Thermodynamics in the Limit of Irreversible Reactions

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Abstract

For many real physico-chemical complex systems detailed mechanism includes both reversible and irreversible reactions. Such systems are typical in homogeneous combustion and heterogeneous catalytic oxidation. Most complex enzyme reactions include irreversible steps. The classical thermodynamics has no limit for irreversible reactions whereas the kinetic equations may have such a limit. We represent the systems with irreversible reactions as the limits of the fully reversible systems when some of the equilibrium concentrations tend to zero. The structure of the limit reaction system crucially depends on the relative rates of this tendency to zero. We study the dynamics of the limit system and describe its limit behavior as $t \to \infty$. If the reversible systems obey the principle of detailed balance then the limit system with some irreversible reactions must satisfy the extended principle of detailed balance. It is formulated and proven in the form of two conditions: (i) the reversible part satisfies the principle of detailed balance and (ii) the convex hull of the stoichiometric vectors of the irreversible reactions does not intersect the linear span of the stoichiometric vectors of the reversible reactions. These conditions imply the existence of the global Lyapunov functionals and allow an algebraic description of the limit behavior. The thermodynamic theory of the irreversible limit of reversible reactions is illustrated by the analysis of hydrogen combustion.

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1. Introduction

1.1. The problem: non-existence of thermodynamic functions in the limit of irreversible reactions

We consider a homogeneous chemical system with $n$ components $A_i$, the concentration of $A_i$ is $c_i \geq 0$, the amount of $A_i$ in the system is $N_i \geq 0$, $V$ is the volume, $N_i = Vc_i$, $T$ is the temperature. The $n$ dimensional vectors $c = (c_i)$ and $N = (N_i)$ belong to the closed positive orthant $\mathbb{R}^n_+$ in $\mathbb{R}^n$. ($\mathbb{R}^n_+$ is the set of all vectors $x \in \mathbb{R}^n$ such that $x_i \geq 0$ for all $i$.)

The classical thermodynamics has no limit for irreversible reactions whereas the kinetic equations have. For example, let us consider a simple cycle

$$A_1 \xrightleftharpoons[k_{-1}]{k_1} A_2 \xrightleftharpoons[k_{-2}]{k_2} A_3 \xrightleftharpoons[k_{-3}]{k_3} A_1$$
with the equilibrium concentrations \( c_{eq} = (c_{eq1}, c_{eq2}, c_{eq3}) \) and the detailed balance conditions:

\[
k_i c_{eq}^i = k_{-i} c_{eq}^{i+1}
\]

under the standard cyclic convention, here, \( A_{3+1} = A_1 \) and \( c_{3+1} = c_1 \). The perfect free energy has the form

\[F = \sum_i RT V c_i \left( \ln \left( \frac{c_i}{c_{eq}^i} \right) - 1 \right) + \text{const}.
\]

Let the equilibrium concentration \( c_{eq}^1 \to 0 \) for the fixed values of \( c_{eq}^{2,3} \). This means that

\[
\frac{k_{-1}}{k_1} = \frac{c_{eq}^1}{c_{eq}^2} \to 0 \quad \text{and} \quad \frac{k_3}{k_{-3}} = \frac{c_{eq}^1}{c_{eq}^3} \to 0.
\]

Let us take the fixed values of the rate constants \( k_1, k_{+2} \) and \( k_{-3} \). Then the limit kinetic system exists and has the form:

\[A_1 \rightleftharpoons A_2 \quad \rightleftharpoons \quad A_3 \rightleftharpoons A_1.
\]

It is a routine task to write a first order kinetic equation for this scheme. At the same time, the free energy function \( F \) has no limit: it tends to \( \infty \) for any positive vector of concentrations because the term \( c_1 \ln(c_1/c_{eq}^1) \) increases to \( \infty \). The free energy cannot be normalized by adding a constant term because the variation of the term \( c_1 \ln(c_1/c_{eq}^1) \) also increases to \( \infty \), it varies from \(-c_1^0/\varepsilon \) (for the minimizer, \( c_1 = c_{eq}^1/\varepsilon \)) to a large number \( \overline{c}(\ln \overline{c} - \ln c_{eq}^1) \) (for \( c_1 = \overline{c} \)).

The logarithmic singularity is rather “soft” and does not cause a real physical problem because even for \( c_{eq}^1/c_1 = 10^{-10} \) the corresponding large term in the free energy will be just \( \sim 23RT \) per mole. Nevertheless, the absence of the limit causes some mathematical questions. For example, the density,

\[f = F/(RTV) = \sum_i c_i (\ln(c_i/c_{eq}^i) - 1),
\]

is a Lyapunov function for a system of chemical kinetics for a perfect mixture with detailed balance under isochoric isothermal conditions. Here, \( c_i \) is the concentration of the \( i \)th component and \( c_{eq}^i \) is its equilibrium concentration for a selected value of the linear conservation laws, the so-called “reference equilibrium”.

This function is used for analysis of stability, existence and uniqueness of chemical equilibrium since the work of Zeldovich (1938, reprinted in 1996 [24]). Detailed analysis of the connections between detailed balance and the free energy function was provided in [19]. Perhaps, the first detailed proof that \( f \) is a Lyapunov function for chemical kinetics of perfect systems with detailed balance was published in 1975 [22]. Of course, it does not differ significantly from the Boltzman’s proof of his \( H \)-theorem (1873 [2]).

For the irreversible systems which are obtained as limits of the systems with detailed balance, we should expect the preservation of stability of the equilibrium. Moreover, one can expect existence of the Lyapunov functions which are as universal as the thermodynamic functions are. The “universality” means that these functions depend on the list of components and on the equilibrium concentrations but do not depend on the reaction rate constants directly.

The thermodynamic potential of a component \( A_i \) cannot be defined in the irreversible limits when the equilibrium concentration of \( A_i \) tends to 0. Nevertheless, in this paper, we construct the universal Lyapunov functions for systems with some irreversible reactions. Instead of detailed balance we use the weaker assumption that these systems can be obtained from the systems with detailed balance when some constants tend to zero.

1.2. The extended form of detailed balance conditions for systems with irreversible reactions

Let us consider a reaction mechanism in the form of the system of stoichiometric equations

\[
\sum_i \alpha_{ri} A_i \to \sum_j \beta_{rj} A_j \quad (r = 1, \ldots, m),
\]
where $\alpha_{ri} \geq 0$, $\beta_{rj} \geq 0$ are the stoichiometric coefficients. The reverse reactions with positive rate constants are included in the list (2) separately (if they exist). The stoichiometric vector $\gamma_r$ of the elementary reaction is $\gamma_r = (\gamma_{ri})$, $\gamma_{ri} = \beta_{ri} - \alpha_{ri}$. We always assume that there exists a strictly positive conservation law, a vector $b = (b_i)$, $b_i > 0$ and $\sum b_i \gamma_{ri} = 0$ for all $r$. This may be the conservation of mass or of total number of atoms, for example.

According to the generalized mass action law, the reaction rate for an elementary reaction (2) is (compare to Eqs. (4), (7), and (14) in [14] and Eq. (4.10) in [7])

$$w_r = k_r \prod_{i=1}^{n} a_i^{\alpha_{ri}},$$

(3)

where $a_i \geq 0$ is the activity of $A_i$,

$$a_i = \exp \left( \frac{\mu_i - \mu_i^0}{RT} \right).$$

(4)

Here, $\mu_i$ is the chemical potential and $\mu_i^0$ is the standard chemical potential of the component $A_i$.

This law has a long history (see [6, 24, 13, 7]). It was invented in order to meet the thermodynamic restrictions on kinetics. For this purposes, according to the principle of detailed balance, the rate of the reverse reaction is defined by the same formula and its rate constant should be found from the detailed balance condition at a given equilibrium.

It is worth mentioning that the free energy has no limit when some of the reaction equilibrium constants tend to zero. For example, for the ideal gas the chemical potential is $\mu_i(c, T) = RT \ln c_i + \mu_i^0(T)$. In the irreversible limit some $\mu_i^0 \to \infty$. On the contrary, the activities remain finite (for the ideal gases $a_i = c_i$) and the approach based on the generalized mass action law and the detailed balance equations $w_r^+ = w_r^-$ can be applied to find the irreversible limit.

The list (2) includes reactions with the reaction rate constants $k_r > 0$. For each $r$ we define $k_r^+ = k_r$, $w_r^+ = w_r$, $k_r^-$ is the reaction rate constant for the reverse reaction if it is on the list (2) and 0 if it is not, $w_r^-$ is the reaction rate for the reverse reaction if it is on the list (2) and 0 if it is not. For a reversible reaction, $K_r = k_r^+/k_r^-$

The principle of detailed balance for the generalized mass action law is: For given values $k_r$ there exists a positive equilibrium $a_i^{eq} > 0$ with detailed balance, $w_r^+ = w_r^-$. Recently, we have formulated the extended form of the detailed balance conditions for the systems with some irreversible reactions [12]. This extended principle of detailed balance is valid for all systems which obey the generalized mass action law and are the limits of the systems with detailed balance when some of the reaction rate constants tend to zero. It consists of two parts:

- **The algebraic condition:** The principle of detailed balance is valid for the reversible part. (This means that for the set of all reversible reactions there exists a positive equilibrium where all the elementary reactions are equilibrated by their reverse reactions.)

- **The structural condition:** The convex hull of the stoichiometric vectors of the irreversible reactions has empty intersection with the linear span of the stoichiometric vectors of the reversible reactions. (Physically, this means that the irreversible reactions cannot be included in oriented cyclic pathways.)

Let us recall the formal convention: the linear span of empty set is $\{0\}$, the convex hull of empty set is empty.

In our previous work [12] we studied the systems with some irreversible reactions which are the limits of the reversible systems with detailed balance. The structural and algebraic conditions were found. The present paper is focused on the dynamical consequences of these conditions. We prove that the attractors always consist of the fixed points. These limit points (“partial equilibria”) are situated on the faces of the positive orthant of concentrations. These faces and the partial equilibria are described in the paper.
1.3. The structure of the paper

In Sec. 2 we study the systems with detailed balance, their multiscale limits and the limit systems which satisfy the extended principle of detailed balance. The classical Wegscheider identities for the reaction rate constants are presented. Their limits when some of the equilibria tend to zero give the extended principle of detailed balance.

We use the generalized mass action law for the reaction rates. For the analysis of equilibria for the general systems, the formulas with activities are the same as for the ideal systems and it is convenient to work with activities unless we need to study dynamics. The dynamical variables are amounts and concentrations. In a special subsection 2.3 we discuss the relations between concentration and activities, formulate the main assumptions and present formulas for the dissipation rate.

We introduce attractors of the systems with some irreversible reactions and study them in Sec. 3. It includes the central results of the paper. We fully characterize the faces of the positive orthant that include ω-limit sets. On such a face, dynamics is completely degenerated (zero rates) or it is driven by a smaller reversible system that obeys classical thermodynamics.

Hydrogen combustion is the most studied and very important gas reaction. It serves as a main benchmark example for many studies of chemical kinetics. This is already not a toy example but the complexity of this system is not extremely high: in the usual models there are 6-8 components and ∼15-30 elementary reversible reactions. Under various conditions some of these reactions are practically irreversible. We use this system as a benchmark in Sec. 4 and give an example of the correct separation of the reactions into reversible and irreversible part. The limit behavior of this system in time is described.

In Conclusion we briefly discuss the results with focus on the unsolved problems.

2. Multiscale limit of a system with detailed balance

2.1. Two classical approaches to the detailed balance condition

There are two traditional approach to the description of the reversible systems with detailed balance. First, we can start from the independent rate constants of the elementary reactions and consider the solvability of the detailed balance equations as the additional condition on the admissible values of the rate constants. Here, for m elementary reactions we have m constants (m should be an even number, m = 2ℓ, ℓ = m/2) and some equations which describe connections between these constants. This approach was introduced by Wegscheider in 1901 [23] and developed further by many authors [20, 4].

Secondly, we can select a “forward” reaction in each pair of mutually reverse elementary reactions. If a positive equilibrium is known then we can find the reaction rate constants for the reverse reaction from the constants for forward reaction and the detailed balance equations. Therefore, the forward reaction rate constants and a set of the equilibrium activities form the complete description of the reaction. Here we have ℓ + n independent constants, ℓ = m/2 rate constants of forward reactions and n (it is the number of components) equilibrium activities. For these ℓ + n constants, the principle of detailed balance produces no restrictions. This second approach is popular in applied chemical thermodynamics and kinetics [17, 10, 25] because it is convenient to work with the independent parameters “from scratch”.

The Wegscheider conditions appear as the necessary and sufficient conditions of solvability of the detailed balance equations. (See, for example, the textbook [24]). Let us join the forward and reverse elementary reactions and write

$$\sum_i \alpha_{ri} A_i = \sum_j \beta_{rj} A_j \quad (r = 1, \ldots, \ell).$$

The stoichiometric matrix is $\Gamma = (\gamma_{ri})$, $\gamma_{ri} = \beta_{ri} - \alpha_{ri}$ (gain minus loss). The stoichiometric vector $\gamma_r$ is the rth row of $\Gamma$ with coordinates $\gamma_{ri} = \beta_{ri} - \alpha_{ri}$.

Both sides of the detailed balance equations, $w_i^+ = w_i^-$, are positive for positive activities. The solvability of this system for positive activities means the solvability of the following system of linear equations:

$$\sum_i \gamma_{ri} x_i = \ln k_r^+ - \ln k_r^- = \ln K_r \quad (r = 1, \ldots, \ell)$$
(x_i = \ln a_i^{eq}). Of course, we assume that if \( k_i^+ > 0 \) then \( k_i^- > 0 \) (reversibility) and the equilibrium constant \( K_r > 0 \) is defined for all reactions from \([2]\).

**Proposition 1.** The necessary and sufficient conditions for existence of the positive equilibrium \( a_i^{eq} > 0 \) with detailed balance is: For any solution \( \lambda = (\lambda_r) \) of the system

\[
\lambda \Gamma = 0 \quad \left( \text{i.e. } \sum_{r=1}^\ell \lambda_r \gamma_{ri} = 0 \text{ for all } i \right)
\]

the Wegscheider identity holds:

\[
\prod_{r=1}^\ell (k_i^+)^{\lambda_r} = \prod_{r=1}^\ell (k_i^-)^{\lambda_r}.
\]

It is sufficient to use in \([2]\) any basis of solutions of the system \([7]\): \( \lambda \in \{\lambda^1, \cdots, \lambda^q\} \).

### 2.2. Multiscale degeneration of equilibria

We consider the systems with some irreversible reactions as the limits of the fully reversible systems when some reaction rate constants tend to zero. In the reversible systems, the principle of detailed balance implies the Wegscheider identities \([3]\). Therefore, the limit system is not arbitrary. Some consequences of the Wegscheider identities persist though a part of reaction rate constants in these identities become zero. In \([12]\), we compare these consequences with the grin of the Cheshire cat: the whole cat (the reversible system with detailed balance) vanishes but the grin persists.

We can postulate that some reaction rate constants go to zero. However, the reaction rate constants are not independent. They are connected by the Wegscheider identities. The rate constants should tend to zero with preservation of their relations. Therefore, the simple strategy, just to neglect the rates of some of the reactions, cannot be applied for complex reactions. Nevertheless, we can change the variables and use the independent set “reaction rate constants for the forward reactions + equilibrium activities” (see \([17, 10, 25, 12]\)). Every set of positive values of these variables corresponds to a reversible system with detailed balance and no additional restrictions are needed. If the reversible system degenerates to a system with some irreversible reactions then some of the equilibrium activities tend to zero. Let us study this process of degeneration of reversible reactions into irreversible ones starting from the corresponding degeneration of equilibrium activities to zero.

Let us take a system with detailed balance and send some of the equilibrium activities to zero: \( a_i^{eq} \rightarrow 0 \) when \( i \in I \) for some set of indexes \( I \). Immediately we find a surprise: this assumption is not sufficient to find a limiting irreversible mechanism. It is necessary to take into account the rates of the convergency to zero of different \( a_i^{eq} \). Indeed, let us study a very simple example,

\[
A_1 \xrightarrow{k_1} A_2 \xrightarrow{k_2} A_3
\]

when \( a_1^{eq}, a_2^{eq} \rightarrow 0 \).

If \( a_1^{eq}, a_2^{eq} \rightarrow 0, a_1^{eq}/a_2^{eq} = \text{const} > 0 \) and \( a_3^{eq} = \text{const} > 0 \) then the limit system should be \( A_1 \xrightarrow{k_1} A_2 \rightarrow A_3 \) and we can keep \( k_{1, -1, 2} = \text{const} \) whereas \( k_{-2} \rightarrow 0 \).

If \( a_1^{eq}, a_2^{eq} \rightarrow 0, a_1^{eq}/a_2^{eq} \rightarrow 0 \) then the limit system should be \( A_1 \rightarrow A_2 \rightarrow A_3 \) and we can keep \( k_{1, 2} = \text{const} > 0 \) whereas \( k_{-1, -2} \rightarrow 0 \).

If \( a_1^{eq}, a_2^{eq} \rightarrow 0, a_2^{eq}/a_1^{eq} \rightarrow 0 \) then in the limit survives only one reaction \( A_2 \rightarrow A_3 \) (if we assume that all the reaction rate constants are bounded).

We study asymptotics \( a_i^{eq} = \text{const} \times \varepsilon^{\delta_i}, \varepsilon \rightarrow 0 \) for various values of non-negative exponents \( \delta_i \geq 0 \) (\( i = 1, \ldots, n \)). At equilibrium, each reaction rate in the generalized mass action law is proportional to a power of \( \varepsilon \):

\[
w_r^{+} = k_r^+ \text{const} \times \varepsilon^{\sum_i \alpha_{r,i} \delta_i}, \quad w_r^{-} = k_r^- \text{const} \times \varepsilon^{\sum_i \beta_{r,i} \delta_i}.
\]
According to the principle of detailed balance, \( w_r^{eq+} = w_r^{eq-} \) and

\[
\frac{k_r^+}{k_r^-} = \text{const} \times \varepsilon^{(\gamma_r, \delta)} ,
\]

where \( \delta \) is the vector of exponents, \( \delta = (\delta_i) \).

There are three groups of reactions with respect to the given vector \( \delta \):

1. \( (\gamma_r, \delta) = 0 \); 2. \( (\gamma_r, \delta) < 0 \); 3. \( (\gamma_r, \delta) > 0 \).

In the first group \( ((\gamma_r, \delta) = 0) \) the ratio \( k_r^+ / k_r^- \) remains constant and we can take \( k_r^+ = \text{const} > 0 \). In the second group \( ((\gamma_r, \delta) < 0) \) the ratio \( k_r^+ / k_r^- \to 0 \) and we should take \( k_r^- \to 0 \) whereas \( k_r^+ \) may remain constant and positive. In the third group \( ((\gamma_r, \delta) > 0) \), the situation is inverse: \( k_r^+ / k_r^- \to 0 \) and we can take \( k_r^- = \text{const} > 0 \), whereas \( k_r^+ \to 0 \).

These three groups depend on \( \delta \) but this dependence is piecewise constant. For every \( \gamma_r \), three sets of \( \delta \) are defined: (i) hyperplane \( (\gamma_r, \delta) = 0 \), (ii) hemispace \( (\gamma_r, \delta) < 0 \) and hemispace \( (\gamma_r, \delta) > 0 \). The space of vectors \( \delta \) is split in the subsets defined by the values of functions \( \text{sign}(\gamma_r, \delta) (\pm 1 \text{ or } 0) \).

We consider bounded systems, hence the negative values of \( \delta \) should be forbidden. At least one equilibrium activity should not vanish. Therefore, \( \delta_i = 0 \) for some \( j \). Below we assume that \( \delta_i \geq 0 \) and \( \delta_i = 0 \) for a non-empty set of indices \( J_0 \). Moreover, the atom balance in equilibrium should be positive. Here, this means that for the set of equilibrium concentrations \( c_i^{eq} (i \in J_0) \) the corresponding values of all atomic concentrations are strictly positive and separated from zero.

Let the vector of exponents, \( \delta = (\delta_i) \) be given and the three groups of reactions be found. For the reactions of the third group (with \( (\gamma_r, \delta) > 0 \)) the forward reaction vanishes in the limit \( \varepsilon \to 0 \). It is convenient to transpose the stoichiometric equations for these reactions and swap the forward reactions with reverse ones. Let us perform this transposition. After that, \( \alpha_r \) changes over \( \beta_r \), \( \gamma_r \) transforms into \(-\gamma_r \), and the inequality \( (\gamma_r, \delta) > 0 \) transforms into \((\gamma_r, \delta) < 0 \).

Let us summarize. We use the given vector of exponents \( \delta \) and produce a system with some irreversible reactions from a system of reversible reactions and detailed balance equilibrium \( a_i^{eq} \) by the following rules:

1. if \( \delta_i > 0 \) then we assign \( a_i^{eq} = 0 \) and if \( \delta_i = 0 \) then \( a_i^{eq} \) does not change;
2. if \( (\gamma_r, \delta) = 0 \) then \( k_r^\pm \) do not change;
3. if \( (\gamma_r, \delta) < 0 \) then we assign \( k_r^- = 0 \) and \( k_r^+ \) does not change;
4. if \( (\gamma_r, \delta) > 0 \) then we assign \( k_r^+ = 0 \) and \( k_r^- \) does not change. (In the last case, we transpose the stoichiometric equation and swap the forward reaction with reverse one, for convenience, \( \gamma_r \) changes to \(-\gamma_r \) and \( k_r^- \) becomes 0. Therefore, this case transforms into case 3.)

This is a limit system caused by the multiscale degeneration of equilibrium. The multiscale character of the limit \( a_i^{eq} = \text{const} \times \varepsilon^{\delta_i} \to 0 \) (for some \( i \)) is important because for different values of \( \delta \) reactions may have different dominant directions and the set of irreversible reactions in the limit may change.

The general form of the kinetic equations for the homogeneous systems is

\[
\frac{dN_i}{dt} = V \sum_r w_r \gamma_r ,
\]

where \( N_i \) is the amount of \( A_i \), \( N \) is the vector with components \( N_i \) and \( V \) is the volume.

Let us consider a limit system for the degeneration of equilibrium with the vector of exponents \( \delta \). For this system \( (\gamma_r, \delta) \leq 0 \) for all \( r \) and, in particular, \( (\gamma_r, \delta) < 0 \) for all irreversible reactions and \( (\gamma_r, \delta) = 0 \) for all reversible reactions.

**Proposition 2.** A linear functional \( G_\delta(N) = (\delta, N) \) decreases along the solutions of kinetic equations \( \dot{X} = f(X) \) for this limit system: \( dG_\delta(N)/dt \leq 0 \) and \( dG_\delta(N)dt \equiv 0 \) if and only if all the reaction rates for the irreversible reactions are zero.
Proof. Indeed, \[
\frac{dG_\delta(N)}{dt} = V \sum_r w_r(\gamma_r, \delta) \leq 0, \tag{11}
\]
because for reversible reactions \((\gamma_r, \delta) = 0\), and for irreversible reactions \(w_r = w_r^+ \geq 0\) and \((\gamma_r, \delta) < 0\). All the terms in this sum are non-negative, hence it may be zero if and only if each summand is zero. \qed

This Lyapunov function may be used in a proof that the rates of all irreversible reactions in the system tend to 0 with time. Indeed, if they do not tend to zero then on a solution of \((10)\) \(G_\delta(N(t)) \to -\infty\) when \(t \to \infty\) and \(N(t)\) is unbounded. Equation \((11)\) and Proposition \(2\) give us the possibility to prove the extended principle of detailed balance in the following form. Let us consider a reaction mechanism that includes reversible and irreversible reactions. Assume that the reaction rates satisfy the generalized mass action law \((3)\) and the set of reaction rate constants is given. Let us ask the question: Is it possible to obtain this reaction mechanism and reaction rate constants as a limit in the multiscale degeneration of equilibrium from a fully reversible system with the classical detailed balance. The answer to this question gives the following theorem about the extended principle of detailed balance.

**Theorem 1.** A system can be obtained as a limit in the multiscale degeneration of equilibrium from a reversible system with detailed balance if and only if (i) the reaction rate constants of the reversible part of the reaction mechanism satisfy the classical principle of detailed balance and (ii) the convex hull of the stoichiometric vectors of the irreversible reactions does not intersect the linear span of the stoichiometric vectors of reversible reactions.

**Proof.** Let the given system be a limit of a reversible system with detailed balance in the multiscale degeneration of equilibrium with the exponent vector \(\delta\). Then for the reversible reactions \((\gamma_r, \delta) = 0\) and for the irreversible reactions \((\gamma_r, \delta) < 0\). For every vector \(x\) from the convex hull of the stoichiometric vector of the irreversible reactions \((x, \delta) < 0\) and for any vector \(y\) from the linear span of the stoichiometric vectors of the reversible reactions \((y, \delta) = 0\). Therefore, these sets do not intersect. The reaction rate constants for the reversible reactions satisfy the classical principle of detailed balance because they do not change in the equilibrium degeneration and keep this property of the original fully reverse system with detailed balance.

Conversely, let a system satisfy the extended principle of detailed balance: (i) the reaction rate constants of the reversible part of the reaction mechanism satisfy the classical principle of detailed balance and (ii) the convex hull of the stoichiometric vectors of the irreversible reactions does not intersect the linear span of the stoichiometric vectors of reversible reactions. Due to the classical theorems of the convex geometry, there exists a linear functional that separates this convex set from the linear subspace. (Strong separation of closed and compact convex sets.) This separating functional can be represented in the form \((x, \theta)\) for some vector \(\theta\). For the reversible reactions \((\gamma_r, \theta) = 0\) and for the irreversible reactions \((\gamma_r, \theta) < 0\).

It is possible to find vector \(\delta\) with this separation property and non-negative coordinates. Indeed, according to the basic assumptions, there exists a linear conservation law with strongly positive coordinates. This is a vector \(b\) \((b_i > 0)\) with the property: \((\gamma_r, b) = 0\) for all reactions. For any \(\lambda\), the vector \(\theta + \lambda b\) has the same separation property as the vector \(\theta\) has. We can select such \(\lambda\) that \(\delta_i = \theta_i + \lambda b_i \geq 0\) and \(\delta_i = \theta_i + \lambda b_i = 0\) for some \(i\). Let us take this linear combination \(\delta\) as a vector of exponents.

Let us create a fully reversible system from the initial partially irreversible one. We do not change the reversible reactions and their rate constants. Because the reversible reactions satisfy the classical principle of detailed balance, there exists a strongly positive vector of equilibrium activities \(a_i^r > 0\) for the reversible reactions.

For each irreversible reaction with the stoichiometric vector \(\gamma_r\) and reaction rate constant \(k_r = k_i^+ > 0\) we add a reverse reaction with the reaction rate constant

\[ k_r^- = k_i^+ \prod_i (a_i^q)^{-\gamma r_i}. \]

For this fully reversible system the activities \(a_i^r > 0\) provide the point of detailed balance. In the multiscale degeneration process, the equilibrium activities depend on \(\varepsilon \to 0\) as \(a_i^r = a_i^r \varepsilon^\theta\). For the reactions with
Figure 1: Main operations in the application of the extended detailed balance conditions. In the concentration space \( \mathbb{R}^n \) we should find the subspace spanned by all the stoichiometric vectors \( \{ \gamma_r \mid r = 1, \ldots, \ell \} \) (a). In this subspace we have to select the internal coordinates. In span \( \{ \gamma_r \mid r = 1, \ldots, \ell \} \) we have to select the subspace spanned by the stoichiometric vectors of the reversible reactions (b) (the dashed vectors). The stoichiometric vectors of the irreversible reactions are in (b,c,d) solid and bold. Due to the extended principle of detailed balance, span \( \{ \gamma_r \mid r \in J_0 \} \) should not intersect conv\( \{ \gamma_r \mid r \in J_1 \} \) (the dotted triangle in Fig.). For analysis of this intersection, it is convenient to proceed to the quotation space span \( \{ \gamma_r \mid r = 1, \ldots, \ell \} \) (c,d). In this quotation space, span \( \{ \gamma_r \mid r \in J_0 \} \) is \{0\} and two situations are possible: (c) \( 0 \notin \text{conv}\{ \gamma_r \mid r \in J_1 \} \) (the dotted triangle includes the origin) or (d) \( 0 \notin \text{conv}\{ \gamma_r \mid r \in J_1 \} \) (the dotted triangle does not include the origin). In the case (c) the extended detailed balance condition is violated. The case (d) satisfies this condition.

\[ (\gamma_r, \delta) = 0 \] the reaction rate constants do not depend on \( \varepsilon \) and for the reactions with \( (\gamma_r, \delta) < 0 \) the rate constant \( k_r^- \) tends to zero as \( \varepsilon^{-|\gamma_r|} \) and \( k_r^+ \) does not change. We return to the initial system of reactions in the limit \( \varepsilon \to 0 \).

This is a particular form of the extended principle of detailed balance. For more discussion see [12]. Fig. 1 illustrates geometric sense of the extended detailed balance condition: the convex hull of the stoichiometric vectors of the irreversible reactions does not intersect the linear span of the stoichiometric vectors of the reversible reactions. In this illustration, \( \{ \gamma_r \mid r \in J_0 \} \) are the stoichiometric vectors of the reversible reactions and \( \{ \gamma_r \mid r \in J_1 \} \) are the stoichiometric vectors of the irreversible reactions.

2.3. Activities, concentrations and affinities

To combine the linear Lyapunov functions \( G_i(N) = (\delta, N) \) with the classical thermodynamic potential and study the kinetic equations in the closed form we have to specify the relations between activities and concentrations. We accept the assumption: \( a_i = c_i g_i(c, T) \), where \( g_i(c, T) > 0 \) is the activity coefficient. It is a continuously differentiable function of \( c, T \) in the whole diapason of their values. In a bounded region of concentrations and temperature we can always assume that \( g_i > g_0 > 0 \) for some constant \( g_0 \). This assumption is valid for the non-ideal gases and for liquid solutions. It holds also for the “surface gas” in kinetics of heterogeneous catalysis [24] and does not hold for the solid reagents (see for example, analysis of carbon activity in the methane reforming [12]).

The system of units should be commented. Traditionally, \( a_i \) is assumed to be dimensionless and for perfect systems \( a_i = c_i/c_i^0 \), where \( c_i^0 \) is an arbitrary “standard” concentration. To avoid introduction of unnecessary quantities, we always assume that in the selected system of units, \( c_i^0 \equiv 1 \).
If the thermodynamic potentials exist then due to the thermodynamic definition of activity, this hypothesis is equivalent to the logarithmic singularity of the chemical potentials, \( \mu_i = RT \ln c_i + \ldots \) where \( \ldots \) stands for a continuous function of \( c, T \) (all the concentrations and the temperature). In this case, the free energy has the form

\[
F(N, T, V) = RT \sum_i N_i (\ln c_i - 1 + f_{0i}(c, T)),
\]

where the functions \( f_{0i}(c, T) \) are continuously differentiable for all possible values of arguments. Functions \( f_{0i} \) in the right hand side of the representation cannot be restored unambiguously from the free energy function \( F(N, T, V) \) but for a small admixture \( A_i \) it is possible to introduce the partial pressure \( p_i \) which satisfies the law \( p_i = RT c_i + o(c_i) \). This is due to the terms \( N_i \ln c_i \) in \( F \). Indeed, \( P = -\partial F(N, T, V)/\partial V = RT c_i + o(c_i) + P \big|_{c=0} \). Connections between the equation of state, free energy and kinetics are discussed in more detail in [3, 8].

There are several simple algebraic corollaries of the assumed connection between activities and concentrations. Let us consider an elementary reaction \( \sum_i \alpha_i A_i \rightarrow \sum_i \beta_i A_i \) with \( \alpha_i, \beta_i \geq 0 \). Then, according to the generalized mass action law, for any vector of concentrations \( c (c_i \geq 0) \)

1. If, for some \( i, c_i = 0 \) then \( \gamma_i w(c) \geq 0 \);
2. If, for some \( i, c_i = 0 \) and \( \gamma_i < 0 \) then \( \alpha_i > 0 \) and \( w(c) = 0 \).

Similarly, for a reversible reaction \( \sum_i \alpha_i A_i \rightarrow \sum_i \beta_i A_i \)

1. If, for some \( i, c_i = 0 \) and \( \gamma_i > 0 \) then \( \beta_i > 0 \) and \( w^-(c) = 0 \);
2. If, for some \( i, c_i = 0 \) and \( \gamma_i < 0 \) then \( \alpha_i > 0 \) and \( w^+(c) = 0 \).

These statements as well as Proposition [5] and Corollary [1] below are the consequences of the generalized mass action law [3] and the connection between activities and concentrations without any assumptions about extended principle of detailed balance.

Each set of indexes \( J = \{i_1, \ldots, i_j\} \) defines a face of the positive polyhedron,

\[
F_J = \{c|c_i \geq 0 \text{ for all } i \text{ and } c_i = 0 \text{ for } i \in J\}.
\]

By definition, the relative interior of \( F_J, ri(F_J) \), consists of points with \( c_i = 0 \) for \( i \in J \) and \( c_i > 0 \) for \( i \not\in J \).

**Proposition 3.** Let for a point \( c \in ri(F_J) \) and an index \( i \in J \)

\[
\sum_r \gamma_{ri} w_r(c) = 0.
\]

Then this identity holds for all \( c \in F_J \).

**Proof.** For convenience, let us write all the forward and reverse reactions separately and represent the reaction mechanism in the form [2]. All the terms in the sum \( \sum_r \gamma_{ri} w_r(c) \) are non-negative, because \( c_i = 0 \). Therefore, if the sum is zero then all the terms are zero. The reaction rate \( w_r \) with non-zero rate constant takes zero value if and only if \( \alpha_{rj} > 0 \) and \( a_j = 0 \) for some \( j \). The equality \( a_i = 0 \) is equivalent to \( c_i = 0 \). Therefore, \( w_r(c) = 0 \) for a point \( c \in ri(F_J) \) if and only if there exists \( j \in J \) such that \( \alpha_{rj} > 0 \). If \( \alpha_{rj} > 0 \) for an index \( j \in J \) then \( w_r(c) = 0 \) for all \( c \in F_J \) because \( c_j = 0 \) in \( F_J \).

We call a face \( F_J \) of the positive orthant \( \mathbb{R}_+^n \) invariant with respect to a set \( S \) of elementary reactions if \( \sum_{r \in S} \gamma_{rj} w_r(c) = 0 \) for all \( c \in F_J \) and every \( j \in J \).

Let us consider the reaction mechanism in the form [2] where all the forward and reverse reactions participate separately.

**Corollary 1.** The following statements are equivalent:

1. \( \sum_{r \in S} \gamma_{rj} w_r(c) = 0 \) for a point \( c \in ri(F_J) \) and all indexes \( i \in J \);
2. The face \( F_J \) is invariant with respect to the set of reactions \( S \);
3. The face \( F_j \) is invariant with respect to every elementary reaction from \( S \);
4. For every \( r \in S \) either \( \gamma_{rj} = 0 \) for all \( j \in J \) or \( \alpha_{rj} > 0 \) for some \( j \in J \).

We aim to perform the analysis of the asymptotic behavior of the kinetic equations in the multiscale degeneration of equilibrium described in Sec. 2.2. For this purpose, we have to answer the question: how the relations between activities \( a_i \) and concentrations \( c_i \) depend on the degeneration parameter \( \varepsilon \to 0 \)? We do not try to find the maximally general appropriate answer to this question. For the known applications, the answer is: the relations between \( a_i \) and \( c_i \) do not depend on \( \varepsilon \to 0 \). In particular, it is trivially true for the ideal systems. The simple generalization, \( a_i = c_i g_i(c, T, \varepsilon) \), where \( g_i(c, T, \varepsilon) > g_0 > 0 \) are continuous functions, is not a generalization at all, because we can use for \( \varepsilon \to 0 \) the limit case that does not depend on \( \varepsilon \), \( g_i(c, T) = g_i(c, T, 0) \).

This independence from \( \varepsilon \) implies that the reversible part of the reaction mechanism has the thermodynamic Lyapunov functions like free energy. If we just delete the irreversible part then the classical thermodynamics is applicable and the thermodynamic potentials do not depend on \( \varepsilon \). For the generalized mass action law, the time derivative of the relevant thermodynamic potentials have very nice general form. Let, under given condition, the function \( \Phi(N, \ldots) \) be given, where by \( \ldots \) is used for the quantities that do not change in time under these conditions. It is the thermodynamics potential if \( \partial \Phi(N, \ldots)/\partial N_i = \mu_i \). For example, it is the free Helmholtz energy \( F \) for \( V, T = \text{const} \) and the free Gibbs energy \( G \) for \( P, V = \text{const} \).

Let us calculate the time derivative of \( \Phi(N, \ldots) \) due to kinetic equation (10). The reaction rates are given by the generalized mass action law (3) with definition of activities through chemical potential (4). We assume that the principle of detailed balance holds (it should hold for the reversible part of the reaction mechanism according to the extended detailed balance conditions). More precisely, there exists an equilibrium with detailed balance for any temperature \( T \), \( a^{eq}(T) \): for all \( r \), \( w^+_r(a^{eq}) = w^-_r(a^{eq}) = w^{eq}_r(T) \). It is convenient to represent the reaction rates using these equilibrium fluxes \( w^{eq}_r(T) \):

\[
w^+_r = w^{eq}_r \exp \left( \sum \alpha_i \left( \mu_i - \mu_i^{eq} \right) / RT \right), \quad w^-_r = w^{eq}_r \exp \left( - \sum \beta_i \left( \mu_i - \mu_i^{eq} \right) / RT \right),
\]

where \( \mu_i^{eq} = \mu_i(a^{eq}, T) \).

These formulas give immediately the following representation of the dissipation rate

\[
\frac{d\Phi}{dt} = \sum_i \frac{\partial \Phi(N, \ldots)}{\partial N_i} \frac{dN_i}{dt} = \sum_i \mu_i \frac{dN_i}{dt}
= -VR \sum_r \left( \ln w^+_r - \ln w^-_r \right) (w^+_r - w^-_r) \leq 0.
\]

The inequality holds because \( \ln \) is a monotone function and, hence, the expressions \( \ln w^+_r - \ln w^-_r \) and \( w^+_r - w^-_r \) have always the same sign. Formulas of this kind for dissipation are well known since the famous Boltzmann \( H \)-theorem (1873 [2], see also [13]). The entropy increase in isolated systems has the similar form:

\[
\frac{dS}{dt} = VR \sum_r \left( \ln w^+_r - \ln w^-_r \right) (w^+_r - w^-_r) \geq 0.
\]

Let us notice that

\[
\ln w^+_r - \ln w^-_r = \frac{1}{RT} \sum_i \mu_i (\alpha_i - \beta_i) = -\frac{(\gamma_r, \mu)}{RT}.
\]

The quantity \( -\langle \gamma_r, \mu \rangle \) is one of the central notion of physical chemistry, affinity [5]. It is positive if the forward reaction prevails over reverse one and negative in the opposite case. It measures the energetic advantage of the forward reaction over the reverse one (free energy per mole). The activity divided by \( RT \) shows how large is this energetic advantage comparing to the thermal energy. We call it the normalized affinity and use a special notation for this quantity:
Let us apply an elementary identity
\[
\exp a - \exp b = (\exp a + \exp b) \tanh \frac{a - b}{2}
\]
to the reaction rate, \( w_r = w_r^+ - w_r^- \):
\[
w_r = (w_r^+ + w_r^-) \tanh \frac{A_r}{2}.
\]
This representation of the reaction rates gives immediately for the dissipation rate:
\[
\frac{d\Phi}{dt} = -VRT \sum_r (w_r^+ + w_r^-) A_r \tanh \frac{A_r}{2} \leq 0.
\]
In this formula, the kinetic information is collected in the non-negative factors, the sums of reaction rates \( (w_r^+ + w_r^-) \). The purely thermodynamical multipliers \( A_r \), \( \tanh(A_r/2) \) are also non-negative. For small \(|A_r|\), the expression \( A_r \tanh(A_r/2) \) behaves like \( A^2_r/2 \) and for large \(|A_r|\) it behaves like the absolute value, \(|A_r|\).

So, we have two Lyapunov functions for two fragments of the reaction mechanism. For the reversible part, this is just a classical thermodynamic potential. For the irreversible part, this is a linear functional \( G_\delta(N) = (\delta, N) \). More precisely, the irreversible reactions decrease this functional, whereas for the reversible reactions it is the conservation law. Therefore, it decreases monotonically in time for the whole system.

3. Attractors

3.1. Dynamical systems and limit points

The kinetic equations (10) do not give a complete representation of dynamics. The right hand side includes the volume \( V \) and the reaction rates \( w_r \), which are functions of the concentrations \( c \) and temperature \( T \), whereas in the left hand side there is \( \dot{N} \). To close this system, we need to express \( V, c \) and \( T \) through \( N \) and quantities which do not change in time. This closure depends on conditions. The simplest expressions appear for isochoric isothermal conditions: \( V, T = \text{const} \), \( c = N/V \). For other classical conditions (\( U, V = \text{const} \), or \( P, T = \text{const} \), or \( H, P = \text{const} \)) we have to use the equations of state. There may be more sophisticated closures which include models or external regulators of the pressure and temperature, for example.

Proposition 2 is valid for all possible closures. It is only important that the external flux of the chemical components is absent. Further on, we assume that the conditions are selected, the closure is done, the right hand side of the resulting system is continuously differentiable and there exists the positive bounded solution for initial data in \( R^+_n \) and \( V, T \) remain bounded and separated from zero. The nature of this closure is not crucial. For some important particular closures the proofs of existence of positive and bounded solutions are well known (see, for example, [22]). Strictly speaking, such a system is not a dynamical system in \( R^+_n \) but a semi-dynamical one: the solutions may lose positivity and leave \( R^+_n \) for negative values of time. The theory of the limit behavior of the semi-dynamical systems was developed for applications to kinetic systems [9].

We aim to describe the limit behavior of the systems as \( t \to \infty \). Under the extended detailed balance condition the limit behavior is rather simple and the system will approach steady states but to prove this behavior we need the more general notion of the \( \omega \)-limit points.

By the definition, the \( \omega \)-limit points of a dynamical system are the limit points of the motions when time \( t \to \infty \). We consider a kinetic system in \( R^+_n \). In particular, for each solution of the kinetic equations \( N(t) \) the set of the corresponding \( \omega \)-limit points is closed, connected and consists of the whole trajectories (Proposition 1.5). This means that the motion which starts from an \( \omega \)-limit point remains in \( R^+_n \) for all time moments, both positive and negative.

Proposition 4. Let \( N(t) \) be a positive solution of the kinetic equation and \( x^* \) be an \( \omega \)-limit point of this solution and \( x^*_t = 0 \). Then at this point \( \dot{x}_i|_{x^*} = 0 \).
Proof. Let \( x(t) \) be a solution of the kinetic equations with the initial state \( x(0) = x^* \). All the points \( x(t) \) \((−∞ < t < ∞) \) belong to \( \mathbb{R}^n_+ \). Indeed, there exists such a sequence \( t_j \to ∞ \) that \( N(t_j) \to x^* \). For any \( τ \in (−∞, ∞) \), \( N(t_j + τ) \to x(τ) \). For sufficiently large \( j \), \( t_j + τ > 0 \) and the value \( N(t_j + τ) \in \mathbb{R}^n_+ \). Therefore, \( x(τ) \in \mathbb{R}^n_+ \) \((−∞ < τ < ∞) \) and for any \( τ \) the point \( x(τ) \) is an \( ω \)-limit point of the solution \( N(t) \). Let \( x^*_i = 0 \) and \( x_i|_{x^*_i} = v \neq 0 \). If \( v > 0 \) then for small \( |τ| \) and \( τ < 0 \) the value of \( x_i \) becomes negative, \( x_i(τ) < 0 \). It is impossible because positivity. Similarly, If \( v < 0 \) then for small \( τ > 0 \) the value of \( x_i \) becomes negative, \( x_i(τ) < 0 \). It is also impossible because positivity. Therefore, \( x_i|_{x^*_i} = 0 \).

We use Proposition 2 in the following combination with Proposition 3. Let us write the reaction mechanism in the form \((2)\).

Corollary 2. If an \( ω \)-limit point belongs to the relative interior \( riF_J \) of the face \( F_J \subset \mathbb{R}^n_+ \) then the face \( F_J \) is invariant with respect to the reaction mechanism and for every elementary reaction either \( γ_{rj} = 0 \) for all \( j \in J \) or \( α_{rj} > 0 \) for some \( j \in J \).

Proof. If an \( ω \)-limit point belongs to \( riF_J \) then at this point all \( \dot{c}_j = 0 \) for \( j \in J \) due to Proposition 4. Therefore, we can apply Corollary 4.

3.2. Steady states of irreversible reactions

Under extended detailed balance conditions, all the reaction rates of the irreversible reactions are zero at every limit point of the kinetic equations \((10)\), due to Proposition 2. In this section, we give a simple combinatorial description of steady states for the set of irreversible reactions. This description is based on Proposition 2 and, therefore, uses the extended detailed balance conditions.

We continue to study multiscale degeneration of a detailed balance equilibrium. The vector of exponents \( δ = (δ_i) \) is given, \( δ_i ≥ 0 \) for all \( i \) and \( δ_i = 0 \) for some \( i \). There are two sets of reaction. For one of them, \( (γ_r, δ) = 0 \) and in the limit both \( k^+_r > 0 \). In the second set, \( (γ_r, δ) < 0 \) and in the limit we assign \( k^-_r = 0 \) and \( k^+_r \) is the same as in the initial system (before the equilibrium degeneration). If it is necessary, we transpose the stoichiometric equations and swap the forward reactions with reverse ones.

For convenience, let us change the notations. Let \( γ_i \) be the stoichiometric vectors of reversible reactions with \( (γ_r, δ) = 0 \) \((r = 1, \ldots, h) \), and \( ν_l \) be the stoichiometric vectors for the reactions from the second set, \( (ν_l, δ) < 0 \) \((l = 1, \ldots, s) \). For the reaction rates and constants for the first set we keep the same notations: \( w_i, w^+_i, k^+_i \). For the second set, we use for the reaction rate constants \( q_l = q^*_l \) and for the reaction rates \( ν_l = ν^*_l \). (They are also calculated according to the generalized mass action law \(3).\) The input and output stoichiometric coefficients remain \( α_{ri} \) and \( β_{ri} \) for the first set and for the second set we use the notations \( α^*_r \) and \( β^*_r \). Let the rates of all the irreversible reaction be equal to zero. This does not mean that all the concentrations \( a_i \) with \( δ_i > 0 \) achieve zero. A bimolecular reaction \( A + B \to C \) gives us a simple example: \( w = ka_Aa_B \) and \( w = 0 \) if either \( a_A = 0 \) or \( a_B = 0 \). On the plane with coordinates \( a_A, a_B \) and with the positivity condition, \( a_A, a_B ≥ 0 \), the set of zeros of \( w \) is a union of two semi-axes, \( \{a_A = 0, a_B ≥ 0\} \) and \( \{a_A ≥ 0, a_B = 0\} \). In more general situation, the set in the activity space, where all the irreversible reactions have zero rates, has a similar structure: it is the union of some faces of the positive orthant.

Let us describe the set of the steady states of the irreversible reactions. Due to Proposition 2 if \( \sum_l ν_lν = 0 \) then all \( ν_l = 0 \). Let us describe the set of zeros of all \( ν_l \) in the the positive orthant of activities.

For every \( l = 1, \ldots, s \) the set of zeros of \( ν_l \) in \( \mathbb{R}^n_+ \) is given by the conditions: at least for one \( i \) \( α^*_{ri} = 0 \) and \( a_i = 0 \). It is convenient to represent this condition as a disjunction. Let \( J_l = \left\{ i | α^*_{ri} = 0 \right\} \). Then the set of zeros of \( ν_l \) an a positive orthant of activities is presented by the formula \( \bigvee_{i \in J_l} (a_i = 0) \). The set of zeros of all \( ν_l \) is represented by the following conjunction form

\[
\bigwedge_{l=1}^s \left( \bigvee_{i \in J_l} (a_i = 0) \right).
\]  

(16)

To transform it into the unions of subspaces we have to move to a disjunction form and make some cancelations. First of all, we represent this formula as a disjunction of conjunctions:

\[
\bigwedge_{l=1}^s \left( \bigvee_{i \in J_l} (a_i = 0) \right) = \bigvee_{i_1 \in J_1, \ldots, i_s \in J_s} \left( (a_{i_1} = 0) \land \ldots \land (a_{i_s} = 0) \right).
\]  

(17)

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For a cortege of indexes \( \{i_1, \ldots, i_s\} \) the correspondent set of their values may be smaller because some values \( i_j \) may coincide. Let this set of values be \( S_1 = S_1(i_1, \ldots, i_s) \). We can delete from (17) a conjunction \((a_{i_1} = 0) \land \ldots \land (a_{i_s} = 0)\) if there exists a cortege \( \{i_1', \ldots, i_s'\} \) with smaller set of values, \( S_1(i_1, \ldots, i_s) \supseteq S_1(i_1', \ldots, i_s') \). Let us check the corteges in some order and delete a conjunction from (14) if there remain a term with smaller (or the same) set of index values in the formula. We can also substitute in (17) the corteges by their sets of values. The resulting minimized formula may become shorter. Each elementary conjunction represents a coordinate subspace and after cancelations each this subspace does not belong to a union of other subspaces. The final form of formula (17) is

\[
\forall_j (\land_{i \in S_j} (a_i = 0)),
\]

where \( S_j \) are sets of indexes, \( S_j \subset \{1, \ldots, n\} \) and for every two different \( S_j, S_p \) none of them includes another, \( S_j \not\subseteq S_p \). The elementary conjunction \( \land_{i \in S_j} (a_i = 0) \) describes a subspace.

The steady states of the irreversible part of the reaction mechanism are given by the intersection of the union of the coordinate subspaces (18) with \( \mathbb{R}^n_+ \). For applications of this formula, it is important that the equalities \( a_i = 0, c_i = 0 \) and \( N_i = 0 \) are equivalent and the positive orthants of the activities \( a_i \), concentrations \( c_i \) or amounts \( N_i \) represent the same sets of physical states. This is also true for the faces of these orthants: \( F_j \) for the activities, concentrations or amounts correspond to the same sets of states. (The same state may corresponds to the different points of these cones, but the totalities of the states are the same.)

### 3.3. Sets of steady states of irreversible reactions invariant with respect to reversible reactions

In this Sec. we study the possible limit behavior of systems which satisfy the extended detailed balance conditions and include some irreversible reactions. All the \( \omega \)-limit points of such systems are steady states of the irreversible reactions due to Proposition 4 but not all these steady states may be the \( \omega \)-limit points of the system. A simple formal example gives us the couple of reactions: \( A = B, A + B \rightarrow C \). Here, we have one reversible and one irreversible reaction. The conditions of the extended detailed balance hold (trivially): the linear span of the stoichiometric vector of the reversible reaction, \((-1, 1, 0)\), does not include the stoichiometric vector of the irreversible reaction, \((-1, -1, 1)\). For the description of the multiscale degeneration of equilibrium, we can take the exponents \( \delta_A = 1, \delta_B = 1, \delta_C = 0 \).

The steady states of the irreversible reaction are given in \( \mathbb{R}^n_+ \) by the disjunction, \((c_A = 0) \lor (c_B = 0)\) but only the points \((c_A = c_B = 0)\) may be the limit points when \( t \rightarrow \infty \). Indeed, if \( c_A = 0 \) and \( c_B > 0 \) then \( dc_A/dt = k_c c_B > 0 \). Due to Proposition 1 this is not an \( \omega \)-limit point. Similarly, the points with \( c_A > 0 \) and \( c_B = 0 \) are not the \( \omega \)-limit points.

Let us combine Propositions 2 and Corollary 2 in the following statement.

**Theorem 2.** Let the kinetic system satisfy the extended detailed balance conditions and include some irreversible reactions. Then an \( \omega \)-limit point \( x^* \in ri F_J \) exists if and only if \( F_J \) consists of steady states of the irreversible reactions and is invariant with respect to all reversible reactions.

**Proof.** If an \( \omega \)-limit point \( x^* \in ri F_J \) exists then it is a steady state for all irreversible reactions (due to Propositions 2). Therefore, the face \( F_J \) consists of steady-states of the irreversible reactions (Proposition 1) and is invariant with respect to all reversible reactions (Proposition 4 and Corollary 2). To prove the reverse statement, let us assume that \( F_J \) consists of steady states of the irreversible reactions and is invariant with respect to all reversible reactions. The reversible reactions which do not act on \( c_j \) for \( j \in J \) define a semidynamical system on \( F_J \). The positive conservation law \( b \) defines an positively invariant polyhedron in \( F_J \). Dynamics in such a compact set always has \( \omega \)-limit points.

Let us find the faces \( F_J \) that contain the \( \omega \)-limit points in their relative interior \( ri F_J \). According to Theorem 2 these faces should consist of the steady states of the irreversible reactions and should be invariant with respect to all reversible reactions. Let us look for the maximal forms with this property. For this purpose, we always minimize the disjunctive forms by cancelations. We do not list the faces that contain the \( \omega \)-limit points in their relative interior and are the proper subsets of other faces with this property. All the \( \omega \)-limit points belong to the union of these maximal faces.
Let us start from the minimized disjunctive form (18). Equation (18) represents the set of the steady states of the irreversible part of the reaction mechanism by a union of the coordinate subspaces \( \cap_{i \in S} (c_i = 0) \) in intersection with \( \mathbb{R}^n_+ \). It is the union of the faces, \( \cup_j F_j \). If a face \( F_j \) consists of the steady states of the irreversible reactions then \( J \supseteq S_j \) for some \( j \).

The following formula (19) is true on a face \( F_j \) if it contains \( \omega \)-limit points in the relative interior \( riF_j \) (Theorem 2):

\[
(c_i = 0) \Rightarrow \left( \bigwedge_{j \in \gamma_i} a_{j} > 0 \right) \wedge \left( \bigwedge_{j \in \gamma_i} b_{j} > 0 \right).
\]

(19)

Here, \( c_i = 0 \) in \( F_j \) may be read as \( i \in J \). Following the previous section, we use here the notations \( \gamma_{ri} \), \( \beta_{ri} \) and \( \beta_i \) for the reversible reactions and reserve \( \alpha_{ri} \) and \( \beta_i' \) for the irreversible reactions.

The required faces \( F_j \) may be constructed in an iterative procedure. First of all, let us introduce an operation that transforms a set of indexes \( S \subset \{1, 2, \ldots, n\} \) in a family of sets, \( \mathfrak{S}(S) = \{S'_1, \ldots, S'_m\} \). Let us take formula (19) and find the set where it is valid for all \( i \in S \). This set is described by the following formula:

\[
\bigwedge_{i \in S} \left[ (c_i = 0) \wedge \left( \bigwedge_{j \in \gamma_i} a_{j} > 0 \right) \wedge \left( \bigwedge_{j \in \gamma_i} b_{j} > 0 \right) \right].
\]

(20)

Let us produce a disjunctive form of this formula and minimize it by cancelations as it is described in Sec. 3.2. The result is

\[
\bigvee_{j = 1}^{m} \left( \bigwedge_{i \in S'_j} (c_i = 0) \right).
\]

(21)

Because of cancelations, the sets \( S'_j \) do not include one another. They give the result, \( \mathfrak{S}(S) = \{S'_1, \ldots, S'_m\} \). Each \( S'_j \in \mathfrak{S}(S) \) is a superset of \( S \), \( S' \supseteq S \).

Let us extend the operation \( \mathfrak{S} \) on the sets of sets \( S = \{S_1, \ldots, S_p\} \) with the property: \( S_i \not\subseteq S_j \) for \( i \neq j \).

Let us apply \( \mathfrak{S} \) to all \( S_i \) and take the union of the results: \( \mathfrak{S}_0(S) = \bigcup_i \mathfrak{S}(S_i) \). Some sets from this family may include other sets from it. Let us organize cancelations: if \( S', S'' \in \mathfrak{S}_0(S) \) and \( S' \subseteq S'' \) then retain the smallest set, \( S' \), and delete the largest one. We do the cancelations until it is possible. Let us call the final result \( \mathfrak{S}(S) \). It does not depend on the order of these operations.

Let us start from any family \( S \) and iterate the operation \( \mathfrak{S} \). Then, after finite number of iterations, the sequence \( \mathfrak{S}^d(S) \) stabilizes: \( \mathfrak{S}^d(S) = \mathfrak{S}^{d+1}(S) = \ldots \) because for any set \( S \) all sets from \( \mathfrak{S}(S) \) include \( S \).

The problems of propositional logic that arise in this and the previous section seem very similar to elementary logical puzzles [3]. In the solution we just use the logical distribution laws (distribution of conjunction over disjunction and distribution of disjunction over conjunction), commutativity of disjunction and conjunction, and elementary cancelation rules like \( (A \wedge A) \Leftrightarrow A \), \( (A \vee A) \Leftrightarrow A \), \( [A \wedge (A \vee B)] \Leftrightarrow A \), and \( [A \vee (A \wedge B)] \Leftrightarrow A \).

Now, we are in position to describe the construction of all \( F_j \) that have the \( \omega \)-limit points on their relative interior and are the maximal faces with this property.

1. Let us follow Sec. 3.2 and construct the minimized disjunctive form (18) for the description of the steady states of the irreversible reactions.
2. Let us calculate the families of sets \( \mathfrak{S}^d(\{S_j\}) \) for the family of sets \( \{S_j\} \) from (18) and \( d = 1, 2, \ldots, \) until stabilization.
3. Let \( \mathfrak{S}^d(\{S_j\}) = \mathfrak{S}^{d+1}(\{S_j\}) = \{J_1, J_2, \ldots, J_p\} \). Then the family of the faces \( F_{J_i} \) \( (i = 1, 2, \ldots, p) \) gives the answer: the \( \omega \)-limit points are situated in \( riF_{J_i} \) and for each \( i \) there are \( \omega \)-limit points in \( riF_{J_i} \).

3.4. Simple examples

In this Sec., we present two simple and formal examples of the calculations described in the previous sections.

1. \( A_1 + A_2 \Rightarrow A_4 \), \( \gamma = (-1, -1, 1, 0) \); \( A_1 + A_2 \Rightarrow A_5 \), \( \nu = (-1, -1, 0, 0, 1) \). The extended principle of detailed balance holds: the convex hull of the stoichiometric vectors of the irreversible reactions consists of one vector \( \gamma_2 \) and it is linearly independent of \( \gamma_1 \). The input vector \( \alpha \) for the irreversible reaction \( A_1 + A_2 \Rightarrow A_5 \) is \((-1, -1, 0, 0, 0)\). The set \( J = J_1 \) from the conjunction form (16) is defined by the non-zero
coordinates of this \( \alpha^n \): \( J = \{1, 2\} \). The conjunction form in this simple case (one irreversible reaction) loses its first conjunction operation and is just \((c_1 = 0) \lor (c_2 = 0)\). It is, at the same time, the minimized disjunction form \([15]\) and does not require additional transformations. This formula describes the steady states of the irreversible reaction in the positive orthant \( R^4_+ \). For this disjunction form, The family of sets \( S = \{S_i\} \) consists of two sets, \( S_1 = \{1\} \) and \( S_2 = \{2\} \).

Let us calculate \( \mathcal{S}(S_{1,2}) \). For both cases, \( i = 1, 2 \) there are no reversible reactions with \( \gamma_{ri} = 0 \). Therefore, one expression in round parentheses vanishes in \([20]\). For \( S = \{1\} \) this formula gives
\[
(c_1 = 0) \land ((c_3 = 0) \lor (c_4 = 0))
\]
and for \( S = \{2\} \) it gives
\[
(c_2 = 0) \land ((c_3 = 0) \lor (c_4 = 0)).
\]

The elementary transformations give the disjunctive forms:
\[
[(c_1 = 0) \land ((c_3 = 0) \lor (c_4 = 0))] \iff \left[ ((c_1 = 0) \land (c_3 = 0)) \lor ((c_1 = 0) \land (c_4 = 0)) \right],
\]
\[
[(c_2 = 0) \land ((c_3 = 0) \lor (c_4 = 0))] \iff \left[ ((c_2 = 0) \land (c_3 = 0)) \lor ((c_2 = 0) \land (c_4 = 0)) \right].
\]

Therefore, \( \mathcal{S}(S_1) = \{\{1, 3\}, \{1, 4\}\} \), \( \mathcal{S}(S_2) = \{\{2, 3\}, \{2, 4\}\} \) and
\[
\mathcal{S}((S_1, S_2)) = \{\{1, 3\}, \{1, 4\}, \{2, 3\}, \{2, 4\}\}.
\]

No cancellations are needed. The iterations of \( \mathcal{S} \) do not produce new sets from \( \{\{1, 3\}, \{1, 4\}, \{2, 3\}, \{2, 4\}\} \).

Indeed, if \( c_1 = c_3 = 0 \), or \( c_1 = c_4 = 0 \), or \( c_2 = c_3 = 0 \), or \( c_2 = c_4 = 0 \) then all the reaction rates are zero. More formally, for example for \( \mathcal{S}((1, 3)) \) formula \([20]\) gives
\[
[(c_1 = 0) \land ((c_3 = 0) \lor (c_4 = 0))] \land [(c_3 = 0) \land ((c_1 = 0) \lor (c_2 = 0))].
\]

This formula is equivalent to \((c_1 = 0) \land (c_3 = 0)\). Therefore, \( \mathcal{S}((1, 3)) = \{1, 3\} \). The same result is true for \( \{1, 4\}, \{2, 3\}, \{2, 4\} \).

All the \( \omega \)-limit points (steady states) belong to the faces \( F_{(1,3)} = \{c \mid c_1 = c_3 = 0\} \), \( F_{(1,4)} = \{c \mid c_1 = c_4 = 0\} \), \( F_{(2,3)} = \{c \mid c_2 = c_3 = 0\} \), or \( F_{(2,4)} = \{c \mid c_2 = c_4 = 0\} \). The position of the \( \omega \)-limit point for a solution \( N(t) \) depends on the initial state. More specifically, this system of reactions has three independent linear conservation laws: \( b_1 = N_1 + N_2 + N_3 + N_4 + 2N_5 \), \( b_2 = N_1 - N_2 \) and \( b_3 = N_3 - N_4 \). For given values of these \( b_{1,2,3} \) vector \( N \) belongs to the \( 2D \) plane in \( R^5 \). The intersection of this plane with the selected faces depends on the signs of \( b_{2,3} \):

- If \( b_2 < 0, b_3 < 0 \) then it intersects \( F_{(1,3)} \) only, at one point \( N = (0, -b_2, 0, -b_3, b_1 + b_2 + b_3) \) \((N_5 \text{ should be non-negative, } b_1 + b_2 + b_3 \geq 0)\).
- If \( b_2 = 0, b_3 < 0 \) then it intersects both \( F_{(1,3)} \) and \( F_{(2,3)} \) at one point \( N = (0, 0, 0, -b_3, b_1 + b_3) \) \((N_5 \text{ should be non-negative, } b_1 + b_3 \geq 0)\).
- If \( b_2 < 0, b_3 = 0 \) then it intersects both \( F_{(1,3)} \) and \( F_{(1,4)} \) at one point \( N = (0, -b_2, 0, 0, b_1 + b_2) \) \((N_5 \text{ should be non-negative, } b_1 + b_2 \geq 0)\).
- If \( b_2 > 0, b_3 < 0 \) then it intersects \( F_{(2,3)} \) only, at one point \( N = (b_2, 0, 0, -b_3, b_1 + b_2 + b_3) \) \((N_5 \text{ should be non-negative, } b_1 + b_2 + b_3 \geq 0)\).
- If \( b_2 > 0, b_3 = 0 \) then it intersects \( F_{(2,3)} \) and \( F_{(2,4)} \) at the point \( N = (b_2, 0, 0, 0, b_1 + b_2) \) \((N_5 \text{ is non-negative because } b_1 + b_2 + b_3 \geq 0)\).
- If \( b_2 < 0, b_3 > 0 \) then it intersects \( F_{(1,4)} \) only, at one point \( N = (0, -b_2, b_3, 0, b_1 + b_2 + b_3) \) \((N_5 \text{ should be non-negative, } b_1 + b_2 + b_3 \geq 0)\).
- If \( b_2 = 0, b_3 > 0 \) then it intersects \( F_{(1,4)} \) and \( F_{(2,4)} \) at one point \( N = (0, 0, b_3, 0, b_1 + b_3) \) \((N_5 \text{ is non-negative because } b_1 + b_3 \geq 0)\).
4. Example: H$_2$ + O$_2$ system

For the case study, we selected the H$_2$ + O$_2$ system. This is one of the main model systems of gas kinetics. The hydrogen burning gives us an example of the medium complexity with 8 components (A$_1$ = H$_2$, A$_2$ = O$_2$, A$_3$ = OH, A$_4$ = H$_2$O, A$_5$ = H, A$_6$ = O, A$_7$ = HO$_2$, and A$_8$ = H$_2$O$_2$) and 2 atomic balances (H and O). For the example, we selected the reaction mechanism from [21]. The literature about hydrogen burning mechanisms is huge. For recent discussion we refer to [16, 18]. We do not aim to compare the different schemes of this reaction but use this reaction mechanism as an example and a benchmark.

A special symbol “M” is used for the “third body”. It may be any molecule. The third body provides the energy balance. Efficiency of different molecules in this process is different, therefore, the “concentration” of the third body is a weighted sum of the concentrations of the components with positive weights. The third body does not affect the equilibrium constants and does not change the zeros of the forward and reverse reaction rates but modifies the non-zero values of reaction rates. Therefore, for our analysis we can omit these terms. The elementary reactions 10, 11 and 12 are glued in one, 2H$\Rightarrow$H$_2$, after cancelation of the third bodies, and we analyze the mechanism of 18 reaction.

### Table 1: H$_2$ burning mechanism [21]

<table>
<thead>
<tr>
<th>No</th>
<th>Reaction</th>
<th>Stoichiometric vector</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H$_2$ + O$_2$ $\Rightarrow$ 2OH</td>
<td>(-1,-1,2,0,0,0,0,0)</td>
</tr>
<tr>
<td>2</td>
<td>H$_2$ + OH $\Rightarrow$ H$_2$O + H</td>
<td>(-1,-1,1,0,0,0,0,0)</td>
</tr>
<tr>
<td>3</td>
<td>OH + O $\Rightarrow$ O$_2$ + H</td>
<td>(0,1,-1,0,1,-1,0,0)</td>
</tr>
<tr>
<td>4</td>
<td>H$_2$ + O $\Rightarrow$ OH + H</td>
<td>(-1,0,1,0,1,-1,0,0)</td>
</tr>
<tr>
<td>5</td>
<td>O$_2$ + H + M $\Rightarrow$ HO$_2$ + M</td>
<td>(0,-1,0,0,-1,0,0,0)</td>
</tr>
<tr>
<td>6</td>
<td>OH + HO$_2$ $\Rightarrow$ O$_2$ + H$_2$O</td>
<td>(0,1,-1,0,0,0,0,0)</td>
</tr>
<tr>
<td>7</td>
<td>H + HO$_2$ $\Rightarrow$ 2OH</td>
<td>(0,0,2,0,-1,0,0,0)</td>
</tr>
<tr>
<td>8</td>
<td>O + HO$_2$ $\Rightarrow$ O$_2$ + OH</td>
<td>(1,0,0,0,1,0,0,0)</td>
</tr>
<tr>
<td>9</td>
<td>2OH $\Rightarrow$ H$_2$O + O</td>
<td>(0,0,0,0,0,0,1,0)</td>
</tr>
<tr>
<td>10</td>
<td>2H + M $\Rightarrow$ H$_2$ + M</td>
<td>(1,0,0,0,0,0,0,0)</td>
</tr>
<tr>
<td>11</td>
<td>2H + H$_2$ $\Rightarrow$ H$_2$ + H$_2$</td>
<td>(0,0,0,0,0,0,1,0)</td>
</tr>
<tr>
<td>12</td>
<td>2H + H$_2$O $\Rightarrow$ H$_2$ + H$_2$O</td>
<td>(0,0,0,0,0,0,1,0)</td>
</tr>
<tr>
<td>13</td>
<td>OH + H + M $\Rightarrow$ H$_2$O + M</td>
<td>(0,0,0,0,0,0,0,0)</td>
</tr>
<tr>
<td>14</td>
<td>H + O + M $\Rightarrow$ OH + M</td>
<td>(0,0,0,0,0,0,0,0)</td>
</tr>
<tr>
<td>15</td>
<td>2O + M $\Rightarrow$ O$_2$ + M</td>
<td>(0,0,0,0,0,0,0,0)</td>
</tr>
<tr>
<td>16</td>
<td>H + HO$_2$ $\Rightarrow$ H$_2$ + O$_2$</td>
<td>(1,0,0,0,0,0,0,0)</td>
</tr>
<tr>
<td>17</td>
<td>2HO$_2$ $\Rightarrow$ O$_2$ + H$_2$O$_2$</td>
<td>(0,0,0,0,0,0,0,0)</td>
</tr>
<tr>
<td>18</td>
<td>H$_2$O + M $\Rightarrow$ 2OH + M</td>
<td>(0,0,0,0,0,0,0,0)</td>
</tr>
<tr>
<td>19</td>
<td>H + H$_2$O$_2$ $\Rightarrow$ H$_2$ + HO$_2$</td>
<td>(1,0,0,0,0,0,0,0)</td>
</tr>
<tr>
<td>20</td>
<td>OH + H$_2$O$_2$ $\Rightarrow$ H$_2$O + HO$_2$</td>
<td>(0,0,0,0,0,0,0,0)</td>
</tr>
</tbody>
</table>

- If $b_2 > 0$, $b_3 > 0$ then it intersects $F_{(2,4)}$ only, at one point $N = (b_2, 0, b_3, 0, b_1 + b_2 + b_3)$ ($N_5$ is non-negative because $b_1 + b_2 + b_3 \geq 0$).

As we can see, the system has exactly one $\omega$-limit point for any admissible combination of the values of the conservation laws. These points are the listed points of intersection.

For the second simple example, let us change the direction of the irreversible reaction.

2. $A_1 + A_2 \rightarrow A_3 + A_4$, $\gamma_1 = (-1, -1, 1, 1, 0)$, $A_5 \rightarrow A_1 + A_2$, $\nu = (1, 1, 0, 0, -1)$. The extended principle of detailed balance holds. The steady-states of the irreversible reactions is given by one equation, $c_5 = 0$. Formula [20] gives for $E_n(\{3\})$ just ($c_5 = 0$). The face $F_{(5)}$ includes $\omega$-limit points in $r t F_{(5)}$. Dynamics on this face is defined by the fully reversible reaction system and tends to the equilibrium of the reaction $A_1 + A_2 \rightarrow A_3 + A_4$ under the given conservation laws. On this face, there exist the border equilibria, where $c_1 = c_3 = 0$, or $c_1 = c_4 = 0$, or $c_2 = c_3 = 0$, or $c_2 = c_4 = 0$ but they are not attracting the positive solutions.
Under various conditions, some of the reactions are (almost) irreversible and some of them should be considered as reversible. For example, let us consider the H$_2$+O$_2$ system at or near the atmospheric pressure and in the temperature interval 800–1200K. The reactions 1, 2, 4, 18, 19, and 20 are supposed to be reversible (on the base of the reaction rate constants presented in [21]). The first question is: if these reactions are reversible then which reactions may be irreversible?

Due to the general criterion, the convex hull of the stoichiometric vectors of the irreversible reactions has empty intersection with the linear span of the stoichiometric vectors of the reversible reactions. Therefore, if the stoichiometric vector of a reaction belongs to the linear span of the stoichiometric vectors of the reversible reactions, then this reaction is reversible. Simple linear algebra gives that

$$\gamma_3,\gamma_9,\gamma_{18} \in \text{span}\{\gamma_1,\gamma_2,\gamma_4,\gamma_{19},\gamma_{20}\}.$$  

In particular, $\gamma_3 = -\gamma_1 + \gamma_4$, $\gamma_5 = \gamma_1 - \gamma_{18} + \gamma_{19}$, $\gamma_9 = \gamma_2 - \gamma_4$. So, the list of the reversible reactions should include the reactions 1, 2, 3, 4, 5, 9, 18, 19, and 20. The reactions 6, 7, 8, 10, 11, 12, 13, 14, 15, and 17 may be irreversible. Formally, there are $2^8 = 256$ possible combinations of the directions of these 8 reactions (the reactions 10, 11 and 12 have the same stoichiometric vector and, in this sense, should be considered as one reaction). The general criterion and simple linear algebra give that there are only two admissible combinations of the directions of irreversible reactions: either for all of them $k_i^+ = 0$ or for all of them $k_i^- = 0$. Here, the forward and reverse reactions and the notations $k_i^\pm$ are selected according to the Table II. We can immediately notice that the inverse direction of all reactions is very far from the reality under the given conditions, for example, it includes the irreversible dissociation H$_2$ $\rightarrow$ 2H.

Let us demonstrate in detail, how the general criterion produces this reduction from the 256 possible combinations of directions of irreversible reactions to just 2 admissible combinations. We assume that the initial set of reactions is split in two: reversible reactions with numbers $r \in J_0$ and irreversible reactions with $r \in J_1$, rank$\{\gamma_1,\gamma_2,\ldots,\gamma_8\} = d$, rank$\{\gamma_r \mid r \in J_0\} = d_0$. The rank of all vectors $\gamma_r$, $d_i$, must exceed the rank of the stoichiometric vectors of the reversible reactions, $d > d_0$, because if $d = d_0$ then all the reactions must be reversible and the problem becomes trivial.

According to [12], we have to perform the following operations with the set of stoichiometric vectors $\gamma_r$ (Fig. I):

1. Eliminate several coordinates from all $\gamma_r$ using linear conservation laws. This is transfer to the internal coordinates in span$\{\gamma_r \mid r \in J_1\}$;
2. Eliminate coordinates from all $\gamma_r$ ($r \in J_1$) using the stoichiometric vectors of the reversible reactions and the Gauss–Jordan elimination procedure. This is the map to the quotient space span$\{\gamma_j | j = 1,\ldots,\ell\}$/span$\{\gamma_j | j \in J_0\}$. Me denote the result as $\overline{\gamma}_r$;
3. Use the linear programming technique and analyze for which combinations of the signs, the convex hull conv$\{\pm \overline{\gamma}_r \mid r \in J_1\}$ does not include 0.

In the Table II we present the results of the step-by-step elimination. First, the atomic balances give us for every possible stoichiometric vector $\eta = (\eta_1,\ldots,\eta_8)$ two identities:

1. $2\eta_1 + \eta_3 + 2\eta_4 + \eta_5 + \eta_7 + 2\eta_8 = 0$ or $\eta_1 = -\frac{1}{2}(\eta_3 + 2\eta_4 + \eta_5 + \eta_7 + 2\eta_8)$;
2. $2\eta_2 + \eta_3 + \eta_4 + \eta_6 + 2\eta_7 + 2\eta_8 = 0$ or $\eta_2 = -\frac{1}{2}(\eta_3 + \eta_4 + \eta_6 + 2\eta_7 + 2\eta_8)$.

Let us recall that the order of the coordinates $(\eta_1,\ldots,\eta_8)$ corresponds to the following order of the components, (H$_2$, O$_2$, OH, H$_2$O, H, O, HO$_2$, H$_2$O$_2$). Due to these identities, a stoichiometric vector $\eta$ for this mixture is completely defined by six coordinates $(\eta_3,\ldots,\eta_8)$. In the second column of the Table II these 6D vectors are given for all the reactions from the H$_2$ burning mechanism (the Table III).

In five columns No. 3-7, the results of the coordinate eliminations are presented (and the zero-valued eliminated coordinates are omitted). Each elimination step may be represented as a projection:

$$x \mapsto x - x_i \frac{1}{\eta_i} \eta,$$

where $\eta_i$ is a pivot (highlighted in bold in the column preceding the result of elimination), and $\eta$ is the vector that includes the pivot (as the $i$th coordinate). The projection operator is applied to every vector of the
previous column. At the end (the last column), all the stoichiometric vectors of the reversible reaction are transformed into zero, and the stoichiometric vectors of the irreversible reactions with the given direction (from the left to the right) are transformed into the same vector \((-2)\). If we restore all the zeros, then the corresponding 6D vector is \((0,0,0,0,-2,0)\). We have to use the atomic balances to return to the 8D vectors. The coordinate \(x_7\) corresponds to HO\(_2\), \(x_1\) corresponds to H\(_2\), and \(x_2\) corresponds to O\(_2\), hence, \(2x_1 - 2 = 0\) and \(2x_2 - 4 = 0\). The restored 8D vector is \((1,2,0,0,0,0,-2,0)\).

A convex combination of several copies of one vector cannot give zero. Therefore, the structural condition of the extended principle of detailed balance holds. It holds also for the inverse direction of all the irreversible reactions. All other distributions of directions can produce zero in the convex hull and are inadmissible. So, we have the following list of irreversible reactions that satisfies the extended principle of detailed balance for given reversible reactions. (We will not discuss the second list of reverse irreversible reactions because it has not much sense for given conditions.)

\[
\begin{align*}
6 & \quad \text{OH} + \text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O} \\
7 & \quad \text{H} + \text{HO}_2 \rightarrow 2\text{OH} \\
8 & \quad \text{O} + \text{HO}_2 \rightarrow \text{O}_2 + \text{OH} \\
10 & \quad 2\text{H} \rightarrow \text{H}_2 \\
13 & \quad \text{OH} + \text{H} \rightarrow \text{H}_2\text{O} \\
14 & \quad \text{H} + \text{O} \rightarrow \text{OH} \\
15 & \quad 2\text{O} \rightarrow \text{O}_2 \\
16 & \quad \text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2 \\
17 & \quad 2\text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O}_2.
\end{align*}
\]

We assume that all the reaction rate constants for the selected directions are strictly positive. The rate of all these reaction vanish if and only if concentration of H, O and HO\(_2\) are equal to zero, \(c_{5,6,7} = 0\). Indeed, \(c_5 = 0\) if and only if \(w_{10} = 0\), \(c_6 = 0\) if and only if \(w_{15} = 0\), \(a_7 = 0\) if and only if \(w_{17} = 0\). On the other hand, all other reaction rates from this list are zeros if \(c_{5,6,7} = 0\).

### Table 2: Elimination of coordinates of stoichiometric vectors for H\(_2\) burning mechanism

The reversible reactions are collected in the upper part of the Table. The reaction in the lower part of the table are irreversible. The group of equivalent reactions 10, 11, 12 is presented by one of them. In the second column, the first two coordinates (which correspond to H\(_2\) and O\(_2\)) are excluded using the atomic balance. In the following columns the results of the coordinates elimination are presented. For each step, the pivot for elimination is underlined and highlighted in bold in the previous column. The eliminated coordinates at each step are named at the top of each column. Their zero values are omitted.

<table>
<thead>
<tr>
<th>No</th>
<th>H(_2), O(_2)</th>
<th>OH</th>
<th>H(_2)O(_2)</th>
<th>H(_2)O</th>
<th>H</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(2,0,0,0,0,0)</td>
<td>(0,0,0,0,0)</td>
<td>(0,0,0,0)</td>
<td>(0,0,0)</td>
<td>(0)</td>
<td>(0)</td>
</tr>
<tr>
<td>2</td>
<td>(-1,1,0,0,0,0)</td>
<td>(1,1,0,0,0)</td>
<td>(1,1,0,0)</td>
<td>(1,1,0)</td>
<td>(0)</td>
<td>(0)</td>
</tr>
<tr>
<td>3</td>
<td>(-1,0,1,-1,0,0)</td>
<td>(0,1,-1,0)</td>
<td>(0,1,-1)</td>
<td>(1,-1)</td>
<td>(0)</td>
<td>(0)</td>
</tr>
<tr>
<td>4</td>
<td>(1,0,1,-1,0,0)</td>
<td>(0,-1,0,0)</td>
<td>(0,-1,0)</td>
<td>(1,-1)</td>
<td>(0)</td>
<td>(0)</td>
</tr>
<tr>
<td>5</td>
<td>(0,0,-1,1,0,0)</td>
<td>(0,-1,0,1)</td>
<td>(0,-1,1)</td>
<td>(-1,1)</td>
<td>(0)</td>
<td>(0)</td>
</tr>
<tr>
<td>6</td>
<td>(-2,1,0,1,0,0)</td>
<td>(1,0,1,0)</td>
<td>(1,0,1)</td>
<td>(-1,0)</td>
<td>(0)</td>
<td>(0)</td>
</tr>
<tr>
<td>7</td>
<td>(2,0,0,0,-1,0)</td>
<td>(0,0,0,0)</td>
<td>(0,0,0)</td>
<td>(0,0)</td>
<td>(0)</td>
<td>(0)</td>
</tr>
<tr>
<td>8</td>
<td>(0,0,-1,0,1,0)</td>
<td>(0,-1,0,1)</td>
<td>(0,-1,1)</td>
<td>(-1,1)</td>
<td>(0)</td>
<td>(0)</td>
</tr>
<tr>
<td>9</td>
<td>(-1,1,0,0,-1,0)</td>
<td>(1,0,0,-1)</td>
<td>(1,0,-1)</td>
<td>(-1,1)</td>
<td>(0)</td>
<td>(0)</td>
</tr>
<tr>
<td>10</td>
<td>(1,0,0,0,-1,0)</td>
<td>(0,0,0,-1)</td>
<td>(0,0,-1)</td>
<td>(1,-1)</td>
<td>(0)</td>
<td>(0)</td>
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<td>(0,0,0)</td>
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</table>
Let us reproduce this reasoning using formulas from Sec. 3.3. For the lth irreversible reaction, \( J_l \) is the set of indexes \( i \) for which \( \alpha_i \neq 0 \). Let us keep for the irreversible reactions their numbers \( (6, 7, 8, 10, 13, 14, 15, 16, 17) \). For them, \( J_6 = \{3, 7\}, J_7 = \{5, 7\}, J_8 = \{6, 7\}, J_{10} = \{5\}, J_{13} = \{3, 5\}, J_{14} = \{5, 6\}, J_{15} = \{6\}, J_{16} = \{5, 7\}, J_{17} = \{7\} \).

Formula (18) gives for the steady states of the irreversible reactions:

\[
((c_3 = 0) \lor (c_7 = 0)) \land ((c_5 = 0) \lor (c_7 = 0)) \land ((c_6 = 0) \lor (c_7 = 0)) \land (c_5 = 0)
\land((c_3 = 0) \lor (c_5 = 0)) \land ((c_5 = 0) \lor (c_6 = 0)) \land (c_6 = 0) \land ((c_5 = 0) \lor (c_7 = 0)) \land (c_7 = 0).
\]

It is equivalent to

\[
(c_5 = 0) \land (c_6 = 0) \land (c_7 = 0).
\]

Of course, the result is the same, the face \( F_{\{5,6,7\}} \) \((c_5,6,7 = 0, c_i \geq 0)\) is the set of the steady states of all irreversible reaction.

Let us look now on the list of reversible reactions:

1. \( H_2 + O_2 \rightleftharpoons 2OH \)
2. \( H_2 + OH \rightleftharpoons H_2O + H \)
3. \( OH + O \rightleftharpoons O_2 + H \)
4. \( H_2 + O \rightleftharpoons OH + H \)
5. \( O_2 + H \rightleftharpoons HO_2 \)
6. \( 2OH \rightleftharpoons H_2O + O \)
7. \( H_2O_2 \rightleftharpoons 2OH \)
8. \( H + H_2O_2 \rightleftharpoons H_2 + HO_2 \)
9. \( OH + H_2O_2 \rightleftharpoons H_2O + HO_2 \)

If the concentration \( \text{OH} \) \( (c_3) \) is positive then the component \( O \) is produced in the reaction 9. If the concentrations of \( H_2 \) \((c_1) \) and \( \text{OH} \) \( (c_3) \) both are positive then the component \( H \) is produced in reaction 2. If the concentrations of \( H_2O_2 \) \( (c_8) \) and \( \text{OH} \) \( (c_3) \) both are positive then the component \( \text{HO}_2 \) is produced in reaction 2. Due to the reversible reaction 18 any of two components \( H_2O_2 \) and \( \text{OH} \) produces the other component. Moreover, the first reaction produces \( \text{OH} \) from \( H_2 + O_2 \). This production stops if and only if either concentration of \( H_2 \) is zero \((c_1 = 0)\) or concentration of \( \text{O}_2 \) is zero \((c_2 = 0)\).

This means that the set of zeros of the irreversible reactions, \( c_{5,6,7} = 0 \) \((c \geq 0)\), is not invariant with respect to the kinetics of the reversible reactions. This means that from an initial conditions on this set the kinetic trajectory will leave it unless, in addition, \( c_1 = c_6 = 0 \) and either \( c_1 = 0 \) or \( c_2 = 0 \).

The reactions of all irreversible reactions should tend to zero due to Proposition. Therefore, the kinetic trajectory should approach the union of two planes, \( c_{1,3,5,6,7,8} = 0 \) and \( c_{2,3,5,6,7,8} = 0 \) (under condition \( c \geq 0 \)). These planes are two-dimensional and the position of the state there is completely defined by the atomic balances.

If the concentration vector belongs to the first plane, then all the atoms are collected in \( O_2 \) and \( H_2O \). It is possible if and only if \( b_0 \geq \frac{1}{2}b_{11} \). In this case, \( c_4 = \frac{1}{2}b_{11} \) and \( c_2 = \frac{1}{2}(b_0 - \frac{1}{2}b_{11}) \).

If the concentration vector belongs to the second plane, then all the atoms are collected in \( H_2 \) and \( H_2O \). It is possible if and only if \( b_0 \leq \frac{1}{2}b_{11} \). In this case, \( c_4 = b_0 \) and \( c_1 = \frac{1}{2}(b_{11} - 2b_0) \).

Let us reproduce this reasoning formally using the general formalism of Sec. 3.3 Formula (20) gives for \( \mathcal{S}(\{5,6,7\}) \)

\[
(c_5 = 0) \land (\land_{r, \gamma_r > 0} \lor_{j, \alpha_r > 0} (c_j = 0)) \land (\land_{r, \gamma_r < 0} \lor_{j, \alpha_r > 0} (c_j = 0))
\land(c_6 = 0) \land (\land_{r, \gamma_r > 0} \lor_{j, \alpha_r > 0} (c_j = 0)) \land (\land_{r, \gamma_r < 0} \lor_{j, \alpha_r > 0} (c_j = 0))
\land(c_7 = 0) \land (\land_{r, \gamma_r > 0} \lor_{j, \alpha_r > 0} (c_j = 0)) \land (\land_{r, \gamma_r < 0} \lor_{j, \alpha_r > 0} (c_j = 0)) \quad (22)
\]

Vectors \( \gamma_r \) that participate in this formula are the stoichiometric vectors of reversible reactions \((r = 1, 2, 3, 4, 5, 9, 18, 19, 20)\). From the Table 1 we find that \( \gamma_5 > 0 \) for \( r = 2, 3, 4, \gamma_5 < 0 \) for \( r = 5, 19, \gamma_6 > 0 \) for \( r = 9, \gamma_6 < 0 \) for \( r = 3, 4, \gamma_7 > 0 \) for \( r = 5, 19, 20, \) and \( \gamma_7 < 0 \) for all \( r \). Formula (22)
transforms into
\[
(c_3 = 0) \land ((c_1 = 0) \lor (c_3 = 0)) \land ((c_1 = 0) \lor (c_6 = 0)) \land ((c_1 = 0) \lor (c_6 = 0)) \land (c_7 = 0)
\land((c_1 = 0) \lor (c_2 = 0)) \land (c_6 = 0) \land (c_3 = 0) \land ((c_2 = 0) \lor (c_5 = 0)) \land ((c_3 = 0) \lor (c_5 = 0))
\land((c_2 = 0) \lor (c_5 = 0)) \land ((c_5 = 0) \lor (c_8 = 0)) \land ((c_3 = 0) \lor (c_8 = 0)).
\]

After simple transformations it becomes
\[
(c_3 = 0) \land (c_5 = 0) \land (c_6 = 0) \land (c_7 = 0).
\]

Therefore, \(\mathcal{S}\{5, 6, 7\} = \{3, 5, 6, 7\}\). To iterate, we have to compute \(\mathcal{S}\{3, 5, 6, 7\}\). For this calculation, we have to add one more line to formula (22), namely,
\[
\land((c_3 = 0) \land (\land_{r, r_3 > 0} \lor_{j, n_3 > 0} (c_j = 0))) \land (\land_{r, r_3 < 0} \lor_{j, n_3 > 0} (c_j = 0)).
\]

Let us take into account that \(\gamma_{r_3} > 0\) for \(r = 1, 4, 18\) and \(\gamma_{r_3} < 0\) for \(r = 2, 3, 9, 20\), and rewrite this formula in the more explicit form
\[
(c_3 = 0) \land ((c_1 = 0) \lor (c_2 = 0)) \land ((c_1 = 0) \lor (c_6 = 0)) \land (c_8 = 0)
\land((c_4 = 0) \lor (c_5 = 0)) \land ((c_2 = 0) \lor (c_5 = 0)) \land ((c_4 = 0) \lor (c_6 = 0)) \land (c_7 = 0).
\]

Let us take the conjunction of this formula with (22) taken in the simplified equivalent form (23) and transform the result to the disjunctive form. We get
\[
[(c_3 = 0) \land (c_5 = 0) \land (c_6 = 0) \land (c_8 = 0) \land (c_1 = 0)]
\land[(c_3 = 0) \land (c_5 = 0) \land (c_6 = 0) \land (c_7 = 0) \land (c_8 = 0) \land (c_2 = 0)].
\]

This means that \(\mathcal{S}^2\{5, 6, 7\} = \mathcal{S}\{3, 5, 6, 7\} = \{1, 3, 5, 6, 7, 8\}, \{2, 3, 5, 6, 7, 8\}\). The further calculations show that the next iteration does not change the result. Therefore, all the \(\omega\)-limit points belong to two faces, \(F_{(1,3,5,6,7,8)}\) and \(F_{(2,3,5,6,7,8)}\). The result is the same as for the previous discussion. The detailed formalization becomes crucial for more complex systems and for software development.

Let us find the vector of exponents \(\delta = (\delta_i) (i = 1, \ldots, 8)\) from the Table 2. After all the eliminations, the corresponding linear functional \(\hat{\delta}\) is just a value of the 7th coordinate: \(\hat{\delta}(x) = x_7\). Its values are negative \((-2)\) for all irreversible reactions and zero for all reversible reactions (see the last column of the Table 2). The conditions \((\delta, \gamma) = 0\) for the reversible reactions and \((\delta, \gamma) < 0\) for all irreversible reactions do not define the unique vector: if \(\hat{\delta}\) satisfies these conditions then its linear combination with the vectors of atomic balances also satisfy them. Such a combination is a vector
\[
\lambda\delta + \lambda\Pi(2, 0, 1, 2, 1, 0, 1, 2) + \lambda\Omega(0, 2, 1, 1, 0, 1, 2, 2)
\]
under condition \(\lambda > 0\). This transformation of \(\delta\) does not change the signs of \(\hat{\delta}\) on the stoichiometric vectors because of atomic balances.

In our case the only coordinate remains not eliminated, \(x_7\) (the bottom part of the last column of the Table 2). If, for some reaction mechanism and selected sets of reversible and irreversible reaction, there remain several \((q)\) coordinates, then it is necessary to find \(q\) corresponding functionals \(\hat{\delta}\) and the space of possible vectors of exponents is \((q + j)\)-dimensional. Here, \(j\) is the number of the independent linear conservation laws for the whole system, \(j = n - \text{rank}\{\gamma_j\}\), \(n\) is the number of the components, \(\{\gamma_j\}\) includes all the stoichiometric vectors for reversible and irreversible reactions.

To find \(\delta\), we apply the elimination procedures from the Table 2 to an arbitrary vector \(y = (y_i) (i = 1, \ldots, 8)\):
\[
(y_1, y_2, y_3, y_4, y_5, y_6, y_7, y_8) \mapsto (y_1, y_2, 0, y_4, y_5, y_6, y_7, y_8)
\mapsto(y_1, y_2, 0, y_4, y_5, y_6, y_7, 0) \mapsto (y_1, y_2, 0, 0, y_5 - y_4, y_6, y_7, 0)
\mapsto(y_1, y_2, 0, 0, y_6 + y_5 - y_4, y_7, 0) \mapsto (y_1, y_2, 0, 0, 0, y_7 + y_6 + y_5 - y_4, 0).
\]
This sequence of transformations gives us the linear functional
\[ \hat{\delta}(y) = y_7 + y_6 + y_5 - y_4. \]

The corresponding vector of exponents \((0, 0, 0, -1, 1, 1, 0)\) should be corrected because its coordinates cannot be negative. Let us apply (25) with \(\lambda = 2\) (for convenience). The coordinates of this combination are non-negative if and only if \(\lambda_H \geq 0\), \(\lambda_O \geq 0\) and \(2\lambda_H + \lambda_O - 2 \geq 0\). The solutions of these linear inequality on the \((\lambda_H, \lambda_O)\) plane is a convex combination of the extreme points (corners) \((1, 0)\) and \((0, 2)\) plus any non-negative 2D vector: \((\lambda_H, \lambda_O) = \zeta(1, 0) + (1 - \zeta)(0, 2) + (\vartheta_1, \vartheta_2)\); \(\vartheta_{1,2} \geq 0\) and \(1 \geq \zeta \geq 0\). The corresponding vectors of exponents are
\[
(0, 0, 0, -2, 2, 2, 0, 0) + (\zeta + \vartheta_1)(2, 0, 1, 2, 1, 0, 1, 2) + (1 - \zeta + \vartheta_2)(0, 4, 2, 2, 0, 2, 4, 4).
\]
At least one of the exponents should be zero. There are only three possibilities, \(\delta_1\), \(\delta_2\) or \(\delta_4\). For all other \(i\), \(\delta_i > 0\) if \(\vartheta_{1,2} \geq 0\) and \(1 \geq \zeta \geq 0\).

To provide any necessary atomic balance in the limit \(\varepsilon \to 0\) it is necessary that two of \(\delta_i\) are zeros. If \(b_O \leq \frac{1}{2}b_H\), then \(\delta_1 = \delta_4 = 0\). This means that \(\vartheta_{1,2} = 0\), \(\zeta = 0\) and \(\delta = (0, 4, 2, 0, 2, 4, 6, 4)\). It is convenient to divide this \(\delta\) by 2 and write
\[ \delta = (0, 2, 2, 0, 2, 2, 3, 2). \]

For these exponents, the equilibrium concentrations tend to 0 with the small parameter \(\varepsilon \to 0\) as
\[
\begin{align*}
c_H^0 &= c^0_1 = \text{const}, & c_O^0 &= c^0_2 \sim \varepsilon^2, & c_{OH}^0 &= c^0_3 \sim \varepsilon^2, & c_{H_2O}^0 &= c^0_4 = \text{const}, \\
c_H &= c^1_1 \sim \varepsilon^2, & c_O &= c^1_2 \sim \varepsilon^2, & c_{OH} &= c^1_3 \sim \varepsilon^2, & c_{H_2O} &= c^1_4 = \text{const}, \\
\end{align*}
\]
(27)

If \(b_O \geq \frac{1}{2}b_H\), then \(\delta_2 = \delta_4 = 0\). This means that \(\vartheta_{1,2} = 0\), \(\zeta = 1\) and
\[ \delta = (2, 0, 1, 0, 3, 2, 3, 2). \]

For these exponents, the equilibrium concentrations tend to 0 with the small parameter \(\varepsilon \to 0\) as
\[
\begin{align*}
c_H^0 &= c^0_1 \sim \varepsilon^2, & c_O^0 &= c^0_2 = \text{const}, & c_{OH}^0 &= c^0_3 \sim \varepsilon, & c_{H_2O}^0 &= c^0_4 = \text{const}, \\
c_H &= c^1_1 \sim \varepsilon^3, & c_O &= c^1_2 \sim \varepsilon^3, & c_{OH} &= c^1_3 \sim \varepsilon^3, & c_{H_2O} &= c^1_4 \sim \varepsilon^3. \\
\end{align*}
\]
(28)

The linear combination \(\sum \delta_i N_i\) decreases in time due to kinetic equations. This is true for any vector of exponents presented by a linear combination \((\lambda \neq 0)\) of the initial vector \((0, 0, 0, -1, 1, 1, 0)\) with the vectors of the atomic balances. At the same time, any of these combinations give an additional linear conservation law for the system of reversible reactions.

Below are several versions of this function:

- The initial version, \(\hat{\delta}\), obtained from the Table(2) is \((\delta, N) = -N_{H_2O} + N_H + N_O + N_{H_2O}\);
- Vector of exponents, calibrated by adding of the atomic balances \((25)\) to meet the atomic balance conditions for \(b_O \leq \frac{1}{2}b_H\) in the limit \(\varepsilon \to 0\) is \((\delta, N) = 2N_O + 2N_{OH} + 2N_H + 2N_O + 3N_{H_2O} + 2N_{H_2O}\);
- Vector of exponents, calibrated to meet the atomic balance conditions for \(b_O \geq \frac{1}{2}b_H\) is, \((\delta, N) = 2N_{H_2} + N_{OH} + 3N_H + 2N_O + 3N_{H_2O} + 2N_{H_2O}\).

All these forms differs by the combinations of the atomic balances \((25)\) and are, in this sense, equivalent.

5. Conclusion

The general principle of detailed balance was formulated in 1925 as follows [15]: “Corresponding to every individual process there is a reverse process, and in a state of equilibrium the average rate of every process is equal to the average rate of its reverse process.” Rigorously speaking, the chemical reactions have to
be considered as reversible ones, and every step of the complex reaction consists of two reactions, forward and reverse (backward) one. However, in reality the rates of some forward or reverse reactions may be negligible. Typically, the complex combustion reactions, in particular, reactions of hydrocarbon oxidation or hydrogen combustion, include both reversible and irreversible steps. It is a case in catalytic reactions as well. In particular, many enzyme reactions are “partially irreversible”. Although many catalytic reactions are globally irreversible, they always include some reversible steps, in particular steps of adsorption of gases. Many enzyme reactions are also “partially irreversible”.

This work aims to solve the problem of the partially irreversible limit in chemical thermodynamics when some reactions become irreversible whereas some other reactions remain reversible. The main results in this direction are

1. Description of the multiscale limit of a system reversible reactions when some of equilibrium concentrations tend to zero (Sec. 2.2).
2. Extended principle of detailed balance for the systems with some irreversible reactions (Theorem 1).
3. The linear functional $G_\delta$ that decreases in time on solutions of the kinetic equations under the extended detailed balance conditions (Proposition 2 and Eq. (11)).
4. The entropy production (or free energy dissipation) formulas for the reversible part of the reaction mechanism under the extended detailed balance conditions (Eqs. (13), (15)).
5. Description of the faces of the positive orthant which include the $\omega$-limit points in their relative interior and, therefore, description of limiting behavior in time (Theorem 2).

Did we solve the main problem and create the thermodynamic of the systems with some irreversible reaction? The answer is: we solved this problem partially. We described the limit behavior but we did not find the global Lyapunov function that captures relaxation of both reversible and irreversible parts of the system. The good candidate is a linear combination of the relevant classical thermodynamic potential and $G_\delta$ but we did not find the coefficients. In that sense, the problem of the limit thermodynamics remains open.

Nevertheless, one problem is solved ultimately and completely: How to throw away some reverse reactions without violation of thermodynamics and microscopic reversibility? The answer is: the convex hull of the stoichiometric vectors of the irreversible reactions should not intersect with the linear span of the stoichiometric vectors of the reversible reactions and the reaction rate constants of the remained reversible reactions should satisfy the Wegscheider identities (8).

The solution of this theoretical problem is important for the modeling of the chemical reaction networks. This is because some of reactions are practically irreversible. Removal of some reverse reaction from the reaction mechanism cannot be done independently of the whole structure of the reaction network; the whole reaction mechanism should be used in the decision making.

If the irreversible reactions are introduced correctly then we also know that the closed system with this reaction mechanism goes to an equilibrium state. At this equilibrium, all the reaction rates are zero: the irreversible reaction rates vanish and the rates of the reversible reactions satisfy the principle of detailed balance. The limit equilibria are situated on the faces of the positive orthant of concentrations and these faces are described in the paper.

The oscillatory or chaotic attractors are impossible in closed systems which satisfy the extended principle of detailed balance. This general statement can be considered as a simple consequence of thermodynamics. It can be easily proved if the thermodynamic Lyapunov functions (potentials) are given. However, the thermodynamic potentials have no limits for the systems with some irreversible reactions and we do not know a priori any general theorem that prohibits bifurcations at the zero values of some reaction rate constants. In this paper we proved, in particular, that the emergency of nontrivial attractors in systems with some irreversible reactions is impossible if they are the limits of the reversible systems which satisfy the principle of detailed balance. In this sense, the thermodynamic behavior is proven for the systems with some irreversible reactions under the extended detailed balance conditions. Nevertheless, the general problem of the thermodynamic potentials in this limit remains open.
References


