EOS Mixing Rule Parameters

GENPAR
Fitting of Equation of State Mixing Rule Parameters
for Flash and VLE Calculation

DDBSP – Dortmund Data Bank Software Package

Contents

1 Introduction

Generate EOS Mixing Rule Parameters (short GenPar) is the fit program for equation of states mixing rule parameters which can be used to describe phase equilibria up to the critical point of a mixture. This is the advantage over g^E-models which can be used only at moderate pressures and temperatures not to far away from normal boiling points.

The *GenPar* program uses binary data sets from the Dortmund Data Bank parts `VLE` and `HPV` which both contain vapor-liquid equilibrium data. `HPV` contains mostly data where the normal boiling points of at least one component is below 273 K whereas the `VLE` data bank contains all other data sets.

`GenPar` can fit parameters for the equations of state

- Soave-Redlich-Kwong
- Peng-Robinson
- Redlich-Kwong

The supported mixing rules are

- quadratic mixing rules
- six g^E mixing rules:
    - Vidal
    - Tochigi
    - Michelsen
    - PSRK
    - VTPR
    - LCVM
- Panagiotopoulos/Reid

2 Searching for Components and Experimental Data Sets

Figure 1 shows the main screen of *Generate EOS Mixing Rule Parameters*.
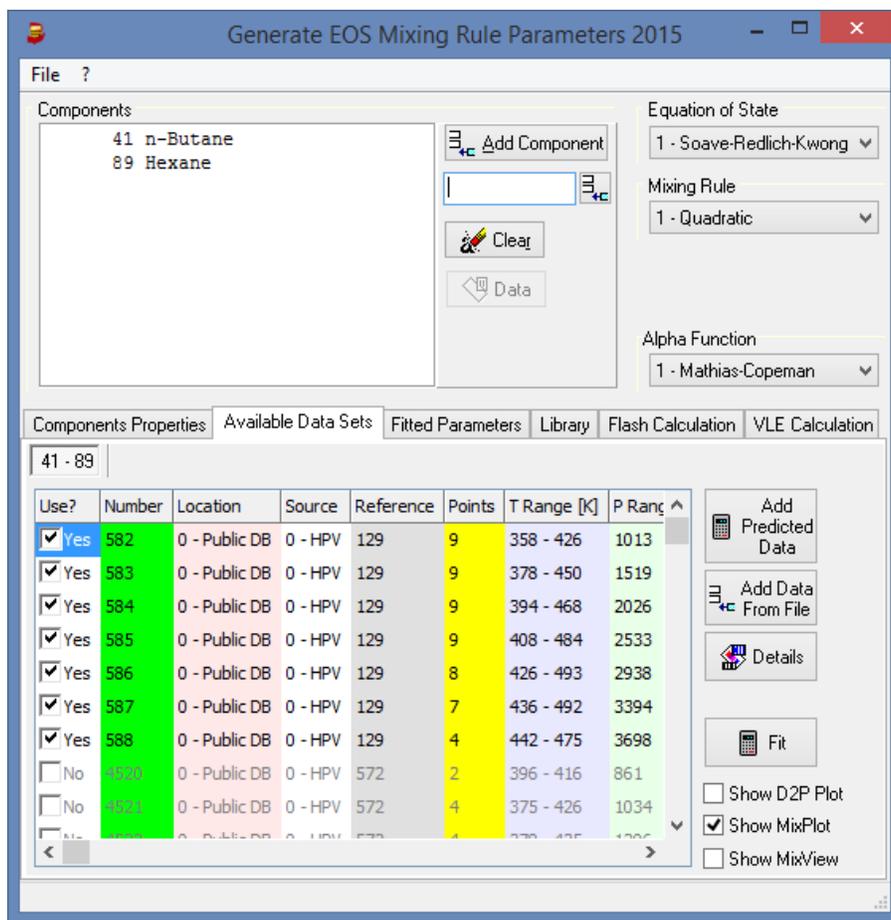
Figure 1: Start Screen

The *Components* group box contains an initially empty list plus these controls:

-

  This button invokes the *Compound Selection* tool (see Figure 2).

-

  If the DDB number of a component is know it can be typed in directly.

-

  This button clears the current component list

-

  If a single component is selected this button display the basic data bank entries like name, CAS registry number, formula etc.
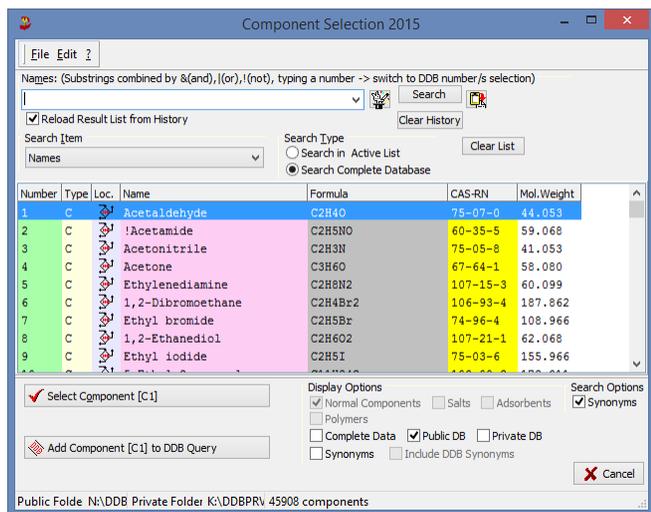
Figure 2: Component Selection

The *Compound Selection* dialog is described in detail in the "Component Management" documentation.

Figure 3: Component List

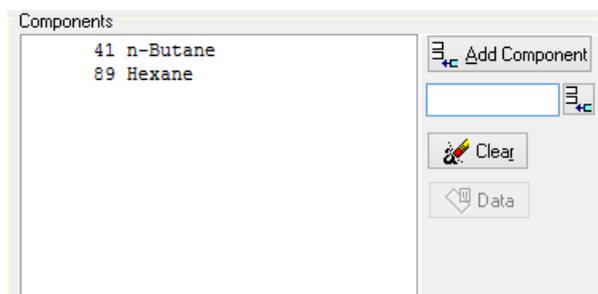After selecting at least two components (see Figure 3) the `VLE` and `HPV` data banks are searched for the binary data sets.

The *Components Properties* card contains the pure component properties that will be used in all operations: fit, flash calculation and VLE calculation. Click on a component in the Components list or use the drop-down control in the card itself to switch between the components.

Figure 4: Available Data Sets, Single System

The *Available Data Sets* card shows the different binary systems and the data sets which have been found in both data banks.

```
  41 n-Butane
  89 Hexane
 161 Toluene
1056 Nitrogen
 237 Propane
```

Figure 5: Component List

If the components list contains more than two entries (see Figure 5) all possible binary component pairs will appear in the list of binary systems (see Figure 6).

Figure 6: Available Data Sets, Many Systems

The data set list contains the following columns:

1. Use?
    These check boxes determine if the data set shall be used for fitting

2. Number
   Data set number

3. Location
   Location of the data bank from which the data set has been loaded (0 stands for a public DDB from DDBST GmbH, 1 stands for a private data bank from a user)

4. Source
   0 if the data sets has been read from the `HPV` data bank and a one for the `VLE` data bank

5. Reference
   Article number

6. Points
   Number of points of the data set

7. T Range [K]
   Temperature range of the data set

8. P Range [kPa]
   Pressure range of the data set.

9. Data Type
   Indicates the data columns of a data set. Column names in parenthesis denotes constant values. So "Pxy(T)" means: pressure, liquid and vapor composition at constant temperature is specified.

The grid has a context menu for modifying selections.

| Select All |
| Select None |
| Swap Selection |
| Select Isothermal Sets |
| Select Isobaric Sets |
| Select Complete Sets Only (x,y,P,T) |
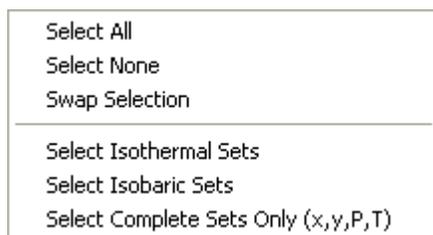
The entry 'Swap Selection' selects previously unused sets and deselects previously checked sets.

The other entries allow to create sublists with matching conditions.

2.1 Add Predicted Data Sets

If the DDB contains no or insufficient data sets for a binary system it is possible to create data sets by predictive methods.
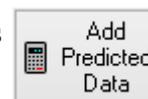
The dialog allows the selection of the predictive methods and the specification of the conditions.
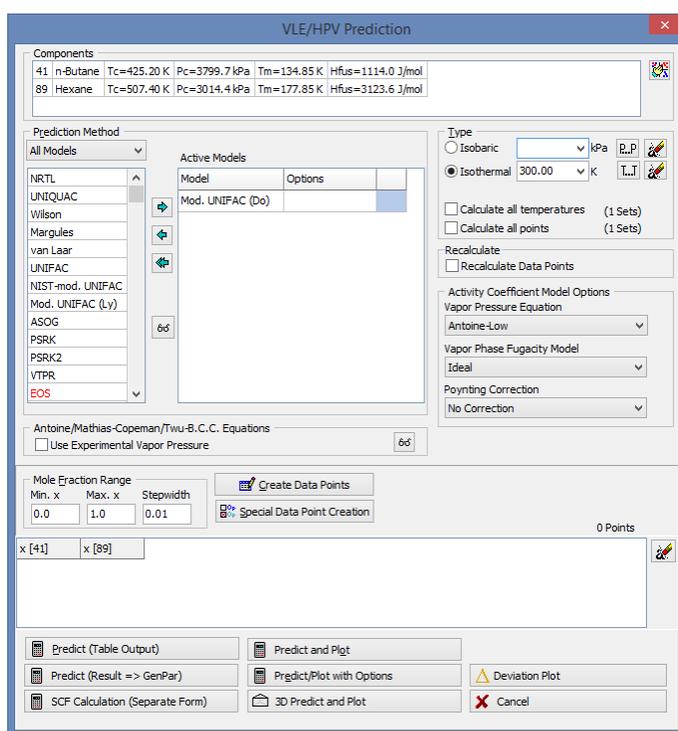
Figure 7: Prediction of Vapor-liquid Equilibria

This dialog is also part of the mixture properties data bank management program and is described in that documentation in detail.

 produces a predicted VLE data set and returns this data set to *Generate EOS Mixing Rule Parameters*. If more than one model is selected or more than one constant condition (temperature and/or pressure) is specified then several data sets are returned to the *GenPar* program.

The location number 205 indicates that the PSRK model created the data set. The "Source" and "Reference" field has to be ignored.

<u>Hint</u>

Many models are restricted to moderate pressures and temperatures near the normal boiling point. Group contribution methods need group assignments and group contributions. g^E models need g^E parameters. There are many possibilities that a calculation can fail.

2.2 Add Data From File

If data are available from other sources or have altered outside the DDB system or saved for any reason it is possible to add data from files. The data have to be in ".qr" format that the Dortmund Data Bank programs reads and writes.

3 Fitting Mixing Rule Parameters

First select the *Available Data Sets* card, the select a binary system (if there are more than two components in the system). When some binary data sets have been selected to be used in the fit process (the "Use?" check boxes are checked) the *Fit* button becomes active:

The step before or after selecting the components and loading the data sets is the selection of the equation of state, the mixing rule, and the α-function.

If a g^E mixing rule has been selected the g^E model has to be specified additionally.

In case of the mixing rule by *Tochigi* the g^E model is fixed to *UNIQUAC (res)*. The Stryjek-Vera alpha function is only available for the Peng-Robinson EOS.

Now the [Fit] button can be pressed. An option dialog will be displayed (see Figure 8). It is possible to use temperature-independent parameters (*none*), and up to five temperature-dependent parameters.

The default starting values ("0"s) for the parameters can be modified. The alpha value of NRTL will always stay constant during the fit process.

It is also possible to load starting values from EOS project files (*.eosproj), fit input files (*.eoi) or fit output files (*.out). All these files are text files with parameter lines beginning with "KIJ".
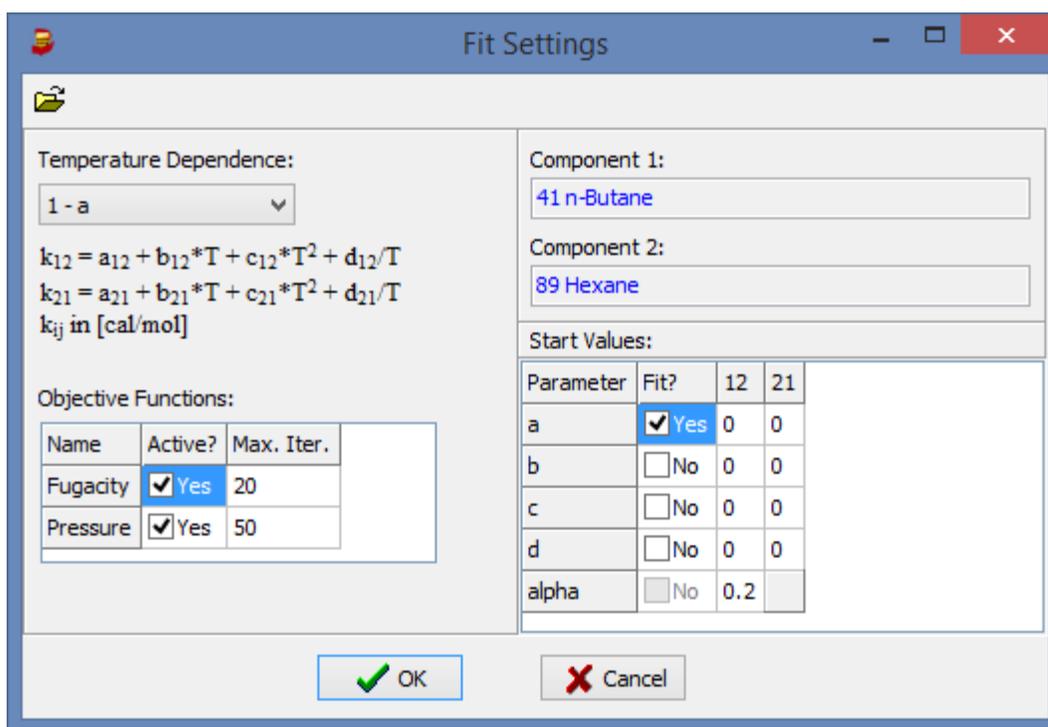
Figure 8: Options for parameter fitting

The optimization process can use up to two objective functions:

- minimize *fugacity* differences
- *minimize pressure* differences.

At least one objective function has to be selected. If both are selected the sum of both objective functions will be minimized.
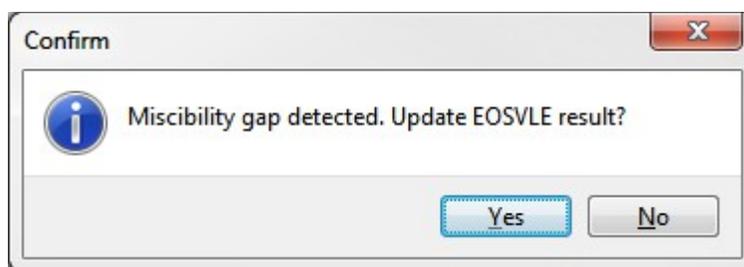
Figure 9: Miscibility gap detection dialog

The optimization process takes a short while. A window with the optimization results (text) is displayed. If the calculation process detects a miscibility gap it is possible to update the VLE calculation results (see Figure 9).

There are up to four result cards:

1. The fit result created by `EOSOPTLP`. This text has the following sections:

    a. Duplicate of the `EOSOPTLP` command file ("INPUT DATA")

    b. The list of data sets used for the fit ("DATA SETS IN FILE")

    c. The specified EOS and mixing rule ("EQUATION OF STATE")

    d. Existing mixing rule parameters ("INTERACTION PARAMETERS....", always 0.)

    e. A list of modified acentric factors or the first Mathias-Copeman parameter for each data set used in the fit. This value is adjusted to pure component vapor pressures of the single sets ("SYSTEM: ???? C1(2)=....").

    f. The minimizing fugacity differences progress report ("MINIMIZING FUGACITY DIFFERENCE")

    g. The minimizing relative pressure deviation ("MINIMIZING RELATIVE PRESSURE DEVIATIONS")

    h. The resulting interaction parameters (= mixing rule parameters, "INTERACTION PARAMETERS FOR ...")

    i. Deviation tables for all used data sets.

2. The second card contains tables of `VLE` data for all temperatures or pressures given in the used data sets. These `VLE` are calculated with the fitted parameters

3. In the cases where a data set contains a miscibility gap a third card gives information on the found `LLE`.

If *Show D2P Plot* is selected the D2P plot output is used to display the experimental `VLE` together with the calculated sets.

Peng-Robinson
(1) n-Butane
(2) Hexane
T [K] =   293.15 283.15 273.15 263.15 253.15
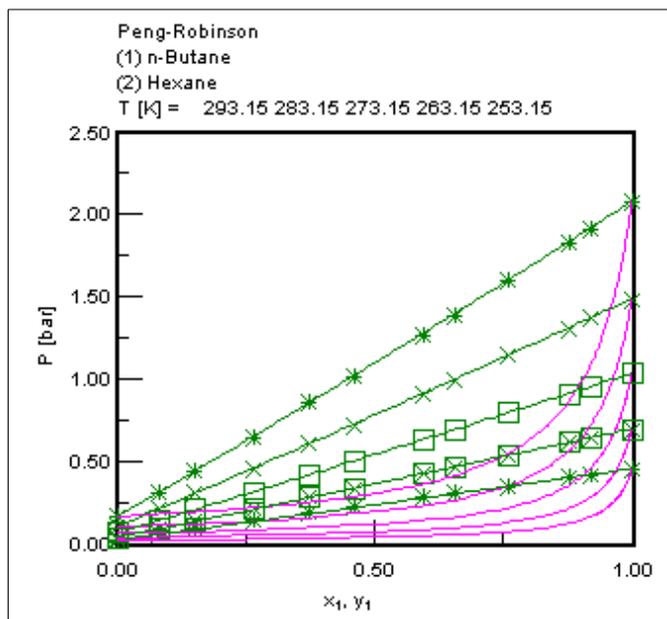
If *"Show MixPlot"* is selected the calculated VLE data together with the experimental data sets are displayed using the standard DDBSP plot window.
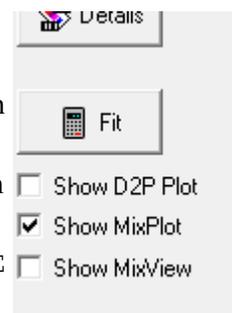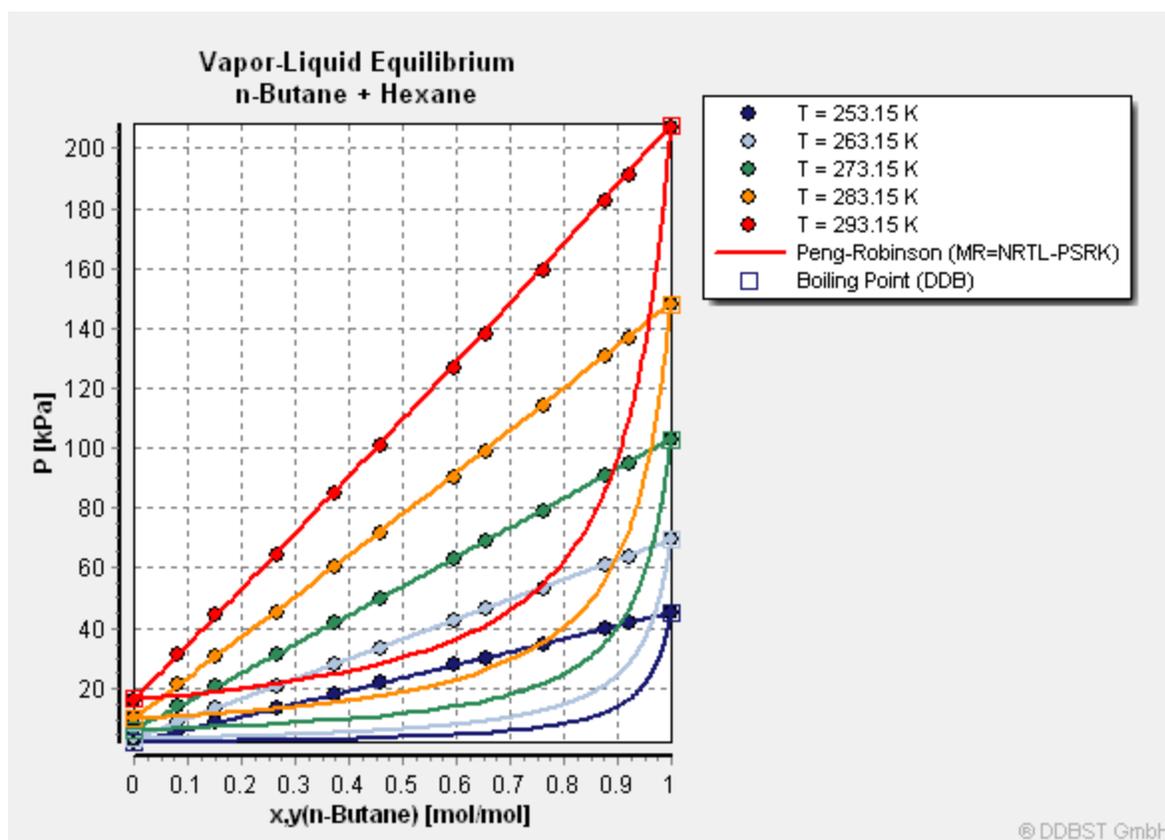
The fitted parameter sets are stored in *GenPar*.

All parameters sets which are created in one program run (a *session*) are collected in that grid. Only one parameter set per component pair is stored here. A new fit overwrites any previously fitted set.

The sets can be stored either in an EOS project file or in a so called library (DDB parameter database). The project files are used to stored a list of components together with their pure component properties and the mixing rule parameters for a specific EOS and mixing rule and g^E model. To be backwards compatible it is possible to load the EPF files which were used in previous versions of the *Generate EOS Mixing Rule Parameters* program. The format of EPF files are described in the appendix.

The fitted parameters can be deleted completely by clicking the *Clear* button or removed line by line by clicking the *Remove Line* button.

4 Working with the Library

The library is essentially a list of parameter sets. It's divided in two parts, a public list which is distributed by DDBST GmbH and a second, private list which can be used by our customers.

Parameter sets cannot be edited directly. Adding data sets is possible only for the private library from the *Fitted Parameters* list (see section Fitting Mixing Rule Parameters) and complete lines (which are parameter sets) can be deleted by the *Remove* button.

5 Project Management

An EOS project file (*.eosproj) can be used to manage all components together with its properties and binary interaction parameters.

Use the *Open Project* menu item of the *File* menu to load an existing project file. This will update the components and the pure component properties and the EOS settings. In addition the *Flash Calculation* and *VLE Calculation* card will contain all the binary interaction parameters that are defined in the project.

To manage the interaction parameters of a project the *VLE Calculation* card can be used. Here parameters can be added from several sources: the pool of just fitted parameters, the parameters available in the public or private library and external parameters can be typed in by hand. Use the ![Kij] button to add fitted or library parameters.

Use the *Save Project As* menu item of the *File* menu to save the binary interaction parameters of the VLE Calculation card to a project file.

Remark: The project file is a text file, so changes that can not be done in the program can be made in a text editor. The file format is described in the appendix.

6 Flash Calculation

Generate EOS Mixing Rule Parameters allows to invoke a two-phase and a three-phase flash calculation.

The two-phase flash calculates composition of the vapor and the liquid phase without considering miscibility gaps whereas the three phase flash tries to find the liquid-liquid equilibrium if it exists.

The flash is calculated either isothermal within a pressure range or isobaric within a temperature range.

The global composition ("Feed") can be specified as mole fraction, mole percent, moles or masses (kilograms), weight fractions or weight percent.

Fill by Newly Fitted Parameters (1.)
Fill by Private Library Parameters (2.)
Fill by Public Library Parameters (3.)
Fill by 1., 2., 3.

Clear All

The parameters used for the flash calculation can be obtained from new fitted parameter sets, from the private or public parameter library or by all three sources. The import can be invoked from a context menu of the parameter grid. The context menu is also shown by the button **Kij** .

Another source is a project file which can be loaded from the *File* menu. And additionally it is possible to type in the parameters by hand.

After completing the input of the global composition and the parameters the flash calculation can be started.

6.1 Two-Phase Flash Results

A two-phase flash gives a text result and a plot result.

The text output contains the following information:

```
EQUATION OF STATE: PENG-ROBINSON
MIXING RULE: PSRK
ALPHA FUNCTION: TWU-BLUCK-CUNNINGHAM-COON
GE-MODEL: NRTL

 I   TC[K] PC[BAR]  OMEGA       C1  ...
 1  304.20   73.76 0.22520   0.82105 ...
 2  425.20   38.00 0.19300   0.40119 ...
 3  507.40   30.14 0.29750   0.38727 ...


 INTERACTION PARAMETERS FOR GE(NRTL) MIXING RULE:

 I  J    AIJ        AJI         BIJ     ...
 1  2  -34.309     1416.6      3.1170   ...
 1  3   2215.6    -4527.7    -11.158    ...
 2  3   145.66    -151.88     0.80876E-01 ...


 ISOBARIC IDEAL GAS HEAT CAPACITY COEFFICIENTS:
 I Eq    A1        A2          A3   ...
 1  9  29370.     34540.     1428.0 ...
 2  9  71340.    0.24300E+06  1630.0 ...
 3  9 0.10440E+06 0.35230E+06 1694.6 ...

DEFINITIONS USED IN THIS PROGRAM:
   IDEAL GAS ENTHALPY = 0 AT T0=298.15 K
   IDEAL GAS ENTROPY  = 0 AT T0=298.15 K AND
P0=1 ATM
THE FOLLOWING PENELOUX CONSTANTS [L/MOL] ARE
USED FOR VOLUME CORRECTIONS:
  -0.00182  -0.00492  -0.00212
```

The first lines specify the equation of state settings together with the used vapor pressure equation for pure components (alpha function).

The used pure component properties follow.

Then the mixing rule parameters are shown.

Pure component heat capacity parameters.

These definitions describe some basic definitions for the used models.

Peneloux constants.

The following line are repeated for every new pressure (isothermal calculations) or new temperatures (isobaric calculations).

```
 TEMPERATURE:      323.15 K
 PRESSURE   :      1.0000 BAR

  I     Z(I)      F*Z      X(I)      L*X      Y(I)      V*Y      K(I)
 -- -------- -------- -------- -------- -------- -------- --------
  1  0.13000  0.13000  0.00159  0.00048  0.18629  0.12952  117.518
  2  0.23000  0.23000  0.06697  0.02041  0.30146  0.20959    4.501
  3  0.64000  0.64000  0.93144  0.28387  0.51225  0.35613    0.550
 -- -------- -------- -------- -------- -------- -------- --------
 N [MOL]      1.00000           0.30476           0.69524
 M [G]          74.24             25.67             48.57
 V [L/MOL]                       0.1327            26.11
 Z=PV/RT                         0.0049            0.9716
 V [L/MOL]    (Corrected)        0.1351            26.11
 Rho [g/ccm]  (Corrected)        0.624             0.003
 H [J/mol]                    -26030.0            2619.9 TOTAL:  -6111.4
 S [J/mol/K]                    -75.90              8.80 TOTAL:   -17.01
```

6.2 Abbreviations – component specific values

I   Component (numbering order from top to bottom as in the Component List)

Z(I)   Total number of moles of component I (normalized to 1 mole of total feed)

X(I)   Mole fraction of component I in the liquid phase

Y(I)   Mole fraction of component I in the vapor phase

K(I)   Y(I)/X(I)

F   Total feed (1 mole)

L   Total number of moles in the liquid phase

V   Total number of moles in the vapor phase

6.3 Abbreviation – system specific values

N [MOL]   Moles (complete, in liquid phase, in vapor phase)
M [G]   Masses (complete, in liquid phase, in vapor phase)
V [L/MOL]   Volume (of liquid phase, of vapor phase)
Z=PV/RT   Compressibility (of liquid phase, of vapor phase)
Rho [g/cm]   Density (of liquid phase, of vapor phase)
H [J/mol]   Enthalpy
S [J/mol/K]   Entropy

`Corrected` means that the Peneloux correction for the density was taken into account.

The plot output contains five different charts:
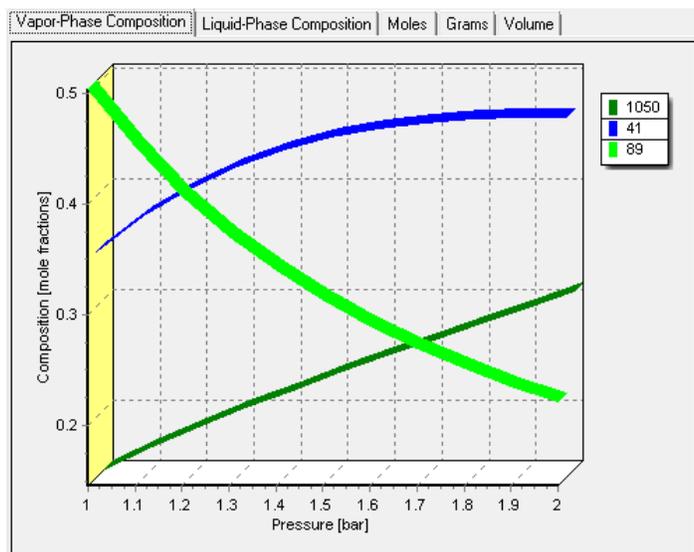
Vapor phase composition.

It can be seen that with increasing pressures the fraction of higher boiling compounds gets lower and the fraction of low-boiling substances gets higher (1050 is Carbon Dioxide, 41 Butane, 89 Hexane).

Figure 10
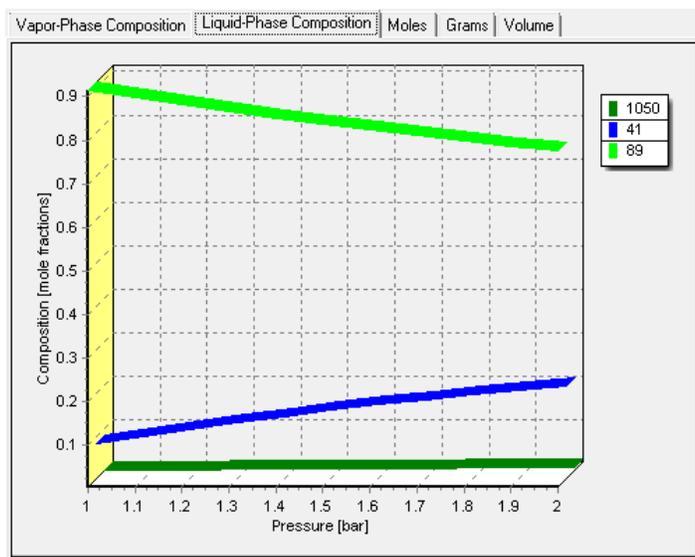
Figure 11

Liquid phase composition

Figure 12
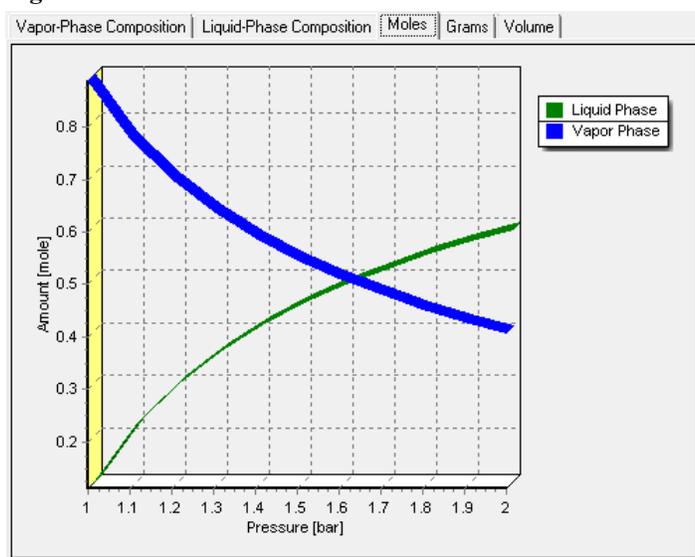
Amount of substance in vapor and liquid phase.

It can be seen that at almost three bar the system has almost no vapor phase anymore.

Figure 13
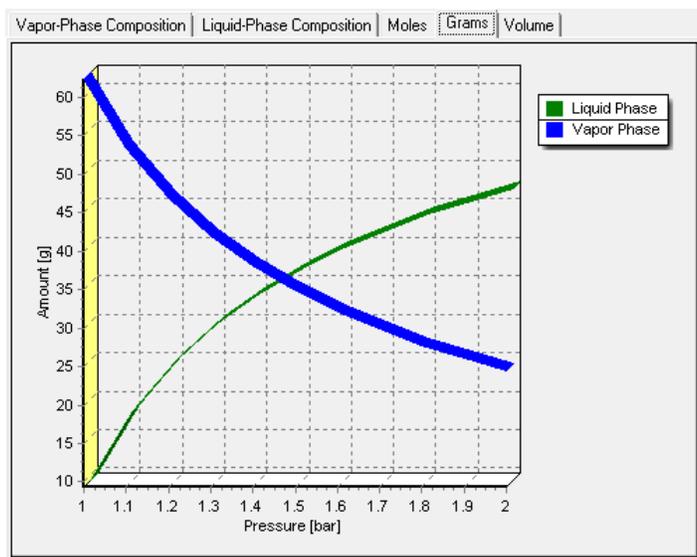
Mass of substance in liquid and vapor phase. Of course this looks very similar to the moles plot.

Figure 14
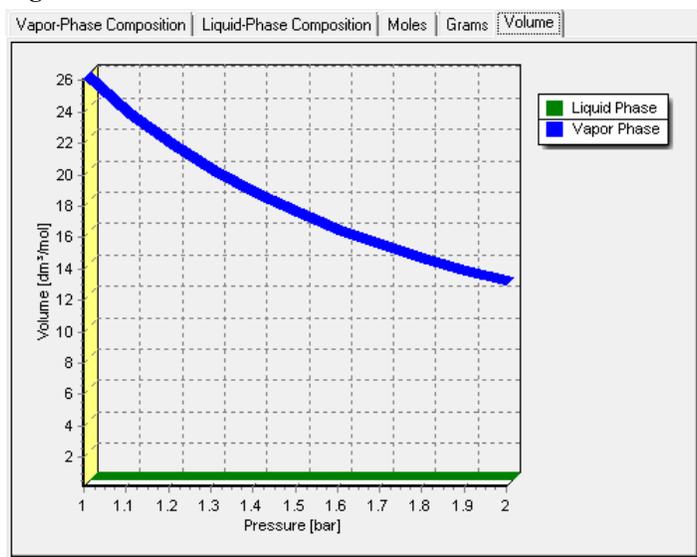
Volume of liquid and vapor phase.

The volume vapor phase is of course very impressed by an increased pressure.

6.4 Three-Phase Flash Result

The three-phase flash calculation creates only a text output. The output starts with the same lines as the two-phase flash.

The data points for the single temperatures or pressure are a little bit different. The `**Result**` line lists the found phases. In most case this will be liquid and vapor, sometimes only vapor, sometimes only liquid and sometimes liquid-liquid.

```
 TEMPERATURE:     323.15 K
 PRESSURE   :      1.0000 BAR

 **RESULT** 2 PHASES: (LIQUID) (VAPOR)

  I     Z(I)     NZ(I)    X1(I)    N1(I)    X2(I)    N2(I)
 -- -------- -------- -------- -------- -------- --------
  1  0.13000  0.13000  0.00159  0.00048  0.18629  0.12952
  2  0.23000  0.23000  0.06697  0.02041  0.30146  0.20959
  3  0.64000  0.64000  0.93144  0.28387  0.51225  0.35613
 -- -------- -------- -------- -------- -------- --------
 N [MOL]      1.00000           0.30476           0.69524
 M [G]          74.24             25.67             48.57
 V [L/MOL]                       0.1327           26.1052
 Z=PV/RT                         0.0049            0.9716

 TOTAL GIBBS ENERGY OF 2 PHASE MIXTURE:  -2601.4     J

  I  X1*PHI1  X2*PHI2   X2/X1
 -- -------- -------- --------
  1 .188     .188     118.
  2 .295     .295     4.50
  3 .490     .490     .550
 -- -------- -------- --------
```

## 6.5 Abbreviations - component specific values

I	Component (numbering order from top to bottom as in the Component List)
Z(I)	Total number of moles of component I (normalized to 1 mole of total feed)
X(I)	Mole fraction of component I in the liquid phase
NZ	Number of moles in the liquid and vapor phase phase
N1	Number of moles in the liquid phase
N2	Number of moles in the vapor phase phase

6.6 Abbreviation – system specific values

N [MOL]	Moles (complete, in liquid phase, in vapor phase)
M [G]	Masses (complete, in liquid phase, in vapor phase)
V [L/MOL]	Volume (of liquid phase, of vapor phase)
Z=PV/RT	Compressibility (of liquid phase, of vapor phase)

Hint

The three-phase calculation is very slow and unstable and not very reliable.

7 VLE Calculation

Generate EOS Mixing Rule Parameters allows to predict a `VLE` data set with EOS mixing rule parameters. These mixing rule parameters might be obtained from new fits or from the library or from a project file.

The grid containing the mixing rule parameters is exactly the same as used in the flash calculation (see section "Flash Calculation" on page 14).

VLE calculations are either isothermal or isobaric and are carried out in one mole percent steps over the entire range from zero mole percent to one hundred mole percent.

For ternary or higher systems it is necessary to specify constant compositions for component 2 and higher.

The calculation yields a table and a plot output:

```
….some lines before this ….
  NO IT    T[K]       P[BAR]      VV [L/MOL] VL       X1      X2      Y1      Y2
  ------------------------------------------------------------------------------
    1  2  323.15     17.194        1.1517    0.1103 0.00000 0.00000 0.00000 0.00000
    2  2  323.15     17.039        1.1658    0.1102 0.01000 0.00000 0.00400 0.00000
    3  1  323.15     16.886        1.1800    0.1102 0.02000 0.00000 0.00803 0.00000
    4  1  323.15     16.733        1.1944    0.1101 0.03000 0.00000 0.01210 0.00000
…. some lines after this ….
```

The lines in the table contain the temperature, the pressure, the volume of the vapor and the liquid phase and the composition of the liquid and the vapor phase.

The plot (D2P format) shows this table graphically.

Soave–Redlich–Kwong
(1) BUTANE
(2) HEXANE
T [K] =   323.15
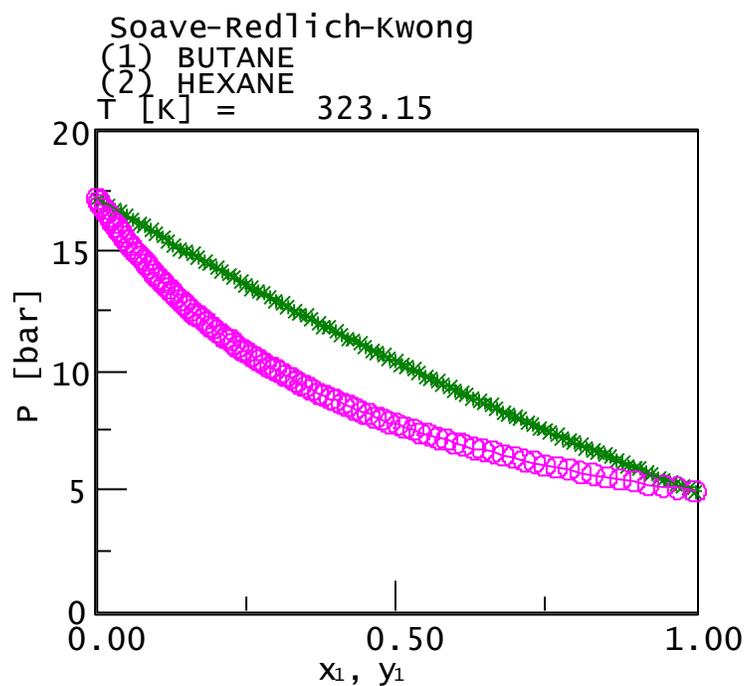
A typical result for a ternary system in the MixPlot format shows the constant composition line (Hexane in this example).

HPV Triangle-Chart
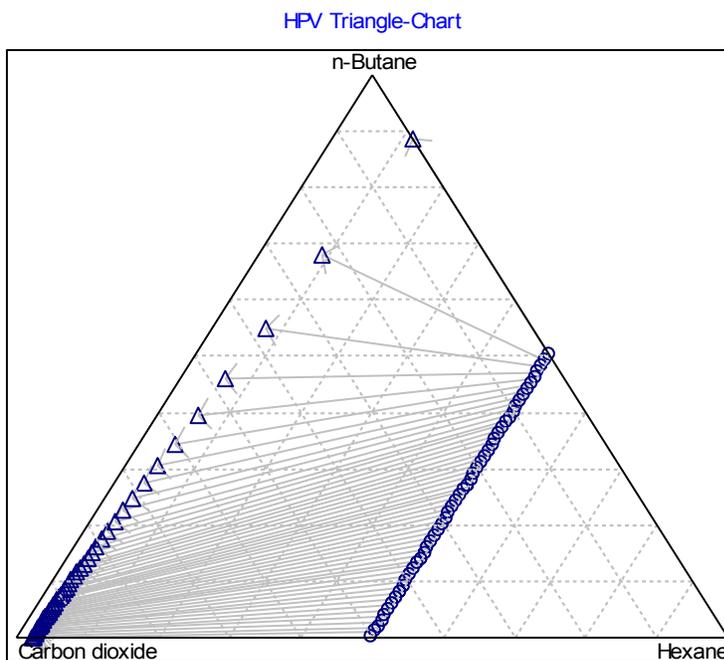
8 Appendix

8.1 The EOS Project File Format

The EOS project file is a text file. The project file contains the EOS specification (EOS, mixing rule, g^E-model, alpha function), the components specification (DDB number, name, pure component properties) and the binary interaction parameters.

The contents can be divided into three blocks: The EOS block, the components block and the interaction parameters block.

The EOS block appears at the beginning of the file and uses the following keywords:

- Model: The EOS model number.
- MIXA: The mixing rule.
- MIXB: The value must be always 1.
- MODG: The g^E-model. The value is 0 if a non-g^E mixing rule is used.
- ALPHA: The alpha function. The value is 0 if the EOS model does not use any alpha function.

All numbers are identical to the numbers displayed in the program.

The components block starts with the specification of the number of components.

- NKOMP

Then the specification of all component with its properties follows. A component block uses the following keywords:

- COMP: The DDB component number.
- TC[K]: The critical temperature in Kelvin.
- PC[BAR]: The critical pressure in bar.
- OMEGA: The acentric factor.
- ALPHA: The parameters of the alpha function (if an alpha function is selected in the EOS block.
- R: The UNIQUAC r-value (used by the UNIQUAC g^E-model).
- Q: The UNIQUAC q-value (used by the UNIQUAC g^E-model).
- VOLUME(WILSON): The Wilson volume in cm³/mol (used by the Wilson g^E-model).
- NAME: The name of the component.

The interaction parameters block contains one line for each binary interaction parameter set. The format is

KIJ $<C_1> <C_2> <N> <a_{12}> <b_{12}> <c_{12}> <a_{21}> <b_{21}> <c_{21}> <Alpha> <T_{min}> <T_{max}>$

with

- C_1: DDB component number of first component
- C_2: DDB component number of second component
- N: number of parameters (1-3)
- a_{ij}, b_{ij}, c_{ij}: interaction parameter between component i and j.
- Alpha: alpha parameter (used by NRTL g^E-model).

- T_{min} / T_{max} :Scope of application (temperature range in Kelvin).

8.2 The EPF File Format

The EPF file is a binary FORTRAN file. It contains numbers for the equation of state, the mixing rule (for EOS-a and EOS-b), and the g^E model.

After these numbers it contains a list of components with the necessary properties:

1. Critical temperature and pressure
2. Acentric factor
3. Mathias-Copeman parameters (c_1, c_2, c_3)
4. UNIQUAC r and q values
5. A volume at 25 °C for the g^E model Wilson

Behind these pure component properties the list of mixing rule parameters follow.

The first record is ten bytes long and contains five short two-byte numbers:

- Number of components
- Equation of state
   1. Soave-Redlich-Kwong
   2. Peng-Robinson
   3. Redlich-Kwong (currently not supported)
- Mixing rule for EOS a parameter
   1. Quadratic
   2. g^E (Vidal)
   3. g^E (Tochigi)
   4. g^E (Michelsen)
   5. g^E (PSRK)
- Mixing rule for EOS b parameter (always 1)
- g^E model
   1. NRTL
   2. Wilson
   3. UNIQUAC
   4. NRTL (Vidal)
   5. UNIQUAC (res.)

The next record contain the pure component properties. Every record contains one short two-byte number, nine double eight-byte floating point numbers, and 48 characters:

- Component DDB number (short)

- T_c
- P_c
- Acentric factor
- Mathias-Copeman constant
- UNIQUAC r and q values
- A volume for Wilson
- The component name

The next record contain the binary mixing rule parameters. The records contain three double eight-byte floating point numbers and fifty characters:

- G_{ij} and G_{ji}
- α (for NRTL)
- A source definition (up to fifty letters).

8.3 Equation of State Formulas

- Soave-Redlich-Kwong

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

with $\alpha(T) = \left[1 + (0.48 + 1.574\omega - 0.176\omega^2)\right]^2$

ω is the acentric factor.

- Peng-Robinson

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

with $a(T) = a\alpha(T)$ and $\alpha(T) = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})\right]^2$

ω is the acentric factor.

- Redlich-Kwong

$$P = \frac{RT}{v - b} - \frac{a}{\sqrt{T}\, v(v + b)} \quad \text{with} \quad \sqrt{a} = \sum_i (x_i \sqrt{a_i}) \quad \text{and} \quad b = \sum_i (x_i b_i) \quad \text{and}$$

$$a_i = 0.42748023 \cdot R^2 \cdot T_{c_i}^{2.5} / P_{c_i} \quad \text{and}$$

$$b_i = 0.08664035 \cdot R \cdot T_{c_i} / P_{c_i}$$

8.4 Mixing Rule Equations

- Quadratic Mixing Rule

$$a = \sum_i \sum_j y_i y_j a_{ij}$$

with $a_{ij} = \left(a_{ii} a_{jj}\right)^{0.5} \left(1 - k_{ij}\right)$

- g^E Mixing Rule Vidal (Huron/Vidal)

$$\frac{\overline{a}^E}{RT} = A_0 \left[\frac{a}{bRT} - \sum x_i \frac{a_{ii}}{b_i RT}\right] = \frac{g_\infty^E}{RT} \qquad A_0 = \ln\frac{v}{v+b} = \ln\frac{1}{2}$$

- g^E Mixing Rule Michelsen

$$\frac{\overline{a}^E}{RT} = A_0 \left[\frac{a}{bRT} - \sum x_i \frac{a_{ii}}{b_i RT}\right] = \frac{g_0^E}{RT} + \sum x_i \ln\frac{b}{b_i} \qquad A_0 = \ln\frac{v}{v+b} = \ln\frac{1.235}{2.235} = -0.593$$

- g^E Mixing Rule PSRK

$$\frac{\overline{a}^E}{RT} = A_0 \left[\frac{a}{bRT} - \sum x_i \frac{a_{ii}}{b_i RT}\right] = \frac{g_0^E}{RT} + \sum x_i \ln\frac{b}{b_i} \qquad A_0 = \ln\frac{v}{v+b} = \ln\frac{1.1}{2.1} = -0.64663$$

- Panagiotopoulos/Reid

$$a = \sum_i \sum_j y_i y_j a_{ij}$$

with $a_{ij} = \sqrt{a_i a_j} \left[1 - k_{ij} + \left(k_{ij} - k_{ji}\right) x_i\right]$

- g^E Mixing Rule LCVM

$$\frac{A^E}{RT} = A_1 \left[\frac{a}{bRT} - \sum x_i \frac{a_{ii}}{b_i RT}\right] = \frac{G_0^E}{RT} + A_1 A_2 \sum x_i \ln\frac{b}{b_i} \quad \text{with}$$

$$A_1 = \frac{1}{\dfrac{0.36}{-0.623} + \dfrac{1-0.36}{-0.52}} = -0.5529 \quad \text{and} \quad A_2 = \frac{1-0.36}{-0.52} = -1.2308$$

- g^E Mixing Rule VTPR

$$\frac{A^E}{RT} = A_0 \left[\frac{a}{bRT} - \sum x_i \frac{a_{ii}}{b_i RT}\right] = G_{0,\text{RES}}^E \quad \text{with}$$

$$A_0 = \frac{1}{2\sqrt{2}} \ln\left(\frac{v+(1-\sqrt{2})b}{v+(1+\sqrt{2})b}\right) = \frac{1}{2\sqrt{2}} \ln\left(\frac{1.22498+(1-\sqrt{2})}{1.22498+(1+\sqrt{2})}\right) = -0.53087 \quad \text{and}$$

RES = Residual Part