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Thermokinetic Behaviour Degenerated from Limit Cycle Oscillation of Isothermal B-Z Reaction System due to Temperature Controlling of Heat Compensation Type

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Abstract : The thermokinetic behavior of the B-Z reaction system was influenced by both the chemical reaction-heat conduction coupling and the temperature undulation due to temperature controlling of heat compensation type. Quantitative research indicated that this kind of temperature fluctuation will lead to limit cycle degeneration and the periodic or quasi-periodic response behavior of the focus near a supercritical Hopf bifurcation .

Keywords: Temperature undulation, thermokinetic behavior, B-Z reaction system.

It has made great progress in clarifying the thermo-kinetic phenomena such as the oscillatory combustion and thermal exploding during past decades[1~2]. Recently, the research domain has been further extended to perturbation both experimentally and theoretically[3]. In contrast to the flow perturbation[3~4], the temperature perturbation received so far little attention. We reported in this paper the corresponding evolution caused by temperature perturbation coupled with B-Z reaction through the relation of rate constants $\{k_i\}$ to temperature T.

A thermokinetic model of B-Z reaction system: degeneration of limit cycle oscillation

Considering the B-Z reaction system in the thermostat as a thermokinetic system, the Oregonator model is used to capture the main qualitative and quantitative features of the B-Z reaction.

$$A+Y \xrightarrow{k_1} X+P\,,\ X+Y \xrightarrow{k_2} 2P\,,\ A+X \xrightarrow{k_3} 2X+2Z\,,\quad 2X \xrightarrow{k_4} P+A\,,\ Z \xrightarrow{k_5} hY\,.$$

Here $A \equiv [BrO_3^-]$, $X \equiv [HBrO_2]$, $Y \equiv [Br^-]$, $Z \equiv [Ce^{4+}]$, $P \equiv [HOBr]$, h is the model parameter, k_1, k_2, k_3, k_4, k_5 denotes the rate constant of elementary steps respectively. The dynamic behaviour of the isothermal B-Z reaction was investigated by means of systematic dynamics analysis[5~6]. The evolution equations take the following form:

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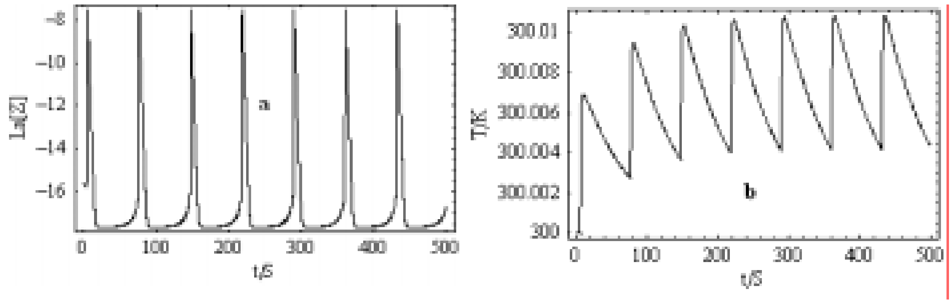
Figure 1 Quasi-periodic oscillation calculated from eqs.(1)-(4): (a) time series for the variable *Z* (b) for variable *T*



parameters value: A=0.04, h=0.65, T_0=300K, Cp=10000, L=150, k_{10}=1.34, k_{20}=1.6*10^9, k_{30}=8*10^3, k_{40}=4*10^7, k_{50}=1

$$dX/dt = k_1AY - k_2XY + k_3AX - 2k_4X^2 \quad (1)$$

$$dY/dt = -k_1AY - k_2XY + hk_5Z \quad (2)$$

$$dZ/dt = 2k_3AX - k_5Z \quad (3)$$

$$Cp \times dT/dt = -\Delta H_1k_1AY - \Delta H_2k_2XY - \Delta H_3k_3AX - \Delta H_4k_4X^2 - \Delta H_5k_5Z - L(T - T_0) \quad (4)$$

where $C_p, L, \Delta H_i$ stands for the heat capacity of the system, the heat conductivity coefficient and the heat effect of i-th elementary reaction respectively. The reaction heat effects of elementary steps could be calculated by means of formation entropies of corresponding components: $\Delta H_1 = -8kJ/mol, \Delta H_2 = -20.6kJ/mol, \Delta H_3 = -15.4kJ/mol$ $\Delta H_4 = -12.6kJ/mol, \Delta H_5 = -100kJ/mol$. The rate constant of a chemical reaction with temperature is governed by the equation:

$$k_i(T) = k_i(T_0)\exp[E_{ai}(T - T_0)/(TT_0R)]$$

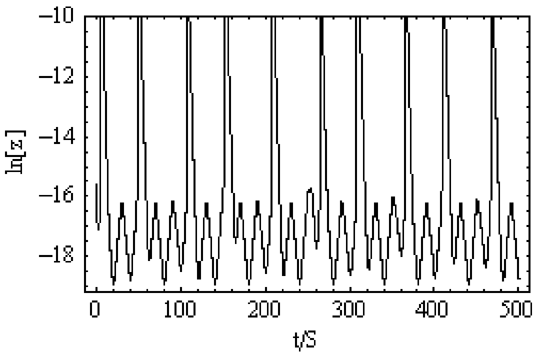
$k_i(T_0)$ is the rate constant at controlled temperature T_0 of the i-th chemical reaction.

The first four steps of the Oregonator model are all related to $Br-O$ bond break, and the activation energy is 30% of bond energy, thus $E_{a1} = E_{a2} = E_{a3} = E_{a4} = 70KJ/mol$. The activation energy of the last step related to C-C bond break by catalysis with Ce(IV) is assumed the lowest , $E_{a5} = 6KJ/mol$. The periodic oscillation degenerate as a quasi-periodic oscillation, see **Figure 1**.

B-Z oscillation degeneration due to temperature controlling

In general, the temperature of thermostat T_0 also undulates in the error range due to temperature controlling of heat compensation type. It is assumed that both the power efficiency *W* of the heater in the thermostated bath and the heat loss rate L_h are constant, the undulation of T_0 will satisfy the equation $C_{p,0} \times dT/dt = \phi W - L_h$, here $C_{p,0}$ denotes the heat content of the thermostated bath and ϕ is a step-function defined:

Figure 2 Quasi-periodic time series of the variable Z calculated from eqs (1-3,6)



E_1=E_2=0.2K, R_{in}=R_{de}=0.04K/S other parameters are the same as **Figure 1**

$$\phi = \begin{cases} 1 & if \quad T_0 < T_c + E_1 \quad and \quad dT_0/dt > 0 \\ 0 & if \quad T_0 \geq T_c + E_1 \\ 0 & if \quad T_0 > T_c\text{-}E_2 \quad and \quad dT_0/dt < 0 \\ 1 & if \quad T_0 \leq T_c\text{-}E_2 \end{cases} \tag{5}$$

There Tc is the desired controlling temperature,[E1,-E2] is the positive and negative error range of the controlled temperature T0 . The T0 is a triangle function:

$$T_0 = \begin{cases} T_c - E_2 + R_{in}T_c \leq T_0 < T_c + E_1 \quad and \quad dT_0/dt > 0 \\ T_c - E_2 < T_0 \leq T_c + E_1 - R_{de}T_c \quad and \quad dT_0/dt < 0 \end{cases} \tag{6}$$

Where R_{in}, R_{de} denotes the rate of the increase and decrease of the temperature of thermostated bath, respectively

$$R_{in} = (W - L_h)/C_p \quad , R_{de} = L_h/C_p$$

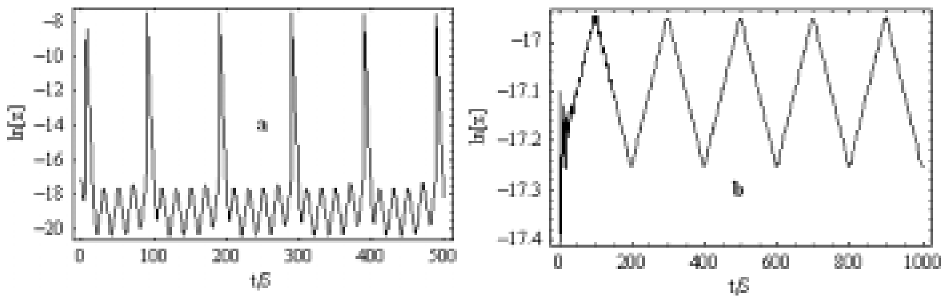
Because the heat content of thermostated bath C_p is large enough in comparison with the heat of B-Z reaction, the time evolution of temperature only plays as a periodic perturbation constrained on the externally controlled variable T_0, intensifying much more the degeneration of B-Z oscillation (**Figure 2).**

Dynamic response of a focus in the B-Z reaction system due to temperature undulation of thermostated bath

The effects of periodic undulation of the temperature on focus were investigated by us, and the focus is near a supercritical Hopf bifurcation induced by temperature controlling of heat compensation type. The response behavior of the periodically driven focus shows the phenomena of bursting (**Figure 3a)**. Bursting can be modeled when the system periodically crossed a supercritical Hopf bifurcation slowly. The amplitude of the triggered response is independent on the excitation frequency and the number of small oscillations of the bursts shows irrespective of the strength of the undulation. This is very different from flow-rate perturbations[7]. When low frequency temperature undulation arrives at a special amplitude, entrainment of B-Z oscillations is calculated. See **Figure**

3b.

Figure 3 Response time series for variable Z calculated from eqs. (1~3,6)



A=0.02, h=0.667, (a) E1=E2=2K, Rin=Rde=0. 4K/S

(b) E1=E2=0.2K, Rin=Rde=0.004K/S

Conclusion

In general, temperature undulation is unavoidable. Our work indicated that this kind of temperature fluctuations will lead to limit cycle degeneration, the bursting and entrainment behavior of the focus near a supercritical Hopf bifurcation of isothermal B-Z reaction system.

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