$t \to \infty$ to a positive PDE whose existence is suggested according to the principle of detailed equilibrium. In general, if there is a positive PDE and the initial conditions are always positive (all $N_i > 0$), for none of the substances does N_i reduce to zero during the reaction time or tend to zero at $t \to \infty$.

2.3 THERMODYNAMIC LIMITATIONS ON NON-STEADY-STATE KINETIC BEHAVIOUR

In the previous section we introduced the Lyapunov functions for chemical kinetic equations that are the dissipative functions G. The function RTG is treated as free energy. Since $\dot{G} \leqslant 0$ and the equality is obtained only at PDE, and for the construction of G it suffices to know only the position of equilibrium $\vec{N}^*$, there exist limitations on the non-steady-state behaviour of a closed system that are independent of the reaction mechanism. If in the initial composition $\vec{N} \neq \vec{N}^*$, the other composition $\vec{N}'$ can be realized during the reaction only in the case when

(a) $\vec{N}'$ satisfies the same balance relationships as for $\vec{N}$

$$\sum_i a_{ij} N_i' = \sum_i a_{ij} N_i$$

for any j or

$$\vec{A}^{\mathrm{T}} \vec{N}' = \vec{A}^{\mathrm{T}} \vec{N} \tag{102}$$

(b)

$$G(\vec{N}) > G(\vec{N}') \tag{103}$$

The latter means that G is a monotonically decreasing function among the solutions for kinetic equations.

With time the system can get from point $\vec{N}$ to point $\vec{N}'$ only in the case when $G(\vec{N}') < G(\vec{N})$. But it is not the only limitation. Let us return to a system of three isomers (isomerization of butenes) (A_1, A_2, and A_3) and specify its PDE. According to Wei [30], at 230°C $N_1^* \cong 0.14$, $N_2^* \cong 0.32$, and $N_3^* \cong 0.54$ (the normalization condition is $N_1 + N_2 + N_3 = 1$, i.e. the law of conservation). In this case

$$\begin{aligned} G &= N_1\left(\frac{\ln N_1}{0.14} - 1\right) + N_2\left(\frac{\ln N_2}{0.32} - 1\right) \\ &\quad + N_3\left(\frac{\ln N_3}{0.54} - 1\right) \\ &= N_1\frac{\ln N_1}{0.14} + N_2\frac{\ln N_2}{0.32} + \frac{N_3 \ln N_3}{0.54} - 1 \end{aligned}$$

Level lines for G [their equations are $G(\vec{n}) = \text{const.}$] in the triangle $N_1 + N_2 + N_3 = 1$ are shown in Fig. 8(a). At $g > \min G(\vec{N})$ on the boundary

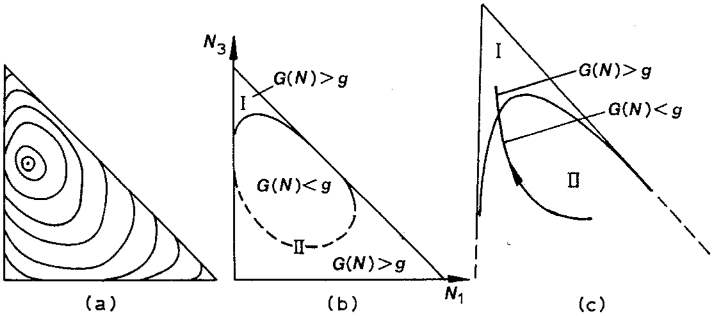


Fig. 8. Thermodynamic limitations on the dynamics of chemical reaction. (a) Level lines of G in the system of three isomers; (b) disconnected multitude of the level; (c) impossibility for the crossing of a connected component for the multitude of the level.

$\vec{D}$ the line $G(\vec{N}) = g$ is no longer a closed curve and at $g > \min\limits_{N_2 = 0} G(\vec{N})$, the level line $G(\vec{N}) = g$ breaks into several segments. Each of these segments separates the triangle into two parts. In one of them $G(\vec{N}) > g$; the other has points with $G(\vec{N}) < g$, but can also have such points where $G(\vec{N}) > g$ [Fig. 8(b)]. One cannot get from region II [Fig. 8(c)] into region I during the reaction, even if, at the initial instant, $G(\vec{N}) > g$. This is due to the fact that it is not possible for the solution of a kinetic equation to cross the $G(\vec{N})$ curve "from the inside" when going from region II into region I [Fig. 8(c)]. In this case, a monotonic character of G along the solution would be broken.

It is clearly seen that, at a vertex of the reaction polyhedron, G achieves its local maximum value (due to the strict convexity of G and the fact that its minimum point is positive). Therefore near each vertex, as well as in the vicinity of some faces, the G function can be used to construct a region that is unattainable from outside. Let us consider the case of one vertex and then a more awkward general situation.

Let $\vec{N}^{\circ}$ be a vertex for the reaction polyhedron with outcoming edges $d_1, \ldots, d_k$. On each edge G is a strictly convex function, therefore it has a unique point of minimum d_i. Let us express the corresponding minimum value of G through M_i

$$M_i = \min N \in d_i \; G(\vec{N}) \tag{104}$$

The maximum value of M_i denoted as $\varepsilon(\vec{N}^{\circ})$ is

$$\varepsilon(\vec{N}^{\circ}) = \max_{1 \leqslant i \leqslant k} M_i \tag{105}$$

A connected component (a "piece") of the surface for the $G(\vec{N}) = \varepsilon(\vec{N}^{\circ})$ level separates inside $\vec{D}$ the unattainability region near $\vec{N}^{\circ}$. This region must be set by several inequalities. One inequality $G(\vec{N}) \geqslant \varepsilon(\vec{N}^{\circ})$ appears to be insufficient, since the $G(\vec{N}) = \varepsilon(\vec{N}^{\circ})$ surface usually consists of several components ("pieces") and we must describe a region near $\vec{N}^{\circ}$ separated by one component. Therefore let us act as follows. We will designate the multitude of all $\vec{D}$ vertices, except $\vec{N}^{\circ}$, through $\vec{\vec{N}}^{\circ}$. Since $\varepsilon(\vec{N}^{\circ})$ is the maximum value for the minima of the G function along the $\vec{D}$ edges d_i from $\vec{N}^{\circ}$, each $d_i (i = 1, \ldots, k)$ has at least one (but not more than two) point where $G(\vec{N}) = \varepsilon(\vec{N}^{\circ})$. Let us take for each d_i that point which is localized closer to $\vec{N}^{\circ}$ and designate it as e_i (if this point is unique it will just be e_i). Then let us construct a convex envelope for all the e_i and the whole of the $\vec{D}$ vertices not coincident with $\vec{N}^{\circ}$

$$\text{conv}\ (\vec{\vec{N}}^{\circ} \cup \{e_i, \ldots, e_n\}) \tag{106}$$

Construction of convex envelopes consists of a system of linear inequalities (it is a typical problem in linear programming; see, for example, ref. 31). In the simplest cases a convex envelope can also be constructed directly. This envelope can also be described parametrically without using inequalities. For example, for a system of $\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_q$ points, their convex envelope consists of linear combinations $\lambda_1\vec{x}_1 + \ldots + \lambda_q\vec{x}_q$ where $\lambda_1, \ldots, \lambda_q$ are non-negative values whose sum equals unity

$$\text{conv}\ \{\vec{x}_1, \ldots, \vec{x}_q\} = \{\lambda_1\vec{x}_1 + \ldots + \lambda_q\vec{x}_q / \lambda_i \geqslant 0,$$
$$(i = 1, \ldots, q), \lambda_1 + \ldots + \lambda_q = 1\}$$

For our purposes, however, it is necessary to set a convex envelope (106) by a system of inequalities. Let these inequalities be

$$\mathrm{l}_j(\vec{N}) \geqslant r_j \qquad j = 1, \ldots, q \tag{107}$$

Here l_j are linear functions and r_j are constants.

A "region of unattainability" $\vec{V}(\vec{N}^{\circ})$ near the vertex $\vec{N}^{\circ}$ is set as follows: $\vec{N}$ lies within $\vec{V}(\vec{N}^{\circ})$ when and only when $G(\vec{N}) > \varepsilon(\vec{N}^{\circ})$ and there exists such $j(1 \leqslant j \leqslant q)$ that $\mathrm{l}_j(\vec{N}) < r_j$

$$\begin{aligned} \vec{V}(\vec{N}^{\circ}) = \{\vec{N} \in \vec{D} \mid G(\vec{N}) &> \varepsilon(\vec{N}^{\circ}) \\ \mathrm{l}_j(\vec{N}) &\leqslant r_j \end{aligned} \tag{108}$$

even if only for $j(1 \leqslant j \leqslant q)\}$.

Let us illustrate the above by a model system of three isomers (butene isomerization). For the analysis we will choose that vertex $\vec{N}^{\circ}$ for which the entire mass of the system is concentrated in A_3: $N_1 = N_2 = 0, N_3 = 1$. Incoming edges correspond to the two possibilities: $N_1 + N_3 = 1$, $N_2 = 0$ [hypotenuse in Fig. 9(a)] and $N_2 + N_3 = 1$, $N_1 = 0$ [a vertical cathetus in Fig. 9(a)] designated as d_1 and d_2, respectively. A minimum G on d_1 is obtained at the point with $N_1/N_3 = N_1^*/N_3^*$, i.e. at $N_1 \cong 0.21$ and $N_3 \cong 0.79$, and it is equal to

$$\begin{aligned} M_1 &\cong 0.21 \ln 1.47 + 0.79 \ln 1.47 - 1 \\ &= \ln 1.47 - 1 \end{aligned}$$

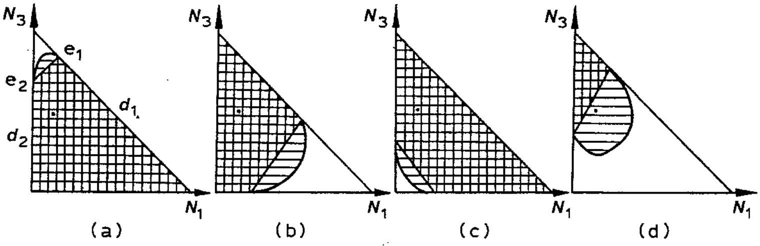


Fig. 9. Construction of the unattainability region for the system of three isomers.

Similarly, the minimum G on d_2 is achieved at $N_2/N_3 = N_2^*/N_3^*$ at a point $N_2 \cong 0.37$, $N_3 \cong 0.63$ and it is equal to

$$M_2 \cong 0.37 \ln 1.16 + 0.63 \ln 1.16 - 1 = \ln 1.16 - 1$$

It is evident that $M_2 < M_1$, hence $\varepsilon(\vec{N}^\circ) = M_1$. A corresponding level line for G is shown in Fig. 9(a). The points e_1 and e_2 are also shown on the figure. Their convex envelope is a vertically hatched tetragon. Horizontal hatches mark its conjunction with a multitude specified by the inequality $G(\vec{N}) \leqslant \varepsilon(\vec{N}^\circ)$. The entire region of the point $\vec{N}^*$ is ω-invariant. It is the other parts of the space near $\vec{N}^\circ$ that is $\vec{V}(\vec{N}^\circ)$, i.e. the desired "unattainability region".

We will now describe the construction of an "unattainability region" near the arbitrary multitude of vertices. Let it be a multitude E for the vertices of the reaction polyhedron. $P(E)$ will be a multitude of $\vec{D}$ edges connecting vertices from E, and $K(E)$ are those connecting elements E with vertices not belonging to E. As before, let $M_d = \min\limits_{N \in d} G(\vec{N})$ be a minimum G on the edge d in the reaction polyhedron. An analog of $\varepsilon(\vec{N}^\circ)$ for the multitude E will be

$$\varepsilon(E) = \max_{d \in K(E)} M_d \tag{109}$$

that is the maximum M_d for the edges going out from E. Let us eliminate from $P(E)$ all the edges for which $M_d \leqslant \varepsilon(E)$. These edges are "cut" by the surface of the $G(\vec{N}) = \varepsilon(E)$ level. If the resultant graph is connected, its vertices are elements of E and its edges are those $P(E)$ for which $M_d > \varepsilon(E)$. We will construct an "unattainability region" $\vec{V}(E)$ which cannot be obtained by conjunction of "unattainability regions" for the sub-multitudes of E (a graph is called connected if, passing along its edges from any vertex, one can get into any others). Let us choose on each edge $d \in K(E)$ a point e_d for which $G(e_d) = \varepsilon(E)$. If there are more than one such points (i.e. two), we will choose that which is nearer to the vertex from E to which this edge belongs. A multitude of polyhedron vertices not belonging to E is designated as $\overline{E}$. Let us construct (describe by linear inequalities) a convex envelope of the multitude

$$\bar{E} \bigcup \{e_d \mid d \in K(E)\} \tag{110}$$

by joining E with the multitude of points e_d at d $K(E)$. Let this convex envelope be set by the inequalities $l_j(\vec{N}) > r_j (j = 1, \ldots, q)$. The "unattainability region" $\vec{V}(E)$ corresponding to E can be described as follows: $\vec{N}$ lies within $\vec{V}(E)$ when, and only when, $G(\vec{N}) > \varepsilon(E)$ and there is at least one j $(1 \leqslant j \leqslant q)$ when $l_j(\vec{N}) < r_j$, i.e.

$$\vec{V}(E) = \{\vec{N} \mid G(\vec{N}) > \varepsilon(E) \text{ and for at least one } j\ (1 \leqslant j \leqslant q)\ l_j(\vec{N}) \leqslant r_j\} \tag{111}$$

The results of the analysis for a system of three isomers for various E are represented in Fig. 9(a)–(b). Here, a convex envelope for the finite multitude (106) is vertically hatched and its union with the multitude $G(\vec{N}) \leqslant \varepsilon(E)$ is horizontally hatched. The whole of the hatched multitude is ω-invariant and the unhatched region is just $\vec{V}(E)$. This example of only four multitudes makes it possible to construct the "unattainability regions" that would not be a union of those for submultitudes. Three multitudes each contain one vertex and a fourth [Fig. 9(d)] includes two vertices, corresponding to the cases when the entire mass is concentrated either in A_1 or in A_2.

Thermodynamic limitations on the non-steady-state kinetic behaviour can be formulated as follows. If the initial non-equilibrium composition is $\vec{N}(0)$, then during the reaction a composition $\vec{N}(t)(t > 0)$ for which $G(\vec{N}(t)) \geqslant G(\vec{N}(^\circ))$ cannot be formed. In addition, it is also impossible that there be formed compositions lying in those "unattainability regions" to which $\vec{N}(0)$ does not belong (one must select the whole of "unattainability regions" whose construction is described above). In other words, there exist several "unattainability regions." For any initial composition $\vec{N}(0)$ there are "unattainability regions" to which it does not belong. During the reaction, a composition from these regions cannot be formed. In addition, for the compositions $\vec{N}$ formed, the condition $G(\vec{N}) \leqslant G(\vec{N}^\circ)$ must be fulfilled.

Thus for closed systems, proceeding from the known equilibrium composition and initial conditions, we can find a thermodynamically forbidden region, i.e. that which would be "non-admittable" for the solution of kinetic equations (18). It is never possible to get from one vertex of the reaction polyhedron into some accurately determined vicinity of the other. In particular, if some initial substance is A (100%), the reaction cannot produce a reaction mixture that would be some other substance completely (100% B) and also have higher content compared with the given content of B. For one reaction, concentrations that cannot be exceeded are equilibrium. For several reactions the case is more complicated. Similar "unattainability regions" exists near certain faces and, more generally, near multitudes of vertices and edges of the reaction polyhedron.

So, what are the thermodynamic limitations on composition variations in the course of a complex reversible reaction following some unknown mechanism?

(1) Starting from positive initial data, we cannot get into boundary points, i.e. during the reaction we cannot obtain a reaction mixture that would not contain at least one of the initial substances. (This was shown in ref. 32 on the basis of Wei's axiomatics [30].)

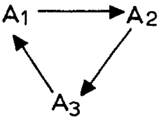
(2) Boundary points cannot be the ω-limit for the solutions starting from positive initial data.

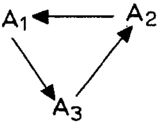
(3) There are no damped oscillations near the point of detailed equilibrium.

(4) According to a given position of the detailed equilibrium point and a given initial composition, we can construct, using the above procedure, a region of compositions that can not be formed during the reaction.

2.4 LIMITATIONS ON NON-STEADY-STATE KINETIC BEHAVIOUR IMPOSED BY THE REACTION MECHANISM

Let the position of the equilibrium point and the reaction mechanism be known. In this case we can use the available information (a list of steps and equilibrium constants k_s^+/k_s^-) to construct stronger, compared with thermodynamic, limitations on the non-steady-state reaction behaviour. Without going into technical details, let us describe the construction of these limitations through a simple example, the same isomerization of n-butenes over Al_2O_3. Let us divide the reaction polyhedron by equilibrium surfaces for individual steps. The regions obtained will be referred to as compartments [Fig. 10(a)]. Inside each compartment, all steps follow a definite direction, i.e. the rate of each step has a fixed sign. Showing a direction the reaction follows by an arrow, every compartment can be prescribed by the oriented graph of predominant directions as shown in Fig. 10(a). Here $A_1 \rightarrow A_2$ means, for example, that for any composition from this compartment the reaction $A_1 \rightleftarrows A_2$ proceeds towards the formation of A_2 from A_1 or, which is the same, $w_1 > 0$. It can be noted that the graphs for all the compartments shown in Fig. 10 are acyclic, i.e. there are no schemes





This is a general fact. For monomolecular (or pseudo-monomolecular) reactions the graphs corresponding to compartments are acyclic. A similar property for the systems having either bi- or termolecular reactions is more complex. It can be formulated as follows. If every edge in the graph of predominant reaction directions for some compartment is ascribed to a positive "rate" constant k and chemical kinetic equations are written with

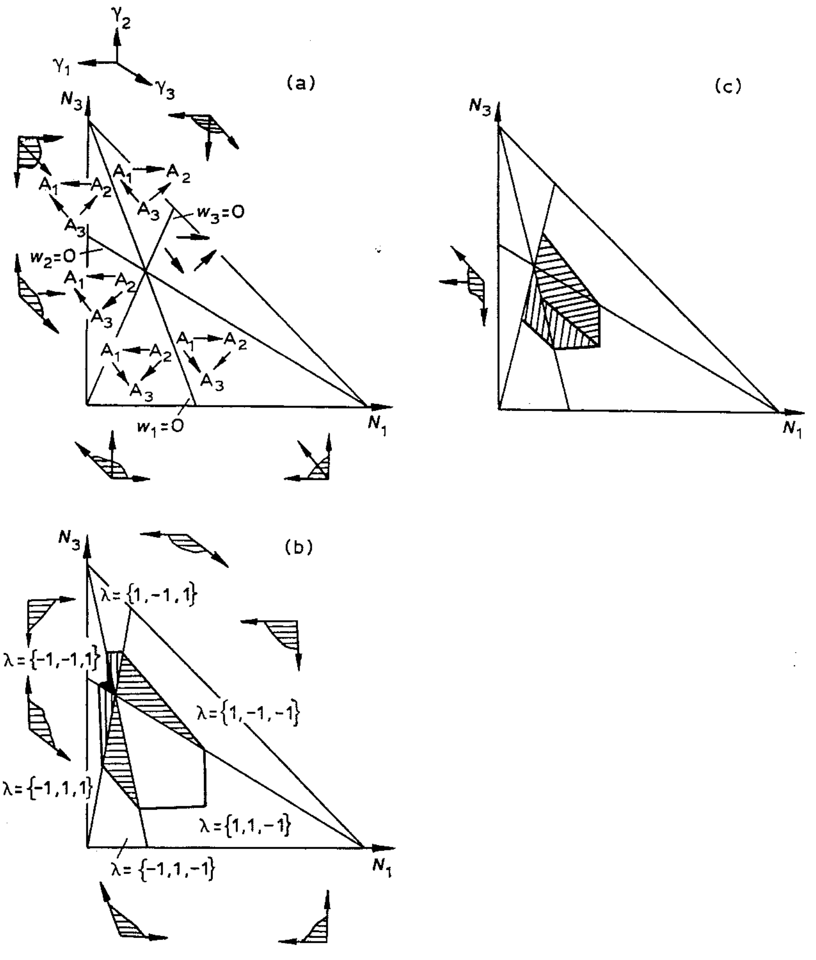


Fig. 10. System of three isomers $A_1 \rightleftarrows A_2 \rightleftarrows A_3 \rightleftarrows A_1$. (a) Compartments and predominant directions of reactions; (b) construction of the minimal ω-invariant set $J(\bar{N}^0)$; (c) sets $J(\bar{N}^0)$ for the reaction mechanisms $A_2 \rightleftarrows A_3$, $A_3 \rightleftarrows A_1$ (horizontally hatched) and $A_1 \rightleftarrows A_2$, $A_3 \rightleftarrows A_1$ (vertically hatched).

such irreversible steps, then at $t \to \infty$ a mixture, which is non-reactive according to this scheme, will be obtained. For example, for the scheme

$$A_1 + A_2 \rightarrow A_3$$

$$A_3 \rightarrow A_2 + A_4$$

the equations will be of the form

$$\dot{N}_1 = -k_1N_1N_2$$

$$\dot{N}_2 = -k_1N_1N_2 + k_2k_3$$

At $t \to \infty$ we will obtain a non-reactive mixture of N_2 and N_4. A graph of the predominant directions corresponds to the direction of the conversion of the initial components either into one substance or a mixture of non-reactive components.

The other way to describe this property is as follows. A convex envelope for the multitude of stoichiometric vectors for the edges in the graph of predominant directions written as if they were direct reaction steps does not contain zero, i.e. there are no such non-negative $\lambda_1, \ldots, \lambda_q$ as

$$\lambda_1 + \ldots + \lambda_q = 1$$

$$\lambda_1\vec{\gamma}_1 + \ldots + \lambda_q\vec{\gamma}_q = 0$$

It can also be interpreted in terms of the bipartite graph for the reaction mechanism (see Sect. 1.3).

In each compartment a sign for all the $w_{s,\sigma}$ has been determined, i.e. we know which of the inequalities $w_{s,\sigma} > 0$ or $w_{s,\sigma} < 0$ take place for the compositions lying inside it. Therefore in any compartment we can write

$$\vec{\gamma}_{s,\sigma} w_{s,\sigma} = |w_{s,\sigma}|\vec{\gamma}_{s,\sigma} \operatorname{sign} w_{s,\sigma}$$

where sign $w_{s,\sigma} = 1$ if $w_{s,\sigma} > 0$ and -1 if $w_{s,\sigma} < 0$. A value for sign $w_{s,\sigma}$ is dictated only by the compartment and does not change if we vary a composition inside it. Since the rate constants are unknown and we do not know $|w_{s,\sigma}|$ either, we can nevertheless write

$$\frac{d\vec{N}}{dt} = S\sum_s |w_s|\vec{\gamma}_s \operatorname{sign} w_s + V\sum_\sigma |w_\sigma|\vec{\gamma}_\sigma \operatorname{sign} w_\sigma$$

This implies that $d\vec{N}/dt$ lies inside a convex cone generated by the vectors $\gamma_{s,\sigma}$ and sign $w_{s,\sigma}$: $d\vec{N}/dt$ is a linear combination of these vectors with positive coefficients. It is possible to construct such a cone for all compartments [Fig. 10(a)]. Since $d\vec{N}/dt$ belongs to this cone, for any initial conditions $\vec{N}^0$ a region can be constructed inside of which lies a solution for kinetic equations that emerges from this point at $t = 0$. For this purpose it is necessary to construct a convex cone generated by the vectors $\vec{\gamma}_{s,\sigma}$, sign $w_{s,\sigma}$ from this point as if it were zero. If this cone is continued up to the compartment boundary [Fig. 10(b)], it is necessary from the intersection points to construct cones corresponding to the neighbouring compartments, etc. A procedure to construct such a set for a system of three isomers is shown in Fig. 10(b). The first cone restored from $\vec{N}^0$ is not hatched. A set obtained at a second step from the boundary of neighbouring compartment is hatched horizontally, a third step is shown by vertical hatches and the last, the fourth one is completely black. After the fourth step no new multitudes are obtained and the construction is completed. The obtained set is ω-invariant and contains a positive semi-trajectory emerging from point $\vec{N}^\circ$. A finite character of the construction procedure is a general fact that is valid for any system. Its proof is cumbersome and hence is omitted.

The multitude constructed for point $\vec{N}^\circ$, and designated as $\vec{J}(\vec{N}^\circ)$, is ω-invariant for all systems of chemical kinetic equations obtained in accordance with the mechanism prescribed and having $\vec{N}^*$ as a PDE. Moreover, it is minimal among the multitudes possessing this property, i.e. if a multitude that is ω-invariant for all systems with a given reaction mechanism and an equilibrium point, contains $\vec{N}^\circ$, it also has $\vec{J}(\vec{N}^\circ)$. In the general case, it is constructed as follows [33].

(1) For each compartment, a signature, i.e. a series of $\lambda_{s,\sigma}$ numbers (one for each step), $\lambda_{s,\sigma} = \operatorname{sign} w_{s,\sigma}$ is written. This multitude is denoted as Λ and the corresponding closed compartment as P_Λ. P_Λ consists of those $\vec{N}$ for which

$$\lambda_{s,\sigma} w_{s,\sigma} \geqslant 0:$$

$$P_\Lambda = \{\vec{N} \mid \lambda_{s,\sigma} w_{s,\sigma} \geqslant 0 \text{ for all values of } s, \sigma\} \tag{112}$$

(2) Each compartment is associated with a convex cone Q_Λ generated by vectors $\lambda_{s,\sigma}$, $\gamma_{s,\sigma}$; this cone consists of vectors of the type

$$\sum_{s,\sigma} x_{s,\sigma} \vec{\gamma}_{s,\sigma} \lambda_{s,\sigma} \tag{113}$$

Where all $x_{s,\sigma} \geqslant 0$ and summation is performed along all reactions (for all values of s, σ). It is necessary to specify a cone Q_Λ by linear inequalities. This is an established problem of linear programming (see, for example, ref. 31) and we will omit the methods of its solution. Let these inequalities be found as $l_j^\Lambda(\vec{N}) \geqslant 0$, where $l_j^\Lambda(\vec{N})$ are linear homogeneous functions.

(3) An operation is constructed that associates each closed multitude M from a reaction polyhedron with the other one $J_0(M)$

$$J_0(M) = \bigcup_\Lambda (((P_\Lambda \cap M) + Q_\Lambda) \cap P_\Lambda) \tag{114}$$

Here it is necessary to find for every compartment P_Λ a multitude $P_\Lambda \cap M$ consisting of those points M that lie in P_Λ. Then the multitude $(P_\Lambda \cap M) + Q_\Lambda$ is constructed. It consists of the points of $\vec{N} + \vec{q}$ type, where $\vec{N} \in P_\Lambda \cap M$, $\vec{q} \in Q_\Lambda$. For every $\vec{N} \in P_\Lambda \cap M$ the multitude $\vec{N} + Q_\Lambda$ is prescribed by the set of inequalities $l_j^\Lambda(\vec{y}) \geqslant l_j^\Lambda(\vec{N})$, therefore the multitude $M + Q_\Lambda$ can be described as

$$(P_\Lambda \cap M) + Q_\Lambda = \{\vec{N}/\text{such } \vec{N}' \in P_\Lambda \cap M \text{ exists as } l_j^\Lambda(\vec{N}) \geqslant l_j^\Lambda(\vec{N}') \text{ for all values of } j\} \tag{115}$$

$(P_\Lambda \cap M) + Q_\Lambda$ comprises those $\vec{N}$ for which there exists $\vec{N}' \in P_\Lambda \cap M$

satisfying the condition $l_j^\Lambda(\vec{N}) \geqslant l_j^\Lambda(\vec{N}')$ at any value of j. In particular

$$\vec{N}^0 + Q_\Lambda = \{\vec{N} | l_j^\Lambda(\vec{N}) \geqslant l_j^\Lambda(\vec{N}^0) \text{ at any value of } j \tag{116}$$

In the construction the internal points of $(P_\Lambda \bigcap M)$ can be eliminated. It suffices to take only boundary points

$$(P_\Lambda \bigcap M) + Q_\Lambda = \partial(P_\Lambda \bigcap M) + Q_\Lambda \tag{117}$$

where ∂ is the symbol for transition to the boundary. If M is prescribed by a finite (alternative) set of inequalities, $(P_\Lambda \bigcap M) + Q_\Lambda$ can also be given by inequalities, even if the initial inequalities are no more linear. Since the method of their construction is cumbersome, it is omitted here. After constructing (describing by inequalities) $(P_\Lambda \bigcap M) + Q_\Lambda$, it is necessary to take its intersection with P_Λ (to add all sets of inequalities with $w_{s,\sigma}\lambda_{s,\sigma} \geqslant 0$ for all s, σ).

(4) A minimal closed ω-invariant set containing $\vec{N}^0$ is constructed as follows. At first $J_0(\{\vec{N}^0\})$ is described, then $J_0(J_0(\{\vec{N}^0\}))$, $J_0(J_0(J_0(\{\vec{N}^0\})))$, etc. This process will be interrupted after a finite number of construction steps. In Fig. 10(b) a white area in the outlined region is $J_0(\{\vec{N}^0\})$. Together with a horizontally hatched section it forms $J_0(J_0(\{\vec{N}^0\}))$, i.e. a horizontally hatched part – points belonging to $J_0(J_0(\{\vec{N}^0\}))$ but lying outside $J_0(\{\vec{N}^0\})$. Similarly, a vertically hatched area belongs to $J_0(J_0(J_0(\{\vec{N}^0\})))$, does not enter $J_0(J_0(\{\vec{N}^0\}))$, and a black area is that of new points in $J_0^4(\{\vec{N}^0\})$ compared with $J_0(J_0(J_0(\{\vec{N}^0\})))$. During the next step of construction no new points appear, i.e. the construction process is interrupted and $J(\vec{N}^0) = J_0^4(\{\vec{N}^0\})$. In justice, it must be emphasized that at finite times closed system behaviour can be rather complicated, i.e. only their limit behaviour is simple. An example is the famous Belousov–Zhabotinskii reaction [13].

Multitudes $J(\vec{N}^0)$ change greatly depending on the reaction mechanism. Therefore we can test (verify) hypothetical reaction mechanisms using these multitudes. If a kinetic curve $\vec{N}(t)$, $\vec{N}(0) = \vec{N}^0$, is obtained, we can say confidently that, when $\vec{N}(t)$ is within experimental accuracy and given limits of the trial, lies outside $J(\vec{N}^0)$, a hypothesis on the reaction mechanism, according to which this $J(\vec{N}^0)$ is constructed, must be eliminated. Multitudes $J(\vec{N}^0)$ for a system of three isomers and various hypothetical (two-step) reaction mechanisms $A_3 \rightleftarrows A_1$, $A_2 \rightleftarrows A_3$ (horizontal hatches) and $A_3 \rightleftarrows A_1$, $A_1 \rightleftarrows A_2$ (vertical hatches) are illustrated in Fig. 10(c). As can be seen, the differences between these multitudes are distinct; they do not even intersect (to be more precise, they intersect along the boundary).

Thus, our knowledge of reaction mechanisms and equilibrium constants makes it possible to construct limitations on the unsteady-state behaviour of chemical reactions. These limitations are essentially stronger compared with ordinary thermodynamic limitations. Since they (in contrasted to thermodynamic limitations) depend on the reaction mechanism, their validity can be tested for experimental curves. Thus hypothetical reaction mechanisms can be tested without calculating rate constants.

In conclusion of the discussion of reaction dynamics in closed systems, it can be suggested that the principal problems here have been solved: closed systems "have been closed". The case is different for open systems. Progress in their study has been extensive. A large number of publications are devoted to the analysis of various dynamic peculiarities (multiplicity of steady states, self-oscillations, stochastic self-oscillations) in various open systems. It can hardly be said that most problems here are completely clear.

3. Formalism of chemical kinetics for open systems

3.1 KINETIC EQUATIONS FOR OPEN SYSTEMS

If, in the system examined, we can neglect spatial differences in the reactant concentrations, a continuous stirred tank reactor (CSTR) model for a reactor can be used. A set of equations is constructed accounting for the process of the totality of reactions under examination at a constant volume. It is then supplemented by a new factor which accounts for the substance exchange with the ambient medium. As usual, concentration equations are used that are analogues to those for substance quantities since the reaction system volume is assumed to be unchanged

$$\begin{aligned} \dot{\vec{c}}^{\,\mathrm{g}} &= \frac{S}{V}\sum_{s} \vec{\gamma}_s^{\,\mathrm{g}} w_s(\vec{c}\,) + \sum_{\sigma} \vec{\gamma}_\sigma^{\,\mathrm{g}} w_\sigma(\vec{c}^{\,\mathrm{g}}) + \frac{v_{\mathrm{in}}}{V}\vec{c}_{\mathrm{in}}^{\,\mathrm{g}} - \frac{v_{\mathrm{out}}}{V}\vec{c}^{\,\mathrm{g}} \\ \dot{c}^{\,\mathrm{s}} &= \sum_{s} \vec{\gamma}_s^{\,\mathrm{s}}\, w_s(\vec{c}\,) \end{aligned} \tag{118}$$

where $\vec{\gamma}_{\mathrm{s}}^{\,\mathrm{g}} \equiv \vec{\gamma}_{\mathrm{s}}^{\,\mathrm{gas}}$, $\vec{\gamma}_{\mathrm{s}}^{\,\mathrm{s}} \equiv \vec{\gamma}_{\mathrm{s}}^{\,\mathrm{sur}}$, v_{in} and v_{out} are the space velocities for the input and output flow of the reaction mixture, respectively, and $\vec{c}_{\mathrm{in}}^{\,\mathrm{g}}$ is the vector whose components are the concentrations of the gaseous substances in the reactor input.

When considering catalytic reaction, the gas-phase processes occurring without a catalyst are often neglected. Equation (118) then takes the form

$$\begin{aligned} \dot{\vec{c}}^{\,\mathrm{g}} &= \frac{S}{V}\sum_{s} \vec{\gamma}_s^{\,\mathrm{g}}\, w_s(\vec{c}\,) + \frac{(v_{\mathrm{in}}\vec{c}_{\mathrm{in}}^{\,\mathrm{g}} - v_{\mathrm{out}}\vec{c}^{\,\mathrm{g}})}{V} \\ \dot{\vec{c}}^{\,\mathrm{s}} &= \sum_{s} \vec{\gamma}_s^{\,\mathrm{s}} w_s(\vec{c}\,) \end{aligned} \tag{119}$$

It is often suggested (without sufficient grounds) that $v_{\mathrm{in}} = v_{\mathrm{out}}$, whereas both volume and pressure remain unchanged during the reaction. Strictly speaking, any catalytic reaction proceeds with changeable volume since gases are partly adsorbed on the catalyst surface. If the pressure is assumed to remain unchanged, we must have $v_{\text{in}} \neq v_{\text{out}}$. Sometimes changes in volume associated with adsorption and desorption can be neglected, particularly under steady-state conditions. When considering unsteady-state behaviour one must remember that, generally speaking, $v_{\text{in}} \neq v_{\text{out}}$. This difference is particularly distinct for the systems with low gas quantities or large catalyst surfaces and also for the "weakly open" systems (see below).

We will make an attempt to determine v_{out} from the equation of state assuming the pressure to remain unchanged

$$P = RT \sum_i c_i^{\text{g}} = \text{const.} \qquad \frac{\mathrm{d}P}{\mathrm{d}T} = 0 \tag{120}$$

Under isothermal conditions we obtain from eqn. (119)

$$v_{\text{out}} = v_{\text{in}} \frac{RT}{P} \sum_i c_{\text{in},i}^{\text{g}} + S \frac{RT}{P} \sum_s \left(w_s(\vec{c}) \sum_i \gamma_{si}^{\text{g}} \right) \tag{121}$$

As usual, the input concentrations are normalized in the following natural way

$$\sum_i c_{\text{in},i}^{\text{g}} = \frac{P}{RT} \tag{122}$$

In this case eqn. (121) for v_{out} takes the form

$$v_{\text{out}} = v_{\text{in}} + S \frac{RT}{P} \sum_s \left[w_s(\vec{c}) \sum_i \gamma_{si}^{\text{g}} \right] \tag{123}$$

Let us designate

$$V_s = \frac{RT}{P} \sum_i \gamma_{si}^{\text{g}} \tag{124}$$

where V_s is the change in the gas volume for the sth step (at a unit rate of this step).

Taking into account eqn. (123), kinetic equations (119) can be written

$$\begin{aligned} \dot{\vec{c}}^{\text{g}} &= \frac{S}{V} \sum_s w_s(\vec{c})(\vec{\gamma}_s^{\text{g}} - V_s \vec{c}^{\text{g}}) + \frac{v_{\text{in}}(\vec{c}_{\text{in}} - \vec{c}^{\text{g}})}{V} \\ \dot{\vec{c}}^{\text{s}} &= \sum_s w_s(\vec{c}) \vec{\gamma}_s^{\text{s}} \end{aligned} \tag{125}$$

These equations are applicable only when the v_{out} value found in accordance with eqn. (123) is non-negative

$$v_{\text{out}} = v_{\text{in}} + S \sum_s w_s(\vec{c}) V_s \geqslant 0 \tag{126}$$

Condition (126) is automatically fulfilled if v_{in} is sufficiently high

$$v_{\text{in}} \; > \; S \max\left(- \sum_s w_s(\vec{c}\,) V_s \right) \tag{127}$$

Here the maximum is taken over all possible concentration values at a given pressure and balance limitation.

If condition (126) is not fulfilled, in the solution of eqn. (119) we can have the case when $v_{\text{out}} < 0$. In this case there is a decrease in the volume of the mixture due to the reaction being faster than its possible increment by virtue of the supply of substance from outside. Remaining in the framework of this model, we can eliminate a negative value for v_{out}, but assuming that $v_{\text{out}} = 0$ at

$$v_{\text{in}} + S \sum_s w_s(\vec{c}\,) V_s \; < \; 0 \tag{128}$$

Otherwise the model must be modified. For example, eqn. (119) can be supplemented by the equations accounting for the pressure drop of the system.

Let us show that, in the steady state found in accordance with eqns. (119) and (123), the condition (127) for the non-negative v_{out} is fulfilled. If $\vec{c}^{\,\text{g}} = \vec{c}^{\,\text{s}} = 0$, then according to eqns. (119) and (123) we obtain

$$\begin{aligned} \vec{c}^{\,\text{g}} \left(\frac{S}{V} \sum_s w_s V_s + \frac{v_{\text{in}}}{V} \right) &= \frac{S}{V} \sum_s \vec{\gamma}^{\,\text{g}}_s w_s + \frac{\vec{c}_{\text{in}} v_{\text{in}}}{V} \\ 0 &= \frac{S}{V} \sum_s \vec{\gamma}^{\,\text{s}}_s w_s \end{aligned} \tag{129}$$

Vectors $\vec{\gamma}_s$ must satisfy balance limitations. For example

$$\sum_{i=1}^{n} m_i \gamma_{si} \; = \; 0$$

where m_i is the molecular weight of substance A_i, if A_i is the gas-phase components, or the molecular weight of a surface substance minus the molecular weight of the catalyst ($\Sigma_{i=1}^{n} m_i N_i$ is the global mass of the gas in the system and of the adsorbed gas). Using this limitation and adding equalities (129) with coefficients m_i, we obtain

$$\sum_i m_i c_i^{\text{g}} \left(\frac{S}{V} \sum_s w_s V_s + \frac{v_{\text{in}}}{V} \right) \; = \; \frac{v_{\text{in}}}{V} \sum_i m_i c_{i,\text{in}}$$

or

$$\rho^{\text{g}} \left(\frac{S}{V} \sum_s w_s V_s + \frac{v_{\text{in}}}{V} \right) \; = \; \rho^{\text{g}}_{\text{in}} \frac{v_{\text{in}}}{V}$$

where ρ^{g} and $\rho^{\text{g}}_{\text{in}}$ are the gas densities in the reactor and its input, respectively. If $v_{\text{in}} \rho^{\text{g}}_{\text{in}} \neq 0$ (its equality to zero indicates that the system is closed), then $\rho^{\text{g}} \neq 0$ and for the steady state we obtain a relationship between v_{in} and v_{out}

$$v_{\text{in}} + S\sum_{s} w_s V_s = v_{\text{out}} = \frac{v_{\text{in}}\rho^{\text{g}}_{\text{in}}}{\rho^{\text{g}}} \tag{130}$$

This corresponds to the fact that, under steady-state conditions, the input and output mass flows are equal.

Thus to examine steady states, eqn. (123) can be used without limitations since it does not result in negative values of v_{out}.

As an example, let us give equations corresponding to two catalytic reactions, namely the simplest reaction of catalytic isomerization and the oxidation of CO (on Pt).

Example 5. The substances are represented by $A_1 = A$, $A_2 = B$, $A_3 = Z$, $A_4 = AZ$, and $A_5 = BZ$ in the reaction mechanism (1) $A + Z \rightleftarrows AZ$, (2) $AZ \rightleftarrows BZ$, and (3) $BZ \rightleftarrows B + Z$ or by $A_{1\text{–}5}$ in the mechanism $A_1 + A_5 \rightleftarrows A_4$, $A_4 \rightleftarrows A_5$, and $A_5 \rightleftarrows A_2 + A_3$. According to the law of acting surfaces, $w_1 = k_1^+ c_1 c_3 - k_1^- c_4$, $w_2 = k_2^+ c_4 - k_2^- c_5$, and $w_3 = k_3^+ c_5 - k_3^- c_2 c_3$. There are no limitations on the constants associated with the principle of detailed equilibrium; all vectors $\vec{\gamma}_s$ are linearly independent

$$\vec{\gamma}^{\,\text{g}}_1 = \begin{bmatrix} -1 \\ 0 \end{bmatrix} \quad \vec{\gamma}^{\,\text{g}}_2 = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \quad \vec{\gamma}^{\,\text{g}}_3 = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

$$\vec{\gamma}^{\,\text{s}}_1 = \begin{bmatrix} -1 \\ 1 \\ 0 \end{bmatrix} \quad \vec{\gamma}^{\,\text{s}}_2 = \begin{bmatrix} 0 \\ -1 \\ 1 \end{bmatrix} \quad \vec{\gamma}^{\,\text{s}}_3 = \begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix}$$

$$\dot{\vec{c}}^{\,\text{g}} = \frac{S}{V}(\vec{\gamma}^{\,\text{g}}_1 w_1 + \vec{\gamma}^{\,\text{g}}_2 w_2 + \vec{\gamma}^{\,\text{g}}_3 w_3) + \frac{v_{\text{in}}\vec{c}^{\,\text{g}}_{\text{in}}}{V} - \frac{v_{\text{out}}\vec{c}^{\,\text{g}}}{V}$$

$$\dot{\vec{c}}^{\,\text{s}} = \vec{\gamma}^{\,\text{s}}_1 w_1 + \vec{\gamma}^{\,\text{s}}_2 w_2 + \vec{\gamma}^{\,\text{s}}_3 w_3$$

or

$$\dot{c}_1 = -\frac{Sw_1}{V} + \frac{v_{\text{in}} c_{1\text{in}}}{V} - \frac{v_{\text{out}} c_1}{V}$$

$$\dot{c}_2 = \frac{Sw_3}{V} + \frac{v_{\text{in}} c_{2\,\text{in}}}{V} - \frac{v_{\text{out}} c_2}{V}$$

$$\dot{c}_3 = -w_1 + w_3$$

$$\dot{c}_4 = w_1 - w_3$$

$$\dot{c}_5 = w_2 - w_3$$

Unlike closed systems (see Sect. 1), the law of conservation, including gas quantities, cannot be used. The system is open with respect to gas and it is for this reason that the balance $c_1 + c_2 + c_3 + c_4 + c_5 = \text{const.}$ cannot be applied. As to the law of catalyst conservation $c_3 + c_4 + c_5 = \text{const.}$ is valid since catalyst is neither introduced nor removed from the system.

Equation (123) for v_{out} takes the form

$$v_{\text{out}} = v_{\text{in}} + S(V_1 w_1 + V_3 w_3)$$

During the second step, the volume is constant since gas does not take part in it at all. Changes in the volumes V_1 and V_3 for the first and third steps are equal

$$V_1 = -\frac{RT}{P}$$

$$V_3 = \frac{RT}{P}$$

Finally

$$v_{\text{out}} = v_{\text{in}} - \frac{w_1 RTS}{P} + \frac{w_3 RTS}{P}$$

[recall that we proceed from the normalization condition (124): $\Sigma c_{i,\text{in}} = P/RT$].

An assumption of constant global gas pressure in the CSTR gives one more law of conservation, i.e. $c_1 + c_2 = \text{const.}$

The laws of conservation for the catalyst amount $c_3 + c_4 + c_5 = b_1 = \text{const.}$ and the gas pressure $c_1 + c_2 = b_2 = \text{const.}$ along with the natural conditions of non-negativity for c account for a convex polyhedron. This polyhedron determined by fixed values of the balances, in this case catalyst and pressure balances, is a balance polyhedron $\vec{D}_\text{o}$. Unlike the polyhedron $\vec{D}$, the structure of the balance polyhedron $\vec{D}_\text{o}$ is, as a rule, rather simple (formally $\vec{D}_\text{o}$ is a particular case of reaction polyhedra). If there exists only one type of active site for the catalyst and accordingly one law of conservation with the participation of concentrations of intermediates, then $\vec{D}_\text{o}$ is a product of two simplexes $\vec{D}_\text{o}$(gas) and $\vec{D}_\text{o}$(surf). The dimensions of $\vec{D}_\text{o}$(gas) and $\vec{D}_\text{o}$(surf) is a unit lower than the number of the corresponding substances, gaseous or those on the catalyst surface. Thus in the case under consideration, $\vec{D}_\text{o}$ consists of the vectors

$$\vec{c} = \begin{bmatrix} \vec{c}^{\,\text{g}} \\ \vec{c}^{\,\text{s}} \end{bmatrix} = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \end{bmatrix}$$

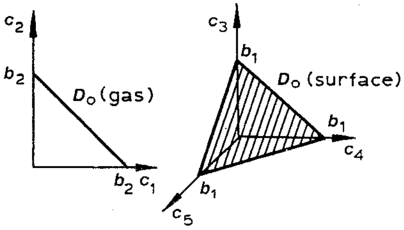
where the vector $\vec{c}^{\,g} = \begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$ lies in the simplex $\vec{D}_o$(gas) and $\vec{c}^{\,s} = \begin{bmatrix} c_3 \\ c_4 \\ c_5 \end{bmatrix}$ enters into the simplex $\vec{D}_o$(surf). $\vec{D}_o$(gas) consists of those $\begin{bmatrix} c_1 \\ c_2 \end{bmatrix}$ for which $c_1 + c_2 = b_2$, $c_1 \geqslant 0$, $c_2 \geqslant 0$ [Fig. 11(a)], and $\vec{D}_o$ (surf) is composed by those $\begin{bmatrix} c_3 \\ c_4 \\ c_5 \end{bmatrix}$ for which $c_3 + c_4 + c_5 = b_1$, $c_3 \geqslant 0$, $c_4 \geqslant 0$, and $c_5 \geqslant 0$ [Fig. 11(b)]. $\vec{D}_o$(gas) is a one-dimensional simplex (segment) and $\vec{D}_o$ (surf) is a two-dimensional one (triangle).

Example 6. The catalytic oxidation of CO on Pt. The substances are represented by $A_1 = O_2$, $A_2 = CO$, $A_3 = CO_2$, $A_4 = Pt$, $A_5 = PtO$, and $A_6 = PtCO$. A detailed mechanism will be a combination of the impact (Eley–Rideal) and adsorption (Langmuir–Hinshelwood) mechanisms (1) $A_1 + 2\,A_4 \rightleftarrows 2\,A_5$, (2) $A_2 + A_4 \rightleftarrows A_6$, (3) $A_5 + A_6 \rightarrow A_3 + 2\,A_4$, and (4) $A_2 + A_5 \rightarrow A_3 + A_4$.

Limitations on the rate constants imposed by the principle of detailed equilibrium (see Sect. 2) have been fulfilled, since steps (3) and (4) are simultaneously taken to be irreversible. Stoichiometric step vectors are

$$\vec{\gamma}_1^{\,g} = \begin{bmatrix} -1 \\ 0 \\ 0 \end{bmatrix} \quad \vec{\gamma}_2^{\,g} = \begin{bmatrix} 0 \\ -1 \\ 0 \end{bmatrix} \quad \vec{\gamma}_3^{\,g} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} \quad \vec{\gamma}_4^{\,g} = \begin{bmatrix} 0 \\ -1 \\ 1 \end{bmatrix}$$

$$\vec{\gamma}_1^{\,s} = \begin{bmatrix} -2 \\ 2 \\ 0 \end{bmatrix} \quad \vec{\gamma}_2^{\,s} = \begin{bmatrix} -1 \\ 0 \\ 1 \end{bmatrix} \quad \vec{\gamma}_3^{\,s} = \begin{bmatrix} 2 \\ -1 \\ -1 \end{bmatrix} \quad \vec{\gamma}_4^{\,s} = \begin{bmatrix} 1 \\ -1 \\ 0 \end{bmatrix}$$



(a) (b)

Fig. 11. Balance polyhedra for catalytic isomerization. (a) For gas; (b) for surface compounds.

In accordance with the law of acting surfaces we have

$$\begin{aligned}
w_1 &= k_1^+ c_1 c_4^2 - k_1^- c_5^2\\
w_2 &= k_2^+ c_2 c_4 - k_2^- c_6\\
w_3 &= k_3 c_5 c_6\\
w_4 &= k_4 c_2 c_5
\end{aligned}$$

Kinetic equations for this system are of the form

$$\begin{aligned}
\dot{\vec{c}}^{\,g} &= \frac{S}{V}\left(\vec{\gamma}_1^{\,g} w_1 + \vec{\gamma}_2^{\,g} w_2 + \vec{\gamma}_3^{\,g} w_3 + \vec{\gamma}_4^{\,g} w_4\right) + \frac{v_{\text{in}} \vec{c}_{\text{in}}^{\,g}}{V} - \frac{v_{\text{out}} \vec{c}^{\,g}}{V}\\
\dot{\vec{c}}^{\,s} &= \vec{\gamma}_1^{\,s} w_1 + \vec{\gamma}_2^{\,s} w_2 + \vec{\gamma}_3^{\,s} w_3 + \vec{\gamma}_4^{\,s} w_4
\end{aligned}$$

or

$$\begin{array}{rcllllll}
\dot c_1 &=& \frac{S}{V} & (-\,w_1 & & &) + \frac{v_{\text{in}} c_{1\,\text{in}}}{V} - \frac{v_{\text{out}} c_1}{V}\\
\dot c_2 &=& \frac{S}{V} & (& -\,w_2 & & -\,w_4) + \frac{v_{\text{in}} c_{2\,\text{in}}}{V} - \frac{v_{\text{out}} c_2}{V}\\
\dot c_3 &=& \frac{S}{V} & (& & w_3 & +\,w_4) + \frac{v_{\text{in}} c_{3\,\text{in}}}{V} - \frac{v_{\text{out}} c_3}{V}\\
\dot c_4 &=& & -2w_1 & -\,w_2\,+ & 2w_3 & +\,w_4\\
\dot c_5 &=& & 2w_1 & & -\,w_3 & -\,w_4\\
\dot c_6 &=& & & w_2\,- & w_3 &
\end{array}$$

An equation for v_{out} is

$$\begin{aligned}
v_{\text{out}} &= v_{\text{in}} + S(w_1 V_1 + w_2 V_2 + w_3 V_3 + w_4 V_4)\\
V_1 &= \frac{-RT}{P},\ V_2 = \frac{-RT}{P},\ V_3 = \frac{RT}{P},\ V_4 = 0
\end{aligned}$$

Ultimately

$$v_{\text{out}} = v_{\text{in}} + S\frac{RT}{P}(-\,w_1 - w_2 + w_3)$$

Remember that here and in what follows we proceed from the condition (124), i.e. $\sum_i c_{i,\text{in}}^g = P/RT$.

The laws of conservation for the catalyst concentration and gas pressure are expressed as: $c_4 + c_5 + c_6 = b_1 = \text{const.}$ and $c_1 + c_2 + c_3 = b_2 = \text{const.}$ Therefore a balance polyhedron is a product of two two-dimensional simplices (triangles).

3.2 "WEAKLY OPEN" SYSTEMS

Sometimes the literature cites postulations implying that, when the velocity of an influx (and correspondingly of an efflux) of substances tends to zero, open systems tend to their corresponding closed systems, demonstrating a similar dynamic behaviour. In fact, this it is not quite true. As usual, even the right-hand sides of CSTR equations (125) do not tend to those of the equations for closed systems. The latter do not contain the summands $S/V \; \Sigma_s w_s(\vec{c}) V_s \vec{c}^{\,g}$. An exclusion is the case when all V_s values are zero, i.e. all reactions proceed with preserved volume (the number of gas molecules in both the right- and left-hand sides of the stoichiometric equation is the same for all steps). For catalytic reactions it never holds true since in every case there are steps with a variable volume, e.g. an adsorption step. But, even in the case when all V_s values are zero, the transition from a closed to an open system cannot be treated as a continuous process. This is due to the fact that closed systems have balance relationships (linear laws of conservation). In open systems even those having low flow velocities, the balance relationships involving the participation of gas-phase components are not fulfilled. This fact can be interpreted as follows. In the transition from open to closed systems a bifurcation occurs and the point $v_{\text{in}} = 0$ is that of bifurcation.

Let us consider open systems at low v_{in} in two stages. First let us assume that both v_{in} and v_{out} are low and time-dependent, but are such that the gas pressure in the reactor is in the range $P_{\max} > P > P_{\min}$ or, equivalently, $b_{\max} > \Sigma\, c_i^g > b_{\min} > 0$, where $b_{\min} = P_{\min}/RT$ and $b_{\max} = P_{\max}/RT$. This agrees well with reality, i.e. even if we want to, we cannot obtain a pressure in the reactor which would be either equal to zero or higher than some very high $P_{\max}$.

Kinetic equations in "weakly" open systems will take the form*

$$\begin{aligned} \dot{\vec{c}}^{\,g} &= \frac{S}{V}\sum_s \vec{\gamma}_s^{\,g} w_s(\vec{c}) + \frac{v_{\text{in}}(t)\vec{c}_{\text{in}}}{V} - \frac{v_{\text{out}}(t)\vec{c}^{\,g}}{V} \\ \dot{\vec{c}}^{\,s} &= \sum_s \vec{\gamma}_s^{\,s} w_s(\vec{c}) \end{aligned} \tag{131}$$

where, in accordance with the assumption, $v_{\text{in}}\Sigma_i\, c_{i,\text{in}} < \varepsilon$ and $v_{\text{out}}\Sigma_i\, c_i^g < \varepsilon$.

Let G be the Lyapunov function corresponding to a closed system at a constant volume (see Sect. 2). We will examine its behaviour using the solutions of eqn. (131).

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* We consider here reactions on the surface. The general case is examined in a similar way.

$$\dot{G} = -S\sum_s w_s \ln\left(\frac{w_s^+}{w_s^-}\right) + \sum_i \frac{\partial G}{\partial c_i^{\mathrm{g}}}\left(\frac{v_{\mathrm{in}} c_{i,\mathrm{in}}}{V} - \frac{v_{\mathrm{out}} c_i}{V}\right) \tag{132}$$

Using the condition of smallness of $v_{\mathrm{in}}\ \Sigma_i c_{i,\mathrm{in}}$ and $v_{\mathrm{out}}\ \Sigma_i c_{i,\mathrm{out}}$ we obtain from eqn. (123)

$$\dot{G} \leqslant -S\sum_s w_s \ln\left(\frac{w_s^+}{w_s^-}\right) + \varepsilon\sum_i \left|\frac{\partial G}{\partial c_i^{\mathrm{g}}}\right| \tag{133}$$

In each reaction polyhedron, the region specified by the inequality

$$-S\sum_s w_s(\vec{c})\ln\left(\frac{w_s^+(\vec{c})}{w_s^-(\vec{c})}\right) + \varepsilon\sum_i \left|\frac{\partial G}{\partial c_i^{\mathrm{g}}}\right| < 0 \tag{134}$$

contains the entire reaction polyhedron, except a certain ε-small vicinity of the PDE and probably a small vicinity of some boundary points of the polyhedron. The latter is attributed to the fact that

$$\frac{\partial G}{\partial c_i^{\mathrm{g}}} = V\ln\left(\frac{c_i^{\mathrm{g}}}{c_i^{\mathrm{g}*}}\right)$$

and tends to ∞ at $c_i^{\mathrm{g}} \to 0$. Let us suggest that the system has no boundary equilibrium point (it is essential). There exist such $t_0 > 0$ and $r > 0$ that, in any reaction polyhedron where the inequalities $b_{\max} > \Sigma_i c_i^{\mathrm{g}} > b_{\min}$ are fulfilled for some its points, a solution of the kinetic equations for the closed system $\vec{c}(t)$ with the initial conditions $\vec{c}(0)$ lying in this polyhedron, belong at $t > t_0$ to the region specified by a $G(\vec{c}) < \delta$ type of inequality and localized at a distance $> r$ from the polyhedron boundary. This follows from the fact that, in the absence of boundary equilibrium points, a positive PDE is the only possible ω-limit one for the solutions of chemical kinetic equations describing closed systems. It is known (see, for example, ref. 34) that, during a finite period of time, the solutions of differential equations are continuously dependent on their right-hand sides, i.e. they vary slightly with small changes of these parts of the equation. It is therefore possible to find such $\varepsilon_0 > 0$ since, at $0 < \varepsilon < \varepsilon_0$, a solution for eqns. (131) describing a "weakly open" system at $t > t_0$ (and hence at $t = t_0$ since a choice of the initial time instant changes nothing) lies in the region specified in the reaction polyhedron corresponding to $\vec{c}(t_0)$ by the $G(\vec{c}) < \delta'$-type inequality (δ' can already differ from δ). This region is localized at a distance $d > r/2$ from the polyhedron boundary (for estimates, one can also take any other positive number that is lower than r). It can be interpreted as follows. The smaller the value of ε, the closer is a solution of eqns. (131) for open systems (at a segment $[0, t_0]$) to the corresponding solution for closed systems. Choosing a sufficiently small value of ε, it is possible to show that $\vec{c}(t_0)$ for an open system will lie in the "region required" specified by any prescribed inequality $G(\vec{c}) < \delta'$ with $\delta' > \delta$.

These regions in all reaction polyhedra can be described by the same inequality. For this purpose let us recall (Sect. 2) that we constructed $G(\vec{c})$ using an arbitrary PDE not necessarily lying in the examined reaction polyhedron and showed that this function is a Lyapunov function for any reaction polyhedron. Now let us introduce one more Lyapunov function which differs from the previous one in every reaction polyhedron by a constant, depending, nevertheless, on this polyhedron. Let us prescribe a function $\vec{c}^*(\vec{c})$ whose value is PDE accounting for the initial conditions $\vec{c}$ (lying in the same reaction polyhedron). Let us determine

$$\tilde{G}(\vec{c}) = G(\vec{c}) - G(\vec{c}^*(\vec{c})) \tag{135}$$

Now $\tilde{G}(\vec{c}^*) = 0$ for any PDE $\vec{c}^*$ irrespective of which reaction polyhedron it belongs to. Using a continuous dependence of the solution $\vec{c}(t)$ for eqns. (131) on the right-hand side of these equations, we can find for any $\delta > 0$ such $t_o > 0$ and $\varepsilon_o > 0$ that, at $t > t_o$ and $0 < \varepsilon < \varepsilon_o$, the solution $\vec{c}(t)$ lies in the region prescribed by the inequality $\tilde{G}(\vec{c}) < \delta$.

PDEs form a surface in the multitude of positive vectors. A multitude formed by the inequality $\tilde{G}(\vec{c}) < \delta$ is a certain vicinity of this surface narrowing towards it at $\delta \to 0$. At first, with sufficiently small ε values, the solution of eqns. (131) behaves like a closed system. For a finite period of time it gets into a small vicinity of the PDE surface, but at the same time remains close to the solution of closed systems. In this vicinity motion is controlled by the substance exchange with the environment and under our assumptions it can be rather complicated. The solution, however, will never leave this area if ε is sufficiently small. Here we proceed from the suggestion that closed systems have no boundary equilibrium points. But if they do exist, then by opening a system they can be made stable. The area of their attraction region tends to zero at $\varepsilon \to 0$. Hence, the presence of boundary points can also be a source of bifurcation when "opening" a system.

Let us consider the case of homogeneous system when v_{in} and v_{out} are low and constant. Let $b(c)$ be a linear function of the concentrations preserved in a closed system. Then for the open system we have

$$\frac{\mathrm{d}b(\vec{c})}{\mathrm{d}t} = v_{\text{in}} b(\vec{c}_{\text{in}}) - v_{\text{out}} b(\vec{c}) \tag{136}$$

and all summands containing $\vec{\gamma}_s$ and w_s reduce to zero in accordance with the law of conservation $b(\vec{c}) = \text{const.}$ for a closed system. Equation (136) is differential with respect to $b(\vec{c})$. After its solution we obtain

$$b(\vec{c}(t)) = \frac{v_{\text{in}} b(\vec{c}_{\text{in}})}{v_{\text{out}}} + \exp\{-v_{\text{out}} t\} \left[b(\vec{c}(0)) - \frac{v_{\text{in}} b(\vec{c}_{\text{in}})}{v_{\text{out}}} \right] \tag{137}$$

At $t \to \infty$, we have $b(\vec{c}(t)) \to v_{\text{in}} b(\vec{c}_{\text{in}})/v_{\text{out}}$ and this result is independent of the smallness of v_{in} and v_{out}. It is only necessary that they will be constant and the system homogeneous. In the case where v_{in} and v_{out} are sufficiently low and $\vec{c}(0)$ is not a boundary PDE, motion takes place at $t \to \infty$ in a small vicinity of the PDE lying inside the reaction polyhedron that corresponds to the balance relationships

$$b(\vec{c}) = b(\vec{c}_{\text{in}}) \frac{v_{\text{in}}}{v_{\text{out}}} \tag{138}$$

We know that a PDE is stable as a linear approximation (see Sect. 2). Whence from eqns. (137) and (138) we establish that, at sufficiently low v_{in} and v_{out} and $t \to \infty$, a solution of the kinetic equations for homogeneous systems tends to a unique steady-state point localized inside the reaction polyhedron with balance relationships (138) in a small vicinity of a positive PDE. If $b(\vec{c}(0)) = b(\vec{c}_{\text{in}})\, v_{\text{in}}/v_{\text{out}}$, then at low v_{in} and v_{out} the function $\vec{c}(t)$ is close to the time dependence of concentrations for a corresponding closed system. To be more precise, if $v_{\text{in}} \to 0$, $v_{\text{out}} \to 0$, $v_{\text{in}}/v_{\text{out}}$, $\vec{c}(0)$, $\vec{c}_{\text{in}}$ are constant and $\vec{c}(0)$ is not a boundary PDE, then we obtain $\max \|\vec{c}(t) - \vec{c}_{\text{cl}}(t)\| \to 0$, where $\vec{c}_{\text{cl}}(t)$ is the solution of the kinetic equations for closed systems, $\vec{c}_{\text{cl}}(0) = \vec{c}(0)$, and $\| \, \|$ is the Euclidian norm in the concentration space.

3.3 STABILIZATION AT HIGH FLOW VELOCITIES

For homogeneous (completely flowing) open systems a steady-state point becomes unique and stable at a very high constant velocity of the flow [35]. In this case the concentrations of gas-phase components rapidly become almost constant and their ratios are close to those for the input mixture. This fact is independent of a concrete type of the $w(\vec{c})$ function. To confirm this postulate, let us consider eqns. (125) for a balance polyhedron $\vec{D}_{\text{o}}$. Since v_{in} is very high, the inequality (127) is fulfilled automatically and we can write

$$\dot{\vec{c}} = \vec{F}(\vec{c}) + \frac{v_{\text{in}}(\vec{c}_{\text{in}} - \vec{c})}{V} \tag{139}$$

where $\vec{F}(\vec{c})$ is independent of v_{in}

$$\vec{F}(\vec{c}) = \sum_{\sigma} w_{\sigma} \left[\vec{\gamma}_{\sigma} - \frac{RT\vec{c}}{P} \left(\sum_{i} \gamma_{\sigma i} \right) \right]$$

As $\vec{D}_{\text{o}}$ is a convex restricted ω-invariant set, it contains at least one steady-state point of eqn. (139). Note that, if starting from some v_{in}, for any two different solutions of eqn. (139) lying in $\vec{D}_{\text{o}}$, $\vec{c}^{\,1}(t)$ and $\vec{c}^{\,2}(t)$, the function $\|\vec{c}^{\,1}(t) - \vec{c}^{\,2}(t)\|$ is monotonically reducing to zero, the steady state is unique, and any solution lying in $\vec{D}_{\text{o}}$ tends to this steady state at $t \to \infty$. It is the distance to this point that will be the global Lyapunov function for eqn. (139) in $\vec{D}_{\text{o}}$. Let us investigate at which values of v_{in} the function $\|\vec{c}^{\,1}(t) - \vec{c}^{\,2}(t)\|$ decreases monotonically.

$$\frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\|\vec{c}^{\,1}(t) - \vec{c}^{\,2}(t)\|^2 = (\vec{c}^{\,1}(t) - \vec{c}^{\,2}(t), \vec{F}(\vec{c}^{\,1}) - \vec{F}(\vec{c}^{\,2})) -$$

$$- \|\vec{c}_1(t) - \vec{c}_2(t)\|^2 \frac{v_{\mathrm{in}}}{V} < 0 \tag{140}$$

Here (,) is the ordinary scalar product that is the sum of coordinate products: $(\vec{x}, \vec{y}) = \Sigma\, x_i y_i$; $\|\ \|^2 = (\,,)$.

Since the inequality (140) must be fulfilled for arbitrarily close $\vec{c}^{\,1}$ and $\vec{c}^{\,2}$ values, we obtain

$$(\vec{\Delta}\,\vec{c}, \vec{F}'_{\vec{c}}\vec{\Delta}\,\vec{c}) - (\vec{\Delta}\,\vec{c}, \vec{\Delta}\,\vec{c})\frac{v_{\mathrm{in}}}{V} < 0 \tag{141}$$

where $\vec{\Delta}\,\vec{c}$ is any non-zero vector satisfying the condition $\Sigma_i \vec{\Delta} c_i = 0$, as vectors of the concentrations $\vec{c}^{\,1}$ and $\vec{c}^{\,2}$ must correspond to the same pressure (they lie in the same $\vec{D}_{\mathrm{o}}$), and $\vec{F}'_{\mathrm{c}} = (\partial F_i/\partial c_j)$ is the matrix of partial derivatives at the point $\vec{c}$.

Due to the convexity of $\vec{D}_{\mathrm{o}}$ (here it is merely a simplex), the local condition (141) is sufficient to claim that eqn. (140) is valid. Inequality (141) is fulfilled if the maximum eigenvalue $\lambda_{\max}$ of the matrix ½ $(\vec{F}'_{\mathrm{c}} + \vec{F}'^{\mathrm{T}}_{\mathrm{c}})$ is lower than v_{in}/V at any $\vec{c}$ from $\vec{D}_{\mathrm{o}}$.

$$\lambda_{\max}\left[\frac{1}{2}(\vec{F}'_{\mathrm{c}} + \vec{F}'^{\mathrm{T}}_{\mathrm{c}})\right] < \frac{v_{\mathrm{in}}}{V} \qquad \text{for any } \vec{c} \in \vec{D}_{\mathrm{o}} \tag{142}$$

An accurate formula for the upper limit of these $\lambda_{\max}$ in $\vec{D}_{\mathrm{o}}$ cannot be given. Hence it is recommended that individual v_{in} values are found for every kinetic model. The stability of the matrix

$$\frac{1}{2}(\vec{F}'_{\mathrm{c}} + \vec{F}'^{\mathrm{T}}_{\mathrm{c}}) - \left(\frac{v_{\mathrm{in}}}{V}\right)\vec{I}$$

can be tested, for example by using the Routh–Hurwitz inequalities.

We can also present simpler estimates for v_{in} when the inequality (142) is fulfilled and $\vec{D}_0$ contains a unique and globally stable steady-state point. Let us apply the Hirsch theorem [29, p. 185]

$$|\lambda_{\max}| < \frac{1}{2}\,n \max_{j,\,i}\left|\frac{\partial F_i}{\partial c_j} + \frac{\partial F_j}{\partial c_i}\right| \qquad (1 \leqslant i, j \leqslant n)$$

(Note that n is the number of substances.)

It follows that a sufficient condition for the validity of eqn. (142) is

$$v_{\mathrm{in}} > \frac{V}{2}\,n \max_{i,\,j,\,c}\left|\frac{\partial F_i}{\partial c_j} + \frac{\partial F_j}{\partial c_i}\right| \qquad (1 \leqslant i, j \leqslant n, c \in D_{\mathrm{o}})$$

It is also possible to apply other estimates for the eigenvalues (see ref. 29, pp. 185–222).

Thus if the flow velocity in a completely flowing (homogeneous) system is higher than a certain value, the balance polyhedron contains a unique steady-state point that is globally stable, i.e. every solution for the kinetic equations (139) lying in $\tilde{D}_0$ tends to it at $t \to \infty$. Note that a critical value for the flow velocity at which this effect is obtained can depend on the choice of balance polyhedron (gas pressure).

A similar claim for heterogeneous systems is, generally speaking, wrong. Indeed, gas concentrations rapidly become close to some values controlled by the balance equations and concentration ratios for the input gas flow. But in close proximity to this value any dynamic behaviour is possible, i.e. a multiplicity of steady states, self-oscillations, etc. The surface state can, however, vary in a rather complicated manner. Figuratively speaking, nontrivial dynamic behaviour of heterogeneous systems cannot be "inhibited" (by a heavy flow).

4. Quasi-stationarity

So far the quasi-steady-state hypothesis introduced in 1913 has remained the most favourable approach to operating with chemical kinetic equations. In short (and not quite strictly), its most applicable version can be formulated as follows. During the reaction, the concentrations of some (usually intermediate) compounds are the concentration functions of the other (usually observed) substances and "adapt" to their values as if they were steady-state values.

As usual, this hypothesis is associated with the names of Bodenstein and Semenov. The latter introduced a concept of partial quasi-stationarity realized for some intermediates. Christiansen described the history of the problem as follows [36] "... the first who applied this theory was S. Chapman and half the year later Bodenstein referred to it in his paper devoted to hydrogen reaction with chlorine. His efforts to confirm his viewpoint were so energetic that this theory is quite naturally associated with his name".

In 1940 Frank–Kamenetskii made an attempt to formulate mathematical conditions for the applicability of this approach [37]. A strict formulation for the problem of a mathematical status for the principle of quasi-stationarity was suggested by Sayasov and Vasilieva [38] in terms of the theory of singularly perturbed differential equations.

Substantiation for this hypothesis is constructed on the availability in the initial set of differential equations with a small parameter ε standing before some derivatives. We will write this set as

$$\begin{aligned} \dot{x} &= \mathrm{f}(x, y) \\ \varepsilon \dot{y} &= \mathrm{g}(x, y) \end{aligned} \qquad (143)$$

Sometimes to reduce the system examined to such a form it is necessary to pass to some new (usually dimensionless) variables or to a new time scale. For example, if the initial set is of the form

$$\frac{dx}{dt} = \varepsilon\, f(x, y)$$

$$\frac{dy}{dt} = g(x, y)$$

then, assuming that $\tau = \varepsilon\, t$, we obtain

$$\frac{dx}{dt} = \varepsilon \frac{dx}{d\tau}$$

$$\frac{dy}{dt} = \varepsilon \frac{dy}{d\tau}$$

and

$$\frac{dx}{d\tau} = f(x, y)$$

$$\varepsilon \frac{dy}{d\tau} = g(x, y)$$

At every fixed value of x we can examine a system of fast motions

$$\frac{dy}{dt} = \frac{1}{\varepsilon} g(x, y) \tag{144}$$

when x acts as a parameter. If at $t \to \infty$ the solution of eqn. (144) tends to the steady state $y_{st}(x)$, it is clear that, by decreasing $\varepsilon > 0$, it can be obtained that the solution of eqn. (144) will get into any given small vicinity of $y_{st}(x)$ for any prescribed time period $T > 0$. Certainly, in the general case the value of ε at which it is achieved depends on the initial conditions and parameter x. If it is possible to obtain an estimate for such ε values that would be valid for a certain region X and the initial conditions y_0, it can be claimed that at $\varepsilon = 0$ the solution of eqns. (143) tends, starting from an arbitrary low $t_0 > 0$, to that for the degenerated equations

$$\begin{aligned} \dot{x} &= f(x, y_{st}(x)) \\ g(x, y) &= 0 \\ y &= y_{st}(x) \end{aligned} \tag{145}$$

Naturally, it holds true as long as the solution remains in the area of x and y for which the above values of ε were obtained.

Rigorous conditions at which the solution of the total equation (143) tend (at $\varepsilon > 0$) to that of the degenerated equation (145) are given by the Tikhonov theorem [39]. Let $y = y_{st}(x)$, i.e. a continuous and continuously differentiated solution for the equations $g(x, y) = 0$ in a certain area $x \in X$ and $y_{st}(x)$ is an asymptotically globally stable steady-state solution for the system of "fast motions" (144): $y(t) \rightarrow y_{st}(x)$ at $t \rightarrow \infty$. Then if the solution $x = x(t)$ of the degenerated system (145) remains in the X area at $0 \leqslant t \leqslant T$, then for any $t_0 > 0$, a solution of the total set (143) $[x(t), y(t)]$ tends to that of the degenerated equation (145) $[x(t), y_{st}(x(t))]$ at $\varepsilon \rightarrow 0$ uniformly on the segment $[t_0, T]$. Functions $x(t)$ for the total and degenerated system tend to each other uniformly throughout the segment $[0, T]$.

Let us emphasize one typical inaccuracy met in the description of the quasi-stationarity hypothesis for chemical systems. It is suggested that the rate of changing the amount of intermediate particles (fast sub-system) tends to or even equals zero. But this is not true since it is not difficult to obtain an expression for $\dot{y}$ by differentiating the relationship $g(x, y) = 0$ and using an implicit function theorem

$$\begin{aligned}\frac{\mathrm{d}g(x, y)}{\mathrm{d}t} &= \frac{\partial g}{\partial x}\dot{x} + \frac{\partial g}{\partial y}\dot{y}\\ &= 0\end{aligned}$$

Here in the general case $\partial g/\partial x$ and $\partial g/\partial y$ are the matrices of the partial derivatives $\partial g_i/\partial x_j$ and $\partial g_i/\partial y_k$. Let us assume that all linear laws of conservation have been eliminated from eqn. (143) and the matrix $\partial g/\partial y$ is inversible. Then

$$\dot{y} = -\left(\frac{\partial g}{\partial y}\right)^{-1}\frac{\partial g}{\partial x}\dot{x}$$

and does not depend on ε (if ε does not enter into the right-hand side). Thus for the solution of a degenerated system, $\dot{y}$ appears to be of the same order as $\dot{x}$ (as usual it is independent of ε).

A source of this mistake is, in particular, the fact that one does not understand that for the solution of a degenerated system the formula

$$\dot{y} = \frac{1}{\varepsilon} g(x, y)$$

is not applicable since quasi-stationarity is only an approximation. With reasonable application of this approximation the errors for $x(t)$ and $y(t)$ are of the order of magnitude as ε but in the expression for $\dot{y}$ containing a large parameter $1/\varepsilon$, they can appear not to be small. Thus the rate of change of the concentrations of intermediates is not obligatorily low compared with that for observed substances. It can be (but need not be) low compared with the rates of formation and consumption for the intermediates, the difference of which determine its value.

The introduction of a quasi-stationarity hypothesis was motivated previously by the fact that concentrations of the intermediates are low and so are the rates of their variations. First, however, rates are often not low and, secondly, generally speaking a low value of the concentrations does not result in a low value of the rates since everything depends on the ratio of the rate constants. This example can show how an inaccurate (even erroneous) approach can lead to a correct and useful result.

Specificity of a concrete system accounts for the source of the appearance of a small parameter ε and for its type. For homogeneous reactions, a small parameter is usually a ratio of rate constants for various reactions; some reactions are much faster than the others. For just such a small parameter Vasiliev et al. [25] distinguished a class of chemical kinetic equations for which the application of the quasi-stationarity principle is correct (they considered a closed system).

For catalytic reactions the fast and slow variables usually considered are the concentrations of surface intermediates on catalysts and gas-phase reactants, respectively. (In the case of high-vacuum conditions, "a vice versa quasi-stationarity" is possible, see below.) But in the equations for heterogeneous catalytic reactions (119)

$$\dot{\vec{c}}^{\,\mathrm{g}} = \frac{S}{V}\sum_s \vec{\gamma}_s^{\,\mathrm{g}} w_s(\vec{c}\,) + \frac{v_{\mathrm{in}}\vec{c}_{\mathrm{in}}^{\,\mathrm{g}}}{V} - \frac{v_{\mathrm{out}}\vec{c}^{\,\mathrm{g}}}{V}$$

$$\dot{\vec{c}}^{\,\mathrm{s}} = \sum_s \vec{\gamma}_s^{\,\mathrm{s}} w_s(\vec{c}\,)$$

a small parameter is not seen at a first glance since S/V need not have a low value, step rates w_s are the same for gas and catalyst and vectors $\vec{\gamma}_s$ have components with values amounting to 0, 1, 2 and (rarely) 3. A key to the solution of this problem can be as follows. The amount of gas (mole) is usually much higher than that of intermediates (mole). Therefore having values for their rates of variation, closer in magnitude, the concentrations of intermediates get into a small vicinity of the steady state (if it is unique and stable) more quickly. Assuming that the pressure in CSTR is constant and the law of catalyst conservation is unique, we can write

$$\sum_i c_i^{\mathrm{g}} = b_{\mathrm{g}} = \text{const.}$$

$$\sum_i c_i^{\mathrm{s}} = b_s = \text{const.}$$

(a more complicated case in which there are several laws of conservation, etc. is considered similarly).

Let us denote

$$N_{\mathrm{tot}}^{\mathrm{s}} = b_{\mathrm{s}}\, S$$

$$N_{\mathrm{tot}}^{\mathrm{g}} = b_{\mathrm{g}}\, V$$

$$\vec{\bar{c}}^{\,\mathrm{g}} = \frac{\vec{N}^{\mathrm{g}}}{N_{\mathrm{tot}}^{\mathrm{g}}}$$

$$\vec{\theta} = \frac{\vec{N}^{\mathrm{s}}}{N^{\mathrm{s}}_{\mathrm{tot}}} \qquad \varepsilon = \frac{N^{\mathrm{s}}_{\mathrm{tot}}}{N^{\mathrm{g}}_{\mathrm{tot}}} \tag{146}$$

At constant b_{s} and b_{g} the rates of steps w_s are functions of $\vec{\bar{c}}^{\,\mathrm{g}}$ and $\vec{\theta}$ and do not depend on ε

$$w_s = k_s^+ \prod_i (\bar{c}_i^{\mathrm{g}} b_{\mathrm{g}})^{\alpha_{si}} \prod_i (\theta_i b_{\mathrm{s}})^{\alpha_{si}} - k_s^- \prod_i (\bar{c}_i^{\mathrm{g}} b_{\mathrm{g}})^{\beta_{si}} \prod_i (\theta_i b_{\mathrm{s}})^{\beta_{si}}$$

The set (119) is rewritten with respect to $\vec{\bar{c}}$ as

$$\begin{aligned} \dot{\vec{\bar{c}}}^{\,\mathrm{g}} &= \frac{1}{b_{\mathrm{s}}} \varepsilon \sum_s \vec{\gamma}_s^{\,\mathrm{g}} w_s(\vec{\bar{c}}^{\,\mathrm{g}}, \vec{\theta}) + \frac{v_{\mathrm{in}} \vec{c}^{\,\mathrm{g}}_{\mathrm{in}}}{N^{\mathrm{g}}_{\mathrm{tot}}} - \frac{v_{\mathrm{out}} \vec{\bar{c}}^{\,\mathrm{g}}}{V} \\ \dot{\vec{\theta}} &= \frac{1}{b_{\mathrm{s}}} \sum_s \vec{\gamma}_s^{\,\mathrm{s}} w_s(\vec{\bar{c}}^{\,\mathrm{g}}, \vec{\theta}) \end{aligned} \tag{147}$$

Let us go to a new time scale $\tau = (\varepsilon/b_{\mathrm{s}})t$. We will then have

$$\begin{aligned} \frac{\mathrm{d}\vec{\bar{c}}^{\,\mathrm{g}}}{\mathrm{d}\tau} &= \sum_s \vec{\gamma}_s^{\,\mathrm{g}} w_s(\vec{\bar{c}}^{\,\mathrm{g}}, \vec{\theta}) + \frac{1}{S} v_{\mathrm{in}} \vec{c}^{\,\mathrm{g}}_{\mathrm{in}} - \frac{b_{\mathrm{g}}}{S} v_{\mathrm{out}} \vec{c}^{\,\mathrm{g}} \\ \varepsilon \frac{\mathrm{d}\vec{\theta}}{\mathrm{d}\tau} &= \sum_s \vec{\gamma}_s^{\,\mathrm{s}} w_s(\vec{\bar{c}}, \vec{\theta}) \end{aligned} \tag{148}$$

If at constant S, b_{s}, b_{g}, $\varepsilon \to 0$ and the system of "fast motions"

$$\frac{\mathrm{d}\vec{\theta}}{\mathrm{d}t} = \sum_s \vec{\gamma}_s^{\,\mathrm{s}} w_s(\vec{\bar{c}}, \vec{\theta}) \tag{149}$$

has at every fixed $\vec{\bar{c}}^{\,\mathrm{g}}$ a unique and asymptotically globally stable steady state, we can apply the Tikhonov theorem and, starting from a certain value of ε, can use a quasi-steady-state approximation.

Generally speaking, ε can be tended to zero by various methods without assuming S, b_{s}, and b_{g} to be constant. In this case, many different asymptotes arise. Their difference is associated with the fact that, at given $\vec{\theta}$ and $\vec{\bar{c}}^{\,\mathrm{g}}$, the values of w are independent of b_{s} and b_{g} and the equations for "slow motions" [the first part of eqn. (148)] contain parameters $1/S$ and b_{g}/S. For example, at fixed b_{g}, S and V, b_{s} can be tended to zero: $b_{\mathrm{s}} \to 0$. Then the rates of elementary reactions which are linear with respect to intermediates, will have an order of smallness ε. But if the reaction also involves the participation of k intermediates as initial reactants, the order of smallness for w is equal to ε^k. Let $k_{\min}$ be the lowest order with respect to intermediates that can be met in elementary reactions of the mechanism examined. Then after going to a new time scale, at $\varepsilon \to 0$ (on finite intervals) the reactions having orders with respect to intermediates above $k_{\min}$ can be neglected. The quasi-steady-state approximation is applicable if $v_{\text{in}} = 0$ and the "fast" subsystem (149) accounting only for the elementary reactions whose order with respect to intermediates is $k_{\min}$ has, for any $\vec{c}^{\,\text{g}}$, a unique and asymptotically globally stable steady state. These asymptotes correspond to the case of "infinitely diluted" or "greatly contaminated" catalysts (the number of active sites per unit surface tends to zero) and were studied in detail by Akramov and Yablonskii [40]. Generally speaking, in this case at $\varepsilon \to 0$ the reaction "vanishes", i.e. all $w_s(\vec{c}) \to 0$ and $\vec{c}^{\,\text{g}}$ variations are determined by the substance flow.

Let us consider two cases for $\varepsilon \to 0$ at which reactions "do not vanish". They are the increase of V (b_s, b_g, and S being constant, $N^\text{g}_\text{tot} \gg N^\text{s}_\text{tot}$) and of b_g (V, S and b_s being constant). The former case has already been considered, namely with increasing V ($N^\text{g}_\text{tot} \gg N^\text{s}_\text{tot}$) the only changeable parameter is the coefficient in eqn. (148) at $\overrightarrow{\mathrm{d}\theta}/\mathrm{d}\tau$ and the right-hand side remains unchanged. To consider the latter case $b_\text{g} \to \infty$ (gas pressure increases), let us use eqn. (121) relating v_{in} to v_{out}

$$v_{\text{out}} = v_{\text{in}} \frac{b_{\text{g,in}}}{b_\text{g}} + \frac{S}{b_\text{g}} \sum_s w_s \sum_i \gamma^\text{g}_{s,i}$$

where

$$b_{\text{g,in}} = b_\text{g}(\vec{c}^{\,\text{g}}_{\text{in}}) = \sum_i c^\text{g}_{\text{in},i}$$

If the initial reactants for an elementary reaction are k gas molecules (as usual $k = 0$ or 1), the reaction rate is $w = b^\text{k}_\text{g} w'(\vec{c}^{\,\text{g}}, \vec{\theta})$, where $w'(\vec{c}^{\,\text{g}}, \vec{\theta})$ is no longer explicitly dependent on b_g. Dividing elementary reactions into groups corresponding to various k values and designating the rates for the kth group as w_{ks}, we obtain

$$\frac{\overrightarrow{\mathrm{d}\bar{c}^{\,\text{g}}}}{\mathrm{d}\tau} = \sum_{k=0} w_{\text{o},s}(\vec{\bar{c}}^{\,\text{g}}, \vec{\theta})(\vec{\gamma}^{\,\text{g}}_{\text{o},s} - V_{\text{o},s}\vec{\bar{c}}^{\,\text{g}}) + b_\text{g} \sum_{k=1} w'_{1,s}(\vec{\bar{c}}^{\,\text{g}}, \vec{\theta})$$

$$(\vec{\gamma}^{\,\text{g}}_{1,s} - V_{1,s}\vec{\bar{c}}^{\,\text{g}}) + b^2_\text{g} \sum_{k=2} \ldots + \frac{v_{\text{in}}}{S} b_{\text{g,in}} \left(\frac{\vec{c}^{\,\text{g}}_{\text{in}}}{b^\text{g}_{\text{in}}} - \vec{\bar{c}}^{\,\text{g}}\right)$$

$$\varepsilon \frac{\overrightarrow{\mathrm{d}\theta}}{\mathrm{d}\tau} = \sum_{k=0} w_{\text{o},s}(\vec{\bar{c}}^{\,\text{g}}, \vec{\theta})\vec{\gamma}^{\,\text{s}}_{\text{o},s} + b_\text{g} \sum_{k=1} w'_{1,s}(\vec{\bar{c}}^{\,\text{g}}, \vec{\theta})\vec{\gamma}^{\,\text{g}}_{1,s} + b^2_\text{g} \sum_{k=2} \ldots$$

At $b_\text{g} \to \infty$, reactions involving the participation of the greatest number of gas molecules ($k = k_{\max}$) become predominant. When choosing a new time scale $\tau' = b_\text{g}^{k_{\max}}\tau$, we can go to the quasi-steady-state approximation at $\varepsilon \to 0$ if the "fast" subsystem corresponding to the case in which $k = k_{\max}$

$$\dot{\vec{\theta}} = \sum_{k=k_{\max}} w'_{k,s}(\bar{\vec{c}}^{\,g}, \vec{\theta})\, \vec{\gamma}^{\,s}_{k,s}$$

has at any fixed $\bar{\vec{c}}^{\,g}$ a unique and global stable steady state. A more comprehensive analysis, taking into account possible partial quasi-stationarity, can be made similarly to the case for $b_s \to 0$ (see ref. 40 and also the example given below).

If $S \to 0$ at constant b_s, b_g, and $V(N^g_{tot} \gg N^s_{tot})$ on the right-hand side of the first equation of eqns. (148) there appears a large parameter $1/S$. Generally speaking, both sets of variables (gas and surface) become "fast" (at $v_{in} \neq 0$). If we return to the initial equations (119), it becomes clear that at $S \to 0$, variations in $\vec{c}^{\,g}$ are determined accurately to the terms of the order by the substance flow

$$\dot{\vec{c}}^{\,g} = \frac{v_{in}\vec{c}^{\,g}_{in}}{V} - \frac{v_{out}\vec{c}^{\,g}}{V} + 0(\varepsilon)$$

or, taking into account eqn. (123), we have

$$\dot{\vec{c}}^{\,g} = \frac{v_{in} b_{g,in}(\vec{c}^{\,g}_{in}/b_{g,in} - \vec{c}^{\,g}/b_g)}{V}$$

It is also possible to consider the case $S \to 0$, with b_s, b_g, and V constant and v_{in} also tends to zero with v_{in}/S remaining unchanged. Then the case $S \to 0$ does not differ from $V \to \infty$, which was considered first, and they can be united into one case $S/V \to 0$ $(N^g_{tot} \gg N^s_{tot})$ with b_g, b_s and v_{in}/S being constant.

The question arises: which of the cases is closest to reality? Let us consider the physical possibilities for various paths for $\varepsilon \to 0$.

(a) $b_s \to 0$, V, S, and b_g are constant. This corresponds to the sequence of systems (with different ε) having the same volume and catalyst surface areas at the same pressure, but different (decreasing) density of active sites on the catalyst surface. The latter is obtained with strong poisoning or dilution of the catalyst.

(b) $b_g \to \infty$, V, S, and b_s are constant. This corresponds to the increase of gas pressure in the system.

(c) $S/V \to 0$, b_g, b_s and v_{in}/S are constant. This means that, starting from approximately equal values of N^g_{tot} and N^s_{tot}, we increase the gas volume in the system or reduce the catalyst surface area by the appropriate changes of $v_{in}(v_{in}/S = \text{const.})$. An apparent barrier for the application of this asymptote is the fact that, generally speaking, S/V is not small. But it is a dimensional value and its smallness depends, for example, on the choice of length units. A real meaning is obtained for the smallness $\varepsilon = N^s_{tot}/N^g_{tot}$. If, for example, ε is already sufficiently small to apply the quasy-steady-state approximation with fairly good accuracy, then the value of S/V cannot yet be very small.

Asymptotes at $\varepsilon \to 0$, corresponding to (a) and (b), are sure to have their meaning with high degrees of catalytic poisoning (a) or high gas pressure (b). But their application suggests that at $\varepsilon \to 0$ the rate ratios for various reactions change and some of them practically disappear (see above). It is not observed for the asymptote (c) which seems to be the most natural.

It is also possible to consider the case $\varepsilon \to \infty$. It is symmetric to the above cases (a)–(c) accurate to the substitution of $\vec{\bar{c}}^{\,g}$, b_g and N_{tot}^g by $\vec{\bar{c}}^{\,s}$, b_s and N_{tot}^s, respectively. This case corresponds to catalytic reactions carried out under high-vacuum conditions. For this case one can observe a "reverse quasi-stationarity", i.e. a fast "adapting" of the concentrations for gaseous substances $\vec{c}^{\,g}$ to those of surface substances $\vec{c}^{\,s}$.

Let us consider all asymptotes for a simple example of catalytic isomerization $A + Z \xrightarrow{1} AZ \xrightarrow{2} BZ \xrightarrow{3} B + Z$. To reduce the calculations, we assume all steps to be irreversible.

$$\dot{c}_A = \frac{S}{V}\left[k_1 c_A c_Z\left(-1 + \frac{1}{b_g} c_A\right) - k_3 c_{BZ} \frac{1}{b_g} c_A\right] +$$

$$+ \frac{b_{g,in} v_{in}}{V}\left(\frac{c_{A,in}}{b_{g,in}} - \frac{c_A}{b_g}\right)$$

$$\dot{c}_B = \frac{S}{V}\left[k_3 c_{BZ}\left(1 - \frac{1}{b_g} c_B\right) + k_1 c_A c_Z \frac{1}{b_g} c_B\right] +$$

$$+ \frac{v_{in} b_{g,in}}{V}\left(\frac{c_{B,in}}{b_{g,in}} - \frac{c_B}{b_g}\right)$$

$$\dot{c}_Z = -k_1 c_A c_Z + k_3 c_{BZ}$$

$$\dot{c}_{AZ} = k_1 c_A c_Z - k_2 c_{AZ}$$

$$\dot{c}_{BZ} = k_2 c_{AZ} - k_3 c_{BZ}$$

where

$$b_g = c_A + c_B = \text{const.}$$

and

$$b_s = c_Z + c_{AZ} + c_{BZ} = \text{const.}$$

Using the laws of conservation and applying variables $\bar{c}$ and θ, we can write

$$\dot{\bar{c}}_A = \frac{S}{b_g V}\left[k_1 b_g b_s \bar{c}_A \theta_Z(-1 + \bar{c}_A) - k_3 b_s \theta_{BZ} \bar{c}_A\right] +$$

$$+ \frac{v_{in}}{V} b_{g,in} \frac{\bar{c}_{A,in} - \bar{c}_A}{b_g}$$

$$\dot{\theta}_Z = -k_1 b_g \bar{c}_A \theta_Z + k_3 \theta_{BZ}$$

$$\dot{\theta}_{BZ} = k_2(1 - \theta_Z - \theta_{BZ}) - k_3\theta_{BZ}$$

$$\bar{c}_B = 1 - \bar{c}_A$$

$$\theta_{AZ} = 1 - \theta_Z - \theta_{BZ}$$

where $\bar{c}_{A,in} = c_{A,in}/b_{g,in}$.

Let us consider the case (a): $b_s \to 0$, b_g, S and V = const. $v_{in} > 0$. Then

$$\bar{c}_A(t) = \bar{c}_{A,in} + [\bar{c}_A(0) - \bar{c}_{A,in}] \exp\left(-\frac{v_{in}b_{g,in}}{Vb_g}t\right) + 0(\varepsilon)$$

Surface coverages θ_Z and θ_{BZ} are determined accurate to $0(\varepsilon)$ from linear equations with variable coefficients

$$\dot{\theta}_Z = -k_1 b_g\left[\bar{c}_{A,in} + (\bar{c}_A(0) - \bar{c}_{A,in}) \exp\left(-\frac{v_{in}b_{g,in}}{b_g V}t\right)\right]\theta_Z +$$

$$+ k_3\theta_{BZ} + 0(\varepsilon)$$

$$\dot{\theta}_{BZ} = k_2 - k_2\theta_2 - (k_2 + k_3)\theta_{BZ} + 0(\varepsilon)$$

The rate constants and b_g, as well as $\bar{c}_{A,in}$ and v_{in}, are assumed to be non-zero and hence the matrix

$$\begin{bmatrix} -k_1 b_g\bar{c}_{A,in} & k_3 \\ -k_2 & -(k_2 + k_3) \end{bmatrix}$$

is non-singular.

As can be seen, at $b_s \to 0$ the asymptotes are rather simple, but no quasi-stationarity exists. As shown above, this is a rather common case for CSTR when $\bar{c}_A(0) = \bar{c}_{A,in}$ and hence $\bar{c}_A(t) = \bar{c}_{A,in} + 0(\varepsilon)$.

If we assume that $v_{in} = 0$ (the system is closed) we obtain the case considered previously. Note that then the asymptotes given are not applicable since a linear part in the equation for c_A becomes singular and the major contribution is made by the terms of the order $0(\varepsilon)$. For this case ($v_{in} = 0$), the quasi-stationarity in the system becomes possible. Proceeding from the assumption that at $b_s \to 0$ we will have v_{in}/b_s = const., it is possible to go to a new time scale $\tau = b_s t$ and obtain

$$\frac{d\bar{c}_A}{d\tau} = \frac{S}{b_g V}\left[k_1 b_g\bar{c}_A\theta_Z(-1 + \bar{c}_A) - k_3\theta_{BZ}\bar{c}_A + \frac{v_{in}b_{g,in}(\bar{c}_{A,in} - \bar{c}_A)}{b_s V b_g}\right]$$

$$b_s\frac{d\theta_Z}{d\tau} = k_1 b_g\bar{c}_A\theta_Z + k_3\theta_{BZ}$$

$$b_s\frac{d\theta_{BZ}}{d\tau} = k_2 - k_2\theta_Z - (k_2 + k_3)\theta_{BZ}$$

Since, it was assumed that v_{in}/b_s = const. at $b_s \to 0$, the right-hand side of the first equation is independent of ε. At any $\bar{c}_A \geqslant 0$ the system of "fast motions" has a unique asymptotically globally stable steady state:

$$\theta_Z = \frac{k_2 k_3}{k_1 b_g \bar{c}_A k_2 + k_2 k_3 + k_3 k_1 b_g \bar{c}_A}$$

$$\theta_{BZ} = \frac{k_1 b_g \bar{c}_A k_2}{k_1 b_g \bar{c}_A k_2 + k_2 k_3 + k_3 k_1 b_g \bar{c}_A}$$

Consequently, starting from some sufficiently low b_s, the quasi-steady-state approximation can be applied after a certain period of time ("boundary layer")

$$\frac{d\bar{c}_A}{d\tau} = \frac{-(S/V)k_1 k_2 k_3 \bar{c}_A}{k_1 b_g \bar{c}_A k_2 + k_2 k_3 + k_3 k_1 b_g \bar{c}_A} + \\ + \frac{v_{in} b_{g,in}}{b_s V b_g}(\bar{c}_{A,in} - \bar{c}_A) \tag{150}$$

Since all reactions are of the same order (first) with respect to intermediates, eqn. (150) coincides in its form (accurate to a scale factor) with that (see below) for the case corresponding asymptote (c) ($S/V \to 0$).

Let us now consider a version of the reverse quasi-stationarity: $b_s \to \infty$, S, V, b_g, and v_{in} being constant. Here a "fast" subsystem is of the form

$$\frac{1}{b_s}\dot{\bar{c}}_A = \frac{1}{b_g}\frac{S}{V}[k_1 b_g \theta_Z \bar{c}_A^2 - (k_1 b_g \theta_Z + k_3 \theta_{BZ})\bar{c}_A] + \\ + \frac{v_{in} b_{g,in}}{b_s v b_g}(\bar{c}_{A,in} - \bar{c}_A)$$

At sufficiently high b_s it has a unique and asymptotically globally stable steady state in the range $0 \leqslant \bar{c}_A \leqslant 1$ near zero. At $b_s \to \infty$, this solution tends to zero like $1/b_s$. Therefore after passing the boundary layer we obtain, accurate to the terms of the order $1/b_s$, $\bar{c}_A = 0(\varepsilon)$, $\dot{\theta}_Z = 0(\varepsilon) + k_3\theta_{BZ}$, $\dot{\theta}_{BZ} = k_2(1 - \theta_Z - \theta_{BZ}) - k_3\theta_{BZ} + 0(\varepsilon)$. At $t \to \infty$, we will have $\theta_Z \to 1 + 0(\varepsilon)$, $\theta_{BZ} \to 0(\varepsilon)$, $\theta_{AZ} \to 0(\varepsilon)$.

Consequently, in this case, the surface is practically free. Let us consider the asymptotes at high ($b_g \to \infty$) and low ($b_g \to 0$) pressures. If $b_g \to \infty$, the equation for $\bar{c}_A$ will have a small parameter $1/b_g$ but not for all summands and on the right-hand side of the equation for θ_Z there appears a large parameter b_g. Let us write

$$\dot{\bar{c}}_A = \frac{S}{V} k_1 b_s \bar{c}_A \theta_Z(-1 + \bar{c}_A) + (1/b_g)[- k_3 b_s \theta_{BZ} \bar{c}_A] + \\ + \frac{v_{in} b_{g,in}}{V}(\bar{c}_{A,in} - \bar{c}_A)$$

$$\frac{1}{b_g}\dot{\theta}_Z = -k_1\bar{c}_A\theta_Z + \frac{1}{b_g}k_3\theta_{BZ}$$

$$\dot{\theta}_{BZ} = k_2(1 - \theta_Z - \theta_{BZ}) - k_3\theta_{BZ}$$

As seen, a fast variable here must consider only θ_Z. At any θ_{BZ} and $\bar{c}_A \neq 0$, the equation for θ_Z has a unique and asymptotically globally stable steady-state solution

$$\theta_Z = \frac{1}{b_g}\frac{k_3\theta_{BZ}}{k_1\bar{c}_A}$$

Quasi-steady-state equations are of the form

$$\theta_Z = 0(\varepsilon)$$

$$\dot{\bar{c}}_A = 0(\varepsilon)$$

$$\dot{\theta}_{BZ} = 0(\varepsilon) + k_2 - (k_2 + k_3)\,\theta_{BZ}$$

Their physical meaning is as follows. At high gas pressures the surface contains almost no unoccupied sites since they are rapidly occupied by adsorbing molecules of A. A value of $\bar{c}_A$ is a low since the quantity of gas is very high compared with that of the catalyst and the adsorption rate is low, hence θ_Z is low.

If $b_g \to 0$ (low pressures) we can write

$$b_g\dot{\bar{c}}_A = b_g\frac{S}{V}k_1 b_s\bar{c}_A\theta_Z(\bar{c}_A - 1) - \frac{S}{V}k_3 b_s\theta_{BZ}\bar{c}_A +$$

$$+ \frac{v_{in}}{V}b_{g,in}(\bar{c}_{A,in} - \bar{c}_A)$$

$$\dot{\theta}_Z = b_g k_1\bar{c}_A\theta_Z + k_3\theta_{BZ}$$

$$\dot{\theta}_{BZ} = k_2(1 - \theta_Z - \theta_{BZ}) - k_3\theta_{BZ}$$

A fast variable here is $\bar{c}_A$. At fixed θ_Z and θ_{BZ}, it is necessary to examine a system of fast motions. This has the steady states

$$(\bar{c}_A)_{1,2} = \frac{1}{2} + \frac{k_3}{2b_g k_1}\frac{\theta_{BZ}}{\theta_Z} + \frac{v_{in}}{2S}\frac{b_{g,in}}{b_g}\frac{1}{k_1 b_s\theta_Z} \pm$$

$$\pm\left[\frac{1}{4}\left(1 + \frac{k_3}{b_g k_1}\frac{\theta_{BZ}}{\theta_Z} + \frac{v_{in}}{S}\frac{b_{g,in}}{b_g}\frac{\theta_Z}{k_1 b_s}\right)^2 - \frac{v_{in}}{S}\frac{b_{g,in}}{b_g}\frac{\bar{c}_{A,in}}{k_1 b_s\theta_Z}\right]^{1/2}$$

A root $(\bar{c}_A)_1$ corresponding to a negative sign, always lies on the segment [0, 1] whereas that of $(\bar{c}_A)_2$ is always above unity. Hence on the segment [0, 1] there exists a unique steady state for the fast subsystem. Since the segment

[0, 1] is ω-invariant (if, at the initial instant, $0 \leqslant \bar{c}_A \leqslant 1$, then this inequality is also valid for the rest of the period) this steady state is stable and the Tikhonov theorem can be used. A solution of the quasi-steady-state equations is of the form

$$\bar{c}_A = \bar{c}_{A,in}\left(\frac{v_{in}b_{g,in}}{k_3\theta_{BZ}b_sS + v_{in}b_{g,in}}\right) + 0(b_g)$$

and θ_Z and θ_{BZ} can be found from the equations

$$\dot{\theta}_Z = 0(b_g) + k_3\theta_{BZ},$$

and

$$\dot{\theta}_{BZ} = k_2(1 - \theta_Z - \theta_{BZ}) - k_3\theta_{BZ}$$

These equations are linear and can be easily integrated. Their characteristic values are $\lambda_1 = k_2$ and $\lambda_2 = -k_3$ and the corresponding eigenvectors will be

$$\begin{bmatrix} +k_3 \\ +k_2 \end{bmatrix} \text{and} \begin{bmatrix} +1 \\ -1 \end{bmatrix}$$

Hence a general solution is

$$\begin{bmatrix} \theta_Z \\ \theta_{BZ} \end{bmatrix} = 0(b_g) + \begin{bmatrix} 1 \\ 0 \end{bmatrix} + C_1\begin{bmatrix} k_3 \\ k_2 \end{bmatrix}\exp(-k_2t) + C_2\begin{bmatrix} +1 \\ -1 \end{bmatrix}\exp(-k_3t)$$

where C_1 and C_2 are arbitrary constants.

Finally, let us consider the case $S/V \to 0$, b_s, b_g and v_{in}/S being constant. After going to a new time scale $\tau = (S/V)t$, we obtain

$$\frac{d\bar{c}_A}{d\tau} = k_1b_g\bar{c}_A\theta_Z(-1 + \bar{c}_A) - k_3\theta_{BZ}\bar{c}_A + \frac{v_{in}}{S}\frac{b_{g,in}}{b_s}(\bar{c}_{A,in} - \bar{c}_A)$$

$$\varepsilon\frac{d\theta_Z}{d\tau} = -k_1b_g\bar{c}_A\theta_Z + k_3\theta_{BZ}$$

$$\varepsilon\frac{d\theta_{BZ}}{d\tau} = k_2(1 - \theta_Z - \theta_{BZ}) - k_3\theta_{BZ}$$

Equations of "fast motions" are linear and have a unique steady-state solution

$$\theta_Z = \frac{k_2k_3}{k_1b_g\bar{c}_Ak_2 + k_2k_3 + k_3k_1b_g\bar{c}_A}$$

$$\theta_{BZ} = \frac{k_1b_g\bar{c}_Ak_2}{k_1b_g\bar{c}_Ak_2 + k_2k_3 + k_3k_1b_g\bar{c}_A}$$

which is stable.

At $\varepsilon = S/V \rightarrow 0$, the Tikhonov theorem is applicable, hence starting from sufficiently small ε, we can use the quasi-steady-state approximation.

Of great importance is the fact that the quasi-steady-state approximation is the solution asymptote of the initial system at $\varepsilon \rightarrow 0$, but it is applied at finite ε. To establish a starting value from which this approximation can be used with the prescribed accuracy is a rather difficult problem in each particular case.

In the intriguingly entitled publication "The steady-state approximation, fact or fiction?" by Farrow and Edelson [41] presents calculated data on the unsteady-state behaviour of a complex chemical reaction including 81 steps. The reaction mixture consists of 50 substances. Numerical calculation shows a great variety of unsteady-state characteristics of a complex reaction. This variety cannot be interpreted in the narrow framework of the quasi-steady-state hypothesis. Nevertheless, the authors discriminate between the ranges of parameters and time intervals within which this hypothesis is confirmed by numerical experiments.

The initial system can be constructed as a series with respect to powers of ε [39]. A zero approximation here is a solution of the degenerated system. This approach is, however, very rarely used since the increase of accuracy results in a significant complication of calculations.

In conclusion, it must be noted that the equations to describe the transient behaviour of heterogeneous catalytic reactions, usually have a small parameter $\varepsilon = N^{\mathrm{s}}_{\mathrm{tot}}/N^{\mathrm{g}}_{\mathrm{tot}}$. Here $N^{\mathrm{s}}_{\mathrm{tot}} = b_{\mathrm{s}} S =$ the number of active sites (mole) in the system and $N^{\mathrm{g}}_{\mathrm{tot}} = b_{\mathrm{g}} V =$ gas quantity (mole). Of most importance is the solution asymptotes for kinetic equations at $N^{\mathrm{s}}_{\mathrm{tot}}/N^{\mathrm{g}}_{\mathrm{tot}} \rightarrow 0$, b_{s}, b_{g} and v_{in}/S being constant. Here we deal with the parameter S/V which is readily controlled in experiments. The case is different for the majority of the asymptotes examined. The parameters with respect to which we examine the asymptotes are difficult for control. For example, we cannot, even in principle, provide an infinite increase (or decrease) of such a parameter as the density of active sites, b_{s}. Moreover, this parameter cannot be varied essentially without radical changes in the physico-chemical properties of the catalyst. Quasi-stationarity can be claimed when these parameters lie in a definite range which does not depend on the experimental conditions.

To answer the question whether quasi-stationarity can be observed in our kinetic model at $\varepsilon \rightarrow 0$ it is first necessary to examine a subsystem of fast motions ("a fast subsystem") so as to establish if it has a unique and stable steady-state solution.

5. Uniqueness, multiplicity and stability of steady states

For heterogeneous catalytic reactions a "fast subsystem" must, as a rule, correspond to the conversions of surface substances. Let these substances be $Z_1, \ldots, Z_n$. A mechanism for surface conversions is of the form

$$\alpha_{p1}Z_1 + \ldots + \alpha_{pn}Z_n \rightleftarrows \beta_{p1}Z_1 + \ldots + \beta_{pn}Z_n \qquad p = 1, \ldots, N$$

This mechanism is obtained after eliminating gas-phase substances from the global one.

Under the assumption of the law of acting surfaces we obtain

$$w_p(\vec{z}) = w_p^+(\vec{z}) - w_p^-(\vec{z}) = k_p^+ \prod_{i=1}^{n} z_i^{\alpha_i} - k_p^- \prod_{i=1}^{n} z_i^{\beta_i}$$

Here all concentrations of gaseous substances are suggested to be constant and are included as co-factors into the rate constants $k_p^{\pm}$.

Kinetic equations take the form

$$\dot{z} = \sum_{p=1}^{n} \gamma_p w_p(z) \tag{151}$$

where the vector $\vec{\gamma}_p$ has the coordinates $(\gamma_p)_i = \beta_{pi} - \alpha_{pi}$. These equations resemble eqns. (18) and (19) describing chemical conversions in closed systems at a constant volume. But there is an essential difference. It is possible that no PDE exist for eqn. (151). A steady-state point for eqn. (151) is not an obligatory PDE. Such coincidence is an exception rather than a rule.

For eqn. (151) at least one positive law of conservation exists corresponding to the constancy of the total amount (or concentration) of catalyst in the system. In the simplest case, this law is expressed as $b_s = \Sigma_i z_i = \text{const.}$ (where z_i is the concentration of Z_i).

Further discussion will be devoted largely to the investigation of the properties for the kinetic models of surface conversions and primarily to the analysis of the number and stability of solutions for eqn. (151).

For this analysis it is of importance to classify mechanisms (their associated kinetic models here are the sets of quasi-steady-state equations) to answer the question of what class of mechanisms possesses a unique and stable solution for the quasi-steady-state equations, and which one can have several solutions, i.e. several steady states.

5.1 LINEAR MECHANISMS

The simplest class of catalytic reaction mechanisms are linear ones. This term was introduced by Temkin (see Chap. 2). Linear mechanisms are those that contain only elementary $Z_i \rightleftarrows Z_j$-type steps. Hence every reaction involves the participation of only one molecule of the intermediate substance.

The theory of linear mechanisms is a sufficiently developed field of catalytic kinetics. Let us present its principal results. In accordance with the law of acting surfaces, kinetic equations for a linear mechanism are of the form

$$\dot{\vec{z}} = \vec{K}\vec{z} \tag{152}$$

where K is the square matrix whose diagonal elements are non-positive and off-diagonal elements are non-negative. By virtue of the existence of the linear law of conservation $\Sigma_i z_i = \text{const.}$, the sums of elements in every column of the matrix $\vec{K}$ are equal to zero. The matrix itself is of the form $\vec{K} = (k_{i,j})$ where the k_{ij} is the rate constant of reactions $Z_j \rightarrow Z_i (i \neq j)$ and

$$k_{ij} = - \sum_{l=i} k_{li} \qquad \text{if } i = j$$

The dynamics for eqn. (152) is determined by the eigenvalues of the matrix $\vec{K}$. It can readily be tested that if at the initial instant $t = 0$ all $z_i \geqslant 0$ then, according to eqn. (152), we also have $z_i \geqslant 0$ at $t > 0$ (it is a special case of the general statements concerning ω-invariance of the orthant for non-negative vectors relative to chemical kinetic equations; see, for example, ref. 7). Therefore for eqn. (152) there exist ω-invariant simplexes of the type $z_i \geqslant 0$, $\Sigma_i z_i = \text{const.} > 0$. In accordance with the existence of these simplices, it is not difficult to obtain the following properties for the eigenvalues of the matrix $\vec{K}$:

(1) real parts of the $\vec{K}$ eigenvalues are non-positive;

(2) $\vec{K}$ has no purely imaginary eigenvalues.

Proof is based on simple geometrical considerations. For example, let us prove property (2). Assume the opposite, then the hyperplane $\Sigma z_i = \text{const.}$ contains a two-dimensional plane where the $\vec{K}$ action reduces to a rotation around a fixed non-negative point. The intersection of this plane with the ω-invariant simplex is a ω-invariant polyhedron that must transform into itself when rotating by an arbitrary angle, which is impossible.

Properties (1) and (2) also result from the estimates of the eigenvalues using Gershgorin circles [29]: any eigenvalue λ of the matrix $\vec{K}$ lie on a complex plane in one of the circles of type $|\lambda - k_{ii}| \leqslant |k_{ii}|$ or otherwise

$$|\lambda + \sum_{j \neq i} k_{ji}| \leqslant \sum_{j \neq i} k_{ij} \tag{153}$$

Let us recall that k_{ji} is the rate constant of reaction $Z_i \rightarrow Z_j$. The number of such Gershgorin circles is the same as the number of substances. The above estimates (153) do not permit us to judge the fold of a zero eigenvalue, since every circle contains 0. Matrix $\vec{K}$ always has a zero eigenvalue with a non-negative eigenvector. It results, for example, from the existance of ω-invariant simplexes. Each such simplex for eqn. (152) has a fixed point $\vec{z}_0$: $\vec{z} = \vec{K}\vec{z}_0 = \vec{0}$; $\vec{z}_0$ is an eigenvector corresponding to a zero eigenvalue. If each of the simplices $z_i \geqslant 0, \Sigma z_i = \text{const.} > 0$ contains a unique fixed point, then the characteristic subspace corresponding to a zero eigenvalue is one-dimensional (it is only slightly less evident than it seems at a first glance and accurately substantiating this statement, a reader can check his knowledge of linear algebra). In the opposite case there exists an additional linear law of conservation, and every simplex decomposes into ω-invariant balance polyhedra of lower dimension.

Let us establish conditions for the existence of additional linear laws of conservation. Consider one invariant plane P; $\Sigma_i z_i = \text{const.} > 0$. Let there exist an additional linear law of conservation $L(\vec{z})$ = const. Each equation $L(\vec{z}) = C$ accounts for a hyperplane in P. With two values $C = C_1, C_2$ this hyperplane is a reference surface for a ω-invariant simplex in P (it is determined in P by the inequalities $z_i \geqslant 0$). Intersections of the hyperplanes $L(\vec{z}) = C_1, C_2$ with this simplex will be faces designated as S_1, S_2. In particular, S_1 and S_2 can consist of one vertex. They correspond to the sets of substances whose concentrations on S_1 and S_2 can be zero. These sets are different, i.e. S_1 and S_2 do not intersect. Faces S_1 and S_2 are invariant [a law of conservation is $L(\vec{z}) = C$], therefore corresponding substances cannot transform into any others whose concentrations on S_1(or S_2) equal zero. Thus, in a linear system, additional laws of conservation can exist only in the case where there are at least two groups of substances with the following properties: (1) the groups have no common substances; (2) substances in each of these groups cannot transform into any others not entering into their group. But inside these groups substances can undergo mutual transformations. Such groups of substances can be called autonomous. The simplest example of such cases is provided by the scheme of two parallel reactions: $A \xrightarrow{1} B$, $A \xrightarrow{2} C$. Here two autonomous groups form substances B and C. An additional linear law of conservation is of the form $(B/k_1) - (C/k_2)$ = const. But for the reaction A → B → C a similar law is absent.

The presence (or absence) of autonomous groups of substances is easily checked. We assume they are absent. As usual, a more rigorous condition compared with the absence of two autonomous groups is fulfilled. It is the condition of an orientally connected reaction graph. (Here we speak about graphs of linear mechanisms when nodes are substances and edges are elementary reactions.)

A graph is called orientally connected (connected digraph) if from any node we can get to any other along its edges moving in the direction of the arrows. Oriented connectivity is closely associated with weak reversibility (see Sect. 5.3) but does not coincide with it.

Let us examine the properties of eqn. (152) under the assumption of oriented connectivity. Let us fix some ω-invariant simplex $\vec{D}_0$: $z_i \geqslant 0$, $\Sigma_i z_i = C > 0$. $\vec{D}_0$ has a unique steady state $\vec{z}^\circ$. Vector $\vec{z}^\circ$ is positive since, due to the connectivity of the reaction digraph, no steady-state points exist on the boundary $\vec{D}_0$. Indeed, if we assume the opposite (some components $\vec{z}^\circ$ are zero), we obtain k_{ji} for such i and j as $z_i^\circ \neq 0$ and $z_j^\circ = 0$. But from this it follows that, moving along the direction of arrows in the graph of the reaction mechanism, we cannot get from the substances for which $z_i^\circ \neq 0$ to those for which $z_j^\circ = 0$, and this is contrary to oriented connectivity (the arrows in the reaction graph correspond, naturally, to the elementary reactions with non-zero rate constants).

As for closed systems, $\vec{D}_0$ has a function monotonically decreasing along the solutions of eqn. (152)

$$G_L(\vec{z}, \vec{z}^\circ) = \sum_i |z_i - z_i^\circ| \qquad (154)$$

Index L is given to G_L to distinguish it from the Lyapunov function for closed systems. Strictly speaking, it is not the Lyapunov function, since it cannot be differentiated on the hyperplanes prescribed by the equations $z_i = z_i^\circ$. Therefore, instead of estimating its derivative by virtue of eqn. (152), let us determine its decrease for a finite period of time τ. Actually, we will find an ergodicity coefficient [42] for the matrix $\exp \tau\vec{K}$

$$G_L(\vec{z}(t + \tau), \vec{z}^\circ) \leqslant G_L(\vec{z}(t), \vec{z}^\circ) \frac{1 - [(k\tau)^m \exp(-(k + q)\tau)]}{nm!} \tag{155}$$

where q is the maximum for the sum of the rate constants for elementary reactions wherein only one of the substances is consumed (the maximum is taken with respect to substances), m is the maximum length of the shortest direct path binding pairs of substances in the reaction graph (for each pair of substances A_1 and A_2 the shortest path from A_1 to A_2 is chosen and the pair for which this path is the longest is found; pairs of A_1 and A_2 and of A_2 and A_1 are thought to be different, since a directed path from the first to the second component of the pair is searched for), and k is the lowest non-zero rate constant.

Estimate (155) can be quite easily improved, but for us its existence is of itself important. Let us denote

$$\lambda_\tau = 1 - \frac{(k\tau)^m \exp[-(k + q)\tau]}{nm!} \tag{156}$$

It is evident that $G_L(\vec{z}(t + l\tau), \vec{z}^\circ) \leqslant G_L(\vec{z}(t), \vec{z}^\circ)\lambda_\tau^l$.

It is essential that the estimate of the type (155) takes place and for the convergence of various trajectories having different $\vec{z}(0)$ but lying in the same $\bar{D}_0(\Sigma z_i(0)$ is the same)

$$G_L(\vec{z}^1(t + \tau), \vec{z}^2(t + \tau)) \leqslant \lambda_\tau G_L(\vec{z}^1(t), \vec{z}^2(t)) \tag{157}$$

For linear systems with variable rate constants*, the estimate (155) becomes meaningless since, although it is possible that a fixed point is absent, eqn. (157) preserves their validity and all trajectories are converging. The only difference, compared with autonomous systems, is that instead of q and k in eqn. (156) their upper and lower, respectively, time limits must be taken. It is natural that $\sup q < \infty$ and $\inf k > 0$ must be fulfilled.

Chapter 4 presents several new results for linear mechanisms. Here we will give a short statement of the fact that a set of quasi-steady-state equations corresponding to a linear mechanism is that of linear algebraic equations. This set has a unique solution and therefore the steady state of the system in which a given reaction takes place following a linear mechanism (at given balances) is unique and stable.

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* Let the reader excuse us for such a word-combination "variable constant", but we have to use it.

For linear sets of differential equations having an ω-invariant limited polyhedron, an eigenvalue for the matrix of the right-hand side can be either zero or have a negative real part, i.e. after eliminating linear laws of conservation, a steady-state point of these systems becomes asymptotically stable.

If the reaction graph is orientally connected, the phase space of a linear system (a balance polyhedron) has a metric (154) in which all trajectories of the system monotonically converge and the distance between them tends to zero at $t \to \infty$. This holds true for both constant and variable coefficients (rate constants), if in the latter case it is demanded that all rate constants have upper and positive lower limits ($0 < \alpha < k(t) < \beta < \infty, \alpha, \beta = \text{const}$).

What reactions have linear mechanisms? Primarily these are enzyme reactions [43, 44]. A typical scheme for enzyme catalysis is the Michaelis–Menten mechanism: (1) E + A → ES; (2) ES → P + S, where S and P are the initial substrate and product, respectively, and E and ES are various forms of enzymes.

5.2 MECHANISMS WITHOUT INTERMEDIATE INTERACTIONS

Linear mechanisms are rather common for heterogeneous catalytic reactions. Examples are given and examined by Cornish-Bowden [43] and Kernevez [44]. Non-linear mechanisms, i.e. those including interactions of several molecules of the same or different surface substances, however, are more frequent. For example, a widely spread step of dissociative adsorption is non-linear.

For us it is important to distinguish between the classes of mechanisms possessing uniqueness of steady state at any value of the reaction parameters. It will be shown that one of these classes is that of mechanisms having no steps consisting of interaction between intermediates. All steps of these mechanisms are of the type $n\,\mathrm{A} \to m\,\mathrm{B}$, i.e. there is one substance on both the right and on the left sides. The difference of these mechanisms from linear mechanisms is that stoichiometric coefficients can be greater than unity. This difference is, however, not very essential since it does not affect the form of metric (154) where trajectories converge. To illustrate this, let the unique linear law of conservation be of the form $\Sigma z_i = \text{const.}$ and the graph of a linear mechanism obtained from the reaction mechanism involving no intermediate interactions by substituting all stoichiometric coefficients by 1 is orientally connected (or, which is the same, its bipartite digraph is connected). The kinetic equations will be

$$\dot{z}_i = -\sum_{j,i} dk_{ijd} z_i^d + \sum_{j,d} dk_{jid} z_j^d \tag{158}$$

where k_{ijd} are the rate constants for the reaction $d\,\mathrm{Z}_i \to d\,\mathrm{Z}_j$. The Jacobian matrix for eqn. (158) will be written as

$$\frac{\partial \dot{z}_i}{\partial z_l} = -\left(\sum_{j,d} d^2 k_{ijd} z_i^{d-1}\right) \delta_{il} + \sum_{d,l} d^2 k_{lid} z_l^{d-1} \tag{159}$$

Note that matrix (159) coincides with that of the kinetic constants for the linear mechanism whose rate constant for the reaction $A_i \to A_j$ is

$$q_{ij}(\vec{z}) = \sum_d d^2 k_{ijd} z_i^{d-1}$$

Each internal point $\vec{z}$ of the balance polyhedron has a set of constants q_{ij} corresponding to the orientally connected graph of the mechanism. Steady-state points (and, more extensively, positive semi-trajectories) on the balance polyhedron boundary are absent since it would contradict the oriented connectivity of the graph for the initial mechanism (a reader can prove this as an exercise). Therefore for any $\tau > 0$ there exist such $\delta > 0$ that, for any solution of eqn. (158) lying in a given balance polyhedron at $t = 0$, we obtain $z_i(t) > \delta$ at $t > \tau$ and all values of i. Let us consider two solutions for eqn. (158), $\vec{z}^{(1)}(t)$ and $\vec{z}^{(2)}(t)$, lying in the same balance polyhedron $\vec{D}_0$.

At every point of $\vec{D}_0$ the Jacobian matrix is that of kinetic constants for a certain linear mechanism (whose exponent is stochastic). Hence at $t > 0$ we have $G_L[\vec{z}^{(1)}(t), \vec{z}^{(2)}(t)] \leqslant G_L[\vec{z}^{(1)}(0), \vec{z}^{(2)}(0)]$ in accordance with the oriented connectivity of the graph for the initial mechanism and the fact that, starting from an arbitrary $\tau > 0$ (at $t > \tau$), the inequalities $0 < \alpha < q_{ij}[\vec{z}(t)] < \beta$ $[\vec{z}(0) \in \vec{D}_0]$ are fulfilled. The latter inequalities have certain α and β independent of $\vec{z}(0)$ and determined only by τ, $\vec{D}_0$ and a set of constants of the initial mechanism. In this case

$$G_L[\vec{z}^{(1)}(t), \vec{z}^{(2)}(t)] \to 0 \text{ when } t \to \infty.$$

When the principal linear law of conservation is of the form $\Sigma m_i z_i =$ const., elementary reactions entering into the mechanism without interactions are $(d/m_i)A_i \to (d/m_j)A_j$ and the corresponding kinetic equations and Jacobian matrix will be

$$\begin{aligned} \dot{z}_i &= -\sum_{j,d} (d/m_i) k_{ijd} z_i^{d/m_i} + \sum_{j,d} (d/m_j) k_{jid} z_j^{d/m_j} \\ J_{il} &= \frac{\partial \dot{z}_i}{\partial z_l} = -\sum_{j,d} \frac{d^2}{m_i^2} k_{ijd} z_i^{d/m_i - 1} \delta_{il} + \sum_{d,l} \frac{d^2}{m_i m_l} k_{lid} z_l^{d/m_l - 1} \end{aligned} \tag{160}$$

Matrix $\vec{J}$ possesses the properties

(1) its non-diagonal elements are non-negative and

(2) the sum of elements of any column with the coefficients m_i is equal to zero

$$\sum_i m_i \frac{\partial \dot{z}_i}{\partial z_l} \equiv 0$$

As in the previous paragraph where we considered the case $m_i \equiv 1$, we obtain (1) eigenvalues of $\vec{J}$ have a non-positive real part and (2) purely imaginary eigenvalues are absent. Further, for any two solutions $\vec{y}^{(1)}$ and

$\vec{y}^{(2)}$, the equations $\dot{\vec{y}} = \vec{J}(t)\vec{y}$, where the matrix $\vec{J}(t)$ satisfies conditions (1) and (2) at any t, the value of $\Sigma_{i=1}^{n} m_i |\vec{y}_i^{(1)} - \vec{y}_i^{(2)}|$ does not increase. But if the condition of oriented connectivity is fulfilled (uniformly with respect to t), for any pair of indices i, j ($i \neq j$) there will exist such a set of the indices $k_1, \ldots, k_m$, as $J_{ik_1}(t), J_{k_1k_2}(t), \ldots, J_{k_mj}(t) > \alpha > 0$ (α = const.) at all t. [It should be noted that the set $k_1, \ldots, k_m$ can also be assumed to be empty if $J_{ij}(t) > \alpha > 0$.] Then for any two solutions $\vec{y}^{(1)}(t)$ and $\vec{y}^{(2)}(t)$ with the same value for the law of conservation, $\Sigma m_i y_i^{(1)} = \Sigma m_i y_i^{(2)}$, we will obtain the distance $\Sigma_{i=1}^{n} m_i |y_i^{(1)}(t) - y_i^{(2)}(t)| \to 0$ at $t \to \infty$.

As in the case $m_i = 1$, in accordance with the above properties of Jacobian matrix (160), it follows that, under the assumption of the oriented connectivity for the reaction mechanism involving no intermediate interactions, the time shift is the phase space (or balance polyhedron) compression in the metric

$$\rho(\vec{z}^{(1)}, \vec{z}^{(2)}) = \sum_{i=1}^{n} m_i |z_i^{(1)} - z_i^{(2)}| \tag{161}$$

Any two solutions lying in the same balance polyhedron converge in the metric (161) and $\rho(\vec{z}^{(1)}(t), \vec{z}^{(2)}(t)) \to 0$ at $t \to \infty$. It results, in particular, in the existence, uniqueness and asymptotic stability (in the large) of the steady state in the balance polyhedron. This was confirmed by Vol'pert et al. [45] and partly and simultaneously by Bykov et al. [46–48]. (Note that all the considerations given also hold for the $n\mathrm{A} \to \Sigma m_i B_i$- type reaction systems.)

Let us consider a structure for the multitude of steady states for eqns. (158) or (160) in the positive orthant. For linear systems $\dot{\vec{z}} = \vec{K}\vec{z}$ it forms either a ray (in the case of the unique linear law of conservation) emerging from zero, or a cone formed at the linear subspace ker K intersection with the orthant. The structure for the multitude of steady states for the systems involving no intermediate interactions is also rather simple. Let us consider the case of only one linear law of conservation $\Sigma m_i z_i = c$ = const. and examine the dependence of steady-state values z_i^{st} on c. Using eqn. (160), we obtain

$$\begin{aligned} \vec{J}(\vec{z}^{\,\mathrm{st}}) \frac{\mathrm{d}\vec{z}^{\,\mathrm{st}}}{\mathrm{d}c} &= 0 \\ \sum m_i \frac{\mathrm{d}z_i^{\mathrm{st}}}{\mathrm{d}c} &= 1 \end{aligned} \tag{162}$$

Let us assume the connectivity of the reaction mechanism digraph. It then follows from eqn. (162) that

$$\frac{\mathrm{d}z_i^{\mathrm{st}}}{\mathrm{d}c} > 0 \tag{163}$$

Consequently, z_i^{st} monotonically depends on the balance $c = \Sigma m_i z_i$. Condition (163) can be rewritten as

$$\frac{dz_i^{st}}{dz_k} > 0 \tag{163'}$$

where z_k is some chosen concentration (degree of coverage). The absence of interaction steps, e.g. of the type

$$\alpha_i Z_i + \alpha_j Z_j + \ldots \rightarrow \beta_k Z_k + \ldots \qquad (\alpha_i, \alpha_j \neq 0) \tag{164}$$

is a sufficient (under oriented connectivity) but not a necessary condition for the validity of eqn. (163). Inequalities (163) can also be fulfilled for some mechanisms involving interaction steps. They can be applied to prove uniqueness of a positive steady state. For this purpose, in addition to eqn. (163) it is necessary to prove that a positive steady state is unique for at least one value of c. As usual, it is simpler to show for c values that are close to zero. In some cases it is possible to find explicit expressions for $z_i^{st}(z_k)$ functions. If this function is unambiguous, the fulfilment of conditions (163) is sufficient for a positive steady state to be unique. Moreover, in this case it suffices that $\Sigma m_i dz/dz_k > 0$.

Let us give an example.

Example 7. Hydrogen oxidation on platinum. In accordance with the range of parametric variations, this reaction can follow two different mechanisms [49].

$$\begin{aligned}
&(1)\ O_2 + 2Z \rightarrow 2ZO\\
&(2)\ H_2 + 2Z \rightleftarrows 2ZH\\
&(3)\ ZO + ZH \rightarrow ZOH + Z\\
&(4)\ H_2 + 2ZOH \rightarrow 2Z + 2H_2O\\
&(5)\ H_2 + ZO \rightarrow Z + H_2O
\end{aligned} \tag{A}$$

or

$$\begin{aligned}
&(1)\ O_2 + 2Z \rightarrow 2ZO\\
&(2)\ H_2 + 2Z \rightleftarrows 2ZH\\
&(3)\ ZO + ZH \rightarrow ZOH + Z\\
&(4)\ ZH + ZOH \rightarrow 2Z + H_2O\\
&(5)\ H_2 + ZO \rightarrow Z + H_2O
\end{aligned} \tag{B}$$

Designating the concentrations of Z, ZO, ZH, and ZOH by z_1, z_2, z_3, and z_4 and assuming that the concentrations of substances in the gas phase of O_2 and H_2 enter as co-factors into the rate constants of the appropriate reactions, we can write a kinetic model for mechanism (A) as

$$\dot{z}_2 = 2k_1 z_1^2 - k_3 z_2 z_3 - k_5 z_2$$

$$\dot{z}_3 = 2k_2 z_1^2 - 2k_{-2} z_3^2 - k_3 z_2 z_3$$

$$\dot{z}_4 = k_3 z_2 z_3 - 2k_4 z_4^2$$

where $z_1 + z_2 + z_3 + z_4 = \text{const}$. Here steady-state concentrations z_i are expressed by the equations ($\dot{z}_2 = \dot{z}_3 = \dot{z}_4 = 0$)

$$z_1 = \left[\frac{z_2(k_3 z_3 + k_5)}{2k_1}\right]^{1/2}$$

$$z_2 = \frac{2k_1 k_{-2} z_3^2}{k_3 z_3 (k_2 - k_1) + k_2 k_5}$$

$$z_4 = \left(\frac{k_3 z_2 z_3}{2k_4}\right)^{1/2}$$

In this case no boundary steady states exist, hence we will have only positive solutions and $k_2 k_5 + k_3(k_2 - k_1)z_3 > 0$. Under this condition it can easily be shown that $\mathrm{d}z_1/\mathrm{d}z_3$, $\mathrm{d}z_2/\mathrm{d}z_3$, and $\mathrm{d}z_4/\mathrm{d}z_3$ are positive, i.e. the internal steady state is unique. In this case condition (163′) is fulfilled and despite the mechanism involving an interaction step between various intermediates, the kinetic model has only one positive steady-state solution.

Mechanism (B) corresponds to the kinetic model

$$\dot{z}_2 = 2k_1 z_1^2 - k_3 z_2 z_3 - k_5 z_2$$

$$\dot{z}_3 = 2k_2 z_1^2 - 2k_{-2} z_3^2 - k_3 z_2 z_3 - k_4 z_3 z_4$$

$$\dot{z}_4 = k_3 z_2 z_3 - k_4 z_3 z_4$$

where, as before, $z_1 + z_2 + z_3 + z_4 = \text{const}$. Steady-state values for its variables can be written from the equations $\dot{z}_2 = \dot{z}_3 = \dot{z}_4 = 0$

$$z_1 = \left[a k_4 z_3^2 + \frac{k_{-2}(b + c z_3) z_3^2}{k_2 (b + c z_3)}\right]^{1/2}$$

$$z_2 = \frac{k_4 [a z_3^2/(b + c z_3)]}{k_3}$$

$$z_4 = \frac{a z_3^2}{b + c z_3}$$

where $a = 2k_1 k_{-2}$, $b = k_2/k_3 k_4 k_5$, and $c = k_2 k_4 - 2k_1 k_4$. For the case in which, along with the boundary steady state ($z_1 = z_2 = z_3 = 0$, $z_4 = \text{const.}$), a positive steady state also exists, it is necessary that $b + c z_3 > 0$. Under this condition $\mathrm{d}z_1/\mathrm{d}z_3$, $\mathrm{d}z_2/\mathrm{d}z_3$, and $\mathrm{d}z_4/\mathrm{d}z_3$ are positive. Hence though mechanism (B) involves an interaction step between various intermediates, it can have only an unique internal steady state.

For mechanisms having interaction steps between various intermediates ($Z_i + Z_j \rightarrow$), it is also possible that the condition of a monotony (163′) is not fulfilled. (Fulfilment of this condition can be thought to be an exception rather than a rule.) Simple mechanisms of this type tolerating the existence of several steady states will be examined comprehensively in Chap. 5.

Let us emphasize the most essential conclusion that can be drawn in this section: a sufficient condition for the uniqueness of steady states in catalytic reactions is the absence of interaction steps for various intermediates in the detailed reaction mechanisms. Their presence is a necessary condition for the multiplicity of steady-state values for the catalytic reaction rates. This principal statement possesses an evident discrimination property. If some experiment is characterized by the multiplicity of steady states and its interpretation suggests a law of acting surfaces, the description of this experiment implies a detailed mechanism that must contain interaction steps of various intermediates.

5.3 QUASI-THERMODYNAMIC HORN AND JACKSON SYSTEMS

Studies of linear systems and systems without "intermediate interactions" show that a positive steady state is unique and stable not only in the "thermodynamic" case (closed systems). Horn and Jackson [50] suggested one more class of chemical kinetic equations possessing "quasi-thermodynamic" properties, implying that a positive steady state is unique and stable in a reaction polyhedron and there exist a global (throughout a given polyhedron) Lyapunov function. This class contains equations for closed systems, linear mechanisms, and intersects with a class of equations for "no intermediate interactions" reactions, but does not exhaust it. Let us describe the Horn and Jackson approach.

Let the reaction mechanism be prescribed in the form

$$\alpha_{s1}A_1 + \ldots + \alpha_{sn}A_n \rightleftarrows \beta_{s1}A_1 + \ldots + \beta_{sn}A_n \tag{165}$$

A combination of symbols A_i with non-negative integer coefficients in the right- and left-hand sides of the stoichiometric equations for reaction steps will be called complexes. Designating each complex by one letter y, the reaction mechanism can be represented as

$$y_k \rightleftarrows y_j \tag{166}$$

for certain pairs y_k, y_j. A list of reactions (166) can also be represented as a graph. For example, for the oxidation of CO on Pt following the Eley–Rideal (impact) mechanism we can write (considering only intermediates and omitting the symbols for the gas-phase components)

$$\begin{array}{ccc} [2Z] \rightleftarrows [2ZO] \\ [ZO] \rightarrow [Z] \end{array} \qquad \begin{pmatrix} y_1 \rightleftarrows y_2 \\ y_3 \rightarrow y_4 \end{pmatrix}$$

For the Langmuir–Hinshelwood (adsorption) mechanism we will have

$$\begin{matrix} [ZO + ZCO] \rightarrow [2Z] \rightleftarrows [2ZO] \\ [ZO] \rightarrow [Z] \rightleftarrows [ZCO] \end{matrix} \qquad \begin{pmatrix} y_6 \rightarrow y_1 \rightleftarrows y_2 \\ y_3 \rightarrow y_4 \rightleftarrows y_5 \end{pmatrix}$$

For each pair of y_j and y_k complexes, w_{jk} represents the rate of reactions $y_j \rightarrow y_k$ (and w_{kj} is similarly the rate of $y_k \rightarrow y_j$ or, which is the same, $y_j \leftarrow y_k$).

A new variable is then introduced which is the rate of "concentration" variation for a given complex. It is determined as the difference of two sums. Rates of all the reactions to "form" this complex are added and from the sum obtained we will subtract that of the rates for all the reactions to "consume" this complex

$$g_j = \sum_k w_{kj} - \sum_k w_{jk} \tag{167}$$

We use quotations for the words complex "concentration", "form", and "consume" since they have no direct physical meaning. The use, by analogy with the Horn–Jackson concept of a "complex" could be attempted of a term "activated complex" from the theory of absolute rates, but after some speculation we decided that this analogy would not be very reasonable. Values of g_j can be interpreted if they are associated with the rates of concentration variations for reactants, namely by giving a designation α_{ij} to the coefficient that the ith substance has when it enters the jth complex. We then obtain

$$\dot{c}_i = \sum_j g_j \alpha_{ij} \tag{168}$$

[We examine conversions only of surface compounds or the reaction at a constant volume; in other cases the analog (168) cannot be written either (see Sect. 1).]

Such a composition of the mixture for which all $g_j = 0$, i.e. the rate of each complex "formation" is equal to that of its "consumption", is called a point of complex balance (PCB).

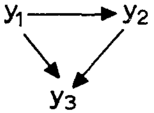
The first of the principal Horn and Jackson results is as follows. If the system obeys the law of mass action (or acting surfaces), then if it has a positive PCB it demonstrates a "quasi-thermodynamic" behaviour, i.e. its positive steady state is unique and stable and a global Lyapunov function exists.

It is evident that each PDE ($w_{kj} = w_{jk}$) is PCB. The opposite is incorrect. For example, though any steady-state point of the linear mechanism is a PCB (complexes are substances, $Z_i = y_i$), the principle of detailed equilibrium for it is not always valid (if the system is open).

A second result consists in the determination of the class of mechanisms which always have a positive PCB. For its description, let us consider a graph of complex conversions. It nodes are y_i and its edges connect those y_j and y_k for which a list of steps has either $y_j \rightarrow y_k$ or $y_k \rightarrow y_j$ reactions. In case both reactions take place ($y_j \rightleftarrows y_k$), the two arrows indicate different reaction directions. A graph is called connected if from any of its nodes we can get into any other by moving along its edges (the orientation of edges does not matter since we can move in both the forward and backward direction). If the graph is unconnected it breaks into several connected fragments (components). Let us denote the number of complexes as M, that of connected graph components for their conversions as l and the number of linearly independent reactions (their stoichiometric vectors) as S. A first Horn and Jackson condition for quasi-thermodynamic behaviour is

$$M - 1 = S \tag{169}$$

The number of complexes minus that of connected components of the graph for their conversions equals the number of linearly independent reactions (stoichiometric vectors). A second Horn and Jackson condition for quasi-thermodynamic behaviour is the weak reversibility of the graph for complex conversions. This graph is called weakly reversible if any of its connected components contain a route to get from any node to any other moving in the direction of its arrows. For example, the scheme



(170)

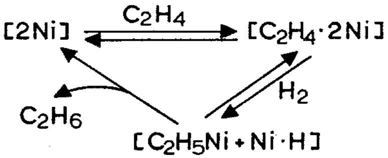
does not seem to be weakly reversible since it is impossible to get from y_3 to y_1 and y_2 and from y_2 to y_1 moving in the direction of the arrows.

Horn and Jackson [50], M. Feinberg [51], Horn [52] and Feinberg and Horn [53] showed that if the scheme of complex conversions is weakly reversible and (most essential) the conditions (169) is fulfilled, the system always has a PCB and hence demonstrates "quasi-thermodynamic" behaviour. The weak reversibility condition seems to be less essential since, for its fulfilment, it is sufficient to suggest that all steps are reversible assuming, if necessary, the rate constant for a reversible step to be sufficiently low. Hence the main difficulty for the application of the results of Horn, Jackson and Feinberg to a concrete reaction system can be the impossibility of fulfilling eqn. (169), which cannot be overcome by small additions to the equations.

Let us check these conditions for the oxidation of CO on Pt. The Eley–Rideal (impact) mechanism has four complexes, $M = 4$, two connected components $[2\mathrm{Z}] \rightleftarrows [2\mathrm{ZO}]$, $[\mathrm{ZO}] \rightarrow [\mathrm{Z}]$, and two stoichiometric vectors $\begin{bmatrix} -2 \\ 2 \end{bmatrix}$, $\begin{bmatrix} 1 \\ -1 \end{bmatrix}$ and they are linearly dependent (proportional), i.e. $S = 1$, $M - l = 4 - 2 = 2 > 1$. In addition, for this mechanism the condition of weak reversibility is not fulfilled. But the mechanism does not involve interaction steps of various intermediates. Hence, though two Horn and Jackson conditions are not fulfilled, a steady state is unique and stable.

For the Langmuir–Hinshelwood mechanism, $M = 6$, $l = 2$, $S = 2$, and eqn. (169) is not fulfilled. It is also impossible to fulfil the condition of weak reversibility.

An interesting example for which eqn. (169) is valid, but the mechanism has an interaction step of various intermediates, is ethylene hydrogenation on nickel, i.e. the Twigg mechanism [54]



(171)

In this case, $M = 3$, $l = 1$, and $S = 3$ but among the stoichiometric vectors only two are linearly independent. Thus $3 - 1 = 2$ and the first Horn and Jackson condition is fulfilled. Also fulfilled is the second condition, i.e. weak reversibility of the graph for complex conversions. Since both conditions are fulfilled, a steady state is unique and stable despite the mechanism having two interaction steps for various intermediates.

Hence, in addition to the systems without intermediate interactions, the conditions for the existence of a PCB account for one more class of mechanisms that always have an unique and stable steady state. In conclusion, let us emphasize that, on the basis of the Rozonoer approach [55, 56], Orlov has recently extended the Horn and Jackson results to the non-ideal systems of a rather general type having a PCB [57, 58].

5.4 CRITERION FOR UNIQUENESS AND MULTIPLICITY ASSOCIATED WITH THE MECHANISM STRUCTURE

There is no doubt that studies for the establishment of new classes of mechanisms possessing an unique and stable steady state are essential and promising. On the other hand, it is of interest to construct a criterion for uniqueness and multiplicity that would permit us to analyze any reaction mechanism. An important contribution here has been made by Ivanova [5]. Using the Clark approach [59], she has formulated sufficiently general conditions for the uniqueness of steady states in a balance polyhedron in terms of the graph theory. In accordance with ref. 5 we will present a brief summary of these results. As before, we proceed from the validity of the law of mass action and its analog, the law of acting surfaces. Let us also assume that a linear law of conservation is unique (the law of conservation of the amount of catalyst).

In accordance with ref. 5, a complex reaction is described by a so-called bipartite graph of its mechanisms having vertices (points) of two types. Type Z corresponds to substances Z_i and type R is ascribed to the reaction $R_p (i = 1, 2, \ldots, n; p = 1, \ldots, N)$. Edges (R_p, Z_i) and (Z_i, R_p) have weights

β_{ip} and α_{ip}, respectively. If the weight equals zero, this edge is absent. Initial information and simple examples of bipartite graphs have been given above (see Sect. 1.3).

Ivanova [5] specifies the following graph elements: a segment $[Z_i, R_p]$; a positive path $[Z_i, R_p, Z_j]^+$ formed by two edges (Z_i, R_p) and (R_p, Z_j) oriented in the same direction from Z_i to Z_j; a negative path $[Z_i, R_p, Z_j]^-$ formed by two edges (Z_i, R_p) and (Z_j, R_p) oriented from Z_i and Z_j to R_p. The positive path corresponds to the formation of Z_j from Z_i due to the reaction R_p, whereas the negative one accounts for the interaction between Z_i and Z_j in the reaction R_p. The paths $[Z_i, R_p, Z_j]^-$ and $[Z_j, R_p, Z_i]^-$ are considered to be different since their orientations are from Z_i to Z_j and from Z_j to Z_i, respectively.

In Sect. 1.3 we described cycles of two types, oriented and non-oriented. The oriented cycle can be passed by if we move in the direction of the arrows. For a cycle of a general type it can be different since it is a sequence of the vertices $Z_1, \ldots, Z_k$ where the pairs of vertices Z_i and Z_{i+1} $(i = 1, \ldots, k-1)$ and also of Z_k and Z_1 are connected by edges. As usual, we will consider simple cycles with no edge and no Z vertex appearing twice.

To study the problem concerning the uniqueness and multiplicity of steady states it is necessary to consider one more type of cycle that is more general compared with oriented cycles. We will call them Clark (or Clark–Ivanova) cycles.

A Clark–Ivanova cycle is a closed sequence of paths where each Z vertex of the cycle is the path origin only once. For brevity, the cycle consisting of the paths $[Z_{i_1}, R_{p_1}, Z_{i_2}]$, $[Z_{i_2}, R_{p_2}, Z_{i_3}]$, . . . $[Z_{i_r}, R_{p_r}, Z_{i_1}]$ will be designated as C $\begin{pmatrix} Z_{i_1}, Z_{i_2}, \ldots, Z_{i_r} \\ R_{p_1}, R_{p_2}, \ldots, R_{p_r} \end{pmatrix}$. The Clark–Ivanova cycle (in what follows, simply the cycle) is called even (odd) if it contains the even (odd) number of negative paths. Let us recall that a negative path corresponds to the interaction of various substances. Therefore an even (odd) cycle must contain the even (odd) number of interaction steps for various substances. A union of the arbitrary number of segments and cycles in which each Z vertex is the origin for only one segment or path is called a subgraph. The number of subgraph Z vertices is called its order. Below we consider the multitude of all subgraphs containing the chosen set of vertices $Z_{i_1}, Z_{i_2}, \ldots, Z_{i_r}$ and $R_{p_1}, R_{p_2}, \ldots, R_{p_r}$. This multitude, Γ, is divided into two non-intersecting multitudes Γ^+ and Γ^- where Γ^- is the multitude of all subgraphs from Γ containing the arbitrary number of segments and the odd number of even cycles, and $\Gamma^+ = \Gamma/\Gamma^-$ is the remaining subgraphs. Then the following numerical functions for the subgraph elements are introduced.

$$B_p^i(z) = \alpha_{ip}(\partial w_p/\partial z_i)$$

for the segment $[Z_i, R_p]$,

$$B_{+p}^{ij}(z) = \beta_{jp}(\partial w_p/\partial z_i)$$

for the positive path $[Z_i, R_p, Z_j]^+$, and

$$B^{ij}_{-p}(z) = -\alpha_{jp}(\partial w_p/\partial z_i)$$

for the negative path $[Z_i, R_p, Z_j]^-$. A value for the cycle $C\begin{pmatrix} Z_{i_1}, \ldots, Z_{i_r} \\ R_{p_1}, \ldots, R_{p_r} \end{pmatrix}$ is called the product of its constituent paths taken with a negative sign. A value for the subgraph will be the product of the values of all its segments and cycles. A coefficient of the subgraph G is expressed as

$$K_G = \prod_{[\,]\in G} \alpha^2_{ip} \prod_{[\,]^-\in G} \alpha_{ip}\,\alpha_{jp} \prod_{[\,]^+\in G} \alpha_{ip}\,\beta_{jp} \tag{172}$$

Here products are taken respectively along all segments $[\,] = [Z_i, R_p]$, positive $[\,]^+ = [Z_i, R_p, Z_j]^+$ and negative $[\,]^- = [Z_i, R_p, Z_j]^-$ paths entering in the subgraph G. Let $F = \|f_{ij}\|$ be the Jacobian matrix for eqn. (151), i.e.

$$f_{ij} = \sum_{s=1}^{N} \gamma_{is} \frac{\partial w_s}{\partial z_j} \tag{173}$$

and $P(\lambda) = (-1)^n \det|F - \lambda E|$. Clark [59] showed that a coefficient of λ^k for the polynomial $P(\lambda)$ is equal to the sum of the values of the possible subgraphs of the $(n - k)$ graph order corresponding to the reaction mechanism. In accordance with this postulate, the following condition, which is sufficient for the uniqueness of the positive steady-state point in eqn. (151), was obtained [5]: if there are no boundary steady-state points (it can be checked), then a positive steady-state point is unique in the case when, for any totality r of the vertices $Z_{i_1}, \ldots, Z_{i_r}$ and any totality r of the vertices $R_{p_1}, \ldots, R_{p_r}$ (r is the rank of the matrix $[\gamma_{ip}]$), the inequality

$$\sum_{G'\in\Gamma^+} K_{G'} \geqslant \sum_{G''\in\Gamma^-} K_{G''} \tag{174}$$

is fulfilled.

A proof for this statement is constructed in accordance with the fact that the latter inequality accounts for the sign of the coefficient in the polynomial $P(\lambda)$ at λ^{n-r}, which in turn is associated with the index of a steady-state point for the vector field (151) [60]. If this coefficient is positive at any point of the positive orthant R^+_n: $z, z_i > 0, i = 1, 2, \ldots, n$, then the steady-state point is unique.

If the boundary of the simplex $D = \{z: z_i \geqslant 0, \Sigma m_i z_i = 1\}$ has one attracting steady-state point and an arbitrary number of unstable points, then if eqn. (174) is fulfilled, D has no internal steady-state points of the system, since a small deformation of the D boundary can provide a region Ω to which a theorem about the relation between the field rotation and the sum of indices for internal steady-state points in Ω is applied [60].

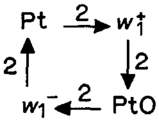
Ivanova also extended the above principal statement to homogeneous flow systems (a homogeneous CSTR). In addition, on the basis of the inequality (174) she formulated: (1) the conditions to distinguish an area of parameters for which a steady state is not unique and (2) those for the existence of an area of parameters for which a positive steady state is unique and unstable.

We apply these conditions to distinguish simple catalytic mechanisms ensuring self-oscillations of reaction rates (see Chap. 5).

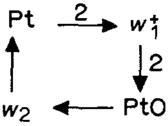
Ivanova and Tarnopolskii have realized a computation of this algorithm, thus making it convenient and applicable for composite reactions [61]. Let us give some examples of this algorithm application.

We will consider simple examples, i.e. the Eley–Rideal and Langmuir–Hinshelwood mechanisms for CO oxidation on Pt. Bipartite graphs corresponding to these mechanisms are represented in Fig. 3. In accordance with the general scheme, let us list segments, paths and cycles of these graphs.

For the Eley–Rideal mechanism [Fig. 3(a)] we have the segments [Pt $\xrightarrow{2}$ w_1^+], [PtO $\xrightarrow{2}$ w_1^-], [PtO $\rightarrow$ w_2], and the paths [Pt $\xrightarrow{2}$ w_1^+ $\rightarrow$ PtO]$^+$, [PtO $\xrightarrow{2}$ w_1^- $\rightarrow$ Pt]$^+$, [PtO $\rightarrow$ w_2 $\rightarrow$ Pt]$^+$. Here there are only positive paths. Negative paths accounting for the interaction steps for various intermediates are absent. The numerals above the arrows symbolize stoichiometric coefficients.



(1)



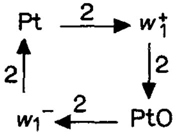
(2)

Cycles in this case are only even (the number of negative paths equals zero). Here the graph contains only second-order cycles. The rank of the stoichiometric matrix is $r = 1$. First-order cycles do not exist here, hence in eqn. (174) the equality is fulfilled identically, i.e. a steady state is always unique.

For the Langmuir–Hinshelwood mechanism [Fig. 3(b)] we have the segments [Pt $\xrightarrow{2}$ w_1^+], [Pt $\rightarrow$ w_2^+], [PtCO $\rightarrow$ w_3], [PtCO $\rightarrow$ w_2^-], [PtO $\xrightarrow{2}$ w_1^-], [PtO $\rightarrow$ w_3],

and the paths [Pt $\xrightarrow{2}$ w_1^+ $\xrightarrow{2}$ PtO]$^+$, [Pt $\rightarrow$ w_2^+ $\rightarrow$ PtCO]$^+$, [PtCO $\rightarrow$ w_2^- $\rightarrow$ Pt]$^+$, [PtO $\xrightarrow{2}$ w_1^- $\xrightarrow{2}$ Pt]$^+$, [PtCO $\rightarrow$ w_3 $\xrightarrow{2}$ Pt]$^+$, [PtO $\rightarrow$ w_3 $\xrightarrow{2}$ Pt]$^+$, [PtCO $\rightarrow$ w_3 $\rightarrow$ PtO]$^-$, [PtO $\rightarrow$ w_3 $\rightarrow$ PtCO]$^-$.

Here the rank of the stoichiometric matrix is $r = 2$. Therefore we will be interested in second-order cycles [Fig. 3(b)]

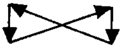


(1)

or, in short

$$\mathrm{C}_1\begin{pmatrix}\mathrm{Pt}, & \mathrm{PtO}\\ w_1^+, & w_1^-\end{pmatrix}$$

Here passing of the cycle corresponds to the arrows



then

$$\mathrm{C}_2\begin{pmatrix}\mathrm{Pt}, & \mathrm{PtCO}\\ w_2^+, & w_2^-\end{pmatrix}, \qquad \mathrm{C}_3\begin{pmatrix}\mathrm{Pt}, & \mathrm{PtO}\\ w_1^+, & w_3\end{pmatrix}, \qquad \mathrm{C}_4\begin{pmatrix}\mathrm{Pt}, & \mathrm{PtCO}\\ w_2^+, & w_3\end{pmatrix}$$

Here all second-order cycles are even. As shown in ref. 5, one of the reasons for the non-uniqueness of steady state [violation of condition (174)] can be the presence of a cycle composed by the positive paths for which $\Pi^r_{j=1}\beta_{i_jp_j} > \Pi^r_{j=1}\alpha_{i_jp_j}$. In our case this cycle (branching cycle) will be the cycle C_3 for which $\beta_{21}\ \beta_{13} = 2 \times 2 = 4$, $\alpha_{11}\ \alpha_{23} = 2 \times 1 = 2$, and the necessary condition for the uniqueness of a steady state is not fulfilled. A comprehensive numerical analysis of several steady states for a given system will be performed in Chap. 5.

Let us give one more example considered in ref. 5. In the scheme of hydrogen reactions with oxygen for the totality of Z vertices corresponding to the substance OH, H, and O and of R vertices corresponding to the reactions

$$\mathrm{OH} + \mathrm{H_2} \rightarrow \mathrm{H} + \mathrm{H_2O}$$

$$\mathrm{H} + \mathrm{O_2} \rightarrow \mathrm{OH} + \mathrm{O}$$

$$\mathrm{O} + \mathrm{H_2} \rightarrow \mathrm{OH} + \mathrm{H}$$

the third-order subgraphs belonging to Γ^- consist of the third-order cycle

$$\mathrm{C}\begin{pmatrix}\mathrm{OH}, & \mathrm{H}, & \mathrm{O}\\ w_1, & w_2, & w_3\end{pmatrix}$$

and the unions of the second-order cycles and segments

$$\mathrm{C}\begin{pmatrix}\mathrm{OH}, & \mathrm{H}\\ w_1, & w_2\end{pmatrix} \bigcup\, [\mathrm{O}, w_3],\ \mathrm{C}\begin{pmatrix}\mathrm{H}, & \mathrm{O}\\ w_2, & w_3\end{pmatrix} \bigcup\, [\mathrm{OH}, w_1],\ \sum_{G''\in\Gamma^-} K_{G''} = 3.$$

The multitude Γ^+ consists of the one subgraph being a union of the segments $[\mathrm{OH}, w_1] \bigcup [\mathrm{H}, w_2] \bigcup [\mathrm{O}, w_3]$, and $\Sigma_{G'\in\Gamma^+} K_{G'} = 1$. In this case inequality (174) is not fulfilled since there are several cycles passing through the same reactions and substances from the same totality. The approach described is sure to merit a more comprehensive description with the greater number of examples.

5.5 SOME CONCLUSIONS

A question arises: in what cases is a unique and asymptotically stable steady state realized?

(1) Closed systems. Here a rest point is always a PDE wherein the rate of every direct reaction is equal to that of the reverse reaction.

(2) Open systems without intermediate interactions, i.e. those having no PDE but the mechanisms do not involve interactions between various intermediates.

(3) Open systems with PCB. An efficient means to establish whether this point exists is to check the equality (169): $M - l = S$ and a weak reversibility (these are sufficient but, generally speaking, not necessary conditions).

Systems (1) enter into class 3 (a PDE point is a PCB). Systems with linear reaction mechanisms belong to both class (2) and class (3) but these classes do not overlap since there are systems without intermediate interactions that do not satisfy the principle of complex balance (e.g. the Eley–Rideal mechanism for CO oxidation on platinum metal). On the other hand, there exist reaction mechanisms containing steps of "intermediate interactions" but at the same time always having a PCB (e.g. the Twigg mechanism for ethylene hydrogenation on nickel).

(4) On the basis of the structure for a bipartite graph of the reaction mechanism, it is possible to formulate a sufficient condition (174) for the uniqueness of a steady state. Applying it to concrete reactions, it is possible to establish the parametric areas for which either a unique steady state exists or there is a multiplicity of such states.

Let us emphasize the following important circumstance. In the introduction we have already spoken about a physico-chemical sense of the conditions obtained for the multiplicity of steady states in the kinetic region. Now we will only stress that for linear mechanisms the steady state is, apparently, unique. If we deal with non-linear mechanisms and kinetic models (rather typical for heterogeneous catalysis), it can be expected that the solution will not be unique. For non-isothermal systems it is a well-known effect [62]. A new fact is the experimental and theoretical establishment of such effects in a purely kinetic region. This behaviour can be observed for an open chemical system that is far from being in equilibrium (a model of such an autocatalytic system was constructed by Zeldovich in 1941 [63]). Multiplicity of steady states is due to model non-linearity. In general it is the non-linearity that is responsible for the complex dynamic behaviour of an open chemical system. Frank-Kamenetskii, the author of the well-known book *Diffusion and Heat Transfer in Chemical Kinetics,* differed with Nalimov who believed that critical effects are possible only under fundamental changes in the reaction mechanism. Frank-Kamenetskii's opinion was that jumpwise transitions from one regime to the other take place under critical conditions that are not associated with variations in the mechanism of the chemical reaction itself but are caused only by its non-linear peculiarities. Recent studies have confirmed his viewpoint [64]. All the results presented are the conditions to determine the areas with unique or multiple positive (either stable or unstable) solutions but so far no general results have been obtained that would permit us to judge the number of positive solutions in the case when there are several. This problem can be solved only for concrete cases, i.e. kinetic models of comparatively small dimension.

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