Chapter 4

Graphs in Chemical Kinetics

1. General description and main concepts

1.1 SIMPLE EXAMPLE

Graph theory has found extensive application in chemical kinetics. It is this subject that is the goal of this chapter.

Let us take a simple example to illustrate the application of graph theory to derive a steady-state kinetic equation for a complex reaction. It is a typical problem for the kinetics of complex reactions. As usual it is solved as follows. Let a mechanism be given for a complex reaction involving the participation of observed substances, i.e. initial reactants and products as well as intermediates. In accordance with the mechanism based on a fundamental law of chemical kinetics, the law of mass action, we obtain a set of differential equations accounting for the kinetics of variable intermediates. Assuming that the known principle of quasi-steady-state concentrations is valid, we go from the above set of differential to that of algebraic equations whose solution provides steady-state concentrations for intermediates. Knowing these values, we can readily obtain a general expression for a steady-state reaction rate as a function of the substance concentrations and temperature. The most cumbersome step in this sequence of operations is the solution of the set of algebraic equations. The application of graph theory not only facilitates this solution (of course, only in the linear case), but also provides the possibility of drawing some general conclusions.

Let us consider a model catalytic isomerization reaction with the detailed mechanism

$$\begin{array}{lcr} (1)\ \mathrm{A + Z \rightleftarrows AZ} & & 1 \\ (2)\ \mathrm{AZ \rightleftarrows BZ} & & 1 \\ (3)\ \underline{\mathrm{BZ \rightleftarrows B + Z}} & & \underline{1} \\ \qquad \mathrm{A = B} & & \end{array} \qquad (1)$$

The equation A = B corresponds to the stoichiometric (brutto) reaction. Here Z, AZ and BZ are the three intermediates through which a complex catalytic reaction proceeds; the substance Z (the active catalytic centre) is also treated as an intermediate.

Intermediates are related by the law of conservation [Z] + [AZ] + [BZ] = 1, since the catalyst quantity in the system is constant. ([Z], [AZ], [BZ] are the dimensionless concentrations of the intermediates.)

Due to the fulfilment of this law of conservation, the number of linearly independent intermediates is not three but one fewer, i.e. it amounts to two. To the right of mechanism (1) we gave a column of numerals. Steps of the detailed mechanism must be multiplied by these numerals so that, after the subsequent addition of the equations, a stoichiometric equation for a complex reaction (a brutto equation) is obtained that contains no intermediates. The Japanese physical chemist Horiuti suggested that these numerals should be called "stoichiometric" numerals. We believe this term is not too suitable, since it is often confused with stoichiometric coefficients, indicating the number of reactant molecules taking part in the reaction. In our opinion it would be more correct to call them Horiuti numerals. For our simplest mechanism, eqn. (1), these numerals amount to unity.

Let us pay attention to the reactions represented in mechanism (1). Here there are monomolecular reactions: direct in the cases of steps (2) and (3) and reverse in the cases of steps (1) and (2). But there are also bimolecular reactions involving the participation of two substances, namely gas and catalyst. These are the direct reaction of step (1) (adsorption of substance A) and the reverse reaction of step (3) (adsorption of substance B). Strictly speaking, mechanisms of heterogeneous catalytic reactions are never monomolecular. They always include, for example, adsorption steps involving at least two initial substances, i.e. gas and catalyst. But if we consider the conversions of only intermediates at a constant composition of the gas phase (note that in heterogeneous catalysis most kinetic experiments are carried out in just this way), a catalytic reaction mechanism can be treated as monomolecular. Every elementary reaction here will involve the participation of no more than one molecule of the intermediate. Temkin called these mechanisms linear since their reaction rates are linearly dependent on the intermediate concentrations. The class of linear mechanisms is particularly wide. It includes practically the whole of the enzyme reaction mechanisms. It is for these reactions that King and Altman used, for the first time, graph theory methods [1]. If some mechanism has steps in which two or more molecules of an intermediate react, it is a linear mechanism. Mechanism (1) is linear. The corresponding graph is represented in Fig. 1. The

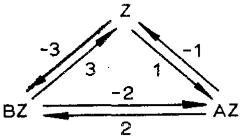


Fig. 1. Graph of a catalytic isomerization mechanism.

nodes of this graph are intermediates and its edges are reactions. The directions of the reactions are indicated by arrows given for the edges.

Let us determine some notations that are essential for the further representation.

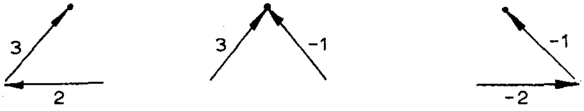
Our graph has a *cycle* that is a finite sequence of graph edges, whose beginning and end coincide. This cycle corresponds to the cyclic conversion of the intermediates. In our case the cycle is unique.

A *tree* is any sequence of graph edges containing no cycles. It corresponds to a certain combination of intermediate conversions. A *spanning tree* (a maximum tree) is a sequence of graph edges containing no cycles and joining all nodes of the initial graph. It suffices to add one more edge to obtain a cycle. Spanning trees are treated as those of the graph node if they enter this node. A spanning tree corresponds to the path of conversions through which a given intermediate is formed from the combination of the rest. Spanning trees of graph nodes corresponding to mechanism (1) are represented in Fig. 2.

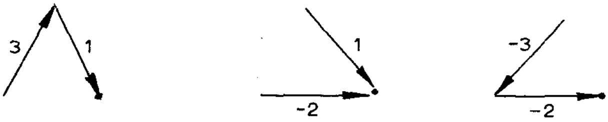
When the reaction has one cycle, its graph has n nodes and n steps. It can easily be shown that every node comprises n spanning trees and their total number will be n^2. For mechanism (1), $n = 3$ and hence the number of spanning trees will be $n^2 = 9$.

Edge weights are obtained if the reaction (both direct and reverse) rates corresponding to the graph edges are divided by the concentrations of the reacting intermediates

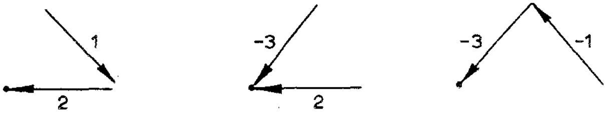
$$b_s^+ = \frac{w_s^+}{[x_i^+]} \tag{2}$$



Spanning trees of node Z



Spanning trees of node AZ



Spanning trees of node BZ

Fig. 2. Spanning trees for the graph of an isomerization mechanism.

$$b_s^- = \frac{w_s^-}{[x_i^-]} \tag{3}$$

where b_s^+ and b_s^- are the edge weights for the direct and reverse reactions and $[x_i^+]$ and $[x_i^-]$ are the concentrations of intermediates reacting in direct and reverse reactions, respectively. Edge weight is the rate of an elementary reaction at a unit concentration of the reacting intermediate. In the literature this characteristic is also called a "reaction frequency" (Schwab), a "kinetic coefficient" (Balandin), and also a probability. Edge (reaction) weight amounts to the rate constant of a reaction or its product by the substance (gas or substrate) concentration.

Let us write reaction rates for mechanism (1) in accordance with the law of mass action (for surface reactions this law is known as "the law of surface action")

$$\begin{aligned} w_1^+ &= k_1^+[\mathrm{A}][\mathrm{Z}] & w_1^- &= k_1^-[\mathrm{AZ}] \\ w_2^+ &= k_2^+[\mathrm{AZ}] & w_2^- &= k_2^-[\mathrm{BZ}] \\ w_3^+ &= k_3^+[\mathrm{BZ}] & w_3^- &= k_3^-[\mathrm{B}][\mathrm{Z}] \end{aligned} \tag{4}$$

Here k_1^+, k_1^-, k_2^+, k_2^-, k_3^+ and k_3^- are the rate constants for the elementary reactions, [A] and [B] the concentrations of the gaseous substances, and [Z], [AZ], and [BZ] the concentrations of the intermediates.

Reaction weights for the isomerization mechanism will be

$$\begin{aligned} b_1^+ &= k_1^+[\mathrm{A}] & b_1^- &= k_1^- \\ b_2^+ &= k_2^+ & b_2^- &= k_2^- \\ b_3^+ &= k_3^+ & b_3^- &= k_3^-[\mathrm{B}] \end{aligned} \tag{5}$$

The *spanning tree weight* is a value amounting to the product of the weights of its constituent edges.

Spanning trees entering into node Z will have the weights

$$B_{\mathrm{Z},1} = b_2^+ b_3^+, \quad B_{\mathrm{Z},2} = b_3^+ b_1^-, \quad B_{\mathrm{Z},3} = b_2^- b_1^- \tag{6}$$

The weights for spanning trees of the node AZ will be

$$B_{\mathrm{AZ},1} = b_1^+ b_3^+, \quad B_{\mathrm{AZ},2} = b_1^+ b_2^-, \quad B_{\mathrm{AZ},3} = b_3^- b_2^- \tag{7}$$

Finally, for the node BZ we will have

$$B_{\mathrm{BZ},1} = b_1^+ b_2^+, \quad B_{\mathrm{BZ},2} = b_2^+ b_3^-, \quad B_{\mathrm{BZ},3} = b_1^- b_3^- \tag{8}$$

The total weight of node spanning trees will be

$$\begin{aligned} \mathrm{Z}: \quad B_{\mathrm{Z}} &= b_2^+ b_3^+ + b_3^+ b_1^- + b_2^- b_1^- \\ \mathrm{AZ}: \quad B_{\mathrm{AZ}} &= b_3^+ b_1^+ + b_1^+ b_2^- + b_3^- b_2^- \\ \mathrm{BZ}: \quad B_{\mathrm{BZ}} &= b_1^+ b_2^+ + b_2^+ b_3^- + b_1^- b_3^- \end{aligned} \tag{9}$$

The total weight of graph spanning trees amounts to

$$B = B_{\mathrm{Z}} + B_{\mathrm{AZ}} + B_{\mathrm{BZ}} \tag{10}$$

Let us write a formula whose application will give us a possibility to simplify essentially the derivation of kinetic equations for complex reactions following a linear mechanism

$$x = \frac{B_{\mathrm{X}}}{B} C \tag{11}$$

Here x is the concentration of the intermediate, B_{X} the total weight of node spanning trees corresponding to a given substance, C the total number of intermediates per unit surface of catalyst (after normalizing, the concentration is usually taken as $C = 1$), and

$$B = \sum_{x} B_{\mathrm{X}}.$$

Relationship (11) was first reported by King and Altman [1]. They examined a linear set of quasi-steady-state equations for the intermediates of the complex enzyme reaction following a linear mechanism. For its derivation the authors applied the well-known Kramer rule.

On the other hand, Vol'kenstein and Gol'dshtein actively applied graph theory methods in a series of the studies in the 1960s [2–4] and introduced this relationship by analogy with the known Mason rule from electrical engineering.

A strict substantiation for this analogy and derivation of this relationship in terms of the Mason rule [5] can be found in refs. 6 and 7. In our monograph [7] we also give proofs for the fact that the terms of eqn. (11) obtained using the Kramer rule are spanning tree weights of various nodes. A brief substantiation for eqn. (11) will be given below.

From the known concentrations of intermediates we can easily determine a rate for any reaction step. For our reaction with an unique cycle the steady-state rate of any step is equal either to that for the consumption of substance A or to that of the formation of substance B (route rate).

For example

$$w = k_2^+ [\mathrm{AZ}] - k_2^- [\mathrm{BZ}] \tag{12}$$

Since $k_2^+ = b_2^+$ and $k_2^- = b_2^-$, eqn. (12) can be written as

$$w = b_2^+ [\mathrm{AZ}] - b_2^- [\mathrm{BZ}] \tag{13}$$

and then

$$\begin{aligned} w &= \frac{b_2^+ B_{\mathrm{AZ}} - b_2^- B_{\mathrm{BZ}}}{B} \\ &= \frac{b_2^+ (b_1^+ b_3^+ + b_1^+ b_2^- + b_3^- b_2^-) - b_2^- (b_1^+ b_2^+ + b_2^+ b_3^- + b_1^- b_3^-)}{b_1^+ b_2^+ + b_2^+ b_3^+ + b_1^+ b_3^+ + b_1^- b_2^- + b_2^- b_3^- + b_3^- b_1^- + b_1^+ b_2^- + b_2^+ b_3^- + b_3^+ b_1^-} \end{aligned} \tag{14}$$

Most factors in the numerator of eqn. (14) cancel out and we obtain the expression

$$w = \frac{b_1^+ b_2^+ b_3^+ - b_1^- b_2^- b_3^-}{b_1^+ b_2^+ + b_2^+ b_3^+ + b_1^+ b_3^+ + b_1^- b_2^- + b_3^- b_2^- + b_3^- b_1^- + b_1^+ b_2^- + b_2^+ b_3^- + b_3^+ b_1^-} \tag{15}$$

After substituting reaction weights from eqn. (5) into eqn. (15), we have

$$w = \frac{k_1^+ k_2^+ k_3^+ [\mathrm{A}] - k_1^- k_2^- k_3^- [\mathrm{B}]}{k_1^+ [\mathrm{A}](k_2^+ + k_3^+ + k_3^-) + k_3^- [\mathrm{B}](k_1^- + k_2^- + k_2^+) + k_2^+ k_3^+ + k_1^- k_2^- + k_3^- k_1^-} \tag{16}$$

Let us analyze the structure of eqn. (16). Its numerator can be written as $K^+[\mathrm{A}] - K^-[\mathrm{B}]$, where $K^+ = k_1^+ k_2^+ k_3^+$ and $K^- = k_1^- k_2^- k_3^-$. In this form it accounts for the stoichiometric equation $\mathrm{A} = \mathrm{B}$ obtained by adding all the steps of the detailed mechanism multiplied by unit stoichiometric numbers. It is interesting that the numerator is absolutely independent of the mechanism "details". Irrespective of the number of steps in our mechanism (a thousand, a million), the numerator of a steady-state kinetic equation always corresponds to the kinetic law of the brutto reaction as if it were simple and obeys the law of mass action. The denominator characterizes a "non-elementary" character accounting for the rate of the catalytic reaction inhibition by the initial substances and products.

If all steps are irreversible ($k_1^- = k_2^- = k_3^- = 0$), eqn. (16) is simplified considerably to

$$w = \frac{k_1^+ k_2^+ k_3^+ [\mathrm{A}]}{k_1^+ [\mathrm{A}](k_2^+ + k_3^+) + k_2^+ k_3^+} \tag{17}$$

Thus this simple example has illustrated the efficiency of graph methods in chemical kinetics.

1.2 TWO FORMALISMS. FORMALISM OF ENZYME KINETICS AND OF STEADY-STATE-REACTION THEORY

As has already been shown, graph theory methods were first used in chemical kinetics by King and Altman who applied them to linear enzyme mechanisms [1]* to derive steady-state kinetic equations. Vol'kenshtein and Gol'dshtein in their studies during the 1960s [2–4] also elaborated a new formalism for the derivation of steady-state kinetic equations based on graph theory methods ("Mason's rule", etc.).

Owing to the classical King–Altman and Vol'kenshtein–Gol'dshtein stu-

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* In ref. 1, a complex mechanism was represented as an open graphical sequence: every graph edge (step) jointed nodes (substances). It is likely that it was Temkin who was the first to suggest the representation of catalytic conversions by a cycle on the graph.

dies, graph theory has become a traditional working instrument for enzyme kinetics (refer, for example, to refs. 8–10). It is the apparatus that was used in the above example in Sect. 1.1.

Here, a graph for the complex reaction mechanism is determined as follows. Every substance x_i participating in the reaction is given a node v_i of the graph $G(\vec{V}, \vec{E})$. Every elementary reaction between the substances x_i and x_j is represented by the edge (v_i, v_j). The edge $\vec{u} = (v_i, v_j)$ corresponds to a certain value $\vec{b}(u)$ that is the reaction weight. Reaction weight was determined above as the rate at unit concentration of the reacting intermediate. The directed graph (i.e. the graph with a given direction) determined in this way is called a graph of the reaction. Apparently, it is the graph for a linear mechanism. This graph can be ascribed to the models usually called natural. They have no differences from the conversion schemes accepted for chemistry.

Apart from enzyme kinetics, this new trend had also appeared in the kinetics of heterogeneous catalysis. In the 1950s, Horiuti formulated a theory of steady-state reactions [11, 12], many of the concepts of which correspond to the graph theory. Independent intermediates, a reaction route, an independent reaction route, all these concepts were introduced by Horiuti.

This can also be said about the Horiuti number (or, as Horiuti called it himself, the stoichiometric number) discussed previously. The Horiuti numbers are the numbers chosen such that, after multiplying the chemical equation for every step by the appropriate Horiuti number and subsequent adding, all intermediates are cancelled. The equation thus obtained is the stoichiometric (brutto) equation. Each set of stoichiometric numbers leading to the elimination of intermediates is called a reaction route. In the general case, the Horiuti numbers form a matrix and its vector columns are the routes.

Horiuti stoichiometric rule. This rule is applied to find the number of linearly independent routes. Stoichiometric numbers must satisfy the equation

$$\vec{\nu}^{\mathrm{T}} \vec{\Gamma}_{\mathrm{int}} = 0 \tag{18}$$

Here $\vec{\nu}^{\mathrm{T}}$ is the transposed matrix of the Horiuti numbers (stoichiometric numbers) and $\vec{\Gamma}_{\mathrm{int}}$ the matrix of the intermediate stoichiometric coefficients. The size for the matrices $\vec{\nu}^{\mathrm{T}}$ and $\vec{\Gamma}_{\mathrm{int}}$ is $(P \times S)$ and $(S \times I_{\mathrm{tot}})$, respectively, where S is the number of steps, I_{tot} the total number of independent intermediates, and P the number of routes. Due to the existence of a conservation law (at least one), the catalyst quantity and the number of linearly independent intermediates will be

$$I = I_{\mathrm{tot}} - 1 \tag{19}$$

The multiplication of the matrices $\vec{\nu}^{\mathrm{T}}(P \times S)$ and $\vec{\Gamma}_{\mathrm{int}}(S \times I_{\mathrm{tot}})$ gives the matrix $\vec{\nu}^{\mathrm{T}} \Gamma_{\mathrm{int}}$ whose size is $(P \times I_{\mathrm{tot}})$. The vector column of the matrix for the

Horiuti numbers $\vec{\nu}$ $(S \times P)$ is the route of a complex reaction. The rank of the matrix $\vec{\Gamma}_{\text{int}}$ cannot be higher than $(S - P)$ since, according to eqn. (19) there are P linearly independent rows of $\vec{\Gamma}_{\text{int}}$. As usual, we have

$$\text{rg}\,\vec{\Gamma}_{\text{int}} = S - P \tag{20}$$

On the other hand, when the law of catalyst conservation is unique, we have

$$\text{rg}\,\vec{\Gamma}_{\text{int}} = I = I_{\text{tot}} - 1 \tag{21}$$

After substituting eqn. (21) in eqn. (20), we obtain

$$P = S - I_{\text{tot}} + 1$$

This relationship for the determination of the number for the linearly independent routes is called the Horiuti stoichiometric rule. Let us apply it.

For the isomerization reaction (1) we have $S = 3$ and $I = 3$, hence $P = 1$. This reaction is one-route and all the Horiuti numbers are equal to unity.

For two-step mechanisms of the type (1) $A + Z \rightleftarrows AZ$ and (2) $B + AZ \rightleftarrows Z + AB$ (the Temkin–Boudart mechanism) we have $S = 2$ and $I = 2$. Hence $P = 1$ and all the Horiuti numbers are unity.

The vinyl chloride synthesis reaction has the detailed mechanism

$$\begin{array}{l} (1)\ C_2H_2 + Z \rightleftarrows ZC_2H_2 \\ (2)\ HCl + ZC_2H_2 \rightarrow Z + C_2H_3Cl \\ (3)\ HCl + Z \rightleftarrows ZHCl \\ (4)\ C_2H_2 + ZHCl \rightarrow Z + C_2H_3Cl \end{array}$$

where Z is the active centre, $I_{\text{tot}} = 3$ and the number of steps $S = 4$. Hence the number of linearly independent routes amounts to

$$\begin{aligned} P &= S - I_{\text{tot}} + 1 \\ &= 4 - 3 + 1 = 2 \end{aligned}$$

Thus, here we have two independent routes. For a linear mechanism of ammonia synthesis on an iron catalyst we will have

$$\begin{array}{ll} (1)\ Z + N_2 \rightleftarrows ZN_2 & 1 \\ (2)\ ZN_2 + H_2 \rightleftarrows ZN_2H_2 & 1 \\ (3)\ ZN_2H_2 + Z \rightleftarrows 2\,ZNH & 1 \\ (4)\ \underline{ZNH + H_2 \rightleftarrows Z + NH_3} & 2 \\ \quad\ N_2 + 3\,H_2 = 2\,NH_3 & \end{array} \tag{22}$$

Here $I_{\text{tot}} = 4$ and $S = 4$. Hence $P = 4 - 4 + 1 = 1$. The reaction mechanism will be one-route. This mechanism contains a non-linear step, a third step, where intermediates react between themselves. Unlike the cases considered above, not all the non-zero Horiuti numbers are equal. Temkin in a series of studies during the 1960s [13–16] popularized the results of the Horiuti theory. Later he used graph theory methods for the representation of complex reaction mechanisms and for the derivation of steady-state kinetic equations. He represented a route of a complex reaction as a graph cycle and the number of linearly independent cycles as the number of routes.

Let us give some examples for the graphs of linear mechanisms. The simplest mechanism of an enzyme catalytic reaction is the Michaelis–Menten scheme

$$\begin{array}{l} (1)\ E + S \rightleftarrows ES \\ (2)\ ES \rightarrow P + S \end{array}$$

where S and P are the substrate and product, respectively, and E and ES the various forms of the enzyme. A graph for the conversion of the intermediates in this mechanism is given in Fig. 3(a).

Graphs of the two-step one-route mechanisms (the Temkin–Boudart mechanisms) for the steam conversion of CO and liquid-phase hydrogenation are illustrated in Fig. 3(b) and (c)

$$\begin{array}{ll} (1)\ Z + H_2O \rightleftarrows ZO + H_2 & (1)\ Z + H_{2,\mathrm{sol}} \rightleftarrows ZH_2 \\ (2)\ \underline{ZO + CO \rightleftarrows Z + CO_2} & (2)\ \underline{ZH_2 + A_{\mathrm{sol}} \rightleftarrows AH_2 + Z} \\ \quad\ CO + H_2O = CO_2 + H_2 & \quad\ A + H_2 = AH_2 \end{array} \qquad (23)$$

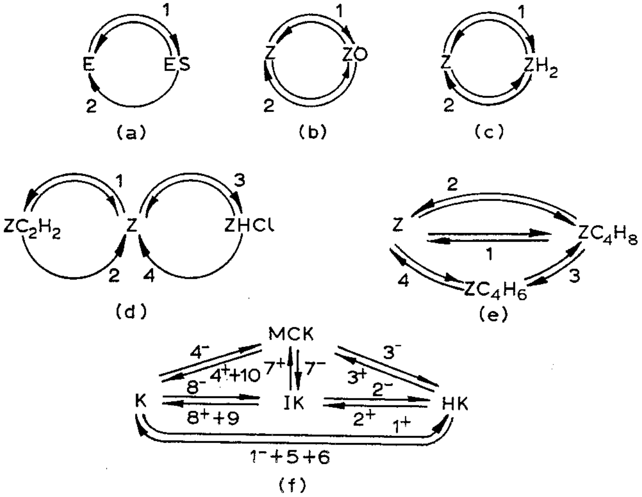


Fig. 3. Graphs of linear catalytic reaction mechanisms. (a), (b), (c), One-route; (d), (e) two-route; (f) multi-route mechanisms.

A detailed mechanism for the synthesis of vinyl chloride on the "mercuric chloride + medical charcoal" catalyst can be represented by the sequence of steps [17]

$$\begin{array}{ll@{\qquad}cc}
 & & \mathrm{I} & \mathrm{II}\\
(1) & \mathrm{Z + C_2H_2 \rightleftarrows ZC_2H_2} & 1 & 0\\
(2) & \mathrm{ZC_2H_2 + HCl \rightarrow Z + C_2H_3Cl} & 1 & 0\\
(3) & \mathrm{Z + HCl \rightleftarrows ZHCl} & 0 & 1\\
(4) & \underline{\mathrm{ZHCl + C_2H_2 \rightarrow Z + C_2H_3Cl}} & 0 & 1\\
 & \mathrm{C_2H_2 + HCl = C_2H_3Cl} & &
\end{array} \tag{24}$$

Here Z is the active site of ($\mathrm{HgCl_2 \cdot HCl}$). Vector-columns of the stoichiometric numbers are given to the right of the equations of the steps. This mechanism corresponds to the graph formed by two cycles having one common node, i.e. the intermediate Z [Fig. 3(d)].

The reaction mechanism for butane dehydrogenation can be represented in simplified form by the steps

$$\begin{array}{ll}
(1) & \mathrm{C_4H_{10} + Z \rightleftarrows C_4H_8Z + H_2}\\
(2) & \mathrm{C_4H_8Z \rightleftarrows C_4H_8 + Z}\\
(3) & \mathrm{C_4H_8Z \rightleftarrows C_4H_6Z + H_2}\\
(4) & \mathrm{C_4H_6Z \rightleftarrows C_4H_6 + Z}
\end{array} \tag{25}$$

This mechanism corresponds to the graph formed by two cycles with one common step (edge) [Fig. 3(e)].

A sample of the *n*-hexane conversions on supported platinum catalysts can be represented by the scheme

$$\begin{array}{ll}
(1) & \mathrm{H + K \rightleftarrows HK}\\
(2) & \mathrm{HK \rightleftarrows IK}\\
(3) & \mathrm{HK \rightleftarrows MCK}\\
(4) & \mathrm{MCK \rightleftarrows MC + K}\\
(5) & \mathrm{HK \rightarrow P + K}\\
(6) & \mathrm{HK \rightarrow B + K}\\
(7) & \mathrm{IK \rightleftarrows MCK}\\
(8) & \mathrm{IK \rightleftarrows I + K}\\
(9) & \mathrm{IK \rightarrow P + K}\\
(10) & \mathrm{MCK \rightarrow B + K}
\end{array} \tag{26}$$

Here H, I, B, MC, and P are *n*-hexane, hexane isomers, benzene, methylcyclopentane, and cracking products, respectively, while K, HK, MCK, and IK are intermediates. The graph for surface conversions is given in Fig. 3(f). Numerals given over the directed edge of the graph point to the number of steps with the help of which one intermediate is formed from the other.

Cycles in the graphs of linear mechanisms are usually called only the "correctly directed" cycles. For example, a sequence of the reactions (1) $A_1 \rightarrow A_2$, (2) $A_2 \rightarrow A_3$, and (3) $A_3 \rightarrow A_1$ is the cycle, whereas the reactions (1) $A_1 \rightarrow A_2$, (2) $A_2 \rightarrow A_3$, and (3) $A_1 \rightarrow A_3$ do not form a cycle. This mechanism is acyclic.

Simple cycles are those that do not contain any repeated points except the initial one. All simple cycles for the most complex of the above graphs, i.e. the graph of *n*-hexane conversions, are presented in Fig 4.

The theory of steady-state reactions operates with the concepts of "a path of the step", "a path of the route", and "the reaction rate along the basic route". Let us give their determination in accordance with ref. 16. The number of step paths is interpreted as the difference of the number of elementary reaction acts in the direct and reverse directions. Then the rate for the direct step is equal to that of the paths per unit time in unit reaction space. One path along the route signifies that every step has as many paths as its stoichiometric number for a given route. In the case when the formation of a molecule in one of the steps is compensated by its consumption in the other step, the steady-state reaction process is realized. If, in the course of this step, no final product but a new intermediate is formed, then it is this

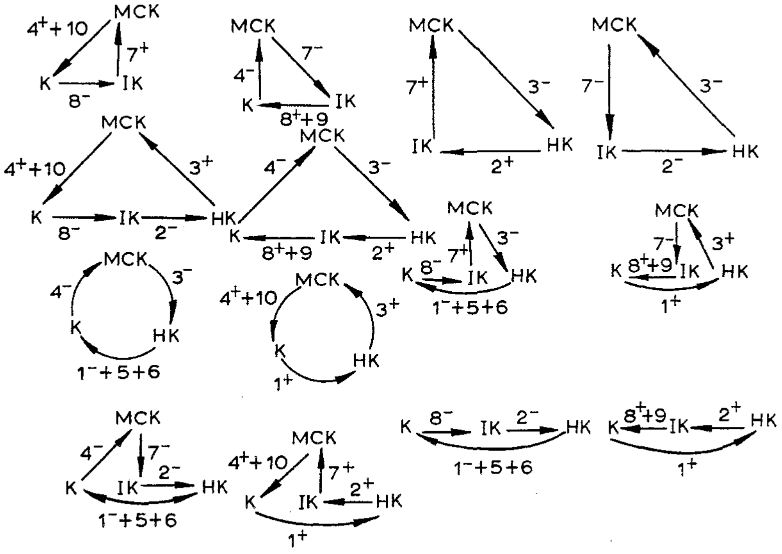


Fig. 4. Simple cycles for *n*-hexane conversion [Fig. 3(f)].

intermediate that must be consumed in the other step. Complete compensation for the formation and consumption of intermediates does signify the completion of a path along some route.

Thus the rate of a steady-state reaction is determined by individual paths along various routes. Every rate, however, can be represented as a linear combination of basic routes and hence a path along this route can be given as a linear combination of paths along the basic routes. Consequently, the paths along the non-basic routes composing a reaction are substituted by equivalent paths along the basic routes. As a result, all paths of the steps for a given time will appear to be adequately determined through basic routes. The reaction rate along the basic route is the number of paths along the basic route per unit time in unit reaction space provided that all paths of the steps are localized along the routes of a given basis. The reaction rate as a whole is set by the rates along the basic routes; similarly, a vector is prescribed by its components along the axes of coordinates.

The application of the concept of "the rate along the basic route" provides a possibility of obtaining a new formulation for the quasi-stationary conditions in terms of the Horiuti theory which is different from the ordinary one, i.e. "the formation of an intermediate is equal to that of its consumption". Temkin called the equations obtained "the conditions for the stationarity of steps". In matrix form they are represented as

$$\vec{\nu}\vec{v} = \vec{w} \tag{27}$$

Here $\vec{\nu}$ is the matrix of the Horiuti (stoichiometric) numbers and $\vec{v}$ and $\vec{w}$ the vector-columns of the rates along basic routes and of the step rates, respectively. Thus the rate of every step is represented as a linear combination of the rates along the basic routes. Here it is recommended that a simple hydrodynamic analogy be used. The total liquid flow along the tube (step) is the reaction rate. This flow consists of individual streams which are the rates along the routes.

It can readily be shown that eqn. (27) is equivalent to the quasi-steady-state condition in its general formulation. In unit time and in unit reaction space there forms $\vec{\Gamma}_{\text{int}}\vec{w}$ of an intermediate, where $\vec{\Gamma}_{\text{int}}$ is the stoichiometric intermediate matrix. Let us recall that the dimension of $\vec{\Gamma}_{\text{int}}$ is $(I_{\text{tot}} \times S)$, where I_{tot} is the total number of independent intermediates and S is the number of steps. After substituting $\vec{w}$ from eqn. (27), we obtain

$$\vec{\Gamma}^{\text{T}}_{\text{int}}\vec{w} = \vec{\Gamma}^{\text{T}}_{\text{int}}(\vec{\nu}\vec{v}) = (\vec{\Gamma}^{\text{T}}_{\text{int}}\vec{\nu})\vec{v} \tag{28}$$

It follows from eqn. (18) that $\vec{\Gamma}^{\text{T}}_{\text{int}}\vec{\nu} = 0$. Consequently, we also have $\vec{\Gamma}^{\text{T}}_{\text{int}}\vec{w} = 0$, which was to be proved.

Temkin applied the identity

$$\begin{aligned}&(w_{+1} - w_{-1})w_{+2}w_{+3}\ldots + w_{-1}(w_{+2} - w_{-2})w_{+3}\ldots + \ldots\\ &= w_{+1}w_{+2}w_{+3}\ldots - w_{-1}w_{-2}w_{-3}\ldots\end{aligned} \tag{29}$$

In this identity the step rates were represented in accordance with eqn. (27) as

$$w_{+s} - w_{-s} = \sum_p \nu_s^{(p)} v^{(p)}$$

where s is the number of the step and its associated graph edges, p is the number of independent routes, $v^{(p)}$ is the rate along the pth route, $\nu_s^{(p)}$ is the Horiuti number along the pth route for the sth step, and w_{+s} and w_{-s} are the rates of the direct and reverse reactions of the sth step, respectively. Temkin [14, 15] obtained the steady-state reaction equation

$$v^{(1)}\left(\frac{\nu_{s_1}^{(1)}}{w_{s_1}} + \frac{w_{-s_1}\nu_{s_2}^{(1)}}{w_{+s_1}w_{+s_2}} + \frac{w_{-s_1}w_{-s_2}\nu_{s_3}^{(1)}}{w_{+s_1}w_{+s_2}w_{+s_3}} + \ldots\right)$$
$$+ v^{(2)}\left(\frac{\nu_{s_1}^{(2)}}{w_{+s_1}} + \frac{w_{-s_1}\nu_{s_2}^{(2)}}{w_{+s_1}w_{+s_2}} + \frac{w_{-s_1}w_{-s_2}\nu_{s_3}^{(2)}}{w_{+s_1}w_{+s_2}w_{+s_3}} + \ldots\right) + \ldots =$$
$$= 1 - \frac{w_{-s_1}w_{-s_2}w_{-s_3}\ldots}{w_{+s_1}w_{+s_2}w_{+s_3}\ldots} \qquad (30)$$

This equation is independent of the order in which the steps are numbered. Temkin suggested an algorithm on the basis of eqn. (30) to obtain an explicit form of the steady-state kinetic equations. For linear mechanisms in this algorithm it is essential to apply a complex reaction graph. In some cases the derivation of a steady-state equation for non-linear mechanisms on the basis of eqn. (30) is also less difficult.

We have made an attempt to illustrate the experience of 15 years (from the mid-1950s to the late 1960s) of the "penetration" of the graph theory methods into two sufficiently close fields, enzyme and heterogeneous catalysis kinetics. From a purely utilitarian viewpoint, we prefer the algorithms approved in enzyme kinetics (see, for example, refs. 9 and 10). For linear mechanisms these algorithms, directly connected with those of the graph theory, are a much more efficient way of obtaining steady-state kinetic equations than the algorithms based on the steady-state reaction theory. This efficiency is constantly increasing as the use of computation analytical methods makes it possible to perform computations of complex analytical calculations. As to non-linear mechanisms, the above approaches are inefficient since neither of these two methods can give an explicit form of the steady-state kinetic equation (here it is impossible in the general case) or a special compact expression that would be convenient for analysis. Non-linear mechanisms will be discussed below.

One must not underestimate, however, the importance of the general results obtained in terms of the steady-state reaction theory. Its informative concepts are used in theoretical kinetics, in particular the concept of Horiuti (stoichiometric) numbers and a new formulation for the steady-state conditions, eqn. (27). In several publications devoted to the use of graph theory in chemical kinetics, quasi-steady-state conditions are used just in this formulation, e.g. in ref. 18. This study suggesting a new algorithm to derive kinetic equations is based on the Vol'kenshtein–Gol'dshtein formalism, but at the same time the authors also use eqn. (27).

In our series of studies of the 1970s [19–27], generalized in our monograph [7] (in what follows we will mostly proceed from the original material), we also used eqn. (27).

1.3 NON-LINEAR MECHANISMS ON GRAPHS

Investigations with the graphs of non-linear mechanisms had been stimulated by an actual problem of chemical kinetics to examine a complex dynamic behaviour. This problem was formulated as follows: for what mechanisms or, for a given mechanism, in what region of the parameters can a multiplicity of steady-states and self-oscillations of the reaction rates be observed? Neither of the above formalisms (of both enzyme kinetics and the steady-state reaction theory) could answer this question. Hence it was necessary to construct a mainly new formalism using bipartite graphs. It was this formalism that was elaborated in the 1970s.

Bipartite graphs of complex reaction mechanisms. A mechanism of a complex chemical reaction can be represented as a graph having nodes of two types, i.e. by a bipartite graph [28, 29]. One of these nodes corresponds, as before, to substances and the other accounts for elementary reactions (N.B. not for the steps, but for elementary reactions). Edges will join a node-substance and a node-reaction if this substance takes part in the reaction. The edge is directed from the node-substance to the node-reaction if the substance is the initial reactant, and vice versa if the substance is the reaction product. If the reaction is described as $\Sigma\alpha_i A_i \rightarrow \Sigma\beta_i A_i$, the number of edges from the node-substance to the node-reaction is α_i; in the opposite case it will amount to β_i. It is evident that non-linear graphs must be applied to non-linear mechanisms (see Chap. 3, Sect. 5.4)

The basic results in the analysis of non-linear mechanisms using graphs, were obtained by Clark [29], who developed a detailed formalism, and Ivanova [30, 31]. On the basis of Clark's approach, Ivanova formulated sufficiently general conditions for the uniqueness of steady states in terms of the graph theory. She suggested an algorithm that can be used to obtain (see Chap. 3, Sect. 5.4)

(1) conditions discriminating the region of parameters where the steady state is not unique (i.e. the condition for the multiplicity of steady states) and

(2) conditions for the existence of such a parametric region where the positive steady state is unique and unstable (i.e. the condition for self-oscillating rates).

Later, Vol'pert and Ivanova [32] suggested methods of searching for some critical phenomena for distributed "reaction–diffusion" systems. It is also possible to describe conditions for the appearance of "dissipative structures" in such systems in terms of graph theory which provides a natural account of the structural peculiarities of chemical reaction mechanisms.

Let us discriminate between the main problems in chemical kinetics solved using graph theory

(1) the algorithmic derivation of steady-state kinetic equations directly from the complex reaction graph. These kinetic equations (structured forms) make it possible to carry out a general analysis of steady-state kinetic equations;

(2) the analysis of the number of independent parameters in kinetic equations;

(3) the algorithmic derivation of a characteristic polynomial required to study relaxation times of complex reactions; and finally

(4) the analysis for the complex dynamic behaviour of chemical systems.

Problems (1)–(3) are efficiently solved for linear mechanisms and the corresponding kinetic models. The major material in what follows will be presented primarily for linear mechanisms.

Problem (4) is typical of non-linear mechanisms. The number of studies in this field is essentially lower since the application of graph theory in non-linear chemical kinetics is new. Our further description will relate to these principal problems.

2. Graphs for steady-state kinetic equations

2.1 SUBSTANTIATION OF THE "MASON RULE"

Let us prove the validity of the "Mason rule" formulated above [see eqn. (11)] for linear mechanisms with many cycles (routes).

A set of quasi-steady-state equations for a linear mechanism is of the form $\vec{b}(\vec{c})\vec{x} = 0$, where $\vec{x}$ and $\vec{c}$ are the vector-columns of the concentrations for the intermediates and observed substances (those participating in the brutto-reaction, i.e. initial substances and products) and $\vec{b}(\vec{c})$ is the matrix of the reaction weights

$$\vec{b}(\vec{c}) = \begin{pmatrix} -b_{11} b_{12} \cdots b_{1n} \\ b_{21} - b_{22} \cdots b_{2n} \\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot \\ b_{n1} b_{n2} \cdots - b_{nn} \end{pmatrix} \qquad (31)$$

Here $b_{ij} = b_{ij}(c) \geqslant 0$, $b_{ii} = \sum_{j \neq i} b_{ji}$. (It is evident that $\vec{c} > 0$.) The element of this matrix b_{ij} is the sum of the reaction weights. As stated above, the reaction weight is equal to its rate at unit concentration of the reacting intermediate.

In addition the law of conservation must be fulfilled for the total amount, C, of intermediates per unit catalyst surface

$$\sum_{r=1}^{n} x_r = C$$

In this case we assume the absence of any additional laws of conservation arising in the case when a linear system has autonomous groups of substances (see Sect. 5.1).

Values of x_r are determined using the set

$$\begin{aligned} x_t \sum_{r=1}^{n} b_{tr} &= \sum_{s=1}^{n} b_{st} x_s \\ \sum_{r=1}^{n} x_r &= C \end{aligned} \tag{32}$$

where b_{tr} is the weight of the reaction consuming x_t and forming x_r and b_{st} is the weight of the reaction in which x_s is consumed and x_t is formed.

Let eqns. (32) correspond to the graph G according to the following rule: every rth intermediate corresponds to a graph node. Let us express it, like the concentration of an intermediate, through x. The nodes x_s and x_t are joined by the edge (x_s, x_t) if the coefficient b_{st} in eqns. (32) does not equal zero.

Graph edges oriented in a definite direction which indicates the order of interconnection between the nodes are called *directed arcs*. Their orientation is indicated by the arrows placed either on the arcs or near them. A graph, a cycle, and a tree containing directed arcs are called directed. A directed cycle is also called a *contour*.

The validity of eqn. (11) is confirmed by the following theorem.

Theorem. If a set of linear equations takes the form of eqns. (32), its solution is determined using the formula

$$x_r = \frac{CD_r}{\sum_{r=1}^{n} D_r}$$

where D_r is the sum of weights for the directed spanning trees of the graph with a root in the node x_r and C is the total amount of intermediates per unit catalyst surface.

Let us prove this theorem proceeding from the Mason rule [5]. For this purpose let us rewrite eqns. (32) as

$$x_1 = \frac{b_{21}x_2 + b_{31}x_3 + \ldots + b_{n1}x_n}{\sum_{r=2}^{n} b_{1r}}$$

$$
\begin{aligned}
x_2 &= \frac{b_{12}x_1 + b_{32}x_3 + \ldots + b_{n2}x_n}{\sum\limits_{\substack{r=1\\ r\neq 2}}^{n} b_{2r}} \\
&\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\
x_{n-1} &= \frac{b_{1,n-1}x_1 + b_{2,n-1}x_2 + \ldots + b_{n,n-1}x_n}{\sum\limits_{\substack{r=1\\ r\neq n-1}}^{n} b_{n-1,r}} \\
x_n &= C - x_1 - x_2 - \ldots - x_{n-1}
\end{aligned}
\qquad (33)
$$

Then for eqns. (33) we construct a Mason graph (a signal graph) in the following way. Nodes of the graph G_{M} (Mason graph) are the nodes x_1, x_2, . . ., x_n corresponding to the variables and the fictitious nodes $x_0, \tilde{x}_1, \ldots, \tilde{x}_n$. The nodes x_i and x_j are joined by the arc (x_i, x_j) whose weight is

$$
a_{ji} = \frac{-b_{ji}}{\sum\limits_{r=1}^{n} b_{ir}} \qquad (34)
$$

The nodes x_n and x_0 are joined by the arc (x_0, x_n) having the weight $(-C)$. The arcs (x_n, x_i) join x_n with x_i and their weight is found from eqn. (34). Further every node x is joined with x_n by the arc whose weight is $(+1)$ and x_i and $\tilde{x}_i$ $(i = 1, \ldots, n)$ are also joined by the arc with the weight equal to $(+1)$.

The node x_0 is the graph G_{M} input and fictitious points $\tilde{x}_i$ are its outputs.

The Mason formula for this graph takes the form

$$
x_i = \frac{1}{\Delta} \sum_k P_k \Delta_k \qquad (35)
$$

where P_k is the kth direct path (walk) from the input node x_0 to the output $\tilde{x}_i$ and Δ is the determinant of eqns. (33) calculated using the formula

$$
\Delta = 1 - \sum C_{k_1} + \sum C_{k_2} - \ldots + (-1)^m \sum C_{k_m} \qquad (36)
$$

Δ_k is the determinant for that part of the graph obtained by eliminating the path P_k from G_{M}. In eqn. (36), $\Sigma\, C_{k_1}$ is the sum of the weights for the whole of the combinations of two uncontacting contours, etc. and $\Sigma\, C_{k_m}$ is the sum of the weights for the whole of the combinations of m uncontacting contours. The weight of contours combination is the product of the weights for the arcs entering into these contours. As can readily be seen, it is far from being evident that the Mason formula, eqn. (35), is analogous to the expression for x_r, eqn. (11) which must be proved.

Equation (36) is well known in combinatorial analysis (see, for example, ref. 33) as the inclusion and exclusion equation to calculate the number of objects possessing a certain, apparently void, set of given properties. Let a given property suggest that the n-node subgraph has a combination of t uncontacting contours. Then eqn. (36) provides a sum for the weights of trees, i.e. of the directed spanning trees in the graph G_M.

Consequently, the determinant will be

$$\Delta = \frac{D}{\prod\limits_k \sum\limits_r b_{kr}} \tag{37}$$

On the other hand, after reducing to a common denominator, the numerator of eqn. (35) will take the form

$$\sum_k P_k \Delta_k = \frac{CD_x}{\prod\limits_k \sum\limits_r b_{kr}} \tag{38}$$

whence the required result is obtained. Let us now prove that eqn. (35) does actually hold.

Let P_i take the form

$$P_i = [x_0, x_n, x_{i_1}, \ldots, x_{i_{k-1}}, x_{i_k}] \tag{39}$$

Its weight is equal to $C \cdot a_{ni_1} \cdot a_{i_1 i_2} \cdot \ldots \cdot a_{i_{k-1} i_k}$. The corresponding determinant Δ_i will be

$$\begin{aligned}\Delta_i &= 1 - \sum_{k_1} C_{k_1} + \sum_{k_2} C_{k_2} - \ldots \\ &= 1 - \left(\sum_{lj} a_{lj} a_{jl}\right) + \ldots \qquad l, j \neq n, i_1, \ldots, i_k\end{aligned} \tag{40}$$

The term in brackets gives the sum of all probable contours that are not in contact with the nodes of the path $P_i - x_n, x_{i_1}, \ldots, x_{i_k}$. This means that the denominators of the contour weights are the sums

$$\sum_{r \neq \alpha} b_{\alpha r}, \alpha \neq n, i_1, \ldots, i_k.$$

After opening the product $\Pi_\alpha \Sigma_r b_{\alpha r}$, $\alpha \neq n, i_1, \ldots, i_k$, we will obtain factors corresponding to the trees with the roots in the nodes $x_n, x_{i_1}, \ldots, x_{i_k}$ for the path P_i. In combination with the path $P_i = x_0, x_{i_1}, \ldots, x_{i_k}$ it provides a multitude of trees with the root in x_{i_k}. The theorem has been proved. Its proof could be carried out in terms of the known Kramer rule (see refs. 1 and, for more detail, 7). An example for the application of eqn. (11) to a simple catalytic isomerization reaction has been given above.

2.2 GENERAL FORM OF STEADY-STATE KINETIC EQUATION FOR COMPLEX CATALYTIC REACTIONS WITH MULTI-ROUTE LINEAR MECHANISMS

Let the graph $G(\vec{x}, \vec{u})$ correspond to the mechanism of a complex catalytic reaction that is linear with respect to intermediates. As before, the graph nodes x account for intermediates and the arcs u correspond to reactions. Every arc $\vec{u}$ of the graph G is ascribed to the number $b^{\pm}$ (b is the reaction weight). For the sake of convenience, we assume that if the arc $\vec{u} = (\vec{x}, \vec{y})$ has a weight $b^+(\vec{u})$, then the weight for the arc $\vec{v} = (\vec{y}, \vec{x})$ will be expressed as $b^-(\vec{u})$. These designations permit us to use an undirected weighted graph as a graph for the detailed mechanism. Each of its edges $\vec{u} = (\vec{x}, \vec{y})$ will account for the conversion of substance y into substance x and simultaneously for the conversion of substance x into y. Therefore the edge weight will be expressed as an ordered pair of the numbers $[b^+(\vec{u})$ and $b^-(\vec{u})]$. If one of the reactions does not take place, the corresponding weight will be equal to zero.

As noted above, a graph of a catalytic reaction must necessarily have cycles, since every intermediate is both consumed and formed. When applying the term "cycle", we will assume that it is a "*simple cycle*", i.e. a cycle containing no repeated nodes. This cycle is also called elementary.

A *connected graph* is a graph in which each point can be connected to the other by a certain sequence of arcs.

An *unconnected graph* is a graph in which not all its nodes can be connected by a certain sequence of arcs.

The definitions for a tree and a spanning tree were given at the beginning of this section. Let us give some further definitions.

(1) Let H be a spanning tree for the undirected graph for the reaction mechanism G. A *directed spanning tree*, $\overline{H}$, for the directed graph of the reaction mechanism is one whose arcs are oriented so that every node of the spanning tree except one, called a root, has one output arc. It can easily be seen that any node of the directed spanning tree is connected by a path with the spanning tree root, i.e. the root can be reached from any node.

(2) A *directed forest* is a term for the unconnected directed graph in which every component of connection is a directed tree with a root*.

Derivation of equation. During the step u, let a mutual conversion of the intermediates x_α and x_β take place at a rate w_u

$$w_u = b^+(\vec{u})x_\alpha - b^-(\vec{u})\, x_\beta \tag{41}$$

Using eqn. (41) whose proof is given above

$$x_r = \frac{CD_r}{\sum_r D_r}$$

where D_r is the sum of the weights for the directed spanning trees of the reaction graph with a root at the node x_r and C is the total amount of intermediates per unit catalyst surface (as usual, $C = 1$). Taking this equation into account, eqn. (41) can be written as

---

* All concepts of graph theory not given here can be found in the monograph 34. A good list of the graph theory concepts required for the investigation of chemical kinetic equations is given in ref. 35.

$$w_u = \frac{b^+(\vec{u})D_\alpha}{\sum\limits_r D_r} - \frac{b^-(\vec{u})D_\beta}{\sum\limits_r D_r}$$

or

$$w_u = \left[b^+(\vec{u}) \sum_k b(\overline{H}_{k,\alpha}) - b^-(\vec{u}) \sum_k b(\overline{H}_{k,\beta}) \right] \sum_r \sum_k b(\overline{H}_{k,r}) \tag{42}$$

where $\overline{H}_{k,\alpha}$ is the kth directed spanning tree with a root at the node α. In this case we have

$$b(\overline{H}_{k,\alpha}) = \prod_{u \in \overline{H}_{k,\alpha}} b^\pm(\vec{u}) \tag{43}$$

The sign $^\pm$ suggests that, for the weight calculation in $(\overline{H}_{k,\alpha})$ we take $b^+(\vec{u})$ or $b^-(\vec{u})$ in accordance with the demands for arc orientation in the spanning tree $\overline{H}_{k,\alpha}$.

Here we deal with the following almost evident statements.

Lemma (1). The product $b^+(\vec{u})b(\overline{H}_{k,\alpha})$ is the weight of a graph having one and only one contour obtained from the directed spanning tree $\overline{H}_{k,\alpha}$ by adding the arc $\vec{u}$.

Indeed, $\overline{H}_{k,\alpha}$ is a directed spanning tree with a root x_α; hence any arc incident with x_α enters x_α. Since the arc u originates from x_α and the directed spanning tree H contains all the graph nodes, the arc u closes exactly one contour.

A similar statement is also valid for the product $b^-(\vec{u})b(\overline{H}_{k,\beta})$. Let us designate the contour from Lemma 1, through $C_{k\alpha\beta}$. Then the inversely directed contour will be designated as $C_{k\beta\alpha}$.

Lemma (2). For the graph $\overline{H}_{k,\alpha} \bigcup \{u^+\}$ obtained by adding the arc u to the directed spanning tree $\overline{H}_{k,\alpha}$, the addition to the contour $C_{k\alpha\beta}$ is the directed forest, apparently with one-node components whose roots are the nodes for the contour $C_{k\alpha\beta}$. The lemma is evident.

Lemma (3). For any graph $\overline{H}_{k,\alpha} \bigcup \{u^+\}$ we will always find a graph $\overline{H}_{k,\beta} \bigcup \{u^-\}$ since the contours $C_{k\alpha\beta}$ and $C_{k\beta\alpha}$ have the same number of nodes and their additions in the graphs $\overline{H}_{k,\alpha} \bigcup \{u^+\}$ and $\overline{H}_{k,\beta} \bigcup \{u^-\}$ are isomorphic. Indeed, for $\overline{H}_{k,\alpha} \bigcup \{u^+\}$, this is a graph obtained by representing the direction for the arcs in the contour of $\overline{H}_{k,\beta} \bigcup \{u^-\}$, i.e. by the substitution of $C_{k\alpha\beta}$ for $C_{k\beta\alpha}$.

Then from eqns. (42) and (43) and lemmas (1)–(3) we immediately obtain a general equation for the rate of step u

$$w_u = \frac{\sum\limits_{\{C(\vec{u})\}} \left(\prod\limits_{v \in C_{k\alpha\beta}} b^+(\vec{v}) - \prod\limits_{v \in C_{k\beta\alpha}} b^-(\vec{v}) \right) \sum\limits_{\overline{H} \in \overline{H}(G, C(\vec{u}))} b(\overline{H})}{\sum\limits_r D_r} \tag{44}$$

Here $\{C(\vec{u})\}$ is the set of simple cycles in the reaction graph passing through the edge u, $\overline{H}$ is the directed forest with roots belonging to $C(\vec{u})$, and $\overline{H}(G, C(\vec{u}))$ is the set of such forests.

The properties of this equation will be examined in what follows.

Let us note that the summation in eqn. (44) is taken with respect to the number of all cycles involving the participation of step u. At the same time, in the Horiuti–Temkin equation ("the steady-state step equation"), which is one more formulation for the quasi-steady state conditions [11, 12]

$$\sum_{p=1}^{P} \nu_s^{(p)} v^{(p)} = w_{+s} - w_{-s} \qquad s = 1, \ldots, S \tag{45}$$

the summation is taken only with respect to the P independent cycles.

2.3 ANALYSIS OF PROPERTIES FOR THE GENERAL STEADY-STATE KINETIC EQUATION OF COMPLEX CATALYTIC REACTIONS

Let us write down the general kinetic equation obtained for the steady-state rate of the step in the form

$$w_u = \frac{\sum_i C_i P_i}{\sum_x D_x} \tag{46}$$

where C_i is the *cyclic characteristics* of the *i*th cycle

$$C_i = \prod_v b^+(\vec{v}) - \prod_v b^-(\vec{v})$$

and P_i is the matching parameter for this cycle

$$P_i = \sum_{\overline{H} \in \overline{H}(G,\, C(u))} b(\overline{H})$$

Let us interpret these important characteristics.

(1) We will first clarify the sense of the "cyclic characteristics". Let us take any cycle of the graph. Note that here a cycle is treated as a simple cycle, i.e. that having no repeated nodes. Each of its edges (step) corresponds to the Horiuti (stoichiometric) number. It can readily be shown that, for the cycle of a linear mechanism, this number will be either $+1$ or -1, depending on whether the step direction coincides with a chosen direction for this cycle. Horiuti numbers for the steps not entering into a cycle are equal to zero. For a one-step mechanism having only one cycle, all Horiuti numbers are equal to $+1$. (If a reaction mechanism also has buffer steps not entering into the cycle, their Horiuti numbers are zero.) Let us add the steps belonging to one simple cycle, multiplying them by the Horiuti numbers. We will obtain a brutto-equation to relate the initial substances and products. We will call this "natural". It will not necessarily be integer-valued. Further we will illustrate it in detail by an example of one-step mechanism. The brutto-equation found can also take the form $0 = 0$. Every simple cycle and its

brutto-equation corresponds to the cyclic characteristics, i.e. the difference between the products of the weights for direct and reverse reactions, respectively.

The sense of the cyclic characteristic is simple. It is a kinetic equation of our brutto-reaction as if it were a step and consists of elementary reactions obeying the law of mass action. For the cycle with the brutto-equation $0 = 0$, the cyclic characteristic is $C = 0$. If all cycles have the same "natural" brutto-equations, their cyclic characteristics are represented as

$$C_p = \prod_i k_i^{+(p)}[1 - (K_{\text{eq}})^{-1} \text{f}^-(\vec{c})/\text{f}^+(\vec{c})]\, \text{f}^+(\vec{c}) \tag{47}$$

where K_p is the equilibrium constant corresponding to the brutto-equation, $\text{f}^+(\vec{c})$ and $\text{f}^-(\vec{c})$ are concentrational dependences for the direct and inverse equations of the brutto-reaction presumed by the elementary reactions, and $k_i^{+(p)}$ the rate constants for the reactions of the pth direct cycle.

Thus cyclic characteristics of various cycles will differ only in values of the factors $(\Pi_i k_i^{+(p)})$. Cyclic characteristics for two different cycles with the same "natural" brutto-equations are proportional to each other

$$\frac{C_1}{C_2} = \frac{\left(\prod_i k_i^{+(1)}\right)}{\left(\prod_i k_i^{+(2)}\right)} \tag{48}$$

In the general case, a complex catalytic reaction can be written in the matrix form

$$\vec{\Gamma}_A \vec{A} + \vec{\Gamma}_X \vec{X} = \vec{0} \tag{49}$$

Here $\vec{A}$ and $\vec{X}$ are the vector-columns of the observed and intermediate substances, respectively, and $\vec{\Gamma}_A$ and $\vec{\Gamma}_X$ the matrices of their stoichiometric coefficients.

As shown above, the stoichiometric (Horiuti) numbers must satisfy the equality

$$\vec{\nu}^T \vec{\Gamma}_X = 0$$

After multiplying all steps of eqn. (49) by the vector $\vec{\nu}^T$ we obtain a set of brutto-reaction equations

$$\vec{\nu}^T \vec{\Gamma}_A \vec{A} = \vec{0} \tag{50}$$

or

$$\vec{\Gamma}_{\text{BR}} \vec{A} = \vec{0}$$

where $\vec{\Gamma}_{\text{BR}}$ is the stoichiometric matrix for the set of brutto-equations.

We have already said that, in principle, the "natural" brutto-equation can have no minimum integer-valued coefficients. Let us illustrate this by an example of the catalytic isomerization reaction, which can follow the following mechanisms

Mechanism I

$$\begin{array}{l} (1)\ \mathrm{A} + \mathrm{Z} \rightleftarrows \mathrm{AZ} \\ (2)\ \mathrm{AZ} \rightleftarrows \mathrm{B} + \mathrm{Z} \\ \hline \qquad \mathrm{A} = \mathrm{B} \end{array}$$

Mechanism II

$$\begin{array}{l} (1)\ \mathrm{A} + \mathrm{Z} \rightleftarrows \mathrm{AZ} \\ (2)\ \mathrm{AZ} \rightleftarrows \mathrm{BZ} \\ (3)\ \mathrm{A} + \mathrm{BZ} \rightleftarrows \mathrm{Z} + 2\,\mathrm{B} \\ \hline \qquad 2\,\mathrm{A} = 2\,\mathrm{B} \end{array}$$

Mechanism III

$$\begin{array}{l} (1)\ \mathrm{A} + \mathrm{Z} \rightleftarrows \mathrm{AZ} \\ (2)\ \mathrm{A} + \mathrm{AZ} \rightleftarrows \mathrm{Z} + 2\,\mathrm{B} \\ \hline \qquad 2\,\mathrm{A} = 2\,\mathrm{B} \end{array}$$

Mechanism I accounts for the "natural" brutto-equation A = B obtained by adding steps of the detailed mechanism, whereas mechanisms II and III correspond to the equation 2 A = 2 B. Cyclic characteristics will, apparently, differ. In the former case $C = K^{+} C_{\mathrm{A}} - K^{-} C_{\mathrm{B}}$, in the latter $C = K^{+} C_{\mathrm{A}}^{2} - K^{-} C_{\mathrm{B}}^{2}$.

(2) The value $\Sigma_{\bar{H}} b(\overline{H}) = P_i$ [see eqn. (46)] is a matching parameter. In the general case it is the sum of factors, i.e. the value characterizing the effect of the substances not involved in a given cycle.

In terms of the graph theory, $b(\overline{H})$ is the weight for the directed graph whose roots belong to a given cycle. For a complex reaction having one cycle and no "buffer" steps, we have $P = 1$ and no matching.

(3) As has been shown above, the cyclic characteristics is a kinetic equation for the brutto-reaction as if it were a simple step. But the denominator $\Sigma_x D_x$ accounts for the "non-elementary" character of this reaction and indicates the rate retardation by catalyst surface intermediates.

Every summand in the denominator is the spanning tree weight. Let us recall that, in this case, the sense of the spanning tree is a non-cyclic sequence of reactions with the help of which a given intermediate is formed of all others. Hence it can easily be shown that (a) every summand of the denominator $\Sigma_x D_x$ and of the matching parameter P_i cannot simultaneously contain weights for the direct and reverse reactions of the same step; (b) every summand of the denominator and of the matching parameter cannot contain weights for two or more reactions involving the participation of the same intermediate; (c) every summand of the denominator is a product of the $(S - P)$ reaction weights, where S is the number of graph edges (steps) and P the number of linearly independent cycles; (d) every summand of the matching parameter P_i is a product of the $(S - S_C) - (P - 1)$ reaction weights where S_C is the number of arcs belonging to a given cycle.

It must be noted that at present the writing of all summmands D_x presents no difficulties because there exist effective computation algorithms.

Equation (46) accounts for the step rate w_u. The steady-state rates for concentration variation of substance A(W_A) and for the step (w_u) are related as

$$W_A = \sum_u \gamma_{u,A} w_u \tag{51}$$

where $\gamma_{u,A}$ is the stoichiometric coefficient for the observed substance A in step u. As a rule, each elementary reaction of complex mechanisms of heterogeneous catalysis involves the participation of no more than one molecule of the observed substance. Therefore $\gamma_{u,A}$ takes a value equal to $+1$, -1 or 0.

Let us apply the general equation (46) for the analysis of various typical cases.

I. One-route mechanisms

$$C = \prod_v b^+(\vec{v}) - \prod_v b^-(\vec{v}) \qquad P = 1$$

It is this one-route mechanism of catalytic isomerization that was used above to illustrate the "operation" of graph theory in chemical kinetics. For a graph of a one-route mechanism see Fig. 5(a).

Let us give one more example, a two-step reaction. Among the class of two-step catalytic reactions suggested by Temkin [36] and studied in detail by Boudart [37], we can find many industrial reactions. For example

(1) $H_2O + Z \rightleftarrows ZO + H_2$

(2) $ZO + CO \rightleftarrows Z + CO_2$

$$\overline{CO + H_2O = CO_2 + H_2}$$

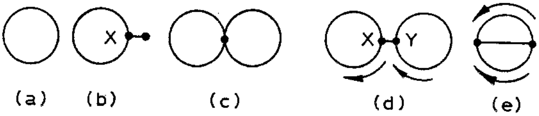


Fig. 5. Graphs of linear mechanisms. (a) One-route mechanism; (b) one-route mechanism with a "buffer" step; (c) two-route mechanism with a common intermediate; (d) two-route mechanism with a "bridge" connecting cycles; (e) two-route mechanism with a common step.

In this case the set of reaction weights will be

$$
\begin{aligned}
b_1^+ &= k_1^+[\mathrm{H_2O}]\\
b_1^- &= k_1^-[\mathrm{H_2}]\\
b_2^+ &= k_2^+[\mathrm{CO}]\\
b_2^- &= k_2^-[\mathrm{CO_2}]
\end{aligned}
$$

and the reaction rate will be written as

$$
\begin{aligned}
W &= \frac{b_1^+ b_2^+ - b_1^- b_2^-}{b_1^+ + b_2^+ + b_1^- + b_2^-}\\
&= \frac{k_1^+ k_2^+[\mathrm{H_2O}][\mathrm{CO}] - k_1^- k_2^-[\mathrm{H_2}][\mathrm{CO_2}]}{k_1^+[\mathrm{H_2O}] + k_1^-[\mathrm{H_2}] + k_2^+[\mathrm{CO}] + k_2^-[\mathrm{CO_2}]}
\end{aligned}
$$

This expression is identical to that from ref. 36. The total number of spanning trees in the graph of the one-step mechanism is equal to n^2 (all steps are assumed to be reversible). We will discriminate between direct, inverse and mixed spanning trees. Direct and inverse will be called the spanning trees consisting of the arcs only with the direct or inverse orientations, respectively. Mixed spanning trees are those containing both direct and inverse arcs. The number of the direct and inverse graph spanning trees is equal to $C_n^{m-1} = n$. Every node has one direct, one inverse and $(n-2)$ mixed spanning trees. Thus the relationship

$$n + n + n(n-2) = n^2$$

is fulfilled.

It is evident that the mixed spanning trees exist only at $n \geqslant 3$. Two-step schemes have no mixed spanning trees.

For the three-step mechanisms (Fig. 1) the weights for direct spanning trees are expressed as

$$
\begin{aligned}
B_{\mathrm{dir}} &= b_1^+ b_2^+ + b_2^+ b_3^+ + b_3^+ b_1^+ &&= k_1^+[\mathrm{A}]k_2^+ + k_2^+ k_3^+ + k_3^+ k_1^+[\mathrm{A}]\\
B_{\mathrm{in}} &= b_1^- b_2^- + b_2^- b_3^- + b_3^- b_1^- &&= k_1^- k_2^- + k_2^- k_3^-[\mathrm{B}] + k_3^-[\mathrm{B}]k_1^- \quad (52)\\
B_{\mathrm{mix}} &= b_1^+ b_2^- + b_2^+ b_3^- + b_3^+ b_1^- &&= k_1^+[\mathrm{A}]k_2^- + k_2^+ k_3^-[\mathrm{B}] + k_3^+ k_1^-
\end{aligned}
$$

where B_{dir}, B_{in} and B_{mix} are the sums of the spanning tree weights for direct, inverse and mixed spanning trees, respectively.

The number of spanning trees is much lower if all steps are irreversible ("strong" irreversibility) or if several (one, two, etc.) steps are irreversible ("weak" irreversibility). In the case of "strong" irreversibility there are no either inverse or mixed spanning trees. If the irreversibility is "weak" and only one step is irreversible, the number of inverse spanning trees reduces to one. In the case in which two or more steps are irreversible there are no inverse spanning trees at all.

For example, for the oxidation of hydrogen on the oxides of the transition metals of Group IV, we have [38]

$$
\begin{aligned}
&(1)\ H_2 + (ZO)_2 \rightarrow ZOZ \cdot H_2O \\
&(2)\ ZOZ \cdot H_2O \rightleftarrows ZOZ + H_2O \\
&(3)\ ZOZ + H_2 \rightarrow Z \cdot Z \cdot H_2O \\
&(4)\ Z \cdot Z \cdot H_2O \rightleftarrows Z \cdot Z + H_2O \\
&(5)\ Z \cdot Z + O_2 \rightarrow (ZO)_2
\end{aligned}
\tag{53}
$$

The corresponding expressions for the reaction weights are

$$
\begin{aligned}
b_1^+ &= k_1^+[H_2] \\
b_2^+ &= k_2^+ \\
b_2^- &= k_2^-[H_2O] \\
b_3^+ &= k_3^+[H_2] \\
b_4^+ &= k_4^+ \\
b_4^- &= k_4^-[H_2O] \\
b_5^+ &= k_5^+[O_2] \\
\prod_v b^+(v) &= k_1^+ k_2^+ k_3^+ k_4^+ k_5^+ [H_2]^2[O_2]
\end{aligned}
$$

Then

$$W = \frac{k_1^+ k_2^+ k_3^+ k_4^+ k_5^+ [H_2]^2[O_2]}{\sum_x D_x} \tag{54}$$

where

$$
\begin{aligned}
\sum_x D_x = {} & k_1^+ k_2^+ k_3^+ k_4^+ [H_2]^2 + k_2^+ k_4^+ k_5^+ (k_1^+ + k_3^+)[O_2][H_2] + \\
& + k_1^+ k_2^+ k_3^+ k_4^- [H_2]^2[H_2O] + k_1^+ k_4^+ k_5^+ k_2^- [H_2][O_2][H_2O] + \\
& + k_1^+ k_3^+ k_5^+ (k_2^+ + k_4^+)[H_2]^2[O_2]
\end{aligned}
$$

If a one-route mechanism is supplemented by a "buffer" step, the graph will have a "hanging" node [Fig. 5(b)].

For this graph the steady-state rate for a one-route mechanism will be expressed as

$$W = \frac{\left(\prod_{i=1}^{n} b_i^+ - \prod_{i=1}^{n} b_i^-\right)}{\sum_x D_x}$$

The only difference is that the weights of the graph arcs going out from the node x must be divided by the value $(1 + K_x)$ where K_x is the ratio of weights of the direct and inverse reactions for the step associated with the "hanging" node.

It is evident that, in the steady-state case, the "buffer" step is in equilibrium and its rate is zero.

II. Two-route mechanisms

(1) Let us consider the mechanism of the reaction of NO and CO on silver [39]

$$\begin{aligned} &(1)\ \mathrm{NO} + \mathrm{Z} \rightleftarrows \mathrm{ZNO} \\ &(2)\ \mathrm{ZNO} + \mathrm{NO} \rightarrow \mathrm{N_2O} + \mathrm{ZO} \\ &(3)\ \mathrm{N_2O} + \mathrm{Z} \rightarrow \mathrm{N_2} + \mathrm{ZO} \\ &(4)\ \mathrm{ZO} + \mathrm{CO} \rightarrow \mathrm{Z} + \mathrm{CO_2} \end{aligned} \tag{55}$$

The reaction graph is represented in Fig. 6. The reaction weights are

$$\begin{aligned} b_1^+ &= k_1^+[\mathrm{NO}] \\ b_1^- &= k_1^- \\ b_2^+ &= k_2^+[\mathrm{NO}] \\ b_3^+ &= k_3^+[\mathrm{N_2O}] \\ b_4^+ &= k_4^+[\mathrm{CO}] \end{aligned}$$

Cyclic characteristics corresponding to the irreversible cycles I [steps (1), (2), (4)] and II [steps (3), (4)] are expressed as

$$\begin{aligned} C_1 &= k_1^+ k_2^+ k_4^+ [\mathrm{NO}]^2[\mathrm{CO}] \\ C_2 &= k_3^+ k_4^+ [\mathrm{N_2O}][\mathrm{CO}] \end{aligned}$$

Matching parameters accounting for cycles I and II, will be $P_{\mathrm{I}} = 1$ and $P_{\mathrm{II}} = k_1^- + k_2^+[\mathrm{NO}]$, respectively.

Then we obtain

$$\begin{aligned} W_{\mathrm{CO}} &= W_{\mathrm{CO_2}} = w_4 \\ &= \frac{k_1^+ k_2^+ k_4^+[\mathrm{NO}]^2[\mathrm{CO}] + k_3^+ k_4^+[\mathrm{N_2O}][\mathrm{CO}](k_1^- + k_2^+[\mathrm{NO}])}{\sum_x D_x} \end{aligned} \tag{56}$$

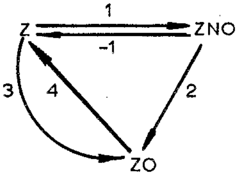


Fig. 6. Graph of the NO + CO reaction over silver.

where

$$\sum_x D_x = k_1^+ k_2^+ [\mathrm{NO}]^2 + k_4^+ [\mathrm{NO}][\mathrm{CO}](k_1^+ + k_2^+) +$$
$$+ k_2^+ k_3^+ [\mathrm{N_2O}][\mathrm{NO}] + k_1^- k_4^+ [\mathrm{CO}] + k_1^- k_3^+ [\mathrm{N_2O}]$$

(2) The mechanism for the synthesis of vinyl chloride, eqns. (24), whose graph is given in Fig. 3(d), also has two routes with one "natural" brutto-equation. Without taking into account the reversibility of steps (1) and (3), the rate of product formation will be

$$\begin{aligned} W &= w_2 + w_4 \\ &= \frac{k_1^+ k_2^+ k_4^+ [\mathrm{HCl}][\mathrm{C_2H_2}]^2 + k_2^+ k_3^+ k_4^+ [\mathrm{HCl}]^2[\mathrm{C_2H_2}]}{k_1^+ k_4^+ [\mathrm{C_2H_2}]^2 + k_2^+ k_4^+ [\mathrm{HCl}][\mathrm{C_2H_2}] + k_2^+ k_3^+ [\mathrm{HCl}]^2} \end{aligned} \tag{57}$$

Among two-route mechanisms, those illustrated in Fig. 5(c) (those having one common intermediate) and in Fig. 5(e) (mechanisms having a common step) are widespread. The graph in Fig. 5(d) accounts for the mechanism in which two cycles are connected by a bridge "arch". It can easily be seen that the steady-state rate corresponding to the "arch" will be zero, i.e. this step is in equilibrium. These typical schemes are present as fragments for multi-route mechanisms.

Essential differences are observed between the two-route mechanism with a common intermediate and the two-route mechanism with a common step (common steps).

In the former case, a step of each cycle can enter into one simple cycle. In the numerator of eqn. (46) for the step rate we will observe only one cyclic characteristic, C, corresponding to this cycle. The presence of an additional cycle affects only the value of the matching parameter P. The cycle rate can vary only quantitatively, but in neither case does the reaction direction vary. This situation corresponds to the so-called "kinetic matching"(see, for example, ref. 40). Assuming that all steps are reversible, the total number of spanning trees amounts to $n_1^2 n_2 + n_1 n_2^2 - n_1 n_2$, where n_1 and n_2 are the number of steps in both cycles.

In the second case the step of each cycle can enter into an additional cycle (also assuming that all steps are reversible). In the numerator of eqn. (46) for the rate of the step of one of the cycles we observe the appearance of the summand W^*. It contains a cyclic characteristic corresponding to the new cycle. In the numerator for the rate of the step of the other cycle there appears the summand $-W^*$. This case corresponds to the so-called "thermodynamic matching" when, due to the appearance of additional cycles, it becomes possible to change both the rate value and its sign (i.e. the reaction direction). It is of interest to note that thermodynamic matching in the pure form is impossible since we will always observe the presence of a summand accounting for the performance of a reaction by "its own" cycle. The total number of spanning trees is calculated using the formula $n_1(n_2 - 1)(n_1 + n_2$

– 2). If both cycles are irreversible, thermodynamic matching is not observed.

Let us emphasize a simple but important circumstance. If multi-route reactions are carried out on a catalyst with an active site of the same type, they must necessarily be characterized by either kinetic or thermodynamic matching. The problem of matching will be discussed in more detail in the next paragraph.

III. Multi-route mechanisms

As an example, let us consider the above fragment of the conversion mechanism for *n*-hexane [its graph is given in Fig. 3(f)]. The weights of some arcs are equal to the sums of those of individual reactions. For example, the weight of the arc from HK to K amounts to $b_{\mathrm{HK\text{-}K}} = b_1 + b_5 + b_6$. Let us write down the rate for step (3). It enters into four cycles (see Fig. 4). Cycle I (HK–MCK–IK–HK) has the cyclic characteristics

$$C_{\mathrm{I}} = b_3 b_{-7} b_{-2} - b_{-3} b_7 b_2$$

The matching parameter P_1 accounting for the connection of the node K with cycle I, will be

$$P_1 = b_4 + b_{-8} + b_1$$

For cycle II (HK–MCK–IK–K–HK) we have

$$C_{\mathrm{II}} = b_3 b_{-7}(b_8 + b_9)b_1 - b_{-3} b_7 b_{-8}(b_{-1} + b_5 + b_6) \qquad P_2 = 1$$

For cycle III (HK–MCK–K–IK–HK) the value of C is equal to

$$C_{\mathrm{III}} = b_3(b_4 + b_{10})b_{-8} b_{-2} - b_{-3} b_{-4}(b_8 + b_9)b_2 \qquad P_3 = 1$$

For cycle IV (HK–MCK–K–HK) it amounts to

$$C_{\mathrm{IV}} = b_3(b_4 + b_{10})b_1 - b_{-3} b_{-4}(b_{-1} + b_5 + b_6)$$

The matching parameter P_4 characterizing the connection of the node IK with cycle IV, takes the form

$$P_4 = (b_8 + b_9) + b_7 + b_{-2}$$

The cyclic characteristics and matching parameters for the cycles being known, we can easily determine a numerator for the steady-state rate. Since the denominator is cumbersome, we omit its description here.

The principal advantage of eqn. (46) is not only the simple derivation of a steady-state kinetic equation directly from the detailed reaction mechanism but the possibility of obtaining from this equation the results which have physicochemical significance. In what follows, we will discuss the most important ones.

2.4 HOW TO FIND THE KINETIC EQUATION FOR REVERSE REACTIONS

This problem, put forward independently by Horiuti (1939) [41] and Boreskov (1945) [42], can be formulated as follows: to find a kinetic equation for a complex reaction in the reverse direction from the known similar expression for the direct reaction rate and applying only thermodynamic relationship for the brutto-reaction. In other words it is necessary to answer the question, in what cases is the equation

$$\frac{W^{+}(\vec{c})}{W^{-}(\vec{c})} = \frac{f^{+}(\overrightarrow{c})}{f^{-}(\overleftarrow{c})} K_{\mathrm{eq}}(T) \tag{58}$$

valid? Here $W^{+}(\vec{c})$ and $W^{-}(\vec{c})$ are the rates of the direct and reverse reactions, respectively, $f^{+}(\overrightarrow{c})$, $f^{-}(\overleftarrow{c})$ are kinetic laws corresponding to the direct and reverse brutto-reactions, $\vec{c}$ is the set of concentrations for all substances, $\overrightarrow{c}$ and $\overleftarrow{c}$ are the sets of concentrations for the initial substances and products, respectively, and $K_{\mathrm{eq}}(T)$ is the equilibrium constant for the brutto-reactions. Horiuti solved this problem in 1939 for a special case, i.e. for the reaction on a hydrogen electrode. It is in connection with this problem that the known concept "stoichiometric number" was introduced. Boreskov, during World War II and not knowing of Horiuti's study, found a solution to this problem for a sequence of reactions under some simplifying assumptions (e.g. one step is rate-determining, the kinetic relationship is a power equation). The Horiuti–Boreskov problem appeared to be rather difficult. In fact, it is the problem of matching kinetic and thermodynamic relationships for complex reactions. So far this problem in its general formulation, i.e. for multi-route non-linear reactions, has not been solved. We will now present the results concerning linear mechanisms.

(1) The cycle is unique

In accordance with eqn. (46) we obtain

$$\begin{aligned}
W &= \frac{C}{\sum_x D_x} = \frac{\prod_i b_i^{+} - \prod_i b_i^{-}}{\sum_x D_x} \\
&= W^{+} - W^{-} \\
&= W^{+}\left(1 - \frac{W^{-}}{W^{+}}\right) \\
&= W^{+}\left(\frac{1 - \prod_i b_i^{-}}{\prod_i b_i^{+}}\right) \\
&= W^{+}\left(1 - \frac{f^{-}(\overleftarrow{c}) \prod_i k_i^{-}(T)}{f^{+}(\overrightarrow{c}) \prod_i k_i^{+}(T)}\right)
\end{aligned}$$

$$= W^+\left(1 - \frac{f^-(\vec{c})}{K_{eq}(T)f^+(\vec{c})}\right) \tag{59}$$

where

$$W^+ = \frac{\prod_i b_i^+}{\sum_x D_x}$$

and

$$W^- = \frac{\prod_i b_i^-}{\sum_x D_x}$$

For this case the Horiuti–Boreskov concept is always valid and does not require an assumption about the rate-determining step.

Let us note that in eqn. (59) the expressions $f^+(\vec{c})$ and $f^-(\vec{c})$ are the kinetic dependences that are written according to the law of mass action for the "natural" brutto-reaction, i.e. for the reaction obtained by a simple addition of all cycle steps, and $K_{eq}(T)$ is the equilibrium constant for this reaction. However, as we mentioned above for the reaction of catalytic isomerization, the "natural" brutto-equation should not necessarily have integer-valued coefficients. For the mechanism

(1) $A + Z \rightleftarrows AZ$

(2) $AZ \rightleftarrows B + Z$

with the "natural" brutto-equation $A = B$ eqn. (59) will take the form

$$W = W^+\left(1 - \frac{1}{K_{eq,m}}\frac{c_B}{c_A}\right) \tag{60}$$

But for the mechanism

(1) $A + Z \rightleftarrows AZ$

(2) $A + AZ \rightleftarrows 2B + Z$

with the "natural" brutto-equation $2A = 2B$, eqn. (59) will be

$$W = W^+\left(1 - \frac{c_B^2}{K_{eq}c_A^2}\right)$$

$$= W^+\left[1 - \left(\frac{c_B}{K_{eq,m}c_A}\right)^2\right] \tag{61}$$

In eqns. (60) and (61), $K_{eq,m}$ is the equilibrium constant for the brutto-reaction with the minimum integer-valued coefficients.

In the general case we can write

$$W = W^{+}\left[1 - \left(\frac{\phi_{\mathrm{m}}(\vec{c})}{K_{\mathrm{eq,m}}}\right)^{\kappa}\right] \tag{62}$$

where $\phi_{\mathrm{m}}(\vec{c})$ and $K_{\mathrm{eq,m}}$ will correspond to the brutto-reaction with the minimum integer-valued coefficients. The value κ can be called the brutto-reaction multiplicity.

Equation (62) is an analog of that obtained by Boreskov [42] but in contrast to it, it does not require the assumption of the existence of a rate-determining step.

(2) There are several cycles

Let us consider the case in which the rate of the step (or steps) of interest is expressed as eqn. (59) or (62). This step participates in simple cycles at a non-zero rate (non-zero cycles) and these cycles correspond to the same "natural" brutto-equation.

Let us interpret it in more detail. According to eqn. (46), the step rate is expressed as

$$w_u = \frac{\sum_i C_i P_i}{\sum_x D_x}$$

The cycle will be characterized by a zero rate in the two cases: (a) the cycle corresponds to the "natural" brutto-equation 0 = 0; then $C = 0$ and (b) the cycle is in equilibrium; then $C = 0$. Cycles with zero rates (zero cycles) do not provide any additional summands in the numerator, whereas the denominator will now have summands accounting for the reaction retardation by the intermediates of these cycles.

Let two cycles have similar "natural" brutto-equations. Then their cyclic characteristics will be expressed as

$$\begin{aligned} C_1 &= \prod_i (b_i^{+})^{\mathrm{I}} - \prod_i (b_i^{-})^{\mathrm{I}} \\ &= \prod_i (b_i^{+})^{\mathrm{I}}\left(1 - \frac{\prod_i (b_i^{-})^{\mathrm{I}}}{\prod_i (b_i^{+})^{\mathrm{I}}}\right) \\ &= \prod_i (b_i^{+})^{\mathrm{I}}\left(1 - \frac{\phi(\vec{c})}{K_{\mathrm{eq}}}\right) \end{aligned} \tag{63}$$

and similarly

$$C_2 = \prod_i (b_i^{+})^{\mathrm{II}}\left(1 - \frac{\phi(\vec{c})}{K_{\mathrm{eq}}}\right) \tag{64}$$

The values $\phi(\vec{c})$ and K_{eq} in eqns. (63) and (64) are the same.

We then have

$$w_u = \frac{(C_1P_1 + C_2P_2)}{\sum\limits_x D_x} = \left(\prod_i (b_i^+)^{\mathrm{I}}P_1 + \prod_i (b_i^+)^{\mathrm{II}}P_2\right)\frac{\left(1 - \dfrac{\phi(\vec{c})}{K_{eq}}\right)}{\sum\limits_x D_x} \tag{65}$$

Thus eqn. (65) takes the form of eqn. (59). It is evident that the same statement can also be made in the case when some step takes part in many cycles with the same "natural" brutto-equation. The representation of type of eqn. (65) will also be valid for the steady-state rate of concentration variation for substance A [see eqn. (51)] if this substance participates in non-zero cycles with the same "natural" brutto-equation.

Let us note one special but widespread case when there are several cycles but they have only common nodes (intermediates). Each cycle has its "own" observed substance that is consumed or formed only in this cycle. The rate of concentration variation for this substance will have only one cyclic characteristic in the numerator, hence its expression by eqn. (59) is valid.

It is possible that the reaction with the only brutto-equation will follow several routes. For example, the reaction of vinyl chloride synthesis

$$C_2H_2 + HCl = C_2H_3Cl$$

can follow two routes [see eqn. (24) and Fig. 3(d)]. In this case "natural" brutto-equations are similar. Apparently, this can be considered to be the rule. Then in the case when all steps are reversible, eqn. (59) for the rate of consumption of a substance is valid.

But, in principle, it is possible that, for the reaction with the only brutto-equation, its different routes correspond to the "natural" brutto-equations having different multiplicities [see eqn. (62)]. Then eqn. (59) would not be valid. The literature lacks studies in which this problem has been examined on the basis of experimental data.

It can be concluded that, for linear multi-route mechanisms, a class has been specified for which the representation of a kinetic equation in the form of the Horiuti–Boreskov equation, eqn. (59), is valid. Note that Khomenko et al. [43] have analyzed a kinetic equation for the two-route reaction, one of which is in equilibrium. For the results of the analysis for a non-linear one-route mechanism, see ref. 44.

2.5 MATCHING OF REACTIONS AND THE REPRESENTATION OF THE KINETIC EQUATION IN THE HORIUTI-BORESKOV FORM

The result obtained provides an interesting aspect in interpreting the matching of the above reactions. If a kinetic equation can be presented in the Horiuti–Boreskov form, we are dealing with *"kinetic matching"*. In this case the addition of an additional cycle affects the value of the rate but cannot result in a reversal of the direction.

But if the kinetic equation cannot be presented in this form, we are dealing with *"thermodynamic matching"* affecting both the value of the rate and its sign (direction). Thus, the typical mechanism

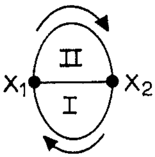
corresponds to the kinetic equations

$$W^{\mathrm{I}} = \frac{C_1 P_1}{\sum_x D_x}$$

and

$$W^{\mathrm{II}} = \frac{C_2 P_2}{\sum_x D_x} \tag{66}$$

and the mechanism



corresponds to the equations

$$\begin{aligned} W^{\mathrm{I}} &= \frac{C_1 P_1 + C^*}{\sum_x D_x} \\ W^{\mathrm{II}} &= \frac{C_2 P_2 - C^*}{\sum_x D_x} \end{aligned} \tag{67}$$

where C^* is the cyclic characteristic of the total cycle obtained after removing the arc (X_1, X_2); $P^* = 1$. Equation (66) is the case of kinetic matching and (67) that of thermodynamic matching. The concept of thermodynamic and kinetic matching is applied in the case when at least two brutto-reactions take place in the system and can affect each other. But multi-route mechanisms can also be realized for cases with only one brutto-reaction. Various cycles can have either common arcs (steps) or only common nodes (intermediates). In this case we can also observe matching: various routes with different characteristics will be matched.

2.6 OBSERVED KINETIC REGULARITIES AND CHARACTERISTICS OF DETAILED MECHANISMS

The analysis of observed kinetic parameters, primarily of the observed reaction rate order, and observed activation energy is an integral part of the kinetic study of complex catalytic reactions.

In accordance with ref. 35, the terms *observed order* and *observed activation energy* can be used correctly only for power kinetic relationships. Here we will examine the relationships between the experimentally observed values $\partial \ln W/\partial \ln A$ and $\partial \ln W/\partial(-1/RT)$ and the characteristics of the detailed mechanism. We believe these relationships to be rather informative. As the subject of the analysis we will take a one-route catalytic reaction with a mechanism that is linear with respect to the intermediates.

Since the steps of these mechanisms usually involve the participation of no more than one molecule of the observed substance, the steady-state rate of its concentration variation will be presented as $W_A = pW$, where p is the number of steps involving the substance participation of A and W the steady-state rate for any step (rate over the route).

2.6.1 *Observed reaction order*

Let us first present some transformational expressions for the steady-state step rate. Every path corresponding to the summand of D_x can include several steps for the consumption of the same substance. The weight of the corresponding spanning tree will then be characterized by the power exponent for the concentration of this reactant with which it enters into this spanning tree. This exponent is the total number of molecules consumed for all steps of a given path.

Assuming that the chosen substance, A, reacts in p steps of the n-step one-route mechanism, let us express the denominator of the steady-state rate as a polynomial with respect to its concentration

$$\sum_x D_x = B_0 + B_1[\mathrm{A}] + B_2[\mathrm{A}]^2 + \ldots + B_p[\mathrm{A}]^p \tag{68}$$

After a similar transformation of the numerator, we can write

$$W = \frac{K[\mathrm{A}]^p - B^-}{B_0 + B_1[\mathrm{A}] + \ldots + B_p[\mathrm{A}]^p} \tag{69}$$

where $B_0, B_1, \ldots, B_p, B^- = \Pi_i b_i^-$ are functions of the composition and temperature which are independent of the concentration of substance A. We then have

$$m_A = \frac{\partial \ln W}{\partial \ln[\mathrm{A}]} = \frac{\partial \ln W}{\partial[\mathrm{A}]} \Big/ \frac{\partial \ln[\mathrm{A}]}{\partial[\mathrm{A}]}$$

$$= \frac{pK[\mathrm{A}]^p}{K[\mathrm{A}]^p - B^-} - \frac{B_1[\mathrm{A}] + 2B_2[\mathrm{A}]^2 + \ldots + pB_p[\mathrm{A}]^p}{B_0 + B_1[\mathrm{A}] + \ldots + B_p[\mathrm{A}]^p}$$

$$= \frac{K[\mathrm{A}]^p(pB_0 + (p-1)B_1[\mathrm{A}] + \ldots + B_{p-1}[\mathrm{A}]^{p-1}) + B^-(B_1[\mathrm{A}] + \ldots + B_p[\mathrm{A}]^p)}{(K[\mathrm{A}]^p - B^-)(B_0 + B_1[\mathrm{A}] + \ldots + B_p[\mathrm{A}]^p)} \tag{70}$$

After several transformations we obtain

$$m_{\mathrm{A}} = 1 - \frac{\sum \text{spanning trees with } [\mathrm{A}]^p}{B_0 + B_1[\mathrm{A}] + \ldots + B_p[\mathrm{A}]^p} + \sum_{i=0}^{p-2} (p - i + 1) \frac{\sum \text{spanning trees containing } [\mathrm{A}]^i}{B_0 + B_1[\mathrm{A}] + \ldots + B_p[\mathrm{A}]^p} + \frac{pB^-}{K[\mathrm{A}]^p - B^-} \tag{71}$$

We can write eqn. (71) as

$$m_{\mathrm{A}} = \frac{\partial \ln W}{\partial \ln[\mathrm{A}]} = \sum_{i=0}^{p-1} (p - i) \frac{\sum \text{spanning trees containing } [\mathrm{A}]^i}{B_0 + B_1[\mathrm{A}] + \ldots + B_p[\mathrm{A}]^p} + \frac{pB^-}{K[\mathrm{A}]^p - B^-} \tag{72}$$

We will now give some preliminary notes that will be necessary for the following discussions.

(I) Let substance A interact with only some of the intermediates. A graph for the one-route mechanism is given in Fig. 7. In this mechanism substance A reacts only in the steps enclosed between the nodes u and $(j + 1)$. For definiteness, we assume that $j > u$. The first step in which A reacts is the step u and the last is the step j. It is evident that $(j + 1 - u) \geqslant p$, which

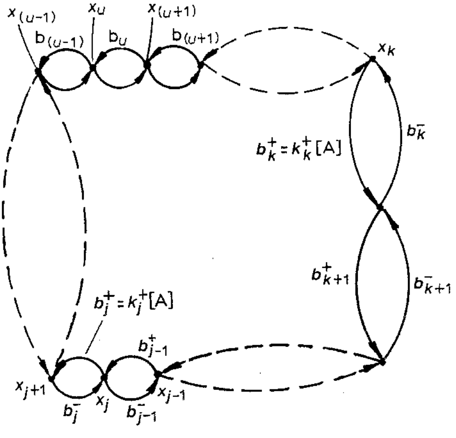


Fig. 7. Graph of a one-route catalytic reaction.

indicates that substance A can react with not all the intermediates localized between the nodes x_u and x_j. Let us represent the number of indices for which x_i interacts with A as I.

(II) For a general proof we will analyze the route all steps of which are reversible. If some step is irreversible, the weights of the spanning trees containing an inverse reaction, must be treated as zero.

Under assumptions (I) and (II), the relationship

$$\sum_{i=0}^{p-1} (p - i) \frac{\sum \text{spanning trees containing } [\mathrm{A}]^i}{B_0 + B_1[\mathrm{A}] + \ldots + B_p[\mathrm{A}]^p} = \sum_i x_i + \sum_i \frac{D^-(i-1)}{\sum_i D_x} \tag{73}$$

is valid.

Here the summation is performed with respect to those values of i for which X_i interacts with A; $D^-_{(i-1)}$ is the sum of the weights for all spanning trees containing an inverse reaction of the $(i - 1)$th step. The validity of eqn. (73) can be proved by using the fact that the summation in the right-hand side exhibits the appearance of the factor $(p - k)$ before every spanning tree containing $[\mathrm{A}]^k$. We omit a strict mathematical proof since it is cumbersome and will write a general formula for the observed order of the reversible n-step reaction taking into account eqns. (72) and (73)

$$m_{\mathrm{A}} = \frac{\partial \ln W}{\partial \ln[\mathrm{A}]} = \sum_i x_i + \frac{\sum_i D_{(i-1)}}{\sum_x D_x} + p\frac{W^-}{W} \tag{74}$$

where $W^- = B^- / \Sigma_x D_x$ is the rate of the inverse reaction and $W = (K[\mathrm{A}]^p - B^-)/\Sigma_x D_x$ is the total reaction rate.

Equation (74) has an interesting physicochemical sense. It appears that the observed order is controlled by three components.

(1) The sum of steady-state coverages of intermediates reacting with A.

(2) The sum of the values for $D^-_{(i-1)}/\Sigma_x D_x$, every summand of which is the ratio of the sum of the spanning trees weight containing an inverse reaction of the $(i - 1)$th step, to the sum of weight for all spanning trees of the reaction graph. The presence of an inverse reaction involving the participation of the intermediate X_i reduces its steady-state coverage. The summation is performed with respect to all $i \in I$. The value $D^-_{(i-1)}/\Sigma_x D_x$ is determined as a "portion" of the inverse reaction for the $(i - 1)$th step. In a similar way the "portion" for the direct reaction in the ith step can be determined.

(3) Reaction reversibility as a whole. It is characterized by the value

$$\frac{\prod_i b_i^-}{\prod_i b_i^+ - \prod_i b_i^-} = \frac{W^-}{W} = \left[K_{\mathrm{eq}} \frac{\mathrm{f}^+(\vec{c})}{\mathrm{f}^-(\overleftarrow{c})} - 1 \right]^{-1}$$

where K_{eq} is the equilibrium constant of the brutto-reaction, $\vec{c}$ and $\overleftarrow{c}$ are the concentration vectors for the initial substances and products, respectively, and $\mathrm{f}^+(\vec{c})$ and $\mathrm{f}^-(\overleftarrow{c})$ are functions for the direct and inverse "natural" brutto-reaction, respectively.

Thus the observed order is "three-step" and is controlled by the sum of intermediates, the reversibility of the previous steps u, and finally by the reaction reversibility as a whole.

Let us give, without proof, the equations

$$\frac{D_i^+ + D_{(i-1)}^-}{\sum_x D_x} = 1 - x_i \tag{75}$$

i.e. the sum of reaction portions involving the participation of the ith intermediate is equal to the concentrations of all the other intermediates and

$$\sum_{i=1}^{n} D_i^+ + \sum_{i=1}^{n} D_i^- = (n-1) \sum_x D_x \tag{76}$$

Assuming that substance A reacts only in one step and applying eqns. (75) and (76), we obtain

$$\frac{D_i^+}{\sum_x D_x} = 1 - m_{\mathrm{A}} + \frac{W^-}{W}$$

If the order for the reaction rate is found according to the product B, we can also determine the contribution of the inverse reaction for the $(i-1)$th step

$$\frac{D_{(i-1)}^-}{\sum_x D_x} = 1 - m_{\mathrm{B}} - \frac{W^+}{W}$$

Here m_{B} is the reaction rate order with respect to substance B [B participates only in the inverse reaction of the $(i-1)$th step].

In the case when the initial substance A takes part in the direct reaction of the ith step and the product B reacts in the inverse reaction of the $(i-1)$th step, the steady-state coverage will be determined as $x_i = m_{\mathrm{A}} + m_{\mathrm{B}}$.

Various particular cases can be easily obtained from eqn. (74). If substance A reacts only in one ith step and at least one step is irreversible, we obtain

$$m_{\mathrm{A}} = x_i + \frac{D_{(i-1)}^-}{\sum_x D_x}$$

If the step $(i - 1)$ is irreversible, we have

$$m_A = x_i \tag{77}$$

It must be noted that an attempt to find a relationship between kinetic orders and surface coverages was made as early as 1958 [45]. Here the exponents for the kinetic equations $W = K[A]^m[B]^n$ were interpreted as

$$m = m' - \frac{\alpha_t}{\alpha_A \theta_A}$$

where m' is the number of particles of A entering into the activated complex, α_A and α_t are the amounts of surface sites occupied by the substance A and the activated complex, respectively, and θ_A is the surface coverage by the substance A. It is evident that if $m' = \alpha_A = \alpha_t = 1$, then $m = 1 - \theta_A$.

Relationship (77) was given by Sokolovskii [46] for the irreversible two-step mechanism

$$(1)\ A + Z \rightarrow AZ$$

$$(2)\ AZ + B \rightarrow AB + Z$$

But the role of eqn. (77) for interpreting the kinetic relationship and, in particular, their relation with surface coverage was first shown clearly by Golodets [47].

If the one-route mechanism is a combination of irreversible steps and the substance A participates in several of these steps, then

$$m_A = \sum_i x_i$$

where the x_i values are the concentrations of the ith intermediates with which A reacts. This relationship can easily be obtained from eqn. (74) by taking into account the irreversibility of all steps.

Let us consider a probable value for the observed order. For the irreversible case it can never be greater than unity irrespective of the number of steps in which the reactant takes part. Reversibility of individual steps increases the observed order but its value will not be greater than p (i.e. the number of steps involving the participation of the reactant A), if the reaction is irreversible as a whole, i.e. $W^- = 0$. This conclusion follows directly from eqns. (74) and (75). But if the total reaction is reversible, the observed order can, in principle, be arbitrarily high. It must be noted, however, that the value $\partial W/\partial[A]$ cannot be determined according to $\partial \ln W/\partial \ln[A]$ near equilibrium since $W^+ \approx W^-$ and $(W^-/W) \rightarrow \infty$.

Examples.

(1) Let us analyze the observed rate orders for hydrogen oxidation on Group IV transition metal oxides. For the steps of the detailed mechanism in accordance with refs. 38, 48, and 49, see eqn. (53); the appropriate kinetic equation is given by eqn. (54).

From eqn. (74) we obtain

$$m_{H_2} = \left(\frac{\partial \ln W}{\partial \ln[H_2]}\right)_{[O_2],[H_2O],T=\text{const.}} = [(ZO)_2] + [ZOZ] + \frac{D_2^-}{\Sigma}$$

$$= \frac{k_2^+ k_4^+ k_5^+ (k_1^+ + k_3^+)[H_2][O_2]}{\Sigma} + \frac{k_1^+ k_4^+ k_5^+ k_2^- [H_2][O_2][H_2O]}{\Sigma}$$

$$m_{O_2} = \left(\frac{\partial \ln W}{\partial \ln[O_2]}\right)_{[H_2],[H_2O],T=\text{const.}} = [ZZ] + \frac{D_4^-}{\Sigma}$$

$$= \frac{k_1^+ k_2^+ k_3^+ k_4^+ [H_2]^2}{\Sigma} + \frac{k_1^+ k_2^+ k_3^+ k_4^- [H_2]^2[H_2O]}{\Sigma}$$

$$m_{H_2O} = \left(\frac{\partial \ln W}{\partial \ln[H_2O]}\right)_{[O_2],[H_2],T=\text{const.}}$$

$$= \frac{-\left(k_1^+ k_2^+ k_3^+ k_4^- [H_2]^2[H_2O] + k_1^+ k_4^+ k_5^+ k_2^- [H_2][O_2][H_2O]\right)}{\Sigma}$$

The fact that $m_{H_2O} \neq 0$ accounts for the effect of water observed experimentally. It can easily be shown that

$$m_{H_2} + m_{O_2} + m_{H_2O} = [(ZO)_2] + [ZOZ] + [ZZ]$$

i.e. it equals the total concentration of the water-free species. At high values of $k_5^+[O_2]$ under the assumption that $k_1^+ = k_3^+$, $k_2^+ = k_4^+$, and $k_2^- = k_4^-$ (which is similar to ref. 23) we obtain

$$\frac{m_{H_2}}{|m_{H_2O}|} = \frac{2}{(b_{H_2O} p_{H_2O})} + 1$$

whence a value for the adsorption coefficient can be determined

$$b_{H_2O} = \frac{k_2^-}{k_2^+} = \frac{k_4^-}{k_4^+}$$

(The available literature data for this coefficient are scarce and inaccurate.) This problem was analyzed more fully in ref. 49.

(2) Let us consider a catalytic reaction of NO with CO on silver. Its detailed mechanism in accordance with ref. 39 is given by eqn. (55) and the appropriate kinetic equation is eqn. (56). It can readily be shown that

$$m_{CO} = \frac{\partial \ln W}{\partial \ln[CO]} = [ZO]$$

$$m_{NO} = \frac{\partial \ln W}{\partial \ln[NO]} = [Z] + [ZNO] + \frac{k_3^+ k_1^- [CO]}{\Sigma}$$

According to the experimental data, the value of m_{CO} is close to unity. Since $m_{CO} = [ZO]$, it can be suggested that in this temperature range the surface is practically completely covered by oxygen and step (3) is rate-determining. For more detail, see ref. 39.

Thus examples (1) and (2) enable us to affirm that the observed rate order or a combination of the observed orders can be used to estimate steady-state concentrations for intermediates.

Also useful can be the ratio of observed orders with respect to various substances. This value is the ratio of surface coverage and its advantage is that it does not contain a cumbersome denominator $\Sigma_x D_x$. In this sense this characteristics for a single-route reaction is similar to the known characteristics of multi-route reactions, i.e. selectivity.

In principle, the observed orders can be used to discriminate between some mechanisms. For example, for the scheme

$$(1)\ \mathrm{A} + \mathrm{B} + \mathrm{Z} \rightarrow \mathrm{ABZ}$$

$$(2)\ \mathrm{ABZ} \rightarrow \mathrm{AB} + \mathrm{Z}$$

we obtain $m_{\mathrm{A}} = m_{\mathrm{B}} = [\mathrm{Z}]$; whereas for the mechanism

$$(1)\ \mathrm{A} + \mathrm{Z} \rightarrow \mathrm{AZ}$$

$$(2)\ \mathrm{AZ} + \mathrm{B} \rightarrow \mathrm{AB} + \mathrm{Z}$$

we have $m_{\mathrm{A}} = [\mathrm{Z}]$, $m_{\mathrm{B}} = [\mathrm{AZ}]$, $m_{\mathrm{A}} + m_{\mathrm{B}} = 1$. (It is evident that these schemes are indistinguishable only at $m_{\mathrm{A}} = m_{\mathrm{B}} = 0.5$.) Having the estimate for the surface coverage obtained from the observed order, we can easily estimate reaction constants.

Now let us present some relationships for the irreversible two-step mechanism

$$(1)\ \mathrm{A} + \mathrm{Z} \rightarrow \mathrm{AZ}$$

$$(2)\ \mathrm{AZ} \rightarrow \mathrm{B} + \mathrm{Z}$$

$$\frac{\partial \ln W}{\partial \ln[\mathrm{A}]} = [\mathrm{Z}]$$

$$\frac{\partial \ln[\mathrm{Z}]}{\partial \ln[\mathrm{A}]} = \frac{\partial^2 \ln W}{\partial (\ln[\mathrm{A}])^2}$$

$$= [\mathrm{AZ}] = 1 - [\mathrm{Z}]$$

Thus we have

$$\frac{\partial \ln W}{\partial \ln[\mathrm{A}]} + \frac{\partial^2 \ln W}{\partial (\ln[\mathrm{A}])^2} = 1$$

2.6.2 Observed activation energy

Let us write an expression for the steady-state rate in the form

$$W = \frac{\prod_i b_i^+ - \prod_i b_i^-}{\sum_i B_{\mathrm{dir},i} + \sum_i B_{\mathrm{inv},i} + \sum_i B_{\mathrm{mix},i}} \tag{78}$$

where $B_{\text{dir},i}$ is the weight of the spanning tree for the node i containing only direct reaction steps, $B_{\text{inv},i}$ is the weight of the spanning tree for the node i containing only inverse reactions, and $B_{\text{mix},i}$ is the sum of the weights for the "mixed" spanning trees of the ith node containing both direct and inverse reactions.

Let us also give a formula for the steady-state concentration of the ith intermediate

$$[\mathrm{X}_i] = \frac{B_{\text{dir},i} + B_{\text{inv},i} + B_{\text{mix},i}}{\sum_i B_{\text{dir},i} + \sum_i B_{\text{inv},i} + \sum_i B_{\text{mix},i}} \tag{79}$$

Let us show that, for a one-route linear mechanism assuming that the rate constant has the Arrhenius dependence on temperature, (i.e. $k_j^{\pm} = k_{0,j}^{\pm} \exp(-E_j^{\pm}/RT)$, the equation

$$\begin{aligned} E_{\text{obs}} &= \frac{\partial \ln W}{\partial(-1/RT)} \\ &= \sum_i x_i E_i^{+} + \frac{\sum_{i=2}^{n+1} (E_i^{+} - E^{-}_{(i-1)}) D^{-}_{(i-1)}}{\sum_i D_x} + \frac{\left(\sum_i E_i^{+} - \sum_i E_i^{-}\right) W^{-}}{W} \\ E_{n+1}^{+} &= E_1^{+} \end{aligned} \tag{80}$$

is valid where E_i^{+} and E_i^{-} are the activation energies for the direct and inverse reactions of the ith step, respectively, and $(-\Delta H_{\text{eq}}) = (\Sigma_i E_i^{+} - \Sigma_i E_i^{-})$ is the thermal effect of the "natural" brutto-reaction. For the derivation of eqn. (80) we will write $\partial \ln W/\partial(-1/RT)$ using eqn. (78) as

$$\begin{aligned} \frac{\partial \ln W}{\partial(-1/RT)} = {} & \frac{\left(\sum_i E_i^{+}\right) \prod_i b_i^{+} - \left(\sum_i E_i^{-}\right) \prod_i b_i^{-}}{\prod_i b_i^{+} - \prod_i b_i^{-}} - \\ & \frac{-\left(\sum_i B_{\text{dir},i}\left(\sum_{j \neq i} E_j^{+}\right) + \sum_i B_{\text{inv},i}\left(\sum_i E_j^{-}\right) + \right. \\ \left. + \sum_i \sum_k \left[\sum_{j=k+1}^{i-1} \left(E_j^{+} + \sum_{j=1}^{k-1} E_j^{-}\right) \prod_{j=1}^{i-1} b_j^{+} \prod_{j=1}^{k-1} b_j^{-}\right)\right]}{\sum_i (B_{\text{dir},i} + B_{\text{inv},i} + B_{\text{mix},i})} \end{aligned}$$

After reducing this expression to a common denominator, we can readily extract $\Sigma_i x_i E_i$ and $(\Sigma_i E_i^{+} - \Sigma_i E_i^{-}) \Pi_i b_i^{-} / (\Pi_i b_i^{+} - \Pi_i b_i^{-})$. It can be shown that the rest of the summands are reduced to the form $\Sigma_i\ (E_i^{+} - E^{-}_{(i-1)} D^{-}_{(i-1)} / \Sigma_x\ D_x)$. Due to the cumbersome calculations, we will not present a strict proof of the validity of eqn. (80).

Let us consider the parameter $\Delta E_i = E_i^{+} - E^{-}_{(i-1)}$ in eqn. (80). It is the energy parameter for the ith intermediate, i.e. the difference between activation energies of two reactions involving the participation of the same intermediate. It can easily be shown that $\Sigma_i(\Delta E_i) = \Sigma_i(-\Delta H_{p,i}) = (-\Delta H_p)$. The value $D^-_{(i-1)}$ was determined above as the contribution of the inverse reaction for the $(i-1)$th step.

By analogy with eqn. (74), let us also consider various particular cases for eqn. (80). If at least one step is irreversible, the equality

$$E_{\text{obs}} = \sum_i x_i E_i^+ + \frac{\sum\limits_{i=2}^{n+1} (E_i^+ - E^-_{(i-1)}) D^-_{(i-1)}}{\sum\limits_x D_x} \qquad E^+_{n+1} = E^+_1$$

will be valid. If $\Delta E_i \approx 0$, the corresponding terms disappear. If all steps are irreversible, we obtain

$$E_{\text{obs}} = \sum_i x_i E_i^+$$

Note that the latter relationship in its particular formulation for a two-step mechanism was reported previously by Il'chenko and Golodets [50].

The expression for the observed activation energy eqn. (80), is similar to that for the observed order, eqn. (74), in its "three-step" character. Here there are also three summands that account for the contribution of intermediates, individual reversible steps, and the total reversibility of the reaction.

It is interesting that eqn. (80) can be written in a form that is similar to the Bronsted equation

$$E_{\text{obs}} = A - B(-\Delta H_p)$$

where A is a complex function of the composition of the gas mixture and B is total reaction reversibility

$$\begin{aligned} B &= \frac{W^-}{W^+ - W^-} \\ &= \frac{1}{(K_{\text{eq}} \mathrm{f}^+(\vec{c})/\mathrm{f}^-(\vec{c}) - 1)} \end{aligned}$$

A value for the reversibility B can easily be found if the equilibrium constant of the brutto-reaction and the gas phase composition are known.

It is possible that this relationship between the thermal effect of the complex reaction and its observed activation energy is responsible for the fact that the Bronsted equation (or its analogs) appear to be valid for some elementary reactions as well. A question arises whether the observed activation energy can be higher than the activation energy of elementary steps.

If all steps are irreversible than in accordance with eqn. (80), E_{obs} cannot be higher than the activation energy of the individual reactions. If only part of the steps is reversible, then E_{obs} can be greater than the maximum activation energy E_i^+, but cannot be higher than $\Sigma_i E_i^+$. And finally, if all the steps are reversible, then E_{obs} can, in principle, be arbitrarily high. As in the case of the observed reaction order, it must be taken into consideration that the value $\partial \ln W/\partial(-1/RT)$ cannot be used to evaluate $\partial W/\partial T$ near equilibrium.

Other conditions being equal, an increase in E_{obs} will be promoted by the endothermicity of the brutto-reaction: $\Sigma_i E_i^+ > \Sigma_i E_i^-$, whereas its decrease will be accounted for by the exothermicity of the brutto-reaction: $\Sigma_i E_i^- > \Sigma_i E_i^+$.

Example.

We shall consider hydrogen oxidation on Group IV transition metal oxides [see eqn. (53) for the mechanism] [38, 48, 49].

Under the assumption that $k_1^+ = k_3^+$, $k_2^+ = k_4^+$, $k_2^- = k_4^-$, and high values for $k_5[O_2]$, the steady-state kinetic equation (54) will take the form

$$W = \frac{k_1^+ k_2^+ [H_2]}{\sum_1}$$

where

$$\sum_1 = 2k_1^+[H_2] + k_2^+(2 + b_{H_2O}[H_2O])$$

Taking into account the simplifications made, we can write

$$E_{obs} = m_{H_2}E_1 + (1 - m_{H_2})E_2 + |m_{H_2O}|q_{H_2O}$$

where E_1 and E_2 are the activation energies for reactions (1) and (2), respectively, and q_{H_2O} is the heat of adsorption of water.

With water eliminated in the cycle, $m_{H_2} = 1$ and $(1 - m_{H_2}) \approx |m_{H_2O}| \approx 0$, we obtain $E_{obs} = E_1$, i.e. the observed activation energy is the same as the activation energy of reaction (1). If we know the observed orders (m_{H_2} and m_{H_2O}), E_{obs}, E_1 (from the experiment at $m_{H_2} = 1$), and also q_{H_2O} (it was determined in ref. 49), we can find E_2.

Thus the known values for the observed reaction rate orders and the observed activation energy can be useful for the determination of the activation energies for individual reactions.

Let us consider the analogy between the expressions for the observed rate order and the observed activation energy. In our opinion, this analogy is essential. It is interesting that the observed values are the derivatives of the complex reaction rate and they prove to be equal to the sum of the three values containing the following three characteristics of the graph

(1) the concentrations of intermediates corresponding to the graph nodes;

(2) the "portion" of the reactions corresponding to the graph arcs, and

(3) the total reversibility of the complex reaction corresponding to the total conversion cycle.

It is possible that this kind of "differentiation on the graph" will also take place in more complicated cases than the one considered.

On the basis of the general formula (46), we can classify the dependences of the reaction rate on the three parameters partial pressure of reactants, temperature, and the total pressure. For such investigations, see Chap. 3, Sect. 3 of ref. 7.

3. Graphs for the analysis of the number of independent parameters

3.1 SIMPLE EXAMPLES

The obtained steady-state kinetic equations (46) are the kinetic model required for both studies of the process and calculations of chemical reactors. The parameters of eqns. (46) are determined on the basis of experimental data. It is this problem that is difficult. The fact is that, in the general case, eqns. (46) are fractions whose numerator and denominator are the polynomials with respect to the concentrations of observed substances (concentration polynomials). Coefficients of these polynomials can be cumbersome complexes of the initial model parameters. These complexes can also be related.

Let us illustrate this by some examples.

(A) Let us take the above isomerization mechanism

(1) $A + Z \rightarrow AZ$;

(2) $AZ \rightarrow BZ$

(3) $BZ \rightarrow B + Z$

(irreversible case). The kinetic equation will take the form [see eqn. (17)]

$$W = \frac{k_1 k_2 k_3 [\mathrm{A}]}{k_1 [\mathrm{A}](k_2 + k_3) + k_2 k_3} = \frac{k_1 [\mathrm{A}]}{1 + [(k_2 + k_3)/(k_2 k_3)]\,[\mathrm{A}]}$$

The initial model contains three reactions, but (+2) and (+3) are of the same type with the weights k_2 and k_3, respectively. On the basis of the isothermal experiment, the rate constants for reactions (+2) and (+3) cannot be determined separately. Among the three parameters of a given simple reaction we can find only two. One is k_1 and the other is complex, $K = (k_2 + k_3)/(k_2 k_3)$, which does not obey the ordinary Arrhenius equation $k = k_0 \mathrm{e}^{-E/RT}$(non-Arrhenius complex). But it is possible that the presence of non-Arrhenius parameters by themselves will not present an obstacle for the determination of the entire reaction rate constants according to the isothermal experimental data. It is only important that the number of Arrhenius complexes in the denominator of the concentration polynomial is not lower than that of the parameters to be determined.

(B) Let us consider a more complex example of a catalytic conversion of methane [51]

$$(1)\ CH_4 + Z \rightleftarrows CH_2Z + H_2$$

$$(2)\ H_2O + CH_2Z \rightleftarrows ZCHOH + H_2$$

$$(3)\ ZCHOH \rightleftarrows ZCO + H_2$$

$$(4)\ ZCO \rightleftarrows Z + CO$$

with the brutto-equation

$$CH_4 + H_2O = CO + 3H_2$$

The equilibrium step

$$Z + H_2O \rightleftarrows ZO + H_2$$

resulting in the "hanging" node [ZO], will not be taken into consideration. The kinetic equation will take the form

$$W = \frac{(k_1^+ k_2^+ k_3^+ k_4^+ [CH_4][H_2O] - k_1^- k_2^- k_3^- k_4^- [CO][H_2]^3)}{\sum} \tag{81}$$

where

$$\begin{aligned}\sum = {} & K_1[H_2O] + K_2[CH_4] + K_3[H_2] + K_4[CH_4][H_2O] + \\ & + K_5[CO][H_2] + K_6[H_2O][CO] + K_7[CH_4][H_2] + K_8[H_2]^2 + \\ & + K_9[CO][H_2]^2 + K_{10}[CH_4][H_2]^2 + K_{11}[H_2O][H_2][CO] + \\ & + K_{12}[CH_4][H_2O][H_2] + K_{13}[H_2]^3\end{aligned}$$

$$K_1 = k_2^+ k_3^+ k_4^+, \quad K_2 = k_3^+ k_4^+ k_1^+, \quad K_3 = k_3^+ k_4^+ k_1^-,$$

$$K_4 = k_1^+ k_2^+ (k_3^+ + k_4^+), \quad K_5 = k_3^+ k_4^- k_1^-, \quad K_6 = k_2^+ k_3^+ k_4^-,$$

$$K_7 = k_4^+ k_1^+ k_2^-, \quad K_8 = k_4^+ k_1^- k_2^-,$$

$$K_9 = k_4^- (k_2^- k_3^- + k_3^- k_1^- + k_1^- k_2^-), \quad K_{10} = k_1^+ k_2^- k_3^-,$$

$$\mathrm{K}_{11} = k_2^+ k_3^- k_4^-, \quad K_{12} = k_1^+ k_2^+ k_3^-, \quad K_{13} = k_1^- k_2^- k_3^-$$

If the mechanism had not contained reactions of the same type, the concentration polynomial Σ would have had $4^2 = 16$ terms among which we would have found no similar ones. Coefficients for the polynomial terms would have been products of the reaction rate constants and would have obeyed the Arrhenius equation. But in the given case we have two direct reactions of the same type, (+3) and (+4), taking place without the participation of gas-phase substances and three inverse reactions of the same type, (−1), (−2) and (−3), involving the participation of the gas-phase hydrogen. Therefore the polynomial Σ has 13 terms. Among these terms two have coefficients that do not satisfy the Arrhenius equation. Among the remaining 11 terms we can identify 8 independent ones, which corresponds to the number of reactions. For example, if we choose K_3, K_5, K_6, K_7, K_8, K_{10},

K_{11}, and K_{12} as independent, the rest of the Arrhenius complexes can be represented as

$$K_1 = \frac{K_3 K_6}{K_5}, \qquad K_2 = \frac{K_3 K_7}{K_8}, \qquad K_{13} = \frac{K_8 K_{10}}{K_7}$$

Non-Arrhenius complexes can be determined using the relationships

$$\begin{aligned} K_9 &= \frac{K_5 K_8}{K_1} + \frac{K_5 K_{11}}{K_6} + \frac{K_{10} K_{11}}{K_{12}} \\ K_4 &= \frac{K_6 K_{12}}{K_{11}} + \frac{K_7 K_{12}}{K_{10}} \end{aligned} \tag{82}$$

Note that

$$\begin{aligned} K^{\pm} &= (K_3 K_5 K_6 K_7 K_8 K_{10} K_{11} K_{12})^{1/3} = k_1^+ k_2^+ k_3^+ k_4^+ k_1^- k_2^- k_3^- k_4^- \\ K^+ &= \frac{K_3 K_6 K_7 K_{12}}{K^{\pm}} = k_1^+ k_2^+ k_3^+ k_4^+ \\ K^- &= \frac{K_5 K_8 K_{10} K_{11}}{K^{\pm}} = k_1^- k_2^- k_3^- k_4^- \end{aligned}$$

Thus the complexes in the numerator are determined on the basis of those in the denominator. They proved to be dependent on the latter and bear no new information. Reaction parameters are found according to the formulas

$$k_1^+ = \frac{K^+}{K_1}, \qquad k_2^+ = \frac{K^+}{K_2}, \qquad k_4^- = \frac{K^-}{K_{13}},$$

$$k_3^+ = \frac{K_6}{k_2^+ k_4^-}, \qquad k_3^- = \frac{K_{12}}{k_1^+ k_2^+},$$

$$k_2^- = \frac{K_{10}}{k_1^+ k_3^-}, \qquad k_4^+ = \frac{K_1}{k_2^+ k_3^+}, \qquad k_1^- = \frac{K_{13}}{k_2^- k_3^-}$$

Though the reaction mechanism here is more complex than in the previous example and the kinetic equation also has non-Arrhenius parameters, it is possible to determine all the reaction rate constants. The fact is that there is a sufficient quantity of the Arrhenius complexes. In this case it appears that all "mixed" complexes, i.e. complexes containing parameters of both direct and inverse reactions, are independent. Here these complexes evidently corresponding to the mixed spanning trees of the graph are coefficients for various concentration characteristics. It is this fact that permitted us to obtain the convenient eqns. (82).

3.2 REASONS FOR DEPENDENCE AND THE IMPOSSIBILITY OF DETERMINING PARAMETERS

A well-known dependence of the equilibrium constants appears in the case in which some step is a linear combination of the others. For example, if we have three steps (1) A ⇄ B, (2) B ⇄ C, and (3) A ⇄ C, where step (3) is a linear combination of the other two, its equilibrium constant satisfies the relationship $K_{\mathrm{eq},3} = K_{\mathrm{eq},1} K_{\mathrm{eq},2}$. Therefore the reaction rate constants also appear to be dependent

$$\frac{k_3^+}{k_3^-} = \frac{k_1^+}{k_1^-}\frac{k_2^+}{k_2^-}$$

These dependences must always be taken into account in the solution of inverse kinetic problems. For example, when finding constants for eqns. (16) and (81) we must take into account that

$$\frac{k_1^+ k_2^+ k_3^+}{k_1^- k_2^- k_3^-} = K_{\mathrm{eq}}$$

and

$$\frac{\Pi k_i^+}{\Pi k_i^-} = K_{\mathrm{eq}},$$

where K_{eq} is the equilibrium constant of the corresponding brutto-reactions.

A different dependence of the parameters in kinetic equations was reported by Horiuti [11] who suggested a method for determining the number of independent parameters. The method consists of the numerical estimation of a rank for some Jacobian matrix. (It is known that this procedure can result in a considerable error.) Later, these problems were analyzed in detail by Spivak and Gorskii [52, 53] but they did not aim at the elucidation of the physico-chemical reasons for the appearance of dependent and undeterminable parameters. It is this aspect that we will discuss below.

We have already noted that a denominator of the steady-state kinetic equation is the concentration polynomial Σ. Each summand of this polynomial is the spanning tree weight and corresponds to some path for the formation of a chosen intermediate from the rest. Among the reaction paths there can be dependent paths due to the reversibility of the sufficiently large number of steps.

For example, in the one-route mechanism all n steps are irreversible and there are n independent spanning trees. If one step is reversible [the number of reactions amounts to $(n + 1)$], there are $(n + 1)$ spanning trees and all of them are independent. But if the mechanism has two reversible steps [the number of reactions is $(n + 2)$], it can readily be shown that the number of spanning trees amounts to $(n + 3)$, i.e. their number is larger than the number of reactions and one spanning tree is dependent. These dependences must be taken into account. In the general case, when all steps of the one-route mechanism are reversible, the polynomial Σ contains n^2 summands, i.e. weights of the spanning trees $B_{k,i}$ formed by various combinations of $2n$ with respect to $(n - 1)$ co-factors $b_j^{\pm}$, and they are determined using the formulae

$$\begin{aligned} B_{k,i} &= \prod_{j=k+1}^{i-1} b_j^+ \prod_{j=1}^{k-1} b_j^- \qquad i = 1, 2, \ldots, n, \\ \prod_{j=1}^{i-1} b_j^+ &= 1,\ b_{n+j}^{\pm} = b_j^{\pm} \qquad j = 1, 2, \ldots \end{aligned} \tag{83}$$

The dimension of the basis for the weights of spanning trees is $2n$; all the rest of $n^2 - 2n$ spanning trees will be dependent. For the spanning tree weights $B_{k,i}$ these dependences can be expressed as

$$B_{k,i} = \prod_{j=k+1}^{i-1} \frac{B^+}{B_{j,j}} \prod_{\substack{j=1 \\ k \neq i,i-1}}^{k-1} \frac{B^-}{B_{j-1,j}} \qquad k,\ i, = 1, 2, \ldots, n \tag{84}$$

where

$$B^+ = \left(\prod_{j=1}^{n} B_{j,j} \right)^{1/(n-1)}$$

and

$$B^- = \left(\prod_{j=1}^{n} B_{j-1,j} \right)^{1/(n-1)}$$

since, in accordance with the spanning tree definition, we have the relationships

$$\begin{aligned} b_j^+ &= \frac{B^+}{B_{j,j}} \\ b_j^- &= \frac{B^-}{B_{j-1,j}} \end{aligned} \tag{85}$$

Here the weights of direct, $B_{j,j}$, and inverse, $B_{j-1,j}$, spanning trees are chosen to be independent. All mixed spanning trees are expressed through them using eqns. (83). It is the dependence of the spanning trees that leads to the dependence of the concentration polynomial coefficients. After choosing any $2n$ independent polynomial terms to $2n$ independent spanning trees, we can abstract summands corresponding to the dependent spanning trees. It must be noted that the chosen $2n$ independent spanning trees are not necessarily direct and inverse ones. For example, in the above example (the catalytic conversion of methane) we have chosen $2n$ independent mixed spanning trees.

The principal fact is that if we have $2n$ of any independent summands, we can easily determine parameters for the whole of reactions (whose number is $2n$). In short, it is necessary that the number of independent summands will be equal to the number of reactions in the detailed mechanism. If this number is smaller, some parameters cannot be determined.

Let us show some reasons for the reduction in the number of independent summands. First, it is the structural peculiarities of a complex graph. The number of its spanning trees can appear to be lower than that of the parameters. Second, a similar type of the kinetic law for individual reactions. These two cases will be discussed in special sections.

The analysis shows that the second case is the most typical. A complex reaction mechanism often includes several reactions subjected to the same kinetic law. For example, it can involve the participation of the same gaseous substance or a reaction in which gaseous substances do not react at all. The weights of these reactions are of the same type. Then the concentrational polynomial of the denominator will have similar terms with factors that, in the general case, will be sums of the products of individual reaction constants. There are non-Arrhenius complexes. We observed them in both the cases in Sect. 3.1. The only difference is that, in the second case, the number of Arrhenius complexes is greater than the number of reactions, whereas in the first it is lower.

It is well-known that the difference of parameter values results in the indeterminacy of parameters. Rate limitation and the steady-state reaction rate will be dependent only on the parameters of "slow" steps. But this case is beyond the scope of our discussion here.

3.3 INDETERMINACY OF PARAMETERS AND GRAPH STRUCTURE

Let us consider a complex catalytic reaction following a multi-route linear mechanism, all steps of which are reversible.

Note that every term of the concentration polynomial in the denominator of eqn. (46) is the spanning tree weight. Let us introduce a concept of "concentration characteristics" for a spanning tree* and define it as a product of the observed reactant concentrations participating in the totality of reactions corresponding to a given spanning tree. Spanning trees with the same characteristics will be referred to as similar whereas those for which there are no similar characteristics will be called individual.

It is evident that spanning trees are individual only in the case where the reaction weights are different. For example, the two-route mechanism

(1) $A + Z \rightarrow AZ$

(2) $AZ + B \rightarrow AB + Z$

(3) $C + Z \rightarrow CZ$

(4) $CZ + D \rightarrow CD + Z$

with different reaction weights $b_1^+ = k_1^+ C_A$, $b_2^+ = k_2^+ C_B$, $b_3^+ = k_3^+ C_C$, and $b_4^+ = k_4^+ C_D$ corresponds to the denominator in eqn. (46)

$$\sum = (k_1^+ k_4^+) C_A C_D + (k_2^+ k_3^+) C_B C_C + (k_2^+ k_4^+) C_B C_D$$

Here all spanning trees are individual.

But spanning trees can also be individual when some weights are similar. For example, the two-route mechanism**

---

* In what follows we will introduce a concept of a "spanning tree colour" adequately corresponding to its concentration characteristics.

** Refer to the mechanism of vinyl chloride synthesis, eqn. (24), with the kinetic eqn. (57).

(1) $A + Z \rightarrow AZ$

(2) $AZ + B \rightarrow AB + Z$

(3) $B + Z \rightarrow BZ$

(4) $BZ + A \rightarrow AB + Z$

with the reaction weights $b_1^+ = k_1^+ C_A$, $b_2^+ = k_2^+ C_B$, $b_3^+ = k_3^+ C_B$, and $b_4^+ = k_4^+ C_A$ corresponds to the denominator of eqn. (46)

$$\sum = (k_1^+ k_4^+) C_A^2 + (k_2^+ k_3^+) C_B^2 + (k_2^+ k_4^+) C_A C_B$$

Here all spanning trees are also individual though some reaction weights are similar. It is evident that all individual spanning trees are of the Arrhenius type, and the similar spanning trees lead to the formation of non-Arrhenius complexes. On the basis of a steady-state kinetic experiment, the factors of the summands in the denominator of eqn. (46) are determined. They differ in their concentration characteristics.

The number of the summands in eqn. (46) will give the number of the parameters under determination. Factors of these summands are the product of the reaction rate coefficients (Arrhenius complexes) or the sums of these products (non-Arrhenius complexes).

Let all the spanning trees be individual. Then all factors in the denominator of eqn. (46) are the Arrhenius complexes K_i.

Here we will have the linear equations

$$\ln b_{i_1} + \ln b_{i_2} + \ldots + \ln b_{i_n} = \ln K_i \qquad i = 1, 2, \ldots, \lambda(G) \tag{86}$$

where $\lambda(G)$ is the number of all directed spanning trees in the reaction graph G.

From eqns. (86) one must choose a set of linearly independent equations and by using known methods find the reaction rate constants.

The analysis, however, shows that, even when all the factors in the denominator of eqn. (46) are Arrhenius factors, reaction rate constants cannot always be determined on their basis. The analysis carried out using graph theory methods shows that it is possible only for definite types of mechanisms, namely for those that correspond to (a) Hamiltonian or (b) strong bi-connected graphs (the latter term is due to Evstigneev) [54].

Let us explain the content and the physico-chemical sense of the above terms.

(a) Hamiltonian graphs are those containing a cycle passing through all their nodes once only. Applied to the complex reaction mechanisms, these graphs are interpreted as follows: there exists a common cycle of conversions (steps) uniting all intermediates. Among Hamiltonian graphs there is a one-route (Fig. 1) and also some two-route [Figs. 5(e) and (6)] mechanisms. A graph represented in Fig. 8(a) and also that of a sufficiently complex enzyme reaction taking place in the presence of two independent inhibitors

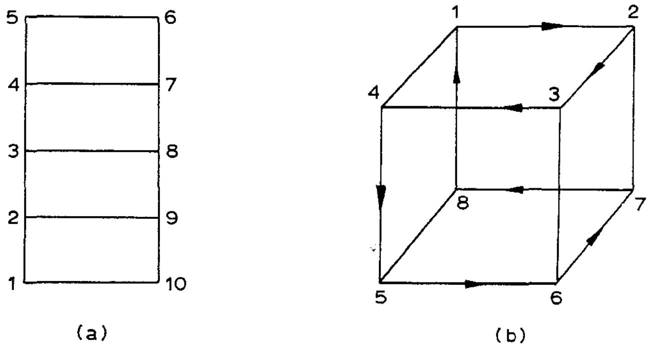


Fig. 8. Hamiltonian graphs. (a) Multi-route reaction; (b) complex enzyme reactions in the presence of two independent inhibitors.

[Fig. 4.8(b), see ref. 9, p. 86] are the Hamiltonian graphs. The Hamiltonian cycle 1–2–3–4–5–6–7–8–1 is marked by arrows.

Non-Hamiltonian graphs of composite mechanisms are widespread, e.g. the graphs of vinyl chloride synthesis and n-hexane conversion [Fig. 3(d) and (f) and Fig. 5(c) and (d)]. The simplest non-Hamiltonian graph is that of the two-step mechanism supplemented by a "buffer" step yielding a non-reactive substance. For the mechanism

$$(1)\ \mathrm{A} + \mathrm{Z} \rightleftarrows \mathrm{AZ} + \mathrm{C}$$

$$(2)\ \mathrm{AZ} + \mathrm{B} \rightleftarrows \mathrm{D} + \mathrm{Z}$$

$$(3)\ \mathrm{Z} + \mathrm{E} \rightleftarrows \mathrm{ZE}$$

the corresponding kinetic equation is

$$W = \frac{(k_1^+ k_2^+ C_\mathrm{A} C_\mathrm{B} - k_1^- k_2^- C_\mathrm{C} C_\mathrm{D})k_3^-}{(k_1^+ C_\mathrm{A} + k_2^+ C_\mathrm{B} + k_1^- C_\mathrm{C} + k_2^- C_\mathrm{D})k_3^- + (k_2^+ C_\mathrm{B} + k_1^- C_\mathrm{C})k_3^+ C_\mathrm{E}} \tag{87}$$

At $k_1^- = k_2^- = 0$

$$W = \frac{k_1^+ k_2^+ C_\mathrm{A} C_\mathrm{B} k_3^-}{(k_1^+ C_\mathrm{A} + k_2^+ C_\mathrm{B})k_3^- + k_2^+ C_\mathrm{B} \cdot k_3^+ C_\mathrm{E}} \tag{88}$$

The denominator of eqn. (88) contains three terms whereas the number of rate constants amounts to four. One of the constants cannot be determined.

(b) Strong bi-connected graph. In non-strict terminology this is a graph without cutpoints, i.e. those graph points whose elimination together with their respective arcs transforms this graph into an unconnected graph. (As far as the graph connectivity is concerned, refer to Sect. 2.2 and ref. 34). In this case conversion cycles will not be connected either by a common step or a common substance. Cutpoints of various graphs are represented in Fig. 5(b) (point X) and (d) (X and Y).

In this case not all the parameters can be determined. An estimate for the number of these indeterminable parameters is obtained as follows. The number is equal to the number of graph cutpoints. (A proof of this results from the Giles theorem [55].) Thus, for the case illustrated in Fig. 5(b), the factors in the denominator of eqn. (46) being known, one cannot determine one constant, whereas in the case shown in Fig. 5(d) two constants cannot be found. This estimate will decrease if the parameters are determined on the basis of the coefficients not only from the denominator but also from the numerator. It can be done since we can also apply some expressions for the rates of variation of substances (in this case reaction cycles differ in their brutto-equations).

As an example, let us describe a two-route mechanism with different brutto-equations.

$$(1)\ \mathrm{A} + \mathrm{Z} \rightarrow \mathrm{AZ}$$

$$(2)\ \mathrm{AZ} + \mathrm{B} \rightarrow \mathrm{AB} + \mathrm{Z}$$

$$(3)\ \mathrm{C} + \mathrm{Z} \rightarrow \mathrm{CZ}$$

$$(4)\ \mathrm{CZ} + \mathrm{D} \rightarrow \mathrm{CD} + \mathrm{Z}$$

This mechanism corresponds to the kinetic equations

$$W_{\mathrm{AB}} = \frac{K_1 C_{\mathrm{A}} C_{\mathrm{B}} C_{\mathrm{D}}}{K_3 C_{\mathrm{A}} C_{\mathrm{D}} + K_4 C_{\mathrm{B}} C_{\mathrm{C}} + K_5 C_{\mathrm{B}} C_{\mathrm{D}}} \tag{89}$$

$$W_{\mathrm{CD}} = \frac{K_2 C_{\mathrm{C}} C_{\mathrm{D}} C_{\mathrm{B}}}{K_3 C_{\mathrm{A}} C_{\mathrm{D}} + K_4 C_{\mathrm{B}} C_{\mathrm{C}} + K_5 C_{\mathrm{B}} C_{\mathrm{D}}} \tag{90}$$

where, as in the previous example, we have

$$K_1 = k_1^+ k_2^+ k_4^+, \quad K_2 = k_2^+ k_3^+ k_4^+, \quad K_3 = k_1^+ k_4^+,$$

$$K_4 = k_2^+ k_3^+, \text{ and } K_5 = k_2^+ k_4^+$$

Whence

$$k_1^+ = \frac{K_1}{K_5}, \quad k_3^+ = \frac{K_2}{K_5}, \quad k_2^+ = \frac{K_4}{K_2} K_5, \quad k_4^+ = \frac{K_3}{K_1} K_5$$

A final conclusion can be formulated as follows. The number of the parameters that cannot be determined from the steady-state kinetic data is the same as the number of steps that do not enter into the cycles. The source of indeterminacy of the parameters implies "buffer" sequences [Fig. 3(b)] and "bridges" between the cycles [Fig. 3(d)]. Note that this estimate refers only to the graph structure when individual reaction weights have not been specified.

The situation becomes radically different when the weights of individual reactions are of the same type, as happens in most cases. Some examples have been given in Sect. 3.1.

One-type weights of individual reactions lead to the fact that some spanning trees will have the same concentration characteristic (see Sect. 3.3) and these spanning trees will be similar.

Graph theory often applies a concept of "graph colour". We will introduce this concept as follows. A set of observed substances reacting with intermediates according to a detailed reaction mechanism will be associated with a set of colours $\alpha_0, \alpha_1, \ldots, \alpha_m$, where α_0 is colourless and corresponds to the case when no substance reacts with an intermediate. Then each arc will be coloured to the colour of the observed substance taking part in the reaction. Every spanning tree will also be characterized by a set of its arc colours. If the spanning tree includes some arcs of the same colour, one can talk about this colour intensity in a given spanning tree. Colour intensity (the number of colour repetitions) is equal to the number of molecules of the substances participating in the reactions corresponding to the spanning tree or to the number of spanning tree arcs (reactions) in which this substance is present. Then the concentration characteristics will be represented by the vector $(r_0, r_1, \ldots, r_m)_T$. Elements of this vector, namely intensities, are the numbers of colour arc α_i in the spanning tree T. This characteristic corresponds identically to the concentration characteristic introduced previously in Sect. 3.3.

Thus the problem of determining spanning trees with different concentration characteristics reduces to the determination of the number of differently coloured spanning trees.

For its solution, let us introduce a concept of the graph of spanning trees $\phi(G)$ for a given graph G. Let T_1 and T_2 be two spanning trees of the graph G. We will say that T_2 is coupled with T_1 if T_2 is obtained from T_1 by removing one of the arcs u and by adding an arc v, i.e. $T_2 = (T_1 \setminus \{u\} \cup \{v\})$.

A graph of the spanning trees $\phi(G)$ of the graph G is called an indirected graph whose nodes correspond to the spanning trees of the graph G in which two points are adjacent if, and only if, their respective spanning trees are coupled.

Let us present a theorem from ref. 56. If $\phi(G)$ has no less than three nodes, then any edge of the graph $\phi(G)$ can become a part of the Hamiltonian cycle in $\phi(G)$. For our purposes, this property is made concrete in the theorem proved in ref. 57.

Theorem. Whatever two spanning trees T_1 and T_2 of the graph with k common arcs may be, there always exists a sequence of $(n - k)$ pairwise coupled spanning trees $T_1 = T_{i_1}, T_{i_2}, \ldots, T_{i_{n-k}} = T_2$, where n is the number of nodes in the graph G.

In accordance with this theorem one can make the following corollaries.

(1) If the graph G contains two spanning trees one of which consists of the

arcs coloured to the colour α [the concentration characteristic is of the form $(n-1, 0, \ldots, 0)$] and the other has arcs with the colour β [the concentration characteristic is of the form $(0, n-1, 0, \ldots, 0)$], it will also have spanning trees with all intermediate concentration characteristics, i.e. with the concentration characteristics of the form

$$(n-2, 1, \ldots, 0)\ (n-3, 2, \ldots, 0), \ldots, (1, n-2, 0, \ldots) \qquad (91)$$

(2) If the graph G contains three spanning trees with the concentration characteristics $(n-1, 0, 0, \ldots)$, $(0, n-1, 0, \ldots)$, $(0, 0, n-1, \ldots)$, it will also have spanning trees with characteristics of the intermediate types

$$\begin{array}{c} (n-1, 0, 0, \ldots) \\ (n-2, 1, 0, \ldots) \qquad (n-2, 0, 1, \ldots) \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ (1, n-2, 0, \ldots)(1, n-3, 1, \ldots) \ldots (1, 1, n-3, \ldots)(1, 0, n-2, \ldots) \\ (0, n-1, 0, \ldots)(0, n-2, 1, \ldots) \ldots (0, 1, n-2, \ldots)(0, 0, n-1, \ldots) \end{array} \qquad (92)$$

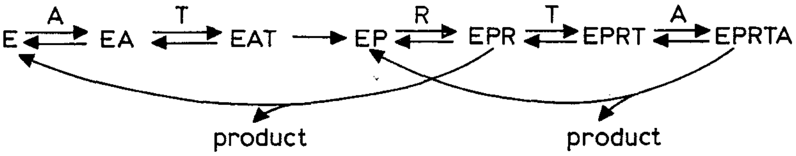
Further generalizations are evident.

It is clear that corollary (1) implies that the graph G contains n groups with different colours (concentration characteristics). Corollary (2) suggests that the graph G comprises $n(n+1)/2$ of these groups. But if one assumes that the graph G contains four similar-coloured spanning trees, the number of its spanning trees will be equal to $n(n+1)(n+2)/6$. This value is greater than the number of arcs in the complete symmetrically directed graph. We believe, however, that this case is extremely rare.

In accordance with corollaries (1) and (2), one can readily find a method to calculate the number of similar spanning trees if they have two, three or four colours. In the graph G, let n_α be the greatest number of the α-coloured arcs that can be met in one spanning tree. Then only those spanning trees that contain $0, 1, 2, \ldots, n$ arcs having the colour α are admissible. The colours of these spanning trees will be obtained if, in eqn. (91), we eliminate the right- and left-hand characteristics with the respective components higher than n_α or n_β. It can be seen from eqn. (92) that, in the case of three colours, these characteristics fill a regular triangle. It is sufficient to eliminate the sections which are also triangular that correspond to the characteristics of the spanning trees with the non-admissible number of the arcs having a given colour. In the case of four colours, the characteristics of spanning trees fill a regular tetrahedron from which it suffices to remove sections that are also tetrahedral and are adjacent to the graph nodes.

To find spanning trees with the greatest number of the similar-coloured arcs, it suffices to give the arcs of the colour required (e.g. α) some low negative weight $(-\varepsilon)$ and the rest of the arcs unit weight and to apply to the graph G an algorithm for the construction of a directed spanning tree having the lowest weight [58]. It is evident that the application of such procedures is efficient only for complex graphs.

Example. A detailed mechanism for one of the reactions catalyzed by aminoacyl-tRNA-synthetase [59] is represented by the set of steps



(93)

where E is enzyme, A is adenosine triphosphate, T is tryptophan and R is tRNA (transporting ribonucleic acid).

A coloured graph for this mechanism is represented in Fig. 9. The colours α, β, δ, and γ correspond to the substances A, T, R and the "colourless" substance (i.e. to the case when the observed substance does not take part in the reaction with an intermediate). A spanning tree colour is represented as four numerals (r_α, r_β, r_δ, and r_γ). Each of these numerals indicates the number of arcs having the corresponding colours. Using the above procedure, let us represent spanning trees having a variety of colours with the help of two regular triangles for the two cases $n_\delta = 0$ and $n_\delta = 1$, respectively (Fig. 10).

Regular triangles eliminate the sets of numerals that do not satisfy limitations for the number of arcs having a specified colour. Then we will have 17 sets of different colours. But not all these sets correspond to real graph spanning trees. After testing, it appears that six sets correspond to the forbidden configurations.

Finally, the denominator has 11 sets of spanning trees, whereas the initial mechanism contains 13 rate coefficients.

This algorithm permits us to determine the number of parameters "manually" on the basis of the reaction graph without derivation of a steady-state kinetic equation. For large-sized and complex-structure graphs it is recommended that the corresponding sets of spanning trees are selected using computations [60].

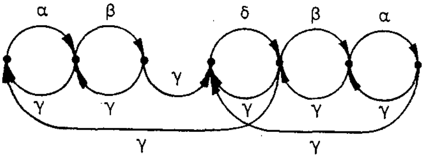


Fig. 9. Graph of reaction catalyzed by aminoacyl-tRNA-synthetase.

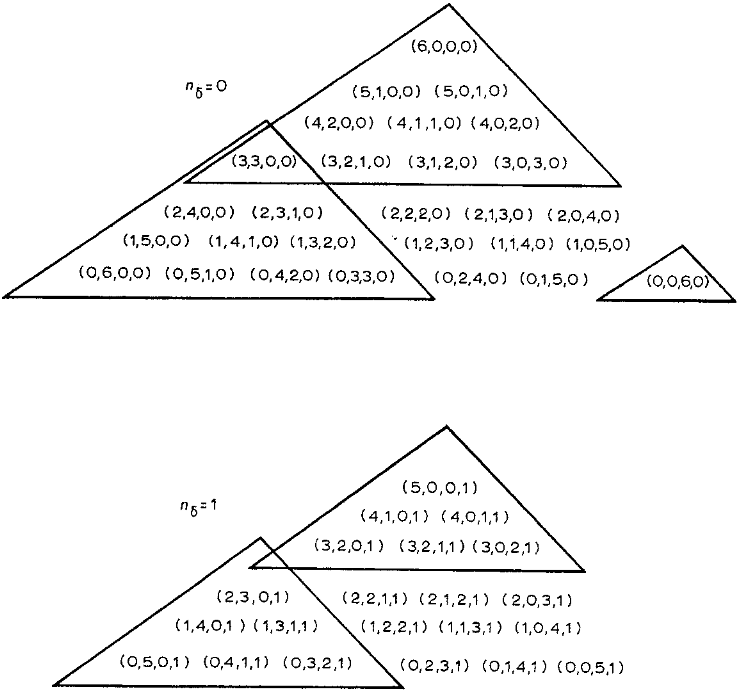


Fig. 10. Variously coloured spanning trees for the mechanism from Fig. 9.

3.5 BRUTTO-REACTION, DETAILED MECHANISM AND THE NUMBER OF PARAMETERS UNDER DETERMINATION

This section is devoted to the relation between the brutto (stoichiometric) equation corresponding to the detailed mechanism and the structure of a kinetic equation. Note that all the detailed mechanisms above can conventionally be divided into two classes. (This division will be applied in what follows.)

(1) Mechanisms in which each step includes at least one observed substance either initial or product (the observed substances can be present in the step as both). For generality, it is suggested that all the steps be reversible.

(2) Mechanisms containing steps having no observed substances.

Let us give some examples.

Mechanisms of class 1. This is a well-known Michaelis–Menten scheme

(1) $\mathrm{E} + \mathrm{S} \rightleftarrows \mathrm{ES}$

(2) $\mathrm{ES} \rightarrow \mathrm{P} + \mathrm{S}$

with the brutto-equation S = P. These are two-step one-route mechanisms that fit the Temkin–Boudart scheme, e.g.

$$(1)\ Z + H_2O \rightleftarrows ZO + H_2$$

$$(2)\ ZO + CO \rightleftarrows Z + CO_2$$

[see eqn. (23)] with the brutto-equation

$$H_2O + CO = H_2 + CO_2$$

It is the one-route mechanism for hydrogen oxidation on the oxides of Group IV transition metals [38]

$$(1)\ H_2 + (ZO)_2 \rightarrow ZOZ \cdot H_2O$$

$$(2)\ ZOZ \cdot H_2O \rightleftarrows ZOZ + H_2O$$

$$(3)\ ZOZ + H_2 \rightarrow ZZ \cdot H_2O$$

$$(4)\ ZZ \cdot H_2O \rightleftarrows ZZ + H_2O$$

$$(5)\ ZZ + O_2 \rightarrow (ZO)_2$$

with the brutto-equation

$$2H_2 + O_2 = 2H_2O$$

A mechanism of this class is also a one-route scheme for SO_2 oxidation over vanadium catalysts having a "buffer" step [61]

$$(1)\ V_2^{5+}O_2^{2-} + SO_2 \rightleftarrows V_2^{5+}O^{2-} + SO_3$$

$$(2)\ V_2^{5+}O^{2-} + SO_2 \rightleftarrows V_2^{5+}SO_3^{2-}$$

$$(3)\ V_2^{5+}SO_3^{2-} + O_2 \rightleftarrows V_2^{5+}O_2^{2-} + SO_3$$

$$(4)\ V_2^{5+}SO_3^{2-} \rightleftarrows V_2^{4+} + SO_3$$

and a one-route catalytic conversion of methane [51]

$$(1)\ CH_4 + Z \rightleftarrows ZCH_2 + H_2$$

$$(2)\ H_2O + ZCH_2 \rightleftarrows ZCHOH + H_2$$

$$(3)\ ZCHOH \rightleftarrows ZCO + H_2$$

$$(4)\ ZCO \rightleftarrows Z + CO$$

with the brutto-equation

$$CH_4 + H_2O = CO + 3H_2$$

We can also give examples of two-route mechanisms belonging to this class: a detailed mechanism for vinyl chloride synthesis [17]

$$(1)\ Z + C_2H_2 \rightleftarrows Z \cdot C_2H_2$$

$$(2)\ Z \cdot C_2H_2 + HCl \rightarrow Z + C_2H_3Cl$$

$$(3)\ Z + HCl \rightleftarrows Z \cdot HCl$$

$$(4)\ Z \cdot HCl + C_2H_2 \rightarrow Z + C_2H_3Cl$$

with the brutto-equation

$$C_2H_2 + HCl = C_2H_3Cl$$

and a mechanism for the NO + CO interaction over silver [39]

$$(1)\ NO + Z \rightleftarrows ZNO$$

$$(2)\ ZNO + NO \rightarrow N_2O + ZO$$

$$(3)\ N_2O + Z \rightarrow N_2 + ZO$$

$$(4)\ ZO + CO \rightarrow Z + CO_2$$

with the brutto-equations

$$2NO + CO = N_2O + CO$$

and

$$N_2O + CO = N_2 + CO_2$$

Every step of these mechanisms contains at least one observed substance and in this case only one of its molecules reacts.

Mechanisms of class 2. A typical mechanism of this class is the model mechanism for the catalytic isomerization treated previously

$$(1)\ A + Z \rightleftarrows AZ$$

$$(2)\ AZ \rightleftarrows BZ$$

$$(3)\ BZ \rightleftarrows B + Z$$

with the brutto-equation A = B. A second step of this mechanism is the mutual conversions of intermediates. It does not contain any observed substances. Some examples for two-route mechanisms of this class can be found in ref. 62. For an example of the multi-route mechanism, see eqn. (26), Fig. 3(f).

The physico-chemical sense of the classification suggested is clear. If the steps such as $AZ \rightleftarrows BZ$ involving no participation of the observed substances ("latent steps") are fast compared with the rest of steps or are not present at all, the mechanism must be attributed to class 1. Otherwise it will belong to class 2.

In our opinion, as one starts studying some reaction mechanism for which no data concerning the mutual conversions of intermediates are available yet, it is reasonable to suggest that this mechanism belongs to class 1. Note that the mechanisms known from the available literature that can be attributed to class 2 are met much more rarely.

Using graph theory terminology presented in Sect. 3.4, mechanisms of class 1 can be called "coloured". It implies that every step has at least one arc-reaction having a colour of the observed substance participating in the reaction.

Mechanisms ascribed to class 2 can be called those with "colourless" steps (i.e. those containing no observed substances).

3.5.1 Brutto-equation and the number of steps

Every graph's cycle corresponds to its "natural" brutto-equation. We will assume that the stoichiometric coefficients in this equation are minimum integer-valued, i.e. for simplicity the multiplicity is taken to be equal to unity (see Sects. 2.3 and 2.4). We suggest that, as in all the above examples, only one molecule of each observed substance (either initial or product) is either consumed or formed.

Then, for a mechanism of class 1, one can give a simple estimate of the number of steps corresponding to a given brutto-equation

$$n_{\max}(n_{\text{in}}, n_{\text{prod}}) \leq s \leq n_{\text{in}} + n_{\text{prod}} \tag{94}$$

where n_{in} and n_{prod} are the numbers of the initial substances and products in the brutto-reaction, respectively, $n_{\max}(n_{\text{in}}, n_{\text{prod}})$ is the maximum number among them, and $n_{\text{in}} + n_{\text{prod}}$ is the total number of molecules in the brutto-equation.

Let us apply estimate (94) to the various mechanisms of class 1 given above. For the Michaelis–Menten mechanism, the brutto-reaction is of the form: $S = P$, $n_{\text{in}} = 1$, $n_{\text{prod}} = 1$, and $s = 1 + 1 = 2$. For CO conversion, the brutto-equation takes the form

$$H_2O + CO = CO_2 + H_2$$

$n_{\text{in}} = n_{\text{prod}} = 2$, $s = 2$. For hydrogen oxidation on Group IV transition metals, we have $s = 5$. Indeed, for the brutto-equation

$$2\,H_2 + O_2 = 2\,H_2O$$

we obtain $s = n_{\text{in}} + n_{\text{prod}} = 5$. For the mechanism of SO_2 oxidation over vanadium catalysts in the cycle we have $s = 3$ (a "buffer" step has not been taken into account). Indeed, for the brutto-equation

$$2\,SO_2 + O_2 = 2\,SO_3$$

we will have $n_{\text{in}} = 3$, $n_{\text{prod}} = 2$, and $s = n_{\max} = n_{\text{in}} = 3$. For the one-route conversion of methane with the brutto-equation

$$CH_4 + H_2O = CO + 3\,H_2$$

we obtain $n_{\text{in}} = 2$, $n_{\text{prod}} = 4$, and $s = 4$.

In the two-route mechanism of vinyl chloride synthesis, the number of steps in each route amounts to two. Indeed, the brutto-equation for each route

$$C_2H_2 + HCl = C_2H_3Cl$$

we have $n_{in} = 2$, $n_{prod} = 1$, and $s = 2$. In the two-route mechanism of NO reaction with CO steps (1), (2), and (4) correspond to the brutto-equation

$$2NO + CO = N_2O + CO_2$$

($n_{in} = 3, n_{prod} = 2, s = n_{max} = n_{in} = 3$), whereas steps (3) and (4) correspond to the brutto-equation

$$N_2O + CO = N_2 + CO_2$$

($n_{in} = n_{prod} = 2$ and $s = 2$).

Thus eqn. (94) is fulfilled in the mechanisms considered as an accurate estimate for the number of steps. More often it is a lower bound (according to the number of molecules either of the initial substances or of products) and rarely will it be an upper bound (according to the number of the initial substances and products).

Although all the mechanisms of class 1 are "coloured" (i.e. every step contains the observed substances), certain reactions can be "colourless". For example, if the number of molecules of the initial substances is greater than that of products (the reaction proceeds with decreasing volume) and the estimate $s = n_{max} = n_{in}$ is fulfilled, then there must be $(n_{in} - n_{prod})$ of "colourless" inverse reactions (see, for example, the SO_2 oxidation where $n_{in} = 3$, $n_{prod} = 2$, and there is one "colourless" inverse reaction). But if $n_{prod} > n_{in}$ (the reaction proceeds with increasing volume) and $s = n_{max} = n_{prod}$, there must be $(n_{prod} - n_{in})$ of "colourless" direct reactions (see, for example, the methane conversion where $n_{in} = 2$, $n_{prod} = 4$, and there are two "colourless" direct reactions). But if $s = n_{in} + n_{prod}$, then in principle there can be s "colourless" reactions. Actually their number is lower (see, for example, the oxidation of hydrogen over Group IV metal oxides where $s = n_{in} + n_{prod} = 5$ and there are two "colourless" reactions).

Certainly, for the mechanisms of class 2 the number of steps can be much greater than that determined in accordance with eqn. (94). Here this estimate will play the role of the lower bound.

Note that if the reactions involve the participation of more than one molecule of the observed substance, then eqn. (94) will need corrections.

3.5.2 Graph colours and kinetic equation structure

The brutto-equation depends on the structure of the kinetic equation and its parameters. In Sect. 2.3 we have already spoken about cyclic characteristics in the numerator of the steady-state kinetic eqn. (46). It is the kinetic equation of the brutto-reaction as if it were a simple step. The form of the cyclic characteristics is independent of the detailed mechanism. But under some suppositions both the structure of the denominator summands and their type also depend on the brutto-equation. Let us first carry out an analysis for a one-route mechanism.

It has already been shown that the denominator of eqn. (46) contains weights of three types of spanning trees: direct, inverse, and mixed. Every spanning tree has its own concentration characteristics and its own colour. In the previous section, the problem of determining the number of independent parameters was associated with estimating the number of variously coloured spanning trees.

As an example, let us consider the catalytic conversion of methane [51] with the brutto-equation

$$CH_4 + H_2O = CO + 3H_2$$

Let this reaction be realized through a one-route linear mechanism. Direct spanning trees are formed by the combination of $(n-1)$ direct reactions of n reactions. It can easily be understood that, irrespective of the reaction mechanism, there must be spanning trees including $[CH_4]$ and those including $[H_2O]$. As far as the spanning tree including $[CH_4][H_2O]$ is concerned, it will be present in the case when "colourless" reactions exist among direct reactions. In our case, as shown above, there are at least two "colourless" direct reactions, i.e. $n_{\text{in}} = n_{\text{prod}} = 2$.

Hence, among the direct spanning trees there will be spanning trees of two colours, i.e. their number will be exactly equal to that of the initial substances. There will be one more two-coloured spanning tree formed due to the fact that the reaction sequence includes a reaction that does not involve the participation of the observed substance. A sum of the weights of direct spanning trees can be written as

$$K_1[CH_4] + K_2[H_2O] + \boxed{K_3[CH_4][H_2O]} \qquad (95)$$

The complex K_3 appears to be the sum of two products of constants (non-Arrhenius complex). The reason for this fact is that the mechanism includes two "colourless" steps. It can be shown similarly that, irrespective of the mechanism, inverse spanning trees must necessarily contain those including $[H_2]^3$ and $[CO][H_2]^2$. The presence of the inverse spanning tree including $[CO][H_2]^3$ shows that the sequence of inverse reactions contain "colourless" reactions. Among inverse spanning trees there are also those of two colours and their number will equal the number of products and probably one more spanning tree (if there are "colourless" reactions). In the general form, the sum of the inverse spanning tree weights will be written as

$$K'_1[H_2]^3 + K'_2[CO][H_2]^2 + \boxed{K'_3[CO][H_2]^3} \qquad (96)$$

The complex K'_3 is non-Arrhenius and is the sum of three products. The reason for this is that the brutto-equation involves three molecules of H_2, and the three steps of the detailed mechanism must be subject to the same type of kinetic law. It is due to this fact that such spanning trees appear.

Equations (95) and (96) contain concentration characteristics $[CH_4]$, $[H_2O]$, $[H_2]^3$, and $[CO][H_2]^2$. It is nothing else than a combination of $(n-1)$ concentrations of the initial substances (products) of n possible ones. In addition, eqns. (95) and (96) contain summands outlined by broken lines. They appear due to the fact that the reaction sequence also contains "colourless" reactions. For the direct sequence the presence of these reactions is obligatory, whereas in the inverse one it is probable.

Let us consider mixed spanning trees. The weight sum can be written here as [see eqn. (81)]

$$\begin{aligned}&K_1''[H_2] + K_2''[CO][H_2] + K_3''[H_2O][CO] + K_4''[CH_4][H_2] + \\ &+ K_5''[H_2]^2 + K_6''[CH_4][H_2]^2 + K_7''[H_2O][H_2][CO] + \\ &+ K_8''[CH_4][H_2O][H_2] \qquad (97)\end{aligned}$$

This expression is apparently considerably dependent on the specificity of the four-step detailed mechanism [51]. It contains several "crossing" terms that depend on the concentrations of both initial substances and products.

Equations of type (97) can also comprise a summand including concentrations of the whole of the brutto-reaction participants, i.e. $K_9''[CH_4][H_2O]$-$[CO][H_2]^3$. It is evident that, in this case, the reaction mechanism must be attributed to class 2 and contains a sufficiently large number of "colourless" reactions. The number of steps here amounts to $s > n_{\text{in}} + n_{\text{prod}}$. The analysis performed using this example can readily be generalized. For a one-route catalytic reaction with one-route linear mechanism the following conclusions can be drawn.

(1) In the denominator of the steady-state kinetic equation (46), several summands generated by direct and inverse spanning trees do not depend on the detailed mechanism. For the inverse case their number is equal to the overall number of the brutto-reaction participants. The form of these summands is defined by the combinations of the $(n-1)$ concentrations of the initial substances (products) of n possible ones.

For example, for the brutto-equation

$$mA + nB = pC + qD$$

the denominator must contain four terms that are independent of the detailed mechanism of the form $K_1[A]^{m-1}[B]^n$, $K_2[A]^m[B]^{n-1}$, $K_3[C]^{p-1}[D]^q$, and $K_4[C]^p[D]^{q-1}$.

(2) If the denominator of eqn. (46) has a term corresponding to the kinetic relationship of the direct (inverse) reaction, it implies that the direct (inverse) sequence of reactions involves steps including no observed substances.

For example, for the brutto-equation

$$mA + nB = pC + qD$$

such terms will be of the form $K_5[A]^m[B]^n$, $K_6[C]^p[D]^q$. In principle it is possible that the term $K_7[\mathrm{A}]^m[\mathrm{B}]^n[\mathrm{C}]^p[\mathrm{D}]^q$ will appear. The presence of such terms whose appearance is, apparently, rare, is the criterion for the mechanism to be attributed to class 2 (mechanisms here include steps containing no observed substances at all).

(3) Coefficients for the terms in the denominator of eqn. (46) can be sums of the constants' products (non-Arrhenius complex).

The reason for the non-Arrhenius type of complex lies in the fact that the brutto-equation comprises several molecules of one or the other substance. For example, for the brutto-equation

$$m\mathrm{A} + n\mathrm{B} = p\mathrm{C} + q\mathrm{D}$$

the factor K_1 in the term $K_1[\mathrm{A}]^{m-1}[\mathrm{B}]^n$ is the non-Arrhenius complex, i.e. the sum of the products of m constants. If $m = 1$ the complex is always Arrhenius. The coefficient of the term $K[\mathrm{A}]^m[\mathrm{B}]^n$ can also be non-Arrhenius if the number of "colourless" reactions in the spanning tree is greater than unity.

(4) Mixed spanning trees generate several terms. It is these terms that are responsible for the detailed mechanism specificity. They can contain mixed products of the concentrations of the initial product substances. Exponential factors for these concentrations will differ from those in the terms generated by direct and inverse spanning trees. For example, for the same brutto-equation

$$m\mathrm{A} + n\mathrm{B} = p\mathrm{C} + q\mathrm{D}$$

mixed spanning trees can generate the terms $K[\mathrm{A}]^\alpha[\mathrm{B}]^\beta[\mathrm{C}]^\gamma[\mathrm{D}]^\delta$, where $\alpha \leqslant m-2, \beta \leqslant n-2, \gamma \leqslant p-2$, and $\delta \leqslant q-2$. Each of these terms depends on the specificity of the reaction sequence. Their interpretation must promote our understanding of the detailed mechanism.

Hence one must understand the importance of special kinetic experiments with mixtures containing high concentrations of products. But the available experimental data here are very limited in number. Note that mixed spanning trees appear only when the number of steps is $s \geqslant 3$.

(5) The number of parameters of eqn. (46) under determination, N_{pud}, can be found using the estimate

$$n_{\mathrm{in}} + n_{\mathrm{prod}} \leq N_{\mathrm{pud}} \tag{98}$$

It is interesting that this estimate coincides with that for the number of steps [eqn. (94)].

But if the sequence of direct (or inverse) reactions contains at least one "colourless" reaction, then eqn. (98) takes the form

$$n_{\mathrm{in}} + n_{\mathrm{prod}} + 1 \leqslant N_{\mathrm{pud}} \tag{98a}$$

In the case in which both of the sequences have "colourless" reactions, we have

$$n_{\mathrm{in}} + n_{\mathrm{prod}} + 2 \leqslant N_{\mathrm{pud}} \tag{98b}$$

(6) All that has been said above refers to the case in which all the mechanism steps are reversible. But if the steps are irreversible we will have

$$N_{\text{pud}} = n_{\text{in}} \tag{99a}$$

when no "colourless" reactions are present or

$$N_{\text{pud}} = n_{\text{in}} + 1 \tag{99b}$$

when they are present.

Hence, in the irreversible case, the number of parameters under determination is equal to that of graph's colours (including the colour of "colourless" reactions).

(7) For the irreversible case, the kinetic equation (46) can be written in a very simple form

$$W = \frac{K}{\sum_{i=1}^{n_{\text{in}}} k_i/C_i} \tag{100a}$$

or

$$W = \frac{K}{1 + \sum_{i=1}^{n_{\text{in}}} k_i/C_i} \tag{100b}$$

In the case in which two reactants react ($n_{\text{in}} = 2$), eqn. (100a) will take the form

$$W = \frac{KC_1C_2}{K_1C_1 + K_2C_2} \tag{100c}$$

For three reactants ($n_{\text{in}} = 3$), eqn. (100a) is represented as

$$W = \frac{KC_1C_2C_3}{K_1C_1C_2 + K_2C_2C_3 + K_3C_3C_1} \tag{100d}$$

and so on.

It is important to understand that the type of eqns. (100) corresponding to the irreversible case depends neither on the detailed mechanism nor even on the type of the brutto-equation. It is dependent only on the number of substances taking part in the brutto-conversion. Note that sometimes it is said that a two-step mechanism is realized if the kinetic relationships satisfy eqn. (100c).

Let us demonstrate the way in which the above considerations can be applied to interpret the detailed mechanism according to the observed kinetic dependences. Let the reaction rate for hydrogen oxidation over oxides be described by eqn. (54) rewritten as

$$W = \frac{K[H_2]^2[O_2]}{K_1[H_2]^2 + K_2[H_2][O_2] + K_3[H_2]^2[O_2] + K_4[H_2]^2[H_2O] + K_5[H_2][O_2][H_2O]} \tag{101}$$

For the brutto-equation

$$2H_2 + O_2 = 2H_2O$$

we have $n_{in} = 3$ and $n_{prod} = 2$. In accordance with eqn. (94), the number of steps for the mechanism must be $3 \leqslant s \leqslant 5$.

Since the denominator contains the term $K_3[H_2]^2[O_2]$, the direct sequence of the reactions must also contain a "colourless" reaction (one or two). Hence $s = 4$ or 5.

The steps of water production can be treated as reversible since there are terms containing $[H_2O]$. But as there is no term with $[H_2O]^2$, it is evident that these two steps are separated by some irreversible step. If $s = 4$, every one of the terms in the denominator of eqn. (101) must be a product of three reaction weights. The terms $K_1[H_2]^2$ and $K_2[H_2][O_2]$ are sure to contain a weight of the "colourless" reaction since their exponential factor is two. This is still more valid at $s = 5$, when these terms will include the weights of two "colourless" reactions.

Some information about the detailed mechanism must be provided by the mixed terms $K_4[H_2]^2[H_2O]$ and $K_5[H_2][O_2][H_2O]$. Judging by their form, one can suggest first that water is not liberated in the step consuming oxygen, and second that in the two steps that consume hydrogen, water is not liberated either. Hence water is liberated in those steps of the decomposition of intermediates that do not involve the participation of the initial gaseous substances.

In our case the catalyst is oxide. It is natural to suggest that the first step in the catalytic cycle is the interaction of an oxide species with hydrogen and that the last step is the reduction of species.

Hence the mechanism can be characterized as follows.

(1) Step 1 is the interaction of the initial catalytic species with hydrogen. In this case water is not formed.

(2) Step 2 is the decomposition of an intermediate formed in step 1 with the liberation of water. The step is reversible.

(3) Step 3 is the interaction of the intermediate formed in step 2. Water is not formed.

(4) Step 4 is similar to step 2.

(5) Step 5 is the reduction of the initial catalytic species (by interaction with oxygen).

The sequence of steps 2 and 3 cannot be reversed since, in this case, two reversible steps of water liberation will become adjacent. As has been shown above, this is not admissible since the denominator of eqn. (101) has no $K[H_2O]^2$ term.

The mechanism suggested has five steps including two "colourless" reactions [steps (2) and (4)]. Note that to interpret data it would be useful to have information concerning the temperature dependence of the complexes. One can say in advance that K and K_1 are the Arrhenius complexes, whereas K_2

is the non-Arrhenius complex. If we had information indicating that K_3 was the non-Arrhenius complex and K_4 and K_5 the Arrhenius complexes, it would further promote the data interpretation. For example, if K_3 is the non-Arrhenius complex, it implies that the direct sequence of reactions has two "colourless" reactions rather than one as has been suggested from the beginning.

Hence in this case, on the basis of the detailed analysis of only the steady-state kinetic equation, we have managed to formulate a reaction mechanism. This mechanism is similar to that suggested in ref. 38.

We believe analysis such as has been demonstrated above will also prove to be useful in more general cases. It must be noted that this analysis places heavy demands on the inverse kinetic problem whose result is to restore summands of the steady-state kinetic equation.

4. Graphs to analyze relaxations. General form of characteristic polynomial

A non-steady-state kinetic model for a complex catalytic reaction with a linear mechanism is described as

$$\dot{\vec{x}} = \vec{B}(\vec{c}\,)\vec{x} \tag{102}$$

where $\vec{x}$ and $\vec{c}$ are the vector-columns for the concentration of the intermediate and observed substances, reepectively, and $\vec{B}(\vec{c})$ is the matrix of the reaction weights.

In addition, a conservation law of the total catalyst amount must be fulfilled

$$\sum_{i=1}^{n} x_i = C$$

Equation (102) is the non-steady-state kinetic model for the conversion of intermediates (for heterogeneous catalysis, for the conversion of surface substances) assuming that the concentrations of the observed substances are constant. As is known, the solution of eqn. (102) is of the form

$$x_i(t) = \sum_{j=i}^{n} x_{ji}^{0} \exp(\lambda_j t) \tag{103}$$

where λ_j are the roots of the characteristic equation (eigen-values).

Note that a characteristic polynomial of the square matrix $\vec{A} = \|a_{ij}\|$ of the order n is called a determinant for a set of linear homogeneous equations

$$\sum_{k=1}^{n} (a_{ik} - \delta_{ik}\lambda)x_k = 0 \qquad i, \ldots, n \tag{104}$$

where δ_{ik} is the Kronecker symbol and λ is the scalar

$$\delta_{ik} = \begin{cases} 1 & \text{if } i = k \\ 0 & \text{in the opposite case} \end{cases}$$

The analysis of the characteristic polynomial (primarily of its roots) is absolutely necessary when studying the non-steady-state behaviour of a complex chemical system. A traditional problem is to study the spectrum of relaxation times $\tau_i = 1/|\mathrm{Re}\lambda_i|$ [63]. A characteristic polynomial can be written as

$$P(\lambda) = (-1)^n(\lambda^n - d_1\lambda^{n-1} + d_2\lambda^{n-2} + \ldots + (-1)^n d_n) \qquad (105)$$

where every coefficient d_i ($i = 1, 2, \ldots, n$) is equal to the arithmetic sum of the whole of the ith order minors from the matrix determinant.

Calculation of the coefficients d_i for a given matrix is a very laborious process. We will give a method to calculate these coefficients proceeding directly from the complex reaction graph. Like a steady-state kinetic equation, a characteristic polynomial will be represented in the general (structuralized) form:

$$\lambda^n - d_1\lambda^{n-1} + d_2\lambda^{n-2} + \ldots + (-1)^n d_n = (-1)^n P(\lambda) \qquad (106)$$

Let us give a determination for the k-spanning tree (k is a positive integer). A k-spanning tree for the graph $G(x,u)$ will be called an unconnected partial graph* containing all the points, i.e. a rooted forest (a set of rooted trees) all of whose arcs are directed towards the roots, i.e. the given graph points x. A rooted tree can also be degenerated, i.e. consisting of one point. When speaking of trees, spanning trees and graphs, here and hereafter we imply that they are directed. The weight of the spanning tree is the product of the weights of its arcs. The weight for the degenerated component is assumed to be equal to unity.

Evstigneev and Yablonskii [64] proved the following theorem: coefficient of λ^k (k is the exponential factor) for the characteristic polynomial $P(\lambda)$ amounts to the sum of the weights for all the k-spanning trees of the reaction graph at $k \neq 0$ and is equal to zero at $k = 0$.

Proof: It suffices to prove that the sum of all the kth order minors amounting to the coefficient of λ^k is at the same time equal to the sum of the weights for all the $(n - k)$-spanning trees of the reaction graphs. At $k = 0$ the coefficient of λ^0 amounts to the $\vec{B}(\vec{c})$ matrix determinant. Since, according to the conservation law, any diagonal element of $\vec{B}(\vec{c})$ satisfies the equality

$$b_{ii} = \sum_{j=1, j\neq i}^{n} b_{ji}$$

the rows of this matrix are linearly dependent and the coefficient equals zero.

Let us give relationships for various coefficients.

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* A partial graph of the graph $G(x, u)$ is the graph $H = (y, v)$ where $y \leqslant x$ and $v \leqslant u$.

(a) $k = 1$. The coefficient of λ is equal to the sum of all the principal $(n - 1)$th order minors. As has been proved in ref. 6, every minor of this type equals the sum of the weights for the spanning trees entering into the point x_k.

(b) $1 < k < n - 1$. The coefficient of λ^k amounts to the sum of the principal $(n - k)$th order minors. It can be shown that every uncancelled term will correspond to the n-point graph having no contours and exactly $(n - k)$ arcs, i.e. a forest consisting of k components. In this case a forest is a non-connected graph whose every connected component is a tree (probably consisting of one point).

(c) $k = n - 1$. The coefficient of λ^{n-1} is equal to the spur of a matrix, i.e. to the sum of the weights for all the reaction graph arcs.

(d) $k = n$. The coefficient of λ^n amounts to the weight of the empty (i.e. having no arcs) n-point graph. According to the determination, its weight equals unity.

Taking into account the above remarks about the characteristic equation coefficients, its general form can be represented as

$$\lambda^{n-1} + \left(\sum_{i=1}^{n} b_i\right) \lambda^{n-2} + \ldots + \left(\sum_{i=1}^{n_k} D_i\right) \lambda^{n-k-1} + \ldots + D = 0 \qquad (107)$$

where n is the number of the graph's arcs and n_k is the number of k-spanning trees. The same type of general form of the characteristic equation can also be obtained from ref. 65 using the concept of the " Coates flow graph" [66].

Example. Let us consider the known mechanism for catalytic isomerization

(1) $\mathrm{A + Z \rightleftarrows AZ}$

(2) $\mathrm{AZ \rightleftarrows BZ}$

(3) $\mathrm{BZ \rightleftarrows B + Z}$

with the reaction weights $b_1^+ = k_1^+[\mathrm{A}]$, $b_1^- = k_1^-$, $b_2^+ = k_2^+$, $b_2^- = k_2^-$, $b_3^+ = k_3^+$, $b_3^- = k_3^-[\mathrm{B}]$. A characteristic equation will be

$$\lambda^2 + \mathrm{d}_1\lambda + D = 0$$

where

$$\begin{aligned} d_1 &= \sum_i b_i = k_1^+[\mathrm{A}] + k_1^- + k_2^+ + k_2^- + k_3^+ + k_3^-[\mathrm{B}] \\ D &= k_1^+[\mathrm{A}](k_2^+ + k_3^+ + k_2^-) + k_3^-[\mathrm{B}](k_1^- + k_2^- + k_2^+) + \\ &\quad + k_2^+k_3^+ + k_1^-k_2^- + k_3^+k_1^- \end{aligned} \qquad (108)$$

If all its steps are irreversible, we obtain

$$\begin{aligned} d_1 &= k_1^+[\mathrm{A}] + k_2^+ + k_3^+ \\ D &= k_1^+[\mathrm{A}](k_2^+ + k_3^+) + k_2^+k_3^+ \end{aligned}$$

Corollaries. (1) Coefficients of the characteristic equation cannot contain terms having simultaneously direct and inverse weights (e.g. they cannot have $b_2^+ b_2^-$) and the terms containing weights of two reaction-arcs emanating from the same point.

(2) In accordance with the Vieta formulas, coefficients of the characteristic equation are related to its roots by the equations

$$\begin{aligned} -d_1 &= \sum_i \lambda_i \\ D &= \prod_i \lambda_i \end{aligned} \tag{109}$$

For an arbitrary j, the equation

$$d_j = \sum_{k=1}^{n_j} \left(\prod_{i(k)=1}^{n} \lambda_{i(k)} \right)$$

is valid where $n_j = C_j^{n-1}$ is the number of combinations of $(n-1)$ elements taken from j.

In the irreversible case, for the above example we will have

$$\begin{aligned} -d_1 &= -k_1^+[\mathrm{A}] - k_2^+ - k_3^+ \\ &= \lambda_1 + \lambda_2 \\ D &= k_1^+[\mathrm{A}](k_2^+ + k_3^+) + k_2^+ k_3^+ \\ &= \lambda_1 \lambda_2 \end{aligned} \tag{110}$$

(3) A useful corollary follows from the comparison of steady-state kinetic and characteristic equations. For example, as has been shown above, for a one-route reaction with a linear mechanism the equation

$$W = \frac{[K^+ f^+(\vec{\bar{c}}) - K^- f^-(\vec{\bar{c}})]C}{\sum} \tag{111}$$

will be valid where

$$\begin{aligned} K^+ &= \prod_{i=1}^{n} k_i^+ \\ K^- &= \prod_{i=1}^{n} k_i^- \end{aligned}$$

The expressions $f^+(\vec{\bar{c}})$ and $f^-(\vec{\bar{c}})$ correspond to the "natural" brutto-reaction and C is the overall number of active centres per unit catalyst surface.

The denominator of eqn. (111) is the determinant for the weights' matrix $\vec{B}(\vec{c})$. But the same determinant is also a free term of the characteristic equation D that equals the product of the roots, i.e. $D = \Pi_{i=1}^{n} \lambda_i$ (n is the number of independent intermediate substances).

It is evident that

$$W\sum = W\prod_{i=1}^{n-1}\lambda_i$$

$$= [K^+f^+(\vec{c}) - K^-f^-(\overleftarrow{c})]C \qquad (112)$$

or

$$\frac{W}{C\prod_{i=1}^{n-1}\tau_i} = K^+f^+(\vec{c}) - K^-f^-(\overleftarrow{c}) \qquad (113)$$

where τ_i is the relaxation time and is equal to $1/|\mathrm{Re}\lambda_i|$.

The expression on the right-hand side of eqns. (112) and (113) is usually written down as a kinetic law for a simple step consisting of two elementary (direct and inverse) reactions satisfying the law of mass action. As a rule, the steady-state rate for a complex reaction does not fit this expression*. It appears that this natural type is satisfied by $W/(\Pi_i\tau_i)$ rather than the steady-state rate W. This value is experimentally observed (W and τ_i from the steady-state and non-steady-state experiments, respectively). This value must have been given some special term.

After differentiating eqn. (113) we obtain

$$\frac{\partial \ln W}{\partial \ln c_j} + \frac{\partial \ln(\prod_i \lambda_i)^{-1}}{\partial \ln c_j} = m_j \frac{K^+f^+(\vec{c})}{K^+f^+(\vec{c}) - K^-f^-(\overleftarrow{c})}$$

$$= m_j(1 - \phi) \qquad (114)$$

where m_j is the total number of jth reactant molecules taking part in all the reactions of the detailed mechanism (or the amount of this reactant molecules in the "natural" brutto-reaction)

$$\phi = \frac{K^-f^-(\overleftarrow{c})}{K^+f^+(\vec{c})} = \frac{1}{K_{\text{eq}}}\frac{f^-(\overleftarrow{c})}{f^+(\vec{c})}$$

in which K_{eq} is the equilibrium constant of the brutto-reaction.

The value $\partial \ln W/\partial \ln c_j$ is the observed order for the reaction rate found from the monoparametric dependences in the non-steady-state experiment. If both the order and the value of $m_j(1 - \phi)$ are known, we can find the value $\partial \ln(\Pi\tau_i)^{-1}/\partial \ln c_j$ from eqn. (114). This value can be called the *observed relaxa-*

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* In early works on kinetics, this equation was also assumed to fit the steady-state rate of composite reaction (see ref. 41).

tion order. For the irreversible case ($\phi = 0$) we will have

$$\frac{\partial \ln\left(\prod_{i=1}^{n-1} \tau_i\right)^{-1}}{\partial \ln c_j} = m_j - \frac{\partial \ln W}{\partial \ln c_j} \tag{115}$$

A general form of the characteristic equation in combination with a steady-state kinetic equation will provide additional possibilities for the interpretation of the observed kinetic relationships.

5. Conclusion

Graph theory provided various fields of physical chemistry and chemical physics with a technique that has been extensively used in theoretical physics (the well-known Feynman diagram technique). It also appeared to be extremely effective in both chemical kinetics and chemical polymer physics. The major advantage of this technique is the extremely simple derivation of equations and the possibility of their direct physical interpretation.

In terms of graph theory, it is convenient to represent several non-empirical and semi-empirical methods of quantum chemistry. Energy and charge characteristics of molecules are treated as various structural characteristics of molecular graphs.

In chemical kinetics, the graph technique is used to obtain steady-state kinetic equations for multi-route linear mechanisms, to analyze the number of independent model parameters and to determine the stability of steady states for open chemical systems. We believe that, in the near future, the possibilities of the "graph analytical" methods will be ever increasing. We are facing a period for a wide application of algorithmic languages intended for operation with graphs. There are two probable ways: (1) the development of special-purpose computers or processors based on microprocessing devices and (2) the application of analytical computation systems. Already at present there exist programs to derive and analyze complex steady-state kinetic equations and characteristic polynomials (see, for example, refs. 60 and 67–69).

The concepts of "graph-molecule" and "graph-reaction" are natural for chemistry, which is a science which pays much attention to the order of arrangement, bonds, and sequences of transformations.

It is possible that in future chemists will develop concepts about a universal dynamic graph accounting for the evolution of complex chemical systems. But already graph theory can give much to chemists. In our opinion, it is quite possible that this theory will become a "chemical esperanto" understandable by chemists of various specialities.

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