

**JOINT KINETICS: A NEW STRATEGY FOR BRIDGING THERMODYNAMICS AND KINETICS  
OF COMPLEX REACTIONS**

Gregory S. Yablonsky<sup>1</sup>, Denis Constaes<sup>2</sup>, Guy B. Marin<sup>2</sup>

<sup>1</sup>Washington University in St. Louis, St. Louis, USA

<sup>2</sup>Gent University, Gent, Belgium

**ABSTRACT**

Joint kinetics is presented as a new strategy for chemical kinetics. Central concepts of joint kinetics based on the analysis of ‘batteries’ of experiments are proposed in a series of our papers, see some review in Yablonsky et al., *Current Opinion in Chemical Engineering*, 29, 83-88. These concepts are “events”, “trends” and “map of events and trends”. “Events” are special features of kinetic dependences observed experimentally or computationally, i.e., extrema and intersections, coincidences and momentary equilibria, “turning points” etc. In analysis of “trends”, a special attention is paid to comparing the reciprocal kinetic dependences which start from the symmetrical initial conditions. Maps of kinetic events and trends are constructed and analyzed. Different events are categorized with an indication which events are unavoidable (“always”- events) and which are never happened (“never”- events). Typical models of chemical kinetics are analyzed for the batch and CSTR-reactors and systems of linear equations based on balances of elements and related to the model-free approach.

In classical chemical kinetics, there is the dogma on the impossibility to predict kinetic behavior based on known equilibrium thermodynamic characteristics. Within the ‘joint kinetics’ this dogma is corrected. In some cases, knowing the equilibrium thermodynamic characteristics and kinetic dependencies which start from some initial conditions, it is possible to predict kinetic behavior from other initial conditions. This statement is illustrated by examples taken from heterogeneous catalysis (two-step catalytic mechanism, three-step Wei-Prater mechanism of isomerization and the water-gas shift reaction). A special attention was paid to revealing the new invariances for non-steady-state chemical reactions, both linear and non-linear. The existence of invariance for the non-linear etherification reaction was justified experimentally. The switching point between thermodynamic and kinetic control in organic reactions is analyzed as well.

For the case of initial state with some equilibrium concentration(s) as initial one(s), the concept of the

“conservatively perturbed equilibrium” (CPE) in chemical kinetics was distinguished using a sequence of first-order reactions (linear mechanism) and non-linear mechanisms as well. In the CPE, some, not all initial concentrations of the closed chemical system are replaced by the corresponding equilibrium concentrations at the same total amount of each chemical element and fixed temperature. Properties of CPE-phenomenon are the following ones: 1. For the substance which initial concentration is taken as the equilibrium one, the concentration extremum in a way to the equilibrium is unavoidable. 2. This extremum can be a momentary partial equilibrium for some steps of the chemical mechanism. 3. In some cases, time of occurrence of this extremum is independent of the perturbation. The CPE-effect was experimentally verified in a batch reactor for the complex esterification reaction. Experimental data obtained are analyzed based on the CPE-effect theory. It is shown that the CPE-phenomenon may lead to the possibility for processes limited by thermodynamic equilibrium achieving a yield higher than the CSTR. This is probably highly important for some industrial processes, for example, processes of the pharmaceutical industry. Also, a phenomenon of the "swapped equilibrium" (SE) is theoretically described. The SE-equilibrium occurs when the initial concentrations of two chemical species are taken as their equilibrium concentrations are swapped.

Keywords: joint kinetics, invariances, conservatively perturbed equilibrium