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CALORIMETRIC CURVES OF B–Z OSCILLATION REACTION SYSTEMS AT DIFFERENT TEMPERATURES

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Abstract

In this paper studies on the oscillation regularity of the classical B–Z reaction system, and the calorimetric curves of the reaction system measured at three temperatures, 25, 27 and 29°C are described. A new way is presented for studying the regularity properties of chemical oscillation phenomena from the viewpoint of reaction heat effects.

Keywords: B–Z oscillation reaction, calorimetric curve, microcalorimeter

Introduction

Since 1958, when B. P. Beloasov first reported that the homogeneous system of citric acid oxidized by bromic acid in the presence of Ce^{3+} as catalyst could produce an oscillation reaction, studies on the phenomenon and properties of chemical oscillation systems have become popular in chemistry. As so far most research reports have been concerned with the oscillation regularity [1–5] of the reacting system by measuring the potential change of an electrode in the reacting system by means of potentiometric method. In this work the classical oscillation regularity of the B–Z reaction system was studied, the calorimetric curves of the reaction system were measured at three temperatures, 25, 27, and 29°C. A new method is presented for studying the regularity and properties of the chemical oscillation phenomenon from the viewpoint of reaction heat effect.

Experimental

Instrument

2277 Thermal Activity Monitor, working temperature range 10–80°C, constancy of temperature $\pm 2\cdot 10^{-4}$°C, minimum detectable power 0.1 μW and baseline stability (over a period of 24 h) 0.2 μW.

Chemical reagents

$KBrO_3$ (analytical grade); $NH_4Ce(SO_4)_2$ (analytical grade); H_2SO_4 (analytical grade); $CH_2(COOH)_2$ Merck AG Darmstadt, Germany.

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Solutions: 0.2530 mol l^{-1} $KBrO_3$; 0.0040 mol l^{-1} $NH_4Ce(SO_4)_2$; 0.5351 mol l^{-1} $CH_2(COOH)_2$; 3.0 mol l^{-1} H_2SO_4, prepared with double distilled water.

Experimental

In this experiment the method of mixing of flows was applied [6]. Reaction liquid (A): mix 5.00 ml $CH_2(COOH)_2$, 1.50 ml H_2SO_4, 2.50 ml $NH_4Ce(SO_4)_2$ solution and 5.00 ml H_2O; Reaction liquid B: mix 5.00 ml $KBrO_3$, 1.50 ml H_2SO_4, 2.50 ml $NH_4Ce(SO_4)_2$ solution and 5.00 ml H_2O. Pump reaction liquid (A) and reaction liquid (B) at the same time into the mixing chamber at a speed of 30 ml h^{-1} with microperpex pump (LKB Sweden). Stop the pump when the mixing chamber is full of reaction liquid.

Results and discussion

According to the FKN mechanism type [7], the vitality maintaining some certain time-space sequential structure of the B–Z reaction system in the reaction process strongly depends on the three reaction chains existing in the system. Because of the mutual dependences and the mutual limitations among these elementary reaction steps and the concentration of various species, the concentrations of some species such as Br^{-1}, HBrO, Ce^{3+}, Ce^{4+} etc. in the system change periodically in a special range when the reaction system is far from the equilibrium state. This means that if the rate of some reaction changes periodically during the process of chemical oscillation, then the heat effect measured in unit time should also behave as a periodical phenomenon. Calorimetric curves (Figs 1–3) well evidence this.

Figures 1, 2 and 3 clearly demonstrate that the period of oscillation shortens gradually with rising temperature. This shows that the rate of reaction increases

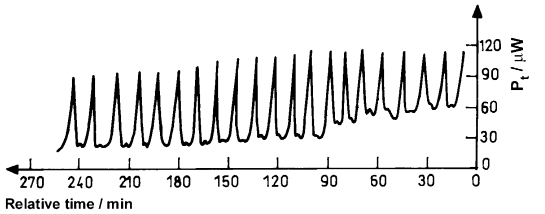

Fig. 1 Calorimetric curve at 25°C

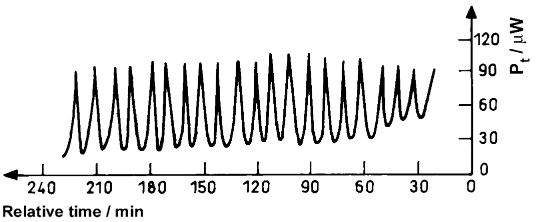

Fig. 2 Calorimetric curve at 27°C

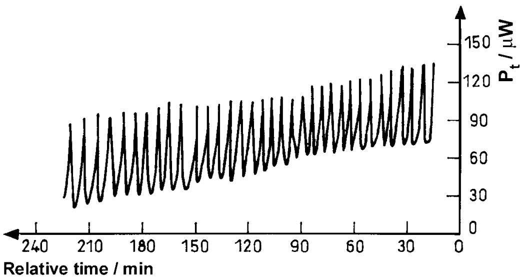

Fig. 3 Calorimetric curve at 29°C

gradually. This conclusion agrees well with those drawn from other studies [8]. In Fig. 1 we can see that there are many infinitesimal thermal waves between two peaks. This also suggests that the reaction process is complicated. By potentiometric method the oscillation cannot be followed as closely as by the calorimetric method described in this paper. However, these infinitesimal thermal waves disappear gradually as the temperature rises and the reaction rate increases.

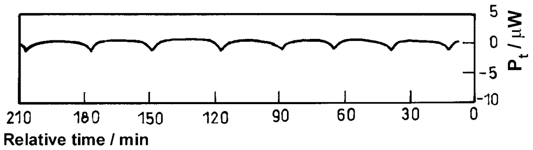

Fig. 4 Calorimetric curve of the reaction system after 20 h (29°C)

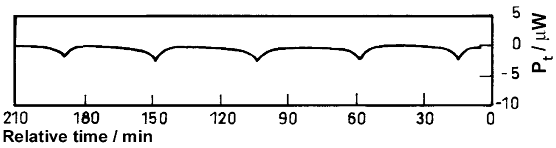

Fig. 5 Calorimetric curve of the reaction system after 40 h (29°C)

An interesting phenomenon is that if after the Microperpex pump is stopped and the tube of sample is left in the reaction liquid, a certain form of thermal oscillation is maintained in the system for a long time (20–43 h). But these thermal oscillations are quite different from those at the beginning (Figs 4 and 5). Similarly, if the Microperpex pump is stopped and the tube of sample is removed from the reaction liquid, the same phenomenon may be observed, but the oscillation time becomes shorter than in the previous case (less than 10 h). This observation may be connected with the fact that due to the escape of part of the gaseous product (a small amount of liquid flowing out of the tube outlet can be observed) some reaction liquid gets into the mixing chamber automatically, and thus a certain form of sequential mechanism of reaction may occur. However, further studies are required to clear up this phenomenon.

In comparison with potentiometric and other methods, the microcalorimeter method has the following advantages in studying the B–Z oscillation reactions:

I. For any reaction system, if there is an oscillation of the concentration of a substance, there should occur an oscillation of energy exchange. So the range of oscillation reactions that can be studied by calorimetric method is much wider than those that can be followed by other methods.

II. Since the microcalorimeter method is direct in measuring the change of heat effect of the system, no effects such as those caused by ion-selective electrode and/or reference electrode used in the potentiometric method on the reaction system are to be taken into account.

III. The microcalorimeter method is very well suited to studies on microsystems. Only 5 ml reaction liquid is needed and only about 1 ml is used in the actual measurement (the volume of the mixing chamber is 1 ml).

The limitations of the microcalorimeter method are:

I. Some oscillation regularity may be inhomogeneous because there is no stirring in the reaction system.

II. Some time is needed until thermal equilibrium is attained after the reaction liquid is put into the mixing chamber, so the induction period of the oscillation cannot be measured accurately. However, in a word by combining the microcalorimeter method with other method, the B–Z oscillation reactions can be studied in more detail.

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