



# Thermodynamics in the limit of irreversible reactions



A.N. Gorban<sup>a,\*</sup>, E.M. Mirkes<sup>b</sup>, G.S. Yablonsky<sup>c</sup>

<sup>a</sup> Department of Mathematics, University of Leicester, Leicester LE1 7RH, UK

<sup>b</sup> Institute of Space and Information Technologies, Siberian Federal University, Krasnoyarsk, Russia

<sup>c</sup> Parks College, Department of Chemistry, Saint Louis University, Saint Louis, MO 63103, USA

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## ABSTRACT

For many complex real physicochemical systems, the 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. Classical thermodynamics has no limit for irreversible reactions, whereas kinetic equations may have such a limit. We represent systems with irreversible reactions as the limits of 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  $t \rightarrow \infty$ . 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. Thermodynamic theory of the irreversible limit of reversible reactions is illustrated by the analysis of hydrogen combustion.

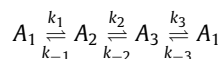
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## 1. Introduction

### 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,  $N_i = Vc_i$ , and  $T$  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  $i$ .)

Classical thermodynamics has no limit for irreversible reactions, whereas kinetic equations have. For example, consider a simple cycle



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

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

\* Corresponding author. Tel.: +44 1162231433.

E-mail address: [ag153@le.ac.uk](mailto:ag153@le.ac.uk) (A.N. Gorban).

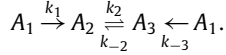
under the standard cyclic convention, which is  $A_{3+1} = A_1$  and  $c_{3+1} = c_1$  here. The perfect free energy has the form

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

Let the equilibrium concentration  $c_1^{\text{eq}} \rightarrow 0$  for fixed values of  $c_{2,3}^{\text{eq}} > 0$ . This means that

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

If we take fixed values of the rate constants  $k_1, k_{\pm 2}$  and  $k_{-3}$  then the limit kinetic system exists and has the form



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

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, the density

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

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  $c_i^{\text{eq}}$  is its equilibrium concentration for a selected value of the linear conservation laws, the so-called reference equilibrium.

This function has been used for analyses of the stability, existence and uniqueness of chemical equilibria since the work of Zeldovich in 1938 [1]. Shapiro and Shapley presented a detailed analysis of the connections between detailed balance and the free energy function [2]. The first detailed proof that  $f$  is a Lyapunov function for chemical kinetics of perfect systems with detailed balance was published in 1975 [3]. Of course this does not differ significantly from the Boltzmann proof of his  $H$ -theorem in 1873 [4].

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

The thermodynamic potential of a component  $A_i$  cannot be defined in the irreversible limit when the equilibrium concentration of  $A_i$  tends to 0. Nevertheless, here we construct 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 systems with detailed balance when some constants tend to zero.

### 1.2. Extended form of detailed balance conditions for systems with irreversible reactions

Consider a reaction mechanism in the form of the following system of stoichiometric equations:



where  $\alpha_{ri} \geq 0$  and  $\beta_{rj} \geq 0$  are the stoichiometric coefficients. The reverse reactions with positive rate constants are included in (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  $\sum_i b_i \gamma_{ri} = 0$  for all  $r$ . This may be the conservation of mass or of the total number of atoms, for example.

According to the *generalized mass action law*, the reaction rate for an elementary reaction (2) is [5] (cf. to [6, Eqs. (4), (7), and (14)] and [7, Eq. (4.10)])

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

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

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

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

This law has a long history [8–10,7]. It was formulated to meet the thermodynamic restrictions on kinetics. For this purpose, 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  $\mu_i^0 \rightarrow \infty$ . 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 reaction mechanism (2) includes reactions with 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 in (2) and 0 if it is not, and  $w_r^-$  is the reaction rate for the reverse reaction if it is in (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 as follows: for given values  $k_r$ , there exists a positive equilibrium  $a_i^{\text{eq}} > 0$  with detailed balance  $w_r^+ = w_r^-$ .

We recently formulated the extended form of the detailed balance conditions for systems with some irreversible reactions [11]. This *extended principle of detailed balance* is valid for all systems that obey the generalized mass action law and are the limits of 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 in which 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 an 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.)

We recall the formal convention: the linear span of the empty set is  $\{0\}$  and the convex hull of the empty set is empty.

We previously studied systems with some irreversible reactions that are the limits of reversible systems with detailed balance and we identified structural and algebraic conditions [11]. Here we focus on the dynamical consequences of these conditions. We prove that attractors always consist of fixed points. These limit points (“partial equilibria”) are situated on the faces of the positive orthant of concentrations. We describe these faces and partial equilibria.

The remainder of the paper is organized as follows. In Section 2 we study systems with detailed balance, their *multiscale* limits and limit systems that satisfy the extended principle of detailed balance. The classical *Wegscheider identities* for 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 analysis of the equilibria for general systems, the formulas with activities are the same as for ideal systems and it is convenient to work with activities unless we need to study dynamics. The dynamical variables are amounts and concentrations. In Section 2.3 we discuss the relations between concentrations and activities, formulate the main assumptions and present formulas for the dissipation rate.

We investigate *attractors* of systems with some irreversible reactions in Section 3 and present the central results of the paper. We fully characterize the faces of the positive orthant that include  $\omega$ -limit sets. On such a face, the dynamics is completely degenerate (zero rates) or is driven by a smaller reversible system that obeys classical thermodynamics.

Hydrogen combustion is a widely studied and very important gas reaction. It serves as a 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 six to eight components and  $\sim 15$ – $30$  elementary reversible reactions. Under various conditions some of these reactions are practically irreversible. We use this system as a benchmark in Section 4 and give an example of correct separation of the reactions into reversible and irreversible parts. The limit behavior of this system in time is described.

In Section 5 we briefly discuss the results with a focus on 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 approaches to the description of 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 an 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,  $m = 2\ell$ ,  $\ell = m/2$ ) and some equations that describe connections between these constants. This approach was introduced by Wegscheider in 1901 [12] and developed further by many authors [13,14].

Second, 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 the 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  $\ell + n$  independent constants,  $\ell = m/2$  rate constants for forward reactions and  $n$  (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 [15–17] because it is convenient to work with independent parameters from scratch.

The Wegscheider conditions appear as the necessary and sufficient conditions of solvability of the detailed balance equations [9]. We join the forward and reverse elementary reactions and write

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

The stoichiometric matrix is  $\Gamma = (\gamma_{ri})$ ,  $\gamma_{ri} = \beta_{ri} - \alpha_{ri}$  (gain minus loss). The stoichiometric vector  $\gamma_r$  is the  $r$ th row of  $\Gamma$  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 is equivalent to the solvability of the following system of linear equations:

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

for  $x_i = \ln a_i^{\text{eq}}$ . 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 condition for the existence of the positive equilibrium  $a_i^{\text{eq}} > 0$  with detailed balance is as follows. For any solution  $\lambda = (\lambda_r)$  of the system*

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

the Wegscheider identity holds:

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

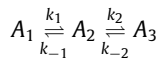
It is sufficient to use in (8) any basis of solutions of system (7):  $\lambda \in \{\lambda^1, \dots, \lambda^q\}$ .

### 2.2. Multiscale degeneration of equilibria

We consider systems with some irreversible reactions as the limits of fully reversible systems when some reaction rate constants tend to zero. In reversible systems, the principle of detailed balance implies the Wegscheider identities (8). Therefore, the limit system is not arbitrary. Some consequences of the Wegscheider identities persist although some of the reaction rate constants in these identities become zero. We previously compared these consequences with the Cheshire cats grin [11]: 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 of neglecting 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” [15–17,11]. 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. We study this process of degeneration of reversible reactions into irreversible ones starting from the corresponding degeneration of equilibrium activities to zero.

We consider a system with detailed balance and send some of the equilibrium activities to zero:  $a_i^{\text{eq}} \rightarrow 0$  when  $i \in I$  for some set of indexes  $I$ . Immediately we surprisingly find that this assumption is not sufficient to find a limiting irreversible mechanism. It is necessary to take into account the rates of the convergence to zero of different  $a_i^{\text{eq}}$ . Consider a very simple example,



when  $a_1^{\text{eq}}, a_2^{\text{eq}} \rightarrow 0$ .

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

keep  $k_{1,-1,2} = \text{const}$ , whereas  $k_{-2} \rightarrow 0$ .

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

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

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

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

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

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

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

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

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

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) hemisphere  $(\gamma_r, \delta) < 0$ , and (iii) hemisphere  $(\gamma_r, \delta) > 0$ . The space of vectors  $\delta$  is split into the subsets defined by the values of functions  $\text{sign}(\gamma_r, \delta)$  ( $\pm 1$  or  $0$ ).

We consider bounded systems, and hence negative values of  $\delta$  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  $c_i^{\text{eq}}$  ( $i \in J_0$ ) 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 let 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  $\varepsilon \rightarrow 0$ . It is convenient to transpose the stoichiometric equations for these reactions and swap the forward reactions with reverse ones. After performing this transposition,  $\alpha_r$  swaps with  $\beta_r$ ,  $\gamma$  transforms to  $-\gamma$ , and the inequality  $(\gamma_r, \delta) > 0$  transforms to  $(\gamma_r, \delta) < 0$ .

To 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  $a_i^{\text{eq}}$  according to the following rules:

1. If  $\delta_i > 0$  then we assign  $a_i^{\text{eq}} = 0$ , and if  $\delta_i = 0$  then  $a_i^{\text{eq}}$  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 the reverse one; for convenience,  $\gamma_r$  changes to  $-\gamma_r$  and  $k_r^-$  becomes 0. Therefore, this case transforms to case 3.)

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

The general form of the kinetic equations for homogeneous systems is

$$\frac{dN}{dt} = V \sum_r w_r \gamma_r, \quad (10)$$

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

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 (10) for this limit system:  $dG_\delta(N)/dt \leq 0$  and  $dG_\delta(N)/dt = 0$  if and only if all the reaction rates for the irreversible reactions are zero.

**Proof.** In fact,

$$\frac{dG_\delta(N)}{dt} = V \sum_r w_r (\gamma_r, \delta) \leq 0, \quad (11)$$

because  $(\gamma_r, \delta) = 0$  for reversible reactions and  $w_r = w_r^+ \geq 0$  and  $(\gamma_r, \delta) < 0$  for irreversible reactions. All the terms in this sum are non-positive and hence it may be zero if and only if each summand is zero.  $\square$

This Lyapunov function may be used to prove 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)  $N(t)$  then  $G_\delta(N(t)) \rightarrow -\infty$  when  $t \rightarrow \infty$  and  $N(t)$  is unbounded. Eq. (11) and Proposition 2 allow us to prove the extended principle of detailed balance in the following form. Consider a reaction mechanism that includes reversible and irreversible reactions. Assume that the reaction rates satisfy the generalized mass action law (3) and that the set of reaction rate constants is given. We ask if it is 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  $(\gamma_r, \delta) = 0$  for the reversible reactions and  $(\gamma_r, \delta) < 0$  for the irreversible reactions. 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 reversible 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. According to the classical theorems of 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  $\theta$ . Then  $(\gamma_r, \theta) = 0$  for the reversible reactions and  $(\gamma_r, \theta) < 0$  for the irreversible reactions.

It is possible to find a vector  $\delta$  with this separation property and non-negative coordinates. 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  $\lambda$  such that  $\delta_i = \theta_i + \lambda b_i \geq 0$  and  $\delta_i = \theta_i + \lambda b_i = 0$  for some  $i$ . We take this linear combination  $\delta$  as a vector of exponents.

We 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.

For each irreversible reaction with the stoichiometric vector  $\gamma_r$  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  $\varepsilon \rightarrow 0$  as  $a_i^{\text{eq}} = a_i^* \varepsilon^{\delta_i}$ . For reactions with  $(\gamma_r, \delta) = 0$ , the reaction rate constants do not depend on  $\varepsilon$  and for 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  $\varepsilon \rightarrow 0$ .  $\square$

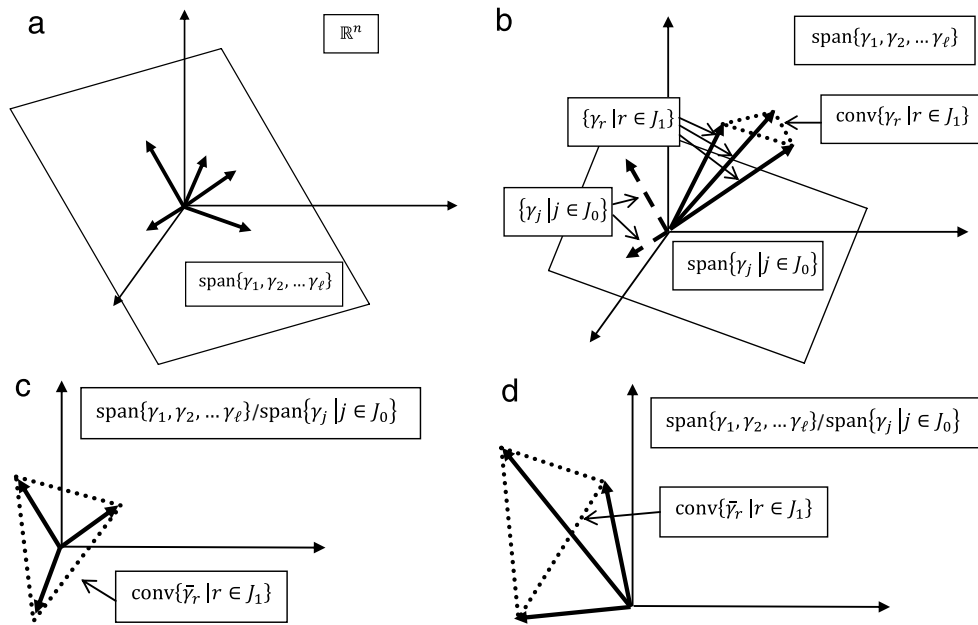
This is a particular form of the extended principle of detailed balance [11]. Fig. 1 illustrates the geometric sense of the extended detailed balance condition: the convex hull of the stoichiometric vectors of the irreversible reactions does not intersect with the linear span of the stoichiometric vectors 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  $G_\delta(N) = (\delta, N)$  (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 [9] and does not hold for the solid reagents (e.g. analysis of carbon activity in methane reforming [11]).

The system of units should also be noted. Traditionally,  $a_i$  is assumed to be dimensionless and for perfect systems  $a_i = c_i/c_i^\circ$ , where  $c_i^\circ$  is an arbitrary “standard” concentration. To avoid the introduction of unnecessary quantities, we always assume that  $c_i^\circ \equiv 1$  in the system of units selected.





**Fig. 1.** Main operations in the application of the extended detailed balance conditions. (a) In the concentration space  $\mathbb{R}^n$  we should find the subspace spanned by all the stoichiometric vectors  $\{\gamma_r \mid r = 1, \dots, \ell\}$ . In this subspace we have to select the internal coordinates. (b) In  $\text{span}\{\gamma_r \mid r = 1, \dots, \ell\}$  we have to select the subspace spanned by the stoichiometric vectors of the reversible reactions (the dashed vectors). The stoichiometric vectors of the irreversible reactions in b, c and d are solid bold lines. Owing to the extended principle of detailed balance,  $\text{span}\{\gamma_r \mid r \in J_0\}$  should not intersect  $\text{conv}\{\gamma_r \mid r \in J_1\}$  (dotted triangle). For analysis of this intersection, it is convenient to proceed to the quotation space  $\text{span}\{\gamma_r \mid r = 1, \dots, \ell\} / \text{span}\{\gamma_r \mid r \in J_0\}$ . In this quotation space,  $\text{span}\{\tilde{\gamma}_r \mid r \in J_0\}$  is  $\{0\}$  and two situations are possible: (c)  $0 \in \text{conv}\{\tilde{\gamma}_r \mid r \in J_1\}$  (the dotted triangle includes the origin) or (d)  $0 \notin \text{conv}\{\tilde{\gamma}_r \mid r \in J_1\}$  (the dotted triangle does not include the origin). In case (c) the extended detailed balance condition is violated. Case (d) satisfies this condition.

If the thermodynamic potentials exist, then owing to the thermodynamic definition of activity (4), this hypothesis is equivalent to the logarithmic singularity of the chemical potentials,  $\mu_i = RT \ln c_i + \dots$ , where  $\dots$  denotes 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 the arguments. Functions  $f_{0i}$  on the right-hand side of (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  $p_i = RTc_i + o(c_i)$ . This is because of the terms  $N_i \ln c_i$  in  $F$ . In fact,  $P = -\partial F(N, T, V) / \partial V = RTc_i + o(c_i) + P|_{c_i=0}$ . Connections between the equation of state, the free energy and the kinetics are discussed in more detail elsewhere [7,18,5].

There are several simple algebraic corollaries of the assumed connection between activities and concentrations. Consider an elementary reaction  $\sum \alpha_i A_i \rightarrow \sum \beta_i A_i$  with  $\alpha_i, \beta_i \geq 0$ . Then, according to the generalized mass action law, for any vector of concentrations  $c$  ( $c_i \geq 0$ ) we have the following:

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  $\sum \alpha_i A_i \rightleftharpoons \sum \beta_i A_i$  we have the following:

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 consequences of the generalized mass action law (3) and the connection between activities and concentrations without any assumptions about the extended principle of detailed balance.

Each set of indexes  $J = \{i_1, \dots, i_j\}$  defines a face of the positive polyhedron

$$F_J = \{c \mid c_i \geq 0 \text{ for all } i \text{ and } c_i = 0 \text{ for } i \in J\}.$$

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.** For a point  $c \in ri(F_j)$  and an index  $i \in J$ , let

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

Then this identity holds for all  $c \in F_j$ .

**Proof.** For convenience, we 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  $w_r$  (3) with a non-zero rate constant takes a 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  $\sum_{r \in S} \gamma_{ri} w_r(c) = 0$  for all  $c \in F_j$  and every  $j \in J$ .

We now consider a reaction mechanism in the form (2) in which all the forward 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 in  $S$ .
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 now analyze the asymptotic behavior of the kinetic equations in the multiscale degeneration of equilibrium described in Section 2.2. For this purpose, we have to determine how the relations between activities  $a_i$  and concentrations  $c_i$  depend on the degeneration parameter  $\varepsilon \rightarrow 0$ . We do not try to find the maximally general appropriate answer to this question. For known applications, the relations between  $a_i$  and  $c_i$  do not depend on  $\varepsilon \rightarrow 0$ . In particular, this is trivially true for 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  $\varepsilon \rightarrow 0$  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 such as 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 a very nice general form. Let the function  $\Phi(N, \dots)$  be given, where  $\dots$  denotes quantities that do not change in time under the given conditions. This is the thermodynamics potential if  $\partial \Phi(N, \dots) / \partial N_i = \mu_i$ . For example, it is the free Helmholtz energy  $F$  for  $V, T = const$  and the free Gibbs energy  $G$  for  $P, V = const$ .

We calculate the time derivative of  $\Phi(N, \dots)$  according to kinetic equation (10). The reaction rates are given by the generalized mass action law (3) with definition of the 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 the equilibrium fluxes  $w_r^{eq}(T)$ :

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

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

These formulas immediately give the following representation of the dissipation rate:

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

The inequality holds because  $\ln$  is a monotone function and hence the expressions  $\ln w_r^+ - \ln w_r^-$  and  $w_r^+ - w_r^-$  always have the same sign. Formulas of this type for dissipation are well known since the famous Boltzmann  $H$ -theorem [4,10]. The entropy increase in isolated systems has a similar form:

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

Note 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 notions of physical chemistry, *affinity* [19]. It is positive if the forward reaction prevails over the reverse one and is 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 the magnitude of this energetic advantage compared to the thermal energy. We call it the *normalized affinity* and use a special notation for this quantity:

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

We apply the elementary identity

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

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

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

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

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

In this formula, the kinetic information is collected in the non-negative factors, the sums of reaction rates  $(w_r^+ + w_r^-)$ . The purely thermodynamic multipliers  $\mathbb{A}_r \tanh(\mathbb{A}_r/2)$  are also non-negative. 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  $|\mathbb{A}_r|$ .

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

### 3. Attractors

#### 3.1. Dynamic systems and limit points

Kinetic equation (10) does not give a complete representation of the 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 the left hand side has  $\dot{N}$ . To close this system, we need to express  $V$ ,  $c$  and  $T$  through  $N$  and quantities that 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 ( $U, V = \text{const}, P, T = \text{const}$  or  $H, P = \text{const}$ ) we have to use the equations of state. There may be more sophisticated closures that 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 in this paper, we assume that the conditions are selected, a closure is performed, the right-hand side of the resulting system is continuously differentiable and there exists a positive bounded solution for the initial data in  $\mathbb{R}_+^n$ , and  $V$  and  $T$  remain bounded and separated from zero. The nature of this closure is not crucial. For some important particular closures, proofs of the existence of positive and bounded solutions are well known [3]. Strictly speaking, such a system is not a dynamic system in  $\mathbb{R}_+^n$  but is semi-dynamic: the solutions may lose positivity and leave  $\mathbb{R}_+^n$  for negative values of time. The theory of the limit behavior of semi-dynamic systems was developed for applications to kinetic systems [20].

We now describe the limit behavior of the systems as  $t \rightarrow \infty$ . 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 definition, the  $\omega$ -limit points of a dynamic system are the limit points of the motions when time  $t \rightarrow \infty$ . We consider a kinetic system in  $\mathbb{R}_+^n$ . In particular, for each solution  $N(t)$  of the kinetic equations, the set of the corresponding  $\omega$ -limit points is closed, connected and consists of the whole trajectories [20, Proposition 1.5]. This means that motion that starts from an  $\omega$ -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 let  $x^*$  be an  $\omega$ -limit point of this solution and  $x_i^* = 0$ . Then  $\dot{x}_i|_{x^*} = 0$  at this point.*

**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  $\mathbb{R}_+^n$ . There exists a sequence  $t_j \rightarrow \infty$  such that  $N(t_j) \rightarrow x^*$ . For any  $\tau \in (-\infty, \infty)$ ,  $N(t_j + \tau) \rightarrow x(\tau)$ . For sufficiently large  $j$ ,  $t_j + \tau > 0$  and  $N(t_j + \tau) \in \mathbb{R}_+^n$ . Therefore,  $x(\tau) \in \mathbb{R}_+^n$  ( $-\infty < \tau < \infty$ ) and for any  $\tau$  the point  $x(\tau)$  is an  $\omega$ -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,  $x_i(\tau) < 0$ . This is impossible because of the positivity. Similarly, if  $v < 0$  then for small  $\tau > 0$  the value of  $x_i$  becomes negative,  $x_i(\tau) < 0$ . This is also impossible because of the positivity. Therefore,  $\dot{x}_i|_{x^*} = 0$ .  $\square$

We use **Proposition 4** in the following combination with **Proposition 3**. (Below we write the reaction mechanism in the form of (2).)

**Corollary 2.** If an  $\omega$ -limit point belongs to the relative interior  $\text{ri}F_j$  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  $\gamma_{ij} = 0$  for all  $j \in J$  or  $\alpha_{ij} > 0$  for some  $j \in J$ .

**Proof.** If an  $\omega$ -limit point belongs to  $\text{ri}F_j$  then all  $\dot{c}_j = 0$  for  $j \in J$  at this point according 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 irreversible reactions are zero at every limit point of kinetic equation (10) according 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 reactions. For one of them,  $(\gamma_r, \delta) = 0$  and in the limit  $k_r^\pm > 0$ . For 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 equilibrium degeneration). If necessary, we transpose the stoichiometric equations and swap the forward reactions with the reverse ones.

For convenience, we change the notation. Let  $\gamma_i$  be the stoichiometric vectors of reversible reactions with  $(\gamma_r, \delta) = 0$  ( $r = 1, \dots, h$ ), and let  $v_l$  be the stoichiometric vectors for reactions from the second set,  $(v_l, \delta) < 0$  ( $l = 1, \dots, s$ ). For the reaction rates and constants for the first set, we keep the same notation:  $w_r, w_r^\pm, k_r^\pm$ . For the second set, we use  $q_l = q_l^+$  for the reaction rate constants and  $v_l = v_l^+$  for the reaction rates. They are also calculated according to the generalized mass action law (3). The input and output stoichiometric coefficients remain  $\alpha_{ri}$  and  $\beta_{ri}$  for the first set and for the second set we use the notation  $\alpha_{li}^v$  and  $\beta_{li}^v$ .

Let the rates of all the irreversible reaction be equal to zero. This does not mean that all the concentrations  $a_i$  with  $\delta_i > 0$  reach zero. A bimolecular reaction  $A + B \rightarrow C$  gives us a simple example:  $w = ka_A a_B$  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,  $a_A, a_B \geq 0$  and 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 a 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 steady states of the irreversible reactions. According to Proposition 2, if  $\sum_l v_l v_l = 0$  then all  $v_l = 0$ . Therefore, we should describe the set of zeros of all  $v_l$  in the positive orthant of activities.

For every  $l = 1, \dots, s$  the set of zeros of  $v_l$  in  $\mathbb{R}_+^n$  is given by the conditions  $\alpha_{li}^v \neq 0$  and  $a_i = 0$  for at least for one  $i$ . 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  $v_l$  in the positive orthant of activities is represented by  $\bigvee_{i \in J_l} (a_i = 0)$ . The set of zeros of all  $v_l$  is represented by the following conjunction form:

$$\bigwedge_{l=1}^s (\bigvee_{i \in J_l} (a_i = 0)). \tag{16}$$

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

$$\bigwedge_{l=1}^s (\bigvee_{i_1 \in J_l, \dots, i_s \in J_s} ((a_{i_1} = 0) \wedge \dots \wedge (a_{i_s} = 0))). \tag{17}$$

For a cortege of indexes  $\{i_1, \dots, i_s\}$ , the corresponding set of values may be smaller because some values  $i_l$  may coincide. Let this set of values be  $S_{\{i_1, \dots, i_s\}}$ . We can delete from (17) a conjunction  $(a_{i_1} = 0) \wedge \dots \wedge (a_{i_s} = 0)$  if there exists a cortege  $\{i'_1, \dots, i'_s\}$  ( $i'_l \in J_l$ ) with a smaller set of values,  $S_{\{i_1, \dots, i_s\}} \supseteq S_{\{i'_1, \dots, i'_s\}}$ . We check the corteges in some order and delete a conjunction from (17) if a term with smaller (or the same) set of index values remains in the formula. We can also substitute the corteges in (17) by their sets of values. The resulting minimized formula may be shorter. Each elementary conjunction represents a coordinate subspace and after cancelations each subspace does not belong to a union of other subspaces. The final form of (17) is

$$\bigvee_j (\bigwedge_{i \in S_j} (a_i = 0)), \tag{18}$$

where  $S_j$  are sets of indexes,  $S_j \subset \{1, \dots, n\}$ , and for every two different  $S_j, S_p$ , neither of them includes the other,  $S_j \not\subseteq S_p$ . The elementary conjunction  $\bigwedge_{i \in S_j} (a_i = 0)$  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 correspond to 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

Here we study the possible limit behavior of systems that 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 according to

**Proposition 2**, but not all these steady states may be the  $\omega$ -limit points of the system. A simple formal example gives us the reaction couple  $A \rightleftharpoons B, A + B \rightarrow C$ . Here, we have one reversible and one irreversible reaction. The conditions of 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 a 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  $t \rightarrow \infty$ . In fact, if  $c_A = 0$  and  $c_B > 0$ , then  $dc_A/dt = k_{-1}c_B > 0$ . According to **Proposition 4**, this is not an  $\omega$ -limit point. Similarly, the points with  $c_A > 0$  and  $c_B = 0$  are not  $\omega$ -limit points.

We combine **Propositions 2** and **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  $\omega$ -limit point  $x^* \in \text{ri}F_J$  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  $x^* \in \text{ri}F_J$  exists, then it is a steady state for all irreversible reactions (according to **Proposition 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, assume that  $F_J$  consists of steady states of the irreversible reactions and is invariant with respect to all reversible reactions. The reversible reactions that do not act on  $c_j$  for  $j \in J$  define a semi-dynamical system on  $F_J$ . The positive conservation law  $b$  defines a positively invariant polyhedron in  $F_J$ . The dynamics in such a compact set always has  $\omega$ -limit points.  $\square$

We now determine the faces  $F_J$  that contain the  $\omega$ -limit points in their relative interior  $\text{ri}F_J$ . 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. We look for the *maximal faces with this property*. For this purpose, we always minimize the disjunctive forms by cancelation. 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.

We start from the minimized disjunctive form (18), which represents the set of steady states of the irreversible part of the reaction mechanism by a union of the coordinate subspaces  $\bigwedge_{i \in S_j} (c_i = 0)$  in intersection with  $\mathbb{R}_+^n$ . This is the union of the faces,  $\bigcup_j F_{S_j}$ . 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 is true on a face  $F_J$  if it contains  $\omega$ -limit points in the relative interior  $\text{ri}F_J$  (**Theorem 2**):

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

Here,  $c_i = 0$  in  $F_J$  may be read as  $i \in J$ . Following the previous section, we use here the notation  $\gamma_{ri}, \alpha_{ri}$  and  $\beta_{ri}$  for the reversible reactions and reserve  $\nu_i, \alpha_{ii}^v$  and  $\beta_{ii}^v$  for the irreversible reactions. The set of  $\gamma_r$  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 we introduce an operation that transforms a set of indexes  $S \subset \{1, 2, \dots, n\}$  in a family of sets  $\mathfrak{S}(S) = \{S'_1, \dots, S'_j\}$ . We use (19) and find the set for which it is valid for all  $i \in S$ . This set is described by the following formula:

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

We produce a disjunctive form of this formula and minimize it by cancelations as described in Section 3.2. This yields

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

Because of cancelations, the sets  $S'_j$  do not include each another and they give the result  $\mathfrak{S}(S) = \{S'_1, \dots, S'_j\}$ . Each  $S'_j \in \mathfrak{S}(S)$  is a superset of  $S, S' \supseteq S$ .

We extend the operation  $\mathfrak{S}$  to the sets of sets  $\mathbf{S} = \{S_1, \dots, S_p\}$  with the property  $S_i \not\subset S_j$  for  $i \neq j$ . We apply  $\mathfrak{S}$  to all  $S_i$  and take the union of the results:  $\mathfrak{S}_0(\mathbf{S}) = \bigcup_i \mathfrak{S}(S_i)$ . Some sets from this family may include other sets from it. We organize cancelations: if  $S', S'' \in \mathfrak{S}_0(\mathbf{S})$  and  $S' \subset S''$ , then we retain the smallest set,  $S'$ , and delete the largest one. We carry out cancelations until this is possible and we call the final result  $\mathfrak{S}(\mathbf{S})$ . The result does not depend on the order of these operations.

We start from any family  $\mathbf{S}$  and iterate the operation  $\mathfrak{S}$ . After a 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 [21]. 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 such as  $(A \wedge A) \Leftrightarrow A, (A \vee A) \Leftrightarrow A, [A \wedge (A \vee B)] \Leftrightarrow A$  and  $[A \vee (A \wedge B)] \Leftrightarrow A$ .

We are now in a position to describe the construction of all  $F_J$  that have the  $\omega$ -limit points in their relative interior and are the maximal faces with this property.

1. We follow Section 3.2 and construct the minimized disjunctive form (18) for a description of the steady states of the irreversible reactions.
2. We calculate the families of sets  $\mathfrak{S}^d(\{S_j\})$  for the family of sets  $\{S_j\}$  from (18) and  $d = 1, 2, \dots$  up to 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 faces  $F_{J_i}$  ( $i = 1, 2, \dots, p$ ) 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 section 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  $\gamma_2$  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 conjunction form (16) is defined by the non-zero coordinates of this  $\alpha^\nu$ :  $J = \{1, 2\}$ . 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  $S_2 = \{2\}$ .

We now calculate  $\mathfrak{S}(S_{1,2})$ . For both  $i = 1, 2$  there are no reversible reactions with  $\gamma_{ri} = 0$ . Therefore, one expression in 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  $\{\{1, 3\}, \{1, 4\}, \{2, 3\}, \{2, 4\}\}$ . In fact, 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  $\mathfrak{S}(\{1, 3\})$ , for example, (20) gives

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

This 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  $\omega$ -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  $\mathbb{R}^5$ . The intersection of this plane with the selected faces depends on the signs of  $b_{2,3}$ :

- If  $b_2 < 0$  and  $b_3 < 0$ , then it intersects  $F_{\{1,3\}}$  at only 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  $b_2 = 0$  and  $b_3 < 0$  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  $b_2 < 0$  and  $b_3 = 0$ , 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  $b_2 > 0$  and  $b_3 < 0$ , then it intersects  $F_{\{2,3\}}$  at only 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  $b_2 > 0$  and  $b_3 = 0$ , 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  $b_2 < 0$  and  $b_3 > 0$ , then it intersects  $F_{\{1,4\}}$  at only 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  $b_2 = 0$  and  $b_3 > 0$ , 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  $b_2 > 0$  and  $b_3 > 0$ , then it intersects  $F_{\{2,4\}}$  at only 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, we 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 principle of detailed balance holds. The steady states of the irreversible reactions are given by one equation,  $c_5 = 0$ . Formula (20) gives just  $(c_5 = 0)$  for  $\mathfrak{S}(\{5\})$ . Face  $F_{\{5\}}$  includes  $\omega$ -limit points in  $riF_{\{5\}}$ . The 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

**Table 1**  
H<sub>2</sub> combustion mechanism [22].

No.	Reaction	Stoichiometric vector
1	H <sub>2</sub> + O <sub>2</sub> ⇌ 2OH	(-1, -1, 2, 0, 0, 0, 0, 0)
2	H <sub>2</sub> + OH ⇌ H <sub>2</sub> O + H	(-1, 0, -1, 1, 1, 0, 0, 0)
3	OH + O ⇌ O <sub>2</sub> + H	(0, 1, -1, 0, 1, -1, 0, 0)
4	H <sub>2</sub> + O ⇌ OH + H	(-1, 0, 1, 0, 1, -1, 0, 0)
5	O <sub>2</sub> + H + M ⇌ HO <sub>2</sub> + M	(0, -1, 0, 0, -1, 0, 1, 0)
6	OH + HO <sub>2</sub> ⇌ O <sub>2</sub> + H <sub>2</sub> O	(0, 1, -1, 1, 0, 0, -1, 0)
7	H + HO <sub>2</sub> ⇌ 2OH	(0, 0, 2, 0, -1, 0, -1, 0)
8	O + HO <sub>2</sub> ⇌ O <sub>2</sub> + OH	(0, 1, 1, 0, 0, -1, -1, 0)
9	2OH ⇌ H <sub>2</sub> O + O	(0, 0, -2, 1, 0, 1, 0, 0)
10	2H + M ⇌ H <sub>2</sub> + M	(1, 0, 0, 0, -2, 0, 0, 0)
11	2H + H <sub>2</sub> ⇌ H <sub>2</sub> + H <sub>2</sub>	(1, 0, 0, 0, -2, 0, 0, 0)
12	2H + H <sub>2</sub> O ⇌ H <sub>2</sub> + H <sub>2</sub> O	(1, 0, 0, 0, -2, 0, 0, 0)
13	OH + H + M ⇌ H <sub>2</sub> O + M	(0, 0, -1, 1, -1, 0, 0, 0)
14	H + O + M ⇌ OH + M	(0, 0, 1, 0, -1, -1, 0, 0)
15	2O + M ⇌ O <sub>2</sub> + M	(0, 1, 0, 0, 0, -2, 0, 0)
16	H + HO <sub>2</sub> ⇌ H <sub>2</sub> + O <sub>2</sub>	(1, 1, 0, 0, -1, 0, -1, 0)
17	2HO <sub>2</sub> ⇌ O <sub>2</sub> + H <sub>2</sub> O <sub>2</sub>	(0, 1, 0, 0, 0, 0, -2, 1)
18	H <sub>2</sub> O <sub>2</sub> + M ⇌ 2OH + M	(0, 0, 2, 0, 0, 0, 0, -1)
19	H + H <sub>2</sub> O <sub>2</sub> ⇌ H <sub>2</sub> + HO <sub>2</sub>	(1, 0, 0, 0, -1, 0, 1, -1)
20	OH + H <sub>2</sub> O <sub>2</sub> ⇌ H <sub>2</sub> O + HO <sub>2</sub>	(0, 0, -1, 1, 0, 0, 1, -1)

face, there exist 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 do not attract the positive solutions.

#### 4. Example: H<sub>2</sub> + O<sub>2</sub> system

For the case study, we selected the H<sub>2</sub> + O<sub>2</sub> system. This is one of the main model systems of gas kinetics. Hydrogen combustion gives us an example of medium complexity with eight components ( $A_1 = \text{H}_2, A_2 = \text{O}_2, A_3 = \text{OH}, A_4 = \text{H}_2\text{O}, A_5 = \text{H}, A_6 = \text{O}, A_7 = \text{HO}_2$  and  $A_8 = \text{H}_2\text{O}_2$ ) and two atomic balances (H and O). For the example, we selected the reaction mechanism described by Vlachos [22]. The literature on hydrogen combustion mechanisms is huge and includes recent discussions [23,24]. We do not aim to compare the different schemes of this reaction but use this reaction mechanism as an example and a benchmark.

The symbol “M” denotes a third body that may be any molecule and provides the energy balance. The efficiency of different molecules in this process differs, and 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 the reaction rates. Therefore, for our analysis we can omit these terms. Elementary reactions 10, 11 and 12 can be considered as a single reaction,  $2\text{H} \rightleftharpoons \text{H}_2$ , after cancelation of the third bodies, and thus we analyze the mechanism of 18 reactions.

Under various conditions, some of the reactions are (almost) irreversible and some of them should be considered as reversible. For example, consider the H<sub>2</sub> + O<sub>2</sub> system at or near atmospheric pressure and in the temperature interval 800–1200 K. Reactions 1, 2, 4, 18, 19, and 20 are supposed to be reversible (according to their reaction rate constants provided by Vlachos [22]). The first question is: if these reactions are reversible, then which reactions may be irreversible?

According to the general criterion, the convex hull of the stoichiometric vectors of the irreversible reactions does not intersect 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,  $\gamma_3 = -\gamma_1 + \gamma_4$ ,  $\gamma_5 = \gamma_1 - \gamma_{18} + \gamma_{19}$  and  $\gamma_9 = \gamma_2 - \gamma_4$ . Therefore, the list of reversible reactions should include reactions 1, 2, 3, 4, 5, 9, 18, 19, and 20. 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 eight reactions (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  $k_r^- = 0$  for all of them or  $k_r^+ = 0$  for all of them. Here, the forward and reverse reactions and the notation  $k_r^\pm$  are selected according to Table 1. It is immediately evident that the inverse direction for all reactions is very far from the reality under the given conditions; for example, it includes the irreversible dissociation  $\text{H}_2 \rightarrow 2\text{H}$ .

We now demonstrate in detail how the general criterion produces this reduction from the 256 possible combinations of directions of irreversible reactions to just two 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  $r \in J_1$ ,  $\text{rank}\{\gamma_1, \gamma_2, \dots, \gamma_\ell\} = d$ ,  $\text{rank}\{\gamma_r \mid r \in J_0\} = d_0$ . The rank of all vectors  $\gamma_r$ ,  $d$ , 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.

**Table 2**

Elimination of coordinates of the stoichiometric vectors for the H<sub>2</sub> combustion mechanism. Reversible and irreversible reactions are shown in the upper and lower parts of the table, respectively. The group of equivalent reactions (10, 11 and 12) is represented by 10. In the second column, the first two coordinates (corresponding to H<sub>2</sub> and O<sub>2</sub>) are excluded using the atomic balance. The following columns show the coordinate elimination results. For each step, the pivot for elimination is underlined and highlighted in bold in the previous column. Coordinates eliminated coordinates in each step are identified at the top of each column. Their zero values are omitted.

No	H <sub>2</sub> , O <sub>2</sub>	OH	H <sub>2</sub> O <sub>2</sub>	H <sub>2</sub> O	H	O
1	<u>(2, 0, 0, 0, 0, 0)</u>	(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)	<b>(1, 1, 0, 0)</b>	(0, 0, 0)	(0, 0)	(0)
3	(-1, 0, 1, -1, 0, 0)	(0, 1, -1, 0, 0)	(0, 1, -1, 0)	<b>(1, -1, 0)</b>	(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)	<b>(-1, 1)</b>	(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)

We have to perform the following operations with the set of stoichiometric vectors  $\gamma_r$  (Fig. 1) [11]:

1. Eliminate several zero coordinates from all  $\gamma_r$  using linear conservation laws. This is transfer to the internal coordinates in  $\text{span}\{\gamma_r \mid r = 1, \dots, \ell\}$ .
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  $\text{span}\{\gamma_j \mid j = 1, \dots, \ell\}/\text{span}\{\gamma_j \mid j \in J_0\}$ . We denote the result as  $\bar{\gamma}_r$ .
3. Use linear programming [25] to analyze for which combinations of the signs the convex hull  $\text{conv}\{\pm\bar{\gamma}_r \mid r \in J_1\}$  does not include 0.

Table 2 presents results for the step-by-step elimination. First, the atomic balances give two identities for every possible stoichiometric vector  $\eta = (\eta_1, \dots, \eta_8)$ :

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  $\eta_2 = -\frac{1}{2}(\eta_3 + \eta_4 + \eta_6 + 2\eta_7 + 2\eta_8)$ .

Recall that the order of the coordinates  $(\eta_1, \dots, \eta_8)$  corresponds to the following order of the components: H<sub>2</sub>, O<sub>2</sub>, OH, H<sub>2</sub>O, H, O, HO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>. According to these identities, a stoichiometric vector  $\eta$  for this mixture is completely defined by six coordinates  $(\eta_3, \dots, \eta_8)$ . The second column of Table 2 lists these 6D vectors for all the reactions in the H<sub>2</sub> combustion mechanism (Table 1).

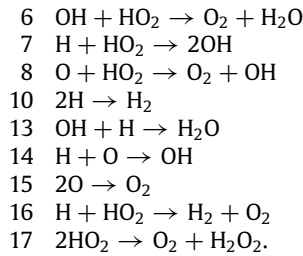
Columns 3–7 contain the coordinate elimination results and the zero-valued eliminated coordinates are omitted. Each elimination step may be represented as a projection,

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

where  $\eta_i$  is a *pivot* (highlighted in bold in the column preceding the elimination result) 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. In the final column, all the stoichiometric vectors of the reversible reaction are transformed to zero, and the stoichiometric vectors of the irreversible reactions with the given direction (from left to right) are transformed to 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<sub>2</sub>,  $x_1$  corresponds to H<sub>2</sub>, and  $x_2$  corresponds to O<sub>2</sub>, and 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 for the extended principle of detailed balance holds. It also holds for the inverse direction for all the irreversible reactions. All the other distributions of the directions can produce zero in the convex hull and are inadmissible. Therefore, we have the following list of irreversible reactions that satisfy the extended principle of detailed balance for given reversible reactions. (We do not discuss the second list of reverse irreversible reactions because it does not make much sense for the given conditions.)





We assume that all the reaction rate constants for the selected directions are strictly positive. The rate of all these reaction vanishes if and only if the concentrations of H, O and HO<sub>2</sub> are equal to zero,  $c_{5,6,7} = 0$ . In fact,  $c_5 = 0$  if and only if  $w_{10} = 0$ ,  $c_6 = 0$  if and only if  $w_{15} = 0$ , and  $a_7 = 0$  if and only if  $w_{17} = 0$ . All the other reaction rates for this list are zero if  $c_{5,6,7} = 0$ .

We reproduce this reasoning using formulas from Section 3.2. For the  $l$ th irreversible reaction,  $J_l$  is the set of indexes  $i$  for which  $\alpha_{li} \neq 0$ . We keep the numbers for the irreversible reactions (6, 7, 8, 10, 13, 14, 15, 16, 17), for which  $J_6 = \{3, 7\}$ ,  $J_7 = \{5, 7\}$ ,  $J_8 = \{6, 7\}$ ,  $J_{10} = \{5\}$ ,  $J_{13} = \{3, 5\}$ ,  $J_{14} = \{5, 6\}$ ,  $J_{15} = \{6\}$ ,  $J_{16} = \{5, 7\}$  and  $J_{17} = \{7\}$ .

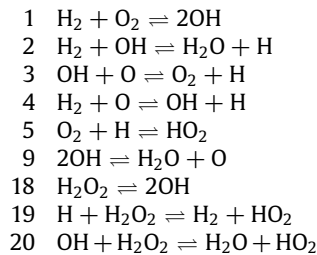
Formula (18) gives the following for the steady states of the irreversible reactions:

$$\begin{aligned}
& ((c_3 = 0) \vee (c_7 = 0)) \wedge ((c_5 = 0) \vee (c_7 = 0)) \wedge ((c_6 = 0) \vee (c_7 = 0)) \wedge (c_5 = 0) \\
& \wedge ((c_3 = 0) \vee (c_5 = 0)) \wedge ((c_5 = 0) \vee (c_6 = 0)) \wedge (c_6 = 0) \wedge ((c_5 = 0) \vee (c_7 = 0)) \wedge (c_7 = 0).
\end{aligned}$$

This is equivalent to

$$(c_5 = 0) \wedge (c_6 = 0) \wedge (c_7 = 0).$$

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 reactions. Consider the following list of reversible reactions:



If the concentration OH ( $c_3$ ) is positive, then the component O is produced in reaction 9. If the concentrations of H<sub>2</sub> ( $c_1$ ) and OH ( $c_3$ ) are both positive, then the component H is produced in reaction 2. If the concentrations of H<sub>2</sub>O<sub>2</sub> ( $c_8$ ) and OH ( $c_3$ ) are both positive, then the component HO<sub>2</sub> is produced in reaction 2. Because of reversible reaction 18, any of the two components H<sub>2</sub>O<sub>2</sub> and OH produces the other component. Moreover, the first reaction produces OH from H<sub>2</sub> + O<sub>2</sub>. This production stops if and only if either the concentration of H<sub>2</sub> is zero ( $c_1 = 0$ ) or the concentration of O<sub>2</sub> is zero ( $c_2 = 0$ ).

This means that the set of zeros for 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 if the initial conditions belong to this set then the kinetic trajectory will leave it unless, in addition,  $c_3 = c_8 = 0$  and either  $c_1 = 0$  or  $c_2 = 0$ .

The rates of irreversible reactions should tend to zero according 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 the 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 contained in O<sub>2</sub> and H<sub>2</sub>O. This is possible if and only if  $b_{\text{O}} \geq \frac{1}{2}b_{\text{H}}$ . In this case,  $c_4 = \frac{1}{2}b_{\text{H}}$  and  $c_2 = \frac{1}{2}(b_{\text{O}} - \frac{1}{2}b_{\text{H}})$ .

If the concentration vector belongs to the second plane, then all the atoms are contained in H<sub>2</sub> and H<sub>2</sub>O. This is possible if and only if  $b_{\text{O}} \leq \frac{1}{2}b_{\text{H}}$ . In this case,  $c_4 = b_{\text{O}}$  and  $c_1 = \frac{1}{2}(b_{\text{H}} - 2b_{\text{O}})$ .

We reproduce this reasoning formally using the general formalism of Section 3.3. Formula (20) gives for  $\mathfrak{S}(\{5, 6, 7\})$

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

The  $\gamma_r$  vectors in this formula are the stoichiometric vectors of the reversible reactions ( $r = 1, 2, 3, 4, 5, 9, 18, 19, 20$ ). From 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  $\gamma_{r7} \neq 0$  for all  $r$ . Formula (22) is transformed to

$$\begin{aligned} & (c_5 = 0) \wedge ((c_1 = 0) \vee (c_3 = 0)) \wedge ((c_3 = 0) \vee (c_6 = 0)) \wedge ((c_1 = 0) \vee (c_6 = 0)) \wedge (c_7 = 0) \\ & \wedge ((c_1 = 0) \vee (c_7 = 0)) \wedge (c_6 = 0) \wedge (c_3 = 0) \wedge ((c_2 = 0) \vee (c_5 = 0)) \wedge ((c_3 = 0) \vee (c_5 = 0)) \\ & \wedge (c_7 = 0) \wedge ((c_2 = 0) \vee (c_5 = 0)) \wedge ((c_5 = 0) \vee (c_8 = 0)) \wedge ((c_3 = 0) \vee (c_8 = 0)). \end{aligned}$$

After simple transformations this becomes

$$(c_3 = 0) \wedge (c_5 = 0) \wedge (c_6 = 0) \wedge (c_7 = 0). \quad (23)$$

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,

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

We 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 a more explicit form:

$$\begin{aligned} & (c_3 = 0) \wedge ((c_1 = 0) \vee (c_2 = 0)) \wedge ((c_1 = 0) \vee (c_6 = 0)) \wedge (c_8 = 0) \\ & \wedge ((c_4 = 0) \vee (c_5 = 0)) \wedge ((c_2 = 0) \vee (c_5 = 0)) \wedge ((c_4 = 0) \vee (c_6 = 0)) \wedge (c_7 = 0). \end{aligned}$$

We take the conjunction of this formula with (22) in the simplified equivalent form (23) and transform the result to the disjunctive form. This yields

$$\begin{aligned} & [(c_3 = 0) \wedge (c_5 = 0) \wedge (c_6 = 0) \wedge (c_7 = 0) \wedge (c_8 = 0) \wedge (c_1 = 0)] \\ & \vee [(c_3 = 0) \wedge (c_5 = 0) \wedge (c_6 = 0) \wedge (c_7 = 0) \wedge (c_8 = 0) \wedge (c_2 = 0)]. \end{aligned} \quad (24)$$

This means that  $\mathfrak{S}^2(\{5, 6, 7\}) = \mathfrak{S}(\{3, 5, 6, 7\}) = \{\{1, 3, 5, 6, 7, 8\}, \{2, 3, 5, 6, 7, 8\}\}$ . 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.

We now search for the vector of exponents  $\delta = (\delta_i)$  ( $i = 1, \dots, 8$ ) from Table 2. After all the eliminations, the corresponding linear functional  $\hat{\delta}$  is just the 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 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  $\delta$  satisfies these conditions, then its linear combination with the vectors of atomic balances also satisfy them. Such a combination is a vector

$$\lambda \delta + \lambda_H(2, 0, 1, 2, 1, 0, 1, 2) + \lambda_O(0, 2, 1, 1, 0, 1, 2, 2) \quad (25)$$

under the condition  $\lambda > 0$ . This transformation of  $\delta$  does not change the sign of  $\hat{\delta}$  on the stoichiometric vectors because of atomic balances.

In our case the only coordinate that is not eliminated is  $x_7$  (bottom part of the last column of Table 2). If, for some reaction mechanism and selected sets of reversible and irreversible reactions, several ( $q$ ) coordinates remain, 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 and  $\{\gamma_r\}$  includes all the stoichiometric vectors for reversible and irreversible reactions.

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

$$\begin{aligned} & (y_1, y_2, y_3, y_4, y_5, y_6, y_7, y_8) \mapsto (y_1, y_2, 0, y_4, y_5, y_6, y_7, y_8) \\ & \mapsto (y_1, y_2, 0, y_4, y_5, y_6, y_7, 0) \mapsto (y_1, y_2, 0, 0, y_5 - y_4, y_6, y_7, 0) \\ & \mapsto (y_1, y_2, 0, 0, 0, y_6 + y_5 - y_4, y_7, 0) \mapsto (y_1, y_2, 0, 0, 0, 0, y_7 + y_6 + y_5 - y_4, 0). \end{aligned} \quad (26)$$

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. We 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 inequalities 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

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

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  $\varepsilon \rightarrow 0$ , it is necessary that two of  $\delta_i$  are zero. If  $b_0 \leq \frac{1}{2}b_H$ , 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  $\varepsilon \rightarrow 0$  ( $\varepsilon > 0$ ) as

$$\begin{aligned} c_{\text{H}_2}^{\text{eq}} = c_1^{\text{eq}} = \text{const}, \quad c_{\text{O}_2}^{\text{eq}} = c_2^{\text{eq}} \sim \varepsilon^2, \quad c_{\text{OH}}^{\text{eq}} = c_3^{\text{eq}} \sim \varepsilon^2, \quad c_{\text{H}_2\text{O}}^{\text{eq}} = c_4^{\text{eq}} = \text{const}, \\ c_{\text{H}}^{\text{eq}} = c_5^{\text{eq}} \sim \varepsilon^2, \quad c_{\text{O}}^{\text{eq}} = c_6^{\text{eq}} \sim \varepsilon^2, \quad c_{\text{HO}_2}^{\text{eq}} = c_7^{\text{eq}} \sim \varepsilon^3, \quad c_{\text{H}_2\text{O}_2}^{\text{eq}} = c_8^{\text{eq}} \sim \varepsilon^2. \end{aligned} \quad (27)$$

If  $b_0 \geq \frac{1}{2}b_H$ , 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  $\varepsilon \rightarrow 0$  ( $\varepsilon > 0$ ) as

$$\begin{aligned} c_{\text{H}_2}^{\text{eq}} = c_1^{\text{eq}} \sim \varepsilon^2, \quad c_{\text{O}_2}^{\text{eq}} = c_2^{\text{eq}} = \text{const}, \quad c_{\text{OH}}^{\text{eq}} = c_3^{\text{eq}} \sim \varepsilon, \quad c_{\text{H}_2\text{O}}^{\text{eq}} = c_4^{\text{eq}} = \text{const}, \\ c_{\text{H}}^{\text{eq}} = c_5^{\text{eq}} \sim \varepsilon^3, \quad c_{\text{O}}^{\text{eq}} = c_6^{\text{eq}} \sim \varepsilon^2, \quad c_{\text{HO}_2}^{\text{eq}} = c_7^{\text{eq}} \sim \varepsilon^3, \quad c_{\text{H}_2\text{O}_2}^{\text{eq}} = c_8^{\text{eq}} \sim \varepsilon^2. \end{aligned} \quad (28)$$

The linear combination  $\sum_i \delta_i N_i$  decreases over time due to kinetic equations. This is true for any vector of exponents represented by 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 gives an additional linear conservation law for the system of reversible reactions.

There are several versions of this function:

- The initial version,  $\hat{\delta}$ , obtained from Table 2 is  $(\delta, N) = -N_{\text{H}_2\text{O}} + N_{\text{H}} + N_{\text{O}} + N_{\text{H}_2\text{O}_2}$ .
- The vector of exponents, calibrated by adding the atomic balances (25) to meet the atomic balance conditions for  $b_0 \leq \frac{1}{2}b_H$  in the limit  $\varepsilon \rightarrow 0$ , is  $(\delta, N) = 2N_{\text{O}_2} + 2N_{\text{OH}} + 2N_{\text{H}} + 2N_{\text{O}} + 3N_{\text{HO}_2} + 2N_{\text{H}_2\text{O}_2}$ .
- The vector of exponents, calibrated to meet the atomic balance conditions for  $b_0 \geq \frac{1}{2}b_H$ , is  $(\delta, N) = 2N_{\text{H}_2} + N_{\text{OH}} + 3N_{\text{H}} + 2N_{\text{O}} + 3N_{\text{HO}_2} + 2N_{\text{H}_2\text{O}_2}$ .

All these forms differ 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 [26]: “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, chemical reactions have to be considered as reversible and every step of a complex reaction consists of two reactions, the forward and reverse (backward). However, in reality the rates of some forward or reverse reactions may be negligible. Typically, complex combustion reactions, particularly hydrocarbon oxidation and hydrogen combustion, include both reversible and irreversible steps. This is also the case in catalytic reactions. In particular, many enzyme reactions are partially irreversible. Although many catalytic reactions are globally irreversible, they always include some reversible steps, in particular gas adsorption steps. Many enzyme reactions are also partially irreversible.

The aim of this study was 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 are as follows:

1. The theory of the multiscale limit of a system of reversible reactions when some of equilibrium concentrations tend to zero (Section 2.2);
2. The extended principle of detailed balance for systems with some irreversible reactions (Theorem 1);
3. The construction of 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) and (15)); and
5. The constructive description of the faces of the positive orthant that include the  $\omega$ -limit points in their relative interior and thus the constructive description of the limiting behavior over time (Theorem 2).

Did we solve the main problem and develop the thermodynamics of systems with some irreversible reactions? The answer is that we solved the problem in part. We described the limit behavior but we did not find a global Lyapunov function that captures relaxation of both reversible and irreversible parts of the system. A 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, we completely solved one problem, namely how to throw away some reverse reactions without violation of the thermodynamics and microscopic reversibility. We found that 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 remaining reversible reactions should satisfy the Wegscheider identities (8).

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

If irreversible reactions are introduced correctly, then we know that a 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 we described these faces.

Oscillatory or chaotic attractors are impossible in closed systems that satisfy the extended principle of detailed balance. This general statement can be considered as a simple consequence of thermodynamics and it can easily be proved if the thermodynamic Lyapunov functions (potentials) are given. However, the thermodynamic potentials have no limits for 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 that the emergence of nontrivial attractors in systems with some irreversible reactions is impossible if they are the limits of the reversible systems that satisfy the principle of detailed balance. In this sense, the thermodynamic behavior is proven for systems with some irreversible reactions under extended detailed balance conditions. Nevertheless, the general problem of thermodynamic potentials in this limit remains open.

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