TWO CONSECUTIVE HETEROGENEOUS REACTIONS OF SECOND ORDER IN WELL MIXED AEROSOL SYSTEM

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The dynamics of concentration changes in well-mixed systems with two consecutive heterogeneous reactions of the second order on the surface of monodisperse aerosol particles is analyzed in the case of mass transfer limitations. A self-consistent set of equations is proposed. All possible variants of concentration changes were classified. Initial concentrations and mass transfer coefficients which lead to these variants were determined. It is shown that number of possible switches increases from one in the case of one binary reaction to three for consecutive reactions of the second order.

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1. INTRODUCTION

In many real systems, e.g. such as atmosphere, mass transfer processes and heterogeneous reactions are interconnected. This poses additional difficulties in building adequate models. In its turn, it leads to excessive simplification or to resource-intensive numerical calculations. For reactions of the second order the nonlinear term appears in kinetics equations. In the most of papers simplification or to resource-intensive numerical calculations. For reactions of the second order the nonlinear term appears in kinetics equations. In the most of papers...

2. SET OF EQUATIONS

Heterogeneous reactions usually go in several steps. We consider tree step mechanism. At first there is formation of adsorbed complexes on the aerosol surface:

\begin{align}
U_1 + V &\rightarrow (U_1)_\text{ads}, \\
V_1 + Particle &\rightarrow (V_1)_\text{ads}, \\
W_1 + Particle &\rightarrow (W_1)_\text{ads}, \\
U_2 + Particle &\rightarrow (U_2)_\text{ads}, \\
W_2 + Particle &\rightarrow (W_2)_\text{ads}. 
\end{align}

(2)

Then there are chemical reactions between adsorbed complexes:

\begin{align}
(U_1)_\text{ads} + (V_1)_\text{ads} &\rightarrow (W_1)_\text{ads}, \\
(U_2)_\text{ads} + (W_1)_\text{ads} &\rightarrow (W_2)_\text{ads}. 
\end{align}

(3)

Subsequently there is decomposition of adsorbed complexes on free molecule and aerosol particle (inverse first step).

Let us at first consider processes nearby aerosol surface. Equations describing surface coverages’ evolution are:

\begin{align}
d\sigma_{u1} &= k_{u1}u_1 (1 - \sigma) - k_{1u1}^u s_1 - k_{1s1}^u s_v + k_{s1}^u s_{w1}, \\
d\sigma_{v1} &= k_{v1}v_1 (1 - \sigma) - k_{1v1}^u s_v - k_{1s1}^u s_1 + k_{s1}^u s_{w1}, \\
d\sigma_{w1} &= k_{w1}w_1 (1 - \sigma) - k_{1w1}^u s_w + k_{s1}^u s_{w1}, \\
d\sigma_{w2} &= k_{w2}w_2 (1 - \sigma) - k_{1w2}^u s_w - k_{2s2}^u s_{w1} + k_{s2}^u s_{w2}, \\
d\sigma_{w3} &= k_{w3}w_3 (1 - \sigma) - k_{1w3}^u s_w + k_{s2}^u s_{w1} - k_{2s2}^u s_{w2}, 
\end{align}

(4-8)

where \( \sigma_{u1}, \sigma_{v1}, \sigma_{w1}, \sigma_{w2}, \sigma_{w3} \) are relative surface coverages, \( \sigma = s_1 + s_v + s_w, \)

\( k_{u1}^u, k_{v1}^u, k_{w1}^u, k_{w2}^u, k_{w3}^u \) are the reaction rates of direct and reverse reactions, \( k_u, k_v, k_w \) are the adsorption and desorption coefficients of the reactant \( c; u_1, v_1, w_1, u_2 \) and \( w_2 \) are concentrations nearby aerosol particle surface.

If processes of adsorption and desorption are fast \((k_c, k_c' \gg k_{1u1}^u, k_{1v1}^u, k_{1w1}^u, k_{1w2}^u, k_{1w3}^u)\) then there is quasi steady state when surface coverages and concentrations nearby surface are related by following equations

\begin{equation}
\sigma_c = \frac{c_c}{a_c}, \\
b_c = 1 + \sum_c \frac{c_c}{a_c},
\end{equation}

(9)

where \( a_c = \frac{k_u}{k_c} \) for all the reactants \( c. \) If the coverages are small we can neglect Langmuir terms:
\[ s_c = \frac{c_x}{a_c}. \]  

The reaction rates \( R_1 \) and \( R_2 \) take the form:

\[ R_1 = \tilde{k}_1 s_n s_v - \tilde{k}_1 s_{n1}, \]  
\[ R_2 = \tilde{k}_2 s_n s_v - \tilde{k}_2 s_{n2}. \]

And, taking into account (10),

\[ R_1 = \eta (u_{11} v_s - K_1 w_{11}), \]  
\[ R_2 = \tilde{r}_2 (w_{12} - K_2 w_{22}), \]

where reaction equilibrium constants are

\[ K_1 = \frac{\tilde{k}_1}{a_{n1}} a_{v1}, \quad K_2 = \frac{\tilde{k}_2}{a_{w2}} a_{w2}, \]

and reaction rates constants are \( \eta = \frac{\tilde{k}_1}{a_{n1}} \), \( \tilde{r}_2 = \frac{\tilde{k}_2}{a_{w2}} \).

Now let us consider local mass transfer on the scale of one particle. Even in well mixed system each particle is surrounded by a boundary layer. Mass transfer through this layer is determined by molecular diffusion [4]. The driving force for this mass transfer is the difference between averaged bulk (volume) concentrations and concentrations nearby surface. Thus flow density for each reactant can be written in the form

\[ j_{\text{f}} = \kappa (c - c_s), \]  
where \( \kappa \) is the mass transfer coefficients that are defined by processes of diffusion and/or thermal motion in Knudsen range [5-6].

The conditions of stoichiometry impose the following constraints on reaction rates and flows densities:

\[ \kappa_{n1} (u_1 - u_{11}) = R_1, \]  
\[ \kappa_v (v - v_0) = R_1, \]  
\[ \kappa_{n1} (w_1 - w_{11}) = -R_1 + R_2, \]  
\[ \kappa_{n2} (u_2 - u_{22}) = R_2, \]  
\[ \kappa_{w2} (w_2 - w_{22}) = R_2. \]

Now we use the concept of local concentrations [1-3]. Local concentration \( \hat{c} \) for each reactant is a result of averaging of concentrations nearby surface over an ensemble of aerosol particles in the physically small volume (that still contains large enough number of particles). Thus local and bulk concentrations are macroscopic variables in contrast to concentrations nearby aerosol surface. Bulk and local concentrations are dimensionless and are measured in mole fractions.

In terms of local concentrations the balance equations have the form

\[ \frac{du_1}{dt'} = -\kappa_{n1} S (u_1 - \hat{u}_1), \]  
\[ \frac{dv}{dt'} = -\kappa_v S (v - \hat{v}), \]  
\[ \frac{dw_1}{dt'} = -\kappa_{n1} S (w_1 - \hat{w}_1), \]  
\[ \frac{dw_2}{dt'} = -\kappa_{w2} S (w_2 - \hat{w}_2), \]  
\[ \frac{dw_2}{dt'} = -\kappa_{w2} S (w_2 - \hat{w}_2), \]

where \( t' \) is the time, and \( S \) is the surface of all aerosol particles.

In the present communication we consider slow mass transfer (small ratio mass transfer coefficient to reactions rate constants). As a result equations (16) (20) are split into conditions of local equilibrium

\[ \hat{u}_1 \hat{v} - K_1 \hat{w}_1 = 0, \]  
\[ \hat{u}_2 \hat{w}_2 - K_2 \hat{w}_2 = 0 \]

and stoichiometric conditions

\[ \kappa_{n1} (u_1 - \hat{u}_1) = \kappa_v (v - \hat{v}), \]  
\[ \kappa_{n1} (w_1 - \hat{w}_1) = -\kappa_{n1} (u_1 - \hat{u}_1) + \kappa_{n2} (u_2 - \hat{u}_2), \]  
\[ \kappa_{n2} (u_2 - \hat{u}_2) = -\kappa_{w2} (w_2 - \hat{w}_2). \]

After introduction of dimensionless time \( t = t' \kappa_{n1} \), we have five differential equations for each reactant

\[ \frac{du_1}{dt} = -\kappa_{n1} S (u_1 - \hat{u}_1), \]  
\[ \frac{dv}{dt} = -\kappa_v S (v - \hat{v}), \]  
\[ \frac{dw_1}{dt} = -\kappa_{n1} S (w_1 - \hat{w}_1), \]  
\[ \frac{dw_2}{dt} = -\kappa_{w2} S (w_2 - \hat{w}_2), \]

\[ \frac{dw_2}{dt} = -\kappa_{w2} S (w_2 - \hat{w}_2), \]

where \( \kappa_v = \frac{\kappa_v}{\kappa_{n1}}, \quad v_1 = \frac{\kappa_{w1}}{\kappa_{n1}}, \quad v_2 = \frac{\kappa_{u2}}{\kappa_{n1}}, \quad v_3 = \frac{\kappa_{w2}}{\kappa_{n1}}, \)

three stoichiometric conditions:

\[ (u_1 - \hat{u}_1) = v_0 (v - \hat{v}), \]  
\[ v_1 (w_1 - \hat{w}_1) = -v_1 (u_1 - \hat{u}_1) + v_2 (u_2 - \hat{u}_2), \]  
\[ v_2 (u_2 - \hat{u}_2) = -v_3 (w_2 - \hat{w}_2) \]

and two equations (26) – (27), which express mass action laws for two reactions.

Initial conditions for bulk concentrations are:

\[ u_1 \big|_{t=0} = u_{10}, \quad v_1 \big|_{t=0} = v_0, \quad w_1 \big|_{t=0} = w_{10}, \]

\[ u_2 \big|_{t=0} = u_{20}, \quad w_2 \big|_{t=0} = w_{20}. \]

Combining equations (31) – (35) yields three conservation laws:

\[ u_1 + w_2 = u_{10} + w_{20}, \]  
\[ u_1 - v = u_{10} - v_0, \]  
\[ w_1 - u_2 + u_1 = w_{10} - u_{20} + u_{10}. \]

3. IRREVERSIBLE REACTION APPROXIMATION

Let us suppose \( K_1 = K_2 = 0 \).

In this case the first reaction is independent on the second one. Thus for the first reaction solution is the
same as in [1]. Let \( \tilde{u}_1 \big|_{t=0} = 0 \) and \( \tilde{v}_1 \big|_{t=0} > 0 \). In this case conditions for switch are:
\[
\begin{align*}
    v_0 &= \frac{1}{\nu_0} u_{00} > 0, \\
    v_{0} - u_{00} &= 0.
\end{align*}
\]
Their compatibility means \( \nu_0 < 1 \).

The evolution of local and global concentrations depends on which reactant of the second reaction is in deficit. In case \( \tilde{u}_2 = 0 \)
\[
\begin{align*}
    \tilde{u}_2 &= u_{20} e^{-\nu_2 t}, \\
    w_1 &= w_{10} + u_{20} \left( e^{-\nu_2 t} - 1 \right) - \Delta_1, \quad \Delta_1 = u_1 - u_{00} = v_0 - \nu_0.
\end{align*}
\]

If both at the beginning \( t = 0 \) and asymptotically, for \( t \to \infty \), the same species is in deficit, the number of switches would be even, otherwise it would be odd.

\[
\tilde{u}_1 = w_{10} + u_{20} \left( \frac{1 - v_2}{v_1} e^{-\nu_2 t} - 1 \right), \\
\tilde{v}_1 \big|_{t=0} = \frac{v_2}{v_1} u_{20} + \frac{1}{v_1} u_{10}, \\
\tilde{v}_1 \big|_{t=\infty} = \begin{cases} 
    \frac{w_{10} - u_{20} + u_{10}, \quad u_{10} > v_0, \\
    w_{10} - u_{20} + v_0, \quad u_{10} < v_0.
\end{cases}
\]

Fig. 1. Changes of local concentrations \( \tilde{u}_1 \) (dash line) and \( \tilde{v} \) (solid line) in irreversible reaction approximation. \( v_0 = 1, v_1 = 0.1, u_{10} = 1, v_0 = 0.49 \)

For the second reaction either \( \tilde{u}_2 = 0 \) or \( \tilde{v}_1 = 0 \).

Mathematically the presence of the first reaction manifests itself in additional terms in the expressions for \( \tilde{u}_1, \tilde{u}_2 \) as compared to the system of one binary reaction. This term leads to possibility of a minimum of
That in its turn leads to possibility of double switching.

Initial values of the volume concentrations which lead to double-switch can be determined from the consideration of the marginal case when \( \tilde{w}_1 = 0 \) at the minimum (\( \tilde{u}_2|_{t=0} = 0 \) and \( \tilde{w}_1|_{t=\infty} = 0 \)). This case separates solution without switching and solution with double-switch [4].

From the extremum condition \( \frac{d}{dz} \tilde{w}_1|_{z=\tau_m} = 0 \) we can determine the point where extremum takes place \( m_T = 1 - 10 \ln \frac{u_{vo}}{u_{v0}} (\nu_1 - \nu_2) \) (we suppose that minimum exists: \( \frac{\nu_1 - \nu_2}{\nu_1 - \nu_2} > 0 \) and \( T_m > 0 \)). And from the condition of switching \( \tilde{w}_1|_{t=\tau_m} < 0 \) we can get inequality for the initial volume concentrations:

\[
\begin{align*}
\frac{w_0}{u_0} & < u_2 - u_0 + \\
& + u_0 \left( 1 - \frac{1}{\nu_1} \right) \left( 1 - \frac{1}{\nu_2} \right) \left[ \frac{u_{vo} (\nu_1 - 1)}{u_{v0} \nu_2 (\nu_1 - 2)} \right] \left( \frac{1}{\nu_1 - 1} \right) \tag{64}
\end{align*}
\]

That suppose \( T_m > 0 \).

Minimum existence condition leads to:

\[
\begin{align*}
\nu_1 & > \nu_2 > 1, \\
\nu_1 & < \nu_2 < 1.
\end{align*}
\]

These inequalities and two inequalities for the initial and final points \( \tilde{w}_2|_{t=0} = 0 \) and \( \tilde{w}_2|_{t=\infty} = 0 \):

\[
\begin{align*}
\frac{w_0}{v_0} & > \frac{v_2}{u_0} - \frac{1}{\nu_1}, \\
\frac{w_0}{v_0} & > u_2 - u_0,
\end{align*}
\]

are necessary and sufficient conditions for double-switch.

If there is switch in first reaction the number of possible switches rises up to three (see Table 2).

**Table 2. Number of possible switches in the second reaction for the second case**

| \( \tilde{w}_1|_{t=\infty} = 0 \) | \( \tilde{a}_2|_{t=\infty} = 0 \) |
|-----------------------------|-----------------------------|
| 0 or 2 switches             | 1 switches                  |
| 1 switches                  | 0 or 2 switches             |

Derivatives of the local concentrations for the second reaction change discontinuously as a result of switch in the first reaction. Values of these changes are:

\[
\begin{align*}
\frac{d\tilde{a}_1}{dt}_{t=\tau_i=0} - \frac{d\tilde{a}_1}{dt}_{t=\tau_i=0} & = \frac{v_0}{v_1} (u_{vo} - v_0) < 0, \tag{68} \\
\frac{d\tilde{a}_2}{dt}_{t=\tau_i+0} - \frac{d\tilde{a}_2}{dt}_{t=\tau_i-0} & = \frac{v_0}{v_2} (u_{vo} - v_0) > 0. \tag{69}
\end{align*}
\]

If \( \tilde{w}_2|_{t=0} > 0 \) this stepwise change can lead to additional switch in the second reaction (see Fig. 3).

**Fig. 3. Changes of local concentrations \( \tilde{w}_2 \) (dash line) and \( \tilde{w}_1 \) (solid line) in irreversible reaction approximation. \( \nu_1 = 1, \nu_2 = 0.1, \nu_3 = 0.6, \nu_4 = 1,\ v_0 = 0.49, \ w_0 = 1.3, \ w_3 = 1.8 \)**

4. CONCLUSIONS

The qualitative change of possible kinetics for a system of consecutive reactions as compared to one reaction of second order is demonstrated. The presence of the switch in the first reaction can lead to additional switch in the second one.

The inequalities separating the manifold of initial values of bulk concentrations into sub-manifolds which lead to different kinetic regimes are given.

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ДВЕ ПОСЛЕДОВАТЕЛЬНЫЕ ГЕТЕРОГЕННЫЕ РЕАКЦИИ ВТОРОГО ПОРЯДКА
В ХОРОШО ПЕРЕМЕШАННОЙ АЭРОЗОЛЬНОЙ СИСТЕМЕ
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Рассмотрена динамика изменения концентраций в полностью перемешанной системе при протекании двух последовательных гетерогенных реакций на поверхности монодисперсных аэрозольных частиц в случае, когда массоперенос реактантов к поверхности аэрозолей является лимитирующим процессом. Получена самосогласованная система уравнений, проанализированы различные варианты изменения концентраций и определены начальные условия и коэффициенты массопереноса, приводящие к этим вариантам. Показано, что за счет последовательности реакций количество возможных переключений возрастает до трёх по сравнению с одной бинарной реакцией.

ДВІ ПОСЛЕДОВАЛЬНІ ГЕТЕРОГЕННІ РЕАЦІЇ ДРУГОГО ПОРЯДКУ В ДОБРЕ
ПЕРЕМІШАНИЙ АЕРОЗОЛЬНІй СИСТЕМІ
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Розглянута динаміка зміни концентрацій у повністю перемішаній системі при протіканні двох послідовних гетерогенних реакцій на поверхні монодисперсних аерозольних часточок у випадку, коли масоперенос реагентів до поверхні аерозолів є процесом, що лімітує. Отримана самоузгоджена систему рівнянь, проаналізовані різні варіанти зміни концентрацій і визначені початкові умови й коекфіцієнти масопереносу, що приводять до цих варіантів. Показано, що за рахунок послідовності реакцій кількість можливих перемикань зростає до трьох у порівнянні з однією бінарною реакцією.