UNIFAC

Documentation

DDBSP – Dortmund Data Bank Software Package

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1 Introduction

This software allows calculating activity coefficients, heats of mixing and excess heat capacity by the activity coefficient models UNIFAC[1], modified UNIFAC (Dortmund)[2] and NIST modified UNIFAC for mixtures with up to fifty components.

It is also possible to calculate the liquid-liquid equilibrium for binary and ternary systems.

The software is an integral part of the Dortmund Data Bank software package and uses the component, the group assignment and other tools from this package. The package therefore includes

1. The main calculation program (described here)
2. A component selection tool (described in "ComponentManagement.pdf")
3. A component editing tool (described in "ComponentManagement.pdf")
4. A UNIFAC interaction parameter editor (described in "GC Model Parameters.pdf")
5. A DDB configuration editing tool (described in "DDBConfiguration.pdf")

The latest UNIFAC parameters have been published in 2003[3], the latest parameter for mod. UNIFAC (Dortmund) have been published 2002[4], 2006[5], 2011 (ionic liquids)[6] and 2016[7].

Most current parameters can be obtained from the UNIFAC Consortium.

1.1 Tutorial

This tutorial shows all functions inside the main calculation software. Additional PDFs are available for editing, adding, and searching components, as well as for modifying/understanding the DDB configuration, and the interaction parameter editor.

[1]Fredenslund A., Jones R.L., Prausnitz J.M., "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures", AIChE J., 21(6), 1086-1099, 1975

[2]Weidlich U., Gmehling J., "A Modified UNIFAC Model. 1. Prediction of VLE, hE, and γ^{∞}", Ind. Eng. Chem. Res., 26(7), 1372-1381, 1987

[3]Wittig R., Lohmann J., Gmehling J., "Vapor-Liquid Equilibria by UNIFAC Group Contribution. 6. Revision and Extension", Ind. Eng. Chem. Res., 42(1), 183-188, 2003

[4]Gmehling J., Wittig R., Lohmann J., Joh R., "A Modified UNIFAC (Dortmund) Model. 4. Revision and Extension", Ind. Eng. Chem. Res., 41(6), 1678-1688, 2002

[5]Jakob A., Grensemann H., Lohmann J., Gmehling J., "Further Development of Modified UNIFAC (Dortmund): Revision and Extension 5", Ind. Eng. Chem. Res., 45(23), 7924-7933, 2006

[6]Nebig S., Gmehling J., "Prediction of phase equilibria and excess properties for systems with ionic liquids using modified UNIFAC: Typical results and present status of the modified UNIFAC matrix for ionic liquids", Fluid Phase Equilib., 302(1-2), 220-225, 2011

[7] Constantinescu D., Gmehling J., „Further Development of Modified UNIFAC (Dortmund): Revision and Extension 6" J. Chem. Eng. Data 2016, 61, 2738−2748.

1.1.1 Building a System

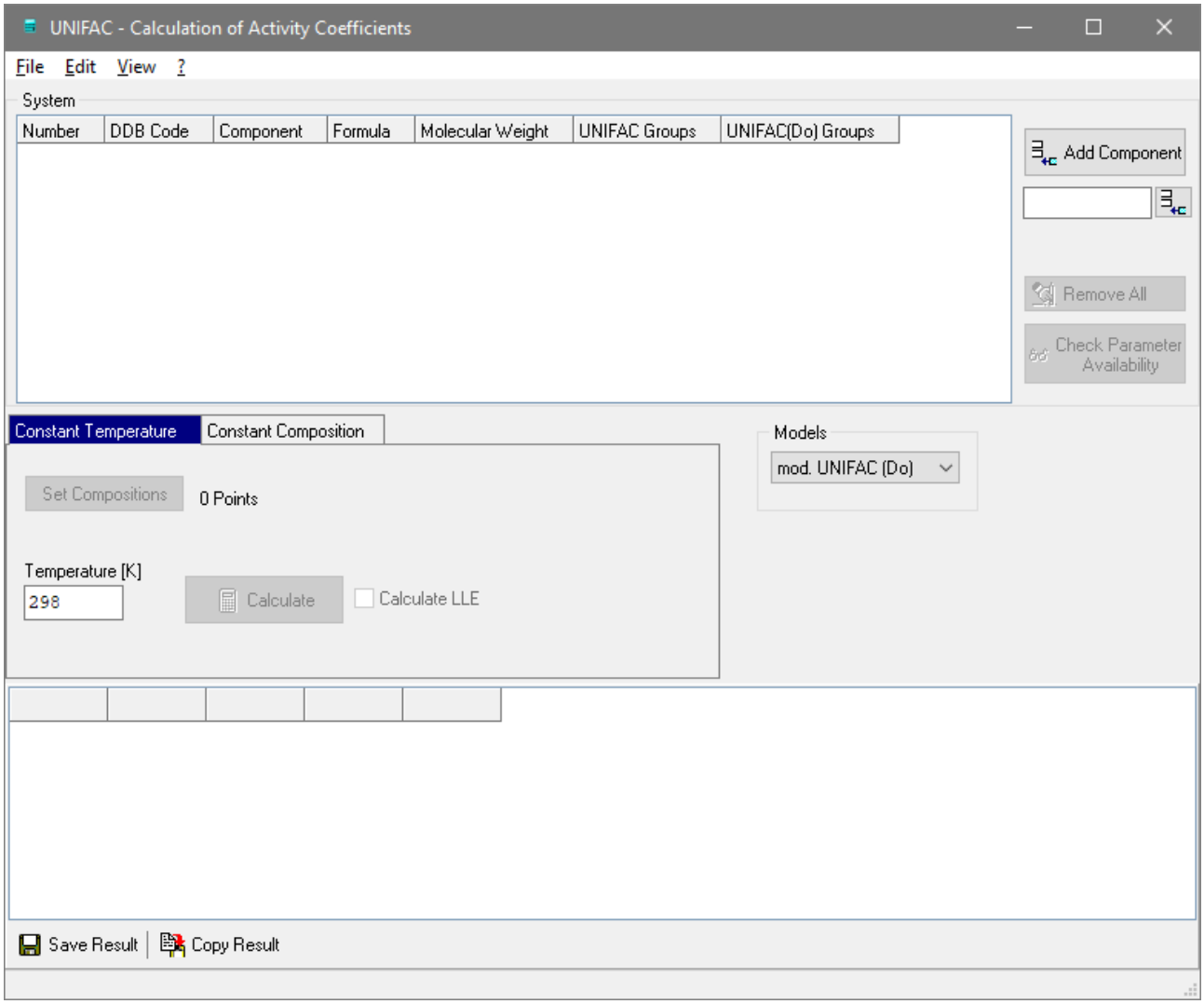


Figure 1: UNIFAC graphical user interface.

A system contains several pure components. Components can be added by the “Add Component” button. It calls the standard DDB component selection package which is described in details in a separate PDF (“Component Management”, Chapter 9).

The dialog allows searching for names, formulas, CAS registry numbers and many more criteria.

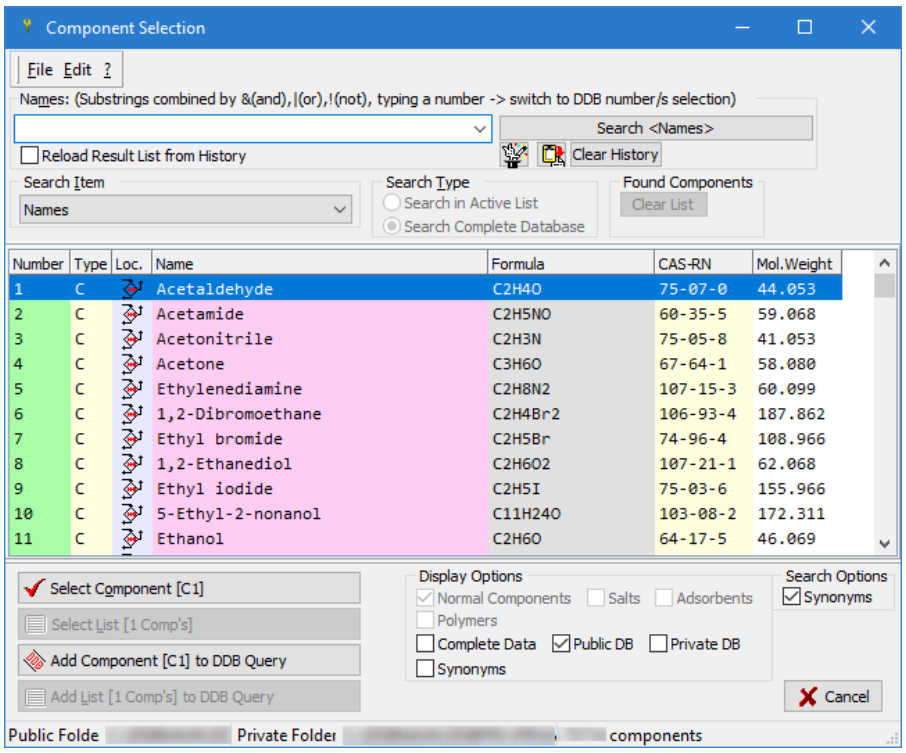


Figure 2: Component selection

The component list shown is the complete list of components available in the Dortmund Data Bank. It includes also many components for which no group assignments are available.

After a component has been selected, it is added to the component list.

	DDB Code	Component	Formula	Molecular Weight	UNIFAC Groups	UNIFA
1	4	Acetone	C3H6O	58.0800	1*CH3; 1*CH3CO	1*CH
2	11	Ethanol	C2H6O	46.0690	1*CH3; 1*CH2; 1*OH	1*CH
3	12	Diethyl ether	C4H10O	74.1228	2*CH3; 1*CH2; 1*CH2O	1*CH
4	17	Aniline	C6H7N	93.1283	5*ACH; 1*ACNH2	5*AC
5	45	Methyl ethyl ketoxime	C4H9NO	87.1216	n.a.	n.a.

Figure 3: Component list

This list displays the DDB internal number, an English name, the empirical formula, the molecular weight, and both the group assignments for UNIFAC and modified UNIFAC (Dortmund). If a group assignment is not given, a “n.a.” is written.

Single components can be removed by double-clicking the line; the complete list can be cleared by clicking the “Remove All” button.

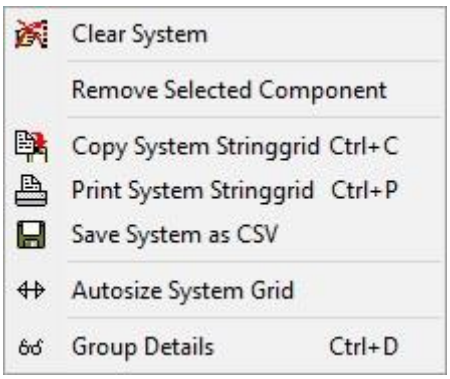


Figure 4: System Table Context Menu

The system table has a context menu which allows

1. Remove all components
2. Remove the selected component
3. Copying, printing, and saving the component list
4. Auto-size the columns of the table
5. Display details of the group assignment

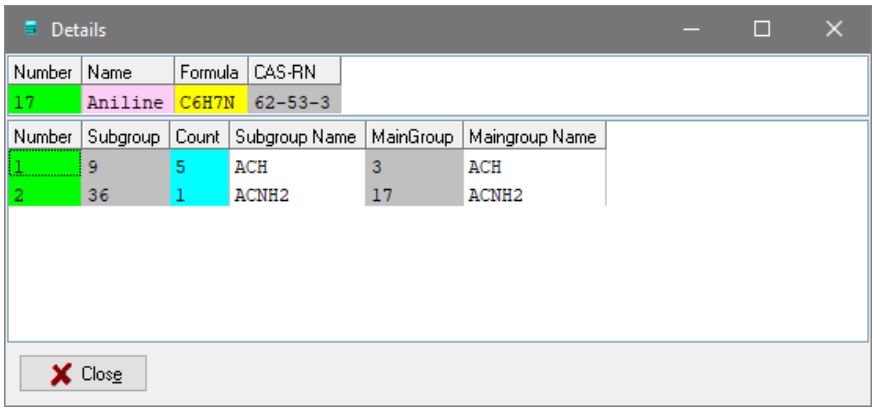


Figure 5: Group assignment details.

The normal display in the component list only displays the sub groups of the components and this dialog adds information about the main groups.

1.1.2 Checking Parameter Availability

UNIFAC needs the component specific group assignment and interaction parameters between all main groups present in the current mixture.

The dialog has two pages. The first page only displays if all parameters are available.

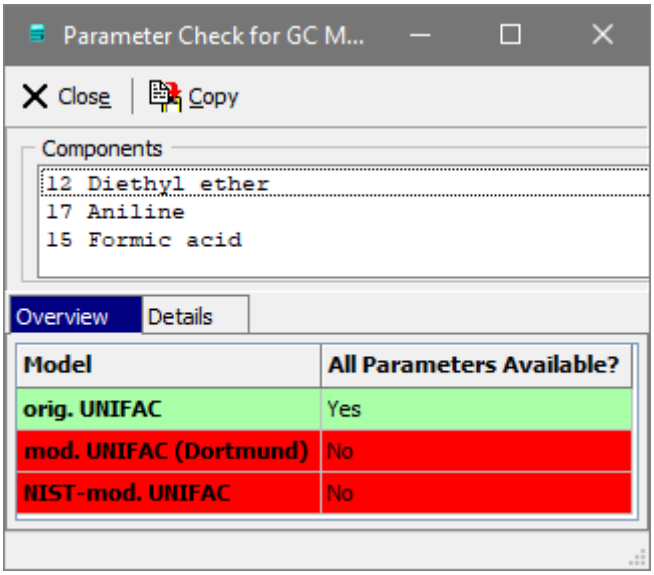


Figure 6: Parameter availability

The second page gives details about the group assignment for all components and all main group interactions. The example shows that for the given system UNIFAC can be used but modified UNIFAC (Dortmund) will fail because of a missing interaction parameter.

UNIFAC

```
Component      12: Diethyl ether
                   Subgroups:    1 (CH3     )    2 (CH2     )   25 (CH2O    )
Component      17: Aniline
                   Subgroups:    9 (ACH     )   36 (ACNH2   )
Component      15: Formic acid
                   Subgroups:   43 (HCOOH   )

List of Main Groups
Maingroups:    1 (CH2     )    3 (ACH     )   13 (CH2O    )   17 (ACNH2   )   20 (COOH    )

Interaction parameters
  1 -   3:  1 parameter/s  (CH2      / ACH     )
  1 -  13:  1 parameter/s  (CH2      / CH2O    )
  1 -  17:  1 parameter/s  (CH2      / ACNH2   )
  1 -  20:  1 parameter/s  (CH2      / COOH    )
  3 -  13:  1 parameter/s  (ACH      / CH2O    )
  3 -  17:  1 parameter/s  (ACH      / ACNH2   )
  3 -  20:  1 parameter/s  (ACH      / COOH    )
 13 -  17:  1 parameter/s  (CH2O     / ACNH2   )
 13 -  20:  1 parameter/s  (CH2O     / COOH    )
 17 -  20:  1 parameter/s  (ACNH2    / COOH    )
```

System has all parameters available.

mod. UNIFAC (Dortmund)

```
Component      12: Diethyl ether
                   Subgroups:    2 (CH2     )    1 (CH3     )   25 (CH2O    )
Component      17: Aniline
                   Subgroups:    9 (ACH     )   36 (ACNH2   )
Component      15: Formic acid
                   Subgroups:   43 (HCOOH   )

List of Main Groups
Maingroups:    1 (CH2     )    3 (ACH     )   13 (CH2O    )   17 (ACNH2   )   44 (HCOOH   )

Interaction parameters
  1 -   3:  2 parameter/s  (CH2      / ACH     )
  1 -  13:  2 parameter/s  (CH2      / CH2O    )
  1 -  17:  2 parameter/s  (CH2      / ACNH2   )
  1 -  44:  1 parameter/s  (CH2      / HCOOH   )
  3 -  13:  2 parameter/s  (ACH      / CH2O    )
  3 -  17:  2 parameter/s  (ACH      / ACNH2   )
  3 -  44:  3 parameter/s  (ACH      / HCOOH   )
 13 -  17:  0 parameter/s  (CH2O     / ACNH2   )
 13 -  44:  1 parameter/s  (CH2O     / HCOOH   )
 17 -  44:  0 parameter/s  (ACNH2    / HCOOH   )
```

Parameters are missing.

1.1.3 Calculation

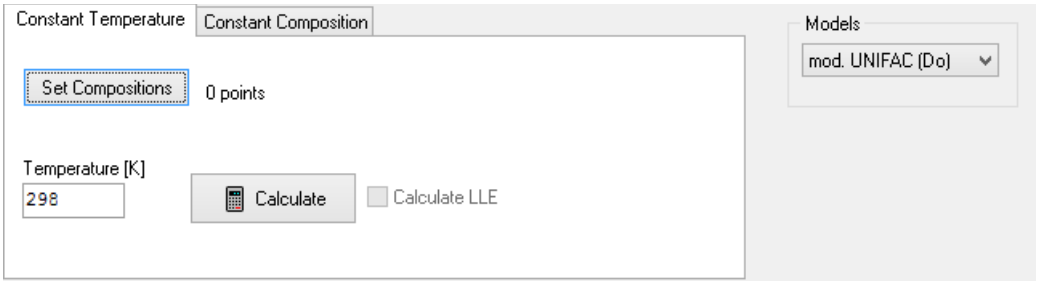


Figure 7: Calculation settings

1.1.3.1 Isothermal Calculation over a Concentration Range

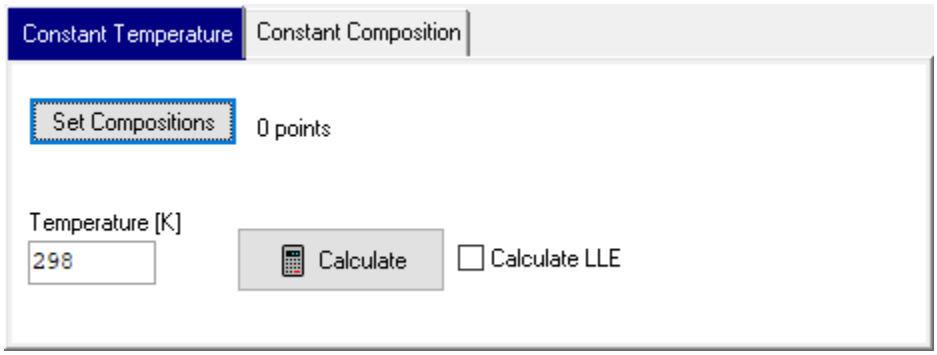


Figure 8: Calculate at constant temperature.

For a constant temperature it is possible to enter compositions manually or let the program calculate some auto-distributed composition points.

The “Set Compositions” button opens a dialog where compositions can be created (“Create Data Points”). In this dialog it is possible to enter compositions directly in the data grid and it allows creating data points over a composition range.

Special case like constant compositions or composition ratios for single or few components are also supported. The composition grid can be copied to the Windows clipboard as well as data can be pasted from the clipboard. This allows creating and managing compositions outside this program. Compositions can also be saved to and restored from files.

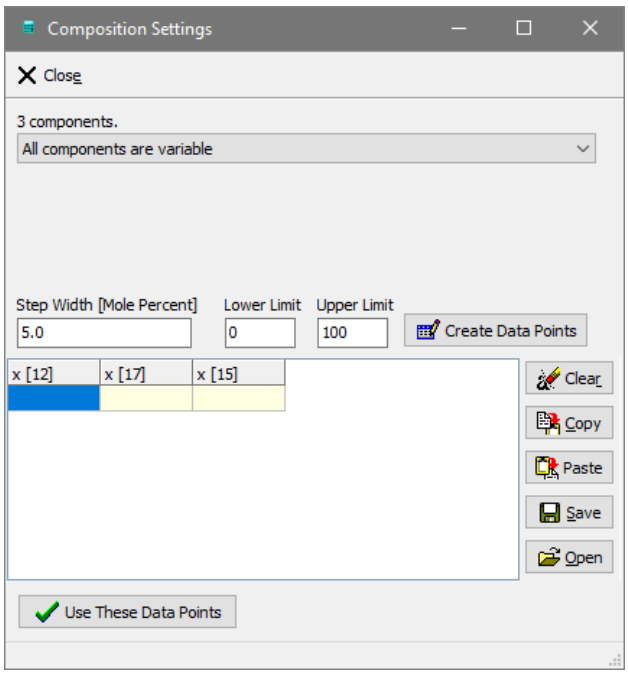


Figure 9: Composition settings

The number of possible data points is limited to 10001. Special compositions can be constant compositions for single components or special composition ratios (specified by integer values like 4 and 5 for a $^4/_5$ ratio) for a list of components.

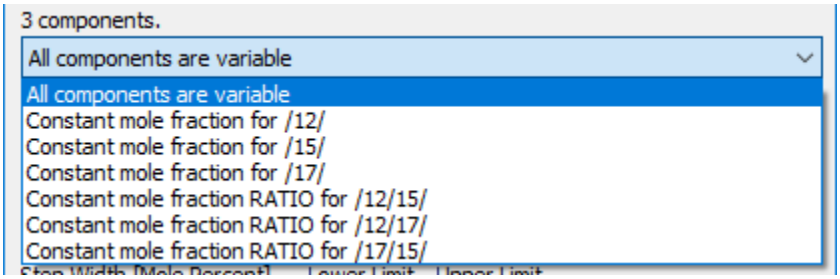


Figure 10: Special compositions

1.1.3.2 Calculation at Constant Compositions over a Temperature Range

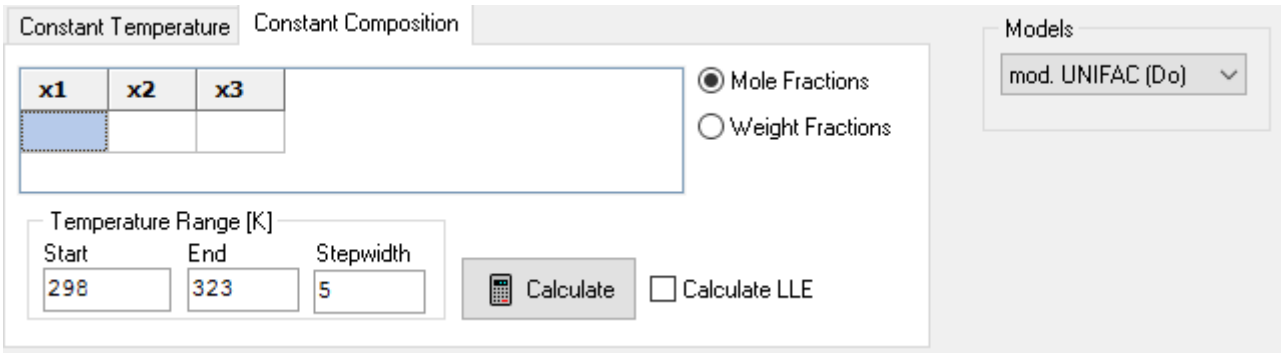


Figure 10: Calculation setting for constant compositions.

This calculation type allows the specification of a single composition line and a temperature range. The composition can be entered as mole fractions and as weight fractions.

1.2 Result Grid

	x1 [mol/mol]	x2 [mol/mol]	x3 [mol/mol]	T [K]	Act.Coeff.1	Act.Coeff.2	Act.Coeff.3	hE [J/mol]	cpE [J/(K*mol)]
1	0	0	1	298	26.7884	1.0746	1.0000	0.000	0.000
2	0	0.05	0.95	298	17.7601	1.0216	1.0012	-268.665	2.050
3	0	0.1	0.9	298	12.6563	0.9914	1.0036	-489.839	3.548
4	0	0.15	0.85	298	9.5280	0.9747	1.0059	-667.330	4.597
5	0	0.2	0.8	298	7.4876	0.9664	1.0077	-805.374	5.287
6	0	0.25	0.75	298	6.0899	0.9633	1.0087	-908.087	5.692

Figure 11: Result grid

The result grid shows all given compositions and the wanted temperatures first followed by the calculated activity coefficients, the heat of mixing and the excess heat capacity.

	z1	z2	T [K]	x1 (ph.1) [mol/mol]	x2 (ph.1)	x1 (ph.2)	x2 (ph.2)	Act.Coeff.1 (ph.1)	Act.Coeff.2 (ph.1)	Act.Coeff.1 (ph.2)	Act.Coeff.2 (ph.2)	hE (ph.1) [J/mol]	hE (ph.2)	cpE (ph.1)	cpE (ph.2
1	0,2	0,8	200					2,4196	1,1458			-2003,950		41,356	
2	0,2	0,8	250	0,04218305	0,95781695	0,62223623	0,37776377	17,2784	1,0130	1,1714	2,5685	-202,310	-620,189	4,478	25,848
3	0,2	0,8	300	0,029029182	0,970970818	0,64305364	0,35694636	25,2549	1,0074	1,1401	2,7403	-27,146	427,373	1,927	16,292
4	0,2	0,8	350	0,028337543	0,971662457	0,57046578	0,42953422	23,9649	1,0079	1,1904	2,2800	67,010	1220,352	2,028	14,769
5	0,2	0,8	400	0,033826493	0,966173507	0,44428349	0,55571651	17,4565	1,0121	1,3291	1,7596	233,437	2210,398	3,768	23,682
6	0,2	0,8	450	0,052803119	0,947196881	0,2552112	0,7447888	8,6400	1,0285	1,7876	1,3080	781,839	3171,535	10,553	35,719
7	0,2	0,8	500					1,5814	1,1837			4733,158		49,024	

Figure 12: Result grid with LLE Calculation

If the LLE calculation is active the initial concentrations are treated as feed. The result grid will then be extended by two phase columns for each component and two activity coefficient/hE/cpE columns for the second phase. The additional columns will be present even if no LLE was found.

The table can be saved as Microsoft Excel (“xls”) file or copied to the Windows clipboard.

1.3 Activity Coefficient Diagram

In case of the calculation at a fixed single composition at different temperatures a diagram with the temperature-dependent activity coefficients is displayed.

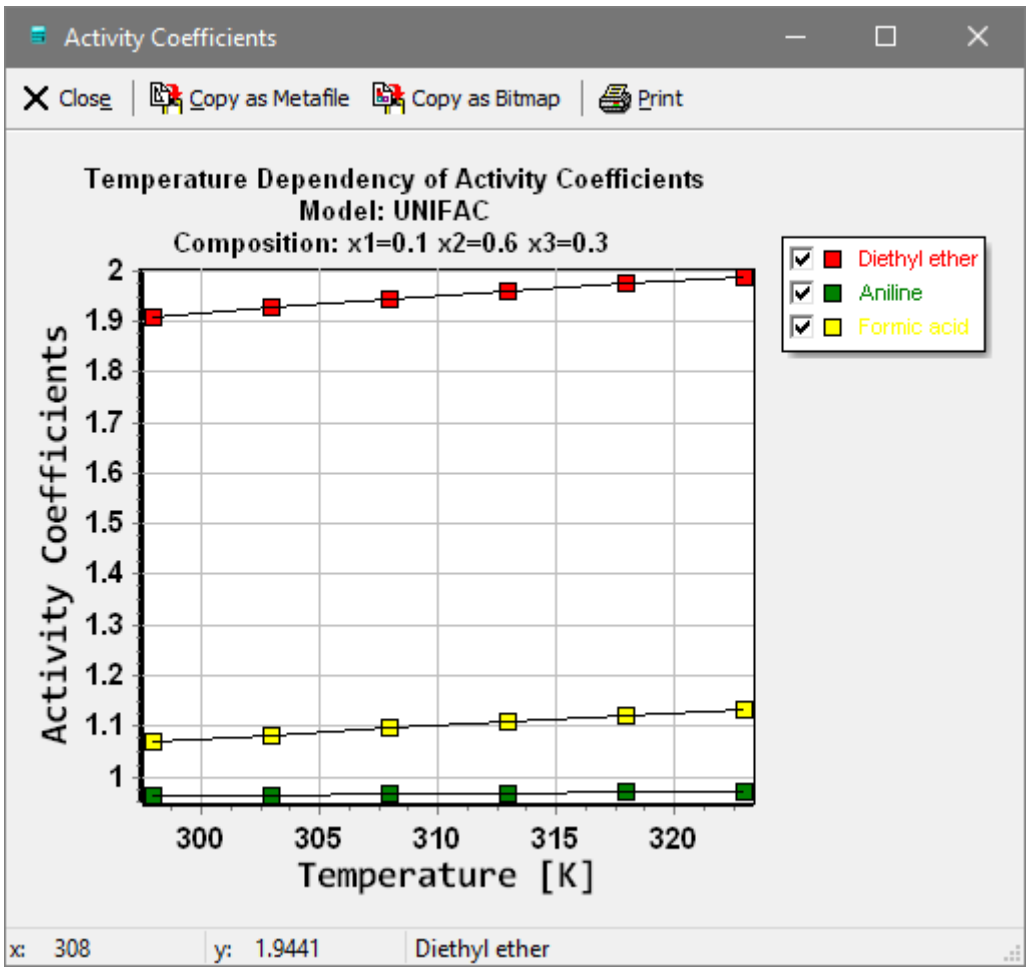
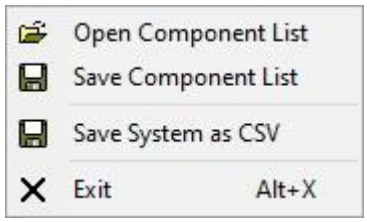
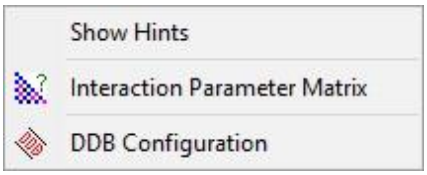


Figure 11: Temperature dependent activity coefficients.

1.4 The Menus

		
Component lists are files containing raw data set numbers. These files have the extension “stl”. The system grid can also be saved as a comma separated file which can be loaded in spread sheet programs.	The system grid (component list) can be copied and printed. “Components” starts the Component Editor (described in “ComponentManagement.pdf”)	“Show Hints” activates additional hints for many items on the form. “Interaction Parameter Matrix” starts the parameter editor (described in “GC Model Parameters.pdf”) “DDB Configuration” starts the configuration program (described in “DDBConfiguration.pdf”)

2 Appendix

2.1 UNIFAC

The UNIFAC group contribution model[8] has been developed to estimate the real vapor-liquid equilibrium behavior. In a group contribution model, the mixture is not seen as a mixture of components but as a mixture of groups. The large advantage is that the number of structural groups is much smaller (dozens) than the number of components (millions). This means that it is possible to calculate most systems of commercial interest with very few group information.

UNIFAC is based on the UNIQUAC equation. Therefore, activity coefficients are calculated from two terms,

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

The combinatorial part is calculated in the same manner as in UNIQUAC,

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

with

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

and

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

For the calculation of the combinatorial part only the relative van der Waals volume r_i and surface q_i together with the mole fractions x_i are needed.

The van der Waals volume and surface can be calculated from group volumes and surfaces,

$$r_i = \sum_k \nu_k^{(i)} R_k$$

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

With $\nu_k^{(i)}$ as the number of structural groups of type k in the molecule i. The residual part has to be calculated from the group activity coefficients Γ_k,

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

The concentration dependency of the group activity coefficients in the mixture Γ_k (and in the pure component $\Gamma_k^{(i)}$) must be calculated in analogy to the `UNIQUAC` equation,

[8] Gmehling J.,Kolbe B., “Thermodynamik”, Verlag Chemie, Weinheim (1987)

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \Theta_m \Psi_m \right) - \sum_m \frac{\Theta_m \Psi_m}{\sum_n \Theta_n \Psi_n} \right].$$

The surface contribution Θ_m and the mole fraction X_m of the group m is defined by

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \qquad X_m = \frac{\sum_j \nu_j^m x_j}{\sum_j \sum_n \nu_{n,j} x_j}$$

and the parameter Ψ_{nm} is defined as

$$\Psi_{nm} = e^{\frac{-a_{nm}}{T}}$$

with a_{nm} as group interaction parameters between the groups n and m. Modified UNIFAC (Dortmund) uses temperature-dependent interaction parameters:

$$\Psi_{nm} = e^{\frac{-a_{nm}}{T} + \frac{-b_{nm} \cdot T}{T} + \frac{-c_{nm} \cdot T^2}{T}}$$