New invariances for chemical reactions from Scaled Incremental Conversion (SIC)

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HIGHLIGHTS

- A new model-free kinetic function is proposed: Scaled Incremental Conversion (SIC).
- The profiles of SIC differences show an extreme value at a particular time point.
- For the linear mechanism A ⇌ B ⇌ C, ratios of SIC differences are time-invariants.
- For some initial conditions the invariants are functions of equilibrium constants.
- In other cases, they are function also of a parametric ratio of kinetic coefficients.

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ABSTRACT

For the two-step chemical reaction A ⇌ B ⇌ C, invariant dependences of a new type have been found. These invariants relate concentration dependences which are started from the single component (single-component-dependences). For constructing the invariants, a three-stage procedure is used:

1. Scaled Incremental Conversion (SIC), χ, is determined for any substance as $\chi = \frac{X(t) - X_o}{X_{eq} - X_o}$, where X_{eq} and X_o are equilibrium and initial concentrations for any substance, A, B, or C, respectively; $X(t)$ is the concentration at any moment of time.
2. Differences of SIC terms $\Delta\chi$ are determined for different pairs of substances. SIC terms are calculated in experiments with symmetrical initial conditions.
3. A generating function of invariants is constructed which produces invariants as ratios of different $\Delta\chi$. These ratios remain constant at any time during the non-steady-state reaction.

It is demonstrated that the variety of invariants obtained depends on the initial conditions used in the procedure. Explicit analytical expressions have been found assuming the same initial conditions, two, and three different initial conditions, respectively.

All invariants are functions of three independent parameters which are ratios of kinetic coefficients. Two of them are equilibrium reaction constants, and the third one is the ratio of kinetic coefficients belonging to different reactions.

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1. Introduction

Searching for invariants is one of the most important goals of many sciences such as chemical kinetics and chemical engineering. Invariants are considered functions of the state variables that remain constant during non-steady-state complex transformations.

There are two well-known linear invariances that are widely used in chemistry and chemical engineering:

- Linear element conservation laws.
- Linear stoichiometric relationships.

Linear element conservation laws are valid regardless of the kinetic and thermodynamic properties of the reaction mechanism,

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Nomenclature

List of symbols

A, B, C...	chemical species A, B, C...
A_o, B_o, C_o...	dimensionless initial/inlet concentrations of A, B, C...
A_{eq}, B_{eq}, C_{eq}	dimensionless equilibrium concentrations of A, B, C...
$A(t), B(t), C(t)$...	dimensionless concentration vs time curve of A, B, C...
$A_i(t), B_i(t), C_i(t)$...	dimensionless concentration vs time curve of A, B, C... starting from the pure chemical species i
k^+	kinetic coefficient of the forward reaction in A ⇌ B $[s^{-1}]$
k^-	kinetic coefficient of the backward reaction in A ⇌ B $[s^{-1}]$
k_i^+	kinetic coefficient of the forward i-th reaction $[s^{-1}]$

k_i^-	kinetic coefficient of the backward i-th reaction $[s^{-1}]$
κ	ratio of kinetic coeficcients, equal to k_1^+/k_2^-
K_i	pure equilibrium constant of the i-th reaction
K_{12}	apparent equilibrium constant, equal to K_1K_2
t	time [s]
t_{ext}	time at the extreme value of the SIC expression[s]
τ	space time [s]
τ_{ext}	space time at the extreme value of the SIC expression [s]
χ_A, χ_B, χ_C	Scaled Incremental Conversion (SIC) of the chemical species A, B, C...
$\chi_{A_i}, \chi_{B_i}, \chi_{C_i}$	Scaled Incremental Conversion (SIC) of the chemical species A, B, C... starting from the pure chemical species i

as well as the way the chemical reactions are carried out. These laws are determined only by the list of chemical substances. As for linear stoichiometric relationships, they can but should not necessarily correspond to the detailed mechanism of a complex chemical reaction. The up to date mathematical framework of application of these linear invariants is presented in recent monographs, (Marin and Yablonsky, 2011, Constales et al., 2017).

1.1. Thermodynamic invariants for non-equilibrium reactions

Since 2011 new types of chemical invariants were described (Yablonsky et al., 2011a, 2011b, Constales et al., 2012). These invariants of thermodynamic origin are closely related to Onsager's famous reciprocal relations (Onsager, 1931a, 1931b). The experimental procedure, real or computational, consists of two symmetric experiments performed from different initial conditions of the reacting mixture, called the "dual experiments". The simplest of these invariants is related to the single reversible reaction A ⇌ B, 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. A 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 the 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 both the forward and backward reaction as first-order, monomolecular reactions, with kinetic coefficients k^+ and k^-, respectively, it was found 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}, $K_{eq} = k^+/k^-$. The equality $B_A(t)/A_B(t) = K_{eq}$ is valid for t > 0, i.e., throughout the course of the reaction. 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 astronomic time t is replaced by the space time τ, defined as the reactor volume divided by the volumetric flow rate (Yablonsky et al., 2011a, 2011b, Constales et al., 2012).

This type of invariant can be observed in more complicated, reversible linear mechanisms, calculated from the ratio of concen-
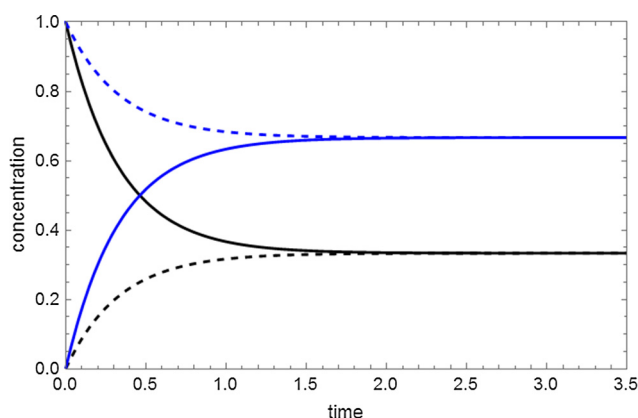

Fig. 1. Concentration profiles of A (black) and B (blue), starting from pure A (solid) and from pure B (dashed), assuming a single step reversible reaction A ⇌ B with k^+ = 2, k^- = 1 s^{-1}. The ratio between $B_A(t)$ (solid blue) and $A_B(t)$ (black dashed) is the equilibrium constant. (For interpretation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

tration profiles of any arbitrary chemical species connected via any number of reversible reactions, as long as these concentration profiles are obtained from dual experiments (Yablonsky et al., 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.

A formal demonstration of this feature is given elsewhere, along with experimental evidence using the water gas shift reaction in a Temporal Analysis of Products (TAP) reactor (Yablonsky et al., 2011b). Even some simple non-linear mechanisms may show similar invariants, calculated from the ratio of selected concentration profiles (Yablonsky et al., 2011a, 2011b, Constales et al., 2012).

1.2. Examples of thermodynamic invariants

Consider the two-step consecutive mechanism:

$$A \underset{k_1^-}{\overset{k_1^+}{\rightleftarrows}} B \overset{k_2^+}{\underset{k_2^-}{\rightleftarrows}} C \qquad (1)$$

The mathematical solution of this mechanism is shown in detail in the Appendix A. The thermodynamic invariants of this two-step mechanism are shown in Table 1, obtained from symmetric initial conditions and assuming all reactions are linear. 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 $A \rightleftarrows C$. The invariants shown in Table 1 are valid in a batch reactor and both the steady-state PFR and CSTR.

1.3. Applications of the invariants

A general dogma in chemical kinetics states that it is not possible to describe the temporal evolution of a reacting system based exclusively on its description under equilibrium conditions. Nevertheless, the thermodynamic, equilibrium-like invariants presented and described in this paper, valid also far from equilibrium, in non-steady-state conditions, show that equilibrium thermodynamic relationships not only describe the final point of the reacting system, but also its temporal evolution. Of course, only the information obtained from equilibrium is not sufficient; some kinetic information is also needed to describe the reacting system (Yablonsky et al., 2011a).

If the equilibrium constant is already known, the invariant expressions can be used to predict kinetic behavior. For the case of a single reversible reaction, if a concentration profile obtained from a given initial condition is known in addition to the equilibrium constant, it is possible to predict kinetic behavior from the symmetric initial condition, as these concentration profiles are proportional by the equilibrium constant. The prediction of kinetic behavior for the Wei-Prater triangular mechanism was done in Constales et al. (2015), using thermodynamic invariants.

1.4. Goal of this paper

The goal of this paper is to present new thermodynamic and non-thermodynamic invariants. These invariants will be obtained using a new kinetic function, closely related to the conversion of reactants. The invariants are calculated from the ratio of the differences of this special kinetic function. Rigorously speaking, the new invariants presented in this paper are valid exclusively for a two-step consecutive mechanism and a triangular mechanism.

2. Scaled Incremental Conversion and its properties

The function that will be used to calculate the invariants is closely related to the widely used term "conversion". For the chemical species A, the Scaled Incremental Conversion (SIC) of A, χ_A, is defined as follows:

$$\chi_A = \frac{A(t) - A_o}{A_{eq} - A_o} \tag{2}$$

where A_{eq} is the equilibrium concentration of A.

At the beginning of the reaction, at time t = 0, $A(0) = A_o$, so the SIC value χ is zero. On the other hand, at the end of the reaction or at equilibrium, $A(t \rightarrow \infty) = A_{eq}$, and the SIC value χ is equal to one.

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

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

For both irreversible and reversible reactions, the SIC values go from zero to one, at the beginning of the chemical reaction and at chemical equilibrium, respectively.

Notice that the SIC expression can be evaluated for any chemical species involved in the reaction. For an irreversible reaction, the equilibrium concentration of the reactant A is zero, $A_{eq} = 0$, and the SIC and the conversion coincide. In Fig. 2 are shown several SIC plots as a function of time, for different chemical species evaluated at different initial conditions, assuming the linear two-step model shown in Eq. (1). As seen in Fig. 2, the SIC value can be larger than one during the chemical reactions; this behavior can be observed for intermediate chemical species, when its concentration value is momentarily equal to its corresponding equilibrium concentration. If the concentration profile of a chemical species shows a maximum, their SIC profile will also show a maximum, both occurring at the same value of time or space time.

2.1. Scaled Incremental Conversion in dual experiments

The time-dependent concentration profile in the SIC definition, see Eq. (2), can be evaluated from different starting reactants. In Table 2 are shown the SIC values of A and B, for two symmetric initial conditions, assuming a single reversible reaction $A \rightleftarrows B$.

Let us focus our attention to the SIC expressions where the concentration profiles of the dual experiments appear, χ_{A_B} and χ_{B_A}. At the beginning of the reaction, at time t = 0, both $A_B(0)$ and $B_A(0)$ are zero, as seen in Fig. 1, and so are χ_{A_B} and χ_{B_A}. At the limit $t \rightarrow \infty$, it is straightforward to check that these last values are both equal to 1. More interestingly, we can demonstrate that these two SIC expressions are equal at any value of time, due to the fact that the ratio of the concentration profiles $B_A(t)$ and $A_B(t)$ is invariant and equal to the equilibrium constant, as shown in Section 1.1:

$$\frac{B_A(t)}{A_B(t)} = \frac{k^+}{k^-} = K_{eq} = \frac{B_{eq}}{A_{eq}} \tag{3}$$

Rearranging Eq. (3), and from Table 2, we have:

$$\chi_{B_A} = \frac{B_A(t)}{B_{eq}} = \frac{A_B(t)}{A_{eq}} = \chi_{A_B} \tag{4}$$

Without loss of generality, we can conclude that the SIC expressions of two chemical species from symmetric initial conditions are always equal.

In a single reversible reaction, the invariant stoichiometric balances of the dual experiments are:
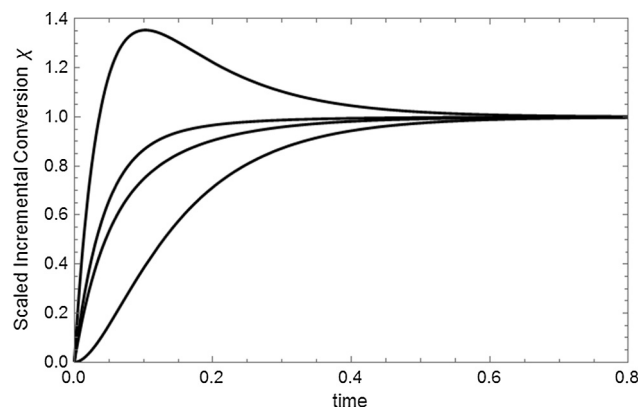

Fig. 2. From top to bottom, the SIC plots of C_B, B_B, B_A and C_A, assuming the two-step mechanism shown in Eq. (1). k_1^+ = 4.5, k_1^- = 10, k_2^+ = 6.5, k_2^- = 12 s^{-1}.

Table 2
SIC expressions for a single reversible reaction, from symmetric initial conditions.

Normalized Conversion of …	Starting from pure A $B_o = 0$	Starting from pure B $A_o = 0$
…A	$\chi_{A_A} = \frac{A_A(t) - A_o}{A_{eq} - A_o}$	$\chi_{A_B} = \frac{A_B(t)}{A_{eq}}$
…B	$\chi_{B_A} = \frac{B_A(t)}{B_{eq}}$	$\chi_{B_B} = \frac{B_B(t) - B_o}{B_{eq} - B_o}$

$$\begin{cases} \text{Starting from pure A}: \begin{cases} A_A(t) + B_A(t) = A_o \\ A_{eq} + B_{eq} = A_o \end{cases} \\ \text{Starting from pure B}: \begin{cases} A_B(t) + B_B(t) = B_o \\ A_{eq} + B_{eq} = B_o \end{cases} \end{cases} \quad (5)$$

Using the stoichiometric balances shown in Eq. (5) for a single reversible reaction, it can be demonstrated that the SIC expressions of A and B in a single experiment, shown in columns in Table 2, are always equal. For instance, starting from pure A, we have:

$$\chi_{A_A} = \frac{A_A(t) - A_o}{A_{eq} - A_o} = \frac{-B_A(t)}{-B_{eq}} = \frac{B_A(t)}{B_{eq}} = \chi_{B_A} \quad (6)$$

This property is only valid for a single reversible reaction, and cannot be extended to other more complex mechanisms. Thus, all SIC expressions shown in Table 2 for a single reversible reaction are equal, at any value of time.

The new invariants presented in the next sections are based on a simple function of four SIC expressions.

3. The invariant generator function

The new thermodynamic and non-thermodynamic invariants are calculated using the invariant generator function F shown in Eq. (7). This function uses four concentration profiles C_i as arguments:

$$F(C_1, C_2, C_3, C_4) = \frac{\Delta \chi_{12}}{\Delta \chi_{34}} = \frac{\chi_1 - \chi_2}{\chi_3 - \chi_4} \quad (7)$$

where χ_i denotes the SIC of the chemical species i, evaluated at a given initial condition.

The plot of the differences of two SIC terms starts at zero at time t = 0, and ends also in zero at the limit t → ∞. In Fig. 3 are shown the differences of some of the SIC plots shown in Fig. 2. The $\Delta \chi$ plots show an extreme value, i.e., a maximum or a minimum. As seen in Fig. 3, the time value when the extremum occurs, t_{ext}, is the same for any difference of SIC terms, and it depends exclusively
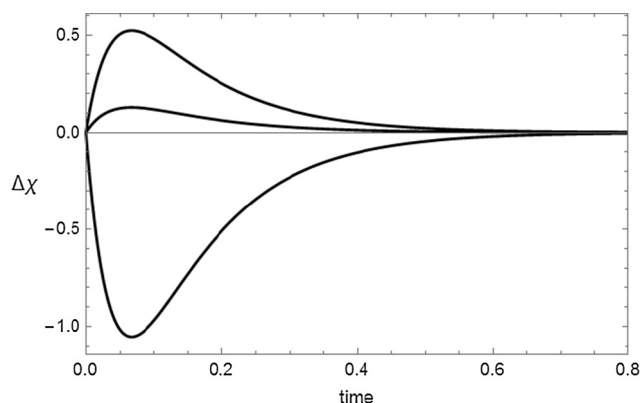

Fig. 3. Difference of SIC plots shown in Fig. 2. From top to bottom, $(\chi_{B_B} - \chi_{C_A})$, $(\chi_{B_B} - \chi_{B_A})$ and $(\chi_{C_A} - \chi_{C_B})$.

on the values of the kinetic coefficients. In a batch reactor and steady-state PFR, this value of time is:

$$t_{ext} = \frac{\ln(\lambda_p / \lambda_m)}{\lambda_p - \lambda_m} \quad (8)$$

whereas in a CSTR, the space time value τ_{ext} when the extremum occurs is:

$$\tau_{ext} = \frac{1}{\sqrt{\lambda_p \lambda_m}} \quad (9)$$

The expressions of both λ_p and λ_m can be found in the Appendix A.

We have found Eqs. (8) and (9) in studies of perturbed equilibrium in the linear two-step mechanism shown in Eq. (1), as the (space-)time when the extreme value occurs, between the initial perturbation and the final equilibrium state, in batch reactor and CSTR, respectively (Branco et al., 2016).

4. Variety of invariant expressions

The ratios of $\Delta \chi$ such as those shown in Fig. 3 yield invariant expressions that depend exclusively on the kinetic coefficients. As the mechanisms studied in this paper have three chemical species A, B and C, and also three single component initial conditions, $(A_o, B_o, C_o) = (A_o, 0, 0), (0, B_o, 0)$ and $(0, 0, C_o)$, there are 9 different concentration profiles, which start from single component initial conditions: A_A, B_A, C_A, from pure A; A_B, B_B, C_B, from pure B, and A_C, B_C and C_C from pure C, arranged in a 3x3 matrix in Eq. (10).

$$\begin{pmatrix} A_A & A_B & A_C \\ B_A & B_B & B_C \\ C_A & C_B & C_C \end{pmatrix} \quad (10)$$

Each of these 9 concentration profiles can be used as arguments of the invariant generator function, Eq. (7). From 9 SIC terms, 9 × 8/2 = 36 combinations of differences of SIC terms exist, and 36 × 35/2 = 630 combinations of ratios of differences of SIC terms exist. However, this number can be greatly reduced taking advantage of the symmetry of the mechanisms studied, as will be seen in the next sections.

All the new invariant expressions can be calculated from different choices of arguments for the invariant generator function F. This variety arises because the SIC expressions of two chemical species from symmetric initial conditions are always equal. Considering the concentration profiles shown in Eq. (10), only those in the main diagonal, A_A, B_B and C_C, have a unique SIC expression. The other six off-diagonal concentration profiles are proportional by equilibrium constants, as seen in Table 1, and are related as follows:

$$\begin{cases} \chi_{B_A} = \chi_{A_B} \\ \chi_{C_A} = \chi_{A_C} \\ \chi_{C_B} = \chi_{B_C} \end{cases} \quad (11)$$

These useful symmetry relationships allow us to reduce the number of invariants; these features will be explained with more detail in the next sections.

5. Invariants in a two-step consecutive mechanism

The new invariants obtained for the two-step consecutive mechanism shown in Eq. (1) will be divided threefold, according to the number of initial conditions involved in the four arguments of the invariant generator function F:

- Thermodynamic invariants, calculated from the same initial condition.
- Non-thermodynamic invariants calculated from two different initial conditions.
- Non-thermodynamic invariants calculated from three different initial conditions.

We define the invariant which depends on only equilibrium constants as "thermodynamic invariant". In this paper, a "non-thermodynamic invariant" is the invariant which is a function of both equilibrium constants and parameter κ, the ratio of kinetic coefficients belonging to different reactions.

5.1. Thermodynamic invariants from the same initial condition

If the four concentration profiles used as arguments in the invariant generator function F are obtained from the same initial condition, only three independent invariant expressions exist; the three arguments are: {A, B, A, C}, {A, B, B, C} and {A, C, B, C}. The invariants obtained from these combinations are shown in Table 3, for two different initial conditions. The invariants in Table 3 depend on two independent parameters: the equilibrium constants K_1 and K_2, so only two of those invariants are independent.

To facilitate the reading of the tables of invariants, we will break down the last of the invariant expressions listed in Table 3. The arguments of this invariant are {A_B, C_B, B_B, C_B}; these concentration profiles are the four arguments of the function F. The invariant expression is obtained evaluating SIC expressions of these concentration profiles, and relating them according to Eq. (7), as follows:

$$F(A_B, C_B, B_B, C_B) = \frac{\chi_{A_B} - \chi_{C_B}}{\chi_{B_B} - \chi_{C_B}}$$

$$= \frac{\left.\frac{A(t)-A_o}{A_{eq}-A_o}\right|_{(A_o,B_o,C_o)=(0,B_o,0)} - \left.\frac{C(t)-C_o}{C_{eq}-C_o}\right|_{(A_o,B_o,C_o)=(0,B_o,0)}}{\left.\frac{B(t)-B_o}{B_{eq}-B_o}\right|_{(A_o,B_o,C_o)=(0,B_o,0)} - \left.\frac{C(t)-C_o}{C_{eq}-C_o}\right|_{(A_o,B_o,C_o)=(0,B_o,0)}}$$

$$= \frac{\frac{A_B(t)}{A_{eq}} - \frac{C_B(t)}{C_{eq}}}{\frac{B_B(t)-B_o}{B_{eq}-B_o} - \frac{C_B(t)}{C_{eq}}} = 1 + \frac{k_1^+}{k_1^-}\frac{k_2^+}{k_2^-} = 1 + K_1 K_2$$

$$= 1 + K_{12} \tag{12}$$

Due to variety, see Section 4, this invariant expression, Eq. (12), can also be obtained from the following combinations of arguments:

$$F(A_B, C_B, B_B, C_B) = F(B_A, C_B, B_B, C_B) = F(A_B, B_C, B_B, B_C)$$
$$= F(B_A, B_C, B_B, B_C) = 1 + K_{12} \tag{13}$$

For simplicity, in the subsequent tables only one argument will be shown.

The invariant expressions shown in Table 3 can be written as simple functions of dimensionless pure or apparent equilibrium constants. The first three invariant expressions, calculated starting from pure A, are functions of the equilibrium constant K_2; these invariants are useful to obtain the invariant expressions calculated

Table 3
Thermodynamic invariants for a two-step consecutive mechanism, calculated from the same initial condition.

Arguments of the F function	Invariant
{A_A, B_A, A_A, C_A}	$-K_2$
{A_A, B_A, B_A, C_A}	$-\frac{K_2}{1+K_2}$
{A_A, C_A, B_A, C_A}	$\frac{1}{1+K_2}$
{A_B, B_B, A_B, C_B}	$\frac{K_{12}}{1+K_{12}}$
{A_B, B_B, B_B, C_B}	K_{12}
{A_B, C_B, B_B, C_B}	$1 + K_{12}$

from pure C, due to the symmetry of the mechanism, just by switching the identification of A and C as chemical species, and also the kinetic coefficients, correspondingly.

Notice that for the two-step mechanism, in contrast to the single reversible reaction, the thermodynamic invariants shown in Table 3 can be calculated from the same initial condition in a single experiment, as long as that the time profile of the concentrations of the three chemical species A, B and C is recorded.

5.2. Non-thermodynamic invariants from two initial conditions

In Table 4 are shown the non-thermodynamic invariants of the two-step consecutive mechanism, using the concentration profiles from two initial conditions: pure A and pure B. These concentration profiles are five: A_A, B_A, C_A, B_B and C_B.

Since the mechanism is described by four parameters: k_1^+, k_1^-, k_2^+ and k_2^-, the non-thermodynamic invariants are function of three

Table 4
Non-thermodynamic invariants for a two-step consecutive mechanism, calculated from two initial conditions: A and B.

Arguments of the F function	Invariant
{A_A, B_A, A_A, B_B}	$\frac{\kappa(1+K_{12})}{\kappa+(1-\kappa)K_1+K_{12}}$
{A_A, B_A, B_A, B_B}	$-\frac{\kappa(1+K_{12})}{(-1+\kappa)(K_1+K_{12})}$
{A_A, B_A, A_A, C_B}	$\frac{\kappa K_2}{1-\kappa+K_2}$
{A_A, B_A, B_A, C_B}	$-\frac{\kappa K_2}{(-1+\kappa)(1+K_2)}$
{A_A, B_A, B_B, C_A}	$-\frac{\kappa K_2(1+K_{12})}{(1+K_2)(\kappa+K_{12})}$
{A_A, B_A, B_B, C_B}	$-\frac{\kappa K_2(1+K_{12})}{(-1+\kappa)(1+K_2)}$
{A_A, B_A, C_A, C_B}	$\frac{\kappa K_2}{1+K_2}$
{A_A, B_B, B_A, B_B}	$-\frac{\kappa+(1-\kappa)K_1+K_{12}}{(-1+\kappa)(K_1+K_{12})}$
{A_A, B_B, A_A, C_A}	$-\frac{K_2(\kappa+(1-\kappa)K_1+K_{12})}{\kappa(1+K_{12})}$
{A_A, B_B, A_A, C_B}	$-\frac{K_2(\kappa+(1-\kappa)K_1+K_{12})}{(-1+\kappa-K_2)(1+K_{12})}$
{A_A, B_B, B_A, C_A}	$-\frac{K_2(\kappa+(1-\kappa)K_1+K_{12})}{\kappa(1+K_2)(1+K_{12})}$
{A_A, B_B, B_A, C_B}	$-\frac{K_2(\kappa+(1-\kappa)K_1+K_{12})}{(-1+\kappa)(1+K_2)(1+K_{12})}$
{B_A, B_B, A_A, C_A}	$\frac{(-1+\kappa)(1+K_2)K_{12}}{\kappa(1+K_{12})}$
{B_A, B_B, A_A, C_B}	$\frac{(-1+\kappa)(1+K_2)K_{12}}{(-1+\kappa-K_2)(1+K_{12})}$
{B_A, B_B, B_A, C_A}	$\frac{(-1+\kappa)K_{12}}{\kappa(1+K_{12})}$
{A_A, B_B, B_B, C_A}	$-\frac{K_2(\kappa+(1-\kappa)K_1+K_{12})}{(1+K_2)(\kappa+K_{12})}$
{A_A, B_B, B_B, C_B}	$-\frac{K_2(\kappa+(1-\kappa)K_1+K_{12})}{(-1+\kappa)(1+K_2)}$
{B_A, B_B, B_B, C_A}	$\frac{(-1+\kappa)K_{12}}{\kappa+K_{12}}$
{A_A, B_B, C_A, C_B}	$\frac{K_2(\kappa+(1-\kappa)K_1+K_{12})}{(1+K_2)(1+K_{12})}$
{B_A, B_B, C_A, C_B}	$-\frac{(-1+\kappa)K_{12}}{1+K_{12}}$
{A_A, C_A, A_A, C_B}	$\frac{\kappa}{(-1+\kappa-K_2)}$
{A_A, C_A, B_A, C_B}	$\frac{\kappa}{(-1+\kappa)(1+K_2)}$
{A_A, C_B, B_A, C_A}	$-\frac{1-\kappa+K_2}{\kappa+\kappa K_2}$
{A_A, C_B, B_A, C_B}	$\frac{-1+\kappa-K_2}{(-1+\kappa)(1+K_2)}$
{B_A, C_A, B_A, C_B}	$\frac{\kappa}{-1+\kappa}$
{A_A, C_A, B_B, C_A}	$\frac{\kappa(1+K_{12})}{(1+K_2)(\kappa+K_{12})}$
{A_A, C_A, B_B, C_B}	$\frac{\kappa(1+K_{12})}{(-1+\kappa)(1+K_2)}$
{A_A, C_B, B_B, C_A}	$\frac{(-1+\kappa-K_2)(1+K_{12})}{(1+K_2)(\kappa+K_{12})}$
{A_A, C_B, B_B, C_B}	$\frac{(-1+\kappa-K_2)(1+K_{12})}{(-1+\kappa)(1+K_2)}$
{B_A, C_A, B_B, C_A}	$\frac{\kappa(1+K_{12})}{\kappa+K_{12}}$
{B_A, C_A, B_B, C_B}	$\frac{\kappa(1+K_{12})}{-1+\kappa}$
{B_A, C_B, B_B, C_A}	$\frac{(-1+\kappa)(1+K_{12})}{\kappa+K_{12}}$
{A_A, C_A, C_A, C_B}	$-\frac{\kappa}{1+K_2}$
{A_A, C_B, C_A, C_B}	$\frac{1-\kappa+K_2}{1+K_2}$
{B_A, C_B, C_A, C_B}	$-\kappa$
{B_A, C_B, C_A, C_B}	$1 - \kappa$
{B_B, C_A, B_B, C_B}	$\frac{\kappa+K_{12}}{-1+\kappa}$
{B_B, C_A, C_A, C_B}	$\frac{-\kappa+K_{12}}{1+K_{12}}$
{B_B, C_B, C_A, C_B}	$\frac{1-\kappa}{1+K_{12}}$

independent dimensionless parameters: two equilibrium constants $K_1 = k_1^+/k_1^-$ and

$K_2 = k_2^+/k_2^-$, and the parametric ratio $\kappa = k_1^+/k_2^-$, as seen in Table 4. Any other ratio of kinetic coefficients can be calculated from both the equilibrium constants and κ; however, it is not possible to resolve single kinetic coefficients using the invariants.

The invariants shown in Table 4 and subsequent tables may be denoted as *kinetic invariants*, as it is not possible to write them as a function of only thermodynamic quantities such as the equilibrium constants. These invariants depend on three independent parameters: the equilibrium constants K_1 and K_2 and the parametric ratio $\kappa = k_1^+/k_2^-$, so only three independent invariants exist.

Notice that the parametric ratio κ can be determined directly from the invariant with the argument $\{B_A, C_A, C_A, C_B\}$, as it is equal to $-\kappa$, as seen in Table 4. The parametric ratio κ can also be determined using two other invariants, namely $\{B_A, C_A, B_A, C_B\}$ and $\{B_A, C_B, C_A, C_B\}$, that are related as follows:

$$F(B_A, C_B, C_A, C_B) = 1 + F(B_A, C_A, C_A, C_B) \tag{14.1}$$

$$F(B_A, C_A, B_A, C_B) = \frac{F(B_A, C_A, C_A, C_B)}{F(B_A, C_B, C_A, C_B)} \tag{14.2}$$

The three invariants described are combinations of three concentration profiles: B_A, C_A and C_B, located at the lower triangular part of the matrix shown in Eq. (10). The invariants obtained from the off-diagonal concentration profiles lead to simple expressions of the parametric ratio κ. The rest of the invariants in Table 4 contain at least one diagonal concentration profile, and depend of the parametric ratio κ and the equilibrium constants.

Some invariant expressions calculated from concentration profiles starting from C can be obtained using the Table 4 and the symmetry relationships shown in Eq. (11). Also, more invariants can be calculated via switching A and C and the kinetic coefficients, correspondingly.

In Table 5 are shown the non-thermodynamic invariants of the two-step consecutive mechanism, using the concentration profiles from two initial conditions: pure A and pure C. These concentration profiles are five: A_A, B_A, C_A, B_C and C_C. Similarly, some invariant expressions calculated from concentration profiles starting from

B can be obtained using the Table 5 and the symmetry relationships shown in Eq. (11). Tables 4 and 5 contain all the invariants obtained from two different initial conditions.

5.3. Non-thermodynamic invariants from three initial conditions

In Table 6 are shown the non-thermodynamic invariants of the two-step consecutive mechanism using concentration profiles from the three different initial conditions. In each one of these invariants, the diagonal concentration profiles A_A, B_B and C_C appear as arguments of the function F. To calculate these invariants, three different experiments are needed.

6. Example

In Fig. 4 are shown three concentration profiles off from the diagonal in the matrix shown in Eq. (10): A_B, C_B and C_A, in solid lines. Notice that the last two tend to the same equilibrium value, independent of the initial conditions. With these off-diagonal concentration profiles, it is possible to calculate the invariants involving the parametric ratio $\kappa = k_1^+/k_2^-$; from Table 4:

$$F(B_A, C_A, C_A, C_B) = -\kappa \tag{15}$$

Table 6
Non-thermodynamic invariants for a two-step consecutive mechanism, calculated from three initial conditions.

Arguments of the F function	Invariant
$\{A_A, B_A, B_B, C_C\}$	$-\frac{\kappa(1+K_{12})(K_2+K_{12})}{(1+K_2)(\kappa+(-1+\kappa)K_1+K_{12})}$
$\{A_A, B_B, A_A, C_C\}$	$-\frac{(1+K_1)K_2(\kappa+(1-\kappa)K_1+K_{12})}{(\kappa+(-1+\kappa)K_1-K_{12})(1+K_{12})}$
$\{A_A, B_B, B_A, C_C\}$	$-\frac{(1+K_1)K_2(\kappa+(1-\kappa)K_1+K_{12})}{(\kappa+(-1+\kappa)K_1)(1+K_2)(1+K_{12})}$
$\{B_A, B_B, A_A, C_C\}$	$\frac{(-1+\kappa)K_{12}(1+K_1+K_2+K_{12})}{(\kappa+(-1+\kappa)K_1-K_{12})(1+K_{12})}$
$\{A_A, B_B, B_B, C_C\}$	$-\frac{(1+K_1)K_2(\kappa+(1-\kappa)K_1+K_{12})}{(1+K_2)(\kappa+(-1+\kappa)K_1+K_{12})}$
$\{A_A, B_B, C_A, C_C\}$	$\frac{(1+K_1)K_2(\kappa+(1-\kappa)K_1+K_{12})}{(1+K_{12})(K_1+K_{12})}$
$\{A_A, B_B, B_C, C_C\}$	$-\frac{(1+K_1)K_2(\kappa+(1-\kappa)K_1+K_{12})}{(1+K_2)(1+K_{12})}$
$\{A_A, C_A, B_B, C_C\}$	$\frac{\kappa(1+K_1)(1+K_{12})}{(1+K_2)(\kappa+(-1+\kappa)K_1+K_{12})}$
$\{A_A, B_C, B_B, C_C\}$	$\frac{(1+K_1)(-1+\kappa-K_2)(1+K_{12})}{(1+K_2)(\kappa+(-1+\kappa)K_1+K_{12})}$
$\{A_A, C_C, B_B, C_A\}$	$\frac{(\kappa+(-1+\kappa)K_1-K_{12})(1+K_{12})}{(\kappa+K_{12})(1+K_1+K_2+K_{12})}$
$\{A_A, C_C, B_B, B_C\}$	$\frac{(\kappa+(-1+\kappa)K_1-K_{12})(1+K_{12})}{(-1+\kappa)(1+K_1)(1+K_2)}$
$\{A_A, C_C, B_B, C_C\}$	$\frac{(\kappa+(-1+\kappa)K_1-K_{12})(1+K_{12})}{(1+K_2)(\kappa+(-1+\kappa)K_1+K_{12}))}$

Table 5
Non-thermodynamic invariants for a two-step consecutive mechanism, calculated from two initial conditions: A and C.

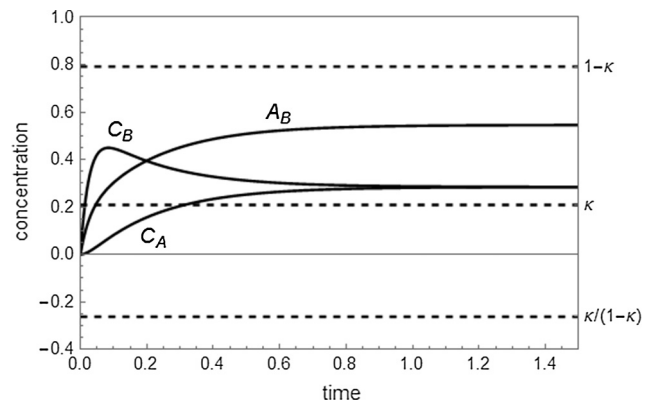| Arguments of the F function	Invariant
$\{A_A, B_A, A_A, C_C\}$	$-\frac{\kappa(K_2+K_{12})}{\kappa+(-1+\kappa)K_1-K_{12}}$
$\{A_A, B_A, B_A, C_C\}$	$-\frac{\kappa(K_2+K_{12})}{(\kappa+(-1+\kappa)K_1)(1+K_2)}$
$\{A_A, B_A, C_A, C_C\}$	$\frac{\kappa(K_2+K_{12})}{K_1+K_{12}}$
$\{A_A, B_A, B_C, C_C\}$	$-\frac{\kappa(K_2+K_{12})}{1+K_2}$
$\{A_A, C_A, A_A, C_C\}$	$\frac{\kappa(1+K_1)}{\kappa+(-1+\kappa)K_1-K_{12}}$
$\{A_A, C_A, B_A, C_C\}$	$\frac{\kappa(1+K_1)}{(\kappa+(-1+\kappa)K_1)(1+K_2)}$
$\{A_A, B_C, A_A, C_C\}$	$\frac{(1+K_1)(-1+\kappa-K_2)}{\kappa+(-1+\kappa)K_1-K_{12}}$
$\{A_A, B_C, B_A, C_C\}$	$\frac{(1+K_1)(-1+\kappa-K_2)}{(\kappa+(-1+\kappa)K_1)(1+K_2)}$
$\{A_A, C_C, B_A, C_A\}$	$\frac{\kappa+(-1+\kappa)K_1-K_{12}}{\kappa(1+K_1)(1+K_2)}$
$\{A_A, C_C, B_A, B_C\}$	$\frac{\kappa+(-1+\kappa)K_1-K_{12}}{(-1+\kappa)(1+K_1)(1+K_2)}$
$\{A_A, C_C, B_A, C_C\}$	$\frac{\kappa+(-1+\kappa)K_1-K_{12}}{(\kappa+(-1+\kappa)K_1)(1+K_2)}$
$\{A_A, C_A, C_A, C_C\}$	$-\frac{\kappa(1+K_1)}{K_1+K_{12}}$
$\{A_A, C_A, B_C, C_C\}$	$\frac{\kappa(1+K_1)}{1+K_2}$
$\{A_A, B_C, C_A, C_C\}$	$-\frac{(1+K_1)(-1+\kappa-K_2)}{K_1+K_{12}}$
$\{A_A, B_C, B_C, C_C\}$	$\frac{(1+K_1)(-1+\kappa-K_2)}{1+K_2}$
$\{A_A, C_C, C_A, B_C\}$	$\frac{-\kappa(1-\kappa)K_1+K_{12}}{(1+K_1)(1+K_2)}$
$\{A_A, C_C, C_A, C_C\}$	$1 - \frac{\kappa(1+K_1)}{K_1+K_{12}}$
$\{A_A, C_C, B_C, C_C\}$	$\frac{\kappa+(-1+\kappa)K_1-K_{12}}{1+K_2}$

Fig. 4. From top to bottom, in solid lines, the concentration profiles A_B, C_B and C_A. From top to bottom, in dashed lines, the invariant values $1-\kappa$, κ and $\kappa/(\kappa-1)$, assuming the two-step mechanism shown in Eq. (1). $k_1^+ = 2.5$, $k_1^- = 8.0$, $k_2^+ = 20.0$, $k_2^- = 12$ s^{-1}.

The first argument in Eq. (15), i.e., the concentration profile B_A, can be calculated from its symmetric concentration profile, A_B, see Eq. (3), or, equivalently, A_B can be substituted directly in the invariant expression in Eq. (15), as the SIC expressions of symmetric concentration profiles are equivalent, see Eq. (11):

$$F(B_A, C_A, C_A, C_B) = F(A_B, C_A, C_A, C_B) = -\kappa \qquad (16)$$

The other two invariants in Table 4 involving the parametric ratio κ can be calculated similarly. The invariants, valid at any value of time, are shown in dashed in Fig. 4.

7. Conclusions

Explicit invariant relationships between single-component-dependences, i.e., concentration dependences which are started from single component conditions, have been found for the two-step chemical reaction $A \rightleftarrows B \rightleftarrows C$. For this purpose, the three-stage procedure was used:

1. Scaled Incremental Conversion (SIC), χ, is determined for any substance as $\chi = \frac{X(t) - X_o}{X_{eq} - X_o}$, where X_{eq} and X_o are equilibrium and initial concentrations for any substance, A, B, or C, respectively; $X(t)$ is the concentration at any moment of time.
2. Differences of SIC terms $\Delta\chi$ are determined for different pairs of substances. SIC terms are calculated in experiments with symmetrical initial conditions.
3. A generating function of invariants is constructed which produces invariants as ratios of different $\Delta\chi$. These ratios remain constant at any time during the non-steady-state reaction.

Three scenarios were analyzed utilizing concentration dependences which that started from the same, two or three different initial conditions.

It was demonstrated that the variety of invariants depends on the initial conditions. Explicit analytical expressions have been found assuming the same initial conditions, two, and three different initial conditions.

At the same initial conditions, invariants are functions of two independent parameters (equilibrium constants), and there are only two independent invariants.

At two and three different initial conditions, invariants are functions of three independent parameters. Two of them are equilibrium reaction constants, and the third one is the ratio of kinetic coefficients belonging to different reactions. In this case, there are only three independent invariants. Consequently, in all cases the number of independent invariants is equal to the number of independent parameters.

Among all invariants, there are three independents invariants of special interest which can be termed simple invariants: two invariants for the same- initial-conditions case:

1. $\{A_A, B_A, A_A, C_A\}$, corresponds to $-K_2$, which is the equilibrium constant of the second reaction $B \rightleftarrows C$.
2. $\{A_B, B_B, B_B, C_B\}$, corresponds to $K_{12} = K_1 K_2$, where K_1 is the equilibrium constant of the first reaction $A \rightleftarrows B$.

The third invariant is from the two-different-initial-conditions case:

3. $\{B_A, C_A, C_A, C_B\}$, corresponds to the ratio of kinetic coefficients of different reactions $\kappa = k_1^+/k_2^-$.

These independent invariants are identical to independent parameters.

Summing up, we'd like to say that finding this new class of invariants opens new problems:

First, we need to understand what is the relationship between these invariants and the invariants of purely thermodynamic origin discovered previously (Yablonsky et al., 2011a, 2011b, Constales et al., 2015), see Constales et al. (2015) as well.

Second, this result was obtained for a two-step reaction using it as an example. However, it can be used as a prototype of 'pseudo-invariant' characteristics of dynamic behavior in more complex linear chemical systems.

Third, new proposed tools of the theoretical analysis, i.e., (a) scaled incremental conversion, $\chi = \frac{X(t) - X_o}{X_{eq} - X_o}$, (b) differences of SIC terms $\Delta\chi$ for different pairs of substances, and (c) a generating function of invariants as a ratio of different $\Delta\chi$ terms, can be applied to the decoding of a complex reaction mechanism and corresponding model. This heuristic approach based on kinetically model-free characteristics can provide researchers with specific invariants, a fruitful source of information on the detailed mechanism.

Acknowledgments

Appendix A

Consider the two-step consecutive mechanism shown in Eq. (1):

$$A \underset{k_1^-}{\overset{k_1^+}{\rightleftarrows}} B \overset{k_2^-}{\underset{}{\rightleftarrows}} k_2^+ C \qquad (1)$$

The mathematical solution of this mechanism was recently published elsewhere (Branco et al., 2016), for the batch reactor. Assuming the initial concentrations of A, B and C as A_o, B_o and C_o, respectively, the equilibrium concentrations of the chemical species, A_{eq}, B_{eq} and C_{eq} are:

$$A_{eq} = \frac{k_1^- k_2^- (A_o + B_o + C_o)}{\lambda_p \lambda_m} \qquad (17)$$

$$B_{eq} = \frac{k_1^+ k_2^- (A_o + B_o + C_o)}{\lambda_p \lambda_m} \qquad (18)$$

$$C_{eq} = \frac{k_1^+ k_2^+ (A_o + B_o + C_o)}{\lambda_p \lambda_m} \qquad (19)$$

where λ_p and λ_m, $\lambda_p > \lambda_m$, are:

$$\lambda_p, \lambda_m = \frac{1}{2}(k_1^+ + k_1^- + k_2^+ + k_2^-$$
$$\pm \sqrt{(k_1^+ + k_1^- + k_2^+ + k_2^-)^2 - 4(k_1^- k_2^- + k_1^+ k_2^- + k_1^+ k_2^+))} \qquad (20)$$

and

$$\lambda_p \lambda_m = k_1^+ k_2^+ + k_1^+ k_2^- + k_1^- k_2^- \qquad (21.1)$$

$$\lambda_p \lambda_m = k_1^+ + k_1^- + k_2^+ + k_2^- \qquad (21.2)$$

The concentration profile of A, A(t), can be written as follows:

$$A(t) = A_{eq} + (A_o - A_{eq} - A_x)e^{-\lambda_p t} + A_x e^{-\lambda_m t} \qquad (22)$$

where A_X is a collection of terms, including the kinetic coefficients and the initial concentrations (Branco et al., 2016). All the concentration profiles can be written similarly to Eq. (22), using the corresponding equilibrium concentration, initial concentration and collection of terms; the definitions of A_X, B_X and C_X can be consulted elsewhere (Branco et al., 2016).

For the CSTR, the solution of the mechanism shown in Eq. (1) is:

$$A(\tau) = \frac{A_o + A_X\tau + \lambda_p\lambda_m A_{eq}\tau^2}{1 + (\lambda_p + \lambda_m)\tau + \lambda_p\lambda_m\tau^2} \tag{23}$$

where for the CSTR, the collection of terms A_X is:

$$A_X = A_o(k_2^+ + k_2^-) + (A_o + B_o)k_1^- \tag{24}$$

The space-time dependent expressions $B(\tau)$ and $C(\tau)$ can be written similarly to Eq. (23), substituting both the inlet and the equilibrium concentrations, correspondingly, as well the A_X expression. The definitions of B_X and C_X are:

$$B_X = (A_o + B_o)k_1^+ + (B_o + C_o)k_2^- \tag{25}$$

$$C_X = C_o(k_1^+ + k_1^-) + (B_o + C_o)k_2^+ \tag{26}$$

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