

# Bond graph modelling for chemical reactors

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## SUMMARY

In this paper we present a bond graph model of a Continuous Stirred Tank Reactor which represents the reaction kinetics as well as the heat and mass transport phenomena in the reactor. The consequences of reticulation of the phenomena and of the systematic use of the power conjugated variables on the formulation of the thermodynamic properties, the reaction kinetics and the energy and mass transport are shown. A classical example of chemical reaction is chosen to illustrate this approach: the equilibrated reaction of Hydrogen and Iodine in Hydrogen Iodide.

**Keywords:** bond-graph, chemical reactor, non equilibrium-thermodynamics.

## 1. INTRODUCTION

The aim of this paper is to present and discuss the port based modelling approach, using the *bond graph language*, also called *thermodynamic or generalized bond graph* [2], in the context of chemical engineering. One of the expected advantages of bond graph modelling is the development of reusable models. This concern is shared with, for instance, E. D. Gilles and co-authors who propose a hierarchical and modular modelling structure for systems arising in chemical engineering and called *network theory* [5], [12] (where the reader may also find detailed references to other modular modelling environments). There, the models are composed of blocks diagrams where the blocks are related by pairs of bilateral signal flows carrying pairs of potential variables and flux variables. The blocks may be of two types: either components which describe storage or coupling elements which generate the flux variables describing the interactions between the components. Bond graph models are also network type models which are composed of multiports related by power bonds representing the (*acausal*) identity between pairs of conjugated variables whose product is the instantaneous energy flow between the multiport elements. In the context of thermodynamics these pairs of power conjugated variables are pairs of intensive variables (the temperature, the pressure and the chemical potentials of components of the systems) and the in-

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stantaneous variation of the extensive variables (the entropy, the volume and the mole number of each species). Let us recall that in the formalism of thermodynamics, extensive variables are those that vary linearly with the size of the system (the quantity of matter) if other conditions are kept constant. The intensive variables are the efforts. The multiport elements belong to one of six possible types and represent storage, balance and continuity equations (the 0- and 1-junctions) or interdomain coupling (the transformer, gyrator and RS-elements). In summary the bond graph language combines the axiomatic foundations of macroscopic physics given by the thermodynamics with a network representation [2]. For modelling processes like reactors, the most used is the so-called pseudo-bond graph representation where the pairs of variables associated to the bonds are not power conjugated: for example, temperature and heat flow, temperature and enthalpy flow, concentrations and molar flows are some choices [10, 7, 9, 20]. In fact pseudo-bond graph models follow closely the usual chemical engineering formulation and resembles to the network models in [5, 12].

There are main departures in the bond graph modelling and the classical model formulation in chemical engineering. Firstly in bond graph models, contrary to the usual model formulation in chemical engineering, the pairs of intensive and extensive variables are systematically written which leads to the definition of some additional variables and relations. But this guarantees the possible interconnection of the submodels as their port variables are the basic variables on which the balance and continuity relations are written. Secondly this leads, for the thermal domain, to write the entropy balance instead of the energy balance and to write explicitly the entropy creation associated with all the irreversible processes involved in the system. Thirdly the multiport approach demands to write the constitutive relations of the energy storage or reaction kinetic for instance, in terms of the pairs of conjugated power variables.

This paper is introductory and aims to present, through the bond graph representation of a classical model of a Continuous Stirred Tank Reactor, the main features of bond graph modelling in chemical engineering for the objective of a modular approach to modelling as well as to discuss some stumbling blocks. The model incorporates the chemical kinetics model of a equilibrated reaction and heat and mass transport phenomena.

In [13], the authors propose the description of the general balanced chemical reaction in a closed well-stirred reactor using the bond-graph formalism. They assume moreover constant internal temperature  $T$  and pressure  $P$  and consequently are interested in the representation of the Gibbs free energy  $G$ . Using Gibbs' relation and the entropy balance, the authors propose a bond-graph model of the reaction. As a consequence, the irreversible entropy production in this bond-graph is not represented and the kinetics of the chemical reaction is represented by a resistive element. Furthermore the authors write the reaction's kinetics in terms of the forward affinity  $A_f$  (corresponding to the direct reaction) and a reverse affinity  $A_r$  (corresponding to the reverse reaction). This representation does not take into account the thermal domain

but only the material one. It is the reason why a resistive element is sufficient. Nevertheless the work of Oster et al. paves the way of the present paper. Further information about chemical reaction and port based modelling can be found in [19].

In [19] [2], the previous model of a chemical reaction is completed by coupling the material domain and the thermal one via a RS element. Hence the model considers the internal energy and allows to represent the first principle (the conservation of energy). In this paper, we establish a bond graph model of a complete chemical reactor using systematically the power conjugate variables. Furthermore, the previously true bond graph models of chemical reactions proposed by [13, 2] have been augmented in order to model a complete *open* continuous stirred reactor where a chemical reaction takes place.

For chemical engineering this approach is novel in the sense that the elementary phenomena are represented as basic multi-port elements which can be locally connected. Furthermore the local use of port-based concepts that satisfy the regular constraints guarantee that the global model consisting of connected basic models also satisfies the basic balance equations (energy,...) due to the bond graph grammar.

The reaction under consideration is the classical example of the gas phase equilibrated hydrogen - iodine reaction  $H_2 + I_2 \rightleftharpoons 2HI$  [17]. The chemical reaction and the jacketed reactor in which the reaction takes place are modelled with the following assumptions:

- The gas is assumed to be an ideal gas with constant heat capacity.
- The kinetics of the forward and reverse reaction satisfy the hypothesis of mass action constitutive relation.
- The reactor is continuous, perfectly stirred and its volume is constant.
- The pressure inside the reactor is assumed to be constant
- The effect of a jacket is partially modelled as heat transfer.
- The three pure components are injected separately at the inlet

The organization of the paper is the following. In section 2 the constitutive relations of the C element are presented. We formulate these relations in terms of chemical potentials for the gas mixture that is involved in the reaction in such a way that the corresponding energy-storing element may admit integral causality assignment. The most difficult task consists in writing the thermodynamical properties with respect to extensive variables as already emphasized in [3], [4]. The chemical reaction is described in section 3: it corresponds to a RS element and a transformer associated with the stoichiometric matrix, following closely [13, 2]. Some comments are made on the dissipative aspect of the chemical reaction. Section 4 is devoted to the discussion on the balance equations written, in the chemical engineering frame, in terms of the energy or, in the bond graph language, in terms of entropy. The *transport* phenomena are considered in section 5: a bond graph model is derived of heat convection and entropy

production due to the mixing of the reactants at the inlet in the mixture. Section 6 deals with the representation of the pressure constraint and section 7 recalls the model of heat conduction for the representation of the thermal exchange with the jacket as well as the complete submodel of the CSTR. Finally in section 8, we present the bond graph model of a tubular reactor obtained by interconnecting through their ports three CSTR submodels, show a simulation results and make some additional comments on the boundary conditions used in our case.

## 2. THE THERMODYNAMIC PROPERTIES OF THE MIXTURE

The thermodynamic properties of the mixture of the three reactants in the reactor are represented by a 3-port energy storing element (denoted by C). Its constitutive relations consist firstly in expressing the thermodynamic properties according to Gibbs' relation [18]:

$$dU = TdS - PdV + \sum_{i=1}^3 \mu_i dn_i \quad (1)$$

where, following the classical Thermodynamics and the assumption of local thermodynamic equilibrium, the internal energy of the mixture is denoted by  $U$ , the states of the reactor are the extensive variables: the volume  $V$ , the entropy  $S$  and the mole number  $n_i$  of each chemical species  $i$  and the conjugated intensive variables are the temperature  $T$ , the pressure  $P$  and the chemical potentials  $\mu_i$ . The constitutive relations of the C-element consist secondly in the calculation of the time variation of the state variables ( $\frac{dS}{dt}$ ,  $\frac{dV}{dt}$ ,  $\frac{dn_i}{dt}$ ) as being equal to the flow variables obtained through the balance equations.

This section deals with the derivation and the use of the preferred integral causal form of the constitutive relations describing the thermodynamic properties of the mixture. This leads to write expressions of the intensive variables (temperature, pressure and chemical potentials) as functions of the extensive variables (entropy, volume and number of moles). This task is not so obvious since thermodynamics properties are classically expressed as functions of the intensive variables, in particular of the temperature and not of the entropy. This is one of the main departure of the bond graph approach from the usual approach in chemical engineering.

In previous papers [3], [4], P. Breedveld deals with the formulation of such constitutive relations in the case of gases composed of a single constituent and described by the ideal gas equation state, the Van-Der-Waals equation and an extension of the latter proposed by H. Paynter [15]. The author has shown under which conditions, this preferred formulation is possible and under which conditions other forms of equations of state can be analytically converted to the desired form.

In the sequel, we shall assume that the mixture of reactants in the reactor constitutes an ideal gas and therefore shall extend the previously cited work to the case a mixture. This is a first step for the study of real mixtures, since the mixture of ideal gases is often chosen as the reference for the derivation of the properties of the real one [18].

### 2.1. The equation of state of the ideal gas mixture

Assuming that a gas composed of a single constituent is *ideal* amounts to assume that its molecules have no interactions with each other. A mixture of ideal gases has the same property. It follows that the equation of state of the mixture is analogous to the one of the pure component :

$$P = \frac{\sum_{i=1}^3 n_i RT}{V} \quad (2)$$

Let us remark now that this equation (2) will provide the relation that gives the pressure  $P$  as a function of the extensive variables as soon as the temperature  $T$  is expressed with respect to extensive variables.

### 2.2. The expression of the temperature

In this section we shall derive the expression of the temperature as a function of the extensive variables by inverting partially the expression of specific entropy of the mixture.

Let us firstly calculate the *specific molar entropy of the pure component* of species  $i$ , denoted by  $s_i^*$ . For a pure ideal gas the differential of the molar entropy is given by:  $ds_i^* = c_{pi}(T) \frac{dT}{T} - R \frac{dP}{P}$ . Assuming for the sake of simplicity, that the *heat capacities  $c_{pi}$  are constant*, the molar entropy of pure component  $i$ , at given temperature  $T$  and pressure  $P$ , has the following expression:

$$s_i^*(T, P) = c_{pi} \ln \frac{T}{T_{ref}} - R \ln \frac{P}{P_{ref}} + s_{iref} \quad (3)$$

where  $T_{ref}$  is a reference temperature,  $P_{ref}$  is a reference pressure and  $s_{iref}$  the reference entropy which shall be specified in the section 2.4.

In the mixture the *partial molar entropy of each species* is denoted by  $s_i$  and is then given by:

$$s_i(T, P, y_i) = s_i^*(T, P) - R \ln y_i \quad (4)$$

where we denote the total number of moles by  $N = \sum_{i=1}^3 n_i$ , the molar fraction by  $y_i = \frac{n_i}{N}$ .

Finally using the homogeneity of the state functions, the *total entropy* of the mixture

denoted by  $S$  is given by:

$$S(T, P, n_1, n_2, n_3) = \sum_{i=1}^3 n_i s_i(T, P, y_i) \quad (5)$$

Using the equation of state (2) by partial inversion of (5) with respect to the temperature, the temperature may be expressed as the following function of the extensive variables:

$$T = T_{ref} \exp \left[ \frac{S + R \sum_{i=1}^3 n_i \ln y_i + RN \ln \frac{NRT_{ref}}{VP_{ref}} - \sum_{i=1}^3 n_i s_{iref}}{\sum_{i=1}^3 n_i c_{pi} - RN} \right] \quad (6)$$

### 2.3. The expression of the chemical potential

Let us first express the partial molar enthalpy of each species  $i$ . For a pure ideal gas the differential of the molar enthalpy is:  $dh_i^* = c_{pi}(T)dT$ . Using again the assumption that the heat capacities are constant, the specific enthalpy of the pure constituent  $i$  at temperature  $T$  and pressure  $P$  is given by:

$$h_i^*(T) = c_{pi}(T - T_{ref}) + h_{iref} \quad (7)$$

where  $T_{ref}$  denotes a reference temperature and  $h_{iref}$  denotes a molar reference enthalpy of constituent  $i$  which shall be specified in the section 2.4.

Hence the enthalpy  $H$  of the ideal gas mixture in the reactor is given by :

$$H(T, n_1, n_2, n_3) = \sum_{i=1}^3 n_i h_i(T) = \sum_{i=1}^3 n_i h_i^*(T) = \sum_{i=1}^3 n_i [c_{pi}(T - T_{ref}) + h_{iref}] \quad (8)$$

For each pure constituent  $i$ , the expression of the chemical potential is  $\mu_i^* = h_i - Ts_i^*$ . In the mixture, one has:

$$\mu_i(T, P, y_i) = \mu_i^*(T, P) + RT \ln y_i \quad (9)$$

By inserting the expressions of  $T$  and  $P$ , with  $y_i = \frac{n_i}{N}$ , the chemical potential is then expressed as a function of the extensive variables.

### 2.4. Choice of the references

In this section, we shall deal with the choice of the reference pressure  $P_{ref}$ , temperature  $T_{ref}$ , specific enthalpies  $h_{iref}^*$  and specific entropies  $s_{iref}^*$  which appear in the expression of the specific enthalpies and enthalpies of the pure species in the equations (3)(7).

Table 1. specific values at  $P_{ref} = 10^5 Pa$  and  $T_{ref} = 600 K$ 

	Hydrogen	Iodine	Hydrogen iodide
entropy $J mol^{-1}$	151.077	286.764	227.233
enthalpy $JK^{-1}mol^{-1}$	0	0	-5961

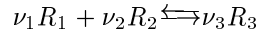
Table 2. heat capacity  $c_p JK^{-1}mol^{-1}$ 

Hydrogen	Iodine	Hydrogen iodide
29.327	37.612	30.348

Let us note furthermore that, as the species are involved in a chemical reaction, the reference specific enthalpies  $h_{iref}$  have to be chosen with regard to the enthalpy of formation of species. They are given in tables for the pressure that we have taken as reference pressure  $P_{ref} = 10^5 Pa$ . As the reaction takes place in gas phase, we have chosen the reference temperature to be  $T_{ref} = 600 K$ . They are given in table 1. For the heat capacities, constant values are chosen. They are given in table 2. The values given in the tables 1 and 2, are taken from the reference [8].

### 3. THE REPRESENTATION OF THE CHEMICAL REACTION

For the representation of the chemical reaction, we shall follow closely the exposition and formulation proposed by Oster et al. in [13] and apply it to our example. The reaction under consideration is the gas phase equilibrated hydrogen - iodine reaction  $H_2 + I_2 \rightleftharpoons 2HI$ . In the sequel, for the sake of defining a general model, we shall index the species by the integers 1, 2, 3: the index 1 stands for hydrogen, 2 for iodine and 3 for hydrogen iodide. And the reaction is denoted by



where the stoichiometric coefficients are  $(\nu_1, \nu_2, \nu_3) = (1, 1, 2)$ .

The kinetics of the forward and reverse reaction are given in the classical form that is used in chemical kinetics. They are assumed to satisfy the hypothesis of the mass action constitutive relation, that is to say the orders of the reactions with respect to each reactant correspond to the stoichiometry of the reactions. The global reaction rate (in  $mol m^{-3} s^{-1}$ ) is then given by  $\mathcal{R} = r_f - r_r$ , the difference between the forward reaction rate:

$$r_f = k_1(T) C_1^{\nu_1} C_2^{\nu_2} \quad (10)$$

and the reverse reaction rate:

$$r_r = k_2(T) C_3^{\nu_3} \quad (11)$$

where  $C_i, i = 1, \dots, 3$  represents the molar concentrations in component  $i$ . The *specific*

rate constants  $k_1(T)$  and  $k_2(T)$  follow the Arrhenius equations:

$$k_j(T) = k_j \exp \frac{-E_j}{RT} \quad (12)$$

where  $k_j$  and  $E_j$  are some constants.

Oster and co-authors have shown [13] that in order to derive a bond graph representation of the reaction kinetics one has to consider the *forward affinity*  $A_f$  and the *reverse affinity*  $A_r$  which are the driving forces of the forward and the reverse chemical reactions according to the approach of irreversible thermodynamics [6].

First of all let us noticed that the affinity vector  $A = \begin{pmatrix} A_f \\ A_r \end{pmatrix}$  is the conjugated power variable to the vector of the *global reaction rates*  $\bar{J} = \begin{pmatrix} J_f \\ J_r \end{pmatrix}$  which may be defined with respect to the forward and reverse reaction rates as follows:

$$\begin{pmatrix} J_f = (r_f - r_r)V \\ J_r = (r_r - r_f)V \end{pmatrix} \quad (13)$$

Furthermore the forward and reverse affinities are defined as linear functions of the chemical potentials and related by the stoichiometric matrix as follows:

$$\begin{pmatrix} A_f \\ A_r \end{pmatrix} = \begin{pmatrix} \nu_1 & \nu_2 & 0 \\ 0 & 0 & \nu_3 \end{pmatrix} \begin{pmatrix} \mu_1 \\ \mu_2 \\ \mu_3 \end{pmatrix} \quad (14)$$

Let us denote by  $J_i$  the rate of change of the number of mole of species  $i$  due to the chemical reaction. According to the stoichiometric coefficients it is related to the global reaction rates as follows:

$$J = \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix} = \begin{pmatrix} \nu_1 & 0 \\ \nu_2 & 0 \\ 0 & \nu_3 \end{pmatrix} \begin{pmatrix} J_f \\ J_r \end{pmatrix} \quad (15)$$

It is easy to see that the relations (14) and (15) define two adjoint relations between pairs of conjugated power variables and may be hence be represented by a transformer with gain being the stoichiometric matrix [13].

It is well known that, although a chemical transformation obeys the conservation of the total mass, the chemical reactants are not conserved but undergo a dissipative transformation to a new product. Following the bond graph language, the chemical reaction kinetics will be described by a resistive-type constitutive relation. Oster et al. consider only isothermal reaction and hence indeed represent the reaction kinetics by a one port resistive element. In order to express the constitutive relations of this element in terms of its port variables the reaction rates are rewritten using (2) and (9),

as follows:

$$\begin{aligned} r_f &= \left(\frac{V}{N}\right)^{\nu_1+\nu_2} \left( k_1(T) \exp\left(\frac{A_f}{RT}\right) \exp\left(-\frac{\nu_1\mu_1^*(T,P)+\nu_2\mu_2^*(T,P)}{RT}\right) \right) \\ r_r &= \left(\frac{V}{N}\right)^{\nu_3} \left( k_2(T) \exp\left(\frac{A_r}{RT}\right) \exp\left(-\frac{\nu_3\mu_3^*(T,P)}{RT}\right) \right). \end{aligned} \quad (16)$$

Using equation (13), the expressions of the reaction rates  $J_f$  and  $J_r$  with respect  $A_f$  and  $A_r$  are then easily deduced. It leads to the bond graph represented in figure 1 where  $J$  represents the vector of the mole number derivative and  $\mu$  the vector of the chemical potential.



Fig. 1. Bond graph representation of the reaction

#### 4. MATERIAL AND ENTROPY BALANCES

##### 4.1. Classical approach in chemical engineering: material and energy balances

In chemical engineering, the dynamic model is classically derived from the mass and energy balances. In the considered example, the material balances are written for the three components:

$$\begin{aligned} \frac{dn_1}{dt} &= F_{e1} - F_{s1} + \bar{\nu}_1(r_f - r_r) \\ \frac{dn_2}{dt} &= F_{e2} - F_{s2} + \bar{\nu}_2(r_f - r_r) \\ \frac{dn_3}{dt} &= F_{e3} - F_{s3} + \bar{\nu}_3(r_f - r_r) \end{aligned} \quad (17)$$

where  $F_{ei}$ ,  $F_{si}$  for  $i = 1, \dots, 3$  respectively denote the inlet and outlet molar flows and  $\bar{\nu}_i$  for  $i = 1, \dots, 3$  denote the signed stoichiometric coefficients: ( $\bar{\nu}_i = -\nu_i$  if it appears on the left side of the reaction scheme,  $\bar{\nu}_i = \nu_i$  in the other case). In the bond graph representation the balance equation (17) is represented by the 0-junction connected to the material port of the energy storing element as represented in figure (2).

Using the assumptions that the pressure as well as the volume are constant, the energy balance is written in terms of the time variation of the enthalpy:

$$\frac{dU}{dt} = \frac{dH}{dt} = \sum_{i=1}^3 (F_{ei}h_{ei}^* - F_{si}h_{si}) + Q \quad (18)$$

where  $h_{ei}$ ,  $h_{si}$  the inlet and outlet specific molar enthalpies and  $Q$  denotes the heat

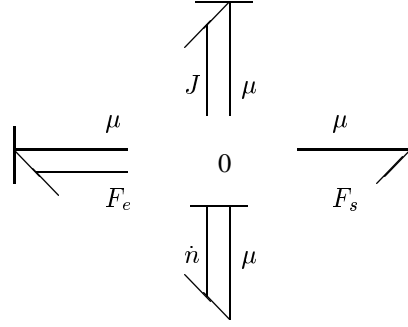


Fig. 2. Bond graph representation of the mass balance

flux coming from the jacket of the reactor which is considered at constant uniform temperature  $T_{jac}$ .

Using the expression of the enthalpy (8) and the energy balance equation (18) the dynamics of the temperature is derived as follows:

$$\sum_{i=1}^3 n_i c_{pi} \frac{dT}{dt} = \sum_{i=1}^3 c_{pi} F_{ei} (T_{ei} - T) + Q - \sum_{i=1}^3 \bar{\nu}_i h_i (r_f - r_r) V \quad (19)$$

where  $\sum_{i=1}^3 \bar{\nu}_i h_i$  is the so-called enthalpy of reaction and  $T_{ei}$  denotes the temperature of the constituent  $i$  at the inlet.

In the bond graph formalism however, as the energy is represented by Gibbs' equation (stated in the definition of the energy-storing element), the entropy balance has to be derived so that the energy and the material balances are satisfied.

#### 4.2. The entropy balance equation

This entropy balance equation may be derived by using Gibbs' equation (1), the energy balance (18) and the material balances (17) :

$$\frac{dS}{dt} = \sum_{i=1}^3 F_{ei} s_{ei}^* - F_{si} s_i + \frac{Q}{T_{jac}} + \sigma \quad (20)$$

where  $\sigma$  is the irreversible entropy production :

$$\sigma = \overbrace{\left( \sum_{i=1}^3 \frac{F_{ei}}{T} (h_{ei}^* - T s_{ei}^* - \mu_i) \right)}^{\sigma_{mixing}} + \overbrace{\left( \frac{Q}{T} - \frac{Q}{T_{jac}} \right)}^{\sigma_{ex}} - \overbrace{\left( \sum_{i=1}^3 \mu_i \bar{\nu}_i (r_f - r_r) \frac{V}{T} \right)}^{\sigma_{reac}} \quad (21)$$

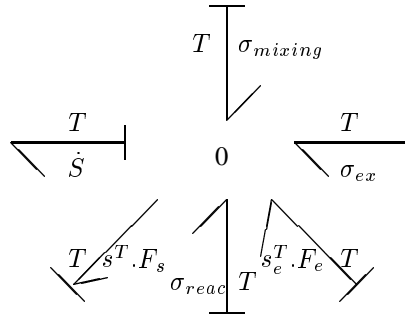


Fig. 3. Bond graph representation of the entropy balance

$\sigma_{mixing}$  is the entropy production due to the mixing of the constituents at the inlet with the mixture in the reactor,  $\sigma_{ex}$  is the entropy production due to the heat transfer between the jacket and the mixture and  $\sigma_{reac}$  is the entropy production due to the chemical reaction. In the bond graph model, the entropy balance given by the equations (20) (21) is represented by the *0-junction* connected at the thermal port of the energy storing element as shown in figure 3 where  $s^T = (s_1 \ s_2 \ s_3)$  and  $s_e^T = (s_{e1} \ s_{e2} \ s_{e3})$ . In the sequel we shall consider with more details some terms of the entropy balance and give their bond graph representation.

## 5. HEAT AND MASS TRANSPORT PHENOMENA

### 5.1. The convective terms

First let us consider firstly the two convective terms of the equation (20). They are represented by two MTF elements which couple the thermal and material domain.

*The entropy convection at the inlet* is represented by the MTF element with gain  $G_e = (s_{1e} \ s_{2e} \ s_{3e})$  formed by molar entropy of the pure constituents at the inlet and couples the 1-junction associated with the molar flows at the inlet with the 0-junction representing the entropy balance. The flow variable at the thermal port of the MTF element is the convected entropy term  $\sum_{i=1}^3 F_{ei} s_{ei}$  is equal to  $G_e F_e$  with  $F_e = \begin{pmatrix} F_{e1} \\ F_{e2} \\ F_{e3} \end{pmatrix}$ .

Its conjugated variable is the temperature of the mixture. By duality, the expression of the effort variable at the material port of the MTF element is  $T G_e^T$  and the conjugated flow variable is the vector of molar flows  $F_e$  at the inlet. The MTF element of the figure 4 represents the convection of the entropy at the inlet.

The entropy convection at the outlet is represented in a similar way by an MTF element with gain  $G = (s_1 \ s_2 \ s_3)$  formed by partial molar entropy (function of the state variables) of the components in the reactor. The convected entropy term  $\sum_{i=1}^3 F_i s_i$  is equal to  $G F_s$  with  $F_s = \begin{pmatrix} F_{s1} \\ F_{s2} \\ F_{s3} \end{pmatrix}$ . On the material port, the conjugated power variables are the vector of outlet molar flows and  $T G^T$ .

### 5.2. The mixing process

Recall that at the inlet, contrary to the outlet, the species are not in thermodynamical equilibrium with the species in the mixture. The mixing of the reactants at the inlet with the mixture is an irreversible process which gives rise to an irreversible entropy production, denoted by  $\sigma_{mixing}$ . This is represented by an RS-element, called "mixing", as shown in figure 4, which relates the 1-junction representing the molar flow of constituents at the inlet and the 0-junction representing the entropy balance. At the material port, the flow variables is the vector of molar flow at the inlet  $F_e$ . Its conjugated effort variable is the driving force for the entropy production  $ex_{ei}^{[T]} - \mu_i$ , the difference between the exergy  $ex_{ei}^{[T]} = h_{ei}^* - T s_{ei}^*$  and the chemical potentials  $\mu_i$  of the constituents of the mixture which is created by the 1-junction to which the RS element is connected. At the thermal port, the effort variable is the temperature of the mixture and the entropy production  $\sigma_{mixing} = \sum_{i=1}^3 \frac{F_{ei}}{T} (h_{ei} - T s_{ei} - \mu_i)$ .

Hence the RS-element is modulated by the state of the constituents at the inlet (the specific enthalpy  $h_{ei}$  and the specific entropy  $s_{ei}$ ).

Using the assumption that the inlet flows are positive and according to the axioms of the irreversible thermodynamics, it can be seen that the entropy production term is non negative, as  $((T_e - T) - T \ln(\frac{T_e}{T}))$  and  $-T R \ln(y_i)$  are non negative.

### 5.3. The heat transfer process

The temperature of the jacket is assumed to be uniform and constant. The associated heat flux  $Q$  is assumed to be proportional to the temperature difference between the jacket and the mixture in the reactor:  $Q = \lambda (T_{jac} - T)$ . The heat transfer conductance, denoted by  $\lambda$ , represents the combined phenomena of heat conduction within the reactor wall and the heat transfer by convection between the reacting mixture, the fluid flowing through the jacket and the reactor wall. The heat transfer process leads to the non negative entropy production  $\sigma_{ex} = Q \left( \frac{1}{T} - \frac{1}{T_{jac}} \right)$ .

For this heat transfer process, we use the bond graph representation proposed in [2], Chap.6, p.139 which make appear explicitly the entropy production  $\sigma_{ex}$  and refer to this reference for further justifications.

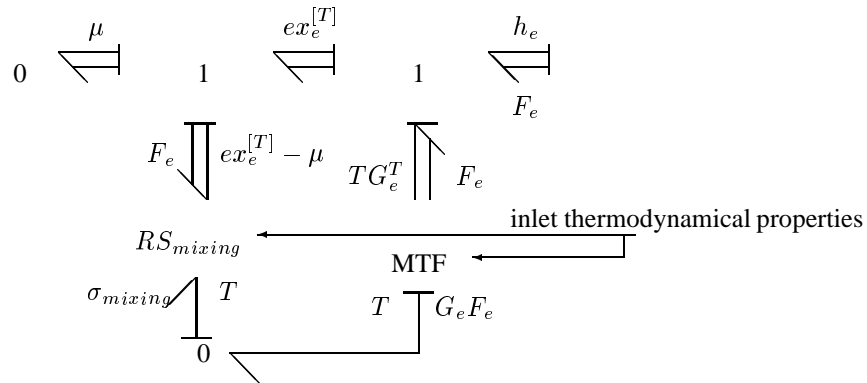


Fig. 4. Bond graph representation of the convective and mixing effects at the inlet

As previously mentioned, this jacket is not completely modelled since it appears in the model as an effort source, which gives the temperature of the jacket. For a more complete model, it will be sufficient to replace this effort source and connect with the modular element which represents the complete model of the jacket.

#### 5.4. The chemical reaction process

The first principle of thermodynamics implies that the "chemical energy" has been transformed in thermal energy in a power continuous way. In the bond graph model of the chemical reaction this is represented by a 2 port element coupling the material domain and the thermal domain and denoted by RS [19][2]. At the material port the power variables are the vector of the forward and reverse affinities and the total reaction rates. The constitutive relations at this port are given by the reaction kinetics already given by equations (13) and (16). At the thermal port they are the temperature of the reacting mixture and  $\sigma_{reac}$  is the irreversible entropy term due to reaction. The port variables satisfy the power continuity relation:

$$A_f J_f + A_r J_r = T \sigma_{reac} \quad (22)$$

According to irreversible thermodynamics [17], the chemical reaction is dissipative and leads to an entropy production:

$$\sigma_{reac} = \frac{1}{T} [A_f \ A_r] \begin{bmatrix} J_f \\ J_r \end{bmatrix} \geq 0 \quad (23)$$

Let us remark that in [2] chap.6, pp.132-133, the author studied in the same context as in [13], the linearized constitutive relations around some operating point. He

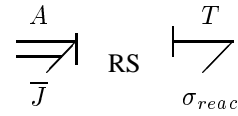


Fig. 5. Bond graph representation of the entropy of the reaction

shows that they can be decomposed into a symmetrical (positive definite) part and an antisymmetric part. Around an equilibrium point, this antisymmetric part disappears. Therefore the RS multiport may also be decomposed in a modulated junction structure and two 1-port RS elements. The figure 5 represents the entropy production due to the reaction.

## 6. THE PRESSURE CONSTRAINT

The Continuous Stirred Tank Reactor is an *open* system for which the following assumptions are made: the reactional volume  $V$  is supposed to be constant as well as the pressure  $P$  being at equilibrium with the pressure of the environment  $P_0$ .

Imposing at the same time both conjugated power variables at the spatial port of the energy storing element is indeed possible as we deal with an open system. The equilibrium in pressure  $P = P_0$  is considered as a constraint on the total model of the CSTR. This constraint may be proven to be of index 1 as shows the following symbolic solution of the problem. Naming  $F_s$  the total outlet molar flow, and recalling that  $F_{si} = y_i F_s$ , the equilibrium in pressure imposes the following total molar flow at the outlet:

$$F_s = \sum_{i=1}^3 (F_{ei} - \bar{v}_i(r_f - r_r)V) + \frac{N}{T \sum_{i=1}^3 n_i c_{pi}} \left( Q + \sum_{i=1}^3 (F_{ei} c_{pi} (T_{ei} - T) - \bar{v}_i h_i (r_f - r_r)V) \right) \quad (24)$$

In the bond graph model, in order to avoid symbolic computations and to preserve the modularity of the model, the constraint is solved numerically and is represented by a 2-port element called “Pressure constraint” and coupling the spatial domain at the port of the energy storing element and the material domain at the 1-junction representing the molar flow at the outlet.

## 7. THE CSTR SUBMODEL

Finally the 20-sim bond graph submodel of the CSTR is obtained by assembling the different submodels through the 0-junctions associated with the balance equations as

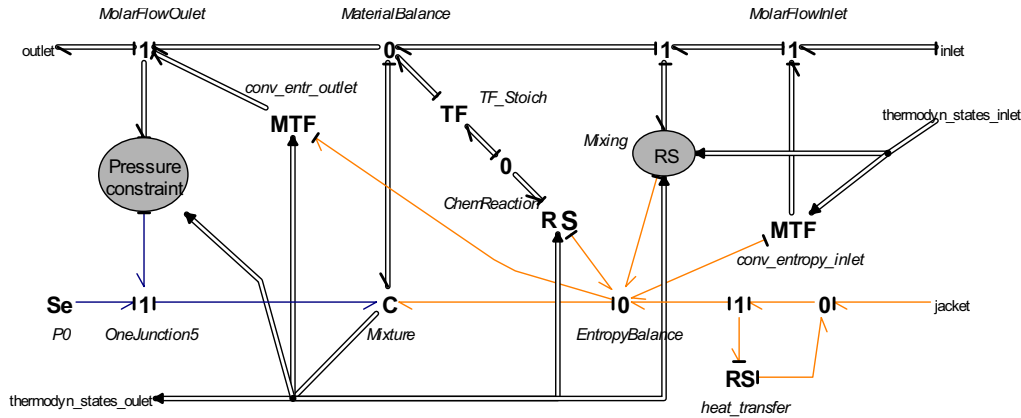


Fig. 6. 20-sim@Bond graph of the CSTR.

depicted in the figure 6.

There are two power ports corresponding to the molar flows at the inlet and at the outlet and an input signal flow of the states of the constituents at the inlet and an output signal flow with the states of the constituents of the mixture. These states are the chemical potential of pure constituents, the specific entropy, the specific enthalpy, the molar fractions, the total number of moles and the volume associated with the energy storing element C. A power port named "jacket" represents the thermal interaction through the jacket. The C-element is connected to the ports through a "generalized" junction structure according to the preceding reactions and representing the chemical reaction as well as the heat and mass transport phenomena. The power continuity of the junction structure can be interpreted as the energy balance given by (18).

The CSTR submodel is equivalent to a fifth order system with one algebraic constraint (of index 1) which may be written as follows:

$$\begin{cases} \begin{pmatrix} \dot{S} \\ \dot{V} \\ \dot{n} \end{pmatrix} = f(S, V, n) + F_s g_c(S, V, n) + g(T_{jac}, F_e, w, S, V, n) \\ 0 = P(S, V, n) - P_0 \end{cases} \quad (25)$$

where  $f$  is the drift vector field,  $g$  is the input vector field,  $g_c$  is the constraint vector field with  $F_s = F_s(S, V, n)$  solving the pressure constraint and  $w$  is the vector of the thermodynamic properties of the species at the inlet.

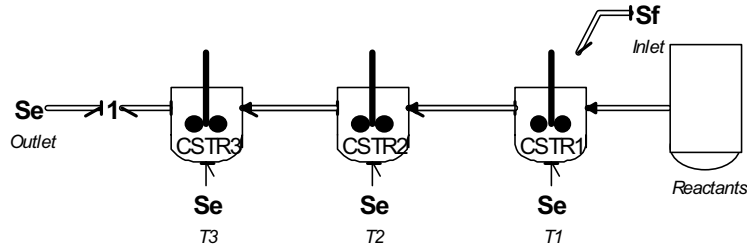


Fig. 7. 20-sim®Bond graph of the cascade of CSTR's.

## 8. THE MODEL OF A CASCADE CSTR AND SIMULATION

As an illustration of the port-based approach to the modelling of chemical reactors, we have chosen to consider the approximation of the model of a tubular reactor by a cascade of Continuous Stirred Tank Reactors as it is a classically done in chemical engineering [11]. The bond graph model and the simulation were implemented in the 20 – sim® bond graph modelling package [21] (figures (6), (7),(8) in this paper are produced using 20-sim and actually generate simulation code) . The bond graph model is then assembled by interconnecting the CSTR submodels by interconnection the power bonds and the signal flows as shown in figure 7.

The bond graph model is connected at the inlet to a source type element consisting of a constant molar flow of the pure constituents and a signal flow of the state of the constituents at the inlet.

In the Figure 8 we show some simulation results for the cascade of 3 of such reactors

The conditions for the simulation are the following :

- the reference temperature and pressure:  $T_{ref} = 600K$ ,  $P_0 = P_{ref} = 100000Pa$
- the volume of the reactor  $V = 29.94m^3$
- the initial total outlet molar flow  $F_{Stot} = 0.974 mol s^{-1}$
- The initial entropy:  $S = 134.58 JK^{-1} s^{-1}$
- the initial mole numbers  $n_1 = 300$ ,  $n_2 = 290$  and  $n_3 = 10$
- the kinetics constants  $k_1 = 3300000 m^3 mol^{-1} s^{-1}$ ,  $k_2 = 2000000 s^{-1}$
- the molar flow at the inlet  $f_1 = f_2 = 0.003 mol s^{-1}$  and  $f_3 = 0.0001 moles s^{-1}$
- the activation energy  $EA_1 = 162602 EA_2 = 177650$
- the heat transfer coefficient  $10 Watt m^{-2} K^{-1}$
- the temperature of the jacket =  $700K$

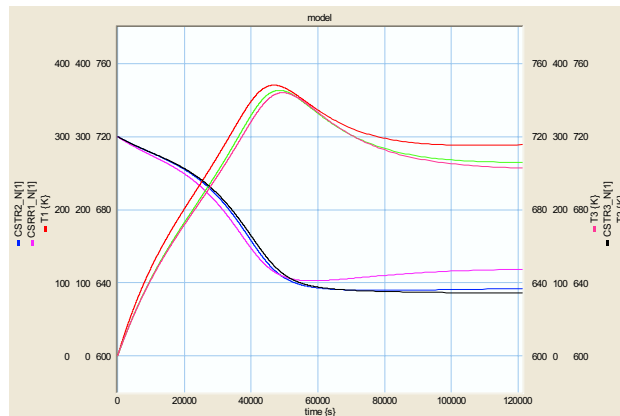


Fig. 8. Evolution of mole number and temperature in reactor 1 , 2 and 3.

## 9. CONCLUSION

We have proposed a generalized Bond graph model of a Continuous Stirred Tank Reactor (CSTR) which may be used as basic lump for the models of homogeneous chemical reactors. As an example we have considered the model of a tubular reactor represented by a cascade of CSTR. The equilibrated hydrogen - iodine reaction is chosen as an example of application. We have discussed the main differences of the bond graph modelling approach with respect to the classical models of chemical engineering. Firstly the thermodynamical properties of the mixture of reactants, represented by an energy storing element denoted by C, have been written on the basis of Gibbs' equations leading to express the intensive variables as functions of the extensive ones. Secondly we have recalled the bond graph models of the kinetics of the reaction, represented by an RS-element with port variables being the global reaction rates and forward and reverse affinity. Its constitutive relations have been written in term of these port variables. Thirdly a special attention was devoted to the bond graph representation of the mass and heat transport phenomena. In particular two-port RS-element represents the mixing process due to the fact that the reactants in the reactor and at the inlet are not in thermodynamical equilibrium. Finally the bond graph model of the reactor has been written and then simulated using the package 20-sim®. In this paper, we have chosen elementary thermodynamic and reaction kinetics properties for which all the computations can be done analytically. In future work we shall investigate more complex situations and how the numerical models of the thermodynamic properties and the reaction kinetics may be included in such port based models. It remains also to demonstrate how such models may be adapted to changes in the

modelling assumptions such as assuming varying pressure inside the reactor or more complex interconnection of CSTR submodels than the cascade interconnection.

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