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EXPERIMENTAL STUDY OF THE BIFURCATION DIAGRAM IN THE BELOUSOV–ZHABOTINSKII REACTION

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In the citric acid $-Mn^{2+}-H_2SO_4-KBrO_3$ system a hysteresis phenomenon in the switching on and off of the oscillations has been observed. The possible bifurcation diagrams of the system are discussed.

В системе лимонная кислота $- Mn^{+2} - H_2SO_4 - KBrO_3$ был определен гистерезис налаживания и разлаживания осцилляций. Обсуждаются возможные диаграммы бифуркации.

Oscillation reactions still arouse much interest among both the theoretical and experimenting investigators. Analysis of the differential equations describing the model systems of chemical reactions showed that oscillations in the chemical systems are related to the existance of a limit cycle.

A stable limit cycle and an unstable node appear in the process of Hopf bifurcation /1/. They form from a stable node, which is the steady state.

In their theoretical papers dealing with model oscillation reaction systems, Tyson /2/ and Othmer /3/ found an unstable limit cycle to occur. The unstable limit cycle and the stable node are formed in the bifurcation process from an unstable node.

On varying one parameter of the system, which may be the concentration of one parent substance, the unstable limit cycle migrates in the concentration space from a stable limit cycle and next combines with the stable limit cycle and both cycles disappear. This is the third type of bifurcation which might occur in the system.

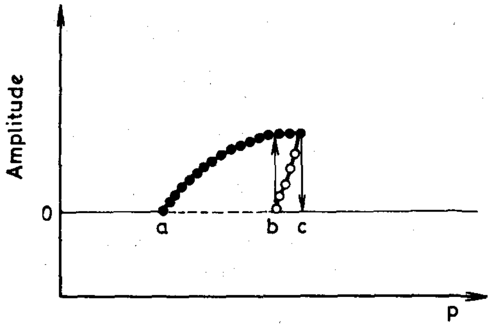

Fig. 1. Bifurcation diagram, —— - stable node, ------- - unstable node, -●-●-●- - stable limit cycle, -o-o-o- - unstable limit cycle

This process is presented diagrammatically in Fig. 1. The bifurcations discussed in this paper appear at points a, b and c. The arrows indicate changes in the system in the bifurcation points. At point "a" the Hopf bifurcation occurs and the system begins to oscillate.

The oscillation amplitude increases with increasing parameter p. At point "b" an unstable limit cycle and a stable node are formed. With further increase in the parameter p the amplitude of the unstable limit cycle increases and at point "c" both cycles disappear. The system jumps to the stable node. Oscillations are suddenly interrupted.

Now, if parameter p decreases, the system will not oscillate up to point "b". At this point the unstable node is formed from the stable node in the bifurcation process and the system jumps to the limit cycle. High-amplitude oscillations occur.

The switching on and off process of oscillations proceeds along a hysteresis curve.

So far hysteresis was found experimentally to occur upon switching on the oscillations in Ref. /4/ in the KIO_3–$HClO_4$–$CH_2 \cdot COOH_2$–$MnSO_4$–H_2O_2 system.

In the present paper the switching on and off process of oscillations was investigated in the H_2SO_4–$MnSO_4$–$KBrO_3$-citric acid system.

EXPERIMENTAL

Studies were carred out in a 70 cm^3 flow-through reactor. The solution was stirred by a magnetic stirrer. The reactor was supplied by means of pumps through separate inlets with two solutions:

Solution A: 6×10^{-3} M $MnSO_4$, 3 M H_2SO_4,
5×10^{-1} to 5×10^{-3} M citric acid,

Solution B: 4×10^{-2} M $KBrO_3$.

The $MnSO_4$, $KBrO_3$ and H_2SO_4 concentrations were constant in all series of measurements.

Variations of the oxidation-reduction potential (Mn^{3+}/Mn^{2+}) were measured as a function of time with a platinum electode using a calomel reference electrode.

The flow rate of solution A was constant and equal to 0.1 $cm^3\ s^{-1}$. For the selected concentration of citric acid the flow rate of solution B was changed stepwise starting from the higher flow rate. If the nature of the processes did not change för 30 min, the flow rate of solution B was somewhat decreased, etc. (Fig. 2). When the flow-rate reached the highest value, it was changed in the reverse order.

RESULTS AND DISCUSSION

The results of measurements are shown in Fig. 2.

Curve "c" represents the points where oscillations become suddenly quenched. Curve "b" displays the points where high-amplitude oscillations appear. The oxcillations start on curve "a". The points lying on this curve were also the points of Mn^{2+} titration by $KBrO_3$.

All 3 curves converge for low citric acid concentrations. Here, 3 cases are possible as shown in Fig. 3.

Figure 3.4 shows the bifurcation diagram below point "d" in Fig. 3.1. This case is difficult to find experimentally since during variation of parameter p the

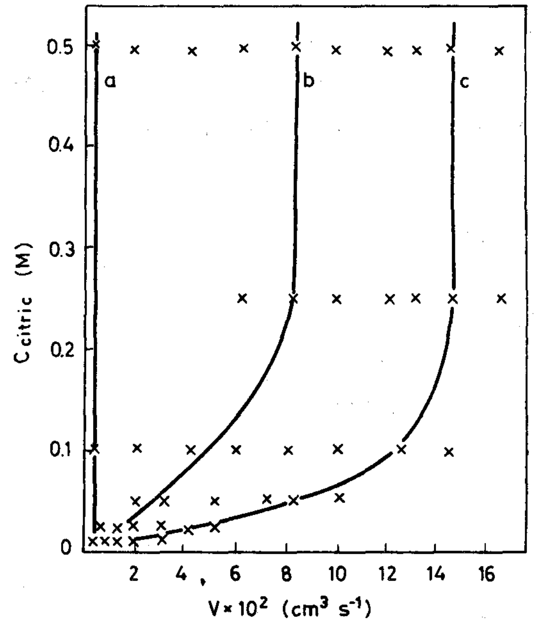

Fig. 2. Experimental positions of curves which are the bifurcation point pattern in the system

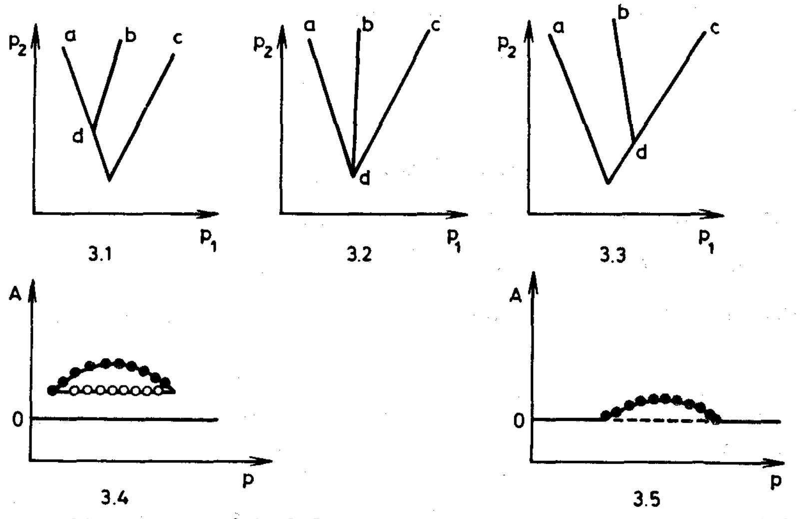

Fig. 3. Possible positions of the bifurcation curves and their corresponding bifurcation diagrams

system is always in the stable node. In order to generate oscillations in the system, it should be disturbed considerably and its transition beyond the unstable limit cycle should be brought about. In Fig. 3.2 all curves converge in one point. In that point the stable node produces a stable limit cycle, an unstable limit cycle and a stable node.

An important question from the chemical point of view arises: how many limit cycles may exist in a chemical system and how many may be formed in one bifurcation?

Figure 3.5 shows the bifurcation pattern for Fig. 3.3 below point "d".

In this case as parameter p increases, the oscillation amplitude increases and then decreases and the oscillations become quenched.

As shown in Fig. 2, in the case under consideration, it is difficult to find experimentally which type of the diagram is valid in the system under investigation. It is highly probable that by varying another one of the system parameters, all three types of bifurcation diagrams may be obtained.

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