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# Predicting kinetic dependences and closing the balance: Wei and Prater revisited

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## HIGHLIGHTS

- The first-order reaction kinetic operator is symmetric in the entropic inner product.
- Using this symmetry and balance relations, kinetic dependences can be predicted.
- Prediction is only possible for suitable basis choices among the trajectories.
- A test for completeness of a reaction scheme is proposed.
- This is illustrated using the classical reaction schemes in Wei and Prater (1962).

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## ABSTRACT

The chemical system of monomolecular reactions among $n$ species, first analysed in the classical paper by Wei and Prater (1962) was revisited. It was shown that using symmetry relationships, based on all the equilibrium constants and $n(n-1)/2$ known dependences, all remaining kinetic dependences can be calculated. A new method of closing the mass balance for such a complex chemical system was developed, using only measurements of one or a few species, and based on symmetry relations. A new method of testing completeness of a kinetic description was proposed, using the properties of the trace sum of components, i.e., the sum of all concentration dependences, each of which is started from maximal initial concentration.

## 1. Introduction

In accordance with the foundations of physical chemistry, the fundamental difference between equilibrium chemical thermodynamics (ECT) and chemical kinetics is always stressed. A traditional ECT problem is calculating the composition of a chemical mixture that reacts in a closed system for an infinitely long time. ECT does not consider time as a characteristic of its theoretical framework. In contrast, chemical kinetics is the science about temporal behaviour of the chemical system, i.e., change of the chemical composition in time. In fact, these statements belong to the paradigm of contemporary physical chemistry.

Some results of theoretical chemical kinetics have been obtained from chemical thermodynamics principles, especially the principle of detailed balance.

(1) the uniqueness and stability of the equilibrium in any closed system, see Zeldovich (1938) and the analysis in Yablonskii et al. (1991).
(2) Analysis of complex monomolecular mechanisms and proof of the absence of damped oscillations near the point of detailed balance by Wei and Prater (1962).
(3) Relations between thermodynamics, symmetries and detailed balance were studied by Boyd (1974).
(4) Some limitations on kinetic behaviour from the given initial conditions, e.g., based on the known set of equilibrium constants that determine the equilibrium composition, the forbidden domain of compositions calculated from the given initial conditions. See Gorban et al. (1982), Gorban et al. (2006) and Gorban (1984).

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(5) Analysis of thermodynamics in the limit of irreversible reactions (Gorban et al., 2013).

Nevertheless, it is generally accepted that it is impossible to predict the temporal evolution of a reacting chemical system based on its description under equilibrium conditions, except for some relations describing the behaviour in the linear vicinity of equilibrium.

Recently, Yablonsky et al. (2011), Yablonsky, Gorban et al. (2011) found an interesting property of time invariance for the ratio of concentration dependences in so-called *dual kinetic experiments*. This result, obtained for constant isothermal processes in batch reactors (BRs), can also be applied to plug-flow reactors (PFRs) in which the space-time is analogous to the astronomic time of BRs. The simplest example of a dual experiment is as follows: in the first experiment we start from a reactor composition with pure species A and measure the temporal or spatial-temporal evolution of the concentration of $B$, $C_{B_A}(t)$. In the second, dual experiment, we start from pure B in unit concentration and measure the evolution $C_{A_B}(t)$ of the concentration of A. It was shown in Yablonsky et al. (2011), Yablonsky, Gorban et al. (2011) that in such dual experiments the ratio of special concentration dependences which start from symmetrical initial conditions is equal to the equilibrium constant of the chosen reaction at any moment in time: $C_{B_A}(t)/C_{A_B}(t) = K_{eq}$ for all $t > 0$. In this, pure A and pure B correspond to starting points of transient regimes, and $K_{eq}$ is the equilibrium constant. This was established not only for the simple reversible first-order reaction $A \leftrightarrow B$ but also for all networks of monomolecular reactions (first-order reactions) a.k.a. linear systems of reactions, and for perturbations in the linear vicinity of nonlinear network near the point of detailed balance. Next, a similar phenomenon was found theoretically for nonlinear single reactions (see Constales et al., 2012) with all realistic stoichiometric coefficients. In all the analysed cases, quotient-like functions of concentrations can be defined that equal the equilibrium constant of the reaction for the whole course of the dual experiments, and not only in the limit of time tending to infinity reaching the equilibrium conditions.

In further studies, this theory was extended to the area of reaction-diffusion models, in particular models of Temporal Analysis of Products (TAP) experiments. As a result, the validity of the theory was proven in water-gas-shift (WGS) reaction studies, (Constales et al., 2011). These reciprocal relations between kinetic curves were analysed form the viewpoint of the thermodynamics of irreversible processes in Yablonsky, Gorban et al. (2011). It was shown that this result is the consequence of Onsager reciprocity, for linear or linearised kinetics with micro-reversibility of type $\dot{x} = Kx$, where $K$ is a symmetric matrix in the special, so-called entropic inner product given (in the perfect isothermal, isochoric case) by $\langle x, y \rangle = \sum_i x_i y_i / C_{eq,i}$, so that $\langle Kx, y \rangle = \langle x, Ky \rangle$ identically. This form of Onsager reciprocity implies that the time shift operator $\exp(Kt)$ is also a symmetric operator, which generates the reciprocity relations between the kinetic curves.

The next step, treated in this paper, is to address the following questions:

(1) Is it possible to find all transient dependences based on the known equilibrium composition or known equilibrium constants using this approach?
(2) How many kinetic dependences do we have to determine in addition to knowing the equilibrium constants for this purpose?
(3) What is the procedure for determining the unknown kinetic dependences based on the known ones?
(4) Are all these procedures successful or not?

In the present paper we will answer these questions or at least some of them. We will present a mathematical formulation of these problems, illustrating them by examples taken from the classical paper (Wei and Prater, 1962).

## 2. Theoretical model

The theoretical model of chemical kinetics which will be analysed in this paper is presented as follows:

$$\frac{dC}{dt} = KC, \qquad (1)$$

where $C$ is a column vector holding the concentrations the $n$ reacting chemical species, and $K$ is a matrix. From the physicochemical viewpoint, this linear model is related to the system of monomolecular reactions or isomerisation reactions $A_i \leftrightarrow A_j$, $i, j = 1, \ldots, n$. Every off-diagonal element of this matrix is the rate coefficient of a reaction, for instance the element (1,2) is the rate coefficient $k_{2\to1}$ of the reaction $A_2 \to A_1$. Due to conservation of matter, each column of the matrix $K$ must sum to zero, so that the diagonal elements hold minus the sum of all rate coefficients occurring in their column away from the diagonal; for instance, element (2,2) holds the value $-(k_{2\to1} + k_{2\to3} + \ldots + k_{2\to n})$. Under some assumptions this model can be applied to the analysis of linear models of reversible reactions in plug-flow reactors (PFRs). This model can also be applied to the analysis of 'pseudomonomolecular' models of Langmuir–Hinshelwood–Hougen–Watson type (LHHW models) for reversible reactions, see Wei and Prater (1962, p. 322). In these models all numerators are linear in the gas concentration (first order); the denominators are polynomials in the concentrations, which are the same for all species. These polynomials reflect the complexity of the catalytic mechanism. It can generally be used for the description of kinetic behaviour related to so-called linear mechanisms, i.e., mechanisms in which every reaction includes only a molecule of an intermediate, e.g., the heterogeneous two-step mechanism $A + Z \leftrightarrow AZ$, $AZ + B \leftrightarrow AB + Z$ with overall reaction $A + B \leftrightarrow AB + Z$, where $Z$ and $AZ$ are free and occupied catalytic active sites, respectively; and also enzyme mechanisms by Michaelis–Menten, $E + S \leftrightarrow ES$, $ES \to P + E$, with overall reaction $S \to P$. The model can furthermore be used in the linear vicinity of nonlinear complex reversible reactions both for batch reactors (closed systems) and PFR.

## 3. Properties of the model

There are two main properties of the theoretical model (1):

(1) Mass balance for the concentrations $C$.
(2) Symmetry for the kinetic operator $K$.

The mass balance for the concentrations in the vector $C$ can be expressed as

$$\sum_{i=1}^{n} C_i = C_t, \qquad (2)$$

where $C_i$ is the concentration of the $i$-th species, $A_i$, and $C_t$ is the total amount of species. In the following discussion, we assume for simplicity that there is only one balance. Completeness, i.e., that all participating species have been identified and are accounted for in the model, can be verified using the balances.

The symmetry of the kinetic operator $K$ follows from the classical principle of detailed balance (PDB) of elementary processes. In accordance with this principle each forward elementary reaction should be equilibrated by its reverse reaction. In 1931, Onsager expressed the concept that this symmetry, also known as reciprocity, directly relates to the PDB. For more details on the connections between the PDB and Onsager reciprocity see Van