



Experimental confirmation of a new invariant for a non-linear chemical reaction

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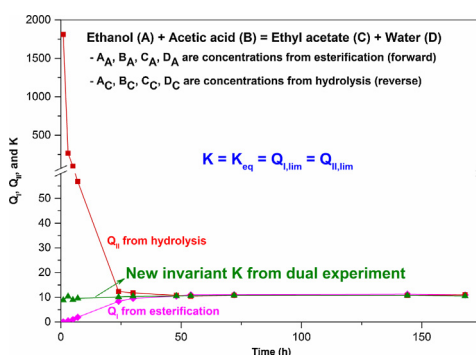
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HIGHLIGHTS

- A non-Onsager invariant is experimentally confirmed for a non-linear reaction.
- The dual kinetics of esterification and hydrolysis are used to obtain the invariant.
- The invariant is valid in all temporal domains and changes in a narrow range.

GRAPHICAL ABSTRACT



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ABSTRACT

The first non-Onsager thermodynamic invariant for a non-linear chemical system was found experimentally in all domains using “the dual kinetic experiment” in a batch reactor in which the reaction of esterification of ethanol with acetic acid was studied jointly with the reaction of hydrolysis of ethyl acetate. In a typical experiment, a glass flask was loaded with 200 mL of 1 mol/L ethanol and acetic acid in acetonitrile for esterification or 1 mol/L ethyl acetate and water in acetonitrile for hydrolysis at 20, 30, and 40 °C. The obtained experimental result is a justification of the theory presented previously (Constaes et al., 2012).

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1. Introduction. Theoretical foundation

1.1. Linear invariants

In many sciences such as chemical kinetics and chemical engineering, searching for invariants is one of the most important prob-

lems. Typically, invariants are defined as functions of variables that remain constant during non-steady-state complex transformations. In the literature on chemistry and chemical engineering, two well-known linear invariances are described and widely used:

- Linear element conservation laws
- Linear stoichiometric relationships

See the classical monograph by Aris (1989) and recent monographs (Marin and Yablonsky, 2011; Constaes et al., 2016).

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Linear element conservation laws governed only by the list of chemical substances are valid regardless of the kinetic and thermodynamic properties of the reaction mechanism, as well as the way the chemical reactions are carried out. Regarding the linear stoichiometric relationships, they correspond to the mechanism of the complex chemical reaction.

1.2. Thermodynamic invariants for non-equilibrium reactions. Onsager invariants

Starting from 2011, new types of chemical invariants were described (Yablonsky et al., 2011a, 2011b; Constaes et al., 2012). It was demonstrated that these invariants have a thermodynamic nature and are closely related to Onsager's famous reciprocal relations described in 1931 (Onsager, 1931a, 1931b). In 1968, Lars Onsager was awarded the Nobel prize for this theoretical discovery.

Onsager reciprocal relations were proven experimentally for many physico-chemical systems. In 1960, Miller wrote a remarkable review on experimental verification of the Onsager reciprocal relations (Miller, 1960) which is topical even now. Analyzing many experimental data related to different cases of irreversible phenomena (thermoelectricity, isothermal diffusion, etc.), Miller found that these reciprocal relations are valid. As for chemical reactions, Miller's point was opposite: "The experimental studies of this phenomenon ... have been inconclusive, and the question is still open from an experimental point".

In our previous studies (Yablonsky et al., 2011a, 2011b; Constaes et al., 2012), a new experimental procedure was proposed, using which invariants for chemical reactions can be obtained and Onsager relations can be tested as well.

The new procedure, whether analytical, or computational, or real, consists of two symmetric experiments performed from different initial conditions of the reacting mixture. Consequently, this procedure is termed as "the dual experiment". The simplest invariant obtained relates to the single reversible reaction $A \rightleftharpoons B$ which occurs in a batch reactor:

- The first experiment is performed in a reactor primed with substance A only
- The second experiment is performed in a reactor primed with substance B only

In both cases, the time-dependent concentrations of A and B are measured, $A(t)$ and $B(t)$, respectively. Special attention was paid to symmetric concentration profiles: the dependences "B produced from pure A", $B_A(t)$, from the first experiment, and "A produced from pure B", $A_B(t)$, from the second experiment. The notation of concentration profiles is as follows: the first capital letter denotes the chemical species, whereas the subscript letter denotes the single component primed in the reactor, in this case: pure A or pure B. Examples of these concentration profiles are shown in Fig. 1.

Assuming that both the forward and backward reactions are first-order, monomolecular reactions, with kinetic coefficients k^+ and k^- , respectively, it was shown that the ratio of the symmetric concentration profiles $B_A(t)/A_B(t)$ is constant, equal to the equilibrium constant of the reversible reaction $K_{eq} = k^+/k^-$. The equality $B_A(t)/A_B(t) = K_{eq}$ holds for any value of time $t > 0$. The same result is valid also for a steady-state plug flow reactor (PFR) and a steady-state continuously stirred tank reactor (CSTR), if the astronomical time t is replaced by the space time (Yablonsky et al., 2011a; Constaes et al., 2012).

The same type of invariants can be observed in more complicated, reversible linear mechanisms, calculated from the ratio of concentration profiles of any two chemical substances connected via any number of reversible reactions, as long as these

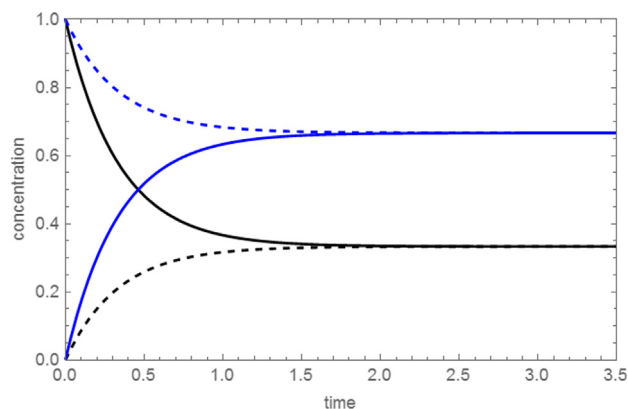


Fig. 1. Concentration profiles of A (black) and B (blue), starting from pure A (solid) and from pure B (dashed), assuming a single step reversible reaction $A \rightleftharpoons B$ with $k^+ = 2$, $k^- = 1 \text{ s}^{-1}$. The ratio between $B_A(t)$ (solid blue) and $A_B(t)$ (black dashed) is the equilibrium constant. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concentration profiles are obtained from dual experiments (Yablonsky et al., 2011a, 2011b). The thermodynamic invariants obtained for complex multi-step mechanisms are twofold:

- Pure equilibrium constants, obtained from the ratio of concentration profiles of chemical species connected via a single step reaction within a complex chemical mechanism
- Apparent equilibrium constants, consisting of products of equilibrium constants of elementary reactions, obtained from the ratio of concentration profiles of chemical species connected via multiple step reactions in a complex chemical mechanism

Considering the two-step consecutive mechanism (Eq. (1)), three thermodynamic invariants can be constructed (Table 1). They are obtained from symmetric initial conditions; notice that the invariant involving the ratio of the concentration profiles of C and A, $C_A(t)$ and $A_C(t)$, respectively, yields the apparent equilibrium constant K_{12} of the global reversible reaction $A \rightleftharpoons C$. The invariants shown in Table 1 are valid in a batch reactor and both the steady-state PFR and CSTR.



In this table, $B_A(t)$ and $C_A(t)$ are temporal dependences of substances B and C which start from the pure component A, respectively; $A_B(t)$ and $C_B(t)$ are temporal dependences of substances A and C which start from the pure component B, respectively; $A_C(t)$ and $B_C(t)$ are temporal dependences of substances A and B which start from the pure component C, respectively.

$B_A(t)/A_B(t) = K_1$, $C_B(t)/B_C(t) = K_2$, $C_A(t)/A_C(t) = K_{12} = K_1 K_2$, where K_1 , K_2 , and K_{12} are equilibrium constants for reactions $A = B$, $B = C$ and $A = C$, respectively.

Yablonsky et al. rigorously showed that for linear or linearized kinetics with microreversibility, $(dx/dt) = kx$, the kinetic operator

Table 1
Thermodynamic invariants in a two-step consecutive mechanism.

Ratio	Invariant
$\frac{B_A(t)}{A_B(t)}$	$K_1 = \frac{k_1^+}{k_1^-}$
$\frac{C_B(t)}{B_C(t)}$	$K_2 = \frac{k_2^+}{k_2^-}$
$\frac{C_A(t)}{A_C(t)}$	$K_{12} = K_1 K_2 = \frac{k_1^+ k_2^+}{k_1^- k_2^-}$

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