JOINT KINETICS: A NEW STRATEGY IN CHEMICAL KINETICS

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Since Guldberg – Waage's and Van't Hoff's times, the chemical equilibrium became one of the favorite topics of physical chemistry and chemical engineering.

Presently, the calculation of chemical equilibrium composition became a basis of solving many problems of chemical and biochemical engineering. Such calculations are performed based on the list of reactions with known equilibrium constants or the list of substances with known thermodynamic potentials using the procedure of Gibbs energy minimization.

The equilibrium of reversible complex chemical reaction is *the detailed balance,* i.e. for every step, the rate of the forward reaction equals the rate of corresponding reverse reaction [1, 2].

The main property of the equilibrium composition is its uniqueness and stability. It means that at the limit of infinite time the chemical composition in a closed chemical system, at fixed amounts of chemical elements and fixed temperature, achieves the same chemical composition, starting from any initial conditions. This composition is unique and stable.

The uniqueness of the equilibrium composition is a fundamental property of physico-chemical systems. This property, still underestimated, is rigorously proven for mass-action-law systems of chemical kinetics. The first qualitative proof was done in 1939 by Y.B. Zeldovich [3]. In the 1960-1970s, the same problem was recognized again and studied extensively. It was posed and solved rigorously by some researchers who have never heard about the pioneering work of Zeldovich. First, the results of Shapiro and Shapley should be mentioned [4]. Aris formulated this problem within the general program of chemo-mathematical activity [5, 6]. Then, Horn and Jackson [7], and Vol'pert [8] and Vol'pert and Khudyaev [9] presented the rigorous proof of the uniqueness and stability of the equilibrium for chemical mass-action law systems which occur in homogeneous media. Later, Gorban showed that all polyhedron boundary equilibrium points of a closed system are unstable [10]. Also, Gorban et al. [11, 12] analyzed the behavior of a closed chemical system with some irreversible reactions presenting it as an asymptotic case of the system in which all reactions are reversible.

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 [13-27]. 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:

(a) System of differential equations for the batch reactor (astronomic time);

(b) System of algebraic equations for the CSTR (space time, or residence time);

(c) System of linear equations based on balances of chemical 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 catalytic isomerization [20] 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 [15, 16, 24, 25]. The existence of invariance for the non-linear etherification reaction was justified experimentally [25]. The switching point between thermodynamic and kinetic control in organic reactions is analyzed as well [22].

For the case of initial state with some equilibrium concentration(s) as initial one(s), the concept of the "conservatively perturbed equilibrium" (CPE) was formulated [26]. 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. It was shown that the extremum time is independent on the initial reaction conditions. Based on the conservatively perturbed equilibrium procedure, some mechanistic details can be extracted, and kinetic parameters can be estimated. A momentary equilibrium in the TAP-studies of reversible adsorption is presented as a source of information about the number of active catalytic centers [18].

Also, a phenomenon of the "swapped equilibrium" (SE) is theoretically described [27]. The SE-equilibrium occurs when the initial concentrations of two chemical species are taken as their equilibrium concentrations but swapped. In complex mechanisms, this implies that the initial concentrations of the other chemical species remain equal to their corresponding equilibrium concentrations; in this case, the SE-phenomenon relates to the CPE-phenomenon previously mentioned. The SE-equilibrium is illustrated for both a single-step and a two-step mechanism with first-order reactions. For the two-step mechanism, invariant expressions are obtained based on the corrected ratios of CPE concentration profiles, while the other two chemical species are under swapped equilibrium conditions. For the related CPE case, invariant expressions are also obtained considering the same two-step mechanism.

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ОСОБЕННОСТИ ЗАДАЧИ ОПТИМИЗАЦИИ СТРАТЕГИЙ УПРАВЛЕНИЯ КАПИТАЛОМ В ТОРГОВЛЕ НА БИРЖЕ

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На примере имитационного моделирования сделан анализ некоторых стратегий игровых ситуаций. В некоторых случаях рассмотрены и результаты аналитических решений. Приведены графики зависимости вероятности событий от финансового результата, финансового результата от числа сделок. В расчетах для различных случаев применен «треугольник Паскаля». Проведен анализ полученных данных. Отмечено, что эффективность стратегий игровых ситуаций зависит от многих факторов и даны пути решения этих проблем.

As an example of imitation modelling the analysis for strategies of game situations was carried out. In some cases the results of analytical decisions were considered. Given are the chartes of dependence of events possibility from final results and the chartes of dependence of the final result for the calculations of different cases "the triangle of Pascal" is issued. The analysis of data recived ws carried out. The effectiveness of strategy for game situations depends on the many factors, but the article gives only some ways of this problems decisions.