Slowing Down in Chemical Tristability Systems

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In this paper two kinds of slowing down in the chemical trista-bility systems are studied. One is the critical slowing down at the edges of tristable region, and the other is the slowing down far from the critical point, which has much to do with the unstable steady-points. The results possess some universal properties.

Keywords   Chemical tristability, critical phenomenon, slowing down

Introduction

Much attention has been paid on the critical phe-nomena in nonlinear chemical reaction.[1-3] The slowing down in chemical bistability has been studied in some papers.[4,5] The chemical tristability system is also a typi-cal nonlinear dissipative system. In previous paper,[6,7] it was pointed out that both the tristability termination point and the bistability termination point[8,9] have the character of second-order-like phase transition. But the difference between bistability and tristability is that the bistability termination point is a stable critical point, and the tristability termination point is an unstable critical point. In this paper, we precede a further study of the slowing down in the chemical tristability, discuss the critical slowing down at the fringe critical point and termination point, and compute the two kinds of critical slowing down phenomena. The result of this study is respectively consistent with the critical exponent at the tangent bifur-cation point and the double-period bifurcation point in the chaotic dynamics. The other kind of unstable slowing down is also studied, which is called the slowing down far from the critical point. This is a critical phenomenon related to so-called strange rejecter. In the end, the two kinds of slowing down are simulated in the computer, and the result of the simulation is consistent with the theory.

Results and discussion

Critical points of tristability system and their slowing down

Assuming in a chemical reaction, only the concen-tration of one ingredient is changeable, however, the concentrations of the rest of the ingredients are constant as to be under environmental control. The reaction rate coefficient is constant because of the constant reaction conditions (*e.g.*, temperature, pressure *etc.*). Thus, from the Law of Mass Action, the rate equation of changeable ingredient concentration x is as follows:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = F(x, q) \tag{1}$$

where q is the control parameter (maybe one or one set) in the system. As Eq. (1) is an autonomic dynamics equation, the system has potential function.[4] The poten-tial function $G(x, q)$ can be determined by the follow-ing equation:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -\frac{\partial G}{\partial x} \tag{2}$$

When $\mathrm{d}x/\mathrm{d}t = 0$, the static equation of this system

is obtained as follows:

$$F(x,q) = 0 \qquad (3)$$

There can be five static values (x_s) in Eq. (3) by adjusting the control parameter q. Three of the five static values are stable (in this case, $(\frac{\partial^2 G}{\partial x^2})x_s > 0$), but the other two are unstable (in this case, $(\frac{\partial^2 G}{\partial x^2})x_s < 0$). This system is called tristability system. From this system, two kinds of critical points can be defined.

(a) The first kind of critical point: for $(\frac{\partial^2 G}{\partial x^2})_c = 0$), where the label "c" stands for this kind of point. There are four critical points of this kind in the tristability system, and it can be demonstrated that this kind of critical points are unstable.[8,9]

(b) The second kind of critical point: The system can be transited from tristability to bistability by further adjusting the control parameter q. This transition point is another critical point (the termination point of the tristability), and the equation is as follows:

$$(\frac{\partial G}{\partial x})_K = (\frac{\partial^2 G}{\partial x^2})_K = (\frac{\partial^3 G}{\partial x^3})_K = 0 \text{ and } (\frac{\partial^4 G}{\partial x^4})_K < 0 \quad (4)$$

This critical point is an unstable inflexion. As shown in Fig.1, K_1, K_2, K_3 and K_4 belong to the first kind of critical point, and K belongs to the second kind of the critical point.

Slowing down at the first kind critical point

The fringe critical point is unstable, and there is

$$F(x_c,q) = -(\frac{\partial G}{\partial x})_c = 0; \quad (\frac{\partial F}{\partial x})_c = -(\frac{\partial^2 G}{\partial x^2})_c = 0 \quad (5)$$

Using the same method as in a previous paper,[9,10] when $F(x, q)$ is expanded in Eq.(1) at the variable x of the critical point to the second power (since the first power is zero), and at q of the critical point to the first power, then integral, the jumping time of the state can be obtained when the system is passing the critical point.
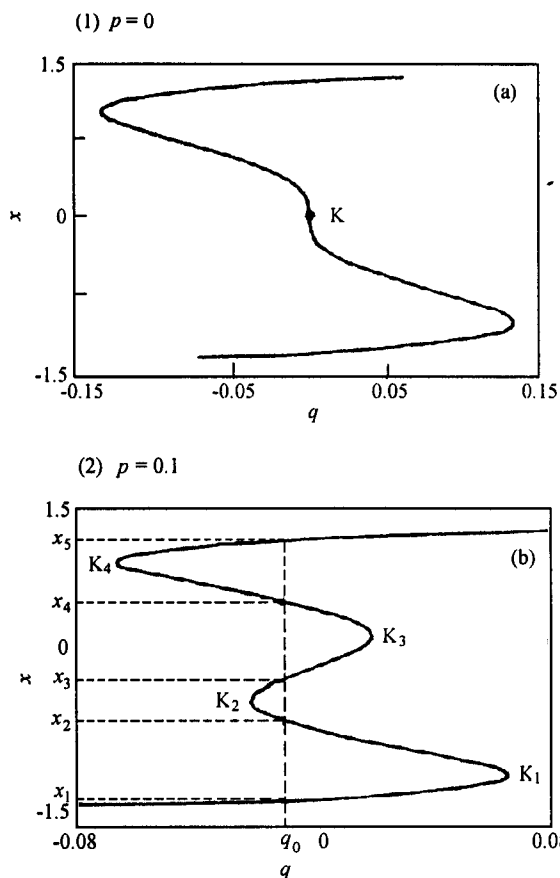
(1) $p = 0$

(2) $p = 0.1$

Fig. 1 Steady-state curve $x - q$ of the tristability system.

$$t_s = \frac{2}{\sqrt{\frac{1}{2}(\frac{\partial F}{\partial q})_c (\frac{\partial^2 F}{\partial x^2})_c (q - q_0)}}$$

$$\text{arctg} \frac{x - x_0}{\sqrt{[2\frac{(\partial F}{\partial q})_c / (\frac{\partial^2 F}{\partial x^2})_c](q - q_0)}} \Bigg|_{x_1}^{x_2} \quad (6)$$

where $x_1 < x_c < x_2$. When $q \to q_0$, the inverse tangent of the above equation goes to π, and therefore the following equation is obtained.

$$t_s \propto |q - q_0|^{-\frac{1}{2}} \quad (7)$$

Eq.(7) is concluded on the basis of the conditions that the fringe critical point in the tristability system should satisfy. The critical exponent is 1/2. This result is identical with the paroxysm chaotic interval diffusion at the tangent bifurcation point in the chaotic dynamics.

Slowing down at the second kind of critical point

The second kind of critical point is an inflexion critical point. The following equation can be obtained with Eq.(4).

$$F(x_K, q_K) = (\frac{\partial F}{\partial x})_K = (\frac{\partial^2 F}{\partial x^2})_K = 0 \quad \text{and}$$

$$(\frac{\partial^3 F}{\partial x^3}) < 0 \tag{8}$$

Firstly $F(x, q)$ is expanded at x_K of critical point in Eq.(1) to the first power, then the following equation is obtained:

$$\frac{d\Delta}{dt} = F(x, q) = (\frac{\partial F}{\partial x})|_{x=x_K}\Delta \tag{9}$$

In the above equation, let $\Delta = x - x_K = ce^{-\frac{t}{t_s}}$ (c is a constant, t_s is characteristic time), and the following equation is obtained:

$$-\frac{1}{t_s} = \frac{\partial F(x, q_K)}{\partial x}|_{x=x_K} \Rightarrow$$

$$t_s = -\frac{1}{\frac{\partial F(x, q_K)}{\partial x}|_{x=x_K}} \tag{10}$$

when $q \to q_K$, $\frac{\partial F(x, q)}{\partial x}|_{x=x_K}$ is expanded to the first power at q_K:

$$\frac{\partial F(x, q_K)}{\partial x}|_{x=x_K} = (\frac{\partial F(x, q)}{\partial x})_K +$$

$$(\frac{\partial^2 F(x, q)}{\partial x \partial q})_K(q - q_K) \tag{11}$$

as $\frac{\partial F(x, q)}{\partial x}|_K = 0$, substituting the above equation to Eq.(10), Eq.(12) can be obtained:

$$t_s = -\frac{1}{\frac{\partial F(x, q)}{\partial x \partial q}|_K(q - q_K)} \tag{12}$$

From the above equation, the critical exponent at the second kind of critical point is 1. This result is con-

sistent with the slowing down at the double-period bifurcation in the chaotic dynamics.[11] Since this critical point is unstable, the characteristic time $t_s < 0$, which is different from the characteristic time in bistability system.

Slowing down at the unstable static state

Assume the reaction concentration x initiated at the tristability area (far from the threshold point) by adjusting the control parameter. The reaction concentration x corresponding to this control parameter q_0 has five steady states: x_1, x_2, x_3, x_4, x_5 ($x_1 < x_2 < x_3 < x_4 \ll x_5$). As shown in Fig. 1, the three steady states of x_1, x_3, x_5 are stable, and the reaction concentration x can stay at these states, but the two steady states of x_2, x_4 are not stable, and the reaction concentration x can stay at these states in the beginning, but when the system encounters slight fluctuation, it will deviate from these states to other steady states. The following will demonstrate the dynamic action when the reaction concentration approaches to unstable state x_m ($m = 2, 4$). The system is first initiated at one of the three stable states. On the basis of this, a rectangular pulse of intensity q_i and time interval T are added (add negative pulse when in high branch state, positive pulse in low branch state, and positive or negative pulse when in middle branch state). The reaction concentration x_0 can be made approach to x_m ($m = 2, 4$) while the pulse just terminates. In this case, Eq. (1) can be expanded to the first power at the unstable state x_m.

$$\frac{dx}{dt} = x_m + (x_0 - x_m)\exp[-(\frac{\partial F}{\partial x})_{x_m}t] \tag{13}$$

As $(\frac{\partial F}{\partial x}) < 0$ at the unstable points, therefore, when $t \to \infty$, the above equation will be "divergent". The system will not go to x_m. Even so, the following conclusion can be made by analysis:

a) When $x_0 > x_4$, the system will go to high branch state x_5.

b) When $x_4 > x_0 > x_2$, the system will go to middle branch state x_3.

c) When $x_0 < x_2$, the system will go to low branch state x_1.

d) The closer the x_0 approaches to x_m ($m = 2, 4$), the longer time it will take for the system to go to

the stable state. This is so-called slowing down far from the critical point.

Numerical result

In the papers,[6,7] the following chemical reaction dynamics equation was obtained:

$$x = F(x,p,q) = -\frac{x^5}{5} + \frac{(1+p)x^3}{3} - px + q \tag{14}$$

where x is the scaling concentration of the changeable ingredient, p and q are the control parameters of the system, which have something to do with the ingredient concentrations a, b, d and the coefficient of the reaction rate. The static equation of the system can be obtained:

$$q = \frac{x_s^5}{5} - \frac{(p+1)x_s^3}{3} + px_s \tag{15}$$

The static curve shown in Fig. 1 is from the above equation. On the basis of dynamics Eq. (14), Runge-Kutta method is used to study the slowing down of the system. Fig. 2—5 are the results of the computer stimulation. Fig. 2 and 3 indicates the slowing down at the fringe critical points K_2 and K_3. Fig. 4 indicates the slowing down at the inflexion critical point. The inflexion critical point is an unstable point, therefore the system will not stay at this point forever. But the slowing down grade at this point is different from that at other unstable point. The curves 1 and 2 in Fig. 4 are the slowing down at other unstable points. The curves 3 and 4 are the slowing down at the inflexion critical point. The slowing down time when $\triangle = x_0 - x_m = 0.00005$ in curve 2 is equivalent to that when $\triangle = x_0 - x_K = 0.10610$ in curve 4. This indicates that the slowing down grade at the inflexion critical point is bigger than that at other unstable points. This agrees to the theory just discussed. The slowing down at the unstable steady point in the tristability system shown in Fig. 5 agrees to the theory discussed in section "Critical points of tristability system and their slowing down" in this paper.

Conclusion

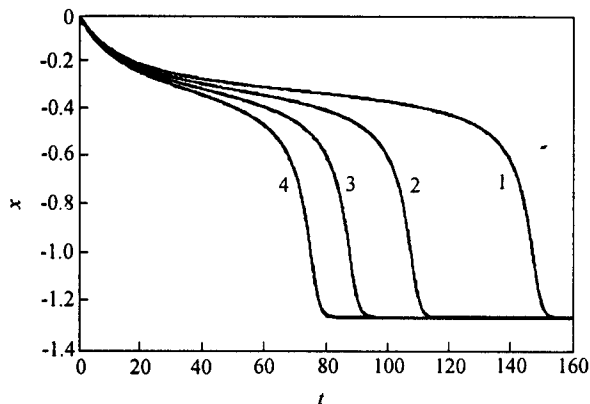In this paper, the slowing down in the chemical

Fig. 2   Slowing down at unstable point K_2, $p = 0$, $q_0 = 0$, $T = \infty$, $x_2 = -0.3170$. 1, $q_t = -0.220$; 2, $q_t = -0.230$; 3, $q_t = -0.230$; 4, $q_t = -0.250$.
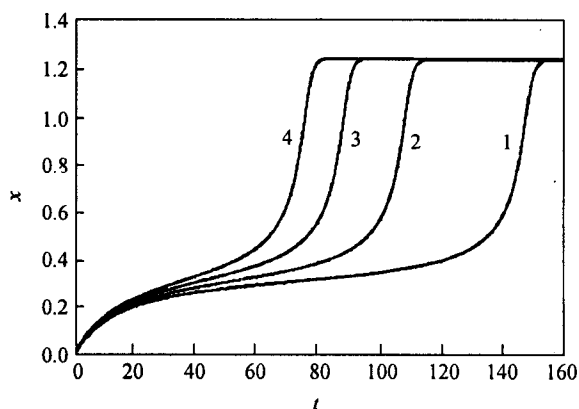

Fig. 3   Slowing down at unstable point K_3, $p = 0.1$, $q_0 = 0$, $T = \infty$, $x_2 = -0.3170$. 1, $q_t = 0.220$; 2, $q_t = 0.230$; 3, $q_t = 0.230$; 4, $q_t = 0.250$.

tristability system has been studied, and the following conclusion can by obtained:

a) The slowing down phenomena existed at the both kinds of critical points. In a previous paper,[12] it was pointed out that the first order phase transition existed at the first kind of critical point. In this paper the critical exponent was computed at this critical point and the value is 1/2. The second kind of critical point is a second-order-like phase transition point and the critical exponent at this critical point is 1. From this, it can be seen that they have some common characters. The difference is that the characteristic time of the termination point in the bistability system is positive, however, in the tristability system is negative.
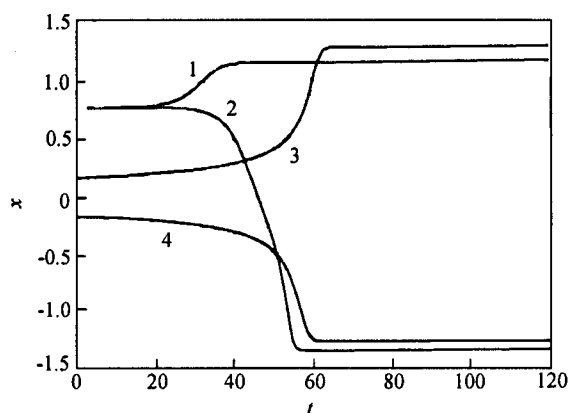
Fig. 4 Slowing down at the point of K and x_m, $T = 2$, $p = 0$, $x_m = 0.77815$, $x_K = 0$: 1, $q_0 = 0.10$, $q_t = 0.98757$, $x_0 = 0.77820$; 2, $q_0 = 0.10$, $q_t = 0.98756$, $x_0 = 0.77821$; 3, $q_0 = 0$, $q_t = 0.750$, $x_0 = 0.1061$; 4, $q_0 = 0$, $q_t = 0.650$, $x_0 = 0.1176$.
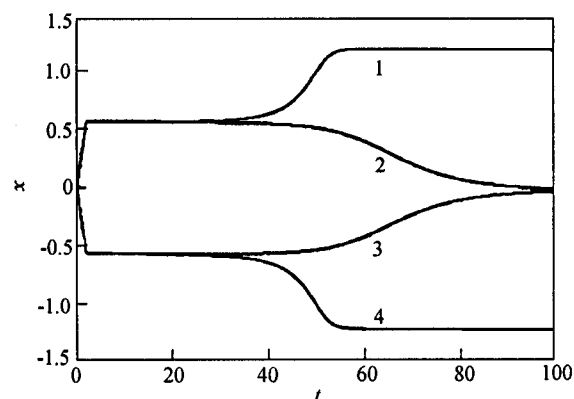

Fig. 5 Slowing down at unstable-state point x_2 and x_4. $T = 2$, $p = 0.10$, $x_1 = -1.2245$, $x_2 = -0.5775$, $x_3 = 0$, $x_4 = +0.5775$, $x_5 = +1.2245$. 1, $q_t = 0.3008$, $x_0 = 0.5778$; 2, $q_t = 0.3007$, $x_0 = 0.5770$; 3, $q_t = 0.3007$, $x_0 = -0.5770$; 4, $q_t = -0.3008$, $x_0 = -0.5778$.

b) Any point in the tristability area can be initiated by the control parameters. Related to this located point,

there are slowing down phenomena far from the critical point. For different located points, there are corresponding slowing down phenomena, which are different from the critical slowing down phenomena.

c) The slowing down phenomena at the unstable steady-state are far away from the above two kinds of critical points. The two unstable steady-states correspond to the maximum value of the potential function. They are called strange rejecters, which are the dividing point of high, middle and low attractors.[11] If the initial value is very close to the strange rejecter, the initial stage of the positive evolution will take a long time to leave the strange rejecter. In this case, the track will reflect the chaotic action determined by the strange rejecter.

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