THERMODYNAMIC TREE: THE SPACE OF ADMISSIBLE PATHS

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Abstract. Is a spontaneous transition from a state x to a state y allowed by thermodynamics? Such a question arises often in chemical thermodynamics and kinetics. We ask the more formal question: is there a continuous path between these states, along which the conservation laws hold, the concentrations remain non-negative and the relevant thermodynamic potential G (Gibbs energy, for example) monotonically decreases? The obvious necessary condition, $G(x) \geq G(y)$, is not sufficient, and we construct the necessary and sufficient conditions. For example, it is impossible to overstep the equilibrium in 1-dimensional (1D) systems (with n components and $n-1$ conservation laws). The system cannot come from a state x to a state y if they are on the opposite sides of the equilibrium even if $G(x) > G(y)$. We find the general multidimensional analogue of this 1D rule and constructively solve the problem of the thermodynamically admissible transitions.

We study dynamical systems, which are given in a positively invariant convex polyhedron and have a convex Lyapunov function G. An admissible path is a continuous curve along which G does not increase. For $x, y \in D$, $x \succcurlyeq y$ (x precedes y) if there exists an admissible path from x to y and $x \sim y$ if $x \succcurlyeq y$ and $y \succcurlyeq x$. The tree of G in D is a quotient space $D/\sim$. We provide an algorithm for the construction of this tree. In this algorithm, the restriction of G onto the 1-skeleton of D (the union of edges) is used. The problem of existence of admissible paths between states is solved constructively. The regions attainable by the admissible paths are described.

Key words. Lyapunov function, convex polyhedron, attainability, tree of function, entropy, free energy

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1. Introduction.

1.1. Ideas and a simple example. "Applied dynamical systems" are models of real systems. We never know such systems in full detail. The available information about the system is incomplete and there are uncertainties of various types: errors in the model structure, errors in coefficients, in the state observation and many others. Nevertheless, there is an order in this world of errors: some information is more reliable, we trust in some structures more and even respect them as laws. Some other data are less reliable. There is an hierarchy of reliability, our knowledge and beliefs (described, for example by R. Peierls [44] for model making in physics). Extracting as many consequences from the more reliable data either without or before use of the less reliable information is a task which arises naturally.

In our paper, we study the systems of chemical kinetics and thermodynamics. For them, we can rank the information in the following way. First of all, the list of reagents and conservation laws should be known. Let the reagents be $A_1, A_2, \ldots, A_n$. The non-negative real variable $N_i \geq 0$, the amount of A_i in the mixture, is defined for each reagent, and N is the vector of composition with coordinates N_i. The conservation laws are presented by the linear balance equations:

$$b_i(N) = \sum_{j=1}^{n} a_i^j N_j = \text{const} \quad (i = 1, \ldots, m)\,. \tag{1.1}$$

We assume that the linear functions $b_i(N)$ $(i = 1, \ldots, m)$ are linearly independent.

The list of the components together with the balance conditions (1.1) is the first part of the information about the kinetic model. This determines the space of states,

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the polyhedron D defined by the balance equations (1.1) and the positivity inequalities $N_i \geq 0$. This is the background of kinetic models and any further development is less reliable.

The polyhedron D is assumed to be bounded. This means that there exist such coefficients λ_i that the linear combination $\sum_i \lambda_i b_i(N)$ has strictly positive coefficients: $\sum_i \lambda_i a_i^j > 0$ for all $j = 1, \ldots, n$.

The thermodynamic functions provide us with the second level of information about the kinetics. Thermodynamic potentials, such as the entropy, energy and free energy are known much better than the reaction rates and, at the same time, they give us some information about the dynamics. For example, the entropy increases in isolated systems. The Gibbs free energy decreases in closed isothermal systems under constant pressure, and the Helmholtz free energy decreases under constant volume and temperature. Of course, knowledge of the Lyapunov functions gives us some inequalities for vector fields of the systems' velocity but the values of these vector fields remain unknown. If there are some external fluxes of energy or non-equilibrium substances then the thermodynamic potentials are not Lyapunov functions and the systems do not relax to the thermodynamic equilibrium. Nevertheless, the inequality of positivity of the entropy production persists and this gives us useful information even about the open systems. Some examples are given in [22].

The next, third part of the information about kinetics is the reaction mechanism. It is presented in the form of the *stoichiometric equations* of the elementary reactions:

$$\sum_i \alpha_{\rho i} A_i \to \sum_i \beta_{\rho i} A_i \,, \tag{1.2}$$

where $\rho = 1, \ldots, m$ is the reaction number and the *stoichiometric coefficients* $\alpha_{\rho i}, \beta_{\rho i}$ $(i = 1, \ldots, n)$ are nonnegative integers.

A *stoichiometric vector* γ_ρ of the reaction (1.2) is a n-dimensional vector with coordinates

$$\gamma_{\rho i} = \beta_{\rho i} - \alpha_{\rho i} \,, \tag{1.3}$$

that is, 'gain minus loss' in the ρth elementary reaction.

The concentration of A_i is an intensive variable $c_i = N_i/V$, where $V > 0$ is the volume. The vector $c = N/V$ with coordinates c_i is the vector of concentrations.

A non-negative intensive quantity, r_ρ, the reaction rate, corresponds to each reaction (1.2). The kinetic equations in the absence of external fluxes are

$$\frac{\mathrm{d}N}{\mathrm{d}t} = V \sum_\rho r_\rho \gamma_\rho \,. \tag{1.4}$$

If the volume is not constant then equations for concentrations include $\dot{V}$ and have different form.

For perfect systems and not so fast reactions the reaction rates are functions of concentrations and temperature given by the *mass action law* and by the *generalized Arrhenius equation*. The mass action law is

$$r_\rho(c, T) = k_\rho(T) \prod_i c_i^{\alpha_{\rho i}} \,, \tag{1.5}$$

where $k_\rho(T)$ is the reaction rate constant.

The generalized Arrhenius equation is

$$k_\rho(T) = A_\rho \exp\left(\frac{S_{a\rho}}{R}\right) \exp\left(-\frac{E_{a\rho}}{RT}\right), \tag{1.6}$$

where $R = 8.314\,472\ \frac{\mathrm{J}}{\mathrm{K\ mol}}$ is the universal, or ideal gas constant, $E_{a\rho}$ is the activation energy, $S_{a\rho}$ is the activation entropy (i.e. $E_{a\rho} - TS_{a\rho}$ is the activation free energy), and A_ρ is the constant pre-exponential factor. A special relation between the kinetic constants is given by the *principle of detailed balance*: For each value of temperature T there exists a positive equilibrium point where each reaction (1.2) is equilibrated with its reverse reaction. This principle was introduced for collisions by Boltzmann in 1872 [6]. Einstein in 1916 used this principle in the background for his quantum theory of emission and absorption of radiation [11]. Wegscheider introduced the principle of detailed balance for chemical kinetics in 1901 [54]. Later, it was used by Onsager in his famous work [43]. For a recent review see [24].

At the third level of reliability of information we select the list of components and the balance conditions, find the thermodynamic potential, guess the reaction mechanism, accept the principle of detailed balance and believe that we know the kinetic law of elementary reactions and the character of dependencies $k_\rho(T)$. However, we still do not know the reaction rate constants.

Finally, at the fourth level of available information, we find the reaction rate constants and can analyze and solve the kinetic equations (1.4) or their extended version with the inclusion of external fluxes.

Of course, this ranking of the available information is conventional, to a certain degree. For example, some reaction rate constants may be known even better than the list of intermediate reagents. Nevertheless, this hierarchy of the information availability, list of components – thermodynamic functions – reaction mechanism – reaction rate constants, reflects the real process of modelling and the stairs of available information about a reaction kinetic system.

It seems very attractive to study the consequences of the information of each level separately. These consequences can be also organized 'stairwise'. We have the hierarchy of questions: how to find the consequences for the dynamics (i) from the list of components, (ii) from this list of components plus the thermodynamic functions of the mixture, and (iii) from the additional information about the reaction mechanism.

The answer to the first question is the description of the balance polyhedron D. The balance equations (1.1) together with the positivity conditions $N_i \geq 0$ should be supplemented by the description of all the faces. For each face, some $N_i = 0$ and we have to specify which N_i have zero value. The list of the corresponding indices i, for which $N_i = 0$ on the face, $I = \{i_1, \ldots, i_k\}$, fully characterizes the face. This problem of *double description* of the convex polyhedra [42, 9, 15] is well know in linear programming.

The list of vertices and edges with the corresponding indices is necessary for the thermodynamic analysis. This is the *1-skeleton* of D. Algorithms for the construction of the 1-skeletons of balance polyhedra as functions of the balance values were described in detail in 1980 [20]. The related problem of double description for convex cones is very important for the pathway analysis in systems biology [46, 16].

In this work, we use the 1-skeleton of D, but the main focus is on the second step, i.e. on the consequences of the given thermodynamic potentials. For closed systems under classical conditions, these potentials are the Lyapunov functions for the kinetic equations. For example, for perfect systems we assume the mass action law. If the

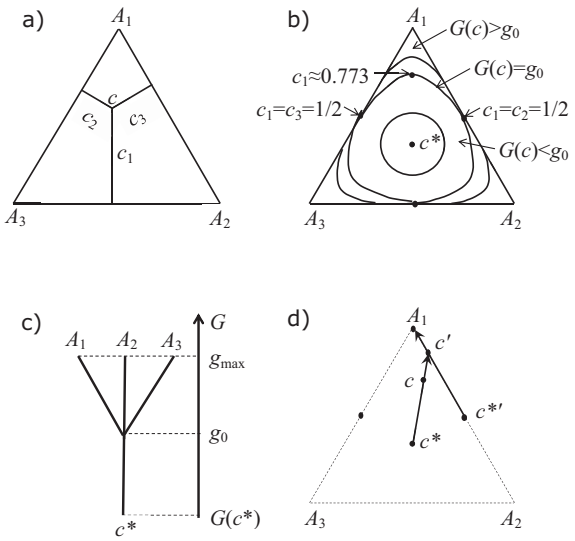

FIG. 1.1. *The balance simplex (a), the levels of the Lyapunov function (b) and the thermodynamic tree (c) for the simple system of three components, A_1, A_2, A_3. Algorithm for finding a vertex $v \succcurlyeq c$ (d).*

equilibrium concentrations c^* are given, the system is closed and both temperature and volume are constant then the function

$$G = \sum_i c_i \left(\ln \left(\frac{c_i}{c_i^*} \right) - 1 \right) \tag{1.7}$$

is the Lyapunov function; it should not increase in time. The function G is proportional to the free energy $F = RTG + \text{const}$ (for detailed information about the Lyapunov functions for kinetic equations under classical conditions see the textbook [55] or the recent paper [27]).

If we know the Lyapunov function G then we have the necessary conditions for the possibility of transition from the vector of concentrations c to c' during the non-stationary reaction: $G(c) \geq G(c')$ because the inequality $G(c(t_0)) \geq G(c(t_0+t))$ holds for any time $t \geq 0$.

The inequality $G(c) \geq G(c')$ is necessary if we are to reach c' from the initial state c by a thermodynamically admissible path, but it is not sufficient because in addition to this inequality there are some other necessary conditions. The simplest and most famous of them is: if D is one-dimensional (a segment) then the equilibrium c^* divides this segment into two parts and $c(t_0)$ and $c(t_0 + t)$ $(t > 0)$ are always on the same side of the equilibrium.

In 1D the overstepping of the equilibrium is forbidden. What is impossible to overstep in one dimension, is possible to circumvent in higher dimensions but in all dimensions the inequality $G(c) \geq G(c')$ is not sufficient if we are to reach c' from the initial state c along an admissible path. Some additional restrictions remain in the general case as well. A two-dimensional example is presented in Fig. 1.1. Let us consider the mixture of three components, $A_{1,2,3}$ with the only conservation law $c_1 + c_2 + c_3 = b$ (we take for illustration $b = 1$) and the equidistribution in equilibrium $c_1^* = c_2^* = c_3^* = 1/3$. The balance polyhedron is the triangle (Fig. 1.1a). In Fig. 1.1b

the level sets of

$$G = \sum_{i=1}^{3} c_i(\ln(3c_i) - 1)$$

are presented. This function achieves its minimum at equilibrium, $G(c^*) = -1$. On the edges, the function G achieves its conditional minimum, g_0, in the middles, and $g_0 = \ln(3/2) - 1$. G reaches its maximal value, $g_{\max} = \ln 3 - 1$, at the vertices.

If $G(c^*) < g \leq g_0$ then the level set $G(c) = g$ is connected. If $g_0 < g \leq g_{\max}$ then the corresponding level set $G(c) = g$ consists of three components (Fig. 1.1b). The critical value is $g = g_0$. The critical level $G(c) = g_0$ consists of three arcs. Each arc connects two middles of the edges and divides D in two sets. One of them is convex and includes two vertices, the other includes the remaining vertex.

A thermodynamically admissible path is a continuous curve along which G does not increase. Therefore, such a path cannot intersect these arcs 'from inside', i.e. from values $G(c) \leq g_0$ to bigger values, $G(c) > g_0$. For example, if an admissible path starts from the state with 100% of A_2, then it cannot intersect the arc that separates the vertex with 100% A_1 from two other vertices. Therefore, any vertex cannot be reached from another one and if we start from 100% of A_2 then the reaction cannot overcome the threshold ∼77.3% of A_1, that is the maximum of c_1 on the corresponding arc (Fig. 1.1b). This is an example of the 2D analogue of the 1D prohibition of overstepping of equilibrium.

For $x, y \in D$, $x \succcurlyeq y$ (x precedes y) if there exists an admissible path from x to y and $x \sim y$ if $x \succcurlyeq y$ and $y \succcurlyeq x$. The tree of G in D is a quotient space $\mathcal{T} = D/\sim$. For the natural projection $D \to D/\sim$ we use the notation π. The tree $D/\sim$ is a 1D continuum. We have to distinguish these connected acyclic graphs which have the same graphical representation but are discrete objects.

If $x \sim y$ then $G(x) = G(y)$. Therefore, we can define the function G on the tree: $G(\pi(c)) = G(c)$. It is convenient to draw this tree on the plane with the vertical coordinate $G(x)$ (Fig. 1.1c). Equilibrium c^* corresponds to a root of this tree, $\pi(c^*)$. If $G(c^*) < g \leq g_0$ then the level set $G(c) = g$ corresponds to one point on the tree. The level $G(c) = g_0$ corresponds to the branching point, and each connected component of the level sets $G(c) = g$ with $g_0 < g \leq g_{\max}$ corresponds to a separate point on the tree. The terminal leaves of the tree correspond to the vertices of D.

Let $x, y \in \mathcal{T}$ and $x \neq y$. The point $z \in \mathcal{T}$ is *between* x and y if $\mathcal{T} \setminus \{z\}$ is not connected, $\mathcal{T} \setminus \{z\} = \mathcal{T}_1 \cup \mathcal{T}_2$, $\mathcal{T}_1$ and $\mathcal{T}_2$ are connected, $x \in \mathcal{T}_1$ and $y \in \mathcal{T}_2$. In other words, z is a *cut point* that separates x from y.

The open segment (x, y) consists of all points that are between x and y. The closed segment $[x, y] = (x, y) \cup \{x, y\}$. These segments are homeomorphic to open and closed segments on the real line.

A continuous curve $\varphi : [0, 1] \to D$ is an admissible path if and only if its image $\pi \circ \varphi : [0, 1] \to \mathcal{T}$ is a path that goes monotonically down in the coordinate g. For each point $x \in \mathcal{T}$, the region attainable by the admissible paths (the *attainable region*) is just a segment $[x, \pi(c^*)]$. On such a segment each point is unambiguously characterized by the value of G. Therefore, if for $c \in D$ we know the value $G(c)$ and a vertex $v \succcurlyeq c$, then we can unambiguously describe the image of c on the tree: $\pi(c)$ is the point on the segment $[\pi(v), \pi(c^*)]$ with the given value of G, $g = G(c)$.

We can find a vertex $v \succcurlyeq c$ by the following algorithm:

- If $c = c^*$ then any vertex v of D precedes c, $v \succcurlyeq c$.

- If $c \neq c^*$ then the first step is the central projection of c onto the border of D with the center at equilibrium c^*. The result is the point c' on a face of D.
- If the projection coincides with the partial equilibrium $c^{*\prime}$ (the minimizer of G on the face) then $G(x) \geq G(c)$ on this face and for any vertices v of the face $v \succcurlyeq c$.
- If $c' \neq c^{*\prime}$ then the second step is the central projection of the point c' on the border of the face with the center at the partial equilibrium $c^{*\prime}$ and so on.
- The dimension of the face decreases at each step, hence, after not more than $\dim D - 1$ steps we will definitely obtain the desired vertex. For our simple example (Fig. 1.1d) this is the vertex A_1.

In order to construct the attainable region for a state c in D we can find the image $\pi(c) \in \mathcal{T}$, and then find the pre-image of the segment $[\pi(c), \pi(c^*)]$ in D. It is obvious (Fig. 1.1c) that every vertex is not attainable from any other vertex.

In this paper, we extend these ideas and observations to any dynamical system, which is given in a positively invariant convex polyhedron and has there a convex Lyapunov function. The class of chemical kinetic equations for closed systems provides us standard and practically important examples.

1.2. A bit of history. It seems attractive to use an attainable region instead of the single trajectory in situations with incomplete information or with information with different levels of reliability. Such situations are typical in many areas of science and engineering. For example, the theory for the continuous–time Markov chain is presented in [2, 21] and for the discrete–time Markov chains in [3].

Perhaps, the first example of this approach was developed in biological kinetics. In 1936, A.N. Kolmogorov [34] studied the dynamics of a pair of interacting populations of prey (x) and predator (y) in the general form:

$$\dot{x} = xS(x, y), \quad \dot{y} = yW(x, y)$$

under monotonicity conditions: $\partial S(x, y)/\partial y < 0$, $\partial W(x, y)/\partial y < 0$. The zero isoclines, the lines at which the rate of change for one population is zero (given by equations $S(x, y) = 0$ or $W(x, y) = 0$), are graphs of two functions $y(x)$. These isoclines divide the phase space into compartments (generically with curvilinear borders).

The geometry of the intersection of the zero isoclines together with some monotonicity conditions, contain important information about the system dynamics that we can extract [34] without exact knowledge of the right hand sides of the kinetic equations. This approach to population dynamics was applied to various problems [38, 4]. The impact of this work on population dynamics was analyzed in the review [49].

In 1964, Horn proposed to analyze the attainable regions for chemical reactors [30]. This approach became popular in chemical engineering. It was applied to the optimization of steady flow reactors [17], to batch reactor optimization by use of tendency models without knowledge of detailed kinetics [13], and for optimization of the reactor structure [28]. An analysis of attainable regions is recognized as a special geometric approach to reactor optimization [12] and as a crucially important part of the new paradigm of chemical engineering [29].

Many particular applications were developed, from polymerization [50] to particle breakage in a ball mill [40] and hydraulic systems [22]. Mathematical methods for the study of attainable regions vary from Pontryagin's maximum principle [39] to linear programming [32], the Shrink-Wrap algorithm [37], and convex analysis.

The connection between attainable regions, thermodynamics and stoichiometric reaction mechanisms was studied in the 1970s. In 1979 it was demonstrated how to utilize the knowledge about partial equilibria of elementary processes to construct the attainable regions [18]. It is possible to use the attainable regions for the discrimination of reaction mechanisms [23] because these regions significantly depend on the mechanism.

Thermodynamic data are more robust than the reaction mechanism and the reaction rates are known with lower accuracy than the stoichiometry of elementary reactions. Hence, there are two types of attainable regions. The first is the thermodynamic one, which use the linear restrictions and the thermodynamic functions [19]. The second is generated by thermodynamics and stoichiometric equations of elementary steps (but without reaction rates) [18, 25]. R. Shinnar and other authors [48] rediscovered this approach. There was even an open discussion about priority [5]. This geometric approach is applied now to various chemical and industrial processes.

Some particular classes of kinetic systems have rich families of the Lyapunov functions. Krambeck [35] studied attainable regions for linear systems and the l_1 Lyapunov norm instead of the entropy. Already simple examples demonstrate that the sets of distributions which are accessible from a given initial distribution by linear kinetic systems (Markov processes) with a given equilibrium are, in general, *non-convex* polytopes [18, 21, 57]. The non-convexity makes the analysis of attainability for continuous time Markov processes more difficult and interesting. This geometric approach to attainability was developed for all the thermodynamic potentials and for open systems as well [20]. Partial results for chemical kinetics and some other engineering systems are summarized in [55, 22].

The tree of the level sets for differentiable functions was studied in the middle of the 20 century by Adelson-Velskii and Kronrod [1, 36] and Reeb [45]. Sometimes these trees are called the *Reeb trees* [14] but from the historical point of view it may be better to call them the Adelson-Velskii – Kronrod – Reeb (or AKR) trees. This idea has application in differential topology (the Morse theory [41]), in topological shape analysis and visualization [14, 33] and in data analysis [51].

Some time ago this tree was recognized as an adequate tool for representation of the attainable regions in chemical thermodynamics [19, 20]. It was applied for analysis of various real systems [31, 56]. Nevertheless, some of the mathematical backgrounds of this approach were delayed in development and publications. Now, the thermodynamically attainable regions are in extensive use in chemical engineering and beyond [12, 13, 17, 22, 28, 29, 30, 31, 32, 35, 37, 39, 40, 47, 48, 50, 56]. In this paper we aim to provide the complete mathematical background for the analysis of the thermodynamically attainable regions.

1.3. The Structure of the Paper. Our results are applicable to any family of dynamical systems that obey a continuous strictly convex Lyapunov function in a positively invariant convex polyhedron.

In Sec. 2 we present several auxiliary propositions from convex geometry. We constructively describe the result of the cutting of a convex polyhedron D by a convex set U: we demonstrate, how it is possible to describe the connected components of $D \setminus U$ by the analysis of the 1D continuum $D_1 \setminus U$, where D_1 is the 1-skeleton of D.

In Sec. 3, we construct the tree of level sets of a strictly convex function G in the convex polyhedron D and study the properties of this tree. The main result of this section is the algorithm for construction of this tree (Sec. 3.3). These constructions are applied to several examples from chemical kinetics in Sec. 4.

2. Cutting of a polyhedron D by a convex set U.

2.1. Connected components of $D \setminus U$ and of $D_1 \setminus U$. Here and below, D is a convex polyhedron in $\mathbb{R}^n$. $\mathrm{Aff}(D)$ is the minimal linear manifold that includes D. $d = \dim \mathrm{Aff}(D) = \dim D$ is the dimension of D. $ri(D)$ is the interior of D in $\mathrm{Aff}(D)$; $r\partial(D)$ is the border of D in $\mathrm{Aff}(D)$.

Let, for $P, Q \subset \mathbb{R}^n$. The Minkowski sum is $P + Q = \{x + y \,|\, x \in P, y \in Q\}$. The convex hull (conv) and the conic hull (cone) of a set $V \subset \mathbb{R}^n$ are:

$$\mathrm{conv}(V) = \left\{ \sum_{i=1}^{q} \lambda_i v_i \;\middle|\; q > 0,\, v_1, \ldots, v_q \in V,\, \lambda_1, \ldots \lambda_q > 0,\, \sum_{i=1}^{q} \lambda_i = 1 \right\};$$

$$\mathrm{cone}(V) = \left\{ \sum_{i=1}^{q} \lambda_i v_i \;\middle|\; q \geq 0,\, v_1, \ldots, v_q \in V,\, \lambda_1, \ldots \lambda_q > 0, \right\}.$$

For a set $D \subset \mathbb{R}^n$ the following two statements are equivalent (the *Minkowski–Weyl theorem*):

1. For some real (finite) matrix A and real vector b, $D = \{x \in \mathbb{R}^n \,|\, Ax \leq b\}$;
2. There are finite sets of vectors $\{v_1, \ldots, v_q\} \subset \mathbb{R}^n$ and $\{r_1, \ldots r_p\} \subset \mathbb{R}^n$ such that

$$D = \mathrm{conv}\{v_1, \ldots v_q\} + \mathrm{cone}\{r_1, \ldots, r_p\} \tag{2.1}$$

.

Every polyhedron has two representations, of type (1) and (2), known as (halfspace) H-representation and (vertex) V-representation, respectively. We systematically use both these representations. Most of the polyhedra in our paper are bounded, therefore, for them only the convex envelope of vertices is used in the V-representation (2.1).

The k-skeleton of D, D_k, is the union of the closed k-dimensional faces of D:

$$D_0 \subset D_1 \subset \ldots \subset D_d = D\,.$$

D_0 consists of vertices of D and D_1 is a one-dimensional continuum embedded in $\mathbb{R}^n$. We use the notation $\widetilde{D_1}$ for the graph whose vertices correspond to the vertices of D and edges correspond to the edges of D, and call this graph the *graph of the 1-skeleton* of D.

The closed segment in $\mathbb{R}^n$ with ends x, y is $[x, y] = \{\lambda x + (1 - \lambda) y \,|\, \lambda \in [0, 1]\}$.

Let U be a convex subset of $\mathbb{R}^n$ (it may be a non-closed set). We use U_0 for the set of vertices of D that belong to U, $U_0 = U \cap D_0$, and U_1 for the set of the edges of D that have non-empty intersection with U. By default, we consider the closed faces of D, hence, the intersection of an edge with U either includes some internal points of the edge or consists from one of its ends. We use the same notation U_1 for the set of the corresponding edges of $\widetilde{D_1}$.

A set $W \subset P \subset \mathbb{R}^n$ is a *path – connected component* of P if it is its maximal path – connected subset. In this section, we aim to describe the path – connected components of $D \setminus U$. In particular, we prove that these components include the same sets of vertices as the connected components of the graph $\widetilde{D_1} \setminus U$. This graph is produced from $\widetilde{D_1}$ by deletion of all the vertices that belong to U_0 and all the edges that belong to U_1.

The closed segment in $\mathbb{R}^n$ with ends x, y is $[x, y] = \{\lambda x + (1-\lambda)y \,|\, \lambda \in [0,1]\}$.

LEMMA 2.1. *Let $x \in D \setminus U$. Then there exists such a vertex $v \in D_0$ that the closed segment $[v, x]$ does not intersect U: $[v, x] \subset D \setminus U$.*

Proof. Let us assume the contrary: for every vertex $v \in D_0$ there exists such $\lambda_v \in (0, 1]$ that $x + \lambda_v(v - x) \in U$. The convex polyhedron D is the convex hull of its vertices. Therefore, $x = \sum_{v \in D_0} \kappa_v v$ for some numbers $\kappa_v \geq 0$, $v \in D_O$, $\sum_{v \in D_0} \kappa_v = 1$.

Let

$$\delta_v = \frac{\kappa_v}{\lambda_v \sum_{v' \in D_0} \frac{\kappa_{v'}}{\lambda_{v'}}} .$$

It is easy to check that $\sum_{v \in D_0} \delta_v = 1$ and

$$x = \sum_{v \in D_0} \delta_v (x + \lambda_v (v - x)) . \tag{2.2}$$

According to (2.2), x belongs to the convex hull of the finite set $\{x + \lambda_v(v - x) \,|\, v \in D_0\} \subset U$. U is convex, therefore, $x \in U$ but this contradicts to the condition $x \notin U$. Therefore, our assumption is wrong and there exists at least one $v \in D_0$ such that $[v, x] \cap U = \emptyset$. □

So, if a point from the convex polyhedron D does not belong to a convex set U then it may be connected to at least one vertex of D by a segment that does not intersect U. Let us demonstrate now that if two vertices of D may be connected in D by a continuous path that does not intersect U then these vertices can be connected in D_1 by a path that is a sequence of edges D, which do not intersect U.

LEMMA 2.2. *Let $v, v' \in D_0$, $v, v' \notin U$, $\varphi : [0, 1] \to (D \setminus U)$ be a continuous path, $\varphi(0) = v$ and $\varphi(1) = v'$. Then there exists such a sequence of vertices $\{v_0, \ldots, v_l\} \subset (D_0 D \setminus U)$ that any two successive vertices, v_i, v_{i+1}, are connected by an edge $e_{i,i+1} \subset D_1$ and $e_{i,i+1} \cap U = \emptyset$.*

Proof. Let us, first, prove the statement: *the vertices v, v' belong to one path – connected component of $D \setminus U$ if and only if they belong to one path – connected components of $D_1 \setminus U$.*

Let us iteratively transform the path φ. On the kth iteration we construct a path that connects v and v' in $D_{d-k} \setminus U$, where $d = \dim D$ and $k = 1, \ldots, d-1$. We start from a transformation of path in a face of D.

Let $S \subset D_j$ be a closed j-dimensional face of D, $j > 1$ and $\psi : [0, 1] \to (D_j \setminus U)$ be a continuous path, $\psi(0) = v$, $\psi(1) = v'$ and $\psi([0, 1]) \cap U = \emptyset$. We will transform ψ into a continuous path $\psi_S : [0, 1] \to (D_j \setminus U)$ with the following properties: (i) $\psi_S(0) = v$, $\psi_S(1) = v'$, (ii) $\psi_S([0, 1]) \cap U = \emptyset$, (iii) $\psi_S([0, 1]) \setminus S \subseteq \psi([0, 1]) \setminus S$ and (iv) $\psi_S([0, 1]) \cap ri(S) = \emptyset$. The properties (i) and (ii) are the same as for ψ, the property (iii) means that all the points of $\psi_S([0, 1])$ outside S belong also to $\psi_S([0, 1])$ (no new points appear outside S) and the property (iv) means that there are no points of $\psi_S([0, 1])$ in $ri(S)$. To construct this ψ_S we consider two cases:

1. $U \cap ri(S) \neq \emptyset$, i.e. there exists $y^0 \in U \cap ri(S)$;
2. $U \cap ri(S) = \emptyset$.

In the first case, let us project any $\psi(\tau) \in ri(S)$ onto $r\partial(S)$ from the center y^0. Let $y \in S$, $y \neq y^0$. There exists such a $\lambda(y) \geq 1$ that $y^0 + \lambda(y)(y - y^0) \in r\partial(S)$. This function $\lambda(y)$ is continuous in $S \setminus \{y^0\}$. The function $\lambda(y)$ can be expressed through the Minkowski gauge functional [26] defined for a set K and a point x:

$$p_K(x) = \inf\{r > 0 \,|\, rx \in K\} \; :$$

$$\lambda(y) = \left(p_{D-y_0}(y-y_0)\right)^{-1} .$$

Let us define for any $y \in ri(S)$, $y \neq y^0$ a projection $\pi_S(y) = y^0 + \lambda(y)(y-y^0)$. This projection is continuous in $S \setminus \{y^0\}$ and $\pi_S(y) = y$ if $y \in r\partial(S)$. It can be extended as a continuous function onto whole $D_j \setminus \{y^0\}$:

$$\pi_S(y) = \begin{cases} \pi_S(y) & \text{if } y \in S \setminus \{y^0\}\,; \\ y & \text{if } y \in D_j \setminus S\,. \end{cases}$$

The center $y^0 \in U$. Because of the convexity of U, if $y \notin U$ then $y^0 + \lambda(y)(y-y^0) \notin U$ for any $\lambda \geq 1$. Therefore, the path $\psi_S(t) = \pi_S(\psi(t))$ does not intersect U and satisfies all the requirements (i)-(iv).

Let us consider the second case, $\psi([0,1]) \cap ri(S) = \emptyset$. There are the moments of the first entrance of $\psi(t)$ in S and the last going of this path out of S:

$$\tau_1 = \min\{\tau \,|\, \psi(\tau) \in S\}, \;\; \tau_2 = \max\{\tau \,|\, \psi(\tau) \in S\}\,,$$

$0 \leq \tau_1 \leq \tau_2 \leq 1$. Let $y^1 = \psi(\tau_1)$ and $y^2 = \psi(\tau_2)$. Let us substitute $\psi(t)$ on the segment $[\tau_1, \tau_2]$ by the linear function:

$$\psi'(\tau) = \begin{cases} y^1 + (\tau - \tau_1)\frac{y^2-y^1}{\tau^2-\tau^1} & \text{if } \tau \in [\tau_1, \tau_2]; \\ \psi(\tau) & \text{if } \tau \notin [\tau_1, \tau_2]\,. \end{cases}$$

The path ψ' connects v and v', does not intersect U and all the points on this path outside S are the points on the path ψ' for the same values of the argument τ.

Inside S, the path ψ' is just a segment $[\psi(\tau_1), \psi(\tau_2)]$. We assumed that $j = \dim S > 1$. Therefore, there exists a point $y^0 \in ri(S)$ that does not belong to $\psi'([0,1])$. Similarly to the previous case, we project the path $\psi'(\tau)$ ($\tau \in [\tau_1, \tau_2]$) from the center y^0 onto $r\partial(S)$. Let us call the new path (after the projection), ψ_S. The path $\psi_S : [0,1] \to D_j \setminus U$ connects v and v', $\psi_S([0,1]) \setminus S \subseteq \psi([0,1]) \setminus S$ and $\psi_S([0,1]) \cap ri(S) = \emptyset$.

Let us start from a given path $\varphi : [0,1] \to D$ and apply this construction to the path φ and $S = D$, then to the resulting path and all the $(d-1)$-dimensional faces S sequentially in some order and so on until we construct a continuous path $\theta : [0,1] \to (D_1 \setminus U)$ which connects v and v'. It can be transformed into a simple path in $D_1 \setminus U$ by deletion of all loops (if they exists). This simple path (without self-intersections) is just the sequence of edges we are looking for. □

Lemmas 2.1, 2.2 allow us to describe the connected components of the d-dimensional set $D \setminus U$ through the connected components of the one-dimensional continuum $D_1 \setminus U$.

PROPOSITION 2.3. *Let $W_1, \ldots, W_q$ be all the path – connected components of $D \setminus U$. Then $W_i \cap D_0 \neq \emptyset$ for all $i = 1, \ldots, q$, the continuum $D_1 \setminus U$ has q path – connected components and $W_i \cap D_1$ are these components.*

Proof. Due to Lemma 2.1, each path – connected component of $D \setminus U$ includes at least one vertex of D. According to Lemma 2.2, if two vertices of D belong to one path – connected component of $D \setminus U$ then they belong to one path – connected component of $D_1 \setminus U$. The reverse statement is obvious, because $D_1 \subset D$ and a continuous path in D_1 is a continuous path in D. □

We can study connected components of a simpler, discrete object, the graph $\widetilde{D_1}$. The path – connected components of $D \setminus U$ correspond to the connected components

of the graph $\widetilde{D_1} \setminus U$. (This graph is produced from $\widetilde{D_1}$ by deletion all the vertices that belong to U_0 and all the edges that belong to U_1).

PROPOSITION 2.4. *Let $W_1, \dots, W_q$ be all the path – connected components of $D \setminus U$. Then the graph $\widetilde{D_1} \setminus U$ has exactly q connected components and each set $W_i \cap D_0$ is the set of the vertices of D of one connected component of $\widetilde{D_1} \setminus U$.*

Proof. Indeed, every path between vertices of D_1 includes a path that connects these vertices and is the sequence of edges. (To prove this statements we just have to delete all loops in a given path.) Therefore, the vertices v_1, v_2 belong to one connected component of $\widetilde{D_1} \setminus U$ if and only if they belong to one path – connected component of $D_1 \setminus U$. The rest of the proof follows from Proposition 2.3. □

We proved that the path – connected components of $D \setminus U$ are in one-to-one correspondence with the components of the graph $\widetilde{D_1} \setminus U$ (the correspondent components have the same sets of vertices). In applications, we will meet the following problem. Let a point $x \in D \setminus U$ be given. Find the path – connected component of $D \setminus U$ which includes this point. There are two basic ways to find this component. Assume that we know the connected components of $\widetilde{D_1} \setminus U$. First, we can examine the segments $[x, v]$ for all vertices v of D. At least one of them does not intersect U (Lemma 2.1). Let it be $[x, v_0]$. We can find the connected component $\widetilde{D_1} \setminus U$ that contains v_0. The point x belongs to the correspondent path – connected component of $D \setminus U$. This approach exploits the V-description of the polyhedron D. The work necessary for this method is proportional to the amount of vertices of D.

Another method is based on projection on the faces of D. Let $x \in ri(D)$. We can take any point $y^0 \in D \setminus U$ and find the unique $\lambda_1 > 1$ such that $x^1 = y_0 + \lambda_1(x - y^0) \in r\partial(D)$. Let $x^1 \in ri(S_1)$, where S_1 is a face of D. If $S_1 \cap U = \emptyset$ then we can take any vertex $v_0 \in S_1$ and find the connected component $\widetilde{D_1} \setminus U$ that contains v_0. This component gives us the answer. If $S_1 \cap U \neq \emptyset$ then we can take any $y^1 \in S_1 \cap U$ and find the unique $\lambda_2 > 1$ such that $x^2 = y_1 + \lambda_2(x - y^1) \in r\partial(S)$. This x^2 belongs to the relative boundary of the face S_2 and so on. At each iteration, the dimension of faces decreases. After $d = \dim D$ iterations at most we will get the vertex v we are looking for (see also Fig. 1.1) and find the connected component of $\widetilde{D_1} \setminus U$ which gives us the answer. Here we exploit the H-description of D.

2.2. Description of the connected components of $D \setminus U$ by inequalities. Let $W_1, \dots, W_q$ be the path – connected components of $D \setminus U$.

PROPOSITION 2.5. *For any set of indices $I \subset \{1, \dots, q\}$ the set*

$$K_I = U \bigcup \left(\bigcup_{i \in I} W_i \right)$$

is convex.

Proof. Let $y^1, y^2 \in K_I$. We have to prove that $[y^1, y^2] \subset K_I$. Five different situations are possible:

1. $y^1, y^2 \in U$;
2. $y^1 \in U$, $y^2 \in W_i$, $i \in I$;
3. $y^1, y^2 \in W_i$, $i \in I$, $[y^1, y^2] \cap U = \emptyset$;
4. $y^1, y^2 \in W_i$, $i \in I$, $[y^1, y^2] \cap U \neq \emptyset$;
5. $y^1 \in W_i$, $y^2 \in W_j$, $i, j \in I$, $i \neq j$.

We will systematically use two simple facts: (i) the convexity of U implies that its intersection with any segment is a segment and (ii) if $x^1 \in W_i$ and $x^2 \in D \setminus W_i$ then the segment $[x^1, x^2]$ intersects U because W_i is a path – connected component of U.

In case 1, $[y^1, y^2] \subset U \subset K$ because convexity U.

In case 2, there exists such a point $y^3 \in (y^1, y^2)$ that $[y^1, y^3) \subseteq U \cap [y^1, y^2] \subseteq [y^1, y^3]$. The segment $(y^3, y^2]$ cannot include any point $x \in D \setminus W_i$ because it does not include any point from U. Therefore, in this case $(y^3, y^2] \subset W_i \subset K$ and $y^3 \in K$ because it belongs either to U or to W_i.

In case 3, $[y^1, y^2] \subset W_i \subset K$ because W_i is a path – connected component of $D \setminus U$ and $[y^1, y^2] \cap U = \emptyset$.

In case 4, $[y^1, y^2] \cap U$ is a segment with the ends x^1, x^2 $(y^1 < x^1 < x^2 < y^2)$ that cuts $[y^1, y^2]$ in three segments. $[y^1, x^1) \subset W_i$, $(x^1, x^2) \subset U$ and $(x^2, y^2) \subset W_i$ because W_i is a path – connected component of $D \setminus U$ and U is convex. The border points $x^{1,2}$ belong either to U or to W_i. Therefore, $[y^1, y^2] \subset K$.

In case 5, $[y^1, y^2] \cap U$ is also a segment with the ends x^1, x^2 $(y^1 < x^1 < x^2 < y^2)$ that cuts $[y^1, y^2]$ in three segments. $[y^1, x^1) \subset W_i$, $(x^1, x^2) \subset U$ and $(x^2, y^2) \subset W_j$ because $W_{i,j}$ are path – connected components of $D \setminus U$ and U is convex. The border points $x^{1,2}$ belong to U, to W_i or to W_j. Therefore, $[y^1, y^2] \subset K$. □

Typically, the set U is represented by a set of inequalities, for example, $G(x) \leq g$. It may be useful to represent the path – connected components of $D \setminus U$ by inequalities. For this purpose, let us first construct a convex polyhedron $Q \subset U$ with the same amount of path – connected components in $D \setminus Q$, $V_1, \ldots, V_q$: $W_i \subset V_i$. We will construct Q as a convex hull of a finite set. Let us select the edges e of D which intersect U but the intersection $e \cap U$ does not include vertices of D. For every such edge we select one point $x_e \in e \cap U$. The set of these points is Q_1. By definition,

$$Q = \mathrm{conv}(U_0 \cup Q_1)\,. \tag{2.3}$$

Q is convex, hence, we can apply all the previous results about the components of $D \setminus U$ to the components of $D \setminus Q$.

LEMMA 2.6. *The set $U_0 \cup Q_1$ is the set of vertices of Q.*

Proof. A point $x \in U_0 \cup Q_1$ is not a vertex of $Q = \mathrm{conv}(U_0 \cup Q_1)$ if and only if it is a convex combination of other points from this set: there exist such $x_1, \ldots, x_k \in U_0 \cup Q_1$ and $\lambda_1, \ldots, \lambda_k > 0$ that $x_i \neq x$ for all $i = 1, \ldots, k$ and

$$\sum_{i=1}^{k} \lambda_i = 1\,, \quad \sum_{i=1}^{k} \lambda_i x_i = x\,.$$

If $x \in U_0$ this is impossible because x is a vertex of D and $U_0 \cup Q_1 \subset D$. If $x \in Q_1$ then it belongs to an edge of D and, hence, may be a convex combination of points D from this edge only. By construction, $U_0 \cup Q_1$ may include only one point from an edge. Therefore, all the points from Q_1 are vertices of Q. □

LEMMA 2.7. *The set $D \setminus Q$ has q path – connected components $V_1, \ldots, V_q$ that may be enumerated in such a way that $W_i \subset V_i$ and $W_i = V_i \setminus U$.*

Proof. To prove this statement about the path – connected components, let us mention that Q and U include the same vertices of D, the set U_0, and cut the same edges of D. Graphs $\widetilde{D_1} \setminus Q$ and $\widetilde{D_1} \setminus U$ coincide. $Q \subset U$ because of the convexity of U and definition of Q. To finalize the proof, we can apply Proposition 2.4. □

PROPOSITION 2.8. *Let I be any set of indices from $\{1, \ldots, q\}$.*

$$Q \bigcup \left(\bigcup_{i \in I} V_i \right) = \mathrm{conv} \left(U_0 \bigcup Q_1 \bigcup \left(\bigcup_{i \in I} \left(D_0 \bigcap V_i \right) \right) \right) \tag{2.4}$$

Proof. On the left hand side of (2.4) we see the union of Q with the connected components V_i ($i \in I$). On the right hand side there is a convex envelope of a finite set. This finite set consists of the vertices of Q, $(U_0 \cup Q_1)$ and the vertices of D that belong to V_i ($i \in I$). Let us denote by R_I the right hand side of (2.4) and by L_I the left hand side of (2.4).

L_I is convex due to Proposition 2.5 applied to Q and V_i. The inclusion $R_I \subseteq L_I$ is obvious because L_I is convex and R_I is defined as a convex hull of a subset of L_I. To prove the inverse inclusion, let us consider the path – connected components of $D \setminus R_I$. Sets V_j ($j \notin I$) are the path – connected components of $D \setminus R_I$ because they are the path – connected components of $D \setminus Q$, $Q \subset R_I$ and $R_I \cap V_j = \emptyset$ for $j \notin I$. There exist no other path – connected components of $Q \subset R_I$ because all the vertices of V_i ($i \in I$) belong to R_I by construction, hence, $D_0 \setminus R_I \subset \cup_{j \notin I} V_j$. Due to Lemma 2.1 every path – connected component of $D \subset R_I$ includes at least one vertex of D. Therefore, V_j ($j \notin I$) are all the path – connected components of $D \setminus R_I$ and $D \setminus R_I = \cup_{j \notin I} V_j$. Finally, $R_I = D \setminus \cup_{j \notin I} V_j = Q \cup (\cup_{i \in I} V_i) = L_I$. □

According to Lemma 2.6, each path – connected component $W_i \subset D \setminus U$ can be represented in the form $W_i = V_i \setminus U$, where V_i is a path – connected component of $D \setminus Q$. By construction, $Q \subset U$, hence

$$W_i = (Q \cup V_i) \setminus U \,. \tag{2.5}$$

If U is given by a system of inequalities then representations (2.4) and (2.5) give us the possibility to represent W_i by inequalities. Indeed, the convex envelope of a finite set in (2.4) may be represented by a system of linear inequalities. If the sets $Q \cup V_i$ and U in (2.5) are represented by inequalities then the difference between them is also represented by the system of inequalities.

The description of the path – connected component of $D \setminus U$ may be constructed by the following steps:

1. Construct the graph of the 1-skeleton of D, this is $\widetilde{D_1}$;
2. Find the vertices of D that belong to U, this is the set U_0;
3. Find the edges of D that intersect U, this is the set U_1.
4. Delete from $\widetilde{D_1}$ all the vertices from U_0 and the edges from U_1, this is the graph $\widetilde{D_1} \setminus U$;
5. Find all the connected components of $\widetilde{D_1} \setminus U$. Let the sets of vertices of these connected components be $V_{01}, \dots, V_{0q}$;
6. Select the edges e of D which intersect U but the intersection $e \cap U$ does not include vertices of D. For every such an edge select one point $x_e \in e \cap U$. The set of these points is Q_1.
7. For every $i = 1, \dots, q$ describe the polyhedron $R_i = \mathrm{conv}(U_0 \cup Q_1 \cup V_{0i})$;
8. There exists q path – connected components of $D \setminus U$: $W_i = R_i \setminus U$.

Every step can be performed by known algorithms including algorithms for the solution of the double description problem [42, 9, 15].

Let us use the simple system of three reagents, $A_{1,2,3}$ (Fig. 1.1) to illustrate the main steps of the construction of the path – connected components. The polyhedron D is here the 2D simplex (Fig. 1.1a). The plane $\mathrm{Aff}D$ is given by the balance equation $c_1 + c_2 + c_3 = 1$. We select $U = \{c \,|\, G(c) \le g_0$ as an example of a convex set (Fig. 2.2a). It includes no vertices of D, hence, $U_0 = \emptyset$. U intersects each edge of D in the middle point, hence, U_1 includes all the edges of D. The graph $\widetilde{D_1} \setminus U$ consists of three isolated vertices. Its connected components are these isolated vertices. Q_1 consists of three points, the middles of the edges $(1/2, 1/2, 0)$, $(1/2, 0, 1/2)$ and $(0, 1/2, 1/2)$ (in

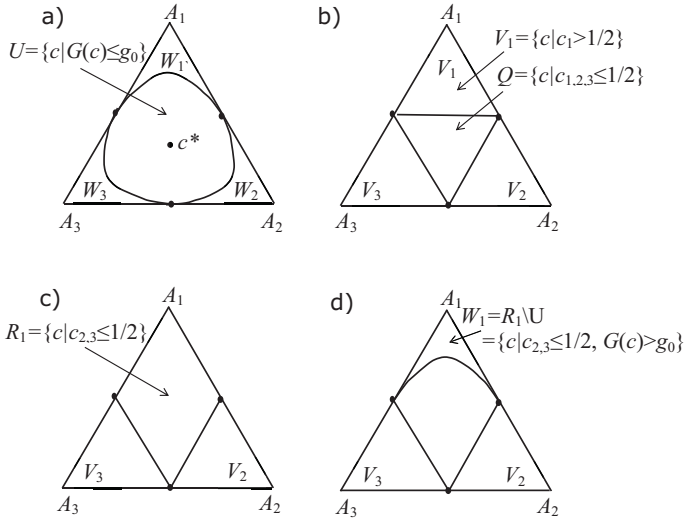

FIG. 2.1. *Construction of the path – connected components W_i of $D\setminus U$ for the simple example. (a) The balance simplex D, the set U and the path – connected components W_i; (b) The polyhedron $Q=\mathrm{conv}(U_0\cup Q_1)$ (2.3) ($U_0=\emptyset$, Q_1 consists of the middles of the edges) and the connected components V_i of $D\setminus Q$: $V_i=\{c\in D\,|\,c_i>1/2\}$; (c) The set $R_1=\mathrm{conv}(U_0\cup Q_1\cup(D_0\cap V_1))$; (d) The connected components W_1 described by the inequalities (as $R_1\setminus U$ (2.4)).*

this example, the choice of these points is unambiguous, Fig. 2.2a).

The polyhedron Q is a convex hull of these three points, that is the triangle given in $\mathrm{Aff}(D)$ by the system of three inequalities $c_{1,2,3}\le 1/2$ (Fig. 2.2b). The connected components of $D\setminus Q$ are the triangles V_i given in D by the inequalities $c_i>1/2$. In the whole $\mathbb{R}^3$, these sets are given by the systems of an equation and inequalities:

$$V_i=\{c\,|\,c_{1,2,3}\ge 0,\ c_1+c_2+c_3=1,\ c_i>1/2\}\,.$$

The polyhedron R_i is the convex hull of four points, the middles of the edges and the ith vertex (Fig. 2.2c). In D, R_i is given by two linear inequalities, $c_j\le 1/2$, $j\ne i$. In the whole $\mathbb{R}^3$, these inequalities should be supplemented by the equation and inequalities that describe D:

$$R_i=\{c\,|\,c_{1,2,3}\ge 0,\ c_1+c_2+c_3=1,\ c_j\le 1/2\,(j\ne i)\}\,.$$

The path – connected components of $D\setminus U$, W_i are described as $R_i\setminus U$ Fig. 2.2d): in D we get $W_i=\{c\,|\,c_j\le 1/2\,(j\ne i),\ G(c)>g_0\}$. In the whole $\mathbb{R}^3$,

$$W_i=\{c\,|\,c_{1,2,3}\ge 0,\ c_1+c_2+c_3=1,\ c_j\le 1/2\,(j\ne i),\ G(c)>g_0\}\,.$$

V_i are convex sets in this simple example, therefore, it is possible to simplify slightly the description of the components W_i and to represent them as $V_i\setminus U$:

$$W_i=\{c\,|\,c_{1,2,3}\ge 0,\ c_1+c_2+c_3=1,\ c_i>1/2,\ G(c)>g_0\}$$

(or $W_i=\{c\,|\,c_i>1/2,\ G(c)>g_0\}$ in D).

In the general case (more components and balance conditions), the connected components V_i may be non-convex, hence, description of these sets by the systems of linear equations and inequalities may be impossible. Therefore, in the general situations, we have to use R_i for description of W_i.

3. Construction of the thermodynamic tree.

3.1. Problem Statement. Let a real continuous function G be given in the bounded polyhedron D. We assume that G is *strictly convex* in D, i.e. the set (the epigraph of G)

$$\mathrm{epi}(G) = \{(x, g) \,|\, x \in D,\, g \geq G(x)\} \subset D \times (-\infty, \infty)$$

is convex and for any segment $[x, y] \subset D$ $(x \neq y)$ G is not constant on $[x, y]$. A strictly convex function on a bounded convex set has a unique minimizer. Let x^* be the minimizer of G in D and $g^* = G(x^*)$ is the corresponding minimal value.

The level set $S_g = \{x \in D \,|\, G(x) = g\}$ is closed and the sublevel set $U_g = \{x \in D \,|\, G(x) < g\}$ is open in D (i.e. it is the intersection of an open set with D). The sets S_g and $D \setminus U_g$ are compact and $S_g \subset D \setminus U_g$.

A continuous path $\varphi[0, 1] \to D$ is admissible if the function $G(\varphi(x))$ does not increase on $[0, 1]$. For $x, y \in D$, $x \succeq y$ (x precedes y) if there exists an admissible path $\varphi[0, 1] \to D$ with $\varphi(0) = x$ and $\varphi(1) = y$. We define the equivalence: $x \sim y$ if $x \succeq y$ and $y \succeq x$.

Definition 3.1. *The tree of G in D is the quotient space $\mathcal{T} = D/\sim$.* We use the notation $\pi : D \to D/\sim$ for the natural projection.

Let $x, y \in D$. According to Corollary 3.5 proven in the next subsection, an admissible path from x to y in D exists if and only if $\pi(y) \in [\pi(x^*), \pi(x)]$. Therefore, to describe constructively the relation $x \succeq y$ in D we have to solve the following problems:

1. How to construct the thermodynamic tree $\mathcal{T}$?
2. How to find an image $\pi(x)$ of a state $x \in D$ on the thermodynamic tree $\mathcal{T}$?
3. How to describe by inequalities a preimage of a segment of the thermodynamic tree, $\pi^{-1}([w, z]) \subset D$ $(w, z \in \mathcal{T})$?

3.2. Coordinates on the thermodynamic tree. We get the following lemma directly from the definitions.

Lemma 3.2. *Let $x, y \in D$. $x \sim y$ if and only if $G(x) = G(y)(= g)$ and x and y belong to the same path – connected component of S_g.*

The path – connected components of $D \setminus U_g$ can be numerated by the connected components of the graph $\widetilde{D_1} \setminus U_g$. The following lemma allows us to apply this result to the path – connected components of S_g.

Lemma 3.3. *Let $g > g^*$, $W_1, \ldots, W_q$ are the path – connected components of $D \setminus U_g$ and $\sigma_1, \ldots, \sigma_p$ are the path – connected components of S_g. Then $q = p$ and σ_i may be enumerated on such a way that σ_i is the border of W_i in D.*

Proof. G is continuous in D, hence, if $G(x) > g$ then there exists a vicinity of x in D where $G(x) > g$. Therefore $G(y) = g$ for every boundary point y of $D \setminus U_g$ in D and S_g is the boundary of $D \setminus U_g$ in D.

Let us define a projection $\theta_g : D \setminus U_g \to S_g$ by the conditions: $\theta_g(x) \in [x, x^*]$ and $G(\theta_g(x)) = g$. The function $G(\theta_g(x))$ is strictly increasing continuous and convex function on the interval $[x, x^*]$. It depends continuously on x in the uniform metrics. Therefore, the solution to the equation $G(y) = g$ on $[x, x^*]$ exists and continuously depends on $x \in D \setminus U_g$.

The fixed points of the projection θ_g are elements of S_g. The image of each path – connected component W_i is a path – connected set. The preimage of every path – connected component σ_i is also a path – connected set. Indeed, let $\theta_g(x) \in \sigma_i$ and $\theta_g(y) \in \sigma_i$. There exists a continuous path from x to y in $D \setminus U_g$. It may be composed

from three paths: (i) from x to $\theta_g(x)$ along the line segment $[x, \theta_g(x)] \subset [x, x^*]$ then a continuous path in σ_i between $\theta_g(x)$ and $\theta_g(y)$ (it exists because σ_i is a path – connected component of S_g and it belongs to $D \setminus U_g$ because $S_g \subset D \setminus U_g$) and, finally, from $\theta_g(y)$ to y along the line segment $[\theta_g(y), y] \subset [x^*, y]$. Therefore, the images of a path – connected component W_i is a path – connected components of S_g that may be enumerated by the same index i, σ_i. This σ_i is the border of W_i in D. □

The equivalence class of $x \in D$ is defined as $[x] = \{y \in D \,|\, y \sim x\}$. Let $W(x)$ be a path – connected component of $D \setminus U_g$ ($g = G(x)$) for which $\theta_g(W(x)) = [x]$. Due to Lemma 3.3 such a component exists and

$$W(x) = \{y \in D \,|\, y \succeq x\}\,. \tag{3.1}$$

Let us define a one-dimensional continuum $\mathcal{Y}$ that consists of pairs (g, M) where $g^* \le g \le g_{\max}$ and M is a set of vertices of a connected component of $\widetilde{D_1} \setminus U_g$. For each (g, M) the fundamental system of neighborhoods consists of sets $V_\rho = \{(g + \gamma, M') \in \mathcal{Y} \,|\, |\gamma| < \rho,\ M' \subseteq M\}$ ($\rho > 0$).

Let us define the preorder structure on $\mathcal{Y}$: $(g, M) \succeq (g', M')$ if $g \ge g'$ and $M \supseteq M'$.

Proposition 3.4. *$\mathcal{Y}$ is a homeomorphic image of $\mathcal{T}$ with preservation of preorder.*

Proof. Let us consider the mapping $\phi : D \to \mathcal{Y}$: $x \mapsto (G(x), W(x) \cap D_0)$. According to Lemmas 3.3, 3.1 and Proposition 2.4, the equivalent points x map to the same pair (g, M) and non-equivalent points map to different pairs (g, M). Let us define the preorder structure on $\mathcal{Y}$: $(g, M) \succeq (g', M')$ if $g \ge g'$ and $M \supseteq M'$. For any $x, y \in D$, $x \succeq y$ if and only if $\phi(x) \succeq \phi(y)$. The fundamental system of neighborhoods in Y may be defined using this preorder. Let us say that (g, M) is compatible to (g', M') if $(g', M') \succeq (g, M)$ or $(g, M) \succeq (g', M')\}$. Then $V_\rho = \{(g', M') \in \mathcal{Y} \,|\, |\gamma - \gamma'| < \rho,\ (g', M')$ is compatible to $(g, M)\}$ ($\rho > 0$). So, $\mathcal{Y}$ has the same preorder and topological structure as $\mathcal{T}$. □

$\mathcal{Y}$ can be considered as a coordinate system on $\mathcal{T}$. Each point is presented as a pair (g, M) where $g^* \le g \le g_{\max}$ and M is a set of vertices of a connected component of $\widetilde{D_1} \setminus U_g$. The map ϕ is the coordinate representation of the canonical projection $\pi : D \to \mathcal{T}$. Now, let us use this coordinate system and the proof of Proposition

Corollary 3.5. *An admissible path from x to y in D exists if and only if*

$$\pi(y) \in [\pi(x^*), \pi(x)]\,.$$

Proof. Let there exists an admissible path from x to y in D, $\varphi[0, 1] \to D$. Then $\pi(x) \succeq \phi(y)$ in $\mathcal{T}$. Let $\pi(x) = (G(x), M)$ in coordinates $\mathcal{Y}$. For any $v \in M$, $\pi(y) \in [\pi(x^*), \pi(v)]$ and $\pi(x) \in [\pi(x^*), \pi(v)]$.

Assume now that $\pi(y) \in [\pi(x^*), \pi(x)]$ and $\pi(x) = (G(x), M)$. Then for any $\pi(x) = (G(x), M)$ the admissible path from x to y in D may be constructed as follows. Let $\bar{v}$ be a vertex of D for which $\pi(\bar{v}) = v$. The straight line interval $[x^*, \bar{v}]$ includes a point x_1 with $G(x_1) = G(x)$ and y_1 with $G(y_1) = G(y)$. Coordinates of $\pi(x_1)$ and $\pi(x)$ in Y coincide as well as coordinates of $\pi(y_1)$ and $\pi(y)$. Therefore, $x \sim x_1$ and $y \sim y_1$. The admissible path from x to y in D may be constructed as sequence of three paths: first, a continuous path from x to x_1 inside the path – connected component of $S_{G(x))}$ (Lemma 3.2), then from x_1 to y_1 along a straight line and after that a continuous path from y_1 to y inside the path – connected component of $S_{G(y)}$. □

To describe the space $\mathcal{T}$ in coordinate representation Y, it is necessary to find the connected components of the graph $\widetilde{D_1} \setminus U_g$ for each g. First of all, this function,

$$g \mapsto \text{ the set of connected components of } \widetilde{D_1} \setminus U_g\,,$$

is piecewise constant. Secondly, we do not need to solve at each point the rather difficult problem of the construction of the connected components of the graph $\widetilde{D_1} \setminus U_g$ "from scratch". The problem of the parametric analysis of these components as functions of g appears to be much simpler. Let us represent the solution of this problem. At the same time, this is the method for the construction of the thermodynamic tree in coordinates (g, M).

3.3. Algorithm for construction of the thermodynamic tree. To construct the thermodynamic tree we need the following information: the graph $\widetilde{D_1}$ of the 1-skeleton of the balance polyhedron D labeled by the values of G. Each vertex v is labeled by the value $\gamma_v = G(v)$ and each edge $e = (v, w)$ is labeled by the minimal value of G on the segment $[v, w] \subset D$, $g_e = \min_{[v,w]} G(x)$. We need also the minimal value $g^* = \min_D\{G(x)\}$ because the root of the tree is (g^*, D_0).

The convex function G achieves its local maxima in D only in vertices. The vertex v is a (local) maximizer of g if $g_e < \gamma_v$ for each edge e that includes v. The leaves of the thermodynamic tree are pairs $(\gamma_v, \{v\})$ for the vertices that are the local maximizers of G.

Let us enumerate the vertices and the edges of $\widetilde{D_1}$ in order of the correspondent γ_v and g_e: $\gamma_{v_1} \geq \gamma_{v_2} \geq \ldots$ and $g_{e_1} \geq g_{e_2} \geq \ldots$. Some of the numbers γ_{v_i}, g_{e_j} may coincide. Let there be l different numbers among them: $a_1 > a_2 > \ldots > a_l$, where each a_k belongs to $\{\gamma_{v_i}\}$ or to $\{g_{e_j}\}$.

The set of connected components of $\widetilde{D_1} \setminus U_g$ is the same for all $g \in (a_{i+1}, a_i]$. For $g \in [g^*, a_l]$ the graph $\widetilde{D_1} \setminus U_g$ includes all the vertices and edges $\widetilde{D_1}$ and, hence, it is connected for this segment. Let us take, formally, $a_{l+1} = g^*$.

Let us construct the connected components of the graph $\widetilde{D_1} \setminus U_g$ starting from the maximal value of G: $a_1 = \max_{x \in D_1} G(x)$. The function G is strictly convex, hence, $a_1 = \gamma_v$ for a set of vertices $A_1 \subset D_0$ but it is impossible that $a_1 = g_e$ for an edge e.

For an interval $(a_2, a_1]$ the connected components of $\widetilde{D_1} \setminus U_g$ are the one-element sets $\{v\}$ for $v \in A_1$.

Let A_i be the set of vertices $v \in D_0$ with $\gamma_v = a_i$ and let E_i be the set of edges of D_1 with $g_e = a_i$ $(i = 1, \ldots, l)$. Let $\mathcal{L}_i = \{M_1^i, \ldots, M_{k_i}^i\}$ be the set of the connected components of $\widetilde{D_1} \setminus U_g$ for $g \in (a_i, a_{i-1}]$ $(i = 1, \ldots, l)$ represented by the sets of vertices M_j^i.

Assume that $\mathcal{L}_{i-1}$ is given. Let us find the set $\mathcal{L}_i$ of connected components of $\widetilde{D_1} \setminus U_g$ for $g = a_i$ (and, therefore, for $g \in (a_{i+1}, a_i]$).

First of all, we add to the set $\mathcal{L}_{i-1} = \{M_1^{i-1}, \ldots, M_{k_{i-1}}^{i-1}\}$ the one-element sets $\{v\}$ for all $v \in A_i$. We will denote this auxiliary set of sets as $\widetilde{L}_0 = \{M_1, \ldots, M_q\}$, where $q = k_{i-1} + |A_i|$. Secondly, let us enumerate the edges from E_i in an arbitrary order: $e_1, \ldots, e_{|E_i|}$. For each $k = 0, \ldots, |E_i|$ we will create an auxiliary set of sets $\widetilde{L}_k$ by the union of some of elements of $\widetilde{L}_0$. Let $\widetilde{L}_{k-1}$ be given and e_k connects the vertices v and v'. If v and v' belong to the same element of $\widetilde{L}_{k-1}$ then $\widetilde{L}_k = \widetilde{L}_{k-1}$. If v and v' belong to the different elements of $\widetilde{L}_{k-1}$, M and M', then $\widetilde{L}_k$ is produced from $\widetilde{L}_{k-1}$ by the union of M and M':

$$\widetilde{L}_k = \widetilde{L}_k \setminus \{M\} \setminus \{M'\} \cup \{M \cup M'\}$$

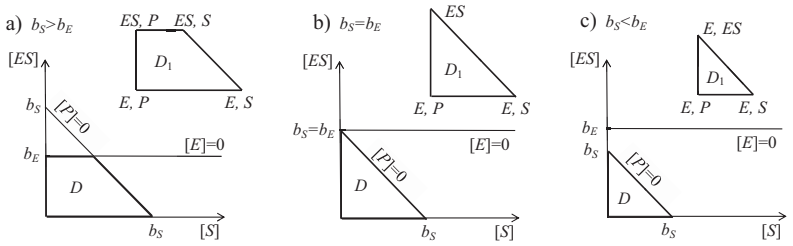

FIG. 3.1. *The balance polygon D on the plane with coordinates $[S]$ and $[ES]$ for the four–component enzyme–substrate system S, E, ES P with two balance conditions, $b_S = [S]+[ES]+[P] =$ const and $b_E = [E] + [ES] =$ const.*

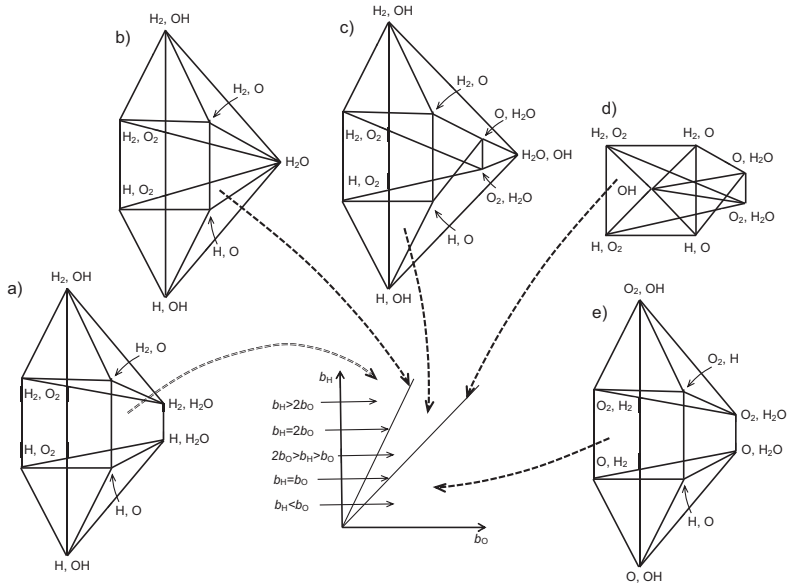

FIG. 3.2. *The graph $\widetilde{D_1}(b)$ of the one-skeleton of the balance polyhedron for the six-component system,* H_2, O_2, H, O, H_2O, OH, *as a piece-wise constant function of $b = (b_H, b_O)$. For each vertex the components are indicated which have non-zero concentrations at this vertex.*

(we delete elements M and M' from $\widetilde{L}_{k-1}$ and add a new element $M \cup M'$). The set $\mathcal{L}_i$ of connected components of $\widetilde{D_1} \setminus U_g$ for $g = a_i$ is $\widetilde{L}_{|E_i|}$.

The described algorithm gives us the sets of connected components of $\widetilde{D_1} \setminus U_g$ for all g and, therefore, we get the tree $\mathcal{T}$. The descent from the higher values of G allows us to avoid the solution of the computationally expensive problem of the calculation of the connected components of a graph.

4. Chemical kinetics: examples.

4.1. Skeletons of the balance polyhedra. In chemical kinetics, the variable N_i is the amount of the ith component in the system. The balance polyhedron D is described by the positivity conditions $N_i \geq 0$ and the balance conditions (1.1) $b_i(N) = \text{const}$ $(i = 1, \ldots, m)$. Under the isochoric (the constant volume) conditions, the concentrations c_i also satisfy the balance conditions and we can construct the

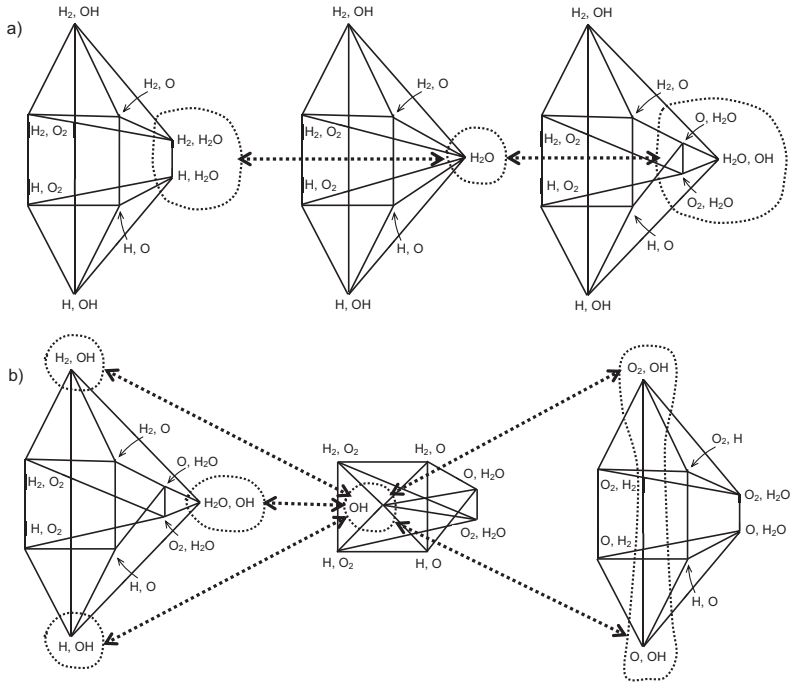

FIG. 4.1. *Transformations of the graph* $\widetilde{D_1}(b)$ *with changes of the relation between* b_{H} *and* b_{O}*: (a) transition from the regular case* $b_{\mathrm{H}} > 2b_{\mathrm{O}}$ *to the regular case* $2b_{\mathrm{O}} > b_{\mathrm{H}} > b_{\mathrm{O}}$ *through the singular case* $b_{\mathrm{H}} = 2b_{\mathrm{O}}$*, (b) transition from the regular case* $2b_{\mathrm{O}} > b_{\mathrm{H}} > b_{\mathrm{O}}$ *to the regular case* $b_{\mathrm{H}} < b_{\mathrm{O}}$ *through the singular case* $b_{\mathrm{H}} = b_{\mathrm{O}}$*.*

balance polyhedron for concentrations. Sometimes, the balance polyhedron is called the *reaction simplex* with some abuse of language because it is not obligatory a simplex when the number m of the independent balance conditions is greater than one.

The graph $\widetilde{D_1}$ depends on the values of the balance functionals $b_i = b_i(N) = \sum_{j=1}^{n} a_i^j N_j$. For the positive vectors N, the vectors b with coordinates $b_i = b_i(N)$ form a convex polyhedral cone in $\mathbb{R}^m$. Let us denote this cone by Λ. $\widetilde{D_1}(b)$ is a piecewise constant function on Λ. Sets with various values on this function are cones. They form a partition of Λ. Analysis of this partition and the corresponding values of $\widetilde{D_1}$ can be done by the tools of linear programming [20]. Let us represent several examples.

In the first example, the reaction system consists of four components: the substrate S, the enzyme E, the enzyme-substrate complex ES and the product P. we consider the system under constant volume. We denote the concentrations by $[S]$, $[E]$, $[ES]$ and $[P]$. There are two balance conditions: $b_S = [S] + [ES] + [P] = \mathrm{const}$ and $b_E = [E] + [ES] = \mathrm{const}$.

For $b_S > b_E$ the polyhedron (here the polygon) D is a trapezium (Fig. 3.1a). Each vertex corresponds to two components that have non-zero concentrations in this vertex. For $b_S > b_E$ there are four such pairs, (ES, P), (ES, S), $(E], P)$ and (E, S). For two pairs there are no vertices: for (S, P) the value b_E is zero and for (ES, E) it should be $b_S < b_E$. When $b_S = b_E$, two vertices, (ES, P) and (ES, S), transform into one vertex with one non-zero component, ES, an the polygon D becomes a triangle

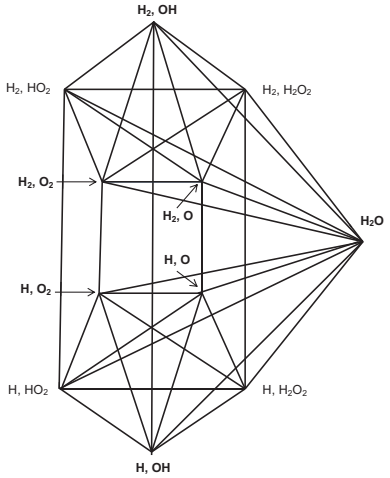

FIG. 4.2. *The graph* $\widetilde{D_1}$ *for the eight-component system,* H_2, O_2, H, O, H_2O, OH, H_2O_2, HO_2 *for the stoichiometric mixture,* $b_H = 2b_O$. *The vertices that correspond also to the six-component mixture are distinguished by bold font.*

(Fig. 3.1b). When $b_S < b_E$ then D is also a triangle and a vertex ES transforms in this case into (ES, E) (Fig. 3.1c).

For the second example, we select a system with six components and two balance conditions: H_2, O_2, H, O, H_2O, OH;

$$b_H = 2N_{H_2} + N_H + 2N_{H_2O} + N_{OH}\,,$$

$$b_O = 2N_{O_2} + N_O + N_{H_2O} + N_{OH}\,.$$

The cone Λ is a positive octant on the plane with the coordinates b_H, b_O. The graph $\widetilde{D_1}(b)$ is constant in the following cones in Λ ($b_H, b_O > 0$): (a) $b_H > 2b_O$, (b) $b_H = 2b_O$, (c) $2b_O > b_H > b_O$, (d) $b_H = b_O$ and (e) $b_H < b_O$ (Fig. 3.2).

The cases (a) $b_H > 2b_O$, (c) $2b_O > b_H > b_O$, and (e) $b_H < b_O$ (Fig. 3.2) are regular: there are two independent balance conditions and for each vertex there are exactly two components with non-zero concentration. In case (a) ($b_H > 2b_O$), if $b_H \to 2b_O$ then two regular vertices, H_2, H_2O and H, H_2O, join in one vertex (case (b)) with only one non-zero concentration, H_2O (Fig. 4.1a). This vertex explodes in three vertices O, H_2O; O_2, H_2O and H_2O, OH, when b_H becomes smaller than $2b_O$ (case (c), $2b_O > b_H > b_O$) (Fig. 4.1a).

Analogously, in the transition from the regular case (c) to the regular case (e) through the singular case (d) ($b_H = b_O$) three vertices join in one, 0H that explodes in two (Fig. 4.1b).

For the modeling of hydrogen combustion, the eight-component model is used usually: H_2, O_2, H, O, H_2O, OH, H_2O_2, HO_2. In Fig. 4.2 the graph $\widetilde{D_1}$ is presented for one particular relations between b_H and $2b_O$, $b_H = 2b_O$. This is the so-called "stoichiometric mixture" where proportion between b_H and $2b_O$ is the same as in the "product", H_2O.

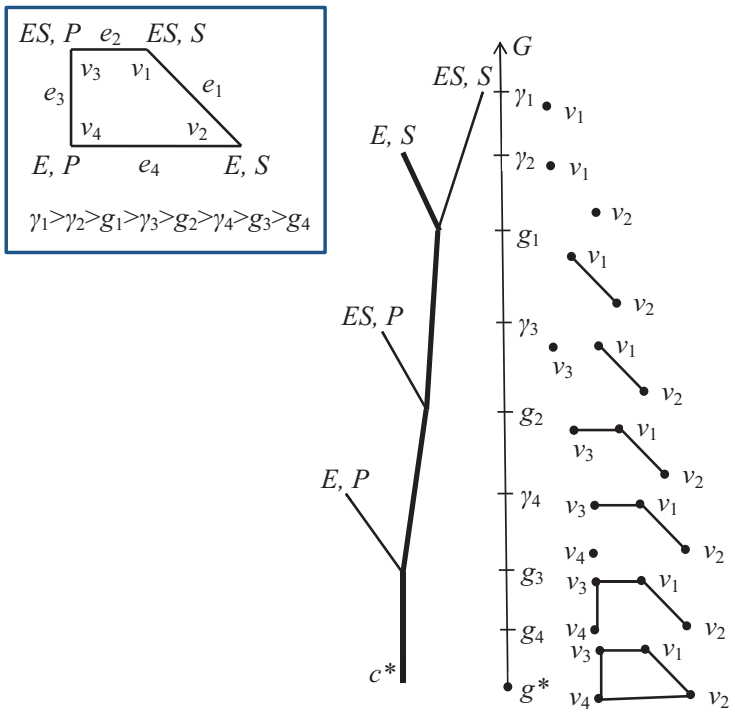

FIG. 4.3. *The thermodynamic tree for the four–component enzyme–substrate system S, E, ES P (Fig. 3.1) with excess of substrate: $b_S > b_E$ (case (a)). The vertices and edges are enumerated in order of γ_v and g_e (starting from the greatest values). The order of these numbers is represented in Fig. On the right, the graphs $\widetilde{D_1} \setminus U_g$ are depicted. The solid bold line on the tree is the thermodynamically admissible path from the initial state E, S (enzyme plus substrate) to the equilibrium.*

4.2. Examples of the thermodynamic tree. In this section, we represents two example of the thermodynamic tree. First, let us consider the trapezium (Fig. 3.1a). Let us select the order of numbers γ_v and g_e according to Fig. 4.3. The vertices and edges are enumerated in order of γ_v and g_e (starting from the greatest values). The tree is presented in Fig. 4.3.

On the right, the graphs $\widetilde{D_1} \setminus U_g$ are depicted for all intervals $(a_{i-1}, a_i]$. For $(\gamma_2, \gamma_1]$ it is just a vertex v_1. For $(g_1, \gamma_2]$ it consists of two disjoint vertices, v_1 and v_2. For $(\gamma_3, g_1]$ these two vertices are connected by an edge. On the interval $(g_2, \gamma_3]$ the graph $\widetilde{D_1} \setminus U_g$ is an edge (v_1, v_2) and an isolated vertex v_3. On $(\gamma_4, g_2]$ all three vertices v_1, v_2 and v_3 are connected by edges. For $(g_3, \gamma_4]$ the isolated vertex v_4 is added to the graph $\widetilde{D_1} \setminus U_g$. For $g \le g_3$ the graph $\widetilde{D_1} \setminus U_g$ includes all the vertices and is connected.

For the second example (Fig. 4.4) we selected the six-component system (Fig. 3.2) with the stoichiometric hydrogen–oxygen ratio, $b_{\mathrm{H}} = 2b_{\mathrm{O}}$. The selected order of numbers γ_i, g_j is presented in Fig. 4.4.

5. Conclusion. The thermodynamic tree is a tool to answer the question: is there a continuous path between two states, along which the conservation laws hold, the concentrations remain non-negative and the relevant thermodynamic potential G (Gibbs energy, for example) monotonically decreases? This question arises often in

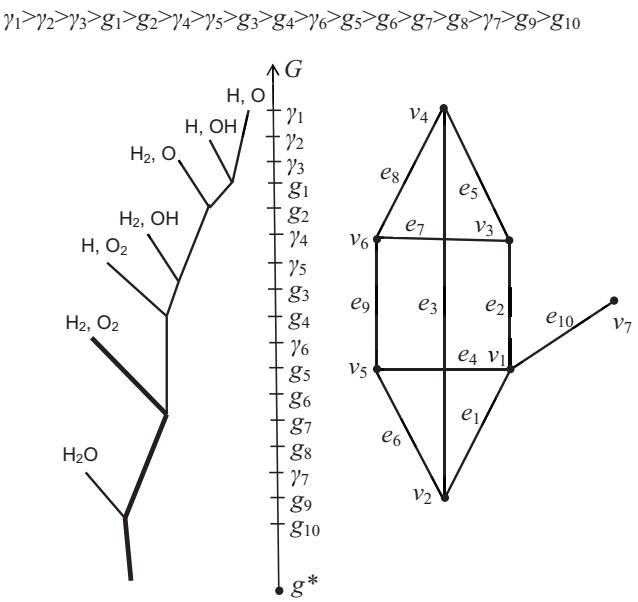

FIG. 4.4. *The thermodynamic tree for the six–component* H_2–O_2 *system,* H_2, O_2, H, O, H_2O, OH *with the stoichiometric hydrogen–oxygen ratio,* $b_H = 2b_O$ *(Fig. 3.2b). The order of numbers* γ_i, g_j *is presented in Fig. On the right, the graph* $\widetilde{D_1} \setminus U_g$ *is represented for* $g = g_{10}$. *For* $g \le g_{10}$, *the graph* $\widetilde{D_1} \setminus U_g$ *includes all the vertices and is connected. The solid bold line on the tree is the thermodynamically admissible path from the initial state* H_2, O_2 *to the equilibrium.*

non-equilibrium thermodynamics and kinetics.

In 1D systems, the space of states is an interval and the thermodynamic tree has two leaves (the ends of the interval) and one root (the equilibrium). In such a system, a spontaneous transition from a state x to a state y is allowed by thermodynamics if $G(x) \ge G(y)$ and x and y are on the same site of the equilibrium, i.e. they belong to the same branch of the thermodynamic tree. This is just a well known rule: "it is impossible to overstep the equilibrium in 1-dimensional systems".

The construction of the thermodynamic tree gives us the multidimensional analogue of this rule. Let $\pi : D \to \mathcal{T}$ be the natural projection of the balance polyhedron D on the thermodynamic tree $\mathcal{T}$. A spontaneous transition from a state x to a state y is allowed by thermodynamics if and only if

$$\pi(y) \in [\pi(N^*), \pi(x)]\,,$$

where N^* is the equilibrium and the closed segment $[\pi(N^*), \pi(x)]$ consists of all points that are between $\pi(N^*)$ and $\pi(x)$, and the ends, $\pi(N^*)$ and $\pi(x)$.

In this paper, we developed methods for solving the following problems:

1. How to construct the thermodynamic tree $\mathcal{T}$?
2. How to find an image $\pi(x)$ of a state $x \in D$ on the thermodynamic tree $\mathcal{T}$?
3. How to describe by inequalities a preimage of a segment of the thermodynamic tree, $\pi^{-1}([w, z]) \subset D$ $(w, z \in \mathcal{T})$?

For this purpose, we analyzed the cutting of a convex polyhedron by a convex set and developed the algorithm for construction of the tree of level sets of a convex function in a convex polyhedron. In this algorithm, the restriction of G onto the

1-skeleton of D is used. This finite family of convex functions of one variable includes all necessary information for analysis of the tree of the level sets of the convex function G of many variables.

Let us now formulate two more problems that also need to be solved:

- To find the maximal and the minimal value of any linear function f in a class of thermodynamic equivalence;
- To evaluate the maximum and the minimum of $\mathrm{d}G/\mathrm{d}t$ in any class of thermodynamic equivalence: $-\overline{\sigma} \le \mathrm{d}G/\mathrm{d}t \le -\underline{\sigma} \le 0$.

For any $w \in \mathcal{T}$, the solution of the first problem allows us to find an interval of values of any linear function of state in the corresponding class of thermodynamic equivalence. We can use the results of Sec. 2.2 to reformulate this problem as the convex programming problem.

The second problem gives us the possibility to consider dynamics of relaxation on $\mathcal{T}$. On each interval on $\mathcal{T}$ we can write

$$-\overline{\sigma}(g) \le \frac{\mathrm{d}g}{\mathrm{d}t} \le -\underline{\sigma}(g) \le 0\,, \tag{5.1}$$

where the functions $\overline{\sigma}(g), \underline{\sigma}(g) \ge 0$ depend on the interval on $\mathcal{T}$.

This differential inequality (5.1) will be a tool for the study of the dynamics of relaxation and may be considered as a reduced kinetic model that substitutes dynamics on the d-dimensional balance polyhedron D by dynamics on the one-dimensional dendrite.

The problem of the construction of the reduced model (5.1) is closely related to the following problem [53]: "Can one establish a lower bound on the entropy production, in terms of how much the distribution function departs from thermodynamical equilibrium?" In 1982, C. Cercignani [8] proposed a simple linear estimate for $\underline{\sigma}(g)$ for the Boltzmann equation (Cercignani's conjecture). After that, these estimates were studied and improved by many authors [10, 7, 52, 53] and now the state of art achieved for the Boltzmann equation gives us some hints how to create the relaxation model (5.1) on the thermodynamic tree for the general kinetic systems. This will be the next step in the study of the thermodynamic trees.

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