# Chemical Reactions

- In this lecture, we shall talk about chemical reaction dynamics, and shall attempt a bond-graphic interpretation thereof.
- Although chemists usually treat reaction dynamics separately from thermodynamics, this separation makes no sense from a bond-graph perspective.
- We shall therefore treat the chemical reaction dynamics and chemical thermodynamics as two facets of one and the same physical phenomenon.

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# Chemical Reactions I

- Chemical reactions are usually represented by ***mass balance equations***, as shown in the following example:

$$\mathbf{C_3H_8 + 5O_2 \rightleftharpoons 3CO_2 + 4H_2O}$$

- ***Stoichiometric coefficients*** are used to ensure that the same number of atoms of each pure substance appears on both sides of the equation. The above example reaction involves 3 carbon atoms, 8 hydrogen atoms, and 10 oxygen atoms.
- Reactions can usually take place in either direction. Consequently, the above equation is an abbreviation for:

$$\mathbf{C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O}$$
$$\mathbf{3CO_2 + 4H_2O \rightarrow C_3H_8 + 5O_2}$$

# Reaction Rates I

- For a reaction to occur, the ***reactants*** must meet at one place at one time. The probability of a reactant to be at any given place is proportional to its concentration, and the probabilities of the different reactants are stochastically independent of each other. Thus, the first of the two reactions is expected to occur with the probability:

$$\boxed{k_1 \cdot c_{C_3H_8} \cdot (c_{O_2})^5}$$

where $c_M$ denotes the concentration of the reactant molecule $M$.

- Similarly, the second reaction is expected to occur with probability:

$$\boxed{k_2 \cdot (c_{CO_2})^3 \cdot (c_{H_2O})^4}$$

# Reaction Rates II

- We denote the probability constants, ***k₁*** and ***k₂***, the so-called ***reaction rate constants***, by writing them on top of the arrows:

$$\begin{aligned} C_3H_8 + 5O_2 &\xrightarrow{k_1} 3CO_2 + 4H_2O \\ 3CO_2 + 4H_2O &\xrightarrow{k_2} C_3H_8 + 5O_2 \end{aligned}$$

- Thus, we are made to believe that we can write:

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{dt}}(c_{\mathrm{C_3H_8}}) &= k_2 \cdot (c_{\mathrm{CO_2}})^3 \cdot (c_{\mathrm{H_2O}})^4 - k_1 \cdot c_{\mathrm{C_3H_8}} \cdot (c_{\mathrm{O_2}})^5 \\
\frac{\mathrm{d}}{\mathrm{dt}}(c_{\mathrm{O_2}}) &= 5k_2 \cdot (c_{\mathrm{CO_2}})^3 \cdot (c_{\mathrm{H_2O}})^4 - 5k_1 \cdot c_{\mathrm{C_3H_8}} \cdot (c_{\mathrm{O_2}})^5 \\
\frac{\mathrm{d}}{\mathrm{dt}}(c_{\mathrm{CO_2}}) &= 3k_1 \cdot c_{\mathrm{C_3H_8}} \cdot (c_{\mathrm{O_2}})^5 - 3k_2 \cdot (c_{\mathrm{CO_2}})^3 \cdot (c_{\mathrm{H_2O}})^4 \\
\frac{\mathrm{d}}{\mathrm{dt}}(c_{\mathrm{H_2O}}) &= 4k_1 \cdot c_{\mathrm{C_3H_8}} \cdot (c_{\mathrm{O_2}})^5 - 4k_2 \cdot (c_{\mathrm{CO_2}})^3 \cdot (c_{\mathrm{H_2O}})^4
\end{aligned}$$

# Reaction Rates III

- The above reaction rate equations are most certainly incorrect though, because it is even less likely to get 6 or even 7 reactants together at one place at any one time, than to get your Ph.D. examining committee of faculty members to agree on a date and time for your exam ( ☺ ).
- Most chemical reactions are only ***balance equations***. In order to determine the reaction equations, we need the individual ***step reactions***.

# Hydrogen-Bromine Reaction I

- Let us look at a very simple reaction, the ***hydrogen-bromine reaction***.

***Balance reaction:***

$$H_2 + Br_2 \rightleftharpoons 2HBr$$

***Step reactions:***

$$\begin{aligned}
&Br_2 \xrightarrow{k_1} 2Br^{\bullet} \\
&2Br^{\bullet} \xrightarrow{k_2} Br_2 \\
&Br^{\bullet} + H_2 \xrightarrow{k_3} HBr + H^{\bullet} \\
&HBr + H^{\bullet} \xrightarrow{k_4} Br^{\bullet} + H_2 \\
&Br_2 + H^{\bullet} \xrightarrow{k_5} HBr + Br^{\bullet}
\end{aligned}$$

# Hydrogen-Bromine Reaction II

***Step reactions:***

$$Br_2 \xrightarrow{k_1} 2Br^\bullet$$
$$2Br^\bullet \xrightarrow{k_2} Br_2$$
$$Br^\bullet + H_2 \xrightarrow{k_3} HBr + H^\bullet$$
$$HBr + H^\bullet \xrightarrow{k_4} Br^\bullet + H_2$$
$$Br_2 + H^\bullet \xrightarrow{k_5} HBr + Br^\bullet$$

***Reaction rate equations:***

$$\frac{d}{dt}(c_{Br_2}) = -k_1 \cdot c_{Br_2} + k_2 \cdot (c_{Br^\bullet})^2 - k_5 \cdot c_{H^\bullet} \cdot c_{Br_2}$$

$$\begin{aligned}\frac{d}{dt}(c_{Br^\bullet}) = {} & 2k_1 \cdot c_{Br_2} - 2k_2 \cdot (c_{Br^\bullet})^2 - k_3 \cdot c_{H_2} \cdot c_{Br^\bullet} \\ & + k_4 \cdot c_{HBr} \cdot c_{H^\bullet} + k_5 \cdot c_{H^\bullet} \cdot c_{Br_2}\end{aligned}$$

$$\frac{d}{dt}(c_{H_2}) = -k_3 \cdot c_{H_2} \cdot c_{Br^\bullet} + k_4 \cdot c_{HBr} \cdot c_{H^\bullet}$$

$$\frac{d}{dt}(c_{H^\bullet}) = k_3 \cdot c_{H_2} \cdot c_{Br^\bullet} - k_4 \cdot c_{HBr} \cdot c_{H^\bullet} - k_5 \cdot c_{H^\bullet} \cdot c_{Br_2}$$

$$\frac{d}{dt}(c_{HBr}) = k_3 \cdot c_{H_2} \cdot c_{Br^\bullet} - k_4 \cdot c_{HBr} \cdot c_{H^\bullet} + k_5 \cdot c_{H^\bullet} \cdot c_{Br_2}$$

# Molecular Mass

- In physics, it is common to express ***mass*** in ***kg***.
- In chemistry, this is inconvenient, since chemical reactions trade substances in a fixed ratio among the involved types of molecules (or atoms).
- Unfortunately, ***1 kg*** of one ***pure chemical substance*** (a substance containing only one type of molecules) contains a different number of molecules than another.
- The ***molecular mass*** of a pure substance is defined as the number of heavy particles (protons and neutrons) contained in a molecule of the pure substance multiplied by the mass of a heavy particle.

# Avogadro's (Loschmidt's) Number

- However, it is inconvenient to work with molecular masses, because the number of molecules of any pure chemical substance in one ***kg*** of substance is very big.
- For this reason, it has become customary to normalize masses differently when dealing with chemical reactions.
- We count the number $L$ of atoms contained in ***12 g*** of $\mathbf{C^{12}}$, where one atom of $\mathbf{C^{12}}$ contains 12 heavy particles.
- Correspondingly, the number of atoms contained in ***2g*** of $\mathbf{H_2}$ is also $L$, since one molecule of $\mathbf{H_2}$ contains two heavy particles, and any heavy particle contains the same mass.
- $L = 6.025 \cdot 10^{23}$ is called ***Avogadro's number*** in the U.S. literature, and ***Loschmidt's number*** in the European literature.

# Molar Mass

- A ***mole*** of a pure chemical substance is the amount of that substance containing $L$ molecules (or atoms).
- The ***molar mass*** of a pure chemical substance is defined as the mass of one mole of that substance.
- Consequently, one mole of $\mathbf{C}^{12}$ has a mass of ***12g***, whereas one mole of $\mathbf{H_2}$ has a mass of ***2g***.
- Given any amount (mass) of a given substance, we can count the ***number of moles*** contained in that amount, and use this as a unit of mass.
- Thus, instead of talking about ***1 kg*** of hydrogen gas, $\mathbf{H_2}$, we can equally well talk about ***500 moles*** of hydrogen gas.

# Molar Concentration

- Until now, we operated on ***concentrations***, without saying explicitly what we meant.
- We shall now become more precise, and define the ***molar concentration*** of a pure chemical substance as the quotient between the ***number of moles*** of a given amount of that substance divided by the ***volume*** that that amount occupies, for example:

$$\boxed{c_{Br_2} = \frac{n_{Br_2}}{V}}$$

- The molar concentration is thus measured in $m^{-3}$.

# Hydrogen-Bromine Reaction III

- Hence we can rewrite our reaction rate equations for the hydrogen-bromine reaction as follows:

$$\frac{d}{dt}(n_{Br_2}/V) = -k_1 \cdot n_{Br_2}/V + k_2 \cdot (n_{Br\cdot})^2/V^2 - k_5 \cdot n_{H\cdot} \cdot n_{Br_2}/V^2$$

$$\begin{aligned}\frac{d}{dt}(n_{Br\cdot}/V) = {} & 2k_1 \cdot n_{Br_2}/V - 2k_2 \cdot (n_{Br\cdot})^2/V^2 - k_3 \cdot n_{H_2} \cdot n_{Br\cdot}/V^2 \\ & + k_4 \cdot n_{HBr} \cdot n_{H\cdot}/V^2 + k_5 \cdot n_{H\cdot} \cdot n_{Br_2}/V^2\end{aligned}$$

$$\frac{d}{dt}(n_{H_2}/V) = -k_3 \cdot n_{H_2} \cdot n_{Br\cdot}/V^2 + k_4 \cdot n_{HBr} \cdot n_{H\cdot}/V^2$$

$$\frac{d}{dt}(n_{H\cdot}/V) = k_3 \cdot n_{H_2} \cdot n_{Br\cdot}/V^2 - k_4 \cdot n_{HBr} \cdot n_{H\cdot}/V^2 - k_5 \cdot n_{H\cdot} \cdot n_{Br_2}/V^2$$

$$\frac{d}{dt}(n_{HBr}/V) = k_3 \cdot n_{H_2} \cdot n_{Br\cdot}/V^2 - k_4 \cdot n_{HBr} \cdot n_{H\cdot}/V^2 + k_5 \cdot n_{H\cdot} \cdot n_{Br_2}/V^2$$

# Molar Flow Rate

- We can define the ***change in molar mass*** as the ***molar flow rate***, for example:

$$\boxed{v_{Br_2} = \frac{d}{dt}(n_{Br_2})}$$

- We can also introduce abbreviations for the expressions on the right hand side of the reaction rate equations:

$$\boxed{v_{k_1} = k_1 \cdot n_{Br_2}} \qquad \boxed{v_{k_2} = k_2 \cdot (n_{Br\cdot})^2 /V} \qquad \boxed{v_{k_3} = k_3 \cdot n_{H_2} \cdot n_{Br\cdot} /V}$$

$$\boxed{v_{k_4} = k_4 \cdot n_{HBr} \cdot n_{H\cdot} /V} \qquad \boxed{v_{k_5} = k_5 \cdot n_{H\cdot} \cdot n_{Br_2} /V}$$

and call these the ***reaction flow rates***.

# Hydrogen-Bromine Reaction IV

- With these abbreviations, we can rewrite our reaction rate equations for the hydrogen-bromine reaction once more:

$$
\begin{aligned}
\nu_{\mathrm{Br}_2} &= -\nu_{k_1} + \nu_{k_2} - \nu_{k_5} && + q \cdot (n_{\mathrm{Br}_2}/V) \\
\nu_{\mathrm{Br}^\bullet} &= 2\,\nu_{k_1} - 2\,\nu_{k_2} - \nu_{k_3} + \nu_{k_4} + \nu_{k_5} && + q \cdot (n_{\mathrm{Br}^\bullet}/V) \\
\nu_{\mathrm{H}_2} &= -\nu_{k_3} + \nu_{k_4} && + q \cdot (n_{\mathrm{H}_2}/V) \\
\nu_{\mathrm{H}^\bullet} &= \nu_{k_3} - \nu_{k_4} - \nu_{k_5} && + q \cdot (n_{\mathrm{H}^\bullet}/V) \\
\nu_{\mathrm{HBr}} &= \nu_{k_3} - \nu_{k_4} + \nu_{k_5} && + q \cdot (n_{\mathrm{HBr}}/V)
\end{aligned}
$$

**These equations are quite beautiful, but unfortunately, they are incorrect!**

$q = dV/dt$

# Thought Experiment

- Let us perform the following thought experiment. We place a mixture of hydrogen and bromine gases in a container of variable volume.
- We wait until no more reactions take place.
- We then expand the volume of the container.
- According to the above equations, the number of moles of each substance would start to grow.
- Evidently, this cannot be. The number of moles can only grow if we add substance, not if we add volume.

# Hydrogen-Bromine Reaction V

- Corrected reaction rate equations for the hydrogen-bromine reaction:

$$\begin{aligned}
\nu_{\mathrm{Br}_2} &= -\nu_{k_1} + \nu_{k_2} - \nu_{k_5} \\
\nu_{\mathrm{Br}^\bullet} &= 2\nu_{k_1} - 2\nu_{k_2} - \nu_{k_3} + \nu_{k_4} + \nu_{k_5} \\
\nu_{\mathrm{H}_2} &= -\nu_{k_3} + \nu_{k_4} \\
\nu_{\mathrm{H}^\bullet} &= \nu_{k_3} - \nu_{k_4} - \nu_{k_5} \\
\nu_{\mathrm{HBr}} &= \nu_{k_3} - \nu_{k_4} + \nu_{k_5}
\end{aligned}$$

- The erroneous term at the end of every reaction equation is simply deleted.

# Hydrogen-Bromine Reaction VI

- We can rewrite these equations in a matrix-vector form:

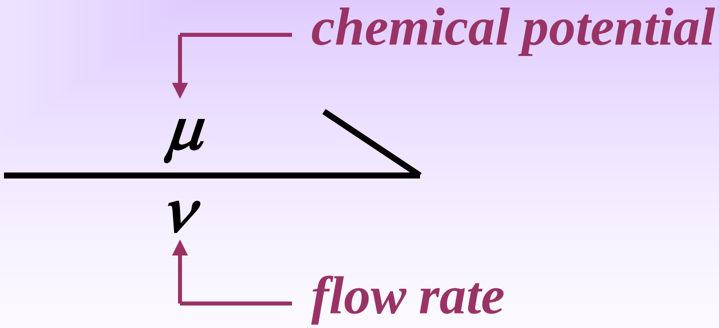
$$\begin{bmatrix} \nu_{Br_2} \\ \nu_{Br\bullet} \\ \nu_{H_2} \\ \nu_{H\bullet} \\ \nu_{HBr} \end{bmatrix} = \begin{bmatrix} -1 & +1 & 0 & 0 & -1 \\ +2 & -2 & -1 & +1 & +1 \\ 0 & 0 & -1 & +1 & 0 \\ 0 & 0 & +1 & -1 & -1 \\ 0 & 0 & +1 & -1 & +1 \end{bmatrix} \cdot \begin{bmatrix} \nu_{k_1} \\ \nu_{k_2}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

or:

$$\underline{\nu}_{mix} = N \cdot \underline{\nu}_{reac}$$

# Chemical Potential

- Molar and reaction flow rates can both be interpreted as ***mass flows***.
- In order to define a chemical bond, we need to come up with an adjugate variable, such that the product of the flow rate with that variable is power.
- This variable is called the ***chemical potential***.



$$g \cdot \dot{M} = \mu \cdot \nu$$

# The Chemical Multi-port Transformer I

- Chemical reaction equations can also be expressed using ***multi-port transformers***:

***Equations:***

$$\boxed{\begin{aligned} \underline{\mu}_{mix} &= M \cdot \underline{\mu}_{reac} \\ \underline{\nu}_{reac} &= M^T \cdot \underline{\nu}_{mix} \end{aligned}}$$

$$\Rightarrow \boxed{M^T = N^{-1}}$$

# The Chemical Multi-port Transformer II

- When we defined the ***TF-element***, we had a choice. We could define the ***m***-coefficient either in the forward direction for the ***flows*** (which is, what we chose), or in the forward direction for the ***efforts***. The two definitions are simply reciprocal, and the bond-graph literature is not consistent in how they do it.
- Even the ***mechanical MTF-elements*** could usually be defined arbitrarily in either way, although efficiency considerations might suggest a preferred direction.
- This is no longer true for the ***chemical MTF-elements***. The reason is that $N^{-1}$ may or may not exist. It happens to exist in the hydrogen-bromine reaction, but in general, the ***N-matrix*** doesn't even have to be square. It has as many rows as there are substances involved in the step reactions, and it has as many columns as there are individual step reactions. In the given example reaction system, both numbers were 5, and furthermore, ***N*** happened to be invertible.

# The Chemical Multi-port Transformer III

- For this reason, we now must define the ***chemical MTF-element*** inversely to how we did it until now:

$\underline{\mu}_{mix}$

$\underline{\nu}_{mix}$

**MTF**

$N$

$\underline{\mu}_{reac}$

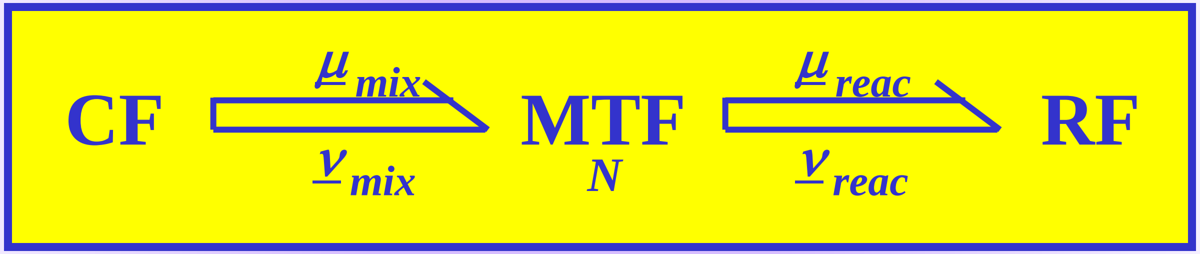
$\underline{\nu}_{reac}$

where:

$$\boxed{\begin{aligned} \underline{\nu}_{mix} &= N \cdot \underline{\nu}_{reac} \\ \underline{\mu}_{reac} &= N^T \cdot \underline{\mu}_{mix} \end{aligned}}$$

# The Chemical Reaction Bond Graph

- We can now plug everything together:



**Capacitive storage of all reactants in the mixture.**

**Transformation of the reactants into each other in the chemical reaction.**

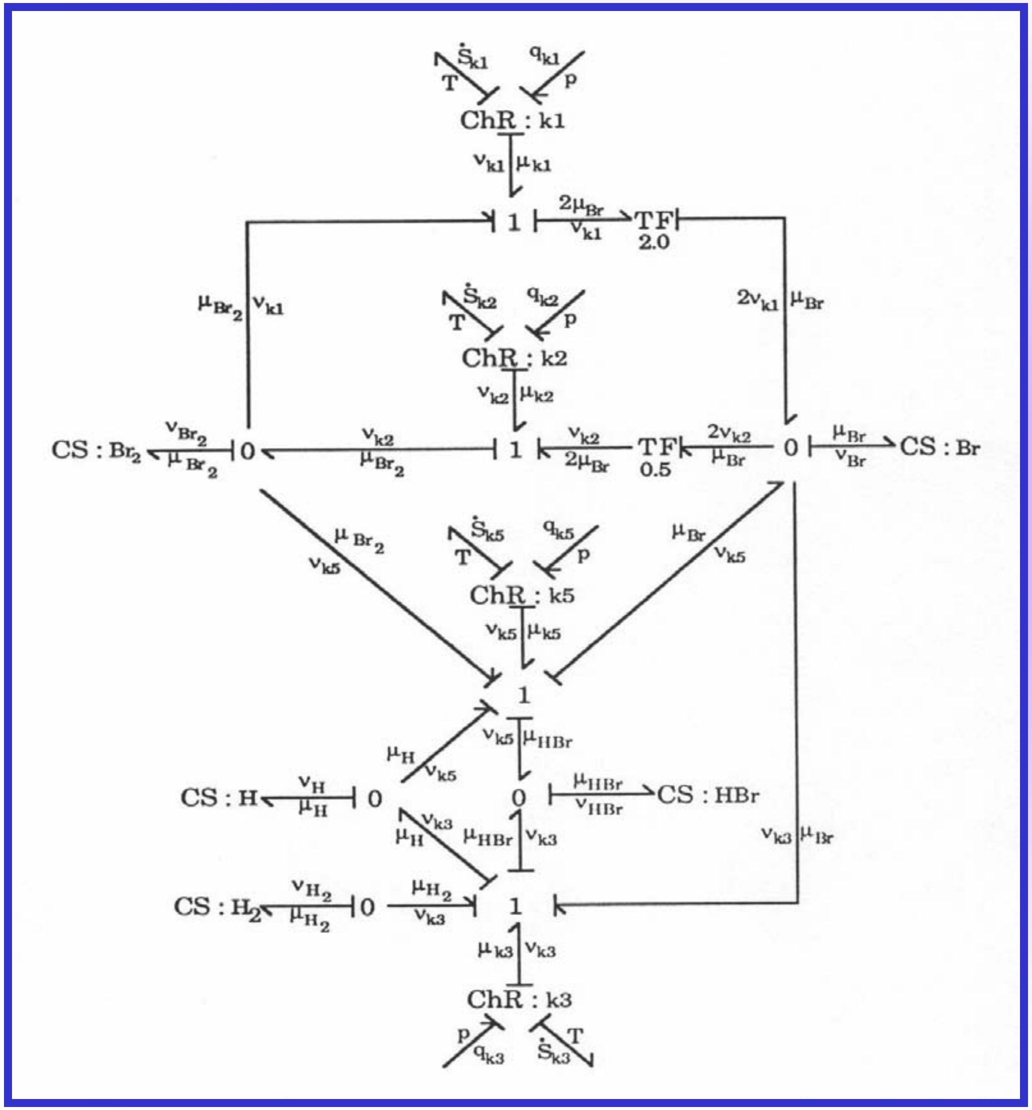
# Hydrogen-Bromine Reaction VII

- We can apply the newly acquired knowledge to the hydrogen-bromine reaction:

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

$$\Rightarrow$$

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



- The bond graph to the left shows a slightly simplified version of the hydrogen-bromine reaction. The least important reaction (reaction #4) was left out, in order to obtain a planar graph.
- The ***CS-elements*** represent the capacitive storages of the five substances involved.
- The ***ChR-elements*** represent the four most important chemical reactions.
- The ***0-junctions*** represent the ***N-matrix***.
- The ***1-junctions*** represent the ***M-matrix***.

# Remarks I

- Contrary to electrical and mechanical systems, both thermodynamics and chemical reactions exhibit equations, whereby the effort and flow variables are totally disconnected.
- In thermodynamics, it was possible to describe both ***conduction*** and ***radiation*** in terms of ***temperature*** alone. Consideration of the entropy flow is only needed, when the thermal domain is coupled to other domains.
- In chemical reactions, the ***reaction rate equations*** describe pure ***mass flow***. The chemical potentials don’t play any role at all, as long as the chemical domain is not coupled to other domains.

# Remarks II

- For these reasons, most researchers dealing with thermodynamics don’t work with entropy flows. They deal with ***temperature*** and ***heat flow*** as two separate phenomena.
- Chemists usually consider either ***reaction dynamics*** as pure mass flow phenomena, or they deal with ***chemical thermodynamics*** as a means to determine the amount of energy needed for or delivered in a reaction, and in order to determine, whether a reaction occurs exothermically or endothermically.
- They hardly ever deal with true thermodynamics, but rather with thermostatics. They concern themselves only with energy flows in the vicinity of the flow equilibrium.

# Remarks III

- Looking at thermodynamics and chemical reactions with a bond-graphic perspective helps to deepen the understanding of the physics behind these phenomena, and helps with preventing errors when coupling these phenomena to those of other domains.
- Since the molar flow rates are measured in numbers per second, the ***chemical potential*** has the dimension of power times seconds, i.e., energy.
- Chemists hardly ever use chemical potentials at all, since they aren’t measurable, in spite of their “physically meaningful” dimension.

# 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.