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 ***RF-element*** and the ***CF-element*** are explained in their full complexity.

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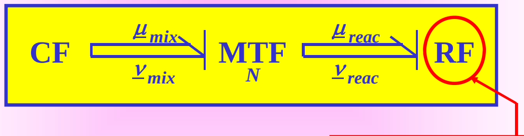
A Structural Analysis of the Generic Chemical Reaction Bond Graphs

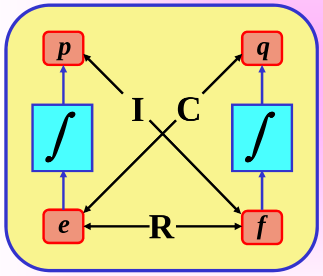
- Let us look once more at the generic chemical reaction bond graph:



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

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: $p \cdot V_i = n_i \cdot R \cdot T$

p, T are e-variables
V_i, n_i are q-variables.

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:

$$p \cdot q_i = \nu_i \cdot R \cdot T$$

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

p, T are e-variables
q_i, ν_i 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

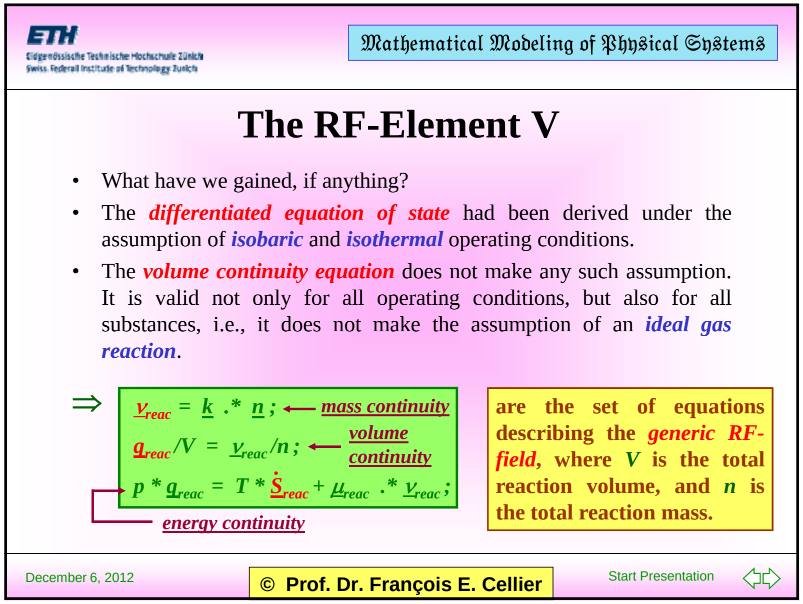
- We know that mass always carries its volume along. Thus:

$$q_i = (V/M) \cdot \dot{M} = (V/n) \cdot \nu_i$$

- 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: $q_i = \nu_i \cdot \dfrac{R \cdot T}{p}$ which is exactly the equation that we had used before.



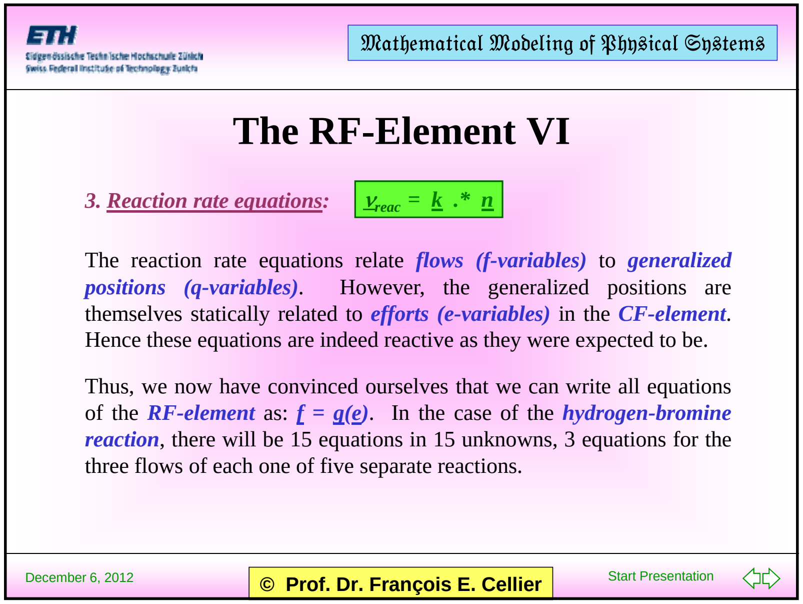
The RF-Element V

- 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***.

$$\Rightarrow \boxed{\begin{aligned} &\underline{v}_{reac} = \underline{k}\ .*\ \underline{n}\,; \longleftarrow \underline{\text{mass continuity}} \\ &\underline{q}_{reac}/V = \underline{v}_{reac}/n\,; \longleftarrow \underline{\text{volume continuity}} \\ &p * \underline{q}_{reac} = T * \underline{\dot{S}}_{reac} + \underline{\mu}_{reac}\ .*\ \underline{v}_{reac}\,; \end{aligned}}$$

energy continuity

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

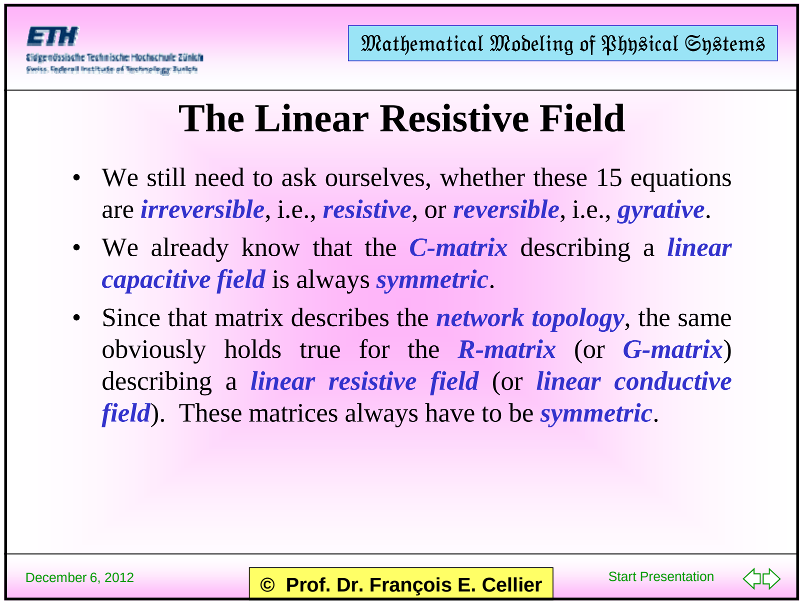


The RF-Element VI

3. Reaction rate equations: $\boxed{\underline{v}_{reac} = \underline{k}\ .*\ \underline{n}}$

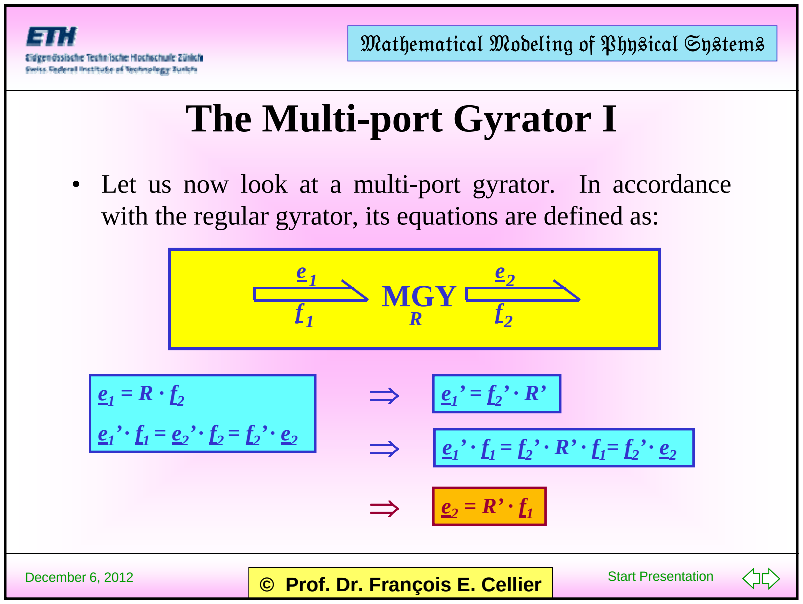
The reaction rate equations relate ***flows (f-variables)*** to ***generalized positions (q-variables)***. However, the generalized positions are themselves statically related to ***efforts (e-variables)*** in the ***CF-element***. Hence these equations are indeed reactive as they were expected to be.

Thus, we now have convinced ourselves that we can write all equations of the ***RF-element*** as: $\underline{f} = \underline{g}(\underline{e})$. 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:

$$\boxed{\begin{aligned} &\underline{e}_1 = R \cdot \underline{f}_2 \\ &\underline{e}_1' \cdot \underline{f}_1 = \underline{e}_2' \cdot \underline{f}_2 = \underline{f}_2' \cdot \underline{e}_2 \end{aligned}}$$

$$\Rightarrow \boxed{\underline{e}_1' = \underline{f}_2' \cdot R'}$$

$$\Rightarrow \boxed{\underline{e}_1' \cdot \underline{f}_1 = \underline{f}_2' \cdot R' \cdot \underline{f}_1 = \underline{f}_2' \cdot \underline{e}_2}$$

$$\Rightarrow \boxed{\underline{e}_2 = R' \cdot \underline{f}_1}$$

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:

with the equations:

$$\boxed{\begin{aligned}\underline{e}_1 &= -R \cdot \underline{f}_2 \\ \underline{e}_2 &= R' \cdot \underline{f}_1\end{aligned}} \quad \text{or:} \quad \boxed{\begin{aligned}\underline{f}_1 &= G' \cdot \underline{e}_2 \\ \underline{f}_2 &= -G \cdot \underline{e}_1\end{aligned}} \quad \text{where:} \quad \boxed{G = R^{-1}}$$

The Multi-port Gyrator III

- In a matrix-vector form:

$$\boxed{\begin{aligned}\underline{f}_1 &= G' \cdot \underline{e}_2 \\ \underline{f}_2 &= -G \cdot \underline{e}_1\end{aligned}} \Rightarrow \boxed{\begin{bmatrix}\underline{f}_1 \\ \underline{f}_2\end{bmatrix} = \underbrace{\begin{bmatrix}0 & G' \\ -G & 0\end{bmatrix}}_{\text{skew-symmetric matrix}} \cdot \begin{bmatrix}\underline{e}_1 \\ \underline{e}_2\end{bmatrix}}$$

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

$$\boxed{M = M_s + M_{as}} \quad \text{where:} \quad \boxed{\begin{aligned}M_s &= (M + M')/2 \\ M_{as} &= (M - M')/2\end{aligned}}$$

Symmetric and Skew-symmetric Matrices

- Example:

$$\boxed{M = \begin{bmatrix}1 & 2 \\ 3 & 4\end{bmatrix}} \Rightarrow \boxed{M' = \begin{bmatrix}1 & 3 \\ 2 & 4\end{bmatrix}}$$

$$\Rightarrow \boxed{M_s = (M + M')/2 = \begin{bmatrix}1 & 2.5 \\ 2.5 & 4\end{bmatrix}} \quad \boxed{M_{as} = (M - M')/2 = \begin{bmatrix}0 & -0.5 \\ 0.5 & 0\end{bmatrix}}$$

is symmetric: $(M_s = M_s')$ *is skew-symmetric: $(M_{as} = -M_{as}')$*

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

The RF-Element VII

- Hence given the equations of the *RF-element*:

$$\boxed{\underline{f} = \underline{g}(\underline{e})}$$

these equations can be written as:

$$\boxed{\underline{f} = G(\underline{e}) \cdot \underline{e}}$$

- Thus:

$$\boxed{\underline{f} = \overbrace{G_s(\underline{e})}^{\text{Conductive part}} \cdot \underline{e} + \underbrace{G_{as}(\underline{e})}_{\text{Gyrative part}} \cdot \underline{e}}$$

The RF-Element VIII

- Example:

$$\begin{aligned} f_1 &= e_1^2 + 2e_2 \\ f_2 &= -e_1 + e_2^2 \end{aligned} \quad \Rightarrow \quad \begin{bmatrix} f_1 \\ f_2 \end{bmatrix} = \begin{bmatrix} e_1 & 2 \\ -1 & e_2 \end{bmatrix} \cdot \begin{bmatrix} e_1 \\ e_2 \end{bmatrix}$$

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

$$G(\underline{e}) = \begin{bmatrix} e_1 & 2 \\ -1 & e_2 \end{bmatrix} = \underbrace{\begin{bmatrix} e_1 & 0.5 \\ 0.5 & e_2 \end{bmatrix}}_{\text{Conduction matrix}} + \underbrace{\begin{bmatrix} 0 & 1.5 \\ -1.5 & 0 \end{bmatrix}}_{\text{Gyration matrix}} = G_s(\underline{e}) + G_{as}(\underline{e})$$

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=constant):

$$\boxed{p \cdot V_0 = n_0 \cdot R \cdot T_0}$$

Isochoric conditions (V=constant):

$$\boxed{p(t) \cdot V = n(t) \cdot R \cdot T(t)}$$

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***:

$$\boxed{ds = (c_p/T) \cdot dT - (dv/dT)_p \cdot dp}$$

where:

ds = change in specific entropy
c_p = specific heat capacity at constant pressure
dT = change in temperature
$(dv/dT)_p$ = 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:

$$\boxed{ds = (c_p/T) \cdot dT}$$

or:

$$\boxed{ds/dT = c_p/T} \Rightarrow \boxed{\Delta s = c_p \cdot \ln(T/T_0)}$$

$$\Rightarrow \boxed{\Delta S = \gamma \cdot \ln(T/T_0)}$$

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:

$$\boxed{\dot{s} = (c_p/T) \cdot \dot{T} - (dv/dT)_p \cdot \dot{p}}$$

- In the case of an *ideal gas reaction*:

$$\boxed{(dv/dT)_p = R/p}$$

- Thus: $\boxed{\dot{s} = c_p \cdot (\dot{T}/T) - R \cdot (\dot{p}/p)}$

$$\Rightarrow \boxed{s - s_0 = c_p \cdot \ln(T/T_0) - R \cdot \ln(p/p_0)}$$

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, ΔT, is computed, from which it is then possible to obtain the *external heat flow*, $\dot{Q} = \Delta T \cdot \dot{S}$, needed to prevent a change in temperature.

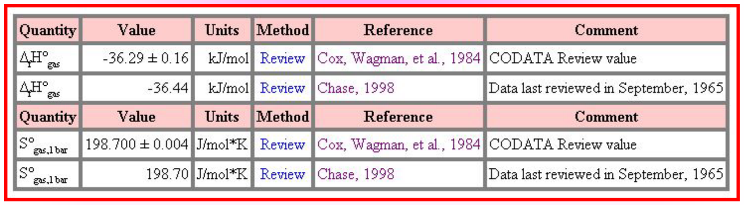
The Enthalpy of Formation

- 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:

$$\boxed{g = h(T,p) - T \cdot s}$$

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



Quantity	Value	Units	Method	Reference	Comment
$\Delta_f H^\circ_{gas}$	-36.29 ± 0.16	kJ/mol	Review	Cox, Wagman, et al., 1984	CODATA Review value
$\Delta_f H^\circ_{gas}$	-36.44	kJ/mol	Review	Chase, 1998	Data last reviewed in September, 1965
Quantity	**Value**	**Units**	**Method**	**Reference**	**Comment**
$S^\circ_{gas,1 bar}$	198.700 ± 0.004	J/mol*K	Review	Cox, Wagman, et al., 1984	CODATA Review value
$S^\circ_{gas,1 bar}$	198.70	J/mol*K	Review	Chase, 1998	Data last reviewed in September, 1965

Tabulation of Chemical Data II

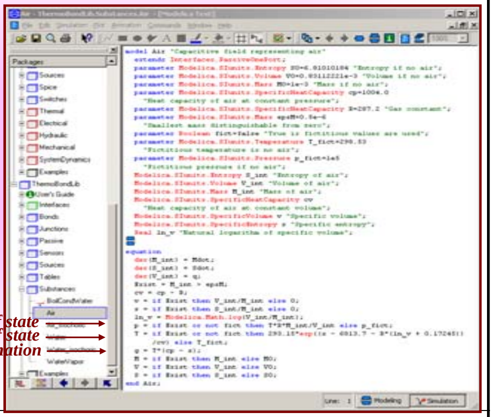
Gas Phase Heat Capacity (Shomate Equation)

$C_p° = A + B{*}t + C{*}t^2 + D{*}t^3 + E/t^2$
$H° - H°_{298.15} = A{*}t + B{*}t^2/2 + C{*}t^3/3 + D{*}t^4/4$ -
$S° = A{*}\ln(t) + B{*}t + C{*}t^2/2 + D{*}t^3/3 - E/(2{*}t^2)$
C_p = heat capacity (J/mol*K)
H° = standard enthalpy (kJ/mol)
$\Delta_f H°_{298.15}$ = enthalpy of formation at 298.15 K
S° = standard entropy (J/mol*K)
t = temperature (K) / 1000.

Temperature (K)	298. - 1100.	1100. - 6000.
A	31.71409	32.88913
B	-13.69992	2.822116
C	23.35567	-0.478035
D	-9.008529	0.032464
E	-0.028758	-3.174958
F	-45.57464	-52.46318
G	240.0428	230.8597
$\Delta H°_{f,298}$ (kJ/mol)	-36.44306	-36.44306
Reference	Chase, 1998	Chase, 1998
Comment	Data last reviewed in September, 1965	Data last reviewed in September, 1965

The Heat Capacity of Air I

We are now able to understand the ***CFAir*** model:

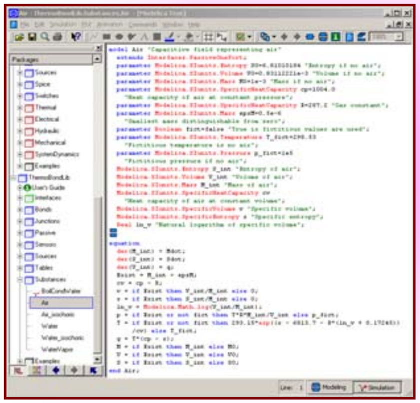


```
model Air "Capacitive field representing air"
  extends Interfaces.PassiveOnePort;
  parameter Modelica.SIunits.Entropy S0=6.81010184 "Entropy if no air";
  parameter Modelica.SIunits.Volume V0=0.831122221e-3 "Volume if no air";
  parameter Modelica.SIunits.Mass M0=1e-3 "Mass if no air";
  parameter Modelica.SIunits.SpecificHeatCapacity cp=1006.0
    "Heat capacity of air at constant pressure";
  parameter Modelica.SIunits.SpecificHeatCapacity R=287.2 "Gas constant";
  parameter Modelica.SIunits.Mass epsM=0.5e-6
    "Smallest mass distinguishable from zero";
  parameter Boolean fict=false "True if fictitious values are used";
  parameter Modelica.SIunits.Temperature T_fict=298.15
    "Fictitious temperature if no air";
  parameter Modelica.SIunits.Pressure p_fict=1e5
    "Fictitious pressure if no air";
  Modelica.SIunits.Entropy S_int "Entropy of air";
  Modelica.SIunits.Volume V_int "Volume of air";
  Modelica.SIunits.Mass M_int "Mass of air";
  Modelica.SIunits.SpecificHeatCapacity cv
    "Heat capacity of air at constant volume";
  Modelica.SIunits.SpecificVolume v "Specific volume";
  Modelica.SIunits.SpecificEntropy s "Specific entropy";
  Real ln_v "Natural logarithm of specific volume";

equation
  der(M_int) = Mdot;
  der(S_int) = Sdot;
  der(V_int) = q;
  Exist = M_int > epsM;
  cv = cp - R;
  v = if Exist then V_int/M_int else 0;
  s = if Exist then S_int/M_int else 0;
  ln_v = Modelica.Math.log(V_int/M_int);
  p = if Exist or not fict then T*R*M_int/V_int else p_fict;
  T = if Exist or not fict then 298.15*exp((s - 6813.7 - R*(ln_v + 0.17245))
    /cv) else T_fict;
  g = T*(cp - s);
  M = if Exist then M_int else M0;
  V = if Exist then V_int else V0;
  S = if Exist then S_int else S0;
end Air;
```

Equation of state
Caloric equation of state
Gibbs energy of formation

The Heat Capacity of Air II



$$\boxed{p = T \cdot R \cdot M/V} \Rightarrow \boxed{p \cdot V = T \cdot R \cdot M}$$

$$\boxed{T = T_0 \cdot \exp((s - s_0 - R \cdot (\ln(v) - \ln(v_0)))/c_v)}$$

$$\Downarrow$$

$$\boxed{T/T_0 = \exp((s - s_0 - R \cdot (\ln(v/v_0)))/c_v)}$$

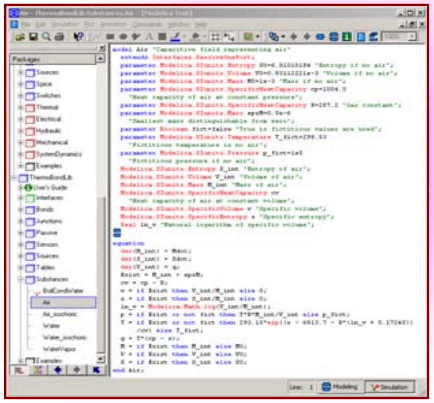
$$\Downarrow$$

$$\boxed{\ln(T/T_0) = (s - s_0 - R \cdot \ln(v/v_0))/c_v}$$

$$\Downarrow$$

$$\boxed{c_v \cdot \ln(T/T_0) = s - s_0 - R \cdot \ln(v/v_0)}$$

The Heat Capacity of Air III



$$\boxed{g = T \cdot (c_p - s)}$$

$$\boxed{h = c_p \cdot T} \Rightarrow \boxed{g = h - T \cdot s}$$

for ideal gases

References

- Cellier, F.E. (1991), *Continuous System Modeling*, Springer-Verlag, New York, Chapter 9.
- Greifeneder, J. (2001), *Modellierung thermodynamischer Phänomene mittels Bondgraphen*, Diplomarbeit, University of Stuttgart, Germany.
- 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.