The robust finite volume schemes for modeling non-classical surface reactions

R. Čiegis

Vilnius Gediminas Technical University, Vilnius, Lithuania
e-mail: rc@vgtu.lt

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New applications

1. Evaluation of immobilized enzyme activity for the scanning electrohemical microscopy, which is based on electrochemical measurements with the scanning ultramicroelectrode.

2. Redox-competition mode for the evaluation of enzymatic kinetics.

Models

The mathematical model describes the NO+CO surface reaction proceeding over supported catalysts.

Assume that reactants $\mathrm{A}_1 = \mathrm{NO}$, $\mathrm{A}_2 = \mathrm{CO}$ of concentrations $a_1(t, x)$, $a_2(t, x)$ occupy domain

$$\Omega = \{x = (x_1, x_2, x_3) : x_i \in [0, l],\ i = 1, 2, 3\}$$

with boundary $\tilde{S} = S_1 \cup S_2$, where

$$S_2 = \{x = (x_1, x_2, x_3) : x_i \in [0, l],\ i = 1, 3,\ x_2 = 0\}$$

and $S_1 = \tilde{S} \setminus S_2$. They diffuse towards catalyst surface S_2.

Suppose that $S_2 = S_{22} \cup S_{21}$, where

$$S_{22} = \{(x_1, x_2, x_3) : x_1 \in [0, x_*),\ x_2 = 0,\ x_3 \in [0, l]\},$$
$$S_{21} = \{(x_1, x_2, x_3) : x_1 \in (x_*, l],\ x_2 = 0,\ x_3 \in [0, l]\},\ \ x_* \in (0, l),$$

are strips that consist of the active and inactive in reaction adsorption sites, respectively.

Denote by $s_2(x),\ x = (x_1, x_3) \in S_{22}$, and $s_1(x),\ x = (x_1, x_3) \in S_{21}$ the surface densities of the active and inactive sites.

Chemical Reactions

Let desorbed reaction products

$$\mathrm{P}_1 = \mathrm{N}_2\mathrm{O}, \quad \mathrm{P}_2 = \mathrm{N}_2, \quad \mathrm{P}_3 = \mathrm{CO}_2$$

of concentrations $p_1(t,x)$, $p_2(t,x)$, and $p_3(t,x)$ diffuse in the same domain.

Let the surface S_1 is impermeable to molecules of reactants and products.

The mechanism of the NO+CO reaction is based on the NO reduction reaction by CO

$$4\mathrm{NO} + 3\mathrm{CO} \to \mathrm{N_2O}{+}3\mathrm{CO_2} + \mathrm{N_2},$$

producing N_2O, CO_2, N_2 and the subreaction

$$\mathrm{CO} + \mathrm{N_2O} \to \mathrm{N_2} + \mathrm{CO_2}$$

via transformation of the adsorbed product $\mathrm{N_2O}$ and involves the following steps:

$$
\begin{cases}
\mathrm{NO} + \mathrm{S} \underset{k_{-1i}}{\overset{k_{1i}}{\rightleftarrows}} \mathrm{NOS}, \qquad \mathrm{CO} + \mathrm{S} \underset{k_{-2i}}{\overset{k_{2i}}{\rightleftarrows}} \mathrm{COS}, \\
\mathrm{NOS} + \mathrm{S} \overset{k_{32}}{\to} \mathrm{NS} + \mathrm{OS}, \qquad \mathrm{NOS} + \mathrm{NS} \overset{k_{42}}{\to} \mathrm{N_2O} + 2\mathrm{S}, \\
2\mathrm{NS} \overset{k_{52}}{\to} \mathrm{N_2} + 2\mathrm{S}, \qquad \mathrm{COS} + \mathrm{OS} \overset{k_{62}}{\to} \mathrm{CO_2} + 2\mathrm{S}, \\
\mathrm{N_2O} + \mathrm{S} \underset{k_{-7i}}{\overset{k_{7i}}{\rightleftarrows}} \mathrm{N_2OS}, \qquad \mathrm{N_2OS} \overset{k_{82}}{\to} \mathrm{N_2} + \mathrm{OS}.
\end{cases} \tag{1}
$$

u_{j2} and u_{j1}, $j = 1, \dots, 5$, are densities of the active and inactive in reaction adsorption sites that are occupied by molecules of adsorbed reactants A_1 and A_2: NOS $(j = 1)$ and COS $(j = 2)$ and molecules of products NS $(j = 3)$, OS $(j = 4)$, N_2OS $(j = 5)$.

$$\partial_t u_{12} = (k_{12} a_1 - k_{32} u_{12})(s_2 - \sum_m u_{m2}) - k_{-12} u_{12} - k_{42} u_{12} u_{32}$$

$$\partial_t u_{22} = k_{22} a_2 (s_2 - \sum_m u_{m2}) - k_{-22} u_{22} - k_{62} u_{22} u_{42}$$

$$\mathrm{NOS} + \mathrm{S} \xrightarrow{k_{32}} \mathrm{NS} + \mathrm{OS}, \quad \mathrm{NOS} + \mathrm{NS} \xrightarrow{k_{42}} \mathrm{N_2O} + 2\mathrm{S},$$

$$2\mathrm{NS} \xrightarrow{k_{52}} \mathrm{N_2} + 2\mathrm{S},$$

$$\partial_t u_{32} = k_{32} u_{12} (s_2 - \sum_m u_{m2}) - k_{42} u_{12} u_{32} - 2 k_{52} u_{32}^2$$

$$\partial_t u_{42} = k_{32} u_{12} (s_2 - \sum_m u_{m2}) - k_{62} u_{22} u_{42} + k_{82} u_{52}$$

$$\partial_t u_{52} = k_{72} p_1 (s_2 - \sum_m u_{m2}) - k_{-72} u_{52} - k_{82} u_{52}$$

Numerical Integration of ODEs

We should preserve the main properties of the solution:

1. Nonnegativity

$$u_{jk}(x_1, t) \geq 0, \quad 1 \leq j \leq 5, \; k = 1, 2.$$

2. Boundedness

$$s_k - \sum_m u_{mk} \geq 0, \quad k = 1, 2.$$

Numerical Integration Techniques

1. Split different processes. Integrate with adaptive time step much smaller than for integration of transport processes.

2. Use adaptive linearizations and a conbination of implicit/explicit approximations.

3. Use robust and efficient state of the art solvers, such as the ODE15s solver (Matlab).

Diffusion

We use the non-classical surface diffusion mechanism (a jump diffusion):

$$q_{ji} = -\kappa_{ji}\Big\{(s_i - \sum_{m=1}^{5} u_{mi})\nabla u_{ji} - u_{ji}\nabla(s_i - \sum_{m=1}^{5} u_{mi})\Big\},\ j = 1, \dots, 5,$$

1D case:

$$q_j = -\kappa\Big\{(s - \sum_{m=1}^{5} u_m)\frac{\partial u_j}{\partial x_1} - u_j\frac{\partial}{\partial x_1}(s - \sum_{m=1}^{5} u_m)\Big\}$$

A parabolic diffusion-convection non-stationary problem

$$\frac{\partial u_j}{\partial t} = \kappa \frac{\partial}{\partial x_1}\Big\{\big(s - \sum_{m=1}^{5} u_m\big)\frac{\partial u_j}{\partial x_1} - u_j \frac{\partial}{\partial x_1}\big(s - \sum_{m=1}^{5} u_m\big)\Big\}.$$

Equivalent forms (for smooth solutions):

$$\frac{\partial u_j}{\partial t} = \kappa \frac{\partial}{\partial x_1}\Big\{\big(s - \sum_{m\neq j} u_m\big)\frac{\partial u_j}{\partial x_1} - u_j \frac{\partial}{\partial x_1}\big(s - \sum_{m\neq j} u_m\big)\Big\}.$$

$$\frac{\partial u_j}{\partial t} = \kappa \Big\{\Big(s - \sum_{m=1}^{5} u_m\Big)\frac{\partial^2 u_j}{\partial x_1^2} + u_j \frac{\partial^2}{\partial x_1^2}\Big(\sum_{m=1}^{5} u_m\Big)\Big\}.$$

1. The Finite Volume Method is used to get a conservative scheme.

2. Implicit/explicit linearization is done (iterations for the explicit terms can be applied for the CN or the fully implicit Euler approximations).

3. The monotone upwind approximation for the convection transport term is used.

4. If $u_j(x,t) = 0$, then $\frac{\partial}{\partial t} u_j \geq 0$ is valid for the differential equation.

Conjugation conditions

1. Mass conservation condition (the fluxes are continuous)
2. Jump conditions (the solutions are discontinuous)

$$
\begin{aligned}
&\kappa_{j1}\Big(\big(s_1 - \sum_{m\neq j} u_{m1}\big)\frac{\partial u_{j1}}{\partial x} - u_{j1}\frac{\partial\big(s_1 - \sum\limits_{m\neq j} u_{m1}\big)}{\partial x}\Big)\Big|_{x_*+0} \\
&= \kappa_{j2}\Big(\big(s_2 - \sum_{m\neq j} u_{m2}\big)\frac{\partial u_{j2}}{\partial x} - u_{j2}\frac{\partial\big(s_2 - \sum\limits_{m\neq j} u_{m2}\big)}{\partial x}\Big)\Big|_{x_*-0} \\
&= \lambda_{2,j1} u_{j1}|_{x_*+0}\big(s_2 - \sum_{m} u_{m2}\big)|_{x_*-0} \\
&\quad - \lambda_{1,j2} u_{j2}|_{x_*-0}\big(s_1 - \sum_{m} u_{m1}\big)|_{x_*+0}, \quad j = 1, \dots, 5.
\end{aligned}
$$

1. FVM approximation (to get a conservative approximation)

2. Four point stencil of the space grid (to approximate discontinuous functions of the boundary of active and non-active regions).

3. A modified factorization algorithm, to solve the obtained systems of linear equations efficiently.

4. Stability analysis of the FVM scheme for some simplified benchmark cases.

We solve the following linear initial-boundary value parabolic problem

$$\partial_t u = \frac{\partial^2 u}{\partial x^2} + f(x,t), \quad 0 < x < 1,\ t > 0,$$
$$\frac{\partial u}{\partial x}\Big|_{x^*-0} = \frac{\partial u}{\partial x}\Big|_{x^*+0} = \alpha\big(u(x^*+0,t) - u(x^*-0,t)\big),$$
$$u(0,t) = 0, \quad u(1,t) = 0,$$
$$u(x,0) = u_0(x), \quad 0 \le x \le 1.$$

We approximate it by the discrete scheme

$$
\begin{aligned}
&\delta_{\bar{t}} U_j^n + A_h U^n = F_j^n, \quad j = 1, \ldots, J-1, \\
&U_0^n = 0, \quad U_J^n = 0, \\
&U_j^0 = u_0(x_j), \quad j = 0, \ldots, J,
\end{aligned}
\tag{2}
$$

where the discrete operator A_h is defined as

$$
A_h U = \begin{cases} -\delta_x \delta_{\bar{x}} U_j, \quad 0 < j \neq K, K+1 < J, \\ \frac{2}{h}\big(\delta_{\bar{x}} U_K - \alpha(U_{K+1} - U_K)\big), \quad j = K, \\ -\frac{2}{h}\big(\delta_x U_{K+1} - \alpha(U_{K+1} - U_K)\big), \quad j = K+1, \end{cases}
$$

THEOREM

The discrete operator A_h is symmetric and positive-definite

$$A_h = A_h^* \geq \lambda_0 I, \quad \lambda_0 > 0. \tag{3}$$

THEOREM

The discrete scheme (2) *is stable and the following stability estimates are valid*

$$\|U^n\| \le \|U^{n-1}\| + \tau\|F^n\|, \tag{4}$$

$$\|U^n\|^2 \le \|U^{n-1}\|^2 + \frac{\tau}{2}\|F^n\|^2_{A_h^{-1}}, \tag{5}$$

where the L_2 *norm is defined as* $\|U\|^2 = (U, U)$ *and* $\|U\|^2_{A_h^{-1}} = \left(A_h^{-1} U, U\right)$.

2D Problems for A_1, A_2, P_1

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$$\begin{cases} \partial_t a_1 = \kappa_{a_1}\Big(\dfrac{\partial^2 a_1}{\partial x_1^2} + \dfrac{\partial^2 a_1}{\partial x_2^2}\Big), \quad (x_1, x_2) \in (0, l) \times (0, l), \\ \partial_n a_1 |_{S_1} = 0, \\ \kappa_{a_1} \partial_n a_1 = -\Big(k_{11} a_1 (s_1 - \sum\limits_m u_{m1}) - k_{-11} u_{11}\Big), \\ \quad x_1 \in (x_*, l),\ x_2 = 0, \\ \kappa_{a_1} \partial_n a_1 = -\Big(k_{12} a_1 (s_2 - \sum\limits_m u_{m2}) - k_{-12} u_{12}\Big), \\ \quad x_1 \in (0, x_*),\ x_2 = 0, \\ a_1(0, x) = a_{10}(x), \quad (x_1, x_2) \in (0, l) \times (0, l), \end{cases}$$

The ODE on the active part of the surface for the u_{12} component

$$\partial_t u_{12} = (k_{12} a_1 - k_{32} u_{12})(s_2 - \sum_m u_{m2}) - k_{-12} u_{12} - k_{42} u_{12} u_{32}$$

The BC for the 2D problem (the flux of a_1 component):

$$\kappa_{a_1} \partial_n a_1 = -\left(k_{12} a_1 (s_2 - \sum_m u_{m2}) - k_{-12} u_{12}\right)$$

1. FVM conservative approximation.
2. Iterations between ODE and PDE steps.
3. AMG solver for the elliptic problems (stability bonus)
4. ADI solvers for the elliptic problems (1D subproblems)