

# The interplay of physical and chemical factors as a source of luminescent travelling fronts in the $\text{H}_2\text{O}_2\text{-SCN}^-\text{-OH}^-\text{-Cu}^{2+}$ oscillatory system

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The  $\text{H}_2\text{O}_2\text{-SCN}^-\text{-OH}^-\text{-Cu}^{2+}$  system [1-3] belongs to the most complex and interesting chemical oscillators, due to its rather untypical lack of connection between the oscillatory and bistable behaviors. In the first reports on this system, the oscillations in the homogenized (batch or flow) systems were described [1], and an advanced model mechanism [2,3], consisting of 26 species engaged in 30 reaction steps, was elaborated. In course of our systematic studies of this process we also discovered other unusual properties of that system, as different oscillatory potentiometric responses of various inert electrodes monitoring reaction course (including  $180^\circ$  phase shift between the Au and Pt electrode) [4] (Fig. 1)

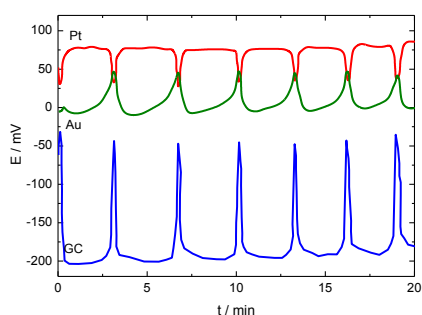


Fig. 1. Untypical differences in the potentiometric oscillatory responses of various inert electrodes for the oscillatory  $\text{H}_2\text{O}_2\text{-SCN}^-\text{-OH}^-\text{-Cu}^{2+}$  system [4].

Furthermore, we discovered, previously excluded in the literature, formation of spatiotemporal patterns in this process, detected upon addition of luminol, as travelling fronts of luminescence (Fig. 2).

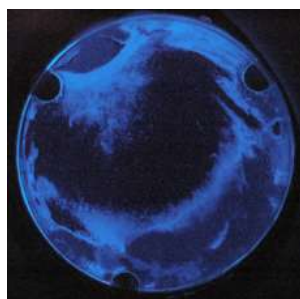


Fig. 2. Exemplary luminescent pattern in the thin layer of the solution with the  $\text{H}_2\text{O}_2\text{-SCN}^-\text{-OH}^-\text{-Cu}^{2+}$  system [5].

In order to understand the above phenomena, with special emphasis on the mechanism of generation of spatiotemporal patterns which is by no means trivial, we performed the following theoretical and experimental studies:

- (i) we simplified the original reaction mechanism, in order to elaborate the model more suitable to the stability (bifurcation) analysis and to the explanation of crucial oscillatory properties of the system studied; our current model involves 9 dynamical variables [6];
- (ii) based on experimental studies, supported with numerical calculations involving our 9-variable model, we were able to explain the potentiometric responses from Fig. 1 in terms of the mixed potential of the inert electrode, being in contact with several redox couples in the solution; the response of the given electrode depends on the relation between current densities of crucial redox couples. A rather sophisticated mechanism of this anomaly can be summarized as follows. These couples, the oscillatory variations of which are shifted in phase for ca.  $180^\circ$ , were identified as  $\text{Cu}(\text{OH})_3^-/\text{Cu}(\text{OH})_2^-$  and  $\text{HO}_2^\bullet/\text{HO}_2^-$ . Since the latter one exhibits the dependence of the charge transfer rate (exchange current density) on the electrode material increasing in the series: GC (glassy carbon) < Au < Pd < Pt (highest electrocatalytic effect for Pt), the GC and Au electrode detect mainly the oscillations of the  $\text{Cu}(\text{OH})_3^-/\text{Cu}(\text{OH})_2^-$  system, and Pd and Pt – those of  $\text{HO}_2^\bullet/\text{HO}_2^-$  system, hence the phase shift in various electrode response (Fig. 3). Besides the better understanding of the  $\text{H}_2\text{O}_2\text{-SCN}^-\text{-OH}^-\text{-Cu}^{2+}$  system, the results may be of more general significance for the interpretation of potentiometric measurement in complex reaction media [6].

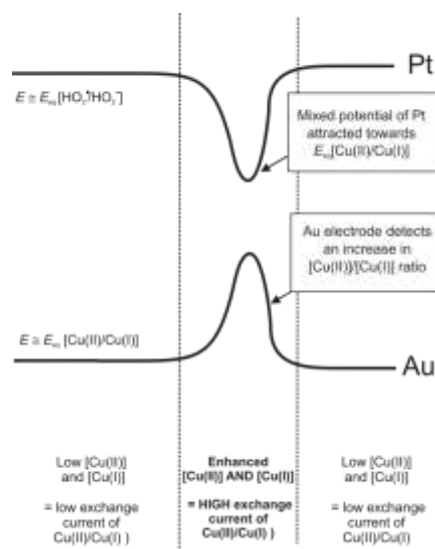


Fig. 3 Principle of the formation of reversed potentiometric peaks in the oscillatory responses of Au and Pt indicator electrodes for the  $\text{H}_2\text{O}_2\text{-SCN}^-\text{-OH}^-\text{-Cu}^{2+}$  system [6]

With respect to further studies, the concordance between the experimental and theoretical electrode response confirm the validity of our simplified kinetic mechanism that can further serve as a basis for modeling spatiotemporal patterns. One of the most important conclusion is that the model mechanism does *not* exhibit excitability, so the mechanism of the pattern generation can be essentially different from those observed in the Belousov-Zhabotinsky oscillatory reaction.

### *Diagnosis of the source of luminescent spatiotemporal patterns*

- (i) Our numerous experiments showed that in vertical tubes, travelling luminescent fronts start usually from the phase boundary solution/air or solution/oxygen bubble, when the local symmetry of the system is broken.
- (ii) In search of other factors that could give rise to pattern formation, we performed a series of thermochemical experiments. They revealed a high exothermicity of the studied reaction, suggesting the eventual role of local temperature gradients in the formation of luminescent patterns (Fig. 4).

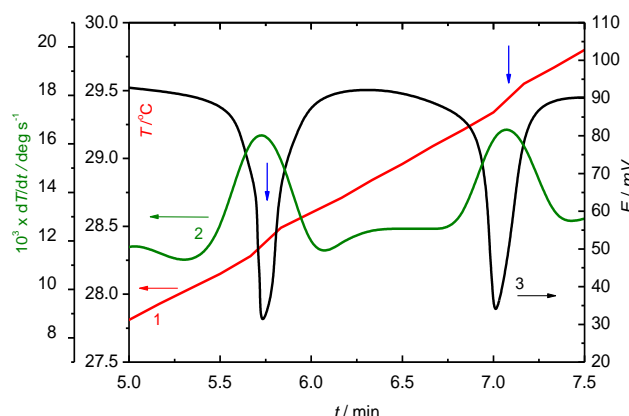


Fig. 4. Variations of the solution temperature  $T$  (curve 1) and its time derivative ( $dT/dt$ ), curve (2) during the oscillatory oxidation of  $\text{SCN}^-$  ions with  $\text{H}_2\text{O}_2$ , monitored simultaneously by variations of the Pt electrode potential (curve 3). Blue arrows indicate locally enhanced  $dT/dt$  slope, concordant with the peak of the Pt electrode potential [7].

- (iii) In view of previous finding, we proposed the novel application of *thermovision camera* for the studies of the surface temperature inhomogeneities (local temperature gradients) associated with the formation of chemical waves; test studies were done for the excitable, thin-layer Belousov-Zhabotinsky system, indicating the thermal map of the concentric wave fronts (Fig. 5), and were extended for the  $\text{H}_2\text{O}_2$ - $\text{SCN}^-$ - $\text{OH}^-$ - $\text{Cu}^{2+}$  thin-layer system (Fig. 6) [7].

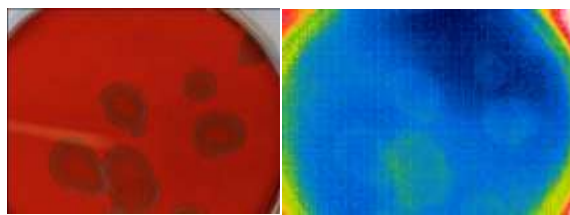


Fig. 5. Optical (left) and infrared (right) images of spatiotemporal patterns in the Belousov-Zhabotinsky reaction [7]

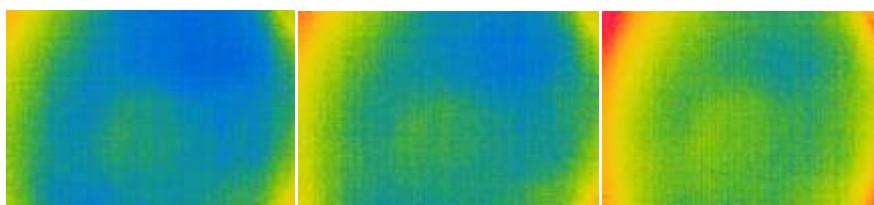


Fig. 6. Exemplary infrared images showing the temporal evolution of temperature gradients of the surface of the thin layer of the solution with  $\text{H}_2\text{O}_2\text{-SCN}^-\text{-OH}^-\text{-Cu}^{2+}$  system [7].

- (iv) In series of following experiments we found that the luminescent patterns can be initiated by local, intentional increase of temperature. Such an increase in the non-perturbed system can also be caused by the high exothermic effect of the chemical reaction, with the inhomogeneous temperature distribution caused by spontaneously formed inhomogeneities in the chemical reaction rate.

Based on the above experimental and theoretical studies we developed a *novel model* for the wave generation and propagation in the  $\text{H}_2\text{O}_2\text{-SCN}^-\text{-OH}^-\text{-Cu}^{2+}$  system [8]. It assumes the interplay of the kinetics of the autocatalytic reaction steps with the enhancement of the reaction rate due to local increase of temperature. In other words, the local kinetics of the system is not isothermal, but the heat evolved during the chemical process enhances the local chemical kinetics through the typical Arrhenius-type dependence. At present stage of our work we are able to choose such (realistic) kinetic and thermodynamic (enthalpic) parameters in the model, that the generated concentration fronts travel with constant velocity through the one-dimensional reactor, similarly to the progress of luminescent fronts in our experiments. One should emphasize that if the effect of increasing temperature on the chemical kinetics is neglected, the wave generated by local perturbation quickly vanishes. This confirms a crucial role of temperature gradient in the progress of the concentration front along the reactor.

Due to this interplay of physical (temperature gradient) and chemical (reaction kinetics) factors, the mechanism of the generation of luminescent fronts in the  $\text{H}_2\text{O}_2\text{-SCN}^-\text{-OH}^-\text{-Cu}^{2+}$  system can be qualified as *thermokinetic* one. So far, thermokinetic oscillations were found rather for fast combustion of various species in the gas phase. We are not aware of any thermokinetic interpretation of spatiotemporal patterns in liquid media. We think that the phenomena studied by us are a rather unique example of instabilities of thermokinetic origin developing in aqueous media and therefore they are worth of presentation.

## References:

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