

Chemical kinetics model analysis

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Abstract

Electric arc discharge method is one of the most effective methods to synthesize fullerenes, despite that the yield is still relatively low. In order to model the fullerene production, a chemical kinetics model has to be involved. A related model is proposed and tested on several cases in the present report.

1 Introduction

One of the most effective ways to produce fullerenes and nanotubes is to synthesize them in an electric arc-discharge cell. In order to improve the yield and reduce the cost of the material, a better understanding of how the fullerenes are formed is needed. Several descriptions of the synthesis processes have been made over the years, the most promising of which appears to be the model suggested by Krestinin and Moravsky (Krestinin and Moravsky, 1998) and its reduced version devised by Scott (Scott, 2004), which is the model that is going to be used in our case.

In this paper the model is described by mathematical equations which construe chemical reactions and reacting species that participate in the fullerene formation process. A numerical method used to calculate the partial differential equations is described together with a simple method that describes the adaptation of the time step. Our main purpose is to keep the calculations as simple as possible. The method used in this case is Euler explicit numerical method.

Several test case scenarios are suggested to test this model and analytical solutions along with their derivations are provided for all of the suggested tests.

Finally, the results of a fullerene kinetics model are presented along with total mass fraction error, which is provided as a test for accuracy of the models.

2 Model

The chemical kinetics model describes the formation of fullerenes in the reaction chamber and is used to calculate the concentration and mass fraction of reacting carbon species. The model is based on the reduced chemical kinetics model and is taken from an article written by C.D. Scott (Scott, 2004). This model consists of reversible and irreversible elementary chemical reactions that are generally expressed as:

$$\sum_{i=1}^{n_g} \nu'_{ir} A_i \xrightleftharpoons[2]{1} \sum_{i=1}^{n_g} \nu''_{ir} A_i, \quad (1)$$

where ν'_{ir} and ν''_{ir} are the stoichiometric mole numbers of reactants and products, respectively, n_g is the number of reacting chemical species, and A_i is the chemical symbol for i -th species.

The i -th species mass fraction is calculated as:

$$\rho \frac{\partial Y_i}{\partial t} = M_i \omega_i, \quad (2)$$

where Y_i is a gas-phase species mass fraction, M_i is a molecular weight for species i and ω_i is chemical production rate of species.

The chemical production rate of the i -th species ω_i can be calculated from the summation of the rate of progress variables q_r for reactions involving the i -th species:

$$\omega_i = \sum_{r=1}^R \nu_{ir} q_r = \frac{dC_i}{dt}, \quad (3)$$

where $\nu_{ir} = \nu''_{ir} - \nu'_{ir}$ and

$$q_r = k_{1r} \prod_{i=1}^{n_g} C_i^{\nu'_{ir}} - k_{2r} \prod_{i=1}^{n_g} C_i^{\nu''_{ir}}. \quad (4)$$

k_{1r} and k_{2r} are forward and reverse rate constants of the r -th reaction and C_i is the molar concentration of the i -th species. Forward k_{1r} and reverse k_{2r} rate constants are calculated from Arrhenius temperature relation:

$$k_{1,2r} = A_{1,2r} T^{\beta_{1,2r}} \exp\left(-\frac{E_{1,2r}}{RT}\right), \quad (5)$$

where A_r represents pre-exponential factor, β_r is the temperature exponent and E_r is the activation energy. Indexes 1 and 2 represent forward and reverse direction respectively. Constants A_r , β_r and E_r are taken from the paper of (Krestinin and Moravsky, 1998) and are listed in Table 1.

2.1 Chemical reactions

In order to be able to calculate the concentrations of species in the domain, a chemical kinetics model equations must be solved. In this case we are going to investigate the formation of small carbon clusters that are according to Scott (Scott, 2004) formed from the following chemical reactions.

2.2 Numerical method

In order to be able to solve the chemical kinetics model Equations (Equations 2, 3, 4 and 5) have to be discretised. The simplest numerical method that can be used for discretisation of ordinary differential equations is Euler explicit method.

Explicit Euler discretisation of an ordinary differential equation:

$$\left(\frac{dy}{dt}\right)_k = \alpha y_k \quad (6)$$

yields:

$$y_{k+1} = y_k - \Delta t \alpha y_k \quad (7)$$

Table 1: The values of constants.

	A_r (cm ³ /(s moles))	β_r	E_r (K)
1	$2.00 \cdot 10^{14}$	0	0
2	$2.00 \cdot 10^{14}$	0	0
3	$2.00 \cdot 10^{15}$	0	9040
4	$2.00 \cdot 10^{14}$	0	0
5	$2.00 \cdot 10^{14}$	0	0
6	$2.00 \cdot 10^{14}$	0	0
7	$2.00 \cdot 10^{14}$	0	0
8	$2.00 \cdot 10^{14}$	0	0
9	$3.20 \cdot 10^{13}$	0	61900
10	$5.00 \cdot 10^{13}$	0	37745
11	$2.00 \cdot 10^{14}$	0	0
12	$4.00 \cdot 10^8$	0	30196
13	$8.30 \cdot 10^{13}$	0	61900
14	$1.40 \cdot 10^{12}$	0	49925
15	$4.00 \cdot 10^{13}$	0	0
16	$4.00 \cdot 10^{12}$	0	0
17	$4.00 \cdot 10^{12}$	0	0
18	$4.00 \cdot 10^{12}$	0	0

for each $k = 1, 2, \dots, n$. Here $\Delta t = t_{k+1} - t_k$ represents time step.

First we insert Equation 4 into Equation 3 and than we descretise the result to get:

$$C_i(t_{k+1}) = C_i(t_k) + \Delta t \sum_{r=1}^R \nu_{ir} \left(k_{1r} \prod_{i=1}^{n_g} C_i^{\nu'_{ir}}(t_k) - k_{2r} \prod_{i=1}^{n_g} C_i^{\nu''_{ir}}(t_k) \right). \quad (8)$$

The mass fraction (Eq. 2) can consequently be discretised as:

$$Y(t_{k+1}) = Y(t_k) + \Delta t \sum_{r=1}^R \nu_{ir} \left(k_{1r} \prod_{i=1}^{n_g} C_i^{\nu'_{ir}}(t_k) - k_{2r} \prod_{i=1}^{n_g} C_i^{\nu''_{ir}}(t_k) \right) \frac{M_i}{\rho}. \quad (9)$$

2.3 Time step adaptation

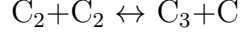
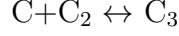
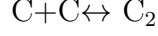
Initial reaction rate values in the fullerene synthesis reactions are significantly different with magnitudes ranging from 10^{17} to 10^2 . Accordingly, the initial time step must be at least 10^{-19} s. As the reaction rates slowly fall towards zero as the system moves towards equilibrium, it is necessary to use the adaptive time step in order to achieve equilibrium in a reasonable computational time.

Adaptation of time step is performed by a very crude but sure method. The concentration of carbon species is first calculated for a given time step as:

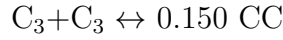
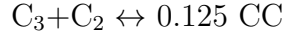
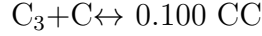
$$C_i^{(1)}(t + dt) = C_i(t) + dt\omega_i. \quad (10)$$

Table 2: Reduced chemical model (Scott, 2004). CC represents carbon cluster (it is assumed here that it consists of 40 carbon atoms) and Z represents soot (it is assumed here that it consists of 80 carbon atoms).

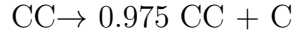
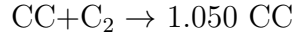
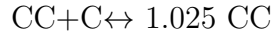
Chemistry of small clusters



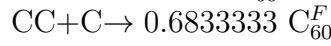
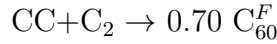
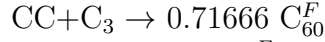
Formation of carbon clusters CC



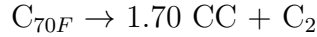
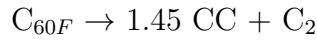
Growth of carbon clusters CC



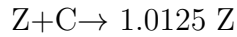
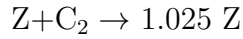
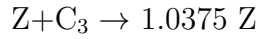
Formation of fullerene molecules C_{60}^F and C_{70}^F



Decay of fullerene molecules C_{60}^F and C_{70}^F



Formation of soot nuclei Z and growth of soot



The time step is then divided into two halves and the concentration is recalculated

$$C_i^{(2)}\left(t + \frac{dt}{2}\right) = C_i(t) + \frac{dt}{2}\omega_i \quad (11)$$

$$C_i^{(2)}\left(t + \frac{dt}{2} + \frac{dt}{2}\right) = C_i^{(2)}\left(t + \frac{dt}{2}\right) + \frac{dt}{2}\omega_{iNEW}. \quad (12)$$

We then calculate the difference between both concentrations

$$|C_i^{(1)} - C_i^{(2)}| = \varepsilon, \quad (13)$$

where ε presents the error of our calculations and is the parameter according to which we adjust the time step. The following criteria is used for the adjustment:

$$dt_{NEW} = \begin{cases} dt; & \text{if } \varepsilon_{MIN} < \varepsilon < \varepsilon_{MAX}, \\ \frac{dt}{2}; & \text{if } \varepsilon > \varepsilon_{MAX}, \\ 2dt; & \text{if } \varepsilon < \varepsilon_{MIN}. \end{cases} \quad (14)$$

ε_{MAX} and ε_{MIN} are the maximum and the minimum allowed errors. The procedure is repeated until the calculated error is small enough.

2.4 Temperature variation

In order to determine the mass fraction dependence of temperature variation, a simple temperature function is constructed:

$$T = T_h - (T_l - T_h) \left(\frac{t}{time} \right)^\gamma, \quad (15)$$

where T , T_h and T_l are current, initial (or high) and final (or low) temperatures, t and $time$ are current time and total time of the calculation, and γ is temperature time variation coefficient. In this instance the function is used only to test the temperature variation influence on the final yield of the material. The optimal temperature profile remains to be determined.

3 Results

Numerical calculations of chemical reactions were performed by solving Equations 2, 3, 4 and 5 for chemical reactions in Table 2. Due to the lack of results for fullerene formation kinetics, the model was tested for a number of simple chemical reactions that can be solved analytically. Analytical solutions of these reactions and their matching numerical results are presented in the following sections. The correspondence between the numerical and the analytical solutions is in all the observed cases satisfactory. Additionally, the conservation of species and convergence was tested for some of the proposed reactions.

3.1 Fullerene chemical kinetics

To analyse quantitatively the process of fullerene formation in the electric arc-discharge cell a reduced chemical kinetics model is used. The model includes 18 chemical reactions (listed in Table 2) which include 7 carbon species.

The initial concentrations and mass fractions of carbon species used to calculate the species concentration in the cell are listed in Table 3 and the values of constants used to calculate the reaction rate constants are listed in Table 1.

Table 3: Species concentrations and mass fractions.

Species	Concentration (mol/m ³)	Mass fraction
C	58.2813657	0.7
C ₂	8.3259093	0.2
C ₃	2.7753031	0.1
CC	0	0
C _{60F}	0	0
C _{70F}	0	0
Z	0	0

As the reaction rates are significantly different for various reactions, an adaptive time step is used for the calculations. The time step is adjusted according to the procedure described in Chapter 2.3.

3.2 Analytical solutions

Analytical solutions for several different types of chemical reactions were calculated in order to test the accuracy of the chemical kinetics model. In the following chapters, the chosen chemical reactions are presented along with their analytical solutions. Time development of species concentrations is depicted in Figures 6, 9, 12, 15 and 18 and is calculated from initial conditions and reaction rate coefficients stated in Tables 4, 5, 6, 7 and 8.

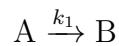
The derivation of analytical solutions for each of the mentioned chemical reactions can be found in Appendix A (GCV, 2009).

3.2.1 1st order reaction

When chemical reactions are classified based on their reaction kinetics, a 1st order reaction is a reaction that has rate proportional to the concentration of one of the reactants. The rate law is then written as:

$$r = k_1 C_A, \quad (16)$$

where r is the reaction rate, k_1 is the rate constant and C_A is the concentration of species A. An example of such a reaction:



is used to verify the results of our chemical kinetics model.

Concentrations of species A C_A and species B C_B are calculated from:

$$C_A = C_{A_0} e^{-k_1 t} \quad (17)$$

$$C_B = C_{A_0} + C_{B_0} - C_A, \quad (18)$$

where C_{A_0} and C_{B_0} denote the initial concentrations of each species.

The time development of species concentrations is presented in Figure 6. The concentrations were calculated with initial conditions and reaction rate constants stated in Table 4.

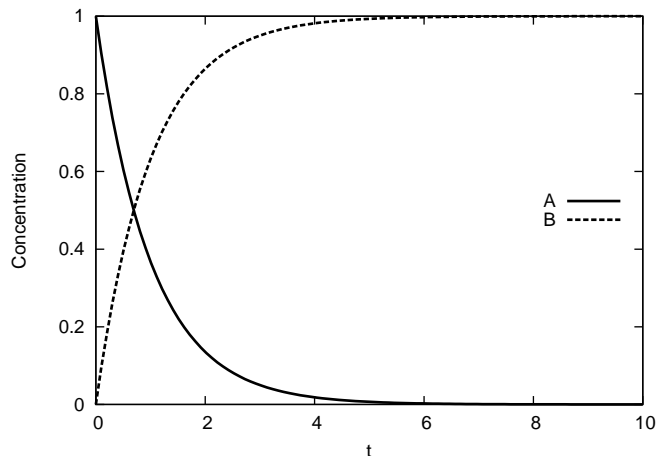


Figure 1: Species concentrations.

Table 4: Initial conditions and reaction rate constants.

Species concentration (mol/m ³)	Reaction rates
$C_{A_0} = 1$	$k_1 = 1 \text{ s}^{-1}$
$C_{B_0} = 0$	

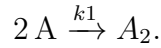
3.2.2 2nd order reaction

2nd order chemical reactions have reaction rates that are proportional to either the concentration of a square of single reactant or to the product of concentrations of two reactants. The rate law is than:

$$r = k_1 C_A^2 \quad \text{or} \quad r = k_1 C_A C_B, \quad (19)$$

where r is the reaction rate, k_1 is the rate constant and C_A and C_B are the concentrations of species A and B respectively.

To verify the accuracy of numerical results, the species concentrations for the following reaction was observed:



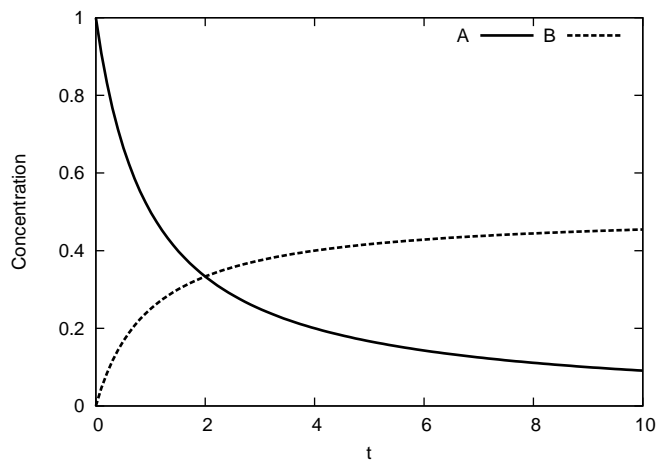
The species concentrations C_A and C_{A_2} were calculated from analytical solutions:

$$C_A = \frac{C_{A_0}}{C_{A_0} k t_1 + 1} \quad (20)$$

$$C_{A_2} = \frac{1}{2}(C_{A_0} - C_A) + C_{A_{2_0}}, \quad (21)$$

where C_{A_0} and $C_{A_{2_0}}$ denote the initial concentrations of each species.

The time development of species concentrations is presented in Figure 9 and is calculated for the initial conditions and reaction rate constant that are presented in Table 5.

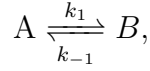
**Figure 2:** Species concentrations.

3.2.3 1st order reversible reaction

1st order reversible reaction is a chemical reaction of the first order which eventually reaches an equilibrium mixture of reactants and products. In our case the observed reaction is:

Table 5: Initial conditions and reaction rate constant.

Species concentration (mol/m ³)	Reaction rates
$C_{A_0} = 1$	$k_1 = 1/(\text{s mol/m}^3)$
$C_{A_{2_0}} = 0$	



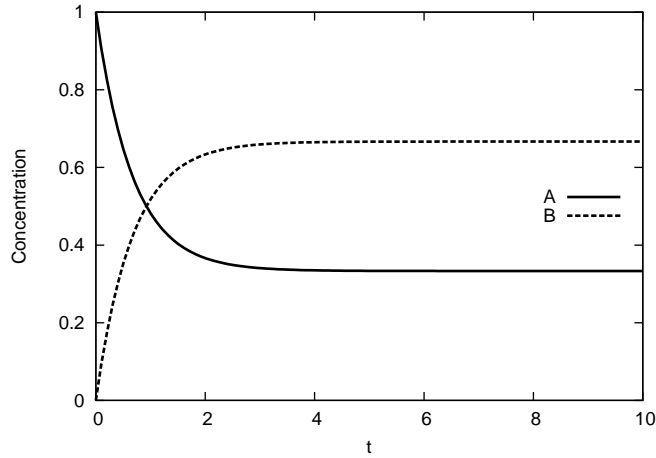
where k_1 is the forward reaction rate constant and k_{-1} is the reverse reaction rate constant. The concentrations of species A and B were calculated analytically:

$$C_A = C_{A_0}e^{-(k_1+k_{-1})t} + \frac{k_{-1}}{k_1+k_{-1}}(C_A + C_B)(1 - e^{-(k_1+k_{-1})t}) \quad (22)$$

$$C_B = C_{B_0}e^{-(k_1+k_{-1})t} + \frac{k_1}{k_1+k_{-1}}(C_A + C_B)(1 - e^{-(k_1+k_{-1})t}). \quad (23)$$

and are presented in Figure 12. Here C_{A_0} and C_{B_0} denote the initial concentrations of each species.

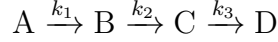
In order to be able to calculate the depicted concentrations (Figure 12), initial conditions and reaction rate constants from Table 6 were used.

**Figure 3:** Species concentrations.**Table 6:** Initial conditions and reaction rate constants.

Species concentration (mol/m ³)	Reaction rates
$C_{A_0} = 1$	$k_1 = 1.0 \text{ s}^{-1}$
$C_{B_0} = 0$	$k_{-1} = 0.5 \text{ s}^{-1}$

3.2.4 Consecutive reactions

In consecutive chemical reactions, products of one reaction are the reactants of another. The following chemical reaction:



was taken and analysed in order to validate the precision of the chemical kinetics model. k_1 , k_2 and k_3 are the reaction rate constants.

The concentrations of the reactants and products were calculated analytically and can be expressed as:

$$C_A = C_{A_0} e^{-k_1 t} \quad (24)$$

$$C_B = \frac{k_1 C_{A_0}}{k_2 - k_1} (e^{-k_1 t} + e^{-k_2 t}) - C_{B_0} e^{-k_2 t} \quad (25)$$

$$C_C = k_1 k_2 C_{A_0} \left(\frac{e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)(k_3 - k_2)} + \frac{e^{-k_3 t}}{(k_1 - k_3)(k_2 - k_3)} \right) \quad (26)$$

$$- \frac{k_2 C_{B_0}}{k_3 - k_2} (e^{-k_2 t} - e^{-k_3 t}) - C_{C_0} e^{-k_3 t},$$

where C_{A_0} , C_{B_0} , C_{C_0} and C_{D_0} are the initial concentrations of each species.

The time development of each species is shown in Figure 15. The initial conditions and reaction rate constants, necessary for the calculations, are listed in Table 7.

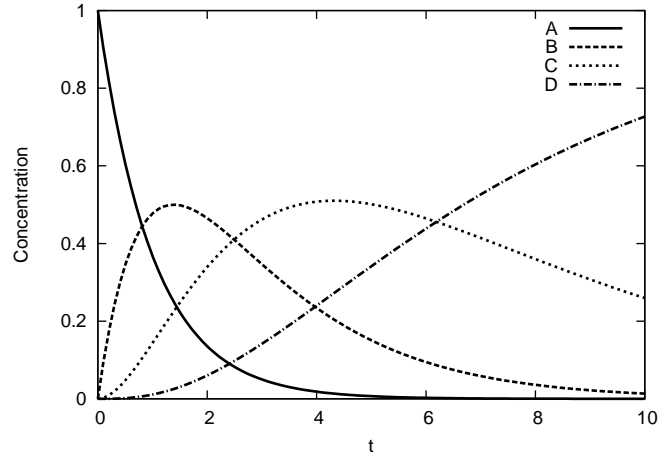


Figure 4: Species concentrations.

Table 7: Initial conditions and reaction rate constants.

Species concentration (mol/m ³)	Reaction rates
$C_{A_0} = 1$	$k_1 = 1.0 \text{ s}^{-1}$
$C_{B_0} = 0$	$k_2 = 0.5 \text{ s}^{-1}$
$C_{C_0} = 0$	$k_3 = 0.2 \text{ s}^{-1}$
$C_{D_0} = 0$	

3.2.5 Reversible and parallel reactions

As a final test, the concentrations of the 1st order consecutive and parallel reactions were calculated analytically. In our case, the following reaction was observed:



where k_1 , k_2 , k_3 , k_4 and k_5 are the reaction rate constants.

The concentrations are calculated analytically and are as follows:

$$C_A = C_{A_0} e^{-(k_1+k_2)t} \quad (28)$$

$$C_B = \begin{cases} C_{B_0}; & \text{if } t = 0, \\ \frac{k_1 C_{A_0}}{k_3+k_4-k_1-k_2} (e^{-(k_1+k_2)t} - e^{-(k_3+k_4)t}) + C_{B_0} e^{-(k_3+k_4)t}; & \text{otherwise.} \end{cases} \quad (29)$$

$$C_C = \begin{cases} C_{C_0}; & \text{if } t = 0, \\ \frac{\alpha}{k_1+k_2-k_5} (e^{-k_5 t} - e^{-(k_1+k_2)t}) + \frac{\beta}{k_3+k_4-k_5} (e^{-k_5 t} - e^{-(k_3+k_4)t}); & \text{otherwise.} \end{cases} \quad (30)$$

$$C_D = C_{A_0} + C_{B_0} + C_{C_0} + C_{D_0} - C_A - C_B - C_C \quad (31)$$

where α and β are

$$\alpha = C_{A_0} \left(k_2 + \frac{k_1 k_3}{k_3 + k_4 - k_1 - k_2} \right) \quad (32)$$

$$\beta = k_3 \left(C_{B_0} + \frac{k_1 C_{A_0}}{k_3 + k_4 - k_1 - k_2} \right). \quad (33)$$

Calculated species concentrations are presented in Figure 18 and are attained with initial conditions and reaction rate constants listed in Table 8.

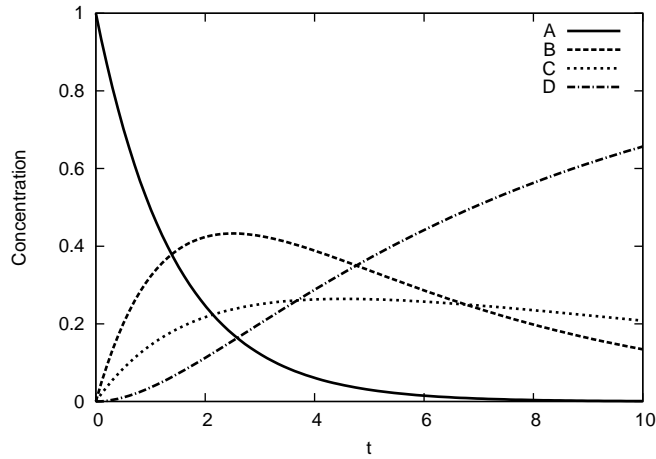


Figure 5: Species concentrations.

Table 8: Initial conditions and reaction rates parameters.

Species concentration (mol/m ³)	Reaction rates
$C_{A_0} = 1$	$k_1 = 0.50 \text{ s}^{-1}$
$C_{B_0} = 0$	$k_2 = 0.20 \text{ s}^{-1}$
$C_{C_0} = 0$	$k_3 = 0.05 \text{ s}^{-1}$
$C_{D_0} = 0$	$k_4 = 0.15 \text{ s}^{-1}$
	$k_5 = 0.10 \text{ s}^{-1}$

3.3 Numerical results

Numerical results are calculated with Euler explicit method (Section 2.2). All of the calculations described below were performed with adaptive time step unless otherwise specified.

The error is defined as a difference between analytically and numerically calculated data:

$$error = \left| \sum_i^n C_{i(analytical)} - C_{i(numerical)} \right| \quad (34)$$

and is calculated for every time step. Furthermore, the accuracy of calculated data is tested by calculating the total mass fraction of the system in each time step. The total mass fraction must be constant since there are no mass sources or losses present in the considered system. The difference between calculated and defined total mass fraction is calculated as:

$$error_{massfraction} = \left| \sum_i^n Y_i - Y_{total} \right|, \quad (35)$$

where n is the number of reacting carbon species. It is assumed here that only the reacting species are present in the system and therefore the total mass fraction Y_{total} of the species is equal to 1.

Three figures are shown for each of the test cases. The first one presents the comparison between analytically and numerically calculated data, the second one shows the obtained error of these calculations and the third figure presents the mass fraction error. Analytical data is depicted with dotted lines whereas numerical data is presented with full lines. In all the cases, initial error can be reduced by adapting the time step by changing the values of maximum and minimum allowed error.

3.3.1 1st order reaction

1st order reaction can be described with the following equation:



Figure 6 shows comparison between analytical and numerical solutions of 1st order reaction. Analytical solutions are depicted with dotted lines whereas numerical solutions are depicted by full lines. The correlation between both solutions at first glance appears to be very good. To test this correlation, an error (Eq. 34) is calculated and is shown in Figure 7. The error reaches the highest value at the beginning of the calculations and then gradually falls. The initial error can be reduced by alternating the initial parameters of the model; namely by

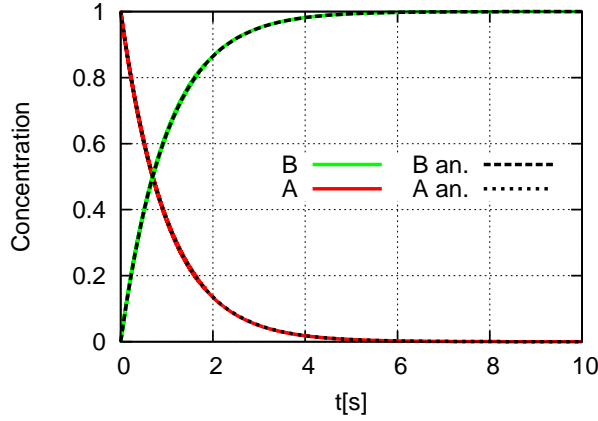


Figure 6: Comparison of analytical and numerical results for species concentrations for 1st order reaction 1.

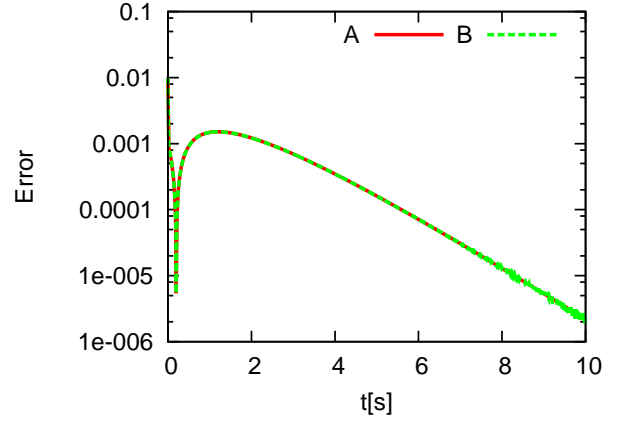


Figure 7: Comparison of analytical and numerical results for species concentrations for 1st order reaction 1.

changing the values of maximum and minimum allowed error in the time step adjustment criteria.

As an additional test, a total mass fraction error is calculated from Equation 35. The results are presented in Figure 8. As can be seen from the Figure 8, the total mass fraction is preserved as the calculated error is the machine precision error.

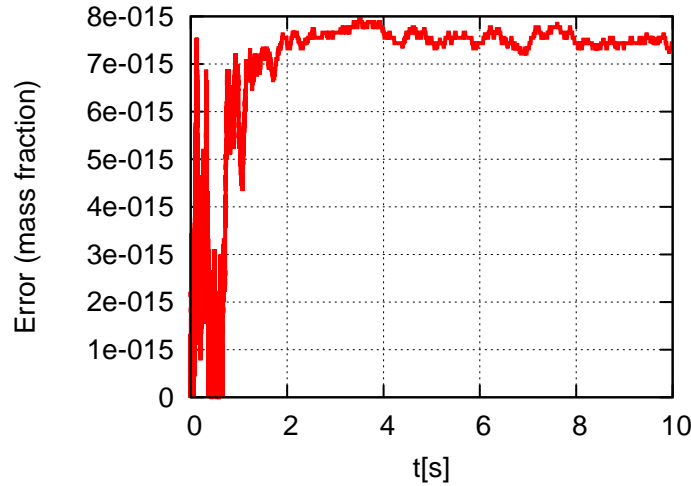


Figure 8: Mass fraction error.

3.3.2 2nd order reaction

2nd order reaction is expressed as:

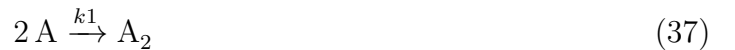


Figure 9 shows a correlation between the analytical and numerical solutions of 2nd order reaction. As in the case of 1st order reaction, analytical solutions are depicted with dotted lines, whereas numerical solutions are depicted by full lines. The correlation is tested by calculating the error (Eq. 34), which is shown in Figure 10. Similarly, as in the case of 1st

order reactions, the error for 2nd order reactions reaches the highest value at the beginning of the calculations, and then gradually falls.

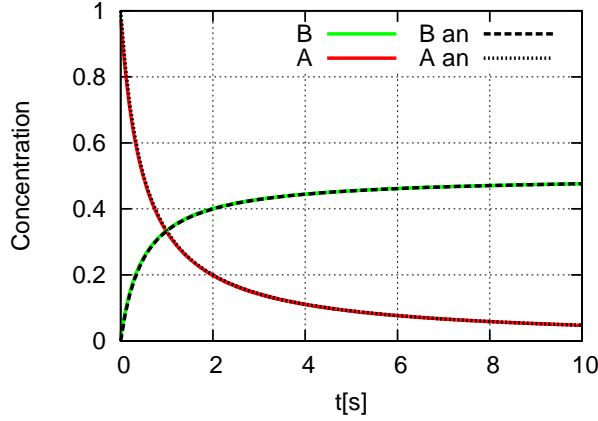


Figure 9: Comparison of analytical and numerical results for species concentrations for 2nd order reaction.

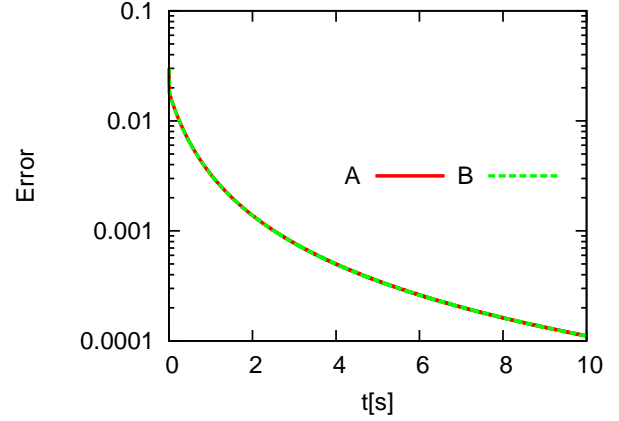


Figure 10: Comparison of analytical and numerical results for species concentrations for 1st order reaction 1.

An additional test was made to verify the total mass fraction conservation by examining the difference between expected and calculated mass fractions. The results shown in Figure 11 confirm that the total mass fraction is preserved as the obtained error is within of the same order of magnitude as the machine precision error.

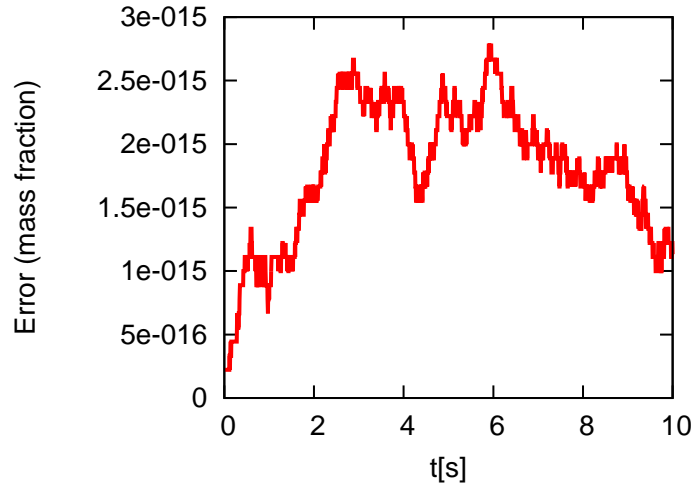


Figure 11: Mass fraction error.

3.3.3 1st order reversible reaction

1st order reversible reaction is described by the following equation:



The correlation between analytically calculated results and by numerical approximation is shown in Figure 12. The correspondence of data is very good but is nonetheless additionally tested by calculating the error (Eq. 34). The results are shown in Figure 13.

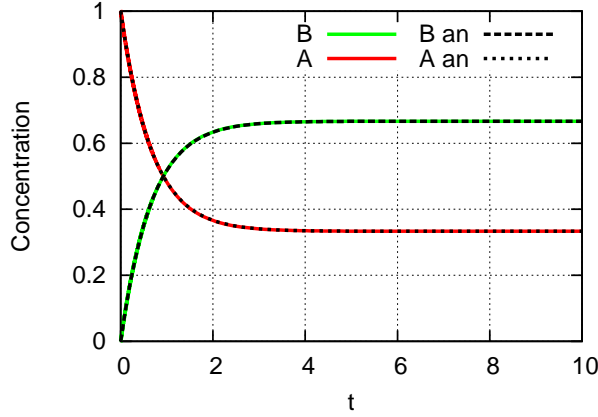


Figure 12: Comparison of analytical and numerical results for species concentrations for 1st order reversible reaction.

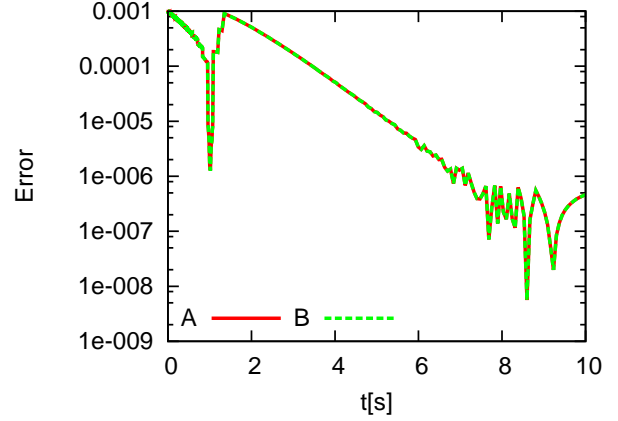


Figure 13: Comparison of analytical and numerical results for species concentrations for 1st order reaction 1.

Another measure by which the accuracy of the calculations can be tested is the mass fraction error. The error is calculated by using the Equation 35. The obtained results are shown in Figure 14 and are in good correspondence with expected values; the mass fraction error for such a reaction must be of the same order of magnitude as the machine precision error.

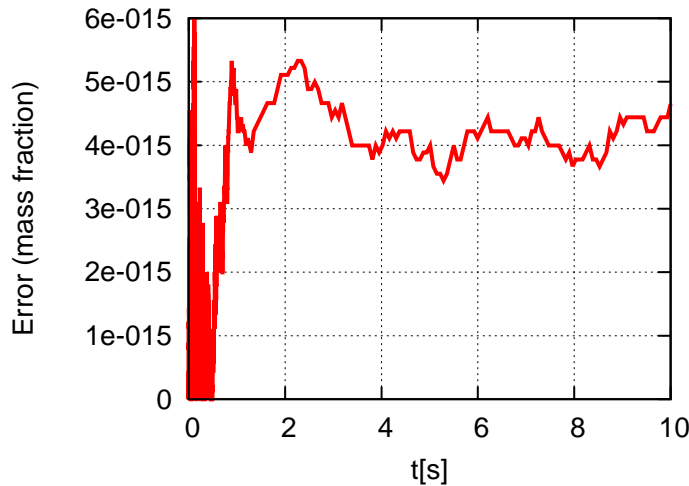


Figure 14: Mass fraction error.

3.3.4 Consecutive reactions

First order consecutive reactions are represented by:



The analytical and the numerical results are shown in Figure 15 and are in good correspondence. The error is depicted in Figure 16 and can be improved by adjusting the adaptive time step criteria. The trend is falling as the time passes and the fractions move towards equilibrium.

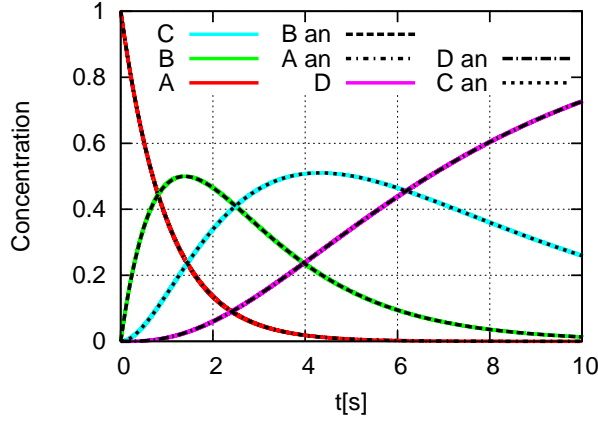


Figure 15: Comparison of analytical and numerical results for species concentrations for consecutive reactions.

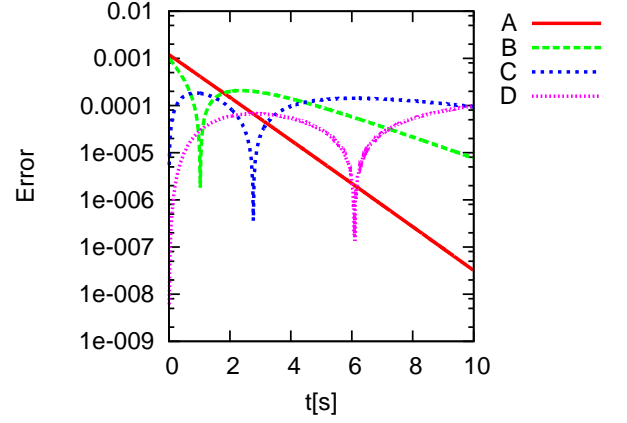


Figure 16: Comparison of analytical and numerical results for species concentrations for 1st order reaction 1.

Again, total mass fraction error is calculated to test the accuracy of the program. The mass fraction error in this case is slightly larger. This is due to the increased number of species and reactions involved, as consequently, more differential equations have to be solved.

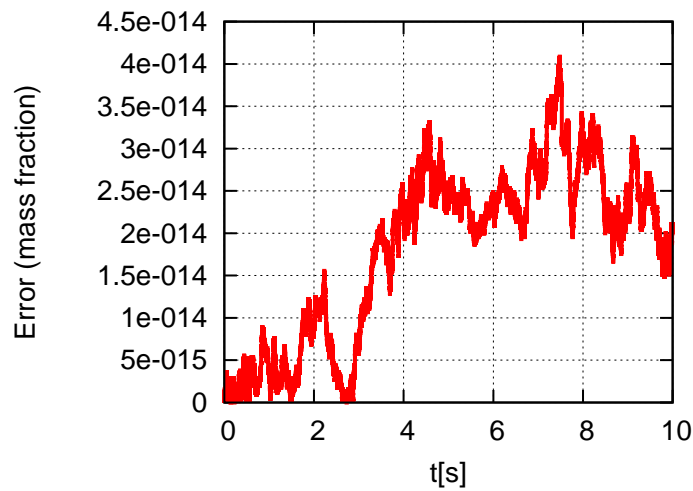


Figure 17: Mass fraction error.

3.3.5 Reversible and parallel reactions

An example of reversible and parallel reactions is also implemented as one of the test case scenarios:



The comparison of analytical and numerical data is depicted in Figure 18. The trend of an error, which is calculated from Eq. 34, is slowly falling as the time passes and the mass fractions approach the equilibrium.

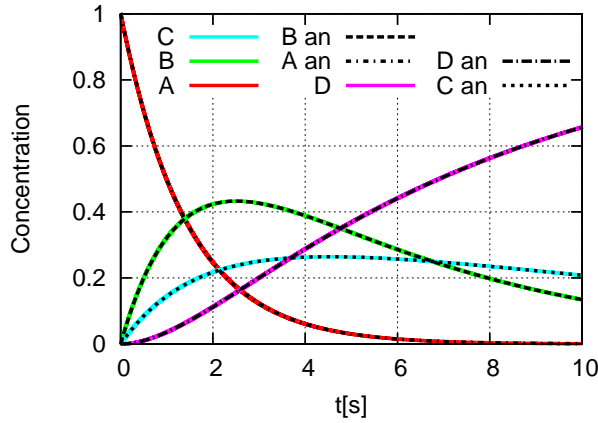


Figure 18: Comparison of analytical and numerical results for species concentrations for reversible and parallel reactions.

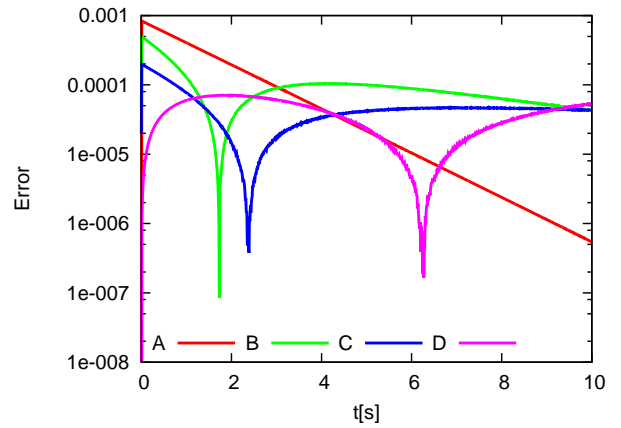


Figure 19: Comparison of analytical and numerical results for species concentrations for 1st order reaction 1.

An additional test was made to test the accuracy of the calculations by appraising the total mass fraction error. The error is slightly larger than for the previous test cases as this one includes more species and reactions that are parallel and reversible at the same time. More differential equations must therefore be solved and the total mass fraction error is consequently larger. The total mass fraction error is shown in Figure 20.

In order to better understand the influence of reaction rate parameters, a comparison between three different sets of reaction rate parameters for the same test case is analysed. The values of reaction rate parameters for each set is given in Table 9. All of the sets are depicted in Figures 21 and 22, where the line colour represents the name of the set in Table 9.

Table 9: Reaction rate parameters sets.

set	k_1 [s ⁻¹]	k_2 [s ⁻¹]	k_3 [s ⁻¹]	k_4 [s ⁻¹]	k_5 [s ⁻¹]
blue	0.50	0.2	0.05	0.15	0.10
red	100	10	1.00	0.10	0.01
green	0.01	0.1	1.00	10.0	100

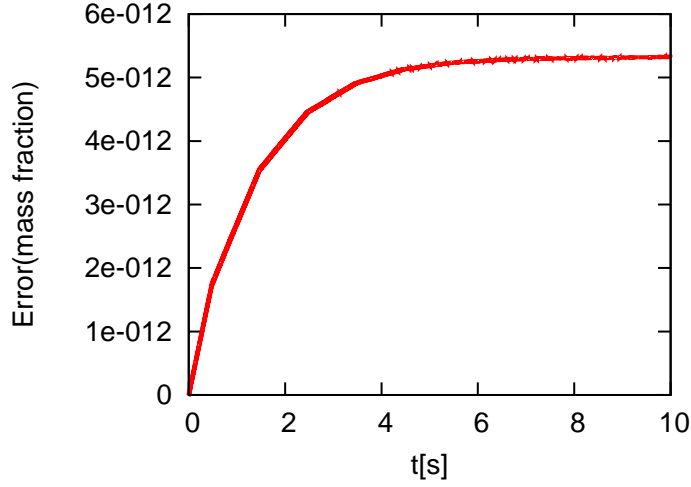


Figure 20: Mass fraction error.

As can be seen in Figures 21 and 22, the reaction rates influence reaction relaxation time; the bigger the parameter value, the shortest the relaxation time is and vice versa; the smaller the parameter value is, the longer the relaxation time is.

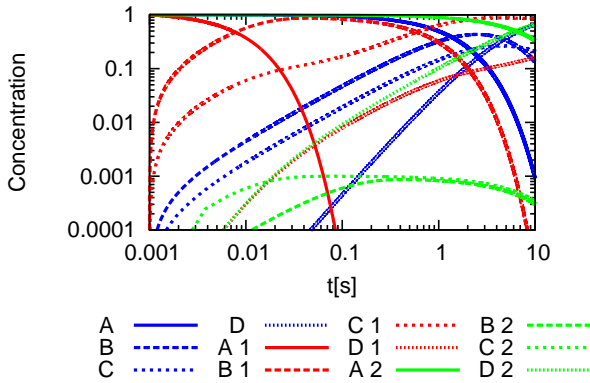


Figure 21: Comparison of different sets of reaction rate parameters in logarithmic scale.

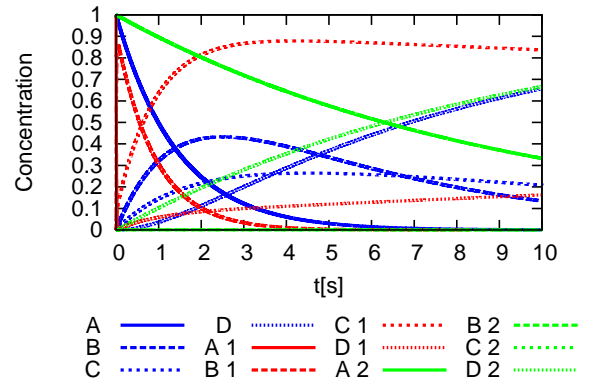


Figure 22: Comparison of different sets of reaction rate parameters.

The reaction rate coefficients are considerably different in different reactions which is why the adaptive time step is used to calculate the species concentrations. Adaptation of time step is shown in Figure 23. The time step grows as the reactions relax towards equilibrium.

3.3.6 Convergence analysis

Error analysis was done for test case number 5 as this is the most complicated of the proposed tests since it involves both consecutive and parallel reactions. The error was calculated for constant time steps ranging from 10^{-3} s to 10^{-9} s. As the time step grows smaller, the error diminishes until it reaches a certain value. The error for each of the species involved in the reactions is shown on a separate figure; the error for species A is shown in Figure 24, the error for species B is shown in Figure 25, the error for species C is shown in Figure 26 and the error for species D is shown in Figure 27.

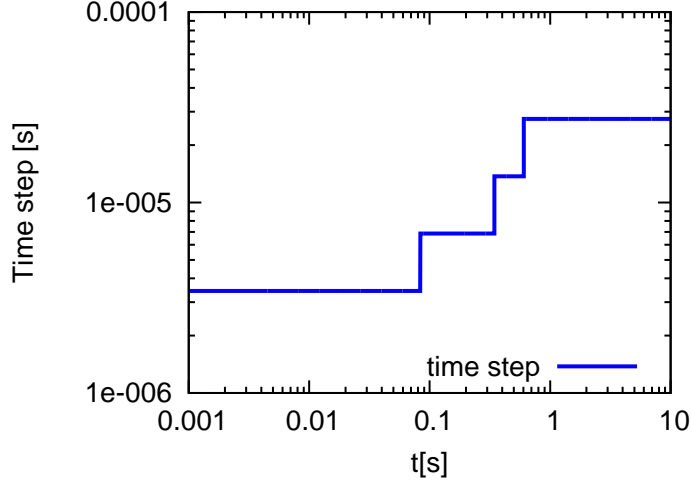


Figure 23: Time step adaptation.

As can be seen from Figures 24 to 27, the error does not change much if the time step is smaller than 10^{-6} s. This means that the initial time step should be at least 10^{-6} s as the error does not lessen when the time step is shorter. Since the errors for less complicated cases are smaller, it also suggests that the time step must be shorter for more complicated examples involving more reactions and more species. We can therefore expect a very short time step for fullerene model.

Since the mass fraction and consequently the concentration of species are calculated as the summation of the time step and the reaction rate coefficient, the adequate time step in each iteration should be a couple of orders of magnitude smaller than the reverse of the reaction rate coefficient. This condition ensures that the product of time step and reaction rate coefficient are relatively small in comparison to either mass fraction or concentration.

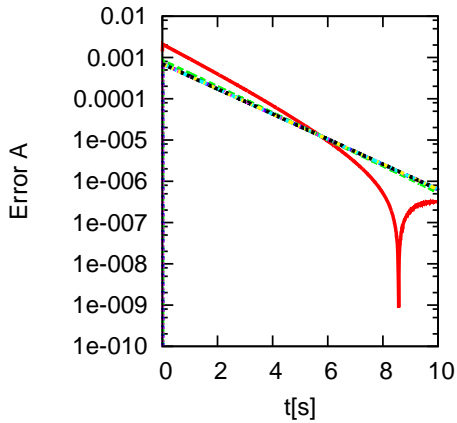


Figure 24: Error for species A.

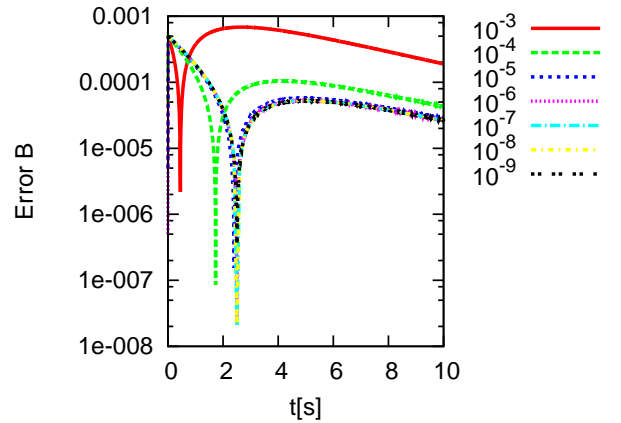


Figure 25: Error for species B.

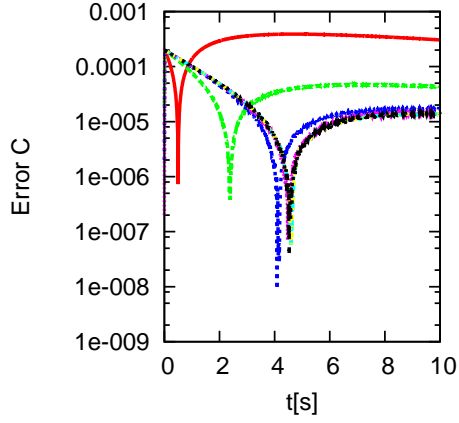


Figure 26: Error for species C.

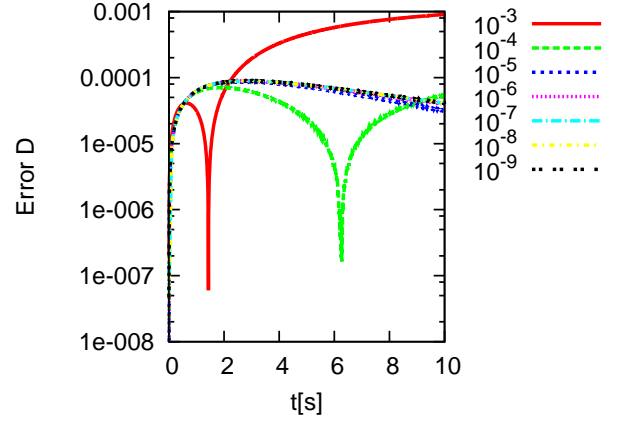


Figure 27: Error for species D.

Table 10: Convergence analysis: species A

time step [s]	2 s	4 s	6 s	8 s	10 s
10^{-2}	$4.1875 \cdot 10^{-3}$	$7.2917 \cdot 10^{-4}$	$1.0534 \cdot 10^{-4}$	$7.7012 \cdot 10^{-6}$	$2.5853 \cdot 10^{-6}$
10^{-3}	$2.1300 \cdot 10^{-3}$	$4.9523 \cdot 10^{-4}$	$1.1472 \cdot 10^{-4}$	$2.6467 \cdot 10^{-5}$	$6.0771 \cdot 10^{-6}$
10^{-4}	$1.9273 \cdot 10^{-3}$	$4.7227 \cdot 10^{-4}$	$1.1572 \cdot 10^{-4}$	$2.8354 \cdot 10^{-5}$	$6.9470 \cdot 10^{-6}$
10^{-5}	$1.9071 \cdot 10^{-3}$	$4.6997 \cdot 10^{-4}$	$1.1582 \cdot 10^{-4}$	$2.8545 \cdot 10^{-5}$	$7.0340 \cdot 10^{-6}$
10^{-6}	$4.0765 \cdot 10^{-4}$	$1.0050 \cdot 10^{-4}$	$2.4775 \cdot 10^{-5}$	$6.1076 \cdot 10^{-6}$	$1.5057 \cdot 10^{-6}$
10^{-7}	$1.9606 \cdot 10^{-4}$	$4.8344 \cdot 10^{-5}$	$1.1921 \cdot 10^{-5}$	$2.9395 \cdot 10^{-6}$	$7.2481 \cdot 10^{-7}$
10^{-8}	$1.7491 \cdot 10^{-4}$	$4.3131 \cdot 10^{-5}$	$1.0636 \cdot 10^{-5}$	$2.6228 \cdot 10^{-6}$	$6.4688 \cdot 10^{-7}$

Table 11: Convergence analysis: species B

time step [s]	2 s	4 s	6 s	8 s	10 s
10^{-2}	$9.8055 \cdot 10^{-3}$	$8.4671 \cdot 10^{-3}$	$5.9360 \cdot 10^{-3}$	$3.9595 \cdot 10^{-3}$	$2.6066 \cdot 10^{-3}$
10^{-3}	$3.6139 \cdot 10^{-3}$	$3.3369 \cdot 10^{-3}$	$2.4419 \cdot 10^{-3}$	$1.6791 \cdot 10^{-3}$	$1.1318 \cdot 10^{-3}$
10^{-4}	$2.9949 \cdot 10^{-3}$	$2.8254 \cdot 10^{-3}$	$2.0936 \cdot 10^{-3}$	$1.4518 \cdot 10^{-3}$	$9.8466 \cdot 10^{-4}$
10^{-5}	$2.9331 \cdot 10^{-3}$	$2.7743 \cdot 10^{-3}$	$2.0587 \cdot 10^{-3}$	$1.4290 \cdot 10^{-3}$	$9.6995 \cdot 10^{-4}$
10^{-6}	$3.6554 \cdot 10^{-4}$	$4.1777 \cdot 10^{-4}$	$3.2262 \cdot 10^{-4}$	$2.2675 \cdot 10^{-4}$	$1.5458 \cdot 10^{-4}$
10^{-7}	$1.9001 \cdot 10^{-6}$	$8.4349 \cdot 10^{-5}$	$7.7025 \cdot 10^{-5}$	$5.6682 \cdot 10^{-5}$	$3.9240 \cdot 10^{-5}$
10^{-8}	$3.4466 \cdot 10^{-5}$	$5.1009 \cdot 10^{-5}$	$5.2468 \cdot 10^{-5}$	$3.9677 \cdot 10^{-5}$	$2.7712 \cdot 10^{-5}$

Table 12: Convergence analysis: species C

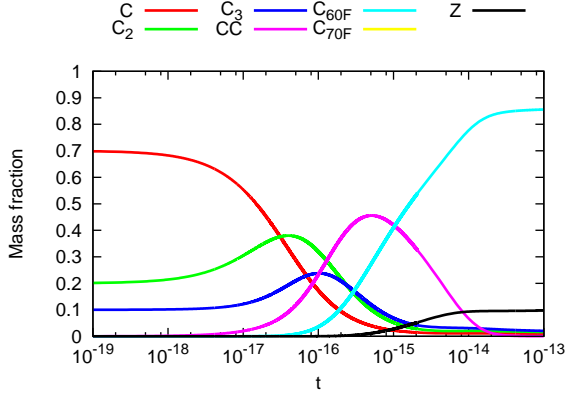
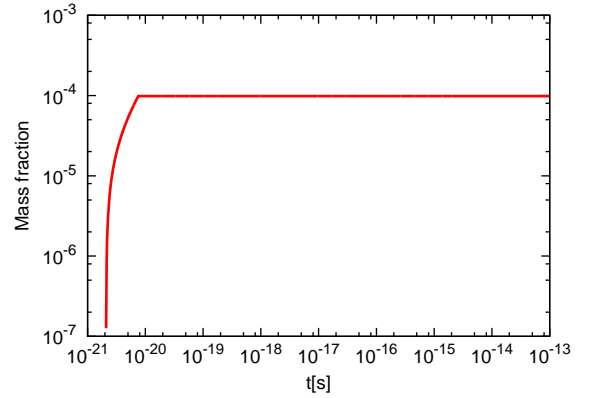
time step [s]	2 s	4 s	6 s	8 s	10 s
10^{-2}	$4.8760 \cdot 10^{-3}$	$5.7458 \cdot 10^{-3}$	$5.5291 \cdot 10^{-3}$	$5.0016 \cdot 10^{-3}$	$4.3910 \cdot 10^{-3}$
10^{-3}	$1.8116 \cdot 10^{-3}$	$2.2256 \cdot 10^{-3}$	$2.1811 \cdot 10^{-3}$	$1.9930 \cdot 10^{-3}$	$1.7622 \cdot 10^{-3}$
10^{-4}	$1.5043 \cdot 10^{-3}$	$1.8737 \cdot 10^{-3}$	$1.8467 \cdot 10^{-3}$	$1.6926 \cdot 10^{-3}$	$1.4997 \cdot 10^{-3}$
10^{-5}	$1.4736 \cdot 10^{-3}$	$1.8385 \cdot 10^{-3}$	$1.8133 \cdot 10^{-3}$	$1.6625 \cdot 10^{-3}$	$1.4734 \cdot 10^{-3}$
10^{-6}	$1.5836 \cdot 10^{-4}$	$2.4535 \cdot 10^{-4}$	$2.5371 \cdot 10^{-4}$	$2.3704 \cdot 10^{-4}$	$2.1223 \cdot 10^{-4}$
10^{-7}	$2.8048 \cdot 10^{-5}$	$1.9770 \cdot 10^{-5}$	$3.2948 \cdot 10^{-5}$	$3.5281 \cdot 10^{-5}$	$3.3730 \cdot 10^{-5}$
10^{-8}	$4.6691 \cdot 10^{-5}$	$2.7885 \cdot 10^{-6}$	$1.0872 \cdot 10^{-5}$	$1.5105 \cdot 10^{-5}$	$1.5884 \cdot 10^{-5}$

Table 13: Convergence analysis: species D

time step [s]	2 s	4 s	6 s	8 s	10 s
10^{-2}	$2.1308 \cdot 10^{-3}$	$6.0579 \cdot 10^{-3}$	$9.4295 \cdot 10^{-3}$	$1.2031 \cdot 10^{-2}$	$1.4005 \cdot 10^{-2}$
10^{-3}	$8.4453 \cdot 10^{-4}$	$2.3423 \cdot 10^{-3}$	$3.6623 \cdot 10^{-3}$	$4.7014 \cdot 10^{-3}$	$5.5000 \cdot 10^{-3}$
10^{-4}	$7.1339 \cdot 10^{-4}$	$1.9686 \cdot 10^{-3}$	$3.0840 \cdot 10^{-3}$	$3.9673 \cdot 10^{-3}$	$4.6487 \cdot 10^{-3}$
10^{-5}	$7.0028 \cdot 10^{-4}$	$1.9312 \cdot 10^{-3}$	$3.0262 \cdot 10^{-3}$	$3.8939 \cdot 10^{-3}$	$4.5636 \cdot 10^{-3}$
10^{-6}	$2.1848 \cdot 10^{-5}$	$1.8978 \cdot 10^{-4}$	$3.5230 \cdot 10^{-4}$	$4.8350 \cdot 10^{-4}$	$5.8509 \cdot 10^{-4}$
10^{-7}	$7.4569 \cdot 10^{-5}$	$5.7122 \cdot 10^{-5}$	$2.6553 \cdot 10^{-5}$	$4.3818 \cdot 10^{-7}$	$2.1645 \cdot 10^{-5}$
10^{-8}	$8.4216 \cdot 10^{-5}$	$8.1818 \cdot 10^{-5}$	$6.4442 \cdot 10^{-5}$	$4.7871 \cdot 10^{-5}$	$3.4709 \cdot 10^{-5}$

3.3.7 Fullerene chemical kinetics model numerical results

Fullerene chemical kinetics model consists of 7 carbon species and 18 chemical reactions, which are listed in Table 2. Initial species concentrations and mass fractions are listed in Table 2 and parameters needed to calculate reaction rate coefficients are listed in Table 3. The calculations are performed until the species reach equilibrium. Thus obtained results are depicted in Figures 28 and 29. The total mass fraction error (Figure 29) is rather high, but that is to be expected due to the large number of chemical reactions and reacting species. The final concentration of C_{60} fullerene is rather high, which is due to the fact that in this model we do not take into account the formation of carbon nanotubes.

**Figure 28:** Carbon species concentrations.**Figure 29:** Total mass fraction error.

Mass fraction dependence of temperature is tested for three different parameters γ ; $\gamma = 0$, $\gamma = 0.5$ and $\gamma = 1$. The results confirm that mass fraction is temperature dependent as different final mass fractions are obtained for when different temperature functions are applied. Results are shown in Figure 30.

What remains to be determined in order to obtain the maximum yield of fullerene C_{60} , is optimal parameter γ .

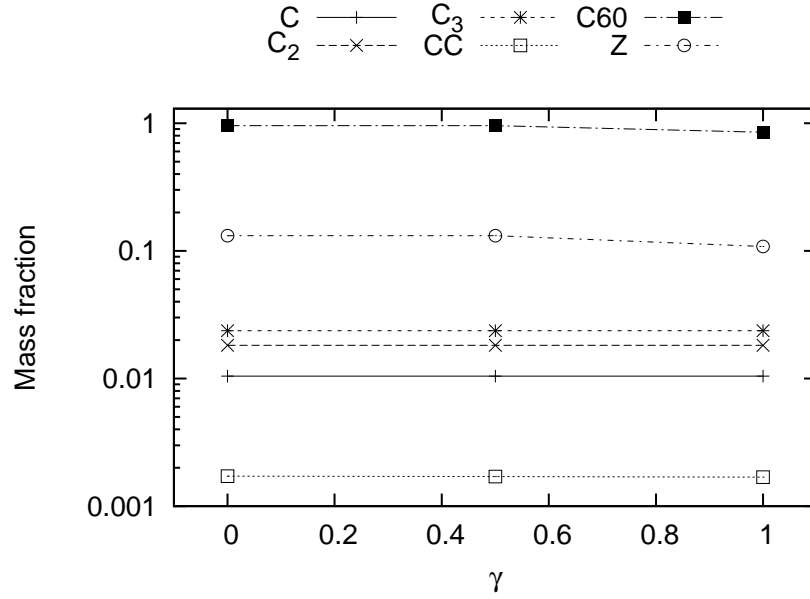


Figure 30: Temperature dependence.

4 Conclusion

Chemical kinetics model is an effective way of modelling fullerene reactor kinetics. Several test cases were devised and tested in order to verify the accuracy of the model. It is shown here that Euler explicit method with adaptive time step works well enough for simple chemical reactions since the obtained results that were tested against analytical solutions gave satisfactory results. Another, more advanced method, will have to be used for more complicated systems, since many ordinary differential equations coupled together quickly become stiff.

A Derivation of analytical solutions of concentration for chemical reactions

A.1 1st order reaction



First order reactions have the following rate equations:

$$-\frac{dC_A}{dt} = k_1 C_A \quad (42)$$

$$\frac{dC_B}{dt} = k_1 C_A. \quad (43)$$

Concentration of species A is obtained by integrating Equation 42:

$$\ln C_A = -k_1 t + \ln C_{A_0} \quad (44)$$

$$C_A = C_{A_0} e^{-k_1 t} \quad (45)$$

and concentration of species B is obtained either by material balance:

$$C_B = C_{A_0} + C_{B_0} - C_A \quad (46)$$

or by integrating Equation 43.

A.2 2nd order reaction



Second order reactions have the following rate equations:

$$-\frac{dC_A}{dt} = k_1 C_A^2 \quad (48)$$

$$2 \frac{dC_{A_2}}{dt} = k_1 C_A^2 \quad (49)$$

Concentration of species A is obtained by integrating Equation 48:

$$\frac{1}{C_A} = k_1 t + \frac{1}{C_{A_0}} \quad (50)$$

$$C_A = \frac{C_{A_0}}{C_{A_0} k_1 t + 1} \quad (51)$$

$$(52)$$

and concentration of species B is obtained either by material balance:

$$C_{A_2} = \frac{1}{2}(C_{A_0} - C_A) + C_{A_{20}} \quad (53)$$

or by integrating Equation 49.

A.3 1st order reversible equation



First order reversible reactions have the following rate equations:

$$\frac{dC_A}{dt} = -k_1 C_A + k_{-1} C_B \quad (55)$$

$$\frac{dC_B}{dt} = k_1 C_A - k_{-1} C_B \quad (56)$$

The concentration of species B can be found by material balance:

$$C_B = C_{A_0} + C_{B_0} - C_A \quad (57)$$

The concentration of species A is obtained by inserting 57 into 55 and integrating the acquired equation:

$$\frac{dC_A}{dt} = -k_1 C_A + k_{-1}(C_{A_0} + C_{B_0} - C_A) \quad (58)$$

$$\frac{dC_A}{dt} - C_A(-k_1 - k_{-1}) = k_{-1}(C_{A_0} + C_{B_0}) \quad (59)$$

$$C_A = C_{A_0} e^{-(k_1+k_{-1})t} + \frac{k_{-1}}{k_1 + k_{-1}}(C_{A_0} + C_{B_0})(1 - e^{-(k_1+k_{-1})t}) \quad (60)$$

Similarly can be done to get the concentration of species B:

$$C_B = C_{B_0} e^{-(k_1+k_{-1})t} + \frac{k_1}{k_1 + k_{-1}}(C_{A_0} + C_{B_0})(1 - e^{-(k_1+k_{-1})t}) \quad (61)$$

A.4 Consecutive reactions



First order consecutive reactions have the following rate equations:

$$\frac{dC_A}{dt} = -k_1 C_A \quad (63)$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \quad (64)$$

$$\frac{dC_C}{dt} = k_2 C_B - k_3 C_C \quad (65)$$

$$\frac{dC_D}{dt} = k_3 C_C \quad (66)$$

The concentration of species D can be found by material balance after differential equations for species A, B, and C have been integrated.

$$C_D = C_{A_0} + C_{B_0} + C_{C_0} + C_{D_0} - C_A - C_B - C_C \quad (67)$$

The differential equations can be solved using Laplace transformation. The Laplace transforms of Equations 66 are:

$$sa - a_0 = -k_1a \quad (68)$$

$$sb - b_0 = k_1a - k_2b \quad (69)$$

$$sc - c_0 = k_2b - k_3c \quad (70)$$

In order to solve these system of equations, determinant of coefficients has to be calculated:

$$D = \begin{bmatrix} s+k_1 & 0 & 0 \\ k_1 & -(s+k_2) & 0 \\ 0 & k_2 & -(s+k_3) \end{bmatrix} = (s+k_1)(s+k_2)(s+k_3) \quad (71)$$

Individual transforms are than:

$$a = \frac{1}{D}D_A = \frac{1}{D} \begin{bmatrix} a_0 & 0 & 0 \\ b_0 & -(s+k_2) & 0 \\ c_0 & k_2 & -(s+k_3) \end{bmatrix} = \frac{a_0}{s+k_1} \quad (72)$$

$$b = \frac{1}{D}D_B = \frac{1}{D} \begin{bmatrix} s+k_1 & a_0 & 0 \\ k_1 & b_0 & 0 \\ 0 & c_0 & -(s+k_3) \end{bmatrix} = -\frac{b_0}{s+k_2} + \frac{k_1a_0}{(s+k_1)(s+k_2)} \quad (73)$$

$$c = \frac{1}{D}D_C = \frac{1}{D} \begin{bmatrix} s+k_1 & 0 & a_0 \\ k_1 & -(s+k_2) & b_0 \\ 0 & k_2 & c_0 \end{bmatrix} \quad (74)$$

$$= -\frac{k_2b_0}{(s+k_2)(s+k_3)} + \frac{k_1k_2a_0}{(s+k_1)(s+k_2)(s+k_3)} - \frac{c_0}{s+k_2}$$

The results are obtained by inversion of Laplace transforms:

$$C_A = C_{A_0}e^{-k_1t} \quad (75)$$

$$C_B = \frac{k_1C_{A_0}}{k_2-k_1}(e^{-k_1t} + e^{-k_2t}) - C_{B_0}e^{-k_2t} \quad (76)$$

$$C_C = k_1k_2C_{A_0} \left(\frac{e^{-k_1t}}{(k_2-k_1)(k_3-k_1)} + \frac{e^{-k_2t}}{(k_1-k_2)(k_3-k_2)} + \frac{e^{-k_3t}}{(k_1-k_3)(k_2-k_3)} \right) \quad (77)$$

$$- \frac{k_2C_{B_0}}{k_3-k_2}(e^{-k_2t} - e^{-k_3t}) - C_0e^{-k_3t}$$

A.5 Reversible and parallel reactions



Reversible and consecutive first order reactions have the following rate equations:

$$\frac{dC_A}{dt} = -(k_1 + k_2)C_A \quad (79)$$

$$\frac{dC_B}{dt} = k_1C_A - (k_3 + k_4)C_B \quad (80)$$

$$\frac{dC_C}{dt} = k_2C_A + k_3C_B - k_5C_C \quad (81)$$

$$\frac{dC_D}{dt} = k_4C_B + k_5C_C \quad (82)$$

Equation 79 is linear and is solved by separating variables:

$$C_A = C_{A_0}e^{-(k_1+k_2)t} \quad (83)$$

Equations 80 and 81 are linear differential equations. By inserting 83 into 80, and integrating, we obtain solutions for species B.

$$\frac{dC_B}{dt} + (k_3 + k_4)C_B = k_1C_{A_0}e^{-(k_1+k_2)t} \quad (84)$$

$$C_B = \begin{cases} C_{B_0}; & \text{if } t = 0, \\ \frac{k_1C_{A_0}}{k_3+k_4-k_1-k_2}(e^{-(k_1+k_2)t} - e^{-(k_3+k_4)t}) + C_{B_0}e^{-(k_3+k_4)t}; & \text{otherwise .} \end{cases} \quad (85)$$

Solution for species C is obtained by inserting 83 and 85 into 81:

$$\frac{dC_C}{dt} + k_5C_C = k_2C_{A_0}e^{-(k_1+k_2)t} + \frac{k_1k_3C_{A_0}}{k_3+k_4-k_1-k_2}e^{-(k_1+k_2)t} \quad (86)$$

$$+ k_3\left(C_{B_0} - \frac{k_1C_{A_0}}{k_3+k_4-k_1-k_2}\right)e^{-(k_3+k_4)t} \quad (87)$$

$$= \alpha e^{-(k_1+k_2)t} + \beta e^{-(k_3+k_4)t} \quad (88)$$

$$\alpha = C_{A_0}\left(k_2 + \frac{k_1k_3}{k_3+k_4-k_1-k_2}\right) \quad (89)$$

$$\beta = k_3\left(C_{B_0} + \frac{k_1C_{A_0}}{k_3+k_4-k_1-k_2}\right) \quad (90)$$

$$C_C = \begin{cases} C_{C_0}; & \text{if } t = 0, \\ \frac{\alpha}{k_1+k_2-k_5}(e^{-k_5t} - e^{-(k_1+k_2)t}) + \frac{\beta}{k_3+k_4-k_5}(e^{-k_5t} - e^{-(k_3+k_4)t}); & \text{otherwise .} \end{cases} \quad (91)$$

The concentration of species D can be found by material balance after differential equations for species A, B, and C have been integrated, or by integrating Equation 82.

$$C_D = C_{A_0} + C_{B_0} + C_{C_0} + C_{D_0} - C_A - C_B - C_C \quad (92)$$

Acknowledgements

The Centre of Excellence for Biosensors, Instrumentation and Process Control is an operation financed by the European Union, European Regional Development Fund and Republic of Slovenia, Ministry of Higher Education, Science and Technology.

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