

New Insights in Chemical Relaxations: Invariants and Conservatively Perturbed Equilibrium.

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Highlights

- New temporal invariants for chemical kinetics have been found.
- The Scaled Incremental Conversion is the building block of the invariants.
- A new, related concept, Conservatively Perturbed Equilibrium, is described.
- The new concepts were applied to a two-step reversible mechanism.

1. Introduction

Searching for invariants is one of the most important goals in many sciences such as chemical kinetics and chemical engineering [1-3]. Invariants are functions of state variables that remain constant during the non-steady-state transformations.

There are two well-known linear invariants that are widely used in chemistry and chemical engineering [4, 5]:

- Linear element conservation laws.
- Linear stoichiometric relationships.

Since 2011, other invariants of thermodynamic origin for first-order, reversible reactions have been found [6-9]. They are related to the famous Onsager's reciprocal relations [10, 11]. For linear or linearized kinetics ($dx/dt = Kx$, with microreversibility, the kinetic operator K is symmetric in the entropic inner product. This form of Onsager's reciprocal relations implies that the shift in time, $\exp(Kt)$, is also a symmetric operator. This generates the reciprocity relations between the kinetic curves, and the ratio of dual kinetic dependences coincides with the equilibrium constant. It was proven experimentally using the catalytic water-gas-shift (WGS) reaction [7].

In this paper new invariants of non-thermodynamic nature for the given mechanism, the two-step consecutive mechanism $A \leftrightarrow B \leftrightarrow C$, are presented. These invariants, specific for the given mechanism, are ratios of linear combinations of concentration dependences which are started from the initial states with only a single component. The invariant expression is based on the 'Scaled Incremental Conversion' (SIC), denoted χ , i.e. a function of modified conversions of different components. For the analyzed mechanism, the invariant is determined by four SIC expressions at initial conditions with only a single component A, B or C, see Fig. 1.

For the case of initial state with some equilibrium concentration(s) as initial one(s), the concept of the "conservatively perturbed equilibrium" was formulated. Obviously, the relaxation to the detailed equilibrium is characterized by the unavoidable extremum (maximum or minimum). Characteristics of such extrema are presented for the Wei-Prater triangular mechanism [6]. It was shown that the extremum time is independent on the initial reaction conditions.

Based on the perturbed equilibrium procedure, some mechanistic details can be extracted and kinetic parameters can be estimated.

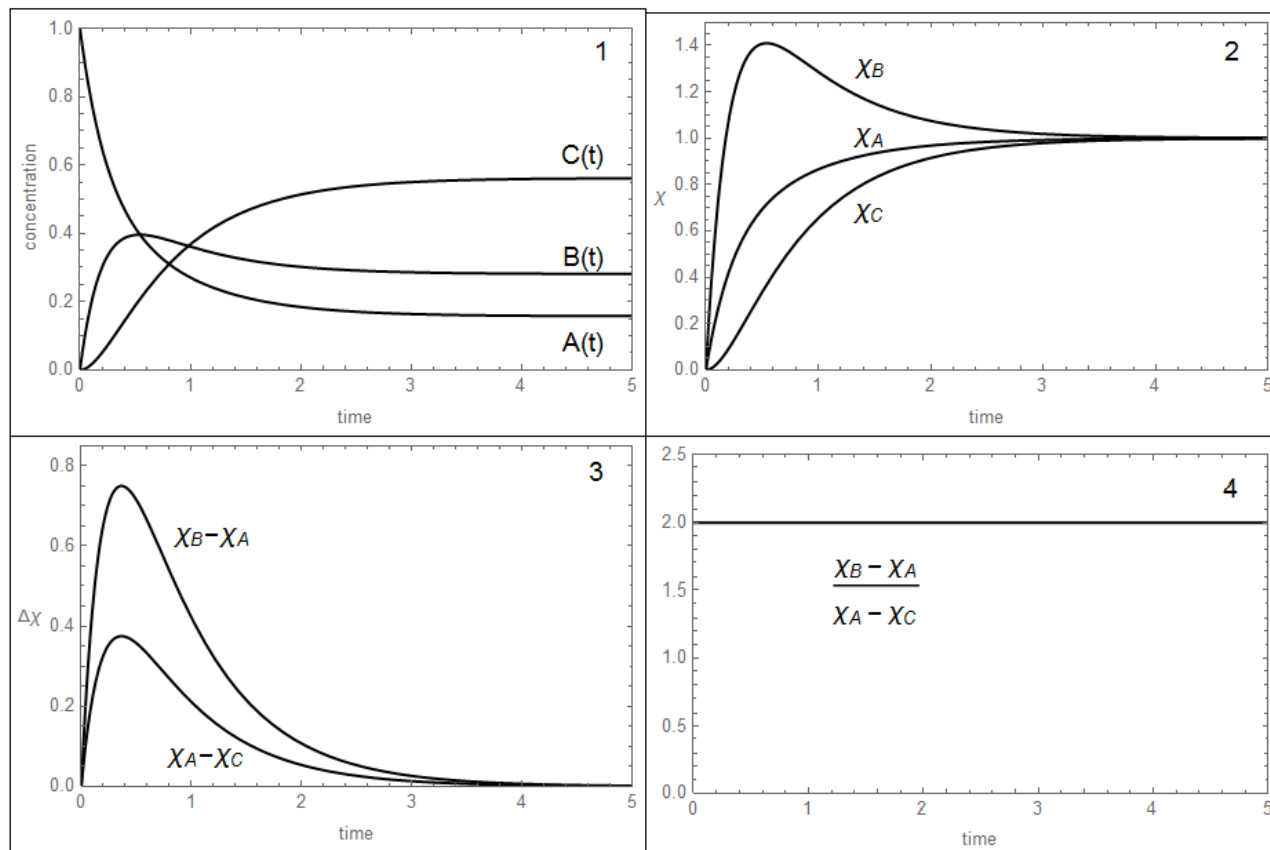


Figure 1. 1) Concentration profiles of A, B and C in a two-step consecutive mechanism $A \leftrightarrow B \leftrightarrow C$, starting from pure A; 2) SIC profiles of A, B and C; 3) Difference of SIC profiles as a function of time; 4) Time invariant from the ratio of SIC differences.

References

- [1] J. Wei, C. Prater, *Adv. Catal.* 13 (1962) 203-392.
- [2] Prigogine I., *Introduction to Thermodynamics of Irreversible Processes*, third ed., Wiley-Interscience, New York, 1967.
- [3] Glansdorff P., Prigogine I., *Thermodynamic Theory of Structure, Stability and Fluctuations*, Wiley-Interscience, New York, 1971.
- [4] Aris R., *Introduction to the Analysis of Complex Reactors*, Prentice Hall, New Jersey, 1965.
- [5] D. Constaes, G.S. Yablonsky, D.R. D'hooge, J.W. Thybaut, G.B. Marin, *Advanced Data Analysis and Modelling in Chemical Engineering*, Elsevier, Amsterdam, 2017.
- [6] G.S. Yablonsky, D. Constaes, G.B. Marin, *Chem. Eng. Sci.* 66 (2011) 111–114.
- [7] G.S. Yablonsky, A.N. Gorban, D. Constaes, V.V. Galvita, G.B. Marin, *Europhys. Lett.* 93 (2011) 20004-20007.
- [8] D. Constaes, G.S. Yablonsky, V. Galvita, G.B. Marin, *Chem. Eng. Sci.* 66 (2011) 4683-4689.
- [9] D. Constaes, G.S. Yablonsky, G.B. Marin, *Chem. Eng. Sci.* 73 (2012) 20-29.
- [10] L. Onsager, *Phys. Rev.* 37 (1931) 405-426.
- [11] L. Onsager, *Phys. Rev.* 38 (1931) 2265-2279.

Keywords

Chemical Relaxation; Temporal Invariant; Chemical Equilibrium; Response Technique.