Convective instabilities in the chlorite-tetrathionate reaction

Tamás Bánsági, Dezső Horváth, and Ágota Tóth

Department of Physical Chemistry, University of Szeged,

P.O.Box 105, Szeged, H-6701, Hungary

The chlorite-tetrathionate autocatalytic reaction exhibits density fingering when the direction of propagation is the same as that of the gravity. The initially planar front loses stability resulting in a fingering structure as a consequence of the product solution being denser than the reactant. We have investigated this phenomenon by varying the concentrations of reactants, the gapwidths, and the viscosity, measured the velocity of the fronts and the dispersion curves describing the linear regime of the evolution of pattern formation. We have determined the characteristics of the most unstable mode and the marginal wavenumber. We have found that the unstable regime and hence the characteristic amplitude and wavelength increases as the concentrations and gapwidths increase. Our results are in a good agreement with the model based on the Navier-Stokes equation coupled with a thin-front approximation describing the chemistry.

An Initial Reduced Scheme for CO Oxidation Exhibiting Complex Oscillations.

R.B.Brad, M.Fairweather, A.S.Tomlin. J.F.Griffiths.

This work concerns the production of reduced chemical reaction schemes from full kinetic descriptions. It aims to develop methodologies for forming compact kinetic descriptions suitable for incorporation in fluid dynamic models of complex chemically reacting flow processes. Experimental data shows that oxidation of carbon monoxide under suitable conditions in a jet stirred reactor demonstrates complex oscillatory behaviour[1]. This has been successfully modelled using the carbon monoxide subset of the comprehensive Leeds Methane Scheme[2], containing 69 reactions. The scheme has then been reduced by first employing a local concentration sensitivity analysis to identify necessary species followed by a principle component analysis of the rate sensitivity matrix to identify necessary reactions[3]. Sensitivity analysis over a varying temperatures, pressures, concentrations and timescales has resulted in a reduced scheme, with under 60% of the original number of reactions, which is accurate over a wide range of conditions. We intend to pursue methods of quasi-steady state analysis and rate of production analysis to further reduce this mechanism.

Refs;

[1] B.R. Johnson. Non-linear Dynamics of Combustion Reactions in a Well Stirred Reactor. Ph.D. Thesis, Department of Chemistry, University of Leeds (1991)

[2] http://www.chem.leeds.ac.uk/Combustion/methane.htm

[3] A.S. Tomlin, T. Turanyi, M.J. Pilling. ‘Mathematical tools for the construction, investigation and reduction of combustion mechanisms’, in Low Temperature Combustion and Autoignition. Ed H.J. Pilling, Elsevier, Amsterdam pp293-437, 1997

pH Oscillations in the Hemin – Hydrogen peroxide – Sulfite Reaction

Nico Fricke, Marcus Hauser, Stefan C. Müller

Abteilung Biophysik, Institut für Experimentelle Physik,
Otto-von-Guericke-Universität, Universitätsplatz 2,
39106 Magdeburg, Germany

The dynamics of the hemin – hydrogen peroxide – sulfite reaction is investigated as a function of the flow rates of the reactants through a continuous-flow stirred tank reactor. During the reaction, either simple periodic or bursting oscillations of the pH value of the reaction medium are induced. These oscillations remain always within the physiological range of pH. The experimental results were compared to results from numerical simulations. To this purpose, we deelopped a reaction mechanism consisting of a well-established auotocatalytic part and two hemin-dependent feedback reactions. The role of the individual feedback steps were evaluated. While the simulated dynamics is good agreement with the one observed in experiments, minor discrepancies remain to be understood.

Quantitative modelling of glycolytic oscillations

Finn Hynne, Sune Danø and Preben Graae Sørensen
Functional Dynamics Group
Department of Chemistry, University of Copenhagen

"The Direct Method" is a powerful, general method of fitting a model of a biochemical pathway to experimental substrate concentrations and dynamical properties measured at a stationary state, when the mechanism is largely known but kinetic parameters are lacking. Rate constants and maximum velocities are calculated from the experimental data by simple algebra without integration of kinetic equations. Using this method, we fit a comprehensive model of glycolysis and glycolytic oscillations in intact yeast cells to data measured on a suspension of living cells of Saccharomyces cerevisiae near a Hopf bifurcation and to a large set of stationary concentrations and other data estimated from comparable batch experiments. The resulting model agrees with almost all experimentally known stationary concentrations and metabolic fluxes, with the frequency of oscillation and with the majority of other experimentally known kinetic and dynamical variables. The functional forms of the rate equations have not been optimized. (Biophysical Chemistry 94:121-163 (2001).)

Encoding and decoding of calcium signals in hepatocytes.

Ann Zahle Larsen[†], Lars Folke Olsen[†] and Ursula Kummer[II]

[†]Celcom, Department of Biochemistry and Molecular Biology, Syddansk Universitet, Campusvej 55, DK-5230 Odense M, Denmark. [II]European Media Laboratory, Schloss-Wolfsbrunnenweg 33, D-69118 Heidelberg, Germany.

Many different agonists use calcium as a second messenger. Despite intensive research in intracellular calcium signalling it is an unsolved riddle how the different types of information, represented by the different agonists, is encoded using the universal carrier calcium. It is also a mystery how the information encoded is decoded again into the intracellular specific information at the site of enzymes and genes. After the discovery of calcium oscillations, one likely mechanism is that information is encoded in the frequency, amplitude and waveform of the oscillations. This hypothesis has received some experimental support. However, the mechanism of decoding of oscillatory signals is still not known. Here, we study a mechanistic model of calcium oscillations which is able to reproduce both spiking and bursting calcium oscillations. We use the model to study the decoding of calcium signals on the basis of cooperativity of calcium binding to various proteins. We show that this cooperativity offers a simple way to decode different calcium dynamics into different enzyme activities.

A model of the oscillatory metabolism of activated neutrophils

Lars F. Olsen[*,†], Ursula Kummer[*], Andrei L. Kindzelskii[‡]
and Howard R. Petty[‡]

[*] European Media Laboratory, Schloss-Wolfsbrunnenweg 33, D-69118 Heidelberg, Germany;
[†] Department of Biochemistry and Molecular Biology, Syddansk Universitet,
DK-5230 Odense M, Denmark ; [‡] Department of Biological Sciences,
Wayne State University, Detroit, MI 48202, USA

Abstract

We present a two-compartment model to explain the oscillatory behaviour observed experimentally in activated neutrophils. Our model is based mainly on the peroxidase-oxidase (PO) reaction catalyzed by myeloperoxidase with melatonin as a cofactor and NADPH oxidase, a major protein in the phagosome membrane of the leukocyte. The model predicts that following activation of a neutrophil an increase in the activity of the hexose monophosphate shunt and the delivery of myeloperoxidase into the phagosome results in oscillations in oxygen and NAD(P)H concentration. The period of oscillation changes from > 200 s to 10-30 s. The model is consistent with previously reported oscillations in cell metabolism and oxidant production. Key features and predictions of the model were confirmed experimentally. The requirement of the hexose monophosphate pathway for 10 s oscillations was verified using 6-aminonicotinamide and dexamethasone, which are inhibitors of glucose-6-phosphate dehydrogenase. The role of the NADPH oxidase in promoting oscillations was confirmed by dose-response studies of the effect of diphenylene iodonium, an inhibitor of the NADPH oxidase. Moreover, the model predicted an increase in the amplitude of NADPH oscillations in the presence of melatonin, which was confirmed experimentally. Successful computer modeling of complex chemical dynamics within cells and their chemical perturbation will enhance our ability to identify new antiinflammatory compounds.

F. Plenge, H. Varela, A.Bonnefon, P. Grauel, K. Krischer and G. Ertl

Fritz–Haber–Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany

Abstract: Experimental observations of spatially unstable limit cycles in reaction-diffusion systems are very rare. One example is the electrochemical oxidation of H_2 on Pt-ring electrodes in the presence of electrosorbing ions (P. Grauel et al., Faraday Discussions 120). A limited system size allows to study the transition from a periodic, inhomogeneous limit cycle to turbulence. Adding a global coupling to the system in the spatially unstable oscillatory state yields a variety of different, to a large extend novel, spatiotemporal patterns, including a spatiotemporal intermittency-type transition to phase clusters. We present a realistic model of the electrochemical processes displaying almost quantitative agreement with experiment in the homogeneous case. The spatiotemporal investigations reproduced many of the patterns in both, the regimes with and without global coupling. The results yield a new understanding of the bifurcation sequences leading to these unusual structures.

Additional Information:
http://www.fhi-berlin.mpg.de/pc/spatdyn/spatdyn.cgi?Research_Projects_Theory
http://www.fhi-berlin.mpg.de/pc/spatdyn/spatdyn.cgi?Research_Projects_H2

PATTERN FORMATION IN AN ASSEMBLY OF COUPLED "BELOUSOV-ZHABOTINSKY CELLS"

Henrik Skødt,
Dept. of Chemistry, Univ. of Copenhagen

A variety of biological phenomena can be described by assemblies of coupled oscillatory cells. Examples are beta cells in the pancreas, neural cells in the visual cortex or other parts of the brain, and distributed yeast cells in a gel.

In this study such a system is emulated by a mask of light on the light-sensitive BZ system so that there are square areas unexposed to light, the "cells", surrounded by areas exposed to light, the "extracellular medium".

This approach takes into account the fact that the cells are not point-like objects, but rather have a distribution of metabolites across the cell.

The obtained results with an array of 2 by 2 cells and also larger arrays show both in-phase and anti-phase synchronisation as well as spiral formation in larger systems. Furthermore can the larger systems exhibit target patterns, a phenomenon not observed in the "extract", i.e. the unmasked system.The results also explain the difficulties in observing bulk oscillations in a layer of yeast cells immobilised in gels.

Modeling of chemical waves in reaction–diffusion systems with excitable dynamics

András Volford
Department of Chemical Physics, Budapest University of Technology and Economics
Budapest, H1521, Hugary
volfi@phyndi.fke.bme.hu

Abstract:

We used two different type of kinetic terms in the reaction−diffusion (RD) systems to describe excitable medium:

a) giving explicitly (in piecewise linear form) the phase portrait of the system
b) giving the reaction equations which describes a Saddle Node Infinite Period Bifurcation (SNIPER).

Coupling this kinetic terms with diffusion, we made model calculations using circular homogeneous media with an obstacle at the center. Later piecewise homogeneous case was examined. Interesting phenomena like wave splitting was found, the examination of which has been started.