

研究简报

化学反应体系中温度场自组织类型和产生阈值的多样性

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Diversity of temperature field self-organization structures and occurring critical values in chemical reaction systems

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Abstract: It is very important for reactor design and control to choose and control the temperature throughout the reaction process. The linear stability analysis showed that control parameters contained in a nonlinear kinetic system of equations resulted in the diversity of temperature self-organization structures and occurring critical values in Lindemann uni-molecular chemical reaction-diffusion-heat conduction systems. The results of numerical simulations also showed that the differences of occurring critical values of Turing bifurcation led to multiple wave number values of spatially periodic structures of temperature field. Without doubt, these significant results should be considered in order to reasonably design, correctly choose the reactor type and optimally control chemical reactors.

Key words: chemical reaction-diffusion-heat conduction; self-organization of temperature field; Lindemann model; design and control of chemical reactor

引 言

化学反应器是一个化学反应发生的场所, 是化学工业生产的核心设备^[1]。因此, 对化学反应器进行合理设计与控制在化工生产中是十分重要的。选择和控制化学反应过程的温度是反应器设计中的重要问题^[2]。无论是等温反应过程还是非等温反应过程, 大多数化学反应器是针对定态操作设计的^[3]。使这类反应器维持在定态而稳定地工作无疑是必须

的。但是, 反应器存在外部的干扰和内部的涨落问题, 这就要求定态反应器具有很好的热稳定性。否则, 定态反应器不仅不能稳定地工作, 而且会导致“热点”的产生, 使局部温度高而引起催化剂中毒与载体损坏等不良后果, 甚至造成失控爆炸事故^[2,4]。以上是从促进反应器的热稳定性方面考虑^[5], 另一方面, 人们不应忽视利用反应器的热不稳定性。这种想法源于这样一个事实: 非定态反应器(如反应器内形成温度场自组织结构)的效率可

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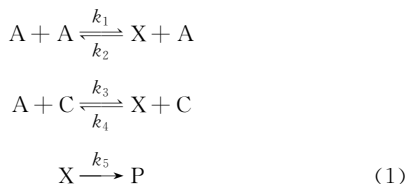
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能大于定态反应器的效率^[4,6]。所以,研究化学反应体系的热稳定性和温度场自组织结构就显得十分必要和重要。

近 30 多年来,物理化学家一直对化学反应体系中的温度分布现象很感兴趣,并进行过理论探索和应用研究^[7-20]。作者曾对化学反应-扩散-热传导体系中的温度场自组织进行了研究,研究结果表明,在适当条件下该体系中分别会出现空间均匀的温度振荡、空间不均匀的温度定态和温度波等自组织结构^[14,18]。在前期研究的基础上,本文从 Lindemann 单分子化学反应体系的非线性动力学方程出发,不仅讨论了体系的热稳定性,而且较为细致地研究了定态温度场失稳后所展示的自组织结构类型及其产生阈值的多样性问题。本文研究结果为化学反应器的设计和控制提供了多种参数控制手段。

1 Lindemann 模型

设在一长度为 l 的无对流传质、空间非均匀非等温、一维空间展布开放体系中进行着某单分子反应,而且该反应遵循 Lindemann 模型机制,反应机理如下^[21]



在某些假定条件下^[18],组分 X 的浓度和体系温度的局域反应-扩散-热传导动力学方程可写为

$$\begin{aligned}
 \frac{\partial c_X}{\partial t} &= k_1 c_A^2 - k_2(T) c_A c_X + k_3 c_C c_A - \\
 &k_4 c_C c_X - k_5 c_X + \frac{D_X \partial^2 c_X}{\partial r^2} \\
 \frac{\partial T}{\partial t} &= \{ \Delta H_1 [k_2(T) c_A c_X - k_1 c_A^2] + \\
 &\Delta H_2 (k_4 c_C c_X - k_3 c_C c_A) - \Delta H_3 k_5 c_X + \lambda \partial^2 T / \partial r^2 \} / C_p \tag{2}
 \end{aligned}$$

其中 $k_2(T) = z_2 \exp[-E_2/(RT)]$,各参数的物理意义见文献 [18]。在 Dirichlet 边界条件或零流边界条件下,体系存在唯一的均匀定态解

$$\begin{aligned}
 c_{X,s} &= \frac{k_3 c_C c_A (\Delta H_1 - \Delta H_2)}{k_4 c_C (\Delta H_1 - \Delta H_2) + k_5 (\Delta H_1 + \Delta H_3)} \\
 k_{2,s}(T_s) &= (k_1 c_A + k_3 c_C) / c_{X,s} - (k_4 c_C + k_5) / c_A \\
 T_s &= E_2 / R \ln [z_2 / k_{2,s}(T_s)]
 \end{aligned} \tag{3}$$

在均匀定态解 [式 (3)] 的邻域内对式 (2) 进行线性化,可以得到线性化方程组的线性化矩阵的

迹、行列式及本征方程根的判别式,分别表示成如下函数形式^[18]

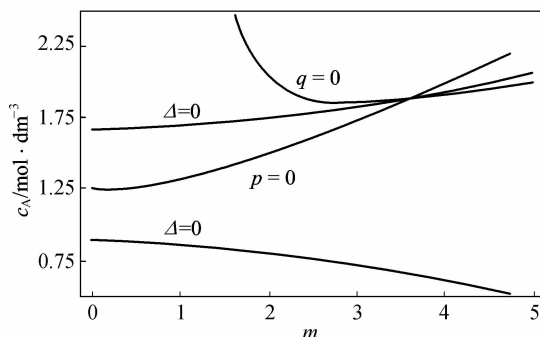
$$\begin{aligned}
 p &= p(k_1, k_3, k_4, k_5, \Delta H_1, \Delta H_2, \Delta H_3, \\
 &C_p, D_X, \lambda, c_A, c_C, l, z_2, E_2, m) \\
 q &= q(k_1, k_3, k_4, k_5, \Delta H_1, \Delta H_2, \Delta H_3, \\
 &C_p, D_X, \lambda, c_A, c_C, l, z_2, E_2, m) \\
 \Delta &= \Delta(k_1, k_3, k_4, k_5, \Delta H_1, \Delta H_2, \Delta H_3, \\
 &C_p, D_X, \lambda, c_A, c_C, l, z_2, E_2, m)
 \end{aligned} \tag{4}$$

2 温度场自组织的多样性分析

用线性稳定性分区图来讨论分支现象是简单方便的^[22-23]。针对 Lindemann 模型体系,在 c_A - m 参数平面上绘制了分区图 (图 1)。图中,曲线 $p=0$ 的上方为 $p>0$ 区, $q=0$ 的上方为 $q<0$ 区, $\Delta=0$ 所围区域为 $\Delta<0$ 区。在零流边界条件下,当 c_A 从小逐渐增大时 (反应体系的均匀定态会由稳定变为不稳定),图 1 (a) 的第一分支是 Hopf 分支 (温度时间周期有序结构),而图 1 (b) ~ (d) 的第一分支皆为 Turing 分支 (温度空间周期有序结构)^[14],第一分支虽然同为 Turing 分支,但其阈值却都不同;另外,由于阈值彼此不同,从而导致它们对应的体系温度场空间周期结构的波数不同。当然,在适当条件下也可形成温度时间-空间周期结构,即温度波^[18]。

3 数值模拟结果

分别把图 2 所示的 3 组参数值代入式 (2),在零流边界条件下用计算机进行数值求解并作图。图 2 (a) 展示的是空间均匀的温度时间周期结构,图 2 (b)、(c) 展示的是定态的温度空间周期结构;而且图 2 (b) 空间周期结构的波数 $m=3$,图 2 (c) 空间周期结构的波数 $m=5$ 。计算机数值模拟结果与前面的分析是一致的。



(a) $\lambda = 0.0625 \text{ dm}^{-1} \cdot \text{K}^{-1} \cdot \text{s}^{-1}, l = 0.03 \text{ dm}$

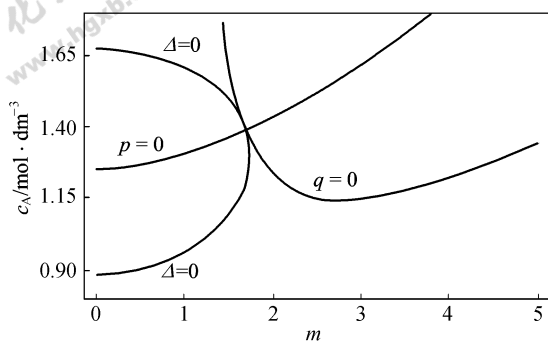
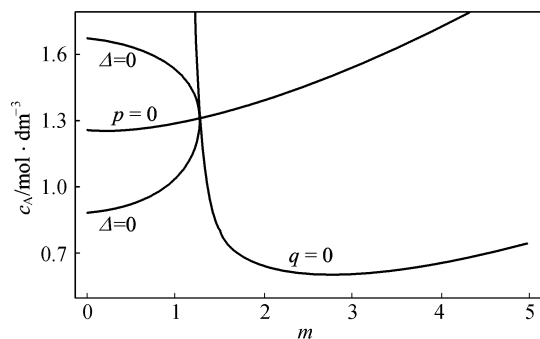
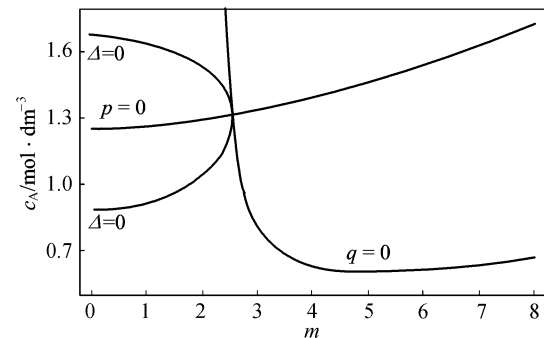
(b) $\lambda = 0.0325 \text{ dm}^{-1} \cdot \text{K}^{-1} \cdot \text{s}^{-1}$, $l = 0.03 \text{ dm}$ (c) $\lambda = 0.0125 \text{ dm}^{-1} \cdot \text{K}^{-1} \cdot \text{s}^{-1}$, $l = 0.03 \text{ dm}$ (d) $\lambda = 0.0125 \text{ dm}^{-1} \cdot \text{K}^{-1} \cdot \text{s}^{-1}$, $l = 0.06 \text{ dm}$

图 1 线性稳定性分区

Fig. 1 Linear stability diagram

$$[\Delta H_1 = 26000 \text{ J} \cdot \text{mol}^{-1}, \Delta H_2 = 30000 \text{ J} \cdot \text{mol}^{-1},$$

$$\Delta H_3 = -30000 \text{ J} \cdot \text{mol}^{-1}, k_1 = 10 \text{ dm}^{-3} \cdot \text{mol}^{-1} \cdot \text{s}^{-1},$$

$$k_3 = 11 \text{ dm}^{-3} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}, k_4 = 100 \text{ dm}^{-3} \cdot \text{mol}^{-1} \cdot \text{s}^{-1},$$

$$k_5 = 50 \text{ s}^{-1}, c_c = 0.4 \text{ mol} \cdot \text{dm}^{-3}, z_2 = 2.5 \times 10^8 \text{ dm}^{-3} \cdot \text{mol}^{-1} \cdot \text{s}^{-1},$$

$$R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}, E_2 = 35000 \text{ J} \cdot \text{mol}^{-1},$$

$$D_X = 0.001 \text{ dm}^2 \cdot \text{s}^{-1}, C_p = 55 \text{ J} \cdot \text{dm}^{-3} \cdot \text{K}^{-1}.$$

$$\text{Boundary conditions: } (\partial c_X / \partial r)_{r=0} =$$

$$(\partial c_X / \partial r)_{r=l} = (\partial T / \partial r)_{r=0} = (\partial T / \partial r)_{r=l} = 0]$$

4 结 论

以上对 Lindemann 模型体系的研究说明，在化学反应-扩散-热传导体系中：

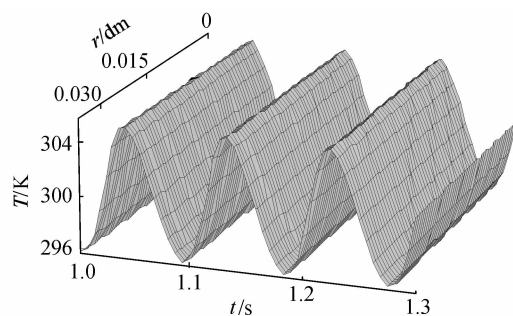
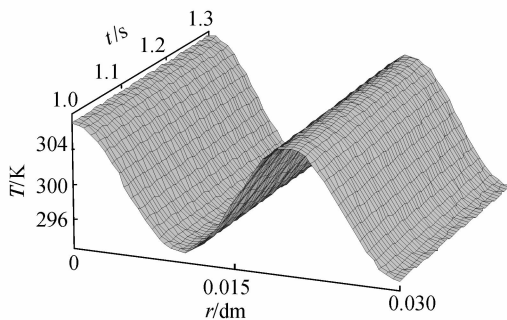
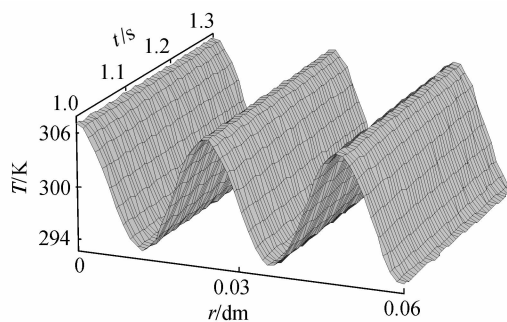
(a) $\lambda = 0.0325 \text{ dm}^{-1} \cdot \text{K}^{-1} \cdot \text{s}^{-1}$, $l = 0.03 \text{ dm}$,
 $c_A = 1.26 \text{ mol} \cdot \text{dm}^{-3}$ (b) $\lambda = 0.0125 \text{ dm}^{-1} \cdot \text{K}^{-1} \cdot \text{s}^{-1}$, $l = 0.03 \text{ dm}$,
 $c_A = 0.62 \text{ mol} \cdot \text{dm}^{-3}$ (c) $\lambda = 0.0125 \text{ dm}^{-1} \cdot \text{K}^{-1} \cdot \text{s}^{-1}$, $l = 0.06 \text{ dm}$,
 $c_A = 0.61 \text{ mol} \cdot \text{dm}^{-3}$

图 2 温度场时空自组织结构 (条件同图 1)

Fig. 2 Self-organization structures of temperature field

(numerical values of parameters and boundary conditions are the same as Fig. 1)

(1) 由诸多控制参数导致了温度场的自组织类型及其产生阈值具有多样性；

(2) 同种分支因不同的产生阈值导致分支特性的细小差异。

本研究拓宽和深化了对于化学反应体系中温度场自组织的认识，能够为化工生产中有关热量衡算及反应器设计与控制工作提供必要的理论指导。

符 号 说 明

c_A, c_C, c_X ——组分浓度, $\text{mol} \cdot \text{dm}^{-3}$

C_p ——等压热容, $J \cdot dm^{-3} \cdot K^{-1}$

D_X ——组分 X 的扩散系数, $dm^2 \cdot s^{-1}$

E_2 ——与 k_2 相应的活化能, $J \cdot mol^{-1}$

$\Delta H_1, \Delta H_2, \Delta H_3$ ——化学反应焓变, $J \cdot mol^{-1}$

k_1, k_2, k_3, k_4 ——基元反应速率常数, $dm^{-3} \cdot mol^{-1} \cdot s^{-1}$

k_5 ——基元反应速率常数, s^{-1}

l ——体系长度, dm

R ——气体常数, $J \cdot mol^{-1} \cdot K^{-1}$

r ——位置坐标, dm

T ——体系温度, K

t ——时间, s

z_2 ——与 k_2 相应的指前因子, $dm^{-3} \cdot mol^{-1} \cdot s^{-1}$

λ ——热导率, $dm^{-1} \cdot K^{-1} \cdot s^{-1}$

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