Thermodynamic theory of kinetic overshoots

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Abstract

Everything that is not prohibited is permissible. So, what is prohibited in the course of chemical
reactions, heat transfer and other dissipative processes? Is it possible to “overshoot” the equilibrium,
and if yes, then how far? Thermodynamically allowed and prohibited trajectories of processes are
discussed by the example of effects of equilibrium encircling. The complete theory of thermodynami-
cally accessible states is presented. The space of all thermodynamically admissible paths is presented
by projection on the “thermodynamic tree”, that is the tree of the related thermodynamic potential
(entropy, free energy, free enthalpy) in the balance polyhedron. The stationary states and limit points
for open systems are localized too.

1 Introduction

In the beginning was $A$, the chemical reagent $A$, 100% of $A$ in a closed vessel. Then $A$ began to transform
in $B$. The substance $B$ transforms in $A$, as well as $A$ transforms in $B$. The conditions are stationary; the
reactions rates are proportional to concentrations. The system goes to equilibrium. Let the concentration
of $A$ and $B$ be equal at this equilibrium (simply for definiteness). One could ask a question: Is it possible
that the amount of $B$ exceed 50% during the way to equilibrium? The answer is obvious: it is impossible.
When concentration of $B$ reaches 50%, the motion stops, because it is equilibrium state. The system
is one-dimensional, and one coordinate (for example, the concentration of $A$) describes the state of the
system in full (for fixed external conditions, for example for fixed volume and temperature). On the line
it is impossible to walk round the equilibrium.

The answer changes, if in the system a third reagent $C$ is present: The equilibrium encircling is
possible if the dimension is more than 1. The second question arises immediately: how far is it possible
to walk around the equilibrium? Is it possible to reach 100% or 90% of $B$? How far the system can go
along the thermodynamically admissible paths, that are the continuous curves, which satisfy the balances
(conservation lows) and the second law (the entropy of isolated system should grow monotonically, i.e. the
related thermodynamic potential of our system should change monotonically, in proper direction). Let
the equilibrium concentrations of $A$, $B$, and $C$ be equal, all these reagents can transform to each other,
and the system is thermodynamically perfect. In this case, on thermodynamically admissible paths the
concentration of $B$ cannot exceed the upper boundary $b_{\text{max}} \approx 77.3\%$ on the way from the state $A = 100\%$
to equilibrium. This global thermodynamic estimation follows from the local condition (the balances
and the second law) and from the continuity of thermodynamically admissible paths.

The questions about global thermodynamical restrictions for kinetic behavior arose several times
[1, 2, 3, 4, 5, 6]. The interest to this problem revives again and again (see, for example, [7, 8]) because
thermodynamic data are much more reliable than kinetic constants, and it is important to extract all the
possible information about dynamic behavior from thermodynamics, both from the practical (industrial)
and the scientific points of view.

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The goal of our talk is to analyze the main theoretical construction that allow to solve the problem of global thermodynamical restrictions on the system dynamics in an explicit form. It is the problem of integration of special differential inclusions: the time derivatives comply with the thermodynamic inequalities and balance equalities at each state, and the whole motion satisfy some global restrictions. It appears that the thermodynamic conditions allow the explicit integration.

2 Thermodynamic tree

Let us consider the chemical system dynamics in the composition space. Coordinates in this space are amounts of reagents. For systems with constant volume we can use the concentration space. The linear conservation laws together with the positivity conditions define a convex polyhedron $D$ in the composition space. For chemical reaction under given condition there exists a thermodynamic Lyapunov function. The function $G$ is assumed to be continuous and strictly convex in $B$. This assumption is crucial, because for non-convex function $G$ computation difficulties of thermodynamic analysis increase drastically. The global minimum of $G$ in $D$ belongs to interior $G$. It is the equilibrium point.

Thermodynamically admissible path is such a continuous function $\varphi : [0,1] \to D$ that the function $G(\varphi(x))$ monotonically decrease (non-increase) on $[0,1]$. The state $y \in D$ is thermodynamically accessible from the state $x \in D$ ($x \succ y$), if there exists such a thermodynamically admissible path $\varphi$ that $\varphi(0) = x$ and $\varphi(1) = y$. The states $x, y \in D$ are thermodynamically equivalent ($x \sim y$), if $x \succ y$ and $y \succ x$. In order to study the structure the thermodynamic accessibility let us glue the thermodynamically equivalent states: Thermodynamic tree is the factor-space $D/\sim$. This space is a one-dimensional continuum with finite number of branching points, that is the tree. The function $G$ is constant on the classes of thermodynamic equivalence, hence, we can define $G$ on $D/\sim$. Similarly, the thermodynamic order $\succ$ can be defined on $D/\sim$, and $y$ is thermodynamically accessible from $x$ if and only if for their images on the thermodynamic tree $(x/\sim) \succ (y/\sim)$. The set of all states thermodynamically accessible from the given $x \in D$ is the preimage in $D$ of the monotone path going on the thermodynamic tree from the point $x/\sim$ to the equilibrium.

3 How to construct the thermodynamic tree?

In this section we consider three main computational problems:

1. How to construct the thermodynamic tree for given $D$ and $G$.

2. How to find the image of the given state $x \in D$ on the thermodynamic tree.

3. How to find maximum of linear function on a class of thermodynamically equivalent states, that is, on the preimage in $D$ of the point from the thermodynamic tree, and on the preimage of a monotone path.

The solution of the third problem gives us the thermodynamically admissible extremal values of various characteristics on the way to equilibrium. After solution of the first two problems this problem turns to the standard problem of optimization: to find a maximum of a linear function on a convex set.

Let $D_1$ be the one-skeleton of $D$, that is the union of all edges of $D$ (including the vertexes). For each $a$ ($\min_{x \in D} G(x) < a < \max_{x \in D} G(x)$) there is one-to-one correspondence between connected components of sets $\{x \in D_1 | G(x) > a\}$ and $\{z \in D/\sim | G(z) > a\}$. A connected component of $\{x \in D_1 | G(x) > a\}$ maps by the natural projection $D \to D/\sim$ onto correspondent connected component of $\{z \in D/\sim | G(z) > a\}$. Hence, for convex functions $G$ the solution of the first problem depends only on two sets of numbers: the values of $G$ in vertexes, and minimal values of $G$ on edges of $D$.

For solution of the second problem, it is sufficient to find such a vertex $v$ that $v \succ x$. In this case the correspondent thermodynamically admissible path can be chosen as a segment of a straight line. For each vertex $v$ and the number $a$ ($\min_{x \in D} G(x) < a < G(v)$) the following two conditions, $v \succ x$ and $G(x) = a$, define the point on the thermodynamic tree uniquely.
4 Localization of stationary states

Thermodynamics allows us to localize the domain in the concentration space where the stationary states for open system can appear. This estimation is rather simple: in this region the external flow should produce \( G \), whereas the intrinsic dynamics decrease \( G \). Let the kinetic equation have the form

\[
\dot{N} = V \dot{w}(c) + v_{\text{in}} c_{\text{in}} - v_{\text{out}} c,
\]

where \( N \) is composition vector, \( c \) is vector of concentrations, \( V \) is the system volume, \( \dot{w} \) describes all the intrinsic processes, \( v_{\text{in}} \) and \( v_{\text{out}} \) are input and output velocities, and \( c_{\text{in}} \) is input vector of concentrations. The point \( c \) might be a stationary point of the open system only in the case when the following inequality is true:

\[
\left( \frac{v_{\text{in}}}{v_{\text{out}}} c_{\text{in}} - c, \nabla G(c) \right) \geq 0,
\]

where \( ( \ , \ ) \) is the standard scalar product.

Is it possible to localize the possible general limit points too [1]. The available information about stoichiometric reaction mechanism can be used for refinement of these estimations.

5 Discussion

As it is well known, the traditional thermodynamic analysis gives many possibilities to analyze the complex chemical process without knowing a kinetic model:

- to find the allowed direction of the chemical process;
- to calculate the equilibrium composition of the complex reaction mixture;
- to apply relationships between parameters of the complex chemical reaction.

The strong advantage of the traditional approach is its simplicity and reliability of data, which it is based on. At the same time, it has the obvious limitation. Using this approach it is impossible to estimate the dynamic of the complex chemical process “beyond the equilibrium”.

In difference from the traditional approach, the advanced thermodynamical analysis of kinetics (let us call it “TAK”) allows to make the further significant step in analysis with no kinetic model. Using TAK, it became possible to estimate an efficiency (selectivity, yield) for the complex chemical reaction “far from equilibrium”, i.e. under non-steady-state conditions in the closed system or under steady-state conditions (or in more complicated attractor regime) in the open system.

Many toy and not only toy example are presented now in [1, 2, 3, 4]. Using TAK, the following problems can be solved:

1. Knowing the initial composition of the complex mixture, to estimate the characteristics of the process “far from equilibrium” and answer the question, is it possible to achieve the desired values of process characteristics.
2. Assuming the desired characteristics of the process, to estimate the corresponding domain of the initial composition.

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