React. Kinet. Catal. Lett., Vol. 15, No. 2, 245–250 (1980)

DYNAMICS OF CHEMICAL REACTIONS AND NONPHYSICAL STEADY STATES

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Received May 13, 1980
Accepted June 17, 1980

Data on the position of nonphysical (lying beyond the region of determination) steady states are shown to be of use for understanding the dynamic behavior of chemical reactions, in particular, the reasons for slow relaxations.

Показано, что информация о положении нефизических (лежащих вне области определения) стационарных состояний полезна для понимания динамического поведения химической реакции, в частности, причин возникновения медленных релаксаций.

Prolonged transient regimes were found experimentally in chemical reactions in greatly different homogeneous (gas and liquid phase) and heterogeneous media. In several cases the non-steady-state kinetic curves have an induction period and are S-shaped. It has been shown previously /1-3/, that such slow relaxations can be of the purely kinetic origin, and for their interpretation one does not need to apply any additonal factors (e. g. processes of exchange between surface and bulk of the catalyst in heterogeneous catalytic reactions /4/). It has been shown that slow relaxations are associated with violating the continuous dependence of ω-limiting sets (i. e. sets consisting of the points which the solution approaches at $t \longrightarrow \infty$) on the parameters and the initial conditions /5/, and of the other peculiarities of the dynamics, i. e. the existence of Poisson-unstable trajectories /6/ completely lying in the reaction polyhedron (the latter is characterized by balance limitations and the condition of nonnegative concentrations). In the presence of the above peculiarities (bifurcations, etc.) and near them, the non-steady-state kinetic dependences are characterized by slow relaxations.

The present paper is devoted to the description of one of the above effects associated with the specificity of chemical systems. The kinetic equations define on the reaction polyhedron not a dynamic system (flux), but only a semi-dynamic system (semi-flux): as a rule, only positive semitrajectories are physically meaningful (at $t > 0$), the extension of solutions for negative times ($t < 0$) usually leads to the formation of "nonphysical" concentrations, and starting from a certain $t_0 < 0$ (at $t < t_0$), the solution leaves the reaction polyhedron. Hence the bifurcations of ω -limiting sets (e.g. the change in the number of steady states) in the polyhedron can occur not only via the usual dynamic route (e.g. through the appearance of nonrough steady-state points), but also through the appearance of new limiting points on the polyhedron boundary, i.e. through the "creeping" of the nonphysical steady state (lying beyond the region of determination) into the physical region.

Consider a simple example, i.e. a reactionn mechanism consisting of the following series of steps:

$$1)\ A_2 + 2Z \rightleftharpoons 2AZ, \qquad 2)\ B + Z \rightleftharpoons BZ,$$

$$3)\ AZ + BZ \longrightarrow AB + 2Z$$

The dynamic model corresponding to the above mechanism is

$$\begin{aligned} [\dot{AZ}] &= 2k_1 p_{A_2} [Z]^2 - 2k_{-1}[AZ]^2 - k_3[AZ][BZ] \\ [\dot{BZ}] &= k_2 p_B [Z] - k_{-2}[BZ] - k_3[AZ][BZ] \qquad (1) \\ [AZ] &+ [BZ] + [Z] = 1 \end{aligned}$$

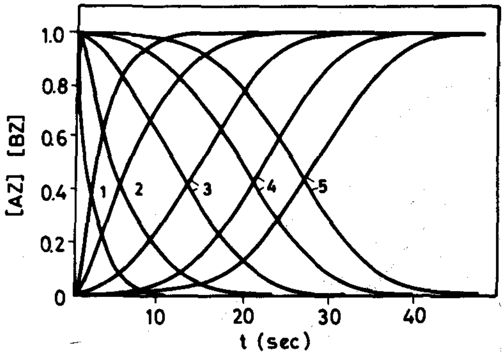

Fig. 1. Dependences [AZ(t)], [BZ(t)] for various rate constants $k_{-1} = 1$ (1), 10^{-1} (2), 10^{-2} (3), 10^{-3} (4) and 10^{-4} s (5)

where p_{A_2} and p_B are the partial pressures of the substances A_2 and B, [AZ], [BZ] and [Z] are the concentrations of various substances on the catalyst surface and $k_{\pm i}$ are reaction rate constants.

At $k_2p_B > 2k_1p_{A_2}$ the steady state is unique and stable /7/: at $k_{-2} = 0$ it is characterized by the total surface coverage by substance B ([BZ] = 1, [AZ] = 0). Let the initial state of the catalyst be such that its surface is practically completely covered by substance A_2 ($[BZ]_{t=0} = 0$, $[AZ]_{t=0} = 0.999$). Let the desorption constant k_{-1} be small. Then the dependences [AZ(t)] and [BZ(t)] are characterized by a distinct induction period. With increasing k_{-1}, the induction period becomes less distinct and finally disappears (Fig. 1).

Upon motion from any initial conditions, the phase trajectories behave as follows: first they reach the vicinity of some special curve rather rapidly, then the motion occurs more slowly along this curve. The meaning of the special curve referred to /1/ as the "main stream" has not been elucidated previously. However, this curve is no more than a specific trajectory (separatrix) which goes to the stable steady state lying in the reaction polyhedron from the unstable steady state positioned

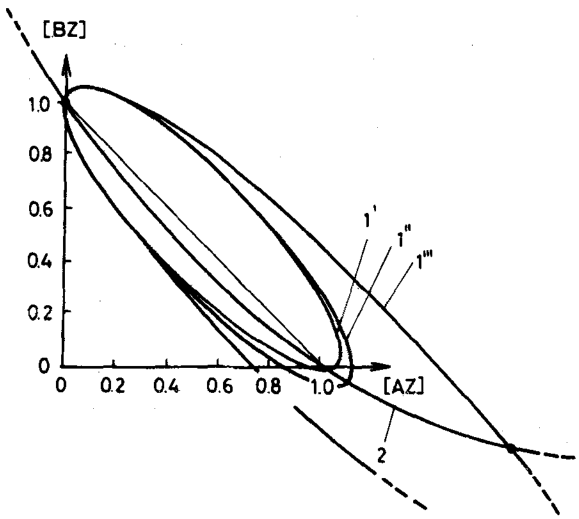

Fig. 2. Steady states and main isoclines of system (1) for various values of parameter k_{-1}: 1 – [AZ] = 0, 1' – $k_{-1} = 10^{-3}$ s, 1'' – $k_{-1} = 10^{-2}$ s^{-1}, 1''' – $k_{-1} = 10^{-1}$ s^{-1}, 2 – [BZ] = 0

outside it. To draw this trajectory, it is necessary to know the position of the steady state located beyond the region of physical determination.

For the example under consideration ($k_1 p_{A_2} = k_2 p_B = 1\ s^{-1}$, $k_2 = 0$, $k_3 = 0.5\ s^{-1}$), besides the boundary steady state ([AZ] = 0, [BZ] = 1), belonging to the reaction polyhedron $S = \{([AZ], [BZ]): [AZ] \geqslant 0, [BZ] \geqslant 0, [AZ] + [BZ] \leqslant 1\}$, there always exists a real steady state lying outside the region of system defined (at $0 < k_1 < 1$ its coordinates are characterized by the inequalities [AZ] > 1, [BZ] < 0). The position of this steady state, the point of intersection of the main isoclines (zero-isoclines) of the system ([AZ] = 0 and [BZ] = 0) is shown in Fig. 2 as a function of the value of parameter k_{-1}. At small values of k_{-1} this point is positioned sufficiently close to the region of our initial conditons (at $k_{-1} = 0$ it becomes the boundary unstable steady-state point). It is the proximity of the initial conditions to the steady state outside the reaction polyhedron that is responsible for the slow transient regime. Note that besides two real steady states, system (1) has also two complex steady states, which at bifurcational values of the parameters /7/ become real, appearing in the reaction polyhedron as a nonrough internal steady state. The proximity of complex roots of system (1) to the reaction polyhedron S is also responsible for the slow relaxation in system /3/.

Similar results can also be obtained from consideration of the more simple reaction mechanism: 1) $A + Z \rightleftharpoons AZ$, 2) $B + Z \rightleftharpoons BZ$, 3) $AZ + BZ \longrightarrow AB + 2Z$.

Thus, the effect of slow relaxations can also be observed when the steady state inside the reaction polyhedron is unique and stable as a whole (all positive solutions tend to it at $t \longrightarrow \infty$). For this it suffices that the "external" (nonphysical) steady state should be close to the polyhedron boundary, and the initial conditions positioned in its vicinity from the opposite boundary side (inside the polyhedron).

We believe that this fact is of general significance. As a rule, the kinetic equations are nonlinear and should have several steady-state solutions, but not all of them are physically meaningful (negative and complex steady-state solutions are possible). But as has been shown, slow transient regimes can also be observed when the physically meaningless stedy-state solutions are positioned near the reaction polyhedron. It is evident that the same situation can also be observed in closed systems, where the positive point of detailed equilibrium is always unique /8-9/. Thus, to understand the dynamics of chemical reactions (in particular, the reasons for the induction periods) in the physically determined region of compositions, the knowledge of the positions of all steady-states of the system may be informative.

REFERENCES

1. V.I. Bykov, G.S. Yablonskii, M.G. Slinko: Dokl. Akad. Nauk SSSR, 229, 6, 1356 (1976).
2. V.I. Elokhin, V.I. Bykov, M.G. Slinko, G.S. Yablonskii: Dokl. Akad. Nauk SSSR, 238, 3, 615 (1978).

3. A.N. Gorban, V.I. Elokhin, V.M. Cheresiz, G.S. Yablonskii: in Proc. All-Union Conference on Non-steady-state Processes in Catalysis, p. 1, pp. 83, Institut Kataliza, Novosibirsk 1979.
4. L.P. Levchenko, N.V. Kulkova, M.I. Temkin: Kinet. Katal., 17, 6, 1542 (1976).
5. A.N. Gorban, V.M. Cheresiz: Dokl. Akad. Nauk SSSR, (In press).
6. V.V. Nemytskii, V.V. Stepanov: Quantitative Theory of Differential Equations, GITL, Moskva 1949.
7. M.G. Slinko, G.S. Yablonskii: in Problems of Kinetics and Catalysis, Vol. 17, pp. 154, Nauka, Moskva 1978.
8. Ya.B. Zeldovich: Zh. Fiz. Khim., 11, 685 (1938).
9. V.M. Basiliev, A.I. Volpert, S.I. Khudyaev: Zh. Vychislit. Mat. Matem. Fiz., 13, 683 (1973).