Chemical Thermodynamics I

- In this lecture, we shall talk about chemical thermodynamics, and shall attempt a bond-graphic interpretation thereof.
- In the previous lecture, we only considered the ***mass flows*** associated with chemical reaction systems. However, these masses also carry ***volume*** and ***heat***.
- Chemical reactions are different from convective flows, because the reaction occurs in a mixture, i.e., masses do not get moved around macroscopically.

Chemical Thermodynamics II

- Yet, some reactions change the overall volume (or pressure) of the reactants, such as in explosive materials, others occur either exothermically or endothermically. It is obviously necessary to keep track of these changes.
- Furthermore, we chose to represent substances in a mixture by separate ***CF-elements***. If we wish to continue with this approach, volume and heat flows indeed do occur between these capacitive fields.

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Causality in Chemical Bond Graphs

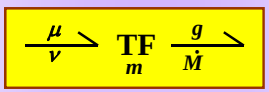
- Let us look once more at the generic chemical reaction bond graph:

Since the ***N-matrix*** cannot be inverted, the ***causality*** of the ***chemical MTF-element*** is ***fixed***.

⇒ ***The CF-element computes the three potentials (T, p, g), whereas the RF-element computes the three flows (Ṡ, q, Ṁ) of each substance involved in the reaction.***

Conversion Between Mass Flow Rate and Molar Flow Rate

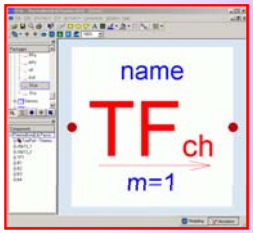
- The molar flow rate is proportional to the mass flow rate. Thus, we are dealing here with a regular transformer.

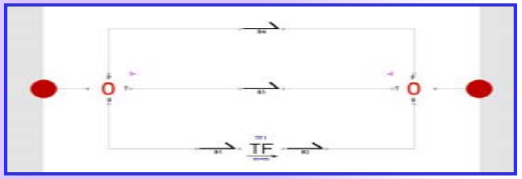


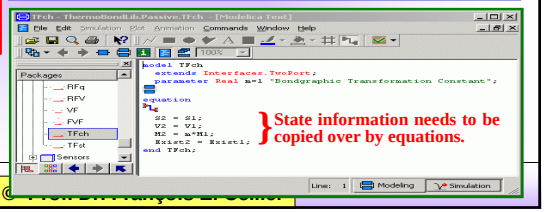
- The transformation constant, ***m***, depends on the substance. For example, since ***1 kg*** of H_2 correspond to ***500 moles***, $m_{H_2} = 0.002$.
- The entropy flow and heat flow don't change.

The TFch-Element

- Hence it makes sense to create the following ***chemical transformation*** element:





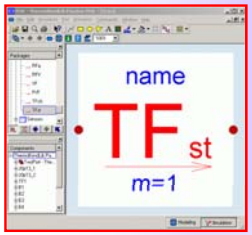


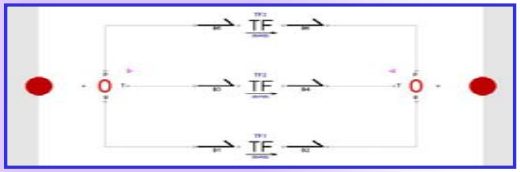
Stoichiometric Coefficients

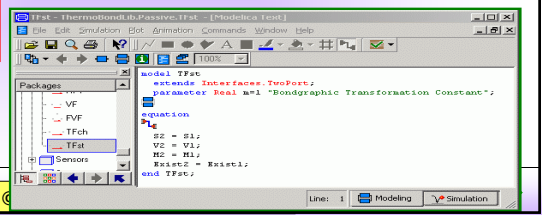
- As we saw in the previous lecture, the generic chemical reaction bond graph can be decomposed into a detailed bond graph showing individual flows between reactants and reactions.
- In such a bond graph, the stoichiometric coefficients are represented by transformers.
- However, since the mass flow rate truly changes in such a transformer (this is not merely a conversion of units), the entropy and heat flows must change along with it.

The TFst-Element

- Hence it makes sense to create the following *stoichiometric transformation* element:

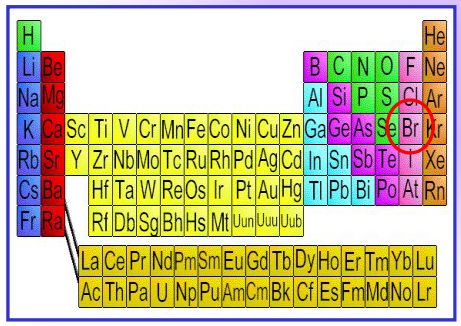






Periodic Table of Elements

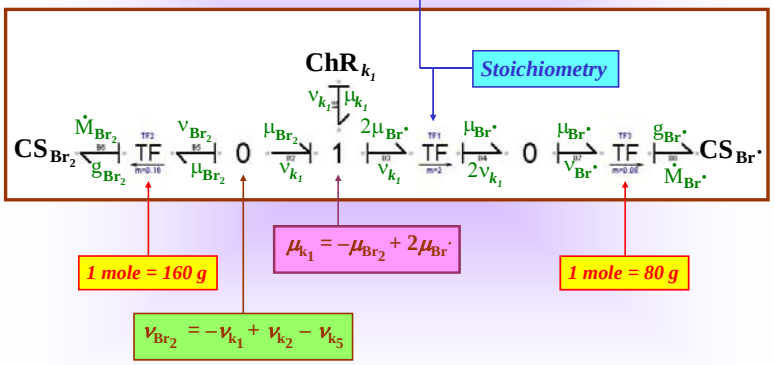
- We can consult the *periodic table of elements*:



Name: Bromine
Symbol: Br
Atomic Number: 35
Atomic Mass: 79.904 amu
Melting Point: -7.2 °C (265.95 °K, 19.04 °F)
Boiling Point: 58.78 °C (331.93 °K, 137.804 °F)
Number of Protons/Electrons: 35
Number of Neutrons: 45
Classification: Halogen
Crystal Structure: Orthorhombic
Density @ 293 K: 3.119 g/cm^3
Color: Red

1 mole = 80 g

$$Br2 \xrightarrow{k_1} 2Br^{\cdot}$$



The Equation of State

- Chemical substances satisfy a so-called *equation of state* that relates the three domains to each other.
- For *ideal gases*, the equation of state can be written as follows:

$$p \cdot V = n \cdot R \cdot T$$

$R = 8.314$ J K^{-1} mole^{-1} is the gas constant

- The equation of state can be written either for *partial pressures* (*Dalton's law*) or for *partial volumes* (*Avogadro's law*).

$$p_i \cdot V = n_i \cdot R \cdot T$$ *Dalton's law*

$$p \cdot V_i = n_i \cdot R \cdot T$$ *Avogadro's law*

Isothermal and Isobaric Reactions I

- If both ***pressure*** and ***temperature*** can be assumed approximately constant, the ***equation of state*** can be conveniently differentiated as follows (using ***Avogadro's law***):

$$p \cdot V_i = n_i \cdot R \cdot T \quad \Rightarrow \quad p \cdot q_i = \nu_i \cdot R \cdot T$$

This equation can be used to compute the ***volume flow*** from the ***mass flow***:

$$q_i = \nu_i \cdot \frac{R \cdot T}{p}$$

Isothermal and Isobaric Reactions II

- This relationship holds for all flows in the ***hydrogen-bromine reaction***, thus:

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

$$\Rightarrow$$

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

describe the corresponding ***partial pressures***.

The Gibbs Equation

- Chemical substances also satisfy the so-called ***Gibbs equation***, which can be written as:

$$p \cdot q_i = T \cdot \dot{S}_i + \mu \cdot \nu_i$$

- Since we already know ν_i and q_i, we can use this equation to compute $\dot{S}_i$.
- The ***entropy flow*** accompanies the ***mass flow*** and the ***volume flow***.
- Due to linearity (***T, p = constant*** $\Rightarrow$ ***μ = constant***), the entropy flow can be superposed to the mass and volume flows.

Isothermal and Isobaric Reactions III

- Entropy flows for the ***hydrogen-bromine reaction***:

$$\begin{bmatrix} \dot{S}_{Br_2} \\ \dot{S}_{Br\bullet} \\ \dot{S}_{H_2} \\ \dot{S}_{H\bullet} \\ \dot{S}_{HBr} \end{bmatrix} = \begin{bmatrix} -1 & +1 & 0 & 0 & -1 \\ +2 & -2 & -1 & +1 & +1 \\ 0 & 0 & -1 & +1 & 0 \\ 0 & 0 & +1 & -1 & -1 \\ 0 & 0 & +1 & -1 & +1 \end{bmatrix} \cdot \begin{bmatrix} \dot{S}_{k_1} \\ \dot{S}_{k_2} \\ \dot{S}_{k_3} \\ \dot{S}_{k_4} \\ \dot{S}_{k_5} \end{bmatrix}$$

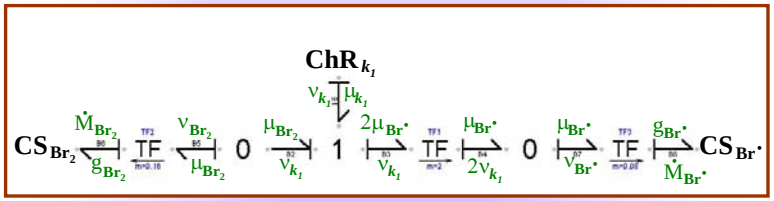
$$\Rightarrow$$

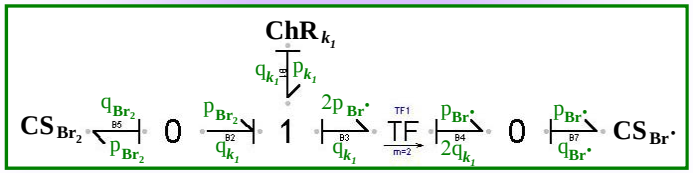
Neither the partial entropies nor the (physically extremely dubious!) "partial temperatures" are used anywhere, except for defining the corresponding power flows.

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

describe the corresponding "***partial temperatures***."

$Br2 \xrightarrow{k_1} 2Br^{\cdot}$





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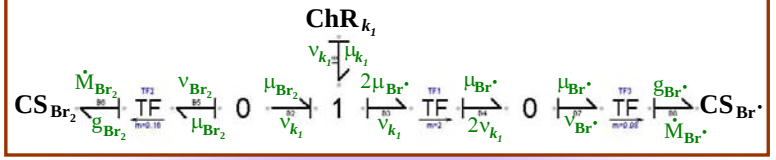
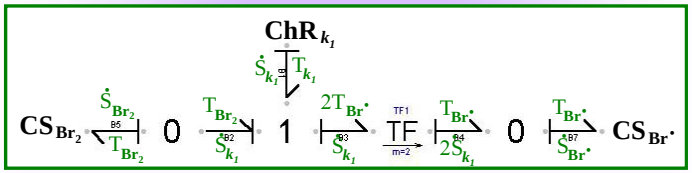
Mathematical Modeling of Physical Systems

$Br2 \xrightarrow{k_1} 2Br^{\cdot}$





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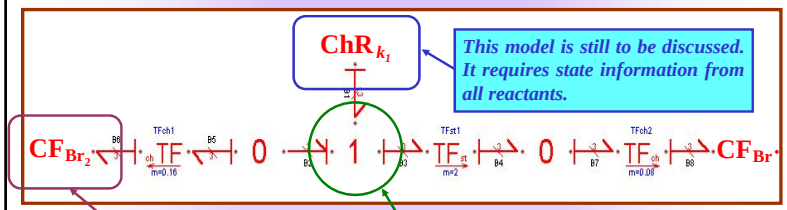
Mathematical Modeling of Physical Systems

$Br2 \xrightarrow{k_1} 2Br^{\cdot}$

- We are now ready to sketch the combined model:



This model is still to be discussed. It requires state information from all reactants.

This is now the standard capacitive field, as it had been introduced in the discussion of the convective flows.

The Bus-1-Junction does not propagate the state information.

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Mathematical Modeling of Physical Systems

The Chemical Reactor Model I

- We already know that the ***chemical reactor*** needs to compute the three flows.
- We already have the equations for this model:

$$\nu_{k_1} = k_1 \cdot n_{Br_2} \quad \leftarrow \text{reaction rate equation}$$
$$q_{k_1} = \nu_{k_1} \cdot (R \cdot T)/p \quad \leftarrow \text{equation of state}$$
$$\dot{S}_{k_1} = (p \cdot q_{k_1} - \mu_{k_1} \cdot \nu_{k_1})/T \quad \leftarrow \text{Gibbs equation}$$

We still need to verify though that no balance equations are being violated!

Mass Balance

- The mass balance is embedded in the ***stoichiometric coefficients***. Whatever gets removed from one reactant, gets added back to another. Hence the total reaction mass will not change.
- This is true for each step reaction separately, since each step reaction must satisfy the stoichiometric constraints.

Energy Balance I

- The way the equations were set up, we already know that:

$$\underline{\mu}_{mix}{}' \cdot \underline{\nu}_{mix} = \underline{\mu}_{reac}{}' \cdot \underline{\nu}_{reac}$$

- and due to the symmetry of the other two domains:

$$\underline{p}_{mix}{}' \cdot \underline{q}_{mix} = \underline{p}_{reac}{}' \cdot \underline{q}_{reac} \qquad \underline{T}_{mix}{}' \cdot \underline{\dot{S}}_{mix} = \underline{T}_{reac}{}' \cdot \underline{\dot{S}}_{reac}$$

- Hence the change in ***internal energy*** can be written as:

$$\begin{aligned}\dot{U} &= \underline{T}_{mix}{}' \cdot \underline{\dot{S}}_{mix} - \underline{p}_{mix}{}' \cdot \underline{q}_{mix} + \underline{\mu}_{mix}{}' \cdot \underline{\nu}_{mix} \\ &= \underline{T}_{reac}{}' \cdot \underline{\dot{S}}_{reac} - \underline{p}_{reac}{}' \cdot \underline{q}_{reac} + \underline{\mu}_{reac}{}' \cdot \underline{\nu}_{reac}\end{aligned}$$

Energy Balance II

- The above equation holds true under all operating conditions, i.e., the topology of the ***chemical reaction network*** is independent of the conditions under which the chemical reaction is performed.
- The ***isothermal*** and ***isobaric*** conditions assumed before only influence the ***CF-field***, i.e., the way in which the three potentials are being computed, and possibly the ***RF-field***, i.e., the way in which the three flows are being computed (we shall discuss in the next class, whether this is indeed true or not).

Volume Flow I

- Under ***isothermal*** and ***isobaric*** conditions, we can write:

$$\begin{aligned}q_{k_1} &= \nu_{k_1} \cdot (R \cdot T)/p \\ q_{k_2} &= \nu_{k_2} \cdot (R \cdot T)/p \\ q_{k_3} &= \nu_{k_3} \cdot (R \cdot T)/p \\ q_{k_4} &= \nu_{k_4} \cdot (R \cdot T)/p \\ q_{k_5} &= \nu_{k_5} \cdot (R \cdot T)/p\end{aligned}$$

$$\begin{bmatrix} p_{k_1} \\ p_{k_2} \\ p_{k_3} \\ p_{k_4} \\ p_{k_5} \end{bmatrix} = \begin{bmatrix} -1 & +2 & 0 & 0 & 0 \\ +1 & -2 & 0 & 0 & 0 \\ 0 & -1 & -1 & +1 & +1 \\ 0 & +1 & +1 & -1 & -1 \\ -1 & +1 & 0 & -1 & +1 \end{bmatrix} \cdot \begin{bmatrix} p_{Br_2} \\ p_{Br\cdot} \\ p_{H_2} \\ p_{H\cdot} \\ p_{HBr} \end{bmatrix} = \begin{bmatrix} +1 \\ -1 \\ 0 \\ 0 \\ 0 \end{bmatrix} \cdot p$$

$$\Rightarrow \quad \underline{p}_{reac}{}' \cdot \underline{q}_{reac} = (\nu_{k_1} - \nu_{k_2}) \cdot (R \cdot T) = \underline{p}_{mix}{}' \cdot \underline{q}_{mix}$$

Volume Flow II

- However under ***isobaric conditions***, we can also write:

$$\begin{aligned}\underline{p}_{mix}{}' \cdot \underline{q}_{mix} &= p \cdot ones(1,5) \cdot \underline{q}_{mix} \\ &= p \cdot ones(1,5) \cdot \underline{\nu}_{mix} \cdot (R \cdot T)/p \\ &= ones(1,5) \cdot \underline{\nu}_{mix} \cdot (R \cdot T) \\ &= ones(1,5) \cdot N \cdot \underline{\nu}_{reac} \cdot (R \cdot T) \\ &= (\nu_{k_1} - \nu_{k_2}) \cdot (R \cdot T) = \underline{p}_{reac}{}' \cdot \underline{q}_{reac}\end{aligned}$$

Entropy Flow I

- Let us now discuss the entropy flow. We are certainly allowed to apply the ***Gibbs equation*** to the ***substances***:

$$\underline{T}_{mix}{}' \cdot \dot{\underline{S}}_{mix} = \underline{p}_{mix}{}' \cdot \underline{q}_{mix} - \underline{\mu}_{mix}{}' \cdot \underline{\nu}_{mix}$$

- Under ***isothermal*** and ***isobaric*** conditions:

$$T \cdot ones(1,5) \cdot \dot{\underline{S}}_{mix} = p \cdot ones(1,5) \cdot \underline{q}_{mix} - \underline{\mu}_{mix}{}' \cdot \underline{\nu}_{mix}$$

- Thus:

$$T \cdot ones(1,5) \cdot N \cdot \dot{\underline{S}}_{reac} = p \cdot ones(1,5) \cdot N \cdot \underline{q}_{reac} - \underline{\mu}_{reac}{}' \cdot \underline{\nu}_{reac}$$

Entropy Flow II

- Therefore:

$$T \cdot (\dot{S}_{k_1} - \dot{S}_{k_2}) = p \cdot (q_{k_1} - q_{k_2}) - \underline{\mu}_{reac}{}' \cdot \underline{\nu}_{reac}$$

- Thus, the ***Gibbs equation*** can also be applied to ***reactions***.

$$\begin{aligned}\dot{S}_{k_1} &= (p \cdot q_{k_1} - \mu_{k_1} \cdot \nu_{k_1})/T \\ \dot{S}_{k_2} &= (p \cdot q_{k_2} - \mu_{k_2} \cdot \nu_{k_2})/T \\ \dot{S}_{k_3} &= (p \cdot q_{k_3} - \mu_{k_3} \cdot \nu_{k_3})/T \\ \dot{S}_{k_4} &= (p \cdot q_{k_4} - \mu_{k_4} \cdot \nu_{k_4})/T \\ \dot{S}_{k_5} &= (p \cdot q_{k_5} - \mu_{k_5} \cdot \nu_{k_5})/T\end{aligned}$$

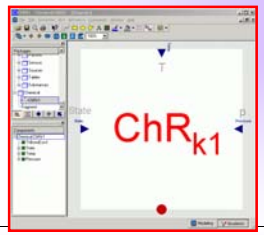
$$\begin{bmatrix} T_{k_1} \\ T_{k_2} \\ T_{k_3} \\ T_{k_4} \\ T_{k_5} \end{bmatrix} = \begin{bmatrix} -1 & +2 & 0 & 0 & 0 \\ +1 & -2 & 0 & 0 & 0 \\ 0 & -1 & -1 & +1 & +1 \\ 0 & +1 & +1 & -1 & -1 \\ -1 & +1 & 0 & -1 & +1 \end{bmatrix} \cdot \begin{bmatrix} T_{Br_2} \\ T_{Br^\bullet} \\ T_{H_2} \\ T_{H^\bullet} \\ T_{HBr} \end{bmatrix} = \begin{bmatrix} +1 \\ -1 \\ 0 \\ 0 \\ 0 \end{bmatrix} \cdot T$$

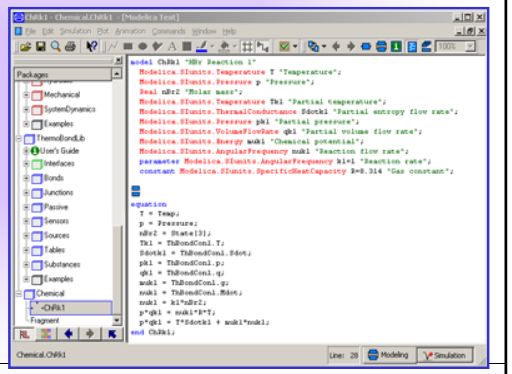
$$\Rightarrow \quad \underline{T}_{reac}{}' \cdot \dot{\underline{S}}_{reac} = T \cdot (\dot{S}_{k_1} - \dot{S}_{k_2}) = \underline{T}_{mix}{}' \cdot \dot{\underline{S}}_{mix}$$

The Chemical Reactor Model II

- We are now ready to program the chemical reactor model.

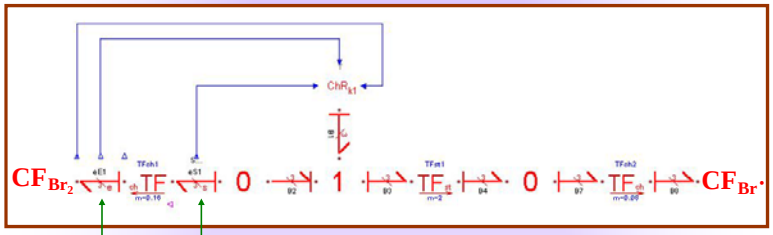
$$\begin{aligned}\nu_{k_1} &= k_1 \cdot n_{Br_2} \\ q_{k_1} &= \nu_{k_1} \cdot (R \cdot T)/p \\ \dot{S}_{k_1} &= (p \cdot q_{k_1} - \mu_{k_1} \cdot \nu_{k_1})/T\end{aligned}$$





The Chemical Reactor Model III

- Consequently:



The activated bonds are awkward. They were necessary because stuff got separated into different and no longer neighboring models that are in reality different aspects of the same physical phenomenon.

The Multi-Bus-Bond

- A clean solution is to create a new bond graph library, the ***ChemBondLib***, which operates on ***multi-bus-bonds***, i.e. vectors of bus-bonds that group all of the flows together.
- Special "blue" ***multi-bus-0-junctions*** will be needed that have on the one side a group of red bus-bond connectors, on the other side one blue multi-bus-bond connector.
- The individual ***CF-elements*** can be connected to the red side, whereas the ***MTF-element*** is connected to the blue side.

The MTF-Element

- The ***MTF-element*** is specific to each reaction, since it contains the ***N-matrix***, which is used six times inside the ***MTF-element***:

$$\underline{\nu}_{reac} = N \cdot \underline{\nu}_{mix}$$
$$\underline{\mu}_{mix} = N' \cdot \underline{\mu}_{reac}$$
$$\underline{q}_{reac} = N \cdot \underline{q}_{mix}$$
$$\underline{p}_{mix} = N' \cdot \underline{p}_{reac}$$
$$\underline{\dot{S}}_{reac} = N \cdot \underline{\dot{S}}_{mix}$$
$$\underline{T}_{mix} = N' \cdot \underline{T}_{reac}$$

The RF-Element

- The ***RF-element*** is also specific to each reaction, and it may furthermore be specific to the operating conditions, e.g. ***isobaric*** and ***isothermal***.
- In the ***isobaric*** and ***isothermal*** case, it could contain the vector equations:

$$\underline{n} = [\, n_{Br_2};\ n_{Br} \cdot {}^2/V;\ n_{H_2} * n_{Br} \cdot /V;\ n_{HBr} * n_{H} \cdot /V;\ n_{H} \cdot * n_{Br_2}/V \,];$$
$$\underline{\nu}_{reac} = \underline{k} \ .* \ \underline{n};$$
$$p * \underline{q}_{reac} = \underline{\nu}_{reac} * R * T;$$
$$p * \underline{q}_{reac} = T * \underline{\dot{S}}_{reac} + \underline{\mu}_{reac} \ .* \ \underline{\nu}_{reac};$$

Conclusions I

- In my ***Continuous System Modeling*** book, I had concentrated on the modeling the reaction rates, i.e., on the ***mass flow equations***. I treated the volume and heat flows as global properties, disassociating them from the individual flows.
- In this new presentation, I recognized that mass flows cannot occur without simultaneous volume and heat flows, which led to an improved and thermodynamically more appealing treatment.

Conclusions II

- Although I had already recognized in my book the ***N-matrix***, relating ***reaction flow rates*** and ***substance flow rates*** to each other, and although I had seen already then that the relationship between the ***substance chemical potentials*** and the ***reaction chemical potentials*** was the transposed matrix, ***M = N'***, I had not yet recognized the ***chemical reaction network*** as a bond-graphic ***Multi-port Transformer*** (the ***MTF-element***).
- Although I had recognized the ***CS-element*** as a capacitive storage element, I had not recognized the ***ChR-element*** as a reactive element.

Conclusions III

- When I wrote my modeling book, I started out with the known reaction rate equations and tried to come up with a consistent bond-graphic interpretation thereof.
- I took the known equations, and fit them into boxes, wherever they fit best … and in all honesty, I didn't goof up very much doing so, because there aren't many ways, using the bond-graphic technique, that would lead to a complete and consistent (i.e., contradiction-free) set of equations, and yet be incorrect.

Conclusions IV

- However, the bond-graphic approach to modeling physical systems is much more powerful than that. In this lecture, I showed you how this approach can lead to a clean and consistent thermo-dynamically appealing description of chemical reaction systems.
- We shall continue with this approach during one more class, where I shall teach you a yet improved way of looking at these equations.

References

- Cellier, F.E. (1991), *Continuous System Modeling*, Springer-Verlag, New York, Chapter 9.
- 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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