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DECOMPOSITION OF THE PROBLEM IN THE NUMERICAL SOLUTION OF DIFFERENTIAL-ALGEBRAIC SYSTEMS FOR CHEMICAL REACTIONS WITH PARTIAL EQUILIBRIA

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The paper considers two simple systems of differential-algebraic equations that appear in the study of chemical kinetics problems with partial equilibria: some of the variables are determined from the condition argmin for some system function state, which depends on all variables of the problem. For such a statement, we can write a differential-algebraic system of equations where the algebraic subproblem expresses the conditions for the minimality of the state function at each moment. It is convenient to use splitting methods in numerical solving, i.e. to solve dynamic and optimization subproblems separately. In this work, we investigate the applicability of differential-algebraic splitting using two simplified systems. The convergence and order of accuracy of the numerical method are determined. Different decomposition options are considered. Calculations show that the numerical solution of the split system of equations has the same order of accuracy as the numerical solution of the joint problem. The constraints are fulfilled with sufficient accuracy if the procedure of the numerical method ends with the solution of the optimization subproblem. The results obtained can be used in the numerical solving of more complex chemical kinetics problems.

Keywords: differential-algebraic systems; optimization; numerical methods.

Introduction

When studying systems of ordinary differential equations with a large spread of time scales, it is often convenient to divide variables into “fast” and “slow” subsystems. This decomposition is usually made by analyzing the spectrum of the Jacobian matrix of the right-hand side [1]. In some cases, however, it is possible to single out “fast” variables from physical considerations, or based on a qualitative analysis of the relationships in the system, to describe which differential equations are used [2, 3]. Algebraic equations approximate the behaviour of the fast subsystem. Decomposition allows decreasing the stiffness of the system and associated problems with its numerical integration. Methods for reducing a system of differential equations to differential-algebraic equations are widely used in chemical kinetics. The mechanisms of chemical transformations of complex molecules, for example, the combustion of hydrocarbons, include thousands of elementary stages and hundreds of components, therefore, in practical calculations, it is necessary to reduce the dimension of the problem by orders of magnitude. Such a reduction becomes possible due to significant differences in the rates of different reactions. Of course, it is necessary to choose the appropriate criteria for separating variables. Since the equations of chemical kinetics (especially in nonisothermal systems) are essentially nonlinear, there exist no universal and rigorous criteria.

The algebraic subsystem expresses the quasi-stationarity of the “fast” subsystem: the rate of change of variables becomes insignificant compared with the “slow” subsystem. Another feature of the “fast” subsystem is the large uncertainty of the kinetic coefficients [4]. As is known from statistical physics, with a sufficiently large number of “fast” variables, we can approximate their behaviour by statistical laws. For example, the local equilibrium approximation is widely used when considering relaxation processes (heat transfer, diffusion, viscous flow) [5].

Similarly, in [6, 7], the “Rate Controlled Constrained Equilibrium” (RCCE) approach was proposed, which considers the “fast” subsystem as equilibrium one for the given values of “slow” variables. Interestingly, similar models were proposed in [8, 9] in the modelling of economic systems in which the time scales of the distribution and production of resources differ significantly. In both cases, the state of the “fast” subsystem is found as a solution to the optimization problem (maximum entropy, minimum free energy). Models of the dynamics of physicochemical systems with equilibrium approximations are widely used in the study of chemical reactors and burners [10–13]. It should be noted that the separation of variables, generally, still requires suitable criteria. The simplest methods of separation are based on estimating the Damkohler number or identifying the regions of the reactor in which processes occur at significantly different rates [14, 15]. The combination of RCCE with other reduction methods and more detailed methods for the partition of variables are discussed in [16–19].

Let us consider the system of differential equations:

$$\frac{d\mathbf{x}}{dt} = \mathbf{g}\left(\mathbf{x}\right). \tag{1}$$

If we can divide $\mathbf{x}$ into “slow” part $\mathbf{y}$ and “fast” part $\mathbf{z}$, then the system is reduced to the form:

$$\frac{d\mathbf{y}}{dt} = \mathbf{g}\left(\mathbf{y}, \mathbf{z}^*\right), \tag{2}$$

$$\mathbf{z}^* = \arg\min_{\mathbf{z}} G(\mathbf{y}, \mathbf{z}), \tag{3}$$

$$\mathbf{h}(\mathbf{y}, \mathbf{z}) = 0. \tag{4}$$

Here G is a function that has the physical meaning of free energy, $\mathbf{h}$ is a vector of equality constraints. In [8], the operator $\arg\min$ is called the “entropy operator” since the author uses the entropy of the system under consideration as an optimization criterion in subproblem (3). In more particular cases, the conditions of partial equilibrium are determined by the free energy; therefore, we can call (2–4) a system with a partial equilibrium operator.

The works [20, 21] propose methods for reformulating an optimization subproblem as a dynamic one (by introducing differential equations for Lagrange multipliers). The papers [22–25] consider methods for solving an optimization problem with linear constraints, which are obtained from solving a kinetic subproblem. In the present paper, different combinations of numerical procedures for kinetic and optimization subproblems are compared. For several (relatively simple) problems, we obtain estimates for the order of accuracy of computational schemes based on the separation of subsystems.

1. Model System (Additive Case)

Let us consider a simple system with three variables: one slow variable y and two fast variables z_1 and z_2. The equation for y is as follows:

$$\frac{dy}{dt} = -\beta_0 y + \beta_1 z_1^* + \beta_2 z_2^*. \tag{5}$$

Here z_1^* and z_2^* are solutions to the optimization problem:

$$\min_{z_1, z_2} G\left(z_1, z_2, y\right), \tag{6}$$

where the function G is an analogue of free energy for the mixture of substances:

$$G\left(z_1, z_2, y\right) = a_1 z_1 \ln(z_1) + a_2 z_2 \ln(z_2) + y \ln(y). \tag{7}$$

Mixture fractions must satisfy the additional relation:

$$y + z_1 + z_2 = 1. \tag{8}$$

We suppose that only non-negative values of z_1 and z_2 have physical sense. It is easy to see that the function G is convex: its minimum exists and is unique. For $y > 0$, the solution to minimization problem (6) smoothly depends on y. In this regard, system of equations (1–3) is a convenient model object for carrying out numerical calculations. The system is equivalent to a reaction vessel, in which the reagent decomposes much more slowly than the competing products transform into each other. The ratio of the products does not depend on the kinetics of their mutual transformations. Reagent conversion completely determines this ratio.

Using the Lagrange multipliers method, we can write conditions of extremum in the following form:

$$a_1 + a_1 \ln(z_1^*) + \lambda = 0, \tag{9}$$

$$a_2 + a_2 \ln(z_2^*) + \lambda = 0, \tag{10}$$

$$y + z_1^* + z_2^* = 1. \tag{11}$$

If $a_1 = a_2$, then the solution is simplified: $z_1^* = z_2^*$, which, along with (8), makes it possible to reduce the problem to a single differential equation. For $a_1 \neq a_2$, analytical solution is much more complex. Further, we consider this particular case.

Using implicit finite-difference approximation, we can write (5) in the form:

$$y^k - y^{k-1} - \tau\left(-\beta_0 y^k + \beta_1 z_1^k + \beta_2 z_2^k\right) = 0. \tag{12}$$

This equation is linear with respect to y, but the variables z_1 and z_2 are non-linearly related to each other. The Lagrange multipliers method allows us to consider them as independent variables. Let us write equations (5, 9–11) in the form:

$$\mathbf{f} = \begin{bmatrix} y^k - y^{k-1} - \tau\left(-\beta_0 y^k + \beta_1 z_1^k + \beta_2 z_2^k\right) \\ a_1 + a_1 \ln(z_1^k) + \lambda^k \\ a_2 + a_2 \ln(z_2^k) + \lambda^k \\ y^k + z_1^k + z_2^k - 1 \end{bmatrix} = 0. \tag{13}$$

Further, we solve the system of equations using the Newton method:

$$\mathbf{x}^s = \mathbf{x}^{s-1} - C\left[\mathbf{J}\left(\mathbf{x}^{s-1}\right)\right]^{-1} \mathbf{f}\left(\mathbf{x}^{s-1}\right). \tag{14}$$

Here $\mathbf{x}$ is a set of variables $[y, z_1, z_2, \lambda]^T$; $\mathbf{J}$ is a Jacobi matrix; the parameter C is a coefficient that holds values of y, z_1, z_2 in a non-negative range. Fig. 1 shows an example of numerical results ($y(0) = 1$, $\beta_0 = 1$, $\beta_1 = 10^{-2}$, $\beta_2 = 10^{-1}$, $a_1 = 1$; $a_2 = 2$; $\tau = 5 \cdot 10^{-3}$). The value of y exponentially decreases in time, and the variables z_1 and z_2 follow a minimum of G. This minimum, however, is local at each moment. Fig. 2 shows that $G(t)$ achieves its minimum value at $t = 1{,}43$. After that, $G(t)$ slowly increases and approaches a stationary value. This inconsistency results from a violation of the detailed balance conditions (the parameters β and a are usually related and cannot be chosen arbitrarily as in the presented case [26]).

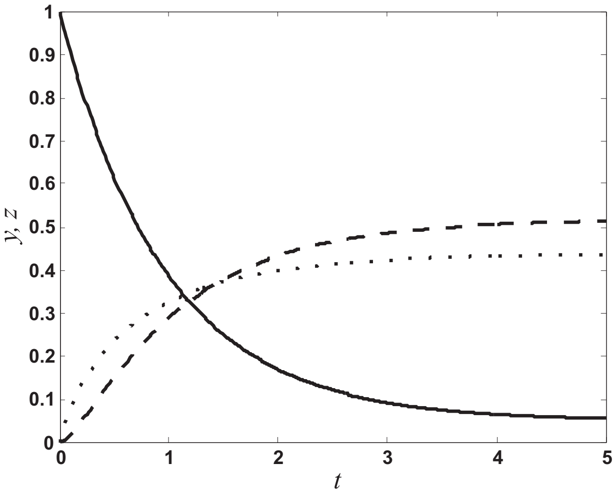

Fig. 1. Numerical solution to equations (5) – (8): solid line denotes y, dotted lines denote z_1 and z_2

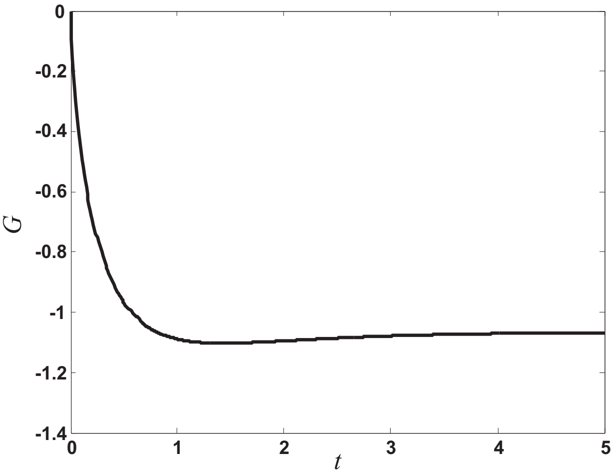

Fig. 2. Dependence of G on time

The joint solution of the differential equations and the optimization problem is relatively simple in this particular case. But for more complex systems, it can turn out to be unsuitable [27]. First, the dimension of the problem can vary, and secondly, the optimization problem conditions can be more complicated (for example, in non-ideal and heterogeneous systems). It is better to use numerical methods for solving differential and optimization subproblems separately. For example, the Runge-Kutta methods can be used to solve a dynamic ("slow") subproblem, while nonlinear programming methods are applied for solving an optimization ("fast") subproblem. Different methods, as a rule, are implemented by different solvers. It is possible to organize data exchange between them to simplify the numerical solution. Thus, we ask the questions: is it possible to decompose problem (5) – (8) into parallel or sequential problems of different classes, and what is the error of such a decomposition?

As mentioned above, the algebraic subsystem often approximates the behaviour of "fast" variables, the relaxation of which is much shorter than the relaxation of "slow" variables. That is, both subsystems can be considered as laws of dynamics on different time scales. Further, we can assume that system (5) – (8) can be approximately solved by splitting into "slow" and "fast" processes. In this case, numerical solution error consists of the error associated with the difference approximation of the derivatives, and the error of time scales decomposition (splitting). Let us consider different options to split problem (5) – (8).

1) Two-step scheme.

First, the dynamic subproblem is solved for fixed values of "fast" variables:

$$y^k - y^{k-1} - \tau g\left(y^k, z_1^{k-1}, z_2^{k-1}\right) = 0. \tag{15}$$

When value of y^k is found, we solve the optimization subproblem:

$$\left[z_1^k, z_2^k\right] = \arg\min_{z_1, z_2} G\left(y^k, z_1, z_2\right), \tag{16}$$

which can be rewritten considering (8) as follows:

$$\left[z_1^k, z_2^k\right] = \arg\min_{z_1, z_2, \lambda} \left[G\left(y^k, z_1, z_2\right) + \lambda(y^k + z_1 + z_2 - 1)\right]. \tag{17}$$

The value of y^k is constant in equation (11). The first step of the scheme solves a one-dimensional problem (calculating y^k), and the second step solves a three-dimensional problem (calculating z_1, z_2 and λ). The differences in the computational speed are negligible in this particular model problem. However, with an increase in the dimension, it is most likely that there exists an advantage of using splitting schemes.

The sequence of steps is insignificant for estimating the value of y. However, as our calculations show, the second step ensures that condition (8) is satisfied; therefore, the splitting error is mainly related to the first step.

2) Three-step scheme.

The first step is the same as in the previous scheme, but the obtained value of y is intermediate:

$$y^{k-1/2} - y^{k-1} - \tau g(y^{k-1/2}, z_1^{k-1}, z_2^{k-1}) = 0. \tag{18}$$

The intermediate value $y^{k-1/2}$ is used to solve the extremum problem:

$$\left[z_1^k, z_2^k\right] = \arg\min_{z_1,z_2,\lambda} \left[G(z_1, z_2, y^{k-1/2}) + \lambda(y^{k-1/2} + z_1 + z_2 - 1)\right]. \tag{19}$$

Finally, values of z_1^k and z_2^k are used to correct the value of y:

$$y^k - y^{k-1} - \tau g(y^k, z_1^k, z_2^k) = 0. \tag{20}$$

On the one hand, the value of y^k is refined by adjusting the variables z; on the other hand, fulfilment of equation (3) is not guaranteed in this case.

Let us refer to scheme (13), (14) as the one-step scheme.

All mentioned schemes are basically different forms of the implicit Euler method. The expected order of approximation with respect to τ is 1, and results of direct computations presented below confirm this. The stability of numerical schemes for differential-algebraic systems was studied in the papers [27–31], where it was shown that simple difference approximations can be inappropriate. However, the proposed numerical schemes are stable, which is easy to show if we approximate variables z by Taylor series:

$$y^k - y^{k-1} - \tau\left[-\beta_0 y^k + \beta_1\left(z_1^{k-1} + \gamma_1(y^k - y^{k-1})\right) + \beta_2\left(z_2^{k-1} + \gamma_2(y^k - y^{k-1})\right)\right] = 0. \tag{21}$$

Here γ is a derivative $\partial z/\partial y$, which has no simple expression, but we can see that γ is non-positive for all values of y, for example, see Fig. 1 (due to equation (8)). Stability conditions of these difference schemes can be reduced to the following expression:

$$|1 + \tau(\beta_0 - \gamma_1\beta_1 - \gamma_2\beta_2)| \geq 1. \tag{22}$$

As long as γ_1 and γ_2 are both non-positive, the proposed numerical schemes are absolutely stable.

The accuracy of different schemes with respect to the value of y is compared in Fig. 3. The three schemes (joint solution and two splitting schemes) have an order of accuracy close to 1. In the optimization problem, the threshold error value $\varepsilon = \sum_{j=1}^{4}|f_j|$ is 10^{-3} for all cases. The average number of iterations required to ensure this error is 30–40 (but it sharply rise in the vicinity of $y = 1$). The splitting practically does not affect the behaviour of the error in determining the value of y.

However, the choice of the scheme affects the error in fulfilling condition (8). Fig. 4 shows behavior of this error in time (the grid step τ is 10^{-2}). The two-step scheme gives approximately the same error as the one-step scheme. The three-step scheme, as expected, gives a much larger error ε with the greatest deviation observed in the domain

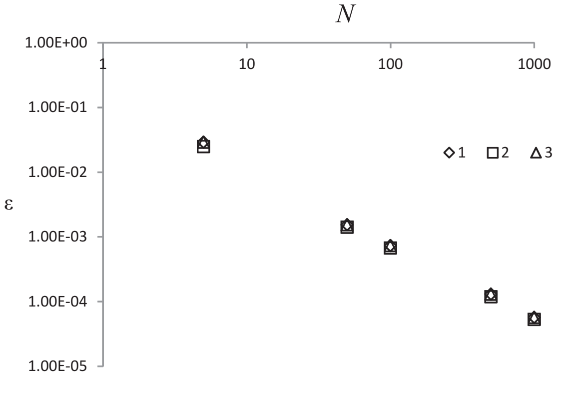

Fig. 3. Dependence of error on a number of time grid points (The legend shows a number of steps of the numerical scheme)

of the highest rate of change in y. With a decrease in the grid step, the error decreases. Thus, using a three-step scheme for the numerical solution of the model system does not give a significant advantage in the accuracy of determining y but gives a much larger violation of the constraint (however, this error is still much less than the threshold error). The two-step scheme turns out to be preferable.

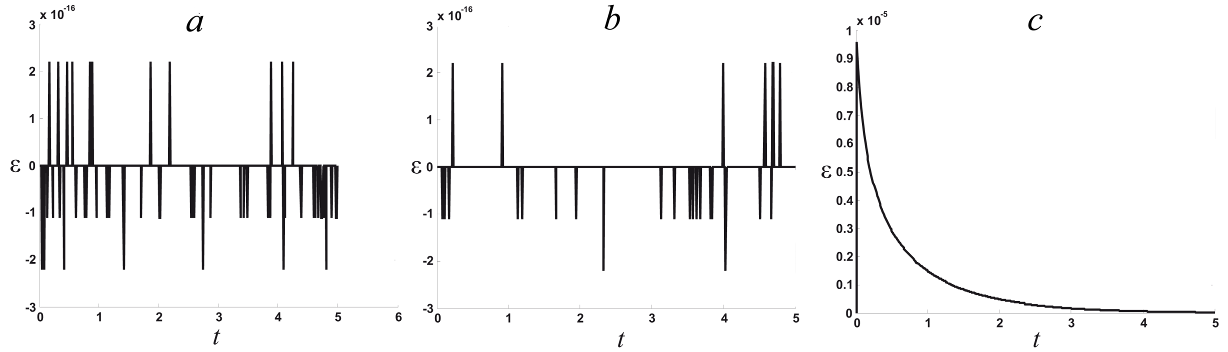

Fig. 4. Numerical error of filfilling equation (8) for different numerical schemes: (a) – one-step scheme; (b) – two-step sheme; (c) – three-step scheme

Most of the computational time for schemes with splitting is occupied by the solution of the optimization problem, so the difference between them is almost negligible. With an increase in the dimension of the problem, the difference in computational time increases as likely as not.

2. Oxidation of Methane (Multiplicative Case)

Let us consider a little more complex non-linear system. It is the isothermal oxidation of methane in the air. The empirical equation describing brutto-reaction rate is as follows:

$$\frac{dn_{CH_4}}{dt} = -\frac{A}{V} e^{-\frac{E_a}{R_g T}} n_{CH_4}^{m_1} n_{O_2}^{m_2}. \tag{23}$$

Here n is the amount of component, mol; A is the preexponential factor; E_a is the activation energy of the reaction; R_g is gas constant; T is the temperature; m is the kinetic order; V is the volume of the reactor. Values of coefficients are listed in Table 1 [32]. Reaction products are carbon oxides, hydrogen and water vapours. The material balance conditions for a closed system are the laws of conservation of elements:

$$n_{CH_4} + n_{CO_2} + n_{CO} = n_C, \tag{24}$$

$$4n_{CH_4} + 2n_{H_2} + 2n_{H_2O} = n_H, \tag{25}$$

$$2n_{O_2} + 2n_{CO_2} + n_{CO} + n_{H_2O} = n_O. \tag{26}$$

Table 1

Values of coefficients included in the kinetic equation of methane oxidation

Coeffcient	Dimensions	Value
A	m^3 mol$^{-(m_1+m_2-1)}$ s $^{-1}$	$8,83{\cdot}10^6$
E_a	J mol^{-1}	$121 \cdot 10^3$
R_g	J mol^{-1} K^{-1}	8,314
m_1	–	1
m_2	–	0,69

We suppose that nitrogen does not participate in chemical reactions. Equations (24) – (26) are linear, so they can be written in a simple matrix form: $\mathbf{An} = \mathbf{b}$, where $\mathbf{A}$ is a matrix of atom indexes, and $\mathbf{b}$ is a vector of amounts of chemical elements. Instead of kinetic equations for reaction products and intermediate species, we use the partial equilibrium approximation:

$$\min G(\mathbf{n}), \tag{27}$$

$$G(\mathbf{n}) = \sum_{j=2}^{N_s} \mu_j(\mathbf{n}) n_j, \tag{28}$$

$$\mathbf{An} = \mathbf{b}, \tag{29}$$

$$\mu_j(\mathbf{n}) = \mu_j^0 + \ln\left(\frac{n_j}{\sigma}\right), \forall j = 2...N_s. \tag{30}$$

Here G is Gibbs free energy, μ is the chemical potential of a mixture component, and σ is a sum of all components. The solution has physical sense only if the amounts of all components are non-negative. It can be shown that, as in the previous example, the function G has a logarithmic singularity on the boundary of the feasible domain, i.e. the extremum is always inside the domain (although it can be very close to the boundary) [26]. The amount of methane (we suppose that methane has index 1) is included in the problem of minimizing G as a parameter.

Note that kinetic equation (23) is suitable only for the complete combustion of methane. For example, with a lack of oxygen, methane cannot react with water vapour and carbon dioxide, as it happens, for example, in reforming processes. To describe these reactions, additional kinetic equations are required.

The one-step scheme equations are as follows:

$$n_{CH_4}^k - n_{CH_4}^{k-1} + \tau K \left(n_{CH_4}^k\right)^{m_1} \left(n_{O_2}^k\right)^{m_2} = 0, \tag{31}$$

$$\mu_j\left(\mathbf{n}^k\right) + \sum_{i=1}^{N_e} \lambda_i^k a_{ij} = 0, \forall j = 2...N_s, \tag{32}$$

$$\sum_{j=1}^{N_s} a_{ij} n_j^k - b_i = 0, \forall i = 1...N_e. \tag{33}$$

Two-step scheme is written by analogy with (15) – (17).

1) The kinetic subproblem is solved to determine the amount of burned methane:

$$n_{CH_4}^k - n_{CH_4}^{k-1} + \tau K \left(n_C^k H_4\right)^{m_1} \left(n_{O_2}^{k-1/2}\right)^{m_2}, \tag{34}$$

$$n_{O_2}^{k-1/2} - n_{O_2}^{k-1} + 2\tau K \left(n_{CH_4}^k\right)^{m_1} \left(n_{O_2}^{k-1}\right)^{m_2}. \tag{35}$$

The calculated amount of oxygen $n_{O_2}^{k-1/2}$ is auxiliary for the kinetic subproblem. At the second step, the amount of oxygen is reduced to the quasi-equilibrium value $n_{O_2}^k$.

We can suggest another option for the first step. Assuming that the oxygen concentration changes slowly, we can reduce the problem to the linear equation:

$$n_{CH_4}^k - n_{CH_4}^{k-1} + \tau K \left(n_{CH_4}^k\right)^{m_1} \left(n_{O_2}^{k-1}\right)^{m_2} = 0. \tag{36}$$

2) The optimization problem is solved at the second step:

$$\mu_j\left(\mathbf{n}^k\right)+\sum_{i=1}^{N_e}\lambda_i^k a_{ij}=0,\forall j=2...N_s, \quad (37)$$

$$\sum_{j=2}^{N_s}a_{ij}n_j^k - b_i - a_{j1}n_{CH_4}^k=0,\forall i=1...N_e. \quad (38)$$

In the three-step scheme, the amount of methane is corrected by solving the kinetic equation with the fixed oxygen amount:

$$n_{CH_4}^k - n_{CH_4}^{k-1} + \tau K\left(n_{CH_4}^k\right)^{m_1}\left(n_{O_2}^{k-1}\right)^{m_2}. \quad (39)$$

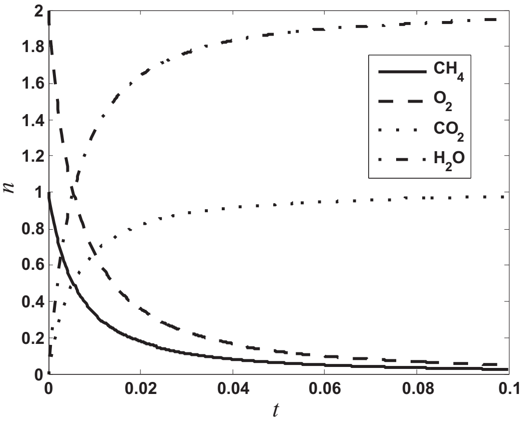

Fig. 5. Dependence of gas mixture composition on time (numerical solution, one-step scheme)

Figs. 5 and 6 show a numerical solution obtained using the one-step scheme ($\tau = 10^{-3}$). Free energy of the system G decreases monotonically, following thermodynamic laws (in this case, detailed balance conditions are not fulfilled, but global equilibrium is close enough to the boundary of the feasible domain where $n_{CH_4} \approx 0$).

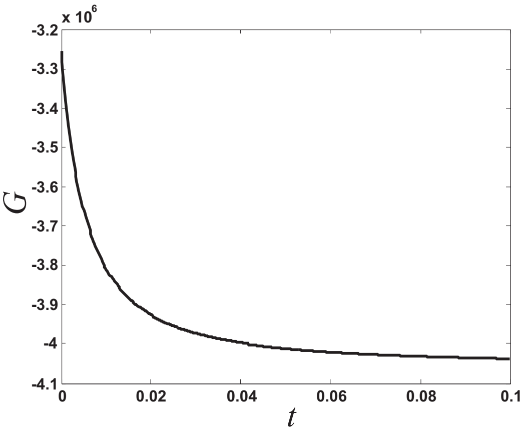

Fig. 6. Dependence of gas mixture free energy G on time (numerical solution, one-step scheme)

Fig. 7 shows the accuracy of different schemes related to methane amount. Interestingly, option № 2 has the worst accuracy. Accuracy even does not improve with decrease in the time step. Apparently, the use of an auxiliary variable (the intermediate amount of oxygen) only increases the splitting error due to nonlinearity. The other three options give close results with an approximation order close to unity. Fig. 8 shows the numerical error of fulfilment of (24) – (26). Option № 4 (three-step scheme) gives the lowest accuracy, which is consistent with the results obtained in the previous section.

Various splitting alternatives were used for the calculations. Option № 1 is the one-step scheme with a joint solution of the kinetic equation and optimization subproblem. Option № 2 is the two-step splitting scheme that solves a nonlinear equation for chemical kinetics. Option № 3 is the two-step scheme in which the chemical kinetics equation is solved using a linear approximation. Finally, option № 4 is the three-step scheme, in which both kinetic problem steps use linear approximation (34). In the initial state, $n_{CH_4} = 1$, $n_{O_2} = 2$, $n_{N_2} = 8$, $n_{CO} = n_{H_2} = n_{CO_2} = n_{H_2O} = 0$. The values of μ^0 were taken from the reference book [33].

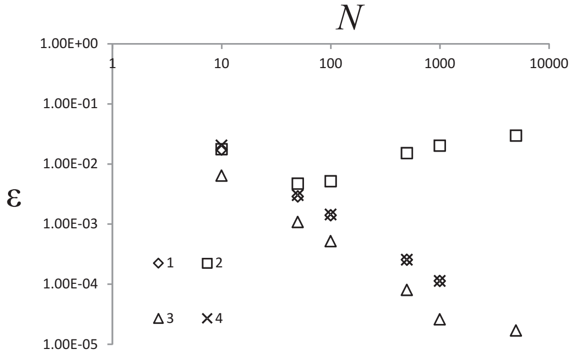

Fig. 7. Dependence of numerical error of the solution to equations (21) – (28) on number of time grid point (legend shows option number of numerical scheme)

Computational time is close for all compared numerical schemes. Option № 3 can be called the best scheme, which gives the least error in calculating the variables and preserves the fulfilment of the constraints.

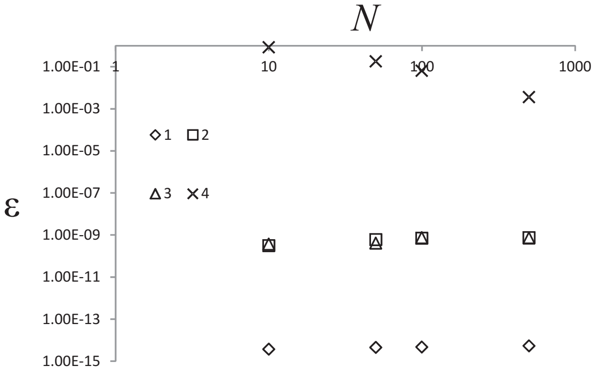

Fig. 8. Dependence of numerical error of fulfilling equations (24) – (26) on the number of time grid points for different numerical schemes (legend shows the option number of a numerical scheme)

We can propose other options for constructing numerical schemes for differential equations with a partial equilibrium operator. For example, the kinetic and optimization subsystems can be solved iteratively: the results of solving one subsystem are substituted into another until the solution converges. For the considered examples, iterations have little effect on the accuracy, and the convergence turns out to be quite fast, so these options are not presented here. Newton's method for solving nonlinear equations systems can be less effective when considering large dimension or heterogeneous systems: in this case, it is better to solve the optimization subproblem, first of all, using methods developed for chemical thermodynamics, such as RAND and its modifications [34], interior-point methods [24], etc. Then it is possible to optimize the numerical solution of equations (2) – (4), entrusting the subsystems to different solvers. In our previous works [15, 35], we used similar methods in the fuel processing modelling.

The examples given in this paper are of limited importance since they are low dimensional and have a small number of connections between subsystems. In addition, the example problems have properties that greatly simplify their solution. Namely, the extremum of G is unique, and its position continuously depends on the parameters of the problem (however, note that these conditions are usually valid for reacting systems). It is interesting to study similar problems for open systems (for example, stationary chemical reactors and systems with diffusion). Numerical schemes for solving such problems will be considered in the following works.

Conclusion

The paper compares numerical schemes for solving systems that include ordinary differential equations and equations of extremum of a convex function. Such systems often arise in the study of complex chemical reactions dynamics. The characteristics of computational schemes based on the decomposition (splitting) are investigated using two model systems. The calculation results show that the most suitable numerical scheme for systems with partial equilibrium is a two-step scheme, in which the dynamic and optimization subproblems are solved separately. In this case, the solution to the dynamic subsystem gives additional constraints for the optimization subproblem. This scheme allows fulfilling the constraints while maintaining the order of accuracy (in the considered examples, the order is close to 1).

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References

1. Gorban A.N., Karlin I.V. Method of Invariant Manifolds for Chemical Kinetics. *Chemical Engineering Science*, 2003, vol. 58, pp. 4751–4768. DOI: 10.1016/j.ces.2002.12.001
2. Maas U., Pope S.B. Simplifying Chemical Kinetics: Intrinsic Low-Dimensional Manifolds in Composition Space. *Combustion and Flame*, 1992, vol. 88, pp. 239–264. DOI: 10.1016/0010-2180(92)90034-M
3. Chen Yulin, Chen Jyh-Yuan. Towards improved Automatic Chemical Kinetic Model Reduction Regarding Ignition Delays and Flame Speeds. *Combustion and Flame*, 2018, vol. 190, pp. 293–301. DOI: 10.1016/j.combustflame.2017.11.024
4. Turanyi T. Applications of Sensivity Analysis to Combustion Chemistry. *Reliability Engineering and System Safety*, 1997, vol. 57, no. 1, pp. 41–48. DOI: 10.1016/S0951-8320(97)00016-1
5. Prigogine I. *Introduction in Thermodynamics of Irreversible Processes.* Izhevsk, Regular and Chaotic Dynamics, 2001. (in Russian)
6. Keck J.C. Rate-Controlled Constrained-Equilibrium Theory of Chemical Reactions in Complex Systems. *Progress in Energy and Combustion Science*, 1990, vol. 30, pp. 125–154. DOI: 10.1016/0360-1285(90)90046-6
7. Jones W.P., Rigopoulos S. Reduction of Comprehensive Chemistry Via Constraint Potentials. *Proceedings of the Combustion Institute*, 2005, vol. 30, pp. 1325–1331. DOI: 10.1016/j.proci.2004.08.198
8. Popkov Yu.S. Positive Dynamic Systems with Entropic Operator. *Automation and Remote Control*, 2003, no. 3, pp. 104–113. (in Russian)
9. Popkov Yu.S. Basics of a Theory of Dynamic Systems with Entropic Operator and Its Applications. *Automation and Remote Control*, 2006, no. 6, pp. 75–105. (in Russian)
10. Koukkari P., Pajarre R. Introducing Mechanistic Kinetics to the Lagrangian Gibbs Energy Calculation. *Computers and Chemical Engineering*, 2006, vol. 30, pp. 1189–1196. DOI: 10.1016/j.compchemeng.2006.03.001
11. Kaganovich B.M., Filippov S.P., Keiko A.V., Shamanskii V.A. Thermodynamic Models of Extreme Intermediate States and their Applications in Power Engineering. *Thermal Engineering*, 2011, vol. 58, pp. 143–152. DOI: 10.1134/S0040601511020054
12. Messerle A.V., Messerle V.E., Ustimenko A.B. Plasma Thermochemical Preparation for Combustion of Pulverized Coal. *High Temperature*, 2017, vol. 55, pp. 352–360. DOI: 10.1134/S0018151X17030142
13. Donskoi I.G. Mathematical Modeling of the Reaction Zone of a Shell-Prenflo Gasifier with the Use of the Models of Sequential Equilibrium. *Solid Fuel Chemistry*, 2016, vol. 50, pp. 191–196. DOI: 10.3103/S0361521916030034
14. Currier N.G., Hyams D.G. A Hybrid Method for Flows in Local Chemical Equilibrium and Nonequilibrium. *50th AIAA Aerospace Sciences Meeting including the new Horizon Forum and Aerospace Exposition*, Nashville, Tennessee, 2012, pp. 2012–1239. DOI: 10.2514/6.2012-1239
15. Rodrigues R. *Modelagem Cinetics e de Equilibrio Combunadas para Simulacao de Processes de Gaseificacao.* Tese de Doutorado, Porto Alegre, 2015.
16. Koniavitis P. Rigopoulos S., Jones W.P. Reduction of a Detailed Chemical Mechanism for a Kerosene Surrogate Via RCCE-CSP. *Combustion and Flame*, 2018, vol. 194, pp. 85–106. DOI: 10.1016/j.combustflame.2018.04.004

17. Lovas T., Navarro-Martinez S., Rigopoulos S. On the Adaptively Reduced Chemistry in Large Eddy Simulations. *Proceedings of the Combustion Institute*, 2011, vol. 33, pp. 1339–1346. DOI: 10.1016/j.proci.2010.05.089
18. Zhuyin Ren, Zhen Lu, Yang Gao, Tianfeng Lu, Lingyun Hou. A Kinetics-Based Method for Constraint Selection in Rate-Controlled Constrained Equilibrium. *Combustion Theory and Modelling*, 2017, vol. 21, pp. 159–182. DOI: 10.1080/13647830.2016.1201596
19. Hiremath V., Pope S.B. A Study of the Rate-Controlled Constrained Equlibrium Dimension Reduction Method and its Different Implementations. *Combustion Theory and Modelling*, 2013, vol. 17, pp. 260–293. DOI: 10.1080/13647830.2012.752109
20. Mohammad Janbozorgia, Wang Haib. Bottom-Up Modeling Using the Rate-Controlled Constrained-Equilibrium Theory: The n-Butane Combustion Chemistry. *Combustion and Flame*, 2018, vol. 194, pp. 223–232. DOI: 10.1016/j.combustflame.2018.04.026
21. Koniavitis P., Rigopoulos S., Jones W.P. A Methodology for Derivation of RCCE-Reduced Mechanisms Via CSP. *Combustion and Flame*, 2017, vol. 183, pp. 126–143. DOI: 10.1016/j.combustflame.2017.05.010
22. Kaganovich B.M., Keiko A.V., Shamansky V.A., Shirkalin I.A., Zarodnyuk M.S. *Technology of Thermodynamic Modelling. Reduction of Dynamic Models to Static Model.* Novosibirsk, Nauka, 2010 (in Russian)
23. Neron A., Lantagne G., Marcos B. Computation of Complex and Constrained Equilibria by Minimization of the Gibbs Free Energy. *Chemical Engineering Science*, 2012, vol. 82, pp. 260—271. DOI: 10.1016/j.ces.2012.07.041
24. Pope S.B. Gibbs Function Continuation for the Stable Computation of Chemical Equilibrium. *Combustion and Flame*, 2004, vol. 139, pp. 222–226. DOI: 10.1016/j.combustflame.2004.07.008
25. Scoggins J.B., Magin T.E. Gibbs Function Continuation for Linearly Constrained Multiphase Equilibria. *Combustion and Flame*, 2015, vol. 162, pp. 4514–4522. DOI: 10.1016/j.combustflame.2015.08.027
26. Feinberg M. Necessary and Sufficient Conditions for Detailed Balancing in Mass Action Systems of Arbitrary Complexity. *Chemical Engineering Science*, 1989, vol. 4, pp. 1819–1827. DOI: 10.1016/0009-2509(89)85124-3
27. Chistyakov V.F., Tairov E.A., Chistyakova E.V., Levin A.A. On Decomposition of Difference Schemes for Numerical Solution of Differential Algebraic Equations. *Bulletin of the South Ural University. Series: Mathematical Modelling, Programming and Computer Software*, 2012, vol. 11, pp. 88–100.
28. Chistyakov V.F. Preservation of Stability Type of Difference Schemes when Solving Stiff Differential Algebraic Equations. *Numerical Analysis and its Applications*, 2011, vol. 4, pp. 363–375. DOI: 10.1134/S1995423911040082
29. Bulatov M.V., Chistyakova E.V. Numerical Solution of Integro-Differential Systems with a Degenerate Matrix Multiplying the Derivative by Multistep Methods. *Differential Equations*, 2006, vol. 42, pp. 1317–1325. DOI: 10.1134/S0012266106090102
30. Bulatov M.V., Tygliyan A.V., Filippov S.S. A Class of One-Step One-Stage Methods for Stiff Systems of Ordinary Differential Equations. *Computational Mathematics and Mathematical Physics*, 2011, vol. 51, pp. 1167–1180. DOI: 10.1134/S0965542511070050
31. Bulatov M.V., Solovarova L.S. On the Loss of L-Stability of the Implicit Euler Method for a Linear Problem. *The Bulletin of Irkutsk State University. Series: Mathematics*, 2015, vol. 12, pp. 3–11.
32. Snegirev A.Yu. Perfectly Stirred Reactor Model to Evaluate Extinction of Diffusion Flame. *Combustion and Flame*, 2015, vol. 162, pp. 3622–3631. DOI: 10.1016/j.combustflame.2015.06.019
33. McBride B.J., Zehe M.J., Gordon S. *NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species.* Cleveland, Glenn Research Center, 2002.

34. Tsanas C., Stenby E.H., Wei Yan. Calculation of Multiphase Chemical Equilibrium by the Modified RAND Method. *Industrial and Engineering Chemistry Research*, 2017, vol. 56, pp. 11983–11995. DOI: 10.1016/j.ces.2017.08.033

35. Donskoy I.G., Shamansky V.A., Kozlov A.N., Svishchev D.A. Coal Gasification Process Simulations Using Combined Kinetic-Thermodynamic Models in One-Dimensional Approximation. *Combustion Theory and Modelling*, 2017, vol. 21, pp. 529–559. DOI: 10.1080/13647830.2016.1259505

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ДЕКОМПОЗИЦИЯ ЗАДАЧИ ПРИ ЧИСЛЕННОМ РЕШЕНИИ ДИФФЕРЕНЦИАЛЬНО-АЛГЕБРАИЧЕСКИХ СИСТЕМ ДЛЯ ХИМИЧЕСКИХ РЕАКЦИЙ С ЧАСТИЧНЫМИ РАВНОВЕСИЯМИ

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В работе рассматриваются две простые системы дифференциально-алгебраических уравнений, которые появляются при исследовании задач химической кинетики с частичными равновесиями: часть переменных определяется из условия argmin для некоторой функции состояния системы, которая зависит от всех переменных задачи. Для такой постановки можно записать дифференциально-алгебраическую систему уравнений, в которой алгебраическая подзадача выражает условия минимальности функции состояния в каждый момент времени. При численном решении удобно провести декомпозицию (расщепление) задачи, т.е. решать динамическую и оптимизационную задачи последовательно. В работе на двух примерах исследуется применимость такой декомпозиции: определяется сходимость и порядок точности численного метода, а также предложены другие варианты декомпозиции. Показано, что численное решение расщепленной системы уравнений имеет такой же порядок точности, как и численное решение совместной задачи. Выполнение ограничений удовлетворяется с достаточной точностью, если временной шаг численного метода заканчивается решением оптимизационной задачи. Полученные результаты могут быть использованы при разработке численных алгоритмов для решения более сложных задач химической кинетики.

Ключевые слова: дифференциально-алгебраические системы; оптимизация; численные методы.

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