

Regression Mix

Model Parameter Regression Simultaneously to Multiple Properties



DDBST

Dortmund Data Bank
Software & Separation
Technology

DDBST - Dortmund Data Bank Software & Separation Technology GmbH

Marie-Curie-Straße 10

D-26129 Oldenburg

Tel.: +49 441 361819 0

support@ddbst.com

www.ddbst.com

Contents

1	Introduction	3
1.1	Supported Data Types	3
1.2	Supported g^E -Models	3
1.3	Supported Cubic EOS Mixing Rules	4
2	Starting the Program	5
2.1	Experimental Data Transfer from a Query Result Window	5
2.2	Starting the Program Directly	5
2.3	Define binary systems	5
3	Main Window	6
3.1	Component List	6
3.2	Model Selection	6
3.2.1	Select g^E Model	7
3.2.2	Select EOS-Model	8
3.2.3	Select External Model	8
3.3	Data (Experimental and Calculated)	9
3.3.1	Calculation Menu	9
3.3.2	Context Menu	9
3.3.3	VLE – Vapor Liquid Equilibrium	10
3.3.4	HE – Heats of Mixing	14
3.3.5	ACT – Limiting Activity Coefficients	14
3.3.6	LLE – Liquid-Liquid Equilibrium	15
3.3.7	AZD – Azeotropic Data	15
3.3.8	CPE – Excess Heat Capacity	16
3.3.9	SLE – Solid Liquid Equilibrium	16
3.3.10	ACTCOEFF – Activity Coefficients (GC2GE)	18
4	Parameter Regression	19
4.1	Active Data Types	19
4.2	Start Fit	19
4.3	Start Parameters	20
4.4	Regression Progress Information	20
4.5	Resulting Regression Parameters	22
4.5.1	Toolbar Options	22
4.5.2	Data Set Action	22
4.5.3	Result Entries	23
4.5.4	Saving parameters in the ParameterDDB	23
4.6	Standard Result Diagrams	23
4.7	Recalculated Data Tables	25
4.8	Custom Result Diagrams	25
4.8.1	Diagram with Residuals	27
4.9	Derived Azeotropic Points	28
5	Appendix	29
5.1	Pure Component Vapor Pressure Correction	29
5.2	Conversion between DDB and Aspen Simulator Equations	30
5.2.1	Introduction	30
5.2.2	Wilson	30
5.2.3	NRTL	31
5.2.4	UNIQUAC	32

1 Introduction

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

1.1 Supported Data Types

DDB Regression Mix 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. Activity coefficients (ACTCOEFF)
5. Liquid-Liquid Equilibrium Data (LLE Data Bank).
6. 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.
7. Excess Heat Capacity (CPE Data Bank).
8. Solid-Liquid Equilibrium Data (SLE Data Bank).
DDB Regression Mix 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 (c_p^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

DDB Regression Mix currently supports the g^E models UNIQUAC¹, NRTL², Wilson³, Margules⁴, and van Laar⁵.

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.

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

UNIQUAC needs component specific volumes and surfaces. DDB Regression Mix uses the values stored in the DDB main component file. To edit these values, it is necessary to use DDB Components.

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 DDB Components.

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

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

DDB Regression Mix 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-Copeman⁶ and Twu-Bluck-Cunningham-Coon⁷ are supported. The Stryjek-Vera⁸ alpha function is available for Peng-Robinson only.

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

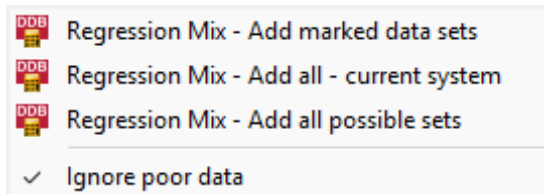
⁸ Stryjek R., Vera J.H., "PRSV: An Improved Peng-Robinson Equation of State for Pure Compounds and Mixtures", Can.J.Chem.Eng., 64, 323-333, 1986

2 Starting the Program

The “Dortmund Data Bank” program can be used to run DDB Regression Mix with selected data from a Query Result window. Additionally, DDB Regression Mix can be used stand-alone and experimental data can added from a query result file (*.qrx or *.qr).

2.1 Experimental Data Transfer from a Query Result Window

The DDB Regression Mix drop-down menu in the query result window of the Dortmund Data Bank program has multiple menu entries for calling DDB Regression Mix with different options.



1. “Add marked data sets” opens a DDB Regression Mix window where only the marked sets are automatically added.
2. “Add all – current system” opens a DDB Regression Mix dialog and all datasets with the same system like the chosen one
3. “Add all possible data sets” opens a DDB Regression Mix dialog and add all usable data sets from the query result (Appears only if different systems are present in 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 DDB Regression Mix 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 DDB Regression Mix project file (*.ddb_rpxml or *.ddbpr) where all information about a previously saved project is included.

DDB Regression Mix 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”.

2.3 Define binary systems

The function in the bottom right corner of the main dialog allows the specification of the binary systems, either by “Add Systems(s)” button (DDB Components) or by typing the known DDB component numbers of the wanted systems in the edit box left of it. This system can be confirmed by pressing the “Enter” button or by the button between the both options. If more than two components were specified at the same time, all binary cross combination will be added. All systems will be shown in the “Systems” combo box, which shows also the total number of binary systems in brackets in the header. If more than one system was added, the wanted one can be chosen here and activated by the “Use” button.

These systems can be used to create calculated data for the fit of model parameters.

3 Main Window

The dialog has the following main parts:

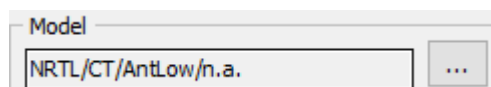
1. List of components (“System”) which, besides the DDB numbers, names, and formula, also shows some additional pure component properties.
2. Model settings including the “Fit Parameters” button and some basic data selections and project management functions.
3. Data Tables (includes a page with results). 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

The screenshot shows a software interface for selecting a g^E model. It features three main sections:

- Gamma Model:** A dropdown menu currently showing 'NRTL'.
- VLE Settings:** A sub-section containing:
 - Vapor Phase Model:** A dropdown menu showing 'Ideal or Marek/Standart for Carboxylic Acids (DCDS)'.
 - Vapor Pressure Equation:** A dropdown menu showing 'Antoine - Low'.
- Poynting Correction:** Two dropdown menus, the first showing 'All Components' and the second showing 'No Correction'.

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

DDB Regression Mix 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 Regression Pure 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 .

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

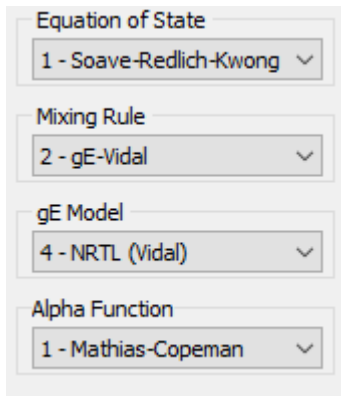
DDB Regression Mix supports:

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 (DDB Regression Pure).

2. Densities by the Yen/Woods⁹ 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.

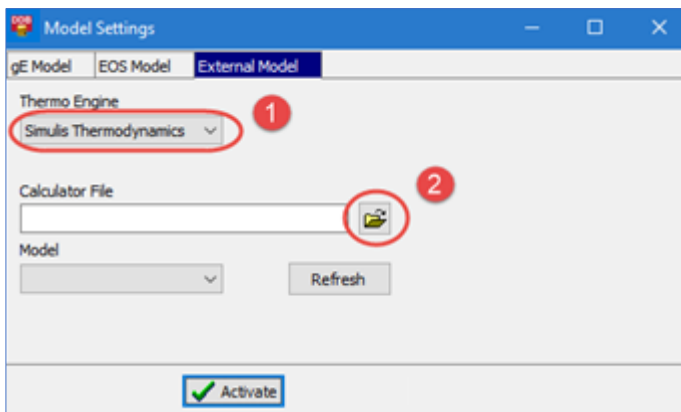
3.2.2 Select EOS-Model



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.

3.2.3 Select External Model

It is also possible to use a third-party thermodynamic engine.



First the desired thermodynamic engine (1) has to be selected. Currently only *Simulis Thermodynamics* and *Aspen and AVEVA SimCentral* are supported.

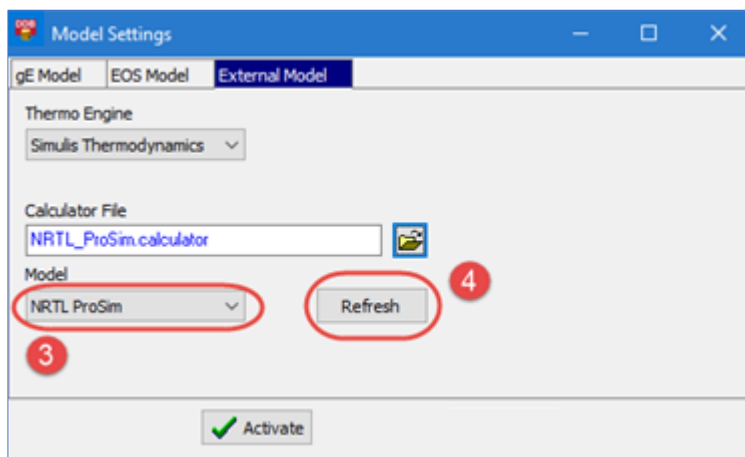
Click on the *Select Calculator File* button (2) to open a *Simulis Thermodynamics* calculator file. Now the well-known *Open Simulis Thermodynamics Calculator File* dialog appears. Click on the *Components Assigned* button to finish the file selection.

For *Aspen* select an *Aspen Plus Backup* file with the file button (2). Currently only UNIQUAC, Wilson and NRTL are supported.

For *AVEVA SimCentral* a *SimCentral AVEVA simulation library* is needed.

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).

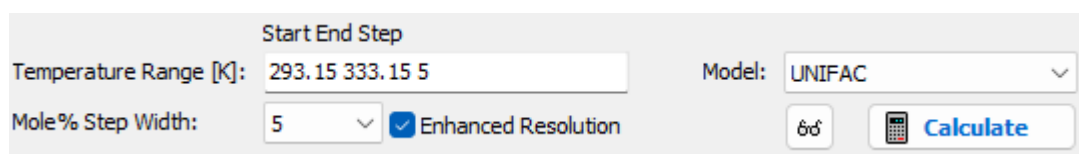


If the *File* field is already filled when the dialog is opened, click on the *Refresh* button (4) to update the model information. If a model is not supported, a text warning is shown.

3.3 Data (Experimental and Calculated)

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 a data table for experimental and calculated data.

3.3.1 Calculation Menu



Every data table is splitted in a tab for experimental and calculated data. Experimental data, which was transferred from the Dortmund Data Bank, is stored in the experimental data table. Datasets, which were calculated in the Dortmund Databank are stored in the calculated datasheet. Additionally each tab for calculated data contains a menu to calculated new data with the supported models.

- “Temperature Range”: The first number is the start value and the second one is the end value of the range. The last number is the step width in which datasets are created.
- “Mole% Step Width”: The concentration steps can be chosen with a drop down menu.
- “Enhanced Resolution”: If this options is used, more concentrations steps will be used in the diluted regions
- “Model”: A drop down menu allows to choose a supported prediction model.
- “Glasses”: Check for parameter availability.
- “Calculate”: Start of the calculation. Results are shown in the data grid.

3.3.2 Context Menu

For both data tables the context menu of each property grid can be used 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
- “Remove data set X”: Removes the marked data set
- “Set All Weights to 1” All points are included with a weight of 1
- “Set All Weights to 0” All points are excluded.

3.3.3 VLE – Vapor Liquid Equilibrium

3.3.3.1 *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 ($x\gamma$).


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.

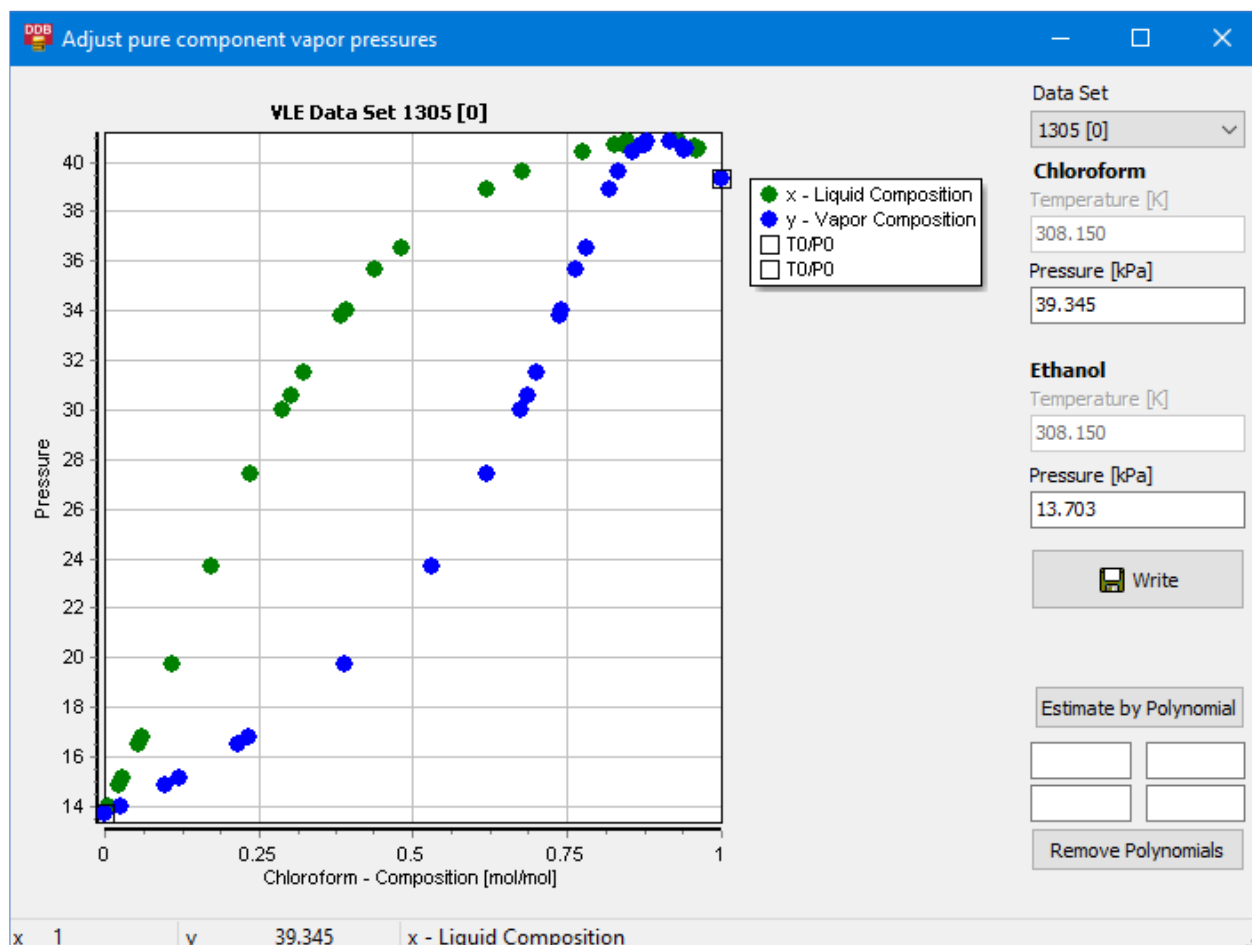
3.3.3.2 *Pure Component Vapor Pressure Correction*

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 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.

3.3.3.3 Data Table

#	x [mol/mol]	y [mol/mol]	T [K]	P [kPa]	Weight	+/-	Cons	Obj	Reference	Objective Functions
-47 [0]	0 - 1		293.15	5.844 - 13.012	1.00	+/-	{??}	O	Niini A., Suom.Tied.Toimit.Ser.A Sci.Nat., 55, 1-52, 1940	((P_exp - P_cal)/P_exp)
-500 [0]	0.0374 - 0.9591	0.1965 - 0.8201	318.15	27.102 - 41.275	1.00	+/-	{+}	O	Brown I., Smith F., Aust.J.Chem., 7, 264-268, 1954	((P_exp - P_cal)/P_exp)
-501 [0]	0.057 - 0.916	0.246 - 0.747	328.15	47.836 - 62.785	1.00	+/-	{+}	O	Yuan K S, Liu R C Y, Deshpande & K. Hn J C K J Chem Eng Data, 8(4), 540-550, 1963	((P_exp - P_cal)/P_exp)

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 reference information(experimental)/ the used model (calculated)
11. the active objective functions

When a node is expanded (with a click on the “+” button in the left-most column) then 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.

3.3.3.4 *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 if the auto options are used. If the “Fit DCDS X” option is used more than one model can freely be chosen.

- Expand All
- Collapse All
-  Copy Selected Cells
-  Check Pure Component Temperature or Pressure
-  Set All Weights to 1
- Set All Weights to 0
-  Set Weight to 0 for Inconsistent Data
-  Remove data set 504 [0]
- Fit DCDS Auto 504 [0]
- Fit DCDS 504 [0]
- Fit DCDS Auto (all data sets)
-  Remove Experimental Data

The results are given in a special “DCDS” Tab Sheet

(1) ACETONE C3H6O

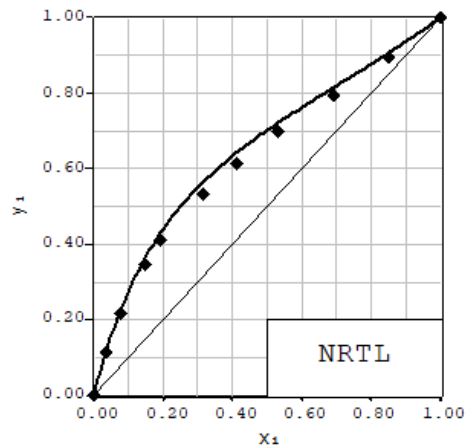
(2) ETHANOL C2H6O

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

CONSTANTS:	A12	A21	ALPHA12	G1	G2	OBJECTIVE 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.

3.3.4 HE – Heats of Mixing

3.3.4.1 Data Table

#	x [mol/mol]	T [K]	P [kPa]	hE [J/mol]	Weight	+/-	Obj	Reference	Objective Functions
1075 [0]	0.209 - 0.773	298.15		717.00 - 1153.00	1.00	+/-	O	Coomber B.A., Wormald C.J., J.Chem.Thermodyn., 8(8), 793-799, 1976	$((hE_{exp} - hE_{cal})/hE_{max})^2$
1076 [0]	0.1053 - 0.829	298.15		444.22 - 1123.32	1.00	+/-	O	Hirobe H., J.Fac.Sci.Univ.Tokyo Sec.1, 1, 155-222, 1926	$((hE_{exp} - hE_{cal})/hE_{max})^2$
1077 [0]	0.0418 - 0.9317	298.15		180.67 - 1110.11	1.00	+/-	O	Nicolaides G.I., Eckert C.A., J.Chem.Energ.Data, 23(2), 152-156, 1978	$((hE_{exp} - hE_{cal})/hE_{max})^2$

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 reference information(experimental) / the used model (calculated)
10. the active objective functions

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

3.3.5 ACT – Limiting Activity Coefficients

3.3.5.1 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.Eng.Chem.
2051 [0]	2 315.950		6.3800	1.00	+/-	O	$(\log(g_{exp}) - \log(g_{cal}))^2$	Thomas F.R., Newman B.A., Nicolaides G.I.

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(experimental) / the used model (calculated)

3.3.6 LLE – Liquid-Liquid Equilibrium

3.3.6.1 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”.

3.3.6.2 Data Table

#	x' [mol/mol]	x'' [mol/mol]	T [K]	P [kPa]	Weight	+/-	Obj	Reference	Objective Functions
3 [0]	0.4888 - 0.851	0.929 - 0.9838	273.15 - 398.15		1.00	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	Peschla R., Garcia B.C., Albert M., Kreiter C., Maurer G., Ind.Eng.Chem.Res., 42(7), 1508-1516, 2003	$(x'_{exp} - x'_{cal})^2 + (x''_{exp} - x''_{cal})^2$
382 [0]	0.4913 - 0.7571	0.9711 - 0.9838	273.15 - 383.15		1.00	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>	Führer H., Ber.Dtsch.Chem.Ges./Abhandl., 57(1), 510-515, 1924	$(x'_{exp} - x'_{cal})^2 + (x''_{exp} - x''_{cal})^2$

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 reference information(experimental) / the used model (calculated)
10. the active objective functions

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

3.3.7 AZD – Azeotropic Data

3.3.7.1 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.

3.3.7.2 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	+/-	<input type="radio"/>	(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	+/-	<input type="radio"/>	(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(experimental) / the used model (calculated)

3.3.8 CPE – Excess Heat Capacity

3.3.8.1 Data Table

	#	x [mol/mol]	T [K]	P [kPa]	cpE [J/molK]	Weight	+/-	Obj	Reference	Objective Functions
	313 [0]	0.09997 - 0.995	298.15		1.32 - 12.04	1.00	+/-	<input type="radio"/>	Ogawa H., Murakami S., Thermochim.Acta, 109, 145-154, 1986	(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 reference information (experimental) / the used model (calculated)
10. the active objective functions

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

3.3.9 SLE – Solid Liquid Equilibrium

3.3.9.1 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

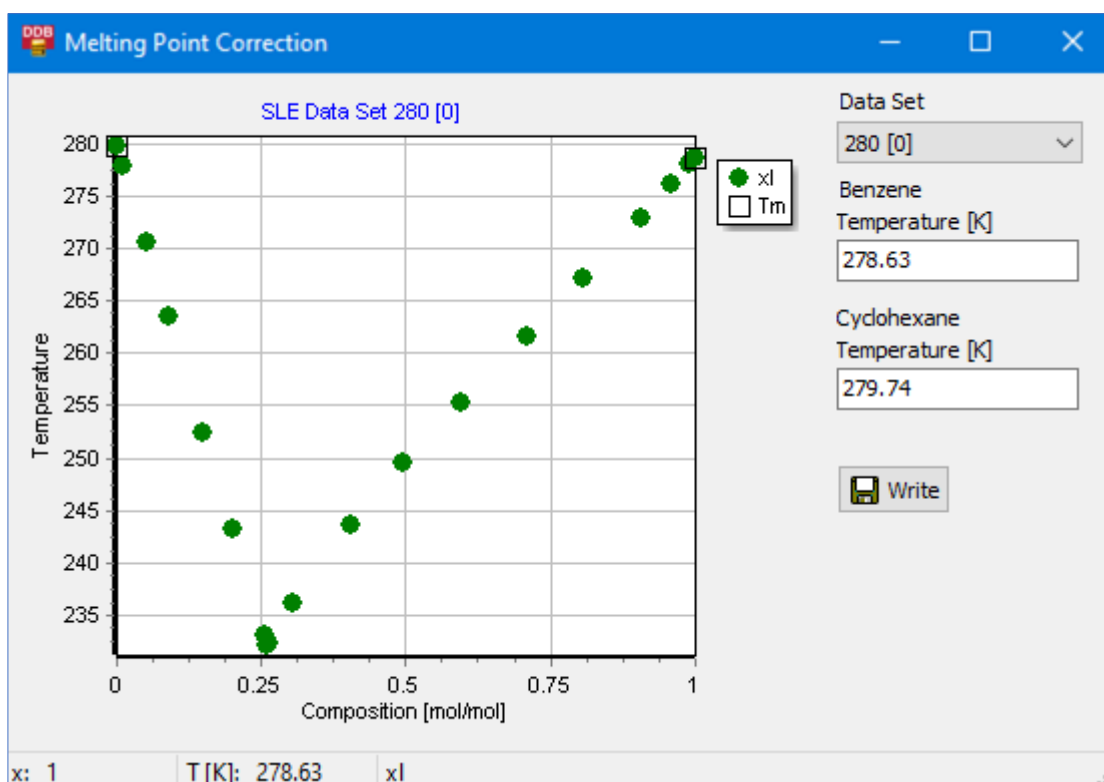
$$\ln x_i^L \gamma_i^L = \frac{-\Delta h_{m,i}}{RT} \left(1 - \frac{T}{T_{m,i}} \right)$$

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.

3.3.9.2 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 3.3.3.2 “Pure Component Vapor Pressure Correction”.

3.3.9.3 Data Table

#	x [mol/mol]	T [K]	P [kPa]	Weight	+/-	Obj	Reference	Objective Functions
6755 [0]	0.1058 - 1	199.89 - 273.15		1.00	+/-	O	Lohmann J., Joh R., Gmehling J., J.Chem.Eng.Data, 42(6), 1170-1175, 1997	$(\log(T_{\text{exp}}) - \log(T_{\text{cal}}))^2$
17103 [0]	0.9746 - 0.9989	270.61 - 273.04		1.00	+/-	O	Knight W.S., Thesis, Princeton Univ., 1962	$(\log(T_{\text{exp}}) - \log(T_{\text{cal}}))^2$

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 reference information (experimental) / the used model (calculated)
9. the active objective functions

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

3.3.10 ACTCOEFF – Activity Coefficients (GC2GE)

The ACTCOEFF tab contains the properties of the old GC2GE program. The calculation allows to calculate the activity coefficients of both components of a binary system over a wide temperature and pressure range. It is possible to fit model only against this calculated data. To emulate the function of GC2GE the datasets are refreshed if the system or the model was changed. This allows a batch fit of all systems.

#	T [K]	x [mol/mol]	Act.Coeff. 1 [-]	Act.Coeff. 2 [-]	Weight	+/-	Obj	Used Model	Objective Functions
1 [201]	293.15	0 - 1			1.00	+/-	<input type="radio"/>	UNIFAC	$(\log(g_{\text{exp}}) - \log(g_{\text{cal}}))^2$
1	293.150	0.00000	11.3307	1.0000	1.00	+/-	<input type="radio"/>		$(\log(g_{\text{exp}}) - \log(g_{\text{cal}}))^2$

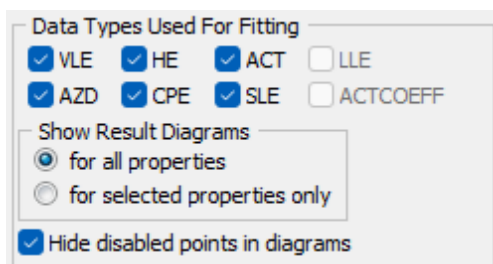
The data table for ACTCOEFF contains one (collapsed) node for each data set. Each node line consists of

1. the data set ID
2. the temperature in K
3. the liquid composition range x_1 for component 1 in mole fractions
4. the activity coefficient of component 1 and 2
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 used model
9. the active objective functions

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

4 Parameter Regression

4.1 Active Data Types



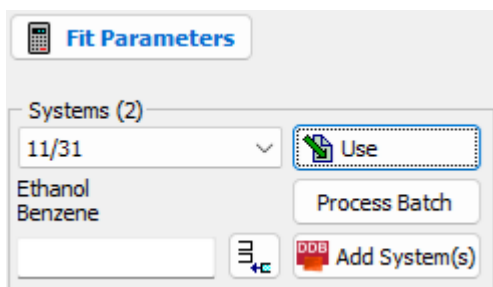
These check boxes allow the user to quickly drop or include selected data types from the regression. A right-click on a check box selects a single property directly.

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 Fit



The Systems drop down menu shows all systems which were added to Regression Mix. The lowest line allows to add other Systems with the help of the DDB Numbers or by DDB components. The “Use” button activates the chosen system. This useful if you only want to fit many systems to calculate activity coefficients.

With a click on the “Fit Parameters” button the start parameters are displayed.

If the “Process Batch” button is used, this fit routine will be done for all given systems.

4.3 Start Parameters

Parameter	Start Value	Initial Step	Constant?	min.	max.	Limits
aij	50	12.5	<input type="checkbox"/> Constant			<input checked="" type="checkbox"/> Respect
aji	60	15	<input type="checkbox"/> Constant			<input checked="" type="checkbox"/> Respect
bij	0	0	<input checked="" type="checkbox"/> Constant			<input checked="" type="checkbox"/> Respect
bji	0	0	<input checked="" type="checkbox"/> Constant			<input checked="" type="checkbox"/> Respect
cij	0	0	<input checked="" type="checkbox"/> Constant			<input checked="" type="checkbox"/> Respect
cji	0	0	<input checked="" type="checkbox"/> Constant			<input checked="" type="checkbox"/> Respect
dij	0		<input checked="" type="checkbox"/> Constant			<input checked="" type="checkbox"/> Respect
dji	0		<input checked="" type="checkbox"/> Constant			<input checked="" type="checkbox"/> Respect
eij	0	0	<input checked="" type="checkbox"/> Constant			<input checked="" type="checkbox"/> Respect
eji	0	0	<input checked="" type="checkbox"/> Constant			<input checked="" type="checkbox"/> Respect
fij	0		<input checked="" type="checkbox"/> Constant			<input checked="" type="checkbox"/> Respect
fji	0		<input checked="" type="checkbox"/> Constant			<input checked="" type="checkbox"/> Respect
alpha	0.3	0	<input checked="" type="checkbox"/> Constant	0.01	1	<input checked="" type="checkbox"/> Respect

Optimizer: LM + SNM (dropdown) Fit Lev. Steps: 80 (input box)

Use Expert Modus Use Fug. Prefit Fit Fug. Steps: 40 (input box)

OK (button)

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.

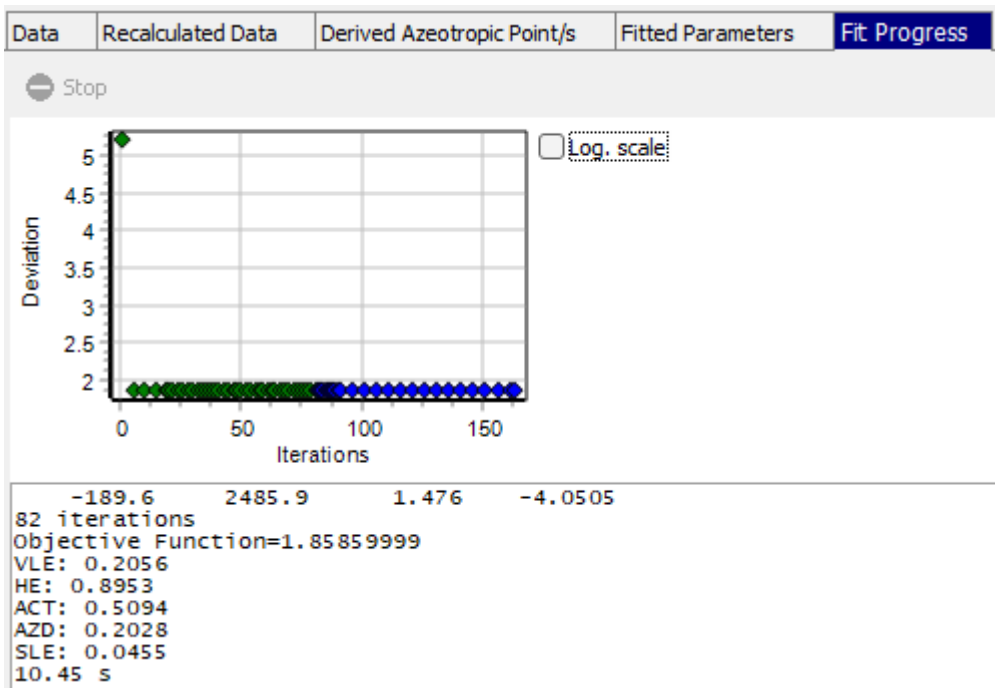
If only LLE-data is active, then the option “Use LLE Prefit” can be selected to perform a special LLE-Fit (internal model only). The option should be unchecked if non-default start parameters are used.

A right click opens the context menu. This allows loading parameter sets for the chosen internal model from the DDB Parameter Organizer.

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

4.4 Regression Progress Information

During the regression a separate tab sheet with a diagram and a multi-line text field is shown. That control is used to present some more detailed information about the iteration progression and the values of the objective function. The diagram shows the size of the objective function against the iteration steps. Different colors represent different optimizer.



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.

4.5 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. Every parameter set starts with a blue colored line. The green color indicates which dataset was used for the last calculation.

Data	Recalculated Data	Derived Azeotropic Point/s	Fitted Parameters	Fit Progress										
Save as XLSX Copy Clear														
6 Sets														
Set no.	6	...												
Model	NRTL/CT/Antoine/n.a.													
Comp. 1	11 Ethanol													
Comp. 2	31 Benzene													
Parameters [cal/mol]	a _{ij}	a _{ji}	b _{ij}	b _{ji}	c _{ij}	c _{ji}	d _{ij}	d _{ji}	e _{ij}	e _{ji}	f _{ij}	f _{ji}	alpha	
1-2	-189.60029	2485.9387	1.4760326	-4.0505323	0	0	0	0	0	0	0	0	0.3	
Obj. Function	Total=1.859 VLE=0.2056 HE=0.8953 ACT=0.5094 AZD=0.2028 SLE=0.04555													
Aspen [K]	a _{ij}	a _{ji}	b _{ij}	b _{ji}	c _{ij}	c _{ji}	d _{ij}	d _{ji}	e _{ij}	e _{ji}	f _{ij}	f _{ji}		
1-2	0.74276637	-2.0383013	-95.410303	1250.9694	0.3	0.3	0	0	0	0	0	0		
PRO/II [K]	a _{ij}	a _{ji}	b _{ij}	b _{ji}	c _{ij}	c _{ji}	alpha							
1-2	0.74276637	-2.0383013	-95.410303	1250.9694	0	0	0.3							
Set no.	5	...												
Model	NRTL/CT/Antoine/n.a.													
Comp. 1	11 Ethanol													
Comp. 2	31 Benzene													
Parameters [cal/mol]	a _{ij}	a _{ji}	b _{ij}	b _{ji}	c _{ij}	c _{ji}	d _{ij}	d _{ji}	e _{ij}	e _{ji}	f _{ij}	f _{ji}	alpha	
1-2	268.12798	1207.4785	0	0	0	0	0	0	0	0	0	0	0.3	

4.5.1 Toolbar Options

The parameters can be saved as

1. Microsoft Excel file in the format the dialog shows (“Save as XLSX”)
2. The parameters can also be copied to the Windows clipboard.

Use the “Clear” button to remove all data sets.

4.5.2 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 internal model was used for fitting also the following entries are available:

4. Aspen INP file for the Aspen simulator (“Save as INP”)
5. DDB parameter data set for the further usage in the DDB system (“Save in ParameterDDB”), see also section 4.5.4 “Saving parameters in the ParameterDDB”
6. IK-CAPE PPDX file (“Save as PPDX”)

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

7. Save: Save the parameters to the currently active external project.
8. “Save as...”: Save the parameters to a new project file.

4.5.3 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.

4.5.4 Saving parameters in the ParameterDDB

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

#	DDB	Store?	Rec'd?	Equation	Components	Parameters [cal/mol]	Tmin [K]	Tmax [K]	Obj. Func.	Source	Comm
1	1 private	<input checked="" type="checkbox"/> Yes	Undef.	17 NRTL gE model	11, 31	A12=-716.25996 A21=3319.7413 B12=3.102213 B21=-6.789637 Alpha=0.3 TRef=0.0	288.15	513.15	Total=0.788978 VLE=0.7890	DDB	Fit by

This dialog has two editable cells

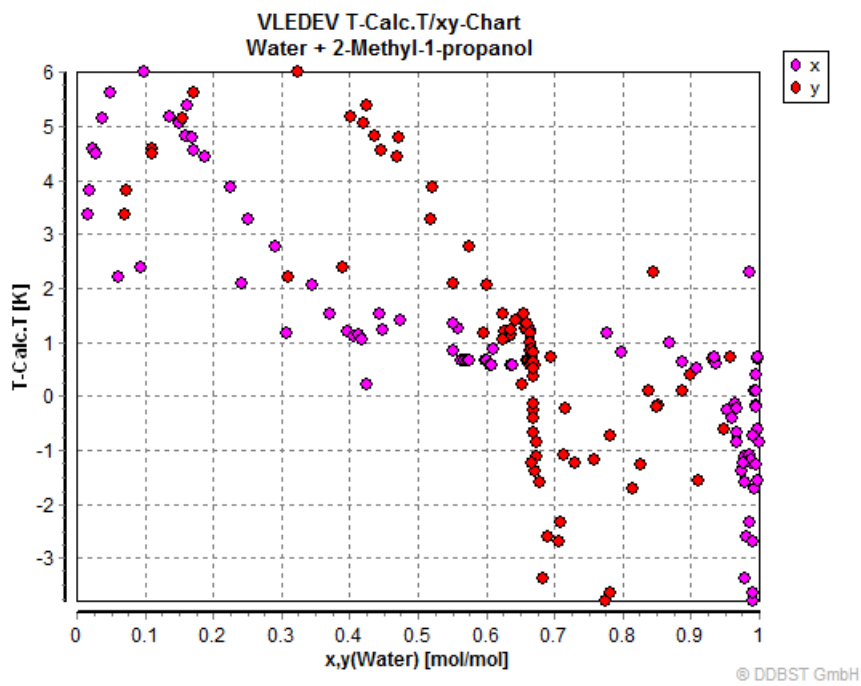
1. “Source” – preset with “DDB”
2. “Comment” – preset with “Fit by DDB Regression Mix”

These can be used to enter detailed descriptions.

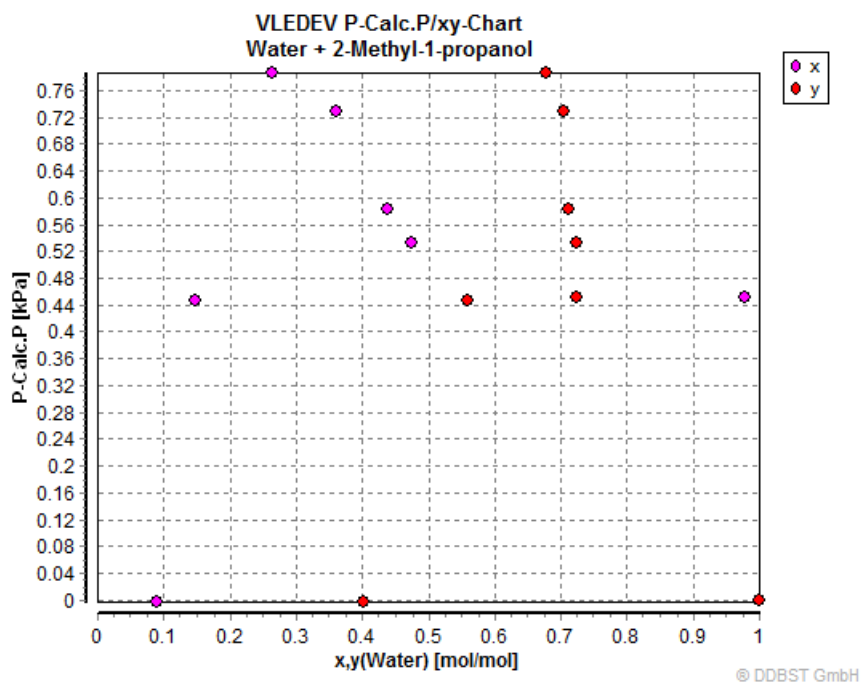
4.6 Standard Result Diagrams

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.

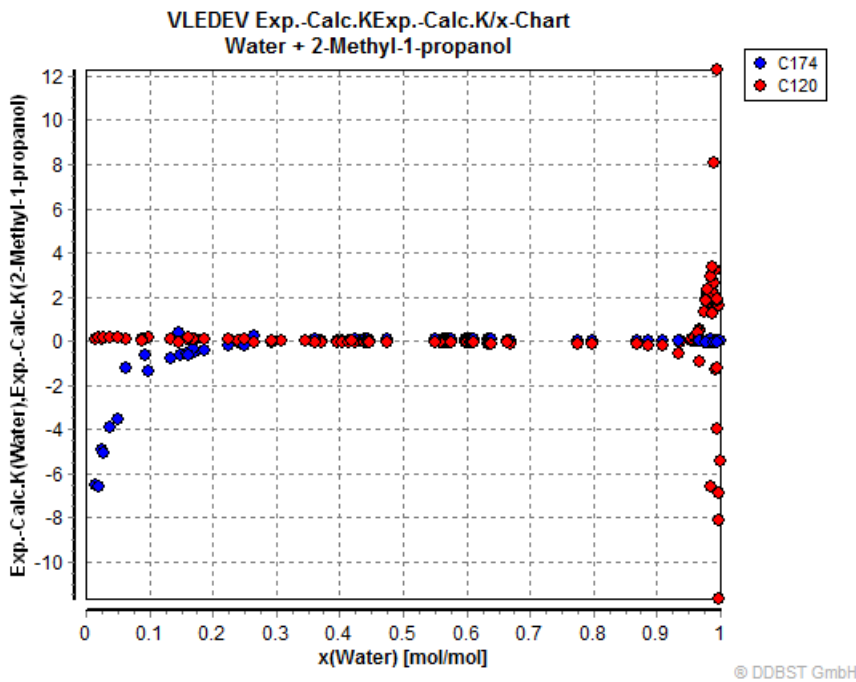
Absolute Temperature Deviations:



Absolute Pressure Deviations:



Absolute K-Factor Errors:



4.7 Recalculated Data Tables

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

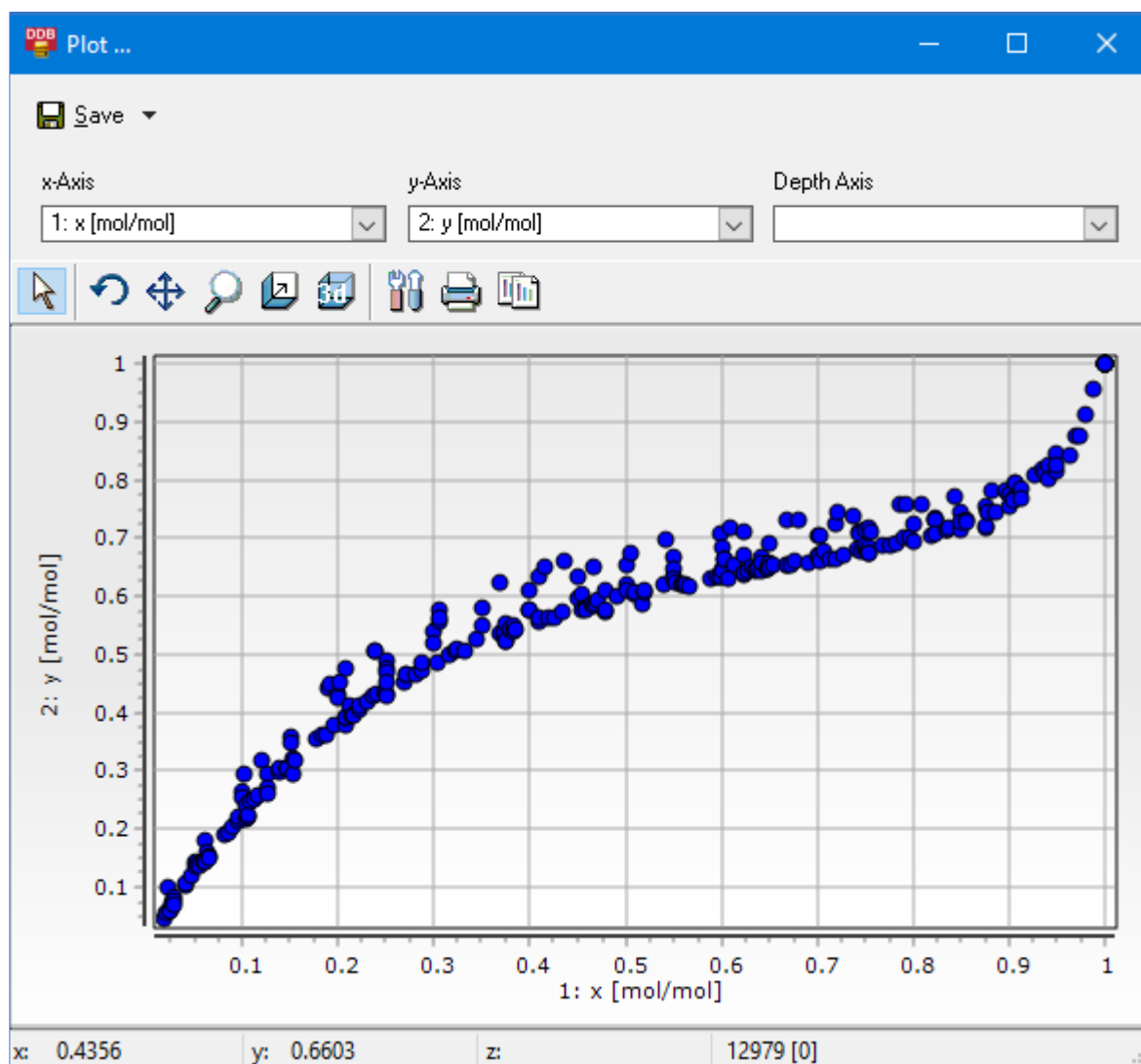
Data	Recalculated Data	Derived Azeotropic Point/s	Fitted Parameters	Fit Progress			
VLE	HE	ACT	AZD	SLE			
#	x1 [mol/mol]	y1 [mol/mol]	T [K]	P [kPa]	Act.Coeff.1	Act.Coeff.2	Calc. Act.Coeff.1
47 [0]							
500 [0]							2.88%
501 [0]							4.22%
502 [0]							

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.

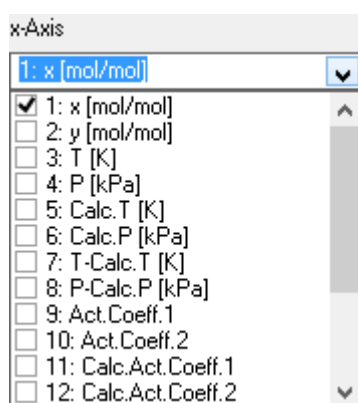
In the case of properties which are originally organized as data sets (HE, VLE, LLE, SLE, CPE, ACTCOEFF) and not as single points (ACT, AZD) the first line shows mean errors and the residual. For every point the residual for the final parameter set is shown. During the calculation each residual is normalized 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.

4.8 Custom Result Diagrams

Besides the standard plots DDB Regression Mix 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 context menu of 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.

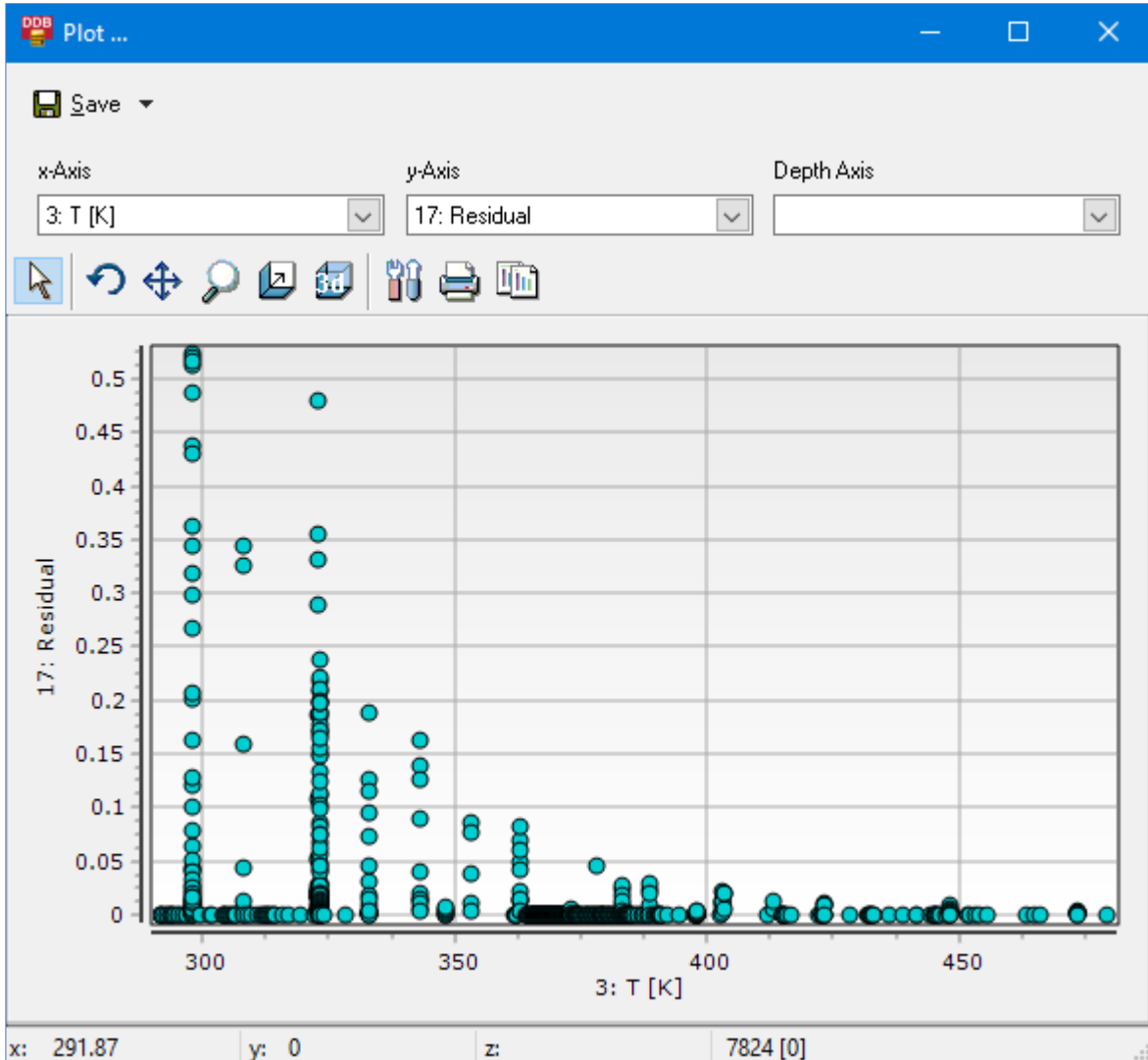
The tool bar enables



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

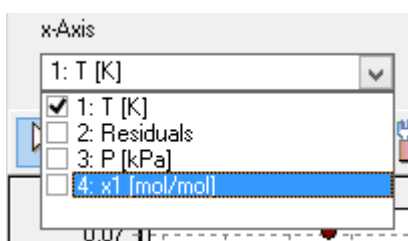
- call the chart editor
- printing
- copying

4.8.1 Diagram with Residuals

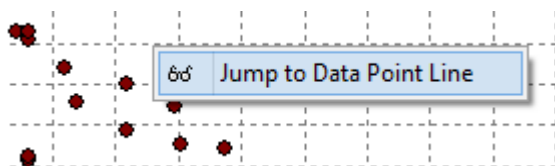


Residuals have no thermodynamic meanings. They are simply the contribution of every single point to the objective function of the optimizer. Such a diagram contains points for all properties together in a single chart and allows finding outliers somewhat easier than the diagrams for the single properties.

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.



4.9 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	48.84	0.75857	0.24143	NRTL	422 [101]
2	322.45	85.95	0.72525	0.27475	NRTL	423 [101]
3	326.87	101.33	0.71460	0.28540	NRTL	424 [101] 1
4	326.76	100.93	0.71486	0.28514	NRTL	425 [101] 1

Buttons: 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”):

Number		Databank	Data Points	Components	Reference	Data Set Number
1	Edit	AZD	1	47 110	64166	422 [101]
2	Edit	AZD	1	47 110	64166	423 [101]
3	Edit	AZD	1	47 110	64166	424 [101] 1
4	Edit	AZD	1	47 110	64166	425 [101] 1
5	Edit	AZD	1	47 110	64166	1301 [101] 1
6	Edit	AZD	1	47 110	64166	1302 [101] 1
7	Edit	AZD	1	47 110	64166	1303 [101] 1
8	Edit	AZD	1	47 110	64166	5147 [101] 1

Mode: Append | Location: Private | Append all data sets

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).

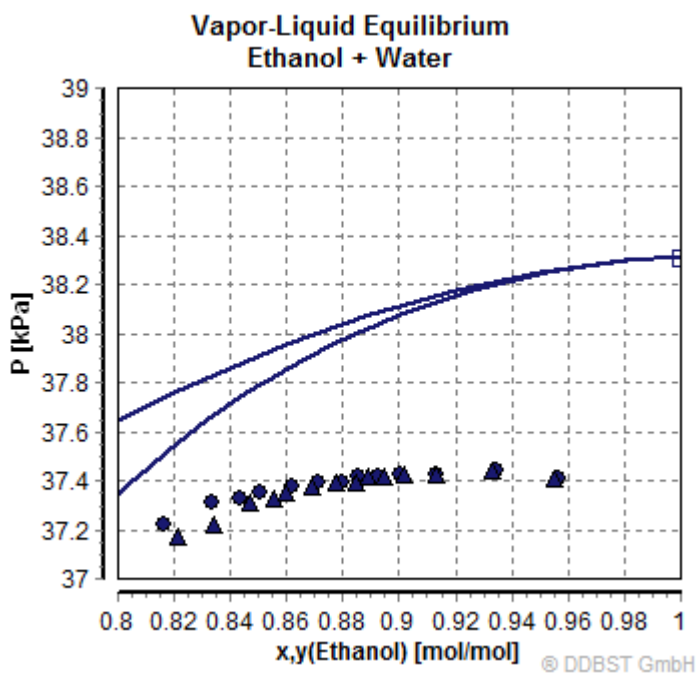
5 Appendix

5.1 Pure Component Vapor Pressure Correction

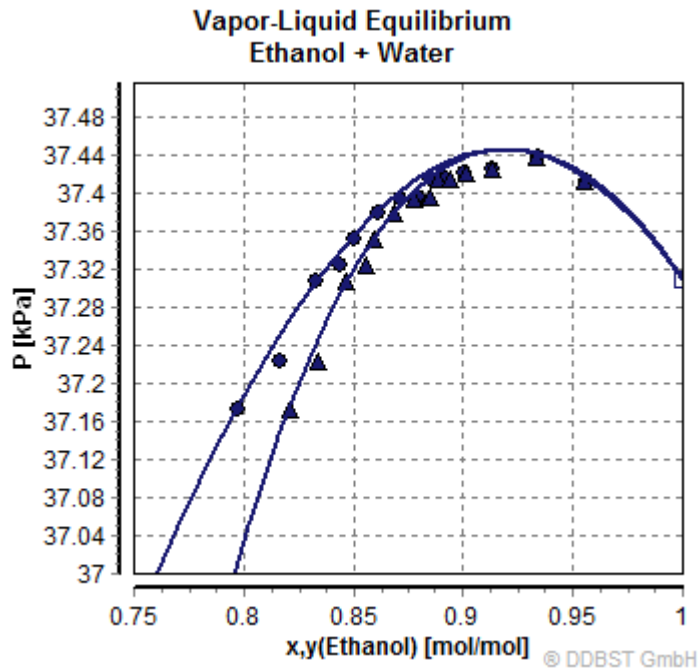
A wrong pressure (here manually modified) leads to a bended curve near the pure components – a forced deviation.

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 Dortmund Data Bank (short DDB) 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 DDB 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

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

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:

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

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 DDB 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 DDB parameters if any of the pure component Wilson volumes are missing.

The last difference is that DDB and Aspen are using different units for the interaction parameters – [cal/mol] in DDB and [K] in Aspen which leads to the conversion factor R (gas constant) in [cal/K/mol]

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

R = 1.9872098 cal/K/mol

5.2.3 NRTL

5.2.3.1 DDB 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

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

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

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

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 DDB and Aspen Parameters

The conversion between DDB and Aspen parameters is mainly a conversion of units. DDB uses [cal/mol] and Aspen uses [K] which leads to the conversion factor R (gas constant) in [cal/K/mol]. DDB 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 DDB parameters. The sequence of parameters is also slightly different.

Aspen parameters	DDB 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 = 1.9872098 cal/K/mol

5.2.4 UNIQUAC

5.2.4.1 DDB 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

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

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

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

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

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 DDB and Aspen Form

The conversion between DDB and Aspen parameters is mainly a conversion of units. DDB 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 DDB parameters into Aspen parameters if these components are encountered.

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

$R = 1.9872098 \text{ cal/K/mol}$