Chemo-bond Graphs

- In this lecture, we shall introduce a fourth bond graph library, the ***ChemBondLib***.
- It is very similar to the ***ThermoBondLib***, but designed for the purpose of modeling chemical reaction networks.

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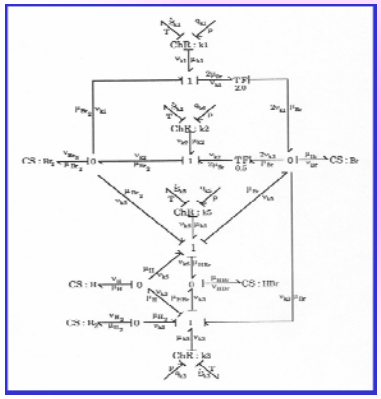
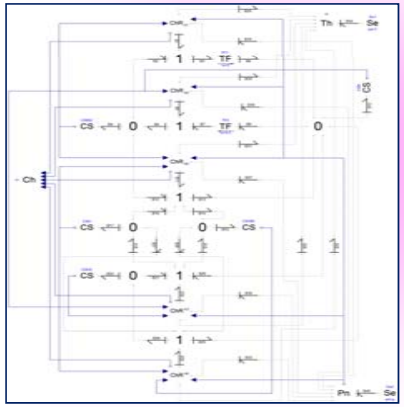
- The stoichiometric transformer
- Model #3: Thermodynamic chemical reaction network
- Model #4: Thermodynamic multi-port transformer
- Simulation efficiency

The Hydrogen-Bromine Reaction

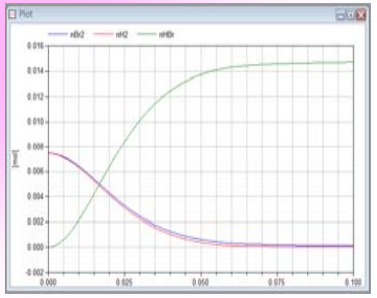


- Let us look once more at the network describing the hydrogen-bromine reaction under isothermal and isobaric conditions.
- The picture to the left is not a program, but only a drawing, as one of the five step reactions has been left out to keep the bond graph planar.
- Also, the activated bonds, passing state information to the five ChR elements were left out in order to keep the bond graph clean and well readable.

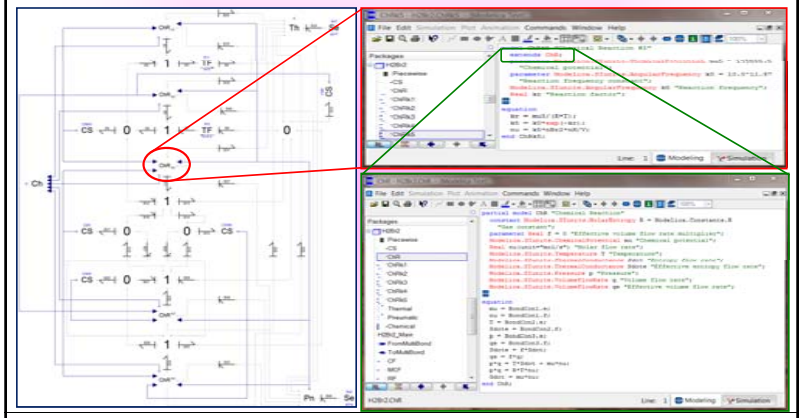
The Hydrogen-Bromine Reaction II



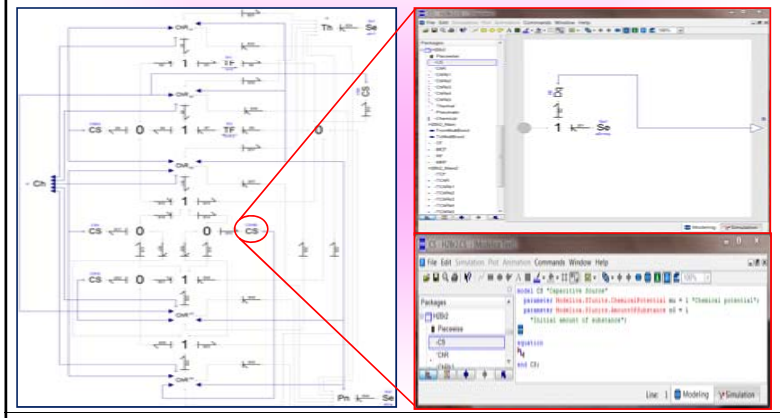
- The complete model is a bit messy.
- Yet, this model can be simulated.



The Hydrogen-Bromine Reaction III



The Hydrogen-Bromine Reaction IV



The Multi-port Transformer

- We have already seen that we can interpret the entire chemical reaction network as a multiport transformer:

$$\begin{pmatrix} \nu_{Br_2} \\ \nu_{Br\bullet} \\ \nu_{H_2} \\ \nu_{H\bullet} \\ \nu_{HBr} \end{pmatrix} = \begin{pmatrix} -1 & 1 & 0 & 0 & -1 \\ 2 & -2 & -1 & 1 & 1 \\ 0 & 0 & -1 & 1 & 0 \\ 0 & 0 & 1 & -1 & -1 \\ 0 & 0 & 1 & -1 & 1 \end{pmatrix} \cdot \begin{pmatrix} \nu_{k_1} \\ \nu_{k_2} \\ \nu_{k_3} \\ \nu_{k_4} \\ \nu_{k_5} \end{pmatrix}$$

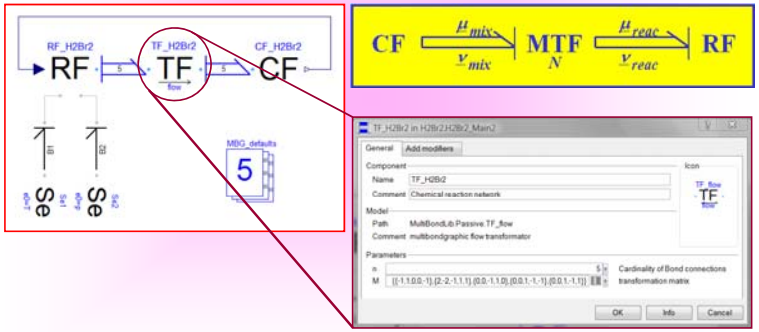
$$\begin{pmatrix} \mu_{k_1} \\ \mu_{k_2} \\ \mu_{k_3} \\ \mu_{k_4} \\ \mu_{k_5} \end{pmatrix} = \begin{pmatrix} -1 & 2 & 0 & 0 & 0 \\ 1 & -2 & 0 & 0 & 0 \\ 0 & -1 & -1 & 1 & 1 \\ 0 & 1 & 1 & -1 & -1 \\ -1 & 1 & 0 & -1 & 1 \end{pmatrix} \cdot \begin{pmatrix} \mu_{Br_2} \\ \mu_{Br\bullet} \\ \mu_{H_2} \\ \mu_{H\bullet} \\ \mu_{HBr} \end{pmatrix}$$

$$\Rightarrow \quad \vec{\nu}_s = \mathbf{N} \cdot \vec{\nu}_r \quad , \quad \vec{\mu}_r = \mathbf{M} \cdot \vec{\mu}_s$$

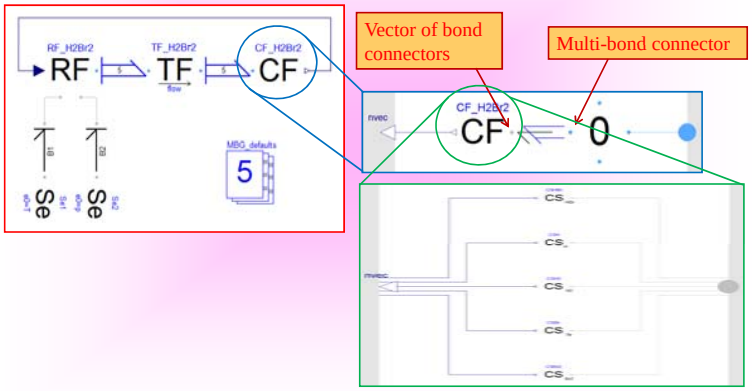
$$\mathbf{M} = \mathbf{N}^T$$

The Hydrogen-Bromine Reaction V

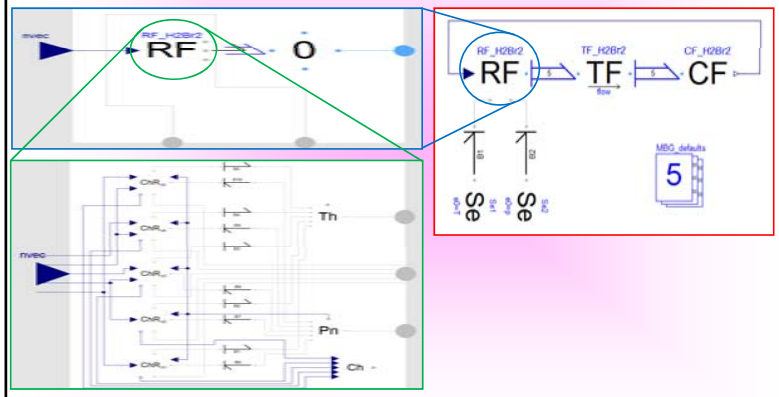
- This gives rise to a second model:



The Hydrogen-Bromine Reaction VI



The Hydrogen-Bromine Reaction VII

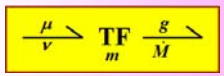


Thermo-bonds

- Until now, we have only modeled the mass flows through the chemical reaction network.
- Yet, the mass flows are also accompanied by volume and heat flows.
- It would simplify the models, if we were to model all three flows through the reaction network simultaneously. In that case, we wouldn't need any separate thermal and pneumatic ports any longer.

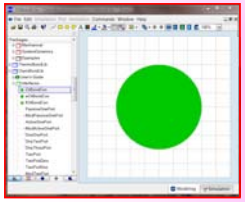
Chemo-bonds

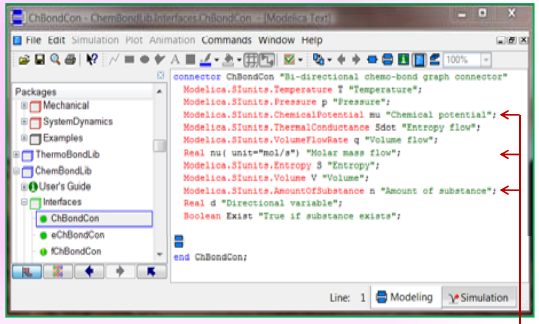
- However, we have a problem. Our thermo-bonds carry the mass flows measured in ***kg/s*** rather than in ***moles/sec***.
- For chemical reactions, this is not practical.
- Remember:



- Thus, we should create a new type of thermo-bonds that measure mass flow in ***moles/sec***.
- These are our new (green) ***chemo-bonds***.

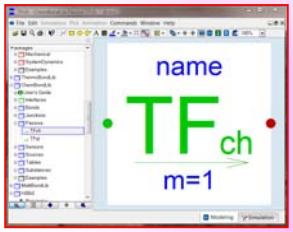
Chemo-bond Connectors



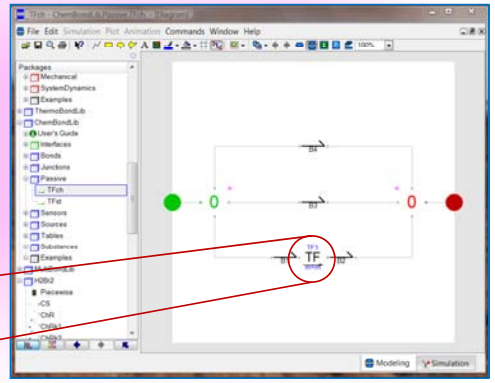


Modified units

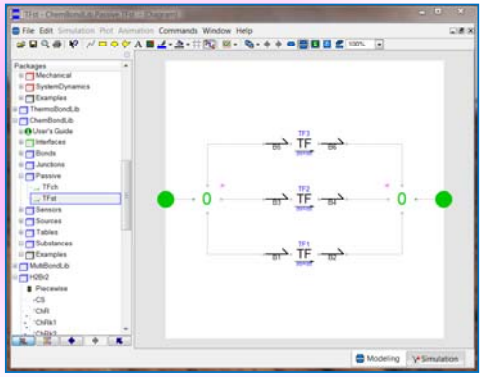
The Chemical Transformer



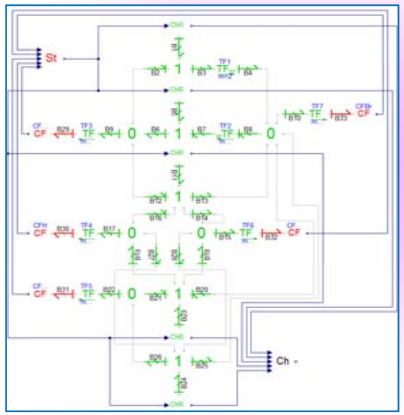
$$\frac{\mu}{\nu} \quad TF_m \quad \frac{g}{M}$$



The Stoichiometric Transformer



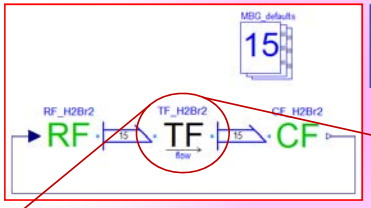
The Hydrogen-Bromine Reaction VIII



- We are now ready to formulate a third model of the H_2Br_2 reaction:
- The model shows once again the complete chemical reaction network.
- However, it is simpler than model #1, as also volume and heat flows are carried through the network.
- The capacitive fields are now the conventional capacitive fields that were introduced earlier.
- The ***St*** model groups the individual states together into a state vector.

The Hydrogen-Bromine Reaction IX

- This gives rise to a fourth model:

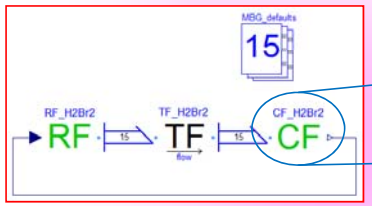


$$Z = zeros(5,5)$$

$$M = \begin{pmatrix} N & Z & Z \\ Z & N & Z \\ Z & Z & N \end{pmatrix}$$

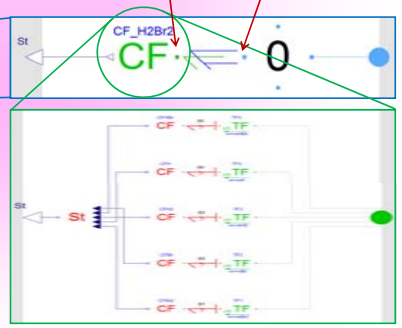
```
protected
  parameter Real N[:,:] = {{-1,1,0,0,-1},{2,-2,-1,1,1},{0,0,-1,1,0},{0,0,1,-1,-1},{0,0,1,-1,1}};
  parameter Real Z[:,:] = zeros(5,5);
  final parameter Real M[:,:] = [ N,Z,Z;  Z,N,Z;  Z,Z,N];
```


The Hydrogen-Bromine Reaction X

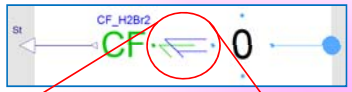


Five chemo-bond vectors of length 3

One multi-bond vector of length 15

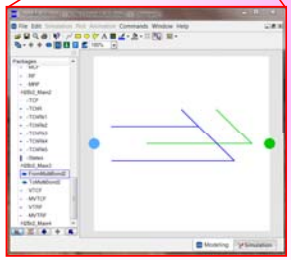


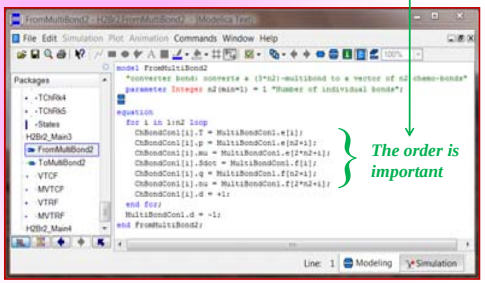
The Hydrogen-Bromine Reaction XI



$$Z = zeros(5,5)$$

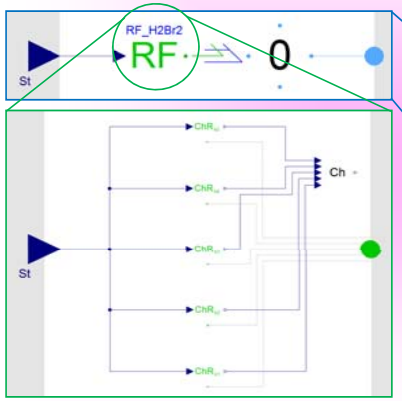
$$M = \begin{pmatrix} N & Z & Z \\ Z & N & Z \\ Z & Z & N \end{pmatrix}$$

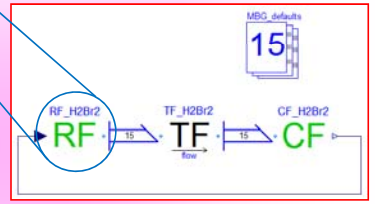




The order is important

The Hydrogen-Bromine Reaction XII





Simulation Efficiency

Model Version	# original equations	# state variables	# algebraic variables
1	1195	8	57
2	1187	8	55
3	3507	16	72
4	2835	16	66

Yet Another Approach …

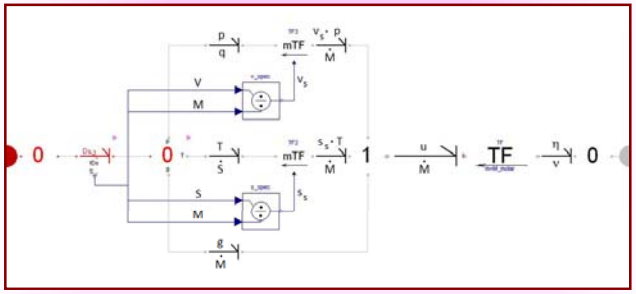
- Remember the formula for the internal energy:

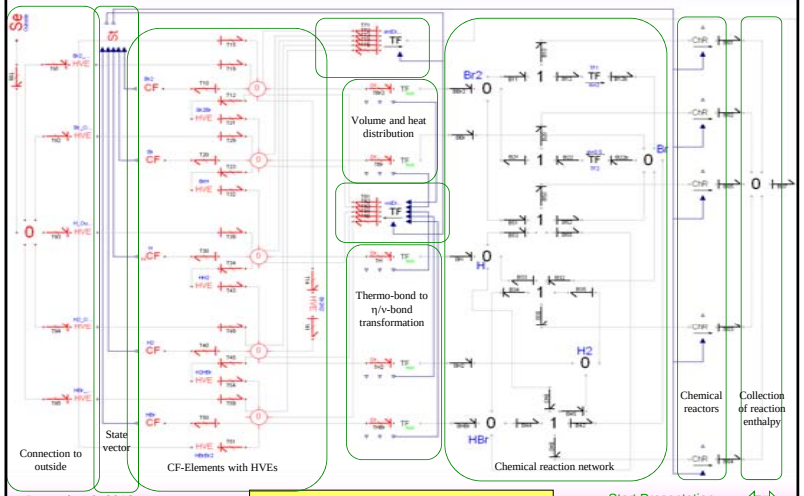
$$U = T \cdot S - p \cdot V + g \cdot m$$

$$\Rightarrow \quad u = T \cdot s - p \cdot v + g$$

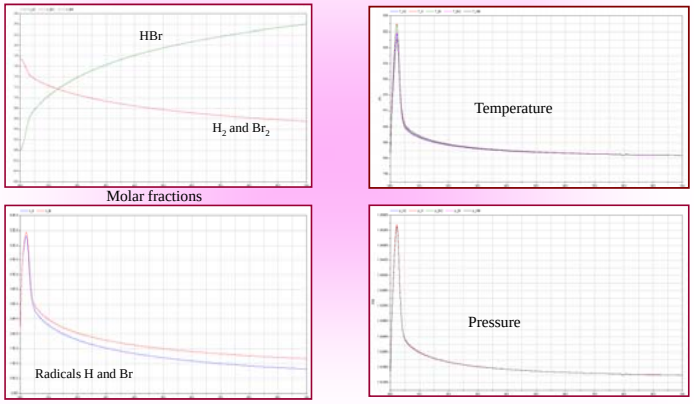
- We can exploit this to merge the three flows back together.

Merging the Three Flows





Simulation Results



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- Greifeneder, J. (2001), *Modellierung thermodynamischer Phänomene mittels Bondgraphen*, Diplomarbeit, University of Stuttgart, Germany.
- Cellier, F.E. and J. Greifeneder (2009), "Modeling Chemical Reactions in Modelica By Use of Chemo-bonds," *Proc. 7th International Modelica Conference*, Como, Italy, pp. 142-150.

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- Greifeneder, J. and F.E. Cellier (2012), "Modeling Chemical Reactions Using Bond Graphs," *Proc. ICBGM'12, 10th SCS Intl. Conf. on Bond Graph Modeling and Simulation*, Genoa, Italy, pp. 110-121.