

Predictive Equation of State

*Vapor-liquid Equilibria, Gas Solubilities and
Phase Flash Calculations*

PSRK - *Predictive Soave-Redlich-Kwong*

VTPR - *Volume-Translated Peng-Robinson*

DDBSP - Dortmund Data Bank Software Package



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Introduction

This software allows the prediction of multicomponent vapor-liquid equilibria (VLE), vapor-liquid-liquid-equilibria (VLLE) and gas solubilities (GLE) with the group contribution equation of state models PSRK^{1,2,3,4,5} and VTPR^{6,7,8,9}.

Both models allow reliable predictions of phase equilibria for polar and non-polar systems as well as asymmetric system over a wide temperature and pressure range. Even systems containing supercritical components can be calculated precisely.

The program PredictiveEOS allows to specify the components of the desired system, to enter necessary data like compositions and temperatures and pressures and it will display the result 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.Comm., 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 an 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 Infinite Dilution with the VTPR Model", Ind.Eng.Chem.Res., 41(23), p5890-5899, 2002

The User Interface

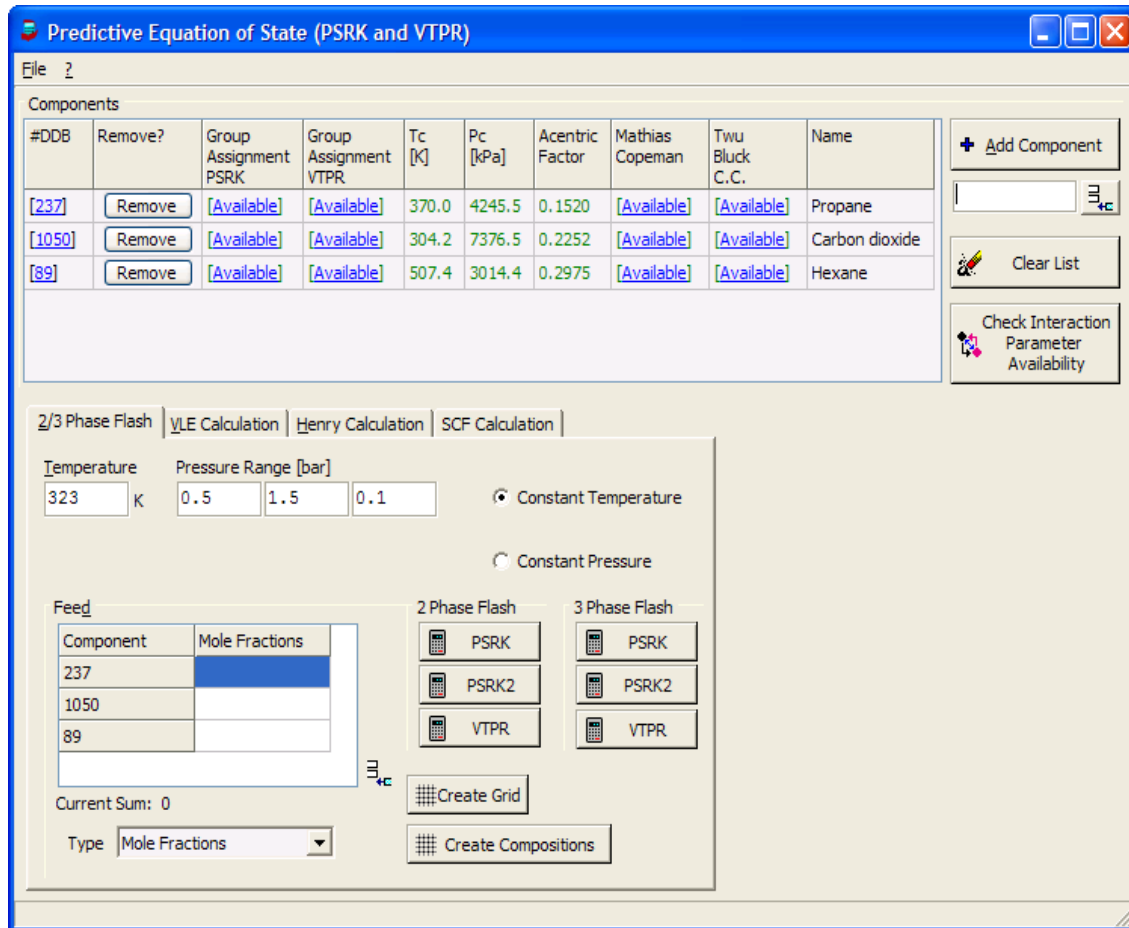


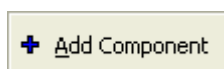
Figure 1 Main Dialog

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

#DDB	Group Assignment PSRK	Group Assignment VTPR	Tc [K]	Pc [kPa]	Acentric Factor	Mathias Copeman	Twu Bluck C.C.	Name
[237]	[Available]	[Available]	370.0	4245.5	0.1520	[Available]	[Available]	Propane
[1050]	[Available]	[Available]	304.2	7376.5	0.2252	[Available]	[Available]	Carbon dioxide
[89]	[Available]	[Available]	507.4	3014.4	0.2975	[Available]	[Available]	Hexane


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.

<i>Column</i>	<i>Explanation</i>
#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.
Tc	Critical temperature (read from component basic file, see component editor)
Pc	Critical pressure (read from component basic file, see component editor)
Acentric factor	Acentric factor (read from component basic file, see component editor) $\omega = -\log_{10} \left[\lim_{T_r=0.7} \left(\frac{P_{vp}}{P_c} \right) \right] - 1.0$
Mathias-Copeman	This column indicates where 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 details. The parameters are stored in the ParameterDDB and can be fitted by the PCPEquationFit program.
Twu-Bluck-C.-C.	This column indicates whether 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 details. The parameters are stored in the ParameterDDB and can be fitted by the PCPEquationFit program.
Name	Component name.

The button  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.

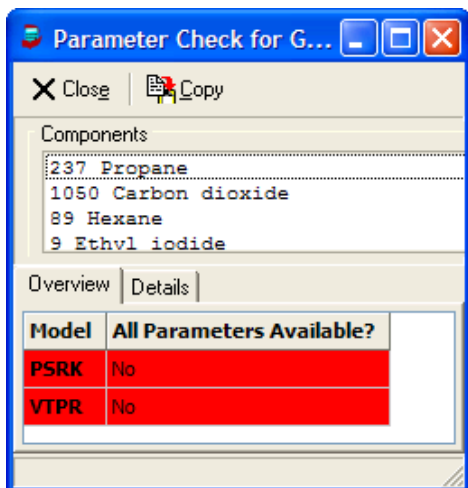


Figure 2 Parameter Check Dialog Overview - Failure

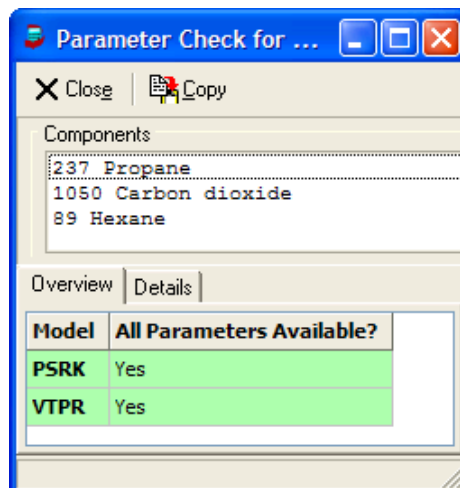


Figure 3 Parameter Check Dialog Overview - Success

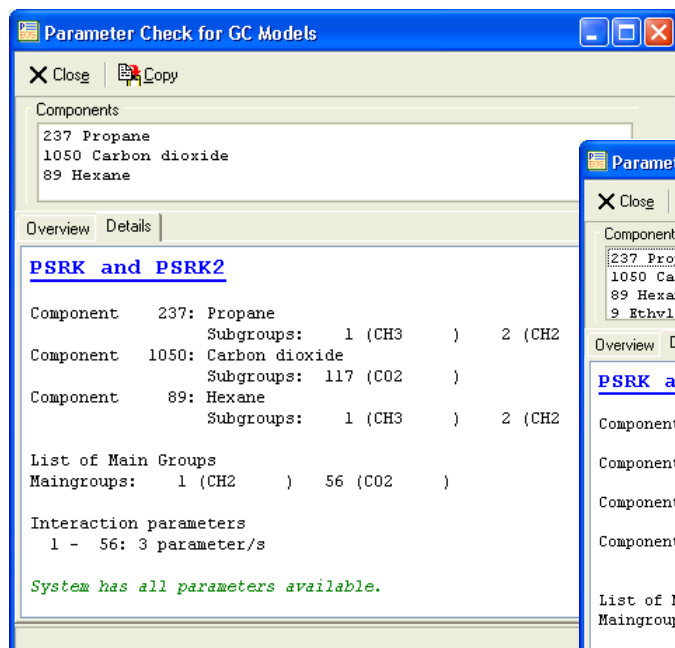


Figure 4 Parameter Check Details- Success

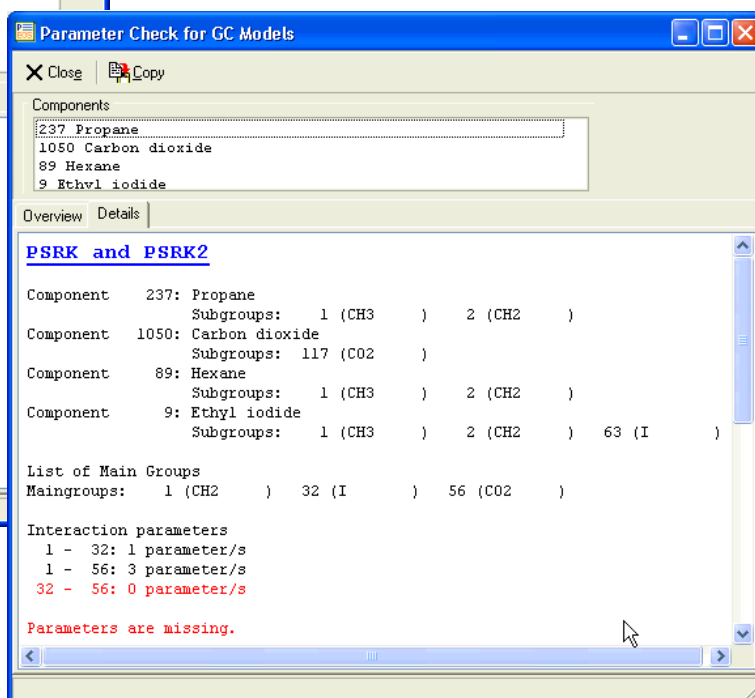


Figure 5 Parameter Check Details - Failure

This details page lists all sub groups of the single components and the resulting list of main groups and if parameters are available 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

For each of the three possible calculations an example is presented.

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, 25 kg NMP and 4 kg of water.

#DDB	Group Assignment PSRK	Group Assignment VTPR	Tc [K]	Pc [kPa]	Acentric Factor	Mathias Copeman	Twu Bluck C.C.	Name
[368]	[Available]	[Available]	419.6	4022.6	0.1870	[Available]	[Available]	1-Butene
[450]	[Available]	[Available]	428.6	4103.7	0.2140	[Available]	[Available]	trans-2-Butene
[460]	[Available]	[Available]	435.6	4205.0	0.2020	[Available]	[Available]	cis-2-Butene
[457]	[Available]	[Available]	422.0	4020.0	0.1900	[Available]	[Available]	Isobutylene
[284]	[Available]	[Available]	721.7	4519.1	0.3577	[Available]	[Available]	N-Methyl-2-pyrrolidone
[174]	[Available]	[Available]	647.3	22048.3	0.3440	[Available]	[Available]	Water

Figure 6 Example System for Flash Calculation

Figure 7 Input Dialog for Flash Calculation

The K-values for the butenes can be predicted at a temperature of 323.15 K in the pressure range $0.5 \text{ bar} < P < 1.5 \text{ bar}$. 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).

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.

```

MODEL: PSRK

KUERZ 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 next part shows the group assignments.

```

KUERZ STRUCT. INFORMATION
368 3 1001 1002 1005 0 0 0 0 0 0 0 0
450 2 2001 1006 0
460 2 2001 1006 0
457 2 2001 1007 0
284 1 1085 0 0
174 1 1016 0 0
    
```

Some group specific information follow.

```

REQUIRED UNIFAC AREAS AND SURFACES:
MAIN- SUB-
GROUP GROUP K R(K) Q(K)
1 1 0.9011 0.8480
1 2 0.6744 0.5400
2 5 1.3454 1.1760
2 6 1.1167 0.8670
2 7 1.1173 0.9880
44 85 3.9810 3.2000
7 16 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)
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
the following peneloux constants [l/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.

```

TEMPERATURE: 323.00 K
PRESSURE : 0.5000 BAR

I Z(I) F*Z X(I) L*X Y(I) V*Y K(I) phi(i),L phi(i),V fug(i)/bar
-----
1 0.10503E+000 0.10503E+000 0.23991E-002 0.12445E-002 0.21564E+000 0.10378E+000 0.89885E+002 0.89051E+002 0.99072E+000 0.10682E+000
2 0.84018E-001 0.84018E-001 0.21090E-002 0.10940E-002 0.17230E+000 0.82924E-001 0.81697E+002 0.80901E+002 0.99026E+000 0.85311E-001
3 0.84018E-001 0.84018E-001 0.23205E-002 0.12037E-002 0.17207E+000 0.82814E-001 0.74154E+002 0.73421E+002 0.99012E+000 0.85186E-001
4 0.16803E+000 0.16803E+000 0.31660E-002 0.16423E-002 0.34573E+000 0.16639E+000 0.10920E+003 0.10819E+003 0.99070E+000 0.17126E+000
5 0.29722E+000 0.29722E+000 0.57060E+000 0.29598E+000 0.25659E-002 0.12349E-002 0.44969E-002 0.43692E-002 0.97160E+000 0.12465E-002
6 0.26168E+000 0.26168E+000 0.41941E+000 0.21756E+000 0.91682E-001 0.44124E-001 0.21860E+000 0.21725E+000 0.99382E+000 0.45558E-001

N [MOL] 1.00000 0.51873 0.48127
M [G] 58.93 33.55 25.38
V [L/MOL] 0.0855 53.21
Z=PV/RT 0.0016 0.9907
V (Corrected) 0.0641 53.20
Rho [g/ccm] (Corrected) 1.0094 0.001
h-h0 [J/mole] -51754E+005 -72967E+002 total (J):-26882E+005
s-s0 [J/mole/K] -12950E+003 -14875E+000 total (J/K):-67249E+002
    
```

Abbreviations in the table:

<i>Short Term</i>	<i>Description</i>
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 $f = \phi_L, i \cdot x_i \cdot P$ $f = \phi_V, i \cdot y_i \cdot P$

Abbreviations below the table:

<i>Short Term</i>	<i>Description</i>
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

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

#DDB	Group Assignment PSRK	Group Assignment VTPR	Tc [K]	Pc [kPa]	Acentric Factor	Mathias Copeman	Twu Bluck C.C.	Name
[1050]	[Available]	[Available]	304.2	7376.5	0.2252	[Available]	[Available]	Carbon dioxide
[485]	[Available]	[Available]	767.0	1070.0	0.8805	[Available]	[Available]	Eicosane

Figure 8 Example System for VLE Calculation

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

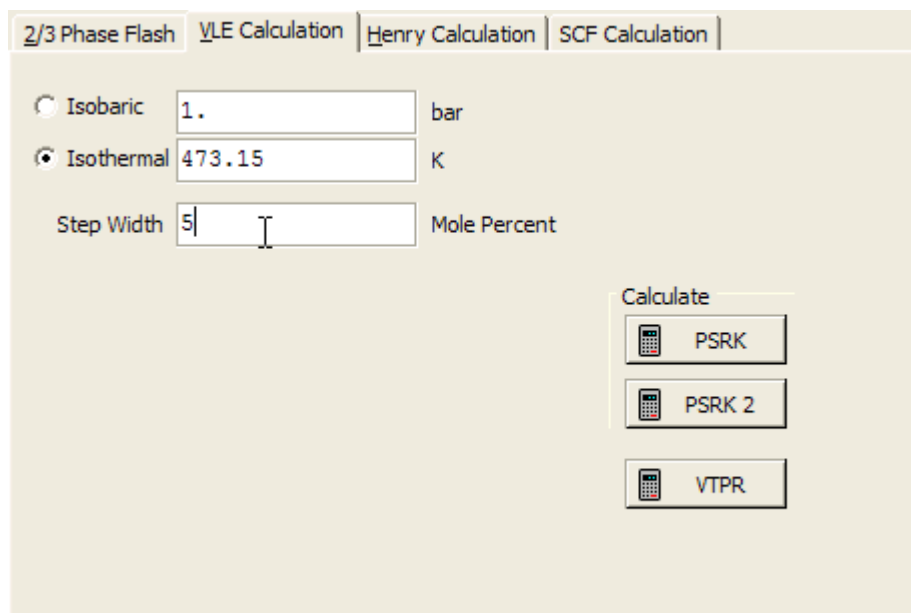


Figure 9 Input Dialog for VLE Calculations

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.

KUERZ	COMPONENT	TC [K]	PC [BAR]	C1	C2	C3
1050	CARBON DIOXIDE	304.20	73.765	0.8250	0.1676	-1.7039
485	EICOSANE	767.00	10.700	1.7295	0.0000	0.0000

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

KUERZ	STRUCT. INFORMATION		
1050	1	1117	0
485	2	2401	18402

The required areas and surfaces are group specific parameters.

REQUIRED UNIFAC AREAS AND SURFACES:					
MAIN-GROUP		SUB-GROUP K		R (K)	Q (K)
56	CO2	117	CO2	1.3000	0.9820
1	CH2	401	20*	1	1.1355
1	CH2	402	20*	2	0.7231

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

REQUIRED UNIFAC INTERACTION PARAMETERS:							
N	M	A (N,M)	A (M,N)	B (N,M)	B (M,N)	C (N,M)	C (M,N)
56	56	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
56	1	-38.672	919.80	0.86149	-3.9132	-0.17906E-02	0.46309E-02
1	1	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000

The following lines are the result of the VLE calculation.

Column	Description
*	Indicates if composition is met precisely

<i>Column</i>	<i>Description</i>
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 mole fraction range has been calculated.

NO	IT	T[K]	P[BAR]	VV [L/MOL]	VL	X1	Y1
* 1	4	473.15	.15296E-01	2564.5	0.60337	0.00000	0.00000
* 2	3	473.15	8.8090	4.4348	0.57786	0.05000	0.99780
* 3	2	473.15	18.094	2.1442	0.55232	0.10000	0.99863
* 4	2	473.15	27.921	1.3795	0.52676	0.15000	0.99886
* 5	2	473.15	38.352	0.99695	0.50117	0.20000	0.99891
* 6	1	473.15	49.456	0.76726	0.47556	0.25000	0.99888
* 7	2	473.15	61.314	0.61406	0.44992	0.30000	0.99879
* 8	1	473.15	74.023	0.50461	0.42425	0.35000	0.99863
* 9	3	473.15	87.696	0.42252	0.39855	0.40000	0.99840
* 10	3	473.15	102.47	0.35873	0.37282	0.45000	0.99808
* 11	2	473.15	118.49	0.30777	0.34706	0.50001	0.99762
* 12	1	473.15	135.97	0.26622	0.32127	0.55001	0.99696
* 13	2	473.15	155.10	0.23180	0.29545	0.60001	0.99602
* 14	2	473.15	176.16	0.20300	0.26962	0.65001	0.99463
* 15	1	473.15	199.38	0.17881	0.24381	0.70001	0.99253
* 16	3	473.15	224.99	0.15866	0.21807	0.75001	0.98924
* 17	3	473.15	252.92	0.14248	0.19253	0.80001	0.98382
* 18	2	473.15	282.15	0.13098	0.16754	0.85001	0.97426
* 19	3	473.15	308.15	0.12685	0.14415	0.90002	0.95547
* 20	-5	473.15	311.62	0.14021	0.12743	0.95002	0.90933
CRITICAL POINT DETECTED							

If an azeotropic point has been identified it will be displayed in the table.

The following lines are special representations of the calculation result table above and are used for plot outputs. They are abbreviated here.

```

YXX
P,x,y, T:473.15 K
x(1),y(1)
Pressure [bar]
 0.15296E-01  0.00000000  0.00000000
 8.8090      0.05000005  0.99780032
.....
=====

```

```

YX
HL(x), T:473.15 K, P = P-bubble
x(1)
HL [J/mole]
 -76738.      0.0000
 -72782.      0.50000E-01
.....

```

```

=====
YX
HV(y), T:473.15 K, P = P-dew
y(1)
HV [J/mole]
 -34.822      0.0000
 -153.46      0.99780
.....
=====
YX
hE(x), T:473.15 K, P:623.27 bar
x(1)
hE(L) [J/mole]
 0.0000      0.0000
 91.070      0.50000E-01

```

```

.....
=====
YX
hE(y), T:473.15 K, P: 0.00 bar
y(1)
hE(V) [J/mole]
  0.0000      0.0000
  0.74852E-01 0.99780
  0.72461E-01 0.99863
.....
=====
YX
vE(x), T:473.15 K, P = P-bubble
x(1)
vE [ccm/mole]
  0.0000      0.0000
 -1.7135      0.50000E-01
.....
=====
YXX
phi(x), T:473.15 K, P = P-bub
phi(1,2),L
x(1)
  0.0000      11194.      0.99718
  0.50000E-01 19.823      0.19816E-02
.....
=====
YXX
phi(y), T:473.15 K, P = P-dew
phi(1,2),V
y(1)
  0.0000      1.0026      0.99718
  0.50000E-01 0.99335      0.85583
.....
=====

```

Beside these tables several plots are generated.

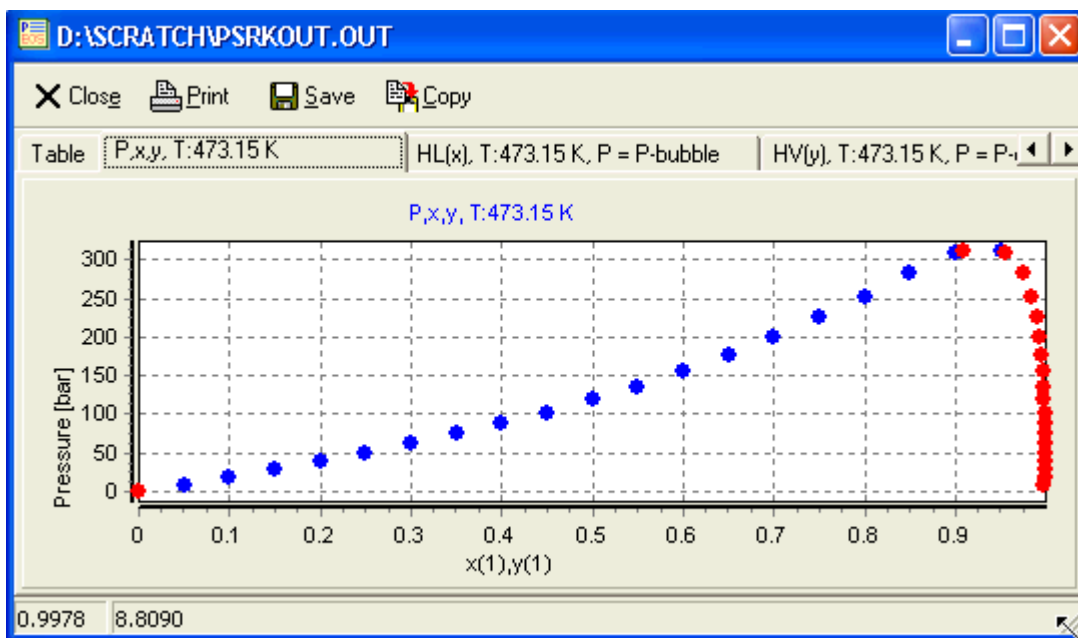


Figure 10 Plot Outputs for VLE Calculation

These plots can be printed, saved and copied to the Windows clipboard.

Example 3 Gas Solubilities

Gas solubilities are calculated as Henry coefficients.

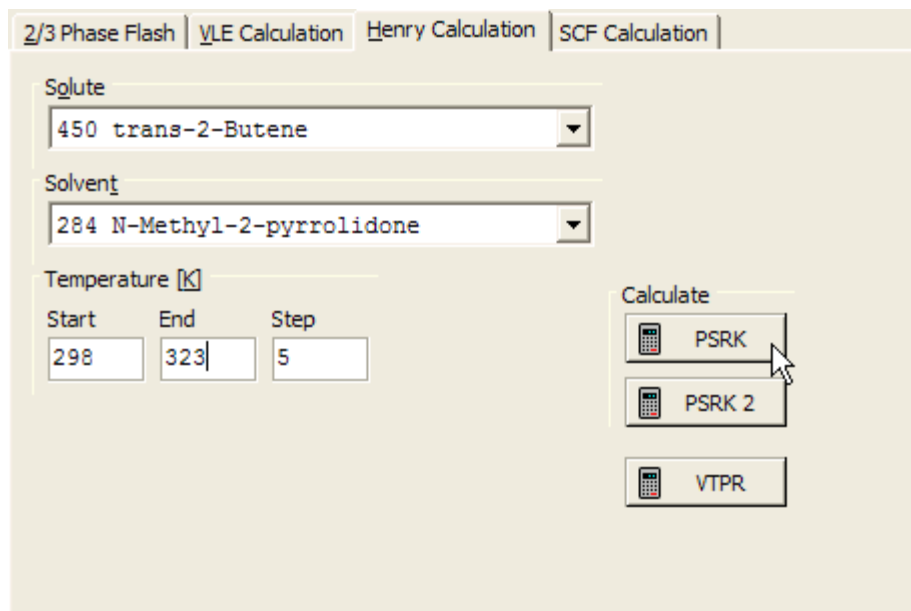


Figure 11 Input Dialog for Henry Calculations

The “Henry Calculation” page allows to specify 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 table

T[K]	HENRY [BAR]	PSAT2 [BAR]	VL [L/MOL]	VV
298.00	9.1089	0.0005	0.12708	54198.
303.00	10.4654	0.0007	0.12743	38248.
308.00	11.9560	0.0009	0.12779	27355.
313.00	13.5853	0.0013	0.12816	19813.
318.00	15.3572	0.0018	0.12854	14525.
323.00	17.2749	0.0025	0.12892	10770.

(SOLVENT IS COMPONENT 2)

with

<i>Column</i>	<i>Description</i>
T	Temperature
Henry	Henry coefficient
PSAT2	Saturated vapor pressure
VL	Liquid volume
VV	Vapor volume

The following lines are other representations of the table above and are used for creating plots.

XY	Henry vs. Temperature	Henry [bar]
	T [K]	298.00 9.1089

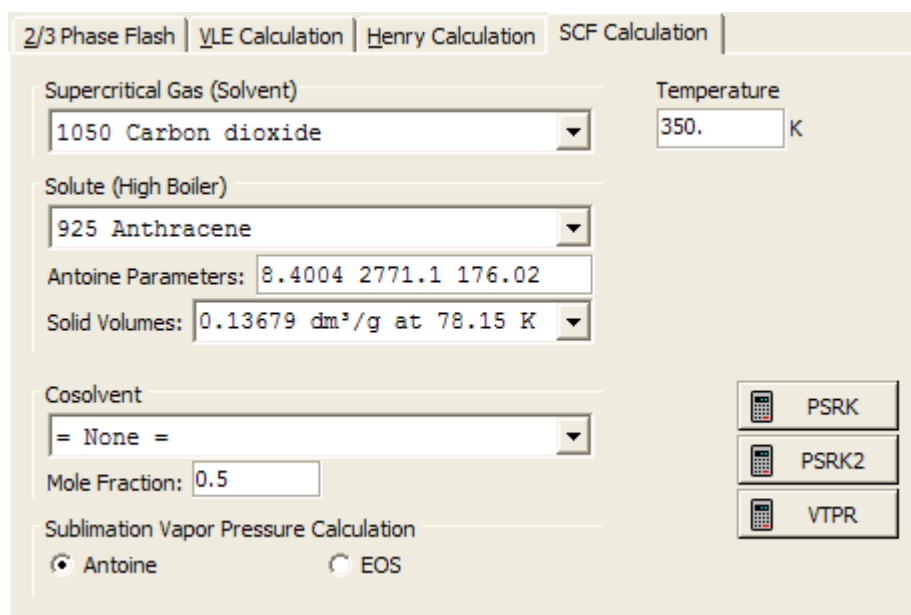
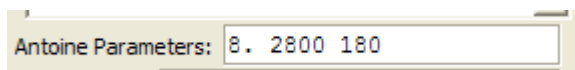


Figure 13: SCF Calculation

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.

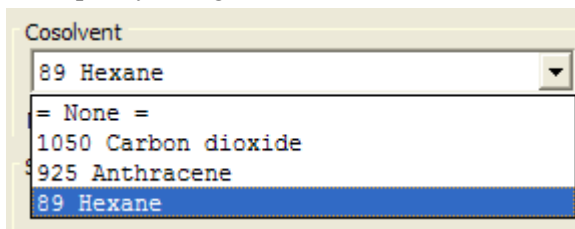
Antoine parameters in mmHg and °C can be entered directly in the edit control if parameters are not available from the Dortmund Data Bank.



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 Cosolvent combo box allows to specify a single additional solvent.



The only necessary information is the mole fraction of this co-solvent.

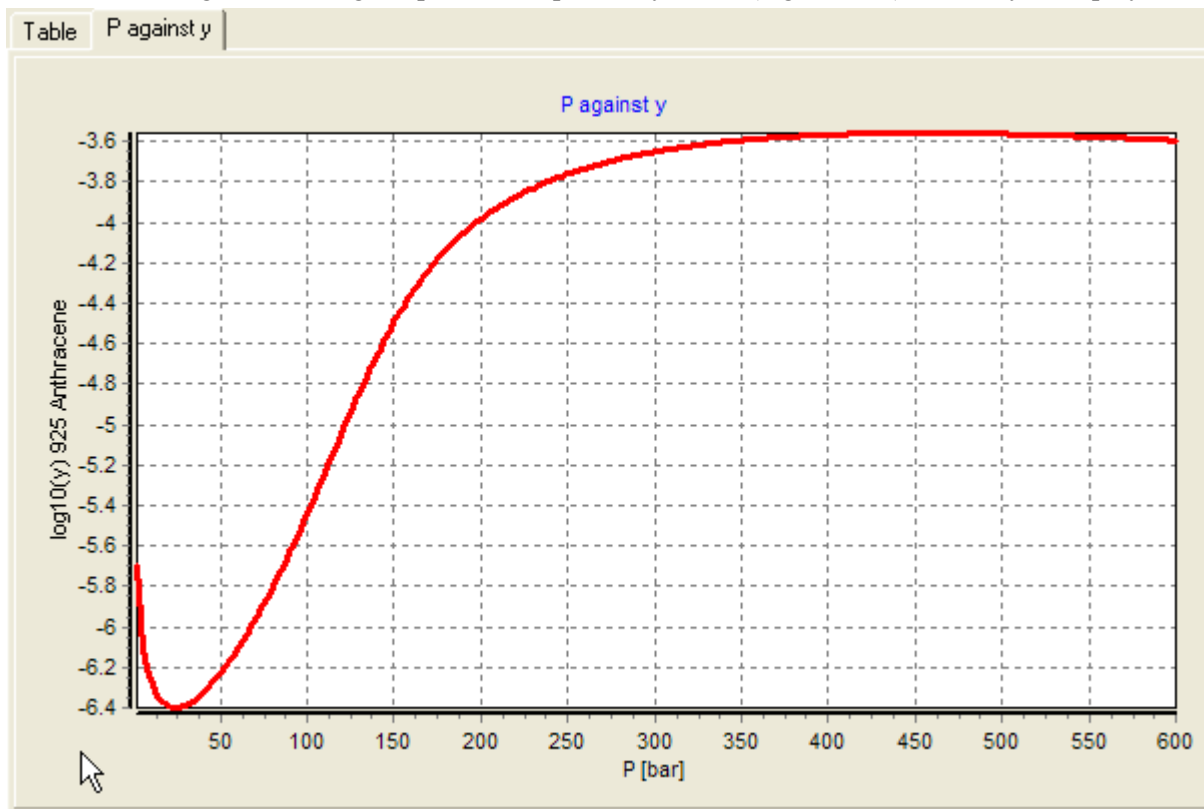
The result of a SCF calculation are a data table and a diagram.

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 for a pressure range from 2 to 600 bar. “VV” is the vapor volume, “PHI” is the fugacity, and “POIN” the poynting factor.

Beside the table a diagram showing the pressure-dependency of the (logarithmic) solubility is displayed.



Known Problems

- 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 solutions for the cubic EOS were 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 its 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.