

# UNIFAC

Documentation

**DDBSP** - Dortmund Data Bank Software Package



DDBST Software & Separation Technology GmbH

Marie-Curie-Straße 10

D-26129 Oldenburg

Tel.: +49 (0) 441 361819 0

Fax: +49 (0) 441 361819 10

E-Mail: [support@ddbst.com](mailto:support@ddbst.com)

[Web: www.ddbst.com](http://www.ddbst.com)

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## Introduction

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

The software is an integral part of the Dortmund Data Bank software package and uses the component, the groups 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 software comes with a list of more than 24000 components from the main DDB component list and approx. 12000 of them have a UNIFAC group assignment and almost 11000 have a group assignment for modified UNIFAC (Dortmund). For most components the DDB provides CAS registry numbers (18800), empirical formula molecular weights (almost all). All other components are applicable in both methods (e. g. salts, metals and metal complexes, etc.).

The latest UNIFAC parameters have been published in 2003<sup>3</sup>, the latest parameter for mod. UNIFAC (Dortmund) have been published 2002<sup>4</sup> and 2006<sup>5</sup>.

Most current parameters can be obtained from the [UNIFAC Consortium](#) at the University of Oldenburg (Chair of Prof. Gmehling).

## 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.

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- 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  $\gamma^{\text{occ}}$ “, *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

## Building a System

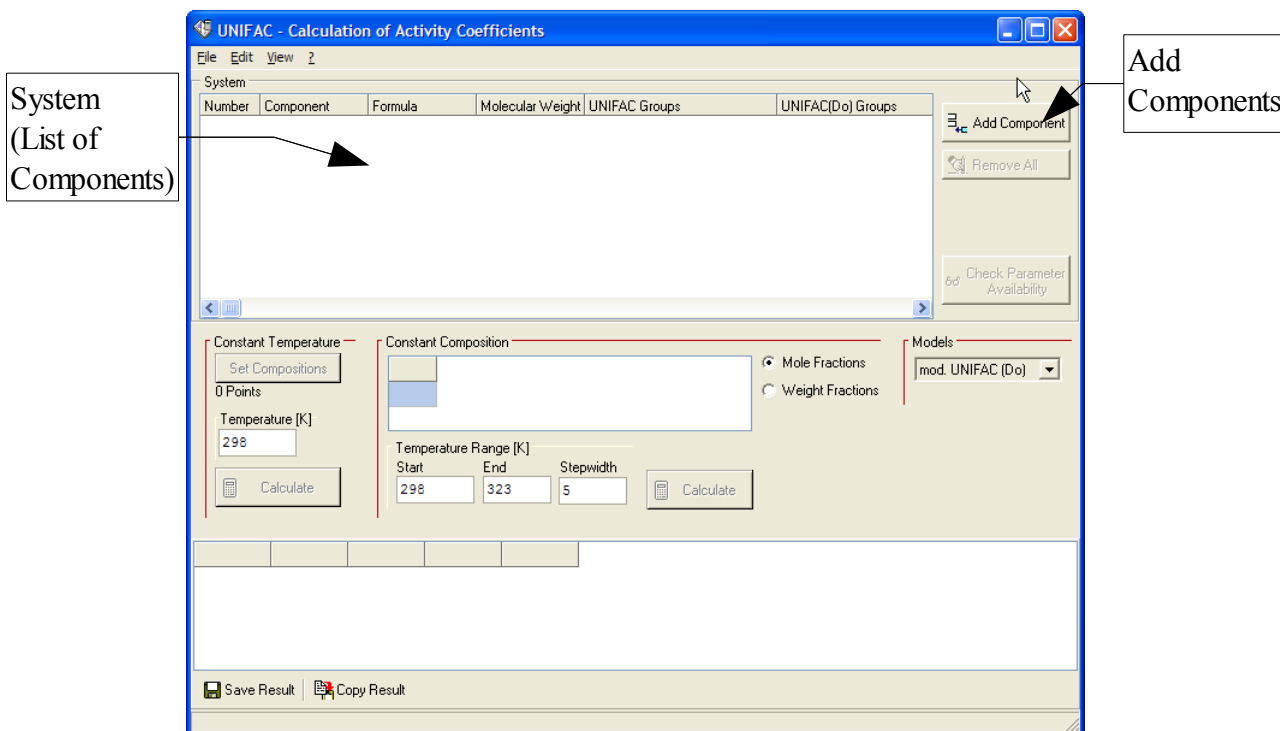


Figure 1: UNIFAC Graphical User Interface

A system contains of several pure components. Component can be added by the “Add Component” button. The 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.

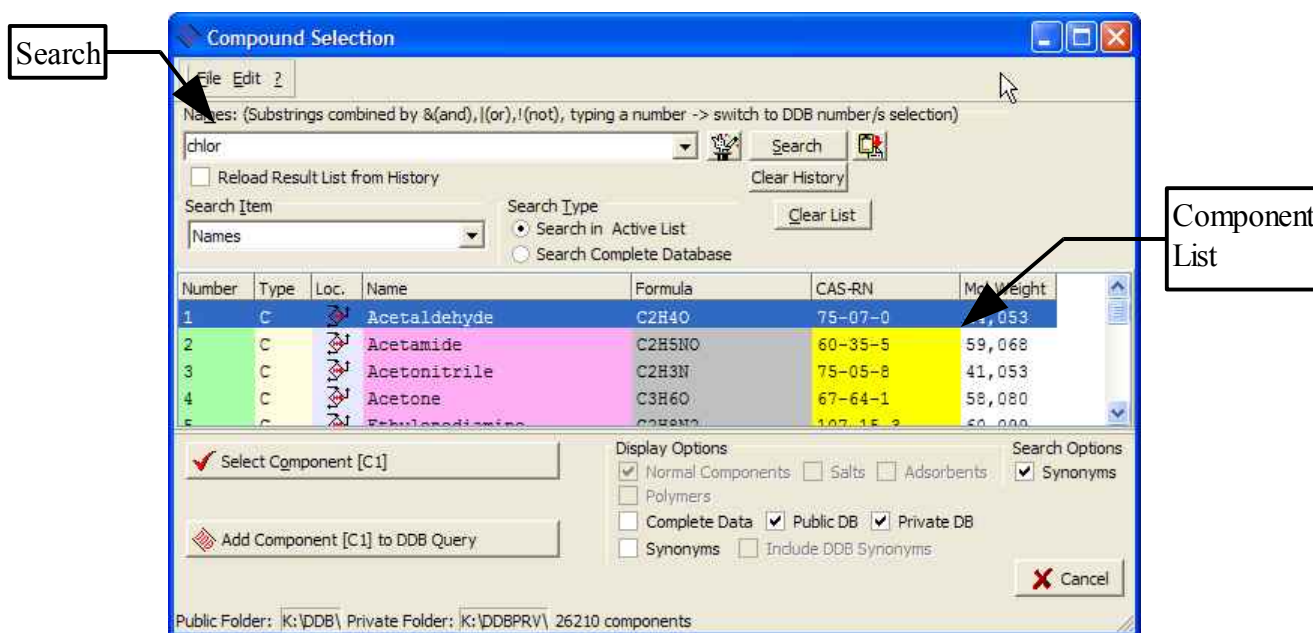
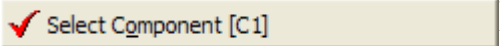


Figure 2: Component Selection

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 (by a double-click or by ) the component is added to the component list.

Number	Component	Form	Group Assignments	Weight	UNIFAC Groups	UNIF.
4	Acetone	C3H6O			1*CH3 1*CH3CO	1*CH
11	Ethanol	C2H6O	46,0690		1*CH3 1*CH2 1*OH (P)	1*CH
12	Diethyl ether	C4H10O	74,1220		2*CH3 1*CH2	1*CH
17	Aniline	C6H7N	93,1280		5*ACH 1*ACNH	5*AC
45	Methyl ethyl ketoxime	C4H9NO	87,1200		n.a.	n.a.

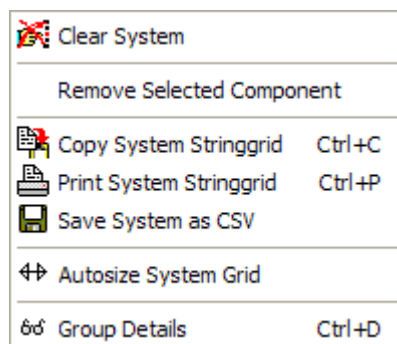
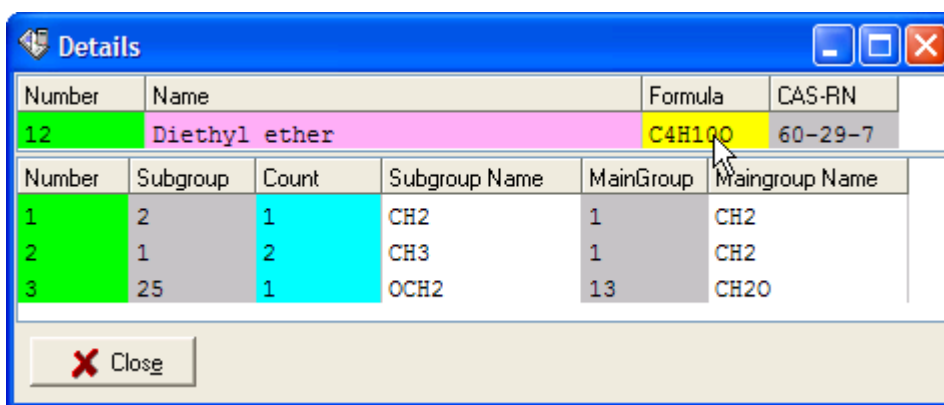
Figure 3: Component List

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.

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

Number	Name	Formula	CAS-RN
12	Diethyl ether	C4H10O	60-29-7

Number	Subgroup	Count	Subgroup Name	MainGroup	Maingroup Name
1	2	1	CH2	1	CH2
2	1	2	CH3	1	CH2
3	25	1	OCH2	13	CH2O

Figure 4: 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.

## 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:

1. The first page only displays if all parameters are available

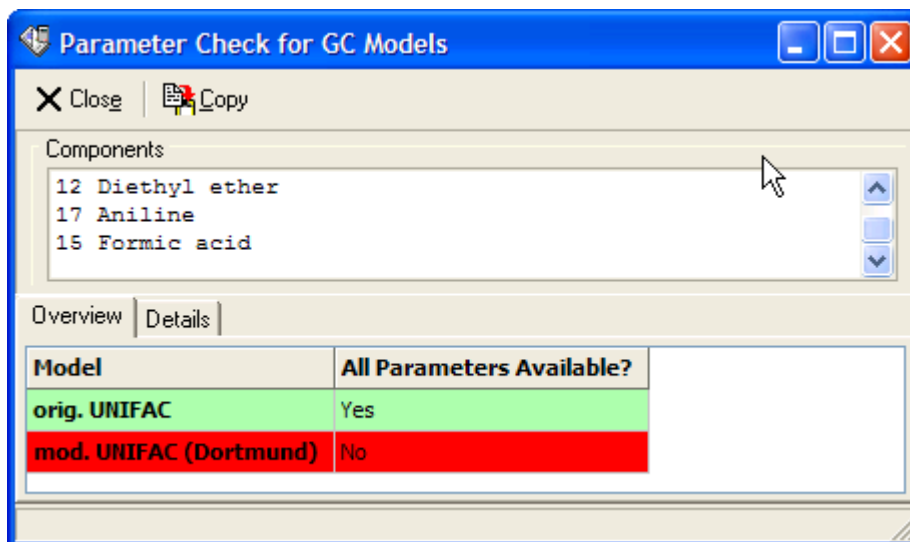


Figure 5: Parameter Availability

2. 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      11: Ethanol
                Subgroups:   1 (CH3   )   2 (CH2   )   14 (OH    )
Component      12: Diethyl ether
                Subgroups:   1 (CH3   )   2 (CH2   )   25 (OCH2  )
Component      17: Aniline
                Subgroups:   9 (ACH   )   36 (ACNH2 )
Component      15: Formic acid
                Subgroups:  43 (HCOOH )
    
```

List of Main Groups

```

Maingroups:   1 (CH2   )   3 (ACH   )   5 (OH    )   13 (CH2O  )   17 (ACNH2 )   20
(COOH   )
    
```

Interaction parameters

```

1 - 3: 1 parameter/s
1 - 5: 1 parameter/s
1 - 13: 1 parameter/s
1 - 17: 1 parameter/s
1 - 20: 1 parameter/s
3 - 5: 1 parameter/s
3 - 13: 1 parameter/s
3 - 17: 1 parameter/s
3 - 20: 1 parameter/s
5 - 13: 1 parameter/s
5 - 17: 1 parameter/s
5 - 20: 1 parameter/s
13 - 17: 1 parameter/s
13 - 20: 1 parameter/s
17 - 20: 1 parameter/s
    
```

*System has all parameters available.*

mod. UNIFAC (Dortmund)

```

Component      11: Ethanol
                Subgroups:   1 (CH3   )   2 (CH2   )   14 (OH (P) )
Component      12: Diethyl ether
                Subgroups:   2 (CH2   )   1 (CH3   )   25 (OCH2  )
Component      17: Aniline
                Subgroups:   9 (ACH   )   36 (ACNH2 )
Component      15: Formic acid
                Subgroups:  43 (HCOOH )
    
```

List of Main Groups

```

Maingroups:   1 (CH2)   3 (ACH)   5 (OH)   13 (CH2O)   17 (ACNH2)   44 (HCOOH)
    
```

Interaction parameters

```

1 - 3: 2 parameter/s
1 - 5: 3 parameter/s
1 - 13: 2 parameter/s
1 - 17: 3 parameter/s
1 - 44: 1 parameter/s
3 - 5: 3 parameter/s
3 - 13: 2 parameter/s
3 - 17: 3 parameter/s
3 - 44: 3 parameter/s
5 - 13: 3 parameter/s
5 - 17: 3 parameter/s
5 - 44: 0 parameter/s
13 - 17: 2 parameter/s
13 - 44: 1 parameter/s
17 - 44: 0 parameter/s
    
```

*Parameters are missing.*

## Calculation

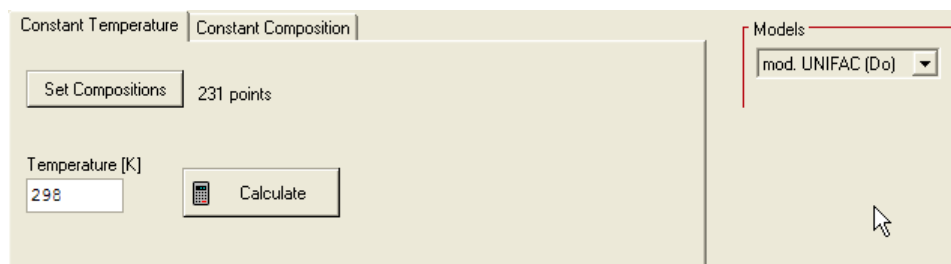


Figure 6: Calculation Settings

### Isothermal Calculation over a Concentration Range

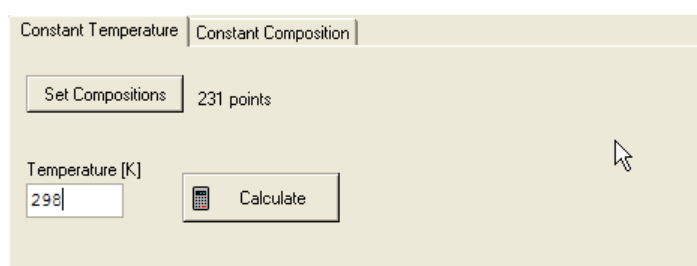


Figure 7: Calculation at Constant Temperature

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

The “Set Compositions” buttons 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.

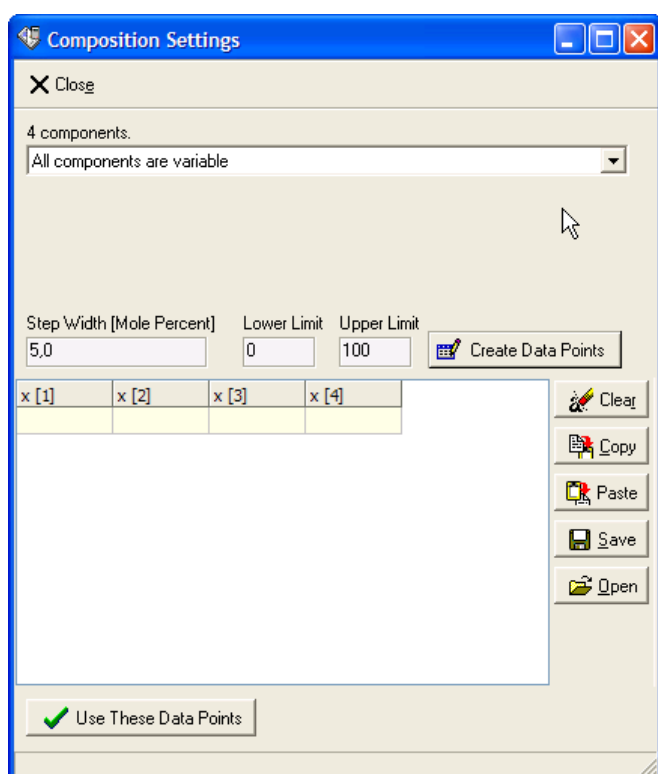


Figure 8: Composition Settings

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 (maybe in Microsoft Excel or OpenOffice Calc).

Compositions can also be saved and restored (“Open”) from files.

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.

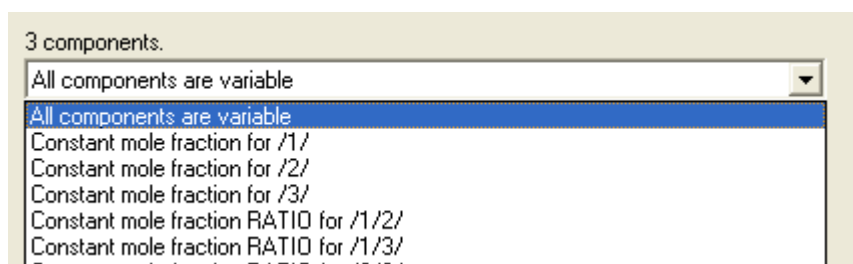


Figure 9: Special Compositions

### Calculation at Constant Compositions over a Temperature Range

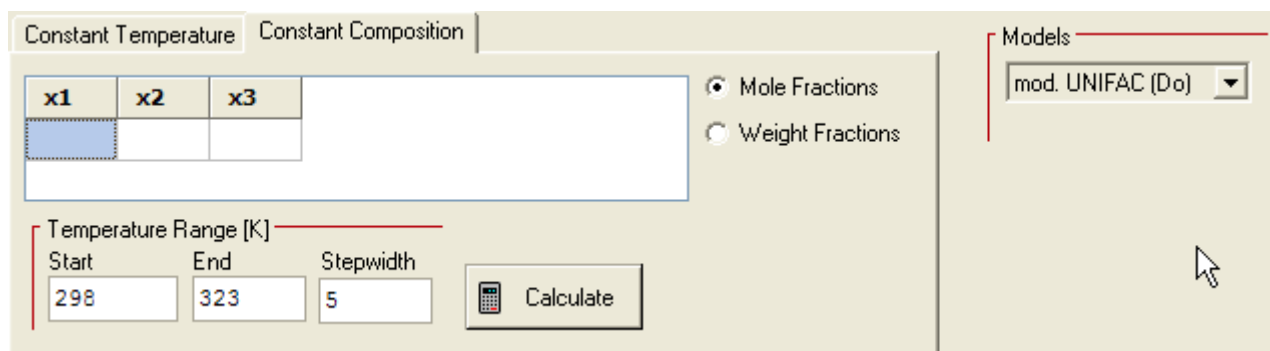


Figure 10: Calculation Setting for Constant Compositions



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.

### Result Grid

	x1 [mol/mol]	x2 [mol/mol]	x3 [mol/mol]	x4 [mol/mol]	T [K]	Act.Coeff.1	Act.Coeff.2	Act.Coeff.3	Act.Coeff.4	hE [J/mol]	cpE [J/(K*mol)]
1	0,0286	0,1286	0,8000	0,0429	298	1,5594	1,5800	1,0105	0,9665	-272,862	0,982
2	0,0357	0,1607	0,7500	0,0536	298	1,5492	1,5301	1,0156	0,9849	-336,916	1,294
3	0,0429	0,1929	0,7000	0,0643	298	1,5417	1,4856	1,0213	1,0078	-398,683	1,634
4	0,0500	0,2250	0,6500	0,0750	298	1,5370	1,4464	1,0271	1,0360	-457,439	2,001
5	0,0571	0,2571	0,6000	0,0857	298	1,5348	1,4119	1,0325	1,0700	-512,644	2,398

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.

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

### 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.

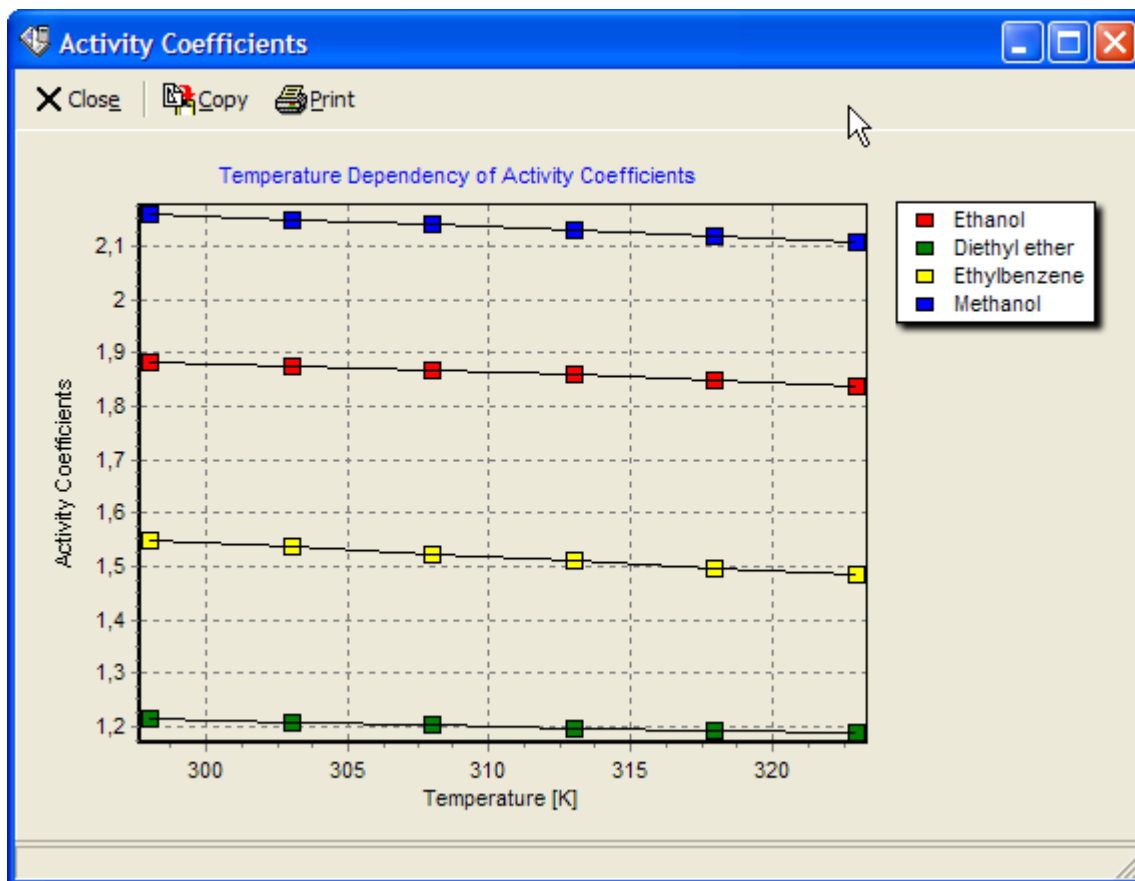


Figure 12: Temperature-dependent Activity Coefficients

### The Menus

<ul style="list-style-type: none"> <li> Open Component List</li> <li> Save Component List</li> <li> Save System as CSV</li> <li> Exit <span style="float: right;">Alt+X</span></li> </ul>	<ul style="list-style-type: none"> <li> Copy System Grid <span style="float: right;">Ctrl+C</span></li> <li> Print System Grid <span style="float: right;">Ctrl+P</span></li> <li> Components</li> </ul>	<ul style="list-style-type: none"> <li>Show Hints</li> <li> Interaction Parameter Matrix</li> <li> DDB Configuration</li> </ul>
<p>Component lists are files containing raw data set numbers. These file have the extension "stl".</p> <p>The system grid can also be saved as a comma separated file which can be loaded in spread sheet programs.</p>	<p>The system grid (component list) can be copied and printed.</p> <p>"Components" starts the Component Editor (described in "ComponentManagement.pdf")</p>	<p>"Show Hints" activates additional hint for many items on the form.</p> <p>"Interaction Parameter Matrix" starts the parameter editor (described in "GC Model Parameters.pdf")</p> <p>"DDB Configuration" starts the configuration program (described in "DDBConfiguration.pdf")</p>

## Appendix

### UNIFAC

The UNIFAC group contribution model<sup>6</sup> 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,

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

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

with  $v_k^{(i)}$  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  $\Gamma_k$ ,

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

---

<sup>6</sup> Gmehling J., Kolbe B., "Thermodynamik", Verlag Chemie, Weinheim (1987)

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

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

The surface contribution  $\theta_m$  and the mole fraction  $X_m$  of the group is defined by

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

$$X_m = \frac{\sum_j v_j^m x_j}{\sum_j \sum_n v_{n,j} x_j}$$

and the parameter  $\Psi_{nm}$  is defined as

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

with  $a_{nm}$  as group interaction parameters between the groups  $n$  and  $m$ .