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 speeds of this tendency to zero. We study the dynamics of the limit system and describe its limit behavior as $t \to \infty$. The *extended principle of detailed balance* provides the physical background of this analysis. If the reversible systems obey the principle of detailed balance then the limit system with some irreversible reactions must satisfy 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 alow 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.
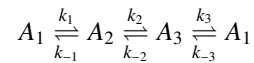
1. Introduction

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 $\mathbb{R}^n$. ($\mathbb{R}^n_+$. (The closed positive orthant 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

$$A_1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_3 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} A_1$$

with the equilibrium concentrations $c^{\mathrm{eq}} = (c_1^{\mathrm{eq}}, c_2^{\mathrm{eq}}, c_3^{\mathrm{eq}})$ and the detailed balance conditions:

$$k_i c_i^{\mathrm{eq}} = k_{-i} c_{i+1}^{\mathrm{eq}}$$

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

$$F = \sum_i RTVc_i \left(\ln\left(\frac{c_i}{c_i^{\mathrm{eq}}}\right) - 1 \right) + const.$$

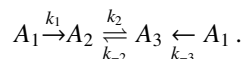Let the equilibrium concentration $c_1^{\mathrm{eq}} \to 0$ for the

fixed values of $c_{2,3}^{\text{eq}} > 0$. This means that

$$\frac{k_{-1}}{k_1} = \frac{c_1^{\text{eq}}}{c_2^{\text{eq}}} \to 0 \text{ and } \frac{k_3}{k_{-3}} = \frac{c_1^{\text{eq}}}{c_3^{\text{eq}}} \to 0 \,.$$

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

$$A_1 \xrightarrow{k_1} A_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_3 \underset{k_{-3}}{\leftarrow} A_1 \,.$$

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 ∞ for any positive vector of concentrations because the term $c_1 \ln(c_1/c_1^{\text{eq}})$ increases to ∞. The free energy cannot be normalized by adding a constant term because the variation of the term $c_1 \ln(c_1/c_1^{\text{eq}})$ on an interval $[0, \overline{c}]$ with fixed $\overline{c}$ also increases to ∞, it varies from $-c_1^{\text{eq}}/e$ (for the minimizer, $c_1 = c_1^{\text{eq}}/e$) to a large number $\overline{c}(\ln \overline{c} - \ln c_1^{\text{eq}})$ (for $c_1 = \overline{c}$).

The logarithmic singularity is rather "soft" and does not cause a real physical problem because even for $c_1^{\text{eq}}/c_1 = 10^{-10}$ 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, for perfect systems with detailed balance under isochoric isothermal conditions the density,

$$f = F/(RTV) = \sum_i c_i(\ln(c_i/c_i^{\text{eq}}) - 1) \,, \qquad (1)$$

is a Lyapunov function for a system of chemical kinetics (here, c_i is the concentration of the ith component and c_i^{eq} 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 [26]). 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].

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. More over, 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

$$\sum_i \alpha_{ri} A_i \to \sum_j \beta_{rj} A_j \quad (r = 1, \dots, m) \,, \qquad (2)$$

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 γ_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 $\sum_i b_i \gamma_{ri} = 0$ 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])

$$w_r = k_r \prod_{i=1}^n a_i^{\alpha_{ri}} \,, \qquad (3)$$

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

$$a_i = \exp\left(\frac{\mu_i - \mu_i^0}{RT}\right) \,. \qquad (4)$$

Here, μ_i is the chemical potential and μ_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 $a_i^{\text{eq}} > 0$ with detailed balance, $w_r^+ = w_r^-$.

Recently, it is found 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.

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 has the modest complexity: 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 we have m constants (m should be an even number, $m = 2\ell$) 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 "direct" 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 direct reaction and the detailed balance equations. Therefore, the direct reaction rate constants and a set of the equilibrium activities form the complete description of the reaction. Here we have $\ell + n$ independent constants, $\ell = m/2$ rate constants of direct reactions and n (it is the number of components) equilibrium activities. For these $\ell + n$ 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 direct and reverse elementary reactions and write

$$\sum_i \alpha_{ri} A_i \rightleftharpoons \sum_j \beta_{rj} A_j \quad (r = 1, \ldots, \ell). \qquad (5)$$

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

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

$$\sum_i \gamma_{ri} x_i = \ln k_r^+ - \ln k_r^- = \ln K_r \quad (r = 1, \ldots \ell) \qquad (6)$$

($x_i = \ln a_i^{\text{eq}}$). Of course, we assume that if $k_r^+ > 0$ then $k_r^- > 0$ (reversibility) and the equilibrium constant $K_r > 0$ is defined for all reactions from (5).

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

$$\lambda \mathbf{\Gamma} = 0 \quad \left(i.e. \ \sum_{r=1}^{\ell} \lambda_r \gamma_{ri} = 0 \ \text{for all} \ i \right) \qquad (7)$$

the Wegscheider identity holds:

$$\prod_{r=1}^{\ell} (k_r^+)^{\lambda_r} = \prod_{r=1}^{\ell} (k_r^-)^{\lambda_r}. \qquad (8)$$

It is sufficient to use in (8) any basis of solutions of the system (7): $\lambda \in \{\lambda^1, \cdots, \lambda^q\}$.

2.2. Multiscale degeneration of equilibria

Let us take a system with detailed balance and send some of the equilibrium activities to zero: $a_i^{\text{eq}} \to 0$ 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,

$$A_1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_3$$
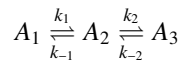
when $a_1^{\text{eq}}, a_2^{\text{eq}} \to 0$.

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

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

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

We study asymptotics $a_i^{\text{eq}} = const \times \varepsilon^{\delta_i}$, $\varepsilon \to 0$ 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 ε:

$$w_r^{\text{eq}+} = k_r^+ const \times \varepsilon^{\sum_i \alpha_{ri} \delta_i}, \quad w_r^{\text{eq}-} = k_r^- const \times \varepsilon^{\sum_i \beta_{ri} \delta_i}.$$

According to the principle of detailed balance, $w_r^{\text{eq}+} = w_r^{\text{eq}-}$ and

$$\frac{k_r^+}{k_r^-} = const \times \varepsilon^{(\gamma_r, \delta)}, \qquad (9)$$

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

There are three groups of reactions with respect to the given vector δ:

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

In the first group ($(\gamma_r, \delta) = 0$) the ratio k_r^+/k_r^- remains constant and we can take $k_r^\pm = const > 0$. 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 $k_r^- = const > 0$, whereas $k_r^+ \to 0$.

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

We consider bounded systems, hence the negative values of δ should be forbidden. At least one equilibrium activity should not vanish. Therefore, $\delta_j = 0$ for some j. Below we assume that $\delta_i \geq 0$ and $\delta_j = 0$ 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 are found. For the reactions of

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the third group (with $(\gamma_r, \delta) > 0$) the direct reaction vanishes in the limit $\varepsilon \to 0$. It is convenient to transpose the stoichiometric equations for these reactions and swap the direct reactions with reverse ones. Let us perform this transposition. After that, α_r changes over β_r, γ transforms into $-\gamma$, and the inequality $(\gamma_r, \delta) > 0$ transforms into $(\gamma_r, \delta) < 0$.

Let us summarize. We use the given vector of exponents δ 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 $a_i^{\mathrm{eq}} = 0$ 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 direct reaction with reverse one, for convenience, γ_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 $a_i^{\mathrm{eq}} = const \times \varepsilon^{\delta_i} \to 0$ (for some i) is important because for different values of δ 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

$$\frac{\mathrm{d}N}{\mathrm{d}t} = V \sum_r w_r \gamma_r, \qquad (10)$$

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 δ. 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 (10) for this limit system: $\mathrm{d}G_\delta(N)/\mathrm{d}t \leq 0$ and $\mathrm{d}G_\delta(N)\mathrm{d}t = 0$ if and only if all the reaction rates for the irreversible reactions are zero.*

Proof. Indeed,

$$\frac{\mathrm{d}G_\delta(N)}{\mathrm{d}t} = V \sum_r w_r(\gamma_r, \delta) \leq 0, \qquad (11)$$

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. $\qquad \square$

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 δ. 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

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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, θ) for some vector θ. For the reversible reactions $(\gamma_r, \theta) = 0$ and for the irreversible reactions $(\gamma_r, \theta) < 0$.

It is possible to find vector δ 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 λ, the vector $\theta + \lambda b$ has the same separation property as the vector θ has. We can select such λ 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 δ 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 $a_i^* > 0$ for the reversible reactions. Let us take one such a vector. (A simple remark is needed here: for the components A_j that do not participate in the reversible reactions we have to select arbitrary positive values $a_j^* > 0$.)

For each irreversible reaction with the stoichiometric vector γ_r and reaction rate constant $k_r = k_r^+ > 0$ we add a reverse reaction with the reaction rate constant

$$k_r^- = k_r^+ \prod_i (a_i^*)^{-\gamma_{ri}}.$$

For this fully reversible system the activities $a_i^* > 0$ provide the point of detailed balance. In the multiscale degeneration process, the equilibrium activities depend on $\varepsilon \to 0$ as $a_i^{\text{eq}} = a_i^* \varepsilon^{\delta_i}$. For the reactions with $(\gamma_r, \delta) = 0$ the reaction rate constants do not depend on ε and for the reactions with $(\gamma_r, \delta) < 0$ the rate constant k_r^- tends to zero as $\varepsilon^{-(\gamma_r, \delta)}$ and k_r^+ does not change. We return to the initial system of reactions in the limit $\varepsilon \to 0$. $\qquad \square$

This is a particular form of the extended principle of detailed balance. For more discussion see [12].

2.3. Activities, concentrations and affinities

To combine the linear Lyapunov functions $G_\delta(N) = (\delta, N)$ (11) 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 $a_i = c_i / c_i^\circ$, where c_i° is an arbitrary "standard" concentration. To avoid introduction of unnecessary quantities, we always assume that in the selected system of units, $c_i^\circ \equiv 1$.

If the thermodynamic potentials exist then due to the thermodynamic definition of activity (4), 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

$$F(N, T, V) = RT \sum_i N_i (\ln c_i - 1 + f_{0i}(c, T)), \quad (12)$$

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 (12) 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, $P = -\partial F(N, T, V)/\partial V = RT c_i + o(c_i) + P|_{c_i=0}$. Connections between the equation of state, free energy and kinetics are discussed in more detail in [7, 8].

There are several simple algebraic corollaries of the assumed connection between activities and concentrations. Let us consider an elementary reaction $\sum \alpha_i A_i \to \sum \beta_i A_i$ 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 $\sum \alpha_i A_i \rightleftharpoons \sum \beta_i A_i$

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 3 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 $i \notin J$.

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 direct 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 (3) 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. $\square$

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 direct and reverse reactions participate separately.

Corollary 1. *The following statements are equivalent:*

1. *$\sum_{r \in S} \gamma_{ri} w_r(c) = 0$ 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 no 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 ε, $g_i(c, T) = g_i(c, T, 0)$.

This independence from ε 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 ε. 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 $V, T = const$ and the free Gibbs energy G for $P, V = const$.

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, $w_r^+(a^{eq}) = w_r^-(a^{eq}) = w_r^{eq}(T)$. It is convenient to represent the reaction rates using these *equilibrium fluxes* $w_r^{eq}(T)$:

$$w_r^+ = w_r^{eq} \exp\left(\sum_i \frac{\alpha_{ri}(\mu_i - \mu_i^{eq})}{RT} \right),$$

$$w_r^- = w_r^{eq} \exp\left(\sum_i \frac{\beta_{ri}(\mu_i - \mu_i^{eq})}{RT} \right).$$

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

These formulas give immediately the following representation of the dissipation rate

$$\frac{d\Phi}{dt} = \sum_i \frac{\partial \Phi(N, \ldots)}{\partial N_i} \frac{dN_i}{dt} = \sum_i \mu_i \frac{dN_i}{dt}$$
$$= -VRT \sum_r (\ln w_r^+ - \ln w_r^-)(w_r^+ - w_r^-) \leq 0 \,. \tag{13}$$

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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:

$$\frac{dS}{dt} = VR \sum_r (\ln w_r^+ - \ln w_r^-)(w_r^+ - w_r^-) \geq 0 \,.$$

Let us notice that

$$\ln w_r^+ - \ln w_r^- = \frac{1}{RT} \sum_i \mu_i (\alpha_{ri} - \beta_{ri}) = -\frac{(\gamma_r, \mu)}{RT} \,.$$

The quantity $-(\gamma_r, \mu)$ is one of the central notion of physical chemistry, *affinity* [5]. It is positive if the direct reaction prevails over reverse one and negative in the opposite case. It measures the energetic advantage of the direct 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:

$$\mathbb{A}_r = -\frac{(\gamma_r, \mu)}{RT}$$

Let us apply an elementary identity

$$\exp a - \exp b = (\exp a + \exp b) \tanh \frac{a - b}{2}$$

to the reaction rate, $w_r = w_r^+ - w_r^-$:

$$w_r = (w_r^+ + w_r^-) \tanh \frac{\mathbb{A}_r}{2} \,. \qquad (14)$$

This representation of the reaction rates gives immediately for the dissipation rate:

$$\frac{d\Phi}{dt} = -VRT \sum_r (w_r^+ + w_r^-) \mathbb{A}_r \tanh \frac{\mathbb{A}_r}{2} \leq 0 \,. \qquad (15)$$

In this formula, the kinetic information is collected in the positive factors, the sums of reaction rates $(w_r^+ + w_r^-)$, and the purely thermodynamical multipliers $\mathbb{A}_r \tanh(\mathbb{A}_r/2)$ are also positive. For small $|\mathbb{A}_r|$, the expression $\mathbb{A}_r \tanh(\mathbb{A}_r/2)$ behaves like $\mathbb{A}_r^2/2$ and for large $|\mathbb{A}_r|$ it behaves like the absolute value, $|\mathbb{A}_r|$.

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 (3) 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: $V, T = const$, $c = N/V$. For other classical conditions ($U, V = const$, or $P, T = const$, or $H, P = const$) 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 $\mathbb{R}_+^n$ 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 $\mathbb{R}_+^n$ but a semi-dynamical one: the solutions may lose positivity and leave $\mathbb{R}_+^n$ 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 ω-limit points.

By the definition, the ω-limit points of a dynamical system are the limit points of the motions when time $t \to \infty$. We consider a kinetic system in $\mathbb{R}_+^n$. In particular, for each solution of the kinetic equations $N(t)$ the set of the corresponding ω-limit points is closed, connected and consists of the whole trajectories ([9], Proposition 1.5). This means that the motion which starts from an ω-limit point remains in $\mathbb{R}_+^n$ 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 ω-limit point of this solution and $x_i^* = 0$. 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 $x(t)$ $(-\infty < t < \infty)$ belong to $\mathbb{R}_+^n$. Indeed, there exists such a sequence $t_j \to \infty$ that $N(t_j) \to x^*$. For any $\tau \in (-\infty, \infty)$, $N(t_j + \tau) \to x(\tau)$. For sufficiently large j, $t_j + \tau > 0$ and the value $N(t_j + \tau) \in \mathbb{R}_+^n$. Therefore, $x(\tau) \in \mathbb{R}_+^n$ $(-\infty < \tau < \infty)$ and for any τ the point $x(\tau)$ is an ω-limit point of the solution $N(t)$. Let $x_i^* = 0$ and $\dot{x}_i|_{x^*} = v \neq 0$. If $v > 0$ then for small $|\tau|$ and $\tau < 0$ the value of x_i becomes negative, $x_i(\tau) < 0$. It is impossible because positivity. Similarly, If $v < 0$ then for small $\tau > 0$ the value of x_i becomes negative, $x_i(\tau) < 0$. It is also impossible because positivity. Therefore, $\dot{x}_i|_{x^*} = 0$. $\square$

We use Proposition 4 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 $\gamma_{rj} = 0$ for all $j \in J$ or $\alpha_{rj} > 0$ 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 1. $\square$

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 $\delta = (\delta_i)$ is given, $\delta_i \geq 0$ for all i and $\delta_i = 0$ for some i. There are two sets of reaction. For one of them, $(\gamma_r, \delta) = 0$ and in the limit both $k_r^{\pm} > 0$. In the second set, $(\gamma_r, \delta) < 0$ 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 direct reactions with reverse ones.

For convenience, let us change the notations. Let γ_i be the stoichiometric vectors of reversible reactions with $(\gamma_r, \delta) = 0$ $(r = 1, \ldots, h)$, and ν_l be the stoichiometric vectors for the reactions from the second set, $(\nu_l, \delta) < 0$ $(l = 1, \ldots, s)$. For the reaction rates and constants for the first set we keep the same notations:

w_r, $w_r^{\pm}$, $k_r^{\pm}$. For the second set, we use for the reaction rate constants $q_l = q_l^+$ and for the reaction rates $v_l = v_l^+$. (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_{li}^v and β_{li}^v.

Let the rates of all the irreversible reaction be equal to zero. This does not mean that all the concentrations a_i with $\delta_i > 0$ achieve zero. A bimolecular reaction $A + B \to C$ gives us a simple example: $w = k a_A a_B$ 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, $a_A, a_B \geq 0$, the set of zeros of w is a union of two semi-axes, $\{a_A = 0, a_B \geq 0\}$ and $\{a_A \geq 0, a_B = 0\}$. 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 $\sum_l v_l \nu_l = 0$ then all $v_l = 0$. Let us describe the set of zeros of all v_l in the the positive orthant of activities.

For every $l = 1, \ldots, s$ the set of zeros of v_l in $\mathbb{R}_+^n$ is given by the conditions: at least for one i $\alpha_{li}^v \neq 0$ and $a_i = 0$. It is convenient to represent this condition as a disjunction. Let $J_l = \{i \mid \alpha_{li}^v \neq 0\}$. Then the set of zeros of v_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 v_l is represented by the following conjunction form

$$\wedge_{l=1}^s \left(\vee_{i \in J_l} (a_i = 0) \right) . \tag{16}$$

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:

$$
\begin{aligned}
&\wedge_{l=1}^s \left(\vee_{i \in J_l} (a_i = 0) \right) \\
&= \vee_{i_1 \in J_1, \ldots, i_s \in J_s} \left((a_{i_1} = 0) \wedge \ldots \wedge (a_{i_s} = 0) \right) .
\end{aligned} \tag{17}
$$

For a cortege of indexes $\{i_1, \ldots, i_s\}$ the correspondent set of their values may be smaller because some values i_l may coincide. Let this set of values be $S_{\{i_1, \ldots, i_s\}}$. We can delete from (17) a conjunction $(a_{i_1} = 0) \wedge \ldots \wedge (a_{i_s} = 0)$ if there exists a cortege $\{i_1', \ldots, i_s'\}$ $(i_l' \in J_l)$ with smaller set of values, $S_{\{i_1, \ldots, i_s\}} \supseteq S_{\{i_1', \ldots, i_s'\}}$. Let us check the corteges in some order and delete a conjunction from (17) 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

$$\vee_j(\wedge_{i \in S_j}(a_i = 0)), \qquad (18)$$

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, $S_j \nsubseteq S_p$. The elementary conjunction $\wedge_{i \in S_j}(a_i = 0)$ 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 ω-limit points of such systems are steady states of the irreversible reactions due to Proposition 2 but not all these steady states may be the ω-limit points of the system. A simple formal example gives us the couple of reaction: $A \rightleftharpoons B$, $A + B \rightarrow C$. 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, $(c_A = 0) \vee (c_B = 0)$ 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 $dc_A/dt = k_1^- c_B > 0$. Due to Proposition 4 this is not an ω-limit point. Similarly, the points with $c_A > 0$ and $c_B = 0$ are not the ω-limit points.

Let us combine Propositions 2, 4 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 ω-limit point $x^* \in riF_J$ 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 ω-limit point $x^* \in riF_J$ 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 4) 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 semi-dynamical 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 ω-limit points. $\square$

Let us find the faces F_J that contain the ω-limit points in their relative interior riF_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 faces with this property*. For this purpose, we always minimize the disjunctive forms by cancelations. We do not list the faces that contain the ω-limit points in their relative interior and are the proper subsets of other faces with this property. All the ω-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 $\wedge_{i \in S_j}(c_i = 0)$ in intersection with $\mathbb{R}_+^n$. It is the union of the faces, $\cup_j F_{S_j}$. 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 ω-limit points in the relative interior riF_J (Theorem 2):

$$(c_i = 0) \Rightarrow \left[\left(\wedge_{r, \gamma_{ri} > 0} \vee_{j, \alpha_{rj} > 0} (c_j = 0)\right) \right.$$
$$\left. \wedge \left(\wedge_{r, \gamma_{ri} < 0} \vee_{j, \beta_{rj} > 0} (c_j = 0)\right)\right]. \qquad (19)$$

Here, $c_i = 0$ in F_J may be read as $i \in J$. Following the previous section, we use here the notations γ_{ri}, β_{ri} and β_{ri} for the reversible reactions and reserve ν_l, α_{li}^ν and β_{li}^ν for the irreversible reactions. The set of γ_r in this formula is the set of the stoichiometric vectors of the reversible 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, $\mathfrak{S}(S) = \{S_1', \ldots, S_l'\}$. 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:

$$\wedge_{i \in S} \left[(c_i = 0) \wedge \left(\wedge_{r, \gamma_{ri} > 0} \ \vee_{j, \alpha_{rj} > 0} (c_j = 0) \right) \right.$$
$$\left. \wedge \left(\wedge_{r, \gamma_{ri} < 0} \ \vee_{j, \beta_{rj} > 0} (c_j = 0) \right) \right] . \quad (20)$$

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

$$\vee_{j=1,\dots,k} \left(\wedge_{i \in S'_j} (c_i = 0) \right) . \quad (21)$$

Because of cancelations, the sets S'_j do not include one another. They give the result, $\mathfrak{S}(S) = \{S'_1, \dots, S'_l\}$. 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 $\mathbf{S} = \{S_1, \dots, S_p\}$ with the property: $S_i \not\subset S_j$ for $i \neq j$. Let us apply $\mathfrak{S}$ to all S_i and take the union of the results: $\mathfrak{S}_0(\mathbf{S}) = \cup_i \mathfrak{S}(S_i)$. Some sets from this family may include other sets from it. Let us organize cancelations: if $S', S'' \in \mathfrak{S}_0(\mathbf{S})$ and $S' \subset S''$ 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 $\mathfrak{S}(\mathbf{S})$. It does not depend on the order of these operations.

Let us start from any family $\mathbf{S}$ and iterate the operation $\mathfrak{S}$. Then, after finite number of iterations, the sequence $\mathfrak{S}^d(\mathbf{S})$ stabilizes: $\mathfrak{S}^d(\mathbf{S}) = \mathfrak{S}^{d+1}(\mathbf{S}) = \dots$ 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 ω-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 $d = 1, 2, \dots$, until stabilization.
3. Let $\mathfrak{S}^d(\{S_j\}) = \mathfrak{S}^{d+1}(\{S_j\}) = \{J_1, J_2, \dots J_p\}$. Then the family of the faces F_{J_i} ($i = 1, 2, \dots, p$) gives the answer: the ω-limit points are situated in riF_{J_i} and for each i there are ω-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. $A_1 + A_2 \rightleftharpoons A_3 + A_4$, $\gamma = (-1, -1, 1, 1, 0)$; $A_1 + A_2 \rightarrow A_5$, $\nu = (-1, -1, 0, 0, 1)$. The extended principle of detailed balance holds: the convex hull of the stoichiometric vectors of the irreversible reactions consists of one vector γ_2 and it is linearly independent of γ_1. The input vector α for the irreversible reaction $A_1 + A_2 \rightarrow A_5$ is $(-1, -1, 0, 0, 0)$. The set $J = J_l$ from the conjunction form (16) is defined by the non-zero coordinates of this α^ν: $J = \{1, 2\}$. The conjunction form in this simple case (one irreversible reaction) loses its first conjunction operation and is just $(c_1 = 0) \vee (c_2 = 0)$. It is, at the same time, the minimized disjunction form (18) and does not require additional transformations. This formula describes the steady states of the irreversible reaction in the positive orthant $\mathbb{R}^n_+$. For this disjunction form, The family of sets $\mathbf{S} = \{S_j\}$ consists of two sets, $S_1 = \{1\}$ and $S_2 = \{2\}$.

Let us calculate $\mathfrak{S}(S_{1,2})$. 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

$$(c_1 = 0) \wedge ((c_3 = 0) \vee (c_4 = 0))$$

and for $S = \{2\}$ it gives

$$(c_2 = 0) \wedge ((c_3 = 0) \vee (c_4 = 0)) .$$

The elementary transformations give the disjunctive forms:

$$[(c_1 = 0) \wedge ((c_3 = 0) \vee (c_4 = 0))]$$
$$\Leftrightarrow [((c_1 = 0) \wedge (c_3 = 0)) \vee ((c_1 = 0) \wedge (c_4 = 0))] ,$$

$$[(c_2 = 0) \wedge ((c_3 = 0) \vee (c_4 = 0))]$$
$$\Leftrightarrow [((c_2 = 0) \wedge (c_3 = 0)) \vee ((c_2 = 0) \wedge (c_4 = 0))] .$$

Therefore, $\mathfrak{S}(S_1) = \{\{1,3\}, \{1,4\}\}$, $\mathfrak{S}(S_2) = \{\{2,3\}, \{2,4\}\}$ and

$$\mathfrak{S}(\{S_1, S_2\}) = \{\{1,3\}, \{1,4\}, \{2,3\}, \{2,4\}\} .$$

No cancelations are needed. The iterations of $\mathfrak{S}$ 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 $\mathfrak{S}(\{1,3\})$ formula (20) gives

$$[(c_1 = 0) \wedge ((c_3 = 0) \vee (c_4 = 0))]$$
$$\wedge [(c_3 = 0) \wedge ((c_1 = 0) \vee (c_2 = 0))] .$$

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

All the ω-limit points (steady states) belong to the faces $F_{\{1,3\}} = \{c\,|\,c_1 = c_3 = 0\}$, $F_{\{1,4\}} = \{c\,|\,c_1 = c_4 = 0\}$, $F_{\{2,3\}} = \{c\,|\,c_2 = c_3 = 0\}$, or $F_{\{2,4\}} = \{c\,|\,c_2 = c_4 = 0\}$. The position of the ω-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 $\mathbb{R}^5$. 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 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 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 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 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 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 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 is non-negative because $b_1 + b_3 \geq 0$).

- 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 ω-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. $A_1 + A_2 \rightleftharpoons A_3 + A_4$, $\gamma_1 = (-1, -1, 1, 1, 0)$, $A_5 \rightarrow A_1 + A_2$, $\nu = (1, 1, 0, 0, -1)$. The extended

Table 1: H_2 burning mechanism [21]

No	Reaction	Stoichiometric vector
1	$H_2 + O_2 \rightleftharpoons 2OH$	(-1,-1,2,0,0,0,0,0)
2	$H_2 + OH \rightleftharpoons H_2O + H$	(-1,0,-1,1,1,0,0,0)
3	$OH + O \rightleftharpoons O_2 + H$	(0,1,-1,0,1,-1,0,0)
4	$H_2 + O \rightleftharpoons OH + H$	(-1,0,1,0,1,-1,0,0)
5	$O_2 + H + M \rightleftharpoons HO_2 + M$	(0,-1,0,0,-1,0,1,0)
6	$OH + HO_2 \rightleftharpoons O_2 + H_2O$	(0,1,-1,1,0,0,-1,0)
7	$H + HO_2 \rightleftharpoons 2OH$	(0,0,2,0,-1,0,-1,0)
8	$O + HO_2 \rightleftharpoons O_2 + OH$	(0,1,1,0,0,-1,-1,0)
9	$2OH \rightleftharpoons H_2O + O$	(0,0,-2,1,0,1,0,0)
10	$2H + M \rightleftharpoons H_2 + M$	(1,0,0,0,-2,0,0,0)
11	$2H + H_2 \rightleftharpoons H_2 + H_2$	(1,0,0,0,-2,0,0,0)
12	$2H + H_2O \rightleftharpoons H_2 + H_2O$	(1,0,0,0,-2,0,0,0)
13	$OH + H + M \rightleftharpoons H_2O + M$	(0,0,-1,1,-1,0,0,0)
14	$H + O + M \rightleftharpoons OH + M$	(0,0,1,0,-1,-1,0,0)
15	$2O + M \rightleftharpoons O_2 + M$	(0,1,0,0,0,-2,0,0)
16	$H + HO_2 \rightleftharpoons H_2 + O_2$	(1,1,0,0,-1,0,-1,0)
17	$2HO_2 \rightleftharpoons O_2 + H_2O_2$	(0,1,0,0,0,0,-2,1)
18	$H_2O_2 + M \rightleftharpoons 2OH + M$	(0,0,2,0,0,0,0,-1)
19	$H + H_2O_2 \rightleftharpoons H_2 + HO_2$	(1,0,0,0,-1,0,1,-1)
20	$OH + H_2O_2 \rightleftharpoons H_2O + HO_2$	(0,0,-1,1,0,0,1,-1)

principle of detailed balance holds. The steady-states of the irreversible reactions is given by one equation, $c_5 = 0$. Formula (20) gives for $\mathfrak{S}(\{5\})$ just $(c_5 = 0)$. The face $F_{\{5\}}$ includes ω-limit points in $riF_{\{5\}}$. Dynamics on this face is defined by the fully reversible reaction system and tends to the equilibrium of the reaction $A_1 + A_2 \rightleftharpoons A_3 + A_4$ 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.

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 ($A_1 = H_2$, $A_2 = O_2$, $A_3 = OH$, $A_4 = H_2O$, $A_5 = H$, $A_6 = O$, $A_7 = HO_2$, and $A_8 = H_2O_2$) 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].

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 direct and inverse 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, $2H \rightleftharpoons H_2$, after cancelation of the third bodies, and we analyze the mechanism of 18 reaction.

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

$$\gamma_{3,5,9} \in \text{span}\{\gamma_1, \gamma_2, \gamma_4, \gamma_{18}, \gamma_{19}, \gamma_{20}\}.$$

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 $k_r^- = 0$ or for all of them $k_r^+ = 0$. Here, the direct and inverse reactions and the notations $k_r^{\pm}$ are selected according to the Table 1. 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 spit in two: reversible reactions with numbers $r \in J_0$ and irreversible reactions with $r \in J_1$, $\text{rank}\{\gamma_1, \gamma_2, \ldots, \gamma_\ell\} = d$, $\text{rank}\{\gamma_r \mid r \in J_0\} = d_0$. The rank of all vectors γ_r, d, must exceed the rank of the stoichio-

metric 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 γ_r:

1. Eliminate several coordinates from all γ_r using linear conservation laws. This is transfer to the internal coordinates in $\text{span}\{\gamma_r \mid r = 1, \ldots, \ell\}$;

2. Eliminate coordinates from all γ_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 $\text{span}\{\gamma_r \mid r = 1, \ldots, \ell\}/\text{span}\{\gamma_r \mid r \in J_0\}$. 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 $\text{conv}\{\pm\overline{\gamma}_r \mid r \in J_1\}$ does not include 0.

In the Table 2 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, $(H_2, O_2, OH, H_2O, H, O, HO_2, H_2O_2)$. Due to these identities, a stoichiometric vector η for this mixture is completely defined by six coordinates $(\eta_3, \ldots, \eta_8)$. In the second column of the Table 2 these 6D vectors are given for all the reactions from the H_2 burning mechanism (the Table 1).

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:

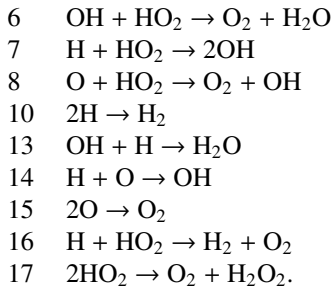$$x \mapsto x - x_i \frac{1}{\eta_i} \eta,$$

where η_i is a *pivot* (highlighted in bold in the column preceding the result of elimination), and η is the vector that includes the pivot (as the ith 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

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.

No	H_2, O_2	OH	H_2O_2	H_2O	H	O
1	(**2**,0,0,0,0,0)	(0,0,0,0,0)	(0,0,0,0)	(0,0,0)	(0,0)	(0)
2	(-1,1,1,0,0,0)	(1,1,0,0,0)	(**1**,1,0,0)	(0,0,0)	(0,0)	(0)
3	(-1,0,1,-1,0,0)	(0,1,-1,0,0)	(0,1,-1,0)	(**1**,-1,0)	(0,0)	(0)
4	(1,0,1,-1,0,0)	(0,1,-1,0,0)	(0,1,-1,0)	(1,-1,0)	(0,0)	(0)
5	(0,0,-1,0,1,0)	(0,-1,0,1,0)	(0,-1,0,1)	(-1,0,1)	(**-1**,1)	(0)
9	(-2,1,0,1,0,0)	(1,0,1,0,0)	(1,0,1,0)	(-1,1,0)	(0,0)	(0)
18	(2,0,0,0,0,-1)	(0,0,0,0,**-1**)	(0,0,0,0)	(0,0,0)	(0,0)	(0)
19	(0,0,-1,0,1,-1)	(0,-1,0,1,-1)	(0,-1,0,1)	(-1,0,1)	(-1,1)	(0)
20	(-1,1,0,0,1,-1)	(1,0,0,1,-1)	(1,0,0,1)	(-1,0,1)	(-1,1)	(0)
6	(-1,1,0,0,-1,0)	(1,0,0,-1,0)	(1,0,0,-1)	(-1,0,-1)	(-1,-1)	(-2)
7	(2,0,-1,0,-1,0)	(0,-1,0,-1,0)	(0,-1,0,-1)	(-1,0,-1)	(-1,-1)	(-2)
8	(1,0,0,-1,-1,0)	(0,0,-1,-1,0)	(0,0,-1,-1)	(0,-1,-1)	(-1,-1)	(-2)
10	(0,0,-2,0,0,0)	(0,-2,0,0,0)	(0,-2,0,0)	(-2,0,0)	(-2,0)	(-2)
13	(-1,1,-1,0,0,0)	(1,-1,0,0,0)	(1,-1,0,0)	(-2,0,0)	(-2,0)	(-2)
14	(1,0,-1,-1,0,0)	(0,-1,-1,0,0)	(0,-1,-1,0)	(-1,-1,0)	(-2,0)	(-2)
15	(0,0,0,-2,0,0)	(0,0,-2,0,0)	(0,0,-2,0)	(0,-2,0)	(-2,0)	(-2)
16	(0,0,-1,0,-1,0)	(0,-1,0,-1,0)	(0,-1,0,-1)	(-1,0,-1)	(-1,-1)	(-2)
17	(0,0,0,0,-2,1)	(0,0,0,-2,1)	(0,0,0,-2)	(0,0,-2)	(0,-2)	(-2)

(-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.)

6 $OH + HO_2 \rightarrow O_2 + H_2O$
7 $H + HO_2 \rightarrow 2OH$
8 $O + HO_2 \rightarrow O_2 + OH$
10 $2H \rightarrow H_2$
13 $OH + H \rightarrow H_2O$
14 $H + O \rightarrow OH$
15 $2O \rightarrow O_2$
16 $H + HO_2 \rightarrow H_2 + O_2$
17 $2HO_2 \rightarrow O_2 + H_2O_2$.

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 $c_{5,6,7} = 0$.

Let us reproduce this reasoning using formulas from Sec. 3.2. For the lth irreversible reaction, J_l is the set of indexes i for which $\alpha_{li} \neq 0$. 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 $F_{\{5,6,7\}}$ $(c_{5,6,7} =$

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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    $O_2 + H \rightleftharpoons HO_2$
9    $2OH \rightleftharpoons H_2O + O$
18   $H_2O_2 \rightleftharpoons 2OH$
19   $H + H_2O_2 \rightleftharpoons H_2 + HO_2$
20   $OH + H_2O_2 \rightleftharpoons H_2O + HO_2$

If the concentration OH (c_3) is positive then the component O is produced in the reaction 9. If the concentrations of H_2 (c_1) and 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 OH (c_3) both are positive then the component HO_2 is produced in reaction 2. Due to the reversible reaction 18 any of two components H_2O_2 and OH produces the other component. Moreover, the first reaction produces 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 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, $c_3 = c_8 = 0$ and either $c_1 = 0$ or $c_2 = 0$.

The reactions of all irreversible reactions should tend to zero due to Proposition 2. 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 $b_O \geq \frac{1}{2}b_H$. In this case, $c_4 = \frac{1}{2}b_H$ and $c_2 = \frac{1}{2}(b_O - \frac{1}{2}b_H)$.

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 $b_O \leq \frac{1}{2}b_H$. In this case, $c_4 = b_O$ and $c_1 = \frac{1}{2}(b_H - 2b_O)$.

Let us reproduce this reasoning formally using the general formalism of Sec. 3.3. Formula 20 gives for

$\mathfrak{S}(\{5, 6, 7\})$

$$(c_5 = 0) \wedge \left(\wedge_{r, \gamma_{r5} > 0} \vee_{j, \alpha_{rj} > 0} (c_j = 0) \right)$$
$$\wedge \left(\wedge_{r, \gamma_{r5} < 0} \vee_{j, \beta_{rj} > 0} (c_j = 0) \right)$$
$$\wedge (c_6 = 0) \wedge \left(\wedge_{r, \gamma_{r6} > 0} \vee_{j, \alpha_{rj} > 0} (c_j = 0) \right)$$
$$\wedge \left(\wedge_{r, \gamma_{r6} < 0} \vee_{j, \beta_{rj} > 0} (c_j = 0) \right) \tag{22}$$
$$\wedge (c_7 = 0) \wedge \left(\wedge_{r, \gamma_{r7} > 0} \vee_{j, \alpha_{rj} > 0} (c_j = 0) \right)$$
$$\wedge \left(\wedge_{r, \gamma_{r7} < 0} \vee_{j, \beta_{rj} > 0} (c_j = 0) \right).$$

Vectors γ_r in this formula participate are the stoichiometric vectors of reversible reactions ($r = 1, 2, 3, 4, 5, 9, 18, 19, 20$). From the Table 1 we find that $\gamma_{r5} > 0$ for $r = 2, 3, 4$, $\gamma_{r5} < 0$ for $r = 5, 19$, $\gamma_{r6} > 0$ for $r = 9$, $\gamma_{r6} < 0$ for $r = 3, 4$, $\gamma_{r7} > 0$ for $r = 5, 19, 20$, and $\gamma_{r7} \not< 0$ for all r. Formula (22) transforms into

$$(c_5 = 0) \wedge ((c_1 = 0) \vee (c_3 = 0)) \wedge ((c_3 = 0) \vee (c_6 = 0))$$
$$\wedge ((c_1 = 0) \vee (c_6 = 0)) \wedge (c_7 = 0) \wedge ((c_1 = 0) \vee (c_7 = 0))$$
$$\wedge (c_6 = 0) \wedge (c_3 = 0) \wedge ((c_2 = 0) \vee (c_5 = 0))$$
$$\wedge ((c_3 = 0) \vee (c_5 = 0)) \wedge (c_7 = 0) \wedge ((c_2 = 0) \vee (c_5 = 0))$$
$$\wedge ((c_5 = 0) \vee (c_8 = 0)) \wedge ((c_3 = 0) \vee (c_8 = 0)).$$

After simple transformations it becomes

$$(c_3 = 0) \wedge (c_5 = 0) \wedge (c_6 = 0) \wedge (c_7 = 0). \tag{23}$$

Therefore, $\mathfrak{S}(\{5, 6, 7\}) = \{3, 5, 6, 7\}$. To iterate, we have to compute $\mathfrak{S}(\{3, 5, 6, 7\})$. For this calculation, we have to add one more line to formula (22), namely,

$$\wedge (c_3 = 0) \wedge \left(\wedge_{r, \gamma_{r3} > 0} \vee_{j, \alpha_{rj} > 0} (c_j = 0) \right)$$
$$\wedge \left(\wedge_{r, \gamma_{r3} < 0} \vee_{j, \beta_{rj} > 0} (c_j = 0) \right).$$

Let us take into account that $\gamma_{r3} > 0$ for $r = 1, 4, 18$ and $\gamma_{r3} < 0$ for $r = 2, 3, 9, 20$, and rewrite this formula in the more explicit form

$$(c_3 = 0) \wedge ((c_1 = 0) \vee (c_2 = 0))$$
$$\wedge ((c_1 = 0) \vee (c_6 = 0)) \wedge (c_8 = 0)$$
$$\wedge ((c_4 = 0) \vee (c_5 = 0)) \wedge ((c_2 = 0) \vee (c_5 = 0))$$
$$\wedge ((c_4 = 0) \vee (c_6 = 0)) \wedge (c_7 = 0).$$

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

$$[(c_3 = 0) \wedge (c_5 = 0) \wedge (c_6 = 0)$$
$$\wedge (c_7 = 0) \wedge (c_8 = 0) \wedge (c_1 = 0)]$$
$$\vee [(c_3 = 0) \wedge (c_5 = 0) \wedge (c_6 = 0) \tag{24}$$
$$\wedge (c_7 = 0) \wedge (c_8 = 0) \wedge (c_2 = 0)]$$

This means that $\mathfrak{S}^2(\{5, 6, 7\}) = \mathfrak{S}(\{3, 5, 6, 7\}) = \{\{1, 3, 5, 6, 7, 8\}, \{2, 3, 5, 6, 7, 8\}\}$. The further calculations show that the next iteration does not change the result. Therefore, all the ω-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 δ satisfies these conditions then its linear combination with the vectors of atomic balances also satisfy them. Such a combination is a vector

$$\lambda\delta + \lambda_H(2, 0, 1, 2, 1, 0, 1, 2) + \lambda_O(0, 2, 1, 1, 0, 1, 2, 2) \tag{25}$$

under condition $\lambda > 0$. This transformation of δ 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, $j = n - \text{rank}\{\gamma_r\}$, n is the number of the components, $\{\gamma_r\}$ includes all the stoichiometric vectors for reversible and irreversible reactions.

To find δ, we apply the elimination procedures from the Table 2 to an arbitrary vector $y = (y_i)$ $(i = 1, \ldots, 8)$:

$$(y_1, y_2, y_3, y_4, y_5, y_6, y_7, y_8) \mapsto (y_1, y_2, 0, y_4, y_5, y_6, y_7, y_8)$$
$$\mapsto (y_1, y_2, 0, y_4, y_5, y_6, y_7, 0) \mapsto (y_1, y_2, 0, 0, y_5 - y_4, y_6, y_7, 0)$$
$$\mapsto (y_1, y_2, 0, 0, 0, y_6 + y_5 - y_4, y_7, 0)$$
$$\mapsto (y_1, y_2, 0, 0, 0, 0, y_7 + y_6 + y_5 - y_4, 0) \tag{26}$$

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 $(0, 0, 0, -1, 1, 1, 1, 0)$ 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 (λ_H, λ_O) plane is a convex combination of the extreme points (corners) $(1, 0)$ and $(0, 2)$ plus any non-negative 2D vector: $(\lambda_H, \lambda_O) = \varsigma(1, 0) + (1 - \varsigma)(0, 2) + (\vartheta_1, \vartheta_2)$, $\vartheta_{1,2} \geq 0$ and $1 \geq \varsigma \geq 0$. The corresponding vectors of exponents are

$$(0, 0, 0, -2, 2, 2, 2, 0) + (\varsigma + \vartheta_1)(2, 0, 1, 2, 1, 0, 1, 2)$$
$$+ (1 - \varsigma + \vartheta_2)(0, 4, 2, 2, 0, 2, 4, 4) \,.$$

At least one of the exponents should be zero. There are only three possibilities, δ_1, δ_2 or δ_4. For all other i, $\delta_i > 0$ if $\vartheta_{1,2} \geq 0$ and $1 \geq \varsigma \geq 0$.

To provide any necessary atomic balance in the limit $\varepsilon \to 0$ it is necessary that two of δ_i are zeros. If $b_O \leq \frac{1}{2}b_H$, then $\delta_1 = \delta_4 = 0$. This means that $\vartheta_{1,2} = 0$, $\varsigma = 0$ and $\delta = (0, 4, 2, 0, 2, 4, 6, 4)$. It is convenient to divide this δ 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 $\varepsilon \to 0$ ($\varepsilon > 0$) as

$$c_{H_2}^{eq} = c_1^{eq} = const, c_{O_2}^{eq} = c_2^{eq} \sim \varepsilon^2, c_{OH}^{eq} = c_3^{eq} \sim \varepsilon^2,$$
$$c_{H_2O}^{eq} = c_4^{eq} = const, c_H^{eq} = c_5^{eq} \sim \varepsilon^2, c_O^{eq} = c_6^{eq} \sim \varepsilon^2,$$
$$c_{HO_2}^{eq} = c_7^{eq} \sim \varepsilon^3, c_{H_2O_2}^{eq} = c_6^{eq} \sim \varepsilon^2 \,. \tag{27}$$

If $b_O \geq \frac{1}{2}b_H$, then $\delta_2 = \delta_4 = 0$. This means that $\vartheta_{1,2} = 0$, $\varsigma = 1$ and

$$\delta = (2, 0, 1, 0, 3, 2, 3, 2) \,.$$

For these exponents, the equilibrium concentrations tend to 0 with the small parameter $\varepsilon \to 0$ ($\varepsilon > 0$) as

$$c_{H_2}^{eq} = c_1^{eq} \sim \varepsilon^2, c_{O_2}^{eq} = c_2^{eq} = const, c_{OH}^{eq} = c_3^{eq} \sim \varepsilon,$$
$$c_{H_2O}^{eq} = c_4^{eq} = const, c_H^{eq} = c_5^{eq} \sim \varepsilon^3, c_O^{eq} = c_6^{eq} \sim \varepsilon^2,$$
$$c_{HO_2}^{eq} = c_7^{eq} \sim \varepsilon^3, c_{H_2O_2}^{eq} = c_6^{eq} \sim \varepsilon^2 \,. \tag{28}$$

The linear combination $\sum_i \delta_i N_i$ decreases in time due to kinetic equations. This is true for any vector of exponents presented by a linear combination (25) ($\lambda \neq 0$) of the initial vector $(0, 0, 0, -1, 1, 1, 1, 0)$ 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 $(\delta, N) = -N_{H_2O} + N_H + N_O + N_H O_2$;

- 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 $(\delta, N) = 2N_{O_2} + 2N_{OH} + 2N_H + 2N_O + 3N_{HO_2} + 2N_{H_2O_2}$;

- Vector of exponents, calibrated to meet the atomic balance conditions for $b_O \geq \frac{1}{2} b_H$ is, $(\delta, N) = 2N_{H_2} + N_{OH} + 3N_H + 2N_O + 3N_{HO_2} + 2N_{H_2O_2}$.

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 some forward or reverse reactions have the negligible rate. 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. Although many catalytic reactions are globally irreversible, they always include some reversible steps, in particular steps of adsorption of gases.

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_δ 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 ω-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_δ 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). 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 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.

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