



Research article

Traveling-waves of metal-containing monomer polymerization without diffusion and heat-transfer



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ABSTRACT

The new approach for modeling kinetics of complex spatial self-propagating traveling-wave reactions is proposed. This approach is intended to replace well-known reaction–diffusion equations and self-propagating high-temperature synthesis (SHS) as methods for mathematical modeling of spatial propagation of chemical reactions. A chemical kinetic model for frontal polymerization of metal-containing monomers under this approach is suggested.

1. Introduction

So far, mathematical modeling of the macro «traveling-waves» of chemical transformation has been made by means of reaction–diffusion equation, or (for exothermic processes) in the context of spatial thermal self-propagation sourced from heat of reaction [1, 2, 3, 4]. In general, the latter method is called self-propagating high-temperature synthesis (SHS) [1, 2]. These approaches outcome in the large number of interesting results in chemical physics, combustion theory, SHS theory, and also in biochemistry and economy. Nevertheless, they offer no universal paradigm for the mathematical modeling of spatial propagation of chemical reactions, focusing on two though important, but particular cases. Those cases when the leading defining moments of process is the physics of diffusion or (and) heat transfer. The chemical kinetics in there is *a priori* secondary since it is responsible either for the “source” term of the production of some components, resulted from the considered process, or, in general, for the total heat of all reactions.

The non-universality fundamental nature of those approaches for the theory of chemical kinetics emphasizes the absence of the general paradigm of modeling the dynamics of chemical transformation by time and space (!) in non-homogeneous (generally, not heterogeneous either) environment. In our opinion, such theory would offer new opportunities for studying complex multistage and multiphase processes of

transformation, as the gnoseological potential of the diffusion and thermal approaches is considerably exhausted over the past eighty years. For example, the thermophysics of metal-containing monomers frontal polymerization is already studied, largely due to SHS-theory, and that cannot be told about its chemical kinetics [5], many of the nuances of which are not covered by a context of neither thermal, nor diffusion models [6].

Here we describe the way for creating the partial differential equations of chemical kinetics with time and spatial variables without appealing to the equations of heat transfer and diffusion. We consider the particular case of chemical reaction taking form of a *one-dimensional traveling wave*, or in other words when the component concentration is formally expressed by function $C_i = C_i \left(t - \frac{x}{w} \right)$, where t is the time variable, x is the spatial variable, w is the rate constant of the traveling wave.

Actually, the approach is based only on a nonconventional view of the well-known fact that the reaction rate constant in the equations of chemical kinetics is usually not a constant, but function of component concentrations and temperature $k = k(C_1, \dots, C_N, T)$. Let us examine that in detail. The rate of reaction $\nu_1 X_1 + \nu_2 X_2 + \dots + \nu_N X_N \rightarrow Y$ is as follows:

$$\frac{d\xi}{dt} = k_A(T) C_1^{\nu_1} C_2^{\nu_2} \dots C_N^{\nu_N}, \quad (1)$$

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where $k_A(T)$ is Arrhenius equation (or one of its versions), ν_i is stoichiometric coefficient of the reaction, C_i is molar concentration of X_i , ξ is conversion such that the following is true:

$$d\xi = \frac{dC_1}{\nu_1} = \frac{dC_2}{\nu_2} = \dots = \frac{dC_N}{\nu_N}$$

Notice that the right part of (1) is true only for the elementary reaction. If the complex reaction occurring in multi steps is considered, then usually exponents are the reaction orders s_i in X_i . Thus follows:

$$\frac{d\xi}{dt} = k_A(T) C_1^{s_1} \dots C_N^{s_N} = [k_A(T) C_1^{s_1 - \nu_1} \dots C_N^{s_N - \nu_N}] C_1^{\nu_1} \dots C_N^{\nu_N} = k(C_1, \dots, C_N, T) \varphi(C_1, \dots, C_N) \quad (2)$$

We reckon that the term “reaction rate constant” in this context looks as unnaturally, as in the phrase, “It has become general practice, however, to express the reaction rates in terms of the concentrations and to include the effects of changing activities in the rate constants” [[7], p.238]. While the multipliers in the right part of (2) have a simple interpretation, the factor $\varphi(C_1, \dots, C_N) = C_1^{\nu_1} \dots C_N^{\nu_N}$ settles “chemical brutto-netto” of transformation, and $k(C_1, \dots, C_N, T) = k_A(T) C_1^{s_1 - \nu_1} \dots C_N^{s_N - \nu_N}$ appears to be the local (in a representative elementary volume (REV) at a given moment in time) intensity of the reaction. This local intensity for complex multi-stage reactions in non-homogeneous environments is actually the central macro-kinetic functional (!) characteristic of their chemical kinetics. Nevertheless, authors are going to follow tradition and to use the term “reaction rate constant” instead of the “local intensity of reaction”.

To sum up, we'll notice that if the reaction appears to be the self-propagating one-dimensional traveling wave, and since the reaction constant is formally expressed as a function of concentration $C_i = C_i \left(t - \frac{x}{w} \right)$, then with $T = Const$ it would also be a traveling wave:

$$\left(\frac{\partial}{\partial t} + w \frac{\partial}{\partial x} \right) k(C_1, \dots, C_N, T) = 0. \quad (3)$$

Besides, as the temperature is normally non-variable, the function can be written down as follows:

$$k = k(C_1, \dots, C_N). \quad (4)$$

If, as in the case of frontal polymerization of metal-containing monomers, chemical transformation releases energy, then the traveling wave of reaction is accompanied by the running thermal wave $T = T \left(t - \frac{x}{w} \right)$. Thereby, (3) is true for a reaction rate constant. Moreover, numerous studies of SHS-systems [1, 2] (in particular, [5]) indicate that in this case the temperature could always be expressed as a function of components concentrations $T \approx \Phi(C_1, \dots, C_N)$. Therefore, (4) is also true.

Further, (4) is used without any special comments. At the same time the less restrictive statements are used instead of (3). This substitution is an attempt to approach the issue at hand from more common positions, open either to further specifications, or discussions.

2. Equations of non-homogeneous chemical macro-kinetics

Even considering the most general situation, it is necessary to mention that diffusional and thermal appearances of reaction for gaseous fluids often allow using known approaches effectively. Therefore, we are going to discuss a complex multiphase process of transformation, such as polymerization of metal-containing monomers (namely metal nitrate acrylamides) that ought not to be compared to gas-phase reactions even in qualitative terms. These monomers appear to be complex molecular formations that could significantly change their inner structure (to lose or to get subunits, rebuild bonds, etc.) during polymerization.

Monomer-polymer melt includes complex associates of tens and hundreds of molecules consisting of interconnected layers, similar to

high-dispersed partly oriented submicroscopic crystallites in solid matter. This polymerization process has a free-radical nature with some specific features. The growing macroradicals change their arrangement or collide with the monomer molecules only upon chain growth (because the reacting monomer particles are lacking in translational diffusion), and crystallographic defects (dislocations, cracks, vacancies) tend to terminate chain growth. Macroradicals grow in line with structural aspects of not only the macroradicals themselves but also of monomers, assuming no diffusion of either of them [5]. Linear dimensions of the defects caused by elementary reactions are comparable to average intermolecular distances.

The matter is situation when it is better to use non-dimensional mass fractions of components y_i ($i = 1, \dots, N$) in mathematical models of chemical kinetics. That also makes easier working with dimensions in appearing non-linear equations and normalizes mass conversation law:

$$\sum_{i=1}^N y_i = 1. \quad (5)$$

From mathematical point of view, hyperbolic (wave) or parabolic (evolutional) equations can be used to characterize process of spatial propagation. This research exploits parabolic equations. In doing so, the authors consider unreasonable to rely on any similarities or connections between propagation of transformation and mechanical motion or thermal physics in continuum. In general, spatial self-propagation of reaction is not connected with any mechanical macro-motion or migration of heat waves. That is why considering reaction rate of spatial propagation as its basic characteristic seems to be the most natural in our case.

Dissimilarity between actual rate of reaction in considered representative elementary volume (REV) and the rate of reaction that would be observed under the condition of homogeneity of the process (i.e. zero concentration gradients of reacting components) can be used to describe “spatial motion of transformation”.

To make this statement formal, we shall consider a monomolecular reaction: one reagent converting to one product. Due to (5) describing the kinetics of either component would be sufficient {reagent, product} = $\{y_1, y_2\}$. Let's define a rate of homogeneous process relative to the product:

$$\frac{dy_2}{dt} = k \cdot (1 - y_2), \quad y_2(0) = 0 \quad (6)$$

And then we shall consider the rate of reaction in non-homogeneous system. Let's suggest that $k = k(t, x)$ and $y_2 = y_2(t, x)$, and pick two neighbor elementary (in terms of local equilibrium thermodynamics [5]) volumes $V(x)$ and $V(x+\Delta x)$ centered at points x and $x+\Delta x$, respectively. To define the rate of spatial reaction propagation we assume that if $k(t, x)$ is the reaction rate constant in the given volume $V(x)$ at the moment t then there is such Δt that $k(t, x) = k(t+\Delta t, x+\Delta x)$ in $V(x+\Delta x)$ at the moment $t+\Delta t$ which also could be written down as:

$$k(t+\Delta t, x+\Delta x) - k(t+\Delta t, x) + k(t+\Delta t, x) - k(t, x) = 0$$

Then, assuming that k is differentiable:

$$\frac{\partial k(t+\Delta t, x)}{\partial x} \Delta x + \frac{\partial k(t, x)}{\partial t} \Delta t = 0 \Leftrightarrow \frac{\partial k(t+\Delta t, x)}{\partial x} \frac{\Delta x}{\Delta t} + \frac{\partial k(t, x)}{\partial t} = 0$$

Evaluating limits:

$$\frac{\partial k(t, x)}{\partial x} w(t, x) + \frac{\partial k(t, x)}{\partial t} = 0 \quad (7)$$

where $w(t, x)$ is instantaneous spatial rate of reaction.

From the equation of homogeneous chemical kinetics (6) we move to the partial differential equation describing non-homogeneous chemical kinetics (the initial condition for (6) transforms to the initial condition determined in every point x of the selected area):

$$\frac{\frac{\partial y_2(x,t)}{\partial t}}{1 - y_2(x,t)} = k(x,t), \tag{8}$$

Differentiating both sides of (8) with respect to t:

$$\frac{\partial}{\partial t} \left(\frac{\frac{\partial y_2(x,t)}{\partial t}}{1 - y_2(x,t)} \right) = \frac{\partial k(x,t)}{\partial t}$$

Then we expand the parentheses on the left side and changing the right side in accordance with (7):

$$\frac{1}{1 - y_2} \frac{\partial^2 y_2}{\partial t^2} + \left(\frac{\frac{\partial y_2}{\partial t}}{1 - y_2} \right)^2 = -w(t,x) \frac{\partial k(y_2)}{\partial x} \tag{9}$$

It should be noted that the rate $w(t, x)$ in our consideration is determined solely by the specificity of chemical transformations. Therefore, its formal assessment should be based on the law of mass action in a non-homogeneous system. In our opinion, despite the fact that the wording of this law has recently attracted the attention of researchers [8], it is still far from ideal. In view of this, in determining $w(t, x)$, one can use either the corresponding phenomenological approach, constructed, for example, on the basis of the principles set forth in [9], or experimental data.

Replacing parentheses on the left side according to equation (8) and multiplying both sides by $(1 - y_2)$ we arrive at

$$\frac{\partial^2 y_2}{\partial t^2} + w(t,x) \frac{\partial k(y_2)}{\partial x} (1 - y_2) + k(y_2)^2 (1 - y_2) = 0. \tag{10}$$

The same goes for the general situation. Consider the system of ordinary differential equations describing chemical kinetics in homogeneous medium

$$\left\{ \frac{dy_i}{dt} = k_i(y_1, \dots, y_N) \varphi_i(y_1, \dots, y_N) \right\}_{i=1}^N \tag{11}$$

Turning to elementary volume we get to the system of partial differential equations in non-homogeneous medium:

$$\left\{ \frac{\frac{\partial y_i}{\partial t}}{\varphi_i(y_1, \dots, y_N)} = k_i(y_1, \dots, y_N) \right\}_{i=1}^N \tag{12a}$$

Then we introduce the chemical motion hypothesis, which is expressed as follows:

$$\left\{ \frac{\partial k_i(t,x)}{\partial x} w(t,x) + \frac{\partial k_i(t,x)}{\partial t} = 0 \right\}_{i=1}^N \tag{12b}$$

Based on (12)_a and (12)_b the result is

$$\left\{ \frac{\partial}{\partial t} \left(\frac{\frac{\partial y_i}{\partial t}}{\varphi_i(y_1, \dots, y_N)} \right) = -w_i(t,x) \frac{\partial k_i(y_1, \dots, y_N)}{\partial x} \right\}_{i=1}^N$$

And after differentiating the left parts of the equations:

$$\left\{ \frac{\partial^2 y_i}{\partial t^2} + w_i(t,x) \frac{\partial k_i(y_1, \dots, y_N)}{\partial x} \varphi_i(y_1, \dots, y_N) - \frac{\partial \varphi_i(y_1, \dots, y_N)}{\partial t} k_i(y_1, \dots, y_N) = 0 \right\}_{i=1}^N$$

Taking into account the additive acceleration (deceleration) factors G_i corresponding to y_i that have no connection with chemical reaction (e.g. describing the rate of the mass loss in certain REV during the “i” component non-uniform motion through the reacting medium) might sum up the above. Considering the system of N components, we can make these equations, which are suggested to refer to as Equations of

Inhomogeneous Chemical Macro-kinetics (EICM):

$$\left. \begin{aligned} & \left\{ \frac{\partial^2 y_i}{\partial t^2} + w_i(t,x) \frac{\partial k_i(y_1, \dots, y_N)}{\partial x} \varphi_i(y_1, \dots, y_N) - \frac{\partial \varphi_i(y_1, \dots, y_N)}{\partial t} k_i(y_1, \dots, y_N) + G_i = 0 \right\}_{i=1}^{N-1} \\ & \sum_{i=1}^N y_i = 1 \end{aligned} \right\} \tag{13}$$

To illustrate facilities provided by this new approach we'll use the simple example (10). The reaction rate constant k within (6) is different from the constant $k = k(y_2)$ within (10) according to the difference in proceeding of homogeneous reaction (6) and non-homogeneous reaction (10). Indeed, assuming their equality leads to

$$\frac{\partial k(y_2)}{\partial x} \rightarrow 0, \text{ but } w(x,t) \frac{\partial k(y_2)}{\partial x} \rightarrow - \frac{\partial k(y_2)}{\partial t}$$

Substituting that into (9) leads to (6). In other words, using (10) instead of (6) ((10) is deduced from (9)) is correct only when reaction is non-homogeneous:

$$\frac{\partial k(y_2)}{\partial x} \neq 0$$

Assuming that $w(t,x) = w = const$, let's find a solution for (10) in a form of the travelling wave $y_2 = y_2(t - \frac{x}{w})$. To do that, we'll assign a variable $\tau = t - \frac{x}{w}$ having the dimension of time, rewrite (10) with that variable and add one more initial condition:

$$\left. \begin{aligned} & \frac{d^2 y_2}{d\tau^2} - \frac{dk(y_2)}{d\tau} (1 - y_2) + k(y_2)^2 (1 - y_2) = 0 \\ & y_2(0) = \delta, \quad \frac{dy_2}{d\tau}(0) = k(\delta)(1 - \delta) \end{aligned} \right\} \tag{14}$$

where the initial condition is set using (8). Note that if $k(0) = 0$ then in order to avoid falling into a stationary point we should set $0 < \delta < 1$. Otherwise, we can assume $\delta = 0$.

To compare the solutions to (6) and (14) let's remove all the units from these equations. Assuming that the reaction rate constant k in (6) is invariable, let's define $\Delta t = \frac{1}{k}$ and $s = \frac{t}{\Delta t}$. To remove the dimensions of (14) we define $\Delta \tau = \frac{1}{k}$ and $s = \frac{\tau}{\Delta \tau}$, k is the reaction rate constant from (6). Besides that, we shall consider 2 expressions for the non-homogeneous reaction rate constant:

$$a) \Delta \tau \cdot k(y_2) = \alpha(1 - y_2), \quad \alpha = const > 0; \quad b) \Delta \tau \cdot k(y_2) = \beta y_2, \quad \beta = const > 0$$

After simple transformations each of obtained equations becomes a system of two first-order equations with a new variable $q = \frac{dy_2}{ds}$:

$$\left. \begin{aligned} & \frac{dy_2}{ds} = q \\ & \frac{dq}{ds} = -\alpha q(1 - y_2) - \alpha^2 (1 - y_2)^3 \end{aligned} \right\}, \quad \begin{pmatrix} y_2(0) \\ q(0) \end{pmatrix} = \begin{pmatrix} 0 \\ \alpha \end{pmatrix} \tag{15}$$

and

$$\left. \begin{aligned} & \frac{dy_2}{ds} = q \\ & \frac{dq}{ds} = \beta q(1 - y_2) - \beta^2 y_2^2 (1 - y_2) \end{aligned} \right\}, \quad \begin{pmatrix} y_2(0) \\ q(0) \end{pmatrix} = \begin{pmatrix} \delta \\ \beta(1 - \delta)\delta \end{pmatrix} \tag{16}$$

Fig. 1 shows plots of solutions for “homogeneous” equation (6), EICM (15) and EICM (16). Notice that given example, despite its simplicity, demonstrates principal steps of modeling within submitted approach.

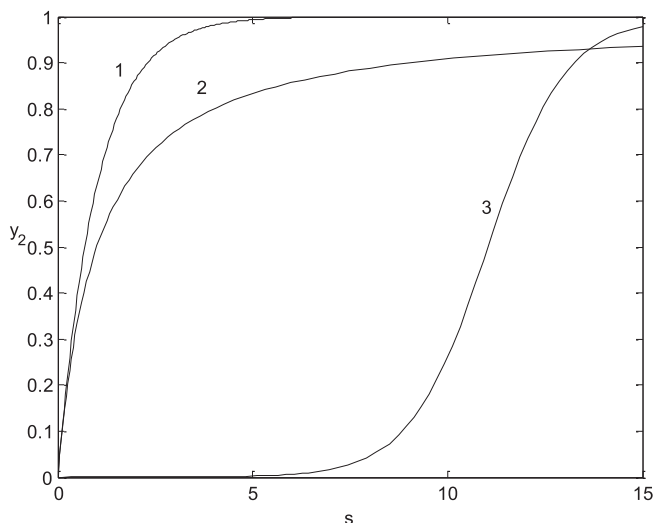


Fig. 1. Curve 1 is a graph of the function $y_2 = 1 - e^{-x}$ that is the solution of the dimensionless equation (6), curve 2 is the graph of the solution (15) at $\alpha = 1$, $\delta = 0$, curve 3 is the graph of the solution (16) at $\beta = 1$, $\delta = 0.00001$.

3. The models of polymerization of metal-containing monomers

The following is objected to compare the mathematical models of homogeneous polymerization of metal-containing monomers and non-homogeneous – frontal, described by means of EICM.

One of the simplest examples of the kinetic process was provided in [6]:



where M is monomer, R_n^* – free radicals, P – generating polymer, k_M^* , k_p^* , k_o^* – kinetic constants.

The system of the ordinary equations of homogeneous chemical kinetics for (17) can be written down as follows:

$$\left. \begin{aligned}
 \frac{dy_1}{dt} &= -k_M^* y_1 - k_p^* y_1 y_2 \\
 \frac{dy_2}{dt} &= k_M^* y_1 - k_o^* y_2^2 \\
 y_1 + y_2 + y_3 &= 1
 \end{aligned} \right\}, \quad 0 \leq t, \quad y_1(0) = 1, \quad y_2(0) = y_3(0) = 0 \tag{18}$$

where y_1, y_2, y_3 are the corresponding mass fractions of monomer, free radicals and polymer. It should be pointed out that y_2 is the mass fraction not only of the free radicals but also of the intermediate compounds that monomer transforms to before becoming the radical (more details in [5]).

The system (18) by means of its third equation is reduced to system of two ordinary differential equations:

$$\left. \begin{aligned}
 \frac{dy_1}{dt} &= -k_M^* y_1 - k_p^* y_1 (1 - y_1 - y_3) \\
 \frac{dy_3}{dt} &= k_p^* y_1 (1 - y_1 - y_3) + k_o^* (1 - y_1 - y_3)^2
 \end{aligned} \right\}, \quad 0 \leq t, \quad y_1(0) = 1, \quad y_3(0) = 0 \tag{19}$$

Changing

$$\Delta t = \frac{1}{k_M^*}, \quad s = \frac{t}{\Delta t}, \quad \frac{d}{dt} = k_M^* \frac{d}{ds}, \quad k_p = \frac{k_p^*}{k_M^*}, \quad k_o = \frac{k_o^*}{k_M^*} \tag{20}$$

leads (19) to a dimensionless look

$$\left. \begin{aligned}
 \frac{dy_1}{ds} &= -y_1 [1 + k_p - k_p (y_1 + y_3)] \\
 \frac{dy_3}{ds} &= [k_o - (k_o - k_p) y_1 - k_o y_3] (1 - y_1 - y_3)
 \end{aligned} \right\}, \quad 0 \leq s, \quad y_1(0) = 1, \quad y_3(0) = 0 \tag{21}$$

Proceeding from (19), let us construct the system of EICM, describing the frontal type of kinetics of the considered process:

$$\left. \begin{aligned}
 \frac{\partial^2 y_1}{\partial t^2} + w_1(t, x) \frac{\partial k_1(y_1, y_3)}{\partial x} \varphi_1(y_1, y_3) - \frac{\partial \varphi_1(y_1, y_3)}{\partial t} k_1(y_1, y_3) &= 0 \\
 \frac{\partial^2 y_3}{\partial t^2} + w_3(t, x) \frac{\partial k_3(y_1, y_3)}{\partial x} \varphi_3(y_1, y_3) - \frac{\partial \varphi_3(y_1, y_3)}{\partial t} k_3(y_1, y_3) &= 0
 \end{aligned} \right\}, \quad 0 \leq t \tag{22}$$

Let's seek for the solution of (22) represented by traveling waves $y_1 = y_1(t - \frac{x}{w})$ and $y_3 = y_3(t - \frac{x}{w})$, assuming that $w_1(t, x) = w_3(t, x) = w \equiv const$, $\tau = t - \frac{x}{w}$. In this case (22) becomes

$$\left. \begin{aligned}
 \frac{d^2 y_1}{d\tau^2} &= \frac{d}{d\tau} [k_1(y_1, y_3) \varphi_1(y_1, y_3)] \\
 \frac{d^2 y_3}{d\tau^2} &= \frac{d}{d\tau} [k_3(y_1, y_3) \varphi_3(y_1, y_3)]
 \end{aligned} \right\}, \quad 0 \leq \tau$$

Whence it follows that

$$\left. \begin{aligned}
 \frac{dy_1}{d\tau} &= C_1 + k_1(y_1, y_3) \varphi_1(y_1, y_3) \\
 \frac{dy_3}{d\tau} &= C_3 + k_3(y_1, y_3) \varphi_3(y_1, y_3)
 \end{aligned} \right\}, \quad 0 \leq \tau, \quad y_1(0) = 1, \quad y_3(0) = 0. \tag{23}$$

It looks like (19) and (23) differ from each other in only “artificially arisen” non-variables C_1 and C_3 . But the principal difference between these systems lies in the variables t and τ . The system (19) describes transformation in homogeneous environment in every spot of it from the moment the reaction began. System (23) describes the structure of the travelling wave of transformation which could be comprehended in two ways (see [6] for the details). First, as spatial propagation of reaction component mass fractions in non-homogeneous system at the moment $t = t_0$ and second, as changing dynamics of those mass fractions in certain REV (in terms of local equilibrium thermodynamics) since its meeting with the travelling wave of reaction. In the latter case, the elementary volume is *a priori* homogeneous. Also the second interpretation shows physical meaning of C_1 and C_3 . If

$$k_1(y_1(0), y_3(0)) \varphi_1(y_1(0), y_3(0)) = k_3(y_1(0), y_3(0)) \varphi_3(y_1(0), y_3(0)) = 0,$$

Then those invariables describe the initiation of the reaction at the moment the travelling wave reaches the considered REV. However, the most significant difference is observed between the rate constants of the homogeneous (19) and non-homogeneous reaction (22). After defining the dimensionless values

$$k_p = \frac{k_p^*}{k_M^*}, \quad k_o = \frac{k_o^*}{k_M^*}, \quad \varphi_1(y_1, y_3) = -y_1 [1 + k_p - k_p (y_1 + y_3)], \tag{24}$$

$$\varphi_3(y_1, y_3) = [k_o - (k_o - k_p) y_1 - k_o y_3] (1 - y_1 - y_3)$$

for (19), we can see that

$$k_1 = k_3 = k_M^* \equiv const,$$

At the same time for (23)

$$k_1(y_1, y_3) = k_M^* \psi_1(y_1, y_3), \quad k_3(y_1, y_3) = k_M^* \psi_3(y_1, y_3)$$

As mentioned in the introduction, frontal polymerization of metal-containing monomers is accompanied by a heat wave $T = T(t - \frac{x}{w}) = T(s)$. According to SHS, such constants a and b could be found that

$$T = T(s) \approx a + by_3(s). \tag{25}$$

Therefore, in this case ψ_i must look like the Arrhenius equation with $T(s)$ substituted by the right part of (25). But the numerical analysis showed that such implicit consideration of the Arrhenius law in (22) leads to the solution that is qualitatively similar to the solution of (19). Hence in the considered approach the Arrhenius law doesn't have that primal role for structuring the travelling waves, as it has in SHS or Combustion Theory. The types of ψ_i equations that are inherent for the situation are still the pending issue. However, taking into account the existing experimental data (some of it is presented in [5]), we shall consider the following:

$$k_1(y_1, y_3) = k_M^*, \quad k_3(y_1, y_3) = k_M^* (1 - y_1 - y_3)^{\frac{1}{2}} \tag{26}$$

Assuming for (23) that

$$\Delta\tau = \frac{1}{k_M^*}, \quad s = \frac{\tau}{\Delta\tau}, \quad \frac{d}{d\tau} = k_M^* \frac{d}{ds}, \quad C_1 = 0, \quad C_3 = 0 \tag{27}$$

Bearing in mind (24) and (26), we can conclude:

$$\left. \begin{aligned} \frac{dy_1}{ds} &= -y_1 [1 + k_p - k_p(y_1 + y_3)] \\ \frac{dy_3}{ds} &= [k_o - (k_o - k_p)y_1 - k_o y_3] (1 - y_1 - y_3)^{\frac{3}{2}} \end{aligned} \right\}, \quad 0 \leq s, \quad y_1(1) = 1, \quad y_3(0) = 0 \tag{28}$$

4. Numerical analysis

The solutions for the systems (21) and (28) were found numerically with the same parameters $k_p = 100, k_o = 7$. Taking into account (20) and (27), it allows comparing the durations of the process in both cases.

The numerical solution for (21) is presented in Fig. 2. It is characterized by the fact that the mass fraction of all intermediate products and radicals do not exceed 0,13 and falls down smoothly by the end of

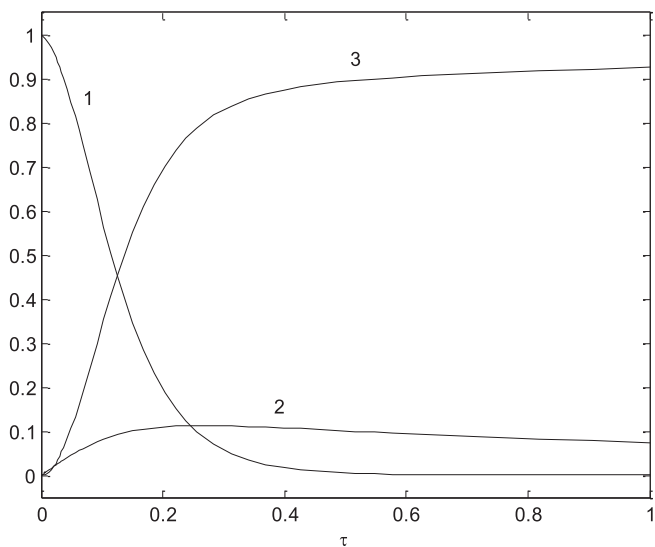


Fig. 2. The solution of system (21) with $k_p = 100, k_o = 7$. Curve 1 is the mass fraction of a monomer y_1 , curve 2 is the mass fraction of active radicals y_2 , curve 3 is the mass fraction of a polymer y_3 .

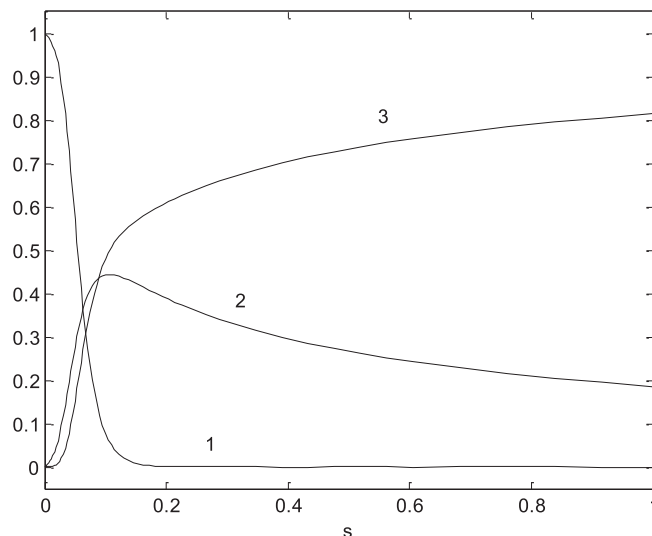


Fig. 3. The solution of system (28) with $k_p = 100, k_o = 7$. Curve 1 is the mass fraction of a monomer y_1 , curve 2 is the mass fraction of active radicals y_2 , curve 3 is the mass fraction of a polymer y_3 .

process. Considering that too big mass fraction of radicals leads to failure of polymerization process for metal-containing monomers, the obtained solution describes a typical homogeneous process [5].

The numerical solution for (28) is presented in Fig. 3. Its particular feature is the clear allocation of the active reacting layer in the reaction front that can be seen from the small part of the figure, where y_2 fraction prevails over the other components. As it was mentioned, y_2 includes not only free radicals, but also the intermediate compounds, and then the lamination of those compounds inside the wave, artificially fastened to the structure of heat wave [5], is naturally coordinates within the transformation wave. It is necessary to highlight that lamination of frontal type of transformation was repeatedly noted by experimenters for the most different reacting systems [5].

The solution in Fig. 3 could also be interpreted as the spatial waves moving across the Ox axis in the negative direction. However, estimating their real scales would require the values of constants w and k_M^* . And it should be mentioned that the danger of termination for the homogeneous polymerization requires moderate mass fraction of radicals, whereas for the frontal polymerization the possibility of termination demands (throughout all process) moderate spatial thickness of the active reacting layer.

5. Conclusion

The aim of this study is development of the mathematical apparatus for the description of spatial self-propagating chemical transformation at the macro level that would be based on the chemical kinetics of the reaction, not the physics of diffusion or (and) heat transfer.

This attempt is the first of a kind, and its effectiveness has yet to be defined. The authors reckon that this work should help “rehabilitating” the macrokinetics as one of the efficient instruments for investigating the complex multi-staged and multi-phased chemical transformations. The skepticism about macrokinetics, which originates from the end of XX century [10], was aroused sufficiently by the intuitively perceived “chemical incorrectness” (or non-constructivity) of macro-level substituting the rate of diffusion or heat transfer for the chemical reaction rate in many particular cases. However, stochastic method (which was proposed as an alternative to the macrokinetics [10] over the last few decades) couldn't go beyond its original range, which was determined as far back as in the second half of the last century. Macro kinetics is a natural instrument for a researcher and a convenient theory for a

technologist to consider complex self-organizing processes (such as frontal polymerization of metal-containing monomers) having a firm macro geometry. This explains the appreciable increase of interest for the macrokinetic models that is observed now in biology, bio-physics, economics, etc.

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Declarations

Author contribution statement

B Yadav: Conceived and designed the experiments; Wrote the paper.
Sergey Zakiev: Conceived and designed the experiments; Performed the experiments.

Vitaly Shershnev: Analyzed and interpreted the data.

Yu. P. Kvrta: Conceived and designed the experiments.

Gulzhian Dzhardimalieva: Contributed reagents, materials, analysis tools or data.

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The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

- [1] P.M. Goldfeder, V.A. Volpert, V.M. Ilyashenko, A.M. Khan, J.A. Pojman, S.E. Solovyov, Mathematical modeling of free-radical polymerization fronts, *J. Phys. Chem. B* 101 (18) (1997) 3474–3482.
- [2] A.I. Volpert, V.A. Volpert, V.A. Volpert, *Traveling Wave Solutions of Parabolic Systems*, 140, American Mathematical Soc, 1994.
- [3] E. Frulloni, M.M. Salinas, L. Torre, A. Mariani, J.M. Kenny, Numerical modeling and experimental study of the frontal polymerization of the diglycidyl ether of bisphenol A/diethylenetriamine epoxy system, *J. Appl. Polym. Sci.* 96 (5) (2005) 1756–1766.
- [4] E. Goli, I.D. Robertson, P.H. Geubelle, J.S. Moore, Frontal polymerization of dicyclopentadiene: a numerical study, *J. Phys. Chem. B* 122 (16) (2018) 4583–4591.
- [5] A.D. Pomogailo, G.I. Dzhardimalieva, Frontal polymerization of metal-containing monomers: achievements and problems, *Polym. Sci. Ser. A* 46 (2004) 250–268.
- [6] S.E. Zakiev, G.I. Dzhardimalieva, A.D. Pomogailo, Nonthermal model for thermal frontal polymerization of metal-containing monomers, *Polym. Sci. Ser. B* 59 (2017) 210–216.
- [7] D. Kondepudi, I. Prigogine, *Modern Thermodynamics: from Heat Engines to Dissipative Structures*, second ed., John Wiley & Sons, Ltd, 2015.
- [8] Hao Ge, Hong Qian, Mathematical formalism of nonequilibrium thermodynamics for nonlinear chemical reaction systems with general rate law, *J. Stat. Phys.* 166 (2017) 190–209.
- [9] B. Delmon, *Introduction a la Cinétique Hétérogène, Éditions TECHNIP, Paris*, 1969.
- [10] E. Kotomin, V. Kuzovkov, *Modern Aspects of Diffusion-Controlled Reactions*, Elsevier Science, 1996.