



Phenomenon of persistent equilibrium in some diffusion and reaction systems

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Abstract

A new phenomenon in the dynamic behavior of diffusion and reaction systems, persistent equilibrium, is presented. In accordance with this phenomenon, for the batch reactor the equilibrium concentration of some substance is persistent during the whole transition isothermal process in which other concentrations are changing. It is shown for acyclic linear mechanism with equal kinetic parameters. The persistent concentration is neither the abundant concentration, nor the asymptotic value. Also, for the one-dimensional diffusional case it is shown that persistent equilibrium is maintained at the middle of the reactor.

Keywords Kinetic model · Persistent equilibrium · Hybrid regime · Conservatively perturbed equilibrium

Introduction

In chemical engineering, typical diffusion and reaction systems are characterized by two types of observed regimes, i.e. non-steady-state and steady-state [1–3], in which temporal values of concentrations are changing and constant, respectively. Generally, the steady-state regime is obtained as the final regime of the non-steady-state one. For simplicity, we don't touch the problem of multiple and unstable steady state regimes here.

There are special cases of non-steady state behavior:

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- (a) The quasi-steady state/quasi-equilibrium regime, in which the *ratio of concentrations is approximately constant* in a certain domain of parameters and times.
- (b) Oscillations, regular or irregular, e.g., chaotic ones, in which the system characteristics such as concentrations are repeated in time, reproducing temporal behavior.

The main result announced in this paper is the following: in diffusion-and reaction systems under isothermal conditions it is possible to observe a *hybrid regime*, i.e. the co-existence of both the steady-state and non-steady-state regimes. It means that some concentrations are changing during the reaction, while other concentrations (at least one) are persistent. In our text, the meaning of a ‘persistent characteristic’ is the following one: it is a characteristic, which is constant during the transition process, from the very beginning to the final state. The ‘persistent’ concentration is neither the approximate characteristic, nor the abundant concentration, nor the asymptotic value which is achieved as the result of the fast reaction. It is the equilibrium concentration taken as the initial concentration for some substances for the batch reactor and the initial concentration at the center of the one-dimensional diffusional reactor. Examples of such behavior will be presented, and the possible reasons of the phenomenon will be discussed. Generally, we consider the *persistent equilibrium* as a new phenomenon in the dynamic behavior of diffusion and reaction systems.

Persistent equilibrium in diffusion systems

The system considered is closed and only the diffusion process occurs. In a closed one-dimensional chamber with a volume V , N molecules are placed, and the equilibrium concentration $C_{eq} = (N/V)$ is achieved after a while.

Consider the following virtual experiment: the initial local concentration at the middle of the chamber is set to the equilibrium concentration $C_{eq} = (N/V)$, and otherwise it is spatially antisymmetric around this value. We prove that this middle concentration will remain constant during the whole relaxation process. It will be the essential feature of the new phenomenon, the *persistent equilibrium*.

We denote by $C(x, t)$ the solution of the linear diffusion problem $C_t = C_{xx}$ over $0 \leq x \leq L$, with closed boundary conditions $C_x = 0$ at $x = 0$ and $x = L$, and initial condition $C(x, 0) = C_0(x)$, which is supposed to be antisymmetric, so that $(C_0(x) + C_0(L - x))/2 = C_{eq}$. Then $C(L - x, t)$ is the solution to the same problem for $C_0(L - x)$, and in view of linearity, $(C(x, t) + C(L - x, t))/2$ is the solution to the same problem for $C(x, 0) = C_{eq}$. But this is C_{eq} always and everywhere. Consequently, $\frac{C(x,t) + C(L-x,t)}{2} = C_{eq}$, and for $x = L/2$, $C\left(\frac{L}{2}, t\right) = C_{eq}$ remains constant over time.

Persistent equilibrium in complex chemical reactions. Examples.

Such behavior is achievable under combination of different factors:

1. Equal kinetic coefficients
2. Special initial concentrations for some substance(s). i.e. the equilibrium ones.
3. Special mechanism of complex reaction.

Equal kinetic coefficients

An assumption on equal kinetic parameters is chosen as the *first constituent* of the kinetic model with persistent behavior. In the paper [4], kinetic models with equal kinetic parameters are distinguished and termed as the egalitarian ones.

Special initial conditions and conservatively perturbed equilibrium

The phenomenon of conservatively perturbed equilibrium (CPE) recently described theoretically [5–7] and justified experimentally [8] is chosen as the *second constituent* for the occurrence of a ‘hybrid’ regime.

In the CPE-phenomenon, some, but not all, the initial concentrations of the closed chemical system are set to the corresponding equilibrium concentrations for the same total amount of each chemical element. The system temperature is constant as well.

The main feature of the CPE phenomenon is the following: for a substance which initial concentration is taken as the equilibrium one, the extremum of concentration on the way to the final equilibrium is inevitable. The value of the transient CPE-extremum can represent important information about the detailed mechanism and kinetic parameters. This information on the CPE-phenomenon can be used for finding the optimal operating conditions of complex reversible chemical transformations [7].

The special mechanism of complex reaction

The goal of this paper is to present the simplest kinetic model which reproduces the *persistent equilibrium* as a new phenomenon in dynamic behavior of complex chemical reactions. The studied model will be linear. As mentioned, all kinetic parameters will be considered equal, i.e. they belong to the class of ‘egalitarian’ models.

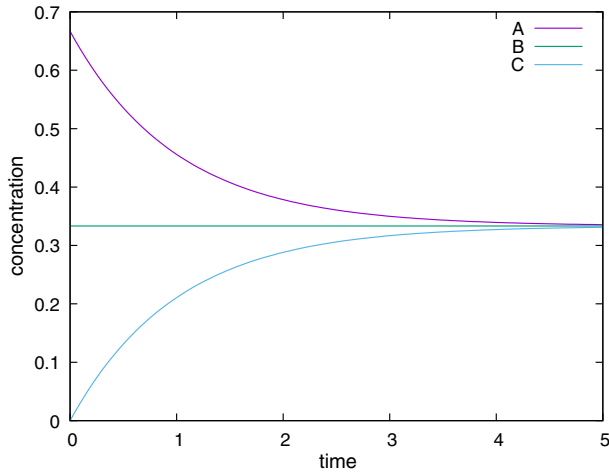


Fig. 1 Three-substance acyclic mechanism

Results

Three-substance acyclic mechanism

Three-substance acyclic mechanism is shown in Fig. 1.

In accordance with the mass-action law, for a batch reactor the kinetic model is expressed as follows:

$$\begin{aligned}\frac{dC_A}{d\tau} &= -k_1^+ C_A + k_1^- C_B; \\ \frac{dC_B}{d\tau} &= k_1^+ C_A - k_1^- C_B - k_2^+ C_B + k_2^- C_C; \\ \frac{dC_C}{d\tau} &= k_2^+ C_B - k_2^- C_C;\end{aligned}\quad (2)$$

Here C_A , C_B , C_C are the concentrations of substances A, B, and C, respectively; τ is residence time. k_1^+ , k_1^- , k_2^+ , k_2^- are the kinetic parameters of the correspondent forward and reverse reactions.

Obviously,

$$C_A + C_B + C_C = C_{A,0} + C_{B,0} + C_{C,0} = 1(\text{dimensionless}), \quad (3)$$

Here $C_{A,0}$, $C_{B,0}$ and $C_{C,0}$ are the initial concentrations of substances A, B, C, respectively. Under assumptions that all kinetic parameters are equal, this kinetic model is transformed into

$$\frac{dC_A}{dt} = -C_A + C_B$$

$$\frac{dC_B}{dt} = C_A - 2C_B + C_C$$

$$\frac{dC_C}{dt} = C_B - C_C$$

Clearly, all equilibrium constants are equal to 1, and all equilibrium concentrations are equal: $C_{A,eq} = C_{B,eq} = C_{C,eq} = 1/3$.

Since $C_A + C_B + C_C = 1$, and $C_A + C_C = 1 - C_B$, the differential equation for C_B is

$$\frac{dC_B}{dt} = 1 - 3C_B$$

The general solution is $C_A(t) = W_1 - W_3e^{-t} + W_2e^{-3t}$, $C_B(t) = W_1 - 2W_2e^{-3t}$, $C_C(t) = W_1 + W_3e^{-t} + W_2e^{-3t}$, where W_1, W_2, W_3 are coefficients which depend on the initial conditions.

Let us start the transient experiment for the following initial conditions: $C_{B,0} = C_{B,eq} = 1/3$ (i.e. substance B is starting at the equilibrium concentration); $C_{A,eq} = 2/3$; $C_{C,eq} = 0$.

In definition with the described terminology, it will be a CPE-experiment.

The analytical solution with these initial conditions can be presented as follows: $C_A = \frac{1}{3} + \frac{1}{3}e^{-t}$, $C_B(t) = \frac{1}{3}$, $C_C(t) = \frac{1}{3} - \frac{1}{3}e^{-t}$.

This solution indicates that the C_B is constant at $1/3$, which is also the equilibrium concentration for every substance, and, consequently, the rate of change of C_B is 0 from the very beginning to the very end of the transient regime.

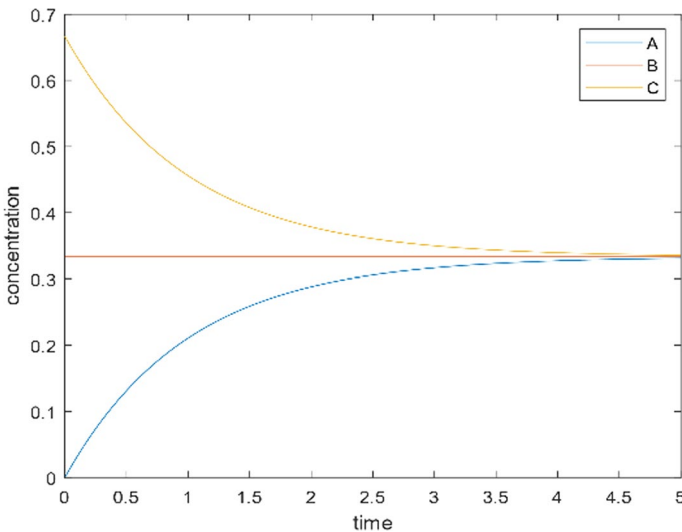


Fig. 2 Three-Substance Acyclic Mechanism, Initial concentration of substance B is equal to its equilibrium concentration

As shown in Fig. 2, the “middle” substance B displays the concentration constancy from $t=0$ to $t=\infty$.

As mentioned, this constancy is caused by the combination of three factors: 1). All kinetic parameters are equal; 2). The assumed mechanism of first order reactions ($A=B=C$) is symmetrical regarding the substance B 3). The initial concentration of substance B is assumed to be ‘unperturbed’, i.e. equal to the equilibrium concentration.

Consequently, at any moment of time the rate of B-production is compensated by the rate of B-consumption.

At any moment of time the rate of reaction $A=B$ is equal to the rate of reaction $B=C$.

It is a physico-chemical reason of persistent behavior of B-concentration. It should be stressed that this constancy is not a result of the classical equilibrium of steps 1 and 2. In both steps, the forward rate is not equal to the reverse rate. Also, it is not the approximate quasi-steady-state behavior.

In this case, both substances A and C are characterized by non-steady-state behavior accompanied by the persistent behavior of substance B. This is an essential feature of the desired ‘hybrid’ regime in which non-steady-state behavior of some substances co-exists with steady-state behavior of another substance.

Summary

The simplest examples of a ‘hybrid’ regime were found in which non-steady-state and persistent behaviour co-exist in the same isothermal experiment, both for one-dimensional diffusion and for acyclic linear mechanism with three substances and equal kinetic parameters.

This could suggest a wide exploration for studying possible persistent behavior in different areas, including neuron networks, electrical systems, or social/economical systems. We are going to study more complex diffusion–reaction systems for detailed analysis of this interesting phenomenon.

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