Predictive Equation of State

Vapor-liquid Equilibria, Gas Solubilities, Excess Enthalpies and
Phase Flash Calculations

PSRK – *Predictive Soave-Redlich-Kwong*

VTPR – *Volume-Translated Peng-Robinson*

DDBSP – Dortmund Data Bank Software Package

DDBST - Dortmund Data Bank Software & Separation Technology GmbH

Marie-Curie-Straße 10

D-26129 Oldenburg

Tel.: +49 441 36 18 19 0

Fax: +49 441 36 18 19 10

support@ddbst.com

www.ddbst.com

Introduction

This software allows the prediction of multicomponent vapor-liquid equilibria (VLE), vapor-liquid-liquid-equilibria (VLLE), gas solubilities (GLE), SCF, P/T-curves, excess enthalpies (HE) and excess volumes (VE) with the group contribution equation of state models PSRK[1,2,3,4,5] and VTPR[6,7,8,9,10,11,12,13,14].

Both models allow reliable predictions of phase equilibria for polar and non-polar systems over a wide temperature and pressure range, PSRK2 and VTPR also in case of asymmetric systems. Even systems containing supercritical components can be calculated precisely.

The program PredictiveEOS allows specifying the components of the desired system, to enter necessary data like compositions, temperatures and pressures and it will display the results in tables and plots. The results can be copied to the Windows clipboard, saved and printed.

[1] Holderbaum T., "Die Vorausberechnung von Dampf-Flüssig-Gleichgewichten mit einer Gruppenbeitragszustandsgleichung", VDI Fortschrittsber.Reihe 3, 243, p1-154, 1991

[2] Holderbaum T., Gmehling J., "PSRK: A group-contribution equation of state based on UNIFAC.", Fluid Phase Equilib., 70, p251-265, 1991

[3] Horstmann S., Jabloniec A., Krafczyk J., Fischer K., Gmehling J., "PSRK Group Contribution Equation of State: Comprehensive Revision and Extension IV, Including Critical Constants and a-Function Parameters for 1000 Components", Fluid Phase Equilib., 227(2), p157-164, 2005

[4] Horstmann S., Fischer K., Gmehling J., "Application of PSRK for Process Design", Chem.Eng.Commun., 192, p336-350, 2005

[5] Gmehling J., Li J., Fischer K., "Further development of the PSRK model for the prediction of gas solubilities and vapor-liquid-equilibria at low and high pressures", Fluid Phase Equilib., 141, p113-127, 1997

[6] Ahlers J., "Entwicklung einer universellen Gruppenbeitragszustandsgleichung", Thesis, Universität, Oldenburg, p1-144, 2003

[7] Ahlers J., Gmehling J., "Development of a universal group contribution equation of state I. Prediction of liquid densities for pure compounds with a volume translated Peng-Robinson equation of state", Fluid Phase Equilib., 191, p177-188, 2001

[8] Ahlers J., Gmehling J., "Development of a Universal Group Contribution Equation of State. 2. Prediction of Vapor-Liquid Equilibria for Asymmetric Systems", Ind.Eng.Chem.Res., 41(14), p3489-3498, 2002

[9] Ahlers J., Gmehling J., "Development of a Universal Group Contribution Equation of State III. Prediction of Vapor-Liquid Equilibria, Excess Enthalpies, and Activity Coefficients at Inifinite Dilution with the VTPR Model", Ind.Eng.Chem.Res., 41(23), p5890-5899, 2002

[10] Schmid B., Gmehling J., "From van der Waals to VTPR: The systematic improvement of the van der Waals equation of state", J.Supercrit.Fluids, 55(2), 438-447, 2010

[11] Schmid B., Gmehling J., "The universal group contribution equation of state VTPR present status and potential for process development", Fluid Phase Equilib., 302(1-2), 213-219, 2011

[12] Schmid B., "Einsatz einer modernen Gruppenbeitragszustandsgleichung für die Synthese thermischer Trennprozesse", Thesis, C.v.O. Universität Oldenburg, 2011

[13] Schmid B., Gmehling J., "Revised parameters and typical results of the VTPR group contribution equation of state", Fluid Phase Equilib., 317, 110-126, 2012

[14] Schmid B., Schedemann A., Gmehling J., "Extension of the VTPR Group Contribution Equation of State: Group Interaction Parameters for Additional 192 Group Combinations and Typical Results", Ind.Eng.Chem.Res., 53(8), 3393-3405, 2014
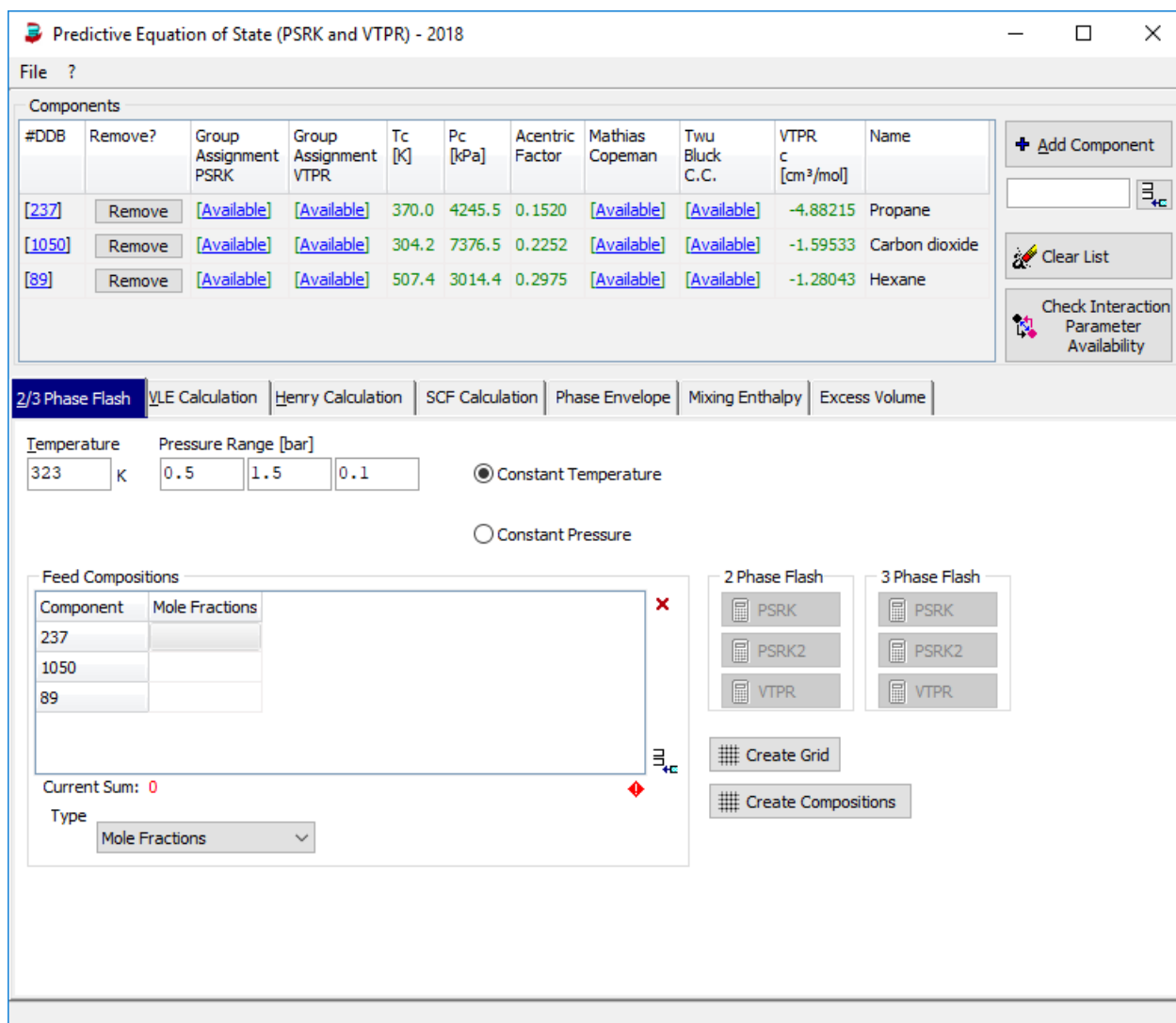
The User Interface

Figure 1: Main dialog

The main program dialog allows to enter the components in the upper half and to specify the calculation specific data in the lower half.

The Component List

The "Add Component" button calls the standard component selection dialog used throughout the DDB software package. The program is described briefly in the *Dortmund Data Bank* documentation.

The component grid is used to display the availability of parameters necessary for the calculation with either VTPR or PSRK.

Column	Explanation
#DDB	This column displays the DDB component number. The number is a link to the component editor.
Group assignment PSRK	This column displays if the PSRK group assignment for the component is available. The text is a link to the group editor (a part of the component editor).
Group assignment VTPR	This column displays if the VTPR group assignment for the component is available.
T_c	Critical temperature (read from component basic file, see component editor)
P_c	Critical pressure (read from component basic file, see component editor)
Acentric factor	Acentric factor (read from component basic file, see component editor) $$\omega = -\log_{10}\left[\lim_{T_r=0.7}\frac{P_{vp}}{P_c}\right] - 1.0$$
Mathias-Copeman	This column indicates if Mathias-Copeman constants for the description of the pure component vapor pressures are available. Mathias-Copeman constants are used in PSRK and can be replaced by the acentric factor if not available. The link shows the parameter dataset in detail. The parameters are stored in the ParameterDDB and can be fitted using the PCPEquationFit program.
Twu-Bluck-C.-C.	This column indicates if Twu-Bluck-Cunningham-Coon (TBCC) constants for the description of the pure component vapor pressures are available. TBCC parameters are used in VTPR. The link shows the parameter dataset in detail. The parameters are stored in the ParameterDDB and can be fitted by the PCPEquationFit program.
Name	Component name.

The button "Check interaction parameter availability" is needed for checking the availability of the interaction parameters between the structural groups a component is built of. The dialog has an overview page and a details page.
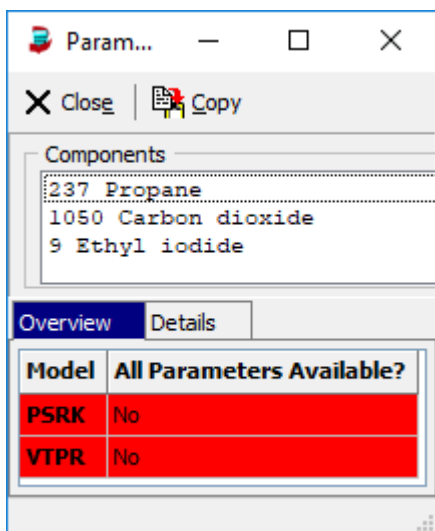
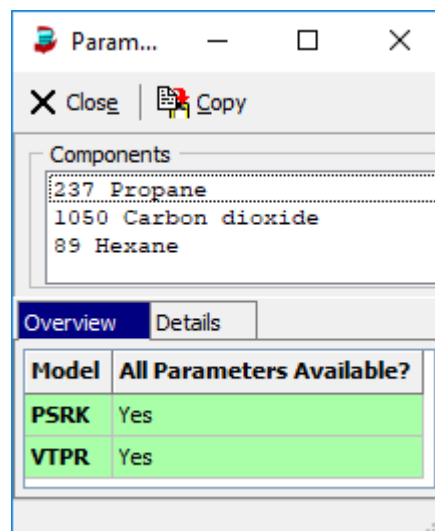**Figure 2:** Parameter check dialog overview - failure

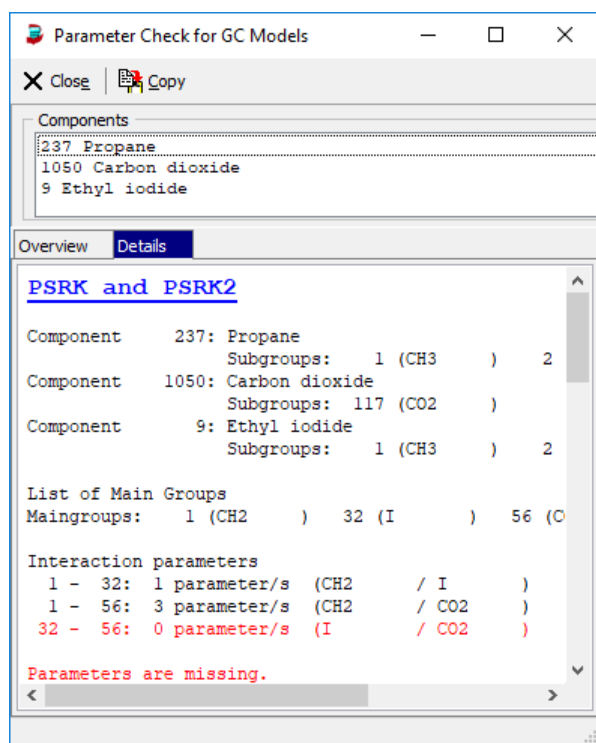**Figure 3:** Parameter check dialog overview – success

Figure 4: Parameter check dialog details – failure
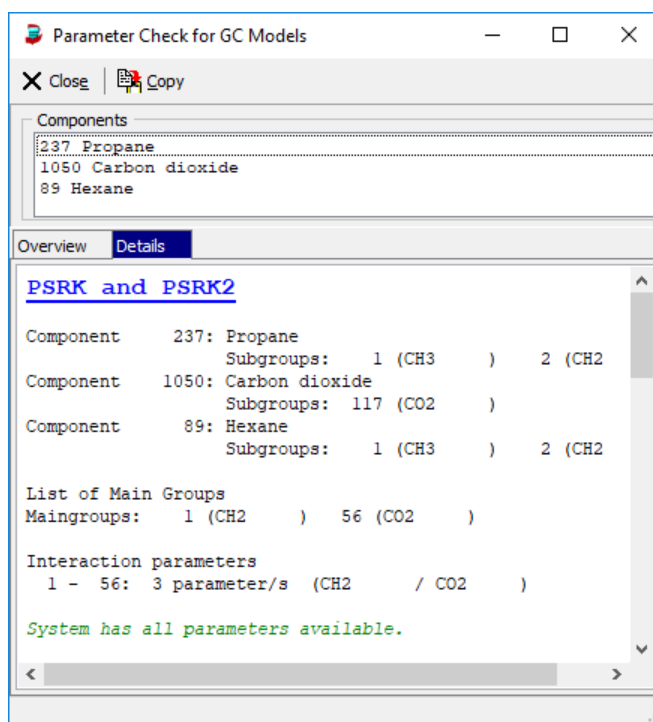
Figure 5: Parameter check dialog details – success

This details page lists all sub groups of the components and the resulting main groups and, if available, the group interaction parameters for all binary main group combinations.

The group assignments, the critical data (T_c, P_c), and the interaction parameters must be available.

The Mathias-Copeman and the Twu-Bluck-Cunningham-Coon parameters can be replaced by the acentric factor, but this will lead to higher deviations.

The Calculations

An example is presented for each calculation type.

Example 1: Flash Calculation

Consider a mixture of 5 kg 1-Butene, 4 kg cis-2-Butene, 4 kg trans-2-Butene, 8 kg iso-Butene, 2 kg NMP and 4 kg of water.

#DDB	Remove?	Group Assignment PSRK	Group Assignment VTPR	Tc [K]	Pc [kPa]	Acentric Factor	Mathias Copeman	Twu Bluck C.C.	VTPR c [cm³/mol]	Name
[368]	Remove	[Available]	[Available]	419.5	4022.6	0.1932	[Available]	[Available]	-4.52300	1-Butene
[450]	Remove	[Available]	[Available]	428.6	4103.7	0.2140	[Available]	[Available]	-4.19844	trans-2-Butene
[460]	Remove	[Available]	[Available]	435.6	4205.0	0.2020	[Available]	[Available]	-2.91929	cis-2-Butene
[457]	Remove	[Available]	[Available]	417.9	4009.8	0.1897	[Available]	[Available]	-4.23079	Isobutylene
[284]	Remove	[Available]	[Available]	721.7	4519.1	0.3577	[Available]	[Available]	17.64607	N-Methyl-2-pyr
[174]	Remove	[Available]	[Available]	647.3	22048.3	0.3440	[Available]	[Available]	4.39615	Water

Figure 6: Example system for the flash calculation.

Figure 7: Input dialog for flash calculations.

The K-values for the butenes can be predicted at a temperature of 323.15 K in the pressure range 0.5 bar < P < 1.5 bar. A step width of 0.5 bar was chosen. With these specified conditions a **2 Phase Flash** or a **3 Phase Flash** calculation can be done by pressing the corresponding button (PSRK, PSRK2, or VTPR).

```
MODEL: PSRK (UNIFAC)

#DDB COMPONENT                         TC[K]  PC[BAR]     C1       C2       C3
 368 1-BUTENE                         419.60   40.226  0.7682  -0.2460   0.9846
 450 TRANS-2-BUTENE                   428.60   41.037  0.8088   0.1826  -0.8876
 460 CIS-2-BUTENE                     435.60   42.050  0.7908   0.0588  -0.2841
 457 ISOBUTYLENE                      422.04   40.200  0.6090   1.0440  -2.2039
 284 N-METHYL-2-PYRROLIDONE           721.70   45.191  1.0170   0.0000   0.0000
 174 WATER                           647.30  220.483  1.0783  -0.5832   0.5462
```

The result output starts with the list of components showing the DDB component number, the name, critical temperature and pressure and the Mathias-Copeman or the Twu-Bluck-Cunningham-Coon constants.

The next part shows the group assignments.

```
#DDB      STRUCT. INFORMATION
 368       3  1001  1002  1005
 450       2  2001  1006
 460       2  2001  1006
 457       2  2001  1007
 284       1  1085
 174       1  1016
```

Some group specific information follow.

```
REQUIRED UNIFAC AREAS AND SURFACES:
MAIN-           SUB-
GROUP           GROUP K              R(K)    Q(K)
   1 CH2           1 CH3          0.9011  0.8480
   1 CH2           2 CH2          0.6744  0.5400
   2 C=C           5 CH2=CH       1.3454  1.1760
   2 C=C           6 CH=CH        1.1167  0.8670
   2 C=C           7 CH2=C        1.1173  0.9880
  44 NMP          85 NMP          3.9810  3.2000
   7 H2O          16 H2O          0.9200  1.4000
```

The next part shows the interaction parameters between the PSRK or VTPR main groups.

```
REQUIRED UNIFAC INTERACTION PARAMETERS:
 N  M    A(N,M)      A(M,N)       B(N,M)     B(M,N)     C(N,M)      C(M,N)
 UNIT    [K]         [K]          [-]        [-]        [1/K]       [1/K]
 1   1   0.0000      0.0000       0.0000     0.0000     0.0000      0.0000
 1   2   86.020     -35.360       0.0000     0.0000     0.0000      0.0000
 1  44   220.30      13.890       0.0000     0.0000     0.0000      0.0000
 1   7   1318.0      300.00       0.0000     0.0000     0.0000      0.0000
 2   2   0.0000      0.0000       0.0000     0.0000     0.0000      0.0000
 2  44   86.460     -16.110       0.0000     0.0000     0.0000      0.0000
 2   7   270.60      496.10       0.0000     0.0000     0.0000      0.0000
44  44   0.0000      0.0000       0.0000     0.0000     0.0000      0.0000
44   7   832.20     -452.20       0.0000     0.0000     0.0000      0.0000
 7   7   0.0000      0.0000       0.0000     0.0000     0.0000      0.0000

 N  M    A(N,M)      A(M,N)       B(N,M)     B(M,N)     C(N,M)      C(M,N)
 UNIT [cal/mol]   [cal/mol]    [cal/molK] [cal/molK] [cal/molK^2] [cal/molK^2]
 1   1   0.0000      0.0000       0.0000     0.0000     0.0000      0.0000
 1   2   170.94     -70.268       0.0000     0.0000     0.0000      0.0000
 1  44   437.78      27.602       0.0000     0.0000     0.0000      0.0000
 1   7   2619.2      596.16       0.0000     0.0000     0.0000      0.0000
 2   2   0.0000      0.0000       0.0000     0.0000     0.0000      0.0000
 2  44   171.81     -32.014       0.0000     0.0000     0.0000      0.0000
 2   7   537.74      985.86       0.0000     0.0000     0.0000      0.0000
44  44   0.0000      0.0000       0.0000     0.0000     0.0000      0.0000
44   7   1653.8     -898.62       0.0000     0.0000     0.0000      0.0000
 7   7   0.0000      0.0000       0.0000     0.0000     0.0000      0.0000
the following Peneloux constants [1/mol] are used for volume corrections:
 0.00625   0.00720   0.00798   0.00733   0.03266   0.00647
```

The next parts are the calculation results and repeated for all temperatures and pressures.

Abbreviations in the table:

Short Term	Description
I	Component (numbering order from top to bottom as in the main form's 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
phi(i),L	Liquid phase fugacity coefficient
phi(i),V	Vapor phase fugacity coefficient
fug(i)	Fugacity $\quad f = \Phi_{L}, i \cdot x_i \cdot P$ $\qquad\quad\; f = \Phi_{V}, i \cdot y_i \cdot P$

Abbreviations below the table:

Short Term	Description

Short Term	Description
N	Mole fraction (complete, liquid phase, vapor phase)
M	Mass (complete, liquid phase, vapor phase)
V	Volume (liquid phase, vapor phase)
Z	Compressibility (liquid phase, vapor phase)
V (corrected)[*]	Volume (liquid phase, vapor phase)
Rho (corrected)[*]	Density (liquid phase, vapor phase)
h-h0	Real part of enthalpy (liquid phase, vapor phase, complete system)
s-s0	Real part of entropy (liquid phase, vapor phase, complete system)

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

Example 2: Vapor-liquid equilibrium calculation

The isothermal vapor-liquid equilibrium prediction for the system carbon dioxide and *n*-eicosane at 473.15 K

#DDB	Remove?	Group Assignment PSRK	Group Assignment VTPR	Tc [K]	Pc [kPa]	Acentric Factor	Mathias Copeman	Twu Bluck C.C.	VTPR c [cm³/mol]	Name
[1050]	Remove	[Available]	[Available]	304.2	7376.5	0.2252	[Available]	[Available]	-1.59533	Carbon dioxide
[485]	Remove	[Available]	[Available]	767.0	1070.0	0.8805	[Available]	[Available]	93.8913	Eicosane

Figure 8: Example system for the VLE calculation

(stepsize liquid mole fraction: 0.05) with the modified PSRK model (PSRK 2 button) gives the following results.

Figure 9: input dialog for VLE calculations.

The component list displays the DDB number, the name, the critical temperature and pressure and the Mathias-Copeman constant resp. the Twu-Bluck-Cunningham-Coon constants.

```
Model: PSRKLi

List of components:
-------------------
No.  #DDB  Name
-----------------------
(1)  1050  Carbon dioxide
(2)   485  Eicosane

Critical data / Mathias-Copeman alpha function parameters:
----------------------------------------------------------
#DDB  Tc [K]  Pc [kPa]  C1        C2         C3
----------------------------------------------------------
1050   304.2  7376.46   0.872721  -0.722187  2.58732
 485   767    1070      1.7295     0          0
```

The structural information block shows the group assignments of all components.

```
Groups:
-------
#DDB  Groups
--------------------
1050  1   1117
 485  2   2401  18402
```

The required volumes and surfaces are group specific parameters.

```
Required R and Q values:
-----------------------
Maingroup  Name    Subgroup  Name    R         Q
-----------------------------------------------------------
       56  CO2          117  CO2     1.3       0.982
        1  CH2          401  CH3     1.20662   1.13552
        1  CH2          402  CH2     0.903059  0.72309
```

The interaction parameters have to be present for all main group pairs.

```
Required interaction parameters:
-------------------------------
N   M   A[N][M]  B[N][M]  C[N][M]    A[M][N]   B[M][N]  C[M][N]
----------------------------------------------------------------
1  56   919.8    -3.9132  0.0046309  -38.672   0.86149  -0.0017906
```

The following lines are the result of the VLE calculation.

Column	Description
*	Indicates if composition is met precisely
NO	Sequential number
IT	Number of iterations used
T	Temperature
P	Pressure
VV	Vapor volume
VL	Liquid volume
X1	Liquid mole fraction of component 1 (carbon dioxide in this example)
Y1	Vapor mole fraction of component 1

The output is finished if a critical point has been identified or the complete composition range has been calculated. If an azeotropic point has been identified it will be displayed in the table. Beside these tables several plots are generated. These plots can be printed, saved and copied to the Windows clipboard.
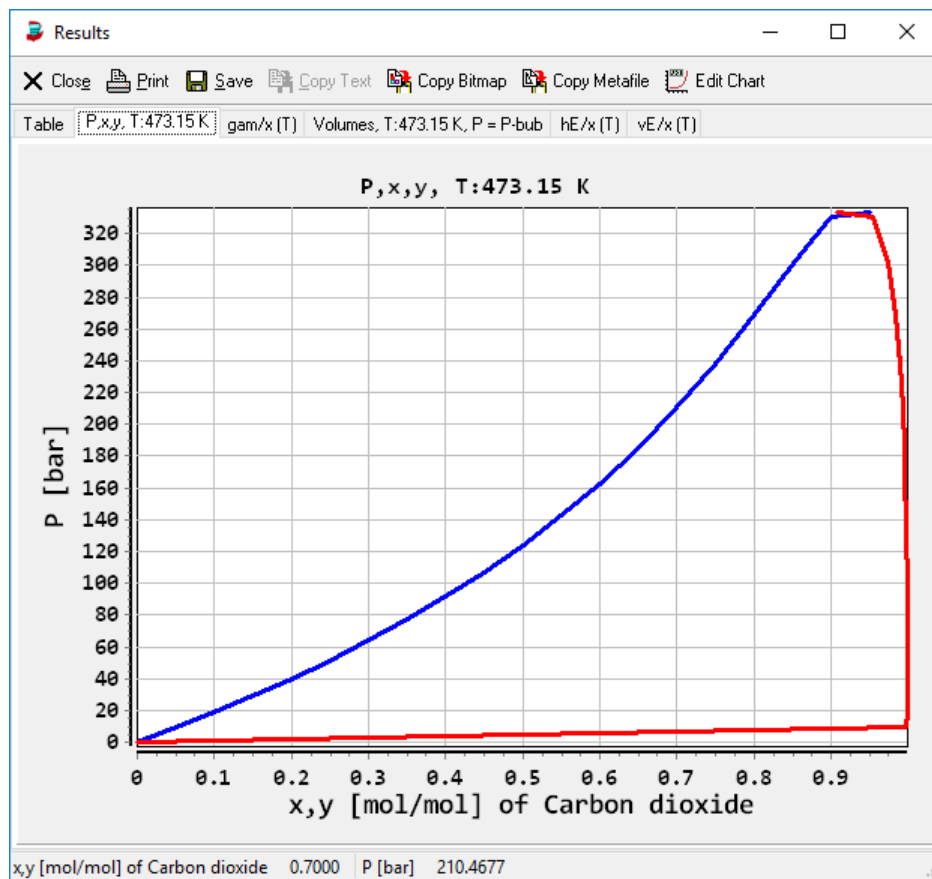
Figure 10: Plot window

Example 3: Gas Solubilities

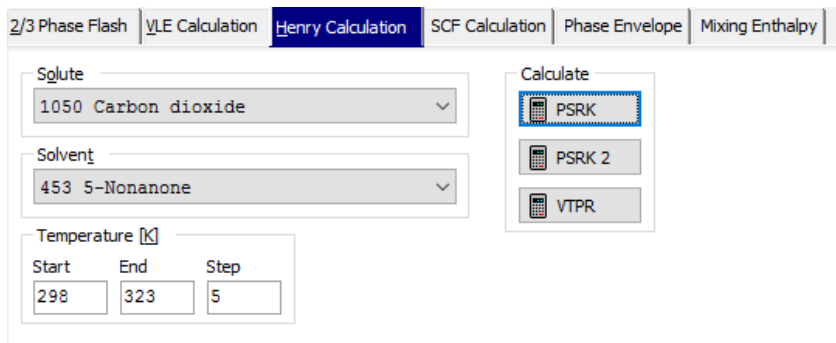Gas solubilities are calculated as Henry coefficients.

Figure 11: Input dialog for Henry calculations.

The "Henry Calculation" page allows specifying a solute and a solvent. Both can be selected from the entire component list. Additionally a temperature range and a step width have to be specified.

The result of a calculation is (after the same heading lines as shown for the VLE calculation) a data table

```
Calculation of Henry coefficients
Solute:    1050  Carbon dioxide
Solvent:    453  5-Nonanone

    T [K]   H12 [bar] Psat2 [bar]   vL [l/mol]   vV [l/mol]
---------------------------------------------------------------
   298.00     54.5180      0.0020      0.17668    12095.312
   303.00     58.7669      0.0027      0.17730     9217.368
   308.00     63.1058      0.0036      0.17793     7088.175
   313.00     67.5214      0.0047      0.17857     5498.029
   318.00     72.0003      0.0061      0.17924     4299.759
   323.00     76.5293      0.0079      0.17992     3389.035
```

With

Column	Description
T	Temperature
Henry	Henry coefficient
PSAT2	Saturated vapor pressure
VL	Liquid volume
VV	Vapor volume
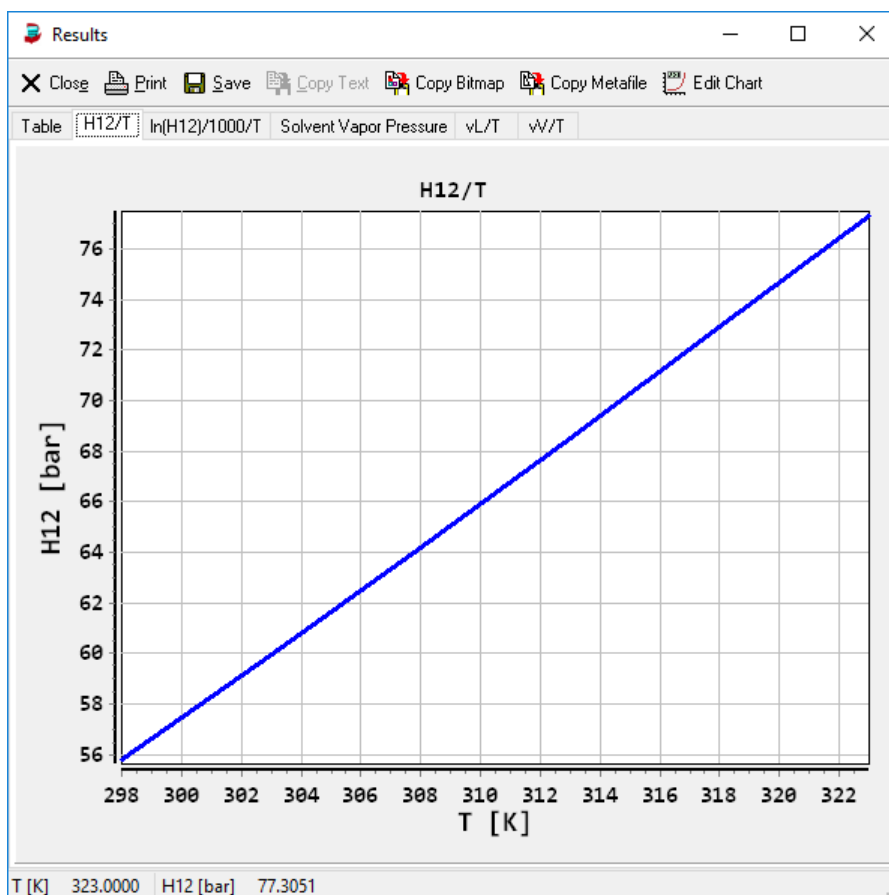
Figure 12: Plot outputs for Henry calculations.

Example 4: Solubilities in Supercritical Solvents (SCF calculation)

This type of calculation allows the prediction of the solubility of solids like anthracene in a supercritical solvent like carbon dioxide.

Figure 13: SCF calculation.

Additionally needed data are sublimation equation parameters either for the Antoine equation or vapor pressure parameter for either the Mathias-Copeman (PSRK) or the Twu-Bluck-Cunningham-Coon equation (VTPR). For the latter equation additionally a heat of fusion value and a melting temperature are needed.

Antoine parameters in mmHg and °C can be entered directly in the edit control if parameters are not available from the Dortmund Data Bank.

The solid volumes in liters per square meter are directly read from the Dortmund Data Bank (pure component properties). If this data bank is not available or doesn't contain the necessary data it is possible to enter data directly.

The co-solvent combo box allows specifying a single additional solvent.
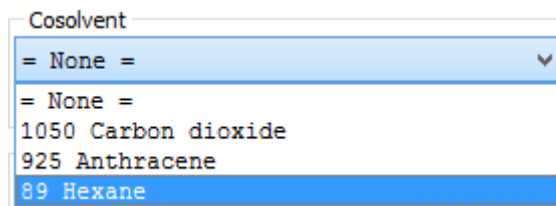
The only necessary information is the mole fraction of this co-solvent.

The result of a SCF calculation is a data table and a diagram.

```
P[bar] VV[l/mol]    Y(2)     log(y2)  PHI(2)    POYN(2)    Y(1)
--------------------------------------------------------------------------
 2.00  14.47   0.19903E-05  -5.7011   0.93463    1.0090   0.99999801
 4.00   7.192  0.10748E-05  -5.9687   0.87313    1.0180   0.99999893
 6.00   4.767  0.77423E-06  -6.1111   0.81531    1.0272   0.99999923
 8.00   3.554  0.62773E-06  -6.2022   0.76097    1.0364   0.99999937
10.00   2.826  0.54314E-06  -6.2651   0.70990    1.0457   0.99999946
.....
```

The table contains the solubilities of the high-boiling component in the "Y(2)" column as mole fractions. The calculation is automatically performed for a pressure range from 2 to 600 bar. "VV" is the vapor volume, "PHI" the fugacity and "POIN" the Poynting factor.

Beside the table a diagram showing the pressure-dependency of the (logarithmic) solubility is displayed.
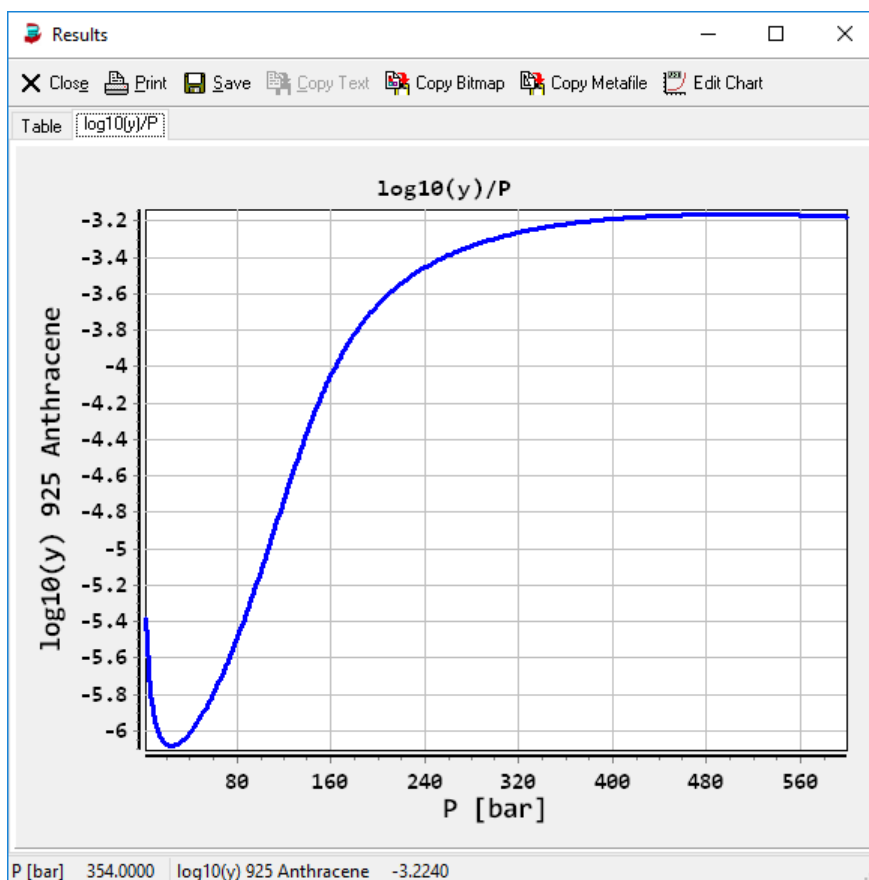
Figure 14: Calculation result.

Example 5: Phase Envelope Calculation

Phase envelopes are dew point and bubble point curves of a mixture at a given constant composition.

Figure 15: Phase envelope calculation input dialog.

The result is a pressure vs. temperature diagram showing the both curves and a table with the compositions, the pressure and temperature.
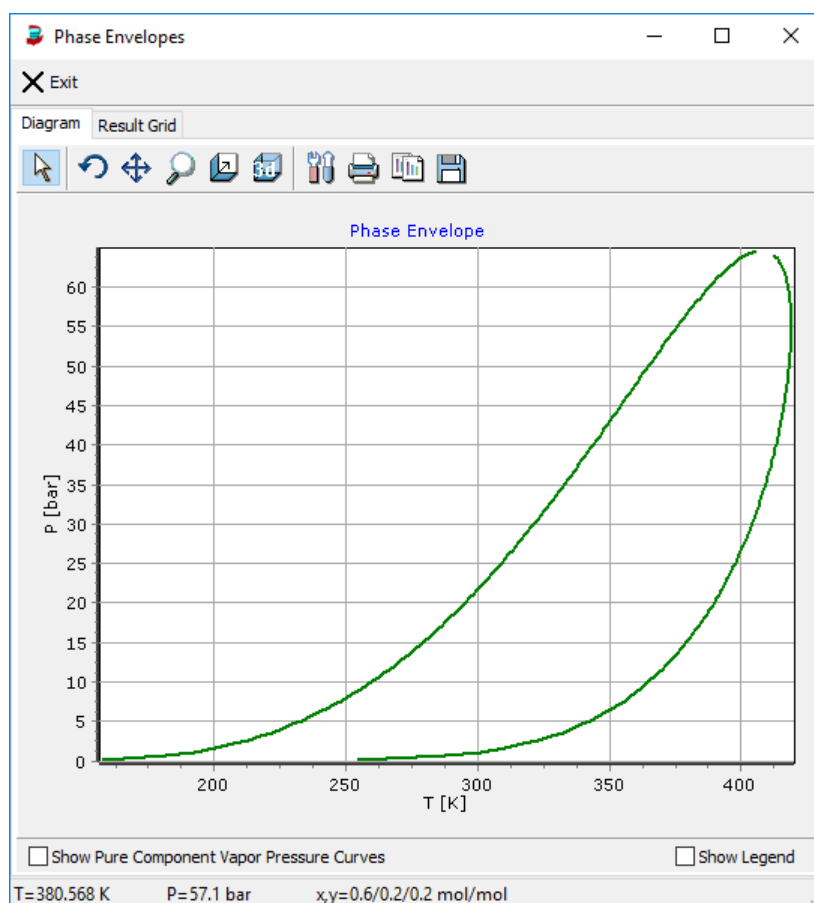
Figure 16: Calculation result window.

Example 6: Excess Enthalpy Calculation

The excess enthalpy can be calculated from the "Mixing Enthalpy" tab.

Figure 17: Calculation input tab for the excess enthalpy calculation.

The result is obtained as table and graph as described before:
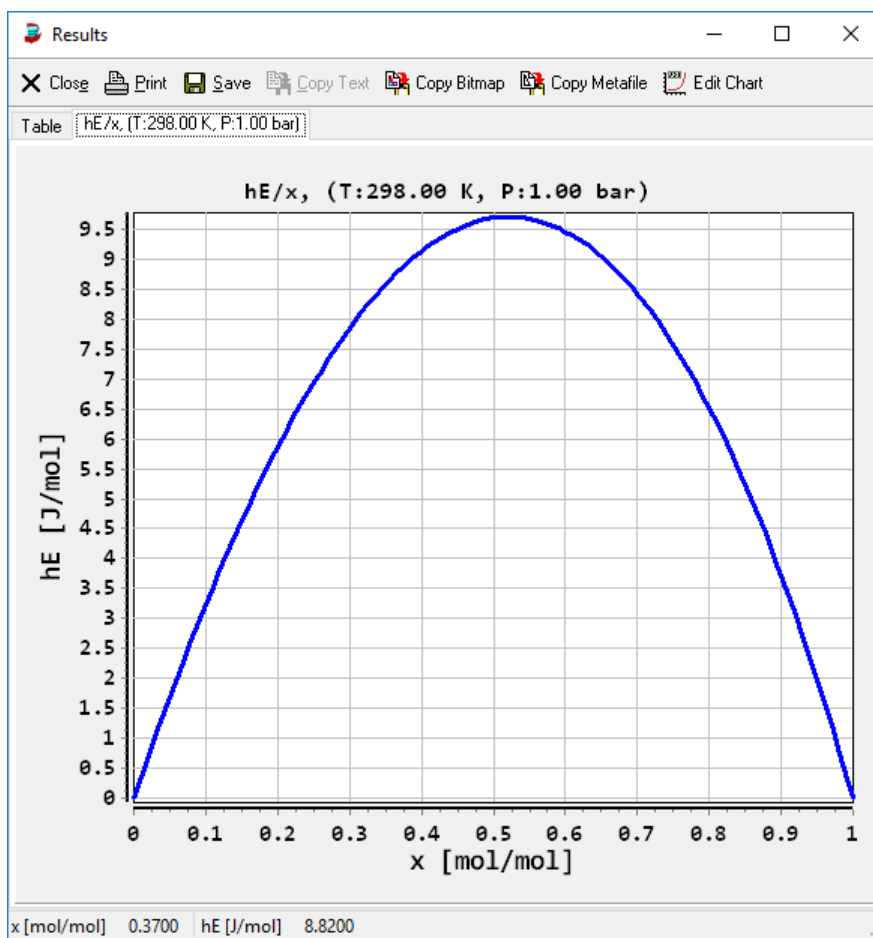
Example 7: Excess Volume Calculation

The excess volumes can be calculated in the "Excess Volume" page:

Figure 18: Calculation input tab for the excess volume calculation

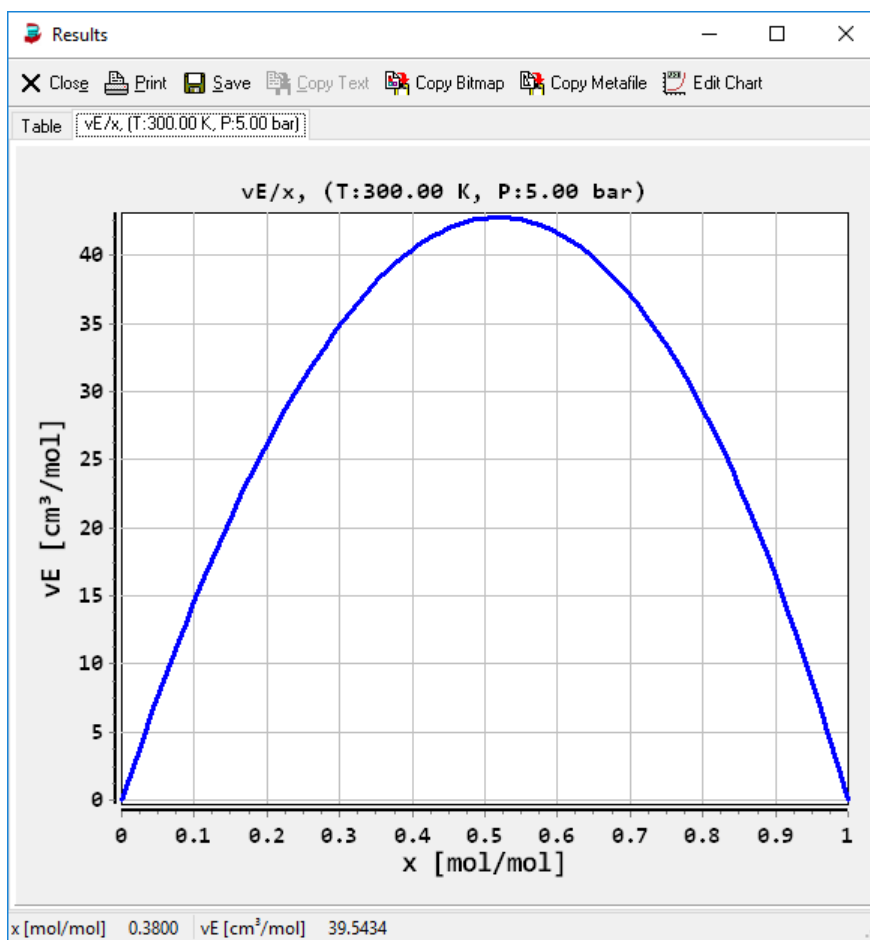The result is available as table and as diagram:

Figure 19: Excess volume diagram

Known Issues

- Sometimes the 3 Phase Flash Algorithm reports miscibility gaps where no LLE is present. The reason for this problem seems to be that more than one (obviously liquid) real solution for the cubic EOS is found and the stability calculation gives plausible results.

- Performing 2 Phase Flash calculations under conditions where only one phase exists results in plot options that are somewhat misleading. Although, for example, no vapor phase was found it's possible to plot the vapor density against the temperature. The density values displayed are all 0.0 because this is the initialized value for the variable. More plausible plot options will be presented in the next version.