METHOD OF SPLINE-INTEGRATION: APPLICATION IN CHEMICAL KINETIC EQUATIONS

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Abstract. The work is dedicated to the solution of the chemical kinetic equations that are applied in the combustion process modeling, represented by ODE’s that are complex and stiff. The $\theta$-method with the transformation of ODE’s in algebraic equations and the application of Newton-Rafson method are traditionally used for its solution. In this work the spline-integration method by the second power polynomials without correction (SK) and with correction (CK) is proposed instead of the $\theta$-method. Its calculate algorithms are presented. The precision and computational volume indicators had been elaborated. The simulations for the reacting medias: “H2+O2” and “Ar+C2H2+CH4+NH3” had shown that the spline-integration method (in CK version) is at least in two times more economic than the $\theta$-method. But SK version for the great integration intervals generates the oscillations in the solution increasing of computational volume.

Keywords: mathematical modeling, stiff equations, spline-integration, combustion.

In the combustion process modeling, a important part belongs to the chemical kinetic equations that describe the substance transformations in the reacting medias (Oran & Boris, 1987). As a rule, these medias are complex and include many species (up to 100) between which occur hundreds chemical reactions. Therefore these equations (ODE’s type) are sufficiently complicated. In order to solve it the universal (relatively of the reacting media) algorithms and software’s (for example, Kee et al, 2000; Krioukov et al, 1997) with transformation of symbolic form of reactions in chemical kinetic equations are used. The modern computers easily solve these equations for one-dimensional problems. But simulation of the combustion processes in real units (combustion chambers, gas generators) demands as a rule two- or three- dimensional approaches. In this case the computational volume becomes gigantic.

For example, Blom & Verwer (2000) used only 26 species and 55 reactions (but in the 3D-approach) and had involved simultaneously the computational resources of several universities and research institutions for the modeling of the NOx formation processes in the atmosphere. Therefore to search and to apply the new numerical methods (or known methods, but still not applied in the universal software’s) in order to reduce the calculation volume is an important problem. It is know that the method of Gear (1971) or the $\theta$-method (Pirumov & Kamzolov, 1966) is already used for the solution of the chemical kinetic equations during several decades. In present paper the method of spline-integration (Sallam, 2000) together with $\theta$-method, applying them into the invariant software, are searched (Krioukov et all, 1977) for the conditions of adiabatic reactor. The chemical kinetic equations are presented in the exponential form:

$$\frac{d\gamma_j}{dt} = -e^{\gamma_i} \sum_j \nu_{ij} \Omega_j + \sum_q \sum_j \nu_{pj} \Omega_j \equiv f_{\gamma_i}; \quad i, q = 1, ..., n_s; \quad j = 1, ..., m_r; \quad (1)$$

where: $\Omega_j = k_j(P / R_0 T)^{r_j} \exp \left( -\sum_p n_{pj} T_p \right); \quad \gamma_i = \ln(r_i); \quad P$ - pressure; $R_0$ - universal gas constant; $t$ - time; $m_r$ - index of participation in reaction $j$ of catalytic particle $M$ ($m_r = 1$ if particle $M$ participates in $j$-th reaction; $m_r = 0$ - in the absence of particle $M$); $r_i$ - molar fraction of $i$-th species; $\nu_{ij}, n_{pj}$ - stoichiometric coefficients of reactions; $n_s$ - total substance number; $m_r$ - total reaction number.
One of the equations (that describes the predominant species alteration) is substituted by the normalization relation:

$$F_x \equiv 1 - \sum_i e^{-\gamma_i} = 0$$

(2)

Also the energy equation was enclosed in the model that is presented in this work by form:

$$F_T = T - T_{aq} - \sum_q \left( I_p \mu_q - H_{aq}^q \right) r_q \left/ \sum_q C_{aq}^q r_q \right. = 0 \quad q = 1, \ldots, n_i;$$

(3)

where $I_p$ - mass enthalpy of the propellant; $H_{aq}^q$, $C_{aq}^q$ - the molar enthalpy and specific heat of reference of $q$-th species; $T_{aq}$ - the reference temperature (Krioukov et al., 1997).

Then the system to compare the numerical methods composes for $(n_s - 1)$ ordinary differential equations and two algebraic equations. The unknown variables are $\gamma$ and $T$.

2. Integration of the chemical kinetic equations

2.1 Description of $\theta$-method and algorithm of solution

The system of ODE’s (1) is stiff and can only be solved by implicit methods (Oran & Boris, 1987). The method of Gear (1971) is the most popular between them. In our model the method of Pirumov & Kamzolov (1966) or $\theta$-method is used. In accordance with this method the Eq. (1) are presented in the form of finite differences:

$$\frac{\gamma_i^{n+1} - \gamma_i^n}{h} = s f_i(\gamma_i^n) + (1 - s) f_i(\gamma_i^{n+1})$$

(4)

where: $n$ is step number; $h$ – integration step; $s$ – approximation parameter.

Attributing the value $s = 0.5$ we get the trapezoidal method. The scheme of Pirumov uses the value of $s = 0.4$ that allows to diminish the initial data errors. Considering the application of the Newton’s method the Eq. (4) lead to the transcendental equations:

$$F_i^{n+1} \equiv \gamma_i^{n+1} - \gamma_i^n - h \left( s f_i(<\gamma_i^n>) + (1 - s) f_i(<\gamma_i^{n+1}>) \right) = 0$$

(5)

where: $<\gamma_k>$ $\equiv$ $\gamma_1$, $\gamma_2$, $\ldots$, $\gamma_{n_s}$; $\gamma_i^n$, $\gamma_i^{n+1}$ are values of $\gamma$ in beginning and in end of step $h$.

It is observed that the Eqs. (2, 3) already are ready to apply the Newton’s method. The values $\gamma_i^{n+1}$, $T^{n+1}$ are unknown in each integration step and are determined by the equations (with some null approach of $\gamma_i^{n+1}$, $T^{n+1}$):

$$\begin{bmatrix}
\frac{\partial F_i}{\partial x_k}
\end{bmatrix} \Delta x_k^{n+1} = - F_i^m \quad x = \gamma, T; \quad i, k = 1, \ldots, (n_s + 1)$$

(6)

where $m$ is iteration number.

During of integration the Jacobian calculated once is used for some steps (saving scheme) reducing the computational volume. In the algorithm are used the calculation indicators:

- the number of iterations $(m_n)$ in the $n$-th step;
- the maximum difference between the iterations $\max_{i} \left| \Delta x_i^{n+1}/x_i^n \right| ;$
- the maximum alteration of $x_i$ in a step $\max_{i} \left| (x_i^{n+1} - x_i^n)/x_i^n \right| ;$
- the number of steps $(I_J)$ without recalculation of the Jacobian.

The control parameters of the integration step (and therefore of the volume and precision of calculations) are:

- the admissible alteration ($\Delta_x$) of the unknowns to increase the step;
- the admissible error ($\varepsilon_x$) to conclude the iterations in step;
- the admissible maximum number of iterations ($m_n$);
- the admissible minimum number ($J_2$) of index $I_J$ to increase the step;
- the admissible iteration number \( (m_a) \) to save the Jacobian.

The iterative process in a step is concluded: if \( m_n > m_p \) or \( \max_i \left| \Delta x_i^{n+1} / x_i^n \right| < \varepsilon_N \).

The Jacobian is recalculated in the \( n \)-th step if \( m_n > m_a \).

The integration step increases: if \( an mm > m_n \) and \( \max_i \left| \Delta x_i^{n+1} / x_i^n \right| < \varepsilon_N \) and \( I_j > J_2 \) and \( \max_i \left| \left( x_i^{n+1} - x_i^n \right) / x_i^n \right| \leq \Delta_x \).

The integration step diminishes: if \( \max_i \left| \Delta x_i^{n+1} / x_i^n \right| > 3\varepsilon_N \) or \( \max_i \left| \left( x_i^{n+1} - x_i^n \right) / x_i^n \right| > 3\Delta_x \).

In other cases the integration step is conserved.

For \( \theta \)-method the following control parameters had been established: \( \Delta_x = 0.005 \); \( \varepsilon_N = 10^{-5} \); \( m_p = 12 \); \( J_1 = 3 \); \( m_a = 7 \) that were chosen by the mathematical experiments (Krioukov et al., 1997), to know:
- the values \( \Delta_x > 0.005 \) causes the significant calculation errors, but if \( \Delta_x < 0.005 \) increases the calculation volume;
- the same effects had shown for \( \varepsilon_N > 10^{-5} \) and \( \varepsilon_N < 10^{-5} \). Besides for \( \varepsilon_N > 10^{-5} \) the integration step size can oscillate increasing the calculation volume;
- the value \( m_p \) in interval \( m_p = 8...16 \) not affect the calculation volume. But out of this interval, this volume rises because of increase of the calculations: of Jacobian (\( m_p < 8 \)) or of right parts of the kinetic chemistry equations (\( m_p > 16 \)). Therefore, the value \( m_p = 12 \) was chosen;
- the same reasons determine the choice of value \( m_a \) that does not influence in the calculation volume in the interval: \( 5 < m_a < 9 \).

In the algorithm the analytical calculation of the derivatives of Jacobian is performed. In this case the iterative process is converged more quickly and the congealed Jacobian is used in a more number of integration steps than in version of numerical calculation of derivatives. Moreover, the analytical determination of derivatives for the exponential form of equations demands minor calculation volume. The partial derivatives of \( \gamma_k, T \) for the system (1-3) are:

\[
\frac{\partial F_i}{\partial t_k} = \delta_i^k + h \cdot (1 - s) \left[ e^{\gamma_i} \sum_j v_{ij} (\delta_k^j - n_k) \Omega_j - \sum_p \sum_j v_{ij} n_{ij} \Omega_j \right] \quad i, k = 1, ..., n_i; \quad j = 1, ..., 2m_c; \quad (7)
\]

\[
\frac{\partial F_i}{\partial T} = e^{-\gamma_k}; \quad \frac{\partial F_T}{\partial T} = 1; \quad (8)
\]

\[
\frac{\partial F_i}{\partial T} = h \cdot (1 - s) \left[ e^{\gamma_i} \sum_j v_{ij} \Omega_j \left( \frac{n_j - \overline{n_j}}{T} + \frac{E_j}{R_o T^2} \right) - \sum_p \sum_j v_{ij} \Omega_j \left( \frac{n_j - \overline{n_j}}{T} + \frac{E_j}{R_o T^2} \right) \right] \quad (9)
\]

\[
\frac{\partial F_i}{\partial t_k} = \left( \overline{I}_p \mu_k - H_k \overline{r}_p \right) r_k - C_{pp}^{\overline{r}} \left( T - T_{ap} \right) \sum_q C_{pp}^{\overline{r}} \overline{r}_q = 0 \quad k, q = 1, ..., n_i; \quad (10)
\]

where, \( \delta_i^k \) - Kronecker symbol.

For the increment \( (\Delta x_i^{n+1}) \) calculation is used the preliminary LU-decomposition of Jacobian.

2.2 Method of spline-integration

In the method of spline-integration by quadratic polynomials the variables \( \gamma_i \) in each integration step \( (\tau_n, ..., \tau_{n+1}) \) are presented by expression:

\[
\gamma_i^{n+1}(\tau) = \tilde{a}_i^{n+1} + \tilde{b}_i^{n+1} \tau + \tilde{c}_i^{n+1} \tau^2
\]

or normalizing:

\[
\gamma_i^{n+1}(\tilde{\tau}) = a_i^{n+1} + b_i^{n+1} \tilde{\tau} + c_i^{n+1} \tilde{\tau}^2
\]
where: \( \tau = (\tau - \tau_0)/h_n; \quad 0 \leq \tau \leq 1 \); and \( \gamma^{n+1}_i(0) = \gamma^n_i; \quad \gamma^{n+1}_i(1) = \gamma^{n+1}_i \) - values of \( \gamma_i \) in beginning and end of the step; \( a^{n+1}_i, b^{n+1}_i, c^{n+1}_i \) - polynomial coefficients to determine.

The two versions of the method are analyzed in this work.

SK - Integration without correction. We admit that in the boundaries between steps the variables \( \gamma_i \) and its derivatives are equal:

\[
\frac{\partial \gamma_i^{n+1}(1)}{\partial \tau} = \frac{\partial \gamma_i^{n+1}(0)}{\partial \tau} ;
\]

Using Eq. (13) we easily obtain:

\[
a^{n+1}_i = a^n_i + b^n_i + c^n_i ; \quad b^{n+1}_i = (b^n_i + 2c^n_i) \frac{h_{n+1}}{h_n};
\]

i.e. beginning the calculation in the interval \((\tau_i, ..., \tau_{i+1})\) the values \( a^{n+1}_i, b^{n+1}_i \) are known. Then in the resolution by the spline-integration method, only the coefficients \( c^{n+1}_i \) are unknown and the Eq. (1) can be written in the form:

\[
\frac{d(a^n_i + b^n_i \tau + c^n_i \tau^2)}{d\tau} = h_{n+1} f_i(\gamma_k) = h_{n+1} f_i(\gamma_{k+1})
\]

(15)

where \( h_{n+1} = \tau_{i+1} - \tau_i; \quad i = 1, ..., n_i \) (except \( i = z \)). Accepting that the Eq. (15) will be satisfied in the points \( \tau_{n+1} \) (i.e. \( \tau_{n+1} = 1 \)), deriving its terms to the left and reducing the terms to the right, we obtain the system:

\[
F^{n+1}_i = b^{n+1}_i + 2c^{n+1}_i - h_{n+1} f_j(\gamma^{n+1}_j) = 0
\]

(16)

that is necessary to solve in each step together with the Eqs. (2,3). To solve the system of Eqs. (16), the Newton-Rafson method is also used and the partial derivatives are calculated for the Jacobian:

\[
\frac{\partial F_i}{\partial c_k} = 2\delta_i^k + h_{n+1} \left[ e^{\gamma_i} \sum_j \gamma_{ji} (\delta_i^j - n_{ji}) \Omega_j - \sum_p \sum_j \gamma_{pi} n_{pj} \Omega_j \right]
\]

(17)

The remaining derivatives do not modify therefore \( \frac{\partial \gamma_i}{\partial c_k} = \delta_i^k \). The initial values to integrate in the step \((n+1)\) are determined by formulas:

\[
c^{n+1}_i = c^n_i \left( h_{n+1}/h_n \right)^2
\]

(18)

going on the second derivative of interval \((\tau_i, ..., \tau_{i+1})\) for interval \((\tau_i, ..., \tau_{i+2})\).

CK - Integration with the correction. In this version after solution of the Eqs. (16) by SK-version and determination of the values \( b^{n+1}_i, c^{n+1}_i, \gamma^{n+1}_i \) the correction of coefficients \( b^{n+2}_i \) is accomplished. Instead of Eq. (14) are used the coefficients \( b^{n+2}_i \) that calculate executing the interpolation for points \( \gamma^{n-1}_i, \gamma^n_i, \gamma^{n+1}_i \). In this case we obtain:

\[
b^{n+2}_i = (q_i + 2s_i) \left( h_n + h_{n+1} \right)/h_{n+2}.
\]

(19)

where: \( s_i = \left( \frac{h_n (\gamma^{n-1}_i - \gamma^n_i) - \gamma^n_i + \gamma^{n+1}_i}{h_n^2 + h_n h_{n+1}} \right) \left( \frac{h_n (h_n + h_{n+1})}{h_n^2 + h_n h_{n+1}} \right) \); \( q_i = (\gamma^n_i - \gamma^{n+1}_i - s_i h_n^2)/h_n \).

The value \( c^{n+2}_i \) for the first iteration in step \( h_{n+2} \) is determined by Eq. (18) substituting \( n \) for \((n+1)\).

3. Numerical simulations

3.1. Reacting medias and the precision and computational volume indicators

To compare the spline-integration method and \( \theta \)-method the two reacting medias had been established:

a) \( O_2 \) and \( H_2 \) with species: \( H, H_2, O_2, HO, OH, HO_2 \) and 10 elementary reactions (LEEDS, 2000) occurred between them with the conditions: oxidizing excess coefficient \( \alpha_{ox} = 2.016; P = 1 \text{atm} \quad T_{in} = 1000 \text{K}; \)
b) enriched air (60% of O$_2$ and 40% of N$_2$) and mixture C$_2$H$_2$ (10%) + CH$_4$ (80%) + NH$_3$ (10%) with 30 substances: N, N$_2$, NO, NO$_2$, NH, NH$_2$, NH$_3$, HNO, H, H$_2$, O, O$_2$, H$_2$O, O, CO, OH, HCO, H$_2$CO, HO$_2$, CO$_2$ among others and 121 elementary reactions (LEEDS, 2000) in conditions: $\alpha_{ox} = 1; P = 1$ atm $e$ $T_m = 1400K$.

In Figure (1) for the reacting media (b) are shown the temperature and the alteration of reagents O$_2$, N$_2$, C$_2$H$_2$, CH$_4$, NH$_3$ in the adiabatic conditions. At first the acetylene that is not steady is destroyed. As a result (until $\tau = 0.2 ms$) the species O$_2$ slightly diminishes and increases $T$ (less than 1700K) forming thus the intermediate substances H$_2$, H, CH$_3$, CH$_2$, etc (as products of pyrolysis C$_2$H$_2$). With the temperature increase the methane (in interval $\tau = 0.2...0.45 ms$) starts to react with O$_2$ forming H$_2$O, CO and H$_2$. When the temperature is approached to $\approx 2100K$ the chained reaction mechanism becomes active and in a interval ($\tau = 0.45...0.55 ms$) the temperature obtains its equilibrium value ($T \approx 3000K$).

![Figure 1. The alteration of species (O$_2$, N$_2$, NH$_3$, C$_2$H$_2$, CH$_4$) and of temperature by time.](image)

In the preliminary simulations for the SK and CK schemes the best control integer parameters had been chosen: $m_p = 16; J_2 = 3; m_a = 9$. In comparison with the $\theta$-method the values $m_a$ and $m_p$ had been increased because the values $c_i$ are smaller than the values $\gamma_i$ and high precision is necessary to determine them. Also for comparison of methods the two error indicators had been taken: the deviation from the equilibrium state ($\delta_m$) and the atom conservation errors ($\delta r_j, \delta r_k$). The first indicator is determined by formula:

$$\delta_m = \frac{1}{n_s + 1} \left[ \sum e r_i^d - r_i^e + |T_e - T_s| \right]$$

(20)

where the superior indices denote: $e$ - chemical equilibrium data and $d$ – chemical kinetic data.

This indicator is applicable when it is known beforehand that the chemical equilibrium (what is certain for the reacting media “O$_2$+H$_2$”) is established into the reacting system. The indicators for the atom conservation are more applicable. They are true for any closed reacting systems, therefore in the chemical reactions the atoms are not transformed. For each type of atoms the atom conservation indicator can be expressed by formula:

$$\delta r_j = \frac{\left( \sum a_{i=} r_j^d + r_j^d \right) - \left( \sum a_{i=} r_j^e + r_j^e \right)}{\left( \sum a_{i=} r_j^e + r_j^e \right)}$$

(21)

where $a_{i=}$ is the number of $k$-th atom in $i$-th substance.

Also it is useful to introduce the total error indicator for atoms: $\delta r_k = \sum \delta r_j$. In general, the computational volume includes all the logical and arithmetical operations that are performed during calculation. But in our software are enclosed many operators and subroutines that are not linked with the numerical method and the use of indicators of type “total calculation time” there are not reflected advantages or imperfections of the numerical method. Therefore the indicators (more adjusted to the searched schemes) had been chosen that are correspond to the two fragments: calculation of direct parts of the chemical kinetic Eq. (1); calculation of the Jacobian.

The calculation of direct parts is fulfilled once in each step of integration and once in each iteration of the Newton’s method. It is observed that for simple reacting systems of type (a) the computational volume of calculation of Jacobian ($V_J$) is smaller in comparison with the necessary volume for iteration ($V_i$). But for complex reacting systems the value $V_J$ can be essentially more than $V_i$. Therefore we will evaluate in the numerical simulations the computational volume by means of two indicators that reflect the volumes $V_j$ and $V_i$, to know: $N_p$ - the sum of total number of iterations with number of the integration steps; $N_J$ - the amount of calculation of Jacobian.
3.2. Comparison of the $\theta$, SK and CK methods for reacting media “H$_2$ + O$_2$”

For this reacting media the $\theta$-method and the methods of spline-integration: with correction (CK) and without correction (SK) and had been analyzed. The calculation precisions were evaluated by the deviation from the equilibrium state ($\delta_e$) because this equilibrium is evident in the end of the combustion process. The influences of: admissible error ($\varepsilon_\gamma$); admissible alteration ($\Delta_x$) and integration interval ($\tau_f$) on the values $\delta_e$, $N_p$ and $N_J$ (being $\tau_f = 10^{-4}$ s, $\Delta_x$ (SK, CK) $= 0.01$, $\Delta_x (\theta) = 0.005$) had been determined in simulations. In the Figure (2) are shown the dependences $N_p = f(\varepsilon_\gamma)$, $N_J = f(\varepsilon_\gamma)$ for the three numerical schemes. For $\theta$-method was chosen the parameter $\Delta_x$ ($\theta$) $= 0.005$ because for $\Delta_x (\theta) > 0.005$ the average error $\delta_e (\theta)$ is inadmissible. The Table (1) showed that almost for all $\varepsilon_\gamma$ the errors $\delta_e$ had been constant. 

The CK scheme shows the minimum errors: $\delta_e (SK) \approx \delta_e (\theta)/4 \approx \delta_e (SK)/15$. However for the great values ($\varepsilon_\gamma=10^{-4}$) $\delta_e (SK) \approx \delta_e (\theta)$ is observed. The schemes SK and CK are more economic than the $\theta$-method at least in two times (Fig.(2)). Indicators $N_J$ are equal for the all schemes but in the high precision region for the $\theta$-method the essential increase of $N_J$ is observed. This effect is induced by necessity to accomplish greater number of iterations in the integration step (with posterior calculation of the Jacobian) than for the SK and CK schemes. The values $c_i \approx (0.001...0.01) << \gamma$ and comparing the formula (7) with (17) it is observed that the Jacobian’s for all methods are almost equal. Therefore the values $\varepsilon_{i,0}^{n+1}$ assure of solution for less number of iterations. Considering relation $c_i << \gamma$ we choose for posterior simulations the values: 

$$\varepsilon_\gamma (\theta) = \max_i \left| \frac{(1 - \gamma_i^{n+1,m+1} - \gamma_i^{n+1,m})}{\gamma_i^{n+1}} \right| = 10^{-5}$$

for $\theta$-method

and $$\varepsilon_\gamma (SK, CK) = \max_i \left| \frac{(c_i^{n+1,m+1} - c_i^{n+1,m})}{\gamma_i^{n+1}} \right| = 0.5 \times 10^{-6}$$ for spline-integration schemes.

To determine the influence of parameter $\Delta_x$ on the errors $\delta_e$ the simulations with $\gamma = 10^{-4}$s varying $\Delta_x$ in interval 0.001... 0.08 had been accomplished. The errors ($\delta_e$) and computational volumes for three schemes are shown in Tab. (2) and in Fig. (3).

### Table 1 - Influence of $\varepsilon_\gamma$ on the errors $\delta_e$ for the three numerical schemes.

<table>
<thead>
<tr>
<th>Parameter $\varepsilon_\gamma$</th>
<th>$10^{-7}$</th>
<th>$5 \cdot 10^{-7}$</th>
<th>$10^{-6}$</th>
<th>$5 \cdot 10^{-6}$</th>
<th>$10^{-5}$</th>
<th>$5 \cdot 10^{-5}$</th>
<th>$10^{-4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_e (SK).10^4$</td>
<td>9.06</td>
<td>9.13</td>
<td>9.13</td>
<td>9.13</td>
<td>8.75</td>
<td>8.75</td>
<td>8.75</td>
</tr>
<tr>
<td>$\delta_e (CK).10^4$</td>
<td>2.69</td>
<td>2.69</td>
<td>2.69</td>
<td>2.69</td>
<td>2.74</td>
<td>4.04</td>
<td>7.92</td>
</tr>
<tr>
<td>$\delta_e (\theta).10^4$</td>
<td>46.5</td>
<td>46.5</td>
<td>46.5</td>
<td>46.5</td>
<td>46.5</td>
<td>46.5</td>
<td>46.5</td>
</tr>
</tbody>
</table>

The CK scheme shows the minimum errors: $\delta_e (CK) \approx \delta_e (SK)/4 \approx \delta_e (\theta)/15$. However for the great values ($\varepsilon_\gamma=10^{-4}$) $\delta_e (SK) \approx \delta_e (\theta)$ is observed. The schemes SK and CK are more economic than the $\theta$-method at least in two times (Fig.(2)). Indicators $N_J$ are equal for the all schemes but in the high precision region for the $\theta$-method the essential increase of $N_J$ is observed. This effect is induced by necessity to accomplish greater number of iterations in the integration step (with posterior calculation of the Jacobian) than for the SK and CK schemes. The values $c_i \approx (0.001...0.01) << \gamma$ and comparing the formula (7) with (17) it is observed that the Jacobian’s for all methods are almost equal. Therefore the values $\varepsilon_{i,0}^{n+1}$ assure of solution for less number of iterations. Considering relation $c_i << \gamma$ we choose for posterior simulations the values: 

$$\varepsilon_\gamma (\theta) = \max_i \left| \frac{(1 - \gamma_i^{n+1,m+1} - \gamma_i^{n+1,m})}{\gamma_i^{n+1}} \right| = 10^{-5}$$

for $\theta$-method

and $$\varepsilon_\gamma (SK, CK) = \max_i \left| \frac{(c_i^{n+1,m+1} - c_i^{n+1,m})}{\gamma_i^{n+1}} \right| = 0.5 \times 10^{-6}$$ for spline-integration schemes.

To determine the influence of parameter $\Delta_x$ on the errors $\delta_e$ the simulations with $\gamma = 10^{-4}$s varying $\Delta_x$ in interval 0.001... 0.08 had been accomplished. The errors ($\delta_e$) and computational volumes for three schemes are shown in Tab. (2) and in Fig. (3).

### Table 2 - Influence of parameter $\Delta_x$ on the errors $\delta_e$ for three numerical schemes.

<table>
<thead>
<tr>
<th>$\Delta_x$</th>
<th>0.001</th>
<th>0.002</th>
<th>0.005</th>
<th>0.01</th>
<th>0.02</th>
<th>0.04</th>
<th>0.08</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_e (SK).10^4$</td>
<td>3.25</td>
<td>3.44</td>
<td>4.63</td>
<td>9.13</td>
<td>28.7</td>
<td>73.7</td>
<td>137</td>
</tr>
<tr>
<td>$\delta_e (CK).10^4$</td>
<td>3.04</td>
<td>3.01</td>
<td>2.71</td>
<td>2.69</td>
<td>6.89</td>
<td>10.88</td>
<td>82.2</td>
</tr>
<tr>
<td>$\delta_e (\theta).10^4$</td>
<td>10.6</td>
<td>18.7</td>
<td>46.2</td>
<td>94.9</td>
<td>210</td>
<td>446</td>
<td>604</td>
</tr>
</tbody>
</table>
For the equal values $\Delta x$ all the schemes present the same computational volumes (for $\theta$-method the indicators $N_p$ and $N_J$ are a little more). For small values of $\Delta x$ the high computational volumes are observed and with the increase of $\Delta x$ they diminish drastically. Table (2) shows that the same values $\Delta x$ generate the very small errors $\delta_m$ for the schemes with the spline-integration (approximately in 40 times smaller than for $\theta$-method). Fixing, for instance, the admissible value ($\delta_m = 0.5\%$) for all schemes obtain: $\Delta x (\theta) = 0.005$; $\Delta x (SK, CK) = 0.04$. Then we conclude that for the SK and CK schemes the computational volumes are: $N_p \approx 1000$, $N_J = 30$ and for the $\theta$-method: $N_p \approx 2800$, $N_J = 27$, i.e. in this case the spline-integration methods are more economic in 2.5 times.

From practical point of view it is interesting to evaluate the influence of the integration interval on computational volume after the chemical equilibrium is reached. The results of these simulations for $\tau_f = 10^{-4}s \div 10^{-2}s$ (with $\epsilon_N (\theta) = 10^{-5}$, $\epsilon_N (SK,CK) = 0.5 \times 10^{-6}$, $\Delta x (\theta) = 0.005$ and $\Delta x (SK,CK) = 0.01$) are presented in Fig. (4). Suddenly the SK scheme presented the unexpected results when starting with $\tau_f = 10^{-3}s$ the essential increase of the indicator $N_p(SK)$ is observed that for $\tau_f = 10^{-2}s$ became more than $N_p(\theta)$ and moreover in 10 times increased value $N_J$ (of 28 to 270).

The cause of this effect is oscillations that appear in SK scheme because of error in coefficients $b_i$ when the reacting system reaches the chemical equilibrium state. In this case $b_i^{n+1} \neq 0$ although the reacting media composition must to be constant. Then the value $c_i^{n+1}$ has to “compensate” the tendency to change the composition attributing the contrary signal to the signal of the coefficient $b_i^{n+1}$. As a result in the step end the derivative $d\gamma_i^{n+1}/d\tau$ (i.e. $b_i^{n+2}$) change its signal and then in step ($n+2$) the value $c_i$ also change signal generating the sequence $c_i^{n+3} \approx -c_i^{n+2}$; $c_i^{n+4} \approx -c_i^{n+3}$ and etc., as shows Fig. (5). These oscillations prevent to increase integration step in SK scheme that leads to computational volume increase. The average errors $\delta_m$ remain constant with alteration $\tau_f$ being $\delta_m(SK) = 9 \times 10^{-4}$; $\delta_m(CK) = 2.7 \times 10^{-4}$ e $\delta_m(\theta) = 46 \times 10^{-4}$. Figure (4) shows that between the computational volumes of CK scheme and $\theta$-method the relation is almost constant being $N_p(CK) \approx N_p(\theta)/2$. 

Figure 3. Alteration of computational volume in function of $\Delta x$ (--- CK; … SK; --- $\theta$).

Figure 4. Alteration of computational volume in function of $\tau_f$ (--- CK; … SK; --- $\theta$).
3.3. Comparison of the $\theta$ and CK methods for the reacting media: “Air enriched + (C$_2$H$_2$ + CH$_4$ + NH$_3$)”

The numerical simulations for this media had been performed only for $\theta$-method and for the scheme with correction (CK), because SK method is not efficient because of oscillations in the solution. The calculation precision was tested through the atom conservation errors ($\delta r_r$, $\delta r_\Sigma$) because for the complex medias the deviation from the equilibrium state ($\delta_\nu$) does not serve as indicating of precision. Three series of simulation had been realized, changing of admissible error ($\varepsilon_N$); admissible alteration ($\Delta x$) and integration interval ($\tau_f$).

In Figure (6) the dependences $N_p = f(\varepsilon_N)$, $N_J = f(\varepsilon_N)$ (being $\tau_f = 10^{-3}$s, $\Delta_x(CK) = 0.01$, $\Delta_x(\theta) = 0.005$) are presented in interval $\varepsilon_N = 10^{-7}...10^{-4}$. It is verified that indicator $N_J(\theta)$ is bigger than $N_J(CK)$ when error $\varepsilon_N \approx 10^{-7}$ but with the increase of value $\varepsilon_N$ this difference diminishes. For the $N_p$ - indicator is observed that with growth $\varepsilon_N$ this indicator almost linearly diminishes in the both numerical schemes, leaving the ratio $N_p(\theta)/N_p(CK) \approx 2$. As seen, observed (Table (3)) that the ratio $\delta r_r(\theta)/\delta r_r(CK) \approx 3$ almost does not depend on value $\varepsilon_N$. 

![Figure 6: Computational volume in function of admissible error $\varepsilon_N$](image)

![Figure 7: Alteration of computational volume in function of $\Delta x$](image)
Table 3 - Influence of the parameter (ε) on the errors δr∑ for two numerical schemes.

<table>
<thead>
<tr>
<th>Parameter ε(θ)</th>
<th>10^{-7}</th>
<th>5.10^{-7}</th>
<th>10^{-6}</th>
<th>5.10^{-6}</th>
<th>10^{-5}</th>
<th>5.10^{-5}</th>
<th>10^{-4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>δr∑(θ), 10^{3}</td>
<td>15,15</td>
<td>15,93</td>
<td>15,88</td>
<td>15,49</td>
<td>15,74</td>
<td>15,73</td>
<td>15,75</td>
</tr>
<tr>
<td>δr∑(CK), 10^{3}</td>
<td>5,69</td>
<td>6,07</td>
<td>5,89</td>
<td>6,00</td>
<td>5,44</td>
<td>6,28</td>
<td>5,49</td>
</tr>
</tbody>
</table>

To determine the influence of parameter Δx on the calculation errors and on computational volume the simulations had been accomplished with τf = 10^{-4}, εN(θ) = 10^{-5} e εN(CK) = 0,5.10^{-6} varying Δx in interval 0,001÷0,08. In Figure (7) is shown the computational volume data for the both scheme. It is perceived that for small values (Δx < 0,01) the both methods demand the great number of iterations (Np) that quickly diminish with increase of indicator Δx, maintaining Np(CK) always less than Np(θ). For the values Δx > 0.01 the Np is almost constant. It is observed that Nf(θ) is almost two times bigger than Nf(CK) and, in the both schemes the value Nf grows until Δx ≈ 0,02 and later remains constant.

Figure 8. Variation of δrN and δrH in function of Δx (--- CK, ---θ).

Figure 9. The computational volume in function of τf (--- CK, --- θ).

In Figure (8) are shown the alterations of the atom conservation errors δrN and δrH in function of Δx. For small Δx (until Δx < 0,005) the difference between δrN(θ), δrH(θ) and δrN(CK), δrH(CK) is surprising. For example for Δx = 0,005, the ratio δrN(θ)/δrN(CK) = 40, showing a great advantage of the spline-integration method in this region. But with the increase of Δx this advantage is diminished. The same behavior is characteristic for the errors δrO and δrC, also for the total error δr∑. As a rule for the scientific and practical necessities it is demanded to keep the value δr∑ around 0,005. In this aspect we can mark that to get the ratio: δr∑(θ) ≈ δr∑(CK) ≈ 0,005 the calculations would be performed with Δx ≈ 0,003 (for θ-method) and with Δx=0,01 (for CK scheme). In this case using Fig. (7) we determine the computational volumes: Np = 10000, Nf = 90 (θ-method); Np = 4500, Nf = 90 (scheme CK).

Also influence of the integration interval on computational volume and on the atom conservation errors was searched. The results of these simulations changing τf of 10^{-4} to 10^{-2} (with εN(θ) =10^{-5}, εN(CK) = 0,5.10^{-6}, Δx(θ)= 0,005
and $\Delta x(CK) = 0.01$ are shown in Fig (9). It is verified that for CK scheme the total iteration number ($N_p$) and the number calculation of Jacobian ($N_J$) are kept almost constant in the interval $\tau_f$. However for $\theta$-method the values $N_p$ and $N_J$ grow linearly, thus showing the advantage of CK scheme. The difference between $N_p(\theta)$ and $N_p(CK)$ is increased of 2 times up to 3 times. For all the integration intervals the atom conservation errors are remained constant with ratio $\frac{\delta r_i(\theta)}{\delta r_i(CK)} \approx 2 \div 4$.

4. Conclusion

The two versions (SK and CK) of the spline-integration method had been implanted in software invariant “ERD” in order to compare with $\theta$-method that traditionally are used in the codes of this type. The tests of three methods had been performed in conditions of adiabatic reactor for reacting medias “H$_2$+O$_2$” and “Air enriched + (C$_2$H$_2$+CH$_4$+NH$_3$)” in large intervals: of admissible errors $\varepsilon_{N}$; of admissible alteration $\Delta x$; of permanence time $\tau_f$. The numerical simulations for the both reacting medias were shown that:
- scheme CK demands less the computational volume than the $\theta$-method at least in two times (and with the essentially high precision);
- scheme SK (in general being better than $\theta$-method) has the significant oscillations for great $\tau_f$ that leads to drastic growth of computational volume.

5. Acknowledgement

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6. References

LEEDS Reaction Kinetics Database, 2000, School of Chemistry, University of Leeds.