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State-of-the-Art in the Theory of Kinetics of Complex Reactions

Principles of the theory of kinetics of complex reactions are based on the investigations of Ostwald, Van’t Hoff, Bodenstein, Shpitalskii, Michaelis, Semenov, Hinselwood, Christiansen, and many others. After the works by Horiuti [1, 2] and Temkin [3, 4], a fairly consistent theory applicable to complex steady-state and quasi-steady-state reactions of any type has been formed in the second half of the 20th century, although refinements have been introduced until quite recently [5]. For about a century, one of the most important questions under discussion was the choice of criteria for the use of quasi-steady-state and quasi-equilibrium approximations in studying reaction kinetics in closed systems (very popular in catalysis with metal complexes and enzymatic catalysis), but now a certain clarity in this issue has been achieved. Significant influence on the understanding of features in the kinetics of complex, multi-route reactions was produced by methods of graph theory, which have been applied to the representation of the mechanisms of complex reactions, their classification, derivation of kinetic equations, and analysis of the dynamic behavior of reacting systems [6, 7]. Considerable progress has been achieved in understanding the nature of an elementary act (R. Bell, M.J. Evans, M. Polanyi, H. Eyring, K. Fukui, R. Hoffmann, H. Taube, J. Polanyi et al.) and in formulating the selection rules for elementary steps and the criteria of the elementarity of steps in the reaction mechanism [6]. Said issues will be briefly discussed in this chapter. Nonlinear mechanisms and related features in the dynamic behavior of kinetic models will be considered in more detail in Chapter 6.

1.1 Main concepts of the Horiuti–Temkin theory of steady-state reactions

The kinetics of reactions involving metal complexes and reactions in catalysis with metal complexes are studied in open, semi-open, and closed reactors operating under stationary, quasi-stationary, or nonstationary conditions. Most popular are the gas-phase-open (semi-open) reactors for gas–liquid systems and the closed reactors for various liquid-phase and gas–liquid reactions, in which various processes are carried out under steady-state and quasi-steady-state conditions, respectively. These regimes are described by the Horiuti–Temkin theory of steady-state reactions, an important part of which is the analysis of the stoichiometry of mechanisms and an important point is the concept of a reaction route. Therefore, it is natural to begin this presentation by considering the main principles of this theory.
1.1.1 Reaction mechanism: Stoichiometry and routes

*Reaction mechanism* is a system of elementary steps (consecutive, parallel-consecutive), within the framework of which a given set of initial reactants is converted into reaction products, that is, a certain overall (brutto) reaction equation is implemented. In a broader sense, the concept of “reaction mechanism” involves, besides the set of steps, the necessary notions concerning the structures of all intermediate species and transition states, estimations of rate constants for each step (i.e., of the reactivity of substances participating in this step) and, eventually, estimations of the effect of parameters \( (C, P, T) \) on the dynamic behavior of the given reacting system.

Thus, the reaction mechanism concept is dual, including two components [8]:

(i) a set of steps (usually called the mechanistic reaction scheme), which determines a *structure* of the mechanism – that is, the interplay of reactants and intermediate species – thus providing a *topological* component of the reaction mechanism;

(ii) notions about the structures and reactivities of all reactants and intermediates, which determine the *chemical* (or physicochemical) component of the reaction mechanism.

As will be shown below (see Chapter 7), there is no hierarchical subordination between the two components and they are equally necessary for establishing the reaction mechanism.

In an analysis of mechanisms, it is commonly accepted to consider reactants and products (referred to jointly as the *reaction participants* that enter into the overall equations) and intermediate species (intermediates). A strict definition of intermediate species was formulated based on topological characteristics of a reaction network [6]. According to this, let us define an *intermediate* as a compound that is formed in one step (or in several steps) and disappears as a result of participation in some other steps. Intermediate species \( (X_i) \) can be either *observable*, that is, involved in the material balance of reactants and products (entering into overall equations), or *unobservable*, that is, not making any significant (i.e., exceeding experimental error) contribution to the material balance. The character of unobservable (or Bodenstein type) intermediate species allows them to be excluded from the stoichiometry of the overall equation of the process. Evidently, overall equations not involving intermediates can be obtained only for steady-state or quasi-steady-state processes, that is, in cases where \( \frac{dC_{X_i}}{dt} = 0 \) or \( \frac{dC_{X_i}}{dt} \approx 0 \), respectively. If the rates of variation of the concentrations of intermediates are nonvanishing, the corresponding \( X_i \) components will enter into the overall equations.

There are linear and nonlinear steps and, accordingly, linear and nonlinear mechanisms. By definition, the equations of linear steps involve no more than one intermediate compound to the left and right of the arrow, and the linear mechanisms consist of only linear steps.

In cases where the set of initial reactants and products (i.e., reaction participants) is known, it is possible to determine the maximum number \( Q_{\text{max}} \) of linearly independent overall equations of chemical reactions. For this purpose, we have to write a molecular (or atomic) matrix \( H \) of dimension \( N \times l \) (where \( N \) is the number of reaction participants and \( l \) is the number of elements and/or atomic groups entering into reactants and products, which remain unchanged during the reaction). According to the so-called Gibbs stoichiometric rule [5, 9], we have

\[
Q_{\text{max}} = N - \text{rank}H,
\]  

(1.1)

where \( \text{rank}H \) is the matrix rank that characterizes the number of linearly independent elements and/or atomic groups (i.e., the number of linearly independent stoichiometric conservation laws).

Not all of the overall equations possible for the given set of reaction participants are represented by reactions in a particular reacting system. Therefore, in the general case, the number \( Q \) of linearly independent equations is \( Q \leq Q_{\text{max}} \). The corresponding stoichiometric rule was originally formulated in
1946 by Brinkly [10] as follows:

\[ \text{rank } B \leq N - \text{rank} H, \]

where \( B \) (in what follows, \( B_r \)) is called the stoichiometric matrix of overall equations. The rank of the stoichiometric matrix \( B_m \) of the reaction mechanism obeys the following relation:

\[ \text{rank} B_m \leq N + I - \text{rank} H, \]

where \( I \) is the number of unobservable intermediates including a catalyst (active center).

In order to describe the kinetics of a complex reaction proceeding in a steady-state or quasi-steady-state regime, it is important to establish a set of overall equations determined by the reaction mechanism, the number of which \((Q_r)\) can be smaller than or equal to \( Q_{\text{max}} \) [11]. In a chemical experiment, the overall equations are established using the results of an analysis of the material balance of the process. The necessity of writing the set of overall equations based on the reaction mechanism rather than on the material balance alone is demonstrated by the following example.\(^1\)

**Example 1.1**

Consider a process with the material balance described by Eq. (1.2) and the reaction scheme described by Eqs (1.3)–(1.5):\(^2\)

\[
\begin{align*}
A & \rightleftharpoons B, \\
A + M & \xrightleftharpoons{\kappa_1}{\kappa_{-1}} MA, \\
MA + A & \xrightleftharpoons{\kappa_2}{\kappa_{-2}} MB + B, \\
MB & \xrightleftharpoons{\kappa_3}{\kappa_{-3}} M + B,
\end{align*}
\]

where \( M \) is the catalyst and \( MA \) and \( MB \) are intermediates. Upon summing the equations of steps (for steady-state or quasi-steady-state regimes), the catalyst and intermediates vanish and we arrive at the following overall equation:

\[ 2A \rightleftharpoons 2B. \] (1.6)

From the standpoint of stoichiometry and material balance, Eqs (1.2) and (1.6) are equivalent, whereas from the standpoint of kinetics, the rate of converting reactant \( A \) into \( B \) is determined by the overall Eq. (1.6). It is this rate \( r \), defined as a difference between the rates of processes in the forward \((r^+)\) and reverse \((r^-)\) directions \((r = r^+ - r^-)\), that corresponds to the mechanism described by Eqs (1.3)–(1.5). Assuming that \([A], [B] \gg [M]_{\Sigma}\) and \([M]_{\Sigma} \gg [MA], [MB] ([M]_{\Sigma} \equiv [M])\), we obtain the following formula for the rate of a steady-state or quasi-steady-state regime:

\[
r = r^+ - r^- = -\frac{1}{2} \frac{d[A]}{dt} - \frac{1}{2} \frac{d[B]}{dt} = \frac{(k_2 k_3 [A]^2 - k_{-1} k_{-2} k_{-3} [B]^2) [M]_{\Sigma}}{k_2 [A] k_3 + k_{-1} k_3 + k_{-1} k_{-2} [B]}.
\] (1.7)

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\(^2\)Mechanisms of close types are inherent in the skeletal isomerization of n-butane [12, 13] and isobutane [14].
In the case of equilibrium \((r^+ = r^-)\), formula (1.7) yields the following equilibrium constant for reaction (1.6):

\[
K = \frac{[B_{\text{eq}}]^2}{[A_{\text{eq}}]^2}.
\]

The rate of the forward reaction can be expressed via that of the reverse reaction using the following de Donde relation:

\[
RT \ln \frac{r^-}{r^+} = \Delta \mu (\Delta \mu = -A), \tag{1.8}
\]

where \(A\) is the chemical affinity and \(\Delta \mu\) is the change in the chemical potential according to the overall reaction equation. An expression for \(\Delta \mu\) should also be written using an equation that follows from the reaction mechanism, in the given case, Eq. (1.6). Note that relation (1.8) is valid only for single-route reactions (see below).

The general algorithm of finding overall equations for the reaction mechanisms of any complexity is called (Horiuti) the method of routes [1–7, 9, 15] and is a constituent part of the Horiuti–Temkin theory of steady-state reactions [1–4]. This algorithm determines a relationship between the stoichiometry of a mechanism and that of the overall reaction equation. The mathematical principles of this theory are presented in more detail elsewhere [5, 9]. Here, we dwell on the basic concepts and corollaries of the theory.

The reaction route is defined as a sequence of steps entering into the complex reaction mechanism, such that, upon summing the equations of these steps multiplied by the so-called stoichiometric numbers \(v_j\) of steps, the obtained overall equation contains no intermediates that play important roles as participants of the mechanism of the given complex reaction.

The term ‘reaction route’ also refers to a vector with components representing the stoichiometric numbers \(v_j\) of steps. For example, the reaction route vector for a mechanism described by Eqs (1.3–1.5) is a set of three components: \(v_{1,3} = 1, v_{1,4} = 1, v_{1,5} = 1\) or \(v^{(1)} = (1, 1, 1)\). A different set of stoichiometric numbers, \(v^{(1)} = (0.5, 0.5, 0.5)\), is provided by the equation \(A = B\), but the above example shows that this equation contradicts the kinetics of the steady-state process under consideration.

The condition for writing the overall equation without intermediates is formally determined by the following set of equations:

\[
f_i = \sum_j \beta_{ij}^* \cdot v_j^{(p)} = 0, \tag{1.9}
\]

where \(\beta_{ij}^*\) is the stoichiometric coefficient of the \(i\)th intermediate at the \(j\)th step of the reaction mechanism and \(v_j^{(p)}\) is the stoichiometric number of the \(j\)th step in the \(p\)th route. Function \(f_i\) is written for each set of linearly independent intermediates. Note that, in generally, the stoichiometric coefficient \(\beta_{ij}^*\) in Eq. (1.9) (and any other \(\beta_{ij}\) value) is the difference of the stoichiometric coefficients for the same substance that enters into the reaction equation on the right and left sides. For a \(j\)th step described by the equation

\[
\sum_i \alpha_{ij}A_i = \sum_i \gamma_{ij}A_i,
\]

we have \(\beta_{ij} = \gamma_{ij} - \alpha_{ij}\). In particular, for a reaction considered in Section 6.3,

\[
A + X_i \xrightarrow{\text{\(j\)th step}} 2X_i + B,
\]

this coefficient is \(\beta_{ij}^* = 2 - 1 = 1\).
The system of Eqs (1.9) can also be written in a matrix form as follows:

\[
\overline{B}_X^T G = 0, \quad (1.10)
\]

where \(\overline{B}_X^T\) is the transposed matrix of stoichiometric coefficients of the linearly independent intermediates and \(G\) is the \(S \times \nu^{(p)}\) matrix of the stoichiometric numbers of steps, where \(S\) is the number of steps. Note that matrix \(B_X\) is a block of the matrix \(B_m\) of stoichiometric coefficients of the reaction mechanism. The second block in this matrix represents the matrix \(B_N\) of stoichiometric coefficients of the reaction participants (reactants and products) with a dimension of \(S \times N\) (where \(S\) is the number of steps and \(N\) is the total number of participants):

\[
B_m = ||B_N : B_X||. \quad (1.11)
\]

In order to determine the stoichiometric numbers of steps, Eq. (1.10) can be rewritten as follows:

\[
\overline{B}_X^T \nu^{(p)}_j = 0, \quad (1.12)
\]

where \(\nu^{(p)}_j\) is the vector of stoichiometric numbers of \(j\)th step in the \(p\)th route. Since the number of unknowns (equal to the number of steps \(S\)) in the system of Eqs (1.12) is greater than the number of equations (equal to the number of linearly independent intermediates \(N_X\)), the number of linearly independent solutions of system (1.12) or the number of linearly independent routes \(P\) is:

\[
S - N_X = P. \quad (1.13)
\]

**Example 1.2**

Consider the following mechanistic reaction scheme:

\[
(1) \quad A \xrightleftharpoons[k_1]{k_{-1}} X, \\
(2) \quad 2X \xrightleftharpoons[k_2]{k_{-2}} P, \quad (1.14)
\]

which involves one independent intermediate \(X\) (so that \(N_X = 1\)), two steps \((S = 2)\), and a single route \((P = 2 - 1 = 1)\). The matrix of stoichiometric coefficients of intermediates \(B_X\) can be written as the row-vector \(\beta^*_y = [1 -2]\). Using the condition that \(\overline{B}_X^T \nu_j = 0\) and multiplying the row-vector \(\beta^*_y\) and column-vector \(\nu = [\nu_1 \nu_2]\), we obtain the following equation:

\[
\nu_1 - 2\nu_2 = 0, \quad (1.15)
\]

which has a single linearly independent solution. Setting \(\nu_1 = 1\), we obtain \(\nu_2 = 0.5\); for \(\nu_1 = 2\) we have \(\nu_2 = 1\) and so on. In order to exclude \(X\) from the overall equation, let us sum reaction steps (1) and (2) multiplied by \(\nu^{(1)} = [1 0.5]\) or \(\nu^{(2)} = [2 1]\). This yields the following overall equations for routes \(\nu^{(1)}\) and \(\nu^{(2)}\):

\[
\nu^{(1)} = A = 1/2 P; \\
\nu^{(2)} = 2A = P.
\]

Evidently, a change in the Gibbs energy \(\Delta \mu^{(p)}\) on route \(\nu^{(p)}\) is as follows:

\[
\Delta \mu^{(p)} = \sum \nu^{(p)}_j \Delta \mu_j. \quad (1.16)
\]
According to Eq. (1.8), we have:

\[
\frac{r^-}{r^+} = \prod \left( \frac{W_j^-}{W_j^+} \right)^{\nu_j},
\]

where \( W_j^\pm \) are the rates of the elementary step in the forward and reverse directions. This yields

\[
\frac{r_1^-}{r_1^+} = \left( \frac{W_1^-}{W_1^+} \right) \left( \frac{W_2^-}{W_2^+} \right)^{1/2}
\]

for route \( \nu^{(1)} \) and

\[
\frac{r_2^-}{r_2^+} = \left( \frac{W_1^-}{W_1^+} \right)^2 \left( \frac{W_2^-}{W_2^+} \right)
\]

for route \( \nu^{(2)} \).

Let us assume step (1) of mechanism (1.14) to be the rate controlling (limiting) and step (2) to be a quasi-equilibrium step \( (W_2^-/W_2^+ \simeq 1) \). Then, considering an equilibrium brutto process \( (r_1^- = r_1^+) \) and using Eq. (1.18), we obtain the following equilibrium constant for the overall equation according to route \( \nu^{(1)} \):

\[
K^{(1)} = K_1 K_2^{1/2} = \frac{[P_{eq}]^{1/2}}{[A_{eq}]},
\]

while Eq. (1.19) for \( r_2^- = r_2^+ \) yields the following equilibrium constant for route \( \nu^{(2)} \):

\[
K^{(2)} = K_1^2 K_2 = \frac{[P_{eq}]}{[A_{eq}]^2}.
\]

Analogous equations for \( K^{(1)} \) and \( K^{(2)} \) can be obtained assuming that step (2) is the limiting stage. Thus, once the route is set [Eqs (1.18) and (1.19)], we obtain the overall equations corresponding to this route irrespective of which step is assumed to be limiting.

For the kinetic equations obtained in the experiment, the overall equations are not chosen arbitrarily. For example, in the case of mechanism (1.14) with \( r^+ \propto [A] \) (rate-controlling step (1)), the overall equilibrium equation corresponds to \( \nu^{(1)} (\nu_1 = 1) \), while for \( r^+ \propto [A]^2 \) (rate-controlling step (2)) the overall equation refers to \( \nu^{(2)} (\nu_2 = 1) \). Thus, once the limiting step is experimentally established or set \textit{a priori}, the overall equations would correspond to the routes in which the stoichiometric numbers of limiting steps are equal to unity. Therefore, for determining \( r^- \) from the known \( r^+ \) (and vice versa), one should use the overall equations that correspond to the actual kinetics. Thus, the choice of a route in the presence of a limiting step is determined by the reaction kinetics.

For any single-route nonlinear mechanism with a rate limiting step, Eq. (1.17) yields the following formula:

\[
\frac{W_{l^-}}{W_{l^+}} = \left( \frac{r^-}{r^+} \right)^{\frac{1}{\nu_l}},
\]

where \( l \) refers to the limiting step. Using this expression and Eq. (1.8), it is possible to obtain a relationship between the ratio of the rates of forward and reverse reactions and the thermodynamic potential \( (\Delta \mu) \), that
is, determine the equilibrium constant of the overall equation of the given route in the following form:

\[ W_l = W_l^+ \left[ 1 - \left( \frac{\prod C_i^{\beta_i}}{K^{(p)}} \right) \right]. \]

Such relationships were originally obtained by Horiuti [2] and Boreskov (see [7]).

3 For mechanism (1.14) and route \( \nu^{(2)} \) with a limiting second step \( (\nu_2 = 1) \), we obtain:

\[ W_2 = W_2^+ \left[ 1 - \left( \frac{[P]/[A]^2}{K^{(2)}} \right) \right]. \]

Using the Boreskov equation [7]

\[ W_l = W_l^+ \left[ 1 - \left( \frac{\prod C_i^{\beta_i}}{K_{\text{min}}^{(m)}} \right)^m \right], \]

it is possible to determine the so-called multiplicity coefficient \( (m) \) of the limiting step by comparing the experimental ratio \( (W/W^+) \) to the quantity \( \prod C_i^{\beta_i}/K_{\text{min}}^{(m)} \), where \( \prod C_i^{\beta_i} \) and \( K_{\text{min}} \) are the concentration product and equilibrium constant, respectively, for the overall equation with minimum integer coefficients with respect to the key reactant. In this case, we have \( m = 1/\nu_l \), where \( \nu_l \) is the stoichiometric number of the route with minimum integer coefficients. In particular, for mechanism (1.14) with a limiting second step, the multiplicity coefficient according to Boreskov is \( m = 2 \), since the stoichiometric number for the second step in overall equation (with minimum integer coefficients with respect to reactant \( A \)) is 0.5 (route \( \nu^{(1)} \)).

In the general case, the Horiuti stoichiometric rule (1.13) is written as follows [4]:

\[ P = S - I + W, \]

where \( I \) is the total number of intermediates and \( W \) is the number of linearly independent stoichiometric conservation laws (or the number of linear relations between intermediates); evidently, \( N_X = I - W = \text{rank} B_X \). For catalytic reactions with the same type of catalysts (or active centers), we have \( W = 1 \), which implies that there is a single stoichiometric conservation law – a material balance with respect to the catalyst. The case of two catalysts participating in the reaction mechanism corresponds to \( W = 2 \). If intermediates of different natures are involved in the reaction, then the determination of \( P \) requires finding the rank of matrix \( B_X \) and using Eq. (1.13).

Thus, in order to find the overall equations of routes, it is necessary to have a basis set of linearly independent routes (vectors of stoichiometric numbers), that is, to know the number \( P \) of these routes. Various vector sets \( \nu^{(p)} \) (columns of the matrix \( G \) of stoichiometric numbers) lead to different sets of overall route equations, which are equally adequate in describing the mechanism of a complex reaction. The structure of solutions for Eqs (1.19) or (1.10) was considered in [6, 16], according to which there are three possible variants.

**Variant 1:** \( S = N_X, P = 0 \)

In this case, the system of equations has a single, trivial solution with \( \nu_j = 0 \) (all stoichiometric numbers are zero). This variant corresponds to the case of autocatalytic (catalyst is a product) or autoinhibitory (catalyst is a reactant) reactions.

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Example 1.3

According to a three-step mechanism of the oxidative chlorination of alkynes [17],

\[
\begin{align*}
(1) & \quad \text{RC≡CH} + \text{CuCl} \rightleftharpoons X_1 + \text{HCl}, \\
(2) & \quad X_1 + 2\text{CuCl}_2 \rightleftharpoons X_2 + \text{CuCl}, \\
(3) & \quad X_2 \longrightarrow \text{RC≡CCl} + 2\text{CuCl},
\end{align*}
\]

(1.21)

the corresponding matrix \( B_X \) includes three intermediates (because, formally, CuCl is also an intermediate):

\[
B_X = \begin{bmatrix}
-1 & 1 & 0 \\
1 & -1 & 1 \\
2 & 0 & -1
\end{bmatrix}; \quad \text{rank } B_X = N_X = 3 \text{ (i.e., } S = N_X). 
\]

If we remove the column of coefficients for CuCl from matrix \( B_X \) and introduce this column into the matrix of participants (\( B_N \)), then the rank of the new stoichiometric matrix of intermediates is \( \text{rank } B'_X = 2 \) and \( P = S - N'_X = 1 \). Thus we obtain two equations for three unknown quantities:

\[
\nu_1 - \nu_2 = 0; \quad \nu_2 - \nu_3 = 0.
\]

Setting \( \nu_3 = 1 \), we obtain \( \nu_1 = 1 \) and \( \nu_2 = 1 \), so that \( \nu = (1 \ 1 \ 1) \). The overall equation (1.22) for a single route is as follows:

\[
\text{RC≡CH} + 2\text{CuCl}_2 \longrightarrow \text{RC≡CCl} + \text{HCl} + 2\text{CuCl}. \quad (1.22)
\]

**Variant 2:** \( S > N_X \) (and there are steps that do not enter into any route)

Solutions of Eqs (1.10) are nonzero and there always are some routes, but one or several steps have \( \nu_j = 0 \) in all vectors (routes) and, hence, these steps do not enter into any route. This situation also arises in autocatalytic or autoinhibitory reactions, provided that one of reactants or products is an intermediate and enters into matrix \( B_X \) (for an example, see [16]), as well as in the presence of equilibrium steps (buffer step) involving the formation of compounds unaccounted for in overall equations (dead end), which do not directly participate in steps of the mechanism but enter into the material balance with respect to the catalyst. Steps that do not enter into any route form a *defect* of the mechanism [6, 18], and this feature is used in the classification of mechanisms [18]. The typical example is a nonbranching chain process with a reversible step of chain initiation in the absence of other steps of chain termination.

**Variant 3:** \( S > N_I \) (and each step is involved in some route)

Using matrices \( B_N \) and \( G \), we find matrix \( B_r \) of stoichiometric coefficients of the overall equations of routes and, thus, write the overall equations as

\[
B_r^T = B_N^T G,
\]

(1.23)

where the dimension of matrix \( B_r \) is \( P \times N \) and, as was noted above, \( \text{rank } B_r = Q_r \leq Q_{max} \) [11]. The number of the linearly independent overall equations of routes can also be determined from the following relation:

\[
Q_r = \text{rank } B_r = \text{rank } B_m - N_X. \quad (1.24)
\]
A comparison of the number $Q_{\text{max}}$ of equations, number $Q_r$ of the overall route equations, and number $P$ of routes shows that $Q_{\text{max}} \geq Q_r$, $Q_r \leq P$, and $Q_{\text{max}} \geq (\leq) P$. It should be noted that, since the considerations in [19, 20] did not allow for the (rather rare) possibility of $Q_{\text{max}} > Q_r$, it was ascertained that $Q_{\text{max}} \leq P$.

**Example 1.4**

The reaction of carbon with water vapor leads to the formation of three products (CO, CO$_2$, and H$_2$):

$$\text{C}_{\text{solid}} + \text{H}_2\text{O} \longrightarrow \text{CO}, \text{CO}_2, \text{H}_2.$$

According to the Gibbs stoichiometric rule (1.1), the number of independent reactions in this system is $Q_{\text{max}} = 2$, which implies that only two overall equations can be independent on the given set of reaction participants. An answer to the question as to which are these equations is provided by an analysis of the reaction mechanism. Let us consider the following simplified mechanism:

\begin{align*}
(1) & \quad \text{C}_{\text{solid}} + \text{H}_2\text{O} + z \underset{\text{zCO + H}_2}{\longrightarrow} z\text{CO}, \\
(2) & \quad z\text{CO} \underset{\text{z + CO}}{\longrightarrow} z + \text{CO}, \quad (1.25) \\
(3) & \quad z\text{CO} + \text{CO} \underset{\text{z + CO}_2 + \text{C}_{\text{TB}}}{\longrightarrow} z + \text{CO}_2 + \text{C}_{\text{TB}},
\end{align*}

where $z$ is an active center on the carbon surface. According to this mechanism, $\text{rank}B_X = 1$ ($N_X = 1$) and $P = S - N_X = 2$, which implies that the number of independent routes is $P = 2$. Multiplying the row-vector of stoichiometric coefficients $\beta_{ij}^* = [1 \quad -1 \quad -1]$ for the intermediate $z\text{CO}$ and column-vector $\nu^{(p)} = [\nu_1 \quad \nu_2 \quad \nu_3]$ and equating the product to zero, we obtain an equation with three unknowns:

$$\nu_1 = \nu_2 + \nu_3,$$

which has an infinite number of solutions, two of which are linearly independent (two solutions, two routes). Let us consider various sets of solutions defined by setting certain $\nu_2$ and $\nu_3$ values, for example, $\nu_2 = 1$, $\nu_3 = 0$ and $\nu_2 = 0$, $\nu_3 = 1$, which correspond to $\nu^{(1)} = (1 \ 1 \ 0)$ and $\nu^{(2)} = (1 \ 0 \ 1)$, respectively. The other possible sets of $\nu_j$ can be obtained by summing and subtracting $\nu^{(1)}$ and $\nu^{(2)}$:

$$\nu^{(3)} = (2 \ 1 \ 1) = \nu^{(1)} + \nu^{(2)}; \quad \nu^{(4)} = (0 \ -1 \ 1) = \nu^{(2)} - \nu^{(1)}.$$

Upon writing the corresponding matrix $G$ as

$$G = \begin{pmatrix}
1 & 1 & 2 & 0 \\
1 & 0 & 1 & -1 \\
0 & 1 & 1 & 1
\end{pmatrix},$$

and using Eq. (1.23), we obtain the stoichiometric matrix $B_r$ of overall equations and write these equations as follows:

\begin{align*}
\nu^{(1)} & \quad \text{C}_{\text{solid}} + \text{H}_2\text{O} = \text{CO} + \text{H}_2; \\
\nu^{(2)} & \quad \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2; \\
\nu^{(3)} & \quad \text{C}_{\text{solid}} + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2; \\
\nu^{(4)} & \quad 2\text{CO} = \text{CO}_2 + \text{C}_{\text{solid}}.
\end{align*}
All these equations follow from the proposed reaction mechanism, but only two of them are linearly independent (since $Q_r = \text{rank} B_r = 2$). In this example, we have the case of $P = 2$, $Q_r = 2$ and $Q_{\text{max}} = 2$.

Although the standard values $\Delta G^{(p)}$ (standard chemical potentials) of the overall equations are different, no one of these equations is preferred from the standpoint of kinetics as long as all the steps are reversible. All steps of the mechanism in both forward and reverse directions will determine the reaction rate for each overall equation (see below).

If irreversible steps appear, we can formally select the routes with negative $\nu_j$ that refer to these irreversible steps, but it is more expedient from both chemical and thermodynamic standpoints to choose the routes so that their directions would correspond to the positive direction of irreversible steps. In this case, the overall equations will not proceed in thermodynamically forbidden directions (see Section 1.4).

Using these overall equations, it is possible to calculate the yields of reaction product and selectivities of their formation. For example, if steps (2) and (3) in mechanism (1.25) under the given process conditions is irreversible, then route $\nu^{(4)}$ will be thermodynamically forbidden in one direction and kinetically prohibited in both directions. ■

**Example 1.5**

The reaction of ethylene hydrogenation at $T = 25^\circ C$ is thermodynamically allowed in the forward direction. A simplified mechanism of this reaction

$$C_2H_4 + H_2 \longrightarrow C_2H_6$$

in solutions of transition metal complexes can be described by the following scheme:

1. $M + H_2 \leftrightarrow M(H)_2$,
2. $M(H)_2 + C_2H_4 \leftrightarrow \text{HMC}_2H_5$,
3. $\text{HMC}_2H_5 \longrightarrow M + C_2H_6$, (1.27)
4. $\text{HMC}_2H_5 + H_2 \longrightarrow M(H)_2 + C_2H_6$,

for which we can distinguish three intermediates (including the catalyst) and write one law of conservation as $[M]_\Sigma = [M] + [M(H)_2] + [\text{HMC}_2H_5]$. The rank of the stoichiometric matrix of intermediates is $\text{rank} B_X = 2$ ($N_X = 2$) and, hence, $P = S - N_X = 4 - 2 = 2$. On the given set of reactants and products ($H_2$, $C_2H_4$, $C_2H_6$), we have a single linearly independent overall equation (since $Q_{\text{max}} = 1$, $P > Q_{\text{max}}$).

Upon multiplying matrix $B_X^T$ (with two linearly independent rows)

$$B_X^T = \begin{bmatrix} 1 & 0 & 1 & 0 \\ 1 & -1 & 0 & 1 \end{bmatrix}$$

by column-vector $\nu = (\nu_1, \nu_2, \nu_3, \nu_4)$, we obtain two equations with four unknowns:

$$\nu_1 = \nu_3; \quad \nu_2 = \nu_1 + \nu_4.$$ (1.28)

Rewriting these equations as

$$\nu_1 = \nu_3; \quad \nu_2 = \nu_3 + \nu_4,$$ (1.29)
and setting the values of \( v_3 \) and \( v_4 \), let us calculate the values of \( v_1 \) and \( v_2 \). As a result, we obtain a basis set of routes, for example, in the form of matrix \( G_1 \), and the corresponding overall equations of routes:

\[
G_1 = \begin{bmatrix}
1 & 0 & 1 & 1 \\
0 & 0 & 1 & 1 \\
\end{bmatrix} \Rightarrow \begin{bmatrix}
v^{(1)} \\
v^{(2)} \\
\end{bmatrix} C_2H_4 + H_2 = C_2H_6;
\]

\[
C_2H_4 + H_2 = C_2H_6.
\]

The overall equations for both routes are the same, and each route yields the reaction product. Evidently, only one equation is linearly independent. Indeed, rank \( B_r = Q_r = 1 \) and, in the given case, \( Q_r = Q_{max} \).

By selecting the proper sets of stoichiometric numbers, we can reduce the system of overall equations to the basis set of such equations, the number of which is \( Q_r \). In this case, some \( (P - Q_r) \) of the overall equations will refer to “empty” routes (with the overall equation \( 0 = 0 \)), the reaction rate over which is the rate of the cyclic conversion of intermediates that leads to neither reactant consumption nor product formation. This set of routes is called the stoichiometric basis set of routes.

Let route \( v^{(3)} \) be characterized by set \( v^{(3)}(1 -1) = v^{(1)} - v^{(2)} \), so that

\[
G_2 = \begin{bmatrix}
1 & 1 & 1 \\
1 & 0 & 1 \\
0 & -1 & 1 \\
\end{bmatrix} \Rightarrow \begin{bmatrix}
v^{(1)} \\
v^{(3)} \\
\end{bmatrix} C_2H_4 + H_2 = C_2H_6;
\]

\[
0 = 0
\]

Since step (4) is irreversible \( (W_4^- = 0) \), the reaction rate over this route is negative. The number of empty routes in this case is \( P^{(0)} = S - \text{rank}B_m \).

Let us briefly consider alternative approaches to an analysis of the stoichiometry of reaction mechanisms. Corio [21, 22] analyzed the stoichiometry of mechanisms using the Gibbs rule in the form of Eq. (1.1), which was written in the following form:

\[
K = \rho + \pi + I = s + m,
\]

where \( \rho \) is the number of reactants, \( \pi \) is the number of products \( (\rho + \pi = N) \), \( I \) is the total number of intermediates, \( K = N + I \), \( s \) is the number of linearly independent reactions \( (\text{rank}B_m) \), and \( m \) is the number of linearly independent stoichiometric conservation laws \( (m = \text{rank}H) \), where \( H \) is the atomic matrix for the total number \( K \) of substances \( (\text{in Eq. (1.20) this number is denoted} W) \). Barbara and Corio [23] also suggested a method for finding overall equations, but without allowing for the case that \( Q_{max} \) can be greater than \( Q_r \).

Interesting observations concerning the number of linear conservation laws were reported by Korzukhin [24]. Since \( \text{rank}B_m \leq (N + I) - \text{rank}H \), the total number \( L \) of these laws can be greater than the total number of the stoichiometric conservation laws \( (m = \text{rank}H) \), provided that \( L = (N + I) - \text{rank}B_m > \text{rank}H \). Then, \( L - m \) is the number of the linear kinetic laws of conservation, the number of which for catalytic reactions can be determined from the following equation \( [9, 11] \):

\[
L - m = I - \text{rank}B_X - K^*, \tag{1.30}
\]

where \( K^* \) is the number of catalysts (or the types of active centers).
1.1.2 Kinetics: Reaction rates with respect to substances and over routes

Any study of kinetics is aimed at finding the type and constants of a kinetic model, which has the form of a system of algebraic, algebraic-differential, or differential equations that describe the dependence of the net rates of consumption or production of participants \( r_N \) or the reaction rates for the overall equations of routes \( r_p \) as functions of the concentrations of participants and the temperature, or the dependences of the concentrations of participants and intermediates on the time and the temperature. The system of equations that quantitatively describes the entire set of chemical and physical stages, including the formation of a catalyst, is necessary for an analysis of the kinetic behavior of a process under non-steady-state conditions [25].

The theory of steady-state reactions employs the concepts of a run over step and run over route. According to [20], the number of runs over step is defined as the difference between the numbers of elementary acts (reactions) in the forward and reverse directions per unit time. Then, the rate of a given step \( W_j = W_j^+ - W_j^- \) is the number of runs over step per unit volume of the reaction space. The run over route implies that the number of runs over every step in the given route is equal to the stoichiometric number \( v_j(p) \) of this step in the route. All runs over routes can be represented as linear combinations of runs over routes of the basis set. Then, the reaction rate over a basis-set route (or the rate for the overall equation of this route) is defined as the number of runs over this route per unit volume of the reaction space, provided that the runs over all steps are distributed over routes of the given basis set.

Now let us derive a relationship between the rates of steps and the rates over basis-set routes \( r_p \), which is very important in the theory of steady-state reactions. The rate with respect to a substance is naturally related to the rates over basis-set routes via matrix \( B_p \), as follows [19]:

\[
    r_N = B_p^T r_p \tag{1.31}
\]

\[
    \text{or } r_N = \sum_p \beta_{ij} r_p \]

where \( r_N \) and \( r_p \) are the column-vectors of reaction rates with respect to substances and over routes, respectively. On the other hand, the \( r_N \) values are related to the rates of steps by the following system of equations:

\[
    r_N = B_N^T W_j, \tag{1.32}
\]

where \( W_j \) is the column-vectors of the step rates. The condition of steady-state (or quasi-steady-state) reactions in open and closed systems can be written as

\[
    r_X = B_X^T W_j = 0, \tag{1.33}
\]

where \( r_X \) is the column-vector of reaction rates with respect to unobservable intermediates. Then, equating expressions (1.31) and (1.32) and multiplying the obtained equation by \( B_N \) from the left, we arrive at the so-called condition of the steady state of steps (M.I. Temkin [4, 9]):

\[
    W_j = G r_p, \tag{1.34}
\]

or

\[
    W_j = W_j^+ - W_j^- = \sum_p v_j(p) r_p \quad (j = 1, 2, 3, \ldots, S). \tag{1.35}
\]

This system of equations is equivalent to Eq. (1.33) and presents an alternative form of the Bodenstein principle \( \frac{dC_X}{dt} = 0, r_X = 0 \), where \( C_X \) and \( r_X \) are the vectors of concentrations and reaction rates, respectively; the Bodenstein condition is considered; see below). Upon solving system (1.35) that consists
of \( S \) equations with \( S = P + N_I \) unknowns, we obtain \( P \) reaction rates \( r_p \) over basis-set routes and \( N_I \) unknown concentrations of intermediates. The \( r_p \) values can be determined using the Temkin algorithm \([9, 26, 27]\) or the method of graphs (for linear mechanisms, see below). It is also possible to determine \( C_{X_i} \) using condition (1.33) and solving the corresponding system of algebraic equations, and then to substitute these \( C_{X_i} \) values into Eqs (1.35) for \( W_j \) of steps with required \( r_p \) values. In the case of a large number of routes at small \( N_I \), it is convenient to use the condition of \( r_{X_i} = 0 \), while in the case of a large set of \( X_i(N_I) \) and a small number of routes, it is more convenient to use system (1.35), since a solution of the set of linear equations using the Cramer rule directly yields the required \( r_p \) values.

**Example 1.6**

Let us derive equations for the rates over basis-set routes and substances for the reaction used in Example 1.4. Consider routes \( \nu^{(1)} \) and \( \nu^{(2)} \) with the following matrix \( G_1 \) of stoichiometric numbers:

\[
G_1 = \begin{bmatrix}
1 & 1 \\
1 & 0 \\
0 & 1
\end{bmatrix}
\Rightarrow \begin{align*}
\nu^{(1)} & \quad \text{solid} + H_2 = CO + H_2; \\
\nu^{(2)} & \quad CO + H_2O = CO_2 + H_2.
\end{align*}
\]

Using condition (1.34) of the steady state of steps, we obtain the following system of equations:

\[
\begin{bmatrix}
W_1 \\
W_2 \\
W_3
\end{bmatrix} = \begin{bmatrix}
1 & 1 \\
1 & 0 \\
0 & 1
\end{bmatrix} \begin{bmatrix}
r_1 \\
r_2
\end{bmatrix}.
\] (1.36)

Taking the product in (1.36) we obtain the following set of three equations (\( S = 3 \)) with three unknowns ([z CO], \( r_1, r_2 \)):

\[
\begin{align*}
W_1 &= W_1^+ - W_1^- = r_1 + r_2; \\
W_2 &= W_2^+ - W_2^- = r_1; \\
W_3 &= W_3^+ - W_3^- = r_2,
\end{align*}
\] (1.37)

from which it follows that the rates \( r_1 \) and \( r_2 \) over the basis set routes are \( W_2 \) and \( W_3 \), respectively, and that step (1) (\( W_1 = W_2 + W_3 \)) proceeds via both routes. Let us introduce the step weight \( \omega_j \) (or \( \omega_{-j} \)), which is defined as the ratio of the step rate in one direction to the concentration \([X_i]\) of an intermediate product involved in this step:

\[
\omega_j = \frac{W_j^+}{[X_{i,j}]}; \quad \omega_{-j} = \frac{W_j^-}{[X_{i+1,j}]},
\]

Taking into account the material balance equation \([z]_\Sigma = [z] + [z CO] \), assuming that the relative concentrations obey the relation \([z]_\Sigma = 1\), and solving system (1.37), we obtain the following expressions:

\[
r_1 = W_2 = \frac{\omega_2(\omega_1 + \omega_{-3}) - \omega_{-2}(\omega_{-1} + \omega_2)}{D};
\] (1.38)

\[
r_2 = W_3 = \frac{\omega_3(\omega_1 + \omega_{-2}) - \omega_{-3}(\omega_{-1} + \omega_2)}{D};
\] (1.39)

\[
D = \omega_{-1} + \omega_2 + \omega_3 + \omega_1 + \omega_{-2} + \omega_{-3}.
\] (1.40)
As can be seen, the rate over the basis-set route contains the rates of all steps of the given mechanism (including the rates of reverse steps) not entering in $W_2$ and $W_3$ in the numerators of expressions (1.38) and (1.39). The rates $r_N$ for substances can be found using relation (1.31), written as

$$
\begin{bmatrix}
  r_C \\
  r_{H_2O} \\
  r_{CO} \\
  r_{H_2} \\
  r_{CO_2}
\end{bmatrix}
= \begin{bmatrix}
  -1 & 0 \\
  -1 & -1 \\
  1 & -1 \\
  1 & 1 \\
  0 & 1
\end{bmatrix}
\times \begin{bmatrix}
  r_1 \\
  r_2
\end{bmatrix},
$$

which yields $-r_C = r_1$; $-r_{H_2O} = r_1 + r_2$; $-r_{CO} = r_1 - r_2$; $-r_{H_2} = r_1 + r_2$; $-r_{CO_2} = r_2$.

In order to describe the reaction, it is sufficient to select two key substances (i.e., linearly independent columns in matrix $B_N$), for example, CO$_2$ and H$_2$. For matrix $G_2$ with routes $v^{(1)}$ and $v^{(4)}$ we have

$$
G_2 = \begin{bmatrix}
  v^{(1)} & v^{(4)}
\end{bmatrix}
\Rightarrow
\begin{cases}
  \text{C solid} + H_2O = CO + H_2, & r'_1, \\
  2CO = CO_2 + \text{C solid}, & r_4.
\end{cases}
$$

In this case, we obtain

$$
W_1 = W_1^+ - W_1^- = r'_1; \\
W_2 = W_2^+ - W_2^- = r' - r_4; \\
W_3 = W_3^+ - W_3^- = r_4; \\
r'_1 = W_1 = \frac{\omega_1(\omega_2 + \omega_3) - \omega_{-1}(\omega_{-2} + \omega_{-3})}{D}; \\
r_4 = W_3 = \frac{\omega_3(\omega_1 + \omega_{-2}) - \omega_{-3}(\omega_{-1} + \omega_2)}{D}.
$$

A comparison of expressions (1.38), (1.39) and (1.41), (1.42) shows that: (i) the structure of equations does not change in the case of using a route with a negative stoichiometric number; and (ii) similar to system (1.37) we have $r_2 = r_4$ and $W_1 = W_2 + W_3$. The expression for $r'_1$ (at which $v_j$ are positive) contains the rates of all reverse steps. Then, we have

$$
\begin{bmatrix}
  r_C \\
  r_{H_2O} \\
  r_{CO} \\
  r_{H_2} \\
  r_{CO_2}
\end{bmatrix}
= \begin{bmatrix}
  -1 & 1 \\
  -1 & 0 \\
  1 & -2 \\
  1 & 0 \\
  0 & 1
\end{bmatrix}
\times \begin{bmatrix}
  r'_1 \\
  r_4
\end{bmatrix},
$$

which yields $r_C = r_4 - r'_1$; $-r_{H_2O} = r'_1$; $r_{CO} = r'_1 - 2r_4$; $-r_{H_2} = r'_1$; $r_{CO_2} = r_4$. Let us compare the rates of formation, e.g., for hydrogen ($r_{H_2}$) via the two sets of routes. For the first set we have $r_{H_2} = r_1 + r_2$, while for the second set $r_{H_2} = r'_1$. Adding equations (1.38) and (1.39) yields formula (1.41), which shows that the rates for substances are invariant with respect to the sets of routes. It is important to bear in mind that both an expression for the rate and a value of the rate over a given route have sense only provided that the entire basis set of routes is defined.
For better understanding the reasons for which we can include steps with negative $\nu_i$ (i.e., reactions proceeding in thermodynamically prohibited directions) into the route, let us also consider the sets of routes $\nu^{(1)}$ and $\nu^{(5)}$:

$$G_3 = \begin{bmatrix} \nu^{(1)} & \nu^{(5)} \\ 1 & 0 \\ 1 & 1 \\ 0 & -1 \end{bmatrix} \Rightarrow \nu^{(1)} \quad C_{\text{solid}} + H_2O = CO + H_2;$$
$$\nu^{(5)} \quad C_{\text{solid}} + CO_2 = 2CO.$$

In this case, we have

$$W_1 = W_1^+ - W_1^- = r_1'';$$
$$W_2 = W_2^+ - W_2^- = r_1 + r_5;$$
$$W_3 = W_3^+ - W_3^- = -r_5,$$

which yields

$$r_5 = -W_3 = \frac{\omega_{-3}(\omega_2 + \omega_{-1}) - \omega_{3}(\omega_{-2} + \omega_1)}{D}. \quad (1.44)$$

Thus, the use of a negative rate over the route also leads to invariant rates with respect to substances. For example, according to matrix $G_3$, the rate of CO$_2$ formation is $r_{CO_2} = -r_5 = r_4$ (cf. equation (1.42) obtained using basis set $G_2$).

In the case of a reversible multi-route reaction, the rate over the route can be presented as the difference between rates in the forward and reverse directions: $r_p = r_p^+ - r_p^-$ [for example, $r_2 = r_2^+ - r_2^-$ (1.39)], but the ratio of rates $r_p^+/r_p^-$ in this case is no longer related to the chemical affinity $A_p$ on route $\nu^{(p)}$, since $A_p$ includes only the chemical affinities of steps entering into the given route,

$$A_p = \sum A_{j}^{(p)}$$

and does not include the chemical affinities of other steps that enter into the kinetic equation of rate over the route. Therefore, for a reversible multi-route reaction, we have

$$RT \ln (r_p^+/r_p^-) \neq A_p.$$  

In Example 1.6 above, the rate of the first step was

$$W_1 = r_1 + r_2,$$

so that the fraction of the affinity of the first step was distributed between two routes, whereas the equation of affinities for the second route,

$$A^{(2)}_\Sigma = A_1 + A_3$$

does not reflect the condition $W_1 = W_2 + W_3$. In this case, the relation $r_2^+/r_2^- = 1$ in equilibrium (see Eq. 1.39) does not lead to an expression for the equilibrium constant of the overall equation of the second route. The equilibrium of one route leads automatically to the equilibrium of all other routes. Indeed, for the equilibrium of step 3 ($W_3 = 0$) in Example 1.4, the rate over route $\nu^{(2)}$, is zero and $\omega_3(\omega_1 + \omega_{-2}) = \omega_{-3}(\omega_{-1} + \omega_2)$. However, the equality $r_2 = 0$ is only possible for $W_1 = W_2 = 0$, but this implies that the overall equation of route $\nu^{(1)}$ is also at equilibrium, as well as the overall equation of all other derivative routes.
Example 1.7

Let us obtain the kinetic equations of rates over the basis-set routes and substances for Example 1.5 [reaction scheme (1.27)]. For the first basis set of routes with matrix $G_1$, we have

\[ W_1 = W_1^+ - W_1^- = r_1; \]
\[ W_2 = W_2^+ - W_2^- = r_1 + r_2; \]
\[ W_3^+ = r_1; \]
\[ W_4^+ = r_2; \]
\[ r_1 = W_3^+ = \frac{[M] \sum \omega_1 \omega_2 \omega_3}{D}; \tag{1.45} \]
\[ r_2 = W_4^+ = \frac{[M] \sum \omega_1 \omega_2 \omega_4}{D}; \tag{1.46} \]
\[ D = \omega_1 \omega_3 + \omega_2 \omega_3 + \omega_1 \omega_2 + \omega_1 \omega_3 + \omega_1 \omega_2 + \omega_1 \omega_4 + \omega_1 \omega_2. \tag{1.47} \]

Then, evidently, for the overall equations of routes $v^{(1)}$ and $v^{(2)}$, we have $r_{C_2H_6} = r_1 + r_2$, and

\[ r_{C_2H_6} = \frac{[M] \sum \omega_1 \omega_2 (\omega_3 + \omega_4)}{D}. \tag{1.48} \]

By the same token, for the basis set of routes with matrix $G_2$, we have

\[ W_1 = r_1' + r_3; \]
\[ W_2 = r_1'; \]
\[ W_3^+ = r_1' + r_3; \]
\[ W_4^+ = -r_3. \]

Ethane is formed via the first route at a rate of

\[ r_1' = W_2 = \frac{[M] \sum \omega_1 \omega_2 (\omega_3 + \omega_4)}{D}. \tag{1.49} \]

Thus, $r_{C_2H_6} = r_1 + r_2 = r_1'$, and we again infer that the rates for substances are invariant with respect to the selection of routes, since

\[ W_3^+ + W_4^+ = r_1 + r_2 \text{ (for } G_1); \]
\[ W_3^+ + W_4^+ = r_1' \text{ (for } G_2). \]

As is known, for a cyclic route with a zero overall equation (empty route), such as that for the mechanism

\[ A \rightleftharpoons B \rightleftharpoons C \rightleftharpoons A, \]

the chemical affinity ($A_p$) is zero and the equilibrium constant for the overall equation of this three-step reaction is $K = K_1 K_2 K_3 = 1$ [15]. This circumstance imposes certain relationships between rate constants of elementary steps, which can be used to estimate the constants for kinetic models in multi-route
reactions with empty routes as was originally pointed out by Avetisov et al. [28]. Let us consider mechanism (1.27) analogous to that in Example 1.5, but with all stages being reversible. The equations of rates over routes \(v^{(2)}\) (matrix \(G_1\)) and \(v^{(3)}\) (matrix \(G_2\) with an empty route) are

\[
\begin{align*}
    r_2 &= W_4 = W_4^+ - W_4^- \\
    r_3 &= -W_4 = W_4^- - W_4^+
\end{align*}
\]

only differing in the sign and containing a term \((\omega_1 \omega_3 \omega_{-4} - \omega_{-1} \omega_{-3} \omega_4)\) in the numerator that refers to the empty route:

\[
    r_3 = \frac{(\omega_1 \omega_3 \omega_{-4} - \omega_{-1} \omega_{-3} \omega_4) + (\omega_1 + \omega_{-3})(\omega_{-2} \omega_{-4} - \omega_2 \omega_4)}{D}.
\]

From thermodynamic considerations, we infer that \(k_1 k_3 k_{-4} = k_{-1} k_{-3} k_{4}\) and the concentrations of products and reactants for the empty route cancel each other so that

\[
    \omega_1 \omega_3 \omega_{-4} = \omega_{-1} \omega_{-3} \omega_4
\]

and

\[
    r_3 = -r_2 = \frac{(\omega_1 + \omega_{-3})(\omega_{-2} \omega_{-4} - \omega_2 \omega_4)}{D}.
\]

Thus, while the chemical affinity for the empty route \(v^{(3)}\) is zero \((A_3 = 0)\), the rate over route \(v^{(3)}\) is not zero and the empty route is not an equilibrium one.

If a mechanism involves reversible steps that do not enter into any route – i.e., steps with zero stoichiometric numbers \(v_j\) (“defect” of the mechanism) – then, according to equation (1.34), the rates of these steps are zero and, hence, they are equilibrium steps. For example, if we add a “dead-end” step to the mechanism according to scheme (1.27),

\[
    (5) \quad M + C_2H_4 \rightleftharpoons MC_2H_4,
\]

for which \(v_5^{(1)} = 0\) and \(v_5^{(2)} = 0\), then

\[
    W_5^+ - W_5^- = v_5^{(1)} r_1 + v_5^{(2)} r_2 = 0
\]

and, hence, \(W_5^+ = W_5^-\).

The rate of an \(n\)-step reversible single-route reaction with a linear mechanism according to Temkin [3, 27] is expressed as follows:

\[
    r = \frac{W_1^+ \cdot W_2^+ \cdot \ldots \cdot W_n^+ - W_1^- \cdot W_2^- \cdot \ldots \cdot W_n^-}{v_1 \cdot W_2^+ + \ldots + W_n^+ + W_1^- \cdot v_2 \cdot \ldots \cdot W_n^- + W_1^+ \cdot W_2^- \cdot \ldots \cdot W_n^+}{v_1 \cdot W_2^- + \ldots + W_n^-}
\]

(1.50)

All stoichiometric numbers for linear single-route mechanisms are \(v_j = 1\), but their position in terms of the denominator helps the memorizing of the algorithm of writing the denominator in formula (1.50). For a catalytic process, this formula (written in terms of step weights) has the following form:

\[
    r = \frac{[M](\omega_1 \cdot \omega_2 \cdot \ldots \cdot \omega_n - \omega_{-1} \cdot \omega_{-2} \cdot \ldots \cdot \omega_{-n})}{\omega_2 \cdot \ldots \cdot \omega_n + \omega_{-1} \cdot \omega_{-2} \cdot \ldots \cdot \omega_{-n}}.
\]

(1.51)

where \([M]\) is the concentration of active centers (active complexes).
Thus, the theory of steady-state and quasi-steady-state reactions employs three equivalent conditions of a steady-state process:

- The condition of zero total rate of variation of the concentration of $X_i$ intermediate:
  \[ r_x = B^T_X W_j = 0 \quad \text{and} \quad \frac{dC_x}{dt} = 0, \]
  (in both open and closed systems);
- The Horiuti condition (1.10) of excluding intermediates from overall equations:
  \[ B^T_X G = 0, \]
  which is valid only provided that the total rate of $X_i$ accumulation (see the first condition above) is zero;
- The condition of the steady state of steps:
  \[ W_j^+ - W_j^- = \sum_p \nu_j^p r_p. \]

Now let us perform the stoichiometric and kinetic analysis of a more complicated, nonlinear mechanism of a catalytic reaction that involves two active catalysts (types of active centers).

**Example 1.8**

The reaction of acetylene hydrochlorination

\[ C_2H_2 + HCl \rightarrow CH_2=CHCl \]  \hspace{1cm} (1.52)

is catalyzed by Cu(I) and Hg(II) chloride complexes (for simplicity, CuCl and HgCl$_2$) in an HCl–H$_2$O solution and probably proceeds according to the following scheme [29]:

1. $C_2H_2 + HgCl_2 \rightleftharpoons X_1$;
2. $X_1 + HCl \rightarrow CH_2=CHCl + HgCl_2$;
3. $C_2H_2 + CuCl \rightleftharpoons X_2$;
4. $X_2 + HCl \rightarrow CH_2=CHCl + CuCl$;
5. $X_1 + CuCl \rightarrow X_2 + HgCl_2$.

The corresponding matrix $B_m$ consists of two blocks ($B_N$ and $B_X$):

\[ B_m = \begin{bmatrix}
  C_2H_2 & HCl & CH_2=CHCl & HgCl_2 & X_1 & CuCl & X_2 \\
  -1 & 0 & 0 & -1 & 1 & 0 & 0 \\
  0 & -1 & 1 & 1 & -1 & 0 & 0 \\
  -1 & 0 & 0 & 0 & 0 & -1 & 1 \\
  0 & -1 & 1 & 0 & 0 & 1 & -1 \\
  0 & 0 & 0 & 1 & -1 & -1 & 1 \\
\end{bmatrix} \]

\[ B_N \quad B_X \]
If \( \text{C}_2\text{H}_2 \) and \( \text{HCl} \) groups are selected to be the groups retained during the reaction under consideration, the rank of the atomic (molecular) matrix \( H_{\text{part}} \) of reaction participants (reactants and products) is \( \text{rank} H_{\text{part}} = 2 \) and, hence, \( Q_{\text{max}} = N - \text{rank} H_{\text{part}} = 3 - 2 = 1 \), i.e., there is a single overall equation [reaction (1.52)]. The reaction involves two catalysts \( (W = 2) \), obeys two material balances \( ([\text{CuCl}]_\Sigma = [\text{CuCl}] + [X_2]) \) and \( [\text{HgCl}_2]_\Sigma = [\text{HgCl}_2] + [X_1] \) and, hence, there are only two linearly independent columns in matrix \( B_X \), so that \( \text{rank} B_X = N_f = 2 \). From this it follows that the number of linearly independent routes (i.e., the rank of the matrix of stoichiometric numbers \( G \)) is \( P = S - N_f = 5 - 2 = 3 \) or \( P = S - I + W = 5 - 4 + 2 = 3 \) [see Eqs (1.13) and (1.14)]. The total number of conservation equations \( (L = N + I - \text{rank} B_m = 7 - 3 = 4) \) in this case is equal to the number of stoichiometric conservation laws, since \( \text{rank} H_{\text{part}} = 2 \) and \( \text{rank} B_X = 2 \).

Let us find the corresponding matrix \( G \). For this purpose, let us select and use two linearly independent columns for \( X_1 \) and \( X_2 \) as matrix \( B_X \) and write the condition \( B_X^T v_j = 0 \) as follows:

\[
\begin{bmatrix}
1 & -1 & 0 & 0 & -1 \\
0 & 0 & 1 & -1 & 1
\end{bmatrix}
\begin{bmatrix}
v_1 \\
v_2 \\
v_3 \\
v_4 \\
v_5
\end{bmatrix} = 0.
\]

Equation (1.54) yields a set of two equations with five unknowns,

\[
\begin{align*}
v_2 + v_5 &= v_1 \\
v_5 &= v_4 - v_3
\end{align*}
\]

which has three linearly independent solutions (i.e., three sets of the stoichiometric numbers of routes). Setting the sequences of whole numbers and zeros for \( v_1, v_3, \) and \( v_4 \), we obtain the corresponding values of \( v_2 \) and \( v_5 \). Choosing the basis-set routes, for example, \( v^{(1)}, v^{(2)} \) and \( v^{(3)} \), we write the matrix \( G \) as

\[
G = \begin{bmatrix}
1 & 0 & 1 & 1 & 1 \\
0 & 1 & 0 & 1 & 1 \\
0 & 1 & 0 & 1 & 1 \\
0 & 0 & 1 & 1 & 0
\end{bmatrix},
\]

and determine routes \( v^{(4)} \) and \( v^{(5)} \) as the difference \( (v^{(3)} - v^{(2)}) \) and sum \( (v^{(1)} + v^{(2)}) \), respectively, of the given sets of stoichiometric numbers.

The overall equations for the first three routes (basis \( G_1 \)), that is, matrix \( B_p \), can be found using Eq. (1.23). From this matrix \( B_p \), it follows that the first three independent routes correspond to three identical equations:

\[
B_p = \begin{bmatrix}
C_2H_2 & \text{HCl} & \text{CH}_2=\text{CHCl} \\
-1 & -1 & 1 \\
-1 & -1 & 1 \\
-1 & -1 & 1
\end{bmatrix}
\Rightarrow
\begin{align*}
v^{(1)} & \Rightarrow C_2H_2 + \text{HCl} \rightarrow \text{CH}_2=\text{CHCl}; \\
v^{(2)} & \Rightarrow C_2H_2 + \text{HCl} \rightarrow \text{CH}_2=\text{CHCl}; \\
v^{(3)} & \Rightarrow C_2H_2 + \text{HCl} \rightarrow \text{CH}_2=\text{CHCl},
\end{align*}
\]

so that \( \text{rank} B_p = Q_p = 1 \). Equation (1.24) also yields \( Q_p = \text{rank} B_m - N_f = 3 - 2 = 1 \), since mechanism (1.53) has only three linearly independent steps.
By the same token, using routes \( \psi^{(1)}, \psi^{(2)} \) and \( \psi^{(4)} \) and the corresponding matrix \( G_2 \), we arrive at matrix \( B_p' \) with an “empty” third route,

\[
B_p' = \begin{pmatrix}
\psi^{(1)} & \psi^{(2)} & \psi^{(4)} \\
C_2H_2 & HCl & CH_2=CHCl \\
\begin{bmatrix}
-1 & -1 & 1 \\
-1 & -1 & 1 \\
0 & 0 & 0
\end{bmatrix}
\end{pmatrix} \Rightarrow \psi^{(4)} = 0 = 0,
\]

in which case the rate over the empty route is nonzero.

The basis set of routes can be reduced to a stoichiometric basis set, that is, a set with two empty routes, by adopting negative stoichiometric numbers for irreversible steps (4) and (5). Selecting matrix \( G_3 \) as

\[
G_3 = \begin{pmatrix}
\psi^{(1)} & \psi^{(2)} & \psi^{(4)} & \psi^{(6)} \\
1 & 1 & 0 & 0 \\
1 & 0 & 1 & 0 \\
0 & -1 & 0 & 0 \\
0 & 0 & -1 & 0 \\
0 & 1 & -1 & 0
\end{pmatrix}
\]

and writing the sets of equations (1.34) of the steady state of steps for matrices \( G_1, G_2, \) and \( G_3 \),

\[
W_1 = r_1 + r_3 \\
W_2 = r_1 \\
W_3 = r_2 \\
W_4 = r_2 + r_3 \\
W_5 = r_3
\]

\[
W_1 = r_1 + r_4 \\
W_2 = r_1 + r_6 \\
W_3 = r_2 - r_4 \\
W_4 = r_2 \\
W_5 = r_4
\]

\[
W_1 = r_1 + r_4 \\
W_2 = r_1 + r_6 \\
W_3 = r_2 - r_4 \\
W_4 = r_2 \\
W_5 = r_4 - r_6,
\]

we can express the rate of vinyl chloride formation \( (r_{VC}) \) via basis set routes using matrix \( B_p (r_N = B_p^T r_p) \) as follows:

\[
G_1 : \quad r_{VC} = r_1 + r_2 + r_3 = W_2 + W_4 \quad (or \ W_1 + W_3); \\
G_2 : \quad r_{VC} = r_1 + r_2 = W_2 + W_4 \quad (or \ W_1 + W_3); \\
G_3 : \quad r_{VC} = r_1 = W_2 + W_4 \quad (or \ W_1 + W_3).
\]

Evidently, the \( r_{VC} \) value must be invariant with respect to the basis set of routes, so that in all cases \( r_{VC} = W_2 + W_4 \) (or \( W_1 + W_3 \)). An expression for \( r_{VC} \) can be obtained by solving sets of Eqs (1.57) for unknowns [X_1], [X_2], and \( r_p \). In the latter case, the set of equations (for \( G_3 \)) is readily reduced to a set of three equations with three unknowns \( (r_1, [X_1], [X_2]) \):

\[
W_1 + W_3 = r_1; \quad W_2 + W_4 = r_1; \quad W_3 + W_5 = W_4,
\]

from which the \( r_1 \) value is readily determined by the Cramer method. Assuming that the step rates obey the relations

\[
[CuCl]_\Sigma \gg [X_2], \quad [HgCl_2]_\Sigma \gg [X_1], \quad [CuCl]_\Sigma \cong [CuCl], \quad [HgCl_2]_\Sigma \cong [HgCl_2],
\]
we eventually obtain

\[
\begin{align*}
r_1 &= \frac{k_1k_2[HgCl_2]_2[HCl]P_{C_2H_2}}{k_{-1} + k_2[HCl] + k_5[CuCl]_\Sigma} + \frac{k_3k_4[CuCl]_2[HCl]P_{C_2H_2}}{k_{-3} + k_4[HCl]} \\
&+ \frac{k_1k_4k_5[HgCl_2]_2[CuCl]_2[HCl]P_{C_2H_2}}{[k_{-3} + k_4[HCl]](k_{-1} + k_2[HCl] + k_5[CuCl]_\Sigma)},
\end{align*}
\]

(1.58)

where \(P_{C_2H_2}\) is the partial pressure of acetylene.

It is also possible to use the relation \(r_s = B^T X W_j = 0\) (Bodenstein condition) and determine \([X_1] \) and \([X_2] \) by solving a system of two equations for two linearly independent concentrations of intermediates \(X_j\). Substituting these \([X_1] \) and \([X_2] \) values into equations for the rates of steps (2) and (4), in which vinyl chloride is formed, we eventually obtain

\[
r_{VC} = W_2 + W_4 = k_2[HCl][X_1] + k_4[HCl][X_2].
\]

The values of \([X_1] \) and \([X_2] \) determined in this way are as follows:

\[
[X_1] = \frac{k_1[HgCl]_2P_{C_2H_2}}{k_{-1} + k_2[HCl] + k_5[CuCl]_\Sigma}; \tag{1.59}
\]

\[
[X_2] = \frac{k_1k_4[CuCl]_2P_{C_2H_2}}{k_{-3} + k_4[HCl]} + \frac{k_1k_4k_5[HgCl_2]_2[CuCl]_2P_{C_2H_2}}{[k_{-3} + k_4[HCl]](k_{-1} + k_2[HCl] + k_5[CuCl]_\Sigma)}. \tag{1.60}
\]

As a result, we eventually also obtain Eq. (1.58) for \(r_{VC}\). The empty route \(N_0\) in the stoichiometric basis set of routes includes the irreversible step (4) with a negative stoichiometric number. Note that the sets of non-empty basis-set routes (overall equations of vinyl chloride formation) in all variants are written in accordance with the thermodynamically allowed directions of steps.

Assuming that steps (1) and (3) are quasi-equilibrium \((W_{-1} \gg W_2, W_3; W_{-3} \gg W_4, W_5)\), the rate of vinyl chloride formation is described by the following equation with two terms in the right-hand side:

\[
r_{VC} = k_2K_1[HgCl_2]_2[HCl]P_{C_2H_2} + k_4K_3[CuCl]_2[HCl]P_{C_2H_2}, \tag{1.61}
\]

in which a synergistic effect caused by step (5) disappears and the rates of reactions on two independent centers (catalysts) are merely added.

In concluding this section, it is expedient to emphasize the following important features of the method of routes:

(i) An elementary step in one direction is characterized by the rates \((r_i)\) with respect to all substances – participants of the step and by the reaction rate \(W_j^{\pm}(r_i = \sum \beta_i W_j^{\pm})\) that is invariant with respect to these substances. The reaction rate constant of the step refers to the latter invariant rate \(W_j\). Similarly, for a multistep process proceeding under steady-state and quasi-steady-state conditions, it is necessary to use the rates with respect to substances \((r_N)\) and rates for overall equations \((r_p)\), which also characterize the whole process in the case of a single-route mechanism.

(ii) The method of routes can also be used to find the overall equations proceeding from the process mechanism, with the rates for substances being invariant with respect to the selection of the basis set of routes (see Examples 1.7 and 1.9).

(iii) The theory of routes shows that a reaction mechanism plays the determining role, while the overall equations merely follow from the mechanism. For a completely reversible process, the question as
to what is the overall equation according to which product is formed is incorrect. The issue to be discussed is what a sequence of steps is, a run over which ensures the formation of this product (as described by one of the overall equations).

(iv) Formally speaking, all the reaction routes and overall equations are equivalent. At the same time, for the overall equations to have a clear chemical sense, to not contradict thermodynamically-allowed directions, and to obey the observed kinetics, it is expedient to take these considerations into account when selecting a basis set of routes. “Reasonable” overall equations are determined with allowance for the mechanism, kinetics (see Examples 1.1 and 1.2), and thermodynamic constraints (Example 1.3).

Features of the kinetics of multi-route reactions, which are related to the possibility of different conjugation of routes, will be considered in Chapter 3, which is specifically devoted to multi-route catalytic reactions (see Section 3.4).

1.1.3 Kinetic polynomial

Since the system of equations (1.34) for the condition of the steady state of steps in the general case has no solutions for nonlinear mechanisms, a new representation of this condition supplemented by the equations of material balance with respect to reaction intermediates $X_i$ was proposed in the form of so-called kinetic polynomial [30–33] (see also M.Z. Lazman and G.S. Yablonsky, Adv. Chem. Eng., 34, 47 (2008)).

Considering an $n$-step single-route catalytic reaction,

$$W_j^+ - W_j^- = \sum_j v_j r, \quad j = 1, 2, 3, \ldots, n;$$

$$\sum X_i = \text{const} \left( [M]_\Sigma \text{ for solutions; } 1 \text{ for surfaces} \right),$$

of the weights of and excluding $[X_i]$, we obtain a polynomial with respect to $r$, with coefficients representing polynomials of step weights ($\omega_j$):

$$B_0 + B_1 r + B_2 r^2 + \cdots + B_k r^k = 0 \ (N = 0, 1, \ldots, k). \quad (1.62)$$

This polynomial can be used to describe the dependence of the observed reaction rate on the parameters measured and to solve the inverse problem of kinetics [34], i.e., to restore the polynomial coefficients and find the reaction rate constants $k_i$ of steps, since the structure of coefficients $B_N$ for the known mechanism is determined. Let us consider some examples.

**Example 1.9**

- For the reaction mechanism (1.14) with a set of $v = (2, 1)$, we can write

$$W_1^+ - \omega_{-1}[X] = 2r;$$

$$\omega_2[X]^2 - W_2^- = r. \quad (1.63)$$

Upon excluding $[X]$, we obtain the following polynomial:

$$B_0 - B_1 r + B_2 r^2 = 0, \quad (1.64)$$

where $B_0 = k_2 k_1^2[A]^2 - k_{-2} k_{-1}^2[P]; B_1 = 4k_1 k_2[A] + k_{-2}^2; \quad$ and $B_2 = 4k_2$. For $r = 0$, we have $B_0 = 0$ and $K_2^2 K_2 = [P_{eq}]/[A_{eq}]^2$, which is evidence for the validity of the requirements of thermodynamics in writing the polynomial. ■
**Example 1.10**

For the reaction scheme

\[
\begin{align*}
A + 2M & \rightleftharpoons 2X; \\
X + B & \rightarrow M + P
\end{align*}
\]

(1.65)

with the overall equation

\[A + 2B = 2P,\]

a system of equations (1.34) can be written as follows:

\[
\begin{align*}
\omega_1 [M]^2 - \omega_{-1} [X]^2 &= r, \\
\omega_2 [X] &= 2r, \\
[M] + [X] &= [M]_\Sigma.
\end{align*}
\]

(1.66)

Expressing \([X]\) from the second equation and substituting it into the first one, we obtain the following polynomial:

\[B_0 - B_1 r + B_2 r^2 = 0,\]

(1.67)

where

\[
B_0 = k_1 k_2^2 [M]_\Sigma^2 [A] [B]^2; \quad B_1 = k_2^2 [B]^2 + 4k_1 k_2 [A] [B] [M]_\Sigma; \quad B_2 = 4k_1 [A] - 4k_{-1}.
\]

The dependence of the polynomial coefficients on \([M]_\Sigma\) and the steady-state and quasi-steady-state concentrations \([A], [B]\), allows the task of estimating the rate constants to be solved. In the case of multi-route reactions, the kinetic polynomials can be written for the rates \(r_p\) over routes.

**Example 1.11**

For the mechanism

\[
\begin{align*}
A + 2Z_1 & \rightleftharpoons 2Z_2, \\
Z_2 & \rightleftharpoons Z_1 + P_1, \\
2Z_2 & \rightleftharpoons 2Z_1 + P_2
\end{align*}
\]

with the matrix of stoichiometric numbers

\[
G = \begin{bmatrix}
1 & 1 \\
2 & 0 \\
0 & 1
\end{bmatrix} \Rightarrow \begin{bmatrix}
\nu^{(1)} \\
\nu^{(2)}
\end{bmatrix} = \begin{bmatrix}
A = 2P_1 \\
A = P_2
\end{bmatrix}
\]

and the system of equations (1.34) written as

\[
\begin{align*}
(1) \quad \omega_1 [Z_1]^2 - \omega_{-1} [Z_2]^2 &= r_1 + r_2; \\
(2) \quad \omega_2 [Z_2] - \omega_{-2} [Z_1] &= 2r_1; \\
(3) \quad \omega_3 [Z_2]^2 - \omega_{-3} [Z_1]^2 &= r_2; \\
(4) \quad [Z_1] + [Z_2] &= 1,
\end{align*}
\]

(1.68)
we obtain the following polynomial with respect to $r_1$:

$$B_0 + B_1 r_1 + B_2 r_1^2 = 0,$$

where

$$B_0 = (\omega_{-1} + \omega_2)\omega_{-2}^2 - (\omega_{-1} + \omega_3)\omega_2^2;$$

$$B_1 = 4[(\omega_{-1} + \omega_3)\omega_{-2} - (\omega_{-1} + \omega_3)\omega_2] - (\omega_2 + \omega_{-2})^2;$$

$$B_2 = 4(\omega_3 - \omega_{-3} + \omega_{-1} - \omega_1).$$

The polynomial form can also be used to represent the dependences of concentrations $[X_i]$ and the relaxation time (used for an analysis of the relaxation regimes) on the reaction parameters [35].

1.1.4 Determining the number of independent parameters in a kinetic model. The problem of identifiability of parameters

A necessary stage in any kinetic investigation is evaluating the parameters (constants) of an adopted kinetic model from experimental data, which is referred to as the inverse problem of chemical kinetics.

For some objective and subjective reasons, the solution of the inverse kinetic problem is a rather ambiguous procedure. Indeed, there appears to be a possibility of equally well describing the experimental data by different sets of parameters within the same mechanism [5, 36–40].

Objective factors that account for the appearance of ambiguity in solving the inverse kinetic problem are:

(i) nonlinearity of adopted models with respect to their parameters (for steady-state and quasi-steady-state systems); (ii) rigidity of the sets of differential equations (for non-steady-state processes) [39]; and (iii) the deficiency of experimental data that are related to the presence of both fast stages and active intermediates whose concentrations cannot be measured [40].

Subjective factors include poor quality of experiments (large errors), absence of statistically justified experimental planning (i.e., unpredictable informativity), and inadequate choice of a functional determining the proximity of the experimentally measured and calculated values of the observable variables [39, 40].

The first question is to what extent the structure of a given model allows its parameters to be unambiguously estimated a priori for conditions of the proposed type of experiment, proceeding from a hypothetical mechanism? If the unambiguous determination of parameters is impossible, then it is necessary to establish which rate constants or complexes of these constants can be determined independently and to understand reasons of the non-identifiability of parameters. Possible approaches to the problem of the aperiodic identifiability of parameters are considered in [41–47].

Methodology of an analysis of the aprioric identifiability of parameters is based on the concept of a matrix of the sensitivity of a response function $\eta$ (typically, the concentration $C$ or the reaction rate $r$) with respect to the required rate constants $k_i$, that is, the Jacoby matrix, the partial derivatives of $\eta$ with respect to $k_i$:

$$J_{m \times S} = \left\{ \frac{\partial \eta}{\partial k_i} \right\},$$

where $m$ is the number of response functions and $S$ is the number of rate constants.

There are two types of non-identifiability of parameters of a model [42, 43]. The local non-identifiability implies that (i) only some functions of the model parameters (constants) rather than all these parameters can be determined using an adopted experimental scheme, and (ii) the number of elements in a complete set of
the independent parametric functions (basis set) is smaller than the number of parameters. This type corresponds to the matrix \( J \) of an incomplete rank and the corresponding model is called an incomplete-rank model (IRM). The global non-identifiability means that (i) we deal with a complete-rank model (CRM) such that all parameters of the model can, in principle, be determined, but (ii) the problem of determining the parameters has no single solution. Both types of non-identifiability of parameters of a model are related to the invariance of a measured response with respect to some transformations of the model parameters – continuous and discrete transformations for the local and global non-identifiability, respectively. Let us consider some examples of the analysis of models for the non-identifiability of parameters.

**Example 1.12**

Consider a simple scheme of a two-step enzymatic or catalytic reaction, which is known as the Michaelis–Menten scheme and will be repeatedly used in what follows:

\[
E + S \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} X_1 \xrightarrow{k_2} E + P,
\]

(1.69)

where \( E \) is an enzyme [45]. Under quasi-steady-state conditions, the rate of the \( S \rightarrow P \) conversion can be expressed as follows:

\[
r = \frac{d[P]}{dt} = \frac{k_1k_2[E]_0[S]}{k_1[S] + k_{-1} + k_2} = \frac{k_2[E]_0[S]}{[S] + \frac{k_{-1} + k_2}{k_1}}.
\]

(1.70)

Apparently, the parameters to be determined in this simple case are \( k_2 \) and \( K_m = \frac{k_{-1} + k_2}{k_1} \), or \( \gamma_1 = \frac{k_{-1} + k_2}{k_1k_2} \) and \( \gamma_2 = \frac{1}{k_2} \). These two independent quantities result from an analysis of the non-identifiability of parameters of the given model. In this case, we deal with the local non-identifiability of an IRM type, where only two of the three columns of the \( J \) matrix are linearly independent. If the scheme of mechanism (1.69) is complicated to include steps corresponding to the conversion of intermediates,

\[
E + S \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} X_1 \xrightarrow{k_2} X_2 \xrightarrow{\ldots} X_n \xrightarrow{k_{n+1}} E + P,
\]

(1.71)

the number of independent parametric functions will remain unchanged:

\[
\gamma_1 = \frac{k_{-1} + k_2}{k_1k_2}; \quad \gamma_2 = \left( \frac{1}{k_2} + \ldots + \frac{1}{k_{n+1}} \right).
\]

Indeed, any complication of the mechanism without involving additional measurements (only \([S]\) or \([P]\)) does not increase the informativity of kinetic data. ■

**Example 1.13**

Let us return to Example 1.1, where the measured variables were \([A]\) and \([B]\) and the six elementary reactions included three pairs of the same type: (3) and (−5), (−3) and (5), (2) and (−2). This circumstance makes the system locally non-identifiable. If the equilibrium constant \( K \) of the overall reaction

\[
2A = 2B \quad (K = K_1K_2K_3)
\]

is known, we can obtain three linearly independent solutions (parametric functions) defined as \( \gamma_1 = k_1 \), \( \gamma_2 = k_2K_1 \), and \( \gamma_3 = k_3K_1K_2 \). ■
The reaction schemes in Examples 1.12 and 1.13 involved steps of the same type, the weights of which had an identical form \((\omega_1 = k_1, \omega_2 = k_2, \omega_n = k_n)\) in Example 1.12. As a result, like terms and the coefficients representing sums of the products of rate constants appear in the concentration polynomial in the denominator of the equation of steady-state kinetics. These complexes of rate constants (parametric functions) are non-Arrhenius complexes of the constants in various powers \([48]\). If the number of Arrhenius complexes is equal to or greater than the number of parameters to be determined, then the problem of determining \(k_i\) becomes solvable, whereas if the number of these complexes is smaller than the number of \(k_i\), there appears a local non-identifiability of parameters.

**Example 1.14**

An interesting example was proposed by Yablonsky et al. \([48]\) which is related to an analysis of a four-step mechanism of the heterogeneous catalytic conversion of methane:

\[
\begin{align*}
(1) & \quad \text{CH}_4 + Z \rightarrow \text{ZCH}_2 + \text{H}_2; \\
(2) & \quad \text{H}_2\text{O} + \text{ZCH}_2 \rightarrow \text{ZCHOH} + \text{H}_2; \\
(3) & \quad \text{ZCHOH} \rightarrow \text{ZCO} + \text{H}_2; \\
(4) & \quad \text{ZCO} \rightarrow \text{Z} + \text{CO}
\end{align*}
\]

with an overall equation of

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2.
\]

The conversion rate according to this overall equation can be expressed as follows:

\[
r = \frac{k_1k_2k_3k_4[\text{CH}_4][\text{H}_2\text{O}] - k_{-1}k_{-2}k_{-3}k_{-4}[\text{CO}][\text{H}_2]^3}{D},
\]

where

\[
D = K_1[\text{H}_2\text{O}] + K_2[\text{CH}_4] + K_3[\text{H}_2] + K_4[\text{CH}_4][\text{H}_2\text{O}] + K_5[\text{CO}][\text{H}_2] + K_6[\text{H}_2\text{O}][\text{CO}] + K_7[\text{CH}_4][\text{H}_2] + K_8[\text{H}_2]^2 + K_9[\text{CO}][\text{H}_2]^2 + K_{10}[\text{CH}_4][\text{H}_2]^2 + K_{11}[\text{H}_2\text{O}][\text{H}_2][\text{CO}] + K_{12}[\text{CH}_4][\text{H}_2][\text{H}_2] + K_{13}[\text{H}_2]^3;
\]

- \(K_1 = k_2k_3k_4;\)  \(K_2 = k_3k_4k_1;\)  \(K_3 = k_3k_4k_{-1};\)  \(K_4 = k_1k_2(k_3 + k_4);\)  \(K_5 = k_3k_{-4}k_{-1};\)
- \(K_6 = k_3k_{-4};\)  \(K_7 = k_4k_{-2};\)  \(K_8 = k_4k_{-1}k_{-2};\)  \(K_9 = k_{-4}(k_{-3}k_{-3} + k_{-1}k_{-3} + k_{-1}k_{-2});\)
- \(K_{10} = k_{-1}k_{-2}k_{-3};\)  \(K_{11} = k_2k_{-3}k_{-4};\)  \(K_{12} = k_1k_2k_{-3};\)  \(K_{13} = k_{-1}k_{-2}k_{-3};\)

This scheme contains two similar reactions of desorption \((\omega_1 = k_3, \omega_4 = k_4)\) and three similar reactions of \(\text{H}_2\) with \(X_i(\omega_1 = k_{-1}P_{\text{H}_2}, \omega_{-2} = k_{-2}P_{\text{H}_2}, \omega_{-3} = k_{-3}P_{\text{H}_2}).\) Accordingly, the polynomial \(D\) includes two parameters \((K_4\) and \(K_5)\) of a non-Arrhenius type. Among the eleven Arrhenius complexes, we can separate eight independent parameters \((K_3, K_5, K_6, K_7, K_8, K_{10}, K_{11}, K_{12})\) according to the number of elementary reactions. The other three complexes can be represented as linear combinations of these independent parametric functions: \(K_1 = K_3K_6/K_5;\) \(K_2 = K_3K_7/K_8;\) \(K_{13} = K_8K_{10}/K_7.\) Complexes in the numerator are determined via those in the denominator as

\[
K^\pm = (K_3K_5K_6K_7K_8K_{10}K_{11}K_{12})^{1/3} = k_1k_2k_3k_{-1}k_{-2}k_{-3}k_{-4};
\]

\[
K^+ = K_3K_6K_7K_{12}/K^\pm = k_1k_2k_3k_4;
\]

\[
K^- = K_5K_8K_{10}K_{11}/K^\pm = k_{-1}k_{-2}k_{-3}k_{-4}.
\]
Note that, if all the 13 complexes were determined as independent, the solution would be ambiguous and deprived of a physicochemical sense, since the constants \( K_1, K_2, K_4, K_9, \) and \( K_{13} \) are combinations of the independent values. In complicated cases, the independent complexes should be determined using the approach described above. As will be shown below, the total number of parameters to be determined in linear mechanisms can also be evaluated using methods of the graph theory (see Section 1.3).

**Example 1.15**

Let us consider the case of a global non-identifiability which is encountered in the investigation of non-steady-state processes [46, 47]. An analysis of the mechanism of a non-steady-state consecutive reaction

\[
A \xrightarrow{k_1} X_1 \xrightarrow{k_2} X_2 \xrightarrow{k_3} B \tag{1.74}
\]

shows that we deal with a CRM case in which all three constants \( k_i \) can be determined, but the solution is not single-valued. The concentrations of \( A \) and \( B \) do not vary with the time upon interchanging \( k_2 \) and \( k_3 \). If the concentration of \( X_2 \) is additionally measured, then we can also find a single solution for \( k_2 \) and \( k_3 \).

An analysis showed that it is not just a symmetry in the arrangement of points in the space of parametric functions (\( k_2 \) and \( k_3 \)) that accounts for the global non-identifiability [46]. There are some other discrete transformations (besides the permutation) for which the parametric functions are invariant.

**Example 1.16**

The typical scheme of a parallel-consecutive mechanism with similar steps [46]

\[
A_1 \xrightarrow{k_1} A_2 \xrightarrow{k_2} A_3 \xrightarrow{k_3} A_3 \tag{1.75}
\]

in which only one parameter \( [A_3] = f(t) \) is measured, corresponds to a locally identifiable model with three independent parametric functions:

\[
\gamma_1 = k_3, \quad \gamma_2 = k_1 + k_2 + k_3, \quad \gamma_3 = k_2(k_1 + k_3).
\]

However, it was established that there is a linear discrete transformation, which provides an additional solution for the constants \( k_1^*, k_2^* \) and \( k_3^* \):

\[
k_1^* = k_2 - k_3, \quad k_2^* = k_1 + k_3, \quad k_3^* = k_3;
\]

\[
\gamma_1 = k_3^*, \quad \gamma_2 = k_1^* + k_2^* + k_3^*, \quad \gamma_3 = k_2^*(k_1^* + k_3^*).
\]

It is believed that *a priori* analysis for the identifiability of parameters in kinetic models will become a necessary part of any kinetic investigation, the more so that the corresponding numerical methods of analysis are already available [49].

### 1.2 Quasi-steady-state and quasi-equilibrium approximations in chemical kinetics

An important method of describing the kinetics of homogeneous reactions in closed and semi-open systems is stationary concentrations, or the *quasi-steady-state approximation*, which allows kinetic models
analogous to those for steady-state processes to be formulated in the case of nonstationary concentrations of reactants and products [7, 15, 50–54]. This approximation was originally used by Chapman in 1913 and then developed by Bodenstein and Semenov [50]. Known as the Bodenstein quasi-steady-state principle or condition, this approximation is now widely used in investigations of the reaction kinetics in homogeneous acid catalysis, nucleophilic and enzymatic catalysis, and homogeneous catalysis with metal complexes, as well as in polymerization, gas- and liquid-phase oxidation, chlorination, and other processes. However, this approximation is still actively discussed by physicists, chemists, and mathematicians. Following the pioneering work by Frank-Kamenetskii [55], significant contributions to deeper insights into the essence of the quasi-steady state were made by specialists in the enzymatic catalysis (see, e.g., [6]) and in many other fields [53, 57, 58] (see also monographs [7, 15] and references cited therein). A detailed analysis of this issue using a computational experiment was recently given in [59].

Under steady-state conditions (open systems) with unobservable intermediates $X_i$ (which either do not leave a reactor that is closed for both a catalyst and these intermediates or do not enter into the equations of material balance for the catalyst and intermediates), the system obeys relations

$$B^T_j G = 0 \quad (1.10)$$

and

$$B^T_j W_j = 0 \quad (1.33),$$

which allows $C_{X_i}$ to be determined for linear mechanisms (i.e., those with steps involving no more than one $X_i$ on both left and right sides) and the expressions for $r_X$ and $r_p$ to be obtained. For example, in the case of a mechanism

$$A \underset{k_1}{\overset{k_2}{\rightleftharpoons}} X \underset{k_{-1}}{\rightarrow} P \quad (1.76)$$

with the overall equation $A = P$ for $dC_X/dt = 0$ we have $k_1 C_A - k_{-1} C_X - k_2 C_X = 0$ and

$$C_X = \frac{k_1 C_A}{k_{-1} + k_2} \quad (1.77).$$

In this case, the rate of process (1.76) is determined by the following equation:

$$r = |r_A| = r_p = k_2 C_X = \frac{k_1 k_2 C_A}{k_{-1} + k_2} \quad (1.78).$$

What are the experimental and theoretical criteria for the conditions $dC_{X_i}/dt \equiv 0$ and $B^T X G = 0$ to be applicable to a closed system, i.e., for the quasi-steady-state approximation to be valid? Is it possible to obtain equations for $dC_A/dt$ and $dC_P/dt$ in a closed system that would be analogous to Eq. (1.78)? Evidently, the condition that intermediates $X_i$ are unobservable is ensured provided that $C_X \ll C_A, C_P$ [for mechanism (1.76)]. Then, the balance equation $C_{0A} = C_A + C_X + C_P$ yields $C_{0A} - C_A \approx C_P$ and, hence,

$$|dC_A/dt| \approx |dC_P/dt|, \quad k_2 C_X \approx k_1 C_A - k_{-1} C_X,$$

which implies that $dC_X/dt \approx 0$. Thus, the condition that

$$\sum C_{X_i} \ll C_A$$

is both necessary and sufficient for the validity of the Bodenstein principle ($dC_{X_i}/dt = 0$) or the condition of quasi-steady state in a closed system. The approximate equality

$$|dC_A/dt| \approx |dC_P/dt|$$
also implies that
\[
\frac{dC_X}{dt} \ll \left| \frac{dC_A}{dt} \right|.
\]

Differentiation of Eq. (1.77) yields the following relation:
\[
\frac{dC_X}{dt} = \frac{k_1}{k_{-1} + k_2} \frac{dC_A}{dt},
\]
from which it is seen that the inequality
\[
\frac{dC_X}{dt} \ll \left| \frac{dC_A}{dt} \right|
\]
is possible for
\[
\frac{k_1}{k_{-1} + k_2} = \epsilon_1 \ll 1.
\]

It is very important to emphasize that, in a multistep reaction, the condition \(dC_X/dt \equiv 0\) must be obeyed for each \(X_i\) and over a long interval of time, since in certain intervals the equality of \(|r_A|\) and \(r_P\) can be provided merely by the summation of \(C_{X_i}\) derivatives with opposite signs:
\[
\sum \frac{dC_{X_i}}{dt} = 0.
\]

Equation (1.79) also shows that, on attaining a quasi-steady state (at \(t > t_{\text{max}}\) for \(C_X\)) the rate of decrease in \(C_X\) is proportional to the rate of decrease in \(C_A\). Under these conditions \((C_X \ll C_A, \epsilon_1 \ll 1)\), it is possible to obtain a system of equations that describes the process (1.76) proceeding in a quasi-steady-state (SS) regime \([57, 58]\):
\[
\begin{align*}
\frac{dC_{P}^{\text{SS}}}{dt} &= k_{\text{eff}}^{\text{SS}} C_{A}^{\text{SS}} \quad \text{(1.80)} \\
-\frac{dC_{X}^{\text{SS}}}{dt} &= k_{\text{eff}}^{\text{SS}} C_{X}^{\text{SS}} \quad \text{(1.81)} \\
-\frac{dC_{A}^{\text{SS}}}{dt} &= k_{\text{eff}}^{\text{SS}} C_{A}^{\text{SS}} \quad \text{(1.82)}
\end{align*}
\]

Evidently, the quasi-steady-state approximation is only applicable for \(t > t_{\text{max}}\) (maximum on the \(C_X = f(t)\) curve), since Eqs (1.77), (1.79) and (1.81) are not valid in the initial interval of time \((t \to 0)\), where \(C_X\) vanishes rather than tends to \(C_{0X} = \epsilon C_{0A}\) [see Eq. (1.77)].

The above relationships indicate that the inequalities \(C_X \ll C_A\) and \(\epsilon_1 \ll 1\) can serve, respectively, the experimental and theoretical criteria for the validity of the quasi-steady-state approximation. Now we will consider in more detail various criteria that were discussed in the literature.

### 1.2.1 Theoretical criteria of quasi-steady-state intermediate concentrations and quasi-equilibrium steps

Once the rate constants of steps are known, it is possible to analyze the behavior of intermediates and the applicability of the quasi-steady-state approximation using various criteria.
1.2.1.1 Frank-Kamenetskii criteria [55]

In order to understand the physical essence of the quasi-steady-state approximation, it is important to know one of the criteria proposed by Frank-Kamenetskii [55], which follows from Eq. (1.81) (for more detail, see [15]). According to this criterion of a quasi-steady state (SS) condition, it is necessary that the lifetime of an intermediate X (or the time to its disappearance), which can be expressed as

\[ \tau = \frac{1}{k_{-1} + k_2}, \]

would be much shorter than the characteristic time \( \tau_X \) of the variation of \( C_X \) (\( \tau_X = 1/k_{\text{eff}}^{SS} \)). The criterion \( \tau \ll \tau_X \) or \( k_{\text{eff}}^{SS} \ll (k_{-1} + k_2) \) is valid for \( k_1 \ll (k_{-1} + k_2) \). The condition \( \tau \ll \tau_X \) is analogous to the relation

\[ \frac{d \ln C_X^{SS}}{dt} \ll k_{-1} + k_2 \]  

[1.83]

[see Eq. (1.81)], since

\[ \frac{d \ln C_X^{SS}}{dt} = k_{\text{eff}}^{SS}. \]

Variables \( C_X \) for the intermediates with short lifetimes are called fast, in contrast to slow variables \( C_A \) and \( C_p \). Thus, the inequality \( k_1 \ll (k_{-1} + k_2) \) that leads to the condition \( \tau \ll \tau_X \) in the case under consideration is also the necessary and sufficient condition for the validity of the quasi-steady-state approximation.

1.2.1.2 Wong’s criterion [56]

Let us transform the equation for \( \frac{dC_X}{dt} \) as written for mechanism (1.76),

\[ \frac{dC_X}{dt} = k_1 C_A - (k_{-1} + k_2) C_X, \]  

[1.84]

and write it as

\[ \delta_1 = \frac{dC_X}{dt} \frac{k_1 C_A}{k_{-1} + k_2} - C_X, \]  

[1.85]

or

\[ \delta_1 + C_X = \frac{k_1 C_A}{k_{-1} + k_2}. \]  

[1.86]

The value of \( \delta_1 \) is what determines the error of the quasi-steady-state approximation (or the method of stationary concentrations). The necessary and sufficient condition for this approximation can be written as \( \delta_1 \ll C_X \) (Wong’s criterion), which also implies the validity of the Frank-Kamenetskii criterion written as

\[ \frac{dC_X}{dt} \ll C_X \text{ or } \frac{d \ln C_X}{dt} \ll k_{-1} + k_2. \]

Another important conclusion following from Wong’s criterion is that a negligibly small value (in comparison to \( C_X \)) is the product of \( \frac{dC_X}{dt} \) and a small parameter:

\[ \delta_1 = \frac{dC_X}{dt} \frac{1}{k_{-1} + k_2} \ll 1 \quad (\delta_1 \to 0). \]

Alternatively, Wong’s criterion can be written in terms of the relative rate \( \Delta \) as

\[ \Delta = \frac{dC_X}{dt} \frac{1}{(k_{-1} + k_2) C_X} \ll 1. \]  

[1.87]
The rate of variation of the $C_X$ value can also be compared to the rate of formation of intermediate X ($k_1 C_A$) [56]. The relative rate $\Delta_1$ must obey the condition

$$\Delta_1 = \frac{dC_X}{dt} \left/ k_1 C_A \right. \ll 1. \quad (1.88)$$

The value of $\Delta_1$ tends to zero for $dC_X/dt \ll k_1 C_A$, i.e., under conditions where the rate of variation of the $C_X$ value is much smaller than the rate of formation of intermediate X. The $\Delta_1$ value also provides an estimate for the error of determination of the rate of product P formation in the quasi-steady-state approximation:

$$\Delta_1 = \frac{dC_P}{dt} \bigg|_{SS} - \frac{dC_P}{dt}. \quad (1.89)$$

Now let us turn to a more complicated mechanism of a two-step catalytic reaction that was considered above (see Section 1.1):

$$A + E \overset{k_1}{\underset{k_{-1}}{\rightleftharpoons}} EA, \quad (1.90)$$

$$EA \overset{k_2}{\to} P + E. \quad (1.91)$$

This mechanism is known as the Michaelis–Menten scheme since it was studied in detail by these researchers in the enzymatic catalysis [52, 56]. Here, E denotes a homogeneous catalyst such as an enzyme, metal complex, HA acid, etc. (in the heterogeneous catalysis, E is an active surface center), EA is an intermediate compound X ($C_{EA} = C_X$). Writing a differential equation for $C_X$ as

$$\frac{dC_X}{dt} = k_1 C_E C_A - (k_{-1} + k_2)C_X, \quad (1.92)$$

taking into account the material balance for the catalyst ($C_{OE} = C_E + C_X$), and assuming that $C_{0A} \gg C_{0E}$, we obtain an expression analogous to (1.85):

$$\delta_2 = \frac{dC_X}{dt} \left/ k_1 C_A + k_{-1} + k_2 \right. = \frac{k_1 C_{OE} C_A}{k_1 C_A + k_{-1} + k_2} - C_X. \quad (1.93)$$

For $dC_X/dt = 0$ (Bodenstein principle) or, more strictly, for $\delta_2 \ll C_X$ (Wong’s criterion), this yields

$$C_X^{SS} = \frac{k_1 C_{OE} C_A^{SS}}{k_1 C_A^{SS} + k_{-1} + k_2}; \quad (1.94)$$

$$\frac{dC_P}{dt} = k_2 C_X^{SS} = \frac{k_1 k_2 C_{OE} C_A^{SS}}{k_1 C_A^{SS} + k_{-1} + k_2}. \quad (1.95)$$

The latter equation is more frequently written in the following form:

$$\frac{dC_P}{dt} = k_2 C_{OE} C_A \bigg/ C_A + k_m. \quad (1.96)$$

$^4$Equation (1.89) was also derived by S.M. Brailovskii and A.F. Fel’dman (S.M. Fel’dman, *Diploma*, Lomonosov Institute of Fine Chemical Technology, Moscow, 1970) in the general case with an arbitrary number of intermediates $X_i$. The derivation of equation for $\Delta_1$ in the case of a single intermediate X in the same study was more rigorous than in [53].
where $k_m = \frac{k_{-1} + k_2}{k_1}$ is the Michaelis constant. In this case, the lifetime of intermediate $X$ is given by the following formula:

$$\tau = \frac{1}{k_1 C_{0A} + k_{-1} + k_2}. \quad (1.97)$$

A detailed analysis of conditions for the validity of the quasi-steady-state approximation and an estimation of the error of this approximation were performed by Wong [56]. In particular, it was shown that, for $C_{0A} \gg C_{0E}$, the error in description of the reaction rate by Eq. (1.96) tends to zero. The relative rate is

$$\Delta_2 = \frac{dC_X/dt}{k_1 C_{0E} C_A} \ll 1 \quad (1.98)$$

also tends to zero in this case for $dC_X/dt \ll k_1 C_{0E} C_A$.

### 1.2.1.3 Bodenstein’s criterion

The equation $dC_X/dt = 0$ provides a sufficient condition for attaining a quasi-steady state, since it ensures the vanishing of all errors ($\delta_1, \delta_2, \Delta, \Delta_1, \Delta_2$). On the other hand, it is a very rough criterion, since $C_X$ is a finite but variable quantity and the equation

$$C_X = \frac{k_1 C_A}{k_{-1} + k_2}$$

yields relation (1.79). In addition, Eqs (1.81) and (1.82) show that

$$\frac{d \ln C_{A}^{SS}}{dt} = \frac{d \ln C_X^{SS}}{dt} = k_{eff}^{SS}. \quad (1.99)$$

The proximity of $dC_A/dt$ and $dC_P/dt$ values indicates that $dC_X/dt \ll dC_A/dt$ rather than $dC_X/dt = 0$. Therefore, the inaccurate (or even erroneous) approach (adopting the condition $dC_X/dt = 0$) leads to a correct and useful result (see [7, p. 146]) The Bodenstein criterion (condition) is useful for interpreting the quasi-steady-state approximation as the requirement of excluding the time as an explicit variable that controls the concentrations of intermediates in a quasi-steady state. The admission of the equality $dC_X/dt = 0$ in the mathematical description converts some differential equations into algebraic relations, thus making the set of initial differential equations degenerate.

### 1.2.1.4 Eyring’s criterion [58]

This criterion (for brevity, referred to below as Eyring’s $D_E$ criterion) was analyzed in [58, 60]. It is based on a comparison of the rates of formation and consumption of intermediates. In particular, for the mechanism

$$A \xrightarrow{k_1} X \xrightarrow{k_2} P$$

the ratio of these rates is

$$D_E = \frac{k_2 C_X}{k_1 C_A}, \quad (1.100)$$
and for mechanism (1.76) we have

\[ D_E = \frac{(k_{-1} + k_2)}{k_1} \frac{C_X}{C_A}, \]  

(1.101)

where \( C_X \) and \( C_A \) are determined by the exact solution of the corresponding systems of differential equations. The accuracy of the quasi-steady-state approximation is determined by the degree of deviation of the \( D_E \) value from unity. In the case of \( k_{-1} \gg k_2 \), expression (1.101) converts into the approximate equation

\[ D_E = \frac{C_X}{C_A k_1}, \]

which characterizes the deviation of the \( C_X/C_A \) ratio from an equilibrium value and, hence, the degree of the system’s deviation from a quasi-equilibrium state of the first step. The closer \( D_E \) to unity, the more equilibrium is the regime under consideration.

**1.2.1.5 Rozovskii criterion [53]**

For an analysis of factors determining the adequacy and accuracy of the quasi-steady-state approximation and for the estimation of \( k_i \) values that are necessary to ensure the required accuracy, it is suggested to use the ratio

\[ D_R = \frac{C_X}{C_{XX}} \]  

(1.102)

where \( C_X \) is the value provided by an analytical solution of the system of differential equations and \( C_{XX} \) is the concentration of X in a quasi-steady state. An analysis of the conditions under which \( D_R \rightarrow 1 \) (or the \( D_R \) ratio differs from unity by a preset small value) was performed in [53]. It should be noted that, in writing expressions for \( C_{XX} \) in the case of mechanism (1.76), it would be more expedient to use the formula

\[ C_{XX} = \frac{k_1 C_{0A}}{k_1 + k_{-1} + k_2} \exp \left( -k_{eff} t \right), \]  

(1.103)

since the exact solution \( C_A = f(t) \) of the system of differential equations is not equal to \( C_{XX} \) expressed as

\[ C_{XX} = \frac{(k_{-1} + k_2)C_{0A}}{k_1 + k_{-1} + k_2} \exp \left( -k_{eff} t \right). \]

In the case of using a strict solution for \( C_A \) and \( C_X \) in the indicated mechanism, the \( D_R \) criterion is identical to \( D_E \) since

\[ D_R = \frac{C_X}{C_{XX}} = \frac{C_X}{\frac{k_1}{k_{-1} + k_2} C_A} = D_E. \]

Similar to \( D_E \), the \( D_R \) criterion for \( k_{-1} \gg k_2 \) characterizes the approach to a quasi-equilibrium regime. If the concentration \( C_{XX} \) in Eq. (1.102) is replaced by formula (1.103), we obtain a modified Rozovskii criterion \( D_R' \left( D'_R = \frac{C_X}{C_{XX(r)}} \right) \), which differs from \( D_R = D_E \).
1.2.1.6 Interrelation between quasi-steady-state approximation and numerical solutions of the complete system of differential equations

It has been demonstrated that, during a numerical solution of the system of differential kinetic equations by the method of successive approximations (iterative procedure) [56, 61], it is possible to improve the quasi-steady-state description by introducing additional terms. This approach reveals that the quasi-steady-state solution (or solutions) represents the first term in an approximate expansion that can be used for a numerical solution (in the region of establishment of a quasi-steady-state regime for $t > t_{\text{max}}$). Rudakov [57] convincingly demonstrated that the classical Bodenstein method based on the condition of $\frac{dC_i}{dt} = 0$ yields an approximate solution for $k_{\text{eff}}^{SS}$ [see Eqs (1.80–1.82)] that is equivalent to the first term in the expansion of the exact solution (at $t > t_{\text{max}}$) for $k_{\text{eff}}$ into a series in powers of a small parameter $\varepsilon_1 = \frac{k_1}{k_{-1} + k_2}$, and the $C_A, C_X$ and $C_P$ values as given by the following equations:

$$
\begin{align*}
-\frac{dC_A}{dt} &= k_{\text{eff}} C_A; \\
-\frac{dC_X}{dt} &= k_{\text{eff}} C_X; \\
-\frac{dC_P}{dt} &= k_{\text{eff}} (C_{0A} - C_P);
\end{align*}
$$

(1.104)

(1.105)

(1.106)

$$
\begin{align*}
\frac{k_{\text{eff}}}{2} &= \frac{k_1 + k_{-1} + k_2}{2} - \left[ \frac{(k_1 + k_{-1} + k_2)^2}{4} - k_1 k_2 \right]^{1/2}.
\end{align*}
$$

(1.107)

A strict mathematical analysis of the problem of quasi-steady-state was originally performed by Sayasov and Vasil’eva [62] based on the theory of singular perturbed differential equations [63]. According to this approach, the quasi-steady-state hypothesis is justified based on the presence of a small coefficient (parameter) at some derivatives in the system of differential equations (see also [7, 64]). For the reaction under consideration in a closed reactor, the role of this small parameter is played by the above $\varepsilon_1$ value. For example, Eq. (1.84) can be transformed into

$$
\varepsilon_1 \frac{dC_X}{dt} = k_1 (\varepsilon_1 C_A - C_X),
$$

which leads for $\varepsilon_1 \ll 1$ to the following equation:

$$
\varepsilon_1 C_A = C_X.
$$

In the general case, consider a system of differential equations that can be separated into a set of slow motions $\dot{X}_i$ for the concentrations of reactants and products and a set of fast motions $\varepsilon \dot{y}$ for intermediates:

$$
\begin{align*}
\dot{X}_i &= f_i(x, y), \quad i = 1, \ldots, p; \\
\varepsilon \dot{y} &= g_i(x, y), \quad i = 1, \ldots, q.
\end{align*}
$$

(1.108)

If this system transforms for $\varepsilon \to 0$ into a degenerate system such that

$$
\begin{align*}
\dot{X}_i &= f_i(x, y); \\
O &= g_i(x, y),
\end{align*}
$$

(1.109)

then, according to the Tikhonov theorem [63], a solution of system (1.108) tends to the solution of system (1.109) as $\varepsilon \to 0$, provided that the corresponding solution for the set of fast motions $\varepsilon y = g_i(x, y)$ is
robust and the initial conditions occur in the region of attraction of this solution. This theorem is valid for $t \gg \tau$, where $\tau \sim |\varepsilon \ln \varepsilon|$. 

### 1.2.1.7 Small parameters as criteria of the Quasi-steady-state and Quasi-equilibrium approximations

Let us first consider the conditions for attaining the regime of quasi-equilibrium. In the literature, a quasi-equilibrium stage is frequently called pre-equilibrium (PE), that is, a stage preceding the limiting step [65]. This is not a strict term, since in a reversible reaction with one slow (rate-limiting) step, all steps both before and after the limiting step will be fast and quasi-equilibrium [4, 27]. Moreover, the quasi-equilibrium steps can also be involved in multi-route reactions in the absence of a limiting step. For the sake of retaining traditional notation, quantities using the PE index will refer to the quasi-equilibrium steps.

Steps involving the formation of intermediates $X_i$ can be fast and quasi-equilibrium (PE) for both observable and unobservable intermediates. For the reaction mechanism (1.76), the ratio $C_X/C_A = \alpha$ tends to $1 = k_1/(k_2 + k_{1-1})$, and the quasi-equilibrium concentration of $X$ is

$$C_X^{PE} = \frac{K_1}{1 + K_1}(C_{0A} - C_X^{PE}), \quad (1.110)$$

so that

$$\frac{dC_X^{PE}}{dt} = k_2C_X^{PE} = \frac{k_2K_1}{1 + K_1}(C_{0A} - C_P^{PE}) = k_{PE}^{eff}(C_{0A} - C_P^{PE}).$$

It can be readily shown [59] that, under quasi-equilibrium conditions at the first step, the rate of consumption of intermediate $X$ (at $t > t_{max}$ for $C_X$) is

$$-\frac{dC_X^{PE}}{dt} = k_{PE}^{eff}C_X^{PE}.$$ \quad (1.111)

Since we have $C_{0A} - C_P^{PE} \equiv C_X^{PE}$ for large $K_1$ ($K_1 > 10$), it is evident that,

$$\frac{dC_P^{PE}}{dt} \equiv \left| \frac{dC_X^{PE}}{dt} \right|.$$ \quad (1.112)

This is a manifestation of the difference between a quasi-equilibrium regime with observable large $C_X(\alpha > 10)$ and a quasi-steady-state regime. For $K_1 \gg 1$, we obtain $k_{eff}^{PE} = k_2$; while for $K_1 \ll 1$ (unobservable intermediates $X_i$), we have $k_{eff}^{PE} = K_1k_2$, and relation (1.112) is no longer valid. Analogous expressions for $k_{eff}$ are obtained from Eqs (1.78) and (1.80) for $k_{1-1} \gg k_2$. Under these conditions, both quasi-steady-state and quasi-equilibrium regimes can exist. The equality of rates of the first step in the forward and reverse directions essentially implies that we admit the quasi-steady-state approximation with respect to the reactant, that is, $dC_A/dt \equiv 0$ [57]. By analogy with the criterion of quasi-steady-state, one can readily obtain an expression for the quasi-equilibrium criterion $\delta_{PE}$ as

$$\delta_{PE} = \frac{-dC_A/dt}{k_1C_A} = \frac{k_2}{k_1 + k_{1-1} + k_2}. \quad (1.113)$$

Evidently, we have $\delta_{PE} \ll 1$ for

$$\frac{k_2}{k_{1-1} + k_1} = \varepsilon_2 \ll 1.$$
The ratio of constants at which $\varepsilon_2 \ll 1$ provides for a quasi-equilibrium regime. In cases where $\varepsilon_1 \ll 1$ and $\varepsilon_2 \ll 1$, both quasi-steady-state and quasi-equilibrium conditions are satisfied and, hence, the $C_X$ and $C_A$ concentrations correspond to a quasi-steady and quasi-equilibrium state.

Here, it is expedient to consider the problem of reversible fast and slow steps. Under steady-state and quasi-steady-state conditions, the rate of each step is equal to the rate of a single-route reaction (see the condition of the steady state of steps in Section 1.1):

$$W_j^+ - W_j^- = r,$$

or (for a single-route reaction with a nonlinear mechanism)

$$W_j^+ - W_j^- = v_j r.$$

In order to determine the slow and fast steps, the rate of the $j$th step in the forward (or reverse) direction is compared to the value of $r$ (or $v_j r$). If $W_j^+ \gg r$, this step is called fast and quasi-equilibrium so that $W_j^+ \approx W_j^-$. If $W_j^+$ is comparable with $r$ [see Eq. (1.114)], the step is considered as slow (for an irreversible step, $W_j^+ = r$). If there is a single slow step in the mechanism, it is called the rate-controlling or limiting step. The first step is limiting in irreversible reaction provided that $W_1^+ = r$.

The rate of a two-step reaction (1.76) under the quasi-steady-state conditions is given by the formula

$$r = \frac{W_1^+ W_2^+}{W_1^- + W_2^+},$$

If this is supplemented by the condition of quasi-equilibrium ($W_1^+ \gg W_2^+, W_2^+ = r$), then $W_1^- \approx W_1^+$ and

$$r = \frac{W_1^+ W_2^+}{W_1^+ + W_2^+},$$

which implies that

$$\frac{1}{r} = \frac{1}{W_1^+} + \frac{1}{W_2^+},$$

or in the general case (quasi-equilibrium for all $X_i$),

$$\frac{1}{r} = \sum_j \frac{1}{W_j^+},$$

where $r$ is the rate of a single-route reaction (for the overall equation) with a linear mechanism.

An analysis of the relations between constants $k_1, k_{-1}$, and $k_2$ that result in $\varepsilon_1 \ll 1$ and $\varepsilon_2 \ll 1$, led to a conclusion [65] that, at a significant (not less than tenfold) difference in $k_j$, there are only six variants (Nos. I–VI) of relations between constants and four cases of the validity of each or both of the quasi-steady-state ($\varepsilon_1 \ll 1$) and quasi-equilibrium ($\varepsilon_2 \ll 1$) conditions (Table 1.1).

As can be seen, strong conditions determining the implementation of a quasi-steady-state regime are $k_2 \gg k_1, k_{-1}$ (I, II) and $k_{-1} \gg k_1, k_2$ (V, VI), which make $\varepsilon_1 \ll 1$ in the former case the result of a rapid conversion of $X$, and in the latter case due to a quite small $K_1 = k_1/k_{-1}$. There are three variants (I, II, V) that coincide with the “first condition” ($k_2 \gg k_1$) of quasi-steady state according to Rozovskii [53], while variant VI corresponds to the “second condition” ($k_{-1} \gg k_2$) supplemented by the condition $k_{-1} \gg k_1$. Note that writing the second condition as $k_1, k_{-1} \gg k_2$ [53] is incorrect, since the equality of $k_{-1}$ and
Table 1.1  Relationship between rate constants and regimes of process (1.76)

<table>
<thead>
<tr>
<th>Variant No.</th>
<th>Relations between $k_i$</th>
<th>$\varepsilon_1 = \frac{k_1}{k_{-1} + k_2}$</th>
<th>$\varepsilon_2 = \frac{k_2}{k_{-1} + k_1}$</th>
<th>Regime</th>
<th>Limiting step</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$k_2 \gg k_1 \gg k_{-1}$</td>
<td>$\ll 1$</td>
<td>$\gg 1$</td>
<td>SS</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>$k_1 \gg k_{-1} \gg k_1$</td>
<td>$\ll 1$</td>
<td>$\gg 1$</td>
<td>SS</td>
<td>1</td>
</tr>
<tr>
<td>III</td>
<td>$k_1 \gg k_2 \gg k_{-1}$</td>
<td>$\gg 1$</td>
<td>$\ll 1$</td>
<td>PE*</td>
<td>2</td>
</tr>
<tr>
<td>IV</td>
<td>$k_1 \gg k_{-1} \gg k_2$</td>
<td>$\gg 1$</td>
<td>$\ll 1$</td>
<td>PE</td>
<td>2</td>
</tr>
<tr>
<td>V</td>
<td>$k_{-1} \gg k_2 \gg k_1$</td>
<td>$\ll 1$</td>
<td>$\ll 1$</td>
<td>SS, PE</td>
<td>2</td>
</tr>
<tr>
<td>VI</td>
<td>$k_{-1} \gg k_1 \gg k_2$</td>
<td>$\ll 1$</td>
<td>$\ll 1$</td>
<td>SS, PE</td>
<td>2</td>
</tr>
</tbody>
</table>

Note: *Conclusion made in [65]; SS = (quasi)-steady state; PE = quasi-equilibrium (pre-equilibrium).

Table 1.2  Relationship between rate constants and regimes

<table>
<thead>
<tr>
<th>Variant No.</th>
<th>Close parameters</th>
<th>Relations between $k_i$</th>
<th>$\varepsilon_1$</th>
<th>$\varepsilon_2$</th>
<th>Regime</th>
<th>Limiting steps</th>
</tr>
</thead>
<tbody>
<tr>
<td>VII (see I)</td>
<td>$k_1 \approx k_{-1}$</td>
<td>$k_2 \gg k_1 \approx k_{-1}$</td>
<td>$\ll 1$</td>
<td>$\gg 1$</td>
<td>SS</td>
<td>1</td>
</tr>
<tr>
<td>VIII (see IV)</td>
<td>$k_1 \approx k_{-1}$</td>
<td>$k_2 \ll k_1 \approx k_{-1}$</td>
<td>$\approx 1$</td>
<td>$\ll 1$</td>
<td>PE</td>
<td>2</td>
</tr>
<tr>
<td>IX (see II)</td>
<td>$k_2 \approx k_{-1}$</td>
<td>$k_1 \ll k_{-1} \approx k_2$</td>
<td>$\ll 1$</td>
<td>$\approx 1$</td>
<td>SS</td>
<td>1</td>
</tr>
<tr>
<td>X (see III)</td>
<td>$k_2 \approx k_{-1}$</td>
<td>$k_1 \gg k_{-1} \approx k_2$</td>
<td>$\gg 1$</td>
<td>$\ll 1$</td>
<td>PE*</td>
<td>2</td>
</tr>
<tr>
<td>XI (see V, VI)</td>
<td>$k_1 \approx k_2$</td>
<td>$k_{-1} \gg k_1 \approx k_2$</td>
<td>$\ll 1$</td>
<td>$\ll 1$</td>
<td>SS, PE</td>
<td>2</td>
</tr>
</tbody>
</table>

*For $k_1/k_{-1} \geq 100$.

$k_1$ makes the quasi-steady-state regime ($\varepsilon_1 \approx 1$) impossible (see below). The quasi-steady-state regime is possible only provided that $k_{-1} \gg k_1$. This is the only possible variant of a quasi-steady-state regime for $k_1 \gg k_2$. Variant IV is also a non-steady-state regime despite the fact that $k_1, k_{-1} \gg k_2$: this is a quasi-equilibrium regime with the second limiting stage. These conclusions were fully confirmed by the results of computer experiments [59]. Variant III is also a quasi-equilibrium regime ($\varepsilon_2 \ll 1$), but only at a large difference between all constants. At a tenfold difference between constants, the quasi-equilibrium regime in this variant is established later than in other cases, but with a higher yield of product P at the final step. This variant in fact reduces to a process with the irreversible first step under the conditions of almost complete and rapid conversion of A into X, that is, to virtually a single-step conversion reaction (see below).

The aforementioned six special cases are expediently supplemented by the variants of implementation of the quasi-steady-state and quasi-equilibrium regimes under conditions of equal (close) constants. The case where all constants are close ($k_1 \approx k_{-1} \approx k_2$) does not obey the criteria of quasi-steady-state and quasi-equilibrium conditions. The equality of constants in pairs adds five cases (Table 1.2).

In the case of close $k_2$ and $k_{-1}$ values (as well as in variant III), the regime is not strictly quasi-equilibrium (the ratio $C_X/C_A = \alpha$ is not constant during the process). The equality of $k_1$ and $k_2$ (variant XI) ensures (in contrast to the statement made in [53]) the quasi-steady state under quasi-equilibrium conditions ($D_E, D_P \equiv 1, \Delta \equiv 0$) [59].

Thus, the quasi-steady-state regime is attained in the following cases:

- for $k_2 \gg k_1$ (variants I, II, V, VII, VIII, IX);
- for $k_1 \gg k_2$ (variant VI);
- for $k_1 \approx k_2$ (variant XI).

5The expediency of this analysis was pointed out by V.F. Shvets.
The quasi-equilibrium approximation is valid in the following cases:

- for \( k_2 \gg k_1 \) (variant V);
- for \( k_1 \gg k_2 \) (variants IV, VI, VIII and III, X with large values of \( k_1/k_{-1} \));
- for \( k_1 \approx k_2 \) (XI).

Let us consider in more detail a difference between variants of the quasi-equilibrium approximation (see Tables 1.1 and 1.2) that leads to the appearance of \( k_2 \) in the kinetic equation and makes the second step limited in mechanism (1.76). Three variants (V, VI and XI) are characterized by small equilibrium constants \( K_1 \ll 1 \), quasi-equilibrium first stage, quasi-equilibrium low concentrations of X, second limiting step, and the kinetic equation written in the following form:

\[
r = \frac{k_2K_1[A_0 - P]}{1 + K_1} \approx k_2K_1[A_0 - P].
\] (1.120)

Note that, for the indicated variants, the quasi-equilibrium regime is also quasi-steady-state with respect to X.

In two cases (regimes IV and VIII), the quasi-equilibrium concentrations of X are large and the reaction rate is described by the following equations:

\[
r = k_2[A_0 - P]
\] (1.121)

(for variant IV, \( K_1 \gg 1 \), \([A_0 - P] \approx [X]\)) and

\[
r = \frac{k_2K_1[A_0 - P]}{1 + K_1}
\] (1.122)

(for variant VIII, \( K_1 \approx 1 \), \([A_0 - P] \approx [A] + [X]\)).

Variants III and X lead formally to the same result as does variant IV, but the concentrations of X are not quasi-equilibrium. Variant III with \( k_1 \gg k_2 \gg k_{-1} \) \((K_1 \gg 1)\) represents a regime with a fast irreversible first step proceeding under conditions \([A_0 - P] \approx [X]\), followed by the rapid transition to a single-step reaction with the rate given by Eq. (1.121). Variant X with \( k_1 \gg k_2 \approx k_{-1} \) is closer to equilibrium, step (1) is reversible, but the concentration of X is also not quasi-equilibrium. In this case, \( r = k_2[A] \) for \([A] = [A_0 - P] - [X]\).

For a catalytic reaction proceeding under quasi-steady-state conditions \([A] \gg [M]_\Sigma\), where M is a catalyst), according to a two-step scheme

\[
A + M \xrightleftharpoons[k_{-1}]{k_1} X \xrightarrow{k_2} M + P
\]

it is possible to separate three cases (with all constants being different).

**I. Fast reversible step (1) with \( K_1 \ll 1 \) \((k_{-1} \gg k_2 \gg k_1[A] \) and \( k_{-1} \gg k_1[A] \gg k_2 \).**

Here, the limiting step is (2) with

\[
r = k_2K_1[A][M]_\Sigma; [M]_\Sigma \approx [M].
\] (1.123)
II. Fast reversible step (1) with \( k_1[A] \gg k_{-1} \gg k_2 \) or fast irreversible step (1) with \( k_1[A] \gg k_2 \gg k_{-1} \) and \( K_1 \gg 1 \).

Here, the limiting step is (2) with

\[
r = k_2[M]_\Sigma; [M]_\Sigma \cong [X].
\]  

(1.124)

III. Fast step (2) and almost irreversible step (1) with \( K_1 \gg 1 \) \((k_2 \gg k_1[A] \gg k_{-1})\) or \( K_1 \ll 1 \) \((k_2 \gg k_{-1} \gg k_1[A])\).

In this case, the limiting step is (1) and

\[
r = k_1[A][M]_\Sigma; [M]_\Sigma = [M].
\]

Thus, the quasi-equilibrium step (1) as well as a fast irreversible step (1) with \( K_1 \gg 1 \) (case II) lead formally to the same kinetic equation (1.124).

The results presented in Tables 1.1 and 1.2 can be generalized by determining the regions where the reaction proceeds in a quasi-steady-state regime and/or under quasi-equilibrium conditions when constants are varied for preset \( \epsilon_1 \) and \( \epsilon_2 \) values.\(^6\) Equations for \( \epsilon_1 \) and \( \epsilon_2 \) yield the following relations:

\[
\frac{k_{-1}}{k_1} = \frac{1}{\epsilon_1} - \frac{k_2}{k_1} \text{ and } \frac{k_{-1}}{k_1} = \frac{k_2}{k_1} \frac{1}{\epsilon_2} - 1.
\]

For preset \( \epsilon_1 \) and \( \epsilon_2 \) values, these equations determine straight lines that bound the regions of validity of the quasi-steady-state and/or quasi-equilibrium approximations. For example, with \( \epsilon_1 = 0.1 \) and \( \epsilon_2 = 0.1 \) [where \( \epsilon_1 \leq 0.1 \) is the condition for quasi-steady-state (SS) regimes and \( \epsilon_2 \leq 0.1 \) is the quasi-equilibrium (PE) condition], we obtain two straight lines (Figure 1.1) in the coordinates of \( y = k_{-1}/k_1 \) and \( x = k_2/k_1 \).

\[\text{Figure 1.1} \quad \text{Domains of quasi-steady-state (SS) and quasi-equilibrium (pre-equilibrium, PE) regimes for mechanism (1.76)}\]

\(^6\)This analysis was proposed by K.Yu. Odintsov.
In Figure 1.1, a region above the solid line corresponds to quasi-steady states ($\varepsilon_1 \leq 0.1$), while a region on the left from dashed line corresponds to quasi-equilibrium states. A region between these lines above their intersection point corresponds to the validity of both quasi-steady-state (SS) and quasi-equilibrium (PE) approximations.

In [66], the quasi-steady-state condition was considered using the conventional Bodenstein criterion of $dC_{X_i}/dt = 0$, but it was ascertained that the concentrations of intermediates $X_i$ differ only very slightly from the equilibrium values. However, this statement in the general case is incorrect. Small deviations from the equilibrium values of $[X_i]$ take place only in the case of simultaneous validity of the quasi-steady-state and quasi-equilibrium approximations. The condition of quasi-steady-state regimes can be valid far from the equilibrium – and this situation is frequently encountered in practice ($W_j^+ - W_j^- = r$). In this case, Eq. (1.119) is inapplicable and it cannot be considered as a basic result of the quasi-steady-state approximation as stated in [66]. Fully reversible chemical reactions that take place near the equilibrium are very rarely investigated. Note also that a system can occur close to the equilibrium, while not obeying quasi-steady-state criterion, for example, in the case of reaction (1.76) with $K_1 \gg 1$ and large $C_X(C_X/C_A = \alpha > 1)$.

### 1.2.2 Experimental criteria of applicability of quasi-steady-state approximation in various systems

The theoretical criteria of quasi-steady and quasi-equilibrium states provide deeper insight into the nature of these approximations and, if the model constants are known, allow the validity of approximations used for the processing of data to be assessed. On the other hand, for the correct planning and description of a kinetic experiment, it is also important to know the experimental criteria of applicability of the quasi-steady-state approximation.

- The above analysis shows that the necessary and sufficient condition of validity of the quasi-steady-state approximation is expressed by the relations $C_X \ll C_A, C_P$ or
  $$\frac{C_X}{C_A} = \alpha \ll 1.$$  

Equations (1.80)–(1.82) also imply the proximity of the rates of product formation and reactant consumption (for the indicated reaction scheme),
  $$\left| \frac{dC_A}{dt} \right| \cong \frac{dC_P}{dt},$$  

as well as the condition $dC_X/dt \cong 0$ and the validity of criterion $\varepsilon_1 \ll 1$ ($\varepsilon_1 = k_1/(k_{-1} + k_2)$).

Condition (1.125) can be experimentally verified by an analysis of the material balance of the process under consideration:
  $$C_{0A} \cong C_A + C_P.$$  

Violation of the material balance as expressed by an equation of the (1.127) type may be indicative of either the presence of unidentified side products or the deviation from condition (1.125). It should be borne in mind that the employed analytical schemes must ensure the determination of $C_A$ without decomposing $X$ in cases where the formation of $X$ is a reversible step.

As was demonstrated in Section 1.1, the exclusion of concentrations $C_{X_i}$ (of Bodenstein’s intermediates) from the material balance and overall equations (containing only the observable substances) is ensured by the condition of the steady state of steps and the Horiuti stoichiometric rule. Relation (1.126) can also be
quite readily checked by experiment. If this condition is valid over a sufficiently large time interval (e.g.,
corresponding to 70–90% of the product yield recalculated for \( C_{0A} \)) with a preset accuracy, so that the
error \( (\delta) \) defined as

\[
\delta = \frac{\left| \frac{dC_A}{dt} \right| - \left| \frac{dC_P}{dt} \right|}{\left| \frac{dC_A}{dt} \right|} \quad (1.128)
\]
does not exceed the experimental uncertainty (e.g., 5–10%), then it is possible to speak of the applicability
of the quasi-steady-state approximation. It should be noted that criterion (1.128) is applicable to any type
of reaction mechanisms.

- In the case of **homogeneous catalytic reactions** [e.g., such as described by equations (1.90) and
(1.91)], concentration \( C_X \) cannot exceed \( C_{0E} \). For this reason, such systems have to be studied for
\( C_{0A} \gg C_{0E} \). According to Wong’s estimation [56], the error \( \Delta_2 \) of the quasi-steady-state approximation
for \( C_{0A}/C_{0E} > 15 \) does not exceed 1%. For \( C_{0A}/C_{0E} < 10 \), the applicability of this approximation is
doubtful (probably only being valid for very large \( k_2/k_1 \) ratios) and the reaction kinetics should be
described by differential equations.

- In the case of **heterogeneous catalysis** in closed (and open – see, e.g., [7]) systems, the amount of
reactants in the gas phase is usually much greater than the amount (number of moles) of intermediates
(\( C_X^S \)) occurring on the surface of a catalyst and, hence, a regime with \( dC_X^S/dt = 0 \) is also attained.
In this case, the role of a small parameter is played by the ratio

\[
\frac{N_{t_{\text{tot}}}^S}{N_{t_{\text{tot}}}^E} = \varepsilon < 1,
\]
where \( N_{t_{\text{tot}}}^S \) and \( N_{t_{\text{tot}}}^E \) are the total amounts (number of moles) of intermediates on the catalyst surface
and in the gas phase within the reactor volume.

The analysis of **enzymatic reactions** provided additional experimental criterion of the applicability of
the quasi-steady-state approximation. According to Eq. (1.95), there must be a linear relationship between
the reaction rate and the initial concentration of an enzyme. These relations are generally typical of the
enzymatic catalysis [52, 56]. However, on replacing \( C_X^{SS} \) in Eq. (1.95) by \( C_X \) expressed from Eq. (1.93),
we obtain the following equation for the reaction rate:

\[
\frac{dC_P}{dt} = \frac{k_1k_2C_{0E}C_A - k_2\frac{dC_X}{dt}}{k_1C_A + k_{-1} + k_2}, \quad (1.129)
\]
which indicates that the reaction rate in this case is not a linear function of \( C_{0E} \). Although the homogeneous
catalysis encounters many other factors that also lead to nonlinearity of the relation \( r = f(C_{0E}) \), this circumstance
should also be borne in mind when considering the problem of applicability of the quasi-steady-state
approximation. A **linear dependence of the reaction rate on the catalyst concentration is evidence in favor of
the validity of the quasi-steady-state approximation within the limits of experimental errors**.

Kinetic investigations are frequently performed using the **approximation of initial reaction rates** \( (r_i \text{ for } t \to 0) \). These rates are determined from the temporal variation of concentrations \( C_A \) and \( C_P \) and then it
is assumed that the obtained values of \( r_{0A} = \left| \frac{dC_A}{dt} \right|_{t \to 0} \) and \( r_{0P} = \left| \frac{dC_P}{dt} \right|_{t \to 0} \) correspond to a quasi-steady-
state. Since the \( C_X \) value passes through a maximum, and the quasi-steady state is attained for \( t > t_{\text{max}} \) (upon
a certain transient regime), the extrapolation of \( dC_P/dt \) to \( t = 0 \) can lead to an error in determining \( r_{0P} \).
which increases with decreasing $C_{0A}/C_{0E}$ and $C_A/C_E$ ratios. For $C_{0A}/C_{0E} < 10$, the method of initial reaction rates is not recommended for use. For the Michaelis–Menten scheme, the relative error $\delta_C$ due to the neglect of the transient regime depends on the lifetime $\tau$ of intermediate X ($\delta_C = \exp(-t/\tau)$ [56]). A rational method of determining the initial reaction rates $r_{0p}$ for simple mechanisms was proposed by Boeker [67].

1.3 Methods of graph theory in chemical kinetics and in theory of complex reaction mechanisms

The application of the main concepts and methods of graph theory to chemical kinetics and theory of chemical reaction mechanisms in the past five decades constituted a special branch of mathematical chemistry [48, 68, 69] (see also review [6]). Graph-theoretical investigations enable specialists to carry out the following:

(i) construct graphs for reaction mechanisms of any type [48, 68–70] (see also reviews [6, 7]) and reveal the structural (topological) basis of the concept of “reaction mechanism” [8, 72, 73];
(ii) classify, encode, and enumerate the mechanisms of complex reactions [6, 74–79];
(iii) develop a nomenclature of reaction mechanisms [6, 18, 72, 73, 80–83];
(iv) obtain kinetic equations for linear mechanisms under steady-state and quasi-steady-state conditions [6, 7, 15, 70, 76, 84–104];
(v) analyze the identifiability of parameters (and determine the number of independent parameters) for an adopted kinetic model [98];
(vi) study and predict the dynamic behavior and critical phenomena in a system under consideration [7, 98, 105–109];
(vii) assess the complexity of mechanisms [6, 78, 110–112];
(viii) formulate mechanistic hypotheses on graphs [6, 113, 114].

The possibility of applying graphs to the study of mechanisms of complex reactions was originally pointed out by Balandin [80, 115]. Balandin was also the first to apply the elements of topology to reaction mechanisms and proposed the first classification of mechanisms based on their topology [80]. Next, Christiansen [81] used graphs to classify the reaction mechanisms and King and Altman [84] gave a graphical interpretation of the Cramer method for solving systems of linear algebraic equations and used it to derive the kinetic equations of enzymatic processes.

The active use of graphs in chemical and enzymatic kinetics was initiated by Temkin [70] in his work devoted to planar cyclic graphs. Nonplanar graphs were originally used by Balaban et al. [116] for enumerating the possible reactions of isomerization of pentasubstituted ethylcation. At the same time, Volkenstein and Goldstein [86–88] proposed a method (known as the Volkenstein–Goldstein algorithm) for deriving kinetic equations using Temkin’s kinetic graphs (KGS), which was later justified [94] and used to obtain a number of important results for the kinetics of steady-state reactions as described in monographs [6, 7, 98].

1.3.1 Linear mechanisms

As noted above, the class of linear mechanisms contains those for which the reactions of all steps involve no more than one intermediate substance on both the left and right sides of the corresponding equations. The rates of these steps are either independent of or linearly depend on the concentrations of intermediates. Linear mechanisms are naturally described by Temkin’s KGS, the vertices of which represent intermediates and the edges (arcs, links) connecting these vertices correspond to reaction steps. For example, a two-route
mechanism of the catalytic reaction

\begin{align*}
(1) & \quad M + S & \rightleftharpoons MS; \\
(2) & \quad MS & \rightarrow M + P_1; \\
(3) & \quad MS & \rightarrow M + P_2
\end{align*}

(1.130)

(where M is a catalyst) can be presented in the form of KG1 (Figure 1.2), in which directed edges (with arrows) correspond to irreversible reaction steps and undirected edges denote reversible steps. A undirected edge can alternatively be depicted by two oppositely directed edges (variant KG2, Figure 1.2), but – for the sake of simplicity – it is more convenient to use variant KG1 [and bear in mind the reversibility of the corresponding edge (in this case, step 1)]. In the case of noncatalytic reactions, Temkin proposed to use the concept of null-species (0-species) representing a hypothetical intermediate with a concentration equal to unity ([X_0] = 1). Thus, cyclic graphs can be used to represent linear mechanisms of arbitrary complex reactions.

For example, the mechanism

\begin{align*}
(1) & \quad A + B & \rightleftharpoons X_1; \\
(2) & \quad X_1 + C & \rightarrow P_1; \\
(3) & \quad X_1 + D & \rightarrow P_2
\end{align*}

(1.131)

and the equivalent scheme

\begin{align*}
(1) & \quad X_0 + A + B & \rightleftharpoons X_1; \\
(2) & \quad X_1 + C & \rightarrow P_1 + X_0; \\
(3) & \quad X_1 + D & \rightarrow P_2 + X_0
\end{align*}

(1.132)

can be depicted by a graph (KG3, Figure 1.2) with an empty vertex representing null-species X_0.

The mechanisms of both catalytic and noncatalytic reactions can include steps involving the formation of compounds of catalysts and/or intermediates with reactants, products, ligands and other components of the reaction medium, which do not enter into the stoichiometry of overall equations but contribute to the material balance with respect to the catalysts and reactants (see Section 1.1). For example, mechanism (1.130) can be supplemented by the reactions

\begin{align*}
(4) & \quad M + P_1 & \rightleftharpoons MP_1; \\
(5) & \quad M + P_2 & \rightleftharpoons MP_2.
\end{align*}
Such steps and the corresponding compounds are depicted on the graphs by “pendant” vertices, since compounds MP\textsubscript{1} and MP\textsubscript{2} do not belong to intermediates (variant KG4, Figure 1.2).

Using the KGs of linear mechanisms, it is possible to establish the number of linearly independent routes, since the basis set of routes corresponds to the number of linearly independent (simple) cycles of the graph as determined by the so-called cyclomatic number (Euler’s characteristic) \( F \) defined as \[ F = q - \rho + C, \] (1.133)

where \( q = S \) is the number of edges (reaction steps), \( \rho = I \) is the number of vertices (intermediates) (plus an empty vertex with the null-species, where necessary), and \( C \) is the number of graph components (\( C = 1 \) for KGs). Note that Eq. (1.133) is equivalent to Eq. (1.13). In the case of planar graphs (i.e., graphs that can be arranged on a plane), the number of simple cycles is equal to the number of KG faces (e.g., two for KG1 in Figure 1.2).

Possible ways of connecting cycles in KGs (topological characteristics) were used as a basis for the classification of linear multi-route mechanisms, their encoding, and enumeration [6, 74–79]. For example, in cases where the number of linearly independent routes is \( P = F = 2 \), there are only three topologically different ways of connecting cycles (routes) and, accordingly, three classes of mechanisms: class A, whereby cycles are connected by a bridge consisting of one or several steps; class B, in which cycles are shearing a vertex (common intermediate); and class C, in which cycles have one or several common steps (see Figure 1.3, which shows examples with minimum numbers of vertices).

For \( P > 2 \), there appears one more way of connecting cycles – class \( Z \), in which unadjacent cycles are connected via other cycles [6, 78]. In the case of three-route reactions, it is possible to distinguish 15 topologically different classes of graphs based on classes A, B, C and \( Z \) (\( n - A^i B^j C^k Z^v \)):

\[
\begin{align*}
3 - A^2, & 4 - A^2Z, 3 - ABZ, 4 - ACZ, 2 - B^2Z, 3 - BCZ, 4 - C^2Z, \\
2 - A^2B, & 3 - A^2C, 2 - B^2C, 2 - BC^2, 4 - C^3, 4 - A^3, 1 - B^3, 3 - BC^3,
\end{align*}
\]

where \( n \) is the number of vertices with degrees above 2. Tables of graphs with \( P = 2, 3, \) and 4 are presented in [6, 78]. Using this classification, a code has been developed that ensures single-valued identification of KGs.

Now let us introduce some important definitions and consider algorithms developed in order to derive kinetic equations for linear mechanisms based on methods of graph theory. A graph’s cycle is any sequence

![Figure 1.3](image_url) 

**Figure 1.3** Classes of two-route mechanisms
of directed edges that originate from and terminate in the same vertex. A KG cycle corresponds to a cyclic conversion of intermediates. The weight of a cycle is defined as the product of the weights of edges (elementary reactions) entering into this cycle:

\[ C^+ = \prod_j \omega_j; \quad C^- = \prod_j \omega_{-j}. \] (1.134)

It should be recalled that the edge weight (i.e., step weight) is equal to the rate of the \( j \)th step in one direction divided by the concentration of the \( i \)th intermediate participating in this step

\[ \omega_{\pm j} = W^\pm_j/[X_{ij}]. \] (1.135)

Note that, for \([X_i] = [X_0] = 1\), we have \( \omega_{\pm j} = W^\pm_j \). For KG1 and KG2 (Figure 1.2), the weights of cycles, including steps 1, 2 and 1, 3 of mechanism (1.130), are as follows:

\[ C^+_1 = \omega_1 \omega_2; \quad C^+_2 = \omega_1 \omega_3. \]

The directions of cycles on KGs are chosen in accordance with the directions of routes which, in turn, are determined by the directions of steps and the vector of stoichiometric numbers. The directions of two cycles for two routes on KG1 (Figure 1.2) is indicated by arrows.

A tree is any sequence of edges on a graph which contains no cycles. The maximum tree (or frame) is a sequence of edges that passes through all vertices (and contains no cycles). A rooted tree or a tree with root at the \( i \)th vertex (frame of the \( i \)th vertex) is a maximum tree with all edges directed toward \( i \)th vertex. For graph KG5 (Figure 1.4) of a two-route catalytic reaction, the possible rooted trees are presented in Figure 1.5.

Let us define the weight \( D_{ik} \) of the \( k \)th rooted tree at the \( i \)th vertex as a product of the weights of edges entering into this tree:

\[ D_{ik} = \prod_j \omega_j \ (j \in \{i, k\}). \] (1.136)

A root determinant \( D_i \) of the \( i \)th vertex is a sum of the weights of rooted trees (sum of frame weights) at the \( i \)th vertex:

\[ D_i = \sum D_{ik}. \] (1.137)

Several methods have been proposed for determining \( D_i \) (and all \( D_{ik} \)) values [90, 101, 117–120]. A simple algorithm [117, 118] consists of the following operations. First, \( D_i^* \) is determined as a product of

![Figure 1.4](image-url)  
**Figure 1.4** Kinetic graph for a two-route catalytic reaction
the weights of edges originating from all vertices except the $i$th one. For example, for vertex M in KG5 (Figure 1.4) we have

$$D_M^* = (\omega_{-1} + \omega_{-2} + \omega_{3}) (\omega_{-3} + \omega_{4})$$

$$= \omega_{-1} \omega_{-3} + \omega_{2} \omega_{-3} + \omega_{3} \omega_{-3} + \omega_{-1} \omega_{4} + \omega_{-2} \omega_{4} + \omega_{3} \omega_{4}.$$  

Then, a product of the weights of edges that form a cycle (including the product of weights of the forward and reverse steps such as $\omega_{3} \omega_{-3}$) is excluded from $D_M^*$, which yields

$$D_M = \omega_{3} \omega_{4} + \omega_{-1} \omega_{-3} + \omega_{2} \omega_{-3} + \omega_{-1} \omega_{4} + \omega_{2} \omega_{4};$$

$$D_{X_1}^* = (\omega_{1} + \omega_{-2}) (\omega_{-3} + \omega_{4}) = \omega_{1} \omega_{-3} + \omega_{1} \omega_{4} + \omega_{-2} \omega_{-3} + \omega_{-2} \omega_{4};$$

$$D_{X_1}^* = D_{X_1};$$

$$D_{X_2}^* = (\omega_{1} + \omega_{-2}) (\omega_{-1} + \omega_{2} + \omega_{3}) = \omega_{1} \omega_{-1} + \omega_{1} \omega_{2} + \omega_{1} \omega_{3} + \omega_{2} \omega_{-2} + \omega_{2} \omega_{3} + \omega_{3} \omega_{2}.$$  

Finally, cycle products $\omega_{1} \omega_{2}$, $\omega_{1} \omega_{-1}$ and $\omega_{2} \omega_{-2}$, $\omega_{-1} \omega_{-2}$ are removed to leave

$$D_{X_2} = \omega_{-2} \omega_{3} + \omega_{1} \omega_{3}.$$  

A general method for deriving an equation of the rate over route (for an overall equation of this route) for steady-state and quasi-steady-state reactions reduces to obtaining expressions for the concentrations of intermediates $X_i$ by solving a system of linear algebraic equations $B_X^T W_j = 0$ for linearly independent $[X_i]$ (see Section 1.1). This system of equations is solved using the Cramer rule as

$$[X_i] = \frac{\Delta X_i}{\Delta},$$

(1.138)

where $\Delta$ is the determinant of the system of linear algebraic equations (written for the coefficients at the unknowns) and $\Delta X_i$ is a determinant in which the column of coefficients at $X_i$ is replaced by a column of constant free terms.

The diagram method was originally used for determining $\Delta X_i$ and $\Delta$ values by King and Altman [84]. Later, S.J. Mason (see [101, 102]) formulated a general rule that allowed graphs to be used for solving the problems related to linear laws of the $y = ax$ type and the systems of Kirchhoff equations in the theory.
of electric circuits (where \( x \) is the current, \( a \) is the resistance, and \( y \) is the potential difference). In the application to the kinetics of chemical reactions with linear mechanisms, \( x \) is the concentration of the \( i \)th intermediate, \( a \) is the step weight \((a_j^\pm)\), and \( y \) is the step rate \((W_j^\pm)\). The essence of this rule is expressed by the following relation:

\[
\frac{[X_i]}{[X_j]} = \frac{D_i}{D_j}.
\] (1.139)

Volkenstein and Goldstein [86–88] employed an analogy with this rule and used the graphs method to derive kinetic equations for the rate of enzymatic reactions. Yablonsky et al. [7, 94] proved Eq. (1.139) and showed its relationship to the Cramer rule. Upon expressing \( \Delta X \) and \( \Delta \) in terms of step weights and relating these quantities for a catalytic reaction as \( \Delta_x = \Delta_{X_i}^* [M] \) (i.e., explicitly introducing the concentration \([M]\) of a catalyst in KG5), we obtain

\[
[X_i] = [M] \frac{\Delta_{X_i}^*}{\Delta} = [M] \frac{D_i}{D_M},
\] (1.140)

where \( D_i = \Delta_{X_i}^* \) and \( D_M = \Delta \).

Using Eqs (1.138) and (1.140), it is possible to obtain the following relations:

\[
\frac{[X_i]}{[X_j]} = \frac{\Delta_{X_i}}{\Delta_{X_j}} = \frac{\Delta_{X_i}^*}{\Delta_{X_j}^*} = \frac{D_i}{D_j}.
\] (1.141)

For noncatalytic reactions, the concentration of intermediate \( X_i \) is written using the concentration of a null-species at the empty vertex:

\[
[X_i] = [X_0] \frac{D_i}{D_0} = \frac{D_i}{D_0}.
\] (1.142)

If all \([X_i]\) in a catalytic reaction are related to \([M]\), we obtain the following expression for the total concentration of the catalyst:

\[
[M]_\Sigma = [M] \left( 1 + \sum_{i \neq M} \frac{D_i}{D_M} \right) = [M] \frac{\sum_i D_i}{D_M},
\] (1.143)

where

\[
[M] = \frac{[M]_\Sigma D_M}{\sum_i D_i}.
\] (1.144)

Equations (1.143) and (1.144) imply that

\[
[X_i] = \frac{[M]_\Sigma D_i}{\sum_i D_i}.
\] (1.145)

For heterogeneous processes with all \([X_i]\) normalized to \([X]_\Sigma\) and expressed via the surface fractions \( \Theta_{X_i} \), we obtain

\[
\Theta_{X_i} = \frac{D_i}{\sum_i D_i}.
\] (1.146)
Allowance for pendant vertices in the material balance with respect to a catalyst can be made by finding the root determinants for these vertices and including them into $\sum_i D_i$, so that $[\text{M}]_\Sigma$ would also refer to the substances occurring in the pendant vertices. Since the graph edges incident to pendant vertices for steady-state and quasi-steady-state reactions represent equilibrium steps, the second approach consists of introducing a supplementary function $F_i$, called the complexity of an intermediate (or any vertex of a cyclic graph), which is defined as follows [6, 68]:

$$F_i = \frac{|X_i|}{[X_i]} = 1 + \frac{\sum S [X_S]}{[X_i]} = 1 + \sum_S \frac{\omega_S}{\omega_{-S}},$$

(1.147)

where $[X_i] + \sum_S [X_S] = |X'_i|$, $[X_S]$ is the concentration of a compound occupying a pendant vertex linked to the graph by step $S$, and $\omega_S$ and $\omega_{-S}$ are the weights of the edge (step) incident to the pendant vertex and directed from $X_i$ to $X_S$. Evidently, the $\omega_S/\omega_{-S}$ ratio includes the equilibrium constant $K_S$ and the concentrations of reaction participants that enter into $\omega_S$ and $\omega_{-S}$. For vertex M in KG4 (Figure 1.2), we obtain

$$F_M = 1 + K_3 [P_1] + K_4 [P_2].$$

Formula (1.145) can be modified by taking into account that $|X'_i| = [X_i]F_i$, which yields

$$[X_i] = \frac{[M]_\Sigma D_i}{\sum_i F_i D_i}$$

(1.148)

1.3.1.1 Algorithms of deriving kinetic equations for steady-state and quasi-steady-state processes

Relations (1.139) and (1.148) lead to the following expression for the rate of any step in the reaction mechanism:

$$W_j = W_j^+ - W_j^- = \omega_j [X_i] - \omega_{-j} [X_i + 1].$$

For a catalytic reaction, we have

$$W_j = \left[ \frac{\omega_j D_i}{D_M} - \frac{\omega_{-j} D_i + 1}{D_M} \right] [\text{M}]$$

(1.149)

$$W_j = \frac{[\omega_j D_i - \omega_{-j} D_i + 1][M]_\Sigma}{\sum_i F_i D_i}.$$ 

(1.150)

Then, using the condition of the steady-state of steps as expressed by Eqs (1.34) and (1.35), one can readily establish a relationship between the step rate and the rate over a route and thus find $r_p$ [91].

Another algorithm was proposed by Volkenstein and Goldstein [86–88] and modified by Yablonsky et al. [7, 48]. According to this, a step belonging to one of the routes (with $W_j = r_p$) is selected on the graph of a multi-route reaction and the rate of this step is expressed as

$$W_j = \frac{[M]_\Sigma \sum_{n=1}^{K} (C_{pn}^+ - C_{pn}) D_{pn}}{\sum_i D_i}.$$  

(1.151)
(or in terms of $\sum F_i D_i$ in the case of a graph with pendant vertices), where $C_{pm}^\pm$ is the weight of the $n$th cycle over route $P$ involving the $j$th step; $D_{pm}$ is the determinant of a subgraph obtained upon the contraction of the $n$th cycle over route $P$ to one vertex with a root in the vertex obtained upon the contraction; and $K$ is the number of cycles passing through the $j$th step. If the rate over route $P$ is described by a combination of steps rates $W_j$, then Eq. (1.151) is written for all of these steps.

**Example 1.17**

Consider graph KG5 (Figure 1.4) for a two-route reaction with two simple cycles and let these cycles be the basis set. The first route includes steps (1) and (2), while the second route includes steps (1), (3) and (4). It is evident from the graph that $W_2 = r_1$ and $W_4 = r_2$. It is also natural that $W_3 = r_2$, but it is expedient to select irreversible step (4) in order to simplify the considerations. According to the second algorithm based on relation (1.151), we begin with writing the weights of cycles $C_{pm}$ as

$$C_{11}^+ = \omega_1 \omega_2; \quad C_{11}^- = \omega_1 \omega_3 \omega_4; \quad C_{12}^+ = 0; \quad C_{12}^- = \omega_2 \omega_3 \omega_4;$$

$$C_{21}^+ = \omega_1 \omega_3 \omega_4; \quad C_{21}^- = 0; \quad C_{22}^+ = \omega_2 \omega_3 \omega_4; \quad C_{22}^- = 0.$$  

Then we write expressions for the $D_{pm}$ values of subgraphs as $D_{11} = \omega_3 + \omega_4$ (a sum of the weights of trees entering into the vertex obtained upon the contraction of cycle 1), $D_{12} = 1$ (one vertex corresponds to $D_{pm} = 1$), $D_{21} = 1$, and $D_{22} = 1$. Finally, using the values of $D_M, D_{X_1}$ and $D_{X_2}$ determined as described above, we can write the following expressions for $r_1$ and $r_2$:

$$r_1 = \frac{[M] \sum (\omega_1 \omega_2 - \omega_1 \omega_3 \omega_4 - \omega_2 \omega_3 \omega_4)}{\sum D_i}; \quad (1.152)$$

$$r_2 = \frac{[M] \sum \omega_1 \omega_2 \omega_4 + \omega_3 \omega_4}{\sum D_i}; \quad (1.153)$$

$$\sum D_i = D_M + D_{X_1} + D_{X_2} = \omega_2 \omega_4 + \omega_3 \omega_4 + \omega_2 \omega_3 + \omega_3 \omega_4 + \omega_2 \omega_4 + \omega_2 \omega_3 + \omega_1 \omega_4.$$  

For a single-route reaction, the step rate is $W_j = v_s r$. In the case of a linear mechanism, we have all $v_s = 1$ and, accordingly,

$$r = \frac{[M] \sum (C^+ - C^-)}{\sum D_i}. \quad (1.154)$$

It is useful to know that, as pointed out in [7], the cyclic characteristic $C = C^+ - C^-$ in this case corresponds to the law of mass action written for an overall equation of the single-route reaction that is considered as the elementary step. For example, in the mechanism (1.3)–(1.5) with an overall equation of $2A = 2B$, the cyclic characteristic is

$$C = C^+ - C^- = k_1 k_2 k_3 [A]^2 - k_{-1} k_{-2} k_{-3} [B]^2 = k^+ [A]^2 - k^- [B]^2.$$  

Denominators (denoted by $D$ in Section 1.1) in the kinetic equations (1.38), (1.39), (1.45) and the like represent the sums of weights of the corresponding trees ($D = \sum D_i$). In formulas (1.50) and (1.51), denominators $D$ are equal to the determinants of vertices $D_M$ and $D_0$, respectively.
The method of graphs is conveniently applied to single-route reactions with a limiting step (i.e., with all other steps obeying the quasi-equilibrium condition). In this case, the weight of a graph edge corresponding to a quasi-equilibrium step (similar to the case of a graph with edges incident to pendant vertices) is given by the ratio \( \omega_j / \omega_{-j} \). For example, the step

\[
A + X_i \xrightleftharpoons[k_{-j}]{k_j} X_{i+1} + P
\]

is characterized by the following ratio:

\[
\frac{\omega_j}{\omega_{-j}} = \frac{k_j [A]}{k_{-j} [P]} = K_j \frac{[A]}{[P]}
\]

Let us denote the product of edge weights on a path from the \( i \)th to \( k \)th vertex by \( D_{ik} \) and call this value the determinant of the \( k \)th vertex. By definition, determinants of an empty vertex (null-species) and a vertex with the initial catalytically active center are assigned the values \( D_{ii} = 1 \). Consider an example of the mechanism of an enzymatic reaction with two pendant vertices (graph KG6, Figure 1.6), which involves inhibitor E and has a limiting step (3) [100]:

\[
\begin{align*}
E & \xrightleftharpoons[1]{A} \xleftarrow[5]{1} EA & \xrightarrow[2]{B} EAB & \xrightarrow[3]{4} E + P; \\
E & \xrightarrow[1]{5} EI & \xrightarrow[4]{4} EAI
\end{align*}
\]

According to Eq. (1.150), the rate of the reaction of product P formation can be expressed as

\[
r = \frac{[E]_0 \omega_3 D_{EAB}}{\sum D_i F_i} = \frac{[E]_0 \omega_3 D_{EAB}}{D_{EE} F_E + D_{EA} F_{EA} + D_{EAB}}.
\]

Determinants of the vertices in this graph are as follows:

\[
\begin{align*}
D_E &= D_{E \rightarrow E} = (D_E = D_{EE}); & D_{EA} &= D_{E \rightarrow EA} = K_1[A]; \\
D_{EAB} &= D_{E \rightarrow EA \rightarrow EAB} = K_1 K_2[A][B]; & D_{EI} &= D_{E \rightarrow EI} = K_4[I]; \\
D_{EAI} &= D_{E \rightarrow EA \rightarrow EAI} = K_1 K_5[A][I]; & F_E &= 1 + K_4[I]; & F_{EA} &= 1 + K_5[I],
\end{align*}
\]

Figure 1.6  Kinetic graph for scheme (1.156)
where $K_i$ are the equilibrium constants of formation of complexes with catalyst E. Substituting these $D_{ik}$ into formula (1.157) yields

$$r = \frac{k_3 K_1 K_2 [A][B][E]}{1 + K_4[I] + (1 + K_5[I])K_1[A] + K_1 K_2[A][B]}.$$  

(1.158)

Evidently, in the presence of a limiting stage, the kinetic equation can be derived without using $F_i$. In this case, a sum in the denominator of formula (1.157) is replaced by the sum of $D_{ik}$ for all vertices of the given graph ($\sum D_{ik}$), including the pendant vertices:

$$\sum D_{ik} = \Sigma D_i F_i.$$  

Taking into account the quasi-equilibrium character of all steps except (3), the three-step mechanism (1.156) can be reduced to a two-step mechanism

$$A + B + E \rightleftharpoons EAB \rightarrow P + E$$  

(1.159)

represented by a graph with three pendant vertices corresponding to the formation of compounds EA, EI and EAI from E (KG7, Figure 1.7). In this case, we can obtain an equation that is equivalent to (1.158) with different $K_i$ that are related to the constants entering into (1.158).

Methods that can be used to simplify the reaction schemes with quasi-equilibrium steps were proposed in [89, 100]. Graphs were also used to find relationships between the equilibrium constants and complexity

$$F = \frac{[M] \Sigma}{[M]} = \sum D_i$$

during the analysis of complicated systems of equilibrium complex formation reactions [122] and to describe the kinetics of non-steady-state reactions [123, 88]. However, the latter approach, based on the Laplace–Carson transform, did not receive further attention—probably because of a considerable difficulty in the transition from reaction rate images to originals in the case of graphs with more than three vertices.

### 1.3.2 Nonlinear mechanisms

In the graphs of linear mechanisms, the vertices of two intermediates (including a null-species) are connected by an edge (reaction step). Relations between elements of a set, in which the elements appear
in pairs, are called binary relations. Any edge on a graph determines a pair of vertices. However, if a mechanism is nonlinear, binary relations are not valid and, for example, a step of the type

\[ X_1 + X_2 \rightarrow 2X_3 \]  

(1.160)
cannot be presented on a KG according to the above approach. In this situation, Temkin [27] suggested using supplementary edges (dashed lines on KGs), but the choice of main and supplementary edges was arbitrary [71]. There are many alternative variants of describing nonlinear mechanisms (see, e.g., [6, 71]), but the author believes that the most convenient approach to the representation of any mechanisms is that employing bipartite graphs (BGs). BGs were originally used by Balandin [80], Volpert [105], and Clarke [106, 107].

The BG of a reaction mechanism is constructed as follows. Each substance is represented by a vertex of type \( w \) and each elementary reaction (step) is represented by a vertex of type \( u \). Reversible steps are represented by two mutually reciprocal elementary reactions and, accordingly, depicted by two vertices \( u_j \). Thus, the set of vertices is subdivided into two subsets, each containing the vertices of one (\( w \) or \( u \)) type. Vertices of one subset are non-adjacent, while vertices \( w_i \) and \( u_j \) are adjacent.

The multiplicity \( (m) \) of an edge of a BG is defined as the stoichiometric coefficient of the \( i \)th substance in the \( j \)th reaction step. If vertices of the \( w \) type are depicted by open symbols (circles with indicated substance) and the \( u \) type vertices are depicted by black symbols (e.g., squares), then an elementary reaction (step) can be represented by a graph (Figure 1.8) with all directed edges (also called segments). Segments \([X_1, u]\) and \([X_2, u]\) reflect the participation of species \( X_1 \) and \( X_2 \) in step \( u \) on the left of the arrow, while segment \([u, X_3]\) corresponds to the formation of substance \( X_3 \) via reaction \( u \). The multiplicity of an edge, which is equal to the stoichiometric coefficient of a substance (e.g., \( m = 2 \) for \( X_3 \)) can be indicated either by writing the stoichiometric coefficient at the corresponding arrow

\[ \circ \rightarrow \overset{2}{\bullet} \rightarrow X_3 \]

or by using the corresponding number of arrows [124]:

\[ \circ \rightarrow X_3 \quad \text{or} \quad \circ \equiv X_3 \]

A reversible reaction is represented by two vertices \( (u_j \) and \( u_{-j} \)) and, hence, depicted by two graphs with opposite directions of arrows. The cycles on BGs can be either directed or undirected. The directed cycles (with the arrows in all segments pointing in the same direction) are called circuits. All cycles (including circuits) of a BG contain even numbers of segments.

![Figure 1.8 Elementary step (1.160)]
Assuming that elementary reactions are predominantly mono- and bimolecular (see Section 1.4), we can separate nine types of elementary reactions that are distinguished by their stoichiometry [6]:

(1) \( A \rightarrow C \);

(2) \( A \rightarrow 2C \);

(3) \( 2A \rightarrow C \);

(4) \( 2A \rightarrow 2C \);

(5) \( A \rightarrow C + D \);

(6) \( 2A \rightarrow C + D \);

(7) \( A + B \rightarrow C \);

(8) \( A + B \rightarrow 2C \);

(9) \( A + B \rightarrow C + D \).

Graphical representations of these reactions are shown in Figure 1.9. For example, reaction (7) involving intermediates \( X_i \) can be depicted as follows:

(10) \( A + B \rightarrow X_i \);  

(11) \( A + X_i \rightarrow X_j \);  

(12) \( A + X_j \rightarrow C \);  

(13) \( X_i + X_j \rightarrow C \);  

(14) \( X_i + X_j \rightarrow X_k \).

Figure 1.10 shows a BG for the typical mechanism of a catalytic reaction with irreversible steps:

\[
A + M \xrightarrow{(1)} MA; \\
B + M \xrightarrow{(2)} MB; \\
MA + MB \xrightarrow{(3)} 2M + P. 
\]

BG is essentially the reaction network of a given mechanism, which includes all substances and reaction steps and reflects all relations between substances. The mutual one-to-one correspondence between stoichiometric matrices \( B_m \) and BGs was proved in [6, 125]. Sakamoto et al. [124] developed an algorithm of writing a set of differential equations for a given BG. By analogy with a Temkin’s KG, it is possible to construct a BG that images a given mechanism in the space of intermediates and is equivalent to the \( B_X \) matrix of this mechanism [6, 125].
Let us remove from graph BG1 the vertices corresponding to the substances (A, B, P) that enter into overall equations and also remove the corresponding incident edges (segments ([A, 1], [B, 2], [3, P]) (Figure 1.10, left). The obtained graph $BG_X1$ (Figure 1.10, right) is called a bipartite network or subnetwork of intermediates. Note that vertices A and B are characterized by zero in-degrees, while vertex P has zero out-degree. Let us consider some other examples of BGs. Figure 1.11 shows graphs BG2 and $BG_X2$ for mechanism (1.21) with three irreversible steps, where A is $RC\equiv CH$ and P is $RC\equiv CCl$. Upon removal of the terminal vertices of reaction participants (A, CuCl$_2$, HCl and P), we obtain graph $BG_X$ of the subnetwork of intermediates. Removal of the CuCl vertex that corresponds to a dual species of intermediate and product (see Example 1.3) yields graph $BG_X2$.

Figures 1.12 and 1.13 show graphs BG3 and $BG_X3$ for the mechanism (1.53) of vinyl chloride synthesis with the participation of two catalysts. As can be seen, graphs representing a subnetwork of intermediates reveal a topological structure of mechanisms and their features that can serve as criteria for classification. Indeed, $BG_X1$ is a cyclic graph with two circuits and contains no pendant vertices of the $u$ type (catalytic reaction), whereas $BG_X2$ is a noncyclic graph with a linear topology and pendant vertices $u_1$ and $u_3$ (noncatalytic reaction). The mechanisms of chain reactions can also differ by the presence of circuits and pendant vertices of type $u$ (mixed topology).

A useful concept for the classification of mechanisms on the topological basis is provided by a *simple submechanism of the network of intermediates* [6, 7, 18, 72, 73]. A submechanism of a reaction mechanism
is defined as a subset of the steps of this mechanism, for which a vector \( \nu_j \) can be found that has no zero components. Submechanisms correspond to subgraphs \( BG_X^* \) of graph \( BG_X \). The set of submechanisms (subgraphs \( BG_X^* \)) is obtained as a result of decomposition of the reaction mechanism on the space of intermediates. Since the number of subgraphs is finite, the number of submechanisms (in contrast to the number of routes) corresponding to a fraction of subgraphs is also limited (finite). Submechanisms that cannot be further subdivided into two (or more) simpler ones are called simple submechanisms (SSMs). The set of such SSMs is an important characteristic of both BGs and KGs. Special software (GERM) for finding SSMs was developed in [125]. Figure 1.14 shows the subgraphs for four SSMs of graph \( BG_X^3 \) for the aforementioned mechanism (1.53). As can be seen, all these SSMs contain circuits. SSM1–SSM3 represent routes of the vinyl chloride formation and SSM4 is an empty route. The elementary reaction steps \((u_1, u_2)\), \((u_3, u_4)\), \((u_{-1}, u_4, u_5)\), and \((u_1, u_{-3}, u_5)\) enter into SSM1–SSM4 with the vectors of stoichiometric numbers containing only positive components.

The number of steps \( S_{SSM} \) in an SSM is given by formula

\[
S_{SSM} = \text{rank} B_X(\text{SSM}) - 1,
\]

where \( B_X(\text{SSM}) \) is the matrix of stoichiometric coefficients for the intermediates entering into the SSM [125]. The topological characteristics of SSMs and their relationships in \( BG_X \) constitute a basis for the classification of reaction mechanisms [16, 18, 72, 73].
1.3.3 Other fields of application of kinetic and bipartite graphs in chemical kinetics and in theory of complex reaction mechanisms

In the context of an analysis of the identifiability of parameters of kinetic models (see Section 1.1), Yablonsky et al. [48] proposed an algorithm for determining the number of independent parametric functions for linear mechanisms on KGs. This algorithm is based on determining the “color” of KG trees. According to this, colored steps are defined as those involving one of the observed substances – initial reactants or products if the corresponding reactions are reversible (on KGs, the weights of these steps include the concentrations of reaction products). Uncolored steps are those in which the observed substances do not interact with intermediates (\(X_i \rightarrow X_k\), \(X_i \rightarrow X_k + P\)). The uniformity of the weights of steps (like colors of the graph edges) result in some trees being similar (having the same sets of colors). The tree color is characterized by a set of figures indicating the number of edges with the same color. An analysis of the sets of these values (assigned according to certain rules) allows one to determine the numbers of trees of different colors among real trees of the KG – that is, the number of independent parametric functions. Using this approach, interesting laws have been established that relate the coloration of KG edges to the structure of a kinetic equation for single-route mechanisms, i.e., to the form of terms \((\Sigma D_i)\) in the denominator of the kinetic equation [48].

Let us consider the application of the graph-theoretical approaches to assessing the complexity of reaction mechanisms. The notion of complexity in this context belongs to intuitively determined properties. In its application to the theory of complex reaction mechanisms, it would be expedient to speak of the complexity of a kinetic equation (and the whole kinetic model), which would determine the probability of identifying the model from experimental data and the possibility of evaluating the model parameters. The complexity of a model is intuitively taken into account in the stage of discrimination between a set of hypothetical mechanisms, the simplest of which are considered first. Evidently, the complexity of a kinetic model in this sense depends on the numbers of intermediates, colored and uncolored steps, routes, and pendant vertices and on the ways of connecting routes (i.e., on the class of the mechanism).

It was suggested to characterize the complexity of linear mechanisms (as the complexity of a kinetic model of a steady-state multi-route reaction [6, 78, 110, 111]) in terms of the complexity index \(E\) (kinetic index). This value is determined by counting the numbers of weights (or rate constants) of steps in the
fractional rational expressions for the rates over routes, obtained using the algorithm of Yablonsky et al. [7, 48] (Eq. (1.151)). According to this, the complexity index is calculated using the following formula:

\[ E = P(I - 1)T^d_p + I \sum_{p=1}^P T^n_p, \]  

(1.162)

where \( P \) is the number of linearly independent routes (KG cycles), \( I \) is the number of intermediates (graph vertices), \( T^d_p \) is the number of trees contributing to the denominator (\( \Sigma D_i \)) of the kinetic equation, and \( T^n_p \) is the number of trees in the specific subgraphs contributing to the numerator (\( D_{pk} \)) of the kinetic equation. The second term in expression (1.162) can be calculated using the following relation:

\[ I \sum_{p=1}^P T^n_p = 2I \sum_{p=1}^P \sum_{k=0}^{k_{\text{max}}} D_{pk}, \]  

(1.163)

where \( k \) is the number of a cycle passing through the step, the rate of which is equal to the rate over route \( \nu^{(p)} \). Expressions for calculating the \( T^d_p \) and \( T^n_p \) values without the derivation of kinetic equations are given in [6, 111].

An increment \( \Delta E \) in the complexity index due to the appearance of pendant vertices in the KG of a mechanism can be evaluated as

\[ \Delta E = P(I - 1) \sum_{i=1}^I T_i P_i, \]  

(1.164)

where \( T_i \) is the number of trees at the \( i \)th vertex of the initial KG without pendant vertices and \( P_i \) is the number of pendant vertices at the \( i \)th vertex of the KG.

A detailed analysis of the effect of the numbers of routes and vertices, the ways of connecting routes, and the class of a mechanism on the \( E \) value was performed in [6, 8, 78, 111]. The influence of the topological structure of a mechanism on the complexity of a kinetic model was clearly illustrated [8] in the case of three-route mechanisms with the KGs depicted in Figure 1.15, which are characterized by the same numbers of vertices (\( I = 4 \)) and steps (\( S = 6 \)). The reaction rate over route I of the catalytic reaction mechanism of class \( B^3 \) according to formula (1.151) is

\[ r^{(1)} = \frac{[\mathcal{K}] \Sigma (C_{10}^+ - C_{10}^-)D_{10}}{\sum D_i}. \]  

(1.165)

Figure 1.15 Kinetic graphs for three-route mechanisms of classes \( B^3 \) and \( C^3 \).
In the more general form, this expression can be written as follows [7]:

\[ r^{(1)} = \frac{[\mathcal{K}]_{\Sigma} W_{I} P_{I}}{\sum D_{i}}, \tag{1.166} \]

where \( W_{I} \) is the cyclic characteristic of route I (\( W_{I} = C_{10}^{+} - C_{10}^{-} \)) and \( P_{I} \) is the conjugation parameter (root determinant of cycle I). For the given mechanism, \( D_{10} = P_{I} \), \( [\mathcal{K}]_{\Sigma} \) is the total catalyst concentration, \( W_{I} = \omega_{1} \omega_{2} - \omega_{-1} \omega_{-2} \), and \( P_{I} = (\omega_{4} + \omega_{-5})(\omega_{6} + \omega_{-5}) \).

The value of index \( \mathcal{E}^{*} \) calculated for one route using formula (1.166) is \( \mathcal{E}^{*} = 128 \). If the concentration \( [\mathcal{K}] \) of the free catalyst is known, the equation for \( r_{1} \) can be written in a simpler form as

\[ r^{(1)} = \frac{[\mathcal{K}]_{\Sigma} W_{I} P_{I}}{D_{1}}, \tag{1.167} \]

where \( D_{1}^{(1)} \) is the root determinant of vertex 1 (calculated for cycle I only). In this case, the equation includes only the weights of route I, so that \( \mathcal{E}^{*'} = 6 \) (the complexity index for the first route kinetic equation with the free catalyst concentration \( [\mathcal{K}] \)).

Now let us turn to the mechanism of class C\(^{3}\). Owing to a strong conjugation of routes (due to the presence of common steps), formula (1.151) takes the following form:

\[ r_{1} = \frac{[\mathcal{K}]_{\Sigma} (W_{I} P_{I} + C^{*})}{\sum D_{i}}, \tag{1.168} \]

where \( C^{*} \) is the conjugation factor calculated as

\[ C^{*} = \sum_{l \neq I} W_{l} P_{l} \]

(the sum is taken over all cycles except I, which include step 2 belonging to route I only) and \( P_{I} \) is the value determined for a subgraph with root in cycle \( l \). In this case, \( \mathcal{E}^{*'} = 256 \). It is important to note that, in strongly conjugated mechanisms (including classes C and Z), even the use of an equation with the free catalyst concentration

\[ r_{1} = \frac{[\mathcal{K}] (W_{I} P_{I} + C^{*})}{D_{1}} \tag{1.169} \]

leads to \( \mathcal{E}' = 112 \) (cf. \( \mathcal{E}' = 6 \) for the above mechanism of class B\(^{3}\)). For the complete kinetic model, the complexity index calculated using formula (1.162) for the mechanism of class C\(^{3}\) is \( \mathcal{E} = \mathcal{E}^{*} \times 3 = 768 \).

The index of complexity of a mechanism, which is applicable to the mechanisms of any type (represented by both KGs and BGs) was constructed based on calculations of the information content of the stoichiometric matrix of a given mechanism and stoichiometric matrices of SSMs [112]. The information content index \( I_{\text{mech}} \) takes into account that the complexity of a mechanism increases with growing numbers of steps, and intermediates, the number, dimension, and degree of conjugation of SSMs, and the variety of the types of nonlinear steps. Therefore, it can be expected that the so defined \( I_{\text{mech}} \) value would also be correlated with the complexity of a kinetic model. Indeed, for the mechanisms of classes B\(^{3}\) and C\(^{3}\) (Figure 1.15), \( I_{\text{mech}} = 589.14 \) and 1870.7, respectively [112].

The application of bipartite and other types of graphs to an analysis of the dynamic behavior of reacting systems (multiplicity of steady states, self-sustained oscillation regimes, etc.) will be considered in Chapter 6. Chapter 7, which is devoted to the problems of selecting a rational strategy in the investigations of reaction mechanisms, will also consider the use of KGs and BGs in formulating hypotheses of the mechanisms of catalytic reactions [6, 113, 114].
1.4 Elementary steps – Selection rules

Notions concerning the nature of elementary steps of a chemical reaction and the meaning of a concept of the “reaction mechanism” were formed during the accumulation and generalization of chemical knowledge and the development of a theory of elementary reactions. Steps which had been considered elementary at a certain stage of the development of chemistry proved later to be complex, consisting of still simpler reactions. Evidently, this process will continue, as the methods of detecting short-lived reactive species become more and more perfect. On the other hand, it should be borne in mind that very fast processes involving such species, which occur beyond the limiting step in single-route reactions, may no longer influence the kinetic laws of the overall process and, hence, can be ignored in constructing an adequate kinetic model.

In any case, in writing a reaction mechanism or formulating a set of hypothetical mechanisms, it is necessary to take into account the main theoretical concepts (postulates, laws, principles) and heuristic rules that can elucidate the nature of a particular reaction, i.e., to assess the level of confidence in classifying one or another reaction into elementary steps. Naturally, in assessing this probability, it is important to predict the possible kinetic behavior of the proposed elementary step and estimate whether the rate of this step is acceptable for the overall reaction. A quantitative answer to this question is provided by laborious quantum-chemical calculations, which are especially difficult for catalytic reactions with heavy metal atoms contained in intermediate species. Nevertheless, these calculations are now actively used in the catalysis with metal complexes and even in heterogeneous catalysis (see Chapter 7). In addition to model calculations, quantitative estimations can also be provided by experimental data on the kinetics of elementary steps, but the amount of such information in the catalysis with metal complexes is still very small. For this reason, considerable help in this respect is offered by the simple heuristic rules and generalizations that shed light on the expected kinetic characteristics of elementary steps. If a proposed mechanism involves a stage that appears to be a block of elementary steps, this possibility has also to be substantiated.

There are numerous monographs and handbooks that summarize the following principal theoretical notions concerning the elementary steps of chemical reactions:

- theory of collisions in gases [58, 126–130];
- theory of collisions in liquids [130–132];
- theory of activated complex (or transition-state theory) [50, 58, 127, 130, 133];
- quantum-mechanical theory of reactions in polar liquids [131, 134–136];
- quantum-mechanical selection rules for elementary steps [137–139];
- topological selection rules for elementary steps [6, 77].

It is expedient to begin considering problems related to the elementarity of steps and the main rules of selecting these steps with an analysis of the main concepts of chemical kinetics.

1.4.1 Main postulates, laws, and principles

A very important concept, and one of the main parameters in chemical kinetics, is the concentration of molecules or other particles involved in a reaction. The concentration \( C_i \) is defined as the number of molecules (particles) or moles of the \( i \)th species per unit volume. The number of particles must be sufficiently large so that it would be possible to treat the concentration, using the laws of statistics, as an averaged quantity that is the same in any part of the reaction volume. The statistical character of the concentration and the statistical independence of all particles are also closely related to the fact that a large number of both identical and different particles randomly colliding with each other are involved in the mutual energy exchange. The resulting distribution of particles with respect to their internal degrees
of freedom (energies) and translational velocities (Maxwell–Boltzmann distribution, MBD) leads to the establishment of a statistical (thermodynamic) equilibrium between excited states. These systems are characterized by a single value of the temperature as a parameter determining this distribution. The time of establishment of the thermal equilibrium is shorter than the characteristic times of excited particle formation and disappearance.

The Boltzmann law of the distribution of molecules (particles) with respect to their energies determines the relative fraction \( \frac{N_i}{N} \) of these particles occurring in the \( i \)th state with energy \( E_i \):

\[
\frac{N_i}{N} = \frac{\exp(-E_i/kT)}{Q},
\]

where \( Q \) is the sum over states (statistical sum, partition function) defined as

\[
Q = \sum_i \exp(-E_i/kT)
\]

and \( T \) is the absolute temperature. The Maxwell law of the distribution of molecules with respect to their velocities is expressed as follows:

\[
\frac{dN(v)}{N} = A \exp\left(-\frac{mv^2}{2kT}\right) v^2 dv,
\]

\[
f(v) = A \exp\left(-\frac{mv^2}{2kT}\right),
\]

where \( v \) is the velocity of a molecule, \( m \) is its mass, \( A \) is a constant factor at \( T = \text{const} \), and \( f(v) \) is the velocity distribution function.

If chemical reactions do not violate the thermal equilibrium, that is, the reactions proceed for a time that exceeds the time necessary for the MBD to establish, the reaction kinetics is called equilibrium [130, 127, 140]. These are the reactions in gases at \( T < 1000–1200 \, ^\circ \text{C} \), in solutions, and on solid surfaces. In the liquid phase, the efficiency of MBD establishment increases due to the collisions between reaction participants and intermediates with solvent molecules. The kinetics of all the reactions considered in this book refers to the region of equilibrium (in the above sense) kinetics. The science of nonequilibrium kinetics studies the photochemical and plasmachemical reactions and the combustion and explosion processes, in which definite quantum states of the reactants and reaction products are taken into consideration [140], whereby the molecules in several energy states can simultaneously participate in both the chemical reactions and physical energy transfer processes.

The interaction between several particles (reactant molecules) with the formation of species called reaction products, which proceeds by surmounting a single potential barrier, is referred to as the elementary act of chemical reaction. Being multiply repeated with a large number of molecules, these acts lead to the formation of a measurable amount of products that is called elementary reaction or elementary step. The stoichiometry of the elementary act and step are naturally the same, for example,

\[
A + B \longrightarrow P.
\]
is $1.5kT$. It is commonly accepted that, when the energy of atomic collisions exceeds the average energy of thermal motion ($E > 2kT$), a chemical compound is formed that is characterized by a minimum on the potential energy surface. Thus, if compounds (AB) with $\Delta E > 2kT$ ($\sim$1200 cal/mole) do not appear on the passage from reactants (A, B) to products (P) along the reaction variable trajectory on the potential energy surface, we can speak of the elementary act (1.173) of the product P formation with a single potential barrier along the reaction coordinate. A reaction that is reverse to (1.173) also proceeds along the reaction trajectory via the same saddle point (barrier), but in the reverse direction (starting from P). The elementary reaction act or step is alternatively called the consistent reaction.

In some cases, bimolecular reactions of the type (1.173) or
\[
A + B \longrightarrow C + D \tag{1.174}
\]
are considered as reactions proceeding via the formation of a long-lived excited state [130]
\[
A + B \iff AB^* \rightarrow P_i
\]
with a minimum on the potential energy surface, which corresponds to an AB* associate. Using this approach, it is possible to use methods of the theory of monomolecular reactions (AB* conversion) for calculating the rate constants. However, in this case, we are not dealing with an elementary step, since the reaction proceeds via two potential barriers and is represented by a block of two elementary steps.

A change ($\Delta n_i$) in the amount (number of moles) of the $i$th participant of a step (or the overall reaction equation, see Section 1.1) as a result of the chemical reaction is determined by the rate of formation or consumption (variation of the concentration $n_i$) of this species, the reaction time $t$, and volume $V$, so that $\Delta n_i = f(r_i, t, V)$. Therefore, the reaction rate $r_i$ for this substance is given by the second-order derivative of $n_i$ with respect to $V$ and $t$ [19]:
\[
r_i = \frac{\partial^2 n_i}{\partial V \partial t}. \tag{1.175}
\]
If $r_i$ is the same over the entire volume and $V = \text{const}$ (closed system), then $\Delta n_i \propto V$ and the differentiation with respect to $V$ can be replaced by the division as
\[
r_i = \frac{dn_i}{Vdt} = \frac{dC_i}{dt}. \tag{1.176}
\]
If the reaction proceeds in the open system in a steady-state regime, then $\Delta n_i \propto t$ and the differentiation with respect to time can be replaced by the division as:
\[
r_i = \frac{dn_i}{idV} = \frac{dF_i}{dV}, \tag{1.177}
\]
where $F_i$ is the molar flux ($n_i/t$). Should both these conditions be satisfied (as in gradient-free, continuous-flow ideally stirred-tank reactor, CSTR), then
\[
r_i = \frac{n_i}{V} \quad \text{or} \quad r_i = \frac{\Delta F_i}{V}. \tag{1.178}
\]
The rate of the $j$th step $W_j$ at $V = \text{const}$ is a derivative of the extent of reaction (or chemical variable) $\xi_j$ with respect to the time per unit volume:
\[
W_j = \frac{d\xi_j}{Vdt}, \tag{1.179}
\]
where $\xi_j = \Delta n_i / \beta_i$, from which it follows that
\[
W_j = \frac{dC_i}{dt} \cdot \frac{1}{\beta_i} = \frac{1}{\beta_i} r_i. \tag{1.180}
\]

Let us consider the assumptions, laws, and heuristic rules underlying the theory of elementary reaction steps. The most important laws and postulates in the chemical kinetics are as follows [127, 140].

- **Conservation of mass and elements in the course of chemical reaction.** These laws are expressed as
  \[
  \beta_i \times M_i = 0; \tag{1.181}
  \]
  \[
  \beta_i \times H = 0, \tag{1.182}
  \]
  where $\beta_i$ is the row-vector of stoichiometric coefficients of the reaction participants, $M_i$ is the column-vector of their molecular masses, and $H$ is the atomic (molecular) matrix (see Section 1.1). The mass defect that arises due to the energy evolution or absorption in the course of chemical reactions is negligibly small and can be ignored.

- **Law of energy conservation.**

- **Law of mass action.** According to this law (Guldberg–Waage, Van’t Hoff), the rate of an elementary step in a certain direction is proportional to a product of the concentrations of reactants in powers corresponding to the stoichiometric coefficients in the step rate equation
  \[
  W^+ = k^+ \prod C_i^{\beta_i}. \tag{1.183}
  \]
  For example, in the case of reaction (1.173), we have
  \[
  W^+ = k^+ C_A C_B,
  \]
  where $k^+$ is the rate constant (specific rate at $\prod C_i^{\beta_i} = 1$). The sum of $\beta_i$ corresponds to the molecularity of reaction, while the exponent $\beta_i$ is called the reaction order. In the case of elementary steps, the total order coincides with the molecularity. Other models proposed for description of the elementary step rate (e.g., de Donde’s model, see [7, 127]) did not receive further development in the chemical kinetics.

- **Necessity of collisions between particles (molecules) for chemical transformation.** Even in the case of monomolecular reactions, all theories [129] are based on the Lindemann–Christiansen scheme, according to which a molecule of reactant A in the reaction $A \rightarrow B$ gains an energy that is necessary for its conversion into B as a result of collisions with any molecules M (inert gas, product, or reactant):
  \[
  A + M \xrightleftharpoons[k_{-1}]{k_1} A^* + M; \quad A^* \xrightarrow[K_2]{k_{-1}} B.
  \]
  In the case of a quasi-steady-state process with respect to $[A^*]$, the rate of this conversion is
  \[
  r = \frac{k_1 k_2 [A][M]}{k_{-1} [M] + k_2}. \tag{1.184}
  \]
  For large concentrations (high pressures) of M, we have $k_{-1} [M] \gg k_2$, so that
  \[
  r = \frac{k_1 k_2 [A]}{k_{-1}}.
  \]
At low concentrations of M, the first step with second-order kinetics in the forward direction becomes the limiting step. Since the probability of collisions of two molecules \( z_B^0 = 10^{-10} - 10^{-11} \text{cm}^3/\text{s} \) is significantly greater than that of triple collisions \( z_T^0 = 10^{-33} - 10^{-35} \text{cm}^6/\text{s} \), the probability of trimolecular reactions is low. In known examples, the trimolecular reactions predominantly take place due to combinations (blocks) of bimolecular elementary steps.

Simple considerations based on the theory of gas phase collisions lead to the first, very important, selection rule that is applicable to both gas and liquid phases, according to which the molecularity of elementary steps does not exceed 2 \((\mu \leq 2)\).

Particles in the gas phase exhibit collisions over the entire volume, while molecules in the liquid collide only within a free volume of a cage of solvent molecules. In the first sphere of this cage, a molecule of reactant A is surrounded by 10–12 solvent molecules. In order to collide under these conditions, molecules A and B must initially diffuse from individual solvent cages \( A_{\text{sol}} \) and \( B_{\text{sol}} \) to a common cage \( (AB)_{\text{sol}} \), that is, to form a so-called diffusion pair. Since the free volume \( V_f \) of a cage amounts to 0.2–2 % of the corresponding solvent volume \([130]\), the frequency of collisions within the cage is greater than in the volume of a gas phase. The experimental ratio \( k_{\text{liq}}/k_{\text{gas}} \) of the rate constants for the same bimolecular reaction in nonpolar solvents amounts to 10–150. Apparently, the probability of collision for three molecules in the cage will not be significantly greater than in the gas phase, whereas the probability of formation of a diffusion triad in one cage is much smaller than that for a diffusion pair.

In the reactions of complex molecules such as enzymes, the molecularities of separate steps also do not exceed 2. However, in the case of enzymatic catalysis, the active site of an enzyme can admit multicenter binding and the simultaneous participation of a greater number (e.g., three or four) of active groups in the reaction. Thus, while the reaction with respect to the enzyme–substrate \((ES)\) complex is, for example, bimolecular \((ES + H_2O)\), the cavity of the active site can feature a multicenter process. A strong drop in the entropy of activation in this case is compensated by an increase in the entropy due to a change in the tertiary structure of a protein and its dehydration as a result of the reconstruction caused by the ES complex formation.

- **Principle of microscopic reversibility.** This principle stipulates the reversibility of any elementary act or microscopic process on a molecular level. Upon attaining equilibrium, the sum of elementary acts in the forward direction (macroscopic process) is compensated by the sum of elementary acts in the reverse direction. It is a macroscopic description of large molecular ensembles that takes into account the MBD and statistical thermodynamic characteristics (such as \( \Delta H, \Delta S \)) and, accordingly, leads to irreversibility. A microscopically reversible process in a macroscopic system can be k inetically irreversible. In a macrosystem of reversible steps, each step (reaction) independently attains equilibrium when the chemical potential \( \Delta \mu \) (or the chemical affinity \( A \)) ceases to change:

\[
\frac{dG}{d\xi} = \Delta \mu = -A = 0 \left( \Delta \mu = \sum \beta_i \mu_i \right).
\]

The condition \( \Delta \mu = -A = 0 \) implies the equality of rates of the forward and reverse reactions: \( W^+ = W^- \).

- **Principle of detailed balance.** This principle determines a statistical relationship between the rate constants of an elementary process in the forward \((k^+)\) and reverse \((k^-)\) directions under the MBD conditions as an equilibrium constant of this process \( k^+/k^- = K \). The principle of detailed balance follows from the principle of microscopic reversibility and the equality of step rates \( (W^+ = W^-) \) at the point of chemical equilibrium \((dG/d\xi = 0)\). Thus, the principle of detailed balance is a macroscopic manifestation of the principle of microscopic reversibility. Indeed, proceeding from the latter principle and assuming that \( W^+ = W^- \) at equilibrium, we arrive at the principle of detailed balance – and vice
versa: on accepting that $k^+/k^- = K$ is an equilibrium constant, we obtain the equality of the rates $W^+ = W^-$ at equilibrium. For example, consider reversible reaction (1.173), where

$$\frac{W^+}{W^-} = K \cdot \frac{C_A C_B}{C_P},$$  \hspace{1cm} (1.185)

$$RT \ln \frac{W^+}{W^-} = RT \ln \frac{k^+}{k^-} - RT \ln \frac{C_P}{C_A C_B}.$$  \hspace{1cm} (1.186)

Assuming that $k^+/k^- = K$, we obtain

$$RT \ln \frac{W^+}{W^-} = \Delta G^\circ - RT \ln \frac{C_P}{C_A C_B},$$

or

$$\ln \frac{W^+}{W^-} = \frac{\Delta G^\circ}{RT}. \hspace{1cm} (1.187)$$

Equation (1.187) implies that, for $\Delta G = dG/d\xi = 0$, we have $W^+ = W^-$ (here, $\Delta G = \Delta \mu$).

The above considerations are valid for the ideal gases and ideal solutions. The principle of microscopic reversibility leads to some other important conclusions [15, 51] concerning mechanisms of complex reactions. In particular, it follows that a complex reaction in the forward and reverse directions passes via the same elementary steps and intermediates.

- **Arrhenius law.** This law in the form of the corresponding equation describes the basic property of an elementary step under the MBD conditions – the exponential dependence of the rate constant on the temperature:

$$k = A \exp\left(-\frac{E_{\text{act}}}{RT}\right). \hspace{1cm} (1.188)$$

This equation was experimentally established by Hood in 1885. Theoretically, this type of dependence was predicted by van’t Hoff (1883) based on the equilibrium thermodynamics and then confirmed and substantiated by Arrhenius (1889) within the framework of statistical physics [7]. The classical mechanism of pair collisions between molecules treated as elastic balls leads to the following expression:

$$k = A(T) \exp\left(-\frac{E_{\text{act}}}{RT}\right). \hspace{1cm} (1.189)$$

Taking into account the necessary orientation of molecules, a kinetic equation should be written in a simple form as follows:

$$k = pZ_0 \exp\left(-\frac{E_{\text{act}}}{RT}\right), \hspace{1cm} (1.190)$$

where $p$ is a sterical factor and $Z_0$ is the total number of collisions.

The activation energy $E_{\text{act}}$ of an elementary step entering in Eqs (1.188–1.190) represents a difference between the average energy of interacting particles and that of all particles, while the exponential factor characterizes the fraction of “active” collisions – that is, collisions with the energy $E$ equal to or exceeding the barrier energy. This expression follows from the fact that the main contribution to $E_{\text{act}}$ in the gas phase is due to the translational motion of A and B molecules. In the liquid phase, the character of molecular motions becomes oscillatory. If the total system energy (kinetic and potential) is described by $2S$ terms (for $S$ independent harmonic oscillators), then the fraction of active particles increases. In particular, a
simple approximation \[130, 131\]

\[
\frac{N_{(E \geq E_i)}}{N} = \exp \left( -\frac{E_i}{kT} \right) \frac{(E_i/(kT))^{S-1}}{(S-1)!}
\]

(1.191)
yields the following formula for a bimolecular reaction:

\[
k^{bm} = Z_0 \exp \left( -\frac{E_i}{RT} \right) \frac{(E_i/(RT))^{(S-1)}}{(S-1)!}
\]

(1.192)

Restriction of the expansion in Eq. (1.191) to the first two terms yields an expression analogous to that for the translational motion:

\[
k^{bm} = Z_0 \left( \frac{E}{RT} \right) \exp \left( -\frac{E}{RT} \right).
\]

(1.193)

In this case, the activation energy in the Arrhenius law is \( E_{\text{act}} = E - 0.5RT \).

An expression for \( k^+ \) can be obtained within the framework of the transition state (activated complex) theory. According to this theory, the rate \( W^+ \) of elementary step (1.173) is

\[
W^+ = C^\neq_{AB}/\tau,
\]

(1.194)

where \( C^\neq_{AB} \) is the concentration of activated complexes \((AB)^\neq\) at the barrier top and \( \tau \) is the time of passage over the barrier, which obeys the relation

\[
1/\tau = kT/h
\]

\((kT/h \text{ is the frequency of transitions over the barrier})\). The state of the activated complexes occurring on top of the barrier (i.e., in the transition state) corresponds to their equilibrium with the initial reactants, so that \( C^\neq_{AB} \) can be expressed in terms of the thermodynamic equilibrium constant \( K^\neq_a \) for the formation of activated complex (postulate) under the MBD conditions for all particles (including the activated complex \((AB)^\neq\)):

\[
K^\neq_a = \frac{a^\neq_{AB}}{a_A a_B} = \frac{C^\neq_{AB}}{C_A C_B} \cdot \frac{\gamma^\neq_{AB}}{\gamma_A \gamma_B},
\]

(1.195)

where \( a \) is the activity and \( \gamma \) is the activity coefficient. This relation yields

\[
C^\neq_{AB} = K^\neq_a \frac{\gamma^\neq_{AB}}{\gamma_A \gamma_B} C_A C_B
\]

(1.196)

and

\[
W^+ = kT/h K^\neq_a \frac{\gamma^\neq_{AB}}{\gamma_A \gamma_B} C_A C_B;
\]

(1.197)

\[
k^+ = kT/h K^\neq_a \frac{\gamma^\neq_{AB}}{\gamma_A \gamma_B}.
\]

(1.198)

In an ideal system (gas, solution), all the activity coefficients are \( \gamma_i = 1 \) and, hence, \( K^\neq_a \) is equal to the concentration constant \( K^\neq_C \). Since the transition frequency \( kT/h \) has a dimensionality of \([s^{-1}]\), while \( K^\neq_a \) is dimensionless, the dimensionality of the reaction rate constant is determined by that of the activity factor
$F = \gamma_A \gamma_B / \gamma_{AB}$. In the given case, $F$ has a dimensionality of [L · mole$^{-1}$] (same as $\gamma_i$). This dimensionality is retained in the case where all activity coefficients are $\gamma_i = 1$.

In order to improve the accuracy of description, a transmission coefficient $\chi$ is introduced into Eq. (1.198) so as to specify the fraction of activated complexes that overcome the barrier:

$$k^+ = \chi \frac{kT}{h} \exp\left(-\frac{-\Delta G^{\circ\neq}}{RT}\right) \exp\left(\frac{\Delta S^{\circ\neq}}{R}\right) \exp\left(-\frac{-\Delta H^{\circ\neq}}{RT}\right),$$

(1.200)

where $\Delta G^{\circ\neq}$ ($\Delta \mu^{\circ\neq}$) is a change in the standard free energy (or the chemical potential) upon the formation of the transition state and $\Delta S^{\circ\neq}$ and $\Delta H^{\circ\neq}$ are the changes in the standard entropy and enthalpy, respectively, of activation of the process

$$A + B \rightleftharpoons (AB)^\neq.$$

The value of $\Delta H^{\circ\neq}$ is related to $E_{\text{act}}$ in the Arrhenius equation (1.188) as $\Delta H^{\circ\neq} = E_{\text{act}} - RT$. Then

$$k^+ = \chi \frac{kT}{h} \exp\left(\frac{\Delta S^{\circ\neq}}{R}\right) \exp\left(\frac{\Delta S^{\circ\neq}}{R}\right),$$

(1.201)

where $\Delta S^{\circ\neq}$ is the standard entropy of activation at $V = \text{const}$. Equation (1.201) describes the rate constant of a liquid-phase reaction. In the reactions involving light quantum particles (electron, proton), the transition to products in a reacting system can take place even before the energy reaches the barrier height – that is, by means of the tunneling effect, in which case $\chi > 1$. The preexponential factor $A$ in the Arrhenius equation (1.188) is

$$A = \chi \frac{kT}{h} \exp\left(\frac{\Delta S^{\circ\neq}}{R}\right);$$

(1.202)

$$\Delta S^{\circ\neq} = R \ln \frac{Ah}{\chi ekT}.$$

(1.203)

Despite some inconsistency [50, 127, 140], the transition state theory has proved to be very useful for the creation of a semiempirical theory of chemical reactivity and is still in progress [51, 58, 141]. Quite recently (1999), A. Zewail was awarded the Nobel Prize in Chemistry for developing the method of femtosecond laser spectroscopy and studying the transition states of chemical reactions. Using this technique with characteristic times of $10–100$ fs ($1$ femtosecond $= 10^{-15}$ s) it is possible to measure the characteristics of transition states in some reactions with lifetimes on the order of $\sim 10^{-13}$ s [142].

The law of mass action (1.183) is written in terms of the product of volume concentrations $C_i$. This circumstance is related to the fact that, in the main models of elementary steps (employing the theory of collisions and the transition state theory), the volume of a system plays a determining role, since the frequency of collisions and the number of activated complexes passing over the barrier per unit time depend on the system volume. Within the framework of the transition state theory, the reaction rate can also be expressed in terms of the activities of reactants as in Eq. (1.197). Accordingly,

$$W^+ = \frac{k_0^{+} a_A a_B}{\gamma_{AB}^{\neq}}.$$
where \( k_0 \) is the rate constant that is independent of the properties of a medium. This writing agrees with the principle of microscopic reversibility, since the equation \( W^+ = W^- \) allows the thermodynamic equilibrium constant to be obtained only using activities (or only for an ideal solution, where \( a_i = C_i \)) as

\[
W^- = k_0 \frac{a_P}{\gamma_P^\neq},
\]

because the transition state for the forward and reverse reactions is the same and \( \gamma_P^\neq = \gamma_P^\neq = \gamma_P^\neq \), so that

\[
\frac{k_0^+}{k_0^-} = \frac{a_P}{a_A a_B} = K_a.
\]

It should be noted that, during any variation of the composition of medium (solution), it is easier to maintain the value of activity \( \gamma_P^\neq \) than the value of factor \( F \) (because of a very low concentration of activated complexes). Therefore, it can be expedient to use Eq. (1.204), especially in the case of organic reactions where determination of the activities of components of the medium (reaction participants) is a relatively simple, well developed routine procedure. The use of activities can also be useful in the case of ionic systems (see Chapters 2 and 8).

- **Principle of least motion.** The most important postulates of classical mechanics – the principle of least action (Euler, Maupertuis) and the variational principles (Lagrange, Hamilton) [143] – undoubtedly strongly influenced the first attempts at formulating the general approach to chemical reactivity [144]. In 1850, Kekule suggested that molecules subject to least structural changes in the course of a chemical reaction would react at a greater rate, and in 1924 Mueller and Païtral formulated a close principle of the least deformation of molecules at the elementary reaction step. Eventually, in 1938 Rice and Teller formulated the principle of least motion. According to this, an elementary step proceeds fast, with low activation energy \( E_{\text{act}} \), provided that this step is characterized by
  
  (i) the least motion of nuclei (i.e., a minimum change in the coordinates of these nuclei); and
  (ii) the least motion of electrons (for which rearrangement of the electron shells does not lead to a change in the valence state).

If a system exhibits only an insignificant change in the coordinates of the nuclei, this implies that the potential energy terms of the reactants and products are close. In general, it is true that the closer the terms, the lower the barrier \( (E_{\text{act}}) \). However, this is not always the case. The pathway of least motion may not coincide with the pathway of minimum energy [144]. Indeed, consider the system

\[
A + BC \longrightarrow AB + C.
\]

For the least motion, the approach of reactant A to group B is accompanied by the removal of group C (Figure 1.16, line 1). In some cases, it is energetically more favorable to attach A to BC with subsequent rupture of the B–C bond (curve 2), whereas in other cases it is better first to rupture the B–C bond and then add A to B (curve 3). The principle of least motion for electrons is more universal.

- **Principle of independence of chemical reactions.** The elementary steps proceeding simultaneously in a reacting system must obey a postulate that these chemical reactions are independent of each other. According to this principle, introduced by W. Ostwald, all chemical reactions, including their steps, proceed independently (see, e.g., [51]). Relations between independent reactions are only established
on the level of a material balance, through a change in the concentrations, and the appearance of new substances. According to the same principle, the forward and reverse elementary reactions also proceed independently and this allows a chemical equilibrium to be established (see also the principle of microscopic reversibility).

1.4.2 Energy selection rules for elementary steps

According to the principles and laws considered above, the possibility for a given reaction to occur as an elementary (consistent) process is determined either by the fraction of active species with energies \( E \) equal to or greater than the activation energy \( E \geq E_{\text{act}} \), or by the value of free energy \( \Delta G_{\text{act}} \) that is dependent on the barrier on the potential energy surface \( \Delta H_{\text{act}} \) and the shape of this surface in the region of a saddle point \( \Delta S_{\text{act}} \). There are different reasons for which the \( \Delta G_{\text{act}} \) and \( \Delta H_{\text{act}} \) values may vary. First, we will consider the energy selection rules, that is, the rules in which the thermodynamic characteristics of reactions are manifested.

- **Thermodynamic limitations on elementary reaction steps.** The main restriction in the case of an endothermal reaction is related to the value of the standard change in the enthalpy \( \Delta H^0 \), which determines the lower limit of \( E_{\text{act}} \). Indeed, in most cases, \( E_{\text{act}} \geq \Delta H^0 \) because maxima on the curves of potential energy and free energy are situated at the same value of the reaction coordinate [131]. In cases where the \( \Delta H_{298}^0 \) value is large (e.g., \( \Delta H_{298}^0 = 40000 \) cal/mole) and the preexponential factor for a bimolecular reaction of the \( S_N^2 \) type has a typical value of \( A \sim 10^{11} \text{M}^{-1} \text{s}^{-1} \) (\( A \) usually varies within \( 10^{10} \div 10^{12} \text{M}^{-1} \text{s}^{-1} \)), the rate constant \( k \) at \( T = 298 \) K will amount to

\[
\begin{align*}
  k &= 10^{11} \exp \left( -\frac{40000}{RT} \right) \approx 5 \cdot 10^{-19} \text{M}^{-1} \text{s}^{-1}.
\end{align*}
\]

In order to ensure that the step rate \( (W_j) \) would be no less that 0.01 M/h (value acceptable in practice), the product of reactant concentrations in reaction of type (1.173) must be about

\[
C_A C_B = \frac{W_j}{k} = \frac{0.01}{3600 \cdot 5 \cdot 10^{-19}} = 5.6 \cdot 10^{12} \text{M}^2,
\]

which is unrealistic. For the same rate and \( C_A C_B = 10^{-4} \text{M}^2 \), we have \( k = 2.8 \cdot 10^{-2} \text{M}^{-1} \text{s}^{-1} \), which yields \( E_{\text{act}} \approx 17000 \) cal/mole.
Thus, depending on the reaction temperature and the expected rate of a steady-state or quasi-steady-state process, we can set limitations on the $\Delta H^{\circ}_{298}$ value in selecting a candidate reaction for the elementary step. In the case of a multi-route reaction, the choice of the rate can also take into account that the step rate can be equal to a sum (or difference) of the rates over routes:

$$W_j = \sum_p v_j^{(p)} r_p.$$

In evaluating $\Delta H^{\circ}$ for an elementary step, it is necessary to use data that refer to the states of reaction participants in which they actually occur during the reaction. For example, the exothermal and exoergonic reaction

$$\text{Pd}^{2+}_{\text{aq}} + \text{H}_2(\text{gas}) \rightarrow \text{Pd}^0_{\text{solid}} + 2\text{H}^+;$$

with $\Delta G^{\circ}_{298} = -45.5$ kcal/mole evidently cannot be elementary, since it results in the formation of a solid palladium phase. An elementary step could lead to the formation of an atom ($\text{Pd}^0_{\text{aq}}$) in solution:

$$\text{Pd}^{2+}_{\text{aq}} + \text{H}_2(\text{gas}) \rightarrow \text{Pd}^0_{\text{aq}} + 2\text{H}^+;$$

with $\Delta G^{\circ}_{298} = +38.5$ kcal/mole (hydration of Pd$^0$ does not significantly contribute to the enthalpy of reaction), but the enthalpy of reaction (1.209) is greater than that of reaction (1.208) by 83–90 kcal/mole and, hence, this reaction also cannot be the elementary step.

Use of the $\Delta G^{\circ}$ value as a thermodynamic criterion for the elementary step is not as strict as it is for assessing the possibility of implementing a given brutto process (overall reaction equation). In the latter case, the reaction conditions ($P$, $T$) are selected by estimating $\Delta G^{\circ}_{P,T}$, $K_{eq}$, and the equilibrium product yield (which in all cases should be large). In the case of an elementary step of intermediate X formation via the reaction

$$\text{A} \rightleftharpoons K_1 X \rightarrow k_2 P$$

an admissible concentration of X must provide for a positive affinity ($A > 0$, $\Delta \mu < 0$) on the first step at a sufficiently high rate of product P formation on the second step that also depends on $k_2$ (for more detail, see Section 3.4):

$$W_1 > 0 \text{ at } \frac{W_1^+}{W_1^-} = \frac{K_1}{\prod C_i^{\beta_i}} = \varphi > 1.$$

At the step of formation of intermediate X, we have

$$\varphi = \frac{K_1}{[X]/[A]} > 1. \quad (1.211)$$

For a quasi-equilibrium first step, $K_1 \equiv [X]/[A]$. Assuming that $K_1 = 10^{-3} (\Delta G^{\circ}_{298} = 4090$ kcal/mol) and $[A]_0 = 1\text{M}$, we have $[X] = 0.999 \cdot 10^{-3}\text{M}$. Then, for $W_2 > 0.01\text{M/h}$, we can estimate $k_2$ as

$$k_2 \geq \frac{W_2}{[X]} = \frac{0.01}{3600 \cdot 0.999 \cdot 10^{-3}} = 2.8 \cdot 10^{-3}\text{ s}^{-1}.$$

and find $E_{\text{act}}$ for the monomolecular reaction (with $A = 10^{13} - 10^{15}$ s$^{-1}$) at $T = 298\text{ K}$:

$$k_2 = 5 \cdot 10^{13} e^{-\frac{E_{\text{act}}}{RT}} \Rightarrow E_{\text{act}} \leq 22000\text{ cal/mol}.$$
This value of $E_{\text{act}}$ on the second step allows the proposed first step to be considered as an allowed elementary reaction despite the positive value of $\Delta G^0_{298}$.

In the above example, we dealt with a kinetic conjugation of two elementary steps via a common intermediate $X$, which allows the product $P$ to be synthesized despite a thermodynamically (energetically) unfavorable first step. Speaking of the kinetic conjugation [145] (see Section 3.4), one should distinguish between the two cases:

(i) $\Delta G^0 > 0$ for the first step, $[X]$ is small, and the affinity is $A \sim 0$. The appearance of step $X \rightarrow P$ leads to a decrease in $[X]$, increase in $A$ ($A > 0$), and growth in the difference of $W^+_1 - W^-_1$ (in the limit, up to $W^+_1$ that is a maximum possible rate of the process). An increase in the rate as a result of the conjugation of two steps is ensured, in fact, by making the first step irreversible.

(ii) $\Delta G > 0$ ($A < 0$) for the first step and $[X]/[A] > K$, the reaction goes leftward ($[X]$ is above the equilibrium level). Here, the conjugation of the first and second steps ($X \rightarrow P$) leads to a decrease in $[X]$, so that $\varphi = \frac{K}{[X]/[A]}$ becomes greater than unity and the process direction switches to rightward (forward direction) and at its limit attains the maximum possible rate $W^+_1$. In this case, the conjugation changes the direction of the first step.

Now let us refine some notions in the context of the issues considered above. The rate of any elementary step is the difference between the rates of the forward and reverse reactions: $W_j = W^+_j - W^-_j$. The kinetic reversibility of a step is a macroscopic manifestation of the principle of microscopic reversibility. On the other hand, a kinetically reversible reaction is thermodynamically irreversible, since a spontaneous chemical reaction proceeds only in one direction: toward a decrease in the affinity and increase in the entropy until attaining equilibrium ($A_j = 0$, $dS_j/dt = 0$, closed system).

A kinetically irreversible step can be represented by an elementary step in which the ratio $K_{\text{eq}}/\prod C_i^{\beta_i} = \varphi$ is $\gg 1(W^+_j/W^-_j \gg 1)$ during the entire process up to reaching the degree of reactant conversion $\alpha = 0.999$. For example, if $K_{\text{eq}} \approx 10^{15}$, then we have $\varphi \gg 1$ over the entire process (for the conversion varying from $\alpha = 0$ to $\alpha = 0.999$) and the ratio $W^+_j/W^-_j$ varies within $10^{12} - 10^7$ (decreasing, but still remaining very large). In other words, processes in which

$$W^+_j - W^-_j \cong W^+_j$$

can be considered kinetically irreversible.

- **Empirical dependences of $E_{\text{act}}$ and $\Delta G^{\circ \neq}$ on thermodynamic characteristics of steps.** Based on the results of experimental observations (J. Brønsted, R. Bell, M. Polanyi) and theoretical investigations (R. Bell, M. Evans, M. Polanyi), the so-called *linear free-energy relationships* were formulated, which are also referred to as the Bell–Evans–Polanyi (BEP) rule [51, 144, 146]. This rule reflects relationships between the kinetic and thermodynamic characteristics in a series of analogous elementary reactions:

$$\Delta G^{\circ \neq} = \beta + \alpha \Delta G^0;$$

$$E_{\text{act}} = \beta + \Delta H^0.$$  

(1.212)

(1.213)

Let us consider a series of the curves of potential energy (representing cross sections of the potential energy surface along the reaction coordinate) for reactants and products of the reaction

$$A_i + BC \longrightarrow A_iB + C,$$  

(1.214)

which yields a diagram presented in Figure 1.17. Since the energy of the BC bond rupture ($E_{\text{BC}}$) is independent of $A_i$, we can fit all curves for different $A_i$ at point 2. By the same token, the curves of
A_i B formation from A_i, B and C can be constructed from point 1. On varying group A_i in the given series of analogous reactions and assuming that the energy terms of A_i B + C do not intersect (rule of non-crossing, or repulsion of terms), it is natural to expect a certain relationship between \( \Delta H_i \) and \( E_i \) since an increase in the endothermicity of reaction (1.214) leads to an increase in \( E_{act} \). Polanyi suggested to approximate this relationship using linear equation (1.213) in a certain interval of \( \Delta H_i \), and N.N. Semenov determined coefficients of this equation for several elementary steps with some radicals and molecules (Polanyi–Semenov equation [50, 130]; see Chapter 7):

\[
E_{exo} = 11.5 - 0.25|\Delta H^0|; \quad (1.215)
\]

\[
E_{endo} = 11.5 + 0.75|\Delta H^0|. \quad (1.216)
\]

According to the BEP rule, the elementary steps can be selected more accurately by using \( E_{act} \) rather than \( \Delta H^0 \) as the upper limit.

A question of principal importance is what the form of function \( E_i = f(\Delta H_i) \) should be. As long ago as the 1930s, Polanyi understood that the linear free-energy relationships provide only a rough linear approximation (valid in a narrow interval of thermodynamic quantities \( \Delta G^0 \) and \( \Delta H^0 \)) of more complicated functions such as, for example, a quadratic relation

\[
E = \frac{(A + \Delta H^0)^2}{4A}. \quad (1.217)
\]

An equation of this type was later obtained for the reactions with electron transfer (R. Marcus, 1956) and proton transfer (R. Marcus, 1968) and then refined and theoretically justified by Levich, Dogonadze, and Kuznetsov [134–137]. Parabolic and more complicated power equations for the calculation of \( E_{act} \) of radical reaction steps using \( \Delta H^0 \) values are presented in [130] (for more detail, see Chapter 7).

In developing a theory of the electron transfer in polar solvents, Marcus introduced important concepts of the internal and external barriers by separating \( \Delta G^{\circ \neq} \) into two components as

\[
\Delta G^{\circ \neq} = \Delta G_{\text{int}}^{\neq} + \Delta G_{\text{ext}}^{\neq}. \quad (1.218)
\]

Reactions in polar media are accompanied by changes not only in the internal coordinates of atoms in reacting species, but also in the coordinates of molecules of the solvent (in the general case, of the
medium) along the reaction coordinate, since the solvent (medium) exhibits reorganization around the transition state [131]. Accordingly, the $A$ value in Eq. (1.217) for the reactions with electron transfer is related to the energy of solvent reorganization.

1.4.3 Quantum-chemical selection rules for elementary steps

Any thermodynamically allowed reaction in which the nuclei exhibit insignificant displacement (i.e., the minima of energy terms are close), the electron states change but little (in accordance with the principle of least motion), and the molecularity $\mu$ does not exceed 2 and has a chance to be a consistent process, that is, an elementary reaction step. However, for the $\Delta G^{\neq}$ value to be small and the reaction to proceed at a measurable rate, two conditions must be fulfilled that follow from the quantum-chemical theory. According to these, an effective interaction of two particles with a sufficiently low barrier can take place only provided that their overlapping molecular orbitals (MOs) possess the same symmetry and that the energies of these MOs are close. For example, as will be shown below, the bimolecular reaction

$$H_2 + I_2 = 2HI$$

(1.219)

with small changes in the nuclear coordinates and electron shell structures cannot be an elementary step because it is prohibited with respect to the symmetry of frontier MOs. Below we will consider some quantum-chemical approaches to the problem of chemical reactivity in more detail.

- **Perturbation theory in the approximation of frontier MOs** [137, 139] According to the BEP rule, the knowledge of the energy states of the initial and final products allows the kinetic characteristics of elementary steps (probabilities of elementary acts) to be evaluated. Using the MO perturbation method and operating only with frontier MOs (highest occupied MO, HOMO; lowest unoccupied MO, LUMO) and charges on atoms, molecules, and atomic orbitals (AOs) in MOs, it is possible in some cases to predict the probability, direction, and efficiency of interaction between two reactants.

The more effective the interaction, the lower the activation energy ($E_{act}$) and the higher the probability of a consistent elementary act.

If the energies of the frontier orbitals $\chi_1$ and $\chi_2$ are close, then their interaction energy is determined by the resonance (exchange) integral $\beta_{12}$ defined as

$$\beta_{12} = \int_0^\tau \chi_1 \hat{H} \chi_2 dv,$$

(1.220)

where $\hat{H}$ is the Hamiltonian of the system and $v$ is the volume element in which the orbitals overlap.

In this case, the value of $\beta_{12}$ also determines the splitting of new MOs ($\Psi_1$ and $\Psi_2$) and the stabilization energy ($\epsilon = \beta_{12}$):
In contrast, if the energies of $\chi_1$ and $\chi_2$ differ significantly, then the $\epsilon$ value depends, besides $\beta_{12}$, on the difference of the frontier orbital energies as

$$\epsilon = \frac{\beta_{12}^2}{E_1 - E_2}, \quad (1.221)$$

where $E_1$ and $E_2$ are the energies of the lowest and highest MOs, respectively:

$$\Delta E = E - E_{0S} - E_{0T}, \quad (1.222)$$

which is only valid for the initial interval of the reaction coordinate. Despite the fact that this approximation is only valid for large distances between reactants, where the MOs exhibit no mixing and there is no intermolecular repulsion (so that we can speak about pure MOs of the initial reactants), this approach allows the most probable reaction pathway to be assessed.

The perturbation energy $\Delta E$ for the interaction of reactants S and T (both being molecules or active centers in molecules) is calculated using the following equation:

$$\Delta E = -\frac{q_S q_T}{R_{ST}\epsilon} + \gamma_{ST} \sum_{m\text{OMO}} \sum_{n\text{UMO}} \left( \frac{C_S^2 C_T^2 \beta_{ST}^2}{E_m - E_n} \right), \quad (1.223)$$

which simplifies in the presence of only two frontier MOs (e.g., electron donor and acceptor) to

$$\Delta E = -\frac{q_S q_T}{R_{ST}\epsilon} + \gamma_{ST} \left( \frac{C_S^2 C_T^2 \beta_{ST}^2}{E_1 - E_2} \right). \quad (1.224)$$

Here, $q_S$ and $q_T$ are the effective charges on the S and T centers; $R_{ST}$ is the distance between these centers; $\epsilon$ is the dielectric permittivity of the medium; $\gamma_{ST}$ is the coefficient that takes into account the electron population of $\chi_1$ and $\chi_2$ orbitals; and $C_S$ and $C_T$ are the coefficients at the wave functions of the AOs of S and T centers, respectively, in the wave functions of the frontier MOs $\chi_1$ and $\chi_2$; $\beta_{ST}$ is the exchange integral; and $E_1$ and $E_2$ are the energies of $\chi_1$ and $\chi_2$ orbitals, respectively.

The first term (first-order perturbation) in these equations reflects the Coulomb interaction energy, while the second term (second-order perturbation) describes the energy due to the orbital overlap. Various cases
of different electron populations on the $\chi_1$ and $\chi_2$ orbitals of reacting particles and the corresponding $\gamma_{ST}$ values are presented below:

<table>
<thead>
<tr>
<th>Numbers of electrons on frontier orbitals $\chi_1$ and $\chi_2$</th>
<th>$\gamma_{ST}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 + 2, 0 + 0$</td>
<td>0 (no overlap)</td>
</tr>
<tr>
<td>$2 + 1, 1 + 0$</td>
<td>1</td>
</tr>
<tr>
<td>$2 + 0, 1 + 1$</td>
<td>2 (maximum overlap)</td>
</tr>
</tbody>
</table>

If the difference $E_1 - E_2$ in the denominator of the second term of Eq. (1.224) is small, the overlap population is $\gamma_{ST} = 1$ or 2, and the orbitals possess the same symmetry ($\beta_{12} > 0$), then the orbital geometry is convenient for the overlap (coefficients $C_S$ and $C_T$ exhibit large values in the same regions of space) and the second term is significantly greater than the first, so that we can speak of an orbital-controlled reaction.

In cases where the $E_1 - E_2$ value is large, the second term becomes small even for large $C_S$ and $C_T$. If the $q_S$ and $q_T$ values are also large, then we deal with the case of a charge-controlled reaction. Using these simple estimations by the MO–LCAO methods, it is possible to determine (without calculating the potential energy surface) in what direction (via which centers) a reaction would proceed and whether a high rate at the selected elementary step can be expected. Naturally, all the above considerations concerning the estimation of $\Delta E$ refer only to the elementary steps.

Now let us consider a donor molecule – e.g., SCN$^-$, the typical nucleophile – reacting with an acceptor that possesses a LUMO. If the HOMO of the donor ($\chi_1$) is close to the LUMO ($\chi_2$) of the acceptor, then the reaction is orbital controlled. This reaction involves the acceptor molecule and that center of the nucleophile (donor) which possesses a maximum charge density ($C_i^2$) on the frontier orbitals. In particular, the HOMO ($\Psi_2$) of the SCN$^-$ written in the form of an LCAO is as follows:

$$\Psi_2 = 0.74\varphi_S + 0.33\varphi_C - 0.59\varphi_N;$$

$$C_S^2 = 0.55, \quad C_N^2 = 0.35 \Rightarrow C_S^2 > C_N^2.$$

Accordingly, the reaction with an acceptor will proceed at the S atom:

$$\text{SCN}^- + \text{Ag}^+ \longrightarrow \text{AgSCN}.$$  \hspace{1cm} (1.225)

If the acceptor orbital energy is much higher than the donor orbital energy and the difference $E_1 - E_2$ is large, the reaction is controlled by the Coulomb interaction between charges. In this case, the first (Coulomb’s) term in Eq. (1.224) is greater for that center of the nucleophile, which possesses a higher $q_i$. For calculating $q_S$ and $q_N$, it is necessary to take into account the coefficient $C_i^2$ for these centers on all orbitals, that is, to use both $\Psi_2$ and LOMO ($\Psi_1$) of the nucleophile:

$$\Psi_1 = 0.33\varphi_S + 0.59\varphi_C + 0.74\varphi_N.$$  

The effective charges on the interacting centers are calculated using the following formula:

$$q_i = 1 - 2\left(\sum C_i^2\right),$$

which yields

$$q_S = 1 - 2(0.33^2 + 0.74^2) = -0.313,$$

$$q_N = 1 - 2(0.59^2 + 0.74^2) = -0.7914.$$
Thus, in the \([S\equiv C\equiv N]^-\) anion, the effective (negative) charge on the N atom is greater than that on the S atom: \(|q_N| > |q_S|\) (and \(q_C \approx 0.1\)). Therefore, under the charge control conditions, the nucleophile SCN\(^-\) will interact with the acceptor via nitrogen atom as

\[
\text{SCN}^- + R^+ \rightarrow RNCS.
\]

The MO perturbation method provided a theoretical explanation for several empirical rules and generalizations. In 1958, Ahrland, Chatt and Davies [147] (see also [148]) proposed a classification of metal complexes by separating metal ions into two groups. The first group (a) includes the ions of metal (in most frequently encountered degrees of oxidation) that form the most stable complexes with ligands containing donor atoms of N, O, and F. The second group (b) contains metal ions that form the most stable complexes with ligands containing donor atoms of the third and subsequent periods (P, S, Cl, Br, I). For example, the stability of halide complexes varies depending on the metal in the following order:

\[
\text{Zn}^{2+} \text{[group (a)]: } F^- \gg Cl^- > Br^- > I^-;
\]

\[
\text{Hg}^{2+} \text{[group (b)]: } I^- > Br^- > Cl^- \gg F^-.
\]

Thus, on the passage from Zn\(^{2+}\) to Hg\(^{2+}\), the order of stability is reversed as compared to that in the “normal” series for Zn\(^{2+}\) (consistent with simple electrostatic considerations). A quantitative measure of the “reversed stability” is provided by the value of \((1/n)\lg\beta_n\) [149] for the process of complete replacement of \(n\) chloride ions by bromide ions in an aqueous solution:

\[
MCl_n^z - nBr^- \rightleftharpoons MBr_n^z + nCl^-.
\]  

(1.226)

It turns out [149] that, in addition to metals occurring in the so-called “Ahrland–Chatt triangle”, some other metals also belong to the group with reversed order of stability. Evidently, for ions of the first group, the stability is determined by the charge factor, whereas for the second group of ions, it is the orbital factor. Analogous explanations were obtained for the rule of interaction between hard and soft acids (Pearson, 1963; see [137]), and the Kornblum rule in organic chemistry [146]. In terms of Pearson’s theory, the interaction of hard species (acid and bases, acceptors and donors) corresponds to the charge control, while the interaction of soft species is orbital controlled. The degree of hardness and softness of an acceptor (A) and donor (D) can be assessed using various criteria [139, 150]. In particular, the values of orbital electronegativities \(E_n(A)\) and \(E_m(D)\) (in electronvolts, eV) according to Klopman [139] are as follows:

<table>
<thead>
<tr>
<th>Acceptors: (acids)</th>
<th>Al(^{3+})</th>
<th>Mg(^{2+})</th>
<th>Cr(^{3+})</th>
<th>Fe(^{2+})</th>
<th>H(^+)</th>
<th>Na(^+)</th>
<th>Cu(^{2+})</th>
<th>Zn(^{2+})</th>
<th>Cu(^{+})</th>
<th>Hg(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)</td>
<td>6</td>
<td>2.42</td>
<td>2.06</td>
<td>0.69</td>
<td>0.42</td>
<td>0.0</td>
<td>-0.55</td>
<td>-1.0</td>
<td>-2.3</td>
<td>-4.6</td>
</tr>
<tr>
<td>Donors: (bases)</td>
<td>F(^-)</td>
<td>H(_2)O</td>
<td>OH(^-)</td>
<td>Br(^-)</td>
<td>CN(^-)</td>
<td>SH(^-)</td>
<td>I(^-)</td>
<td>H(^-)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-12.18</td>
<td>-10.7</td>
<td>-10.45</td>
<td>-9.2</td>
<td>-8.78</td>
<td>-8.59</td>
<td>-8.31</td>
<td>-7.37</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In these series, the hardest acid is Al\(^{3+}\), the hardest base is F\(^-\), the softest acid is Hg\(^{2+}\), and the softest base is H\(^-\).

- **Orbital symmetry and selection rules.** The use of the symmetry of orbitals or electron states for determining allowed and forbidden elementary reaction steps is described in detail elsewhere [137–139, 144]. Here we will only consider the main concepts and rules of this approach. The requirement of
identical orbital symmetry for their effective overlap (i.e., for the interaction of components without high energy barriers) is also taken into account when calculating the exchange integrals $\beta_{ST}$ for the MO perturbation method. Even simple comparison of the symmetry of MOs in interacting molecules allows us, in some cases, to judge the possibility of a consistent elementary act. For example, consider reaction (1.219), for which a consistent character implies that an elementary act must involve the rupture and formation of two bonds. Therefore, the process must pass via a four-center cyclic transition state as follows:

\[
\begin{align*}
H - H & \quad \rightarrow \quad H - H \\
+ & \quad \rightarrow \quad H \quad + \\
I - I & \quad \rightarrow \quad I \quad I
\end{align*}
\] (1.227)

Figure 1.18 shows the $\sigma$–MOs of $H_2$ and $I_2$ molecules. If we use a single element of symmetry, as represented by the $P_{\text{intra}}$ plane passing through the center of the molecule and perpendicular to the H–H and I–I bonds, and the symmetry operation of mirror reflection in this plane, then the $\sigma$-MOs of both molecules are symmetric (S) with respect to this operation, whereas their $\sigma^*$-MOs are antisymmetric (A). Thus, consistent (synchronous) overlap within the framework of a cyclic transition state (1.227) between the HOMO of $H_2$ (S) and LUMO of $I_2$ (A) as well as between LUMO of $H_2$ (A) and HOMO of $I_2$ (S) is impossible. Thus, reaction (1.219) with transition state (1.227) cannot be an elementary step.

An analogous simple analysis of the reaction

\[
\begin{align*}
\text{CH}_2\equiv\text{CH}_2 & \quad \rightarrow \quad \text{CH}_2\equiv\text{CH}_2 \\
+ & \quad \rightarrow \quad \text{CH}_2\equiv\text{CH}_2
\end{align*}
\] (1.228)

(2+2 cycloaddition) shows that the occupied and vacant MOs of the two molecules possess different symmetries (Figure 1.19). It is evident that, for this symmetry analysis, it is sufficient to use only a diagram of the $p$ orbitals (Figure 1.19b). It should be recalled that the shaded and open lobes of the orbitals are indicative of the opposite ($\pm$) signs of the angular parts of their wave functions.

The general rules of selecting elementary steps with respect to the symmetry of orbitals in the reacting system were formulated by Woodward and Hoffmann [138] for the elementary reactions passing via cyclic transition states (pericyclic reactions):

\[\text{Figure 1.18} \quad \text{Frontier } \sigma \text{ MOs formed by } s(H_2) \text{ and } p(I_2) \text{ orbitals}\]
These rules are as follows:

*If the occupied bonding MOs of reactants are symmetry-correlated (possess identical symmetry) with occupied bonding MOs of the reaction products, the reaction will proceed as consistent thermally (can be an elementary step). During this reaction, the symmetry of interacting orbitals is conserved along the reaction trajectory on the potential energy surface. Should this correlation be absent, a consistent reaction is possible only in a photochemical regime.* [138]

The class of pericyclic reactions includes consistent reactions of $\sigma$ bond exchange ($\sigma$ bond metathesis) such as

$$
\begin{align*}
H_2 + I_2 & \rightleftharpoons 2HI, \\
M-R + H_2 & \rightleftharpoons MH + RH;
\end{align*}
$$

consistent reactions of addition of HX and X–Y molecules to multiple bonds

$$
\begin{align*}
\text{Cl}_2 + \text{C}_2\text{H}_4 & \longrightarrow \text{ClCH}_2\text{CH}_2\text{Cl}, \\
\text{HCl} + \text{C}_2\text{H}_4 & \longrightarrow \text{CH}_3\text{CH}_2\text{Cl},
\end{align*}
$$

reactions of cycle formation and decay [see also (1.228)]

$$
\begin{align*}
\| + & \rightleftharpoons \text{cycle};
\end{align*}
$$

electrocyclic reactions

$$
\begin{align*}
\| + & \rightleftharpoons \text{cycle}.
\end{align*}
$$
(in which intramolecular $\sigma$ bonds are formed or ruptured), and so-called sigmatropic rearrangements

\[
\begin{array}{c}
\begin{array}{c}
3 \quad 2 \\
4 \quad 6
\end{array}
\end{array} \quad \rightleftharpoons \quad \begin{array}{c}
\begin{array}{c}
3 \quad 2 \\
4 \quad 6
\end{array}
\end{array}
\]

(1.233)

\[
R_1 - C - C = C \quad \longrightarrow \quad R_1 - C = C - C.
\]

(1.234)

The reactions are also classified with respect to (i) the number of AOs of the reactants (or molecular fragments) involved in the formation of a transition state, and (ii) the types of bonds linking the reaction centers. For example, the aforementioned reactions are denoted as $[2\sigma + 2\sigma]$ (1.229), $[2\sigma + 2\pi]$ (1.230), $[2\pi + 2\pi]$ (1.228), $[2\pi + 4\pi]$ (1.231), $[2\sigma + 2\pi]$ (1.232), $[2\sigma + 4\pi]$ (1.233), and $[2\sigma + 2\pi]$ (1.234).

Let us analyze the symmetry of the orbitals of reactants and products for the $[2\pi + 2\pi]$ type reaction (1.228) by considering a pair of reacting ethylene molecules and the corresponding MOs (Figure 1.20) [1.244]. For this purpose, we will use two planes – the local symmetry plane $P_{\text{intra}}$, which is common for both molecules, and the plane $P_{\text{inter}}$ that is lying between the two ethylene molecules and is parallel to their planes. Two pairs of the $\pi$-MOs of ethylene molecules form two occupied MOs representing the combinations of $\pi + \pi'$ and $\pi - \pi'$. Both these combinations are symmetric with respect to the reflection in $P_{\text{intra}}$, while for the reflection in $P_{\text{inter}}$, the former combination is symmetric and the latter is

![Woodward–Hoffmann correlation diagram for concerted cyclodimerization of C$_2$H$_4$](Reprinted from [14] with kind permission from Springer Science+Business Media © 1998)
antisymmetric. The general symmetry of the two \( \pi \)-MOs is SS and SA. For the \( \pi^* \)-MOs, we also obtain two combinations \((\pi^* + \pi^*')\) and \((\pi^* - \pi^*)\), the symmetry of which is illustrated in Figure 1.20. Note that the antisymmetric character of the \( \pi - \pi' \) orbital relative to the \( P_{\text{inter}} \) plane implies the presence of a nodal plane between molecules.

In the product (cyclobutane), we consider \( \sigma \)-MOs of the two newly-formed C–C bonds. The two \( \sigma \)-MOs are symmetric with respect to reflection in the \( P_{\text{inter}} \) plane, while the two \( \sigma^* \)-MOs are antisymmetric in this respect. Thus, the possible combinations of these bonds yield four MOs with the symmetries SS, AS, SA, and AA. As can be seen from Figure 1.20, two ethylene molecules in the ground state (SS, SA) are symmetry-correlated with a cyclobutane molecule in the doubly excited state (SS, SA). The pair of electrons from an orbital of the SA symmetry has to surmount a high energy barrier in order to reach the SA level of cyclobutane, which implies that this reaction is forbidden with respect to orbital symmetry. In order to ensure the formation of a cyclobutane molecule in the ground state, the energy of a pair of electrons from MOs of SA symmetry must be increased so as to reach point C, where the energies of SA and AS orbitals intersect and the electron pair can be transferred to the orbital of AS symmetry (Figure 1.21). The magnitude of this barrier is evaluated as the energy of two bonding \( \pi \) electrons, which is too large for a thermoactivated reaction (270 kJ/mole) [144]. In the case of a photochemical excitation, the \( \pi^*(\text{AS}) \) orbital is populated by electrons (two-electron excitation is also possible) and the symmetries of the occupied MOs of the reactants and products are retained in the course of reaction and, hence, the reaction proceeds as an elementary act.

It was demonstrated by the method of laser spectroscopy [142] that the thermal cycloaddition reaction (1.228) proceeds via two symmetry-allowed steps with the formation of an intermediate biradical (with a lifetime of 700 fs):

\[
2\text{C}_2\text{H}_4 \rightarrow \text{H}_2\text{C} \cdot \text{C} \cdot \text{H}_2 \rightarrow \text{H}_2\text{C} \cdot \text{C} \cdot \text{H}_2
\]  

(1.235)

In contrast to the 2+2 cycloaddition, the 2+4 addition (Diels–Alder reaction) can proceed consistently as an elementary step via a hexa-center cyclic transition state. Even without an analysis of the combinations of reactants and products, the analysis of reactants for their MO symmetry with respect to the \( P_{\text{intra}} \) plane shows that the HOMO of ethylene (\( \pi \)-MO) can overlap with the LUMO of butadiene (\( \pi^*_1 \)- MO), while the LUMO of ethylene (\( \pi^* \)-MO) can overlap with the HOMO of butadiene (\( \pi^*_2 \)-MO) (Figure 1.22).

Based on the rule of conservation of the orbital symmetry, it is also possible to predict the stereochemistry of the reaction products [137, 138]. For example, a thermal process according to scheme (1.232) yields
Figure 1.22 MO overlap in reactions of C$_2$H$_4$ and C$_4$H$_6$ with the formation of six-center transition states

Figure 1.23 Exchange interaction of frontier MOs of reactant in \([2\pi + 2\pi]\) cyclization process

An isomer with groups R in the cis position relative to the ring plane, whereas the photochemical process yields a product with groups R in the trans position. This conclusion can be derived from an analysis of the symmetry of frontier MOs (Figure 1.23). Indeed, for the overlap of an occupied \(\pi\)-MO of one \(\pi\) bond with a free (antibonding) MO of the second \(\pi\) bond, it is necessary to rotate both bonds in the same direction (conrotator), e.g., clockwise to obtain a cis isomer. In an excited state of the diene molecule, the overlap of an occupied \(\pi^*\)-MO with the second bond takes place upon the counter-rotation of bonds (disrotator), which leads to the formation of a trans isomer (photochemical cyclization).

An important reason for the appearance of prohibitions with respect to the symmetry of orbitals is a change in the position of a nodal plane (or the shape of the nodal plane) [144]. For example, a horizontal nodal plane (P$_{\text{inter}}$) in the SA combination in ethylene dimer passes to a vertical nodal plane (P$_{\text{intra}}$) in the AS combination in cyclobutane (Figure 1.21). In other words, the upper bonding electron pair must rearrange so that the horizontal nodal plane becomes the vertical plane, i.e., this pair must receive a kinetic energy sufficient to reach point C.

Correlation diagrams for various diatomic and polyatomic molecules are presented in [137]. It should also be emphasized that a symmetry-forbidden reaction is also prohibited in the reverse direction.

Upon the appearance of substituents in olefin molecules in the \([2\pi + 2\pi]\) cycle formation process

\[
\begin{align*}
\text{H}_2\text{C} &\equiv \text{CH}_2 \\
\text{H}_2\text{C} &\equiv \text{CHCH}_3
\end{align*}
\]

\[\rightarrow\]

\[
\begin{align*}
\text{H}_2\text{C} &\equiv \text{CH}_2 \\
\text{H}_2\text{C} &\equiv \text{CHCH}_3
\end{align*}
\]

(1.236)

the P$_{\text{intra}}$ and P$_{\text{inter}}$ planes cease to be the planes of symmetry, but if the MO energies are weakly disturbed by the introduction of substituents, the main conclusions of the Woodward–Hoffmann theory remain valid. However, if the asymmetry increases due to the introduction of both donor (X) and acceptor (Y)
substituents (X–CH=CH–Y), the reaction no longer belongs to the class of usual pericyclic reactions and may become an allowed thermal process [144].

The symmetry also decreases during the reaction of the addition of HX molecules to multiple bonds. In this case, the overlap is nonzero (as it is in the reactions of H–H and Cl–Cl addition), but the barrier is still high [137]. Apparently, this accounts for the fact that no examples of consistent reactions were reported for X = OH, Cl, Br, I, SR, NR₂, etc. For studying the reactions of this type, it is expedient to use the MO perturbation method together with an analysis of the symmetry of frontier MOs.

The replacement of H by a metal (metal complex) in the HX molecule substantially changes the situation in reactions of M–X fragment addition to multiple bonds (X = H, R, Hal, OH, OR, etc.). Consistent addition of M–X in the case of nontransition metals is still of low probability with respect to the symmetry of frontier MOs. These systems most probably feature pre-coordination due to the free orbitals of a metal and π-MOs of an unsaturated molecule with the subsequent interaction between the M–X bond and one of the p orbitals of the antibonding MO and with an almost synchronous addition of the M–X fragment to the multiple bond. This mechanism is operative, e.g., during the addition of B–H bond in R₂B–H to olefins (Figure 1.24) [139]. Note that these processes are not considered in the Woodward–Hoffmann theory.

In the case of transition metals, the addition of M–X fragments to multiple bonds as well as the metathesis of σ bonds (M–X + H–H) are allowed as consistent processes (Figure 1.25). The participation of a d orbital in the formation of σ bond M–X allows two electrons from the σ-MO to overlap with π*-MO of an olefin or σ*-MO of an X–Y molecule.

The reaction of [2π+2π] cycle formation also becomes allowed provided that a multiple bond in one of the reactants is formed with the participation of a transition metal (Figure 1.26), i.e., a carbene (or carbyne) metal complex reacts with an olefin (or alkyne) [1561]:

\[
\begin{align*}
M=\text{C} & \quad + & \quad \text{C}=\text{C} \\
\text{C}=\text{C} & \quad \rightarrow & \quad [\text{M} \quad \text{C} \quad \text{C}] \quad \rightarrow & \quad \text{M} \quad \text{C} \quad \text{C}
\end{align*}
\]

In this case, the d orbital involved in the formation of a \(d_\pi-p_\pi\) bond in the carbene metal complex can overlap with a bent π bond of the olefin molecule, in which substituents deviate from the olefin plane similar to the case of metal π complexes. The reactions of M–X or M=\text{C} < addition to multiple bonds most probably involve the pre-coordination of olefin (alkyne) to the metal with the formation of a π complex, followed by the consistent addition to the multiple bond via a cyclic transition state.

The possibility of reduction (or removal) of the prohibition with respect to symmetry (that is, lowering the corresponding barrier) due to the coordination of a metal to a substrate was considered for some time (in the 1970s) as a very attractive idea for explaining the nature of the catalytic effect [152, 153]. Indeed, theoretical analysis showed that the participation of both free and occupied d-AOs of a metal can actually
reduce the prohibition in the case of a consistent [2\pi + 2\pi] cycloaddition of olefins

\[
\begin{align*}
\text{M} & \quad \rightarrow \quad \text{M} \\
\pi \text{ complex} & \quad \rightarrow \quad \boxed{\text{M}} + \text{M}
\end{align*}
\]

(1.238)

and in the reaction of \( \text{H}_2 \) addition to a metal-coordinated olefin (Figure 1.27). In the latter case, the antibonding \( \pi^* \)-MO of the olefin occupied by \( d \) electrons of the metal overlaps with \( \sigma^* \)-MOs of \( \text{H}_2 \). However, these ideas have not been confirmed in experiment: there is no one proved case of addition of nondissociated \( \text{H}_2 \) molecules to multiple bonds, and the cyclodimerization of olefins proceeds via a symmetry-allowed formation of metallacyclobutane intermediates as a result of the consistent oxidative addition of two olefin molecules to the metal (Figure 1.28).

Thus, the role of a metal (metal complex) consists in making possible the appearance of new intermediates, the formation and transformation of which proceed as consistent, symmetry-allowed processes with relatively low activation energies.
isolobal analogy. This heuristic principle, which combines the main postulates of quantum chemistry (symmetry rules, energy characteristics of MOs) and the principle of least motion was formulated by Hoffmann [154] (see also [155–157]):

Molecules and/or molecular fragments must readily (with low barriers) react, provided that these species possess the same symmetry of frontier (or hybrid) orbitals, same number of frontier orbitals, same number of electrons on these orbitals, close energies, and similar geometry (spatial arrangement) of interacting orbitals.

Said fragments are called isolobal (from the Greek “λοβοσ” for lobe). Since the isolobal analogy (or principle) does not specify any particular nature of the fragment, this principle is essentially a rule of reactivity that combines all fields of chemistry, including organic, inorganic, element-organic, and organometallic.

For example, groups such as •CH₃ (with unpaired electron on the sp³ hybrid orbital) and •Mn(CO)₅ (with unpaired electron on the d²sp³ hybrid orbital) are isolobal. This implies that they can react in any combination: CH₃–CH₃, CH₃–Mn(CO)₅, and Mn(CO)₅–Mn(CO)₅. If some fragments are isolobal (which is indicated by a special sign as in the example below), this by no means implies that the reaction product will always exist in the form predicted based on the interaction of fragments. The structure can be somewhat modified for sterical or thermodynamic reasons. Nevertheless, the isolobal analogy provides a good prognostic principle that offers a convenient tool for synthetic chemists. It is assumed that isolobal fragments can react in a consistent elementary act, but their interaction most frequently is a multistep process.

Another example of isolobal fragments is as follows:

\[ \text{CH} (\text{carbyne}) \leftrightarrow \text{Co}(\text{CO})₃ \]

Pair interactions of these fragments lead to the following compounds: HC≡CH, HC≡Co(CO)₃, and (CO)₃Co≡Co(CO)₃. The latter compound, Co₂(CO)₆, exists but is highly reactive and readily adds another 2CO via the triple bond Co≡Co and stabilizes in the form of Co₂(CO)₈ with a structure of
All the formed molecules can interact with the like species and with each other. In particular, fragments L may combine in four to yield one molecule

\[
\text{HC}≡\text{CH} + \text{HC}≡\text{CH} \rightarrow \text{HC}≡\text{CH}
\]

(1.239)

The cyclobutadiene molecule is unstable (although it can exist as a reactive intermediate) and exhibits isomerization into a more stable form of tetrahedron:

\[
\begin{align*}
\text{HC} & \equiv \text{CH} \\
\text{HC} & \equiv \text{CH} \\
\end{align*}
\rightarrow
\begin{align*}
\text{CH} \\
\text{CH} \\
\text{CH} \\
\text{CH} \\
\end{align*}
\]

(1.240)

Examples (1.239)–(1.240) formally illustrate the pathway of combining isolobal fragments. In other words, each isolobal fragment L interacts with 3L fragments. All other possible molecules also exist in the form of tetrahedra:

There are tables of isolobal fragments [155, 158]. Evidently, neither the formation of molecules from three or four fragments, nor the interaction of two acetylene molecules (1.239) in the course of a thermal reaction represents an elementary act. These reactions are essentially the blocks of elementary steps.

Sometimes, fragments that are isolobal with respect to almost all parameters possess strongly different orbital energies. Therefore, a simple analysis of the symmetry and electron configurations does not guarantee that the selected fragments would readily interact with the formation of anticipated products.

- **Selection rules related to the conservation or insignificant variation of electron configurations.**

A strong perturbation of the electron configuration leads, in accordance to the principle of least motion, to significant values of \( E_{\text{act}} \) in the following cases [137, 145, 157]:

(i) interaction proceeds via the orbitals of reactants that lead to the formation of products in excited states;

(ii) orbitals of the ruptured and formed bonds are uncorrelated with respect to symmetry;

(iii) absence of the low-lying excited states for reactants with symmetry-forbidden ground states;

(iv) overlap of orbitals is weak or absent (\( \beta_{\text{ST}} \approx 0 \), see MO perturbation method).

The pathway of least motion for elementary steps is a pathway that creates or retains the maximum number of symmetry elements on the passage from reactants to products [137]. Let us consider several examples and rules, in which the principle of least motion is manifested in the conservation of electron configuration.
According to the electron transfer reaction

\[
\text{Co(Phen)}_3^{2+} + \text{Co}^*(\text{Phen})_3^{3+} \rightarrow \text{Co(Phen)}_3^{3+} + \text{Co}^*(\text{Phen})_3^{2+}
\]  

(1.241)

with \(\Delta G_{298}^o = 0\) (symmetric reaction), \(\text{Co}^{2+} (d^7)\) converts into \(\text{Co}^{3+} (d^6)\). The electron configuration (valence shell) in the course of this transfer \((t_{2g}^6 e_g^1 \rightarrow t_{2g}^6 e_g^0)\) remains unchanged, since six electrons on the triply degenerate bonding level \((t_{2g}^6)\) are retained and a single electron is removed from the antibonding \(e_g\) level. The second-order rate constant for reaction (1.241) amounts to \(1.1 \text{ M}^{-1}\text{s}^{-1}\). Because phenanthroline (Phen) belongs to strong ligands, the maximum number of \(7d\) electrons is paired (spin-paired state). In the case of a weak \(\text{NH}_3\) ligand, the situation dramatically changes. Fragment \(\text{Co(NH}_3)_2^{2+} (n = 4, 5, 6)\) occurs in a spin-unpaired (high-spin) \(t_{2g}^5 e_g^2\) state:

\[
\uparrow \uparrow \uparrow \downarrow \uparrow \downarrow \uparrow t_{2g}
\]

A strong complex of \(\text{Co(NH}_3)_6^{3+}\) (which is \(\sim 10^{30}\) times stronger than \(\text{Co(NH}_3)_6^{2+}\) occurs in a spin-paired \(t_{2g}^6 e_g^0\) state like the complex with Phen ligand. Therefore, the \(t_{2g}^5 e_g^2 \rightarrow t_{2g}^6 e_g^0\) electron transfer process is accompanied by a significant reconstruction of the valence shell and, accordingly, \(k = 10^{-9} \text{ M}^{-1} \text{s}^{-1}\).

The degree of \(\text{Co}^{2+}\) conversion into \(\text{Co}^{3+}\), about 50\%, is reached with Phen ligand for 1 s, while for \(\text{NH}_3\) ligand it would take \(\sim 30\) years. Evidently, a step (formally, elementary) with this rate can be excluded from the set of elementary steps to be considered in the analysis of reaction mechanisms.

Reactions of radical species (atoms) with other radicals, radicals with molecules, and stable molecules in the triplet state (such as \(\text{O}_2\)) with other molecules obey the Wigner–Witmer spin conservation rule [137].

The conservation of a valence electron shell in the course of reactions of transition metal complexes is related to the Tolman’s 16/18 electron rule [137]. It was noticed long ago (N. Sidgwick, 1929) that, in stable complex compounds, the total number of electrons surrounding the metal atom is equal to that in the electron shell of the closest inert gas atom. This number was called the effective atomic number (EAN). For \(d\) metals, the number of electrons in the valence shell of an atom bound to ligands is 18 \((d^{10}s^2p^6)\), and this shell is considered stable. For example, in the case of \(\text{Ni(CO)}_4\), we have \(\text{Ni}^{0}(d^{10})\) and CO (two-electron ligand), which yields \(n = 10 + 8 = 18\) e\(^-\).

In coordination compounds of transition metals, the number of electrons \(n\) introduced by each metal atom to the valence electron shell is equal to the number of electrons in its \(d^5sp^3\) shell, that is, corresponds to the given group of elements. For example:

\[
\begin{align*}
\text{V(CO)}_6 & \quad \text{group V} \quad n = 5 + (2 \cdot 6) = 17 \text{ e}^-; \\
\text{Cr(CO)}_6 & \quad \text{group VI} \quad n = 6 + (2 \cdot 6) = 18 \text{ e}^- \\
\text{Mn}_2(\text{CO})_{10} & \quad \text{group VII} \quad n = 7 + (2 \cdot 5) + 1 \quad (\text{from Mn}) = 18 \text{ e}^- 
\end{align*}
\]

By analogy with Mn, the formation of C–C bonds from \(2\text{CH}_3\cdot\) supplements the valence shell of C atom to octet. Because of sterical hindrances, \(\text{V(CO)}_6\) exists as a paramagnetic complex and forms a stable \(\text{V(CO)}_6^-\) anion (18 e\(^-\)), while \(\text{Co}_2(\text{CO})_8\) contains two bridging CO groups and appears as \(\text{Co}_2(\text{CO})_2^-(\mu\text{-CO})_2\). It is commonly accepted that each bridging carbonyl introduces 1 e\(^-\) to the shell of Co, so that we have \(9 \text{ e}^- + (2 \cdot 3) \text{ e}^- + 1 \text{ e}^-\) (from Co) + \((1 \cdot 2) \text{ e}^-\) (from \(\mu\text{-CO}) = 18 \text{ e}^-\). The number \(n\) of
Table 1.3 Numbers of electrons introduced by typical ligands [158]

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Ligand type</th>
<th>CM*</th>
<th>IM*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl, OH, NR, Me, Ph, R, H</td>
<td>X</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>CO, NH₃, PR₃</td>
<td>L</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>L</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>H₂</td>
<td>L</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>η³-C₃H₅</td>
<td>LX</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>η³-CH₃COO</td>
<td>LX</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>η⁴-C₄H₆</td>
<td>L₂</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>η⁵-C₅H₅</td>
<td>L₂X</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>η⁶-C₆H₆</td>
<td>L₃X</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

Note: *IM = ion model; CM = covalent model.

electrons in the valence shell can be calculated using ion models (IMs) and covalent models (CMs) [158]. For example:

\[
\text{HMn(CO)}_5, \text{ CM : } n = 7 + (2 \cdot 5) + 1 \text{ (from H)} = 18 \text{ e}^-; \\
\text{H}^+\text{Mn}^+\text{(CO)}_5, \text{ IM : } n = 6 + (2 \cdot 5) + 2 \text{ (from H}) = 18 \text{ e}^-.
\]

For using IM or CM, it is necessary to come to an agreement on the number of electrons introduced by particular ligands (Table 1.3).

For example, in a simple case of \(\text{MX}_a\text{L}^{c+}_b\), the number of introduced electrons according to the CM is

\[
n = N + a + 2b - c,
\]

while according to the IM this number is

\[
n = N - (a + c) + 2a + 2b = N + a + 2b - c,
\]

where \(a + c\) is the metal oxidation number and \(N\) is the number of its valence electrons (or the group number in the periodic table).

In organometallic chemistry, there are many exceptions to the 18 electron rule, some examples being offered by \(\text{Me}_2\text{NbCl}_3\) \((n = 10)\), \(\text{WMe}_6\) \((n = 12)\), and \(\text{NiCp}_2\) \((n = 20)\). The EAN rule works satisfactorily for small but strong ligands (H, CO, CN). At the ends of transition metal series (Groups 8–11) the tendency to form 16-electron complexes is manifested on the passage from left to right. Nevertheless, the generalization over a large body of experimental material allowed Tolman to formulate the following rule:

**Intermediates formed in the reactions of complex and organometallic compounds usually possess 16- or 18-electron shells. These intermediates usually exist in significant amounts.**

Thus, in reactions involving \(d\) metals that can be considered as elementary steps, the number of valence electrons must typically change by two \((18 \rightarrow 16 \rightarrow 18 \text{ and so on}) [159]\). Complexes with 16 electrons in the valence shell are naturally more reactive with respect to ligand substitution, since they admit substitution according to the associative mechanism:

\[
\begin{align*}
\text{ML}_4 + \cdot\text{L}^* & \rightleftharpoons \text{ML}_4\text{L}^* \\
16 \text{ e}^- & \rightleftharpoons 18 \text{ e}^- \rightleftharpoons 16 \text{ e}^-
\end{align*}
\] (1.242)
For example, Rh(\text{Acac})(\text{C}_2\text{H}_4)_2 (16 \text{ e}^-) exchanges ethylene ($^{13}\text{C}_2\text{H}_4$) by the associative mechanism at a rate constant above $10^4 \text{ s}^{-1}$ ($T = 25^\circ \text{C}, P = 1 \text{ bar}$), while (C$_5$H$_5$)Rh(\text{C}_2\text{H}_4)$_2$ (18 \text{ e}^-) exchanges ethylene by the dissociative mechanism at a rate constant of $\sim 4 \cdot 10^{-10} \text{ s}^{-1}$ [159].

Among the three possible mechanisms of CO insertion into the CH$_3$–Mn bond, the least probable variant, according to the Tolman rule, is (1):

$$\begin{align*}
\text{CH}_3\text{Mn(CO)}_5 & \quad (1) \quad \text{CO} \quad \text{CH}_3\text{Mn(CO)}_6 \quad 20 \text{ e}^- \quad \text{CH}_3\text{COMn(CO)}_5 \quad 18 \text{ e}^- \\
\text{CH}_3\text{Mn(CO)}_5 & \quad (2) \quad \text{CO} \quad \text{CH}_3\text{COMn(CO)}_4 \quad 16 \text{ e}^- \quad \text{CH}_3\text{COMn(CO)}_5 \quad 18 \text{ e}^- \\
\text{CH}_3\text{Mn(CO)}_5 & \quad (3) \quad \text{CO} \quad \text{CH}_3\text{COMn(CO)}_5 
\end{align*}$$

(1.243)

In the presence of $\pi$-allyl, $\pi$-cyclopentadienyl, and $\pi$-indenyl ligands, the associative mechanism for 18-electron complexes is sometimes possible without transition to 20-electron shells, which is due to a change in the type of $\eta$-ligand coordination (on the passage from $\eta^5$ to $\eta^3$ type and from $\eta^3$ to $\eta^1$ type):

$$\begin{align*}
\begin{array}{c}
\text{ML} \\
\hline
\text{ML} \\
\hline
\text{ML} \\
\hline
\text{ML} \\
\hline
\text{ML} \\
\hline
\text{ML} \\
\hline
\text{ML}
\end{array}
\end{align*}$$

(1.244)

The rule of 18-electron-shell stability is also applicable to metal clusters [160], although a more general rule for metal clusters is provided by calculating the Wade “magic” numbers of stable valence shells [160].

For selecting a ligand to be replaced by another one in substitution reactions and evaluating the relative rate of ligand L$_1$ substitution by L$_2$ in the case of flat square and octahedral complexes of $d$ metals, it is also possible to use the Chernyaev law of trans-influence and the Grinberg–Kukushkin law of cis-influence [161–166]. The former law, established by I.I. Chernyaev in 1926 for Pt(II) complexes, says that certain ligands X accelerate the substitution of ligand L$_1$ in trans position relative to X (trans-coordinate X–Pt–L$_1$). The order of efficiency of a given ligand X is retained (to the first approximation) irrespective of the nature of ligand L$_1$. This effect exhibited a kinetic character, and the series of trans-activity were constructed with respect to the rate of ligand L$_1$ substitution. The trans-influence of ligands X decreases in the following series:

$\text{CN}^- \sim \text{CO} \sim \text{C}_2\text{H}_4 \sim \text{NO} > \text{SC(NH}_2)_2, \text{R}_2\text{S}, \text{R}_3\text{P}, \text{NO}_2^-, \text{I}^-, \text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{OH}^- > \text{RNH}_2 > \text{NH}_3 > \text{H}_2\text{O}$.

A strong trans-influence is known for ligands $\text{H}^- (\sim \text{R}_2\text{S})$, $\text{CH}_3^- (\sim \text{SC(NH}_2)_2$), and $\text{C}_6\text{H}_5^- (\sim \text{NO}_2^-)$. Investigations showed that the trans-influence is also manifested by changes in the equilibrium thermodynamic properties and geometric parameters of M–L$_1$ bonds. For this reason, the term trans-influence usually implies the effect of ligand X on the equilibrium characteristics of M–L$_1$ bonds, while the term trans-effect refers to the influence of ligand X on the kinetic properties of ligand L$_1$ in the
substitution reaction. Quantum-chemical models have been developed that explain the role of σ- and π-donor and π-acceptor properties of ligands X and L₁ in the manifestations of both trans-influence and trans-effect [164, 165].

Another phenomenon related to the properties of electron configurations of metal complexes is known as the Jahn–Teller effect (or the structure distortion due to the Jahn–Teller effect) [146]. This effect helps in selecting the type of elementary step or even the direction of transformation of metal complexes. The Jahn–Teller theorem is as follows:

*If the ground-state electron configuration in a nonlinear molecule is degenerate, then the molecule exhibits distortion that removes the degeneracy and increases the stability.*

For example, in octahedral aqua-complexes of Cu²⁺ and Cr²⁺ (with d⁹ and d⁴ configurations), the degeneracy of t₂g and e_g levels is removed as a result of the elongation of axial bonds between metal ions and H₂O molecules (Figure 1.29). Here, two axial water molecules are less strongly bound and more readily replaced by ligands (water molecules or anions) than water molecules in the equatorial plane, the substitution taking place within the framework of the dissociative exchange mechanism.

### 1.4.4 Topological selection rules for elementary steps

In the analysis of ethylene cyclodimerization reaction, it was pointed out that the transition states in elementary steps can possess various structures (depending on the number of reacting centers and the mode of their interaction) and, hence, different topologies. In particular, two ethylene molecules cannot form a (symmetry-forbidden) cyclic transition state A via a thermal reaction, but they can form a linear four-center transition state B:

\[
\begin{align*}
\text{A} & : \begin{bmatrix} \text{H}_2\text{C} & \cdots & \text{CH}_2 \\ \text{H}_2\text{C} & \cdots & \text{CH}_2 \end{bmatrix} \\
\text{B} & : \begin{bmatrix} \text{H}_2\text{C} & \cdots & \text{CH}_2 \\
\text{H}_2\text{C} & \text{CH}_2 \end{bmatrix}
\end{align*}
\]

A transition state formed during the Diels–Alder reaction is a hexa-center cycle. This circumstance poses some questions as to which structures of transition states are realized in the elementary steps studied and what is the possible topology of the redistribution of bonds and unshared electron pairs in the course of consistent reactions.
Here, by the *topology of bond redistribution*, we imply the structure of a graph that is obtained upon superposition of the ruptured and created bonds. Any chemical reaction can be represented by a graph from which atoms and atomic groups not involved in changing bonds are removed. For example, the Diels–Alder reaction can be represented by the following graphical equation that describes the redistribution of bonds:

\[ G_1 \xrightarrow{\text{ reaction }} G_2 \]

This equation type is referred to as the *symbolic* [167] or the *base reaction* [168–171]. Then it is possible to remove bonds that remain unchanged, which yields an equation that reflects the *reaction type* [6]:

\[ G_3 \xrightarrow{\text{ reaction }} G_4 \]

The superposition of graphs \( G_3 \) and \( G_4 \) yields the following graph \( G_5 \):

\[ \Gamma_5 \]

which is called the *topology identifier* (TI) [167] or the *topology of reaction category* [168]. The TI characterizes the topology of bond redistribution and presents a simplified topology of the transition state (in the given case, a hexagonal cyclic topology). If the simultaneous rupture and/or formation of multiple bonds is expected, then graphs \( G_3, G_4, \) and \( G_5 \) contain multiple edges that form additional cycles in the TI.

It is important to note [6] that the *reactions, which can be classified on sufficient grounds as elementary steps, virtually never have mixed (linear-cyclic) or more complicated (polycyclic) TIs*. This conclusion is based on an analysis of databases available for the elementary steps of reactions involving metal complexes and organometallic compounds [6] and on the results [170] obtained from an analysis of the ORAC and REACS databases for about 80,000 organic reactions. It should be noted that the processes with complex topologies referred to as “coarctate” reactions with coarctate transition states [169, 170, 172] apparently do not represent elementary steps. Indeed, these reactions, for example,

\[ \xrightarrow{\text{ reaction }} + \text{HC} \equiv \text{CH} + \text{N=N} + \text{CO}_2, \]
with a TI of the following type \( G_6 \)

\[
\text{TI: } \quad G_6
\]

involve a change in the coordinates of a large number of nuclei, for which the synchronization of many oscillations (in this case, of nine bonds with various directions, which is necessary for the fragmentation of four molecules) seems hardly probable. The given TI \( G_6 \) is a complex polycyclic graph. The molecularity of the reverse reaction \( \mu = 4 \) is also indicative of a low probability that reaction (1.247) represents an elementary step, since the reverse reaction cannot proceed via the same transition state.

As was noted above, the molecularity \( \mu \) of a reverse step estimated with allowance for the basic principle of microscopic reversibility must not exceed 2, but this circumstance was ignored during the analysis of coarctate reactions. According to R. Ponec (see, e.g., [6]), the quality of quantum-chemical calculations of the potential energy surfaces used to justify the elementarity of coarctate reactions was insufficient for distinguishing between multistep and consistent mechanisms.

Let us consider the application of the above-described procedure to an analysis of transition states for the reaction of olefin epoxidation in the reaction with a molybdenum peroxy complex [173]:

\[
O\{\text{[Mo]}\} + C\rightleftharpoons O\{\text{[Mo]}\} + O\text{C}
\]

Assuming that this is an elementary step that proceeds via a transition state \( C \) according to the scheme

\[
\begin{bmatrix}
1 \\
O \\
2 \\
O\{\text{[Mo]}\} \\
3 \\
C \\
4 \\
O \\
5 \\
\end{bmatrix}
\]

we obtain a TI with the following complex (bicyclic) structure:

\[
\begin{bmatrix}
1 \\
O \\
2 \\
O\{\text{[Mo]}\} \\
3 \\
C \\
4 \\
O \\
5 \\
\end{bmatrix}
\]

Then, it can be suggested that this is not an elementary reaction. Based on an analysis of reaction kinetics [174, 175], the following two-step mechanism was proposed:

\[
\begin{align*}
&O\{\text{[Mo]}\} + C \quad \rightleftharpoons \quad O\{\text{[Mo]}\} + O\text{C} \\
&\text{O\{[Mo]\} + C} \quad \overset{1}{\rightleftharpoons} \quad O\text{C} \quad \overset{2}{\rightleftharpoons} \quad \text{O\{[Mo]\} + O\text{C}}
\end{align*}
\]
Let us consider the topology of transition states for the two steps:

\[
\begin{align*}
\text{TI:} \\
(1.251) \\
\end{align*}
\]

As can be seen, the first step (1.251) exhibits a mixed (linear and cyclic) topology. It can be suggested that there is one more elementary step, at which the M–O bond in the peroxy complex exhibits pre-rupture as

\[
\begin{align*}
\text{TI:} \\
(1.252) \\
\end{align*}
\]

which has a linear TI structure (\(\bullet \rightarrow \bullet \rightarrow \bullet\)). The resulting electrophilic center (\(-\text{O}^+\)) is added to olefin with a cyclic TI:

\[
\begin{align*}
\text{TI:} \\
(1.253) \\
\end{align*}
\]

The intermediate compound (1.254) is converted into the reaction product in the second step (1.250) via a linear transition state (1.252).

Thus, an analysis of the topological structure (as represented by the TI) can be used to determine the possible elementary steps, that is, to find reactions which, from the standpoint of topology, have a high probability to be elementary steps according to the following rule:

Reactions whose transition states do not exhibit simple topology (cyclic or linear) are not considered to be elementary steps.

If a reaction involves simultaneous (synchronous) rupture and/or formation of multiple bonds, these bonds are represented on the graphs by double (or triple) edges, for example:
According to the above notions, reaction (1.256) should not be considered as a consistent elementary step. Some other topological criteria of the elementarity of steps have been formulated for pericyclic reactions [176].

The set of topological principles can include a heuristic rule concerning the number of bonds ruptured and formed in the course of an elementary reaction. An analysis of elementary steps in this respect [6, 77] showed that, in an overwhelming majority of cases, the difference of the numbers of ruptured and formed bonds does not exceed one:

\[ |\Delta q| \leq 1 \]

(irrespective of the sign of \( \Delta H^0 \) for the elementary step). According to this rule, reaction (1.256) is not an elementary step since \( |\Delta q| = 2 \).

Based on the above brief review, it is possible to formulate a set of rules for determining thermodynamically allowed elementary thermal reaction steps. To the first approximation, reactions be considered elementary, provided that:

- molecularity of the forward and reverse reactions does not exceed two (\( \mu \leq 2 \));
- number of the ruptured bond does not differ from the number of the formed bond by more than one (bond compensation rule, \( |\Delta q| \leq 1 \));
- occupied frontier MOs of reactants are symmetry-correlated with those of the products (frontier MOs of the donor and acceptor must possess the same symmetry);
- topology of bond redistribution (topological structure of the transition state) is either linear or cyclic.

The principle of least motion can be considered as an additional rule, the expediency of which was demonstrated in Section 1.4.

Let us return to considering reaction (1.219) between hydrogen and iodine. The molecularity of a proposed consistent elementary step is \( \mu = 2 \), the bond compensation index is \( |\Delta q| = 0 \), and the topological structure of the transition state is cyclic. The only criterion for the impossibility of this elementary act, which turns out to be decisive in this case, is prohibition with respect to the symmetry. However, reaction (1.219) proceeds in accordance with the kinetic equation

\[ W^+ = k^+[H_2][I_2] \]

and \( E_{act} \approx 40 \text{ kcal/mole} \) (at \( T = 500–600 \text{ K} \)). Then we have to consider the two possible variants with the dissociation of \( I_2 \) molecule.

(i) Chain mechanism:

\[ I_2 \xrightarrow{K_0} 2I; \]
\[ \text{I} + \text{H}_2 \xrightleftharpoons[k_1]{\text{H}} \text{HI} + \text{H}; \quad (1.260) \]
\[ \text{H} + \text{I}_2 \xrightarrow[k_2]{\text{H} \cdot \cdot \cdot \text{H}} \text{HI} + \text{I}. \quad (1.261) \]

The activation energy of this process according to the equation
\[
W^+ = k_1 K_0^{1/2}[\text{H}_2][\text{I}_2]^{1/2}
\]
amounts to \(\sim 54\) kcal/mole and the reaction order with respect to \([\text{I}_2]\) differs from that observed in experiment. The other variants of radical chain termination are low probable, since \([\text{I}]/[\text{H}] \approx 10^{12}\) at \(T = 600\)K.

(ii) Radical mechanism, which includes the \(\text{IH}_2\) complex formation and its subsequent decomposition at the limiting step via a symmetry-allowed transition state \(|\text{I} \cdot \cdot \cdot \text{H} \cdot \cdot \cdot \text{H} \cdot \cdot \cdot \text{I}|\): 

\[
\begin{align*}
\text{I} + \text{H}_2 & \xrightleftharpoons[k_1]{\text{H}} \text{IH}_2; \\
\text{IH}_2 + \text{I} & \xrightarrow[k_2]{\text{H} \cdot \cdot \cdot \text{H}} 2\text{HI}; \\
W^+ & = k_2 K_0 K_1 [\text{H}_2][\text{I}_2]; \\
E_{\text{act}} & = E_2 + \Delta H_0^0 + \Delta H_1^0. \quad (1.263) \quad (1.264) \quad (1.265)
\end{align*}
\]

Since the experimental activation energy is \(E_{\text{act}} \approx 40\) kcal/mole [177] and \(\Delta H_0^0 = 35.5\) kcal/mole, we obtain \(E_2 + \Delta H_1^0 \approx 4.5\) kcal/mole. At a small estimated value of \(\Delta H_1^0\) (about \(-0.4\) kcal/mole), we have \(E_2 \approx 5\) kcal/mole.[7] Estimating the values of preexponential factors for the rate constants and equilibrium constant of steps (1.259), (1.263), and (1.264) in the second variant of the proposed mechanism, we eventually obtain the observed rate constant \(k_{\text{obs}} = k_2 K_0 K_1 = 2 \cdot 10^{-4}\) L\(\cdot\)mole\(^{-1}\)\(\cdot\)s\(^{-1}\) at \(T = 600\)K, which is close to the experimental value of \(k^+\) in Eq. (1.258).

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