12th Homework - Solution

- In this homework, we shall model chemical reactions using reaction rate equations only.
- We shall program the reaction rate equations directly in the equation window and learn to use ***Modelica's*** matrix notation.

Hydrogen-Bromine Reaction

- We wish to simulate the ***hydrogen-bromine reaction*** described during the lectures. We concentrate on mass flows only, i.e., we only model the reaction rate equations.
- We wish to plot the molar masses of the five species as functions of time.
- We shall program the reaction rate equations in the ***equation window*** of ***Dymola***, making use of a ***matrix-vector notation***, i.e., the chemical reaction network is described by the corresponding ***N-matrix***.

- Although the reactions are occurring under ***isothermic conditions***, we still wish to take the ***Arrhenius' law*** into account, and program the reaction rate constants as functions of temperature:

$$
\begin{aligned}
ak_1 &= 1.39 \cdot 10^8 \cdot \sqrt{T} \cdot \left(\frac{189243.0}{R \cdot T}\right)^{1.97} \\
k_1 &= ak_1 \cdot \exp\left(\frac{-189243.0}{R \cdot T}\right) \\
k_2 &= \frac{k_1}{K(T)} \\
k_3 &= 10^{11.43} \cdot \exp\left(\frac{-82400.0}{R \cdot T}\right) \\
k_5 &= 10^{11.97} \cdot \exp\left(\frac{-149800.0}{R \cdot T}\right) \\
k_4 &= 0.1 \cdot k_5
\end{aligned}
$$

- where ***R*** is the gas constant (***R = 8.314 J K^{-1} mole^{-1}***).

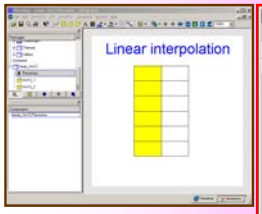
- Reaction k_2 contains a temperature dependence ***K(T)*** that was experimentally found:

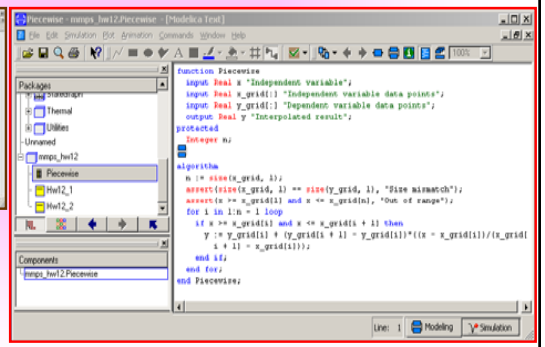
Abs. Temperature T [K]	Equilibrium Const. K [mole m^{-3}]
300.0	7.7446×10^{-29}
400.0	1.9543×10^{-20}
500.0	2.2182×10^{-15}
600.0	5.2844×10^{-12}
700.0	1.3867×10^{-9}
800.0	9.0782×10^{-8}
900.0	2.3768×10^{-6}
1000.0	3.2509×10^{-5}
1100.0	2.7861×10^{-4}
1200.0	1.6788×10^{-3}
1300.0	7.6913×10^{-3}
1400.0	2.8510×10^{-2}
1500.0	8.8716×10^{-2}
1600.0	2.4044×10^{-1}
1700.0	5.8344×10^{-1}
1800.0	1.7947
1900.0	2.6061
2000.0	4.9431

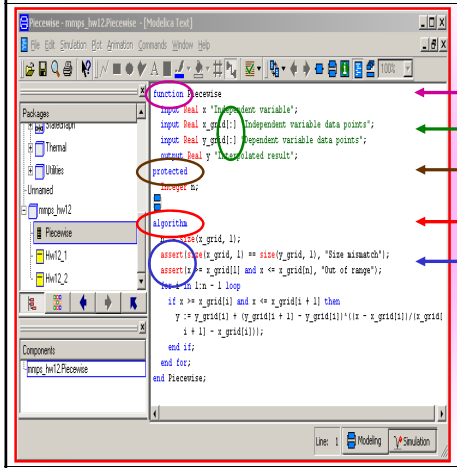
- Program ***K(T)*** using a table-lookup function.

- The initial molar masses of Br_2 and H_2 are both equal to ***0.0075***. The total reaction volume is ***V = 0.001 m^3***. The temperature is ***T = 800 K***.
- Simulate the system during ***5000 seconds***. You need to reduce the tolerance value for the ***DASSL integration algorithm*** to ***10^{-10}***.
- Plot on one graph the molar masses of Br_2, H_2, and HBr during the first ***0.1 seconds***.
- Plot on a second graph the molar mass of $H^{\bullet}$ during the first ***0.2 seconds***.
- Plot on a third graph the molar mass of $Br^{\bullet}$ during the first ***0.3 seconds***.

- We shall need a ***table look-up function***. We can program it manually.







We use a function.

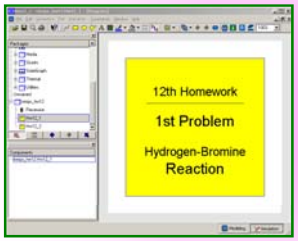
The colon here means that the array will adjust its dimension upon invocation.

Protected variables are hidden from the outside. They are strictly local.

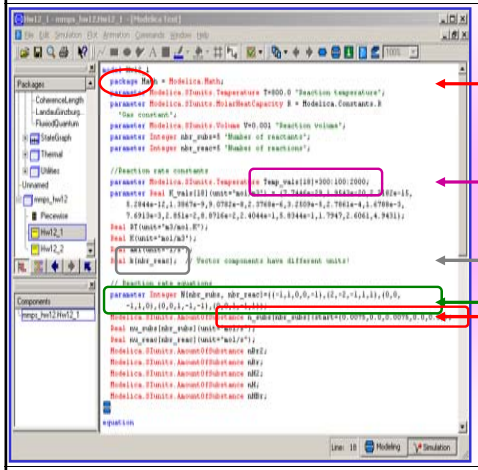
The algorithm instruction allows users to encode sequential code. While equations are declarative, algorithms are procedural.

Assert is a clean way to ensure proper usage of the function. If the assert clause is not met, the simulation dies with the indicated error message.

- We can now create the model for the ***hydrogen-bromine reaction***.



The problem is modeled entirely in the equation window. The code is a bit long. The declarations and equations shall be explained separately.



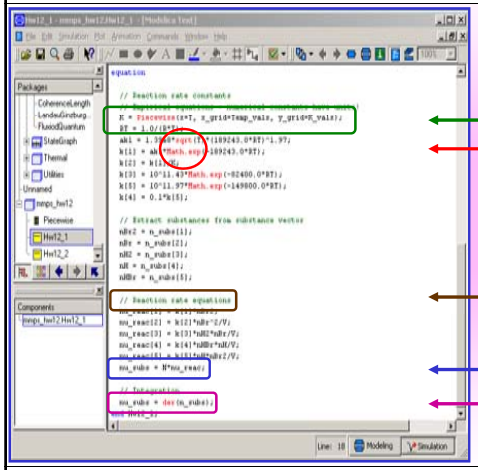
This is an abbreviation. Whenever I write "Math," I mean "Modelica.Math."

For convenience, I use the Matlab notation here.

Array sizes can be parameter expressions.

The Modelica notation is used here to declare this two-dimensional array. The Matlab notation would have worked equally well.

Initial conditions for the state vector.



Call of interpolation function.

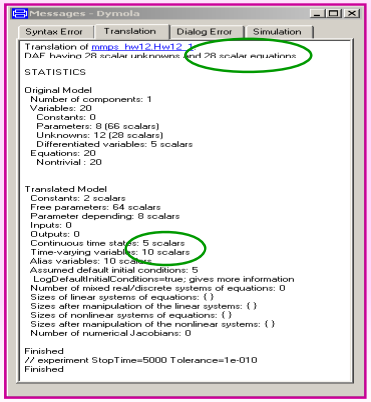
Sqrt is an intrinsic Modelica function, whereas exp is a function that is contained in the Modelica.Math library.

Comment.

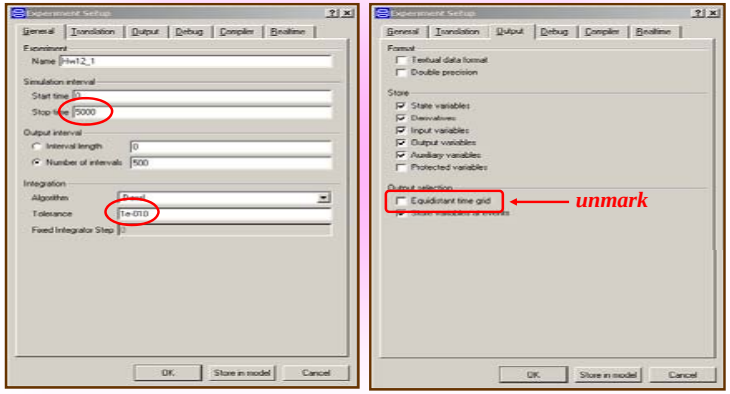
Matrix multiplication.

Matrix integration.

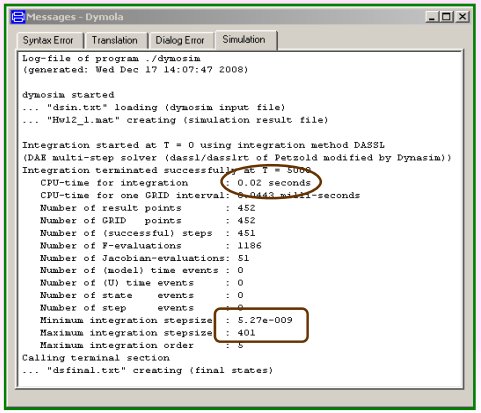
- We are now ready to compile the model.



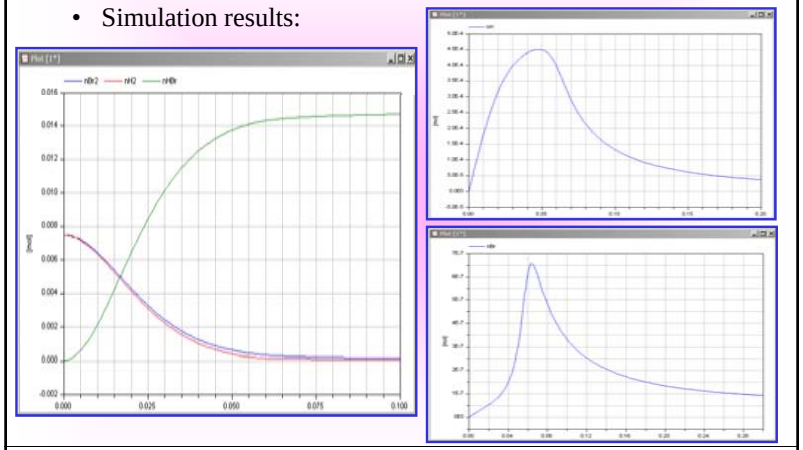
- We require some simulation control.



- We can now simulate the model.



- Simulation results:



Oxy-hydrogen Gas Reaction

- When oxygen and hydrogen gases are mixed in similar proportions, a spark can bring the mixture to explosion. The process can be described by the following set of step reactions:

$$H_2 + O_2 \xrightarrow{k_0} H^\bullet + HO_2^\bullet$$
$$H_2 + OH^\bullet \xrightarrow{k_1} H^\bullet + H_2O$$
$$O_2 + H^\bullet \xrightarrow{k_2} OH^\bullet + O^\bullet$$
$$H_2 + O^\bullet \xrightarrow{k_3} H^\bullet + OH^\bullet$$
$$OH^\bullet + W \xrightarrow{a_1}$$
$$H^\bullet + W \xrightarrow{a_2}$$
$$O^\bullet + W \xrightarrow{a_3}$$

W stands for the wall. At the wall, the unstable atoms $H^\bullet$ and $O^\bullet$, as well as the unstable radical $OH^\bullet$ can be absorbed. The absorption rates are proportional to the molar masses of the absorbed species:

$$\nu_{OH^\bullet} = -a_1 \cdot n_{OH^\bullet}$$

- The reaction rate constants at the given temperature are as follows:

$k_0 = 60.0$
$k_1 = 2.3 \cdot 10^{11}$
$k_2 = 4.02 \cdot 10^{9}$
$k_3 = 2.82 \cdot 10^{12}$
$a_1 = 920.0$
$a_2 = 80.0$
$a_3 = 920.0$

Model the system in the ***Dymola equation window*** using a matrix-vector notation.

Simulate the system during 0.1 seconds. The initial conditions are $n_{H_2} = 10^{-7}$, and $n_{O_2} = 0.5 \cdot 10^{-7}$. The reaction volume is $V = 1.0\ m^3$.

You need to reduce the tolerance value of the ***DASSL integration algorithm*** to 10^{-17}.

- Plot the molar masses of H_2, O_2, and H_2O on one plot. Plot the molar masses of the other four species on separate plots.

- Let us find the ***N-matrix***:

$$H_2 + O_2 \xrightarrow{k_0} H^\bullet + HO_2^\bullet$$
$$H_2 + OH^\bullet \xrightarrow{k_1} H^\bullet + H_2O$$
$$O_2 + H^\bullet \xrightarrow{k_2} OH^\bullet + O^\bullet$$
$$H_2 + O^\bullet \xrightarrow{k_3} H^\bullet + OH^\bullet$$
$$OH^\bullet + W \xrightarrow{a_1}$$
$$H^\bullet + W \xrightarrow{a_2}$$
$$O^\bullet + W \xrightarrow{a_3}$$

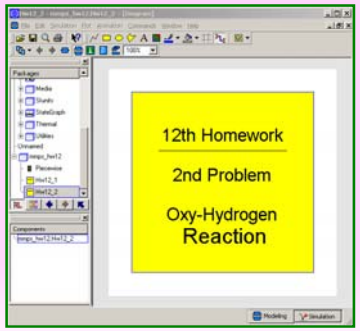
$$N = \begin{array}{c} \begin{matrix} k_0 & k_1 & k_2 & k_3 & a_1 & a_2 & a_3 \end{matrix} \\ \begin{bmatrix} -1 & -1 & 0 & -1 & 0 & 0 & 0 \\ -1 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1 & -1 & 1 & 0 & -1 & 0 \\ 0 & 0 & 1 & -1 & 0 & 0 & -1 \\ 0 & -1 & 1 & 1 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \end{array} \begin{matrix} H_2 \\ O_2 \\ H_2O \\ H^\bullet \\ O^\bullet \\ OH^\bullet \\ HO_2^\bullet \end{matrix}$$

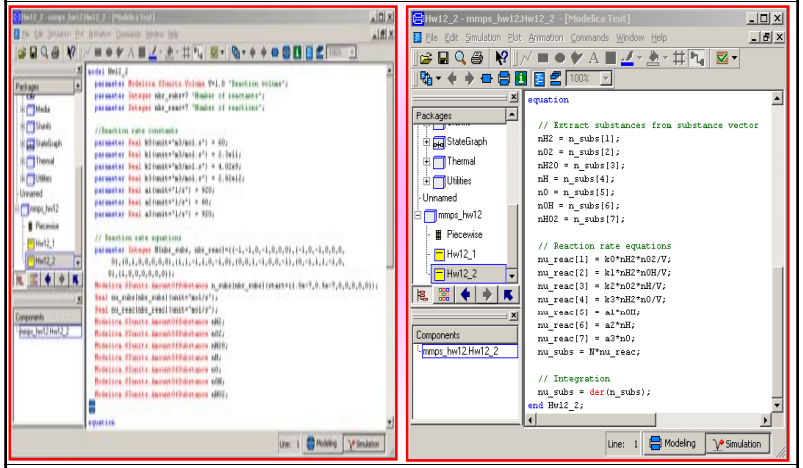
- Let us find the ***reaction rates***:

$$H_2 + O_2 \xrightarrow{k_0} H^\bullet + HO_2^\bullet$$
$$H_2 + OH^\bullet \xrightarrow{k_1} H^\bullet + H_2O$$
$$O_2 + H^\bullet \xrightarrow{k_2} OH^\bullet + O^\bullet$$
$$H_2 + O^\bullet \xrightarrow{k_3} H^\bullet + OH^\bullet$$
$$OH^\bullet + W \xrightarrow{a_1}$$
$$H^\bullet + W \xrightarrow{a_2}$$
$$O^\bullet + W \xrightarrow{a_3}$$

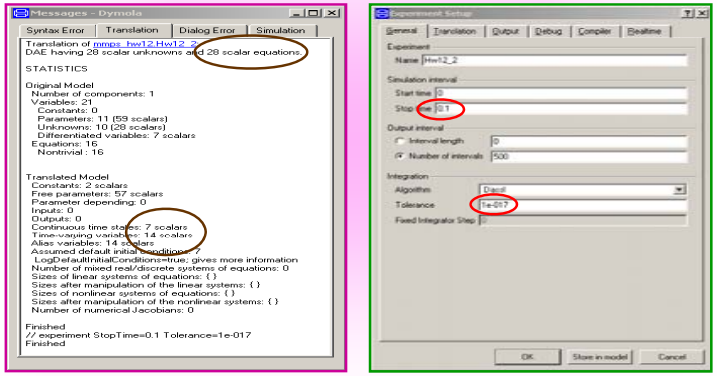
$$\nu_1 = k_0 \cdot n_{H_2} \cdot n_{O_2} / V$$
$$\nu_2 = k_1 \cdot n_{H_2} \cdot n_{OH^\bullet} / V$$
$$\nu_3 = k_2 \cdot n_{O_2} \cdot n_{H^\bullet} / V$$
$$\nu_4 = k_3 \cdot n_{H_2} \cdot n_{O^\bullet} / V$$
$$\nu_5 = a_1 \cdot n_{OH^\bullet}$$
$$\nu_6 = a_2 \cdot n_{H^\bullet}$$
$$\nu_7 = a_3 \cdot n_{O^\bullet}$$

- We are now ready to program:





- Translation and simulation control:



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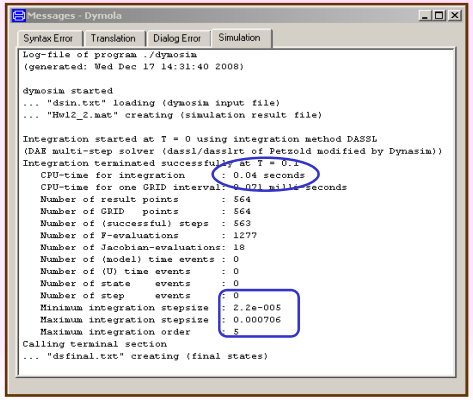
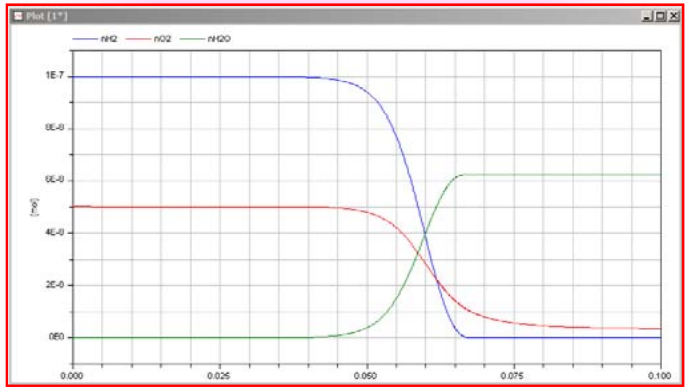
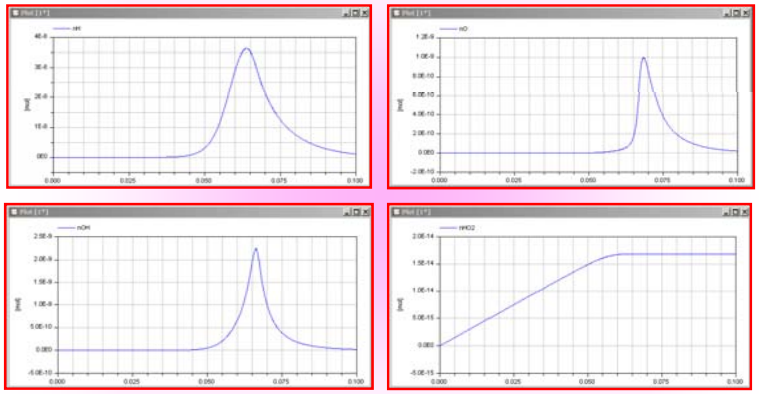


- Simulation results:





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References

- Tiller, M.M. (2001), *Introduction to Physical Modeling with Modelica*, Kluwer Academic Publishers, Chapter 6.5: *Language Fundamentals*.