

# Model kinetic systems with multiple stationary states and their stability in an ideally stirred flow reactor — tristable system

A. TOCKSTEIN

*Department of Physical Chemistry, Institute of Chemical Technology,  
CS-532 10 Pardubice*

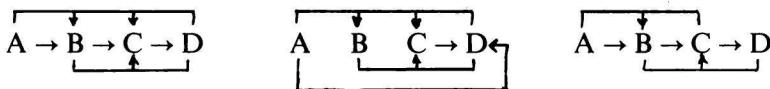
Received 26 June 1989

*Dedicated to Professor E. Treindl, DrSc., in honour of his 60th birthday*

Some more complicated systems were formed by parallel arrangement of autocatalytic blocks of the type  $A \rightarrow B \rightarrow C$  or  $A \rightarrow B \rightarrow C \rightarrow D$  in an ideally stirred flow reactor. For one of them the tristability was evidenced at a discontinuous change in flow rate. This model represents a simple kinetic model for tristability.

В идеально перемешиваемом проточном реакторе из автокаталитических блоков типа  $A \rightarrow B \rightarrow C$  или  $A \rightarrow B \rightarrow C \rightarrow D$  были с помощью параллельного упорядочения составлены более сложные системы. У одного из них демонстрировалась тристабильность при дисконтинуальном изменении проточных скоростей. Данная система представляет собой простую кинетическую модель тристабильности.

Several authors [1] have experimentally found kinetic systems which in an ideally stirred flow reactor show the bistable behaviour depending on the flow rate. Besides chemically little realistic models [2—9], some simple and chemically realistic models [10] have been put forward for the bistable behaviour. These models are based on simple autocatalytic blocks of the type  $A \rightarrow B \rightarrow C$  or  $A \rightarrow B \rightarrow C \rightarrow D$  which can be arranged in the following ways



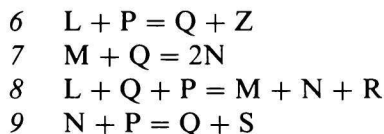
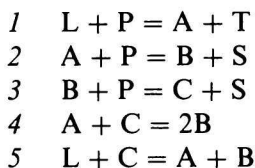
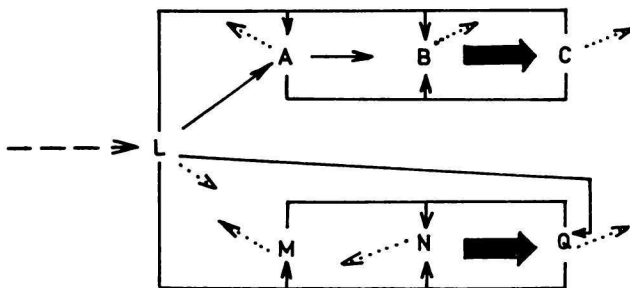
The aim of this study has been to combine always two such bistable blocks for forming the more complicated systems which could be able to show the multistable, and especially the tristable behaviour. As a matter of fact, the tristable systems have already been described experimentally in few cases [1, 11], but an appropriate theoretical model has not been found yet.

### Theoretical

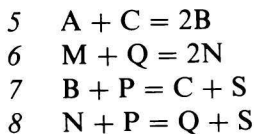
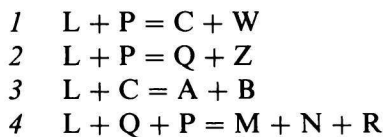
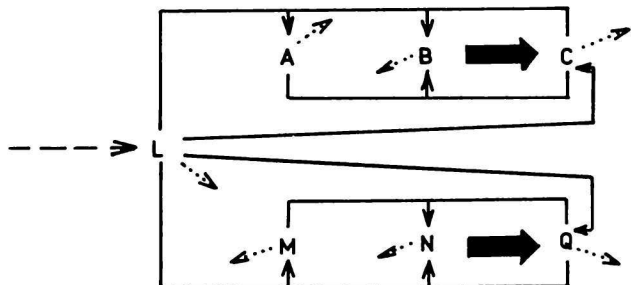
We have chosen four kinetic systems S1, S2, S3, and S4 as models. Their stoichiometry and graphical representation is given subsequently.

The outlet of all components in the systems is designated by dotted line while the inlet of the starting component L is marked by dashed line, the bold arrow means a very fast step which is in line with the Bodenstein principle. Reagent P is present in pseudoconstant concentration and is not denoted in the schemes. The products of its transformation S, W, Z, R, T are also not denoted.

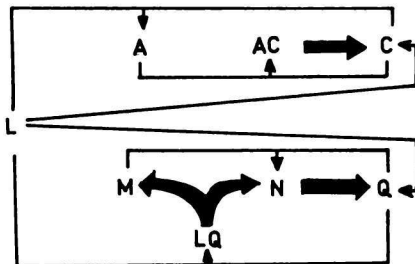
System S1



System S2



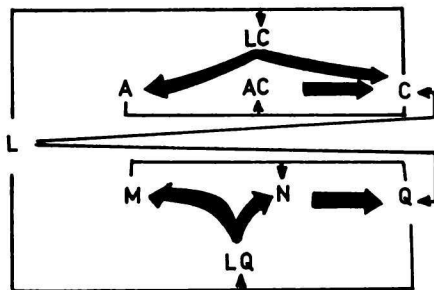
## System S3



- 1  $L + P = C + W$
- 2  $L + P = Q + Z$
- 3  $L + C = 2A$
- 4  $A + C = AC$
- 5  $AC + P = 2C + S$

- 6  $L + Q = LQ$
- 7  $LQ + P = M + N + R$
- 8  $M + Q = 2N$
- 9  $N + P = Q + S$

## System S4



- 1  $L + P = C + W$
- 2  $L + P = Q + Z$
- 3  $L + C = LC$
- 4  $A + C = AC$
- 5  $LC + P = A + C + S$

- 5'  $AC + P = 2C + S$
- 6  $L + Q = LQ$
- 7  $LQ + P = M + N + R$
- 8  $M + Q = 2N$
- 9  $N + P = Q + S$

The reason for construction of systems S3 and S4 containing adducts LQ, AC or LC, LQ, AC is as follows: If system S1 or S2 were to be made by different oxidation numbers of a certain element and particles L, A, B, C, M, N, Q should be different, the existence of seven oxidation numbers would be necessary, which could be put into life with difficulties. On the other hand, for systems S3 and S4

the existence of six oxidation numbers is sufficient because adducts have been taken into consideration. For instance, if we consider the permanganate oscillator for which the tristability was found experimentally some time ago [11], particles L, M, A, N, C, Q ought to represent the oxidation numbers 7, 6, 5, 4, 3, 2 and agent P acts in step 7 of systems S3 and S4 as oxidant and in other steps as reductant.

For all these systems we calculated the stationary concentrations of individual reaction components as functions of flow rate by using different combinations of rate constants of particular steps and simultaneously we ascertained the stability of individual parts of the corresponding curves.

For solving the stationary states the corresponding kinetic equations were annulled and the system of algebraic equations thus formed was transformed in the dependence of one chosen relative stationary concentration of component C  $c^o(C) = [C]^o/a$  on flow rate  $f = v/(aV)$  where  $v$  is the rate of feed of solution of the component L present in concentration  $a$  into reactor of volume  $V$ . The roots of this algebraic equation were sought for every chosen level  $f$  by using the method of halving of the interval on a digital computer. In some cases, a high precision of calculation had to be used because the flow branch in the systems S3 (Figs. 2a, b) or S4 possessed a pair of roots which differed from each other as far as on the eighth decimal place and one of them had physical meaning while the other corresponded to negative concentration.

The stability of individual branches was so determined that the corresponding system of kinetic equations was integrated numerically by the Runge—Kutta method by using an automatically chosen length of step and initial conditions corresponding always to the calculated stationary values for all reaction components except one. For this one reaction component the initial value was put either a little lower or a little higher than the calculated stationary concentration and it was examined by integrating whether this concentration approached the stationary value or receded from it in the course of time. The first case indicates stability of the investigated branch whereas the second one corresponds to instability.

## Results and discussion

In Fig. 1 are the results obtained for the systems S1 and S2, which are valid also for the system S4 and in Fig. 2 are results obtained for the system S3. As

for systems S1 and S2, we can obtain the  $f$ — $c^\circ$  relationships between the flow rate and relative stationary concentration of component C which are of different form according to the choice of rate constants. We can derive them qualitatively from the basic geometrical formation given by contact of two beaks. Individual types may be obtained graphically by using different types of breaking and separation of particular branches. The equation of the  $f$ — $c^\circ$  relationship for system S4 is identical with the  $f$ — $c^\circ$  equation obtained for system S2, owing to which system S4 does not bring anything new.

Two types of the  $f$ — $c^\circ$  relationship (Figs. 2a, b) appeared for system S3, one with closed curve (isole), another without it.

The type of diagram in Figs. 1 and 2 is determined by the fact which of both parallel subsystems LAC or LMQ prevails in temporal development of the system at low rates, which depends on the choice of rate constants of individual steps. In cases represented in Figs. 1a, c subsystem LAC prevails while in case b it is subsystem LMQ. In Fig. 2a subsystem LMQ prevails and conversely it is subsystem LAC that prevails in Fig. 2b. The stable parts of individual branches are drawn in full lines and the instable branches in dashed lines.

It is obvious from the figures that a sufficiently great discontinuous change in flow rate makes possible to get inside the closed curve and as the case may be, to reach its stable branch (which would not be attainable at a continuous change in flow rate) and thus to produce a conditioned tristable system. As the flow rate changes discontinuously during experimental investigation of the systems in an ideally stirred flow reactor, such conditioned tristable systems may appear. For this reason, the calculations of behaviour of the kinetic system were so performed for the chosen model systems that the corresponding stationary concentrations were chosen as the initial ones for a certain value of flow rate. Then the value of flow rate was changed for reaching the required level and the system was solved by the Runge—Kutta method. The results are represented in Figs. 1 and 2 by means of dotted and dashed arrows which give the magnitude of the change in flow rate and the direction in which the system tends towards a certain stable branch.

Thus it results in cases in Figs. 1a, b, and c, *i.e.* for the systems S1 and S2, resp. S4 that the continuous as well as discontinuous changes in flow rate always lead to equal branches and the system manifests only bistable behaviour. On the other hand, conveniently great discontinuous changes in flow rate in the system S3 (Fig. 2b) result in tristable behaviour owing to which this system represents a simple kinetic model of tristability at appropriate values of rate constants. Otherwise it is bistable (Fig. 2a).

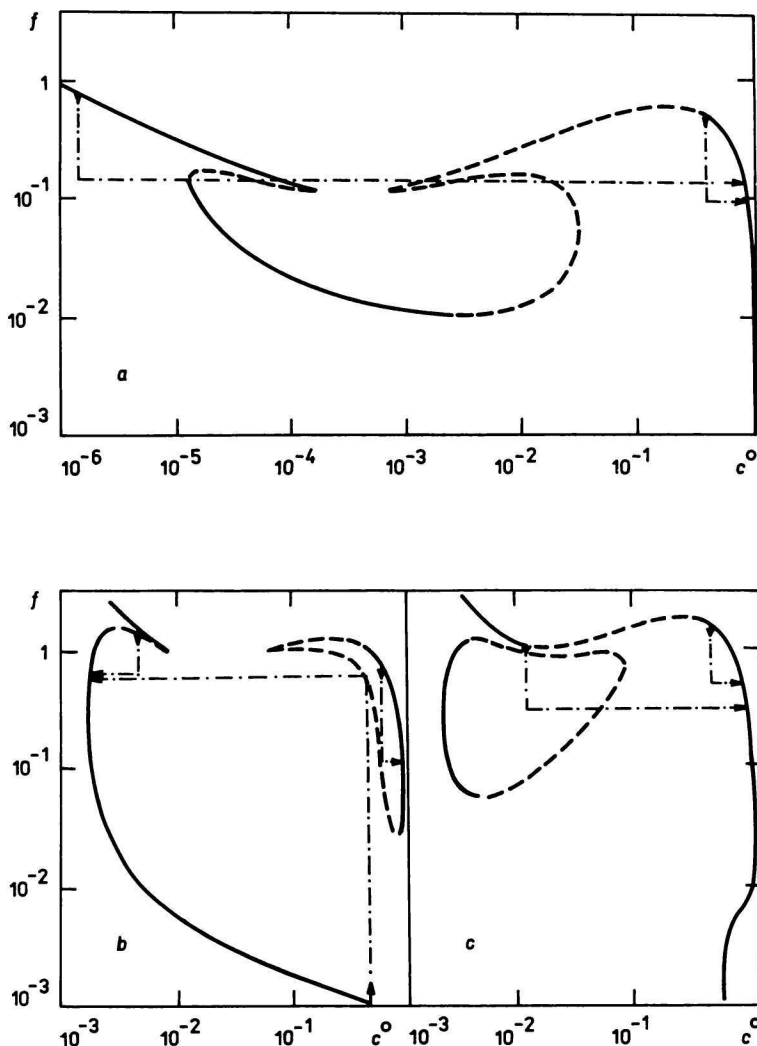


Fig. 1. Variation of relative stationary concentration of component C with relative flow rate  $f$ .

a) System S1, relative rate constants:  $k_1 = k_2 = k_6 = 10^{-3}$ ,  $k_4 = 10$ ,  $k_5 = k_8 = 1$ ,  $k_7 = 0.5$ .

b) System S2,  $k_1 = k_2 = 10^{-2}$ ,  $k_3 = k_4 = k_5 = 5$ ,  $k_6 = 10$ .

c) System S2,  $k_1 = k_2 = 10^{-2}$ ,  $k_3 = k_5 = 5$ ,  $k_4 = k_6 = 10$ .

— Stable branch, - - - - - unstable branch, - · - · - changes in  $f$  and tendency of development of the system.

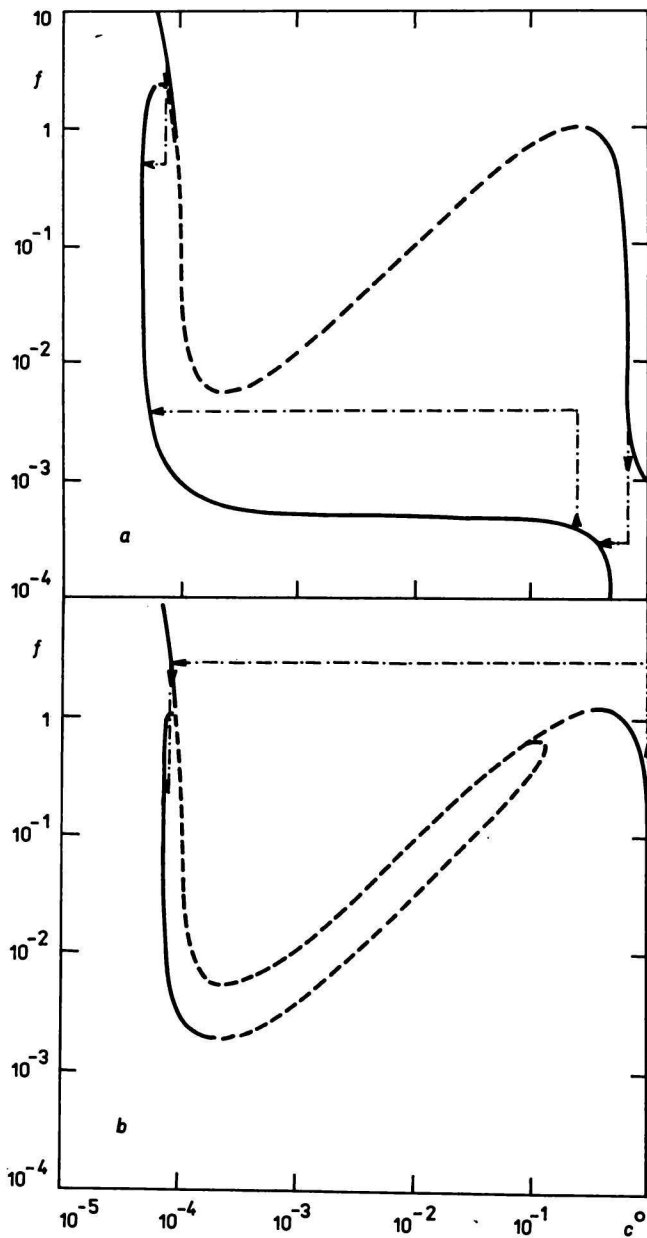


Fig. 2. Variation of relative stationary concentration of component C with relative flow rate  $f$ . System S3, relative rate constants: a)  $k_1 = k_2 = 10^{-3}$ ,  $k_3 = k_4 = k_6 = k_8 = 10$ . b)  $k_1 = k_2 = 10^{-3}$ ,  $k_3 = k_4 = 10$ ,  $k_6 = k_8 = 5$ . Denotation of lines as in Fig. 1.

## References

1. Field, R. J. and Burger, M., *Oscillations and Travelling Waves in Chemical Systems*, p. 231. J. Wiley, New York, 1985.
2. Boissonade, J., *J. Chem. Phys.* 73, 540 (1976).
3. Merkin, J. H., Needham, P. J., and Scott, S. K., *Proc. R. Soc. London, A* 398, 101 (1985).
4. Gray, P. and Scott, S. K., *Chem. Eng. Sci.* 38, 29 (1983).
5. Gray, B. F. and Scott, S. K., *J. Chem. Soc., Faraday Trans. 1* 81, 1563 (1985).
6. Gray, B. F. and Scott, S. K., *Chem. Eng. Sci.* 39, 1087 (1984).
7. Balakotaiah, V., *Proc. R. Soc. London, A* 411, 193 (1987).
8. Lin, K. F., *Can. J. Chem. Eng.* 57, 476 (1979).
9. Boissonade, J. and DeKepper, P., *J. Phys. Chem.* 84, 501 (1980).
10. Tockstein, A., *Chem. Phys. Lett.* 152, 464 (1988).
11. Nagy, A. and Treindl, L., *J. Phys. Chem.* 93, 2807 (1989).

Translated by R. Domanský