JOINT KINETICS: A NEW STRATEGY FOR CHEMICAL KINETICS.

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Highlights

- Unavoidable transient extrema.
- The CPE-experiment.
- Hydrogen and CO over-equilibria.
- Kinetic invariances.

1. Introduction

Joint kinetics (JK), as formulated in a series of papers [1-13], is presented as a new strategy for chemical kinetics. Central concepts of JK have been introduced based on the analysis of 'batteries" of experiments. These concepts are "events", "trends" and "map of events. "Events" are kinetic experiment and corresponding kinetic dependences with special features found computationally and/or theoretically, i.e., extrema and intersections, coincidences and momentary equilibria, "turning points" etc. Maps of kinetic events and trends are constructed and analyzed. Different events are categorized with an indicationhich events are unavoidable (always'- events) and which never happened (never' -events). .

2. Methods

Mathematical models of chemical kinetics as systems of ordinary differential equations and algebraic equations have been analyzed using analytic and computer methods. Conceptual results, i.e. dual relationships and predicted over-equilibria, have been verified experimentally in special kinetic experiments.

3. Results and discussion.

Within Joint Kinetics, two approaches have been established and developed.

3A. Dual-Experiment Approach.

The "batteries" of kinetic experiments are performed and analyzed, e.g., the experiments which start from symmetrical initial conditions [1, 3-7].

In classical chemical kinetics, there has been, and still exists, a traditional view that *one cannot* predict *kinetic* behavior based on known *equilibrium* thermodynamic characteristics. Based on JK- findings, 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. In [4-6], the developed theory was justified in both computer and real experiments using the catalytic Water-Gas-Shift (WGS) – reaction, dual electrochemical dependencies and esterification reaction. Also, the mixed "kinetic-thermodynamic" invariances have been found, i.e., functions of both kinetic constants and equilibrium constants [7]. Intersection points of kinetic dependencies were interpreted as an additional source for extracting the reaction coefficients [2].

3B. Conservatively Perturbed Equilibrium

Within JK, in a virtual experiment with special initial conditions a new kinetic phenomenon was found, i.e., the *Conservatively Perturbed Equilibrium (CPE)* [1, 8, 9]. In such an experiment using a closed chemical system (a batch reactor) with the complex reversible reaction, the initial concentrations of *(n-2)* substances are chosen to be equal to the equilibrium ones for these substances. The concentrations of the two remaining substances must meet mass conservation requirements. In a batch reactor, the relaxation curve for each of the *(n-2)* mentioned substances must have the following special property: starting from the equilibrium concentration as the initial value, it achieves the equilibrium concentration again via an extreme value (maximum or minimum) in the transient regime. Such behavior is unavoidable for each substance whose initial concentration is taken as the equilibrium one. The CPE-effect was justified experimentally [10].

Potentially, the obtained over-equilibria are interesting for increasing the efficiency of industrial reactions. It was illustrated by modelling the methane reforming processes (dry reforming + steam reforming) [11]. Also, the phenomenon described can be used both experimentally and computationally to reveal details of complex chemical mechanisms [10, 12-13].

4. Conclusions

Joint kinetics bridges the gap between thermodynamic equilibrium and non-steady-state kinetic behavior.

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