

Modeling Chemical Reactions Using Bond Graphs

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Abstract

This article offers a general methodology for modeling basic chemical reactions and carries forward a series of papers on modeling thermodynamic behavior using true rather than pseudo-bond graphs. In order to make processes of heating and expansion within the mixture visible, our approach does not deal with one overall volume and the overall entropy –as would be normal for classical chemistry– but rather with separated entities, one for each compound. Furthermore, assumptions of quasi-stationary or equilibrium conditions are minimized to ensure the largest possible degree of generality in the conclusions reached.

It will be shown, that chemical reactions can be modeled as transformative behavior, which makes their external behavior linear and therefore allows for superposing several chemical reactions.

While the mass flows (respectively molar flows) are assumed to be determined directly from Arrhenius' equation and the underlying stoichiometry, the determination of entropy and volume flow processes needed a more extensive discussion.

A bondgrapher's Modelica model of the HBr-synthesis based on the assumption of ideal gas serves as an example of the presented theory of chemical reaction dynamics.

1 INTRODUCTION

Dealing with macroscopic mass flows, the mass that flows through the system has to be modeled explicitly, as it carries with it its stored internal free energy, which is thus transported from one location to another in a non-dissipative fashion. In the most general sense, thermodynamics ought to be described by distributed parameter models. Since bond graphs are geared to be used for the description of lumped parameter models only, a simplifying assumption will be made, in that the system to be modeled is compartmentalized, whereby each compartment is considered to be homogeneous.

New bond-graphic macro-elements were introduced in the previous papers [1][2][3][4] to describe the energy storage within a compartment as well as the mass (and

energy) flows between neighboring compartments. The first of them [1] discussed the modeling of conductive as well as convective flows of a single homogeneous substance through a homogeneous medium. The second one [2] discussed the phenomena associated with phase change, i.e., it discussed –from a bondgrapher's perspective– phenomena such as evaporation and condensation, solidification, melting, and sublimation. The third paper in the series [3] dealt with the difficult problem of modeling multi-element systems. Therefore the assumption of homogeneous, ideally mixed compartments was needed. 'Ideally mixed' here means that the molecules are distributed at random, i.e., a prediction of what molecule becomes a neighbor of which other molecules is not possible. These conceptual systems have been modeled by introducing one energy storage element for each component of the mixture and by connecting them using pressure-volume-exchange and heat-exchange elements. The latest of the previous papers [4] introduced the corresponding thermal-bond-library for Dymola [5].

2 BONDS, MULTI-BONDS, AND THERMO-BONDS

In this section, a short summary of the three types of bonds that populate our three bond graph libraries, *BondLib* [8], *MultiBondLib* [9], and *ThermoBondLib* [4], is provided.

The basic bonds are our regular (black) bonds as shown in Fig. 1.

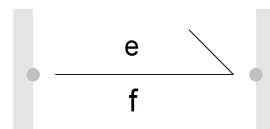


Fig. 1: Regular bonds.

Regular bonds carry two variables, the effort, e , and the flow, f . Their connectors, the gray dots to the left and the right of the bond carry a third variable, the directional variable, d . The directional variable is set by the bonds. It assumes a value of +1 at the side of the harpoon, and a value of -1 at the opposite end of the bond. The directional variable is used by the junction models to sum either the flows or the efforts up correctly.

The efforts and flows of the regular bonds don't carry units in order to make them usable for all application areas. In Dymola, variables not carrying units can be connected to variables carrying units. They then inherit (and propagate) the units of their connecting variables. Thus, if a bond gets connected to an electrical resistor model, the bond inherits units of Volts for the effort variable and units of Amperes for the flow variable and propagates those units across junctions throughout the bond graph. When two variables get connected, that carry incompatible units, the compiler complains.

MultiBondLib operates on (blue) multi-bonds, i.e., vectors of unit-less efforts and flows as shown in Fig. 2.

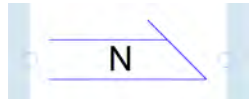


Fig. 2: Multi-bonds.

Multi-bonds (or vector-bonds, as they are also sometimes called) represent generalizations of regular bonds. Here, the effort and the flow are vectors of length N . They are most commonly used for the description of 2D and 3D mechanical systems, but the concept is completely general. For this reason, also our multi-bonds don't carry units by themselves, but rather inherit them in connections to elements belonging to a particular domain, such as mechanics.

Whereas the dynamics of electrical or mechanical phenomena can be fully captured by two variables each, thermodynamic phenomena require three independent variables for their description. Traditionally, physicists dealing with thermodynamic models make use of the temperature, T , the pressure, p , and the mass, M as their three "state variables." From a bond-graphic point of view, this approach is a bit inconvenient. We are used to think in terms of power flows.

The internal energy of matter can be written as:

$$U = T \cdot S - p \cdot V + g \cdot M \quad (1)$$

where S denotes the entropy, V is the volume, and g represents the Gibbs potential. The change of internal energy in a transition can be written as:

$$\Delta U = T \cdot \Delta S - p \cdot \Delta V + g \cdot \Delta M \quad (2)$$

When matter gets transported from place A to place B, it carries with it its internal energy, represented by its entropy S , its volume V , and its mass M . It thus makes sense to represent the transport of matter (convective flow) by three parallel bonds, one representing the flow of *entropy*, the second denoting the flow of *volume*, and the third carrying the flow of *mass*. This is shown in Fig. 3.

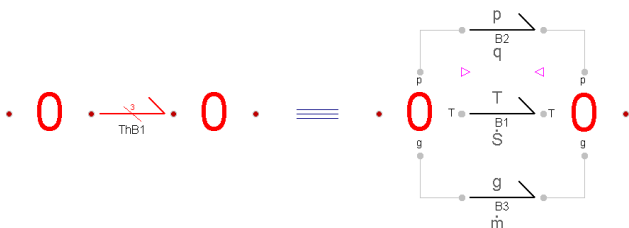


Fig. 3: Thermo-bonds.

ThermoBondLib operates on (red) thermo-bonds. Although it would have been perfectly possible to represent convective flows by multi-bonds (Dymola does not impose the restriction that all components of a vector must carry the same units), we chose a different route.

Thermodynamics is such a fundamental field of physics that it seemed justified to create a special bond to denote convective flow. This bond, contrary to the regular and multi-bond, carries units of its own, i.e., the compiler will complain immediately if a user by mistake tries to connect an entropy flow to a volume port or vice-versa. Also it is convenient to be able to carry the state information across the bond together with the energy flow variables. To this end, the red thermo-bond connectors carry 11 variables instead of only 7. They carry three scalar effort variables (T , p , and g), three scalar flow variables ($Sdot$, q , and $Mdot$), three scalar state variables (S , V , and M), the directional variable, d , and a Boolean variable, called *Exist*, that denotes whether there is still mass at the input thermo-port of the bond. The final variable in the set is useful because many models operate on specific quantities, such as specific entropy or specific volume, and Dymola takes it very odd when we try to compute a specific entropy by dividing the entropy by a mass that has meanwhile assumed a value of zero.

The thermo-bond connector model is given in Fig. 4.

```
connector ThBondCon "Bi-directional thermo-bond graph connector"
  Modelica.SIunits.Temperature T "Temperature";
  Modelica.SIunits.Pressure p "Pressure";
  Modelica.SIunits.SpecificEnthalpy g "Gibbs potential";
  Modelica.SIunits.ThermalConductance Sdot "Entropy flow";
  Modelica.SIunits.VolumeFlowRate q "Volume flow";
  Modelica.SIunits.MassFlowRate Mdot "Mass flow";
  Modelica.SIunits.Entropy S "Entropy";
  Modelica.SIunits.Volume V "Volume";
  Modelica.SIunits.Mass M "Mass";
  Real d "Directional variable";
  Boolean Exist "True if substance exists";
end ThBondCon;
```

Fig. 4: Thermo-bond connector model.

The entropy flow variable carries the unit *ThermalConductance* instead of the (compatible) unit *EntropyFlowRate* because Modelica so far failed to include *EntropyFlowRate* in its library of physical quantities and their units.

3 SUMMARY OF THERMODYNAMIC MACRO-ELEMENTS

In this section, a short summary of macro-elements introduced in previous papers will be offered.

To represent the relationship between the three thermodynamic dimensions of storage and potential a new bond graph element was introduced, called thermodynamic capacitive field, or C-field (cf. Fig. 5).

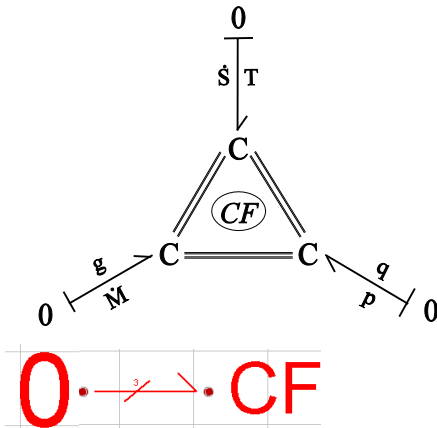


Fig. 5: C-field (Bond graph and iconic representation).

The exchange of heat (by conduction) is modeled using the Heat-Exchange (**HE**) element. The exchange of volume (to obtain a pressure equilibrium) between neighboring media with a movable membrane in between them is modeled using the Pressure-Volume-Exchange (**PVE**) element. Besides these two mass free exchanges there exist a couple of different mass-flow types. All of them have in common that they are driven by a difference in at least one of their potential variables. It is important to note that any kind of mass flow always carries volume and entropy, creates mixing entropy within the absorbing C-field, and does not change the total volume and mass present in the system. This is true even for mixtures containing different components¹, as changing the number of molecules within a volume or changing the composition yields a different internal pressure and not a change in volume. The changing pressure may ultimately lead to a volume change if the system is open; however, this is a consequence of pressure-volume exchange with the environment and not an immediate effect caused by the mass flow.

There is a distinction made between (externally) forced mass flows and free (not externally forced) mass flows. The former are modeled using the **RF** respectively **FMF** element, whereby we discriminate between **RFq** and **FMFq** (versus **RFm** and **FMFm**), symbolizing R-fields driven by an externally specified volume flow (versus mass flow). Modeling a pump would suggest use of a **RFq** element, while modeling stochastically described phenomena, such as phase changes, are best described using an **RFm** element. The internal representation of both types of models is essentially the same except for the place where the external forcing variable enters the model. Free mass flows are based on potential differences in at least one of the three thermodynamic potentials. This is similar to the previously discussed **HE** and **PVE** elements, however without a membrane within the compartments (thereby inducing a mass flow). Most of the convective processes can be described using free mass-flow elements.

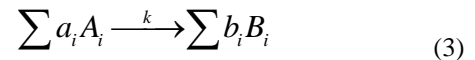
¹ To describe mixtures containing different components, the concept of the mixture-information (**MI**) element is used [3].

These elements have been coined mass exchange (**ME**) and volume exchange (**VE**) element, respectively. There could exist a third such element, the entropy exchange element. However, the three potentials are not independent of each other, as the Gibbs potential can be expressed as a function of temperature and pressure.

4 MASS FLOW EQUATIONS IN CHEMICAL REACTIONS

4.1 Reaction rate

Chemical reactions are given in the following form:



where a_i , and b_i are called stoichiometric coefficients and A_i and B_i represent the reactants respectively products of the reaction. k is called the reaction rate and is of a stochastic nature. It describes the consistency in between the intensity of activation, Ea , i.e., the energy required to produce disintegration of a molecule, the temperature T –representing the kinetic energy of the molecule (cf. Browns movements)– and the collision frequency, k_∞ . Arrhenius found, that most reaction rates are exponential in temperature with k_∞ and Ea being assumed constant:

$$k = k_\infty \cdot e^{-\frac{Ea}{R \cdot T}} \quad \text{respect.} \quad k = k_0 \cdot T^m \cdot e^{-\frac{Ea}{R \cdot T}} \quad (4)$$

While the dependence between temperature and reaction rate could be interpreted using physical knowledge, Arrhenius' law still is of empirical nature, i.e. there is no physical explanation for the exact formula. Obviously, the reaction rate also depends on the pressure, not only on the temperature, as increasing the pressure equals increasing the density and therefore means increasing the probability of two molecules hitting one another. However, this is not accounted for within the reaction rate, but within the molar flow rate (cf. Section 4.3).

One problem with Arrhenius' law concerns the value of the temperature to be used in Eq.(4). While the different components involved in the chemical reaction might be at different temperatures, Arrhenius' equation references only one (medium) temperature, which can e.g. be determined by calculating the steady-state temperature of the reactants – or using a first-order approximation, as volume-fraction weighted average of the different temperature values (cf. Section 7).

4.2 Molar and mass flows

From Eq.(3) it follows, that for a_l molecules of component A_l , a_i molecules of component A_i , $i > l$, are needed to process the reaction. Furthermore, it follows that a_i molecules of the components A_i , $i \geq l$ lead to b_i molecules of the components B_i . For this reason chemists operate on numbers of molecules instead of amount of mass, i.e., the activity of such a reaction will be specified as a molar

flow ν , rather than as a mass flow \dot{M} . A molar flow rate ν for an indicated reaction means that $a_i \cdot \nu$ molecules of component A_i are consumed within one time unit, creating $b_i \cdot \nu$ molecules of component B_i . Consequently all flow rates will be specified in mol/sec instead of kg/sec. This is not as bad as it seems, as there exists a constant relationship between *mol* and *kg* for each component, called the molar mass. One mol ($L=6.025 \cdot 10^{23}$ molecules) of a specified component with molar mass \bar{M} gram/mol weighs \bar{M} gram. L is called Loschmidt's or Avogadro's number. In bond graph modeling this means that each mass flow bond (Gibbs potential g and mass flow \dot{M}) can be easily transformed to a molar flow bond (chemical potential μ and molar flow ν) using a transformer with transforming factor \bar{M} (the molar mass), cf. Fig. 6.



Fig. 6: Molar Transformer.

It follows that the mass within the C-fields could be replaced by the number of molecules n stored in the C-field. This transformation might make sense if the whole bond graph does only concern chemical reactions, but it is impractical if the world around should be included in the model also. For this reason, it makes more sense to couple chemical reaction to the outside using molar transformers, i.e., the chemical reaction network operates on molar flow rates, but the C-fields represent mass in kg. They are connected to the chemical reaction network via molar transformers.

4.3 Molar flow rate

For a reaction to take place, it is necessary that the reactant molecules hit one another. Assuming independent surface probabilities, the probability of such a hit is given by:

$$\prod_{A_i} \left(\frac{n_{A_i}}{n_{tot}} \right)^{a_i} \quad (5)$$

n_{A_i} thereby specifies the number of mol of reactant A_i within the compartment, whereas n_{tot} gives the total number of mol ($6.025 \cdot 10^{23}$ molecules) present in the compartment, i.e., n_{tot} counts all molecules no matter if they are part of a reaction or not.

Together with the reaction rate, this leads to the reaction's molar flow rate:

$$\nu = k \cdot V_{tot} \cdot \prod_{A_i} \left(\frac{n_{A_i}}{n_{tot}} \right)^{a_i} \quad (6)$$

As chemical reactions are determined by their molar flow rate and the linear factors a_i and b_i , it makes sense to chose a bondgraphic representation of such a chemical reaction that is based on the molar flow rate, a corresponding potential, a 1-junction representing the sums given in Eq.(3) and transformers to enforce the multiples given by

a_i and b_i . This is exemplarily shown in Fig. 7. The ChR-Element represents the chemical reaction and is nothing else than a modulated transformer element. It will be discussed in more detail in Subsection 6.2

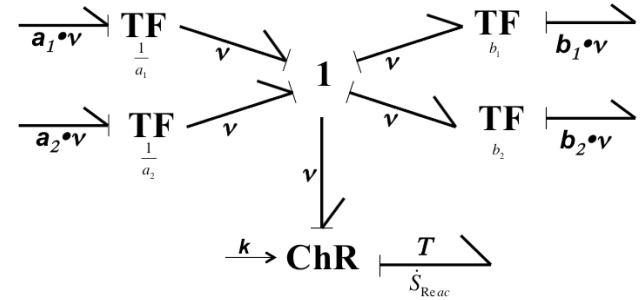
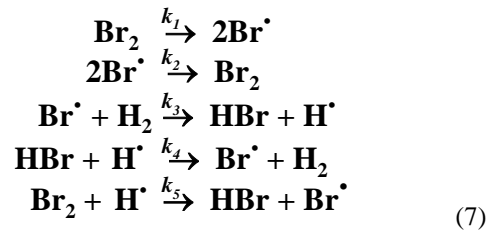


Fig. 7: Chemical Reaction using the molar flow ν as bondgraphic flow variable, transformers to enforce the coefficients a_i and b_i and a modulated transformer representing the chemical reaction (ChR).

4.4 Parallel reactions

Normally, chemical reactions do not appear alone. That is, there are several chemical reactions in parallel to one another. To illustrate this, let us discuss the following step reactions of the hydrogen-bromine reaction:



For each of the five reactions, a ν_i can be determined by Eq.(6). On the other hand, it is possible to calculate a molar flow for each of the corresponding molecules (i.e. C-fields). This leads to the following matrix notation:

$$\begin{bmatrix} \nu_{\text{Br}_2} \\ \nu_{\text{Br}^\cdot} \\ \nu_{\text{H}_2} \\ \nu_{\text{H}^\cdot} \\ \nu_{\text{HBr}} \end{bmatrix} = \begin{bmatrix} -1 & +1 & 0 & 0 & -1 \\ +2 & -2 & -1 & +1 & +1 \\ 0 & 0 & -1 & +1 & 0 \\ 0 & 0 & +1 & -1 & -1 \\ 0 & 0 & +1 & -1 & +1 \end{bmatrix} \cdot \begin{bmatrix} \nu_{k_1} \\ \nu_{k_2} \\ \nu_{k_3} \\ \nu_{k_4} \\ \nu_{k_5} \end{bmatrix} \quad (8)$$

In a bondgraphic interpretation this means that we can add up linearly all of the flows being created within the different reactions towards the different reactants. This is shown in Fig. 8. Each reaction is marked using a green rectangle. The reactants arrive from the left leading each into a 0-junction. The bonds from the five reactions are connected to those five 0-junctions, i.e., the reaction flows are superposed in those 0-junctions to form the reactants' molar flow rates ν_i . Thus the five 0-junctions together implement the above matrix of flow rate transformations. An additional 0-junction sums up the five reaction enthalpy flows.

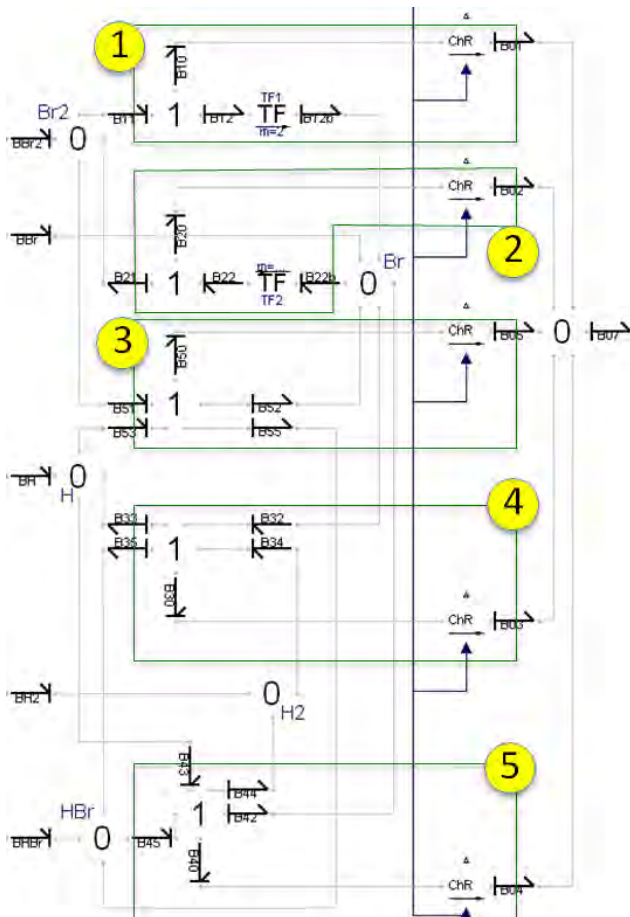


Fig. 8: Reaction Network built from the five HBr-Step reactions.

5 REACTION BOND POTENTIALS

Up to now, we did not answer the question, which variable should be used as adjugate of the molar flow rate. In order to decide this question, let us discuss a few special cases first that will help us reach a meaningful decision.

5.1 Rearrangement and tautomerism reactions

The simplest case of chemical reactions is given by one reactant being converted to one product. In practice, those kind of chemical reactions can be found e.g. in dissociation processes ($R_2 \rightarrow 2R$) or in organic chemistry, as exemplarily shown in Fig. 9 (R represents a monovalent "rest" molecule).

If the reaction rate is known, this kind of reaction can be modeled as a forced mass flow (specified by the molar flow rate) from the C-field of the single reactant to the C-field of the single product, as shown in Fig. 10. The corresponding volume and entropy flows are thereby determined as the product of molar flow and molar specific volume (i.e., the inverse density) and molar specific entropy, respectively.

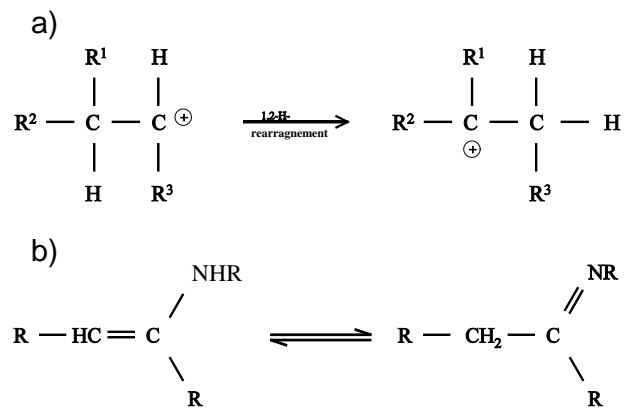


Fig. 9: Wagner-Meerwein rearrangement (a) [6] and Enamin-Imin tautomerism (b).

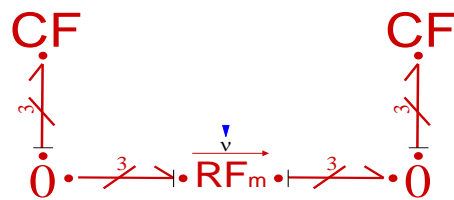
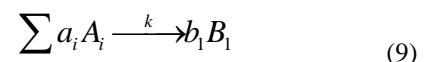


Fig. 10: Bond graph of rearrangement and tautomerism reactions (for simplicity, the transformation from molar to mass flows is not shown).

As one can see easily, we do not need any chemical network nor a discussion of the reaction enthalpy. Both, the molar as well as the corresponding volume flow entering on the left hand side must be conserved, i.e., only the entropy is changing in accordance with the first law of thermodynamics.

5.2 The basic single-product reaction

Let us now consider a reaction converting n reactants to one single product, with the reverse reaction being neglected:



From a bondgrapher's point of view, this can be described as n thermo-bonds being fused into one single thermo-bond, i.e., all input flows are summed up and are being sent to one destination. We shall see later that the most difficult issue is how to correctly distribute volume and entropy flows among different products. Thus, the single-product reaction represents a simplified case.

In this special case, we can use the molar free enthalpy as potential variable and obtain the bond graph shown in Fig 11.

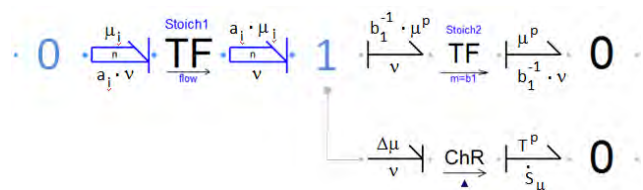


Fig. 11: Mass-flow bond graph of single-product reaction.

The transformer on the left represents the stoichiometric transformation of molar flows of the reactants. The individual molar flows of the reactants were grouped together into a multi-bond for compactness. The transformer to the right represents the stoichiometric coefficient of the single product.

The **ChR** element represents the chemical reaction. It computes on the primary side the molar flow rate (nonlinear equation), and, in the case the chemical potential decreases ($\Delta\mu > 0$), it generates on the secondary side reaction enthalpy. This element is syntactically similar to the classical resistive source, but contrary to an electrical or mechanical resistor, that always generates entropy (irreversible thermodynamics), the ChR element can also consume enthalpy (if the stoichiometrically weighted chemical potential of the product is bigger than the sum of stoichiometrically weighted chemical potentials of the reactants). It is thus a thermodynamically reversible element.

Notice that the bond graph assumes that the reactants come with their own potential variables that are being determined by the C-field to the left. A reaction can only take place as long as there is reactant mass available in the C-field, i.e., as long as the reactant mass *exists*.

As the total volume must be preserved and the volume flow into the product is a direct consequence of the corresponding mass flow, the bond graph for the volumes can be given as shown in Fig. 12.

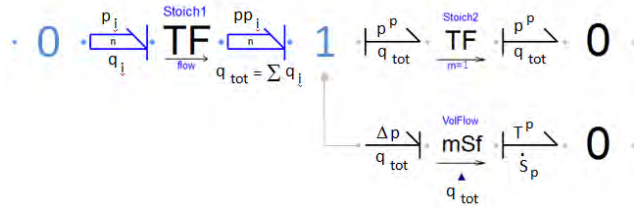


Fig. 12: Volume-flow bond graph of single-product reaction.

The **mSf** element is an aspect of the chemical reaction. It computes the volume flow from the corresponding molar flow. The transformer above the **mSf** element is not needed because the volume flow must be preserved. The multiport transformer on the left converts partial volumes (primary side) to partial pressures (secondary side). The pressure values, p_i , on the leftmost multi-bond are the pressures of the individual C-fields. These may temporarily differ slightly from one another, but they are true pressure values, not partial pressures. In contrast, the pressure values on the multi-bond to the right of the multiport transformer, pp_i , are partial pressures. Enthalpy is being generated if the total pressure decreases in the reaction ($\Delta p > 0$) and is being consumed if it increases.

Finally, the entropy needs to be looked at. The corresponding entropy-flow bond graph is shown in Fig. 13.

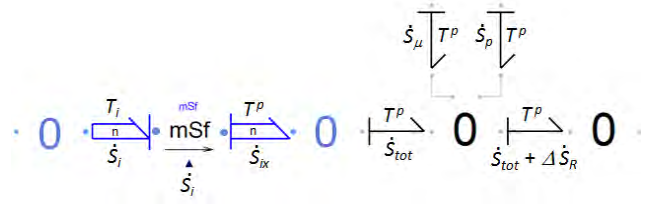


Fig. 13: Entropy-flow bond graph of single-product reaction.

Mass flows evidently carry their heat along. Thus, each mass flow induces a corresponding heat flow. An **mSf** multiport modulated flow source element is used to compute the corresponding entropy flows, such that:

$$T_i \cdot \dot{S}_i = T^p \cdot \dot{S}_{ix} \quad (10)$$

where T_i is the temperature of the i^{th} reactant C-field, and T^p is the temperature of the product C-field. The partial heat flows (entropy flows) get summed up in the (blue) multiport 0-junction. At the next 0-junction to the right, the enthalpy flows generated (or consumed) by the mass-flow and volume-flow bond graphs are injected.

If $\dot{S}_{tot} + \Delta \dot{S}^R > \dot{M}^p \cdot s_s$, with s_s the specific entropy of the product at (T^p, p^p) , the reaction is exothermic. If $\dot{S}_{tot} + \Delta \dot{S}^R < \dot{M}^p \cdot s_s$, the reaction is endothermic.

5.3 Fictitious potentials

In order to generalize the approach discussed in the previous subsection (5.2) towards several products, it is necessary to find a method that determines the volume and entropy flows to the different products.

The first approach solving this problem [7] introduced fictitious reaction potentials, i.e., it calculated iteratively the one temperature and pressure values for which the volume flows of the products equal the sum of the volume flows of the reactants such that the overall energy balance is satisfied.

Although this technique could be applied successfully to small models, the approach suffers from the fact that each reaction has to be handled separately, i.e., a reaction network, as shown in Fig. 8, had to be split up into separate reactions.

5.4 Molar intrinsic energy

The main problem in generating reaction networks for volume and entropy flows is that each reactant “owns” its own specific volume and entropy values (given as functions of temperature and pressure).

To deal with this issue, another approach has meanwhile been developed. The main ideas behind this new approach are as follows:

- The chemical reaction does not change the overall volume, i.e., the volume balance can be implemented outside the reaction core.
- Inside the reaction system only the energy levels matter, i.e., the separation into entropy and free Gibbs enthalpy is not really needed.

As volume and entropy flows are functions of the corresponding (molar) mass flow, it is possible to convert both the volume and the entropy flow into equivalent mass flows. The corresponding potentials are temperature times specific entropy and pressure times specific volume. The transformation is shown in Fig. 14.

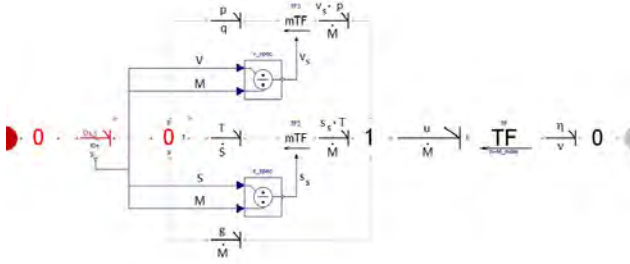


Fig. 14: TF_{mol} Element.

The red thermo-bond to the left is a state sensor element. It extracts the state information (S , V , and M) that is being carried along with the thermo-bond. The red/black 0-junction to its right splits the three flows that are carried by the thermo-bond into separate flows of heat, volume, and mass. The two division boxes compute the specific volume, v_s , and the specific entropy, s_s . The two modulated transformers convert the heat and volume flows to equivalent mass flows, and the 1-junction in the center sums the three potentials up on a combined mass flow.

The resulting mass flow carries as its potential variable the specific intrinsic energy, u .

$$u = T \cdot s + g - p \cdot v \quad (11)$$

Unfortunately, Eq.(11) carries a minus sign for the volume flow. This problem can be solved in two ways: As discussed in [1], it may make sense to define all pressures in the systems negative for convenience. Negative pressures are not physically meaningful, but they simplify the construction of the bond graph. Alternatively, care must be taken to turn around the bond representing volume flow at the 1-junction. Thus, when dealing with positive pressure values, the modeler must remember to account for the minus sign whenever a coupling between volume- and entropy-flow bonds takes place. This is especially true for all types of movements from one pressure level to another generating entropy (friction).

The transformer to the right of Fig. 14 converts absolute mass flows to molar mass flows. Since the potential variable on the primary side has changed, the potential variable must also change on the secondary side. Thus, the molar mass flow rate is no longer accompanied by the chemical potential, μ , but rather by the molar-specific enthalpy, η .

6 CHEMICAL REACTION ELEMENT

6.1 General principles of chemical reactions

Discussing chemical reactions, the following principles must be observed:

1. All mass flows can be determined using the Arrhenius law considering their stoichiometric weights.
2. All incoming flows have the same thermodynamic state as the corresponding emitting C-fields, and consequently, the inflows are known.
3. The sum of all incoming energy, volume, and mass equals the sum of all outgoing corresponding flows.
4. The thermodynamic state of the receiving C-fields does not influence the chemical reaction itself, and merging flows can create mixture entropy.

Chemical reactions are reversible, i.e. for each reaction, there exists a reverse reaction, such that:

$$R^{-1} [R(x)] = x \quad (12)$$

In the equilibrium point, the two reaction rates compensate one another. We can write:

$$i \cdot R(x) + j \cdot R^{-1}(x) = (i - j) \cdot R(x) = (j - i) \cdot R^{-1}(x) \quad (13)$$

The equilibrium point of a chemical reaction depends on the reaction condition and is reached when both reactions –the forward and the reverse reaction– are showing the same molar flow rate, i.e. in the equilibrium, the reactions do not stop but are compensated by the reverse reactions.

This implies that, when either the temperature or the pressure changes, a chemical reaction might start “running backward.”

In the example shown in Fig. 8, the reactions $k2$ and $k4$ are the reverse reactions of $k1$ and $k3$, respectively. The equilibrium point of the reactions $k5$ and $k6$ is so close to the $k5$ product side that we neglected the reverse reaction $k6$.

As the reverse reaction rates superpose additively, it would have been possible to only define ChR-Elements determining the superposed reaction rates of the reactions $k1$ and $k2$ as well as $k3$ and $k4$.

6.2 ChR Dymola Model

As shown in Fig. 15, the chemical reaction model **ChR** is a bond graph two-port, as introduced in [8], extended by a multidimensional information cut. The (inflow) bond on the left-hand side carries the molar flow rate, ν , and the molar intrinsic enthalpy, η . The (outflow) bond on the right-hand side carries an entropy flow together with a temperature.

The amount of power transported through the ChR-Element is available as information out-port. If the out-port is connected to an integrator, the reaction enthalpy, ΔH_{Reac} , is being computed.

Finally, the model features an information in-port carrying the volume, V_{tot} , of the compartment and the number of moles being stored in each C-field. As discussed in Section 4.3, this information is necessary to calculate the molar flow rate v . To increase readability of the graphical model, this information is provided by a single Element, called **State** for all **ChR**-Elements. Consequently, **State** features on its left side as many information inputs, as there are C-fields present in the compartment. Additionally to the already discussed information out-port carrying the overall volume and molar numbers, the **State**-element provides separately also another out-port vector delivering the volume fractions. This second out-port will be used for the heat and volume balancing distribution discussed in Section 7.

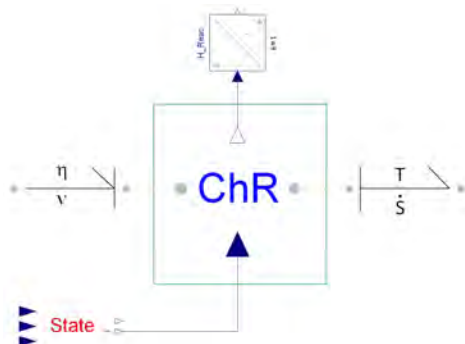


Fig. 15: ChR-Model (general version).

Unfortunately, it is necessary to build one **ChR**-Element for each reaction as the equation for v is different for each of them. The basic ChR element is therefore a partial model. Thus, we end up with separate **ChR_{k1}**, **ChR_{k2}**, ... models.

Note: It is possible to connect only parts of the n_i vector carried by the **State**-Element into the **ChR**-Element, which however requires the **State**-Element to offer one more variable, namely the sum of all n_i .

7 ENTROPY AND VOLUME DISTRIBUTION

In this section, we analyze the distribution of entropy out-ported by the **ChR**-Elements as well as the volume balance.

7.1 The mixture

Let us start by looking at the reactants represented by C-fields (cf. Fig. 5). Inputs to a C-field are the three flow variables: mass flow, entropy flow, and volumetric flow. On this basis, the C-field calculates the three potentials: the Gibbs free energy, g , the temperature, T , and the pressure, p . As each reactant is represented by its own C-field, each reactant has its own volume, mass, temperature, and pressure. Due to the different thermodynamic behavior of different reactants, the same amount of volume or entropy flow leads to different temperature and pressure values.

However in a mixture, the pressure and temperature of different reactants will equilibrate as the molecules transporting the corresponding energy are in contact with each other. Consequently, the C-Fields (**CF**) need to be connected via temperature-pressure equilibration (heat-volume exchange: **HVE**) elements as shown in Fig. 16. The three bonds at the bottom of Fig. 16 (B21, B22 and B23) are the connections to the chemical reaction network.

Note: For larger settings, it may be sufficient to connect each **CF** to a few other neighboring **CF** elements for equilibration to occur. There is no need to connect every **CF** element with all other **CF** elements.

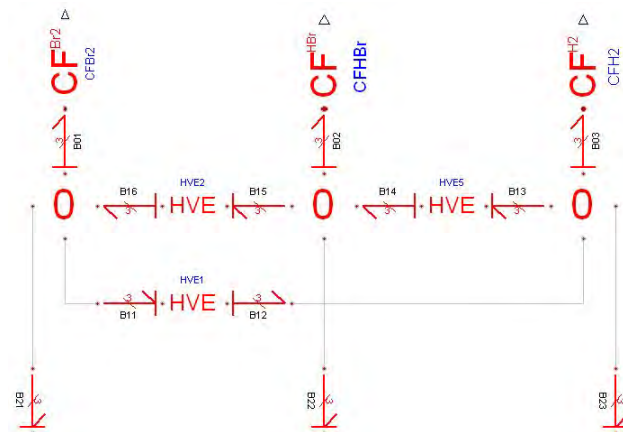


Fig. 16: Temperature-pressure equilibration between C-Fields.

With this setting, it is possible to simulate any adiabatic-isochoric process, as there is no connection to the outside. If for example an isothermal or isobaric boundary condition is wanted, the outside (represented by an **Se**-Element) must be connected to the CF-Elements also, as shown in Fig. 17. The conductance values of the HVE-outside connections (green box) have to be selected depending on the boundary condition and exhibit different parameter values from the HVE-inside connections (blue box). The internal pressure/temperature equilibration normally occurs very fast, whereas the exchange to the outside is much slower (at least as far as the temperature is concerned).

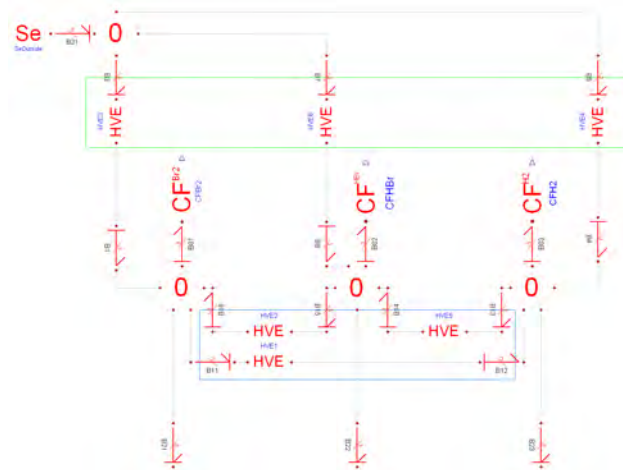


Fig. 17: Changing the boundary conditions.

7.2 Entropy distribution

The reaction network (e.g. in Fig. 8) together with the TF_{mol} Element (cf. Fig. 14) guarantees that the molar flow of each reactant is accompanied by the correct volume and entropy flows corresponding to the current state. However as chemical reactions normally free up or consume energy, there will be additional entropy ($\Delta H_{\text{Reac}} = T \cdot S$) to be distributed among the C-fields belonging to the system.

From a conceptual point of view, there are two approaches possible:

1. All energy from the reactant compounds moves towards the product compounds, i.e., the product compounds have to absorb the additional entropy (or deliver the missing entropy). This situation may apply in the case of a continuous stirred tank reaction (CSTR), where reactants are constantly added to the reaction chamber from the outside and where the products are constantly removed from it.
2. The reaction core radiates the additional entropy to its surrounding, i.e. towards all molecules. As radiation only cares about areas and distances, it can be assumed that the energy is distributed among all compounds in the mixture in proportion to their volume fraction

$$c_i = \frac{V_i}{V_{\text{ges}}} \quad (14)$$

The latter situation may apply in the case of a batch reaction, where the reactants and the products share the same space.

Fig. 18 shows the bond graph model, TF_{ent} , for a mixture containing three compounds assuming the latter approach.

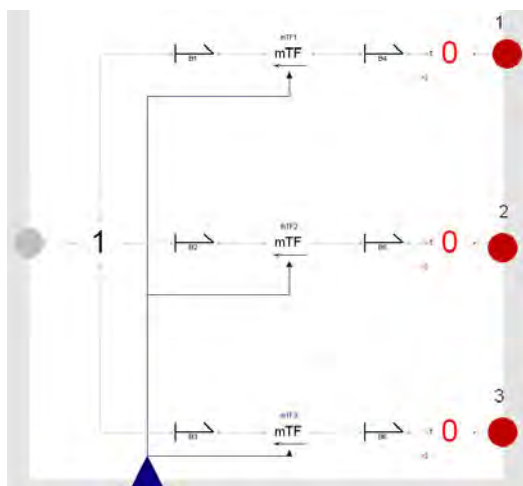


Fig. 18: Entropy distribution.

The entropy flow coming in on the left is the entropy flow shown at the right-hand side of Fig. 8. The three modulated transformers distribute the entropy flow to the three compounds (C-fields) in accordance with their volume fraction, which is computed by the **State** element of Fig. 15. The thermo-bond 0-junctions on the right-hand side of Fig. 18 are connected to the 0-junctions adjacent to the **CF**-Elements representing the three compounds.

7.3 Volume balance

From an energy-based point of view, the model is ready to be built now. Unfortunately, the volume balance may still be violated when doing so, as each compound carries its own specific volume, i.e. at a given temperature and pressure condition, 1 *mol* of a compound A_1 may occupy a different amount of volume from 1 *mol* of a compound B_1 . Even worse: the amount of moles does not have to remain constant if chemical reactions are present. To avoid this change in overall volume, it is necessary to determine the difference in volume flows and add (or remove) this difference from the overall entity.

The second step can make use of the same mechanism used already for the entropy distribution: Distribute the difference volume proportional to the existing volume fractions, i.e., just scale to whole system. This algorithm is only a first-order approximation as the correct distribution would distribute in such a way that the pressure of all C-Fields would in- or decrease by the same amount. However as pressure differences get equilibrated quickly by the HVE elements, this approximation error gets rectified rapidly. For ideal gases, the approximation is correct anyway, as 1 *mol* of an ideal gas always occupies the same volume (at a given pressure).

Let us now look at the first step, i.e., determine the volume difference to be distributed. This can be accomplished easily by connecting all volume bonds to a single 0-junction that will automatically calculate the remaining volume flow. Fig. 19 shows this procedure exemplarily for two compounds.

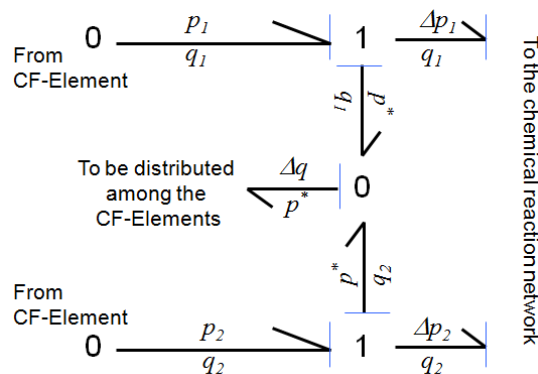


Fig. 19: Difference volume determination.

As the blue causality strokes show, the volume flows q_1 and q_2 are determined by the chemical reaction, while the pressures p_1 and p_2 are determined by the corresponding **CF**-Elements. Δq then gets calculated automatically, we just have to offer p^* .

For the special case of using the ideal gas assumption, p^* can be calculated as weighted sum of the partial pressures, as described by the law of Boyle-Mariotte:

$$p^* = \frac{\sum (p_i \cdot V_i)}{\sum V_i} \quad (15)$$

Since in practice the different p_i values will be nearly identical, this formula can be used as a good approximation for the general case as well.

Let us assume that all the C-Fields show the same pressure p^* , i.e. $p_1 = p_2 = p^*$ and consequently, $\Delta p_1 = \Delta p_2 = 0$. In this case, the bonds running towards the chemical network do not carry any power, but only loop back the values of the volume flows. In consequence, this means that, even without difference volume determination, there is no volume-power passed towards the ChR element, as the chemical network is doing a similar job on its own as the difference volume determination bond graph does.

Fig. 20 shows a difference volume determination and distribution for a mixture containing three compounds. The determination 1-0-junction-combination thereby is shown on the right-hand-side, while the mTF-Elements for the distribution towards the CF-0-junctions are shown towards the left-hand side, i.e. the process runs in opposite direction.

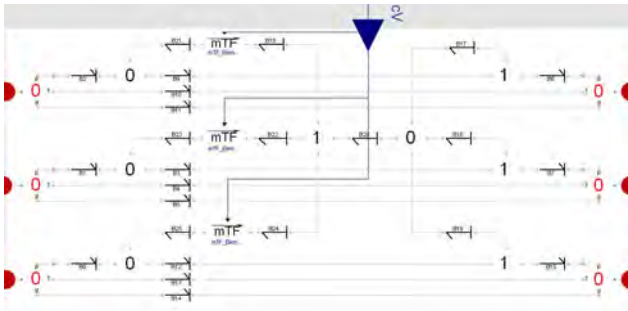


Fig. 20: Network guaranteeing the volume balance.

The awkward thing about this implementation is that we need to interrupt the connection in between CF and chemical reaction network of each compound. This indeed becomes quite confusing if a larger number of C-Fields is present.

However, we can do this job mathematically also, as it is not necessary to eliminate the volume flows from the chemical reaction network, as the latter will just pass them through anyway. Consequently, the determination can also be done using flow sensors and enforcing the difference volume flow independently. This is implemented in the model shown in Fig. 21, which uses the **mSf**-Element, shown in Fig. 22. The three thermo-bond 0-junctions in Fig. 21 are directly connected to the 0-junctions to which the corresponding **CF**-Elements are connected.

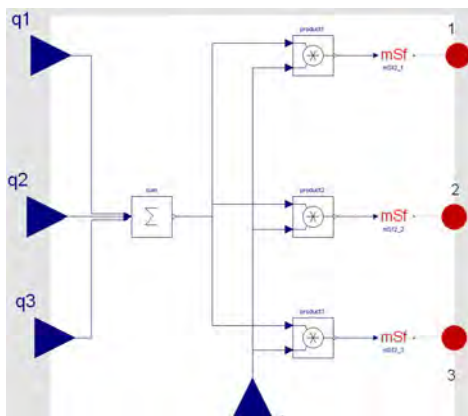


Fig. 21: Model ensuring the volume balance.

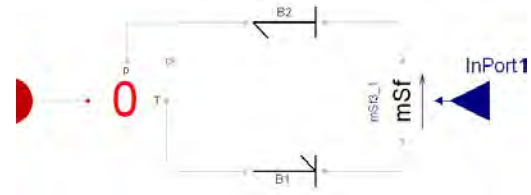


Fig. 22: mSf-element used in Fig. 21.

8 EXAMPLE

As example we implemented the hydrogen-bromine-synthesis already introduced.

8.1 Equations and assumptions

We used the ideal gas assumption and therefore, the equations of the C-Fields became as shown in Eq.(16). v_s and s_s are the mass specific volume and entropy variables (volume, respectively entropy divided by the corresponding mass). v_0 and s_0 are constants, representing the values of v_s and s_s at T_0 , the temperature toward which the data of the molecules was determined. Finally, c_p is the heat capacity (per kg) and ΔHf_0 is the (standard) enthalpy of formation.

$$R \cdot \bar{M} = \mathcal{R} = 8.134 \frac{J}{mol K}$$

$$p \cdot v_s = R \cdot T$$

$$s_s - s_0 = (c_p - R) \cdot \ln\left(\frac{T}{T_0}\right) + R \cdot \ln\left(\frac{v_s}{v_0}\right)$$

$$g - \Delta Hf_0 = T \cdot (c_p - s_s) - c_p \cdot T_0 \quad (16)$$

Inside the **ChR**-Elements the following equations got implemented:

$$k_1 = k_0 \cdot \sqrt{\frac{T}{T_0}} \cdot \left(\frac{\mu_1}{R \cdot T}\right)^{1.97} \cdot e^{-\frac{\mu_1}{RT}}$$

$$k_3 = k_0 \cdot e^{-\frac{\mu_3}{RT}} \quad ; \quad k_5 = k_0 \cdot e^{-\frac{\mu_5}{RT}}$$

$$v_1 = k_1 \cdot n_{Br_2} \quad ; \quad v_2 = \frac{k_1}{K(T)} \cdot \frac{n_{Br}^2}{V}$$

$$v_3 = k_3 \cdot \frac{n_{H_2} \cdot n_{Br}}{V} \quad ; \quad v_4 = 0.1 \cdot k_5 \cdot \frac{n_{HBr} \cdot n_H}{V}$$

$$v_5 = k_5 \cdot \frac{n_{Br_2} \cdot n_H}{V} \quad (17)$$

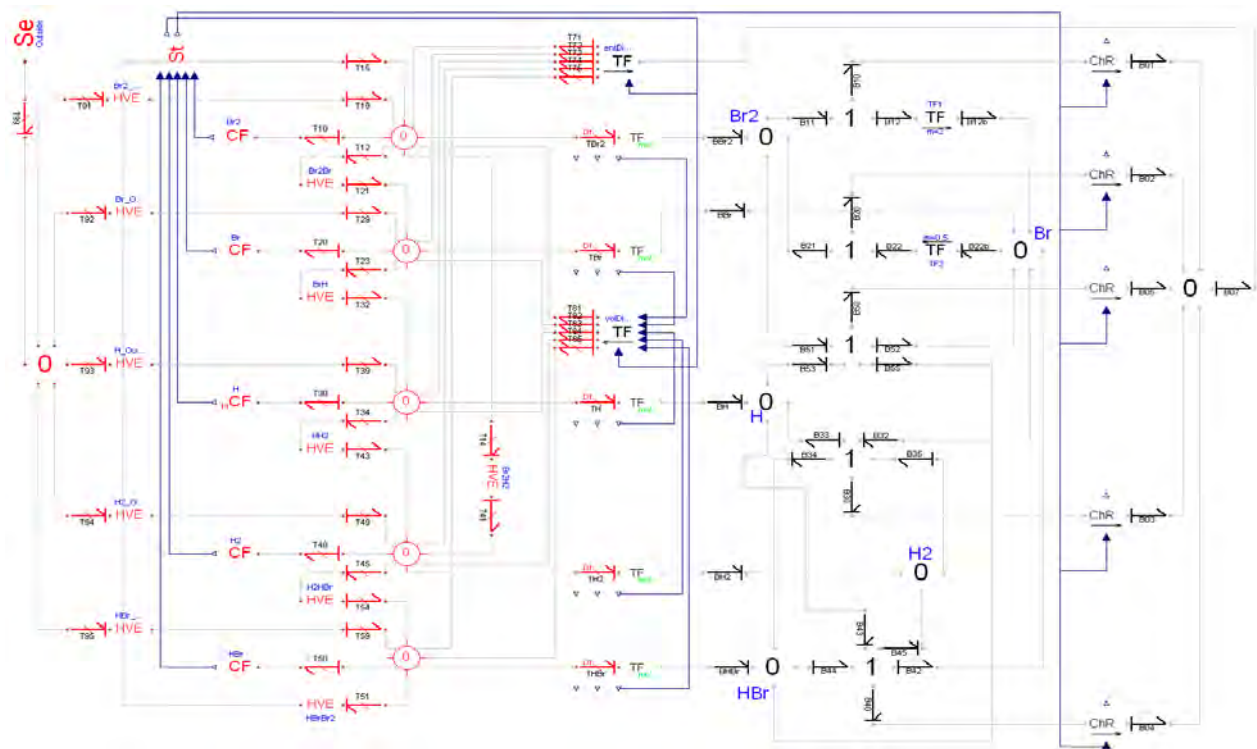


Fig. 23: Overall model of the hydrogen-bromine-synthesis.

8.2 Model

Fig. 23 shows the overall model of the hydrogen-bromine synthesis. Depending on the conductance values of the HVE connecting the outside Se with the CF-elements, different boundary conditions can be simulated, such as e.g. adiabatic-isochoric (no exchange with the outside) or isothermal-isobaric (open system).

From left to right:

- Connection to outside
- CF-Elements with HVEs
- Volume and entropy distribution
- Thermo-bond to η/v -bond transformation
- Chemical reaction network
- Chemical reactors ChR
- Collection of reaction enthalpy

8.3 Simulation results

Fig. 24 shows the development of the molar numbers over time under isochoric and quasi-isothermal conditions. The term quasi-isothermal thereby is used to describe the behavior of an endless heat conductivity towards the outside, i.e. as shown in Fig. 26, the temperature rises in the beginning, but returns to the outside condition after some time. While the amount of HBr molecules is increasing, the number of Br_2 and H_2 molecules is decreasing (correspondingly).

Only small values of the two radicals H and Br are ever observed (Fig. 25). However due to the temporarily rising temperature, the reactions producing those radicals become temporarily more active and in consequence,

there is a peak in the trajectories, which is responsible for the rapidly changing derivatives observed in the trajectories of Fig. 24.

Having in mind the thermodynamic dependencies of temperature and pressure, the trajectories of the pressures, shown in Fig. 27 do not require too much of an explanation.

Note: The simulation time is given in msec.

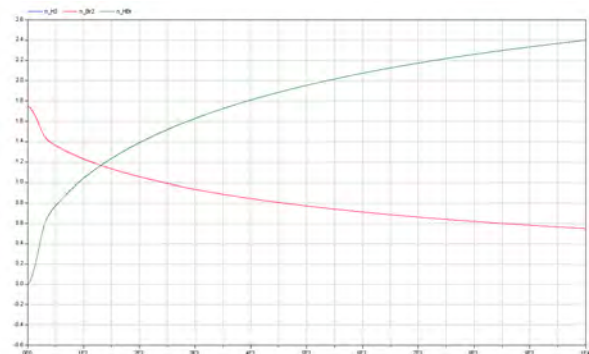


Fig. 24: Molar numbers n_i over time (isochoric).

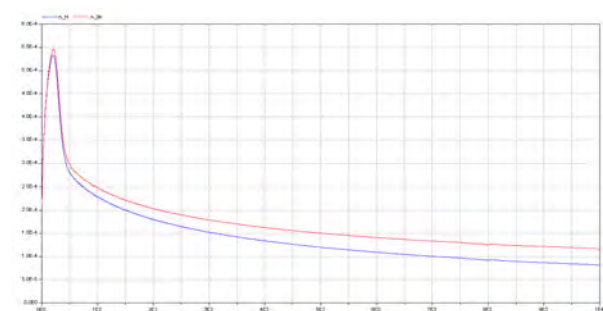


Fig. 25: n_H and n_{Br} over time (isochoric).

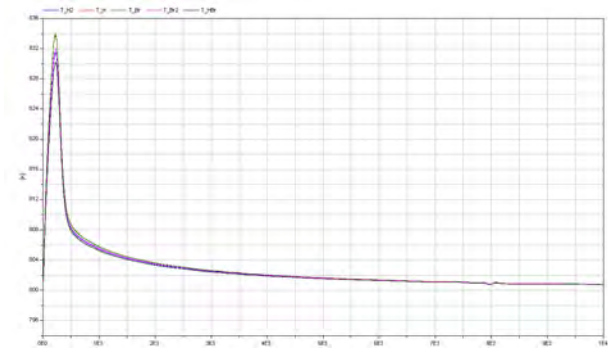


Fig. 26: Temperature over time (isochoric).

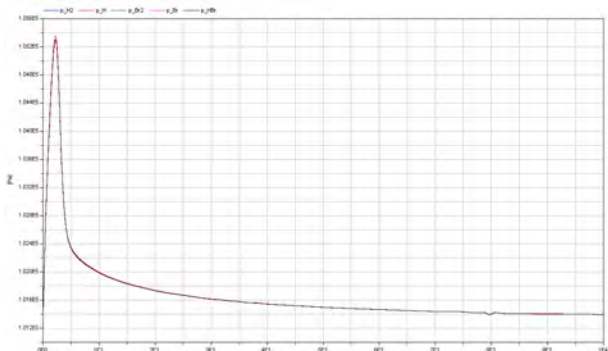


Fig. 27: Pressure over time (isochoric).

9 CONCLUSIONS

This paper introduced a general approach for modeling chemical reactions using bond graphs. To this end, a number of macro-elements got introduced and implemented in Dymola. The latter were used to demonstrate the applicability of this approach by means of a small example.

10 REFERENCES

- [1] Greifeneder, Jürgen and François E. Cellier: Modeling Convective Flows Using Bond Graphs. Proceedings *ICBGM'2001, International Conference on Bond Graph Modeling and Simulation*, Phoenix, AZ, pp. 276--284, SCS, ISBN: 1-56555-221-0, 2001.
- [2] Greifeneder, Jürgen and François E. Cellier: Modeling Multiphase Systems Using Bond Graphs. Proceedings *ICBGM'2001, International Conference on Bond Graph Modeling and Simulation*, Phoenix, AZ, pp. 285--291, SCS, ISBN: 1-56555-221-0, 2001.
- [3] Greifeneder, Jürgen and François E. Cellier: Modeling Multi-Element Systems Using Bond Graphs. Proceedings *European Simulation Symposium and Exhibition (ESS)*, Marseille 2001, pp. 758--766, SCS, ISBN: 90-77039-02-3, 2001.
- [4] Cellier, François E. and Jürgen Greifeneder: Object-Oriented Modeling of Convective Flows Using the Dymola Thermo-Bond-Graph Library. Proceedings *ICBGM'2003, International Conference on Bond Graph Modeling and Simulation*, Orlando, FL, Seiten 198--204, SCS, ISBN: 1-56555-257-1, 2003.
- [5] Dymola: <http://www.dynasim.se/>
- [6] Meerwein, H., Unkel, W. and Liebig, Justus: *Ann. Chem.*, 376, pp. 152-163, 1910.
- [7] Greifeneder, Jürgen: Modellierung thermodynamischer Phänomene mittels Bondgraphen. Diploma Thesis, University of Stuttgart, Germany, 2001.
- [8] Cellier, François E. and Angela Nebot: The Modelica Bond Graph Library, Proceedings *4th International Modelica Conference*, Hamburg, Germany, Vol. 1, pp. 57-65, 2005.
- [9] Zimmer, Dirk and François E. Cellier: The Modelica Multi-bond Graph Library, Proceedings *5th International Modelica Conference*, Vienna, Austria, Vol. 2, pp. 559-568, 2006.

11 BIOGRAPHIES



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