12^{th} Homework

- 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
- Oxy-hydrogen Gas Reaction

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:

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

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

- Reaction $\boldsymbol{k_2}$ 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 $\mathbf{Br_2}$ and $\mathbf{H_2}$ 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 $\mathbf{Br_2}$, $\mathbf{H_2}$, and **HBr** during the first ***0.1 seconds***.
- Plot on a second graph the molar mass of $\mathbf{H^\bullet}$ during the first ***0.2 seconds***.
- Plot on a third graph the molar mass of $\mathbf{Br^\bullet}$ during the first ***0.3 seconds***.

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:

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

W stands for the wall. At the wall, the unstable atoms $\mathbf{H^\bullet}$ and $\mathbf{O^\bullet}$, as well as the unstable radical $\mathbf{OH^\bullet}$ 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 $\mathbf{H_2}$, $\mathbf{O_2}$, and $\mathbf{H_2O}$ on one plot. Plot the molar masses of the other four species on separate plots.

References

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