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## FAST HETEROGENEOUS CATALYTIC REACTIONS IN A BATCH REACTOR: PERTURBATIVE APPROACH

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The novel theoretical technique to study heterogeneous catalytic reactions in a batch reactor is presented. The analytical solution for the corresponding mathematical problem is obtained using the method of singular asymptotic expansion.

### 1. Introduction

A batch reactor, that is a closed vessel where the reactants are mixed, is constructively the simplest type of reactor and in its “mini”-form is a part of equipment of every chemical laboratory. The industrial use of batch reactors is commonly limited to producing small quantities of material or producing several different products from one piece of equipment. Therefore, they are often used in the pharmaceutical and dyestuff industries and in the production of certain specialty chemicals, with desired flexibility [1]. In planning the production capacities the estimation of the time necessary to carry out the reaction (as well as the length of “non-productive” period – filling, emptying, and cleaning of reactor) is of special importance. The modeling of the time evolution of the reaction systems involved is, therefore, desirable.

However, opposite to homogeneous reactions the heterogeneous catalytic reactions under batch conditions are studied insufficiently. Indeed, for heterogeneous reactions, mass transfer to the surface of the porous catalyst particles, freely moving or packed in a bed, generates greater complications [1, 2]. Even for perfect mixing, the heterogeneous character of the reaction implies three-dimensional mesoscopic transport in a vicinity of a single catalyst particle. Although sophisticated simulations are possible of particular reactor systems, exploration of the parameter space to find optimal conditions or those with desirable features, is problematic. Exploration can be improved by approximate models, especially with analytic forms for parametric dependencies, that can serve as guides to the parameter space.

Our point is that for the fast heterogeneous reaction, when the mesoscopic mass transfer becomes rate determining, the reaction of arbitrary order manifests itself as “quasi-first-order” [2], thereby introducing an effective simplification. The crucial feature of our model is the distinction between the bulk and “local” concentrations of reactants. The local concentration of reactant is a result of averaging of concentrations of this reactant at the surfaces of catalytic particles over “physically infinite small volume”. For the perfect mixing this concentration has the same value for all points inside the tank. It rapidly reaches its equilibrium value due to fast exchange with the catalytic surface and fast chemical reaction on the surface. That is, the local concentration is a macroscopic time-dependent variable. If the catalyst particles are identical, the local concentration coincides with the concentration at the surface of each particle, the latter having the same value for all particles. From the formal point of view the local concentration represents the “reverse reaction term” in the “quasi-first-order” [1] reaction rate (see above). It’s worth mentioning that the value of this local concentration is determined self-consistently in the course of solution.

It is useful to have a pseudo zero-dimensional time-dependent model for the evolution of composition, treating the mesoscopic transport phenomenologically, that is, in terms of mass transfer coefficients [3, 4]. Such a model permits simulation and optimization of the design of a batch reactor, especially, when the selectivity considerations are of importance. The contacting patterns (see, e.g. [1], p.319–320) are conveniently described in terms of local

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concentrations of the reactants. To achieve the most desirable contacting pattern for a multiple reaction in a batch reactor, a very precise planing of the regimes of feeding and/ or removal of the product (products) is needed. This, in turn, demands a clear understanding of the time behavior of the reactant's concentrations as well as of dependence on external parameters. Recently [5], to study the dispersion effects in continuous flow tubular reactors for heterogeneous catalytic reactions, the authors adapted the concept of auxiliary dependent variable(s) called F-functions or modified Thiele moduli (mTm). These mTm(s) are found from the transformation from bulk and surface concentrations, to differences representing the driving forces for physical processes. This novel theoretical technique was first applied by [6] in solid state mixtures for precipitation reactions. In the case of initially segregated reactants, a simplification was possible leading to a single modified Thiele modulus describing the nonlinear dynamics of each binary reaction in a multicomponent, multiple reaction system. Furthermore, when there is a kinetic difference or an asymmetry in the transport coefficients, one of the modified Thiele moduli is controlling, and asymptotically all the others are slaved to it. Thus, it is sufficient to optimize the dynamics of the controlling modified Thiele modulus alone.

The purpose of this paper is to explore the possibility that such a technique may be applicable to the batch reactor as well. As it is our objective to develop an approximate ordinary differential equations (ODE) model for which successively improved approximations are possible, we start from extreme parametric conditions, some of which are accurate to a great extent and permit the simplification of the physical description. In particular, we are looking for parametric regimes in which the modified Thiele modulus formulation simplifies. A prerequisite for this is the depletion of the surface concentration of one or the other of the reactants. If this occurs, then reaction is intensified if there is a time period, when surface concentration switches from depletion of one reactant to the other. In the present communication a single binary reaction is considered. However, for system of several reactions, if such a time exists for one of them, then the modified Thiele modulus for that reaction will be controlling, and yields and selectivities, will, conceivably, be slaved to its dynamics. If the reactions are fast and nearly irreversible, always one of the reagents will effectively be depleted. In this case, depending on the initial conditions, it may be possible a crossover for local concentrations of the reagents.

## 2. Basic system of equations for a binary reaction in a batch reactor

For a single binary heterogeneous catalytic reaction in a batch reactor the mass balance equations are

$$\frac{\partial u}{\partial t} = -Sj_u(u, \tilde{u}), \quad (1)$$

$$\frac{\partial v}{\partial t} = -Sj_v(v, \tilde{v}), \quad (2)$$

$$\frac{\partial w}{\partial t} = -Sj_w(w, \tilde{w}), \quad (3)$$

where  $u, v, w$  and  $\tilde{u}, \tilde{v}, \tilde{w}$  are the bulk and surface concentrations, respectively,  $S$  is the active catalyst surface per unit volume. The terms proportional to fluxes  $j_u, j_v, j_w$  refer to the disappearance (appearance) from the bulk of all species by the mass transfer to (from) the surface of the randomly distributed catalyst particles. These fluxes are driven by the difference between bulk and surface concentration, due to the occurrence of surface reaction. If the catalyst particles are identical, we may identify the surface concentrations with the "local concentrations", defined above. It is typical chemical engineering practice to write these fluxes in terms of mass transfer coefficients  $k_u, k_v, k_w$ , which are either empirically determined or estimated by correlations [3,4]:

$$j_u = k_u(u - \tilde{u}), \quad (4)$$

$$j_v = k_v(v - \tilde{v}), \quad (5)$$

$$j_w = k_w(w - \tilde{w}). \quad (6)$$

Since the mass transfer transients are short, it is typical presume that mass transfer and surface reaction are always in a pseudo-steady state, represented by

$$\frac{j_u}{m} = \frac{j_v}{n} = j_w = g' \left[ \frac{\left(\frac{u}{a_1}\right)^m \left(\frac{v}{a_2}\right)^n}{\left(1 + \frac{\tilde{u}}{a_1} + \frac{\tilde{v}}{a_2} + \frac{\tilde{w}}{a_3}\right)^{m+n}} - K' \frac{\frac{w}{a_3}}{1 + \frac{\tilde{u}}{a_1} + \frac{\tilde{v}}{a_2} + \frac{\tilde{w}}{a_3}} \right], \quad (7)$$

where  $m, n$  are stoichiometric coefficients,  $g'$  is the reaction rate constant, and  $K'$  is the equilibrium constant in the mass action law. The parameters  $a_1, a_2, a_3$  are surface concentrations reflecting saturation of the species. Eq. (7) is the kinetic mass-action law for surface reaction, with the assumption of Langmuire-type kinetics [7, 8]: the right-hand side represents the combined effect both of the catalytic reaction on the surface and the adsorption-desorption process.

For convenience, we take all surface coverages to be small relative to the number of active sites, i.e.  $\frac{\tilde{u}}{a_1} + \frac{\tilde{v}}{a_2} + \frac{\tilde{w}}{a_3} \ll 1$ . Rescaling the reaction parameters, we take  $g = \frac{g'}{a_1 a_2}$  and

$K = \frac{K' a_1 a_2}{a_3}$ . Presuming the reaction rate  $g$  to be fast leads to the surface quasi-equilibrium:

$$\tilde{u}^m \tilde{v}^n - K \tilde{w} = 0. \quad (8)$$

For further analysis it is convenient to rewrite the equations in non-dimensional form. All concentrations are measured in atomic or molecular fractions and are already non-dimensional.

The natural time scale for mesoscopic mass transfer is  $\tau = \frac{1}{S k_v}$ . We denote also

$$t' = \frac{t}{\tau}; \nu_0 = \frac{k_u}{k_v}; \nu_1 = \frac{k_w}{k_v}.$$

To simplify the formulae, we consider here the simplest possible stoichiometry,  $m = n = 1$ . This limitation is not necessary and will be dropped in the next subsections. The system of equations is

$$\frac{\partial u}{\partial t} = -\nu_0 (u - \tilde{u}), \quad (9)$$

$$\frac{\partial v}{\partial t} = -(v - \tilde{v}), \quad (10)$$

$$\frac{\partial w}{\partial t} = \nu_1 (\tilde{w} - w), \quad (11)$$

$$\nu_0 (u - \tilde{u}) = \nu_1 (\tilde{w} - w) = (v - \tilde{v}) = \varphi, \quad (12)$$

$$\tilde{u} \tilde{v} = K \tilde{w} \quad (13)$$

and the initial conditions

$$u|_{t=0} = u_0; v|_{t=0} = v_0; w|_{t=0} = 0. \quad (14)$$

It is instructive to start with considering the strictly irreversible reaction,  $K = 0$ .

Let us first suppose  $\tilde{u} = 0, \tilde{v} \neq 0$  for  $t = 0$ . Then it follows from eq. (13) and initial conditions eq. (14)

$$\tilde{v}|_{t=0} = v_0 - \nu_0 u_0 \quad (15)$$

and for  $\tilde{v}|_{t=0}$  to be positive it should be

$$v_0 - \nu_0 u_0 > 0. \quad (16)$$

For the present case it is natural to assume that  $\tilde{u} = 0$  at least for some  $t > 0$  as well; then the solutions for  $u, v$  and  $\tilde{v}$  are easily obtained

$$u = u_0 \exp\{-\nu_0 t\}, \quad (17)$$

$$v = v_0 + u_0 [\exp\{-v_0 t\} - 1], \quad (18)$$

$$\tilde{v} = v_0 - u_0 + u_0(1 - v_0) \exp\{-v_0 t\}. \quad (19)$$

Note, that the solution for  $\tilde{v}$  is a monotonic function of the time. Let us take its limit for  $t \rightarrow \infty$ :

$$\tilde{v}|_{t \rightarrow \infty} = v_0 - u_0. \quad (20)$$

If  $v_0 - u_0 > 0$ ,  $\tilde{v}$  remains positive, and the present case persists for all times. However, if  $v_0 - u_0 < 0$ , there is some time  $t = T$ , when there is a "switch" to the case  $\tilde{v} = 0$ :

$$T = \frac{1}{v_0} \ln \frac{(1 - v_0)u_0}{u_0 - v_0}. \quad (21)$$

For inequality eq. (16) to be compatible with  $v_0 < u_0$ , it should be  $v_0 < 1$ ; the later inequality is therefore the necessary condition for the "switch" to exist (the "kinetic asymmetry" mentioned in Introduction). At the moment  $t = T$  the concentrations  $u$  and  $v$  take the values

$$u|_{t=T} = \frac{u_0 - v_0}{1 - v_0}, \quad (22)$$

$$v|_{t=T} = \frac{u_0 - v_0}{1 - v_0} v_0 \quad (23)$$

which may be considered as initial conditions for  $t > T$ . Now, for  $t > T$   $\tilde{v} = 0$ , and solutions for  $u, v$  and  $\tilde{u}$  take the form

$$v = (u_0 - v_0) \frac{v_0}{1 - v_0} \exp\{-(t - T)\}, \quad (24)$$

$$u = (u_0 - v_0) \left[ 1 + \frac{v_0}{1 - v_0} \exp\{-(t - T)\} \right], \quad (25)$$

$$\tilde{u} = (u_0 - v_0) [1 - \exp\{-(t - T)\}]. \quad (26)$$

If we denote  $w_T$  the product yield before the "switch"

$$w_T = \int_0^T \phi dt \quad (27)$$

then the partitioning ratio  $w_T/w_\infty$  appears to be a linear function of  $u_0/v_0$

$$\frac{w_T}{w_\infty} = \frac{1 - v_0 \frac{u_0}{v_0}}{1 - v_0} \quad (28)$$

It is interesting to note that an analogous dependence was found numerically for the "fractional conversion" (the fraction of product produced between the inlet and crossover point  $x$ ) for the tubular reactor model [9] in the limit of irreversible reaction.

It is easy to check, that while  $\frac{\partial \tilde{u}}{\partial t}, \frac{\partial \tilde{v}}{\partial t}$  are discontinuous,  $\frac{\partial u}{\partial t}, \frac{\partial v}{\partial t}$  are continuous at the "switch point". For  $t \rightarrow \infty$ ,  $u = \tilde{u} = u_0 - v_0$ . Comparing this with eq. (20) one easily notes, that the asymptotic state is always a complete depletion of the reactor on the reactant, which is in deficit initially (with respect to stoichiometric ratio). On the other hand, whether there is a "switch point", or not, depends not only on concentrations and stoichiometry, but on the ratio of mass-transfer coefficients as well. For  $K = 0$  the reaction is effectively first-order for all times. But contrary to the common practice, the selection of the excess reactant is self-consistent (and even may change at the "switch point").

However, such a simple picture does not stand any generalization (several reactions, etc.). Even more, the  $K$ , being small indeed for practically important reactions, is still finite. Therefore, the extension of the F-formalism [5, 6] (see above) on the processes in a batch reactor may be desirable.

The basic system eqs. (9)–(13) is reformulated in terms of functions  $\psi_1, \psi_2$  and supersaturation  $\varphi$ . The auxiliary functions  $\psi_1, \psi_2$  are

$$\psi_1 = \nu_0 \tilde{u} - \tilde{v} = \nu_0 u - v, \quad (29)$$

$$\psi_2 = \nu_1 \tilde{w} + \tilde{v} = \nu_1 w + v \quad (30)$$

and we obtain from (9)–(12)

$$\frac{\partial \psi_1}{\partial t} = -(\nu_0 - 1)\varphi, \quad (31)$$

$$\frac{\partial \psi_2}{\partial t} = (\nu_1 - 1)\varphi, \quad (32)$$

$$\frac{\partial \varphi}{\partial t} = -\varphi - \frac{\partial \tilde{v}}{\partial t}. \quad (33)$$

From eqs. (31), (32) immediately follows

$$\frac{\partial}{\partial t} [(\nu_1 - 1)\psi_1 + (\nu_0 - 1)\psi_2] = 0, \quad (34)$$

that is, a conservation law

$$(\nu_1 - 1)\psi_1 + (\nu_0 - 1)\psi_2 = \nu_0(\nu_1 - 1)u + (\nu_0 - \nu_1)v + \nu_1(\nu_0 - 1)w = \nu_0(\nu_1 - 1)u_0 + (\nu_0 - \nu_1)v_0 \quad (35)$$

which is an evident consequence of the closeness of the batch reactor.

Eliminating  $\varphi$  from eqs. (31) and (33) yields

$$-\frac{\partial^2 \psi_1}{\partial t^2} = \frac{\partial \psi_1}{\partial t} - (\nu_0 - 1) \frac{\partial \tilde{v}}{\partial t}. \quad (36)$$

Introducing, as in [5,6] the mTm's

$$F_1 = \frac{\frac{1}{\nu_0 \tilde{u}}}{\frac{1}{\tilde{v}} + \frac{1}{\nu_0 \tilde{u}} + \frac{1}{\nu_1 \tilde{w}}}; F_2 = \frac{\frac{1}{\nu_1 \tilde{w}}}{\frac{1}{\tilde{v}} + \frac{1}{\nu_0 \tilde{u}} + \frac{1}{\nu_1 \tilde{w}}}. \quad (37)$$

we may express  $\frac{\partial \tilde{v}}{\partial t}$  as a linear combination of  $\frac{\partial \psi_1}{\partial t}, \frac{\partial \psi_2}{\partial t}$ , or, using eq. (34), through  $\frac{\partial \psi_1}{\partial t}$  only:

$$(\nu_0 - 1) \frac{\partial \tilde{v}}{\partial t} = -[F_1(\nu_0 - 1) + F_2(\nu_1 - 1)] \frac{\partial \psi_1}{\partial t}. \quad (38)$$

Substituting (38) into the right-hand side of eq. (36) for  $\frac{\partial \tilde{v}}{\partial t}$ , we obtain

$$\frac{\partial^2 \psi_1}{\partial t^2} + [1 + (\nu_0 - 1)F_1 + (\nu_1 - 1)F_2] \frac{\partial \psi_1}{\partial t} = 0. \quad (39)$$

On the other hand, using the definition of  $F_1, F_2$ , eq. (37), and the MAL eq. (13), the local concentrations  $\tilde{u}, \tilde{v}$  and  $\tilde{w}$  are readily expressed as functions of  $F_1$  and  $F_2$ :

$$\tilde{u} = \frac{1}{\nu_1} K \frac{1 - F_1 - F_2}{F_2}, \quad (40)$$

$$\tilde{v} = \frac{\nu_0}{\nu_1} K \frac{F_1}{F_2}, \quad (41)$$

$$\tilde{w} = \frac{\nu_0}{\nu_1^2} K \frac{F_1}{F_2} \frac{1 - F_1 - F_2}{F_2}. \quad (42)$$

From eqs. (40), (41) and the definition of  $\psi_1$ , eq. (29), it also follows

$$\psi_1 = \frac{\nu_0}{\nu_1} K \frac{1 - 2F_1 - F_2}{F_2}. \quad (43)$$

Substituting eq. (43) into eq. (39) for  $\psi_1$ , we rewrite the latter equation in terms of  $F_1, F_2$  only:

$$\frac{\partial^2}{\partial t^2} \left( \frac{1-2F_1}{F_2} \right) + [1 + (\nu_0 - 1)F_1 + (\nu_1 - 1)F_2] \frac{\partial}{\partial t} \left( \frac{1-2F_1}{F_2} \right) = 0, \quad (44)$$

The additional link between  $F_1, F_2$  is obtained by substituting eqs. (40)–(42) into the conservation law eq. (35) for  $\tilde{u}, \tilde{v}$  and  $\tilde{w}$ :

$$\frac{\nu_0}{\nu_1} \frac{K}{F_2^2} [(\nu_1 - 1)(1 - F_1 - F_2)F_2 + (\nu_0 - \nu_1)F_1F_2 + (\nu_0 - 1)F_1(1 - F_1 - F_2)] = \nu_0(\nu_1 - 1)u_0 + (\nu_0 - \nu_1)v_0. \quad (45)$$

It is worth mentioning that the closed system eqs. (44), (45) for  $F_1, F_2$  is an exact consequence of the basic nonlinear system of three first order ordinary differential equations eqs. (9)–(11) and three (nonlinear) algebraic equations eqs. (12), (13). An analogous, though more cumbersome reduction is possible for arbitrary stoichiometry,  $m \neq n \neq 1$ .

It follows from the above consideration for  $K \rightarrow 0$  that  $F_1$  is very close to unity before “switch point”, very close to zero after this moment and varies very fast in the immediate vicinity of the “switch point”. In this limit the function  $F_2$  is very close to zero for all times.

Now, let us consider the initial conditions. Substituting initial values  $u, v$  and  $w$  in eqs. (12), (13) we obtain a (nonlinear) system of equations for the initial values of local concentrations  $\tilde{u}, \tilde{v}$  and  $\tilde{w}$ , which we denote as  $\tilde{u}_0, \tilde{v}_0$  and  $\tilde{w}_0$ , respectively:

$$\nu_0(u_0 - \tilde{u}_0) = \nu_0 - \tilde{v}, \quad (46)$$

$$\nu_1 \tilde{w}_0 = \nu_0 - \tilde{v}, \quad (47)$$

$$\tilde{u}_0 \tilde{v}_0 = K \tilde{w}_0. \quad (48)$$

We are interested in the approximate solutions for small  $K$ .

In accord with the above consideration for  $K = 0$ , there are two possibilities for the initial state: if

$$u_0 \nu_0 - \nu_0 + \frac{\nu_0}{\nu_1} K < 0, \quad (49)$$

then in the local equilibrium the reactant U is nearly depleted at the surface of the particle, and the local concentrations are

$$\tilde{v}_0 = (\nu_0 - u_0 \nu_0) + \frac{\nu_0}{\nu_1} K \frac{u_0 \nu_0}{\nu_0 - u_0 \nu_0}, \quad (50)$$

$$\tilde{u}_0 = \frac{\nu_0}{\nu_1} K \frac{u_0}{\nu_0 - u_0 \nu_0}, \quad (51)$$

$$\tilde{w}_0 = \frac{\nu_0}{\nu_1} u_0 - \frac{\nu_0^2}{\nu_1^2} K \frac{u_0}{\nu_0 - u_0 \nu_0}. \quad (52)$$

If, on the other hand,

$$u_0 \nu_0 - \nu_0 + \frac{\nu_0}{\nu_1} K > 0 \quad (53)$$

the initial values of the local concentrations are

$$\tilde{v}_0 = \frac{\nu_0}{\nu_1} K \frac{\nu_0}{u_0 \nu_0 - \nu_0}, \quad (54)$$

$$\tilde{u}_0 = u_0 - \frac{1}{\nu_0} \nu_0 + \frac{1}{\nu_1} K \frac{\nu_0}{u_0 \nu_0 - \nu_0}, \quad (55)$$

$$\tilde{w}_0 = \frac{1}{\nu_1} \nu_0 - \frac{\nu_0}{\nu_1^2} K \frac{u_0}{u_0 \nu_0 - \nu_0}. \quad (56)$$

To match with the above  $K = 0$  consideration we will start from the “local deficit” of U, that is with the initial conditions eqs. (50)–(52). On the other hand, we assume  $u_0 > \nu_0$ , that

is the asymptotic ( $t \rightarrow \infty$ ) state corresponds to the deficit of V. Let us denote the asymptotic values of the U, V and W concentrations as  $u_\infty, v_\infty$  and  $w_\infty$  respectively. Then, as a consequence of stoichiometry, we have

$$w_\infty = v_0 - v_\infty = u_0 - u_\infty \quad (57)$$

Because the supersaturation  $\varphi$  asymptotically vanishes, we have

$$\tilde{u}|_{t \rightarrow \infty} = u_\infty; \tilde{v}|_{t \rightarrow \infty} = v_\infty; \tilde{w}|_{t \rightarrow \infty} = w_\infty; \quad (58)$$

therefore the asymptotic values of concentrations also satisfy the MAL, eq. (13):

$$u_\infty v_\infty = K w_\infty. \quad (59)$$

Solving the system eqs. (57), (59) and assuming, in accord with the above  $K=0$ -consideration,

$$u_0 - v_0 + K > 0, \quad (60)$$

the approximate (for small  $K$ ) expressions for asymptotic concentrations are readily obtained

$$\tilde{v}_\infty = \frac{K v_0}{u_0 - v_0}, \quad (61)$$

$$\tilde{u}_\infty = u_0 - v_0 + \frac{K v_0}{u_0 - v_0}, \quad (62)$$

$$\tilde{w}_\infty = v_0 - \frac{K v_0}{u_0 - v_0}. \quad (63)$$

Now we are able to write down the boundary conditions for  $F_1, F_2$  (see eq. (44); of course, they are not independent because of eq. (45)). First we consider  $t=0$ . Introducing a small parameter  $\varepsilon_1$

$$\varepsilon_1 = \frac{v_0 \tilde{u}}{v_1 \tilde{w}} = \frac{v_0}{v_1} \cdot \frac{K}{v_0 - u_0 v_0} \ll 1 \quad (64)$$

and denoting

$$a = \frac{v_1 \tilde{u}}{\tilde{v}} = \frac{v_0 u_0}{v_0 - u_0 v_0}, \quad (65)$$

using eqs. (50)–(52) the initial conditions for  $F_1, F_2$  at  $t \rightarrow \infty$  may be written as

$$F_1|_{t=0} = \frac{1}{1 + \varepsilon_1(1+a)}; F_2|_{t=0} = \frac{\varepsilon_1}{1 + \varepsilon_1(1+a)}. \quad (66)$$

Quite analogously for  $t \rightarrow \infty$ , introducing the small parameter  $\varepsilon_2$

$$\varepsilon_2 = \frac{\tilde{v}_\infty}{v_1 \tilde{w}_\infty} = \frac{K}{v_1(u_0 - v_0)} \ll 1 \quad (67)$$

and denoting

$$b = \frac{v_1 \tilde{w}_\infty}{v_0 \tilde{u}_\infty} = \frac{v_1 v_0}{v_0(u_0 - v_0)} \quad (68)$$

using eqs. (61)–(63) the boundary conditions for  $F_1, F_2$  may be written as

$$F_1|_{t \rightarrow \infty} = \frac{\varepsilon_2 b}{1 + \varepsilon_2(1+b)}; F_2|_{t \rightarrow \infty} = \frac{\varepsilon_2}{1 + \varepsilon_2(b+1)}. \quad (69)$$

To solve the system of equations (44), (45) with the boundary conditions (66), (69) the method of singular asymptotic expansions [10, 11] is used. Finally the following matched asymptotic expansions for  $F_1, F_2$  in three adjacent domains are obtained.

For  $t < t_0 - \varepsilon$

$$F_1 = 1 - \varepsilon_1 \left[ \frac{v_1 - 1}{v_0 - 1} p_{21} + \frac{v_0(v_1 - 1)u_0 + (v_0 - v_1)v_0}{(v_0 - 1)(v_0 - u_0 v_0)} p_{21}^2 \right], \quad (70)$$

$$F_2 = \varepsilon_1 p_{21}, \quad (71)$$

where

$$p_{21} = \frac{v_0 - v_0 u_0}{v_0 - u_0 + u_0 (1 - v_0) \exp\{-v_0 t\}}. \quad (72)$$

For  $t_0 - \varepsilon < t < t_0 + \varepsilon$

$$F_1 = \frac{1}{2} - \frac{1}{2\varepsilon} \frac{t - t_0}{\left[4Q + \left(\frac{t - t_0}{\varepsilon}\right)^2\right]^{1/2}}, \quad (73)$$

$$F_2 = \frac{\varepsilon}{\left[4Q + \left(\frac{t - t_0}{\varepsilon}\right)^2\right]^{1/2}}. \quad (74)$$

where

$$Q = \frac{v_1 \varepsilon^2}{v_0 (v_0 - 1) K} \left[ v_0 (v_1 - 1) u_0 + (v_0 - v_1) v_0 \right]. \quad (75)$$

For  $t_0 + \varepsilon < t$

$$F_1 = \varepsilon_2 \left[ -\frac{(v_1 - 1)}{(v_0 - 1)} q_{21} + \frac{v_0 (v_1 - 1) u_0 + (v_0 - v_1) v_0}{v_0 (v_0 - 1) (u_0 - v_0)} q_{21}^2 \right], \quad (76)$$

$$F_2 = \varepsilon_2 q_{21}. \quad (77)$$

where

$$q_{21} = \frac{1}{1 - \exp[-(t - t_0)]}. \quad (78)$$

The small parameter  $\varepsilon$  for the transition period is linked to either  $\varepsilon_1$ , or  $\varepsilon_2$ :

$$\varepsilon^2 = \varepsilon_1 \frac{\exp(v_0 t_0) - 1}{v_0} = \varepsilon_2. \quad (79)$$

From the latter equality, using the definitions of  $\varepsilon_1, \varepsilon_2$ , eqs. (64), (67) we obtain

$$\frac{u_0 - v_0}{u_0 (1 - v_0)} = \exp(-v_0 t_0). \quad (80)$$

One easily checks that the latter equation for  $t_0$  coincides with the formula eq. (21) for the "switch" time  $t = T$ , determined above from zero-order (in  $K$ ) approximation.

The eqs.(70)-(78) allow one to obtain the detailed evolution of the reacting system. Substitution of the latter equations for  $F$ 's in the corresponding time intervals into eqs.(40)-(42) yields the local concentrations; substitution of  $\tilde{u}, \tilde{v}$  and  $\tilde{w}$  into eqs. (9), (10) and (11), respectively gives the overall concentrations  $u, v$  and  $w$  by a straightforward integration. Therefore the full solution of the problem is obtained.

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Kharkov University Bulletin. 2001. №532. Chemical Series. Issue 7(30). П.О.Мchedлов-Петросян, Г.А.Хоменко, В.Б.Дж.Зиммерман. Быстрая гетерогенная каталитическая реакция в непроточном химическом реакторе: подход теории возмущений.

Предложен новый теоретический метод изучения гетерогенных каталитических реакций в непроточном химическом реакторе. Аналитическое решение соответствующей математической задачи получено методом сингулярных асимптотических разложений.