

Final Report on the
"New perspectives in the design and study of nonlinear chemical phenomena"
research project (119360, 2016-2021)

The aim of the project was to design and control pure reaction-diffusion patterns and look for new perspectives in the construction and coupling of oscillatory chemical reactions. We have published 12 papers mainly Q1, one is D1 in prestigious journal, with a total impact factor over 50. We have presented our results at most important international conferences organized on the field of nonlinear dynamics (Dynamics Days Europe, Gordon Research Conference). The main results of this five-year project are the followings: demonstration of the appearance of wave phenomena in a minimal bromate oscillator; inducing forced oscillations in the bromate-sulfite-Co(II)-histidine system; generation of spatially localized moving and stationary pH patterns in two-side-fed reaction-diffusion systems; experimental realization of reaction-diffusion waves and stationary Turing patterns in closed two-layer gel reactors; construction of a new reactor design, that is a hydrogel with flow-through channels to create a spatiotemporal non-equilibrium system and the investigation of a new oscillatory family based on perborate chemistry. In the frame of our research project two Ph.D. thesis have also been prepared and defended successfully.

1. Design and control of pure reaction-diffusion patterns

Kinetic and Diffusion-Driven Instabilities in the Bromate–Sulfite–Ferrocyanide System

Mixed Landolt-type pH oscillators are versatile systems to study a wide range of dynamic phenomena, including multistability, oscillations, and spatiotemporal patterns. We have reported numerical simulations and experiments performed in an annular shape open one-side-fed gel reactor to characterize the spatiotemporal dynamics observed in the bromate–sulfite–ferrocyanide (BSF) reaction-diffusion system. Two types of instabilities, kinetic and diffusion-driven, were identified in the model. Two hydrogen ion-consuming pathways support the negative feedback loop in the mechanism: the partial oxidation of sulfite to dithionate and the oxidation of ferrocyanide by bromate ions. The input feed concentrations can conveniently control the time scale of the oxidation of ferrocyanide by bromate ions, thus it provides a more flexible way to find spatiotemporal oscillations. Long-range activation due to the relatively fast diffusion of hydrogen ions compared to the other reactants can also result in oscillations in this mechanism. We have shown that the spatial extent of the reaction–diffusion medium along the direction of the diffusive feed (the thickness) acts as a general control parameter of the dynamics. Oscillations originated in kinetic or in diffusive instabilities and can only develop in a narrow range of thickness. This properly explains the experimentally often observed spatial localization of the oscillations. A reciprocal relationship is found between the two main control parameters of the dynamics: the thickness and the hydrogen ion input feed concentration. The 10-variable model with the proper description of the coupled CSTR/gel system provides a solid starting point to study the other interesting phenomena observed

in the BSF reaction-diffusion system, namely calcium waves in the presence of calcium ions and ethylenediaminetetraacetate, or stationary patterns in the presence of sodium-polyacrylate.

Published papers:

- I. Molnár, I., Szalai: Kinetic and Diffusion-Driven Instabilities in the Bromate-Sulfite-Ferrocyanide System, *Journal of Physical Chemistry A* 121:(9) pp. 1900-1908., 2017
- J. Horváth, I. Szalai, P. De Kepper: Designing Stationary Reaction-Diffusion Patterns in pH Self-Activated Systems, *Accounts of Chemical Research* 51 : 12 pp. 3183-3190., 2018

Spatial self-organization in minimal bromate oscillators

A minimal bromate oscillator (MBO) consists of bromate, bromide, and a catalyst, which can be cerium(IV), manganese(II), ferroin, or tris(2,2-bipyridine)ruthenium(II). These systems do not show periodic behavior in batch and have only a narrow range of oscillation in a CSTR compared to the versions extended with a substrate. We have demonstrated both experimentally and numerically that the simplest variants of bromate oscillators are capable of producing nontrivial spatiotemporal phenomena, like spatial bistability and waves. Numerical simulations indicate that the formation of waves is more expected in the ferroin catalyzed MBO than in the cerium catalyzed one. This has been supported by experiments, where periodic wave trains are observed in OSFRs with different geometries. We have pointed out that the wave dynamics depends not only on the characteristic chemical timescales but also on the diffusive ones as well. The extended reactivity of the ferroin catalyst towards the oxybromine species causes intensive matter exchange that occurs between the reaction-diffusion medium and its environment.

Published papers:

- I. Molnár, K. Kurin-Csörgei, I. Szalai: Spatiotemporal dynamics of minimal bromate oscillators in an open one-side-fed reactor, *Physical Chemistry Chemical Physics* 20 (20), 13851-13857, 2018

Dynamics of pH-Oscillators in a Two Side Fed Reactor

We presented a method to generate localized pH patterns in the presence of antagonistic gradients maintained by the counter-diffusion of different chemicals. The interplay of gradients and the self-activatory process was successfully used to create a spatially organized system where sharp thresholds separate a localized high extent of reaction zone from the outer nonreactive regions. At this configuration we have demonstrated the formation of spatial bistability, the coexistence of two stable spatial steady states, characterized by different spatial concentration distributions at the same boundary conditions. In the high extent of the spatially organized reaction zone, kinetic and diffusion driven instabilities may lead to the formation of different reaction-diffusion patterns. The proposed approach has been tested by numerical simulations and in experiments performed in two-side-fed reactors. Experimental evidence was provided by using various pH-oscillators, namely the bromate-sulfite-ferrocyanide, the iodate-sulfite-ferrocyanide, the iodate-sulfite-thiourea, and the hydrogen peroxide-sulfite-ferrocyanide reactions. We anticipate that this method can be applied to any chemical or biochemical reaction-diffusion system, where the diffusive gradients of the reagents of the positive feedback process can be maintained. This is the case in most of the reactions, which are known as CSTR oscillators. To initiate Turing instability, we have added a

large molecular weight hydrogen ion binding agent. We have created a system where the Wolpert mechanism is used to localize Turing patterns. The spatially periodic pH-pattern is an example of the rational combination of the two developmental concepts.

Published papers:

- B. Dúzs, I. Szalai: Design of localized spatiotemporal pH patterns by means of antagonistic chemical gradients, RSC Advances 8 : 73 pp. 41756-41761., 2018

Front dynamics of pH-oscillators with initially separated reactants

We have performed a numerical and experimental investigations on the dynamics of pH-oscillators when the reactants are separated initially in space. In this configuration, the front is initiated by placing two gels containing the primary reactants of the pH-oscillators in contact. pH-oscillators consist of four initial reagents, an oxidant, the protonated, and the unprotonated form of a reductant and a component that induces a hydrogen ion-consuming reaction. These chemicals are distributed asymmetrically at the beginning. The oxidant mixed with the unprotonated reductant and the hydrogen ion-consuming species is on one side. The other part of the system consists of an equilibrium mixture of the protonated and unprotonated form of the reductant and the hydrogen ion-consuming species. When these two parts get in contact, the reaction between the oxidant and the protonated reductant occurs at the interface and results in positive feedback for hydrogen ion production. As the reactants diffuse toward each other, they can react and form an autocatalytic front and even spatiotemporal oscillations under appropriate conditions. We have performed experiments with two different oxidants (bromate and hydrogen peroxide) and different H^+ -consuming reactions induced by ferrocyanide, thiourea, and hydrogen carbonate. This strategy is potentially applicable for the other types of oscillatory reactions, which show oscillations only in the presence of a continuous supply of the reagents.

Published papers:

- B. Dúzs, I. Szalai: Front dynamics of pH-oscillators with initially separated reactants, Reaction Kinetics, Mechanisms and Catalysis 123 (2), 335-349, 2018

Turing Patterns and Waves in Closed Two-Layer Gel Reactors

We have proposed a new way to study reaction-diffusion waves and stationary Turing patterns using a closed two-layer gel reactor. The two compartments are initially filled with complementary sets of reactants of the chlorine dioxide–iodine–malonic acid–poly(vinyl alcohol) reaction. The asymmetrical loading generates concentration gradients and the patterns form at the interface between the two parts. These easy-to-perform experiments allow us to study a wide range of dynamical phenomena without requiring a specific reactor design or the use of sophisticated equipment. Complementary information on pattern formation has been gathered by using two geometrically different configurations of compartments. We demonstrate that three variants of the initial distribution of the chemicals can be equally applied and this flexibility provides a way to introduce additional reagents to perturb the dynamics of the systems. Because of its technical simplicity, the two-layer gel reactors can be appropriately used to establish demonstration experiments to illustrate the process of Turing-type pattern formation.

Published papers:

- B. Dúzs, P. De Kepper, I. Szalai: Turing Patterns and Waves in Closed Two-Layer Gel Reactors, ACS Omega 4 : 2 pp. 3213-3219., 2019

Design of simple hydrogel device with flow-through channels

We proposed and constructed a new reactor design, a hydrogel with flow-through channels, to create a spatiotemporal non-equilibrium system. This simple reactor provides a new way to perform a chemical reaction at out-of-equilibrium conditions or even create a chemically fueled device. We presented experimental evidence for the formation of various types of RD phenomena in this new reactor. First, we used a two-channel set up to create stationary stripes standing perpendicular to the direction of the concentration gradients, which is maintained by the different compositions in the two flows, using the bromite-sulfite pH-autocatalytic reaction and the precipitate formation between calcium and carbonate ions. In the latter case, the final sharp precipitate zone contains mainly spherical, cubic, and flower-shaped crystals. The spherical and flower forms are typical for the metastable vaterite, while the cubic is typical for calcite. Next, we created dynamical structures, spatiotemporal waves by homogeneous chemical oscillators (in the bromate-sulfite-ferrocyanide (BSF) and the in chlorite-iodide-malonic acid (CIMA) systems), long-lasting, dynamic precipitate patterns in the reaction between aluminum ions and hydroxide ions, and stationary Turing patterns in the chlorite-iodide-malonic acid reaction. We have noticed the appearance of diffusive coupling between spatially separated reaction-diffusion zones by using three flow-through channels. To clarify the effects of the reactor geometry on the dynamics, numerical simulations were carried out. Published papers:

- B. Dúzs, I. Szalai: A simple hydrogel device with flow-through channels to maintain dissipative non-equilibrium phenomena, Communications Chemistry 3 (1), 1-6, 2020

Investigation of the the effect of time-periodic boundary conditions

During the final year of the project, we have focused on investigating the effect of time-periodic boundary conditions in open gel reactors. The experimental study of chemical reaction-diffusion systems has often been made in open one-side-fed reactors (OSFR) or open two-side-fed reactors (TSFR). The central part of these reactors is a porous material, often a hydrogel, which acts as a convection-less medium for the development of reaction-diffusion phenomena. In an OSFR configuration, the porous medium is in contact with the content of a continuous stirred-tank reactor (CSTR). The CSTR content feeds the porous material with fresh reagents, which allows to maintain sustained far-from-equilibrium conditions. In a TSFR configuration, the gel is sandwiched between two separated open tanks of reagents.

We selected a simple but chemically relevant model of pH oscillators, which contains relatively simple redox reactions. These reactions can produce large amplitude pH oscillations in a CSTR, and hydrogen or hydroxide ions play a crucial role in the positive feedback of its mechanism. Their robust pattern forming capacity has been experimentally demonstrated in OSFR and TSFR configurations. We explored an autonomous and a non-autonomous way to generate time-periodic boundary conditions in an OSFR. The autonomous way is due to the capability of the reaction to produce oscillations in a CSTR. The oscillatory state of the CSTR content can be used to set time-periodic boundary conditions for the gel. The other, non-autonomous method is to apply a

sinusoidal perturbation on the input feed concentration of hydrogen ions when the unperturbed CSTR content is on a stationary, low-extent-of-reaction state. In a TSFR, we apply a similar non-autonomous perturbation in one of the tanks. Our investigation shows that this latter method is a more flexible way to study time periodic boundary conditions, but the damping effect of the tank on the amplitude of the periodic concentration forcing is a significant limitation.

A natural way to create time-periodic boundary conditions is to use a parameter set, where the CSTR content oscillates. In a thin gel, the CSTR oscillations are followed by the oscillations of gel content without any significant time delay. When the thickness of the gel reaches the size at which oscillations may develop in the gel even at stationary state in the CSTR, the dynamics become more complex. During the complex oscillatory cycle, two oscillations with quite different periods are superimposed. Our simulations confirmed that periodic boundary conditions created by low-frequency forcing on the CSTR might result in the modulation of spatiotemporal oscillations and forced spatiotemporal bursting in the gel part. Synchronization can also be observed at high-frequency forcing in a TSFR. The use of time-periodic boundary conditions may open a new perspective in the control and design of spatiotemporal phenomena in open one-side-fed and two-side-fed reactors.

Published papers:

- B. Dúzs, I. Molnár, I. Lagzi, and I. Szalai: Reaction-Diffusion Dynamics of pH Oscillators in Oscillatory Forced Open Spatial Reactors, ACS Omega
<https://doi.org/10.1021/acsomega.1c04269>, 2021

2. New perspectives in the design, study, and coupling of oscillatory reactions

Oscillatory transformation in the oxidation states of cobalt observed in the bromate-sulfite-Co(II)-Histidine CSTR System

We have reported a new version of oscillatory phenomena that can appear in coupled oscillators. Oscillations in the oxidation states of the center ion bound in a chelate complex were generated in a combined system when the participants of the oscillator as a dynamical unit and the components of the complex formation interacted with each other through a redox reaction. It was demonstrated that when the bromate-sulfite pH-oscillator and the Co(II)-histidine complex were mixed in a continuous stirred tank reactor, periodic changes in the pH were accompanied by periodic transitions in the oxidation number of the cobalt ion between +2 and +3. The oscillatory build-up and removal of the Co(III)-complex were followed by recording the light absorption at the wavelength characteristic for this species with simultaneous monitoring of the pH-oscillations. The dual role of the sulfite ion in the explanation of this observation was pointed out.

Published papers:

- K. Kurin-Csörgei, E. Poros, J. Csepiova; M. Orbán: Periodic Changes in the Oxidation States of the Center Ion in the Cobalt-Histidine Complex Induced by the BrO_3^- - SO_3^{2-} pH, Chaos 28, 053114, 2018

From master–slave to peer-to-peer coupling in chemical reaction networks

Design strategy of linking a driving pH oscillator (master system) to a pH-sensitive complexation, precipitation, or protonation equilibrium (slave system) has been widely used to create and control concentration oscillations of chemical entities which are not part of the pH oscillatory system. We have studied how the components of these equilibria affect the characteristics of the driving pH oscillators. By varying the concentration of pH-sensitive species, we could control the strength of the chemical feedback. To illustrate these transition and coupling strategies, we investigated the hydrogen peroxide–thiosulfate–copper(II) system when EDTA was added to the system. It has been reported previously that the coupling between the periodic protonation of EDTA and the complexation of copper(II)-ions by EDTA results in amplified pH oscillations. We pointed out that the binding of the catalyst in an inert form lowers the effective concentration of the catalyst in the high pH phase of the reaction. This lowering of the Cu(II) concentrations results in the observed increase of the pH amplitudes and even finally in the quenching of the oscillations.

Published papers:

- G. Holló, B. Dúzs, I. Szalai, I. Lagzi: From Master-Slave to Peer-to-Peer Coupling in Chemical Reaction Networks., *Journal of Physical Chemistry A* 121:(17) pp. 3192-3198., 2017

Pulse-coupled BZ oscillators with external inhibitory forcing

Coupling of oscillators to each other can result in a variety of collective dynamical behaviors, in which the frequencies generally differ from those measured in the individual oscillators: inhibitory interactions lead to a lower frequency, while excitatory interactions produce behaviors with increased frequency. We have explored the dynamics of two pulse-coupled Belousov-Zhabotinsky oscillators by numerical simulations when frequency modulators (which can increase or decrease the frequency of the oscillators) are combined with coupling agents. New dynamical regimes emerge with a host of complex temporal patterns when frequency modulation is antagonistic to the natural frequency change resulting from the excitatory or inhibitory coupling. We have analyzed the properties of the patterns and showed the correlation between the frequency modulation strength and the pattern characteristics.

Published papers:

- V. Horváth and I. R. Epstein: Pulse-coupled Belousov-Zhabotinsky oscillators with frequency modulation, *Chaos* 28, 045108, 2018

Perborate chemistry based oscillators

We have reported that sodium perborate, similarly to some oxyhalogens, permanganate, or peroxides, can also be used as a major reactant in constructing oscillatory reactions. It was proven by the successful replacement of hydrogen-peroxide with sodium perborate which resulted in the extension of the number of chemical oscillators with two members. We recorded potential and pH oscillations in the perborate - thiosulfate - Cu(II) flow system, and potential oscillations in the strongly alkaline Cu(II)-catalyzed perborate - thiocyanate batch reaction. Our experimental and numerical results showed that this is not a simple replacement of the oxidant, but the development

of oscillations is supported by the catalytic effect of borate on peroxide chemistry. Our numerical simulations pointed out the crucial catalytic effect of the perborate species.

Published papers:

- K. Kurin-Csörgei, E. Poros-Tarcali, I. Molnár, M. Orbán, I. Szalai: Chemical Oscillations With Sodium Perborate as Oxidant, *Frontiers in Chemistry* 8, 889, 2020