

# Computer Simulation of Chemical Kinetics

(Wednesday, 21. March 2007)

## 1. Summary

Concentration-time profiles of various reaction mechanisms are calculated and visualized on a PC. Using such simulations, the effect of parameters like initial concentrations, kinetic constants, or temperature can be studied and a more detailed understanding of chemical reaction kinetics can be achieved.

## 2. Introduction

Chemical kinetics investigates the time development of chemical reactions and with the parameters like temperature, pressure, solvent, etc, which affect such reactions. Kinetic investigations are for example used in order to find the optimal conditions for a reaction, i.e. for *optimizing the yield* of a reaction, or in order to determine the *reaction mechanism* of a given chemical reaction. In this computer experiment we investigate the correlation between reaction mechanism and the development in time of concentrations of the different reactants for various chemical reactions.

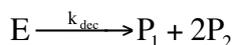
Any chemical reaction, as complex it might be, consists of a series of so-called *elementary reactions*. These simple reactions can either find place simultaneously (parallel reactions) or sequentially (consecutive reactions). Each one of these steps can be described using *simple kinetic equations* that give the change of concentrations of the reactants per time unit (the *reaction rate*). In the case of the simple reaction



as many molecules A and B disappear per time unit as molecules C are formed. Since the conversion per time unit is proportional to the probability for a reactive collision of molecules A and B and, therefore, the product of their concentrations, the kinetic equations for this reaction is written as

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = +\frac{d[C]}{dt} = k[A][B] \quad (1)$$

The proportional coefficient k is called the *kinetic constant* of the reactions. Another example is the decay reaction (for example radioactive decay)



Here, the same considerations as above lead to the following kinetic equations:

$$-\frac{d[E]}{dt} = \frac{d[P_1]}{dt} = +\frac{1}{2} \frac{d[P_2]}{dt} = k_{dec}[E] \quad (2)$$

The kinetics of a complex, multilevel reaction is thus represented by a system of coupled differential equations, where every single differential equation describes one simple elementary reaction step. Integration of such a system of differential equations reveals the rate law, which describes the concentrations of reactants as a function of time. If no agreement between observed and calculated concentration profiles is achieved, then the assumed reaction mechanism must be wrong. On the other hand, observed and calculated concentration profiles agree well, the assumed reaction mechanism seems to be reasonable and should be confirmed by doing additional investigation. It is important to emphasize that at this point, an agreement doesn't *prove* the validity of the assumed reaction mechanism. General information about chemical kinetics can be found in Ref. [1].

### 3. Mathematical Methods

The integration of a system of coupled differential equations is difficult and can be done analytically (see for example reference [2]) only in very simple cases. If an analytical treatment is not possible, the integration has to be carried out numerically. Various algorithms exist how numerical integrations can be carried out. The probably most common methods are the *method of Euler* and the *Runge-Kutta method* (see references [3,4]). Such methods work well for many systems, but breakdown when chemical instabilities exist or when the boundary conditions required for integration are not physically realistic.

A simpler alternative to the methods mentioned above is a *stochastic method*. This is the method used in the program package CKS, which we will use in our investigations. (CKS [5], The program is available for Windows systems as well as for Mac OS 9 and can be downloaded from [http://www.almaden.ibm.com/st/computational\\_science/ck/msim/?cks-download](http://www.almaden.ibm.com/st/computational_science/ck/msim/?cks-download)). With this method, simple reaction schemes can be investigated as well as explosions, nucleations, large ranges of rates or concentrations, etc. The mathematical foundation of stochastic methods for kinetics simulations can however not be discussed in this instruction. A nice introduction to this method can be found in Ref [6], pages 109 – 114. For a more detailed treatment, the original literature has to be consulted (see references [7,8]).

### 4. Using the Program CKS

We discuss the use of program CKS by applying it to a simple kinetic problem. Assume, we have the reaction equation

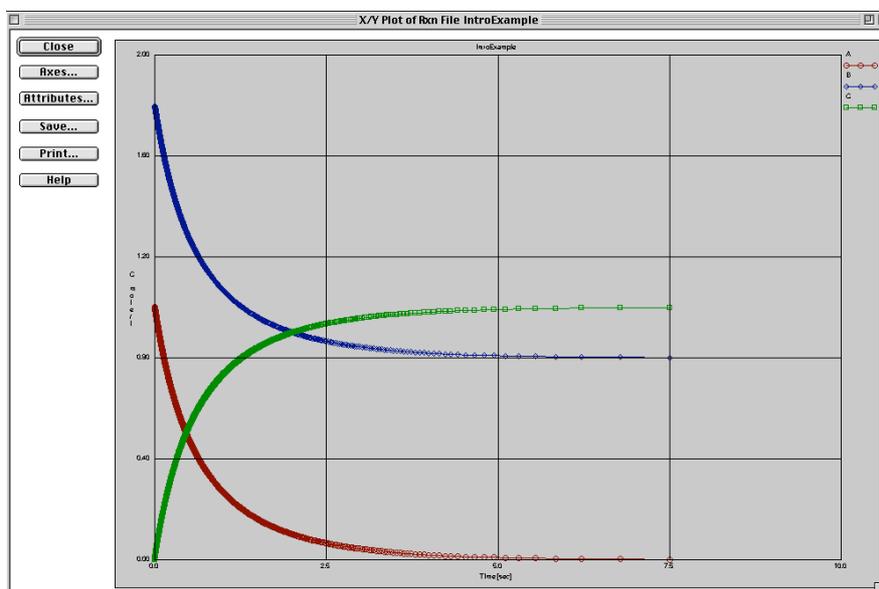


following the kinetic equation given in (1). The reaction is temperature independent and the kinetic constant  $k$  is 1.0. We assume, the concentrations (in mole/l) at the beginning are as follows:  $A=1.0$ ,  $B=1.8$ ,  $C=0.0$ .

We now want to simulate this reaction system using CKS.

- Start the program CKS
- Choose Create under File
- Save the simulation system as Intro in your own data folder
- Choose the default units
- Then, add a reaction step:  $A + B \Rightarrow C$  and enter the appropriate rate constant (1.0). The rate law should be derived stoichiometrically and the reaction should be temperature independent.
  - There have to be spaces between the symbols of chemical species like A or B and the + or  $\Rightarrow$  signs.
  - Forward, backwards, and reversible reactions are denoted using the symbols  $\Rightarrow$ ,  $\Leftarrow$ , and  $\Leftrightarrow$ , respectively.

- Now, choose Simulation settings... under Simulation. The appearing menu consists of three sections:
  - The General section lets you define the total amount of molecules, the record interval (the frequency, how often the concentration will be written to file), and a random number seed. A larger amount of molecules reduces the noise in the calculated concentrations.
  - The Limits section contains the maximal number of steps that will be calculated and a time limit. The limit first met will stop the simulation. Entering 0.0 to the time limit disables it.
  - Finally there is an Equilibrium detect section. Here it is decided if the program should attempt to detect a chemical equilibrium. Use the default values.
- Now, the simulation can be started by choosing Start under Simulation. The first time, the concentrations of the reactants have to be given. Choose 1.0 for A, 1.8 for B and 0.0 for C. In subsequent simulations, these parameters can be changed under Edit/Reaction Conditions...
- After the simulation has finished, click on Ok and plot the results (Plot Results under Results). Choose concentrations and select A, B, and C. This should reveal a plot like this:

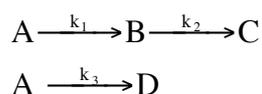


## 5. Tasks

### 5.1. Simple reactions

- Set up a simulation system for a consecutive reaction  $A \xrightarrow{k_1} B \xrightarrow{k_2} C$  and solve this system different concentrations and kinetic constants. Also try extreme cases like  $k_1 \gg k_2$  and  $k_1 \ll k_2$ .  
At the beginning use the kinetic constants  $k_1 = k_2 = 1$  and the concentrations  $[A]_0 = 1$ ,  $[B]_0 = [C]_0 = 0$ .

- b. This reaction scheme can be altered by adding a side reaction:

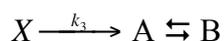


Begin with the concentrations  $[A]_0 = 1$ ,  $[B]_0 = [C]_0 = [D]_0 = 0$  and the kinetic constants  $k_1 = k_2 = k_3 = 1$ . Find parameters such that  $B(t)$  becomes maximal.

## 5.2. Simple chemical equilibrium

- a. Setup a simulation for simplest type of a chemical equilibrium:  $A \rightleftharpoons B$  with rate constants  $k_{\text{forward}}$  and  $k_{\text{backward}}$ . Try different initial concentrations and different kinetic constants. Calculate the time needed in order to reach equilibrium concentrations. Determine the equilibrium constant.

- b. Now we assume that A is produced by a preceding reaction:



use as initial concentrations  $[X]_0 = 1$ ,  $[A]_0 = 0$ ,  $[B]_0 = 0$ . Use the same values for  $k_{\text{forward}}$  and  $k_{\text{backward}}$  as in a and choose different values for  $k_3$ . Investigate cases where  $k_3 \gg k_{\text{forward}}$ ,  $k_{\text{backward}}$  and  $k_3 \ll k_{\text{forward}}$ ,  $k_{\text{backward}}$ . How does  $k_3$  affect the equilibrium?

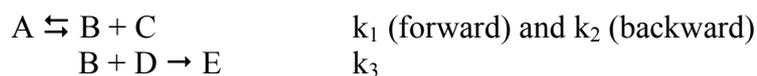
## 5.3. Reversible second order reaction

- a. We now investigate the reversible second order reaction:  $H_2 + I_2 \rightleftharpoons 2HI$  with kinetic constants  $k_1$  and  $k_2$  for forward and backward reaction, respectively. Create a new simulation entry for this reaction scheme. Run simulations with either only educts or only products available as initial concentrations. The total concentration should be 0.1 mol/l. The kinetic constants at different temperatures are given as:

| temperature[K] | $k_1$ [l/mol s]      | $k_2$ [l/mol s]      |
|----------------|----------------------|----------------------|
| 600            | $2.14 \cdot 10^{-4}$ | $2.75 \cdot 10^{-6}$ |
| 700            | $3.02 \cdot 10^{-2}$ | $5.5 \cdot 10^{-4}$  |

Discuss the equilibriums achieved at 600 and 700 K. How much time does it take until the equilibrium is reached?

- b. A well known reaction scheme corresponds to a variation of the preceding mechanism:



This reaction scheme corresponds to an  $S_N1$  reaction. The kinetic constants are given as follows:

$$\begin{aligned}
 k_1 &= 0.1 \text{ s}^{-1} \\
 k_2 &= 0.6 \text{ l mol}^{-1} \text{ s}^{-1} \\
 k_3 &= 1.0 \text{ l mol}^{-1} \text{ s}^{-1}
 \end{aligned}$$

The initial concentrations are:

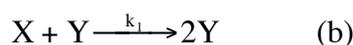
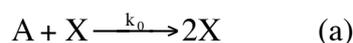
$$\begin{aligned}
 [A]_0 &= 0.5 \text{ mol/l} \\
 [B]_0 &= [C]_0 = [E]_0 = 0.0 \text{ mol/l} \\
 [D]_0 &= 1.0 \text{ mol/l}
 \end{aligned}$$

What is the maximal concentration of the reactive intermediate B?

## 5.4. Oscillating reactions

### a. *The Lotka-Volterra mechanism:*

We consider a simple example of an autocatalytic reaction which can exhibit oscillations:



Steps (a) and (b) in this scheme are auto-catalytic. The concentration of A should be chosen large enough such that it changes only slowly. Oscillations are found in the intermediates X and Y.

Try the following setup: choose as kinetic constants  $k_0 = 0.001$  and  $k_1 = k_2 = 1.0$ . The initial concentrations are  $[A]_0 = 1000$ ,  $[B]_0 = 0$ ,  $[X]_0 = 1$ ,  $[Y]_0 = 0.5$ . Plot only the concentrations of X and Y. Choose the following simulation parameters:

**Set Simulation Options: LotkaVolterra**

**General Settings**

Total number of molecules:

Record state at intervals of:  events

Random number seed:

**Limits**

Stop when total number of events exceeds:

Stop when time in simulation exceeds:  sec

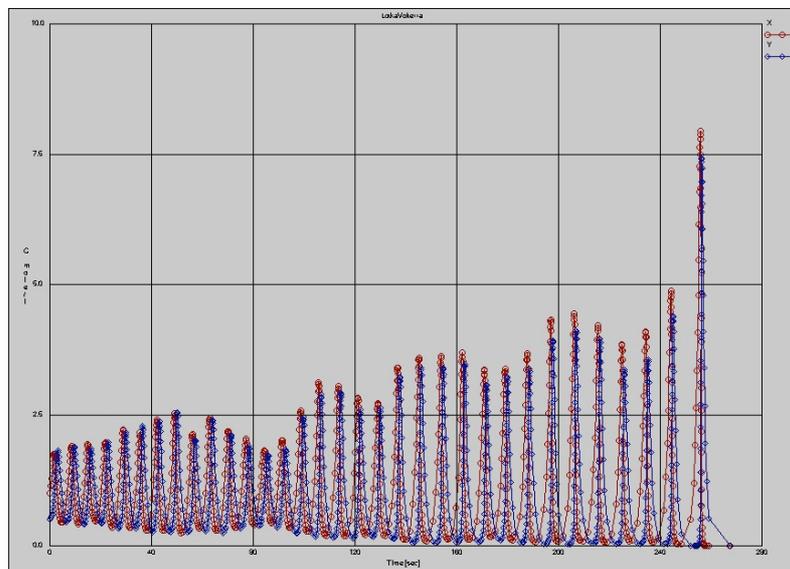
**Equilibrium Detect**

Enabled      Equil. test cycle length:  events

Disabled      Selection frequency:  percent

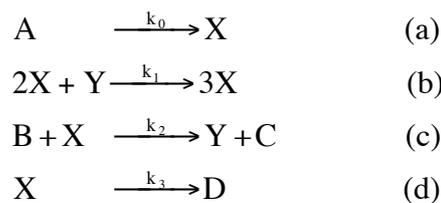
The chosen conditions should reveal concentrations for X and Y as shown in the following picture:



Change the kinetic constants and the initial concentrations and document your observations.

**b. The Brusselator**

This reaction scheme was introduced by Prigogine and co-workers in 1971. It consists of the following reaction steps:



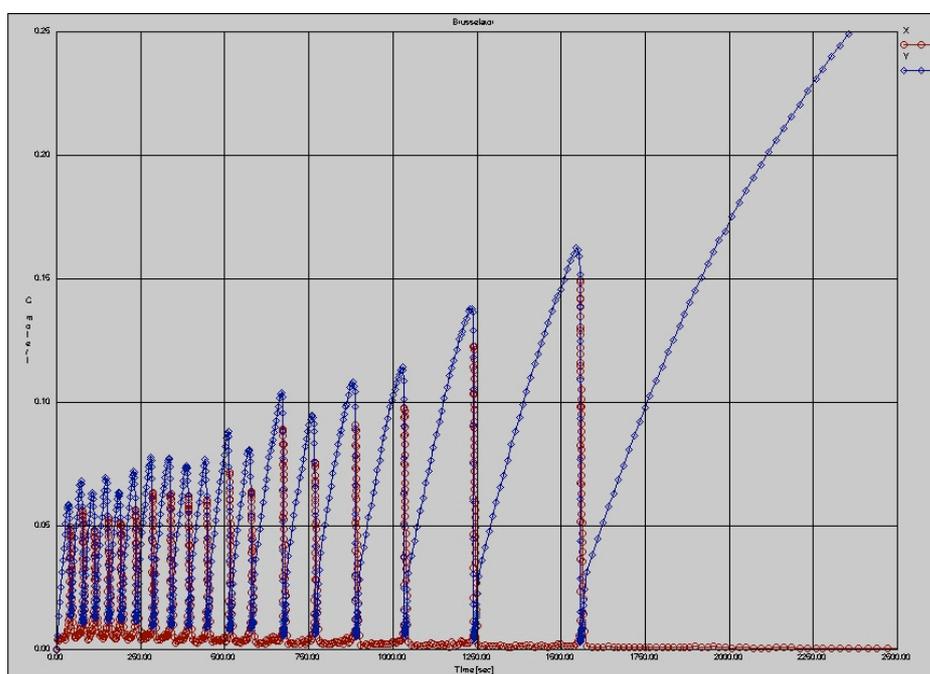
A and B are educts, X and Y are intermediates which exhibit oscillations, and C and D are products.

Use the following parameters:

$$k_0 = 0.001, k_1 = 1000, k_2 = 0.02, k_3 = 0.2$$

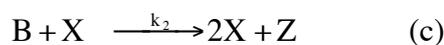
$$[A]_0 = 3, [B]_0 = 30, [C]_0 = [D]_0 = [X]_0 = [Y]_0 = 0$$

The suggested simulation parameters lead to oscillations in X and Y as shown below. Again, change the initial concentrations and document your observations.



### c. *The Oregonator*

The Belousov-Zhabotinski reaction was one of the first oscillating reactions discovered. The reaction is very complex and consists of 18 reaction steps with 21 species participating. A strong simplification of this reaction type is achieved with the Oregonator that is described using the following reaction scheme:



The intermediates X, Y, and Z show oscillations.  
 Try the following kinetic constants and initial concentrations:

$$k_0 = 5 \cdot 10^{-4}, k_1 = 8, k_2 = 8 \cdot 10^{-3}, k_3 = 1,0, k_4 = 1.5$$

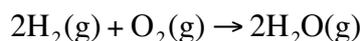
$$[A]_0 = 1000, [B]_0 = 900, [C]_0 = [D]_0 = [X]_0 = [Z]_0 = 0, [Y]_0 = 1$$

How do changes in the initial concentrations affect the reaction?

## 5.5. Explosions

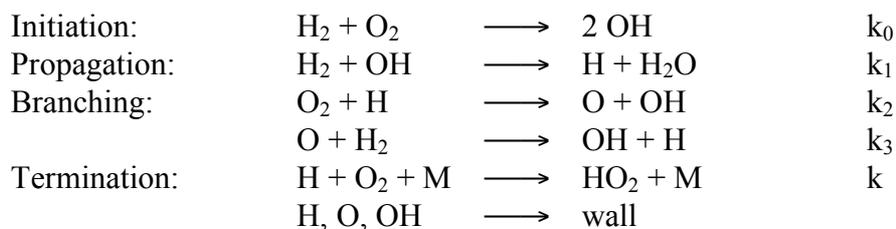
### 5.5.1. Explosion due to chain branching: the Hydrogen-Oxygen Reaction

As an example we consider the “bang gas” reaction (Knallgas-Reaktion):

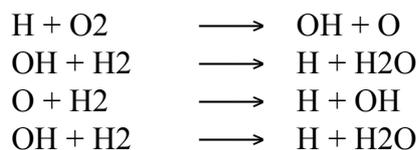


Despite the simple reaction equation, the mechanism of this reaction is extremely complex and is not yet fully understood.

The reaction can be divided into the following steps:



Initially, OH radicals are generated which react with  $\text{H}_2$  and produce H. The subsequent branching reactions increase the radical concentration:



As a net reaction we get:  $\text{H} + \text{O}_2 + 3\text{H}_2 \longrightarrow 3\text{H} + \text{H}_2\text{O}$ , i.e. one H produces three H. If branching occurs more rapidly than termination, an exponential growth can develop which ends in an explosion. The conditions for an explosion can therefore to some extent be correlated to concentrations of radicals: at high concentrations of the reactive radicals H, O, and OH, explosions are likely to happen.

At 800K the kinetic constants have the following values:

$$k_0 = 2.5 \cdot 10^{-1} \text{ l}\cdot\text{mol}^{-1}\text{s}^{-1}$$

$$k_1 = 1.2 \cdot 10^9 \text{ l}\cdot\text{mol}^{-1}\text{s}^{-1}$$

$$k_2 = 5.1 \cdot 10^6 \text{ l}\cdot\text{mol}^{-1}\text{s}^{-1}$$

$$k_3 = 5.6 \cdot 10^7 \text{ l}\cdot\text{mol}^{-1}\text{s}^{-1}$$

The initial concentration should be chosen as:

$$[\text{O}_2] = 0.0017 \text{ mol l}^{-1}$$

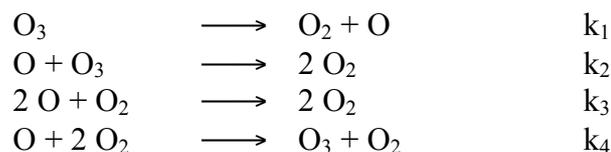
$$[\text{H}_2] = 0.0033 \text{ mol l}^{-1}$$

In the same input box, also change the temperature to 800K.

- Enter the reaction scheme (only the steps initiation, propagation, and branching) into CKS
- Compute the kinetics using the given parameters
- Change the oxygen concentration, i.e. choose oxygen concentrations that are much larger/smaller than the hydrogen concentration. How does this affect the reaction?
- Which important factors have been neglected in the applied model?

### 5.5.2. Explosion of Ozone

Here we simulate the explosion of ozone by taking into account thermo-chemical data and monitoring temperature and pressure. The considered reaction scheme is:



Create a new simulation and enter the four reaction steps. Choose the following start concentrations under *Edit -> Reaction Conditions...*:  $[\text{O}]_0 = 0.0$ ,  $[\text{O}_2]_0 = 0.0$ ,  $[\text{O}_3]_0 = 0.1$ . The volume should be kept constant in this simulation while the pressure will vary (this is defined in the same box). Also in this box, you can choose if the reaction should a) occur at constant temperature, b) at variable temperature starting at some defined temperature, or c) according to two more protocols. Choose option b) with a starting temperature of 500K and a temperature convergence of 0.5K. The simulation settings should then be chosen as depicted here:

**Set Simulation Options: OzoneOrig**

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**General Settings**

Total number of molecules:

Record state at intervals of:  events

Random number seed:

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**Limits**

Stop when total number of events exceeds:

Stop when time in simulation exceeds:  sec

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**Equilibrium Detect**

Enabled      Equil. test cycle length:  events

Disabled      Selection frequency:  percent

The kinetics is temperature dependent and follows the Arrhenius equation:

$$k = A e^{-\frac{E_A}{RT}}$$

A is a pre-exponential factor (frequency factor),  $E_A$  is the activation energy and R is the gas constant. For the considered reaction, these data are given below.

|             |                             | A-factor [l/mol s] | Temp. Exp. | $E_A$ [kcal/mol] |
|-------------|-----------------------------|--------------------|------------|------------------|
| $O_3$       | $\longrightarrow O_2 + O$   | 1.0E13             | 0.0        | 25.0             |
| $O + O_3$   | $\longrightarrow 2 O_2$     | 1.0E10             | 0.0        | 5.0              |
| $2 O + O_2$ | $\longrightarrow 2 O_2$     | 1.0E9              | -1.5       | 0.0              |
| $O + 2 O_2$ | $\longrightarrow O_3 + O_2$ | 1.0E10             | -1.5       | 0.0              |

Under *Edit -> Reaction scheme..* check *Temperature dependent* for every step and enter the corresponding data.

Moreover, thermo-chemical data of the involved species have to be given to the program. Since temperature changes during the reaction, a temperature dependent enthalpy has to be considered. In a simple approach, the enthalpy is given by:

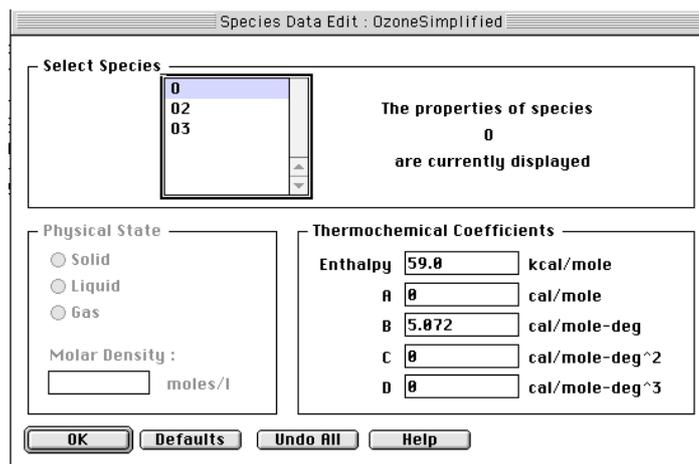
$$\Delta H_f(T) = \Delta H_f(0) + C_p \cdot T$$

The assumed linear dependence on the temperature is a big simplification. More accurate formula consists of 5 or even more terms.

For each species this data can be entered under *Edit -> Species Data....* The needed values are:

| species        | Enthalpy [kcal/mol]<br>(Enthalpy in CKS input) | $C_p$ [cal/mol·deg]<br>(parameter B in CKS input) |
|----------------|--|---|
| O              | 59.0   | 5.072   |
| O <sub>2</sub> | 0.0  | 7.395   |
| O <sub>3</sub> | 34.0   | 9.0   |

As shown below, parameters A, C, and D are set to 0.0.



Now the simulation can be started. After the simulation is finished, inspect not only the time profile of the concentrations but also the time development of temperature and pressure. Discuss your findings.

## Literature

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