Thermodynamics in the limit of irreversible reactions

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A B S T R A C T

For many complex real physicochemical systems, the detailed mechanism includes both reversible and irreversible reactions. Such systems are typical in homogeneous combustion and heterogeneous catalytic oxidation. Most complex enzyme reactions include irreversible steps. Classical thermodynamics has no limit for irreversible reactions, whereas kinetic equations may have such a limit. We represent systems with irreversible reactions as the limits of fully reversible systems when some of the equilibrium concentrations tend to zero. The structure of the limit reaction system crucially depends on the relative rates of this tendency to zero. We study the dynamics of the limit system and describe its limit behavior as $t \to \infty$. If the reversible systems obey the principle of detailed balance then the limit system with some irreversible reactions must satisfy the *extended principle of detailed balance*. It is formulated and proven in the form of two conditions: (i) the reversible part satisfies the principle of detailed balance and (ii) the convex hull of the stoichiometric vectors of the irreversible reactions does not intersect the linear span of the stoichiometric vectors of the reversible reactions. These conditions imply the existence of the global Lyapunov functionals and allow an algebraic description of the limit behavior. Thermodynamic theory of the irreversible limit of reversible reactions is illustrated by the analysis of hydrogen combustion.
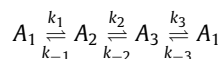
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1. Introduction

1.1. The problem: non-existence of thermodynamic functions in the limit of irreversible reactions

We consider a homogeneous chemical system with n components A_i. The concentration of A_i is $c_i \geq 0$, the amount of A_i in the system is $N_i \geq 0$, V is the volume, $N_i = Vc_i$, and T is the temperature. The n-dimensional vectors $c = (c_i)$ and $N = (N_i)$ belong to the closed positive orthant $\mathbb{R}_+^n$ in $\mathbb{R}^n$. ($\mathbb{R}_+^n$ is the set of all vectors $x \in \mathbb{R}^n$ such that $x_i \geq 0$ for all i.)

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

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

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

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

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

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

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

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

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

$$A_1 \xrightarrow{k_1} A_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_3 \underset{k_{-3}}{\leftarrow} A_1.$$
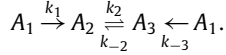
It is a routine task to write a first-order kinetic equation for this scheme. At the same time, the free energy function F has no limit: it tends to ∞ for any positive vector of concentrations because the term $c_1 \ln(c_1/c_1^{eq})$ increases to ∞. The free energy cannot be normalized by adding a constant term because the variation of the term $c_1 \ln(c_1/c_1^{eq})$ on an interval $[0, \bar{c}]$ with fixed $\bar{c}$ also increases to ∞; it varies from $-c_1^{eq}/e$ (for the minimizer $c_1 = c_1^{eq}/e$) to a large number $\bar{c}(\ln \bar{c} - \ln c_1^{eq})$ (for $c_1 = \bar{c}$).

The logarithmic singularity is rather "soft" and does not cause a real physical problem, because even for $c_1^{eq}/c_1 = 10^{-10}$ the corresponding large term in the free energy will be just $\sim 23RT$ per mole. Nevertheless, the absence of the limit causes some mathematical questions. For example, the density

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

is a Lyapunov function for a system of chemical kinetics for a perfect mixture with detailed balance under isochoric isothermal conditions. Here, c_i is the concentration of the ith component and c_i^{eq} is its equilibrium concentration for a selected value of the linear conservation laws, the so-called reference equilibrium.

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

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

The thermodynamic potential of a component A_i cannot be defined in the irreversible limit when the equilibrium concentration of A_i tends to 0. Nevertheless, here we construct universal Lyapunov functions for systems with some irreversible reactions. Instead of detailed balance, we use the weaker assumption that these systems can be obtained from systems with detailed balance when some constants tend to zero.

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

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

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

where $\alpha_{ri} \geq 0$ and $\beta_{rj} \geq 0$ are the stoichiometric coefficients. The reverse reactions with positive rate constants are included in (2) separately (if they exist). The stoichiometric vector γ_r of the elementary reaction is $\gamma_r = (\gamma_{ri})$, $\gamma_{ri} = \beta_{ri} - \alpha_{ri}$. We always assume that there exists a strictly positive conservation law, a vector $b = (b_i)$, $b_i > 0$ and $\sum_i b_i \gamma_{ri} = 0$ for all r. This may be the conservation of mass or of the total number of atoms, for example.

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

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

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

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

Here, μ_i is the chemical potential and μ_i^0 is the standard chemical potential of component A_i.