

# 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<sup>1</sup>, modified UNIFAC (Dortmund)<sup>2</sup> 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)<sup>6</sup> 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.

<sup>&</sup>lt;sup>1</sup>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

<sup>&</sup>lt;sup>2</sup>Weidlich U., Gmehling J., "A Modified UNIFAC Model. 1. Prediction of VLE, hE, and γ<sup>∞</sup>", Ind. Eng. Chem. Res., 26(7), 1372-1381, 1987

<sup>&</sup>lt;sup>3</sup>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

<sup>&</sup>lt;sup>4</sup>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

<sup>&</sup>lt;sup>5</sup>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

<sup>&</sup>lt;sup>6</sup>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

<sup>&</sup>lt;sup>7</sup> 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

🛢 UNIFAC - Calcula	tion of Activity (	Coefficients	5			—		×
<u>File Edit View ?</u>								
System						_		
Number DDB Code	Component	Formula	Molecular Weight	UNIFAC Groups	UNIFAC(Do) Groups	∃₄∊	dd Compo	nent
								+
								_
						<u></u> F	lemove All	
						aa Ch	neck Paran	neter
							Availabili	(y
Constant Temperature	Constant Comp	osition			Models			
					mod. UNIFAC (Do) 🗸 🗸			
Set Compositions	0 Points							
Temperature [K]	Calculate	Calc	culate LLE					
230	m caloudo							
🔚 Save Result 🛛 🛱	Copy Result							

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.

Y Co	mpon	ent S	election			_		×	
<u> </u>	dit <u>?</u>								
Names:	(Subs	trings	combined by &(and),  (or), !(not)	, typing a number	-> switch to DDB num	ber/s selection)			
	✓ Search <names></names>								
Rela	Reload Result List from History								
Search	<u>I</u> tem			Search Type	F	ound Components	5		
Names			~	Search in Ac	tive List	Clear List			
				Search Comp	olete Database				
Number	Type	Loc.	Name		Formula	CAS-RN	Mol.Weight	~	
1	С	€	Acetaldehyde		C2H4O	75-07-0	44.053		
2	С	₹	Acetamide		C2H5NO	60-35-5	59.068		
3	С	₹	Acetonitrile		C2H3N	75-05-8	41.053		
4	С	₹	Acetone		C3H60	67-64-1	58.080		
5	C	₹	Ethylenediamine		C2H8N2	107-15-3	60.099		
6	c	₹	1,2-Dibromoethane		C2H4Br2	106-93-4	187.862		
7	C	₹	Ethyl bromide		C2H5Br	74-96-4	108.966		
8	C	₹	1,2-Ethanediol		C2H6O2	107-21-1	62.068		
9	C	•€	Ethyl iodide		C2H5I	75-03-6	155.966		
10	С	•€	5-Ethyl-2-nonanol		C11H240	103-08-2	172.311		
11	с	€	Ethanol		C2H60	64-17-5	46.069	~	
🖌 Sel	✓ Select Component [C1] Display Options Search Options Search Options [2] Search Options [2] Synonyms								
🗐 Se	Select List [1 Comp's] Polymers								
🚸 Ad	Add Component [C1] to DDB Query     Complete Data								
Ad 🗐	d <u>L</u> ist (	1 Con	np's] to DDB Query				🗙 Ca	ncel	
Public F	Oublic Folder components								

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
ź	11	Ethanol	C2H6O	46.0690	1*CH3; 1*CH2; 1*OH	1*CH
3	12	Diethyl ether	C4H100	74.1228	2*CH3; 1*CH2; 1*CH20	1*CH
4	17	Aniline	C6H7N	93.1283	5*ACH; 1*ACNH2	5*AC
Ę	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

🛢 Details — 🗆 🗙										
Number	Name	Formul	a CAS-RN							
17	Aniline	C6H71	₹ 62-53-3							
Number	Subgroup	Count	Subgroup Name	MainGroup	Maingroup Name					
1	9	5	ACH	3	ACH					
2	36	1	ACNH2	17	ACNH2					
×	X Close									

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.

Parameter Check for GC	м — 🗆 🗙				
Components					
12 Diethyl ether 17 Aniline 15 Formic acid					
Overview Details					
Model	All Parameters Available?				
orig. UNIFAC	Yes				
mod. UNIFAC (Dortmund)	No				
NIST-mod. UNIFAC	No				
	.:				

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.

UNIFA	<u>vc</u>											
Compone	ent	12:	Diethyl Subgrou	ether	1 (CH	3)		2 (CH2	)	25 (CH20	)	
Compone	ent	17:	Aniline		e (ac	- , + \	2	<ul> <li>составляется с составляется с состав С составляется с соста с составляется с сост с с составляется с с с с с составляется с с с с с с с с с с с с с с с с с с с</li></ul>	, ,	,	,	
Compone	ent	15:	Formic Subgrou	acid mps: /	43 (HC	оон)	5	o (Acanz	,			
List of Maingro	f Mair oups:	n Group 1 (	s CH2	) 3	(ACH	)	13	(CH20	)	17 (ACNH2	)	20 (COOH
Interac	ction	parame	ters									
1 -	3:	1 para	meter/s	(CH2	/	ACH	)					
1 -	13:	1 para	meter/s	(CH2	/	CH2O	)					
1 -	17:	1 para	meter/s	(CH2		ACNH2	)					
1 -	20:	1 para	meter/s	(CH2		COOH	)					
3 -	13:	1 para	meter/s	(ACH		CH2O	)					
3 -	17:	1 para	meter/s	(ACH		ACNH2	)					
3 -	20:	1 para	meter/s	(ACH		COOH	)					
13 -	1/:	1 para	meter/s	(CH20		ACNH2	)					
13 -	20:	1 para	meter/s	(CHZO	, <i>'</i> ,	COOH	)					
T/ -	20:	i para	meter/s	(ACNH)	2 /	COOH	)					

System has all parameters available.

#### mod. UNIFAC (Dortmund)

Component	12: Diethyl	ether							
	Subgroug	ps: 2	(CH2	)	1 (CH3	)	25 (CH2O	)	
Component	17: Aniline								
	Subgroug	ps: 9	(ACH	) 3	6 (ACNH2	)			
Component	15: Formic a	acid							
_	Subgroup	ps: 43	(HCOOH	)					
Tist of Main C	201109								
Maingroups.	1 (CEO )		7.CU )	1.2	1000		17 (3 (3)(1))	) 44 /BCO	он V
Maingroups:	I (CH2 )	) 5 (.	асп )	13	(CHZU	)	I/ (ACMHZ	) 44 (ACO	Jn )
Interaction pa	rameters								
1 - 3: 2)	parameter/s	(CH2	/ ACH	)					
1 - 13: 2 ;	parameter/s	(CH2	/ CH2C	))					
1 - 17: 2 ;	parameter/s	(CH2	/ ACNH	12)					
1 - 44: 1	parameter/s	(CH2	/ HCOC	)H )					
3 - 13: 2	parameter/s	(ACH	/ CH2C	)					
3 - 17: 2	parameter/s	(ACH	/ ACNH	12 j					
3 - 44: 3	parameter/s	(ACH	/ HCOC	)H )					
13 - 17: 0	parameter/s	(CH20	/ ACNH	(2)					
13 - 44: 1	parameter/s	(CH2O	/ HCOC	)H )					
17 - 44: 0	parameter/s	(ACNH2	/ HCOO	)H j					
	-	-							

Parameters are missing.

)

#### 1.1.3 Calculation

Constant Temperature	Constant Composition	Models
Set Compositions	0 points	mod. UNIFAC (Do) 🗸
Temperature [K]	Calculate LLE	

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.

Composition Settings —		×
× Clos <u>e</u>		
3 components.		
All components are variable		$\sim$
Chan Width Didels Descentil - Lawren Limit - Line on Limit		
5.0 0 100 mt Create Da	ta Points	5
		_
x [12] x [17] x [15]	2 🖉 🖸	lea <u>r</u>
	B <mark>≹</mark> ⊆	ору
	P:	aste
		ave
		)pen
✓ Use These Data Points		

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  $\frac{4}{5}$  ratio) for a list of components.

3 components.	
All components are variable	~
All components are variable	
Constant mole fraction for /12/	
Constant mole fraction for /15/	
Constant mole fraction for /17/	
Constant mole fraction RATIO for /12/15/	
Constant mole fraction RATIO for /12/17/	
Constant mole fraction RATIO for /17/15/	

Figure 10: Special compositions

# 1.1.3.2 Calculation at Constant Compositions over a Temperature Range

Constant Temperature Constant Composition	Models
x1     x2     x3       Image: Sector of the	mod. UNIFAC (Do) 🗸 🗸
Temperature Range [K]	
Start     End     Stepwidth       298     323     5     Image: Calculate	

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]	т [К]	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]	×1 (ph.1) [mol/mol]	x2 (ph.1)	×1 (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

Image: Component List       Image: Component List       Save Component List       Image: Component List       Save System as CSV       Image: Component List       Image: Component List	Copy System Grid Ctrl+C         Print System Grid Ctrl+P         Components	Show Hints Interaction Parameter Matrix DDB Configuration
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<sup>8</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,

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

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  $\Gamma_k$ ,

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

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,

<sup>&</sup>lt;sup>8</sup> 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  $\Theta_m$  and the mole fraction  $X_m$  of the group *m* is defined by

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

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*. Modified UNIFAC (Dortmund) uses temperature-dependent interaction parameters:

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