

Fit of g^E Model Parameters to Activity Coefficients Obtained from Group Contribution Methods

UNIQUAC, NRTL, Wilson
original UNIFAC, modified UNIFAC, ASOG

DDBSP - Dortmund Data Bank Software Package



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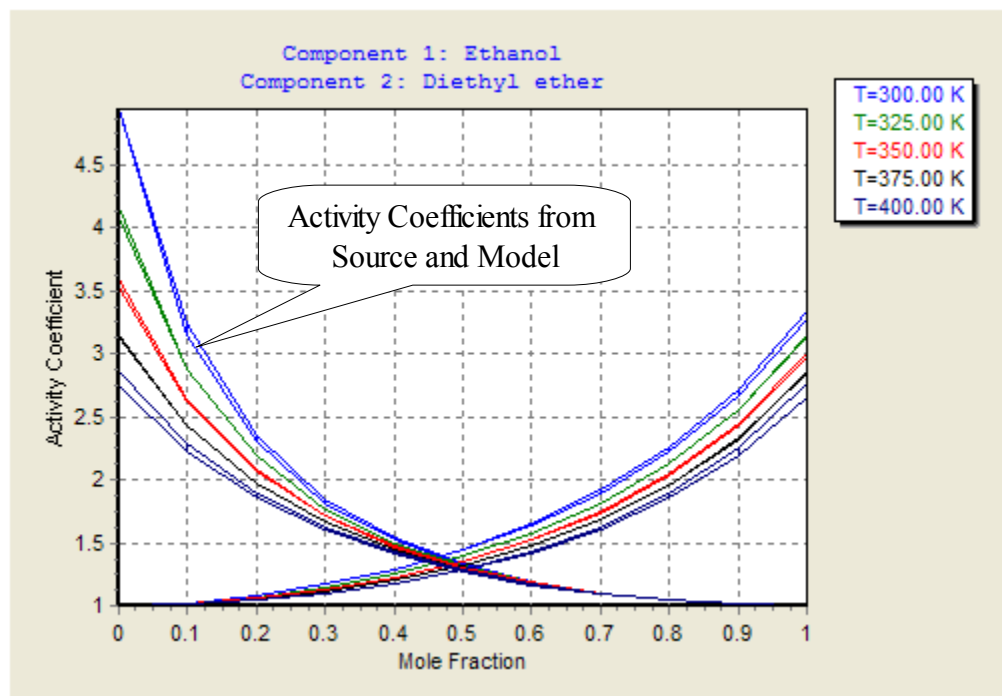
Table of Contents

Introduction.....	3
Development Status.....	3
Component Selection.....	4
Calculating Activity Coefficients.....	6
Fitting.....	7
Starting Values.....	7
Objective Function.....	8
Loops.....	8
Fitting.....	8
Batch Fitting.....	9
Results.....	10
Export to ParameterDDB.....	11
Export to Aspen INP Files.....	11
Import Aspen Components.....	11
The UNIFAC Consortium.....	12

Introduction

This program fits g^E model (Wilson, NRTL, and UNIQUAC) parameters to activity coefficients obtained from group contribution models (original UNIFAC, modified UNIFAC (Dortmund), modified UNIFAC (Lyngby), and ASOG for binary systems.

This software can obtain parameters for a high number of systems in a short time. These parameters have the same quality as the underlying activity coefficient model, the program neither adds or loses quality. There's still a slight degradation of precision because of a remaining fit deviation.



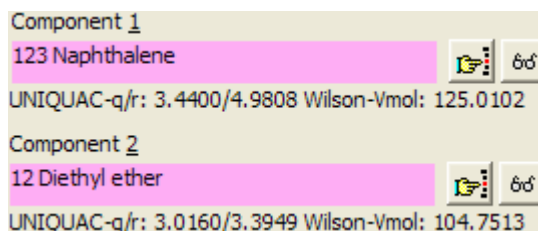
This deviation normally doesn't exceed 1 percent (absolute mean error in the activity coefficients).

The software is integrated in the standard DDB software package using the DDB's component list, the parameter files, and the standard software components.

Development Status

This program is still in an early development status although fully functional. Development is continued and will result in new updated versions relatively soon. Progress reports will be available on DDBST's web site (www.ddbst.com).

Component Selection



This part of the main dialog allows to specify the two components of the binary systems either the standard component selection dialog or by typing a known DDB component number.

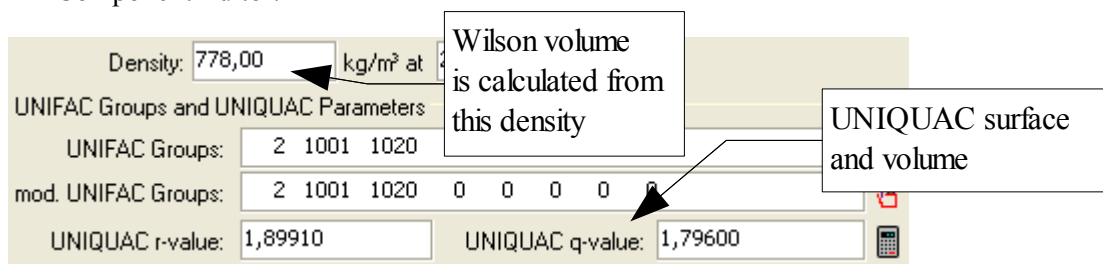
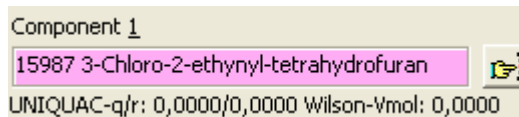
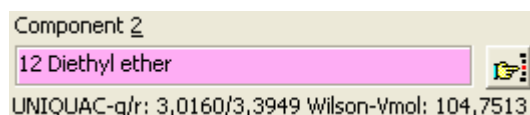
11 | | → Press Return → 11 Ethanol |

The program displays some data relevant data for the g^E models

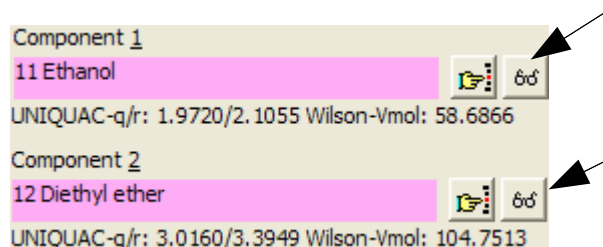
- UNIQUAC: Molecular surface and volume
- Wilson: Liquid volume at approx. 298 K

If any of these values are 0 the corresponding model cannot be used.

The values are stored in the basic component file and can be modified by the DDB Component Editor.




The two buttons with glasses at the right side of the component names open a dialog with additional information

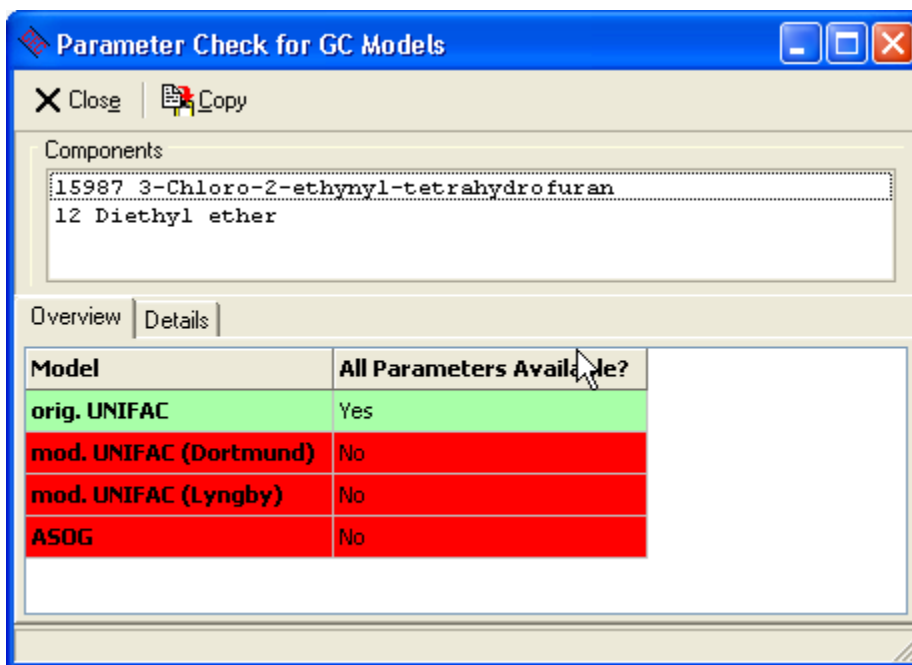


about necessary component specific data.

Component Details: Ethanol			
X Exit			
UNIQUAC-r	2.1055		
UNIQUAC-q	1.9720		
V Wilson	58.6866		
UNIFAC groups			
3	1 time 1 CH3 [CH2]	1 time 2 CH2 [CH2]	1 time 14 OH [OH]
mod. UNIFAC (Dortmund) groups			
3	1 time 1 CH3 [CH2]	1 time 2 CH2 [CH2]	1 time 14 OH (P) [OH]
mod. UNIFAC (Lyngby) groups			
3	1 time 1 CH3 [CH2]	1 time 2 CH2 [CH2]	1 time 12 OH [OH]
ASOG groups			
2	2 times 1 CH2 [CH2]	1 time 6 OH [OH]	

The UNIQUAC volumes and surfaces and the Wilson volume is repeated here but the lines about the group assignment (group numbers and names) for the four supported group contribution models add new important information. These groups must be available for all the components. Otherwise a group contribution model can't be used.

The button  Interaction Parameters opens a dialog with information of the availability of group assignments and interaction parameters for the different group contribution methods.



Green lines indicate that this model can be used to calculate activity coefficients – group assignment and interaction parameters are available. Red lines indicate either a missing group assignment or missing interaction parameters. The “Details” page allows to identify the problem.

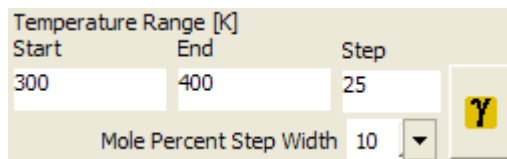
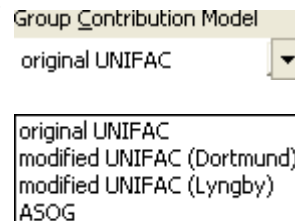
Calculating Activity Coefficients


Four different models are currently available for the calculation of activity coefficients:

- original UNIFAC
- modified UNIFAC (Dortmund)
- modified UNIFAC (Lyngby)
- ASOG

The first two models are maintained by the UNIFAC consortium (www.unifac.org). The program recalculates the activity coefficient table on any model change and displays an error message if a calculation fails because of missing parameters or group assignments.

The last settings are the temperature range and the step width of the composition.



If any of these values is changed the  has to be used to force the program to recalculate the activity coefficient table.

Fitting

The program allows to fit parameters for the g^E models UNIQUAC, NRTL, and Wilson.

gE Model
UNIQUAC

NRTL
UNIQUAC
Wilson

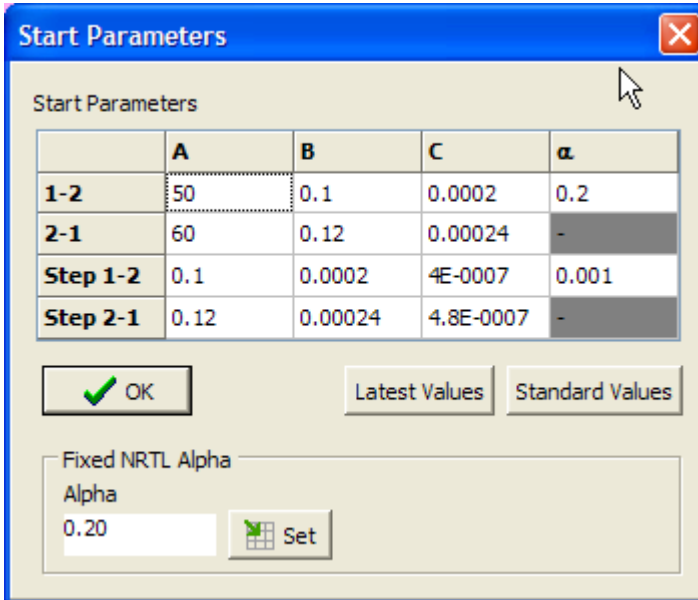
For all three methods the temperature dependence of the parameters can be set to

- none (1 parameter, A_{12}, A_{21})
- linear (2 parameters, $A_{12}, A_{21}, B_{12}, B_{21}$)
- quadratic (3 parameters, $A_{12}, A_{21}, B_{12}, B_{21}, C_{12}, C_{21}$)


Temperature Dependency
none

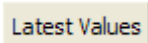
Starting Values

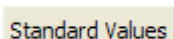
Starting values for the parameters can be modified by  :




	A	B	C	α
1-2	50	0.1	0.0002	0.2
2-1	60	0.12	0.00024	-
Step 1-2	0.1	0.0002	4E-0007	0.001
Step 2-1	0.12	0.00024	4.8E-0007	-

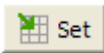
Fixed NRTL Alpha
Alpha
0.20 

The grid is editable and allows to enter starting values as well as initial step widths. A parameter can be fixed by setting the step width to 0. The  buttons allows using the parameters from the last fit and the

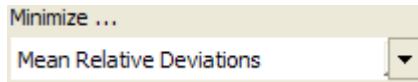
 resets the parameters to some useful values.

Fixing the NRTL α parameter can either be done by simply setting the step width to zero in the data grid or by entering a value in the “Alpha” edit field in

Fixed NRTL Alpha
Alpha
0.20 

the “Fixed NRTL Alpha” box and selecting the  button. This makes nothing else than storing the α in the right cell of the data grid and setting the step width to 0.

Objective Function

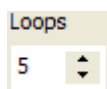


The objective function can be set to

- Average Absolute Deviations
- Root Mean Square Deviations
- Mean Relative Deviation

All three objective function have different advantages and downsides.


Loops



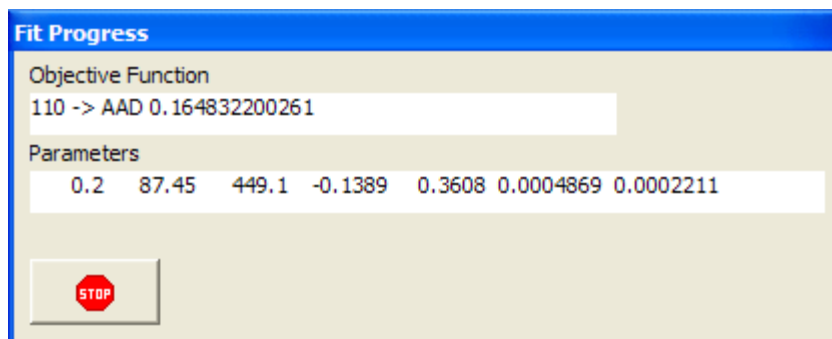
The “Loops” setting is used to restart the fit procedure up to four times. This is a useful and often necessary feature because the changes in the objective function are rather small near the minimum and the optimization process is starving before reaching a *global* minimum. The re-start uses the obtained parameters from the previous fit but starts with the step widths of the initial fit.

This procedure guarantees in many cases a better minimum (in deviations) than a single fit.

Fitting

The  button starts the fit. The used algorithm is Simplex-Nelder-Mead (SNM). This optimization algorithm is known to be robust and will not fail. The drawback of this stability is that the SNM method needs a lot of function calls and can be slow.

The currently obtained objective function value and the parameters are displayed in a separate window.



The  button allows stopping the current fit process.

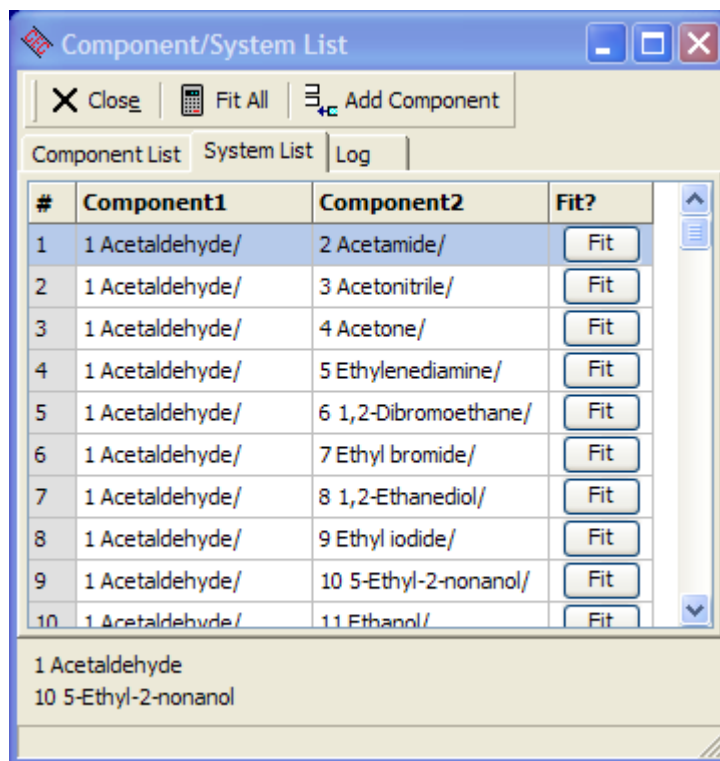
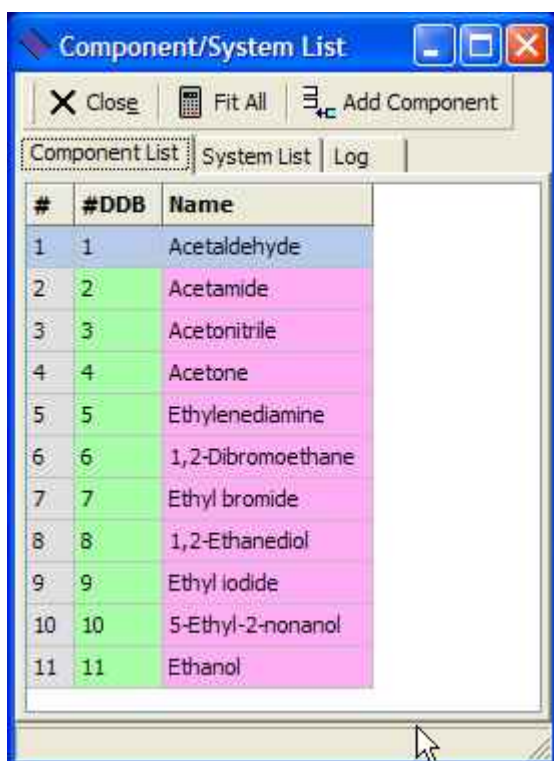
The sequence of the parameters are always

- NRTL α first (if NRTL has been selected)
- A_{12} and A_{21} (temperature-independent parameter)
- B_{12} and B_{21} (linear temperature-dependent parameter)
- C_{12} and C_{21} (quadratically temperature-dependent parameter)

Batch Fitting


The program allows to fit multiple systems in a row. These systems will be build from component lists which can be created by other DDB software like the component management program, the Artist structure editor, or the DDB main retrieval program.

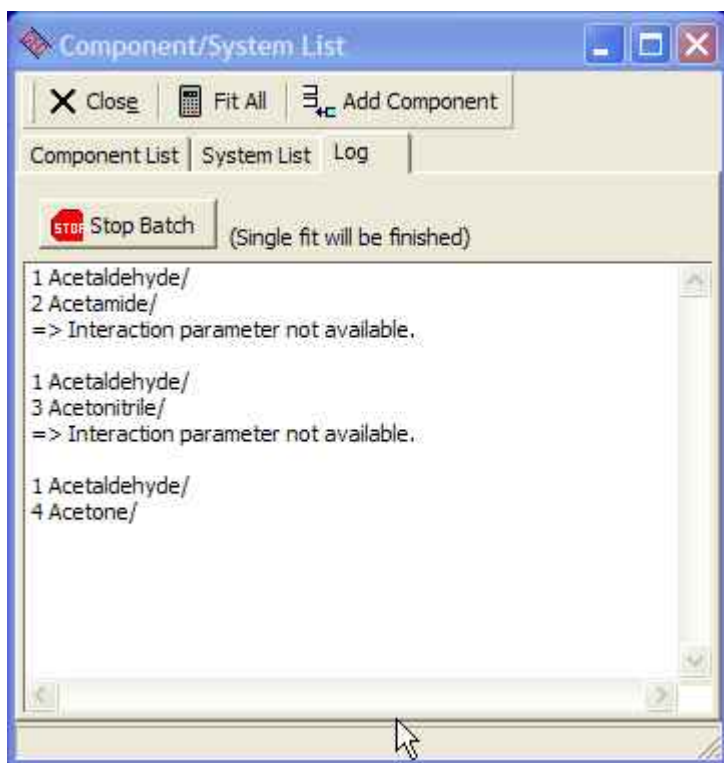
The dialogs

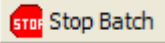


display both the list of components and the list of binary systems built from these components. The



button in the single grid rows will start a fit only for the single binary system displayed in the single row whereas the  button in the tool bar will start a batch fit for all the systems. This batch fit produces a protocol which is displayed in the third page of this dialog.



The batch fit can be stopped by the  button. A single fit will be finished before the batch stops. Any results from the already executed fits are saved in the “Result” windows (see next chapter) and are not lost.

The log window itself only stores information on the success of a fit or an error message if a fit can't be performed due to, for example, missing group/group interaction parameters of a UNIFAC model.

Results

The obtained parameters are also displayed in a table. This table is used to collect all fit results.

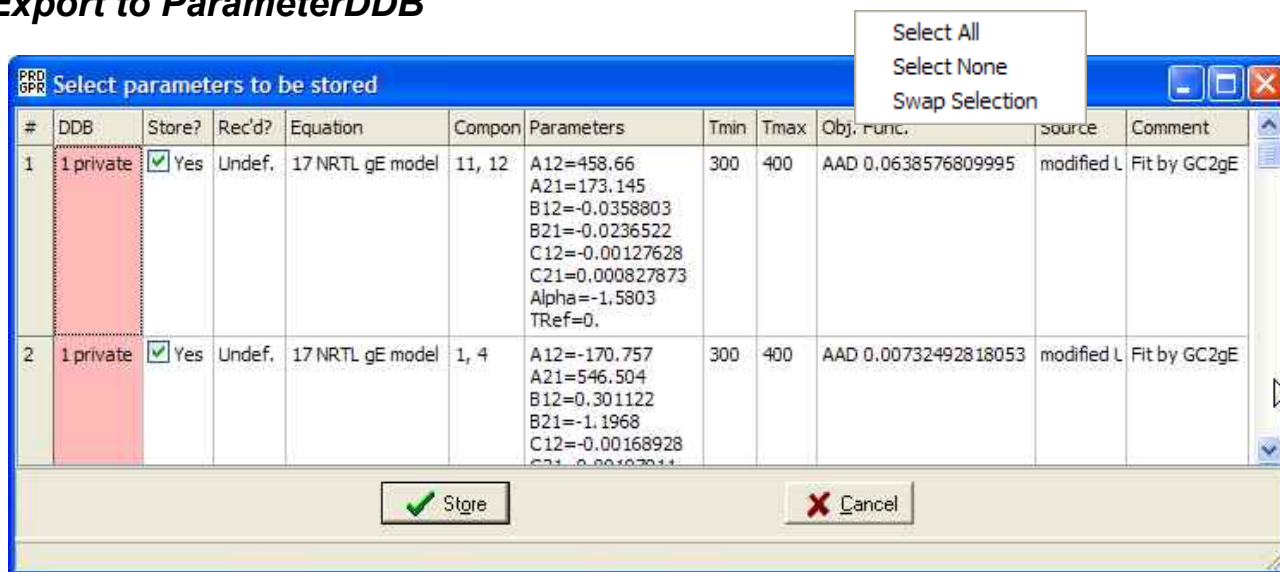
1 Set	A	B	C	α
Model	NRTL			
1-2	458.65983	-0.0358802	-0.0012762	-1.5803432
2-1	173.14463	-0.0236521	0.00082787	-1.5803432
Comp1	11 Ethanol			
	r=2.1055	q=1.9720	Vmol=58.69	
Comp2	12 Diethyl ether			
	r=3.3949	q=3.0160	Vmol=104.7	
Obj. Function	AAD 0.0638576809995			
Parameters are given in [cal/mol]				

The parameters sets can be saved as Microsoft Excel file, as Aspen INP file, to the ParameterDDB, and copied

to the Windows clipboard.

The parameters saved in the Aspen INP file are fully Aspen compatible whereas all other locations store the parameters in a DDB software specific format. The ParameterDDB management software supports to copy g^E model parameters in the DDB format as well as in the Aspen and the compatible EPCON's System7 format. Additionally, DDBST provides a tool for exporting data from the ParameterDDB to EPCON's System7 which directly supports their file format.

Export to ParameterDDB



This export is displaying an additional selection dialog where all fitted parameter sets are listed. Single datasets can be included and excluded here before storing the entire list.

This ParameterDDB is also used to export parameters in various other formats.

Export to Aspen INP Files

This export only needs the specification of a file name to create an INP file. This fit program is able to perform a match of the internal (DDB) components with the Aspen IDs and will write appropriate Aspen names in the INP file. If a match can't be found a unique identifier is used which can be easily modified in Aspen.

Import Aspen Components

This feature allows to import components from Aspen simulator files. Supported files are the INP, the BKP, and the APT files.

This fit program will not only load the component identifiers but it also loads group assignments which will be matched automatically to DDB group assignments.

After a fit has been performed the program will write an INP file with the appropriate Aspen component identifiers allowing to seamlessly import the fitted g^E model parameters.

The UNIFAC Consortium

This program fully supports the parameter files developed by the UNIFAC consortium (www.unifac.org).