Conditions for the critical phenomena in a dynamic model of an electrocatalytic reaction

Natalia Firstova, Elena Shchepakina
Department of Technical Cybernetics, Samara National Research University,
34, Moskovskoye shosse, Samara 443086, Russian Federation
E-mail: firstova.natalia@yandex.ru, shchepakina@smr.ru

Abstract. In the paper, a detailed study of the critical phenomena mechanism in a model of an electrocatalytic reaction is carried out. The use of the geometric theory of integral manifolds allows us to show the relationship between the critical regime and the stability loss delay of the slow integral manifold of the corresponding differential system. The asymptotic formula for the critical value of the control parameter is obtained.

1. Introduction
In this paper we investigate the Koper–Sluyters electrocatalytic reaction mechanism underlying an electrochemical reactor. The electrochemical reactor, in contrast to its closest analogue — diaphragm electrolyzer, has much more technical and technological degrees of freedom and has been designed for the electrochemical transformation of a variety of liquids (not only water or aqua-systems over a wide range of solute concentrations, but also milk, vegetable and mineral oils, solutions of carbohydrates, ammonia, alcohols, surfactants, organic and inorganic fertilizers, herbicides, pesticides, and many others). The application area of electrochemically activated solutions is quite broad and includes medicine, petrochemical industry, manufacture of beverages, drinking water purification.

The Koper–Sluyters electrocatalytic reaction is a chemical reaction corresponding to the following kinetic scheme [1]:

\[ X_{\text{bulk}} \xrightarrow{D/\delta} X_{\text{sur}} \xrightarrow{k_a} X_{\text{ads}} \xrightarrow{k_e} P + n e^- . \]

Here \( X \) is a single species which diffuses towards the electrode, where it successively adsors and is electrochemically oxidized; \( X_{\text{sur}} \) and \( X_{\text{bulk}} \) are the parts of \( X \) on the electrode surface and outside the electric double layer, respectively; \( X_{\text{ads}} \) is the adsorbed part of \( X \); \( D \) is the diffusion coefficient of \( X \); \( \delta \) is the thickness of the Nernst diffusion layer; \( k_a, k_d, k_e \) are the rate constants for adsorption, desorption and electron transfer, respectively. The oxidation products \( P \) are assumed not to be adsorbed nor to leave neighborhood of the interface.

In paper [1], simple models of the Koper-Sluyters reaction were investigated in order to determine the possible origins of instabilities and oscillations. For proposed models three different kinds of external electrochemical cell control were considered: potentiostatic control, ohmic resistance control and galvanostatic control. The relations of the proposed models to the previously studied models and experiments were also discussed here.
The case of potentiostatic control of the Koper–Sluyters reaction was also investigated in [2]. The authors showed the existence of two types of the oscillations, small amplitude harmonic oscillations and large amplitude relaxation oscillations. It was noted that for a very narrow range of electrode potentials the electrocatalytic reaction behaviour is similar to a canard. However, neither numerically nor analytically the canard’s existence has been shown. The aim of the present paper is to fill this gap.

The dimensionless dynamic model of the Koper–Sluyters reaction in the case of potentiostatic control described by the system

\begin{align}
\frac{du}{dt} &= -k_a e^{\gamma \theta/2} u (1 - \theta) + k_d e^{-\gamma \theta/2} \theta + 1 - u = f(u, \theta), \\
\beta \frac{d\theta}{dt} &= k_a e^{\gamma \theta/2} u (1 - \theta) - k_d e^{-\gamma \theta/2} \theta - k_e e^{\alpha_0 \zeta E \theta} = g(u, \theta),
\end{align}

here \( u \) is the dimensionless interfacial concentration of \( X \); \( \theta \) is the dimensionless amount of \( X \) that is adsorbed on the electrode surface; \( E \) is the interfacial potential; \( \beta \) is the coverage ratio of the adsorbate; \( \alpha_0 \) is the symmetry factor for the electron transfer; \( \zeta \) is the universal gas constant, \( F \) is Faraday's constant, and \( T \) is the temperature. The physical meaning of the parameter \( \gamma \) has always been a subject of dispute. In most of the literature it is interpreted as an interaction parameter. Positive \( \gamma \) signifies attractive and negative \( \gamma \) signifies repulsive adsorbate interactions.

The typical values of the parameter \( \beta \) are small [1,2], hence, the geometric theory of singular perturbations [3–5] can be applied for the qualitative study of (1), (2).

2. Analysis of the slow integral manifold

Recall, that a slow integral manifold of a singular perturbed system is an invariant surface of slow motions whose dimension is equal to that of the slow subsystem [4,5].

The zero-order approximation of the slow integral manifold, the slow curve, of the system (1), (2) is determined by the expression \( g(u, \theta) = 0 \) and has the form

\[ k_a e^{\gamma \theta/2} u (1 - \theta) - k_d e^{-\gamma \theta/2} \theta - k_e e^{\alpha_0 \zeta E \theta} = 0 \]

or

\[ u = \frac{(k_d e^{-\gamma \theta/2} + k_e e^{\alpha_0 \zeta E \theta}) \theta}{k_a e^{\gamma \theta/2} (1 - \theta)}. \] (3)

The slow curve has a stable (or attractive) and unstable (or repulsive) parts, which are zero-order approximations of the stable and unstable slow integral manifolds, respectively. The stable and unstable parts are divided by jump points [4,5], at which we have

\[ \begin{cases} g(u, \theta) = 0, \\ \frac{\partial g(u, \theta)}{\partial \theta} = 0. \end{cases} \] (4)

For (1), (2) the system (4) has the form

\[ \begin{cases} k_a e^{\gamma \theta/2} u (1 - \theta) - k_d e^{-\gamma \theta/2} \theta - k_e e^{\alpha_0 \zeta E \theta} = 0, \\ k_a u (1 - \theta) \frac{e^{\gamma \theta/2}}{2} - k_a e^{\gamma \theta/2} - k_d e^{-\gamma \theta/2} + k_d e^{-\gamma \theta/2} \frac{\theta}{2} - k_e e^{\alpha_0 \zeta E \theta} = 0. \] (5)

The shape of the slow curve depends on the values of the parameters. We will consider \( \gamma \) as a control under the fixed values of all other parameters.
The following cases are possible.

For $0 < \gamma < 4$ the system (5) has no solutions. Therefore, the slow manifold is either entirely stable or entirely unstable. Due to the fact that

$$\frac{\partial g(u, \theta)}{\partial \theta} < 0,$$

i.e.,

$$k_a u (1 - \theta) \frac{\gamma}{2} e^{\gamma \theta/2} - k_a u e^{\gamma \theta/2} - k_d e^{-\gamma \theta/2} + k_d e^{-\gamma \theta/2} \theta \frac{\gamma}{2} - k_e e^{\alpha_0 \zeta E} \theta < 0,$$

the slow curve is stable in this case, see Figure 1. Hence, the trajectories of the system (1), (2) are attracted to the slow curve and then follow along it as $t \to \infty$. In the case when $\gamma \approx 4$, the slow curve is stable too [6] and has a shape represented in Figure 2.

The critical points of the system (1), (2) are determined by the system

$$
\begin{align*}
-k_a e^{\gamma \theta/2} u (1 - \theta) + k_d e^{-\gamma \theta/2} \theta + 1 - u &= 0, \\
k_a e^{\gamma \theta/2} u (1 - \theta) - k_d e^{-\gamma \theta/2} \theta - k_e e^{\alpha_0 \zeta E} \theta &= 0.
\end{align*}
$$

Thus, for $\gamma > 4$ two jump points, $A_1$ and $A_2$, divide the slow curve into three parts $S_1^s$, $S_2^u$, $S_3^s$ (see Figure 3) which are zeroth order approximations for the corresponding slow integral manifolds $M_1^s$, $M_2^u$, $M_3^s$. Manifolds $M_1^s$ and $M_3^s$ are stable and $M_2^u$ is unstable. Each manifold $M_1^s$, $M_2^u$, and $M_3^s$ is at the same time part of some trajectory of the system (1), (2) [5].

A trajectory, starting from an initial point in the basin of attraction of the stable slow integral manifold $M_1^s$ (or $M_3^s$), tends rapidly to it and then follows $M_1^s$ (or $M_3^s$) with the velocity of order $O(1)$ as $\beta \to 0$. The further behaviour of the trajectory will depend on the location of the critical point of the system (1), (2).

The critical points of the system (1), (2) are determined by the system

$$
\begin{align*}
-k_a e^{\gamma \theta/2} u (1 - \theta) + k_d e^{-\gamma \theta/2} \theta + 1 - u &= 0, \\
k_a e^{\gamma \theta/2} u (1 - \theta) - k_d e^{-\gamma \theta/2} \theta - k_e e^{\alpha_0 \zeta E} \theta &= 0.
\end{align*}
$$

\[ \text{(6)} \]
From the system (6) we get:

\[ u = 1 - k_e e^{\alpha_0 \xi E \theta}. \]  

Substituting (7) into the second equation of the system (6), we obtain the equation that determines the value \( \theta = \theta^* \):

\[ k_a e^{\gamma \theta^*/2} (1 - k_e e^{\alpha_0 \xi E} \theta)(1 - \theta) - k_d e^{-\gamma \theta^*/2} \theta - k_e e^{\alpha_0 \xi E} \theta = 0. \]  

Thus, we obtain the critical point

\[ A \left( \theta^*, 1 - k_e e^{\alpha_0 \xi E \theta^*} \right), \]

where \( \theta^* \) is the solution of the equation (8).

The Jacobian matrix of the system (1), (2):

\[
\begin{pmatrix}
\frac{\partial f(u,\theta)}{\partial u} & \frac{\partial f(u,\theta)}{\partial \theta} \\
\frac{\partial g(u,\theta)}{\partial u} & \frac{\partial g(u,\theta)}{\partial \theta}
\end{pmatrix},
\]

has the characteristic equation

\[ \lambda^2 + \lambda \xi_1 + \xi_2 = 0, \]

with the discriminant

\[ D = \xi_1^2 - 4 \xi_2, \]

where

\[ \xi_1 = \frac{k_a}{\beta} e^{-\gamma \theta^*/2} \left( 1 - k_e e^{\alpha_0 \xi E} \theta^* \right) \left( 1 - \frac{\gamma}{2} (1 - \theta^*) \right) + \frac{k_d}{\beta} e^{-2 \gamma \theta^*/2} \left( 1 - \frac{\gamma \theta^*}{2} \right) 
\]

\[ + \frac{k_e}{\beta} e^{\alpha_0 \xi E} + k_d e^{\gamma \theta^*/2} (1 - \theta^*) + 1, \]

\[ \xi_2 = \frac{k_a}{\beta} e^{-\gamma \theta^*/2} \left( 1 - k_e e^{\alpha_0 \xi E} \theta^* \right) \left( 1 - \frac{\gamma}{2} (1 - \theta^*) \right) + \frac{k_d}{\beta} e^{-2 \gamma \theta^*/2} \left( 1 - \frac{\gamma \theta^*}{2} \right) 
\]

\[ + \frac{k_e}{\beta} e^{\alpha_0 \xi E} + \frac{k_a k_e}{\beta} e^{\gamma \theta^*/2} (1 - \theta^*) e^{\alpha_0 \xi E}. \]

The type of the critical point and its coordinates depends on the value of the parameter \( \gamma \).

Let us consider the most interesting case when \( \gamma > 4 \). Without loss of generality the parameters of the system are chosen to be \( \epsilon = 0.2, \gamma = 8.99, k_a = 10, k_d = 100, a_0 = 0.05, f = 38, 7, E = 0.207564 \) unless other values are specified in figure captions.

In [6], it has been shown that the critical point is a stable focus when it lies on the stable part of the slow curve (Figure 4) and it is an unstable focus when it situated on \( S_2^\circ \). In the second case, the relaxation oscillations are observed in the system, see Figure 5.

The transition between these two situations corresponds to the case when the critical point coincides with the jump point, the stable equilibrium of the system becomes unstable, and at the same instant the stable limit cycle is originated, i.e., the Andronov–Hopf bifurcation occurs, see Figure 6. With further minor modifications of the control parameter, say \( k_e \), the critical point shifts on the unstable part of the slow curve, staying in small (of order \( O(\beta) \) as \( \beta \to 0 \)) neighbourhood of the jump point. As parameter \( k_e \) changes further, this limit cycle grows, and at a value \( k_e = k_e^* \) (so-called canard point) it becomes the canard cycle [7] (Figures 7, 8) with the following canard explosion [8–10]. Recall that the trajectories which at first move along the stable slow integral manifold and then continue for a while along the unstable slow integral manifold are called canards [4,5].
At the first sight the threshold in the qualitative behaviour of the solutions of the system corresponds to the Andronov–Hopf bifurcation point. However, when the value of the control parameter is close to the Andronov–Hopf bifurcation point, the size of the limit cycle is so small that the behaviour of the system’s solution is practically indistinguishable from the slow mode. If, in the case of slow regime, the trajectories approach the stable equilibrium, practically coinciding with the jump point, in the later case they tend to a small limit cycle, again nearly coinciding with the same jump point. Only when the control parameter attains the canard point, provided the equilibrium is on the unstable part of the slow curve and in the sufficiently small vicinity of the jump point, the qualitative change of the system’s behaviour can be observed. Namely, the growth of the limit cycle occurs in such a way that it becomes possible to speak of the existence of the canard trajectory. In other words, the appreciable change in size and/or in form of the limit cycle is observed for small variations of the control parameter, i.e. the canard explosion takes place. Thus, the canard point is the critical value of the control parameter.
3. Asymptotic expression for the critical value of the control parameter

The canards and the parameter value $k^*_c$ allow asymptotic expansions in powers of the small parameter $\beta$ [4,5,11]:

$$u = \Phi(\theta, \beta) = u_0(\theta) + \beta u_1(\theta) + \beta^2 u_2(\theta) + \ldots,$$

$$k^*_c = \chi(\beta) = \chi_0 + \beta \chi_1 + \beta^2 \chi_2 + \ldots. \tag{10}$$

In order to find these asymptotic expansions for the canard and the canard point we substitute the formal expansions (9) and (10) into the invariance equation [5]

$$\frac{du}{d\theta} g(u, \theta) = \beta f(u, \theta),$$

which follows from the system (1), (2). As a result we obtain the following equation:

$$\left(k_a e^{\gamma \theta/2}(1 - \theta)(u_0 + \beta u_1 + \beta^2 u_2 + \ldots) - (\chi_0 + \beta \chi_1 + \beta^2 \chi_2 + \ldots)e^{\alpha_0 \zeta E \theta} - k_d e^{\gamma \theta/2} \theta\right)$$

$$\times \left(u'_0 + \beta u'_1 + \beta^2 u'_2 + \ldots\right) = -\beta k_a e^{\gamma \theta/2}(1 - \theta)(u_0 + \beta u_1 + \beta^2 u_2 + \ldots)$$

$$+ \beta \left(k_d e^{\gamma \theta/2} \theta + 1 - u_0 - \beta u_1 - \beta^2 u_2 + \ldots\right). \tag{11}$$

On setting equal the coefficients of powers of $\beta$ in the equation (11) we find the functions $u_0(\theta), u_1(\theta), \ldots$. To obtain the values $\chi_0, \chi_1, \ldots$ we require the continuity of the functions $u_i(\theta)$ ($i = 0, 1, \ldots$) at the jump point. This requirement means that we glue the stable and the unstable integral manifolds at the jump point, and, as a result, construct the canard passing through this point. As a result we have:

$$u_0(\theta) = \frac{(k_a e^{-\gamma \theta/2} + \chi_0 e^{\alpha_0 \zeta E \theta}) \theta}{k_a e^{\gamma \theta/2}(1 - \theta)}, \tag{12}$$

$$u_1(\theta) = \frac{-k_a u_0(\theta)(1 - \theta)e^{\gamma \theta/2} + k_d e^{-\gamma \theta/2} \theta + 1 - u_0(\theta) + \chi_1 e^{\alpha_0 \zeta E \theta} u_0'(\theta)}{k_a e^{\gamma \theta/2} u_0'(\theta)}, \tag{13}$$

$$\chi_0 = \frac{k_a(1 - \theta) e^{\gamma \theta/2} - k_d e^{-\gamma \theta/2} \bar{\theta}}{(k_a(1 - \theta) e^{\gamma \theta/2} - 1)e^{\alpha_0 \zeta E \bar{\theta}}}. \tag{14}$$
\[ x_1 = -k_au_1(\bar{\theta})(1 - \bar{\theta})e^{\gamma\bar{\theta}/2} + u_1(\bar{\theta}) + k_au_1(\bar{\theta})u'_1(\bar{\theta})(1 - \bar{\theta})e^{\gamma\bar{\theta}/2}, \tag{15} \]

where the value \( \theta = \bar{\theta} \) corresponding to the jump point can be calculated from the system (5).

The equations (12)–(15) define the first-order approximations for the canard passing through the jump point \( (u(\bar{\theta}), \bar{\theta}) \) and the canard point of the system (1), (2). It should be noted that we can construct the canard either in the jump point \( A_1 \) (by gluing the stable slow integral manifold \( M_1 \) and the unstable one \( M_2 \), see Figures 9, 10) or in \( A_2 \) (by gluing the stable slow integral manifold \( M_3 \) and \( M_2 \), see Figures 7, 8). If it is necessary to glue stable and unstable slow invariant manifolds at both jump points simultaneously, we should use two control parameters and as a result we obtain a canard cascade [12].

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{figure9.png}
\caption{The slow curve (the red line) and the canard (the black line) of the system (1), (2); \( k_e = 2.40855 \).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.45\textwidth]{figure10.png}
\caption{Plots of \( \theta(t) \) (the solid orange line), \( u(t) \) (the dashed blue line) for \( k_e = 2.40855 \).}
\end{figure}

4. Conclusion

We have explored the dynamic model of the electrocatalytic reaction under the influence of constantly present small perturbations. The critical regime separating the basic types of the regimes, slow and relaxation, was modelled with the help of the integral manifolds of variable stability. This approach was used in [12-21] for modelling of the critical phenomena in chemical systems.

We showed that in the differential system the critical regime corresponds to the phenomenon of the delayed loss of stability, when the trajectory, passing through a jump point, continues its motion for a while on the unstable slow manifold. The asymptotic formula for the critical value of the control parameter has been derived.

The obtained results are of utmost importance for several applications in chemical kinetics, as they can be used to determine the dynamics of the process in the chemical system for given initial conditions.

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