UDC 517.938

H.M. Hubal
Lutsk National Technical University

CONSTRUCTION AND STUDY OF THE SYSTEM OF DIFFERENTIAL EQUATIONS THAT DESCRIBES OSCILLATORY CHEMICAL REACTIONS BASED ON DIFFUSION

Губаль Г. М. Побудова та дослідження системи диференціальних рівнянь, яка описує коливальні хімічні реакції з урахуванням дифузії. У статті побудовано та досліджено систему нелінійних диференціальних рівнянь з частинними похідними другого порядку, яка описує коливальні хімічні реакції з урахуванням дифузії.

Ключові слова: дифузія, концентрація, система диференціальних рівнянь, крайові умови.

Губаль Г. Н. Построение и исследование системы дифференциальных уравнений, описывающей колебательные химические реакции с учетом диффузии. В статье построено и исследовано систему нелинейных дифференциальных уравнений с частными производными второго порядка, описывающей колебательные химические реакции с учетом диффузии.

Ключевые слова: диффузия, концентрация, система дифференциальных уравнений, краевые условия.

Hubal H. M. Construction and study of the system of differential equations that describes oscillatory chemical reactions based on diffusion. In the article, the system of non-linear partial differential equations of the second order describing oscillatory chemical reactions based on diffusion are constructed and investigated.

Keywords: diffusion, concentration, system of differential equations, boundary conditions.

Introduction. When studying oxidation-reduction self-oscillatory reactions in a flask, it is obvious that solution changes its colour simultaneously in the whole flask if there is a sufficient mixing. If the reaction goes without intense mixing, then the eye does not notice periodic changes in the colour of the solution. Even with weak mixing, the colour of the solution changes synchronously throughout the volume.

If there would be no oscillations at each point, and the alignment of the initial heterogeneities in the concentrations resulting in the spread of the phase difference would only occur due to the thermal diffusion of molecules, then establishment of a state with equal concentration of substances in the whole flask would continue to be considerably longer. However, due to convection flows and turbulent diffusion [1], when mixing the equilibrium of concentrations occurs much faster. For example, as a result of turbulent diffusion, the smoke from a cigar in concentrations sufficient to act on a human smell spreads around the room in a few seconds, and the effect of only one molecular diffusion would lead to the same result only in a few days.

As a result of the mixing, the molecules of the reactants pass from one elemental volume to neighbouring ones, together with the whole larger volumes of the solution, as well as there are differences (larger gradients) of the concentrations that increase the diffusion rate.

The analysis of oscillatory chemical reactions based on diffusion shows that as a result of the redistribution of the molecules of the reactants in space, there is not only the alignment of the initial spatial heterogeneities along the amplitude, but also the phases of oscillations in different elemental volumes become the same, i.e. there is a mutual synchronization of many connected oscillatory systems in space in oscillatory chemical reactions based on diffusion.

Main part. Consider how we can explain the synchronization of small deviations of concentrations from their stationary levels in space.

Let there be the substance P_1 in surplus in some very small elemental volume. The substance P_1 being in surplus, in the process of the reaction the consumption of the substance P_1 is almost invisible. The molecules of the substance P_1 with some constant rate λ_0 turns into the molecules of the substance X (it being the zero-order reaction). The substance X turns into the substance Y (it being the second-order reaction; the greater the concentration of the substance Y, the greater its rate as indicated by the reverse arrow above Y in the scheme given below). The molecules of the substance Y irreversibly decay resulting in the formation of the substance P_2 (it being the first-order reaction).

The kinetic scheme of the periodic oscillatory chemical reaction that goes in a homogeneous environment:

$$P_1 \xrightarrow{\lambda_0} X \xrightarrow{\lambda_1} \overset{\swarrow}{Y} \xrightarrow{\lambda_2} P_2,$$

where λ_0, λ_1, λ_2 are constant rates.

© Губаль Г. М.

For simplicity, we denote by P_1, P_2, X, Y the concentrations of the corresponding substances.

Since we consider this chemical reaction in a very small elemental volume, then in this case, we can write

$$X = X(t), \quad Y = Y(t).$$

We write the system of differential equations that describes this reaction

$$\begin{cases} \dfrac{dX}{dt} = \lambda_0 - \lambda_1 XY, \\ \dfrac{dY}{dt} = \lambda_1 XY - \lambda_2 Y, \\ \dfrac{dP_2}{dt} = \lambda_2 Y. \end{cases} \tag{1}$$

Since the first two differential equations do not depend on P_2, then they can be considered separately. The first differential equation of this system of differential equations shows that the rate of change of the concentration *X* is determined by the constant rate of formation of the substance (λ_0) while transforming P_1 to X and by decrease while transforming *X* to *Y*. The second differential equation of the system of differential equations takes into account the increase of *Y* due to *X* and the decrease while transforming *Y* to P_2.

First we find out whether the reaction can go so that the rate of formation P_2 can remain constant. This is the case when the concentrations $\overline{X}$ i $\overline{Y}$ do not change in time, i.e.

$$\frac{d\overline{X}}{dt} = 0, \quad \frac{d\overline{Y}}{dt} = 0.$$

For these conditions, we obtain the following system of algebraic equations that connect equilibrium concentrations $\overline{X}$ and $\overline{Y}$ from system of differential equations (1):

$$\begin{cases} \lambda_0 - \lambda_1 \overline{X}\overline{Y} = 0, \\ \lambda_1 \overline{X}\overline{Y} - \lambda_2 \overline{Y} = 0. \end{cases}$$

The solution of the system has the form

$$\overline{X} = \frac{\lambda_2}{\lambda_1}, \quad \overline{Y} = \frac{\lambda_0}{\lambda_2}. \tag{2}$$

Suppose that this reaction can go not only in very small elemental volume (or at a point) where the change of the concentration of each substance is synchronous but also in a sufficiently large volume. For simplicity, we suppose that this finite large volume is one-dimensional, that is we suppose that the reactor is a very narrow tube which has the length *l* and the section *S* (see the scheme of the one-dimensional reactor, Fig. 1). This tube has such a small radius that the going of the reaction can be considered synchronous in its arbitrary cross-section. Suppose also that the substance P_1 is distributed in surplus throughout its length *l*. Denote by *u* the only spatial coordinate, the origin combining with the left end of the tube. Then the right end of the tube has the coordinate $u = l$.

Consider the elemental volume $\Delta V(u)$ and calculate the balance of the concentrations *X* and *Y* in it. It is obvious that *X* and *Y* are functions of the coordinate and time:

$$X = X(u,t), \; Y = Y(u,t).$$

The rate of change of concentrations in the elemental volume $\Delta V(u)$ is determined by the decrease and increase of the concentrations *X* and *Y* as a result of chemical transformations and the running of the molecules *X* and *Y* across the boundaries of the elemental volume $\Delta V(u)$. These boundaries have the coordinates u and $u + \Delta u$.

© Губаль Г. М.

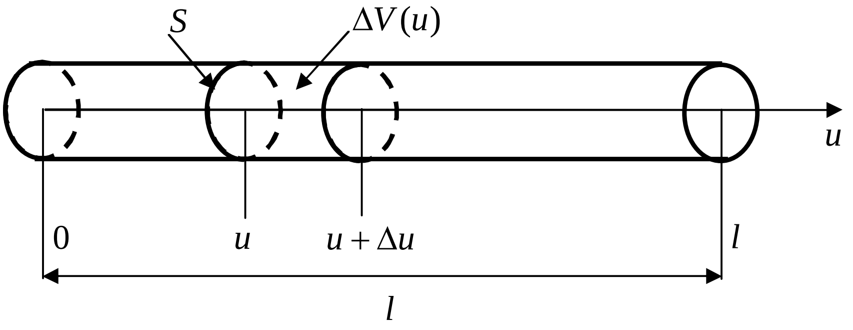

Fig.1

By Nernst’s law, the mass of the substance X (or the number of molecules) that penetrates through the section of the tube that is, the reactor with the coordinate $u+\Delta u$ into the elemental volume $\Delta V(u)$ for a small period of time from t to $t+\Delta t$ is proportional to the gradient $\frac{\Delta X(u+\Delta u,t)}{\Delta u}$ of the concentration of the substance X in the direction $-u$ (that is, the increment of the mass $\Delta M_{u+\Delta u}$ of the substance X for time Δt in the elemental volume $\Delta V(u)$ due to diffusion through the tube section with the coordinate $u+\Delta u$):

$$\Delta M_{u+\Delta u} = D\frac{\Delta X(u+\Delta u,t)}{\Delta u}S\Delta t,$$

where D is the coefficient of diffusion. The value D is determined by the properties of the dissolved substance and the solution and does not depend on the concentration in the large boundaries of its change.

The following mass passes through the second boundary of the elemental volume $\Delta V(u)$ with the coordinate u in the direction u (opposite to $-u$ so there is the minus sign in the formula given below) for time from t to $t+\Delta t$ (that is, the increment of the mass ΔM_u of the substance X for time Δt in the elemental volume $\Delta V(u)$ due to diffusion through the tube section with the coordinate u):

$$\Delta M_u = -D\frac{\Delta X(u,t)}{\Delta u}S\Delta t.$$

The total quantity (mass) of the substance X that penetrates the elemental volume $\Delta V(u)$ through its two limits due to diffusion for time Δt (that is, the total increment of the mass ΔM of the substance X for time Δt in the elemental volume $\Delta V(u)$ due to diffusion) is

$$\Delta M = \Delta M_{u+\Delta u} + \Delta M_u.$$

The corresponding increment of the concentration ΔX of the substance X inside the volume $\Delta V(u)$ due to diffusion is

$$\Delta X = \frac{\Delta M}{\Delta V(u)} = \frac{\Delta M}{S\Delta u} = \frac{\frac{\Delta X(u+\Delta u,t)}{\Delta u} - \frac{\Delta X(u,t)}{\Delta u}}{\Delta u}D\Delta t = \frac{\Delta\left(\frac{\Delta X(u,t)}{\Delta u}\right)}{\Delta u}D\Delta t.$$

The rate of change of the concentration of the substance X inside the considerable elemental volume due to running of molecules (diffusion) across the boundaries with coordinates u, $u+\Delta u$ at $\Delta u \to 0$ $(\Delta V(u) \to 0)$, $\Delta t \to 0$:

$$v_2 = \lim_{\substack{\Delta u\to 0\\ \Delta t\to 0}} \frac{\Delta X}{\Delta t} = D\frac{\partial}{\partial u}\left(\frac{\partial X(u,t)}{\partial u}\right) = D\frac{\partial^2 X(u,t)}{\partial u^2}.$$

It is necessary to add the rate of change of the concentration due to chemical transformations to this rate (see the first differential equation of system of differential equations (1)):

© Губаль Г. М.

$$v_1 = \lambda_0 - \lambda_1 XY.$$

Thus, full rate of change of the concentration of the substance *X*:

$$\frac{\partial X}{\partial t} = v = v_1 + v_2 = \lambda_0 - \lambda_1 XY + D\frac{\partial^2 X(u,t)}{\partial u^2}.$$

Similarly, we calculate full rate of change of the concentration of the substance *Y* (taking into account the second differential equation of system of differential equations (1)).

Then the system of differential equations for the rates of change of concentrations in the volume $dV(u)$:

$$\begin{cases} \dfrac{\partial X}{\partial t} = \lambda_0 - \lambda_1 XY + D_1 \dfrac{\partial^2 X}{\partial u^2}, \\ \dfrac{\partial Y}{\partial t} = \lambda_1 XY - \lambda_2 Y + D_2 \dfrac{\partial^2 Y}{\partial u^2}, \end{cases} \tag{3}$$

where D_1 and D_2 are coefficients of diffusion for the substances *X* and *Y*.

System of equations (3) is a system of second-order non-linear partial differential equations.

We linearize system of differential equations (3).

Taking into account that small deviations *x* and *y* from stationary values of concentrations $\overline{X}$ and $\overline{Y}$ are the functions *u* and *t*, we obtain

$$\begin{aligned} X(u,t) &= \overline{X} + x(u,t), \\ Y(u,t) &= \overline{Y} + y(u,t). \end{aligned} \tag{4}$$

Substituting expressions (4) and (2) into system of differential equations (3), we obtain the following system of differential equations for small deviations *x* and *y*:

$$\begin{cases} \dfrac{\partial x}{\partial t} = -\dfrac{\lambda_1 \lambda_0}{\lambda_2} x - \lambda_2 y - \lambda_1 xy + D_1 \dfrac{\partial^2 x}{\partial u^2}, \\ \dfrac{\partial y}{\partial t} = \dfrac{\lambda_1 \lambda_0}{\lambda_2} x + \lambda_1 xy + D_2 \dfrac{\partial^2 y}{\partial u^2}. \end{cases}$$

Neglecting the terms containing values of the second order of smallness *xy*, we obtain the linearized system of differential equations for small deviations of concentrations *x* and *y*:

$$\begin{cases} \dfrac{\partial x}{\partial t} = -2\delta x - \dfrac{\omega^2}{2\delta} y + D_1 \dfrac{\partial^2 x}{\partial u^2}, \\ \dfrac{\partial y}{\partial t} = 2\delta x + D_2 \dfrac{\partial^2 y}{\partial u^2}, \end{cases} \tag{5}$$

where the coefficients δ and ω are expressed in terms of constant rates λ_0, λ_1 and λ_2:

$$\frac{\lambda_1 \lambda_0}{\lambda_2} = 2\delta, \quad \lambda_1 \lambda_0 = \omega^2.$$

Note that in system of differential equations (5) unlike system of differential equations (3), variables *x* and *y* can change their sign (since they are small deviations of concentrations which are either positive or negative or zero), whereas variables *X* and *Y*, which are concentrations, can only be positive.

System of differential equations (5) is solved taking into account the boundary conditions at the ends of the reactor which are impervious to molecules of the substances *X* and *Y*:

$$\left.\frac{\partial x}{\partial u}\right|_{u=0} = \left.\frac{\partial x}{\partial u}\right|_{u=l} = 0,$$
$$\left.\frac{\partial y}{\partial u}\right|_{u=0} = \left.\frac{\partial y}{\partial u}\right|_{u=l} = 0.$$

If initial small deviations of concentrations, at $t=0$ $x(u,0)$ and $y(u,0)$, from equilibrium are defined the same everywhere, then the oscillations will be carried out synchronously throughout the length of the reactor and there will be no diffusion along the u-axis because in any neighbouring pair of points u and $u+du$, the concentration difference at any time is zero. System of differential equations (5) has solutions that describe damped oscillations, that is the small deviations $x(u,t)$ і $y(u,t)$ in this case will vary equally throughout the length of the reactor.

If the initial concentrations at different points of the tube differ from each other, then there is diffusion that will try to align the concentrations at neighbouring points (or at elemental volumes).

To study the dependence of the damping of oscillations on the nature of the initial distribution of small deviations of concentrations $x(u,0)$, $y(u,0)$, it is convenient to define the initial distribution (the initial data) in the form of the cosines:

$$\left.x(u,t)\right|_{t=0} = x_0 \cos\frac{n\pi}{l}u,$$
$$\left.y(u,t)\right|_{t=0} = y_0 \cos\frac{n\pi}{l}u,$$

where x_0 and y_0 are constant numbers.

Since the differential equations of oscillatory chemical reactions are non-linear, then conclusions obtained here are true when the deviations of concentrations $x(u,t)$ and $y(u,t)$ are small compared to stationary values of the concentrations $\overline{X}$ and $\overline{Y}$.

If the least initial heterogeneities increase, then oscillations in different phases appear in separate elemental volumes of the reactor. Then the colour the liquor of does not change synchronously throughout the volume. However, it is enough weak mixing (for example, convection flow rate is 1 cm/s, the reactor radius is 1 cm and $l=10$ cm), so that only initial zero tone can increase, another heterogeneities quickly damp and, therefore, the reaction goes synchronously in the whole volume.

The oscillations of concentrations inside the cell pass in the entire volume of the cell synchronously at zero tone if the periods of such oscillations are of the order of several hours and $\delta \le 0{,}1\omega$. If oscillatory heterogeneities appear in the cell, then they are quickly dissolved under the action of only one molecular diffusion. The oscillations of concentrations in the cell appear, for example, in dark reactions of photosynthesis [3] or in glycolysis [2].

If the space is heterogeneous, for example, it is heated or illuminated unevenly, then with small these heterogeneity the diffusion will also lead to smoothing of heterogeneities and synchronous oscillation modes.

Conclusions. The system of non-linear partial differential equations of the second order describing oscillatory chemical reactions based on diffusion are constructed and investigated.

The boundary conditions at the ends of the reactor are defined.

1. Bakunin O.G. Turbulence and diffusion. From chaos to structures / O.G. Bakunin // Moscow: Fizmatlit, 2010.
2. Bar-Even A., Flamholz A., Noor E., Milo R. Rethinking glycolysis: on the biochemical logic of metabolic pathways / A. Bar-Even, A. Flamholz, E. Noor, R. Milo // Natural Chemical Biology. – Vol. 8. – 2012. – P. 509–517.
3. Tanaka A., Makino A. Photosynthetic research in plant science / A. Tanaka, A. Makino // Plant and sell physiology. – Vol. 50, Issue 4. – 2009. – P. 681–683.

© Губаль Г. М.