RecPar

Model Parameter Regression Simultaneously to Multiple Properties

DDBSP – Dortmund Data Bank Software Package

DDB

DDBST
Dortmund Data Bank
Software & Separation
Technology

Contents

1   Introduction

RecPar is a regression tool that allows the user to fit binary interaction parameters to different phase equilibrium data and some excess properties simultaneously. RecPar can currently handle binary systems only.

1.1   Supported Data Types

RecPar can use

1. Vapor-Liquid Equilibrium Data (VLE and HPV Data Bank).
   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. Heats of Mixing (HE Data Bank).

3. Activity coefficients at infinite dilution (ACT Data Bank)

4. Liquid-Liquid Equilibrium Data (LLE Data Bank).

5. Azeotropic Data (AZD Data Bank).
   AZD are handled as special VLE data points. Currently only full azeotropic data points containing temperature, pressure, and composition are supported.

6. Excess Heat Capacity (CPE Data Bank).

7. Solid-Liquid Equilibrium Data (SLE Data Bank).
   RecPar can handle only eutectic systems correctly.

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. It will *not* result in usable parameters if they 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 UNIQUAC[1], NRTL[2], Wilson[3], Margules[4], and van Laar[5].

NRTL can be used without any additionally needed parameters and is the preset method. The model 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.

The Wilson model implementation needs to extract a ratio of pure component liquid volumes (which can be hypothetical). These volumes are calculated from the density value which can be edited in the Component Editor.

The models Margules and van Laar are simple models which do not need further constants.

[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
[5] Van Laar J.J., "Über Dampfspannungen von binären Gemischen", Z.Phys.Chem.(Leipzig), 72(6), 723-751, 1910

For g^E-models the following temperature function is used:

$$G_{ij} = \exp\left(-\frac{T_{ij}}{RT}\right)$$

$$T_{ij}[\text{cal/mol}] = a_{ij} + b_{ij}T + c_{ij}T^2 + d_{ij}T \cdot ln(T) + e_{ij}T^3 + \frac{f_{ij}}{T}$$

1.3   Supported Cubic EOS Mixing Rules

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 following temperature function is used:

$$K_{ij}[\text{K}] = a_{ij} + b_{ij}T + c_{ij}T^2 + \frac{d_{ij}}{T} + \frac{e_{ij}}{T^2}$$

As g^E mixing rules Vidal, Tochigi, Michelsen, PSRK, VTPR and LCVM are supported. In this case the following temperature function is used:

$$G_{ij} = \exp\left(-\frac{T_{ij}}{RT}\right)$$

$$T_{ij}[\text{cal/mol}] = a_{ij} + b_{ij}T + c_{ij}T^2 + \frac{d_{ij}}{T} + e_{ij}T \cdot ln(T) + f_{ij}T^3$$

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

For Soave-Redlich-Kwong and Peng-Robinson the original alpha functions (using the acentric factor ω), Mathias-Copeman[6] and Twu-Bluck-Cunningham-Coon[7] are supported. The Stryjek-Vera[8] alpha function is available for Peng-Robinson only.

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[6] Mathias P.M., Copeman T.W., "Extension of the Peng-Robinson Equation of State to Complex Mixtures: Evaluation of the Various Forms of the Local Composition Concept", Fluid Phase Equilib., 13, 91-108, 1983

[7] Twu C.H., Bluck D., Cunningham J.R., Coon J.E., "A Cubic Equation of State with a New Alpha Function and a New Mixing Rule", Fluid Phase Equilib., 69, 33-50, 1991

[8] Stryjek R., Vera J.H., "PRSV: An Improved Peng-Robinson Equation of State for Pure Compounds and Mixtures", Can.J.Chem.Eng., 64, 323-333, 1986

2   Starting the Program

The "Dortmund Data Bank" program can be used to run RecPar with selected data from a Query Result window. Additionally, RecPar can be used stand-alone and experimental data can added from a query result file (*.qr).

2.1   Experimental Data Transfer from a Query Result Window

The RecPar drop-down menu in the query result window of the Dortmund Data Bank program has multiple menu entries for calling RecPar with different options.
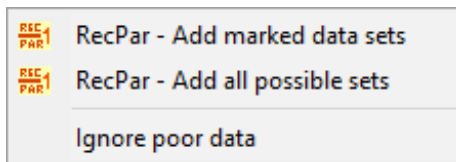
1. "Add marked data sets" opens a RecPar window where only the marked sets are automatically added.

2. "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   Starting the Program Directly

If RecPar is started directly, data can be added either by opening a data file or by dropping a query result file.

The "Load Data" button can be used to add data from a query result file. Furthermore, it is also possible to load a RecPar project file (*.ddb_rpxml) where all information about a previously saved project is included.

RecPar allows the user also to import RecVal/3 projects with the "Import RecVal Project" button. RecVal/3 main project files have the extension ".rvi". Additional files have the extension ".rvd", ".rvo", and ".rvp".

3   Main Window
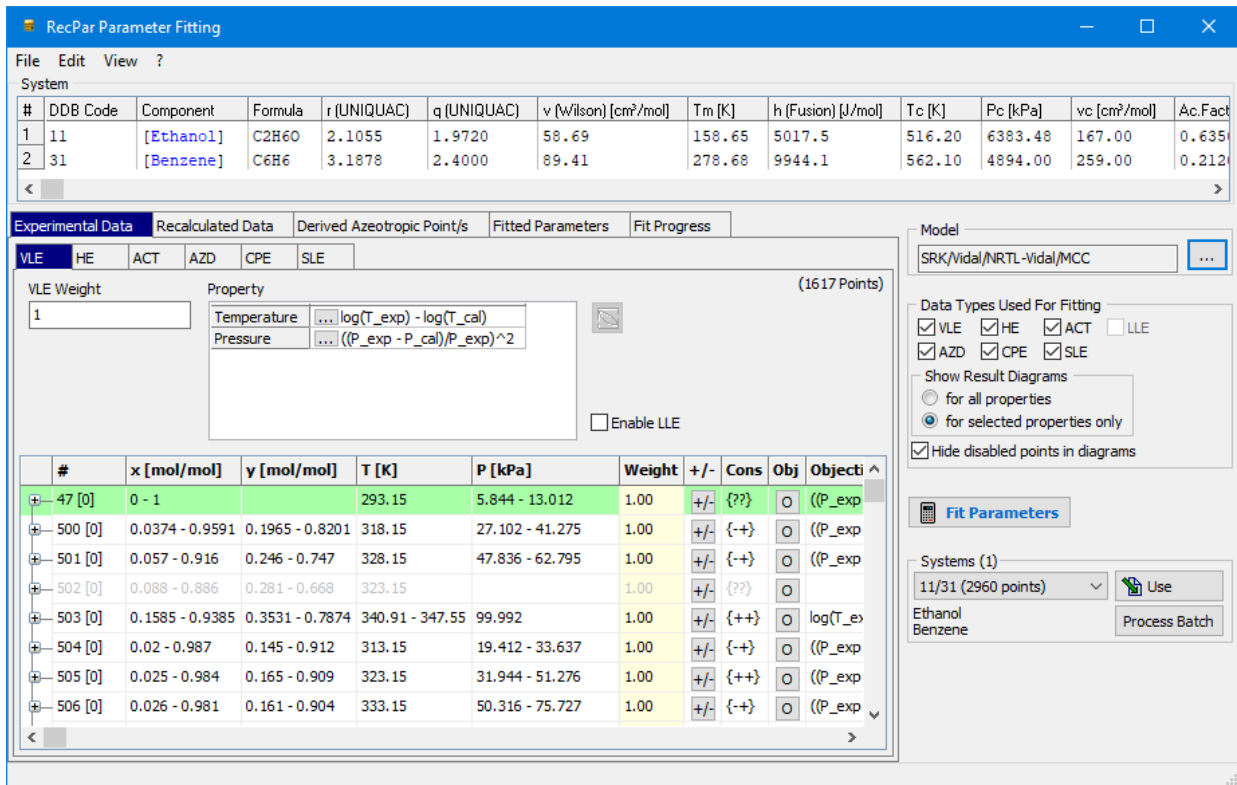
The dialog has the following main parts:

1. List of components ("System") which, besides the DDB numbers, names, and formula, also shows some additional pure component properties.

2. Model settings including the "Fit Parameters" button and some basic data selections and project management functions.

3. Experimental Data Tables (includes a page with results). This part allows property specific settings like data point's weights or the type of contribution to the objective function.

3.1   Component List

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, 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

The *Model* area displays a short summary of the selected model.
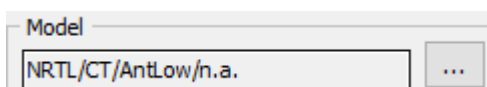
Push the ellipsis button on the right side to open a model selection dialog. In the dialog, either a g^E model, a cubic equation of state model or an external model can be selected.

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 considering the vapor phase association.

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

3.2.1.2 Vapor Pressure Equation

The following pure component vapor pressure equations (see the PCPEquationFit documentation for the equation details) are supported:

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).

2. Antoine – Low: This option searches the list of available Antoine parameter sets for that one which 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).

3. DIPPR 101 equation

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

5. Cox equation

6. Extended Antoine (Aspen)

3.2.1.3 Poynting Correction

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

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

RecPar supports:

1. 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 data bank ("PCP Equation Fit" program).

2. Densities by the Yen/Woods[9] correlation.

3. Densities (fixed) taken from the basic data (usually at 25 °C).

4. Densities calculated with the DIPPR 100 equation.

5. Densities calculated with the DIPPR 119 equation.

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

3.2.2 Select EOS-Model
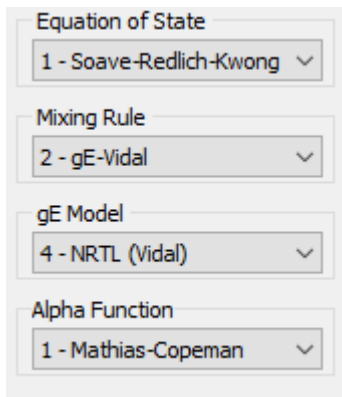
In the settings page for the EOS model the base cubic equation of state, the mixing rule, the g^E model (if applicable) and the alpha function (if applicable) can be selected. For further details on the EOS models and the mixing rules see the *GenPar* documentation.

3.2.3 Select External Model

It is also possible to use a third-party thermo engine.
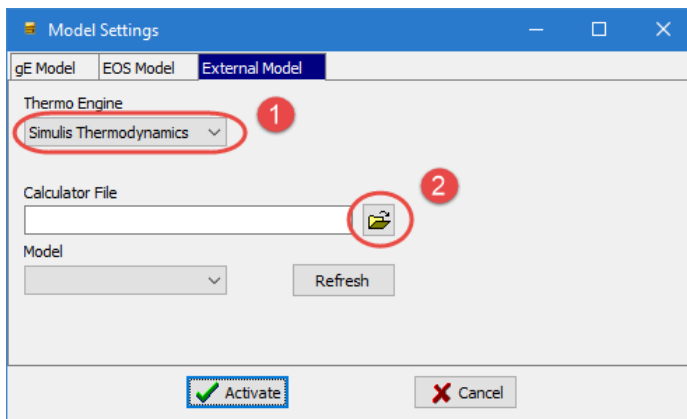
First the desired thermo engine (1) has to be selected. Currently only *Simulis Thermodynamics* is supported.

Click on the *Select Calculator File* button (2) to open a *Simulis Thermodynamics* calculator file. Now the well-known *Open Simulis Thermodynamics Calculator File* dialog appears. Click on the *Components Assigned* button to finish the file selection.

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[9] Yen L. C., Woods S. S., "A Generalized Equation for Computer Calculation of Liquid Densities", AIChE J., 12(1), 95-99, 196

Now the active model should be displayed (3).
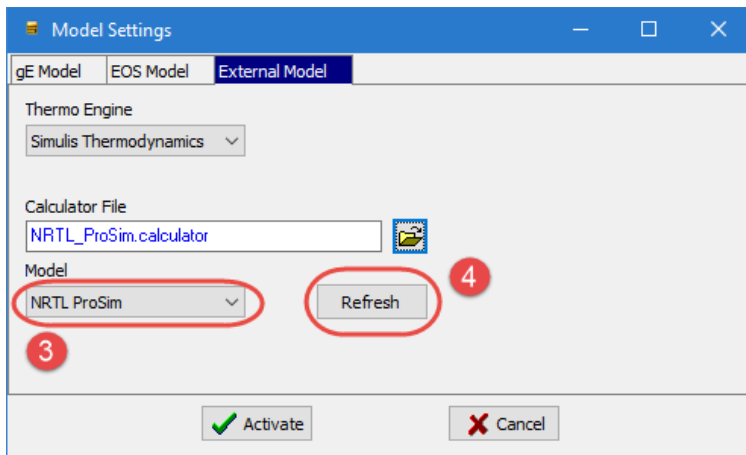
If the *Calculator File* field is already filled when the dialog is opened, click on the *Refresh* button (4) to update the model information.

3.3   Experimental Data

The data tables are different for each data type. Common settings are the data type weight, a list of data type specific properties used in the objective functions for the parameter regression and the data table.

Use the context menu of each property grid to add or remove an objective function property. If no objective function property is active then that data type will have no contribution – which is the same effect as setting the data type weight or all data point weights to zero. Use the ellipsis button next to a property entry to modify the objective function calculation rule.

The following context menu entries are available for all data tables:

- "Expand All": Expand all data sets and shows the data points
- "Collapse All": Collapse all data sets
- "Copy Selected Cells"
- "Remove <TYPE> Data": Removes all data sets from this data type
- "Set All Weights to 1" All points are included with a weight of 1
- "Set All Weights to 0" All points are excluded.

3.3.1 VLE – Vapor Liquid Equilibrium

3.3.1.1   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*γ).

Temperature for isobaric data sets and pressure for isothermal data sets are preselected after data have been added. The other properties can be selected manually by the context menu.

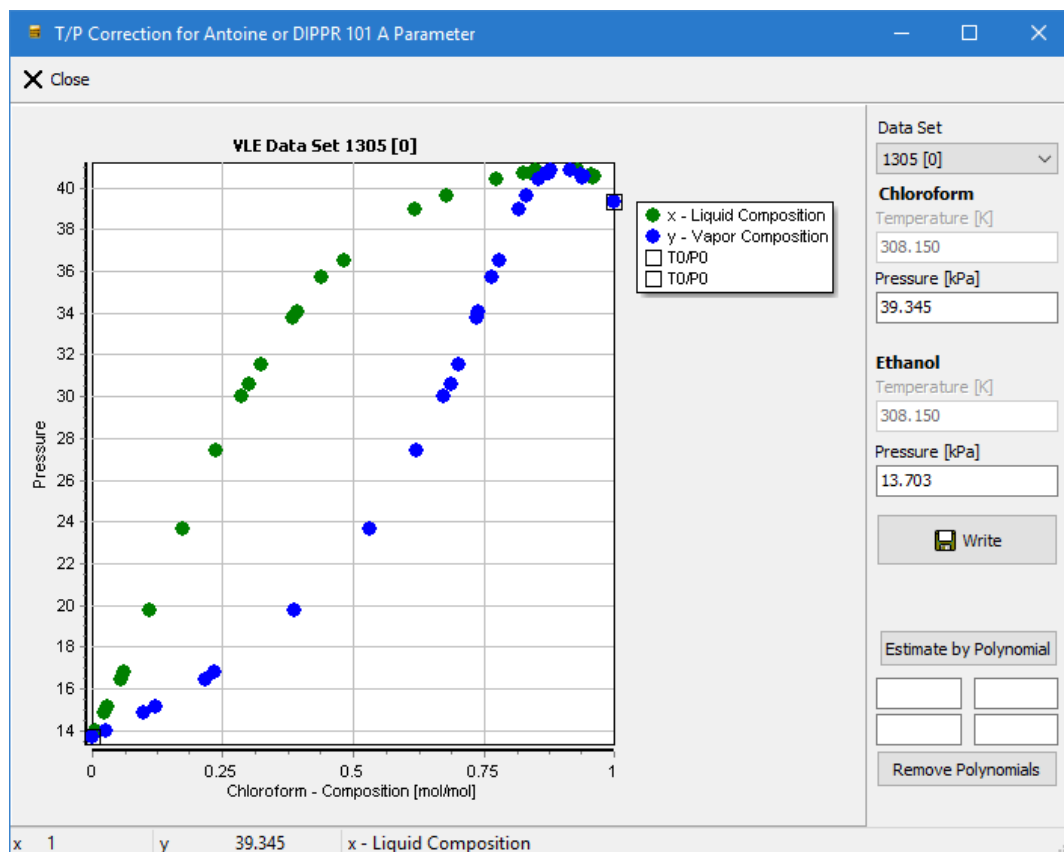### 3.3.1.2   *Pure Component Vapor Pressure Correction*

If the experimental VLE data set contains 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 the program automatically adopts the experimental pure component pressure and temperature by modifying the Antoine "A" or DIPPR 101 "A" parameters. If experimental pure component data are not available the adjustment can be done manually.

This button opens the adjustment dialog.

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

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

3.3.1.3 Data Table

#	x [mol/mol]	y [mol/mol]	T [K]	P [kPa]	Weight	+/-	Cons	Obj	Objective Functions	^
⊞ 422 [0]	0.05 - 0.95	0.143 - 0.845	308.15	30.704 - 49.183	1.00	+/-	{++}	O	((P_exp - P_cal)/P_exp)^2	
⊞ 423 [0]	0.05 - 0.95	0.138 - 0.824	322.45	58.875 - 87.579	1.00	+/-	{++}	O	((P_exp - P_cal)/P_exp)^2	

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. an "O" button to set the objective function for all points of the data set

10. the active objective functions

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.

⊟ 423 [0]	0.05 - 0.95	0.138 - 0.824	322.45	58.875 - 87.579	1.00	+/-	{++}	O	((P_exp - P_cal)/P_exp)^2
Kireev V.A., Sitnikov I.P., Zh.Fiz.Khim., 15(4), 492-499, 1941									
20	0.05000	0.13800	322.450	58.875	1.00				((P_exp - P_cal)/P_exp)^2

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 functions for the data point.
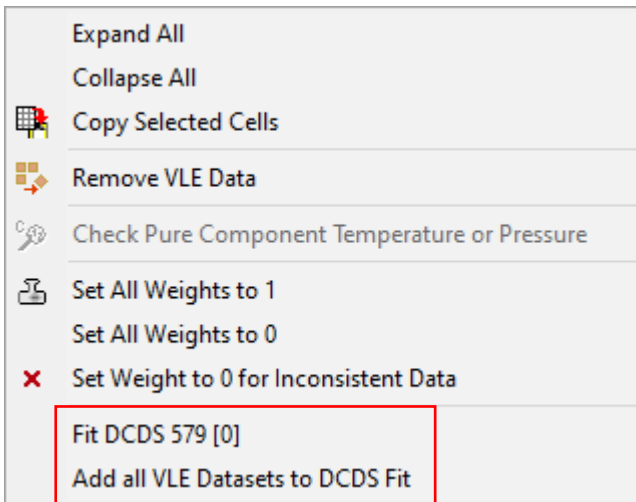
When VLE data is added two consistency tests are performed automatically – a point-to-point test (first position) and an area test. The possible entries are then

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)

There is the special option "Set Weight 0 for Inconsistent Data" in the context menu of the data table to exclude these data sets from the fit. In most cases, consistent data sets are of higher quality will be easier to fit and give better results.

3.3.1.4 DECHEMA Chemistry Data Series Fit

The Context menu of the VLE data grid contains an option to make a DECHEMA Chemistry Data Series (DCDS) fit for g^E-models for the marked set or for all VLE data sets. The fit uses the options from the Model Selection.

	Expand All
	Collapse All
🖳	Copy Selected Cells
🔲	Remove VLE Data
🔍	Check Pure Component Temperature or Pressure
⚒	Set All Weights to 1
	Set All Weights to 0
✗	Set Weight to 0 for Inconsistent Data
	Fit DCDS 579 [0]
	Add all VLE Datasets to DCDS Fit

The results are given in a special "DCDS" Tab Sheet

```
(1) ACETONE                                           C3H6O
---------------------------------------------------------------------
(2) ETHANOL                                           C2H6O
---------------------------------------------------------------------

Wagner 2.5-5 ( Parameter and Temperature Range )
(1)    -7.6707      1.9659    -2.4454    -2.8999   -59- 235 C
(2)    -8.3380      0.0872    -3.3058    -0.2599   -19- 241 C

PRESSURE=  760.00 MM HG   (  1.013 BAR  )

LIT: Amer H.H., Paxton R.R., van Winkle M., Ind.Eng.Chem., 48(1),
     142-146, 1956

                                                         OBJECTIVE
CONSTANTS:      A12        A21      ALPHA12     G1      G2   FUNCTION

   NRTL      41.2186   374.6399    0.3007     1.81    1.72  0.06382 G
```
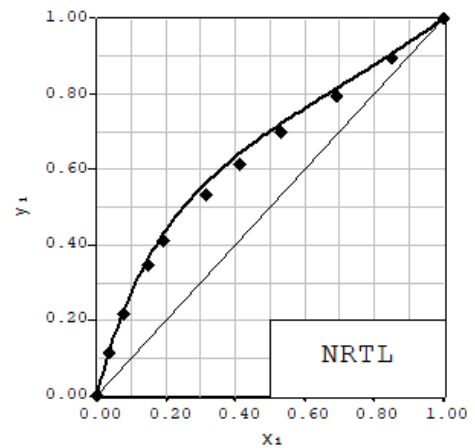


```
     EXPERIMENTAL DATA              NRTL
      T DEG C    X1       Y1       DIFF T  DIFF Y1

        78.30 0.0000   0.0000      -0.03   0.0000
        76.40 0.0330   0.1110      -0.22  -0.0021
        74.00 0.0780   0.2160      -0.25   0.0106
        70.80 0.1490   0.3450      -0.12   0.0192
        69.10 0.1950   0.4100      -0.05   0.0222
        65.60 0.3160   0.5340       0.12   0.0307
        63.40 0.4140   0.6140       0.29   0.0297
        61.30 0.5320   0.6970       0.40   0.0249
        59.00 0.6910   0.7960       0.50   0.0188
        57.30 0.8520   0.8960       0.31   0.0112
        56.10 1.0000   1.0000      -0.02   0.0000

     MEAN DEVIATION:       0.21   0.0154

     MAX. DEVIATION:       0.50   0.0307
```

The Results sheet can be printed. They can also be saved as RTF file or the results can be copied to the clipboard.

3.3.2 HE – Heats of Mixing

3.3.2.1   Data Table

#	x [mol/mol]	T [K]	P [kPa]	hE [J/mol]	Weight	+/-	Obj	Objective Functions
⊞— 385 [0]	0.1154 - 0.9141	298.15		-607.09 - 393.56	1.00	+/-	o	(hE_exp - hE_cal)/hE_max
386 [0]	0.051 - 0.965	298.15		548.47 - 428.61	1.00			(hE_exp - hE_cal)/hE_max

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 functions

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   Data Table

	#	T [K]	Act.Coeff. 1 in 2 [-]	Act.Coeff. 2 in 1 [-]	Weight	+/-	Obj	Objective Functions	Reference
2050 [0]	1	298.150		9.5500	1.00	+/-	o	(log(g_exp) - log(g_cal))^2	Landau I., Belfer A.J., Locke D.C., Ind.En
2051 [0]	2	315.950		6.3800	1.00		o	(log(g_exp) - log(g_cal))^2	Thomas E.R., Newman B.A., Nicolaides G

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 functions

10. the reference information

3.3.4 LLE – Liquid-Liquid Equilibrium

3.3.4.1   Objective Function

The LLE objection function can minimize the difference in the activities of the two phases (the goal

is isoactivity) or by meeting the experimental liquid compositions with the additional option of obtaining the right gap width. Additionally, also the difference of the logarithmic form of the concentrations can be minimized.

The isoactivity criterion also works when the fitted parameters show no miscibility gap. This leads to a stable fitting routine but often also to poor results. It also needs the experimental concentration information for both phases. The other three 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 if no other information is given. But normally this form of minimization gives better results. The logarithmic form of the concentrations should be used for very small concentrations.

When LLE-data sets are added, the LLE Routine creates artificial concentrations for points, which have only information for one phase. These points are created with interpolation and extrapolation of known concentrations for this phase. With the help of this option more data points can be used for the isoactivity criterion and an overfit of the side with more points is avoided. These calculated points are marked in the data table with a grey background color. They can be removed by unchecking the option "Calculate missing LLE-Points".

3.3.4.2   *Data Table*

#	x' [mol/mol]	x" [mol/mol]	T [K]	P [kPa]	Weight	+/-	Obj	Objective Functions
⊞— 3 [0]	0.4888 - 0.851	0.929 - 0.9838	273.15 - 398.15		1.00	+/-	O	((a1'-a1")_cal)^2 + ((a2'-a2")_cal)^2
⊞— 382 [0]		0.9711 - 0.9838	273.15 - 383.15		1.00	+/-	O	

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 functions

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   *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.

3.3.5.2   *Data Table*

	#	T [K]	P [kPa]	y [mol/mol]	Weight	+/-	Obj	Objective Functions			Reference
75 [0]	1	305.650	23.998	0.33800	1.00	+/-	O	(y_exp - y_cal)/y_exp	log(T_exp) - log(T_cal)	log(P_exp) - log(P_cal)	Nielsen R.L., V
403 [0]	2	298.150	16.892	0.30700	1.00	+/-	O	(y_exp - y_cal)/y_exp	log(T_exp) - log(T_cal)	log(P_exp) - log(P_cal)	Ohta T., Koyal

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 functions

10. the reference information

3.3.6 CPE – Excess Heat Capacity

3.3.6.1 Data Table

#	x [mol/mol]	T [K]	P [kPa]	cpE [J/molK]	Weight	+/-	Obj	Objective Functions
⊞— 965 [0]	0.00208 - 0.8988	298.15		0.00 - 14.51	1.00	+/-	o	(cpE_exp - cpE_cal)/cpE_max
⊞— 1145 [0]	0.1759 - 0.9097	293.15		3.92 - 12.90	1.00	+/-	o	(cpE_exp - cpE_cal)/cpE_max

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 functions

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

3.3.7 SLE – Solid Liquid Equilibrium

3.3.7.1 Objective Function

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

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.

3.3.7.2   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.
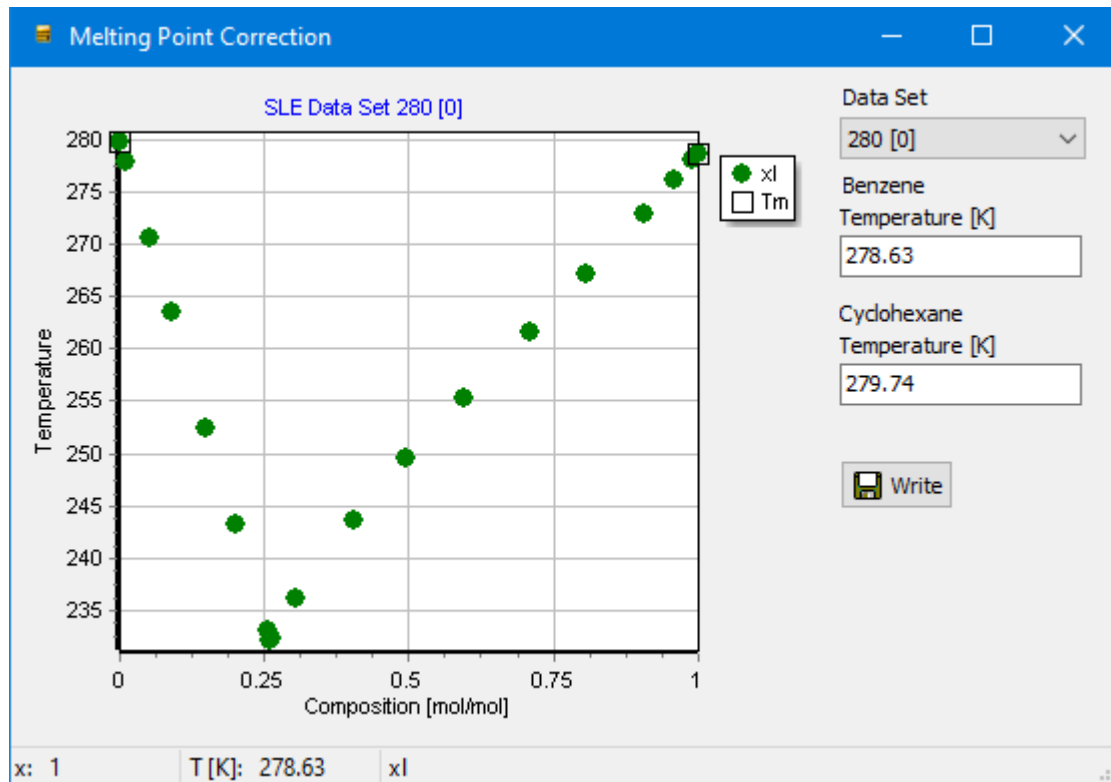
This utility is very similar to the correction of pure component vapor pressures, see section 3.3.1.2 "Pure Component Vapor Pressure Correction".

3.3.7.3   Data Table

#	x [mol/mol]	T [K]	P [kPa]	Weight	+/-	Obj	Objective Functions
⊞— 590 [0]	0 - 1	159.15 - 278.65		1.00	+/-	O	(T_exp - T_cal)/T_exp
⊞— 1372 [0]	0 - 1	159.25 - 278.65		1.00	+/-	O	(T_exp - T_cal)/T_exp

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 functions

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

# 4   Parameter Regression

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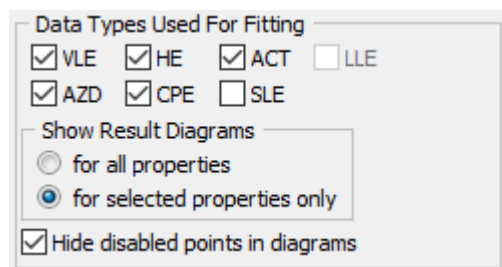
These check boxes allow the user to quickly drop or include selected data types from the regression. A right-click on a check box selects a single property directly.

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.

4.2   Start Parameters
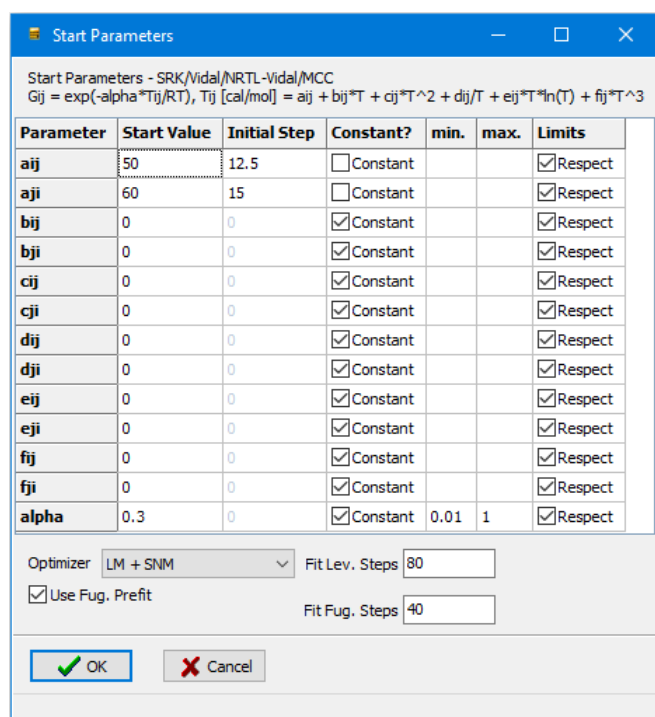
With a click on the "Fit Parameters" button the start parameters are displayed. Depending on the selected model and data default start parameters are suggested.

The parameter equation and the chosen model are shown at the top of the window. All Parameters, which are not flagged constant, are fitted. For these parameters limits can be specified with the three last columns.

At the bottom the Simplex-Nelder-Mead or Levenberg-Marquardt method or a combination of both methods can be chosen as optimizer method. In the case of Levenberg Marquardt a maximum number of steps can be defined with the "Fit Lev. Steps" box.
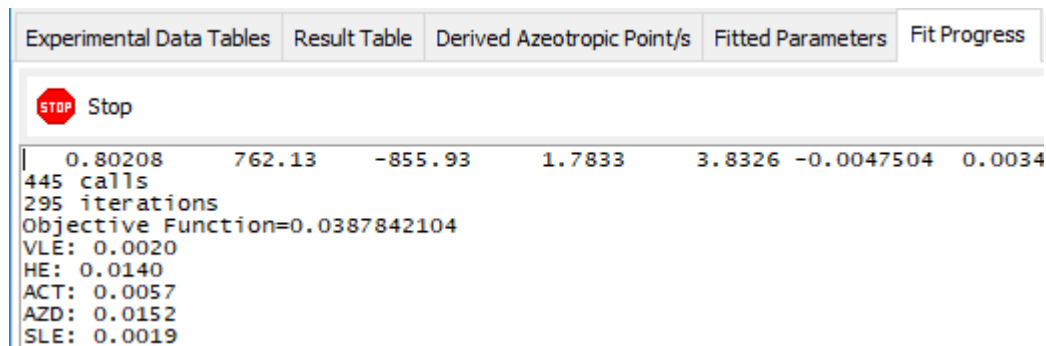
If an internal EOS model should be fitted a fugacity prefit is executed. This is normally only done for the first fit to achieve a working starting parameter set. A maximum number of steps can be defined with the "Fit Fug. Steps" box.

If only LLE-data is active, then the option "Use LLE Prefit" can be selected to perform a special LLE-Fit (internal model only). The option should be unchecked if non-default start parameters are used.

With a click on the "OK" button the parameter fit will start.

4.3   Regression Progress Information

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

|   0.80208      762.13     -855.93      1.7833      3.8326 -0.0047504  0.0034
445 calls
295 iterations
Objective Function=0.0387842104
VLE: 0.0020
HE:  0.0140
ACT: 0.0057
AZD: 0.0152
SLE: 0.0019
```

The first line shows the current parameters, the number of calls to the objective function is shown in the second line and the next line contains the number of iteration steps. The following line shows the total error calculated with the current parameters and then the contributions of the single properties are following. At the end of the fitting, the time elapsed will be given at the bottom.

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.

4.4   Resulting Regression Parameters

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

| Experimental Data Tables | Result Table | Derived Azeotropic Point/s | **Fitted Parameters** | Fit Progress |

| 🖫 Save as XLS | 🧬 Save as INP | 📊 Save in ParameterDDB | 🗄 Save as PPDX | 📋 Copy | 🔀 Clear |

1 Set														
Set no.	1	...												
Model	SRK/Vidal/NRTL-Vidal/MCC													
Comp. 1	11 Ethanol													
Comp. 2	31 Benzene													
Parameters [cal/mol]	aij	aji	bij	bji	cij	cji	dij	dji	eij	eji	fij	fji	alpha
1-2	-4.908999	1623.9368	0	0	0	0	0	0	0	0	0	0	0.3
Obj. Function	Total=172.062 VLE=23.3119 HE=82.4840 CPE=30.3624 ACT=9.3668 AZD=...													

4.4.1 Toolbar Options

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"), see also section 4.4.4 "Saving parameters in the ParameterDDB"

4. IK-CAPE PPDX file ("Save as PPDX")

5. The parameters can also be copied to the Windows clipboard.

Use the "Clear" button to remove all data sets.

4.4.2 Data Set Action

Every data set contains an ellipsis button which shows a menu with the following entries:

1. Replot: Replots all available diagrams for the specific parameter set.

2. Refit: Uses the given parameter set as start parameters for a new fit.

3. Remove: Deletes the given parameter set.

In case an external model was used for fitting also the following entries are available:

4. Save: Save the parameters to the currently active external project.

5. "Save as…": Save the parameters to a new project file.

4.4.3 Result Entries
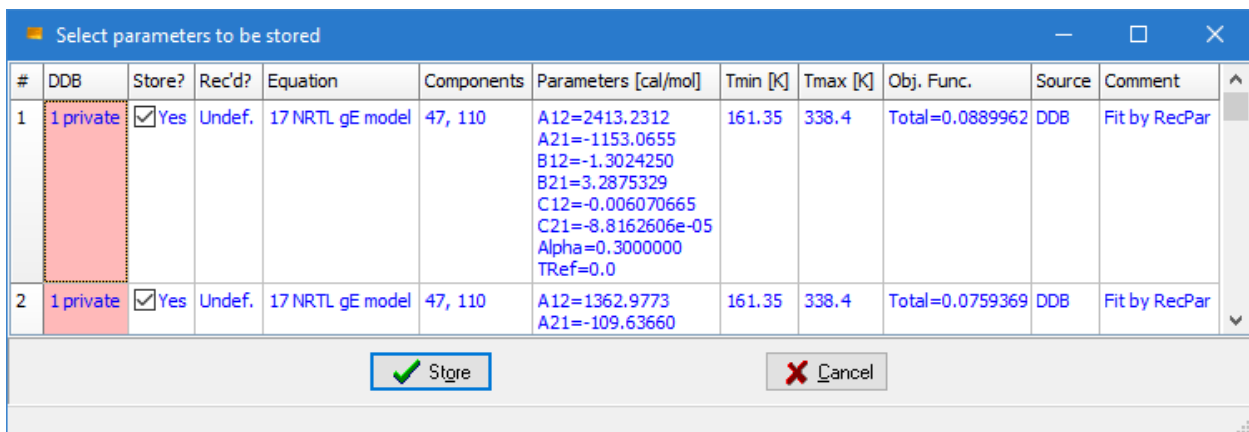
The result dialog shows the following lines

1. The top line shows the internal data set number.

2. The next line contains the model description.

3. Both components with DDB number, name, and – if applicable – some basic properties come next.

4. The parameters in the presentation format follow.

5. 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.

6. In the following lines also the parameters in the Aspen format and/or the PRO/II format are displayed – if available.

4.4.4 Saving parameters in the ParameterDDB

The option is available for internal g^E models only. Parameters are always stored in the private DDB.

An additional selection dialog with all data sets found in the regression result window will be displayed. It allows the selection and deselection of single sets.

#	DDB	Store?	Rec'd?	Equation	Components	Parameters [cal/mol]	Tmin [K]	Tmax [K]	Obj. Func.	Source	Comment
1	1 private	☑Yes	Undef.	17 NRTL gE model	47, 110	A12=2413.2312 A21=-1153.0655 B12=-1.3024250 B21=3.2875329 C12=-0.006070665 C21=-8.8162606e-05 Alpha=0.3000000 TRef=0.0	161.35	338.4	Total=0.0889962	DDB	Fit by RecPar
2	1 private	☑Yes	Undef.	17 NRTL gE model	47, 110	A12=1362.9773 A21=-109.63660	161.35	338.4	Total=0.0759369	DDB	Fit by RecPar

Store   Cancel

This dialog has two editable cells

1. "Source" – preset with "DDB"

2. "Comment" – preset with "Fit by RecPar"

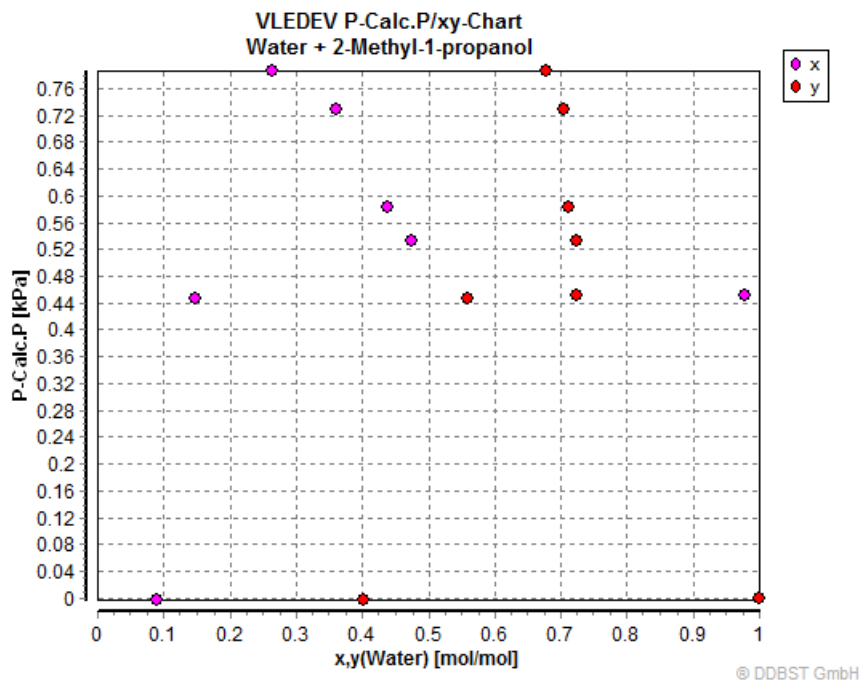These can be used to enter detailed descriptions.

4.5 *Standard Result Diagrams*

All diagrams are standard diagrams already used in the Dortmund Data Bank. Furthermore, some deviation diagrams have been added. Here are some examples for VLE.
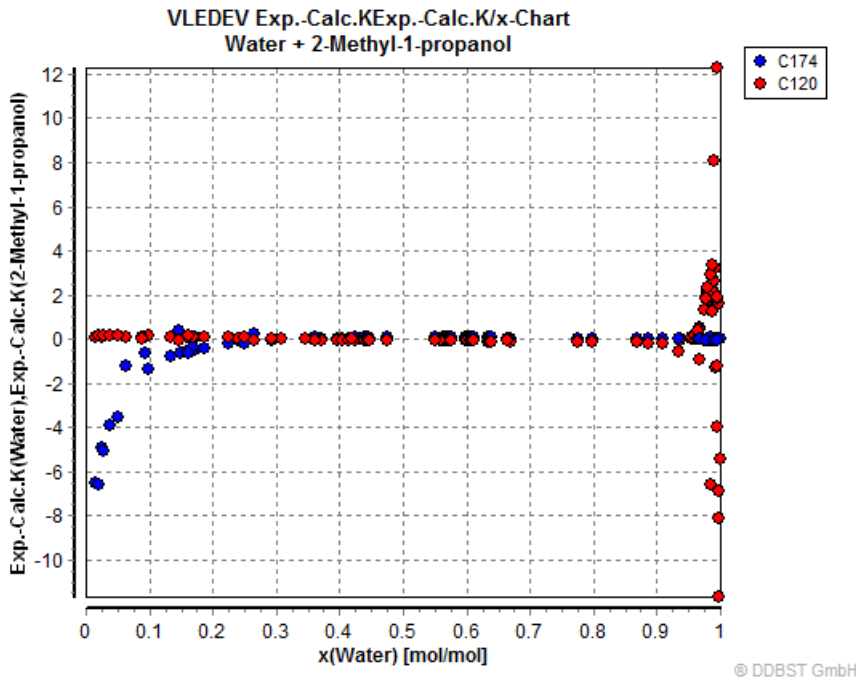
Absolute Temperature Deviations:
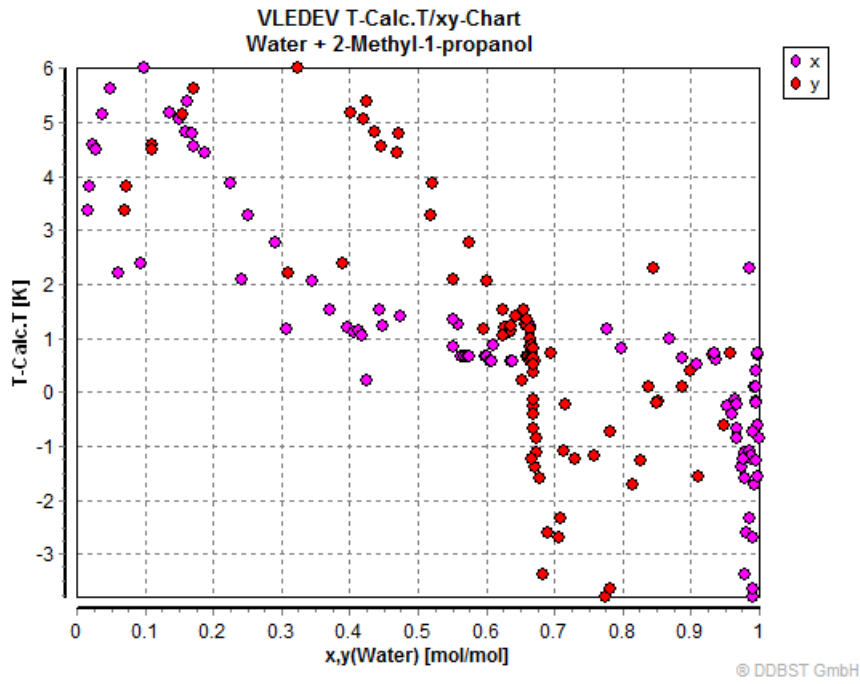
Absolute Pressure Deviations:

Absolute K-Factor Errors:

4.6   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.

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 and the residual. For every point the residual for the final parameter set is shown. During the calculation each residual is normalized with a multiplication with 1000 and divided by the number of objective function contributions for the given property. So, properties with many data points – which leads to many objective function contributions – will not be overweighted.

4.7   Custom Result Diagrams

Besides the standard plots RecPar supports a special diagram type where the axes can be selected arbitrarily from the available data table columns. They can be created with "Diagram" button in the result sheet.
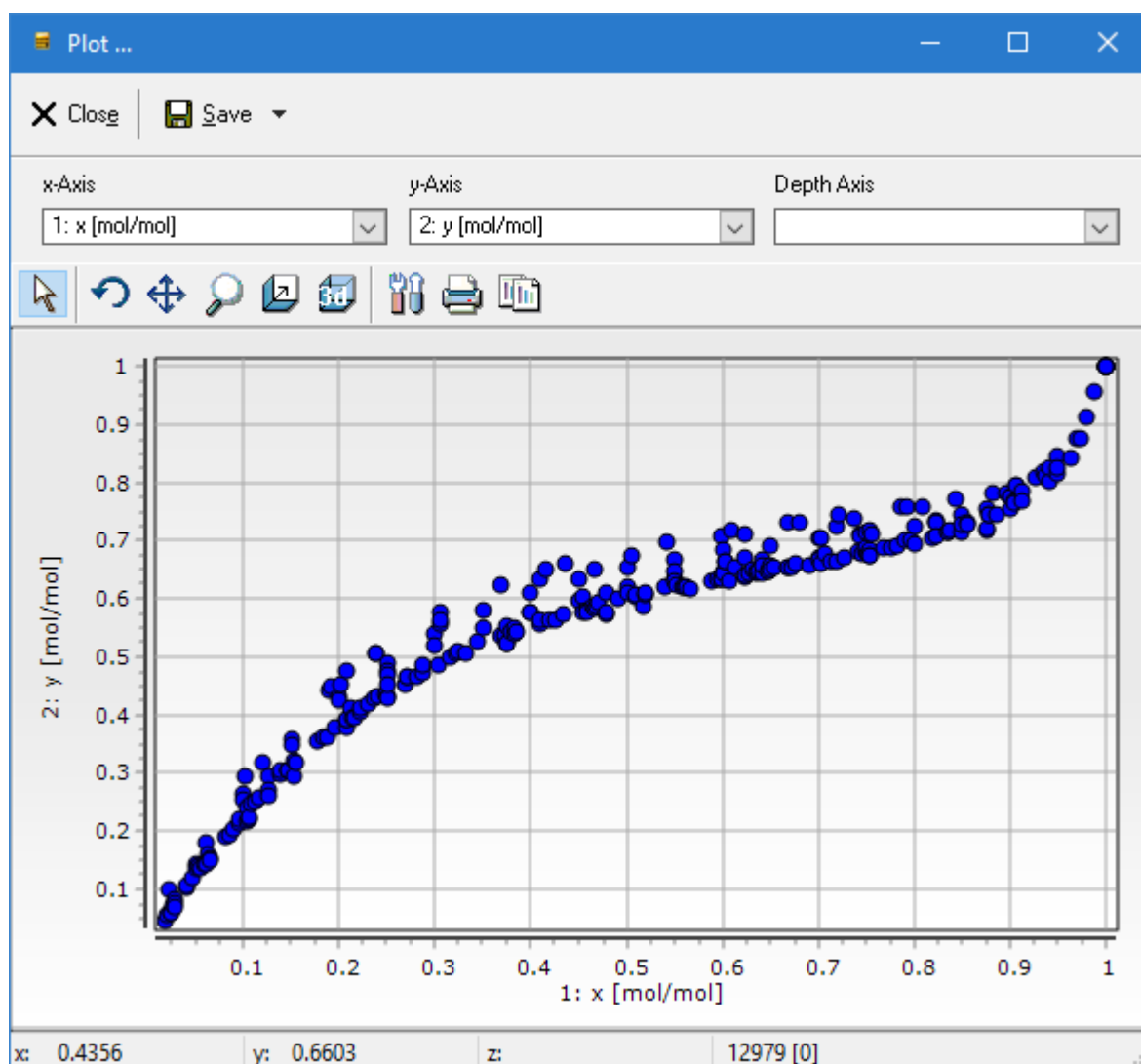
The combo boxes for x-Axis, y-Axis, and Depth-Axis all contain all possible columns and enable free selections of what to plot versus each other.
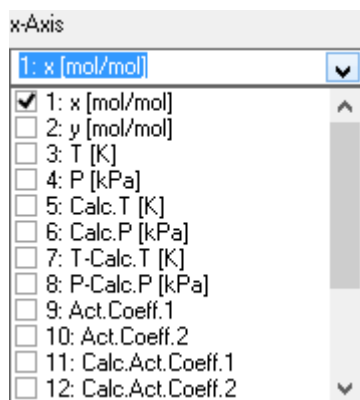
It is also possible to select multiple properties for a single axis which is common practice for liquid and vapor composition (x and y) versus temperature and pressure. The combo boxes have a context menu where all items can be selected or deselected, and, additionally their selection can be inverted.

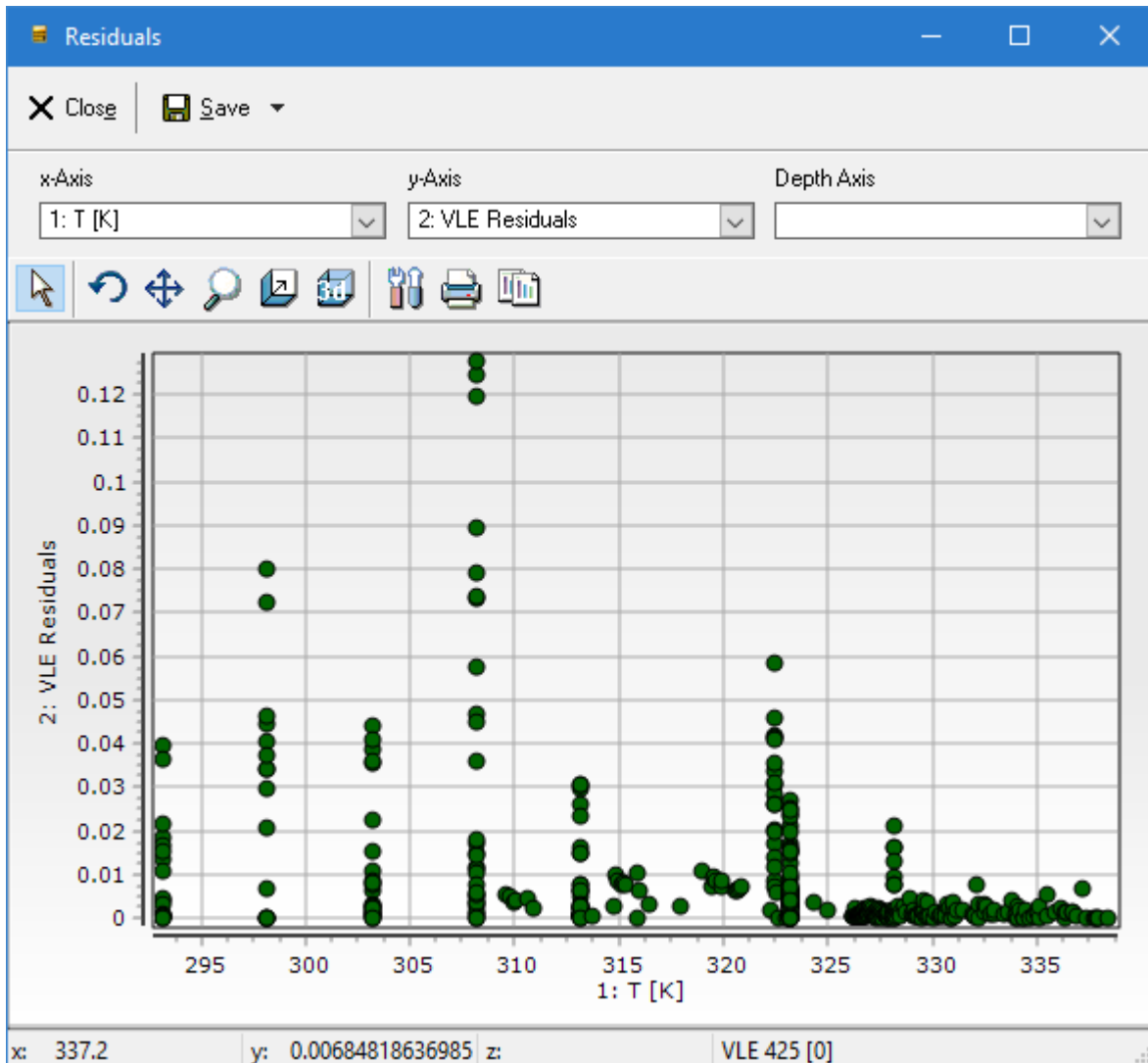The diagrams switches to a 3D representation if something in the Depth-Axis combo box is selected.

The tool bar enables

- zooming and panning/moving
- rotating (in 3D mode)
- changing depth (in 3D mode)

- call the chart editor
- printing
- copying

### 4.7.1 Diagram with 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.
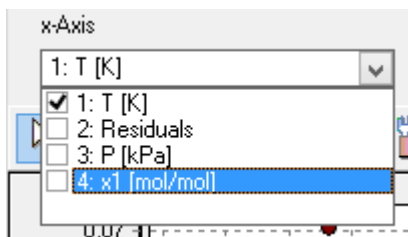
A context menu allows jumping to the line of the currently selected point.
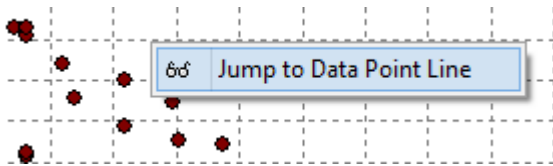
4.8   Derived Azeotropic Points

If a regression shows that a mixture has 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	49.03	0.68699	0.31301	NRTL	422 [101]
2	322.45	87.05	0.63315	0.36685	NRTL	423 [101]
3	326.47	101.33	0.61809	0.38191	NRTL	424 [101] 1
4	326.36	100.93	0.61849	0.38151	NRTL	425 [101] 1

Edit in Mixture Data Editor | Save to File | Copy Grid

These derived data points can now be saved as data file ("Save to File", 'qr' format, readable in most DDB software), it can be copied to the Windows clipboard ("Copy Grid"), and it can be transferred directly to EditMixtureData where it can be added to the DDB ("Edit 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   Appendix

5.1   Pure Component Vapor Pressure Correction

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.
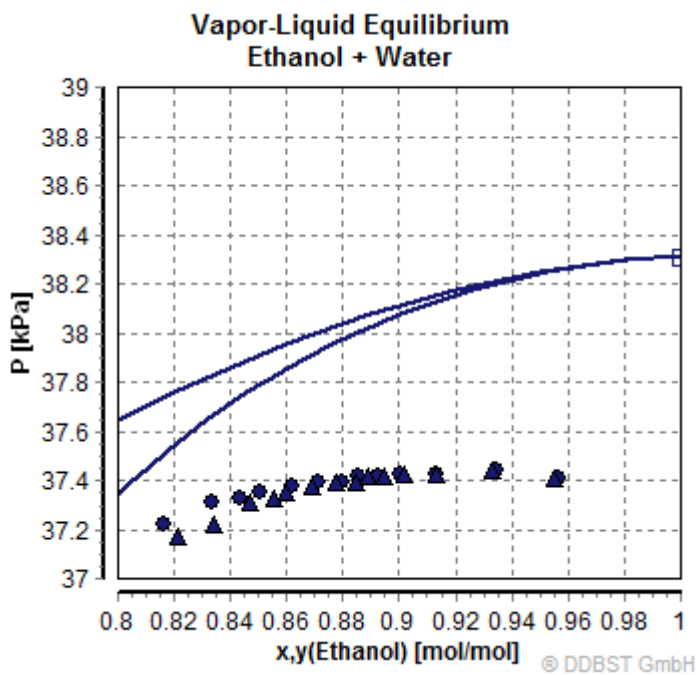
The corrected pure component vapor pressures give a much better fit result – in this case even the only correct result.
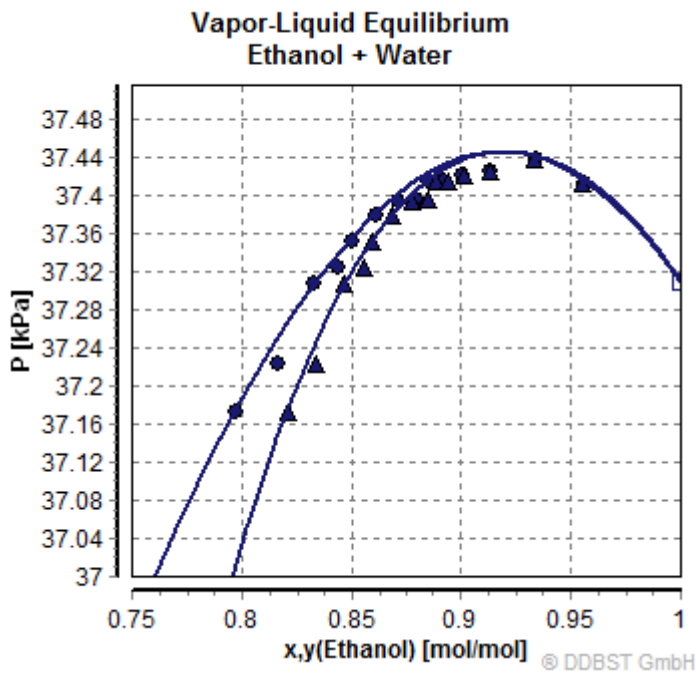
5.2   Conversion between DDB and Aspen Simulator Equations

5.2.1 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.

5.2.2 Wilson

5.2.2.1   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

$$\Lambda_{ij} = \frac{v_j}{v_i}\exp\left(-\Delta\lambda_{ij}/T\right)$$

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:

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

5.2.2.2   Aspen Form

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

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

5.2.2.3   *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 cannot be converted to the Aspen equation.

On the other hand, Aspen incorporated the ratio of molar volumes at 25°C $\frac{v_j}{v_i}$ 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 [cal/K/mol]

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

R = 1.9872098 cal/K/mol

5.2.3 NRTL

5.2.3.1   *DDBSP Form*

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

with

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

where α_{ij} is the non-randomness parameter $\alpha_{ij} = \alpha_{ji}$ and

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

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

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

5.2.3.2   Aspen Form

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

with

$$G_{ij} = \exp\left(-S_{ij}\tau_{ij}\right)$$

and

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

and

$$S_{ij} = c_{i,j} + d_{i,j}(T - 273.15)$$

which is the non-randomness parameter.

5.2.3.3   Conversion between DDBSP and Aspen Parameters

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 [cal/K/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
$a_{i,j}$	$\dfrac{b_{ij}}{\text{R}}$
$b_{i,j}$	$\dfrac{a_{ij}}{\text{R}}$
$c_{i,j}$	α_{ij}
$d_{i,j}$	0
$e_{i,j}$	$\dfrac{d_{ij}}{\text{R}}$
$f_{i,j}$	$\dfrac{c_{ij}}{\text{R}}$

R = 1.9872098 cal/K/mol

5.2.4 UNIQUAC

5.2.4.1   DDBSP Form

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

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

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

with

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

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

$\tau_{ij} = \exp\left(-\Delta u_{ij}/T\right)$ Interaction parameters between component i and j [cal/mol]

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

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

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

r_i Relative van der Waals volume of component i

q_i Relative van der Waals surface of component i

5.2.4.2   Aspen Form

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

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

The combinatorial part is determined by

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

The coordination number is $z = 10$.

The residual part is determined by

$\ln\gamma_i^R = q_i\left(1 - \ln\sum_j F_j\tau_{j,i} - \sum_j \frac{F_j\tau_{i,j}}{\sum_k F_k\tau_{k,j}}\right)$ or $\ln\gamma_i^R = q_i'\left(1 - \ln\sum_j F_j'\tau_{j,i} - \sum_j \frac{F_j'\tau_{i,j}}{\sum_k F_k'\tau_{k,j}}\right)$

with

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

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

$F_i = \frac{q_i x_i}{\sum_j q_j x_j}$ or $F_i' = \frac{q_i' x_i}{\sum_j q_j' x_j}$ Surface fraction, the F' version is used for alcohol and water.

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

5.2.4.3   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 [cal/K/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
$a_{i,j}$	$-\dfrac{b_{ij}}{R}$
$b_{i,j}$	$-\dfrac{a_{ij}}{R}$
$c_{i,j}$	$-\dfrac{d_{ij}}{R}$
$d_{i,j}$	$-\dfrac{c_{ij}}{R}$

R = 1.9872098 cal/K/mol