

RecPar

g^E Model Parameter Regression Simultaneously to Multiple Properties

DDBSP – Dortmund Data Bank Software Package



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1 Introduction

RecPar is a regression tool that allows the user to fit g^E model parameter and cubic EOS mixing rule parameters simultaneously to different phase equilibrium data and some excess properties. RecPar currently can handle binary systems only.

1.1 Supported Data Types

RecPar can use

1. Vapor-Liquid Equilibrium Data (VLE and HPV Databank).
The only needed data are liquid composition and the presence of either temperatures or pressures. Full data (liquid and vapor composition, temperatures and pressures are both present) will give better results, in most cases.
2. Azeotropic Data (AZD Databank).
AZD are handled as special VLE data points. Currently only full azeotropic data points containing temperature, pressure, and composition are supported.
3. Liquid-Liquid Equilibrium Data (LLE Databank).
RecPar can handle single phase data but then needs good starting values for the parameters already giving an LLE. If both phases of the miscibility gap are given, RecPar will find the LLE through the isoactivity criterion.
4. Solid-Liquid Equilibrium Data (SLE Databank).
RecPar can handle only eutectic systems correctly.
5. Heats of Mixing (HE Databank).
6. Excess Heat Capacity (CPE Databank).

Heats of mixing and excess heat capacities *must be used only as additional data* to VLE, SLE, or LLE data because they only describe the first (h^E) and second derivative (cP^E) of the activity coefficient with the temperature and will *not* result in usable parameters if used as sole source even if the regression seems to work and the calculated line match the experimental value.

1.2 Supported g^E Models

RecPar currently supports the g^E models

1. UNIQUAC¹
2. NRTL²
3. Wilson³
4. Margules⁴ (limited to VLE data)

1 Abrams D.S., Prausnitz J.M., "Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems", AIChE J., 21(1), 116-128, 1975

2 Renon H., Prausnitz J.M., "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures", AIChE J., 14(1), 135-144, 1968

3 Wilson G.M., "Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing", J.Am.Chem.Soc., 86, 127-130, 1964

4 Margules, Max, "Über die Zusammensetzung der gesättigten Dämpfe von Mischungen", Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften Wien; Mathematisch-Naturwissenschaftliche Klasse II, 104, 1243–1278,

The equation of van Laar is currently neglected because this model is of no practical importance.

NRTL can be used without any additionally needed parameters and is the preset method. The selection is registered and restored on subsequent program invocations.

UNIQUAC needs component specific volumes and surfaces. RecPar uses the values stored in the DDB main component file. To edit these values it is necessary to use the Component Editor.

UNIQUAC r-value: UNIQUAC q-value:

The Wilson model can also be used without any additional properties in the Aspen form of the equation (which RecPar uses) but in the DDB system it is necessary to extract a ratio of pure component liquid volumes (which can be hypothetical). These “Wilson” volumes are also available through the Component Editor.

Density: kg/m³ at K

Margules is a simple model also needing no further constants. The model of van Laar is currently not supported because of its negligible importance and its limitations.

1.2.1 Temperature Dependencies

RecPar can regress temperature-independent, linear temperature-dependent, and quadratic temperature-dependent parameters.

Additional temperature-dependencies include a logarithmic term, a cubic term and term with T^{-1} . The latter is used by PRO/II and the logarithmic term by Aspen. The “Quick Select” combo box contains short cuts to the common T dependencies used either by the old DDB software or by the simulators.

Temperature Dependency

a_{ij} $d_{ij} \cdot T \cdot \ln(T)$

$b_{ij} \cdot T$ $e_{ij} \cdot T^3$

$c_{ij} \cdot T^2$ f_{ij} / T

Quick Select: PRO/II

If a term is chosen that is not supported by a specific process simulator the parameters cannot be used in that software. RecPar notices if the selected equation form is compatible with either Aspen or Pro/II or older DDBSP software.

1.3 Supported EOS Mixing Rule Models

RecPar supports the cubic equation of state models Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), Peng-Robinson 1978 (PR78) and Redlich-Kwong (RK).

As K_{ij} mixing rules the quadratic mixing rule and Panagiotopoulos/Reid are supported. In this case the temperature dependency displayed below is used. The parameters unit is K.

Temperature Dependency

a_{ij} d_{ij} / T

$b_{ij} \cdot T$ e_{ij} / T^2

$c_{ij} \cdot T^2$

Quick Select: PRO/II

As g^E mixing rules Vidal, Tochigi, Michelsen, PSRK, VTPR and LCVM are supported. In this case the temperature dependency displayed below is used. The parameters unit is cal/mol.

Temperature Dependency

a_{ij} d_{ij} / T

$b_{ij} \cdot T$ $e_{ij} \cdot T \cdot \ln(T)$

$c_{ij} \cdot T^2$ $f_{ij} \cdot T^3$

Quick Select: PRO/II

The supported g^E models are NRTL, Wilson, UNIQUAC, NRTL (Vidal) and UNIQUAC (res.).

For SRK and PR the original alpha functions (using the acentric factor), Mathias-Copeman and Twu-Bluck-Cunningham-Coon are supported. The Stryjek-Vera alpha function is available for PR only.

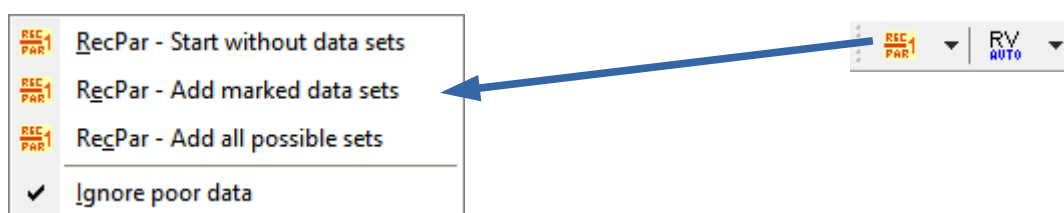
2 First Use

The “Dortmund Data Bank” program can be used to run RecPar with selected data from a Query Result window. Additionally it can be used stand-alone and experimental data can be entered or pasted directly in the program.

This document does not repeat the steps to perform a data search and obtaining a query result.

2.1 Experimental Data Transfer

The drop-down in the query result dialog menu of the Dortmund Data Bank program has three menu entries for calling RecPar with different options.



1. “Start without data sets” opens an empty RecPar dialog where data sets can be added by drag-and-drop from the query result window.
2. “Add marked data sets” opens a RecPar dialog where only the marked sets are automatically added. Further sets can then be added through drag-and-drop.
3. “Add all possible data sets” opens a RecPar dialog and add all usable data sets from the query result.

The option *Ignore poor data* can be used to omit data flagged as doubtful, poor or unreliable.

2.2 Editing or Pasting Experimental Data

If RecPar is started directly an empty form is displayed where data can be added either by opening a data file or by using an import/editor form. These functions are described in detail in the chapter 5 “Entering Own Data“.

3 The RecPar Main Dialog

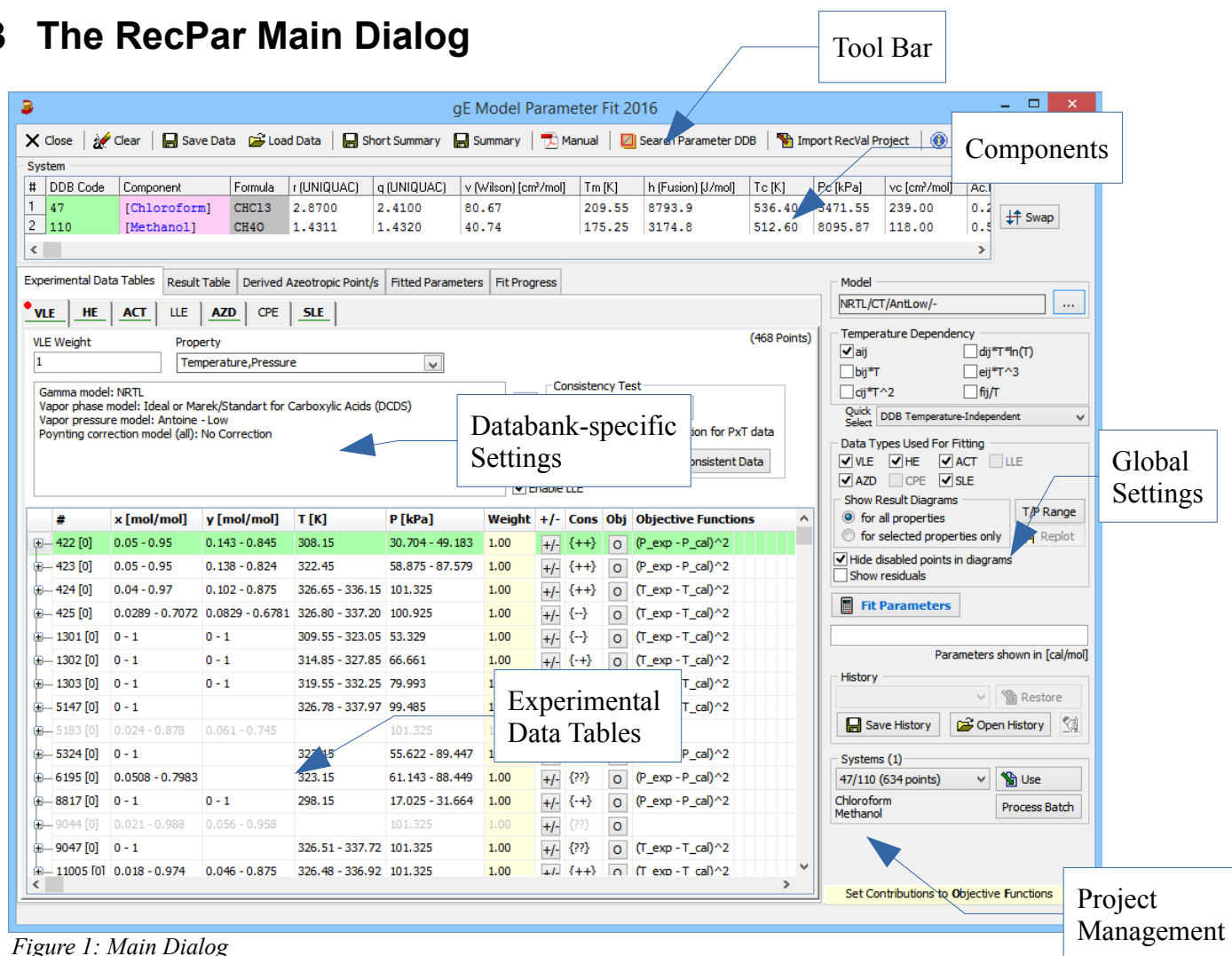


Figure 1: Main Dialog

The dialog has the following main parts:

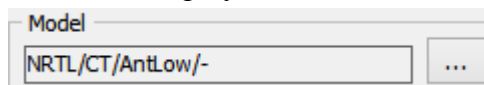
1. List of components which, besides the DDB numbers, names and formula also shows some essentially needed pure component properties.
2. Experimental Data Tables (includes a page with results). This part allows property specific settings like data points weights or the type of contribution to the objective function.
3. Model settings including the “Fit Parameters” buttons and some basic data selections and project management functions.

3.1 List of Components

The list of components is not only used to display the current system but also includes some basic values like the R and Q values (needed for UNIQUAC), the Wilson volume (see chapter 7.2.2 Wilson for details), the melting temperature and heat of fusion (needed for SLE calculation), and critical data and acentric factor (required for EOS calculation).

3.2 Model Selection

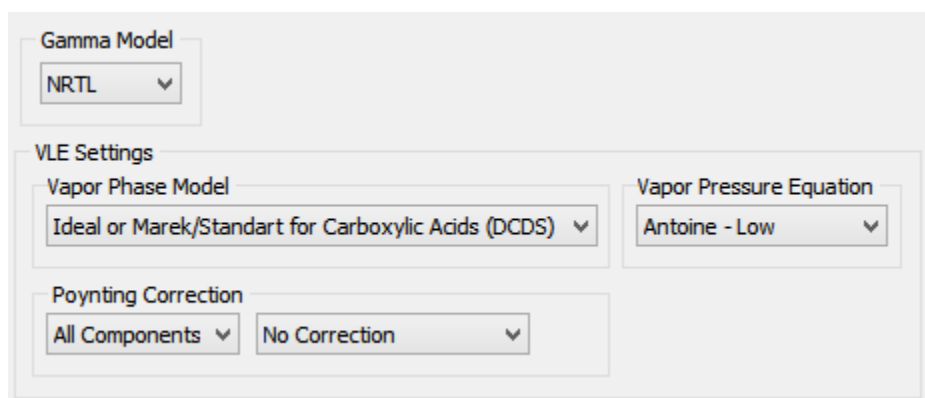
A short summary of the selected model is displayed in the *Model* area



A more elaborate summary can be found on the VLE experimental data page.

Push the button () to open a model selection dialog. In the dialog you can either select a g^E model or an EOS model.

3.2.1 Select g^E Model



In the g^E model settings page the gamma model (required for all mixture properties) can be changed. For VLE (and AZD) calculations further model options are available.

3.2.1.1 Vapor Phase Model

RecPar supports an ideal vapor phase but automatically switches to the Marek/Standart method for an internally stored list of carboxylic acids taking the vapor association into account.

The other methods include different cubic equations of state with the quadratic mixing rule and the Hayden-O-Connell method.

3.2.1.2 Vapor Pressure Equation

RecPar supports a variety of pure component vapor pressure equations:

1. Antoine – Best Match: This option searches the list of available Antoine parameter sets for that one that covers the needed temperature range best (highest overlap or closest).

$$P=10^{A-\frac{B}{T+C}}$$

2. Antoine – Low: This options searches the list of available Antoine parameter sets for that one that has the lowest lower validity range (this option was implemented to mimic the behavior of RecVal which uses a low temperature and a high temperature set of Antoine parameters).

$$P=10^{A-\frac{B}{T+C}}$$

3. DIPPR 101: These are DIPPR⁵ parameters fitted by DDBST staff to DDB pure component properties data (PCP data bank).

$$P = e^{A + \frac{B}{T} + C \ln T + DT^E}$$

4. Wagner 25 and Wagner 36 are both variants of the Wagner equation (2.5-5 and 3-6 form)

$$P = \exp \left(\ln P_c + \frac{A(1-T_r) + B(1-T_r)^{1.5} + C(1-T_r)^{2.5} + D(1-T_r)^5}{T_r} \right)$$

$$P = \exp \left(\ln P_c + \frac{A(1-T_r) + B(1-T_r)^{1.5} + C(1-T_r)^3 + D(1-T_r)^6}{T_r} \right)$$

5. Cox equation

$$P = \exp \left[\ln 101.325 + e^{A + B \left(\frac{T}{T_B} \right) + C \left(\frac{T}{T_B} \right)^2} \left(1 - \frac{T_B}{T} \right) \right]$$

3.2.1.3 Poynting Correction

The Poynting correction needs pure component densities resp. volumes v_i .

RecPar supports

$$Poy_i = \exp \frac{v_i (P - P_i^s)}{RT}$$

- densities calculated with the DIPPR 105 equation. These aren't original DIPPR parameters. The parameters are regressed by DDBST personnel with the help of the DDB pure component properties databank ("PCP Equation Fit" program).

$$\rho = \frac{A}{B \left(1 + \left(1 - \frac{T}{C} \right)^D \right)}$$

- densities by the Yen/Woods⁶ correlation,
- densities (fixed) taken from the basic data (usually at 25 °C),
- densities calculated with the DIPPR 100 equation,
- densities calculated with the DIPPR 119 equation.

It is possible to use different poynting correction models for each component.

⁵ See [DIPPR on the AIChE Web Site](#)

⁶ Yen L. C., Woods S. S., "A Generalized Equation for Computer Calculation of Liquid Densities", AIChE J., 12(1), 95-99, 1967

3.2.2 Select EOS Model

In the EOS model settings page the base cubic equation of state, the mixing rule, the g^E model (if applicable) and the alpha function (if applicable) can be selected.

For further details on the EOS models and the mixing rules see the *GenPar* documentation.

3.3 Experimental Data

The data tables are different for the different properties. Common settings are only the data bank weight and a list of properties used in the objective functions for the parameter regression. The list of properties is, of course, different.

3.3.1 VLE – Vapor-Liquid Equilibrium

3.3.1.1 VLE Specific Settings

3.3.1.1.1 Properties for the Objective Function


The regression routine can minimize the differences between estimated and experimental (or derived) activity coefficients, vapor compositions, temperatures, pressures, K factors, g^E/RT , and activities ($x^*\gamma$).

Temperature for isobaric data sets and pressures for isothermal data sets are preselected after data have been added to the RecPar dialog. The other properties can be selected manually.

3.3.1.1.2 Consistency Test

For VLE data two consistency tests are available, the point-to-point test and the area test. A detailed description of both tests is given in the “Dortmund Data Bank” manual. RecPar allows setting all data point weights to zero for data sets where both consistency tests have failed.


3.3.1.1.3 Pure Component Vapor Pressure Corrections

 If the experimental VLE data set contain pure component temperatures and pressures it is recommended to use that experimental data point for the VLE calculation instead of the temperature or pressure calculated by the vapor pressure equation.

This avoids offsets between calculated and experimental data points leading to artificial errors in pressures and temperatures.

For the Antoine and DIPPR 101 equations RecPar automatically adopts the experimental pressure and temperature by modifying the Antoine “A” or DIPPR 101 “A” parameters. If experimental data are not available RecPar has a dialog where these correction can be entered manually.

The dialog shows the experimental VLE data set (dew and bubble point curve) as circles and the pure component vapor pressure as rectangles on the left and right borders.

If the rectangles seem to be at a wrong place they can be moved by entering new vapor pressures for one or both components. Clicking the  Write button will

store the changed pure component vapor pressure or temperature.

The “Estimate by Polynomial” function uses five points of the VLE curves on both sides and for both the dew point and bubble point curves and extrapolates to the pure components.

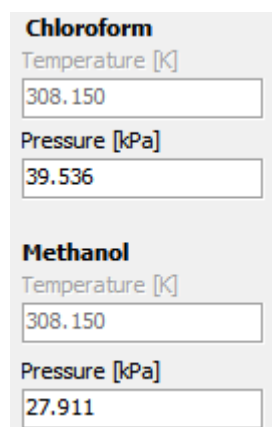


Figure 2: Entering Corrected Pressures

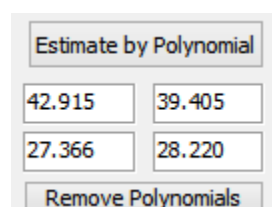
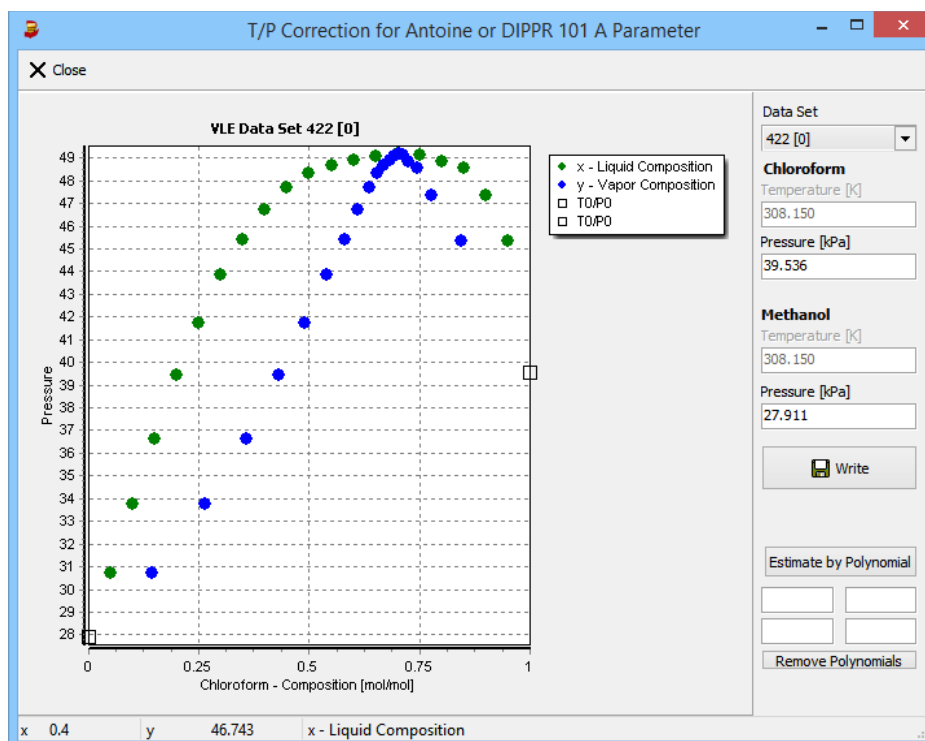



Figure 3: Temperature/Pressure Correction for Antoine A Parameter

These polynomials normally only give a rather rough estimate and can be only useful if the data set contains quite some data near at high mole fractions of the particular component.

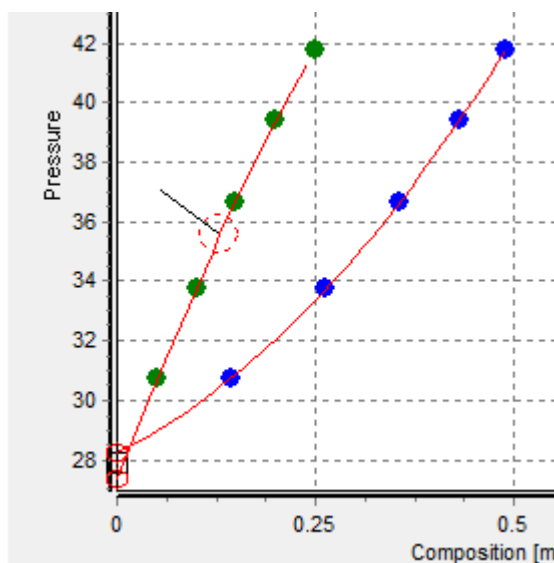


Figure 4: Estimation by Polynomial

The parameter of the equations Wagner and Cox can't be corrected this way and will always be used unmodified.

3.3.1.2 Data Table

The data table for VLE contains one (collapsed) node for each data set. Each node line consists of

1. the data set ID
2. the liquid composition range x_1 for component 1 in mole fractions (the liquid composition of component 2 is always $1.0 - x_1$)
3. the vapor composition range y_1 for component 1 in mole fractions
4. the temperature range in K
5. the pressure range in kPa
6. the data set weight (if equal for all points in the set)
7. a button to enable/disable all points of the data set
8. the consistency test result (see below)
9. a button to set the objective function for all points of the data set
10. the active objective function

When a node is expanded (with a click on the “+” button in the left-most column) then the first child row contains the reference information. All following child rows represent a data point with a consecutive number, liquid composition x_1 , vapor composition y_1 , temperature, pressure, data point weight (modifiable), a button to enable/disable the data point, a button to set the objective function for the data point, and the active objective function for the data point.

Two consistency tests are performed – a point-to-point test (first position) and an area test. The possible entries are then

1. “+”: Data set is consistent
2. “-”: Data set is **in**consistent

3. “*”: Consistency test hasn't been performed
4. “?”: Consistency test gave no results (mostly for incomplete data sets like PxT sets with a missing vapor composition)

The consistency tests are performed automatically in the Query Result if “Add all possible sets” has been selected.

In most cases, consistent data sets are of higher quality, will be easier to fit and give better results.

3.3.2 HE – Heats of Mixing

3.3.2.1 HE Specific Settings

HE Weight	Property
<input type="text" value="1.0"/>	<input type="text" value="Heat of Mixing"/>

3.3.2.1.1 Objective Function

The single possible setting for heats of mixing is switching off and on if heats of mixing should be used. Switching off means that h^E data have no contribution – which is the same effect as setting the data bank weight or data point weight to zero.

Property
<input type="text" value="Heat of Mixing"/>
<input checked="" type="checkbox"/> Heat of Mixing

3.3.2.2 Data Table

The data table for HE contains one (collapsed) node for each data set. Each node line consists of

1. the data set ID
2. the liquid composition range x_1 for component 1 in mole fractions
3. the temperature range in K
4. the pressure range in kPa
5. the heat of mixing in J/mol
6. the data set weight (if equal for all points in the set)
7. a button to enable/disable all points of the data set
8. a button to set the objective function for all points of the data set
9. the active objective function

When a node is expanded then reference and data point information similar to VLE is displayed.

3.3.3 ACT – Limiting Activity Coefficients

3.3.3.1 ACT Specific Settings

ACT Weight	Property
<input type="text" value="1.0"/>	<input type="text" value="Limiting Activity Coefficient (Logarithmic Scale)"/> ▾

3.3.3.1.1 Objective Function

The only possible setting for limiting activity coefficients is switching off and on if limiting activity coefficients should be used. Switching off means that ACT data have no contribution – which is the same effect as setting the data bank weight or data point weight to zero.

<input type="text" value="Limiting Activity Coefficient (Logarithmic Scale)"/> ▾
<input checked="" type="checkbox"/> Limiting Activity Coefficient (Logarithmic Scale)

3.3.3.2 Data Table

The data table for ACT contains one line for each data set (single data point). Each line consists of

1. the data set ID
2. a consecutive number
3. the temperature in K
4. the limiting activity coefficient of component 1 in component 2
5. the limiting activity coefficient of component 2 in component 1
6. the data point weight (modifiable)
7. a button to enable/disable the data point
8. a button to set the objective function for the data point
9. the active objective function
10. the reference information

3.3.4 LLE – Liquid-Liquid Equilibrium

3.3.4.1 LLE Specific Settings

LLE Weight	Property
<input type="text" value="1.0"/>	<input type="text" value="Isoactivity"/> ▾

3.3.4.1.1 Objective Function

The LLE objection function can minimize the difference in the activities of the two phases (goal is isoactivity) or by meeting the experimental liquid compositions with the additional option of obtaining the right gap width.

<input type="text" value="Isoactivity"/> ▾
<input type="checkbox"/> Mole Fractions of Both Phases
<input type="checkbox"/> Mole Fractions of Both Phases plus Gap Width
<input checked="" type="checkbox"/> Isoactivity

The criterion “Isoactivity” is stable – any starting parameter will achieve useful parameters during the regression. The drawback is that coexistent phase information (tie lines) are necessary. The other two properties can be used with information from a single phase only but they need starting

values which already estimate a miscibility gap. If not, the parameter regression can obtain no usable objective function and the iteration will most probably fail.

3.3.4.2 Data Table

The data table for LLE contains one (collapsed) node for each data set. Each node line consists of

1. the data set ID
2. the mole fraction range $x_{1,L1}$ of component 1 in phase 1
3. the mole fraction range $x_{1,L2}$ of component 1 in phase 2
4. the temperature range in K
5. the pressure range in kPa
6. the data set weight (if equal for all points in the set)
7. a button to enable/disable all points of the data set
8. a button to set the objective function for all points of the data set
9. the active objective function

When a node is expanded then reference and data point information similar to VLE is displayed.

3.3.5 AZD – Azeotropic Data

3.3.5.1 AZD Specific Settings

AZD Weight	1.0	Property	Vapor Composition, Temperature, Pressure
Further Settings see VLE Page			

3.3.5.1.1 Objective Function

The parameter regression is simply a VLE regression with the small limitation that the vapor composition has to be the same as the liquid composition.

Vapor Composition, Temperature, Pressure	▼
<input checked="" type="checkbox"/> Vapor Composition <input checked="" type="checkbox"/> Temperature <input checked="" type="checkbox"/> Pressure	

3.3.5.2 Data Table

The data table for AZD contains one line for each data set (single data point). Each line consists of

1. the data set ID
2. a consecutive number
3. the temperature in K
4. the pressure in kPa
5. the azeotropic composition y_1 for component 1 in mole fractions
6. the data point weight (modifiable)
7. a button to enable/disable the data point
8. a button to set the objective function for the data point

9. the active objective function
10. the reference information

3.3.6 CPE – Excess Heat Capacities

3.3.6.1 CPE Specific Settings

CPE Weight	Property
<input type="text" value="1.0"/>	<input type="text" value="Excess Heat Capacity"/>

3.3.6.1.1 Objective Function

The only possible setting for excess heat capacities is switching off and on if excess heat capacities should be used. Switching off means that cp^E data have no contribution – which is the same effect as setting the data bank weight or data point weight to zero.

Excess Heat Capacity	▼
<input checked="" type="checkbox"/> Excess Heat Capacity	

3.3.6.2 Data Table

The data table for CPE contains one (collapsed) node for each data set. Each node line consists of


1. the data set ID
2. the liquid composition range x_1 for component 1 in mole fractions
3. the temperature range in K
4. the pressure range in kPa
5. the excess heat capacity in J/(mol*K)
6. the data set weight (if equal for all points in the set)
7. a button to enable/disable all points of the data set
8. a button to set the objective function for all points of the data set
9. the active objective function

When a node is expanded then reference and data point information similar to VLE is displayed.

3.3.7 SLE – Solid-Liquid Equilibrium

Only data for eutectic mixtures (pure solids) can be used.

3.3.7.1 SLE Specific Settings

SLE Weight	Property	
<input type="text" value="1.0"/>	<input type="text" value="Melting Temperatures"/>	

3.3.7.1.1 Objective Functions

Both the melting temperature and the activity coefficients are possible as properties for the objective function for solid-liquid equilibria.

Melting Temperatures	▼
<input checked="" type="checkbox"/> Melting Temperatures <input type="checkbox"/> Activity Coefficients	


The activity coefficients are derived by the equation

$$\ln x_i^L \gamma_i^L = \frac{-\Delta h_{m,i}}{RT} \left(1 - \frac{T}{T_{m,i}} \right)$$

This equation is valid only for the side where component i is the pure solid. Heats and temperatures of transitions are also taken into account – if available.

There's a remaining insecurity if there are only few points in the original data sets and the location of the eutectic points isn't clear. Then, as a result, it cannot be seen clearly what component is the pure solid and the wrong activity coefficient might be used. It's normally safer to use the melting temperature T_m only.

3.3.7.1.2 Melting Point Correction

The button  invokes a dialog where pure component melting points can be corrected. If a melting is present in the experimental data it will be used; if it is missing a default value from the basic component file is used. If this does not match the current melting point of the SLE data set it can be changed here.

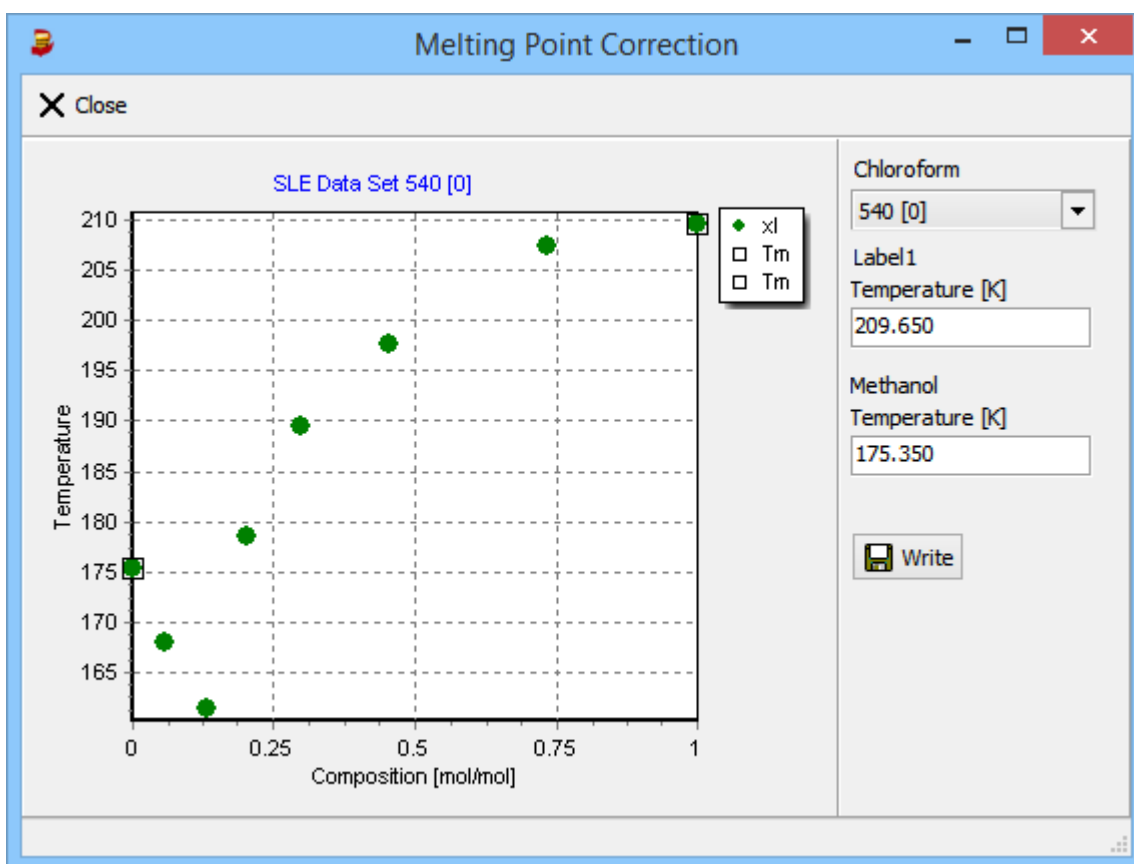


Figure 5: Melting Point Correction

This utility is very similar to the correction of pure component vapor pressures, see chapter “Pure Component Vapor Pressure Corrections“.

3.3.7.2 Data Table

The data table for SLE contains one (collapsed) node for each data set. Each node line consists of

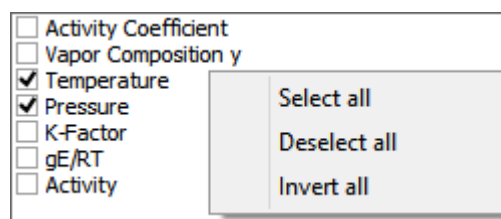
1. the data set ID
2. the liquid composition range x_1 for component 1 in mole fractions
3. the temperature range in K
4. the pressure range in kPa
5. the data set weight (if equal for all points in the set)
6. a button to enable/disable all points of the data set
7. a button to set the objective function for all points of the data set
8. the active objective function

When a node is expanded then reference and data point information similar to VLE is displayed.

3.3.8 Common Controls to All Data Types

The properties selector for the objective function has a context menu that allows

- selecting all properties,
- deselecting all,
- and invert the selection.



In the data grid the objective function selection button pop ups a menu repeating the entries from the properties selector. If the button in a node line of a data set is used then the change is applied to all data points of the data set.

The “Weights” column has yellow cells that allow entering weight for all data points of the current set in one step. If the field is empty then at least one data point within the data set has a different weight than other points.

3.4 Models

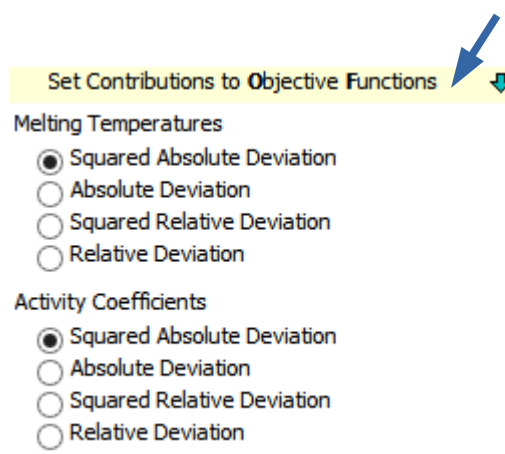
3.4.1 Objective Functions

For all available objective functions it is possible to set how they are summed up.

The possible choices are

- Squared Absolute Deviation
- Absolute Deviation
- Squared Relative Deviation
- Relative Deviation

On first use all “Squared Absolute Deviation” is set for all properties contributing to the objective functions.



There's one exception: A relative deviation is not possible for the LLE objective function “Mole fraction of both phases”.

Although a relative deviation can be selected only the equivalent absolute error is used.

The settings are stored and will be restored in subsequent RecPar sessions.

3.4.2 Parameter Regression

3.4.2.1 Active Data Types

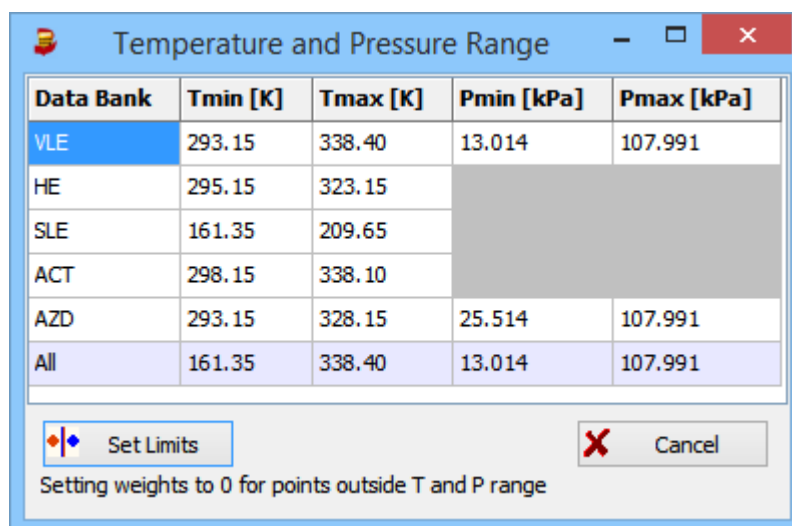
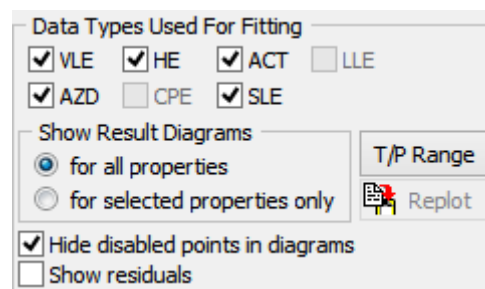
These check boxes allow quickly drop or include selected data types from the regression. A right-click on a check box selects a single property directly.

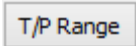
The “Show Result Diagrams” option controls how many diagrams are shown after a regression has been performed.

- “for all properties” will show diagrams for all available data types even if they haven't been used for the fit.
- “for selected properties only” will show only diagrams for the data types used in the regression.

“Hide disabled points...” allows hiding data points with no contribution to the objective function.

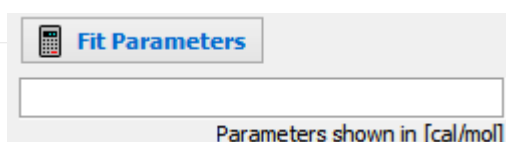
The “Show residuals” shows and hides a further result diagram with residuals (contributions to the objective function). Residuals have no thermodynamic meaning but the diagram might show outliers prominently.



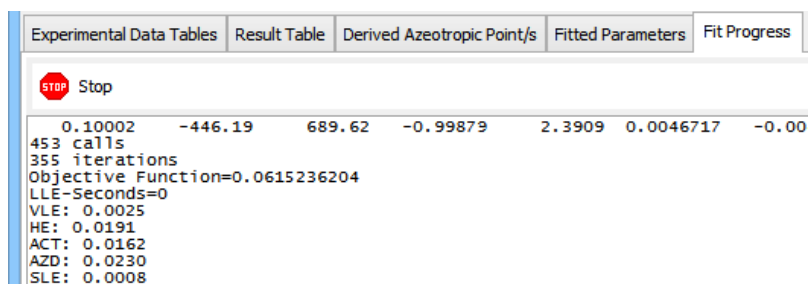
The “T/P Range” button  opens a dialog where the minimum and maximum temperature and pressure of all available data is shown and it allows setting new limits and setting the weight of data points outside this given limit to 0 so that they are not used for the regression anymore.

3.4.2.2 Regression Progress Information

The line below the “Fit Parameters” button shows the obtained parameters during the regression and also after the regression.



During the regression a separate tab sheet with a multi-line text field is shown. That control is used to present some more detailed information about the iterations and the objective function.



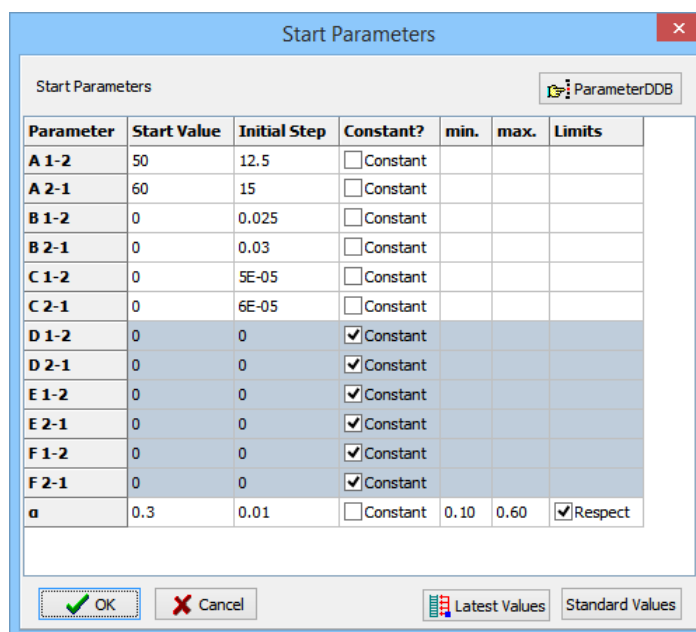
```
Experimental Data Tables | Result Table | Derived Azeotropic Point/s | Fitted Parameters | Fit Progress
STOP Stop
0.10002 -446.19 689.62 -0.99879 2.3909 0.0046717 -0.00
453 calls
355 iterations
Objective Function=0.0615236204
LLE-Seconds=0
VLE: 0.0025
HE: 0.0191
ACT: 0.0162
AZD: 0.0230
SLE: 0.0008
```

The first line shows the current parameters, the number of calls to the objective function is shown in the second line, the next line contains the number of iteration steps, the following line shows the total error calculated with the current parameters, the “LLE seconds” entry shows the time needed for calculating the LLE contribution, and then the contributions of the other properties are following.

These values are *scaled* and a combination of several contributions and will not represent concrete values assignable to specific properties. The numbers however may be useful to see the contributions of the single properties in comparison to the other properties and see if there are some imbalances in the weighting of the single properties.

4 Parameter Regression

4.1 Start Parameters



The start parameters are displayed when a fit is about to start. RecPar uses default start parameters (nearly the same as RecVal/3) and so a parameter regression can be started right-away.

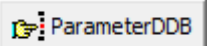
It is also possible to use the parameters from previous regression as starting parameters.

This is especially useful for subsequent regressions, going from temperature-independent to temperature-dependent parameters.

This will normally speed-up the regression (although speed is normally only an issue for many hundred available points and difficult objective functions).

Other settings are only available for NRTL. It is possible to set limits for the α value.

Starting values are especially important if LLE data are the only available data. If the objective function is finding the correct compositions directly it is necessary to start with parameters already estimating a miscibility gap.

The  button allows searching the DDB parameter data bank for existing parameters.

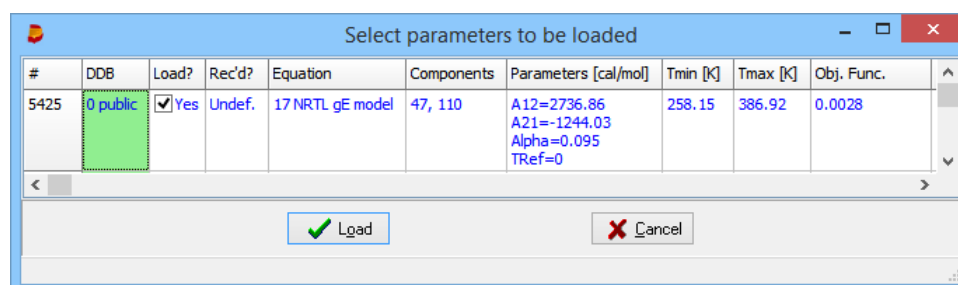


Figure 6: Using stored parameters as starting values

4.2 Regression Results

The regression results are collected in a separate tab sheet and therefore it is not necessary to store every obtained single parameter set.

The parameters can be saved as

1. Microsoft Excel file in the format the dialog shows (“Save as XLS”)
2. Aspen INP file for the Aspen simulator (“Save as INP”)
3. DDB parameter data set for the further usage in the DDB system (“Save in ParameterDDB”)
4. GPF file, a DDB specific file for parameters (soon obsolete, “Save as GPF”)
5. The parameters can also be copied to the Windows clipboard.

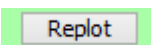
The dialog also allows clearing all  or single sets .

The parameters are not cleared/removed if the model settings change. Only the explicit usage of the “Clear” or the “Remove” button or exiting the entire program removes all fitted parameter sets.

1 Set	a	b	c	d	e	f	a	
Model	NRTL		Set No. 2		Ideal	AntLow	Remove	Replot
IA 1-2	1991.8164	3.0311336	-0.01662206	0.0000000	0.0000000	0.0000000	0.3000000	
IA 2-1	913.99697	-11.253248	0.02551783	0.0000000	0.0000000	0.0000000	0.3000000	
Comp1	47 Chloroform							
				poy=-				
Comp2	110 Methanol							
				poy=-				
Obj. Function	Total=0.00282612 VLE=0.0001 HE=0.0020 AZD=0.0004 SLE=0.0004							
Aspen	a	b	c	d	e	f		
IA 1-2	1.5253214	1002.3181	0.3	0	0	-0.008364522		
IA 2-1	-5.6628384	459.93985	0.3	0	0	0.012841035		
Pro/II								
IA 1-2	Equation form not compatible							
IA 2-1	Equation form not compatible							

parameters are given in [cal/mol], Aspen and PRO/II parameters in [K]

Figure 7: List of Fitted Parameters

The  button in the data grid shows again all available diagrams for the specific parameter set.

4.2.1 Result Dialog Entries

The result dialog shows the following lines

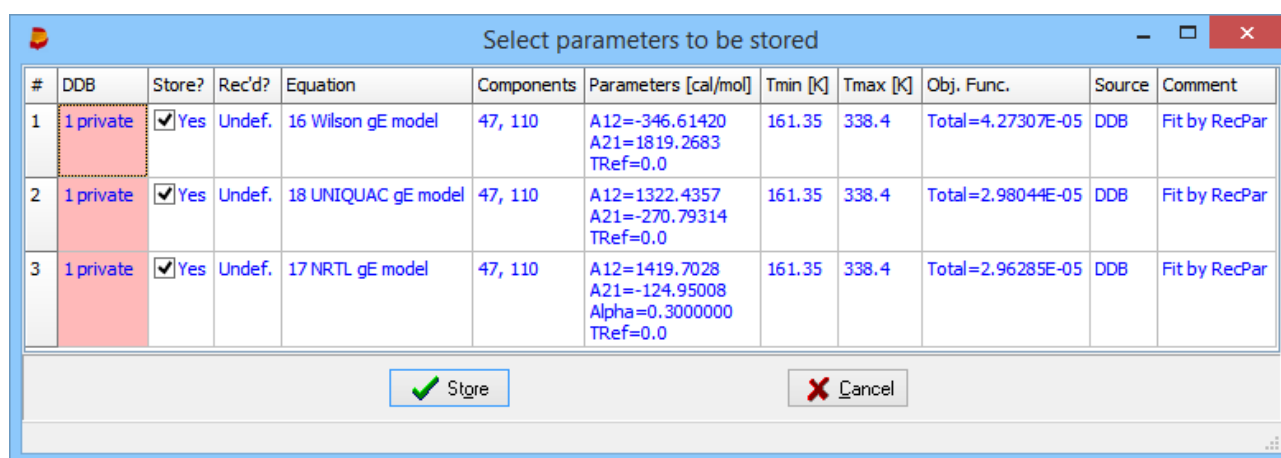
1. The top line shows the equation name (NRTL etc.), a consecutive number, the “Remove” and the “Replot” buttons. For a gE model result it does also contain the vapor phase model and the vapor pressure model used for VLE regression.
2. The parameters in the typical DDB format follow
3. Both components with DDB number, name, and – if applicable – some basic properties and the poynting correction model come next.

4. The next line shows the objective function – the final error. This value does not represent a concrete thermodynamically useful value, it should be used only for the comparison of different models and temperature dependencies with otherwise the same settings.
5. The parameter in the Aspen simulator format follow – if possible.
6. Finally the parameter in the PRO/II simulator format follow – if possible.

4.2.2 Saving parameters in the ParameterDDB

Parameters are always stored in the private DDB.

RecPar shows an additional selection dialog with all data sets found in the regression result window and allows the selection and deselection of single sets.



This dialog has two editable cells

1. “Source” – preset with “DDB”
2. “Comment” – preset with “Fit by RecPar”

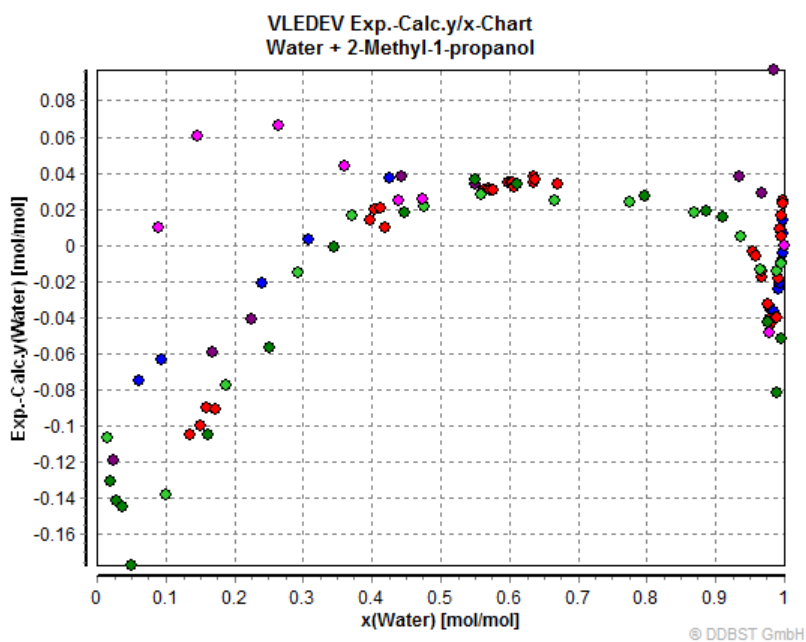
	Source	Comment
71	DDB	Fit by RecPar/1

These can be used to enter detailed descriptions.

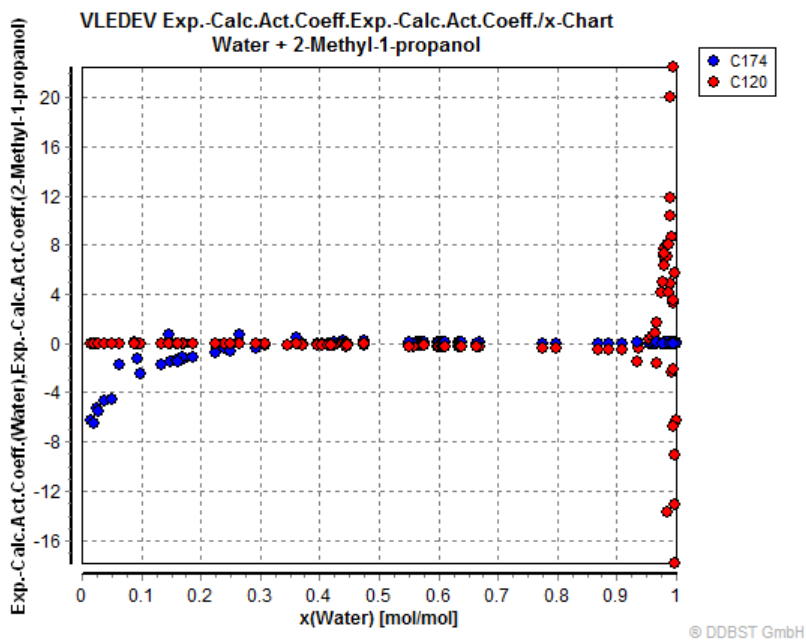
4.2.3 Result Diagrams

All diagrams are standard diagrams already used in the Dortmund Data Bank. For VLE some deviation diagrams have been added:

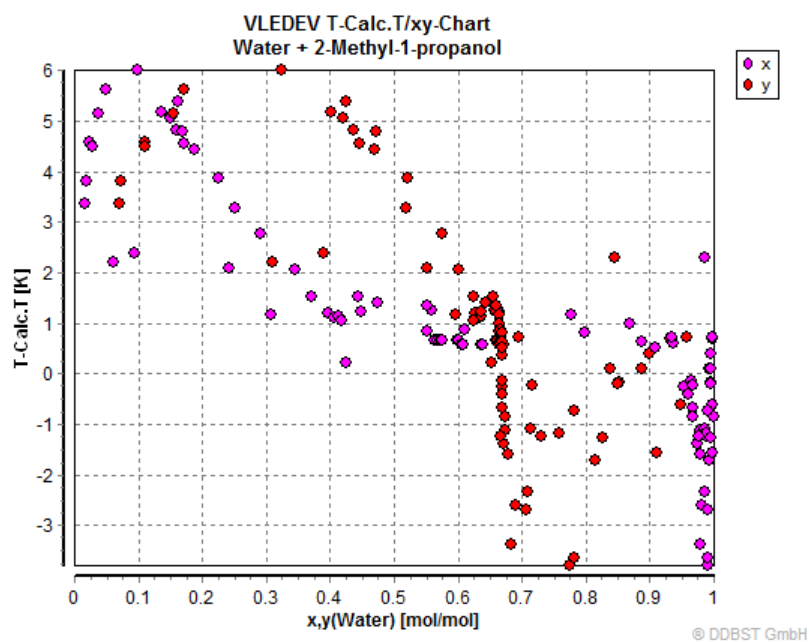
Absolute deviation in vapor composition



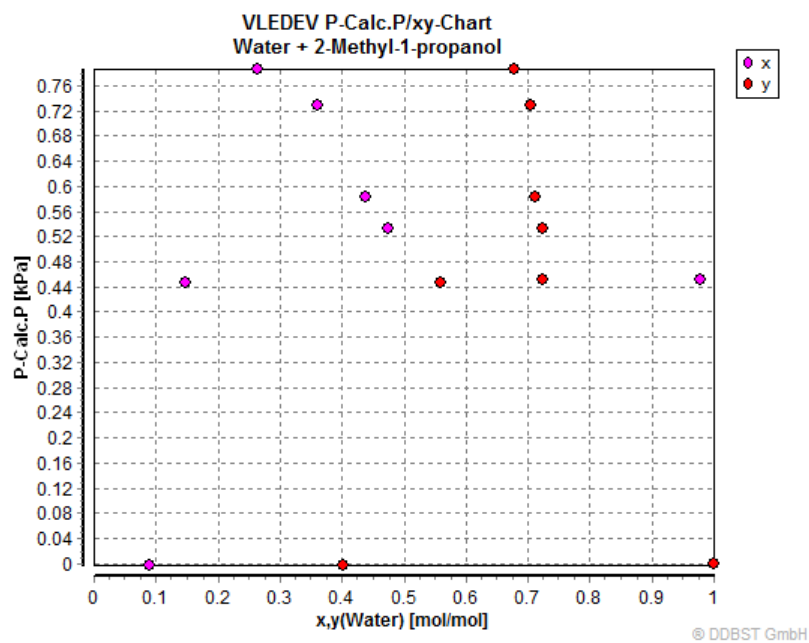
Absolute Deviations in the Activity Coefficients



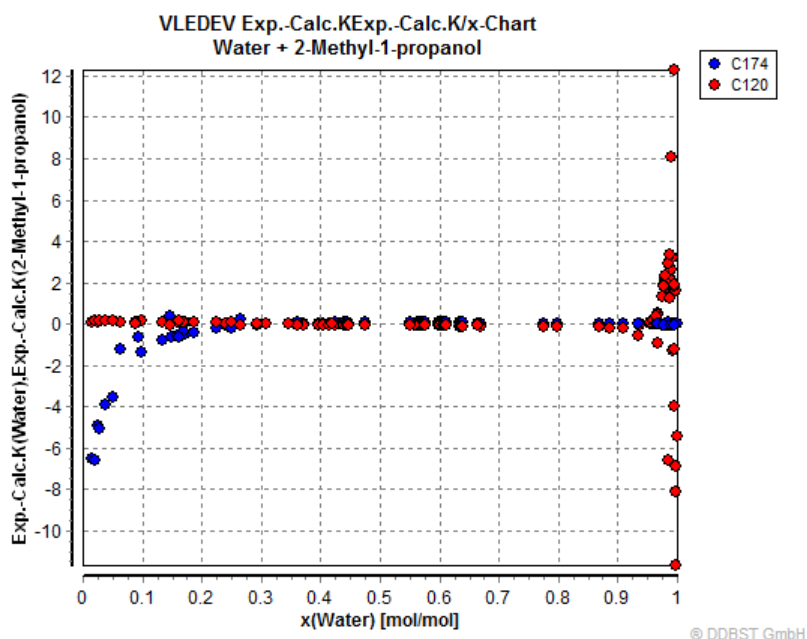
Absolute Temperature Deviations



Absolute Pressure Deviations



Absolute K-Factor Errors



4.3 Result Tables

After a regression a table with experimental and calculated values is available.

The tables are similar to the data tables with experimental data points but contain sometimes, especially for vapor-liquid equilibria, some information about the additionally used data.

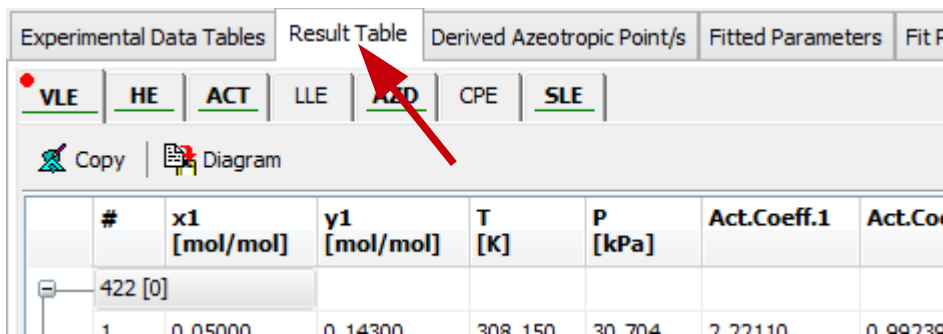


Figure 8: Result Tables Page

In the case of properties which are originally organized as data sets (HE, VLE, LLE, SLE, CPE) and not as single points (ACT, AZD) the first line shows mean errors.

Calc. Act.Coeff.1	Calc. Act.Coeff.2	y1,calc [mol/mol]
3.24%	3.33%	2.57%
2.59650	1.00159	0.16197

Figure 9: Mean Errors

4.4 Custom Result Diagrams

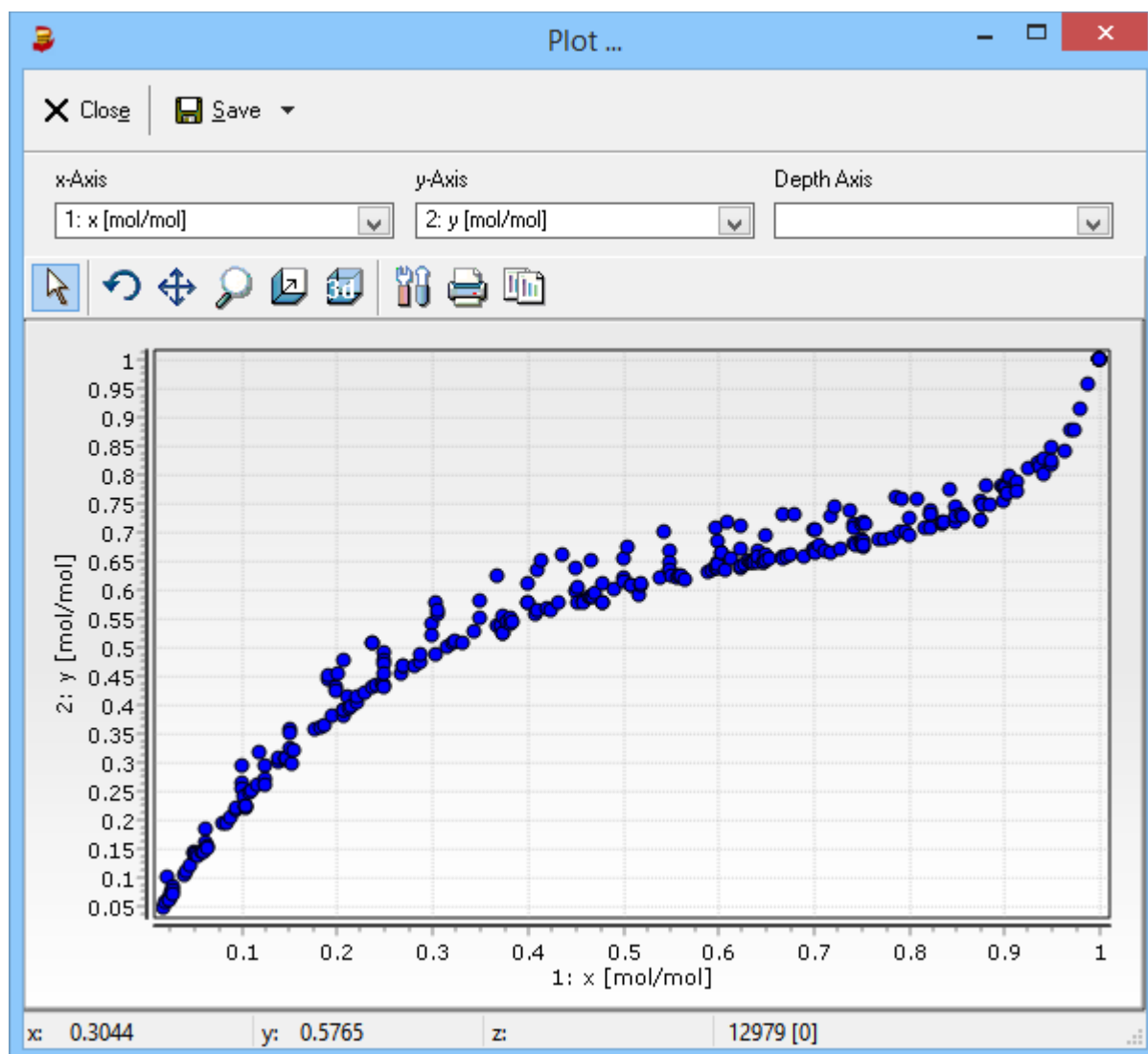
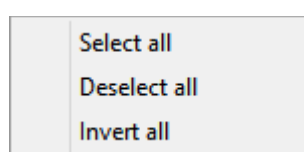


Figure 10: Custom Result Diagram

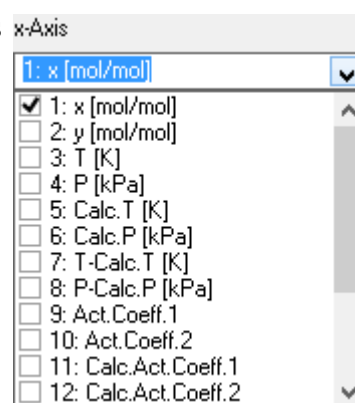
Besides the standard plots RecPar supports a special diagram type where the axes can be selected arbitrarily from the available data table columns. The combo boxes for x-Axis, y-Axis, and Depth-Axis all contain all possible columns and enable free selections of what to plot versus each other.

It is also possible to select multiple properties for a single axis which is common practice for liquid and vapor composition (x and y) versus temperature and pressure.

The diagrams switches to a 3D representation if something in the Depth-Axis combo box is selected.



The combo boxes have a context menu where all items can be selected or deselected, and, additionally their selection can be inverted.



The tool bar



enables

- zooming and panning/moving
- rotating (in 3D mode)
- changing depth (in 3D mode)
- call the chart editor
- printing
- copying

4.5 Diagram With Residuals

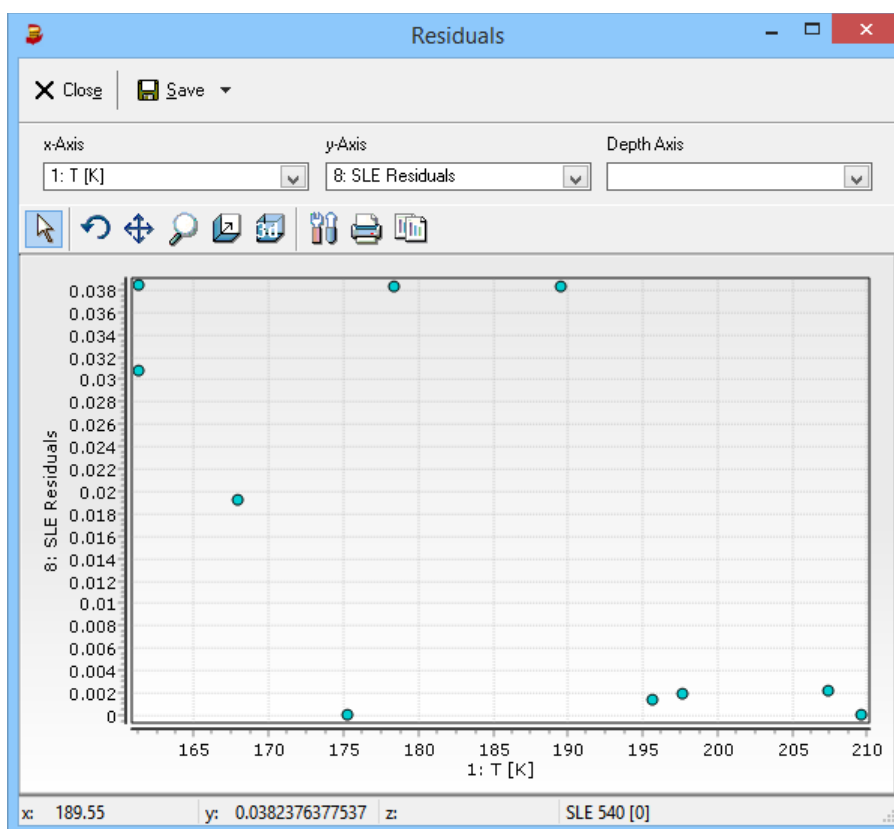
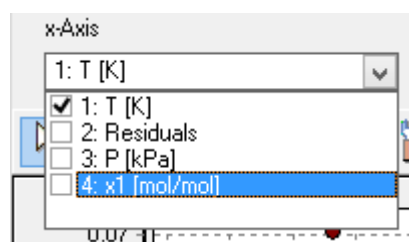


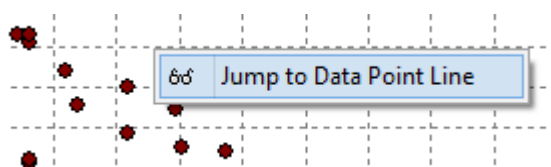
Figure 11: Residuals

Residuals have no thermodynamic meanings. They are simply the contribution of every single point to the objective function of the optimizer. Such a diagram contains points for all properties together in a single chart and allows finding outliers somewhat easier than the diagrams for the single properties.

The residuals can be shown dependent on the temperature, the pressure, and the composition.



A context menu





allows jumping to the line of the currently selected point.

4.6 Derived Azeotropic Points

If a regression shows that a mixture shows azeotropic behavior an additional calculation of the temperature- or pressure-dependent composition for every given data set is performed and the result is displayed by an azeotropic point curve as table.

A typical result gives this data table with azeotropic data points:

#	T [K]	P [kPa]	y1 [mol/mol]	y2 [mol/mol]	Model	VLE Data Set ID
1	308.15	48.52	0.70607	0.29393	UNIQUAC	422 [102]
2	322.45	85.06	0.64559	0.35441	UNIQUAC	423 [102]
3	327.24	101.32	0.62484	0.37516	UNIQUAC	424 [102] 1
4	327.13	100.93	0.62532	0.37468	UNIQUAC	425 [102] 1

 Edit in Mixture Data Editor |
  Save to File

These derived data points can now be saved as data file (“Save to File”, 'qr' format, readable in most DDB software) and it can be transferred directly to EditMixtureData where it can be added to the DDB (“Edit in EditMixtureData”):

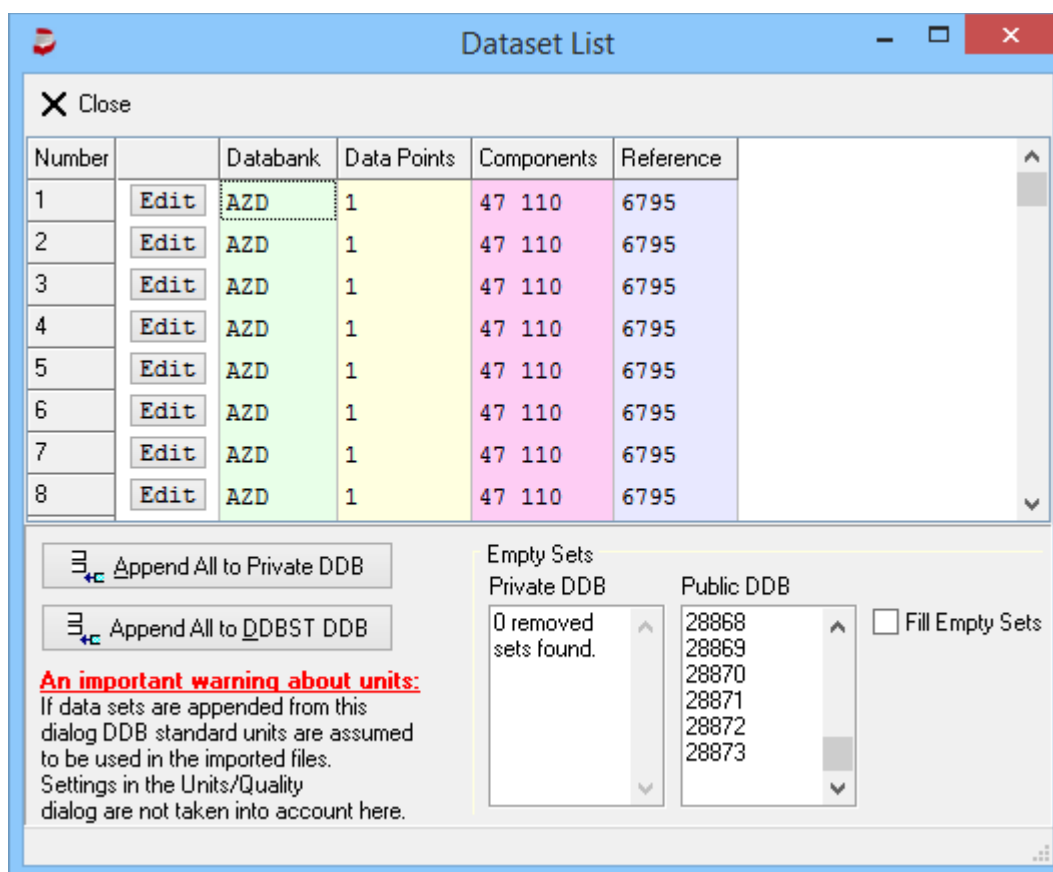
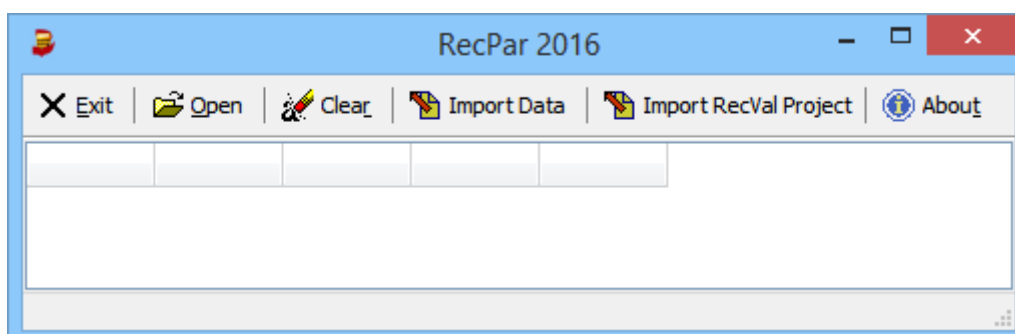


Figure 12: Data set list in EditMixtureData

This dialog in the editor allows appending all sets automatically to the private or public DDB and it allows transferring the single values to the normal editor for azeotropic points (“Edit” button in the data grid).

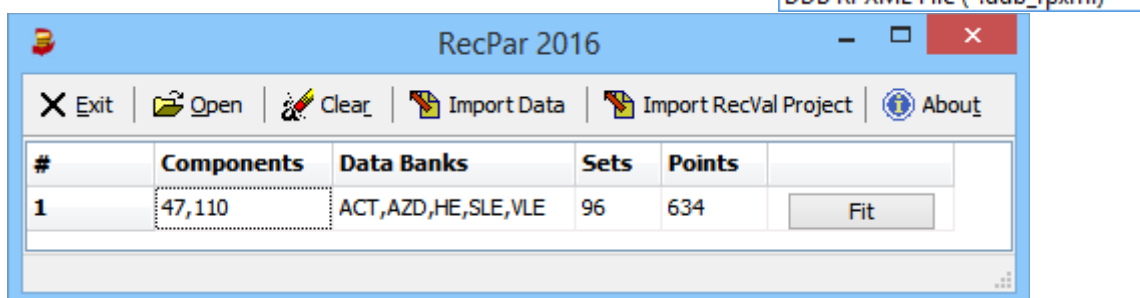
5 Entering Own Data

If RecPar is started directly a data set collector form is shown first.




This form is used to store entered or loaded data sets. Data files have to be in the qr format of the Dortmund Data Bank program. Besides loading data files only it is also possible to load RecPar project files (extension “ddb_rpxml”) where all information about a previously saved project is included.

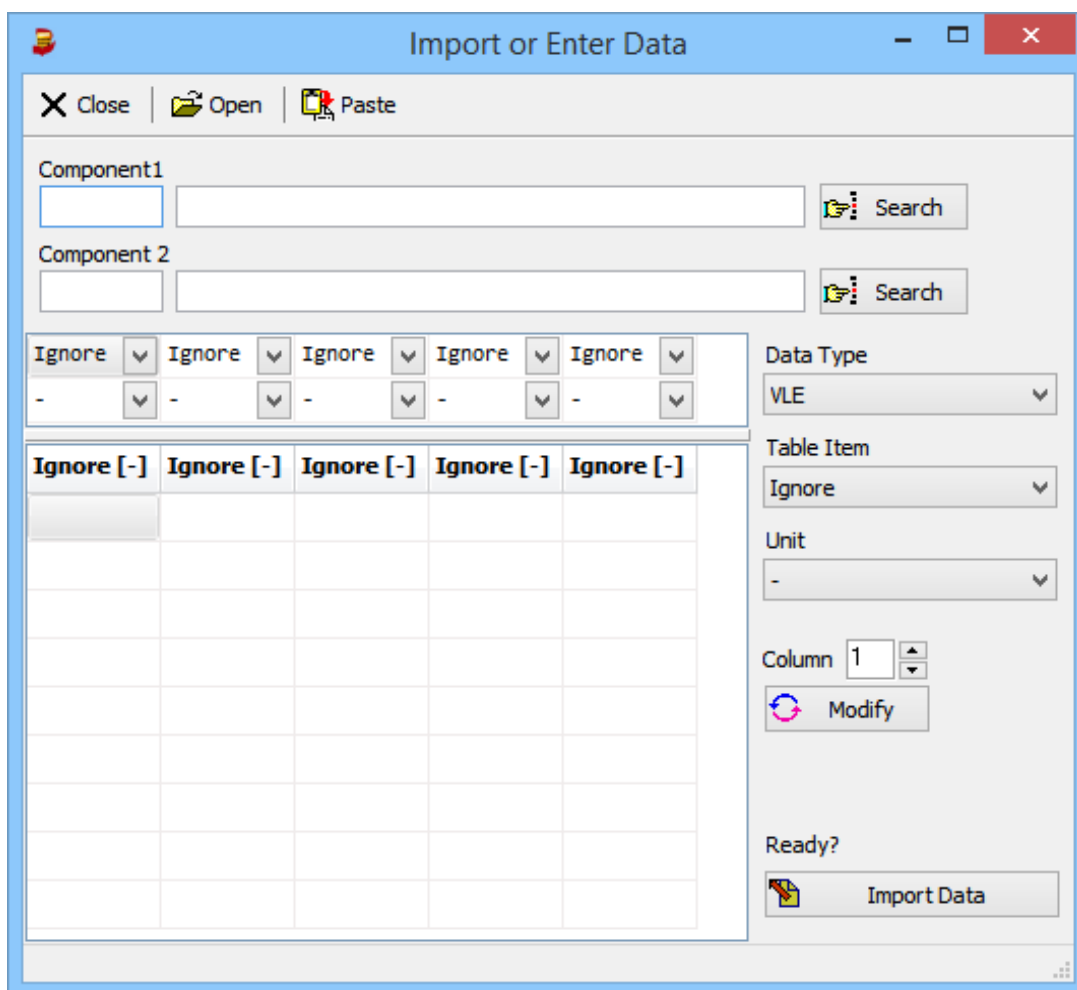
After loading a data or project files this collector form is hidden and the stand regression form is shown. After closing the regression form the collector form will be shown again and shows the the information about the loaded data sets.



It is now possible to restart the regression (“Fit” button) or load further data. If the additional data are for the same binary mixtures the data sets will be merged. Data for another mixture will be shown in additional lines.

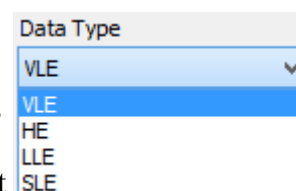
Besides loading own data it is also possible to enter own data directly into RecPar. The

 **Import Data** button opens a separate dialog with the options to enter data or to paste data from spread sheet or other programs.



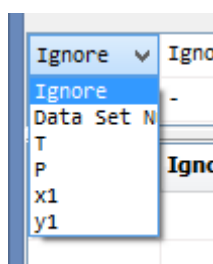
This dialog allows entering, loading, or pasting VLE, heats of mixing (HE), LLE, and SLE data.

The “Open” button allows selecting Excel files (xls format). The data tables should contain only the needed experimental data and no headers or footers or any additional information. If an Excel table contains more information it is better to copy and paste the data table (“Paste” button).



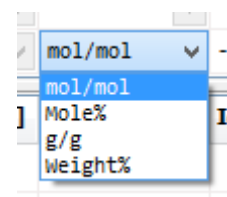
The data type has to be entered – the program cannot decide itself which kind of data has been entered or pasted.

In addition, it is necessary to specify the data type for each single column.



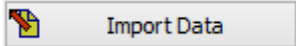
The list of data types changes somewhat depending on the pre-selection of the phase equilibrium:

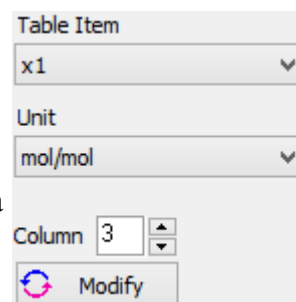
1. VLE: T, P, x_1 , y_1
2. LLE: T, P, x_{1l} , x_{1r} , y_1
3. SLE: T, P, x_{1l} , x_{s1} , y_1
4. HE: T, P, hE , x_1



It is also possible to tell a column to be a data set number or to be ignored. Duplicate properties have to be avoided (two T columns for example).

If the column property has been selected it is also necessary to specify the unit of the data. Besides using the selectors above the data grid it is also possible to use the selectors and the at the right side of the table.

The last step is to specify the two components of the the mixture and then the  button orders the program to load the given data into its internal structures and display it in the data set collector form where the regression can be started.

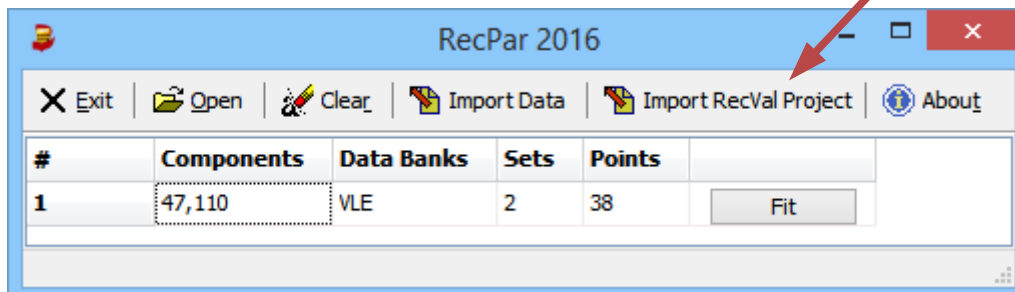


The screenshot shows a configuration panel for a 'Table Item'. It includes a dropdown menu for 'Table Item' with 'x1' selected, a dropdown for 'Unit' with 'mol/mol' selected, a 'Column' field with the value '3' and up/down arrows, and a 'Modify' button with a circular arrow icon.

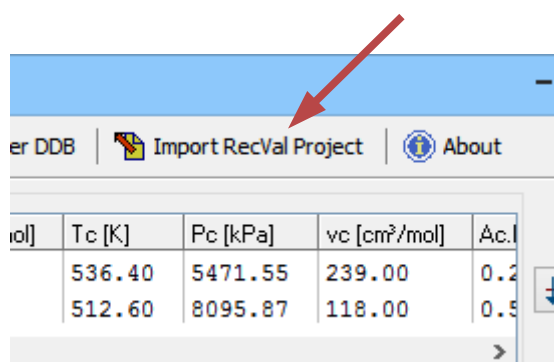
The input form only allows to enter data set by set. The collector form will combine data from different sets if they are for the same mixture.

6 Import RecVal/3 Projects

RecPar allows the user to import RecVal/3 projects either from the main form visible if RecPar is started directly (or the main regression dialog is closed)



or in the fit dialog:



RecVal/3 main project files have the extension “.rvi”. Additional files have the extension “.rvd”, “.rvo”, and “.rvp”.

7 Appendix

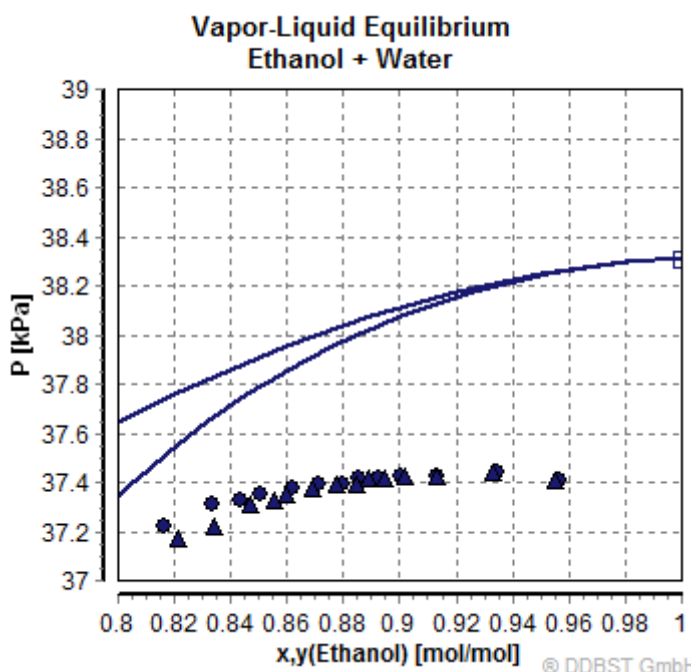
7.1 Pure Component Vapor Pressure Correction?

Wrong Pressure

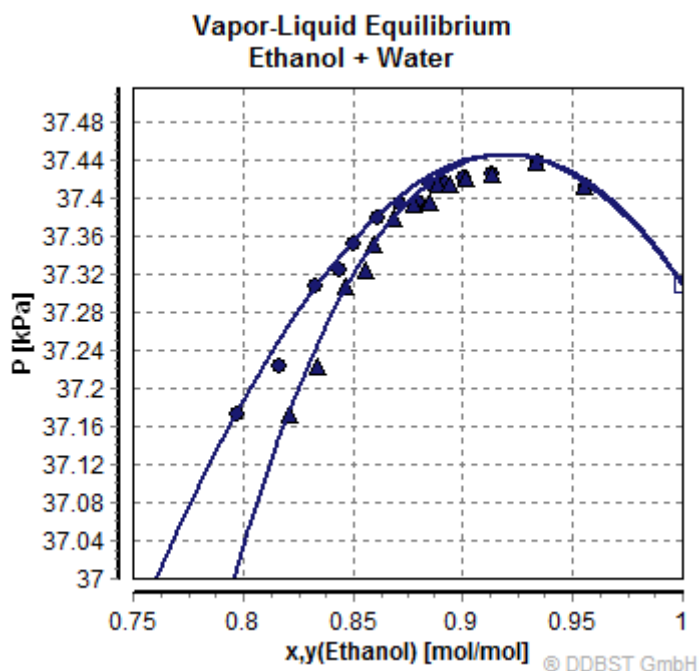
A wrong pressure (here manually modified) leads to a bended curve near the pure components – a forced deviation.

This example shows that a vapor pressure that is only approx. 1 kPa too high prohibits the calculation of a pressure maximum azeotrope where one exists for sure.

The deviations between experimental data and the vapor pressure curve can have multiple reasons like out-of-range calculations with the vapor pressure equation or simply slightly-off thermometer calibrations.



Corrected Pressure



The corrected pure component vapor pressures gives a much better fit result – in this case even the only correct result.

7.2 Conversion between DDB and Aspen Simulator Equations

7.2.1 Introduction

This section describes the different forms of the g^E model equations used in the Aspen simulator (short Aspen) and the DDB software package (short DDBSP) for the three models Wilson, NRTL, and UNIQUAC. Wherever it is possible a conversion of parameters is described.

7.2.2 Wilson

7.2.2.1 DDBSP Form

$$\ln \gamma_i = -\ln \left(\sum_j x_j \Lambda_{ij} \right) + 1 - \sum_k \frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}}$$

with

$$\Lambda_{ij} = \frac{v_j}{v_i} e^{-\Delta \lambda_{ij}/T}$$

v_i Molar volume of liquid pure component i at 25°C

$\Delta \lambda_{ij}$ are interaction parameters between component i and j [cal/mol] and can be made temperature-dependent:

$$\Delta \lambda_{ij} = a_{ij} + b_{ij} T + c_{ij} T^2 + d_{ij} T \cdot \ln T + e_{ij} T^3 + \frac{f_{ij}}{T}$$

7.2.2.2 Aspen Form

$$\ln \gamma_i = 1 - \ln \left(\sum_j x_j \Lambda_{i,j} \right) - \frac{\sum_k x_k \Lambda_{k,j}}{\sum_j x_j \Lambda_{k,j}}$$

$$\Lambda_{i,j} = \exp \left(a_{i,j} + \frac{b_{i,j}}{T} + c_{i,j} \ln T + d_{i,j} T \right)$$

7.2.2.3 Conversion between DDBSP and Aspen Parameters

The Aspen form does not support the terms for e_{ij} and f_{ij} in the temperature-dependency of the interaction parameters. Therefore parameter sets where e_{ij} or f_{ij} are non-zero can not be converted to the Aspen equation.

On the other hand, Aspen incorporated the ratio of molar volumes at 25°C $\left(\frac{v_j}{v_i} \right)$ within the parameter $a_{i,j}$. This makes it impossible to convert Aspen-style Wilson parameters into DDBSP parameters if any of the pure component Wilson volumes are missing.

The last difference is that DDBSP and Aspen are using different units for the interaction parameters

– [cal/mol] in DDBSP and [K] in Aspen which leads to the conversion factor R (gas constant) in $\frac{\text{cal}}{\text{K}\cdot\text{mol}}$.

Aspen parameters	DDBSP parameters
$a_{i,j}$	$\ln\left(\frac{v_j}{v_i}\right) - \frac{b_{ij}}{R}$
$b_{i,j}$	$-\frac{a_{ij}}{R}$
$c_{i,j}$	$-\frac{d_{ij}}{R}$
$d_{i,j}$	$-\frac{c_{ij}}{R}$

$$R = 1.9858775 \frac{\text{cal}}{\text{K}\cdot\text{mol}}$$

7.2.3 NRTL

7.2.3.1 DDBSP Form

$$\ln y_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_n x_n \tau_{nj} G_{nj}}{\sum_k G_{kj} x_k} \right)$$

with

$$G_{i,j} = \exp(-\alpha_{ij} \tau_{ij})$$

and

$$\tau_{ij} = \frac{\Delta g_{ij}}{T}$$

Δg_{ij} are interaction parameters for component i and j [cal/mol]

$$\Delta g_{ij} = a_{ij} + b_{ij} T + c_{ij} T^2 + d_{ij} T \cdot \ln T + e_{ij} T^3 + \frac{f_{ij}}{T}$$

α_{ij} is the non-randomness parameter: $\alpha_{ij} = \alpha_{ji}$.

7.2.3.2 Aspen Form

$$\ln y_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_l x_l \tau_{lj} G_{lj}}{\sum_k G_{kj} x_k} \right)$$

with

$$G_{ji} = \exp(-S_{ji} \tau_{ji})$$

and

$$\tau_{ji} = a_{j,i} + \frac{b_{j,i}}{T} + e_{j,i} \ln T + f_{j,i} T$$

and

$$S_{ji} = c_{ji} + d_{ji}(T - 273.15) \quad (\text{non-randomness parameter})$$

7.2.3.3 Conversion between DDBSP and Aspen Forms

The conversion between DDBSP and Aspen parameters is mainly a conversion of units. DDBSP uses [cal/mol] and Aspen uses [K] which leads to the conversion factor R (gas constant) in $\frac{\text{cal}}{\text{K} \cdot \text{mol}}$.

DDBSP does not support a temperature-dependent non-randomness parameter which means that the Aspen parameter $d_{i,j}$ is always 0 and an Aspen parameter set including a temperature-dependency of the non-randomness parameter cannot be converted into DDBSP parameters.

The sequence of parameters is also slightly different.

Aspen parameters	DDBSP parameters
$a_{i,j}$	$\frac{b_{ij}}{R}$
$b_{i,j}$	$\frac{a_{ij}}{R}$
$c_{i,j}$	α_{ij}
$d_{i,j}$	0
$e_{i,j}$	$\frac{d_{ij}}{R}$
$f_{i,j}$	$\frac{c_{ij}}{R}$

$$R = 1.9858775 \frac{\text{cal}}{\text{K} \cdot \text{mol}}$$

7.2.4 UNIQUAC

7.2.4.1 DDBSP Form

$$\ln y_i = \ln y_i^C + \ln y_i^R$$

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

$$\ln y_i^R = q_i \left(1 - \ln \frac{\sum_j q_j x_j \tau_{ji}}{\sum_j q_j x_j} - \sum_j \frac{q_j x_j \tau_{ij}}{\sum_k q_k x_k \tau_{kj}} \right)$$

with

$\ln y_i^C$ Combinatorial part of the activity coefficient of component i

$\ln y_i^R$ Residual part of the activity coefficient of component i

$\tau_{ij} = e^{-\Delta u_{ij}/T}$ Interaction parameters between component i and j [cal/mol]

$$\Delta u_{ij} = a_{ij} + b_{ij} T + c_{ij} T^2 + d_{ij} T \cdot \ln T + e_{ij} T^3 + \frac{f_{ij}}{T}$$

$$V_i = \frac{r_i}{\sum_j r_j x_j} \quad \text{Volume fraction}$$

$$F_i = \frac{q_i}{\sum_j q_j x_j} \quad \text{Surface fraction}$$

r_i Relative van der Waals volume of component i

q_i Relative van der Waals surface of component i

7.2.4.2 Aspen Form

The activity coefficient is calculated from a residual and a combinatorial part.

$$\ln y_i = \ln y_i^C + \ln y_i^R$$

The combinatorial part is determined by

$$\ln y_i^C = \ln \frac{V_i}{x_i} + \frac{z}{2} q_i \ln \frac{F_i}{V_i} + l_i - \frac{V_i}{x_i} \sum_j x_j l_j$$

The coordination number is $z = 10$

The residual part is determined by

$$\ln y_i^R = q_i \left(1 - \ln \sum_j F_j \tau_{j,i} - \sum_j \frac{F_j \tau_{i,j}}{\sum_k F_k \tau_{k,j}} \right) \quad \text{or} \quad \ln y_i^R = q'_i \left(1 - \ln \sum_j F'_j \tau_{j,i} - \sum_j \frac{F'_j \tau_{i,j}}{\sum_k F'_k \tau_{k,j}} \right)$$

with

$$l_i = 5(r_i - q_i) - (r_i - 1)$$

$$V_i = \frac{r_i x_i}{\sum_j r_j x_j} \quad \text{Volume fraction}$$

$$F_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad \text{or} \quad F'_i = \frac{q'_i x_i}{\sum_j q'_{j,i} x_j} \quad \text{Surface fraction, the F' version is used for alcohols and Water.}$$

$$\tau_{j,i} = \exp\left(a_{j,i} + \frac{b_{j,i}}{T} + c_{j,i} \ln T + d_{j,i} T\right)$$

7.2.4.3 Conversion between DDBSP and Aspen Form

The conversion between DDBSP and Aspen parameters is mainly a conversion of units. DDBSP uses [cal/mol] and Aspen uses [K] which leads to the conversion factor R (gas constant) in $\frac{\text{cal}}{\text{K} \cdot \text{mol}}$.

There's one bigger difference regarding alcohols and Water containing mixtures. Aspen uses a slightly different equation form for alcohols and Water mainly caused by a different relative van der Waals surface constant (q') making it impossible to convert DDBSP parameters into Aspen parameters if these components are encountered.

Aspen parameters	DDBSP parameters
$a_{i,j}$	$-\frac{b_{ij}}{R}$
$b_{i,j}$	$-\frac{a_{ij}}{R}$
$c_{i,j}$	$-\frac{d_{ij}}{R}$
$d_{i,j}$	$-\frac{c_{ij}}{R}$

$$R = 1.9858775 \frac{\text{cal}}{\text{K} \cdot \text{mol}}$$

7.3 Chemical Theory (Marek et al.)

The chemical theory⁷ can be used to describe the dimerization and cross dimerization of carboxylic acids in the vapor phase. The dimerization (or cross dimerization) constants can be calculated via the equation

$$K = e^{A + \frac{B}{T}} \quad \text{with T in K and parameters in mmHg}^{-1}.$$

The dimerization and cross dimerization constants are found in the following table.

⁷ Marek J., Standard G., Coll. Czech. Chem. Commun. 19, 1074 (1954)

7.3.1 Dimerization Constants (Chemical Theory)

DDB Number	Component Name	Emp. Formula	A	B
15	Formic Acid	CH ₂ O ₂	-24.7367	7098.9
598	Trifluoroacetic Acid	C ₂ HF ₃ O ₂	-24.8679	7029.8
295	Chloroacetic Acid	C ₂ H ₃ ClO ₂	-24.7021	7633.1
84	Acetic Acid	C ₂ H ₄ O ₂	-23.9952	7290.0
298	Acrylic Acid	C ₃ H ₄ O ₂	-24.9669	7635.4
141	Propionic Acid	C ₃ H ₆ O ₂	-24.9669	7635.4
235	Butyric Acid	C ₄ H ₈ O ₂	-23.2561	7000.0
307	Isobutyric Acid	C ₄ H ₈ O ₂	-23.2561	7000.0
232	Metacrylic Acid	C ₄ H ₆ O ₂	-23.2561	6999.9
324	Valeric Acid	C ₅ H ₁₀ O ₂	-23.0374	6891.6
268	Hexanoic Acid	C ₆ H ₁₂ O ₂	-22.7749	6776.5
425	Benzoic Acid	C ₇ H ₆ O ₂	-19.5576	5423.7
745	Heptanoic Acid	C ₇ H ₁₄ O ₂	-22.5815	6677.5
738	2-Ethyl Hexanoic Acid	C ₈ H ₁₆ O ₂	-22.2500	6543.9
269	Octanoic Acid	C ₈ H ₁₆ O ₂	-22.2500	6543.9
801	Nonanoic Acid	C ₉ H ₁₈ O ₂	-21.9897	6428.8
499	Decanoic Acid	C ₁₀ H ₂₀ O ₂	-21.7272	6311.4

7.3.2 Cross Dimerization Constants (Chemical Theory)

DDB Number	Component Name	Emp. Formula	A	B
15	Formic Acid	CH ₂ O ₂	-23.8451	7352.15
84	Acetic Acid	C ₂ H ₄ O ₂		