On the Modelling of Particles Aggregation in Disperse Reaction-Diffusion Systems

Arnold M. Brener*[a], Ablakim S. Muratov[b], Vladimir G. Golubev[a]

[a]State University of South Kazakhstan, Tauke Khan, 5, Shymkent, 160012, Kazakhstan
[b]University "Miras", Ilyaeva str., 3, Shymkent, 160012, Kazakhstan
amb_52@mail.ru

The work deals with the theoretical foundation and development of the engineering methods for calculating the kinetics of the aggregation of insoluble products in chemical apparatus in terms of joint chemical reactions and coagulation processes in the working zone of reactors. The models of aggregation of a disperse phase in systems with chemical reactions have been developed. Regularities of aggregation process in systems with a chemical source of first and second orders of insoluble phase monomers have been studied.

1. Introduction

Currently, the use of chemical apparatuses and reactors formation, aggregation and sedimentation of insoluble phases in the working volume of the chemical apparatuses becomes more and wider, particularly in the range of modern processes (Liu, 2008). In many cases processes of chemical technologies are accompanied by formation of the new solid disperse phase. It can be phase transition, as in cases of crystallization or desublimation, or it can be formation of low soluble substances during chemical reactions (Voloschuk and Sedunov, 1975). As a whole, it is possible to allocate a lot of directions of a modern science dealing with processes and apparatuses in which the problems of the kinetics and dynamical characteristics of reactors with formation of a dispersed solid phase in a working zone are relevant (Blackman and Marshall, 1994). They are: 1) purification of gas pollution from fine particles and dust (Friedlander, 2000); 2) production of nano-dispersed powders for constructional and functional bioceramics; 3) creation of sorbents, catalysts, drugs and molecular grids with given structure (Bodmeier and Paeratakul, 1989); 4) creation of methods for optimal engineering of technological processes dealing with a method of chemical sedimentation (Logan, 2012); 5) elaboration of polymeric films for molecular covering the products of chemical industry (Menon and Pego, 2004). At the same time, the known theoretical models of aggregation of dispersed phase and sedimentation are of little use for engineering calculations, as they are too complex and involve the need to use a set of parameters some of which are difficult for finding (Spicer and Pratsinis, 1996).

In this paper, we propose a simple mathematical model, which opens, in our opinion, the prospects for creating a calculation method of aggregation of insoluble solids in systems with chemical reactions of pseudo-first and of second orders. As the result we can obtain expressions for calculating the evolution both of the total number of clusters in the system and of the average cluster order with allowance for the kinetic constants of the given chemical reaction and elements of the aggregation of the matrix.

2. First-order reaction

Let us consider the first-order reaction occurring in solution according to a conventional scheme

$$A \rightarrow B \tag{1}$$

In accordance with a relaxation approach (Brener, 2006), the kinetic equation for the reaction (1) can be written as (Brener et al., 2009)

$$\frac{dA}{dt} = -\int_0^t \eta_c \exp(-\frac{t-t_1}{\tau_c})A(t_1)dt_1 \tag{2}$$

For sufficiently small chemical relaxation time, we get the following expression for the concentration of the reaction product (Boehm et al., 1998)

$$B = A_0\left(1 - \exp\left(-t/\tau_c\right)\right) \tag{3}$$

Further, let us there exists a process of the nucleation of an insoluble dispersed phase of the reaction product in the system

$$B \to C \tag{4}$$

Primary nucleation process is quite complex and theoretically poorly described, although his analysis is involved by many researchers (Ernst, 1986). However, here we will describe the kinetics of this process, approximately, namely, using the delay time of formation of the insoluble phase with respect to the time of formation of the reactants for a certain period of nucleation. The time of formation of the equilibrium concentration of the reaction product in the solution is not accounted. It seems acceptable for poorly soluble substances (Slemrod, 1990).

Thus, the following kinetic equation can be written

$$\left.\frac{dC}{dt}\right|_n = \frac{d(\Delta B)}{dt} = \frac{dB}{dt} = \frac{A_0}{\tau_c}\exp\left(-\frac{t-\tau_n}{\tau_c}\right) \tag{5}$$

Here τ_c is the typical relaxation time of chemical reaction, and τ_n is the typical time of primary nucleation.

Smoluchowski equation for coagulation of the insoluble phase with account of the chemical source reads as follows (Brener, 2011)

$$\frac{dC_i}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} N_{j,i-j}C_j(t)C_{i-j}(t) - \sum_{j=1}^{\infty} N_{i,j}C_i(t)C_j(t) + \Phi_i(t) \tag{6}$$

$$\frac{dC_1}{dt} = -\sum_{j=1}^{\infty} N_{1,j}C_1(t)C_j(t) + \Phi_1(t) \tag{7}$$

Assume for simplicity, that during the primary nucleation only monomers of the insoluble phase can arise (Wong et al., 2009), i.e.

$$\Phi_i(t) = 0 \atop i\neq 1 \tag{8}$$

From this assumption it follows (Davies et al., 1999)

$$\frac{dC_1}{dt} = -\sum_{j=1}^{\infty} N_{1,j}C_1(t)C_j(t) + \chi\frac{A_0}{\tau_c}\exp\left(-\frac{t-\tau_n}{\tau_c}\right) \tag{9}$$

Let us introduce the generating function of the form (Wattis, 2006)

$$\tilde{C}(t,z) = \sum_{i=1}^{\infty} C_i(t)\exp(-iz) \tag{10}$$

In the case of constant coagulation kernels, the kinetic equation in terms of the generating function takes the form

$$\frac{\partial\tilde{C}}{\partial t} = \frac{1}{2}\tilde{C}(t,z) - \tilde{C}(t,0)\tilde{C}(t,z) + \sum_{i=1}^{\infty}\Phi_i(t)\exp(-iz) \tag{11}$$

$$\frac{\partial \tilde{C}}{\partial t} = \frac{1}{2}\tilde{C}(t,z) - \tilde{C}(t,0)\tilde{C}(t,z) + \chi \frac{A_0}{\tau_c}\exp\left(-\frac{t-\tau_n}{\tau_c} - z\right) \tag{12}$$

Let us introduce now the designations (Yu Jiang and Hu Gang, 1989a)

$$M_0 = \sum C_i = \tilde{C}\Big|_{z=0} \quad ; \qquad M_1 = \sum iC_i = \frac{\partial \tilde{C}}{\partial z}\Big|_{z=0} \tag{13}$$

Thus, the kinetic equation for a total concentration of clusters of different orders takes the form of (Yu Jiang and Hu Gang, 1989b)

$$\frac{dM_0}{dt} = -\frac{1}{2}M_0^2 + \frac{A_0\exp(\tau_n/\tau_c)}{\tau_c}\exp\left(-\frac{t}{\tau_c}\right) \tag{14}$$

For obtaining the analytical solution of Eq. (14) it is convenient to introduce transformed variable s and the special control parameter E_0

$$s = \exp(-t/\tau_c); \quad E_0 = \frac{A_0\exp(\tau_n/\tau_c)}{\tau_c} \tag{15}$$

Thus Eq. (14) can be rearranged to the form of Riccati equation (Bittanti et al., 1991)

$$\frac{dM_0}{ds} = \frac{\tau_c}{2s}M_0^2 - E_0 \tag{16}$$

The solution of Eq. 16 can be expressed through Bessel functions I_0 and K_0 (Jin and Jjie, 1996)

$$M_0 = -\frac{2s}{\tau_c}\frac{dU/ds}{U}; \quad U = U_1 I_0\left(\sqrt{2E_0\tau_c s}\right) + U_2 K_0\left(\sqrt{2E_0\tau_c s}\right) \tag{17}$$

The found solution has theoretical interest but it is unlikely useful for practical calculations (Leyvraz, 2003). Figures 1, 2 depict some results of numerical experiments for calculating the evolution of the total clusters concentration of various orders in the system during the aggregation in the system with monomers forming by the first order reaction scheme.
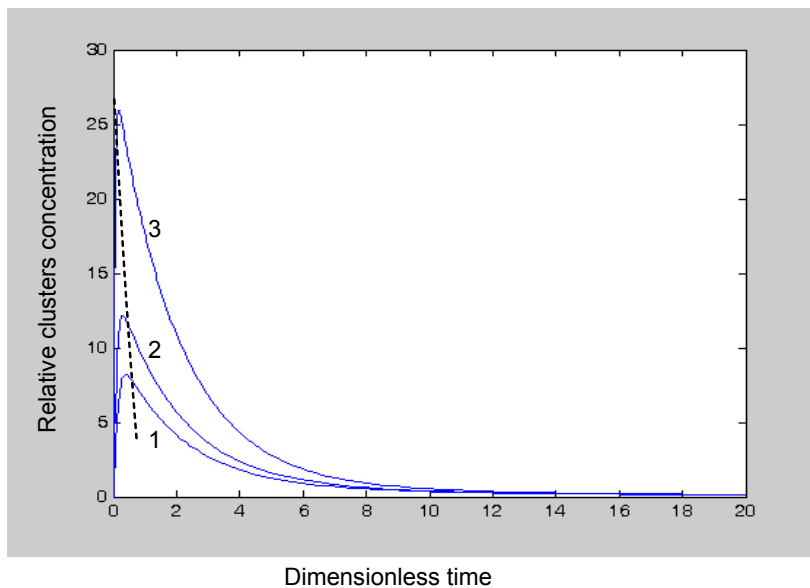

Figure 1: Evolution of the total clusters concentration of insoluble phase in the first order system for a long time (E_0=1- 80; 2- 200; 3-800)
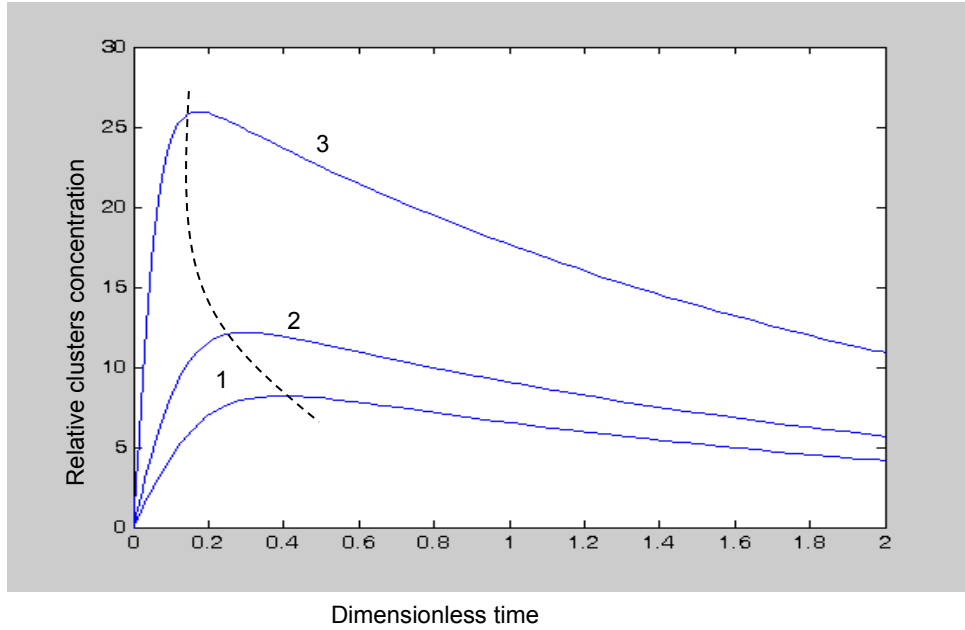
Dimensionless time

Figure 2: Evolution of the total clusters concentration of insoluble phase in the first order system for small time (E_0=1- 80; 2- 200; 3-800)

While processing the results of numerical experiments, it was found that the time moments, at which extrema of the total number of clusters in the system of first-order reaction can be observed, are determined on the parameter E_0 :

$$(t/\tau)_{\max} = 0,437 E_0^{-0,286}$$ (18)

3. Second-order reaction

Let us consider the scheme of second-order reaction as follows

$$A + B \rightarrow C$$ (19)

The total concentration of reactants reads

$$\rho_0 = A_0 + B_0$$ (20)

After obvious rearrangements the kinetic equation takes the following form

$$\frac{d^2C}{dt^2} = -k_2 \frac{dC}{dt}(\rho_0 - 2C)$$ (21)

Thus, we obtain the expression for the evolution of the product concentration

$$C = \frac{A_0 B_0 (1 - \exp(k_2(A_0 - B_0)t))}{B_0 - A_0 \exp(k_2(A_0 - B_0)t)}$$ (22)

If $A_0 = B_0$ then

$$C = \frac{\rho_0^2 k_2 t}{2(2 + \rho_0 k_2 t)}$$ (23)

If the reaction product is insoluble, it begins again the aggregation of primary monomers according to the mechanism described above, but it occurs with the other type of chemical source of monomers:

$$\frac{dC_1}{dt} = -\sum_{j=1}^{\infty} N_{1,j} C_1(t) C_j(t) + \frac{k_2 A_0 B_0 (A_0 - B_0)^2 \exp(k_2(A_0 - B_0)(t - \tau_n)/\tau_c)}{(B_0 - A_0 \exp(k_2(A_0 - B_0)(t - \tau_n)/\tau_c))^2} \tag{23}$$

In order to analyze of this problem it can be used the same method as before. The kinetic equation for a total concentration of clusters of different orders takes now the form

$$\frac{dM_0}{dt} = -\frac{1}{2} M_0^2 + \frac{A_0 B_0 (1 - E_0 \exp((A_0 - B_0)t/\tau_c))}{B_0 - A_0 E_0 \exp((A_0 - B_0)t/\tau_c)} \tag{24}$$

Eq. (24) can be also resolved with the help of Bessel functions. This method however leads to the very bulk relations. So, it is more expedient apparently to use numerical experiments as before. The more so, that in this case we succeeded to distinguish also the convenient control parameter.

$$E_0 = \exp\left(-(A_0 - B_0)\frac{\tau_n}{\tau_c}\right) \tag{25}$$

Figure 3 depicts some results of numerical experiments for calculating the evolution of the total clusters concentration of various orders in the system with the second-order chemical source of monomers.
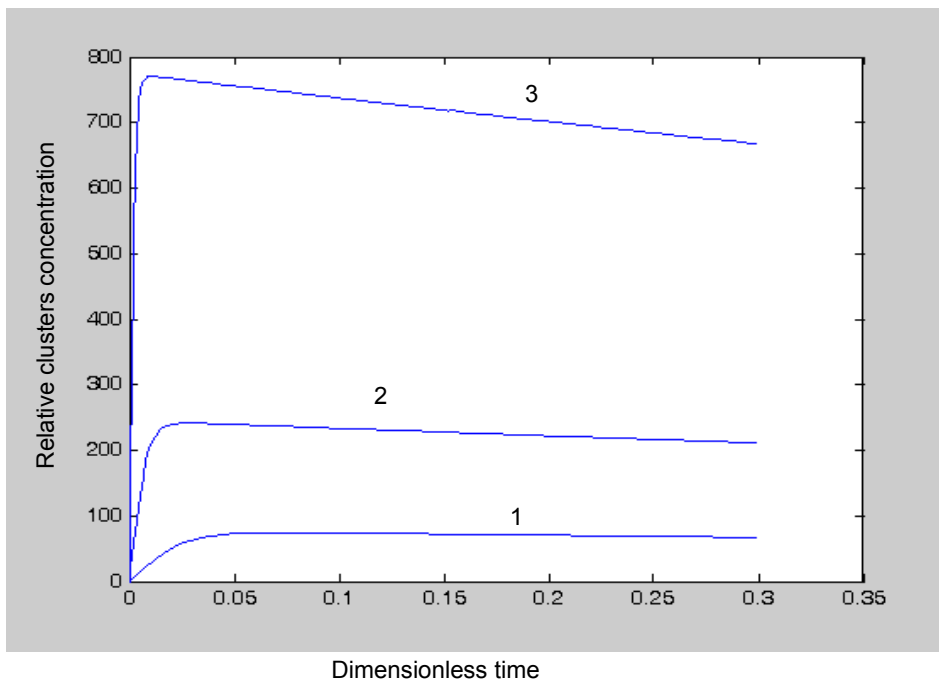

Figure 3: Evolution of the total clusters concentration of insoluble phase in the second- order system for a small time (E_0=1- 800; 2- 1000; 3-4000)

The graphs show that the order of the reaction does not affect essentially the qualitative character of the evolution of the total number of clusters. It may be noted only a slower decline in the total number of clusters after the peak of coagulation.

4. Conclusions

The paper discusses the modified equations for calculating the kinetics of aggregation of the dispersed phase in the chemical reaction system based on the Smoluchowski equation for the binary coagulation. The basic process control parameters of the aggregation process in the systems with a chemical source of insoluble monomer phase of first and second-orders have been determined, and their validity has been confirmed with the help of numerical experiment. It was shown that order of chemical reaction did not change the character of aggregation process of insoluble product of the reaction. Particularly, in both cases the time moment, which is corresponded to the peak of the total number clusters of insoluble phase in the system, is determined by the

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one control parameter. Relations for calculating this parameter however are different depending on the order of chemical reaction.

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