The effect of autocatalyst removal on reaction-diffusion fronts

Thesis of the PhD dissertation

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1 Introduction

Reaction-diffusion fronts arise from the spatiotemporal coupling of autocatalytic reactions and diffusion. The effect of reversible and irreversible partial binding of the autocatalyst on the properties of reaction-diffusion fronts in two and three spatial dimensions is studied in my dissertation. Two phenomena are investigated with theoretical methods in this work: a planar front propagating through the homogeneous reactant mixture loses stability when some of the autocatalyst is removed and spatial gradients develop transverse to the direction of propagation resulting in a cellular structure. The removal of the autocatalyst for spherical fronts, on the other hand, may result in stationary standing fronts and lead to the stabilization of the spherical structure. For reactions in closed systems, the solution ahead of the front is unstable which can be stabilized by running the reaction in an open reactor. Systems where the dominant cell size is smaller than those studied previously can provide more optimal conditions for the investigation of lateral instability of reaction diffusion fronts in bistable systems. The effect of temperature, as a potential control parameter, on the lateral instability is therefore studied experimentally.

The requirements for the onset of instability according to previous experimental and theoretical works are: the order of the autocatalyst in the empirical rate law should be greater than one and the autocatalyst must diffuse slower than the reactants. The diffusion coefficient of the autocatalyst is usually in the same order or higher than the diffusion coefficient of the reactants, therefore, the selective lowering of the apparent diffusion coefficient is achieved experimentally by binding the autocatalyst to immobile species in systems exhibiting lateral instability. The first observation of lateral instability under isothermal conditions occurred in the iodate–arseneous acid reaction. A different, but more efficient immobilization of the autocatalyst, has been utilized in the study of cellular fronts of the acid-catalyzed chlorite–tetrathionate reaction in two and three spatial dimensions. The parameters affecting the transport of species can also have an influence on the stability of reaction fronts, therefore, in autocatalytic reactions involving ions, constant electric field separating the components may induce lateral instability even in systems where planar fronts are stable in the absence of electric field. A rigorous study has shown that the ratio of diffusion coefficients at the onset of instability is directly proportional to the concentration of the autocatalyst behind the front and this concentration is the most significant parameter determining the onset of instability. The partial immobilization employed in the experimental system represents a reversible removal of the autocatalyst since it lowers the final concentration behind the front analogous to the application of a constant electric field. We have examined the effect of reversible and irreversible removal of the autocatalyst on the lateral instability of the cubic autocatalysis, which may be considered as a prototype for experimental studies mentioned above. We have tried to identify the parameters that have major effects on the emergence of cellular structure.

The acid-catalyzed chlorite–tetrathionate reaction run in a polyacrylamide/polymethacrylate hydrogel may give rise to cellular structures via the loss of stability of planar fronts. The lateral instability of this system has already been extensively investigated at room temperature but the effect of bistability on the spatiotemporal pattern formation has not been addressed experimentally. At room temperature the inherent cell size is 1–2 cm, which is slightly larger than that desired for studies of the reaction in a continuously-fed unstirred reactor, therefore, we have examined the possibility of optimizing the cell size for future experiments in bistable systems. The temperature is expected to be a simple control parameter to adjust the desired pattern size, since we anticipate that at higher temperature the cell size should be smaller.

Reaction balls can be considered as the isothermal analogues of flame balls in engineering science. The exothermic heat release and the temperature dependent reaction rate provide the positive feedback for flames similar to the role of the autocatalyst in an autocatalytic reaction in isothermal solutions. We are interested in what order of autocatalysis would support reaction balls and whether these structures can be stabilized similarly to flame balls.

2 Applied methods

2.1 Numerical methods

The differential equations of reaction diffusion fronts in nonlinear dynamic systems are rarely solvable analytically, therefore, the properties of the solutions are studied often with the qualitative methods of differential equations without explicitly solving the equations. Linear stability analysis was carried out on reaction fronts arising in cubic autocatalytic systems with different removals of the autocatalyst and the dispersion relation characterizing the initial patterns were calculated. For the numerical simulation of the reaction-diffusion systems we solved the time-independent differential equations in one spatial dimension by shooting and relaxation methods. The optimization of the variables for the shooting method was accomplished with the bisection method and the conjugate gradient method. The initial value problem of the time dependent partial differential equations in two spatial dimensions were solved by explicit Euler method. The CVODE package was utilized for the integration and the eigenvalue problem was solved with the Maple package.

2.2 Experimental methods

The effect of temperature on the lateral instability was studied in a thermostated Plexiglas reactor. The front evolution was monitored by a black and white CCD camera (Panasonic WV-BP310/G) with an imaging board (AverPro 2000). Standard imaging techniques were utilized to determine the front position.

3 New scientific results

3.1 The effect of reversible and irreversible binding of the autocatalyst on the lateral instability of reaction fronts

3.1.1 Irreversible removal

I. *Novel boundary conditions have been applied to enhance the accuracy in calculating the dispersion relation characterizing the initial patterns based on the linear stability analysis.* [1]

Exponential distributions for the concentration of species have been introduced at the boundaries which are governed by the eigenvectors resulting from linear stability analysis. The calculated dispersion curves are in excellent agreement with those obtained from the direct integration of the full two-dimensional problem.

3.1.2 Reversible removal

II. *The region of lateral instability for a wide range of parameters has been determined by linear stability analysis and the arising spatiotemporal patterns have been characterized by dispersion curves.* [2]

The calculations show that the velocity of front propagation dramatically decreases upon increasing the concentration of the complexing agent, since the amount of mobile autocatalyst decreases leading to the loss of stability of planar fronts and the emergence of cellular patterns. The results of the linear stability analysis are presented on the ratio of diffusion coefficients vs. concentration of complexing agent phase plane showing the regions of cellular and stable planar fronts. We have calculated the onset of instability for various dissociation constants and binding. As the concentration of complexing agent increases, the critical ratio of the diffusion coefficients—the smallest ratio of the diffusion coefficient of the reactant and the autocatalyst for a given concentration of the complexing agent and dissociation constant where lateral instability exists—decreases. The domain of lateral instability slightly decreases on increasing the dissociation constant of the complex. We have found that lateral instability may occur even in systems where the autocatalyst diffuses faster than the reactant if sufficient concentration of the complexing agent is applied.

III. *We have demonstrated that the flux of the autocatalyst governs the appearance of lateral instability: two parameters—the concentration of the autocatalyst and the ratio of the diffusion coefficients—affect the onset of lateral instability.* [2]

The concentration of the autocatalyst decreases behind the reaction front because of the reversible removal of the autocatalyst. The flux of the autocatalyst along the front, i.e., the product of the ratio of the diffusion coefficients and the concentration gradient of the autocatalyst, decreases on increasing the concentration of the complexing agent and decreasing

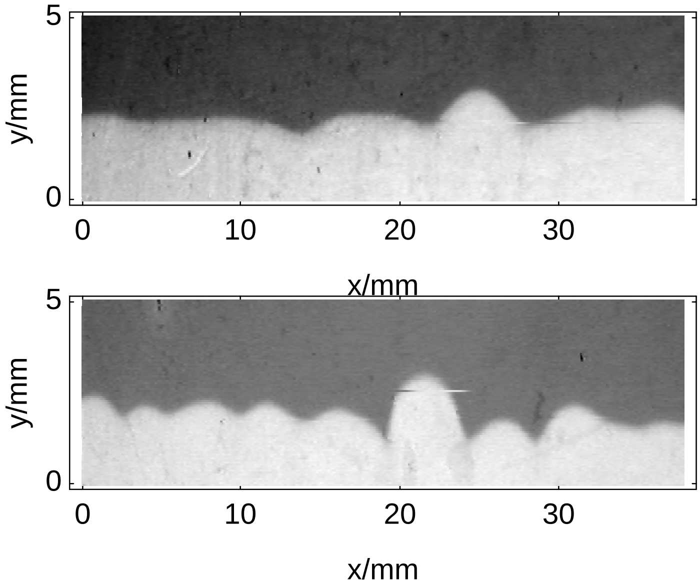

Figure 1: Images of fronts taken at temperature of 35 °C, 82 minutes after initiation (top) and at temperature of 50 °C, 49 minutes after initiation. Lighter regions correspond to the product mixture behind, and darker ones to the reactant mixture ahead of the front.

the dissociation constant of the complex. The onset of lateral instability thus also depends on the concentration of the autocatalyst behind the front which is in good agreement with previous experiments and former studies on electric field effects.

3.2 Temperature–controlled cellular fronts

IV. *We have experimentally confirmed our prediction based on the simple model of the reaction that the time and length scale shorten on increasing temperature, while the onset of instability is independent of it.* [3]

We have examined the effect of temperature in the range of 30-55 °C on the spatiotemporal pattern formation of the chlorite–tetrathionate reaction carried out in a polyacrylamide/polymethacrylate hydrogel. Figure 1. illustrates that the increase in temperature results in the formation of patterns of significantly smaller wavelengths on a faster time scale. We have also carried out experiments around the onset of instability determined previously at room temperature but we have found no change in its value on increasing temperature proving that the onset of instability is independent of temperature. The results can be explained with the simple model of the reaction by considering the temperature dependence of diffusion coefficients based on the Stokes-Einstein equation and that of the rate coefficient of the empirical rate law based on the Arrhenius equation. The exponential dependence of the rate coefficient significantly affects the shortening of the time scale and the decrease in the size of the patterns.

V. *The dispersion relation, which quantitatively describes the pattern formation, has been* *determined from the experimental data of the reaction fronts in a convection-free medium.* [3]

The front evolution was monitored by collecting frames at appropriate time intervals and from which we determined the dispersion relation describing the temporal evolution of the cellular structure. The wavelength of the most unstable mode increases on increasing temperature corresponding to decreasing cell size. As the temperature increases, the growth rate of the most unstable mode also increases, in agreement with the experimental observations, since pattern formation is faster at higher temperature.

3.3 Numerical study of reaction balls

VI. *We have demonstrated the existence of reaction balls for autocatalysis with order greater than six. The solutions are temporally unstable to perturbations in the radial direction.* [4]

The solutions have been determined for boundary conditions derived from the physical properties of the system: the concentration of the autocatalyst continuously decreases in the radial direction from the origin of the sphere and it becomes zero at infinity, while the concentration gradients are zero at the origin. Using numerical methods, we have proved that the steady solution satisfying the boundary conditions does not exist for kinetic orders with respect to the autocatalyst less than or equal to five. For higher orders, there are an infinite number of solutions satisfying the required boundary conditions and one of them is a unique, fast decaying solution, which is inversely proportional to the radial distance as it goes to infinity. All steady solutions are temporally unstable, i.e., for perturbations of the concentration distribution the system cannot return to its original state.

VII. *We have proved that the decay of autocatalyst can stabilize the reaction balls, the properties of which depend on the ratio of the diffusion coefficients besides the rate and the order of the decay for a given autocatalysis.* [5]

Using irreversible decay the unstable reaction balls can be stabilized, i.e., the perturbation of the concentration profiles leads to the relaxation of the system back to its original state. We have calculated the concentration profiles and the radii of reaction balls with respect to the decay rate for different decay orders with the smallest integer order of the autocatalyst. The radius of the reaction ball monotonously increases when the decay order is greater than or equal to the kinetic order of the autocatalyst. For smaller decay orders, there is a critical decay rate above which there is no reaction ball solution, below which there are two reaction balls with different radii. The smaller reaction balls are always unstable, while the reaction balls with greater radii may become stable. As the ratio of the diffusion coefficient of autocatalyst to that of the reactant decreases, stable solutions also exist for higher decay rate increasing the region of stability.

4 Publications related to the dissertation

[1]. Á. Tóth, D. Horváth, É. Jakab, J. H. Merkin, S. K. Scott: Lateral instabilities in cubic autocatalytic reaction fronts: The effect of autocatalyst decay, *J. Chem. Phys.*, **2001,** 114, 9947–9952. (IF=3,147)

[2]. É. Jakab, D. Horváth, Á. Tóth, J. H. Merkin, S. K. Scott: The effect of reversible binding of autocatalyst on the lateral instability of reaction fronts, *Chem. Phys. Lett.*, **2001,** 342, 317–322. (IF=2,364)

[3]. É. Jakab, D. Horváth, Á. Tóth: Temperature-controlled cellular fronts, *Phys. Chem. Chem. Phys.*, **2002,** 4, 1307–1309. (IF=1,787)

[4]. É. Jakab, D. Horváth, J. H. Merkin, S. K. Scott, P. L. Simon, Á. Tóth: Isothermal flame balls, *Phys. Rev. E*, **2002,** 66, 016207-1–016207-8. (IF=2,235)

[5]. É. Jakab, D. Horváth, J. H. Merkin, S. K. Scott, P. L. Simon, Á. Tóth: Isothermal flame balls: Effect of autocatalyst decay, *Phys. Rev. E*, **2003,** 68, 036210-1–036210-9. (IF=2,235)

5 Lecture and poster presentations related to the dissertation

1. D. Horváth, **É. Jakab**, Á. Tóth, J. H. Merkin, S. K. Scott: The effect of autocatalyst removal on lateral instability, Gordon Research Conference on ’Oscillations and Dynamic Instabilities in Chemical Systems’, Bristol, RI, USA, 2000. (poster)

2. **Jakab É.**, Horváth D., Tóth Á.: Autokatalizátor reverzíbilis megkötésének hatása a laterális instabilitásra, XXIII. Kémiai Előadó Napok, Szeged, 2000. (oral presentation in Hungarian)

3. D. Horváth, **É. Jakab**, Á. Tóth, J. H. Merkin, S. K. Scott: The effect of autocatalyst removal on lateral instability, Workshop on Nonlinear Chemistry in Complex Reactors, Palermo, 2001. (poster)

4. **É. Jakab**, D. Horváth, Á. Tóth: Temperature-controlled cellular fronts, European Science Foundation, Project REAKTOR, Workshop 2, Leeds, UK, 2001. (poster)

5. **É. Jakab**, D. Horváth, Á. Tóth: Temperature-controlled cellular fronts, Faraday Discussion 120, Nonlinear Chemical Kinetics: Complex Dynamics and Spatiotemporal Patterns, Manchester, UK, 2001. (poster)

6. **É. Jakab**, D. Horváth, Á. Tóth, J. H. Merkin, S. K. Scott, P. L. Simon: Isothermal flame balls, Gordon Research Conference on ’Oscillations and Dynamic Instabilities in Chemical Systems’, Oxford, UK, 2002. (poster)
7. **Jakab É**.: Autokatalizátor elvonásának hatása frontreakciókra, Reakciókinetikai és Fotokémiai Munkabizottság, Balatonalmádi, 2002. (oral presentation in Hungarian)

6 Lecture and poster presentations not related to the dissertation

1. **Jakab É.**, Berkesi O., Peintler G., Nagypál I.: A Raman spektroszkópia kvantitatív alkalmazása, XXXIII. Komplexkémiai Kollokvium, Paks, 1998. (oral presentation in Hungarian)

2. **É. Jakab**, L. Fülöp, G. Peintler, O. Berkesi, I. Nagypál: FT-Raman spectroscopy as a powerful quantitative analytical tool to study equilibria under extreme conditions: the sulphate-hydrogen sulphate case, 7th Austrian-Hungarian International Conference on Vibrational Spectroscopy, Balatonfüred, 1999. (poster)