Non-local phenomena under heat and mass transfer in the high rate processes

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The paper deals with the theoretical description of intensive regimes of heat and mass transfer which are typical for high rate transport phenomena in chemical reactors. The operation cycle in case of high-intensity fast processes is short and the entire process can be performed under transient conditions. Problems of modeling high-intensity processes involve construction of equations with retarded and divergent arguments, which takes account of the actual mechanism of transfer phenomena in the medium. In our paper non-local equations of the heat and mass transfer in technological processes are developed. The conditions of validity of the obtained equations and their solutions are discussed. The generalization of relaxation transfer cores applied to multicomponent systems is developed. It is established that the time dependence of the cross transfer cores is non-monotonous and has a maximum. This is a specific phenomenon caused by the effect of thermal diffusion or the Soret effect. The new methodology of calculating the intensity of heat and mass transfer processes accompanied by cross effects has been carried out.

1. Mathematical model

Consideration of the relaxation time and long-range interaction of structural components of a medium is a great practical and theoretical problem (Rudyak, 1987, p. 270) that is very relevant in cases of high-intensity fast processes. In this connection, the control of high-intensity process is limited and it is important to calculate correctly and select the best values of determining parameters. The time nonlocality of transfer processes under high-intensity conditions can be described by the model of relaxation cores of transfer [6]. Relaxation cores of transfer are the cores of integral transforms that, in the statistical theory of dissipation processes, relate fluxes with thermodynamic forces [1, 6]. Noteworthy are the wide possibilities of modeling by relaxation cores of transfer under a minimum of phenomenological approaches, which makes the method good for a study of the effect of the spatial-time nonlocality on the heat- and mass-transfer phenomena. The total structure of the component mass fluxes and heat flux in an *n*-component system according to this method has the following form according to (Jou, Casas-Vazquez and Criado-Sancho, 2001, p. 225):

$$J(R,t) = J(R,t_0) + \sum_{k=1}^{n+1} \iint dt_1 dR' N_{ik}(R, R', t, t_1) F_k(R', t), \tag{1}$$

where J are the substances fluxes; N_{ik} are the relaxation transfer cores; F_k are the thermodynamic forces; t is a time; R is a space vector.

Limiting one self to the time nonlocality in the multicomponent system, one can write expressions for the *n* linearly independent mass fluxes (Kim, Brener, 1996, p. 260).

$$J_i = -\sum_{k=1}^{n}\int_0^t dt_1 N_{ik}(R, t-t_1)\nabla\left(\frac{\nu_k(R,t_1)}{T}\right) - \int_0^t dt_1 N_{ih}(R, t-t_1)\frac{\nabla T}{T^2}, \tag{2}$$

$$J_h = -\sum_{k=1}^{n}\int_0^t dt_2 N_{hk}(R, t-t_2)\nabla\left(\frac{\nu_k(R,t_1)}{T}\right) - \int_0^t dt_2 N_{hh}(R, t-t_2)\frac{\nabla T}{T^2}, \tag{3}$$

where ν_k are the chemical potentials; T is the temperature.

To obtained a compact description and simplify transformations, let us assume $\nu_{n+1} = -1$. Then, in expressions (2), (3), one can replace the subscript *h* by *n* + 1 and write a unified form for the mass fluxes and heat flux in the multicomponent system (Brener, Muratov, Tashimov, 2004, p. 326):

$$J_i = -\sum_{k=1}^{n+1}\int_0^t dt_1 N_{ik}(R, t-t_1)\nabla\left(\frac{\nu_k(R,t_1)}{T}\right). \tag{4}$$

To analyze the total structure of the transfer equations, we use the special model equation, derived in (Brener, 2006, p. 566):

$$\frac{\partial I_{ik}}{\partial t} = \eta_{ik}\nabla\left(\frac{\nu_k}{T}\right) - \frac{I_{ik}}{\tau_{ik}}, \tag{5}$$

where τ_{ik} are the relaxation times and

$$I_{ik} = \int_0^t dt_1 N_{ik}(R, t-t_1)\nabla\left(\frac{\nu_k(R,t_1)}{T}\right). \tag{6}$$

Using (10), as a result of the repeated differentiation up to derivatives of the (*n*+ 1)-th order, the following relationships are obtained:

$$\frac{\partial^p J_i}{\partial t^p} = \sum_{j=0}^{p-1}(-1)^{j+1}\frac{\partial^{p-1-j}}{\partial t^{p-1-j}}\left(\sum_{k=1}^{n+1}\frac{\eta_{ik}\nabla(\nu_k/T)}{\tau_{ik}^j}\right) + (-1)^{p+1}\sum_{k=1}^{n+1}\frac{I_{ik}}{\tau_{ik}^p}. \tag{7}$$

Subsequent transformations are based on the conservation laws:

$$\frac{\partial \nu_i}{\partial t} + \nabla \cdot J_i = 0 \,. \tag{8}$$

Acting on expression (7) by the nabla operator and using (8), one can obtain, as a result, the differential equation of the (*n* + 2)-th order for the potential of each of the components of the system:

$$L\left(\frac{\partial^{n+2}(\nu_i)}{\partial t^{n+2}}, \frac{\partial^{n+1}(\nu_i)}{\partial t^{n+1}}, \ldots, \frac{\partial \nu_1}{\partial t}; \nu_i, .., \nu_n \right) = 0 \,. \tag{9}$$

The generalization of model approach (Kim, Brener, 1996, p. 261) to calculating relaxation cores for multiple components can be presented as

$$\frac{\partial N_i}{\partial t} = -N_i \tau_{ii}^{-1} + \sum_{\substack{k=1 \\ k \neq i}}^{n} N_k \tau_{ik}^{-1} \,. \tag{10}$$

Here, for filling to the Onsager principle, it is assumed that $\tau_{ik} = \tau_{ki}$.

The matrix of set (10) is symmetrical; therefore, all its eigenvalues are real. In this connection, by analogy with the result (Brener, 2006, p. 570), solution of (10) can be represented as the sum of the forward and cross components of the cores of transfer:

$$N_i = \sum_{k=1}^{n} N_{ik} \,, \tag{11}$$

where all items are real exponents and *Nik* = *Nki*. Hence, a relationship of the form of (9) again occurs.

The nonlinear generalization of flow equations (1) can be represented in a nonlocal quadratic form with tensor cores (Brener, 2006, p. 571):

$$\begin{aligned} J_i = &-\sum_{k=1}^{n+1} \int_0^t dt_1 N_{ik}^{(1)}(R, t - t_1) \cdot \nabla \left(\frac{\nu_k(R, t_1)}{T} \right) - \\ &- \sum_{k=1}^{n+1} \sum_{p=1}^{n+1} \int_0^t \int_0^t dt_1 dt_2 N_{ikp}^{(2)}(R; t - t_1; t - t_2) : \nabla \left(\frac{\nu_k(R, t_1)}{T} \right) \nabla \left(\frac{\nu_p(R, t_2)}{T} \right) \,. \end{aligned} \tag{12}$$

In the weakly nonlinear approximation, one can assume

$$\left\| N_{ikp}^{(2)} \right\| = \varepsilon \left\| N_{ik}^{(1)} \right\| \left\| N_{ip}^{(1)} \right\|, \tag{13}$$

where ε is the series expansion parameter. As the parameter, one can use the ratio of the two Knudsen numbers that are calculated by two specific spatial scales for the elastic and inelastic molecular collisions, respectively.

The simple non-linear generalization of the model (10) considering the cross effects in a two-component system looks as follows

$$\begin{cases} \dfrac{\partial N_m}{\partial t} = -N_m\left(1-\varepsilon_m N_m\right)\tau_m^{-1} + N_h\left(1-\varepsilon_h N_h\right)\tau_\times^{-1}, \\ \dfrac{\partial N_h}{\partial t} = N_m\left(1-\varepsilon_m N_m\right)\tau_\times^{-1} - N_h\left(1-\varepsilon_h N_h\right)\tau_h^{-1} \end{cases} \tag{14}$$

2. Model results

The solution of submitted model for a two-component system can be written in the form

$$N_m = N_{mm} + N_{mh}, \tag{15}$$

$$N_h = N_{hh} + N_{hm}, \tag{16}$$

where

$$N_{mm} = \frac{\eta_m}{\lambda_2 - \lambda_1}\left[\left(\lambda_2 + \frac{1}{\tau_m}\right)\exp(\lambda_1 s) - \left(\lambda_1 + \frac{1}{\tau_m}\right)\exp(\lambda_2 s)\right], \tag{17}$$

$$N_{hh} = \frac{\eta_h}{\lambda_2 - \lambda_1}\left[\left(\lambda_2 + \frac{1}{\tau_h}\right)\exp(\lambda_1 s) - \left(\lambda_1 + \frac{1}{\tau_h}\right)\exp(\lambda_2 s)\right], \tag{18}$$

$$N_{mh} = N_{hm} = \frac{\eta_\times}{\tau_\times(\lambda_2 - \lambda_1)}\left[\exp(\lambda_1 s) - \exp(\lambda_2 s)\right] \tag{19}$$

In the approximation of system quasi non-equilibrium, from the condition of attenuation of distortions, it is follows that both characteristic quantities $\lambda_{1;2}$ should be negative. From this, one can obtain the inequality for direct and cross relaxation times:

$$\tau_\times > \sqrt{\tau_m \tau_h}\ . \tag{20}$$

Let us introduce the dimensionless parameters that characterize the correlations of relaxation times of the forward and cross distortions:

$$\alpha_1 = \frac{\tau_m}{\tau_h}; \quad \alpha_2 = \frac{\tau_m}{\tau_\times}; \quad z = \alpha_2\sqrt{\alpha_1} \tag{21}$$

Figure 1 depicts the typical curves for the time history of relaxation transfer cores under the different quantities of the parameters obtained by numerical experiment.

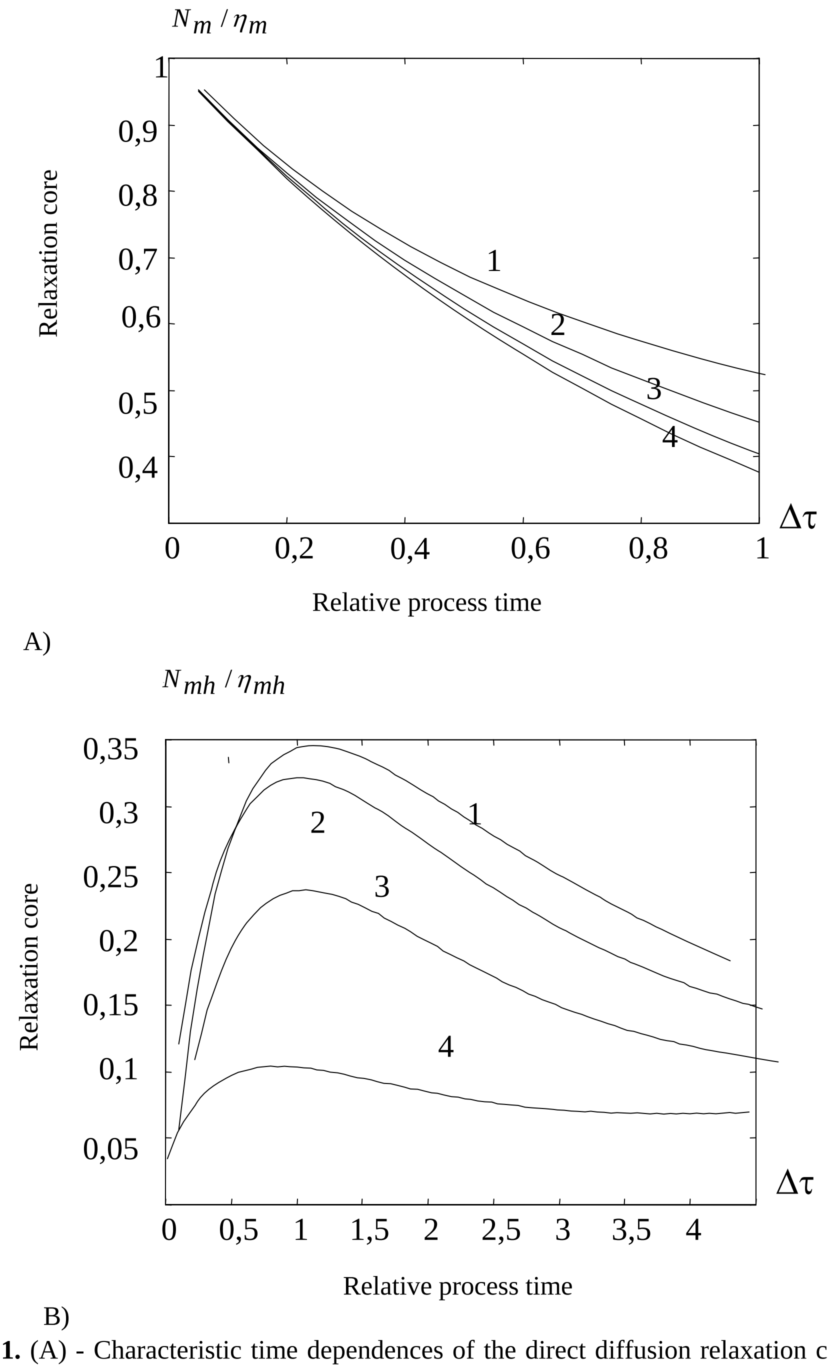


Figure 1. (A) - Characteristic time dependences of the direct diffusion relaxation core of transfer at α_1 = 1.4 and (B) - the development of cross relaxation distortion at α_1 = 0.6; z = (1) 0.2, (2) 0.4, (3) 0.6, (4) 0.8.

The time dependence of the cross core of transfer has a maximum (Fig. 1 - B). This is a specific phenomenon caused by the effect of thermal diffusion or the Soret effect. The maximum of the time dependence of the cross core of transfer determines the period of increase in the initial distortions of the temperature and concentration fields that is due to influence of thermodynamic cross effects. From this, one can obtain the formula for the specific period of increase in distortions:

$$\Delta t_{\uparrow} = \frac{\ln(\lambda_2/\lambda_1)}{\lambda_1 - \lambda_2}. \tag{22}$$

3. Practical recomendations

In a compact form the calculations order for one-dimension tubular through-reactor with allowing for the non-local phenomena can be described as follows.
The simplified system of heat and mass transfer reads:

$$\tau_1 \frac{\partial^2 \nu}{\partial t^2} = (-1 + \tau_1 \mathrm{N}_1)\frac{\partial \nu}{\partial t} + D\Delta \nu \ , \tag{23}$$

$$\tau_2 \frac{\partial^2 T}{\partial t^2} = (-1 + \tau_2 \mathrm{N}_2)\frac{\partial T}{\partial t} + a\Delta T \ , \tag{24}$$

Let us introduce the extended variables using scales of the relaxations times order: t; $\theta = \frac{t}{\tau}$; x. Thus solutions of (23), (24) look as follows

$$\nu = \nu_0 + \tau_1 \nu_1, \ T = T_0 + \tau_2 T_1. \tag{25}$$

The zero and first approximations are determined from the equations

$$\frac{\partial^2 \nu_0}{\partial \theta^2} = -\frac{\partial \nu_0}{\partial \theta}, \ \frac{\partial^2 T_0}{\partial \theta^2} = -\frac{\partial T_0}{\partial \theta}; \tag{26}$$

$$\frac{\partial^2 \nu_1}{\partial \theta^2} = \frac{\partial \nu_1}{\partial \theta} + N_1 \frac{\partial \nu_0}{\partial \theta} + \frac{\partial^2 \nu_0}{\partial x^2}, \ \frac{\partial^2 T_1}{\partial \theta^2} = \frac{\partial T_1}{\partial \theta} + N_1 \frac{\partial T_0}{\partial \theta} + \frac{\partial^2 T_0}{\partial x^2}. \tag{27}$$

From these equations it follows the characteristic solutions.
Zero-order:

$$\nu_0 = \nu_0(x)\big|_{t=0} + C_\nu \exp(-\theta); \ T_0 = T_0(x)\big|_{t=0} + C_T \exp(-\theta). \tag{28}$$

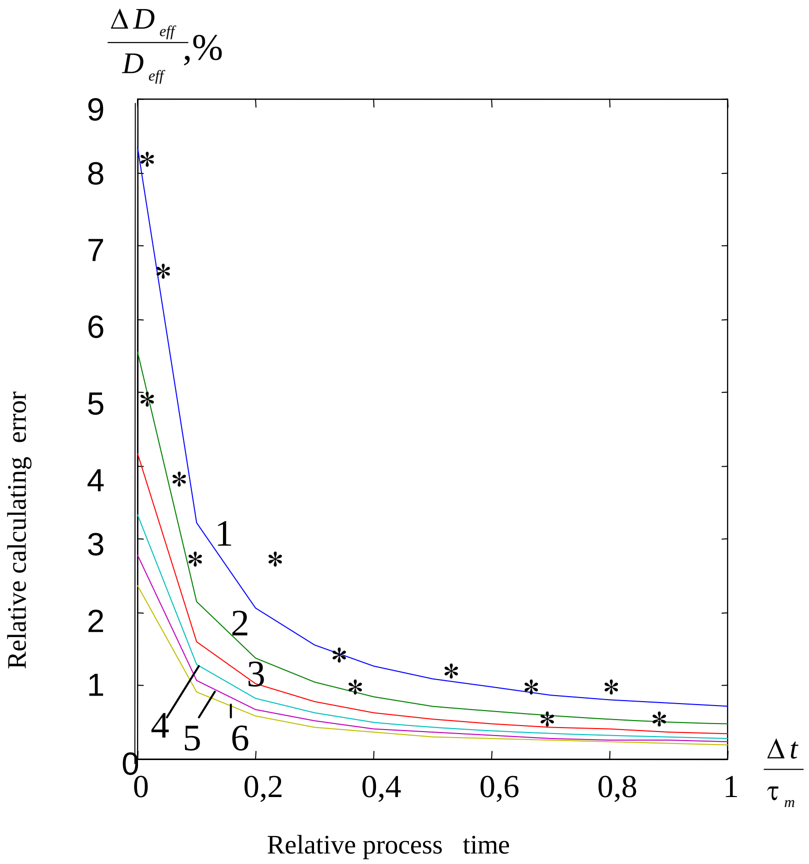
First order:

$$\nu_1 = (C_\nu + A_\nu \theta)\exp(-\theta); \ T_1 = (C_T + A_T \theta)\exp(-\theta). \tag{29}$$

The effective mass diffusivity is calculated with amendment to non-local phenomena:

$$D_{ef} = \chi D_{ef}(0). \tag{30}$$

According to this approach the engineering methodology for calculating chemical reactors with accounting of non-local phenomena and cross effects was carried out. Figures 2 and 3 depict some results of the above investigations.



$1 - \alpha_1 = 0{,}4$; $2 - \alpha_1 = 0{,}6$; $3 - \alpha_1 = 0{,}8$; $4 - \alpha_1 = 1{,}0$; $5 - \alpha_1 = 1{,}2$; $6 - \alpha_1 = 1{,}4$

Figure 2. The relative deviation of the effective mass diffusivity from the nominal under calculating with accounting to non-local phenomena

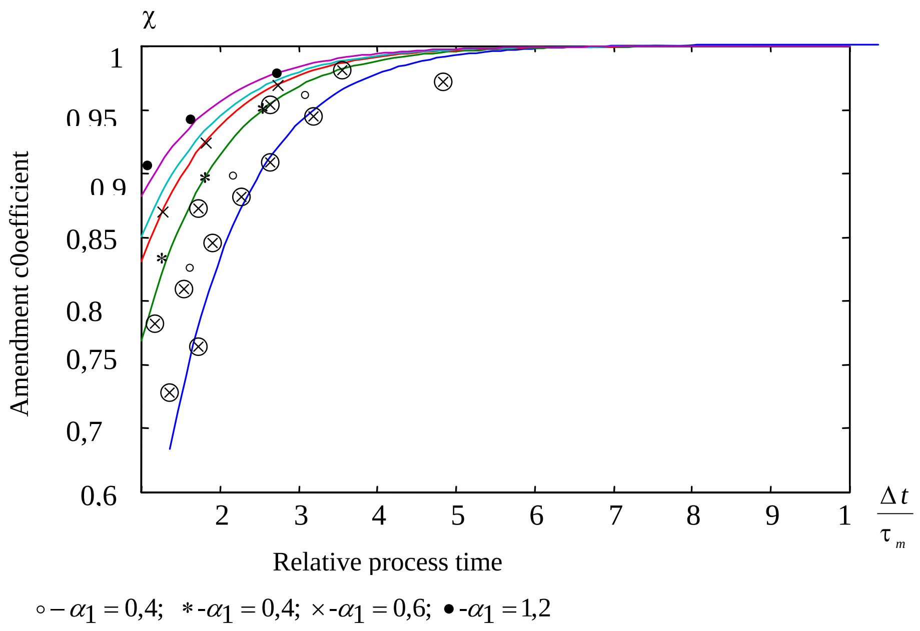


Figure 3. Amendment coefficients under calculating effective diffusivities for high rate processes.

The nonlinearity and the high order of the obtained equations are unusual and complicate their practical use. Yet their capability to describe the various effects caused by the nonlinearity of the medium and cross effects is rather wide and can justify subsequent investigations. That work is likely to be of importance to practice in process engineering including biotechnology processes. It seems that methods for describing transport phenomena in complex systems such as biological or biotechnological systems may be interesting for specialists in biotechnology.

4. References

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