Constitutive Equations in Energy Systems Models

Flow sheet

Flow Thermodynamic State
T, P, X

Reformer
Water Fuel
Air

Anode
Cathode

Burner
O₂

CO₂

H₂O

Gas Turbine

CO₂ separation

Compression power savings

Process unit:
Size
Support (e.g., catalyst)
Conversion of mass and energy
A process unit model

State variables inlet
\[ \dot{N}, T, P, \tilde{c}_i \]

Simulation Equation
\[ f_m(\dot{N}_n, T_n, P_n, \tilde{c}_n, \pi_p) = 0 \]

State variable outlet
\[ \dot{N}, T, P, \tilde{c}_i \]

Constitutive Equations

• How to characterize the flow between two unit operations?
  - Transfer of mass

• How to calculate the thermodynamic state of a stream?

• How to know what is the temperature, the pressure, the enthalpy, the speed, the volume, the state (liquid or vapor), the viscosity of a fluid with a single component (like water)

• How to define the properties of a mixture of fluid

• How to calculate the thermodynamic transformations in the process units
State variables of a stream: Gibbs Phase rule

- For a stream with N compounds: degrees of freedom
  - only N+2 variables are required to characterise the state. (Gibbs phase rule, Degree of freedom of a flow)
  - in which at least one will characterise a flow
    - i.e. 1 extensive variable

- Examples:
  \[ T, P, m_i \]
  \[ P, h, m, c_i \quad \text{for} \quad i = 1, \ldots, N - 1 \]
  \[ P, V, m_i \quad \text{for} \quad i = 1, \ldots, N \]

Thermodynamic properties (other state variables)

- Other State variables
  - Density, Specific volume (v)
  - Enthalpy (h), entropy (s), Specific Heat (s)
  - Viscosity, thermal conductivity, diffusion coefficient, surface tension

- Phase equilibrium (L-V, L-L, L-L-V)
  - Saturation point, dew point
  - Heat of vaporisation
  - Saturating pressure
  - Phase distribution coefficient

- Chemical reactions
  - Heat of reaction
  - Equilibrium constants

- To be calculated by the constitutive equations from the N+2 state variables
Constitutive equations

- To represent properties and interactions forces between the molecules
  - Thermodynamic properties are related with the energy storage mode in the molecules.
    - Nuclear forces
    - Links between atoms:
      - Reaction heat
      - Heat of formation
      - Equilibrium
    - Interactions between molecules
- **Energy of the molecules**
  - Translation: perfect gases
  - Rotation, vibration
    - Contributions to $C_p$, $H$, $S$
- **Interactions between molecules**
  - Attraction, repulsion
    - Equations of State
    - Corrections wrt perfect gases
    - Phase changes
    - Transport phenomena

- **Estimating thermodynamic properties of a pure component**

  - **Correlations between properties**
    - Thermodynamic Theory
      - Example: Clapeyron
        \[
        \frac{dP_{vp}}{dT} = \frac{\Delta H_v}{T \Delta V_v} = \frac{\Delta H_v}{\left( RT^2 / P_{vp} \right) \Delta Z_v} \
        \frac{d \ln P_{vp}}{d(1/T)} = -\frac{\Delta H_v}{R \Delta Z_v} \
        \]
    - Polynomial correlation (experimental):
      \[
      c_{pi}(T) = a_i + b_i \cdot T + c_i \cdot T^2 + d_i \cdot T^3 + \frac{e_i}{T} \\
      T_{min_i} \leq T \leq T_{max_i} 
      \]
    - Molecular structure analysis
      - Substance sub-sets
      - Group contribution
Constitutive equations: Empirical

- Represent properties and interactions forces between the molecules
  - For specific substances
    - i.e. see NIST web book, refprop
    - http://webbook.nist.gov/chemistry/
  - May be really detailed, according to the amount of experiments available
    - Applied from pure components
  - Difficult to implement in a systematic manner in a software (not generic)
- Example: Refprop software

Systematic implementation in software

- Model: Generic formulation
  - Independent of the components
  - Mixtures of components
  - Based on thermodynamic theory
- Model parameters
  - Compounds data base
  - To be estimated if missing
- Allows to calculate
  - Thermo-properties
  - Fluid phase changes
Systematic implementation: Enthalpy calculations

Gas ideal

\[ H_{id}^g(T,P,x_i) = \sum_i x_i \Delta H_{f}^{0} + \int_{T_{ref}}^{T} \left( \sum_i x_i \cdot C_{p_i}(T) \right) dT \]

\[ C_{p_i}(T) = a_i + b_i \cdot T + c_i \cdot T^2 + d_i \cdot T^3 \]

Liquid ideal

\[ H_{id}^l(T,P,x_i) = \sum_i x_i \Delta H_{f}^{0} + \int_{T_{ref}}^{T} \left( \sum_i x_i \cdot C_{p_i}(T) \right) dT - \sum_i x_i \cdot \Delta H_{vap_i}(T) \]

\[ \Delta H_{vap_i}(T) = \Delta H_{vap_i}(T_{i}^{b}) \cdot \left( \frac{T_{i}^{crit} - T}{T_{i}^{crit} - T_{i}^{b}} \right)^{0.38} \]

Mixture liquid - vapor

\[ H_{id}^{l-v}(T,P,x_i) = \alpha \cdot H_{id}^g(T,P,x_i) + (1 - \alpha) \cdot H_{id}^l(T,P,x_i) \]

T0: reference temperature

Perfect gas: 25°C 1 atm

Systematic implementation: Entropy calculation

- For a gas state

\[ ds = cp \frac{dT}{T} - \left( \frac{\delta v}{\delta T} \right)_P dP \]

\[ s_i = s_{i}^{0f} + \int_{T_0}^{T} \frac{C_{p_i}(T)}{T} dT - R \ln \frac{P_i}{P_0} \]

- This shows that the properties can be deduced if we know
  - the correlation equations
  - the data characterising the components
  - the fundamental rules of thermodynamics.
Equation of state: explanation

- Interactions between molecules:
  - Attraction: lowers the pressure for the same volume
  - Repulsion: minimum volume, quasi incompressible
- Perfect gases

\[ PV = nRT \Rightarrow PV - nRT = 0 \]

- Example: van der Waals equation

\[
P = \frac{RT}{V - b} - \frac{a}{V^2}
\]

Repulsion  Attraction

Equation of state: derived from van der Waals eq.

Redlich-Kwong

\[
P = \frac{RT}{V - b} - \frac{a}{\sqrt{TV}(V + b)}
\]

Soave

\[
P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)}
\]

Peng-Robinson

\[
P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)}
\]
Parameters calibration: Values of $a(T)$ and $b$:

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)}$$

- At the critical point
  $$\left(\frac{\partial P}{\partial V}\right)_{T=T_c} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T=T_c} = 0$$

- 2 equations to calculate $a$ and $b$ at $T=T_c$
- $a$ and/or $b$ may be a function of $T$
- e.g. $b(T)$ calibrated to fit a given property like $P_{vap}$

Soave example cont.

Equations of state detailed example

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)}$$

$$Z = \frac{PV}{RT} \quad A = \frac{aP}{(RT)^2} \quad B = \frac{bP}{RT}$$

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0$$

$$\frac{H - H^0}{RT} = \frac{U - U^0}{RT} + \frac{PV}{RT} = V \left(\frac{\partial U}{\partial V}\right)_T + \frac{PV - RT}{RT}$$

$$\frac{H - H^0}{RT} = \int V \left(\frac{\partial P}{\partial T}\right)_V - P dV$$

$$\frac{H - H^0}{RT} = Z - 1 + \int V \left(\frac{\partial P}{\partial T}\right)_V - P dV$$

Thermodynamics
Extending the equations to mixture

Mixing rules

\[
\begin{align*}
a &= \sum_{i}^{N} x_i \sum_{j}^{N} x_j a_{i,j} \\
b &= \sum_{i}^{N} x_i b_i
\end{align*}
\]

Combinaison rules

\[
a_{i,j} = \sqrt{a_i a_j (1 - \delta_{i,j})}
\]

\(\delta\) parameters are calibrated to fit measurements using parameter identification techniques

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Liquid-Vapor Equilibrium

\[
K_i = \frac{c_i^V}{c_i^L} = \frac{y_i}{x_i}
\]

<table>
<thead>
<tr>
<th>Comportement phase vapeur</th>
<th>Mélange ideal</th>
<th>Gaz parfait</th>
<th>(q_i^* = q_i^s = 1)</th>
<th>Gaz réel</th>
<th>(f_i^L = x_i \cdot f_i^L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mélange</td>
<td>Gaz parfait</td>
<td>(K_i = \frac{P_i}{P})</td>
<td>K = (K^f = f(P,T))</td>
<td>K = (f_i^s \cdot \gamma_i)</td>
</tr>
<tr>
<td></td>
<td>non idéal</td>
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<td>Gaz réel</td>
<td>(f_i^L = \frac{x_i \cdot f_i^L}{\gamma_i \cdot P})</td>
<td>K = (f_i^s \cdot \gamma_i)</td>
<td>K = (f_i^s \cdot \gamma_i)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mélange non idéal</td>
<td>Impossible</td>
<td>K = (f_i^s \cdot \gamma_i)</td>
<td>K = (f_i^s \cdot \gamma_i)</td>
</tr>
</tbody>
</table>
Soave example cont.

\[ Z = \frac{PV}{RT} \quad A = \frac{aP}{(RT)^2} \quad B = \frac{bP}{RT} \]

\[ P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)} \]

\[ Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \]

\[ RTd(\ln \phi) = VdP = d(PV) - PdV \]

\[ \Rightarrow \ln \phi = \int \frac{d(PV) - PdV}{RT} = \frac{PV}{RT} - \int \frac{1}{V - b}dV + \int \frac{a(T)}{RT \cdot V(V + b)}dV \]

\[ \ln \phi = Z - 1 - \ln Z - \int_{\infty}^{V} \frac{Z - 1}{V} \]

\[ = Z - 1 - \ln(Z - B) - \frac{A}{B} \ln \frac{Z + B}{Z} \]

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**Evaluation of \( K_i = f(T, P, x, y) \)**

- **Liquid**
  - Compute \( a = a(T, x_i) \) and \( b = b(x_i) \)
  - Compute \( A \) and \( B \)
  - Compute \( Z \) in liquid phase
  - Compute \( \phi_{iL} \)

- **Gas phase**
  - Compute \( a = a(T, y_i) \) and \( b = b(y_i) \)
  - Compute \( A \) and \( B \)
  - Compute \( Z \) gas phase
  - Compute \( \phi_{iV} \)

- \( \Rightarrow K_i = \phi_{iL}/\phi_{iV} \)
**Chemical reactions**

\[ \xi_a A + \xi_b B \rightleftharpoons \xi_c C + \xi_d D \]

- **Equilibrium : Min Gibbs free energy**

\[
g - g_{ref} = RT \ln(\phi) = [PV]_{P0->0}^P \int V_{P0->0} PdV - \int P_{V0->\infty} dP - \int \frac{RT}{P} dP
\]

**Properties of pure components**

- Where to find the properties of the pure components
  - Literature : dedicated papers
  - Compilations : Tables & Graphs
    - e.g. ASHRAE (http://www.ashrae.org)
  - Thermodynamic Data bases
    - e.g. DIPPR (www.aiche.org/dippr)
  - Estimation methods is required because
    - Millions of substances…
    - mixtures …
    - extrapolate properties using models
    - to predict missing information
**Single component values**

- Minimum information needed (values used in empirical correlations)
  - Critical properties
    - $T_c, P_c, V_c$
  - Acentric Factor $\omega$
  - Boiling temperature $T_{eb}$
  - Fusion temperature $T_{fus}$

\[
\omega_i = \log_{10}\left(\frac{P_{sat}(T = 0.7 \cdot T_{ci})}{P_{ci}}\right) - 1
\]

**Corresponding states**

- Reduced coordinates
  - $Tr = T/T_c$ \quad $Pr = P/P_c$ \quad $vr = v/v_c$

- in reduced coordinates phase diagrams coincide for simple compounds: $Ar, CH4, N2, O2$

- For non polar substances or non spherical substances a 3rd parameter is needed.
**Example: corresponding states**

Properties of CH₄, C₂H₆, C₃H₈ and C₄H₁₀ are identical in reduced coordinates

\[ T_r = \frac{T}{T_c}, \quad P_r = \frac{P}{P_c}, \quad \nu_r = \frac{\nu}{\nu_c} \]

**Corresponding states**

- Two detailed equations for two compounds
  - acentric factor of 1 (\(\omega_1\)) near 0 (e.g. argon)
  - acentric factor of 2 (\(\omega_2\)) near 1 (e.g. n-butane)
- The estimation of a given thermodynamic property \(F(T,P)\) for a compound with known \(\omega, T_c\) and \(P_c\) is calculated by:
  - \(T_r = \frac{T}{T_c}\) et \(P_r = \frac{P}{P_c}\)
- \(F\) is computed by corresponding state:
  - \(F = F_1 + (\omega - \omega_1)/(\omega_2 - \omega_1)(F_2 - F_1)\)
    - \(F_1 = F(T_r, P_r)\) for reference compound 1
    - \(F_2 = F(T_r, P_r)\) for reference compound 2

**Fig. 3.3** Facteur de compressibilité du méthane (Δ), de l'éthane (+), du propane (○) et du n-buane (●); représentation en coordonnées réduites.
Equations of state detailed example

**Equation of Soave : estimating properties**

\[
P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b)}
\]

\[a_c = 0.42748 \frac{(RT_c)^2}{P_c}\]

\[a = a_c \left[1 + (0.48 + 1.574\omega - 0.176\omega^2)(1 - \sqrt{T_r})\right]^2\]

\[b = 0.08664 \frac{RT_c}{P_c}\]

\[T_c, P_c, \omega\] are characteristics of the molecules

**Extending the equations to mixture**

Mixing rules

\[a = \sum_{i}^{N} x_i \sum_{j}^{N} x_j a_{i,j}\]

\[b = \sum_{i}^{N} x_i b_i\]

Combinaison rules

\[a_{i,j} = \sqrt{a_i a_j (1 - \delta_{i,j})}\]

\[\delta\] parameters are calibrated to fit measurements using parameter identification techniques
Constitutive equations

- **Equations of state**
  - computes thermodynamic properties
  - same properties from same data (e.g. P, T, x)
  - thermodynamic equations to link properties from basic properties evaluated by equation of states

- **Parameters of the equations**
  - Data bases (measures + calibration)
  - Corresponding states (estimates by interpolation)
  - Group contribution (based on the chem. formula)

- **Mixing rules to represent behaviour of mixtures**

Constitutive equation

- The choice of the dependent state variable is important

\[ h = f(T, P, x_i) \]
\[ s = f(h, P, x_i) \]