Thermodynamics-Package

for

CAPE-Applications

Project of the IK-CAPE

Model Description

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1 <u>Introduction</u>

Inside of this handbook all models included inside the IK-CAPE Thermodynamics Package are documented.

Common abbreviations:

R	gas constant in J/kmol/K
T	temperature in Kelvin
P	pressure in Pascal
T_c	critical temperature in Kelvin
P_c	critical pressure in Pascal
v	volume in m³/kmol
x_i	mol fraction in liquid phase
y_i	mol fraction in vapor phase
γ_i	activity coefficients
φ_i	fugacity coefficients

2 Description of the temperature dependency for pure component property data

2.1 Equations

To describe the temperature dependency of any pure component property at current stage the following functions can be used:

- **POLY : Polynom**

$$f(T) = a_0 + a_1 T + a_2 T^2 + \ldots\ldots\ldots + a_9 T^9$$

- **EPOL : Polynom in exponent**

$$f(T) = 10^{a_0 + a_1 T + a_2 T^2 + \ldots + a_9 T^9}$$

- **WATS : extended Watson equation**

$$f(T) = a_0 (a_2 - T)^{a_1} + a_3$$

- **ANTO : Antoine equation**

$$\ln(f(T)) = a_0 - \frac{a_1}{T + a_2}$$

- **ANT1 : extended Antoine equation**

$$\ln f(T) = a_0 + \frac{a_1}{T + a_2} + a_3 T + a_4 \ln T + a_5 T^{a_6}$$

- **KIRC : Kirchhoff equation**

$$\ln(f(T)) = a_0 - \frac{a_1}{T} + a_2 * \ln T$$

- **SUTH : Sutherland equation**

$$f(T) = \frac{a_0 \sqrt{T}}{1 + \dfrac{a_1}{T}}$$

- **WAGN : Wagner equation**

$$\ln f(T) = \ln a_1 + \frac{1}{T_r} * (a_2 \tau + a_3 \tau^{1.5} + a_4 \tau^3 + a_5 \tau^6)$$

$$T_r = \frac{T}{a_0}$$

$$\tau = 1 - T_r$$

$$a_0 = T_c$$

$$a_1 = P_c$$

- **CPL : Equation for the specific heat capacity of liquids**

$$f(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + \frac{a_4}{T^2}$$

- **ICPL : Equation for the specific heat capacity of liquids**

$$f(T) = a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4 + \frac{a_5}{T}$$

- **VISC : Equation for the dynamic viscosity**

$$f(T) = a_0 e^{\frac{a_1}{T}} + a_2$$

- **RACK : Rackett equation**

$$f(T) = \frac{a_0}{a_1^{1 + (1 - \frac{T}{a_2})^{a3}}}$$

- **KIR1 : extended Kirchhoff equation**

$$\ln(f(T)) = a_0 + \frac{a_1}{T} + a_2 \ln T + a_3 T^{a_4}$$

- **ALYL : Aly-Lee equation**

$$f(T) = a_0 + a_1 \left(\frac{\dfrac{a_2}{T}}{\sinh \dfrac{a_2}{T}} \right)^2 + a_3 \left(\frac{\dfrac{a_4}{T}}{\cosh \dfrac{a_4}{T}} \right)^2$$

- **DIP4 : DIPPR function for HVAP and ST**

$$f(T) = a_1 (1 - T_r)^h$$
with
$$h = a_2 + a_3 T_r + a_4 T_r^2 + a_5 T_r^3$$
$$T_r = \frac{T}{a_0}$$
$$a_0 = T_c$$

- **DIP5 : DIPPR function for KVAP and VISV**

$$f(T) = \frac{a_0 T^{a_1}}{1 + \dfrac{a_2}{T} + \dfrac{a_3}{T^2}}$$

2.2 Extrapolations

To avoid nonsensical results as well as program crashes, one can use the possibility to extrapolate the above given functions beyond the proofed temperature range using one of the given extrapolation methods.

- Linear extrapolation

  For linear extrapolation inside the f(T)-diagram applies for the case $T > T_{upper}$ and $f'(T_{upper}) > 0$

  $$f(T) = f'(T_{upper}) * (T - T_{upper}) + f(T_{upper})$$
  $$f'(T) = f'(T_{upper})$$

and for the case $T < T_{lower}$ and $f\,'(T_{lower}) < 0$

$$f(T) = f\,'(T_{lower}) * (T - T_{lower}) + f(T_{lower})$$
$$f\,'(T) = f\,'(T_{lower})$$

- Extrapolation to the value B

  For $T > T_{upper}$ and $f\,'(T_{upper}) < 0$ applies with $0 \le B < f(T_{upper})$

  $$f(T) = \left[f(T_{upper}) - B\right]\exp\left[\frac{f\,'(T_{upper})}{f(T_{upper}) - B}(T - T_{upper})\right] + B$$

  $$f\,'(T) = f\,'(T_{upper})\exp\left[\frac{f\,'(T_{upper})}{f(T_{upper}) - B}(T - T_{upper})\right]$$

  For $T < T_{lower}$ and $f\,'(T_{lower}) > 0$ gilt mit $0 \le B < f(T_{lower})$

  $$f(T) = \left[f(T_{lower}) - B\right]\exp\left[\frac{f\,'(T_{lower})}{f(T_{lower}) - B}(T - T_{lower})\right] + B$$

  $$f\,'(T) = f\,'(T_{lower})\exp\left[\frac{f\,'(T_{lower})}{f(T_{lower}) - B}(T - T_{lower})\right]$$

- linear extrapolation inside a logarithmic diagram

  $$\ln f(T) = \left[\frac{d\ln f(T)}{dT}\right]_{T=T_{upper}}(T - T_{upper}) + \ln f(T_{upper})$$

  For $T > T_{upper}$ and $f\,'(T_{upper}) < 0$ applies expressed in f(T)

  $$f(T) = \exp\left[\frac{f\,'(T_{upper})}{f(T_{upper})}\left(T - T_{upper}\right) + \ln f(T_{upper})\right]$$

  $$f\,'(T) = f(T)\frac{f\,'(T_{upper})}{f(T_{upper})}$$

- Extrapolation of the Wagner equation for vapor pressure

$$a_0 = T_c$$
$$a_1 = P_c$$

Above the critical point the Wagner equation is extrapolated linear inside the ln(p) vs. 1/T diagram

$$f(T) = a_1 e^{a_2 a_0 \left(\frac{1}{T} - \frac{1}{a_0} \right)}$$

$$f'(T) = -\frac{a_2 a_0}{T^2} f(T)$$

at $T > T_c$ the vapor pressure represents a virtual value.

$$a_0 = T_c$$
$$a_1 = P_c$$

3 Calculation of averages

- **MOLA: average based on mole fractions**

$$average = \sum_i x_i \cdot value_i$$

- **MASS: average based on mass fractions**

$$average = \frac{\sum_i x_{mass,i} * value_i}{\sum_i x_{mass,i}}$$

- **MOLG: logarithmic average based on mole fractions**

$$\ln(average) = \sum_i x_i * \ln(value_i)$$

- **MALG: logarithmic average based on mass fractions**

$$\ln(average) = \frac{\sum_i x_{mass,i} \cdot \ln(value_i)}{\sum_i x_{mass,i}}$$

- **LAMB: average for the heat conductivity of gaseous mixtures**

$$\lambda_m = 0.5 * \left(\sum x_i * \lambda_i + \frac{1}{\sum \frac{x_i}{\lambda_i}} \right)$$

- **VISC: average for the viscosity of gaseous mixtures**

$$\eta_m = \frac{\sum_i x_i * \sqrt{M_i} * \eta_i}{\sum_i x_i * \sqrt{M_i}}$$

- **VOLU: average for density based on volume**

$$\rho_m = \frac{1}{\sum_i \frac{x_i}{\rho i}}$$

- **WILK: average from Wilke for viscosity of gaseous mixtures**

$$average = \sum_i \frac{y_i value_i}{\sum_j y_j F_{i,j}}$$

$$F_{i,j} = \frac{\left[1 + \sqrt{\frac{value_i}{value_j}} \sqrt[4]{\frac{Mol_j}{Mol_i}}\right]^2}{\sqrt{8\left(1 + \frac{Mol_i}{Mol_j}\right)}}$$

- **WAMA: average from Wassiljewa,Mason,Saxena für die heat conductivity of gaseous mixtures**

$$average = \sum_i \frac{y_i value_i}{\sum_j y_j F_{i,j}}$$

$$F_{i,j} = \frac{\left[1 + \sqrt{\frac{\eta_i}{\eta_j}} \sqrt[4]{\frac{Mol_j}{Mol_i}}\right]^2}{\sqrt{8\left(1 + \frac{Mol_i}{Mol_j}\right)}}$$

$\eta = gas\ vis\cos ity$

- **DIST: average for the surface tension based on DIPPR**

$$average = \left[\frac{\sum_i x_i Vol_i \sqrt[4]{value_i}}{\sum_i x_i Vol_i}\right]^4$$

- **DIKL: average for the heat conductivity of liquids based on DIPPR**

$$average = \sum_i \sum_j \frac{2 xv_i\, xv_j}{\dfrac{1}{value_i} + \dfrac{1}{value_j}}$$

$$xv_i = \frac{x_i Vol_i}{\sum_j x_j Vol_j}$$

4 Activity coefficients

4.1 NRTL model

$$\ln \gamma_i = \frac{\sum_j \tau_{j,i} G_{j,i} x_j}{\sum_k G_{k,i} x_k} + \sum_j \frac{x_j G_{i,j}}{\sum_k G_{k,j} x_k} \left(\tau_{i,j} - \frac{\sum_l \tau_{l,j} G_{l,j} x_l}{\sum_k G_{k,j} x_k} \right)$$

$$G_{j,i} = e^{-S_{j,i} \tau_{j,i}}$$

$$\tau_{j,i} = a_{j,i} + \frac{b_{j,i}}{T} + e_{j,i} \ln T + f_{j,i} T$$

$$S_{j,i} = c_{j,i} + d_{j,i} (T - 273.15)$$

4.2 UNIQUAC model

The volume part is defined by:

$$V_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

The surface part is defined by:

$$F_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad \text{and} \quad F'_i = \frac{q'_i x_i}{\sum_j q'_j x_j}$$

For the activity coefficient applies:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

with

$$\ln \gamma_i^C = \ln \frac{V_i}{x_i} + \frac{KZ}{2} q_i \ln \frac{F_i}{V_i} + l_i - \frac{V_i}{x_i} \sum_j x_j l_j$$

and

$$\ln \gamma_i^R = q'_i \left(1 - \ln \sum_j F'_j \tau_{j,i} - \sum_j \frac{F'_j \tau_{i,j}}{\sum_k F'_k \tau_{k,j}} \right)$$

$$l_i = 5 (r_i - q_i) - (r_i - 1)$$

$$\tau_{j,i} = e^{a_{j,i} + \frac{b_{j,i}}{T} + c_{j,i}\ln T + d_{j,i}T}$$

4.3 Wilson model

$$\ln \gamma_i = 1 - \ln\left(\sum_j x_j \Lambda_{i,j}\right) - \sum_k \frac{x_k \Lambda_{k,i}}{\sum_j x_j \Lambda_{k,j}}$$

$$\Lambda_{i,j} = e^{a_{i,j} + \frac{b_{i,j}}{T} + c_{i,j}\ln T + d_{i,j}T}$$

4.4 Flory-Huggins model

$$\ln \gamma_i = 1 + \ln\frac{1}{\bar{r}} - \frac{1}{\bar{r}} + (1 - \varphi_1)\sum_{2i} \varphi_{2i}\chi_{1,2i}$$

$$\ln \gamma_{2k} = 1 + \ln\frac{r_{2k}}{\bar{r}} - \frac{r_{2k}}{\bar{r}} + \varphi_1 r_{2k}\left(\chi_{1,2k} - \sum_{2i}\varphi_{2i}\chi_{1,2i}\right)$$

with

$$\varphi_1 = \frac{x_1}{\bar{r}}$$

$$\varphi_{2i} = \frac{r_{2i}x_{2i}}{\bar{r}}$$

$$\bar{r} = x_1 + \sum_{2i} x_{2i} r_{2i}$$

$$\chi_{1,2i} = \chi^0_{1,2i} + \chi^1_{1,2i}\frac{1}{T}$$

r_i segment number of component i
φ_i volume fraction of component i
$\chi_{1,2i}$ interaction parameter
        solvent(1)-solved species(2i)

4.5 UNIFAC model

The volume part is defined by:

$$V_i = \frac{r_i}{\sum_j r_j x_j}$$

$$r_i = \sum v_k^{(i)} R_k$$

The surface part is defined by:

$$F_i = \frac{q_i}{\sum_j q_j x_j}$$

$$q_i = \sum v_k^{(i)} Q_k$$

For the activity coefficient applies:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R$$

with the combinatorial part

$$\ln \gamma_i^c = 1 - V_i + \ln V_i - 5q_i \left(1 - \frac{V_i}{F_i} + \ln \frac{V_i}{F_i} \right)$$

and the residual part, that describes the interactions between the different functional groups.

$$\ln \gamma_i^R = \sum v_k^{(i)} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right)$$

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \Theta_m \Psi_{km} \right) - \sum \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right]$$

Herein is Θ_m the area fraction of the functional group m

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}$$

with the mole fraction X_m of the functional group m.

$$X_m = \frac{\sum_j v_m^{(j)} x_j}{\sum_j \sum_n v_n^{(j)} x_j}$$

The parameter Ψ_{ji} contains the group interaction coefficient between the groups j and i:

$$\Psi_{j,i} = e^{-\frac{a_{j,i}}{T}}$$

5 Poynting correction

$$\ln F_{p,i} = \frac{v_i^L \left(P - P_i^s \right)}{RT}$$

6 Henry correction

$$\ln H_i = \frac{\sum_j x_j \ln H_{i,j}}{\sum_j x_j}$$

whereas means:
i   Index of the Henry components
j   Index of the non Henry components

$$\ln H_{i,j} = a + \frac{b}{T} + c \ln T + d\,T$$

7 Equations of state

7.1 Redlich-Kwong-Soave equation

The fugacity coefficients can be calculated using the following equation:

$$\ln \varphi_i = \frac{B_i}{b_m}\left(z_m - 1\right) - \ln z_m + \ln \frac{v_m}{v_m - b_m} - \frac{a_m}{b_m RT}\left(2\frac{as_i}{a_m} - \frac{B_i}{b_m}\right)\ln \frac{v_m + b_m}{v_m}$$

using the following mixture rule:

$$a_m = \sum_i x_i \sum_j x_j a_{i,j}$$

$$as_i = \sum_j x_j a_{i,j}$$

and

$$B_i = 2bs_i - b_m$$

$$b_m = \sum_i x_i \sum_j x_j b_{i,j}$$

$$bs_i = \sum_j x_j b_{i,j}$$

Herein means:

$$a_{i,j} = \sqrt{A_i A_j}\left(1 - k_{i,j}\right)$$

$$b_{i,j} = \frac{b_i + b_j}{2}\left(1 - k_{bi,j}\right)$$

The pure component parameters a, b can be received from:

$$A_i(T) = a_i \alpha_i$$

$$\alpha_i = \left[1 + m_i\left(1 - \sqrt{T_r}\right)\right]^2$$

$$m_i = 0.48 + 1.574\omega_i - 0.176\omega_i^2$$

$$a_i = 0.42748\frac{R^2 T_c^2}{P_c}$$

$$b_i = 0.0867 \frac{RT_c}{P_c}$$

7.2 Peng-Robinson equation

Pressure explicit representation:

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

Normal form of the cubic equation for the volume explicit representation:

$$v^3 + \left(b - \frac{RT}{P}\right)v^2 - \frac{3Pb^2 + 2RTb - a}{P}v + \left(\frac{Pb^3 + RTb^2 - ab}{P}\right) = 0$$

Calculation of compressibility:

$$z_m = \frac{Pv_m}{RT}$$

$$z_m = \frac{v_m}{v_m - b_m} - \frac{a_m v_m}{RT\left[v_m(v_m + b_m) + b_m(v_m - b_m)\right]}$$

using the following mixture rules:

$$a_m = \sum_i \sum_j x_i x_j a_{i,j}$$

$$b_m = \sum_i x_i b_i$$

Herein means:

$$a_{i,j} = \sqrt{A_i(T)A_j(T)}(1 - k_{i,j})$$

The pure component parameters a, b can be received from:

$$A_i(T) = a_i \alpha_i$$

$$\alpha_i = \left[1 + m_i\left(1 - \sqrt{\frac{T}{Tc_i}}\right)\right]^2$$

$$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$$

$$a_i = 0.45724 \frac{R^2 Tc_i^{\,2}}{Pc_i}$$

$$b_i = 0.07780 \frac{RTc_i}{Pc_i}$$

8 Fugacity coefficients

8.1 Redlich-Kwong-Soave equation

$$\varphi_i = \frac{\varphi_i^0}{\varphi_i^v}$$

$$\ln \varphi_i^0 = z_i - 1 - \ln \frac{P_i^s}{RT}\left(v_i - b_i\right) - \frac{A_i(T)}{b_i RT} \ln\left(\frac{v_i + b_i}{v_i}\right)$$

and

$$\ln \varphi_i^v = \frac{B_i}{b_m}\left(z_m - 1\right) - \ln z_m + \ln \frac{v_m}{v_m - b_m} - \frac{a_m}{b_m RT}\left(2\frac{as_i}{a_m} - \frac{B_i}{b_m}\right)\ln \frac{v_m + b_m}{v_m}$$

The mixture rules can be find in the previous chapter „Equations of state".

8.2 Peng-Robinson equation

$$\varphi_i = \frac{\varphi_i^0}{\varphi_i^v}$$

with

$$\ln \varphi_i^0 = z_i - 1 - \ln\left[\frac{P_i^S}{RT}(v_i - b_i)\right] - \frac{A_i(T)}{2\sqrt{2}b_i RT}\ \ln\left[\frac{v_i + \left(1 + \sqrt{2}\right)b_i}{v_i + \left(1 - \sqrt{2}\right)b_i}\right]$$

for a pure component at saturated vapor pressure

and

$$\ln \varphi_i^v = \frac{b_i}{b_m}(z_m - 1) - \ln\left[\frac{P}{RT}(v_m - b_m)\right] - \frac{a_m}{2\sqrt{2}b_m RT}\left(\frac{2}{a_m}\sum_j x_j a_{i,j} - \frac{b_i}{b_m}\right)\ln\left[\frac{v_m + \left(1 + \sqrt{2}\right)b_m}{v_m + \left(1 - \sqrt{2}\right)b_m}\right]$$

for a component inside a mixture

8.3 Virial equation

$$\varphi_i = \frac{\varphi_i^0}{\varphi_i^v}$$

$$\varphi_i^0 = \frac{e^{\frac{2}{v}B_{i,i}}}{1+\frac{B_{i,i}}{v}}$$

$$v = \frac{RT}{2P_i^0}\left(1+\sqrt{1+\frac{4P_i^0 B_{i,i}}{RT}}\right)$$

$$\varphi_i^v = \frac{e^{\frac{2}{v}\sum_j y_j B_{i,j}}}{1+\frac{B_m}{v}}$$

$$v = \frac{RT}{2P}\left(1+\sqrt{1+\frac{4PB_m}{RT}}\right)$$

$$B_m = \sum_i \sum_j y_i y_j B_{i,j}$$

$$z_m = 1 + \frac{B_m}{v}$$

with

$B_{i,i}$ = Pure component virial coefficient
$B_{i,j}$ = Cross virial coefficient

8.4 Association in vapor phase

Prerequisites:

- The vapor phase behaves ideal, temperature, pressure and concentration are given
- up to 5 components can build Di-, Tetra- and Hexamers as well as mixed dimers among each other
- any desired number of inerts is allowed

Notation:

"true" concentration

z_{in}
i,j ... components
n   association degree   n=1,2,4,6 for i ≤ 5
$z_{i2} = z_{i4} = z_{i6} = 0$ for i > 5
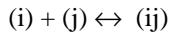
Mixed dimers z_{Mij} i,j ≤ 5

Equilibrium constants:

For each association reaction   n · (i) ↔ (i)$_n$

$$(i) + (j) \leftrightarrow (ij)$$

equilibrium constants

$$K_{in} = \frac{z_{in}}{z_{i1}^n p^{n-1}}$$

$$K_{Mij} = \frac{z_{Mij}}{z_{i1} z_{j1} p}$$

are generated. For each applies:

$$\ln K_{in} = A_{in} + \frac{B_{in}}{T}$$

$$K_{Mij} = 2\sqrt{K_{i2} K_{j2}}$$

Set of equations to calculate the true monomer concentrations:

Material balance:

$$\sum_i \sum_n K_{in} z_{i1}^n p^{n-1} = 1$$

Material rate for each component i:

$$\frac{\sum_n n K_{in} z_{i1}^n p^{n-1} + \sum_{j \neq i, j \leq 5} K_{Mij} z_{i1} z_{j1} p}{\sum_n n K_{1n} z_{11}^n p^{n-1} + \sum_{j \neq i, j \leq 5} K_{M1j} z_{11} z_{j1} p} = \frac{y_i}{y_1}$$

$\rightarrow$ Set of equations for the variable z_{in} to be solved iterative. Afterwards all z_{in} and z_{Mij} can be calculated.

The fugacity coefficients can be calculated afterwards as follows:

$$\varphi_i = \frac{z_{i1}}{y_i}$$

9 Enthalpy

The following abbreviations are used:

h_i^o Reference enthalpy of the pure component
h_i^l Enthalpy of the liquid, component i
h_i^v Enthalpy of the vapor, component i
r_i Enthalpy of vaporization, component i
cp_i specific heat capacity of the ideal gas, component i

$$\Delta h \qquad \int\limits_0^{p^s(T)} \left(\frac{\partial h^v}{\partial p} \right) dp$$

9.1 Enthalpy of liquid with starting phase in liquid

The enthalpy of the liquid follows from:

$$h_l = h^E + \sum_i x_i h_i^l$$

with

$$h_i^l = h_i^0 + \int\limits_{T_{0,i}}^T cl_i dT$$

9.2 Enthalpy of the liquid with starting phase in vapor

The enthalpy of the liquid follows from:

$$h_l = h^E + \sum_i x_i h_i^l$$

If the temperature for the phase change is set equal to the systems temperature, the enthalpy of the pure component can be calculated using:

$$h_i^l = h_i^0 + \int\limits_{T_{0,i}}^T cp_i dT - \int\limits_{p_i^s(T)}^0 \left(\frac{\partial h_i^v}{\partial p} \right) dp - r_i(T)$$

If the temperature for the phase change is predetermined, the enthalpy of the pure component has to be calculated using:

$$h_i^l = h_i^0 + \int\limits_{T_{0,i}}^{T_{ui}} cp_i dT - \int\limits_{p_i^s(T_{ui})}^0 \left(\frac{\partial h_i^v}{\partial p} \right) dp - r_i(T_{ui}) + \int\limits_{T_{ui}}^T cl_i dT$$

9.3 Enthalpy of a gas with starting phase in liquid

The enthalpy of the gas follows from:

$$h_v = \int_0^P \left(\frac{\partial h_v}{\partial p} \right) dp + \sum_i y_i h_i^v$$

If the temperature for the phase change is set equal to the systems temperature, the enthalpy of the pure component can be calculated using:

$$h_i^v = h_i^0 + \int_{T_{0,i}}^T cl_i dT + r_i(T) + \int_{p_i^s(T)}^0 \left(\frac{\partial h_i^v}{\partial p} \right) dp$$

If the temperature for the phase change is predetermined, the enthalpy of the pure component has to be calculated using:

$$h_i^v = h_i^0 + \int_{T_{0,i}}^{T_{ui}} cl_i dT + r_i(T_{ui}) + \int_{p_i^s(T_{ui})}^0 \left(\frac{\partial h_i^v}{\partial p} \right) dp + \int_{T_{ui}}^T cp_i dT$$

9.4 Enthalpy of a gas with starting phase in vapor

The enthalpy of the gas follows from:

$$h_v = \int_0^P \left(\frac{\partial h_v}{\partial p} \right) dp + \sum_i y_i h_i^v$$

with

$$h_i^v = h_i^0 + \int_{T_{0,i}}^T cp_i dT$$

9.5 Enthalpy of a solid component

The enthalpy of a solid component follows from:

$$h_s = \sum_i s_i h_i^s$$

with

$$h_i^s = h_i^0 + \int_{T_{0,i}}^T cs_i dT$$

9.6 The excess enthalpy

$$h^E = -T^2 \frac{\partial \frac{g^E}{T}}{\partial T} = -RT^2 \sum_i x_i \left(\frac{\partial \ln \gamma_i}{\partial T} \right) = -RT^2 \sum_i x_i \frac{1}{\gamma_i} \frac{\partial \gamma_i}{\partial T}$$

The excess enthalpy can be calculated using different methods.

9.6.1 NRTL equation

$$\frac{g^E}{RT} = \sum_i x_i \frac{\sum_j x_j G_{j,i} \tau_{j,i}}{\sum_j x_j G_{j,i}}$$

$$h^E = -T^2 R \sum_i x_i \frac{A_i' B_i - B_i' A_i}{B_i^2}$$

with

$$A_i = \sum_j x_j G_{j,i} \tau_{j,i}$$

$$\frac{\partial A_i}{\partial T} = A_i' = \sum_j x_j \left(G'_{j,i} \tau_{j,i} + G_{j,i} \tau'_{j,i} \right)$$

$$B_i = \sum_j G_{j,i} x_j$$

$$\frac{\partial B_i}{\partial T} = B_i' = \sum_j x_j G'_{j,i}$$

$$G_{j,i} = e^{-S_{j,i} \tau_{j,i}}$$

$$S_{j,i} = c_{j,i} + d_{j,i} (T - 273.15)$$

$$\tau_{j,i} = a_{j,i} + \frac{b_{j,i}}{T} + e_{j,i} \ln T + f_{j,i} T$$

$$\frac{\partial G_{j,i}}{\partial T} = G'_{j,i} = -G_{j,i} \left(\frac{\partial S_{j,i}}{\partial T} \tau_{j,i} + \frac{\partial \tau_{j,i}}{\partial T} S_{j,i} \right)$$

$$\frac{\partial \tau_{j,i}}{\partial T} = \tau'_{j,i} = -\frac{b_{j,i}}{T^2} + \frac{e_{j,i}}{T} + f_{j,i}$$

$$\frac{\partial S_{j,i}}{\partial T} = d_{j,i}$$

9.6.2 UNIQUAC equation

$$\frac{g^E}{RT} = \sum_i x_i \ln V_i + 5\sum_i q_i x_i \ln \frac{F_i}{V_i} - \sum_i q'_i x_i \ln \sum_j x_j F'_j \tau_{j,i}$$

$$h^E = RT^2 \sum_i q'_i x_i \left[\frac{A'_i}{A_i} + \sum_j F'_j \frac{\frac{\partial \tau_{i,j}}{\partial T} A_j - \tau_{i,j} A'_j}{A_j^2} \right]$$

with

$$A_i = \sum_j F'_j \tau_{j,i}$$

$$A'_i = \sum_j F'_j \frac{\partial \tau_{j,i}}{\partial T}$$

$$F'_i = \frac{q'_i x_i}{\sum_j q'_j x_j}$$

and

$$\tau_{j,i} = e^{a_{j,i} + \frac{b_{j,i}}{T} + c_{j,i} \ln T + d_{j,i} T}$$

9.6.3 Wilson equation

$$\frac{g^E}{T} = -R \sum_i x_i \ln \sum_j x_j \Lambda_{i,j}$$

$$h^E = RT^2 \sum_i x_i \left(\frac{\eta'_i}{\eta_i} + \sum_j x_j \frac{\Lambda'_{j,i} \eta_j - \Lambda_{j,i} \eta'_j}{\eta_j^2} \right)$$

$$\frac{\partial \eta_i}{\partial T} = \eta'_i = \sum_j x_j \Lambda'_{i,j}$$

$$\eta_i = \sum_j x_j \Lambda_{i,j}$$

$$\frac{\partial \Lambda_{i,j}}{\partial T} = \Lambda'_{i,j} = \Lambda_{i,j} \left(-\frac{b_{i,j}}{T^2} + \frac{c_{i,j}}{T} + d_{i,j} \right)$$

$$\Lambda_{i,j} = e^{a_{i,j} + \frac{b_{i,j}}{T} + c_{i,j} \ln T + d_{i,j} T}$$

9.6.4 Flory-Huggins equation

$$\frac{g^E}{RT} = x_1 \ln\frac{\varphi_1}{x_1} + \sum_{2i} x_{2i} \ln\frac{\varphi_{2i}}{x_{2i}} + x_1 \sum_{2i} \varphi_{2i}\chi_{1,2i}$$

$$h^E = RTx_1 \sum_{2i} \varphi_{2i}\chi_{1,2i}$$

9.6.5 Redlich-Kister equation

$$h^E = 0.5\sum_{i}\sum_{j} h^E_{i,j}$$

$$h^E_{i,j} = \frac{x_i x_j}{x_i + x_j}\left(A(T) + B(T)x_d + C(T)x_d^2 + D(T)x_d^3 + E(T)x_d^4 + F(T)x_d^5\right)$$

$$x_d = x_i - x_j$$

The temperature dependency of the coefficients in most cases can be characterized well by a polynom:

$$A(T) = a_0 + a_1 T + a_2 T^2 \dots$$

9.7 The isothermal pressure dependency of the enthalpy in vapor phase

9.7.1 Redlich-Kwong-Soave equation

The pressure dependency of the pure component is characterized as follows:

$$\Delta h_i = RT(z-1) + \frac{T\dfrac{da_i}{dT} - a_i}{b_i}\ln\left(1 + \frac{b_i p_i^s}{zRT}\right)$$

The pressure dependency of the mixture:

$$\Delta h_m = RT(z-1) + \frac{T\dfrac{da_m}{dT} - a_m}{b_m}\ln\left(1 + \frac{b_m p}{zRT}\right)$$

9.7.2 Peng-Robinson equation

The pressure dependency of the pure component is characterized as follows:

$$\Delta h_i = RT(z_i - 1) - \frac{1}{2\sqrt{2}b_i}\left(A_i(T) - T\frac{\partial A_i(T)}{\partial T}\right)\ln\left(\frac{v_i + (1+\sqrt{2})b_i}{v_i + (1-\sqrt{2})b_i}\right)$$

with

$$A_i(T) = a_i\left[1 + m_i\left(1 - \sqrt{\frac{T}{Tc_i}}\right)\right]^2$$

$$\frac{\partial A_i(T)}{\partial T} = \left[1 + m_i\left(1 - \sqrt{\frac{T}{Tc_i}}\right)\right]\frac{-a_i m_i}{\sqrt{Tc_i T}}$$

The pressure dependency of the mixture:

$$\Delta h_m = RT(z_m - 1) - \frac{1}{2\sqrt{2}b_m}\left(a_m - T\frac{\partial a_m}{\partial T}\right)\ln\left(\frac{v_m + (1+\sqrt{2})b_m}{v_m + (1-\sqrt{2})b_m}\right)$$

with

$$\frac{\partial a_m}{\partial T} = \sum_i\sum_j x_i x_j (1 - k_{i,j})\frac{1}{2\sqrt{A_i(T)A_j(T)}}\left(A_i(T)\frac{\partial A_j(T)}{\partial T} + A_j(T)\frac{\partial A_i(T)}{\partial T}\right)$$

9.8 The enthalpy of a gas with simultaneous association

$$h_v = RE + \sum_i y_i h_i^v$$

$$RE = \frac{\sum_i\sum_n z_{in}\Delta h_{in} + \sum_i\sum_{j\neq i} z_{Mij}\Delta h_{Mij}}{\sum_i\sum_n nz_{in} + 2\sum_i\sum_{j\neq i} z_{Mij}}$$

$$\Delta h_{in} = -RB_{in}$$

$$\Delta h_{Mij} = -\frac{R}{2}\left(B_{i2} + B_{j2}\right)$$

10 Chemical reactions

10.1 Equilibrium reactions

$$\ln f(T) = a_0 + \frac{a_1}{T} + a_2 \ln T + a_3 T + a_4 T^2 + a_5 T^3$$

- **EQLM**

$$\prod_i x_i^{v_i} = f(T)$$

- **EQVM**

$$\prod_i y_i^{v_i} = f(T)$$

- **EQLC**

$$\prod_i \left(\frac{x_i}{V} \right)^{v_i} = f(T)$$

$$V = \sum_i \frac{x_i}{\rho_i}$$

- **EQVC**

$$\prod_i \left(\frac{y_i}{V} \right)^{v_i} = f(T)$$

$$V = \frac{z \cdot R \cdot T}{P}$$

- **EQLA**

$$\prod_i \left(\gamma_i x_i \right)^{v_i} = f(T)$$

- **EQVP**

$$\prod_i \left(P y_i \right)^{v_i} = f(T)$$

- **EQLF**

$$\prod_i \left(\frac{\varphi_i^0 P_i^s \gamma_i F p_i}{f^0} x_i \right)^{\upsilon_i} = f(T)$$

- **EQVF**

$$\prod_i \left(\frac{\varphi_i^\upsilon P}{f^0} y_i \right)^{\upsilon_i} = f(T)$$

10.2 Kinetically controlled reactions

$$\ln f(T) = a_0 + \frac{a_1}{T} + a_2 \ln T + a_3 T$$

$$\ln \varphi(T) = a_0 + \frac{a_1}{T} + a_2 \ln T + a_3 T$$

- **KILM**

$$\varsigma = V \left(\sum_k f_k \prod_i x_i^{\alpha_{i,k}} \right) \left(\prod_l \left(1 + \varphi_l \sum_i \gamma_{i,l} x_i \right) \right)$$

- **KIVM**

$$\varsigma = V \left(\sum_k f_k \prod_i y_i^{\alpha_{i,k}} \right) \left(\prod_l \left(1 + \varphi_l \sum_i \gamma_{i,l} y_i \right) \right)$$

- **KILC**

$$\varsigma = V \left(\sum_k \frac{f_k}{Vs \sum \alpha_{i,k}} \prod_i x_i^{\alpha_{i,k}} \right) \left(\prod_l \left(1 + \frac{\varphi_l}{Vs} \sum_i \gamma_{i,l} x_i \right) \right)$$

$$Vs = \sum_i \frac{x_i}{\rho_i}$$

- **KIVC**

$$\varsigma = V \left(\sum_k \frac{f_k}{Vs \sum \alpha_{i,k}} \prod_i y_i^{\alpha_{i,k}} \right) \left(\prod_l \left(1 + \frac{\varphi_l}{Vs} \sum_i \gamma_{i,l} y_i \right) \right)$$

$$Vs = \frac{zRT}{P}$$

- **KILW**

$$\varsigma = V\rho_m Vs\left(\sum_k \frac{f_k}{Vs\sum \alpha_{i,k}}\prod_i x_i^{\alpha_{i,k}}\right)\left(\prod_l\left(1+\frac{\varphi_l}{Vs}\sum_i \gamma_{i,l}x_i\right)\right)$$

$$Vs = \sum_i x_i Mw_i$$

- **KIVW**

$$\varsigma = V\rho_m Vs\left(\sum_k \frac{f_k}{Vs\sum \alpha_{i,k}}\prod_i y_i^{\alpha_{i,k}}\right)\left(\prod_l\left(1+\frac{\varphi_l}{Vs}\sum_i \gamma_{i,l}y_i\right)\right)$$

$$Vs = \sum_i y_i Mw_i$$

$$\rho_m = \frac{zRT}{P}$$

10.3 Reactions of general nature

- **COOR**

$$\varsigma = value$$

- **CONV**

$$ratio * M_{ref} = -\varsigma_r \upsilon_{ref}$$

- **STAT**

$$ratio * M_{ref} = \varsigma_r \upsilon_{ref}(ratio - 1)$$