Elaboration of Attainability Region Boundaries in The Model of Extreme Intermediate States

Maxim Zarodnyuk, Alexandre Keiko, Boris Kaganovich

Melentiev Energy Systems Institute of SB RAS
130, Lermontov str., Irkutsk 664033 Russia
max@isem.sei.irk.ru, keiko@isem.sei.irk.ru, thermo@isem.sei.irk.ru

Abstract. A possible application of one-dimensional continuum (thermodynamic tree) in analysis of the model of extreme intermediate states (MEIS) with the constraints on macroscopic kinetics is studied. Properties of stage equilibrium manifolds corresponding to these constraints are revealed.

Keywords: equilibrium thermodynamics, the model of extreme intermediate states, macroscopic kinetic constraints, hierarchy in thermodynamic tree sense, stage equilibrium manifold.

1. Introduction

Non-equilibrium irreversible processes proceed in the majority of open physico-chemical systems. There is a possibility to describe such processes on the basis of equilibrium thermodynamics statements [KKS10]. The model of extreme intermediate states (MEIS) [GKF’06, KF95, KKS10] has been used to formulate and solve various physico-chemical problems at Melentiev Energy Systems Institute for over 25 years. As distinct from the traditional thermodynamic models MEIS is intended both for seeking the final equilibrium point, and to study the entire attainable region.

Recent researches have shown MEIS to be able to take into account such irreversible processes as chemical transformations, diffusion, heat...
exchange, etc. Nitrogen oxides formation in a gas turbine combustion chamber as well as modes of low-grade solid fuel gasification have been successfully analyzed using MEIS along with a number of minor problems. In these studies the imposed constraints on macroscopic kinetic lessen the attainable region and specify the sought partial equilibrium state.

The transformation of the graph of a balance polyhedron into a one-dimensional tree graph (a function tree, by V.I. Arnold and A.S. Kronrod [Arn58, Kro50]) with an account of the extreme values of thermodynamic characteristic function suggested by A.N. Gorban [Gor84] appears to be useful in analysis of MEIS. This transformation provides a method to precisely define the borders of thermodynamically attainable set conditioned by the second law of thermodynamics. However at the solution of real problems the transformation meets great difficulties because of huge number of vertices and edges. Besides, it is proved only for strictly convex characteristic thermodynamic functions [Gor84]. The possibility to reduce the variables space or to pass from the full polyhedron to its faces is physically clear as values of these functions are defined only by macroscopic variables. Ways to reduce the estimates of balance polyhedron size have been considered in [Zar01, Zar00] on the basis of the combinatory account of a balance relation matrix sparseness, redundant constraints on substances amount non-negativity, a relation between components in the initial state.

The present article is devoted to improving MEIS efficiency by introduction of macroscopic kinetic constraints with the help of a tree graph (a thermodynamic tree).

2. The equilibrium thermodynamics application in description of irreversible processes

A full enough substantiation of the equilibrium thermodynamics applicability in description of irreversible processes is done in [KKS10]. The continuity of the equilibrium approach in historical aspect is disclosed. Modern directions of research which the suggested approach competes with are indicated. Among them the interpretation of inter-relations between the equilibrium and the reversibility elucidated in
[Gor07, GK05] is the closest one by its content. The area of MEIS development may be attributed to the novel scientific direction referred like "Model Engineering".

The formal statement of the model of extreme intermediate states with constraints on chemical kinetics has the form:

\[ F(x) = c^T x \to \text{max}, \]

\[ Ax = b, \quad x \geq 0, \]

\[ x \in D_t(x^{\text{in}}) = \{ x : x^{\text{in}} \preceq x \}, \]

\[ \psi_i(x) - K_i^* \leq 0, \]

where \( c \) is a vector ranging usefulness or harmfulness of corresponding components of the composition vector \( x \); \( A \) is the \((m \times n)\) matrix of element contents in the system components, \( m \) – the number of material balances; \( b = Ax^{\text{in}} \); \( x^{\text{in}} \) – the vector of the initial composition (this is often the initial state of the vector \( x \)); \( D_t(x^{\text{in}}) \) – the region (the set) of thermodynamic attainability from \( x^{\text{in}} \); the sign "\( \preceq \)" (precedes or equivalent) in expression (3) is understood in the thermodynamic sense, i.e. \( x^1 \preceq x^2 \), if there is a continuous trajectory from a point \( x^1 \) to a point \( x^2 \), along which the characteristic function \( G(x) \) monotonously does not increase, \( \psi_i(x) \) – the function of a reaction products ratio whose form coincides with the one of the equilibrium constant, \( K_i^* \) – the equilibrium constant of \( i \)-th reaction. Here we consider Gibbs free energy \( G(x) \) as the thermodynamic characteristic function that takes for an ideal gas system at constant temperature \( T \) and pressure \( P \) the form:

\[ G(x) = \sum_{j=1}^{n} \left( G_j^0 + RT \ln \left( \frac{P x_j}{\sigma} \right) \right) x_j, \]
were $G^0_j$ is a mole energy of $j$-th substance, $R$ – the gas constant, $\sigma = \sum_{j=1}^{n} x_j$. For an ideal multiphase system the equation (5) takes the form:

$$
G(x) = \sum_{j=1}^{k_1} \left( G^0_j + RT \ln \left( \frac{P x_j}{\sigma_g} \right) \right) x_j + \sum_{j=k_1+1}^{k_2} G^0_j x_j + \sum_{j=k_2+1}^{n} \left( G^0_j + RT \ln \left( \frac{P x_j}{\sigma_s} \right) \right) x_j, 
$$

(6)

where $x_j$ is the substance amount at $j = 1, k_1$ in the gas phase, at $j = k_1 + 1, k_2$ – in pure condensed phase, and at $j = k_2 + 1, n$ – in a solution phase, $\sigma_g = \sum_{j=1}^{k_1} x_j$, $\sigma_s = \sum_{j=k_2+1}^{n} x_j$.

The solution of problems satisfying the model (1)–(4) is based on E.G.Antsiferov’s two-stage technique. At its first stage, the point $x^{\text{mat}}$ being the solution of linear programming problem (1)–(2), is searched. The point $x^{\text{mat}}$ corresponds to the state with maximum content of the desired system component determined by material balance constraints. On the second stage, the solution of the problem (1)–(3) $x^{\text{ext}}$ is searched at the border of the set (3). Recently the second stage is complemented with consideration of constrains (4) which lead to a reduction of the thermodynamic attainability region.

3. The thermodynamic three

In [Gor84, GKF+06] a short formal description of the exact algorithm of thermodynamic tree construction is given. This transformation is done in the following way. Assume we precisely know that $|D_1^*| = d$. Then to construct the tree $d$ values $\varepsilon_s = \min_{x \in D_1^*} G(x)$, $s = 1, d$ are to be found. They can be arranged into a numerical sequence $\varepsilon = \{\varepsilon_1, \varepsilon_2, ..., \varepsilon_d\}$ such that $\forall k = \overline{1, d} - 1, \varepsilon_k \leq \varepsilon_{k+1}$. The value $\varepsilon_0 = G(x^{e_0})$ is assigned the tree graph root. Nodes $\varepsilon_1, \varepsilon_2, ...$ are placed on "trunk", and open edges corresponding to them are excluded from the polyhedron graph until simple connectedness of $D_1$ is broken. If
there are equalities $\varepsilon_k = \varepsilon_{k+1} = \ldots = \varepsilon_{k+r}$ for any $r > 0$ (which is hardly possible in practice), then all these values are placed in a single node. The number of branches at a node is equal to the number of simply connected sets into which the $D$ polyhedron graph breaks up (the latter is usually two in practice). Since excluded edges are open, the situation when all of them are excluded about any vertex is also a violation of simple connectedness. In this case the branching stops. The end of last branch corresponds to value of function $G(x)$ in this node.

The fruitfulness of the tree concept in equilibrium thermodynamic modeling is illustrated on the example of hexane isomerization. It uses computation results for transformations of three isomers: n-hexane ($x_1$), 2-methylpentane ($x_2$) and 3-methylpentane ($x_3$) at $T = 600$ K and $P = 0.1$ MPa. A graphic interpretation of the problem is presented in fig. 1, a and b. The constructed tree (fig. 1b) substitutes the set $D(x^{in})$ and allows one to study the behavior of both the characteristic thermodynamic function (in this case Gibbs energy), and objective function $F(x)$. The admissible paths from the point $x^{in} = (1, 0, 0)$ to the points $x^{ext}_1$ and $x^{ext}_2$ are shown in fig. 1a and correspond to the paths 1–4 and 1–4–5 on the tree (fig. 1b). Transition from the point 4 to the point 3 as well as from

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**Fig. 1** The material balance polyhedron (a) and the thermodynamic tree (b) for hexane isomerization reactions. $T = 600$ K, $P = 0.1$ MPa

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the points 5 and 6 to point 2 is impossible due to a rise in Gibbs energy of the system. The points 4 and 5 reside at the levels of $G$ (isopotential surfaces: $G(x) = -424.118$ kJ/mole and $G(x) = -425.672$ kJ/mole) on which the extreme compositions $x^e_3$ and $x^e_2$ should be placed.

In order to reduce the size of a balance polyhedron one could apply the method of thermodynamic tree on partial edges [GKF+06, KKS10]. To explain it we need two more notions: 1) $D^{\text{gen}}$ – the edge of the least dimension containing $x^\text{in}$ and $x^\text{ext}$; 2) $d$ – the dimension chosen by the researcher as a reliable one. Then the formal description of the algorithm to construct a thermodynamic tree on partial edges is formulated as follows:

1) Find the edge $D^{\text{gen}}$ of the balance polyhedron.
2) If $|D^{\text{gen}}| \leq d$ then go to $\#4$.
3) If $|D^{\text{gen}}| > d$, direct algorithm is applied to the $D^{\text{gen}}$. The solution is ultimate.
4) Find all edges that include $D^{\text{gen}}$ and have dimension less than $p$.
5) The algorithm of full thermodynamic tree is applied to each of the edges from $\#4$.
6) Choose the maximum value $\varepsilon_k$ from those found. The algorithm stops.

In practice it turns out that when constructing the tree, values $\varepsilon_k$ are arranged in a special (hierarchical) manner. This property affects the thermodynamic tree in the following way. Consider the longest chain of arcs that is called a geodesic in some sources [Ore62]. It appears that all the arcs adjacent to it are incident to pendant vertices that are equivalent to points $D^0$. Thus, branching, at which the vertex is singled out from the polyhedron, occurs at the largest value of $e$ on the edges incident to it. Therefore, to determine the level of $G(x) = G^\text{ext}$ which $x^\text{ext}$ (solution to (1)–(2)) belongs to, it is sufficient to compare two values $\varepsilon^\text{in}$ and $\varepsilon^\text{mat}$ that are the maximum minima of $G(x) = G^\text{ext}$ at all edges incident to $x^\text{in}$ and $x^\text{mat}$, respectively. Then the sought value $G^\text{ext} = \varepsilon^\text{in}$, if $\varepsilon^\text{in} > \varepsilon^\text{mat}$, otherwise $G^\text{ext} = \varepsilon^\text{mat}$.

To explain the particular order of $\varepsilon_k$ we will need the following definition.
**Definition** Let us say that the extreme values $\varepsilon_k = \min_{x \in D_k^1} G(x)$ are arranged hierarchically in the sense of thermodynamic tree (function tree), if at each stage of branching the vertex and simply-connected region subset $D$ turn out to be disconnected.

Such an order in the sequence of extreme values of the thermodynamic characteristic function is uniquely established when studying the isomerization reactions in which simplex appears to be a balance polyhedron. To prove this fact the auxiliary Lemma and Proposition are presented below.

**Lemma** If $G(v_2) > G(v_3)$, then $\varepsilon_1 > \varepsilon_2$, where $\varepsilon_1 = \min_{x \in [v_1,v_2]} G(x), \varepsilon_2 = \min_{x \in [v_1,v_3]} G(x)$, and $v_1, v_2, v_3$, are any three vertices of an $n$-dimensional simplex $S$, $S = \{x : x_0 + \sum_{i=1}^{n} \alpha_i (x_i - x_0), \sum_{i=1}^{n} \alpha_i \geq 0, \alpha_i \leq 1\}$.

The proof of the Lemma is based either on the necessary condition of extremum for a fundamental solution to systems $x_1 + x_2 = b$ and $x_1 + x_3 = b$, or on the rule of Lagrange multipliers. From which we find

$$\begin{aligned}
\arg \min_{x \in [v_1,v_2]} G(x) &= \left( \frac{be^{-c_1^0}}{e^{-c_1^0} + e^{-c_2^0}}, \frac{be^{-c_2^0}}{e^{-c_1^0} + e^{-c_2^0}}, 0, \ldots \right),
\end{aligned}$$

and

$$\begin{aligned}
\arg \min_{x \in [v_1,v_3]} G(x) &= \left( \frac{be^{-c_1^0}}{e^{-c_1^0} + e^{-c_3^0}}, 0, \frac{be^{-c_3^0}}{e^{-c_1^0} + e^{-c_3^0}}, 0, \ldots \right).
\end{aligned}$$

Thus, it is easy to calculate extreme values of the thermodynamic function $G(x)$ of type (5) at these points. In terms of the Lemma condition they relate to one another as follows.
\[ \varepsilon_1 = RTb \ln \left( \frac{e^{G_0^1} e^{G_0^2}}{e^{G_0^1} + e^{G_0^2}} \right) > \varepsilon_2 = RTb \ln \left( \frac{e^{G_0^2} e^{G_0^3}}{e^{G_0^1} + e^{G_0^3}} \right). \]

In fig. 2 thermodynamic trees with the hierarchical located values \( \varepsilon \) are represented. Fat lines allocate the parts equivalent to states which are attainable of \( x^{in} \).

![Fig. 2. Thermodynamic trees with different relationships between \( \varepsilon^{in} \) and \( \varepsilon^{mat} \): a) \( \varepsilon^{mat} > \varepsilon^{in} \), b) \( \varepsilon^{in} > \varepsilon^{mat} \)]

**Proposition**

Values \( \varepsilon_k \) on the one-dimensional faces of simplex have a hierarchy in the sense of thermodynamic tree.

**Proof.** If to arrange the vertices of simplex in ascending order of value \( G(x) \) in them, it is obvious from the Lemma that the lowest value among all \( \varepsilon \) will be \( \varepsilon_1 = \min_{x \in [v_1, v_2]} G(x) \). Since all two-dimensional faces of the simplex are triangles, for each of them the relation \( \varepsilon_1 < \varepsilon_2 < \varepsilon_3 \) holds true, if \( G(v_1) < G(v_2) < G(v_3) \), and \( \varepsilon_1 = \min_{x \in [v_1, v_2]} G(x), \varepsilon_2 = \min_{x \in [v_2, v_3]} G(x) \), \( \varepsilon_3 = \min_{x \in [v_1, v_3]} G(x) \).
Since all vertices in the simplex are incident to one another, the value \( \varepsilon \) on any edge that contains \( v_1 \), will be lower than the values on all edges that contain vertex \( v_n \) (with the largest value of \( G(x) \)) and do not contain \( v_1 \). Thus, by excluding all edges with \( v_1 \) while constructing the tree, it is easy to see that connectedness between \( v_n \) and the rest of vertices will not be broken, i.e. the described hierarchy with regard to \( v_1 \) is observed. The same reasoning is applicable to the rest of vertices. The proposition is proved.

The notion of reversed algorithm appears to be important to construct a thermodynamic tree. Its formal description looks as follows.

1) The graph of a balance polyhedron \( D(x^{in}) \) is constructed.
2) The list of vertices \( D_0 = \{v_1, ..., v_l\} \) is made up.
3) The list of edges \( D_1 = \{D_1^1, ..., D_1^p\} \) is made up.
4) \( \varepsilon_k \) (minimum values of \( G(x) \) on edges), \( k = 1, p \) are computed.
5) Values \( \varepsilon_k \) are arranged in descending order.
6) For each \( \varepsilon_k \) we check whether the vertices connected by edge \( D_1^k \) to different components of linear connectivity, i.e. whether \( \varepsilon_k \) is a branching point.
7) If they belong, the branching point \( \varepsilon_k \) is connected with the nodes incidental by \( D_1^k \), or with the lowest \( \varepsilon \), that correspond to the components to be connected. These components are united into one.
8) We check whether there are disconnected components. If there are no disconnected components point \( x^{ext} \) is connected with the last \( \varepsilon_k \). The algorithm stops.
9) Point \( \varepsilon_k \) is connected with point \( \varepsilon \) that follows in descending order of values and transition to \#6 is made.

The considered above hierarchy was observed in the problems describing various physical-chemical processes and not only isomerization. These problems were solved by the authors using the thermodynamic tree. Existence of the hierarchy provides another advantage that lies in the fact that there is no need to construct the entire tree or its part. It is sufficient to calculate the values of \( G(x) \) on the edges which vertices \( x^{in} \) and \( x^{ext} \) belong to, and compare them.
4. Constraints on macroscopic kinetics

To describe additional thermodynamic constraints on chemical kinetics let us consider such notion as the stage equilibrium manifold (SEM) for ideal physico-chemical systems. In monograph [Gor84] it is defined as a geometrical object in the space of compositions that represents the boundary between the regions where the direct and inverse reactions proceed. Such a manifold should obviously pass through the equilibrium point \( x^m \). In other words condition \( \phi(x^m) = 0 \) should be satisfied, if \( \phi(x) = 0 \) is the SEM equation.

The SEM equations are derived by using Lagrange multipliers rule. The form of Lagrange function is \( L(x, \lambda) = G(x) + \langle b - Ax, \lambda \rangle \); \( \lambda_0 = 1 \), since \( G(x) \) is strictly convex; the inequality constraints are inactive, since \( x^m \in \text{ri} D \), \( \text{ri} D = \{ x : x \notin \partial D \} \) is a relative interior of set \( D \). Differentiation of Lagrange function with respect to \( x \) results in a system of algebraic equations:

\[
\nabla G(x) = A^T \lambda, \tag{7}
\]

where \( A^T \) is the transposed matrix of the material balance. It is important that components \( \nabla G(x) \) have the form \( \frac{\partial G}{\partial x_j} = \frac{G^0_j}{\sigma_j} + RT \ln x_j - RT \ln \sigma \), and the left-hand sides of (7) form a column vector that describes an elemental composition of their associated substances in the initial list. Since the rows of matrix \( A^T \) represent shares of chemical elements in the composition of reagents, then for any reaction of the type

\[
\nu_i^+ A_i = \nu_i^- A_i, \tag{8}
\]

where \( \nu_i^+ \) and \( \nu_i^- \) – the vectors of stoichiometric coefficients of the initial reagents and products of \( i \)-th reaction, respectively, the following relation is fulfilled

\[
\nu_i^+ A^T \lambda = \nu_i^- A^T \lambda.
\]
For the elementary reactions $\nu_{ij} = 1$, if the substance participates in some reaction and $\nu_{ij} = 0$, if it does not participate in it. Based on equation (7) for reaction (8) the equilibrium constants can be calculated via their speeds and the substance amounts in the equilibrium state. Then the stage equilibrium manifold is expressed like

$$\frac{\prod_{j=1}^{n} x_j^{\nu_{ij}^+} \sigma_{\nu_{ij}^-}}{\prod_{j=1}^{n} x_j^{\nu_{ij}^-} \sigma_{\nu_{ij}^+}} = K_i^*.$$  

(9)

As a rule, for the detailed study of physicochemical processes the elementary reactions are analyzed in detail. It is possible to separate four basically different types of such reactions: 1) isomerization, 2) exchange, 3) connection, 4) dissociation.

Chemical equations for theses reactions are as follows:

$$A_1 = A_2;$$  

(10)

$$A_1 + A_2 = A_3 + A_4;$$  

(11)

$$A_1 + A_2 (+M) = A_3 (+M);$$  

(12)

$$A_1 (+M) = A_2 + A_2 (+M)$$  

(13)

respectively. The stage equilibrium manifolds for each type are specified by the expressions

$$x_2 - K^* x_1 = 0,$$  

(14)

$$x_3 x_4 - K^* x_1 x_2 = 0,$$  

(15)
\[ x_3 \sigma - K^* x_1 x_2 = 0, \quad (16) \]

\[ x_2^2 - K^* x_1 \sigma = 0. \quad (17) \]

For the first type of elementary reactions SEM is obviously linear and it is quadratic for the rest of them.

Fig. 3 presents the curves of stage equilibrium for the reaction of carbon monoxide combustion in oxygen. Three types of reactions are observed: (11)–(13). Expression \( \text{CO} + \text{O}_2 \) corresponds to the type of reaction (11), \( \text{CO} + \text{O} + \text{M} = \text{CO}_2 + \text{M} \) – to the type of reaction (12) and \( \text{O}_2 + \text{M} = \text{O} + \text{O} + \text{M} \) – to the type of reaction (13). It is noteworthy that only the dissociation reaction proceeds on the edges with the zero contents of \( \text{CO}_2 \) and \( \text{CO} \).

![Diagram](image)

**Fig. 3.** The polyhedron of the material balance and the curves of stage equilibriums (a), the thermodynamic tree (b) for the reaction of carbon monoxide combustion in oxygen

For the systems with characteristic functions of type (6) without the last sum SEMs have some specific features. First, These functions can be both strictly and not strictly convex. These properties determine whether \( x^{m_1} \) is a relatively interior point. And second, for the substances
in the condensed phase $\frac{\partial G}{\partial x_j} = G^0_j$, therefore, the following effect takes place. In system (7) of Lagrange function for these substances

$$G^0_j = a_j^T \lambda,$$

expressions (15)–(17) do not depend, therefore, on their amount. A simple technique can be suggested for replacing the corresponding components of vector $x$ in these expressions. It is enough to put unities or even more correct, to insert zeros instead of their stoichiometric coefficients in (15)–(17) instead of them, since multipliers $\sigma$ for them are also absent. It should be noted that the SEM properties for the reactions with participation of condensed substances change in accordance with the described above features. For example, if in (11) one of the pairs: $(A_1, A_3), (A_1, A_4), (A_2, A_3), (A_2, A_4)$ is a condensed substance, then (15) becomes linear. The same is observed in (16), if one of the substances: $A_1$ or $A_2$ is condensed.

For physicochemical systems with thermodynamic characteristic functions (6) it is also possible to derive MES equations. In this case the properties of (15)–(17) can vary considerably, their degree can rise to four.

SEM can also be obtained for more complex reactions than elementary ones. Such their properties as the convexity directions will be quite different. It is safe to say solely about the polynomial structure of these manifolds.

**5. Conclusion**

The idea of the tree has proved to be effective for searching $G(x^{ext})$ and refining solutions by MEIS as a whole. Joint application of MEIS and constraints on microscopic kinetics provides further essential increase in accuracy of determination of $x^{ext}$. Surely, widespread application of the idea of the tree calls for further extensive studies, primarily on solving non-convex problems for the analysis of irreversible processes.
It is planned to interpret different MEIS modifications on the basis of the described ideas [KKS10] and apply the idea of constructing a thermodynamic tree to them. It is necessary to generalize the presented statement for the polyhedrons other than simplexes. It is intended to analyze and develop new algorithms aimed to take into consideration kinetic constraints by using the thermodynamic tree.

Acknowledgements

This work was supported by Russian Foundation of Basic Research (grant No. 09-08-00245).

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