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OVER-EQUILIBRIUM AS A RESULT OF CONSERVATIVELY-PERTUBED EQUILIBRIUM (ACYCLIC AND CYCLIC MECHANISMS)

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Finding the optimal mode is a conceptual problem of chemical engineering. In this paper, there were analyzed the transient regimes under conditions of the conservatively – perturbed equilibrium (CPE) recently discovered [1–3]. It is shown that CPE may provide concentration characteristics higher than the equilibrium ones, i. e., "over-equilibrium".

Reversible linear mechanisms with three substances, *A*, *B* and *C* (acyclic (1, 2) and cyclic (3, 4) mechanisms) are considered:

$$A \xleftrightarrow{k_1^+,k_1^-} B \xleftrightarrow{k_2^+,k_2^-} C \qquad (1)$$

$$k_1^+ = 10,\ k_1^- = 2,\ \ k_2^+ = 6,\ \ k_2^- = 2; \qquad (2)$$

$$A \xleftrightarrow{k_1^+,k_1^-} B \xleftrightarrow{k_2^+,k_2^-} C \xleftrightarrow{k_3^+,k_3^-} A \qquad (3)$$

$$k_1^+ = 10,\ k_1^- = 2,\ \ k_2^+ = 6,\ \ k_2^- = 2,\ \ k_3^+ = 1,\ \ k_3^- = 15; \qquad (4)$$

where k^+ and k^- are the rate coefficients for the forward and reversible reactions.

According to the CPE phenomenon, one component, i. e., *B*, is selected so that its initial concentration is equal to its equilibrium value. Remaining two components, *A* and *C*, are selected so that their initial concentrations differ from the equilibrium concentrations maintaining the constant total mass amount.

Graphical dependences are obtained, namely temporal dependencies of concentrations for PFR ("steady-state plug flow reactor") and CSTR ("steady-state continuous stirred tank reactor"): fig. 1 – acyclic system, fig. 2 – cyclic system.

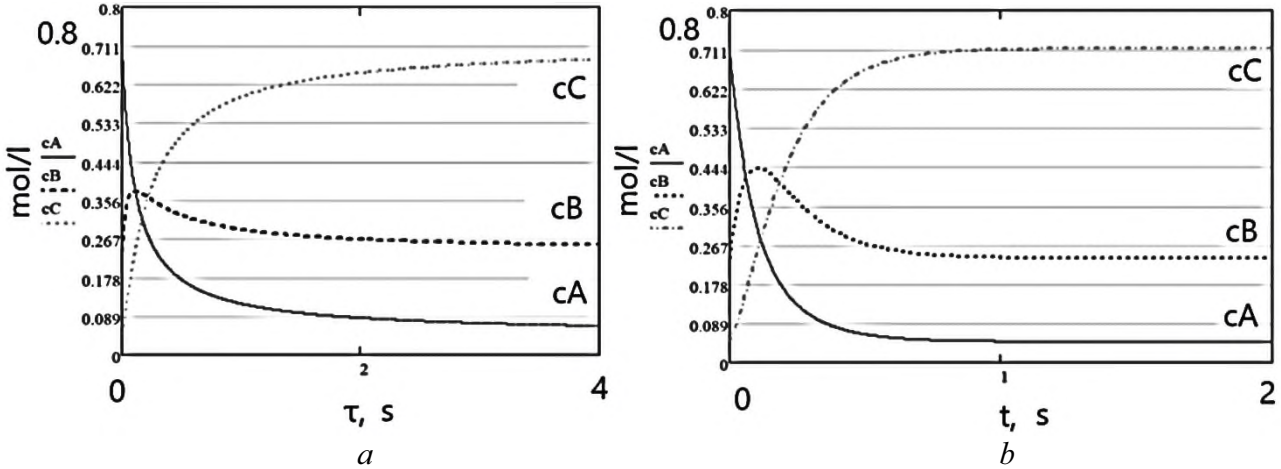
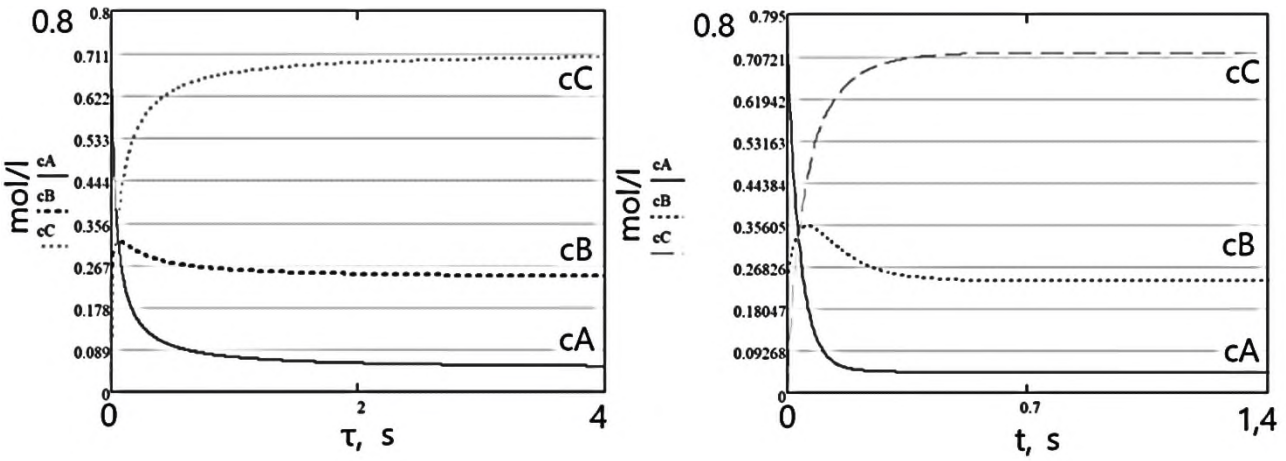


Fig. 1. Temporal concentrations of reactants *(a)* CSTR and *(b)* PFR (acyclic mechanism)



a *b*

Fig. 2. Temporal concentrations of reactants for: *(a)* CSTR and *(b)* PFR (cyclic mechanism)

For the acyclic mechanism, in the CSTR the time of *B*-extremum onset was insignificantly less than in the PFR (about by 2 %), but the extremum *B*-concentration in the PFR was significantly greater than in the CSTR (about 20 %).

For the cyclic mechanism, in the CSTR the time of *B*-extremum onset was less in the CSTR by 6 %, but the extremum *B*-concentration in the PFR was greater than in the CSTR, about 12 %.

The greater the difference between the initial concentrations of the two substances, the greater the "over-equilibrium" concentration of the third substance, the initial concentration of which was the equilibrium one.

Conclusions. In transient regimes, the concentration extrema are always observed for acyclic and cyclic mechanisms in both reactors, PFR and CSTR i. e., CPE-phenomenon is reproduced in both PFR and CSTR. Considering the same rate coefficients for corresponding reactions, the both mechanisms in the PFR are characterized by higher values of "over-equilibrium" than these mechanisms in the CSTR.

1. Yablonsky G. S., Branco D. P., Marin G. B., Constales D. Conservatively Perturbed Equilibrium (CPE) in chemical kinetics. *Chemical Engineering Science*. 2019. Vol. 196. P. 384–390. DOI: https://doi.org/10.1016/j.ces.2018.11.010.

2. Yablonsky G. S., Constales D., Marin G. B. Equilibrium relationships for non-equilibrium chemical dependencies *Chemical Engineering Science*. 2011. Vol. 66. P. 111–114. DOI: https://doi.org/10.1016/j.ces.2010.10.014.

3. Trishch V. R., Beznosyk Yu. O., Bugaieva L. M., Yablonsky G. S. Reactive chemical systems with equilibrium kinetic relations. *Organization of scientific research in modern conditions '2020*: Conference proceedings International scientific conference May, 14–15, 2020. USA, Seattle: KindleDP, 2020. P. 167–172. DOI: https://doi.org/10.30888/979-865-1656-02-8.0.