Chemical Thermodynamics II

• In this lecture, we shall continue to analyze our chemical thermodynamics bond graphs, making use of bond-graphic knowledge that we hadn’t exploited so far.

• This shall lead us to a more general bond-graphic description of chemical reaction systems that is less dependent on the operating conditions.

• The \textit{RF-element} and the \textit{CF-element} are explained in their full complexity.

Table of Contents

• Structural analysis of chemical reaction bond graph
• The chemical resistive field
• Multi-port gyrators
• The chemical capacitive field
• Isochoric vs. isobaric operating conditions
• Equation of state
• Adiabatic vs. isothermal operating conditions
• Caloric equation of state
• Enthalpy of formation
• Tabulation of chemical data
• Heat capacity of air
A Structural Analysis of the Generic Chemical Reaction Bond Graphs

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

\[ \text{CF} \xleftarrow{\mu_{\text{mix}}} \text{MTF} \xrightarrow{N} \xrightarrow{\chi} \text{RF} \]

Is the RF-element truly reactive?

Relations Between the Base Variables

- Let us recall a slide from an early class on bond graphs:

- **Resistor:** \( e = R(f) \)
- **Capacity:** \( q = C(e) \)
- **Inductivity:** \( p = I(f) \)

A reactive element must be describable purely by a (possibly non-linear) static relationship between efforts and flows.
The RF-Element I

- Let us analyze the three equations that make up the RF-element:

  1. **Gibbs equation**:

     \[ p \cdot q_i = T \cdot S_i + \mu \cdot v_i \]

     The *Gibbs equation* is certainly a static equation relating only efforts and flows to each other. It generalizes the “S” of the RS-element.

  2. **Equation of state**:

     \[ p \cdot V_i = n_i \cdot R \cdot T \]

     The equation of state is a static equation relating efforts with generalized positions. *Thus, it clearly belongs to the CF-element!*

The RF-Element II

- By differentiating the equation of state:

  \[ p \cdot q_i = v_i \cdot R \cdot T \]

  we were able to come up with a structurally appropriate equation:

  \[ p, T \text{ are e-variables} \]

  \[ q_i, v_i \text{ are f-variables.} \]

  Yet, the approach is dubious. The *physics* behind the equation of state points to the CF-field, and this is where it should be used.
The RF-Element III

- This also makes physical sense.
- The *equation of state* describes a *property of a substance*. The *CF-field* should contain a complete description of all chemical properties of the substance stored in it.
- The *RF-field*, on the other hand, only describes the transport of substances. A pipe really doesn’t care what flows through it!
- The *RF-field* should be restricted to describing *continuity equations*.
- The *mass continuity* is described by the *reaction rate equations*. The *energy continuity* is described by the *Gibbs equation*. What is missing is the *volume continuity*.

The RF-Element IV

- We know that mass always carries its volume along. Thus:
  \[ q_i = (V/M) \cdot \dot{M} = (V/n) \cdot v_i \]

- Using the *volume continuity equation*, we obtain exactly the same results as using the *differentiated equation of state*, since the equation of state teaches us that:
  \[ p \cdot V_i = n_i \cdot R \cdot T \quad \Rightarrow \quad V/n = R \cdot T / p \]

  thus:
  \[ q_i = v_i \cdot \frac{R \cdot T}{p} \]

  which is exactly the equation that we had used before.
The RF-Element V

- What have we gained, if anything?
- The differentiated equation of state had been derived under the assumption of isobaric and isothermal operating conditions.
- The volume continuity equation does not make any such assumption. It is valid not only for all operating conditions, but also for all substances, i.e., it does not make the assumption of an ideal gas reaction.

\[
\begin{align*}
\nu_{\text{reac}} &= k \cdot n ; \quad \text{mass continuity} \\
\frac{\nu_{\text{reac}}}{V} &= \frac{\nu_{\text{reac}}}{n} ; \quad \text{volume continuity} \\
p \cdot \dot{\nu}_{\text{reac}} &= T \cdot \dot{S}_{\text{reac}} + \mu_{\text{reac}} \cdot \nu_{\text{reac}} ; \quad \text{energy continuity}
\end{align*}
\]

are the set of equations describing the generic RF-field, where \( V \) is the total reaction volume, and \( n \) is the total reaction mass.

The RF-Element VI

3. Reaction rate equations: \( \nu_{\text{reac}} = k \cdot n \)

The reaction rate equations relate flows (\( f \)-variables) to generalized positions (\( q \)-variables). However, the generalized positions are themselves statically related to efforts (\( e \)-variables) in the CF-element. Hence these equations are indeed reactive as they were expected to be.

Thus, we now have convinced ourselves that we can write all equations of the RF-element as: \( f = g(e) \). In the case of the hydrogen-bromine reaction, there will be 15 equations in 15 unknowns, 3 equations for the three flows of each one of five separate reactions.
The Linear Resistive Field

- We still need to ask ourselves, whether these 15 equations are irreversible, i.e., resistive, or reversible, i.e., gyrative.
- We already know that the C-matrix describing a linear capacitive field is always symmetric.
- Since that matrix describes the network topology, the same obviously holds true for the R-matrix (or G-matrix) describing a linear resistive field (or linear conductive field). These matrices always have to be symmetric.

The Multi-port Gyrator I

- Let us now look at a multi-port gyrator. In accordance with the regular gyrator, its equations are defined as:

\[
\begin{align*}
\varepsilon_1 &= R \cdot f_2 \\
\varepsilon_1' \cdot \bar{L}_1 &= \varepsilon_1' \cdot \bar{L}_1 = \bar{L}_1' \cdot \varepsilon_1 \\
\varepsilon_2 &= R' \cdot \bar{L}_1
\end{align*}
\]
The Multi-port Gyrator II

- In order to compare this element with the resistive field, it is useful to have all bonds point at the element, thus:

\[
\begin{align*}
e_1 &= -R \cdot f_2 \\
e_2 &= R' \cdot f_1
\end{align*}
\]

or:

\[
\begin{align*}
L_1 &= G' \cdot e_2 \\
L_2 &= -G \cdot e_1
\end{align*}
\]

where:

\[
G = R^{-1}
\]

The Multi-port Gyrator III

- In a matrix-vector form:

\[
\begin{bmatrix}
L_1 \\
L_2
\end{bmatrix} =
\begin{bmatrix}
0 & G' \\
-G & 0
\end{bmatrix}
\begin{bmatrix}
e_1 \\
e_2
\end{bmatrix}
\]

\[
\text{skew-symmetric matrix}
\]

- Any matrix can be decomposed into a symmetric part and a skew-symmetric part:

\[
M = M_s + M_{as}
\]

where:

\[
M_s = \frac{M + M'}{2} \\
M_{as} = \frac{M - M'}{2}
\]
Symmetric and Skew-symmetric Matrices

- Example:

\[
M = \begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix} \quad \Rightarrow \quad M' = \begin{bmatrix} 1 & 3 \\ 2 & 4 \end{bmatrix}
\]

\[
M_s = (M + M') / 2 = \begin{bmatrix} 1 & 2.5 \\ 2.5 & 4 \end{bmatrix} \quad \text{is symmetric:} \quad (M_s = M_{s'})
\]

\[
M_{as} = (M - M') / 2 = \begin{bmatrix} 0 & -0.5 \\ 0.5 & 0 \end{bmatrix} \quad \text{is skew-symmetric:} \quad (M_{as} = -M_{as'})
\]

\[
M = \begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix} = \begin{bmatrix} 1 & 2.5 \\ 2.5 & 4 \end{bmatrix} + \begin{bmatrix} 0 & -0.5 \\ 0.5 & 0 \end{bmatrix} = M_s + M_{as}
\]

The RF-Element VII

- Hence given the equations of the RF-element:

\[
f = g(e)
\]

these equations can be written as:

\[
f = G(e) \cdot e
\]

- Thus:

\[
f = G_s(e) \cdot e + G_{as}(e) \cdot e
\]
The RF-Element VIII

- Example:

\[
\begin{align*}
  f_1 &= e_1^2 + 2e_2 \\
  f_2 &= -e_1 + e_2
\end{align*}
\]

\[
\begin{bmatrix}
  f_1 \\
  f_2
\end{bmatrix} = \begin{bmatrix}
  e_1 & 2 \\
  -1 & e_2
\end{bmatrix} \begin{bmatrix}
  e_1 \\
  e_2
\end{bmatrix}
\]

\[
G(e) = \begin{bmatrix}
  e_1 & 2 \\
  -1 & e_2
\end{bmatrix} \Rightarrow \quad G'(e) = \begin{bmatrix}
  e_1 & -1 \\
  2 & e_2
\end{bmatrix}
\]

\[
G(e) = \begin{bmatrix}
  e_1 & 2 \\
  -1 & e_2
\end{bmatrix} = \begin{bmatrix}
  e_1 & 0.5 \\
  0.5 & e_2
\end{bmatrix} + \begin{bmatrix}
  0 & 1.5 \\
  -1.5 & 0
\end{bmatrix} = G_s(e) + G_o(e)
\]

Conduction matrix

\[G'(e)\]

Gyration matrix

The CF-Element I

- We should also look at the CF-elements. Of course, these elements are substance-specific, yet they can be constructed using general principles.

- We need to come up with equations for the three potentials (efforts): \(T\), \(p\), and \(g\). These are functions of the states (generalized positions): \(S\), \(V\), and \(M\).

- We also need to come up with initial conditions for the three state variables: \(S_0\), \(V_0\), and \(M_0\).
The CF-Element II

- The reaction mass is usually given, i.e., we know up front, how much reactants of each kind are available. This determines $M_0$ for each of the species, and therefore $n_0$. It also provides the total reaction mass $M$, and therefore $n$.
- In a batch reaction, the reaction mass remains constant, whereas in a continuous reaction, new reaction mass is constantly added, and an equal amount of product mass is constantly removed.
- Modeling continuous reactions with bond graphs is easy, since the chemical reaction bond graph can be naturally interfaced with a convective flow bond graph.

Isochoric vs. Isobaric Operating Conditions

- Chemical reactions usually take place either inside a closed container, in which case the total reaction volume is constant, or in an open container, in which case the reaction pressure is constant, namely the pressure of the environment.
- Hence either volume or pressure can be provided from the outside. We call the case where the volume is kept constant the isochoric operating condition, whereas the case where the pressure is kept constant, is called the isobaric operating condition.
The Equation of State

- The equation of state can be used to compute the other of the two volume-related variables, given the reaction mass and the temperature:

  **Isobaric conditions** \((p=\text{constant})\):
  \[ p \cdot V_0 = n_0 \cdot R \cdot T_0 \]

  **Isochoric conditions** \((V=\text{constant})\):
  \[ p(t) \cdot V = n(t) \cdot R \cdot T(t) \]

Adiabatic vs. Isothermal Operating Conditions

- We can perform a chemical reaction under conditions of thermal insulation, i.e., no heat is either added or subtracted. This operating condition is called the **adiabatic operating condition**.

- Alternatively, we may use a **controller** to add or subtract just the right amount of heat to keep the reaction temperature constant. This operating condition is called the **isothermal operating condition**.
The Caloric Equation of State I

- We need an equation that relates temperature and entropy to each other. In general: \( T = f(S, V) \). To this end, we make use of the so-called caloric equation of state:

\[
ds = \left( \frac{c_p}{T} \right) \cdot dT - \left( \frac{dV}{dT} \right)_p \cdot dp
\]

where:
- \( ds \) = change in specific entropy
- \( c_p \) = specific heat capacity at constant pressure
- \( dT \) = change in temperature
- \( \left( \frac{dV}{dT} \right)_p \) = gradient of specific volume with respect to temperature at constant pressure
- \( dp \) = change in pressure

The Caloric Equation of State II

- Under isobaric conditions \( (dp = 0) \), the caloric equation of state simplifies to:

\[
ds = \left( \frac{c_p}{T} \right) \cdot dT
\]

or:

\[
\frac{ds}{dT} = \frac{c_p}{T} \quad \implies \quad \Delta S = c_p \cdot \ln \left( \frac{T}{T_0} \right)
\]

\[
\Delta S = \gamma \cdot \ln \left( \frac{T}{T_0} \right)
\]

which corresponds exactly to the heat capacitor used in the past.
The Caloric Equation of State III

- In the general case, the caloric equation of state can also be written as:

\[ \dot{s} = \left( c_p/T \right) \cdot \dot{T} - \left( \frac{dv}{dT} \right) \cdot \dot{p} \]

- In the case of an ideal gas reaction:

\[ \left( \frac{dv}{dT} \right) = \frac{R}{p} \]

- Thus:

\[ \dot{s} = c_p \cdot \left( \frac{T}{T} \right) - R \cdot \left( \frac{p}{p} \right) \]

\[ \Rightarrow s - s_0 = c_p \cdot \ln\left( \frac{T}{T_0} \right) - R \cdot \ln\left( \frac{p}{p_0} \right) \]

The Caloric Equation of State IV

- The initial temperature, \( T_0 \), is usually given. The initial entropy, \( S_0 \), can be computed as \( S_0 = M_0 \cdot s(T_0, p_0) \) using a table lookup function.

- In the case of adiabatic operating conditions, the change in entropy flow can be used to determine the new temperature value. To this end, it may be convenient to modify the caloric equation of state such that the change in pressure is expressed as an equivalent change in volume.

- In the case of isothermal conditions, the approach is essentially the same. The resulting temperature change, \( \Delta T \), is computed, from which it is then possible to obtain the external heat flow, \( Q = \Delta T \cdot \dot{S} \), needed to prevent a change in temperature.
The Enthalpy of Formation

- Finally, we need to compute the Gibbs potential, \( g \). It represents the energy stored in the substance, i.e., the energy needed in the process of making the substance.
- In the chemical engineering literature, the enthalpy of formation, \( h \), is usually tabulated, in place of the Gibbs free energy, \( g \).
- Once \( h \) has been obtained, \( g \) can be computed easily:

\[
g = h(T, p) - T \cdot s
\]

Tabulation of Chemical Data I

- We can find the chemical data of most substances on the web, e.g. at: http://webbook.nist.gov/chemistry/form-ser.html.
- Searching e.g. for the substance HBr, we find at the address: http://webbook.nist.gov/cgi/cbook.cgi?ID=C10035106&Units=SI&Mask=1

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The Heat Capacity of Air I

We are now able to understand the CFAir model:

Equation of state
Caloric equation of state
Gibbs energy of formation

November 12, 2003

Tabulation of Chemical Data II

Gas Phase Heat Capacity (Shomate Equation)

\[ C_p^T = A + B/T + C \ln T + D + E T^{-1} \]

\[ H^\circ_p = H^\circ_{p,273} + R T \ln \left( \frac{T}{273} \right) \]

\[ S^\circ_p = S^\circ_p(273) + R \ln \left( \frac{T}{273} \right) \]

\[ C_p = \text{heat capacity (J/mol*K)} \]

\[ \Delta H^\circ_p = \text{enthalpy of formation at 298.15 K} \]

\[ \Delta S^\circ_p = \text{standard entropy (J/mol*K)} \]

\[ t = \text{temperature (K)/1000} \]

Temperature (K) | 298.1000 | 1100.6900
--- | --- | ---
A | 31.71409 | 23.39013
B | -53.09902 | 2.822176
C | 23.35567 | -0.470353
D | -9.605325 | 0.935914
E | -9.028790 | -3.174856
F | 45.64396 | 52.46318
G | 240.04203 | 210.0597
Molar Heat Capacity (J/mol*K) | 3644.086 | 2544.080
Reference

1993

Comment: Data last reviewed in September, 1993
The Heat Capacity of Air II

\[-p = T \cdot R \cdot \frac{M}{V} \quad \Rightarrow \quad -p \cdot V = T \cdot R \cdot M\]

The pressure is defined negatively.

\[T = T_0 \cdot \exp \left( \frac{(s - s_0 - R \cdot (\ln(v) - \ln(v_0)))}{c_v} \right) \]

\[\frac{T}{T_0} = \exp \left( \frac{(s - s_0 - R \cdot (\ln(v/v_0)))}{c_v} \right) \]

\[\ln \left( \frac{T}{T_0} \right) = \frac{(s - s_0 - R \cdot (\ln(v/v_0)))}{c_v} \]

\[c_v \cdot \ln \left( \frac{T}{T_0} \right) = s - s_0 - R \cdot (\ln(v/v_0))\]

The Heat Capacity of Air III

\[g = T \cdot (c_p - s)\]

\[h = c_p T \quad \Rightarrow \quad g = h - T \cdot s\]

for ideal gases
References
