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The symmetry breaking instability in the irreversible Oregonator model for sufficiently low and unequal diffusion coefficients of its three intermediate species has been investigated using the rate constants of Field and Försterling. The effects of diffusion and the control parameters on the shift of Hopf bifurcation points associated with the emergence of heterogeneous waves of short wavelengths are reported. The results are found to be in good agreement with those obtained by Prigogine *et al.* for Brusselator and Turing models.

INTRODUCTION

Many systems in nature exhibit a symmetry breaking instability through a Hopf bifurcation leading to highly ordered spatiotemporal patterns in far from equilibrium situations.[1,2] The Turing instability with the formation of time independent spatial patterns was predicted theoretically[2,3] in nonlinear reaction–diffusion (RD) models. The Turing instability mechanism requires the diffusion coefficients of the different chemical species to be significantly different, whereas under laboratory conditions, the diffusion coefficients are nearly equal. This makes observation of the Turing instability extremely difficult in RD experiments.[4,5] Nicolis and Prigogine[2] reported patterns in numerical simulations of the Brusselator when the diffusion coefficients differ by a factor of 5. Becker and Field[6] obtained stationary patterns with the Oregonator when the diffusion coefficient of the metal ion catalyst is at least ten times larger than that of the other two species. Pearson and Horsthemke[7] very recently reported a Turing instability with nearly equal diffusion coefficients in the Showalter–Noyes–Bar Eli (SNB)[8] model of the BZ reaction. Another numerical work[9] with evidence of spatiotemporal patterns in a two-variable Vander Pol oscillator-like[10] chemical system has been published.

Most RD experiments have revealed traveling waves including both target patterns and spiral waves.[5,11-18] A few experiments have demonstrated stationary patterns, but the origin of these structures is ambiguous due to the presence of convective and interfacial effects.[19] In this paper we report on the effect of diffusion on the Hopf bifurcation in the irreversible Oregonator model,[20] which leads to symmetry breaking of the homogeneous system.

KINETIC MODEL

The irreversible Oregonator[20] is represented by the following five steps:

$$A + Y \rightarrow X + P, \qquad \text{(M1)}$$

$$X + Y \rightarrow 2P, \qquad \text{(M2)}$$

$$A + X \rightarrow 2X + Z, \qquad \text{(M3)}$$

$$2X \rightarrow A + P, \qquad \text{(M4)}$$

$$Z \rightarrow fY. \qquad \text{(M5)}$$

The kinetic equations for a homogeneous system are

$$\frac{dx}{dt} = k_1ay - k_2xy + k_3ax - 2k_4x^2, \qquad (1a)$$

$$\frac{dy}{dt} = -k_1ay - k_2xy + fk_5z, \qquad (1b)$$

$$\frac{dz}{dt} = k_3ax - k_5z, \qquad (1c)$$

where a, p, x, y and z, represent concentrations of the respective species in mol/ℓ; k_i are the rate constants of the forward reactions i ($i = 1 \rightarrow 5$) and f is a stoichiometric factor. We consider that the model is open in the thermodynamic sense and that the concentration of A (i.e., a) is constant.

One obtains the steady state solution of X (i.e., x_0) of this homogeneous system from Eq. (2a) by a numerical method using parameters suggested by Field and Försterling[21]

$$2k_2k_4x_0^2 + [k_2k_3a(f-1) + 2k_1k_4a]x_0 - k_1k_3a^2(f+1) = 0. \qquad (2a)$$

If the steady state value x_0 is known for a given value of f and k_5 one can calculate the corresponding values of y_0 and z_0 using Eqs. (2b) and (2c):

$$y_0 = fk_3ax_0/(k_1a + k_2x_0) \qquad (2b)$$

$$z_0 = k_3ax_0/k_5. \qquad (2c)$$

We now include diffusion coefficients D_x, D_y, and D_z into the kinetic differential equations [Eqs. (1)]. Therefore, we have

$$\delta x/\delta t = k_1ay - k_2xy + k_3ax - 2k_4x^2 + D_x(\delta^2x/\delta r^2), \qquad (3a)$$

$$\delta y/\delta t = -k_1ay - k_2xy + fk_5z + D_y(\delta^2y/\delta r^2), \qquad (3b)$$

$$\delta z/\delta t = k_3ax - k_5z + D_z(\delta^2z/\delta r^2). \qquad (3c)$$

We consider space as well as the time dependent perturbation using r as the geometric coordinate such that

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$$x - x_0 = \delta x \exp(\omega t + ir/\lambda),$$
$$y - y_0 = \delta y \exp(\omega t + ir/\lambda), \quad (4)$$
$$z - z_0 = \delta z \exp(\omega t + ir/\lambda),$$

where λ is the wavelength of the inhomogeneity; ω the characteristic exponent and

$$|\delta x/x_0| \ll 1, \quad |\delta y/y_0| \ll 1, \quad |\delta z/z_0| \ll 1. \quad (4a)$$

Substituting the values of x,y, and z from Eqs. (4) into the kinetic differential Eqs. (3a)–(3c), one obtains

$$(\omega + k_2y_0 - k_3a + 4k_4x_0 + D_x/\lambda^2)\delta x + (k_2x_0 - k_1a)\delta y = 0 \quad (5a)$$

$$(k_2y_0)\delta x + (\omega + k_1a + k_2x_0 + D_y/\lambda^2)\delta y - (fk_5)\delta z = 0 \quad (5b)$$

$$(k_3a)\delta x - (\omega + k_5 + D_z/\lambda^2)\delta z = 0. \quad (5c)$$

Therefore, the corresponding characteristic equation is given by

$$\omega^3 + a_2\omega^2 + a_1\omega + a_0 = 0, \quad (6)$$

where

$$a_2 = k_1a + k_2x_0 + D_y/\lambda^2 + k_2y_0 - k_3a + 4k_4x_0 + D_x/\lambda^2 + k_5 + D_z/\lambda^2, \quad (6a)$$

$$a_1 = (k_5 + D_z/\lambda^2)(k_1a + k_2x_0 + D_y/\lambda^2 + k_2y_0 - k_3a + 4k_4x_0 + D_x/\lambda^2) + (k_1a + k_2x_0 + D_y/\lambda^2) \times (k_2y_0 - k_3a + 4k_4x_0 + D_x/\lambda^2) - k_2y_0(k_2x_0 - k_1a), \quad (6b)$$

$$a_0 = (k_1a + k_2x_0 + D_y/\lambda^2)(k_2y_0 - k_3a + 4k_4x_0 + D_x/\lambda^2)(k_5 + D_z/\lambda^2) - (k_2x_0 - k_1a) \times (k_2k_5y_0 + k_2y_0D_z/\lambda^2 - fk_3k_5a). \quad (6c)$$

The steady state (x_0,y_0,z_0) becomes unstable when the real part of the complex characteristic exponent is positive and the periodic behavior can grow to a finite amplitude. When the real part of the complex characteristic exponent (ω) is zero, this is the Hopf bifurcation, and in this case the coefficients of the characteristic equation should satisfy the following relationship:

$$a_2a_1 = a_0. \quad (7)$$

Therefore, one obtains

$$(k_1a + k_2x_0 + D_y/\lambda^2 + k_2y_0 - k_3a + 4k_4x_0 + D_x/\lambda^2 + k_5 + D_z/\lambda^2)[(k_5 + D_z/\lambda^2)(k_1a + k_2x_0 + D_y/\lambda^2 + k_2y_0 - k_3a + 4k_4x_0 + D_x/\lambda^2) + (k_1a + k_2x_0 + D_y/\lambda^2)(k_2y_0 - k_3a + 4k_4x_0 + D_x/\lambda^2) - k_2y_0(k_2x_0 - k_1a)]$$
$$= (k_1a + k_2x_0 + D_y/\lambda^2)(k_2y_0 - k_3a + 4k_4x_0 + D_x/\lambda^2)(k_5 + D_z/\lambda^2) - (k_2x_0 - k_1a)(k_2k_5y_0 + k_2y_0D_z/\lambda^2 - fk_3k_5a). \quad (8)$$

RESULT AND DISCUSSION

As described above, Eq. (8) represents the Hopf bifurcation in this reaction–diffusion system. To study the effect of diffusion on the Hopf bifurcation, we find it necessary to construct[20] the Hopf curve in the homogeneous system [assuming zero diffusion coefficients in Eq. (8)] for parameters suggested by Field and Försterling.[21] Figure 1 represents the Hopf line in (f–k_5) plane, which separates the unstable and stable regions.

Equal diffusion coefficients

For equal diffusion coefficient values of the intermediates X, Y, and Z, Eq. (8) takes the form

$$d^3 + (p + k_5)d^2 + 0.25(3pk_5 + p^2 + k_5^2 + pq - q^2 - rs)d + (1/8) \times (p^2k_5 + p^2q - q^2p - prs + k_5^2p - fk_5st) = 0, \quad (9)$$

where

$$D_x/\lambda^2 = D_y/\lambda^2 = D_z/\lambda^2 = D/\lambda^2 = d, \quad (9a)$$
$$k_1a + k_2x_0 + k_2y_0 - k_3a + 4k_4x_0 = p, \quad (9b)$$
$$k_1a + k_2x_0 = q, \quad (9c)$$
$$k_2y_0 - k_3a + 4k_4x_0 = p - q, \quad (9d)$$

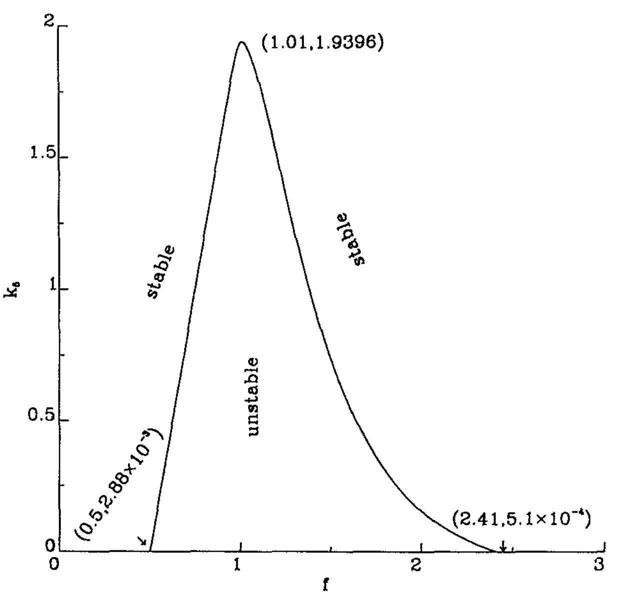

FIG. 1. Stability diagram of the homogeneous irreversible Oregonator model in f–k_5 plane. Stable and unstable regions are separated by Hopf curve. The extreme points of the unstable region are ($0.50, 2.88 \times 10^{-3}$), ($2.41, 5.1 \times 10^{-4}$) and (1.01, 1.9396), respectively; $a = 0.06$ (parameters from Ref. 21).

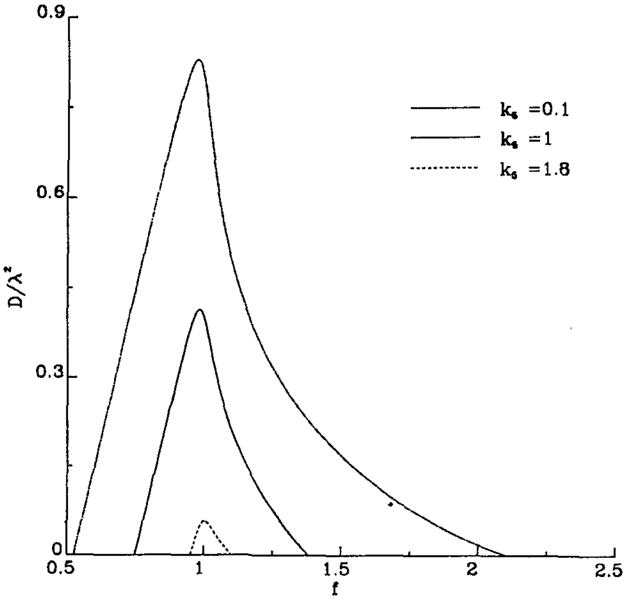

FIG. 2. Hopf bifurcation surface as D/λ^2 vs f plots for three values of k_5; $a = 0.06$ (parameters from Ref. 21).

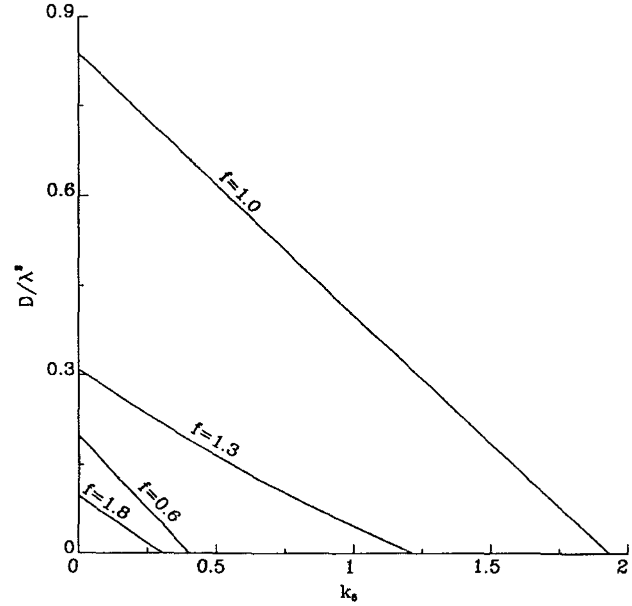

FIG. 3. Hopf bifurcation surface as D/λ^2 vs k_5 plots for four values of f; $a = 0.06$ (parameters from Ref. 21).

$$k_2y_0 = r, \tag{9e}$$

$$k_2x_0 - k_1a = s, \tag{9f}$$

$$k_3a = t. \tag{9g}$$

Equation (9) is solved numerically using parameters from Ref. 21. Since the effect of diffusion manifests itself by creating inhomogeneity, we find it useful to construct the Hopf curves for D/λ^2 vs f (Fig. 2) and d/λ^2 vs k_5 (Fig. 3) at different values of k_5 and f, respectively. Figure 2 demonstrates that for equal diffusion coefficient values of the chemical species, the Hopf bifurcation may generate inhomogeneous waves of small wavelength only when the values of the diffusion coefficients lie within a range of small values. When the diffusion coefficients are not small, the Hopf bifurcation may or may not take place, and in the former case it will create an inhomogeneity of very large wavelength. This means that for large diffusion coefficient values there is high possibility that no symmetry breaking of the RD system will take place even if there is Hopf bifurcation. It is also evident from this diagram that the Hopf boundaries could be shifted by changing the parameters f and k_5 suitably. For a certain value of f, $k_5 = 1$ will produce waves of longer wavelength than at $k_5 = 0.1$.

Figure 3 shows that as k_5 increases, the Hopf bifurcation takes place for lower values of D/λ^2, i.e., for the same values of D the wavelength of the inhomogeneity generated at the Hopf point due to the coupling of chemical reaction and diffusion effects increases as k_5 increases. This result is in agreement with Fig. 2.

Different diffusion coefficients

From Eq. (8) we have,

$$b_6\lambda^6 + b_4\lambda^4 + b_2\lambda^2 + b_0 = 0, \tag{10}$$

where

$$\begin{aligned} b_6 = {} & (k_1a + k_2x_0 + k_2y_0 - k_3a + 4k_4x_0 + k_5)[k_1k_5a + k_2k_5x_0 + k_2k_5y_0 - k_3k_5a + 4k_4k_5x_0 \\ & + (k_1a + k_2x_0)(k_2y_0 - k_3a + 4k_4x_0) - k_2^2x_0y_0 + k_1k_2ay_0] \\ & - k_5(k_1a + k_2x_0)(k_2y_0 - k_3a + 4k_4x_0) + (k_2x_0 - k_1a)(k_2k_5y_0 - fk_3k_5a), \end{aligned} \tag{10a}$$

$$\begin{aligned} b_4 = {} & (k_1a + k_2x_0 + k_2y_0 - k_3a + 4k_4x_0 + k_5)[k_5(D_x + D_y) + (k_1a + k_2x_0 + k_2y_0 - k_3a + 4k_4x_0)D_z \\ & + (k_1a + k_2x_0)D_x + (k_2y_0 - k_3a + 4k_4x_0)D_y] + (D_x + D_y + D_z)[k_1k_5a + k_2k_5x_0 + k_2k_5y_0 - k_3k_5a \\ & + 4k_4k_5x_0 + (k_1a + k_2x_0)(k_2y_0 - k_3a + 4k_4x_0) - k_2^2x_0y_0 + k_1k_2ay_0] - [k_5D_x(k_1a + k_2x_0) \\ & + k_5D_y(k_2y_0 - k_3a + 4k_4x_0) + D_z(k_1a + k_2x_0)(k_2y_0 - k_3a + 4k_4x_0) - D_zk_2y_0(k_2x_0 - k_1a)], \end{aligned} \tag{10b}$$

$$\begin{aligned} b_2 = {} & (k_1a + k_2x_0 + k_2y_0 - k_3a + 4k_4x_0 + k_5)[D_z(D_x + D_y) + D_xD_y] + [k_5(D_x + D_y)(D_x + D_y + D_z) \\ & + D_z(D_x + D_y + D_z)(k_1a + k_2x_0 + k_2y_0 - k_3a + 4k_4x_0) + (k_1a + k_2x_0)D_x \\ & + D_y(k_2y_0 - k_3a + 4k_4x_0)] - [k_5D_xD_y + (k_1a + k_2x_0)D_xD_z + (k_2y_0 - k_3a + 4k_4x_0)D_yD_z], \end{aligned} \tag{10c}$$

$$b_0 = D_z(D_x + D_y)(D_x + D_y + D_z) + D_x D_y (D_x + D_y + D_z) - D_x D_y D_z. \tag{10d}$$

Plots of λ as a function of D_z for small and unequal values of the diffusion coefficients D_x and D_y of the other two species are shown in Fig. 4 for $f = 1$. The figures clearly demonstrate evidence of symmetry breaking phenomena at the Hopf bifurcation due to the coupling of diffusion with reaction in this model in a far from equilibrium situation for small and unequal diffusion coefficients of the species X, Y, and Z.

CONCLUSION

We have shown numerically how diffusion can play a major role in nonlinear chemical systems producing inhomogeneities of small wavelengths at Hopf bifurcation points. People have observed spatial patterns[5,11–18] in unstirred laboratory experiments of the BZ reaction. The present work reports how diffusion and control parameters (f and k_5) shift the Hopf points in the case of a purely RD system maintained far from equilibrium. The results reported here are in good agreement with the findings of Prigogine *et al.*[22,23] for Brusselator and Turing models.

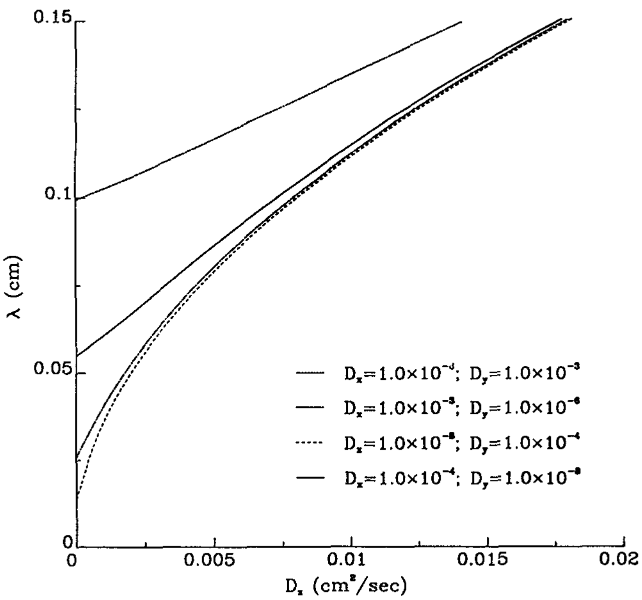

FIG. 4. The wavelength of inhomogeneity (λ) at the Hopf bifurcation points as a function of D_z when D_x and D_y have small and unequal values; $f = 1$ and $a = 0.06$ (parameters from Ref. 21).

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