

Pure Component Equations

Fitting of Pure Component Equation Parameters

DDBSP – Dortmund Data Bank Software Package



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1 Introduction

PCPEquationFit fits parameters for a large variety of equations for pure component properties. Parameters can be stored in and retrieved from a parameter database, they can be plotted, and they can be used for calculations.

PCPEquationFit normally uses the pure component properties data bank which is a part of the Dortmund Data Bank. It can also be used to fit data from other data sources since tables can be pasted from the clipboard or loaded from files.

2 List of Equations

<i>Property</i>	<i>Equation</i>
Liquid Viscosity T [K] η [mPa s]	1. Andrade $\eta = e^{A + \frac{B}{T}}$ 2. Vogel $\eta = e^{A + \frac{B}{T+C}}$ 3. DIPPR 101 $\eta = e^{A + \frac{B}{T} + C \ln T + DT^E}$ 4. PPDS 9 $\eta = E \exp \left[A \left(\frac{C-T}{T-D} \right)^{\frac{1}{3}} + B \left(\frac{C-T}{T-D} \right)^{\frac{4}{3}} \right]$ 5. Extended Andrade $\eta = e^{A + \frac{B}{T} + CT + DT^2 + ET^3}$
Vapor Viscosity T[K] η [mPa s]	1. DIPPR 102 $\eta = \frac{AT^B}{1 + \frac{C}{T} + \frac{D}{T^2}}$ 2. Polynomial $\eta = A + B \cdot T + CT^2 + DT^3 + ET^4$

Property	Equation
Saturated Vapor Pressure T [K] P [kPa]	<p>1. Antoine $P=10^{A-\frac{B}{T+C}}$ (► Other Units: T [°C], P [mmHg])</p> <p>2. Wagner 2.5,5 $P=\exp\left(\ln P_c+\frac{A(1-T_r)+B(1-T_r)^{1.5}+C(1-T_r)^{2.5}+D(1-T_r)^5}{T_r}\right)$</p> <p>3. Wagner 3,6 $P=\exp\left(\ln P_c+\frac{A(1-T_r)+B(1-T_r)^{1.5}+C(1-T_r)^3+D(1-T_r)^6}{T_r}\right)$</p> <p>4. Cox $P=\exp\left[\ln 101.325+e^{A+B\left(\frac{T}{T_B}\right)+C\left(\frac{T}{T_B}\right)^2}\left(1-\frac{T_B}{T}\right)\right]$</p> <p>5. DIPPR 101 $P=e^{A+\frac{B}{T}+C\ln T+DT^E}$ (► Other Units: P [Pa])</p> <p>6. Extended Antoine (Lonza) $P=\exp\left(A+\frac{B}{T+C}+DT+ET^2+F\ln(T)\right)$ (► Other Units: P [bar])</p> <p>7. Extended Antoine (Aspen) $P=\exp\left(A+\frac{B}{T+C}+DT+E\ln(T)+FT^G\right)$ G=1 or G=2</p> <p>8. Extended Antoine (Hysys) $P=\exp\left(A+\frac{B}{T+C}+D\ln(T)+ET^F\right)$ F=1 or F=2</p> <p>9. Rarey2P $P=P_{atm}10^{\left[4.1012+A\left(\frac{T-B}{T-\frac{B}{8}}\right)\right]}$ $B\approx T_b$ $-1 < A < +1$</p> <p>10. Xiang/Tan $P=P_c\cdot\exp\left(\ln T_R\cdot\left(A_1+A_2(1-T_R)^{1.89}+A_3\cdot(1-T_R)^{5.67}\right)\right)$</p> <p>11. PVExpansion: $P=\exp\left(A+\frac{B}{T}+C\ln(T)+DT+ET^2+\frac{F}{T^2}+GT^6+\frac{H}{T^4}\right)$</p> <p>12. Hoffman/Florin: $P=\exp\left(A+B\left(\frac{1}{T}-7.9151\cdot 10^{-3}+2.6726\cdot 10^{-3}\cdot\log_{10}(T)-0.8625\cdot 10^{-6}\cdot T\right)\right)$ (► Other Units: P [Pa])</p>

Property	Equation
Saturated Vapor Pressure by EOS T [K] P [kPa]	<ol style="list-style-type: none"> Mathias-Copeman Constants for EOS $\alpha = \left(1 + m \cdot \left(1 - \sqrt{T_r}\right)\right)^2$ $m = c_1 + c_2 \cdot \left(1 - \sqrt{T_r}\right) + c_3 \cdot \left(1 - \sqrt{T_r}\right)^2$ Twu-Bluck-Cunningham-Coon Constants for EOS $\alpha = T_r^{(c_3 \cdot (c_2 - 1))} \cdot \exp\left(c_1 \cdot \left(1 - T_r^{(c_2 \cdot c_3)}\right)\right) \quad (c_1, c_2, c_3 \text{ used in DDB programs})$ $\alpha = T_r^{(N \cdot (M - 1))} \cdot \exp\left(L \cdot \left(1 - T_r^{(M \cdot N)}\right)\right) \quad (L, M, N \text{ like original authors})$ Melhem-Saini-Goodwin Constants for EOS $\alpha = \exp\left(c_1 \cdot \left(1 - T_r\right) + c_2 \cdot \left(1 - \sqrt{T_r}\right)^2\right)$ Stryjek-Vera Constants for EOS $\kappa = \kappa_0 + \kappa_1 \left(1 + \sqrt{T_r}\right) \left(0.7 - T_r\right)$ $\alpha = \left(1 + \kappa \left(1 - \sqrt{T_r}\right)\right)^2$ Stryjek-Vera-2 Constants for EOS $\kappa = \kappa_0 + \left[\kappa_1 + \kappa_2 \left(\kappa_3 - T_r^{0.5}\right) \left(1 - T_r^{0.5}\right)\right] \left(1 + T_r^{0.5}\right) \left(0.7 - T_r\right)$ $\alpha = \left(1 + \kappa \left(1 - T_r^{0.5}\right)\right)^2$ Schwartzentruber/Renon/Watanasiri Constant for EOS $P_{rm} = 0.37464 + 1.54226 \cdot \omega - 0.26992 \cdot \omega^2$ $\alpha = \left(1 + P_{rm} \cdot \left(1 - \sqrt{T_r}\right) - \left(1 - \sqrt{T_r}\right) \cdot \left(c_1 + c_2 \cdot T_r + c_3 \cdot T_r^2\right)\right)^2$
Liquid Heat Capacity T [K] c _p [J/mol K]	<ol style="list-style-type: none"> Polynomial $c_p = A + BT + CT^2 + DT^3 + ET^4$ PPDS 15 $c_p = R \left(\frac{A}{\tau} + C\tau + D\tau^2 + E\tau^3 + F\tau^4\right)$ with $\tau = 1 - \frac{T}{T_c}$

<i>Property</i>	<i>Equation</i>
Ideal Gas Heat Capacity T [K] c_p [J/mol K]	1. Polynomial $c_p = A + BT + CT^2 + DT^3 + ET^4$ 2. Aly-Lee, DIPPR 107 $c_p = a_0 + a_1 \left(\frac{a_2}{T} \right)^2 + a_3 \left(\frac{a_4}{T} \right)^2$ $\left(\frac{a_2}{\sinh \frac{a_2}{T}} \right)^2 + a_3 \left(\frac{a_4}{\cosh \frac{a_4}{T}} \right)^2$ 3. PPDS 2 $C_p = R \left(B + (C - B) y^2 \left[1 + (y - 1) (D + Ey + Fy^2 + Gy^3) \right] \right)$ with $y = \frac{T}{A + T}$ 4. Shomate $c_p = A + BT + CT^2 + DT^3 + \frac{E}{T^2}$
Solid Heat Capacity T[K] c_p [J/mol K]	Polynomial $c_p = A + BT + CT^2 + DT^3 + ET^4$

Property	Equation
Liquid (Saturated) Density T [K] ρ [kg/m ³]	<ol style="list-style-type: none"> DIPPR 105 $\rho = \frac{A}{B \cdot \left(1 - \frac{T}{C}\right)^D}$ Polynomial $\rho = A + B \cdot T + CT^2 + DT^3 + ET^4$ Tait (pressure-dependent data) $P_{ref} = \max(f(T), 1.01325) \text{ MPa}$ (Wagner-Equation) $\rho_{ref} = f(T) \frac{\text{kg}}{\text{m}^3}$ (DIPPR 105-Equation) $T_{reduced} = 100 \quad T_R = \frac{T}{T_{reduced}}$ $C = c_0 + c_1 T_R$ $B = b_0 + b_1 T_R + b_2 T_R^2 + b_3 T_R^3 + b_4 T_R^4$ $\rho = \frac{\rho_{ref}}{1 - C \ln \left[\frac{B + P}{B + P_{ref}} \right]}$ DIPPR 116 (with additional addend ρ_c, the critical density) $\rho_L = \rho_c + \left[A \tau^{0.35} + B \tau^{\frac{2}{3}} + C \tau + D \tau^{\frac{4}{3}} \right]$ with $\tau = 1 - \frac{T}{T_c}$ DIPPR 119 $\rho = A + B \cdot \tau^{\frac{1}{3}} + C \cdot \tau^{\frac{2}{3}} + D \cdot \tau^{\frac{5}{3}} + E \cdot \tau^{\frac{16}{3}} + F \cdot \tau^{\frac{43}{3}} + G \cdot \tau^{\frac{110}{3}}$ with $\tau = 1 - \frac{T}{T_c}$
Surface Tension T [K] σ [N/m]	<ol style="list-style-type: none"> Polynomial $\sigma = A + BT + CT^2 + DT^3 + ET^4$ Short DIPPR 106 $\sigma = A(1 - T_R)^n$ with $T_R = \frac{T}{T_c}$ $\sigma = A(T - T_c)^B$ Full DIPPR 106 $\sigma = A \left(1 - T_r\right)^{B + CT_r + DT_r^2 + ET_r^3}$ with $T_r = \frac{T}{T_c}$ PPDS 14 $\sigma = A \cdot \tau^B \cdot (1 + C \cdot \tau)$ with $\tau = 1 - \frac{T}{T_c}$

Property	Equation
Second Virial Coefficient T [K] B _{ii} [cm ³ /mol]	1. $B_{ii} = \frac{A}{\sqrt{T}} + \frac{B}{T}$ 2. DIPPR 104 $B_{ii} = A + \frac{B}{T} + \frac{C}{T^3} + \frac{D}{T^8} + \frac{E}{T^9}$
Heat of Vaporization T [K] H _{vap} [J/mol]	1. DIPPR 106 $H_{vap} = A \left(1 - \frac{T}{T_c} \right)^{B+C} + D \left(\frac{T}{T_c} \right)^2 + E \left(\frac{T}{T_c} \right)^3$ 2. Extended Watson $H_{vap} = a(c - T)^b + d$ 3. PPDS 12 $H_{vap} = RT_c \left(A\tau^{\frac{1}{3}} + B\tau^{\frac{2}{3}} + C\tau + D\tau^2 + E\tau^6 \right)$ with $\tau = 1 - \frac{T}{T_c}$
Liquid Thermal Conductivity T [K] λ [W/m K]	1. Polynomial $\lambda = A + BT + CT^2 + DT^3 + ET^4$ 2. PPDS 8 $\lambda = A \left(1 + B\tau^{\frac{1}{3}} + C\tau^{\frac{2}{3}} + D\tau \right)$ with $\tau = 1 - \frac{T}{T_c}$
Vapor Thermal Conductivity T [K] λ [W/m K]	1. PPDS 3 $\lambda = \frac{\sqrt{T_r}}{A + \frac{B}{T_r} + \frac{C}{T_r^2} + \frac{D}{T_r^3}}$ with $T_r = \frac{T}{T_c}$
Isothermal Compressibility	Linear Interpolation
Thermal Expansion Coefficient	Linear Interpolation
Melting Temperature (Pressure Dependency)	Simon-Glatzel Equation $P_m = a \left(\left(\frac{T_m}{T_{m(normal)}} \right)^c - 1 \right)$
Dielectric Constants of Liquids, Permittivity T [K], ε [.]	1. Polynomial $\lambda = A + BT + CT^2 + DT^3 + ET^4$

3 Using the program

3.1 Initial Dialog

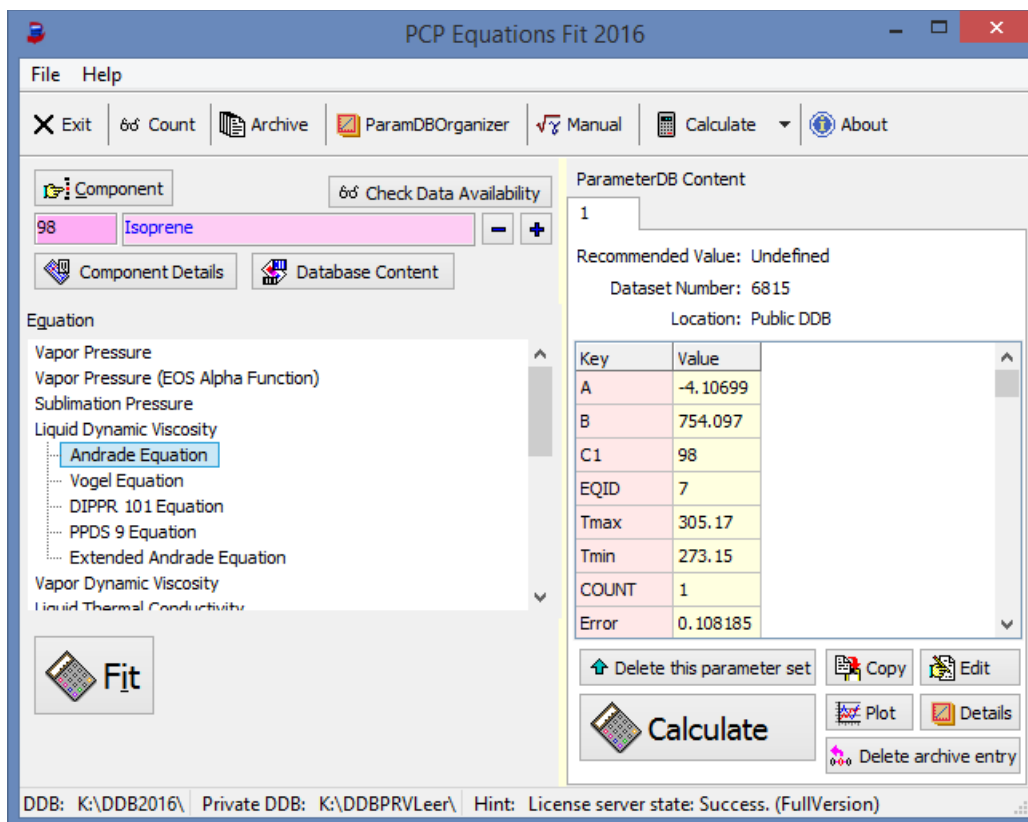
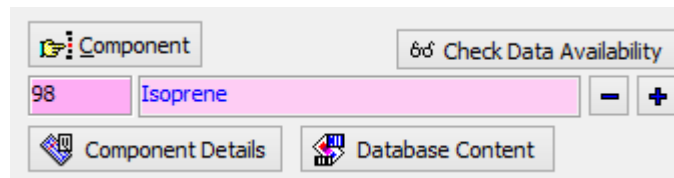


Figure 1 Main PCPEquationFit Dialog

The program's start dialog contains three major parts:

1. The components area allows
 1. selecting components
 2. displaying component details with the component editor
 3. displaying the content of the Dortmund Data Bank for the selected component
 4. verifying if enough data sets or points are available (this is only a hint, since there might be further constraints)
2. The list of equations. The list is organized hierarchically. The methods are summarized below the property they describe.
3. The parameter data set shows the current content of the ParameterDDB.

The toolbar buttons are mainly short cuts for the “File” and “Help” menus.



3.2 File Menu

- Open Component Numbers File**
 This function allows loading a file with a list of DDB component numbers. Such component files can be created, for example, in the component selection dialog or in the main Dortmund Data Bank program from search results. The data set numbers are shown in a separate window.

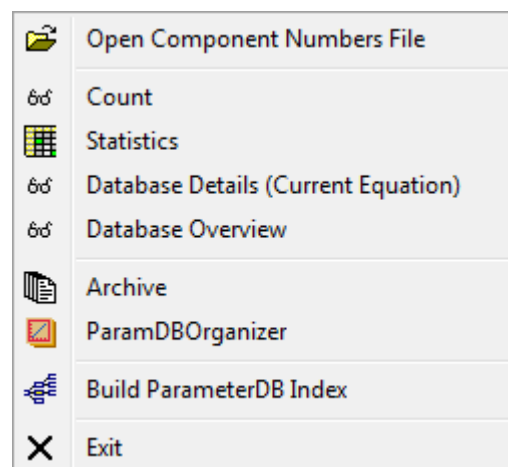
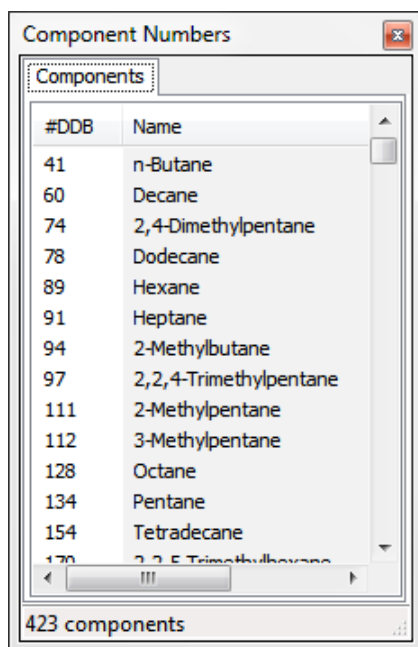


Figure 2: File menu

A click on a line sets the component number in the main fit window.

- Count**
 Count shows the number of available parameter data sets for the current model.

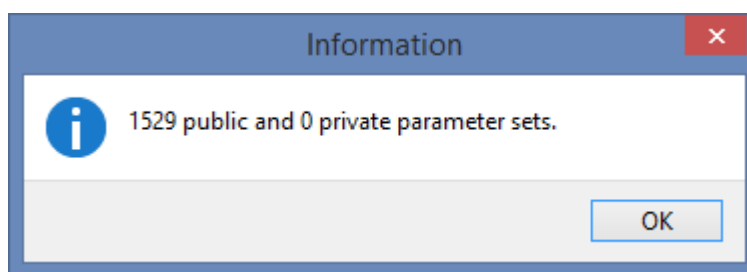


Figure 3: Parameter Data Set Count

- Statistics**
 Statistics creates a table with an overview over all equations.

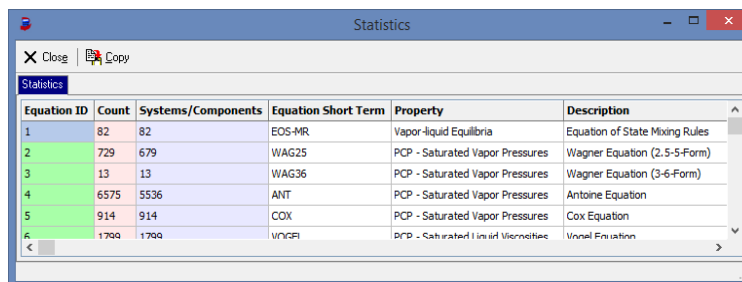


Figure 4: Statistics

- Database Details (Current Equation)**
 This function creates a table with all data sets available for the current equation.

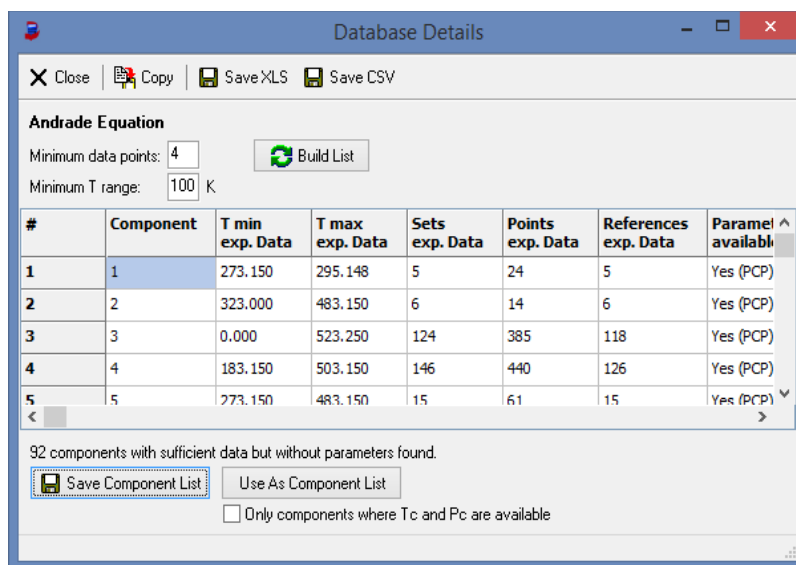


Figure 5: Database Details (Current Equation)

- Database Overview**
 This functions creates a table with the number of components for experimental data in the Pure Component Properties part of the Dortmund Data Bank are available for the single equations.

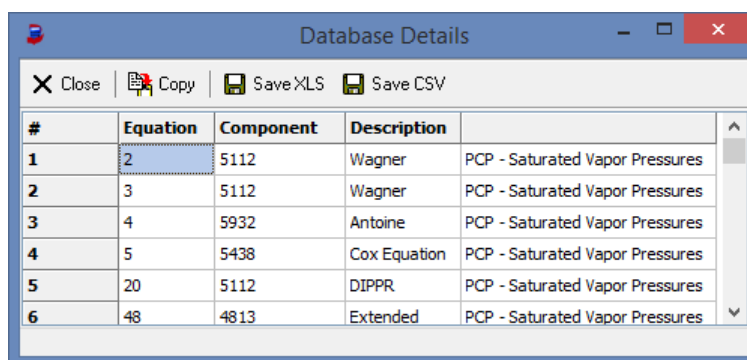


Figure 6: Database Overview

- Archive**
 See chapter “Fit Archive” on page 25.
- ParamDBOrganizer**
 This function call the program for managing the parameter data base. This program is described in a separate PDF (“ParameterDDBOrganizer.pdf”).
- Build ParameterDB Index**
 This will rebuild the component index of the parameter data base. This is normally done automatically when needed. This function is only needed if changes outside PCPEquationFit have been made.

3.3 Help Menu

The help menu contains a button which brings this PDF help up and an “About” button which shows some information about the program.

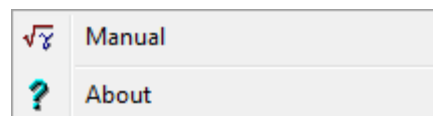
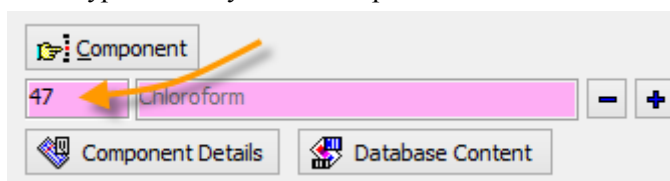



Figure 7: Help menu

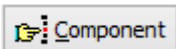
3.4 Component Selection

DDB component numbers can be typed directly in the component field.



After a *Return* the component name is added.

The buttons  allow to navigate through the DDB component list.

The button  calls the component selection dialog

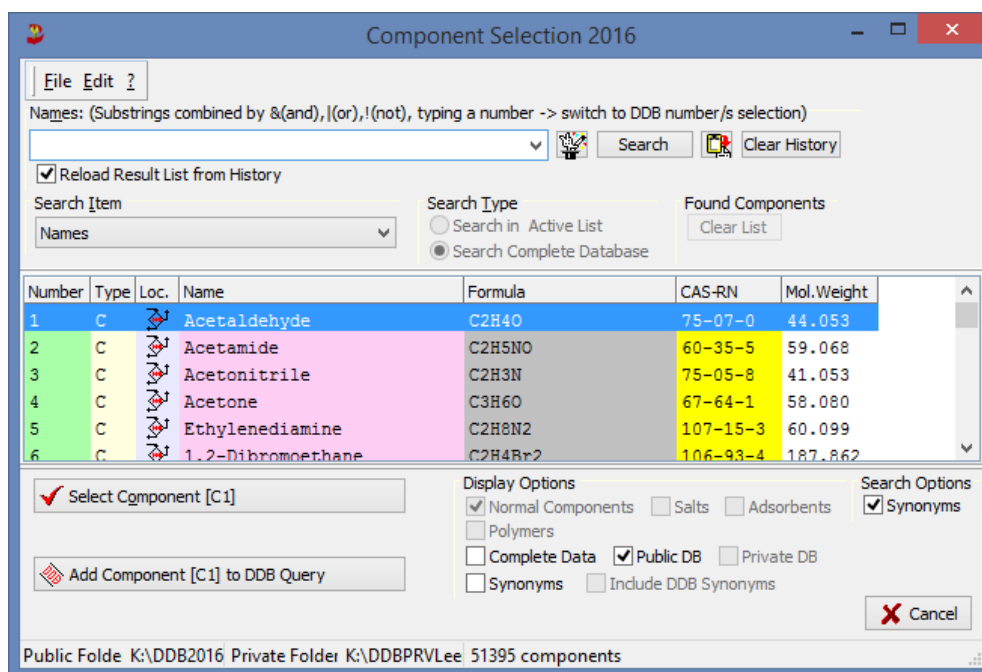
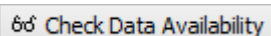


Figure 8 Component Selection

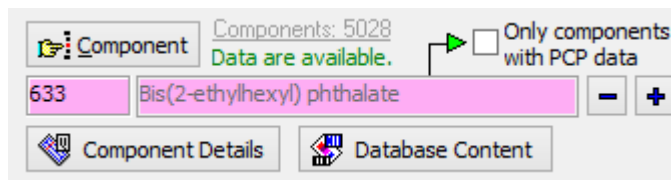
which is described in details in other documents.

3.5 Check Data Availability



This button starts a search in the pure component property data bank for experimental data for the currently selected equation.

When this search is finished the “Check Data Availability” is hidden and information about the availability of data is shown.



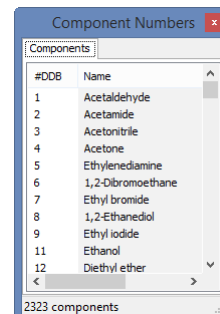
The information lines **Components: 5028** **Data are available.** show for how many components the Dortmund Data Bank contains experimental data sets. The example shows the number of components for the Antoine equation (saturated vapor pressures).

Clicking on the underlined label (“Components 5028”) will open a window with the list of components.

The “Data are available” line indicates that there are enough data points for the specific equation. This number is normally set to <number of parameters + 1>.

If no data are available this text will be displayed: **No data available.**

The check box **Only components with PCP data** should be used in “walk-through” mode where a list of components is in work. If checked this will avoid the display of components without experimental data points.



A detailed description of all component selection features is available in the “Component Management” documentation.

3.6 Fit

After the component and the equation has been selected and the program indicates that enough data points are available (**Data are available.**) the *Fit* button displays a model specific dialog with **almost** the same content for the different models.



The used example for showing a typical fit is the Wagner 2.5-5 equation for saturated vapor pressures.

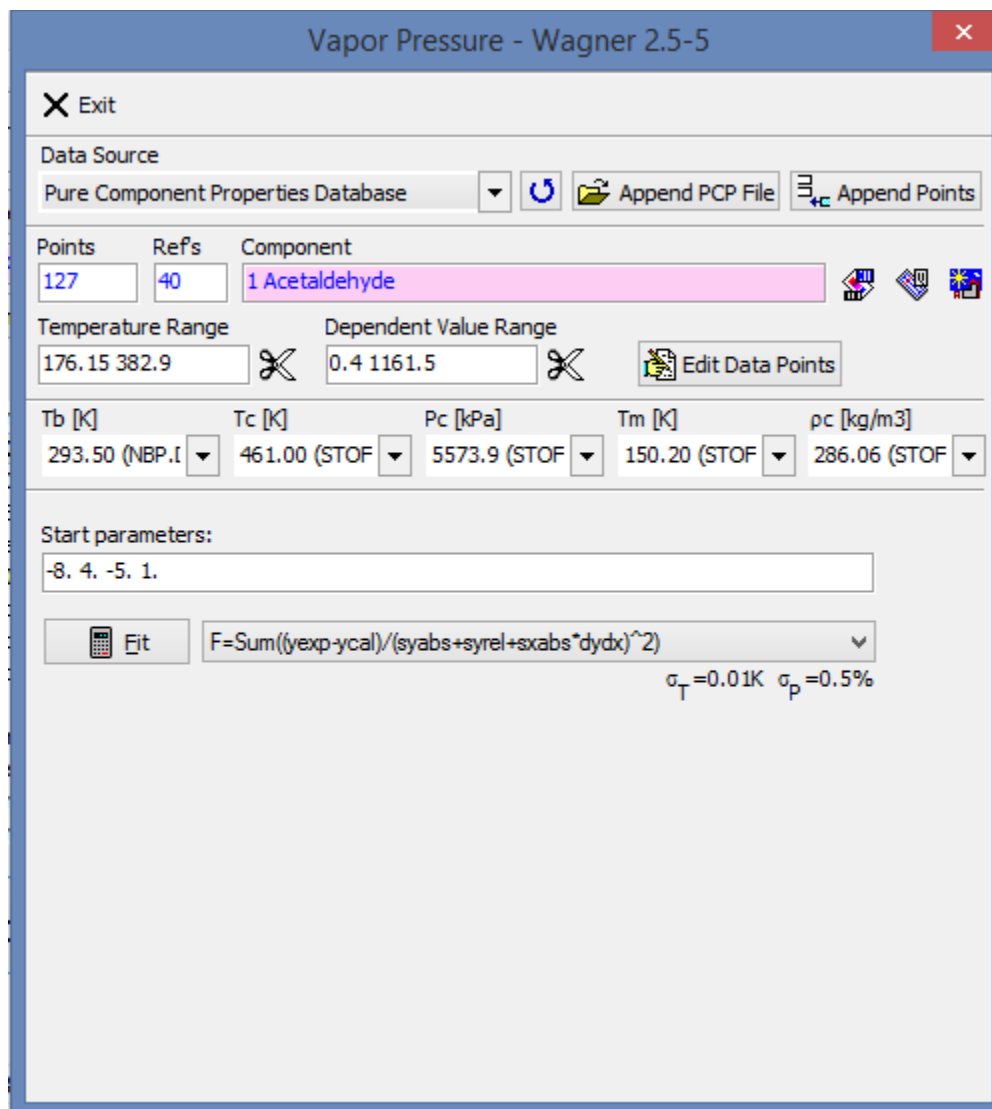
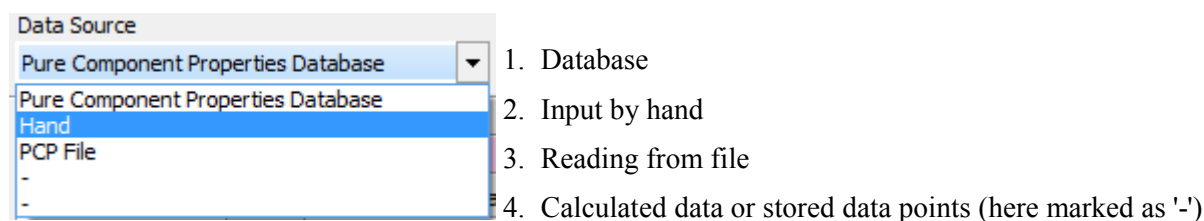



Figure 9 Fit Dialog for Wager 2.5-5 equation

The dialog displays the data source – which is in most cases the pure component properties data bank. All possible sources are



The “Append PCP File” would allow to append data from an external file.

The dialog displays the number of available data points and the number of different references (number of different authors) and repeats the display of the component name. The two buttons besides the name invoke the component editor and the Dortmund Data Bank program.

The temperature and pressure range are also displayed. These limits are editable and can be used to cut points by increasing the lower limit or decreasing the upper limit. The knife button  will actually throw the points outside the given ranges away. The “Edit Data Points” allows to modify the data from the data sources. It uses the “Input by Hand” dialog.

The normal boiling point (T_b), the critical data (T_c , P_c , ρ_c), and the melting point (T_m) are read from pure component basic files (not from the pure component properties data bank).

The lower part of the dialog is model specific but contains in most cases starting parameters and a selection for an objective function where appropriate.

3.6.1 Input by Hand

If this input mode is selected a dialog with a data grid is shown where the user can either type or paste or load data.

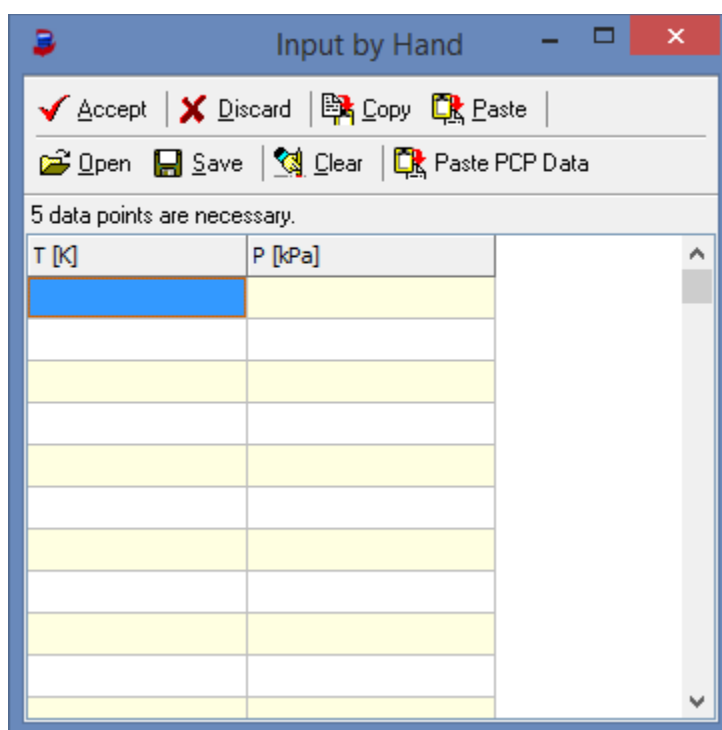


Figure 10 Input by Hand

3.6.2 Fit Results

After pressing the *Fit* button the fit will start and present a “New Parameters” box when it's finished:

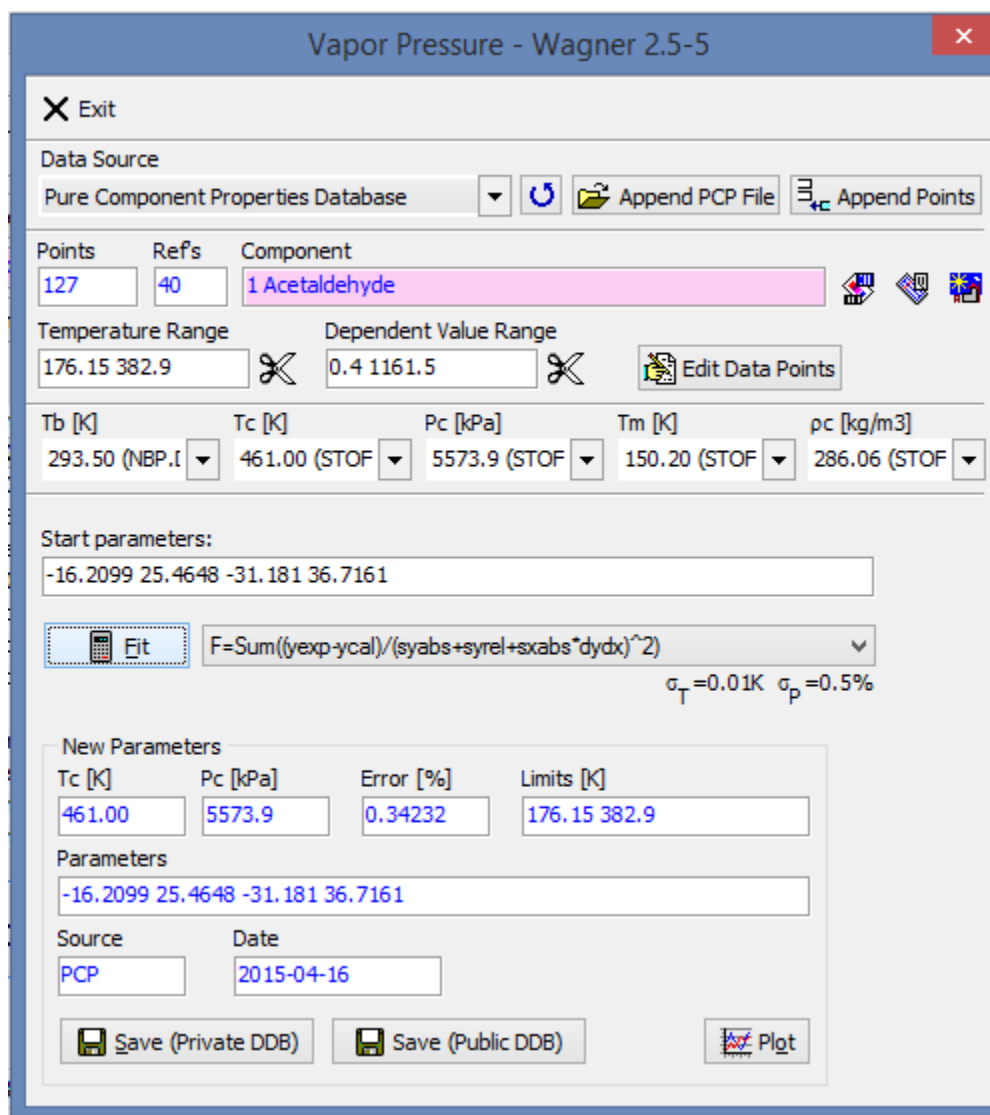


Figure 11 Fit Result

This box shows the new parameters, a mean error, the used temperature limits, the data source and the current date and in some cases additionally used constants like in this example T_c and P_c .

These entries will be stored in the ParameterDDB if one of the “Save” buttons will be pressed.

3.6.3 Plot

For an overview on the fit quality PCPEquationFit provides several plots.

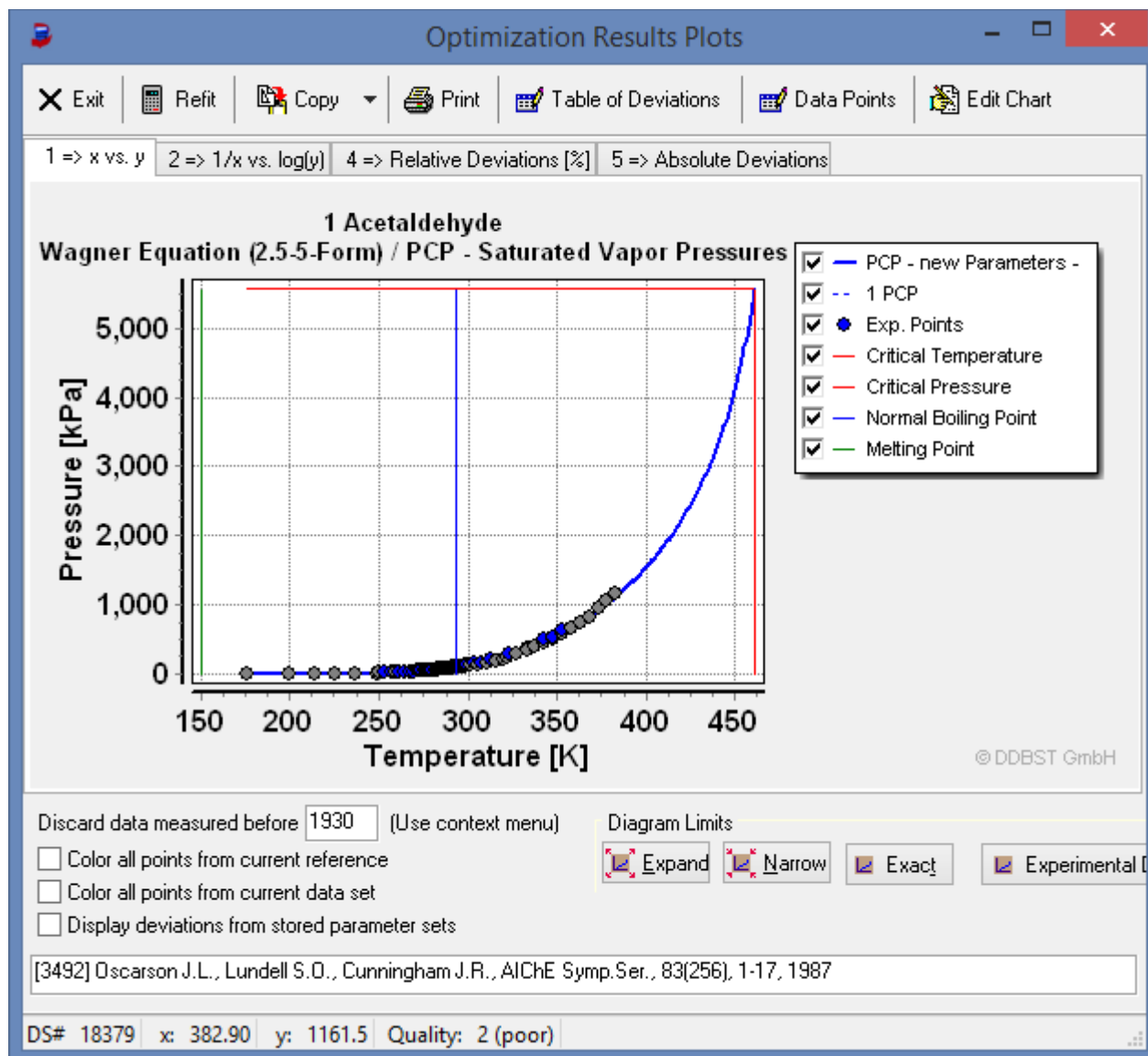
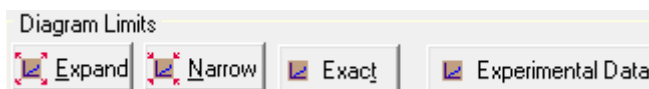


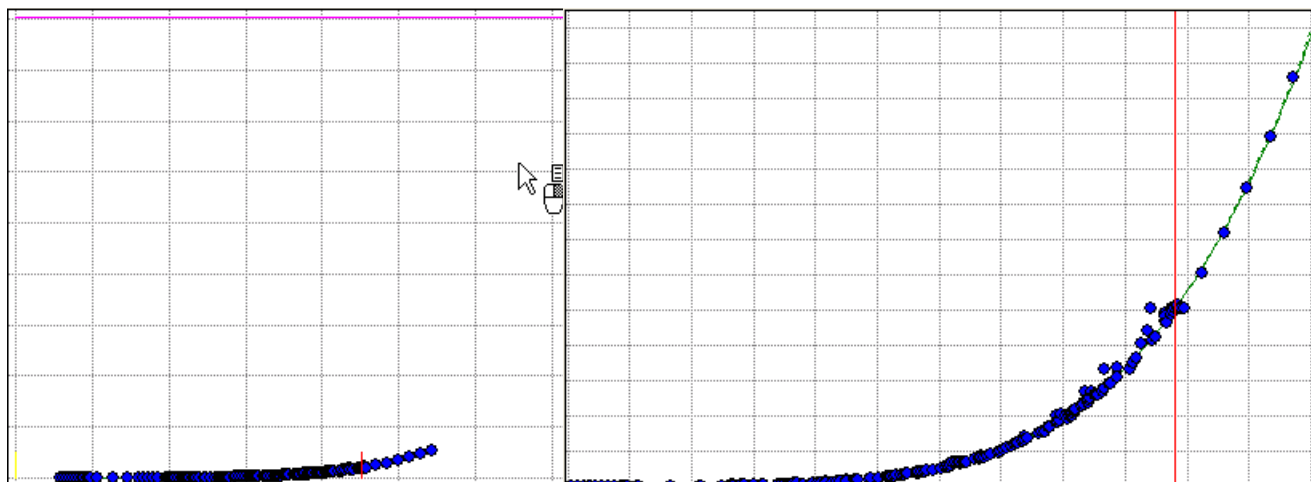
Figure 12 Plot – Fit Result

The list of plots slightly varies from model to model. Always the same is the rubber band drawn from the mouse cursor to the nearest point. Detailed information of this point are displayed in the status line. Additionally the reference is shown below the tool bar.

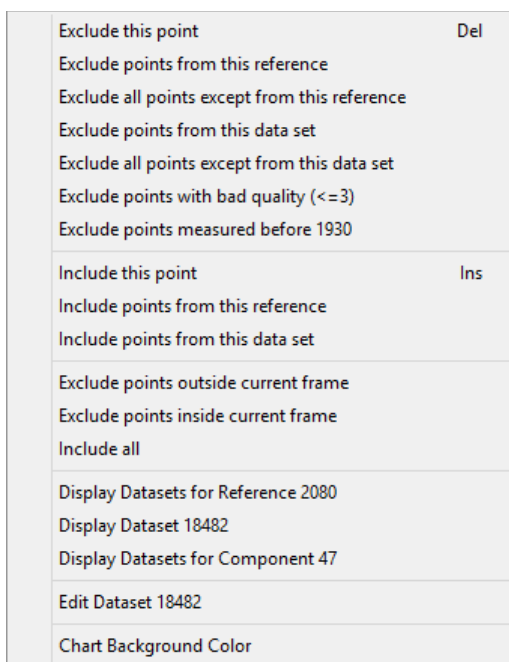
The diagram limit can be widened and narrowed.



The “Experimental Data” button adjusts the diagram so that the experimental data are filling the chart window. This is useful in the cases where critical data and melting points are shown and the experimental data are available only for a smaller range.



Through a context menu on the plot it is possible to



1. Exclude points (either single or by criteria)
2. Include formerly excluded points
3. Display data sets shown in the chart (either single or a list of data sets for the current component or reference)
4. Call the data sets editor
5. Change the background color

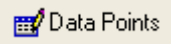
Figure 13 Plot Context Menu

Additionally a complete list of deviations can be created (“Table of Deviations” tool button) and the diagram can be copied to the Windows clipboard or printed.

The screenshot shows a window titled "Grid Output" with a menu bar containing "Close", "Print", "Copy", "Save", and "Mail". Below the menu bar is a table with the following data:

Dataset	Temperature [K]	Pressure [kPa]	Deviation	Relative Deviation [%]	Used
19644	208.95	0.07426058	-0.002558661	-3.45	Yes
19644	214.95	0.1279895	-0.009786889	-7.65	Yes
19644	215.15	0.1275895	-0.0127987	-10.03	Yes
267928	215.15	0.1333224	-0.007065839	-5.30	Yes

Figure 14 Table of Deviations

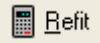
The “Data Points” tool button  opens a dialog where all data points are listed. This dialog can be used to include and exclude data points.

The screenshot shows a window titled "Data Points" with a menu bar containing "Close" and "Update Plot". Below the menu bar is a table with the following data:

Use?	x	y	#Ref	#Set	Quality	Reference
<input checked="" type="checkbox"/>	208.950	0.0742605775595	3291	19644	0	[50702] Drucker C., Jimeno E., Kangro W., Z
<input checked="" type="checkbox"/>	214.950	0.127989500761	3291	19644	0	[50702] Drucker C., Jimeno E., Kangro W., Z
<input checked="" type="checkbox"/>	215.150	0.127589538693	3291	19644	0	[50702] Drucker C., Jimeno E., Kangro W., Z
<input checked="" type="checkbox"/>	215.150	0.133322402835	20568	267928	0	[88253] Confident.Comp.Res.Rep., 1967-19:
<input checked="" type="checkbox"/>	215.450	0.137322068214	3291	19644	0	[50702] Drucker C., Jimeno E., Kangro W., Z
<input type="checkbox"/>	215.850	0.137855365872	3291	19644	0	[50702] Drucker C., Jimeno E., Kangro W., Z
<input checked="" type="checkbox"/>	222.150	0.253312557936	3291	19644	0	[50702] Drucker C., Jimeno E., Kangro W., Z
<input checked="" type="checkbox"/>	227.600	0.458629012108	12368	80399	0	[16033] Lorimer J.W., Smith B.C., Smith G.H.

Figure 15: Data Points Selection

This function has been added because of points occupying exactly the same position (exactly same data) which makes it impossible to select all these points by mouse.

If points have been excluded it is necessary to start a new fit by the “Refit” button . This will return us to the fit dialog allowing to store the modified parameters.

4 Understanding the ParameterDDB Data Set Display

Key	Value
A	-8,41515
B	4,65592
C	-6,26863
D	1,7655
C1	12
Pc	3637,57
Tc	466,7
EQID	2
Tmax	466,74
Tmin	250,046
User	Cordes
COUNT	1
DateD	16
DateM	6
DateY	1994
Error	0,092
SETNUM	12
Source	PCP
LOCATION	0
AUTOSELECT	true
SourceFile	PARAM.WAG

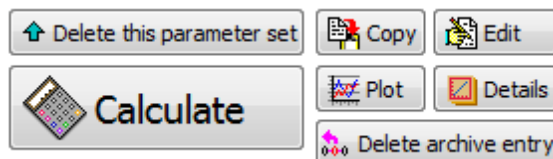
Figure 16 Parameter Data Set

The ParameterDDB contains key/value pairs. The keys describe the values. The grid shows the list of keys and the values belonging to them.

1. The keys “A”, “B”, “C”, “D” and so on are the parameters of the equations.
2. “C1” is the DDB component number. Its name can be found in the component editor.
3. “Pc”, “Tc” are critical temperature and pressure. Other possible entries are e.g. “Tb”.
4. “EQID” is the internal equation number.
5. “Tmax” and “Tmin” are the upper and lower temperature limits of the experimental data used. Please regard these values also as validity range for the equation.
6. “User” specifies the person who stored the parameter dataset.
7. “DateD”, “DateM”, “DateY” specify the date when the dataset has been stored.
8. “Error” gives the model and fit specific error.
9. “Source” specifies the source of the data points which have been used for the fit.
10. “Location” specifies if the parameter set is stored in the public DDB (0) or in the private DDB (1) or, if missing or another number, some other location.
11. “AUTOSELECT” is necessary if more than one dataset is available for a component and a single equation. It specifies the preferred parameter set.

12. “SourceFile” is given in some cases and specifies a file from which the set has been imported.

5 Working with a Parameter Data Set



5.1 Copy

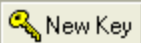
The data set grid will be copied to the windows clipboard as it is displayed in Figure 16 (source) and Figure 17 (destination).

	A	B
1	Key	Value
2	A	-8.42
3	B	4.66
4	C	-6.27
5	D	1.77
6	C1	12

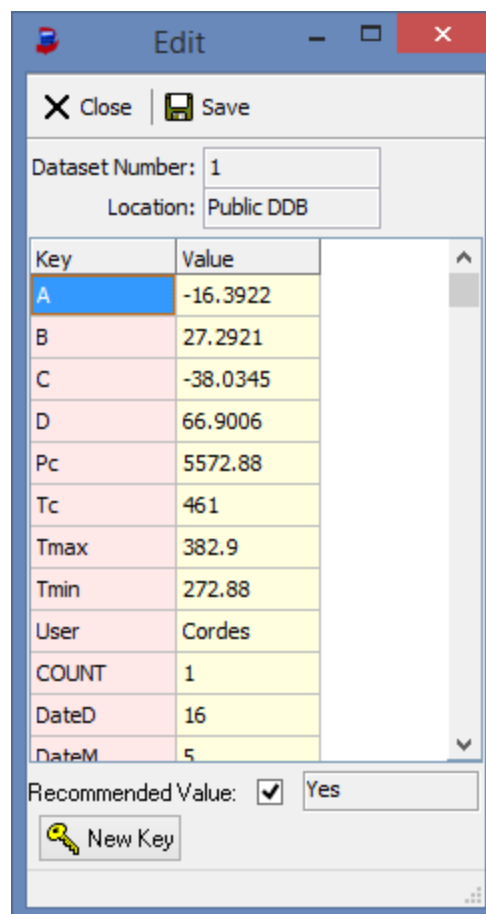
Figure 17 Data set pasted in spreadsheet program

5.2 Edit

The editor is another view on the parameter data set grid. The grid is now editable and new values can be typed in the Value column.

The Key column is not directly editable but new keys () can be added and keys with empty values will be removed automatically when the data set is saved.

The “Recommended Value” check mark should be set if more than one data set is available for the same component and equation and the current data set should be preferred over all others.



5.3 Plot

This plot shows the stored equation parameters together with points from the pure component properties data bank. It's the same plot as used in the fit procedure with the exception that some editing functions are not available – like removal of data points.

5.4 Details

This function displays a more detailed and explanatory view on the current parameter set. It is part of the ParamDDBOrganizer program.

This program is described in detail in the separate document “ParameterDDBOrganizer.pdf”.

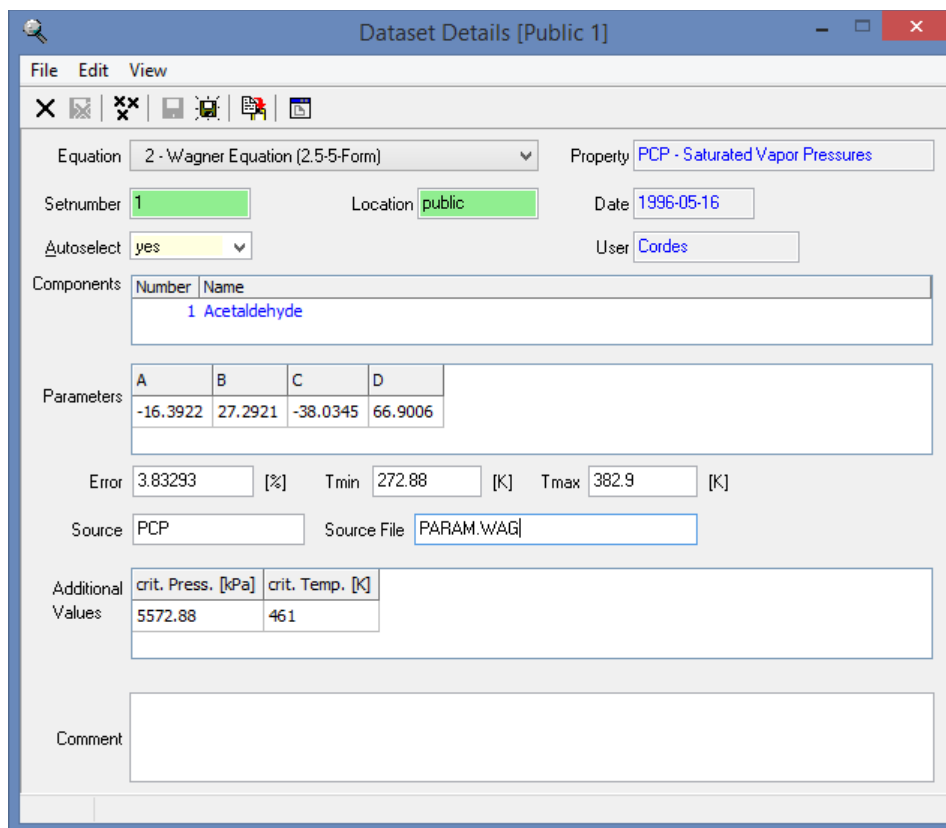


Figure 18 Data set details

5.5 Calculate

Stored parameter sets can be used to calculate the property at arbitrary temperatures.

It is either possible to calculate values in a temperature range where start and end temperature as well as a step width can be specified

Start Temperature	End Temperature	Stepwidth	<input type="button" value="Calculate"/>
275.65 K	320.65 K	1.00 K	

or single values typed in the data grid.

Temperature	Cal
280	
285	
290	

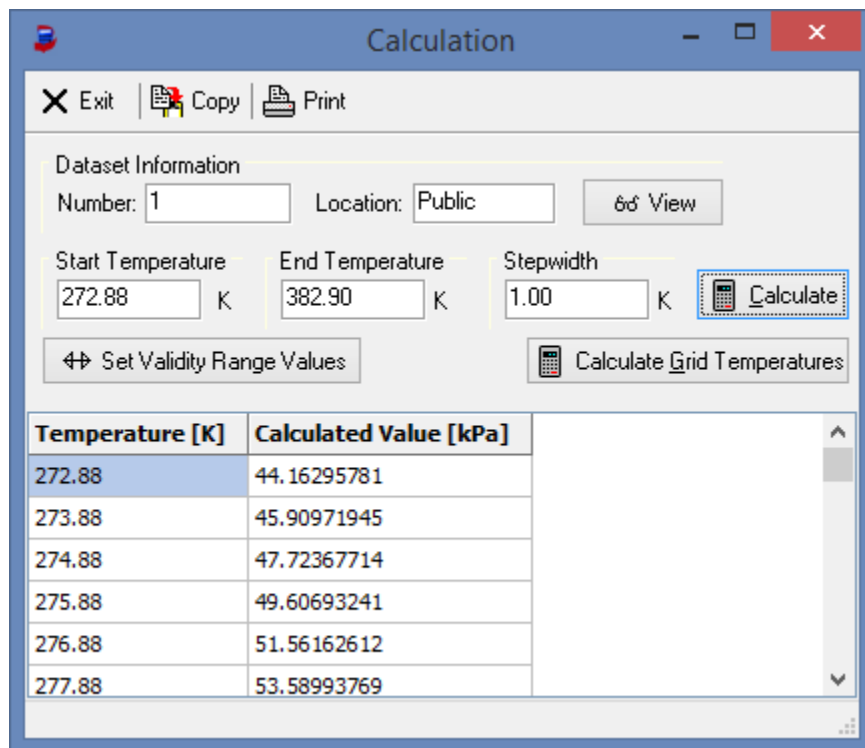
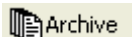


Figure 19: Calculate properties with stored parameters

6 Fit Archive

PCPEquationFit stores a history of fitted parameters and used datasets. This archive is accessible through the tool bar button  Archive .

The archive is intended to be the memory of all fits. It should allow to save the data which have been used for the fit and to restore them and perform a full re-fit under the same conditions as done originally. This goal is currently not perfectly achieved.

The archive dialog itself (Figure 20) shows a list of of parameter sets identified by component number and model description separated for the public and private data banks.

The details grid shows the x and y, the reference number and the dataset number and in the “Used” column a “+” if the value has been used in the fit or a “-” if the point has been excluded.

The “Refit” button creates a fit dialog for the given equation and component with the stored data points (Figure 21).

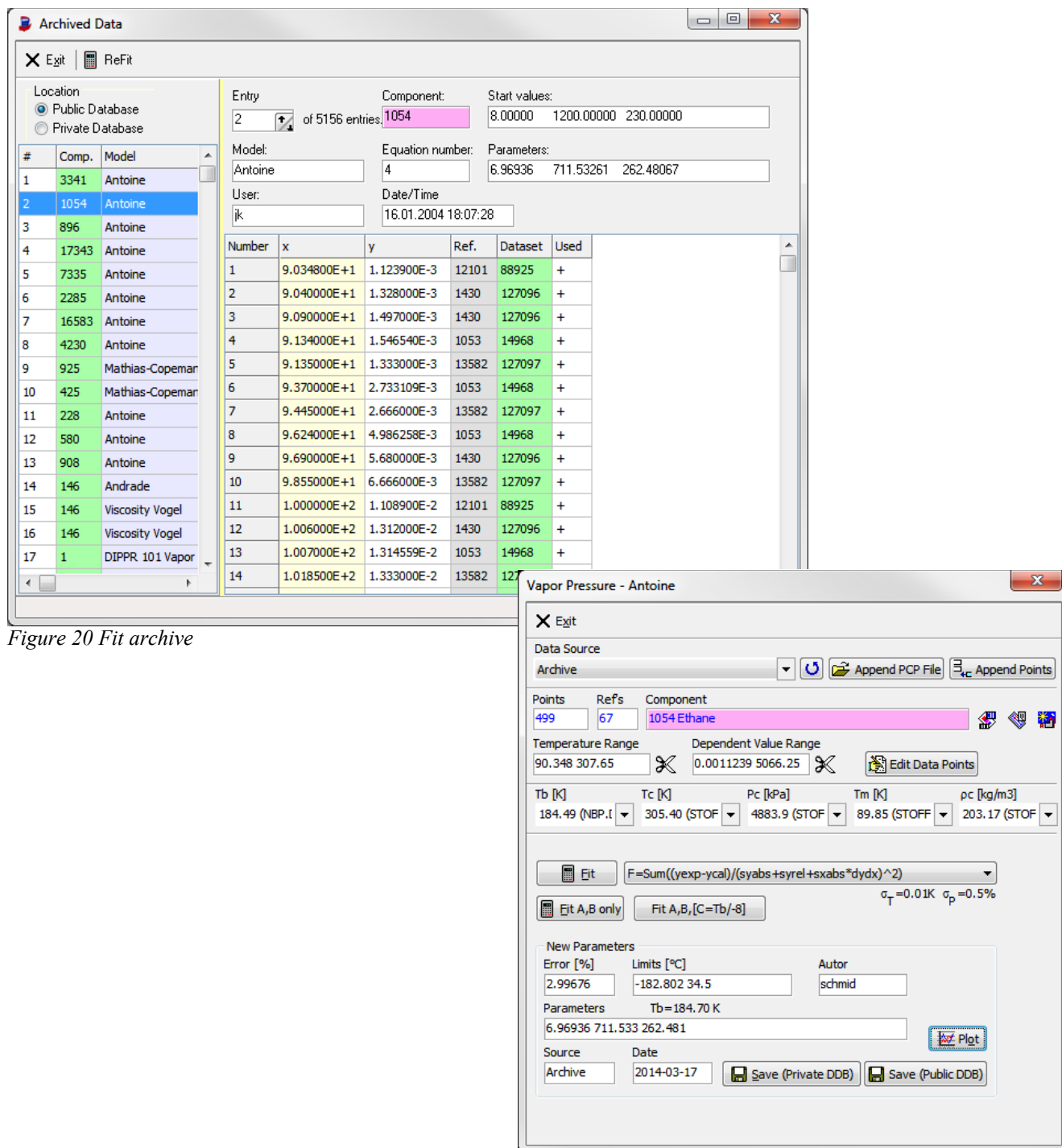


Figure 20 Fit archive

Figure 21 Refit with archived data

7 T_c/P_c Evaluation

PCPEquationFit allows with this function the evaluation of experimental pure component critical data and saturated vapor pressures together with calculated and estimated values.

For a full investigation it is necessary to have at least a parameter set for a vapor pressure equation and the Artist program package should also be present since it is used for displaying estimated critical data.

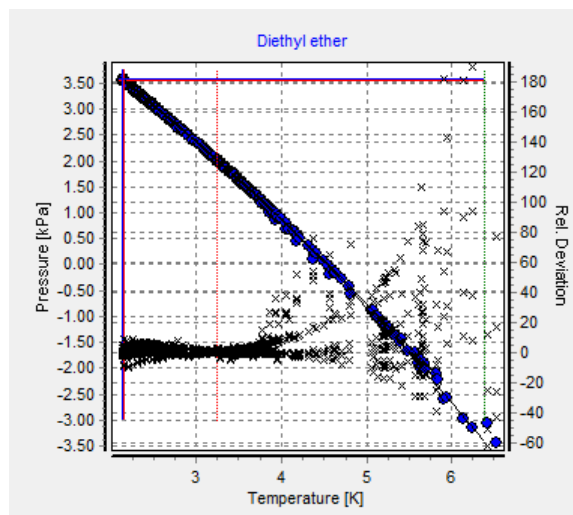
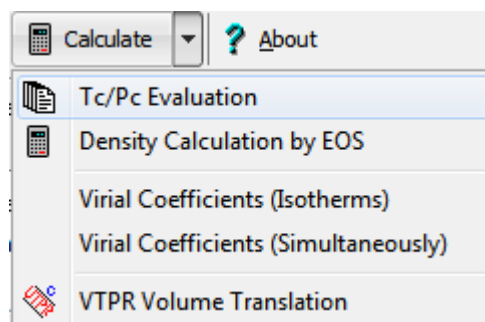


Figure 22 Critical Data Evaluation - Plot

The “Options” page allows selecting vapor pressure equations from PCPEquationFit and T_c and P_c estimation methods from Artist.

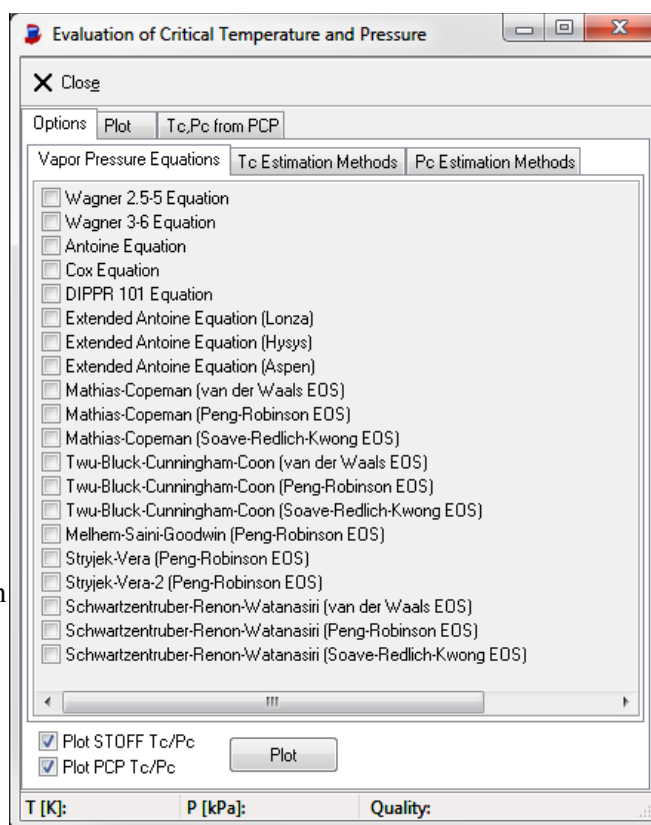


Figure 23 Critical Data Evaluation - Vapor Pressure Equations

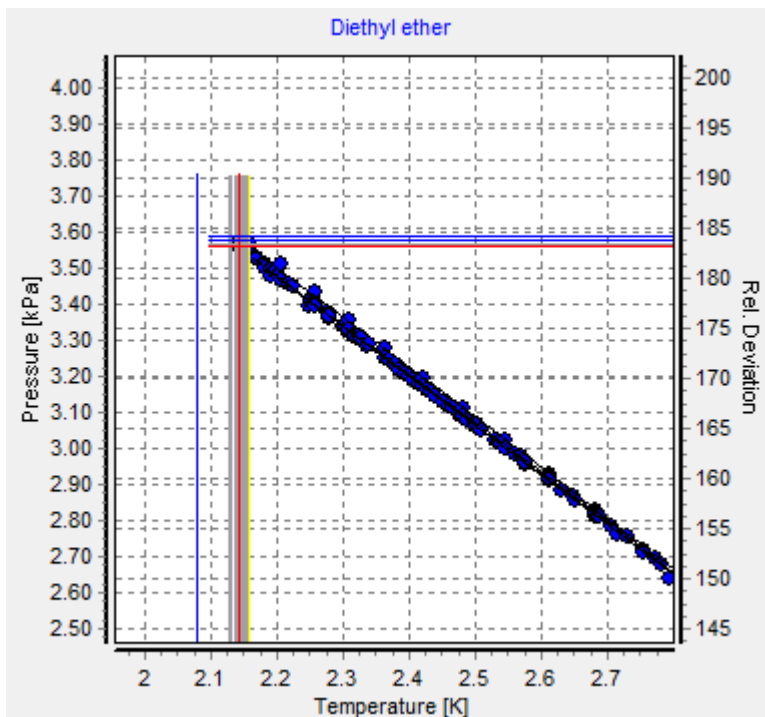


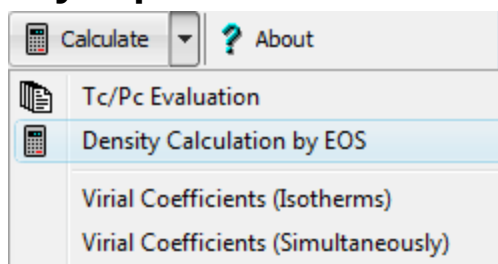
Figure 24: Zoomed in for Critical Point

The resulting diagram shows all experimental, calculated, and estimated data points in a Temperature vs. Pressure plot. Deviations are shown in the same diagram with its scale on the diagram's right side.

The diagram allows switching between “T vs. P” and “1000/T vs. $\log_{10} P$ ” and the display of the deviations can be switched on and off.

The important point is the end point of the vapor pressure curve. The experimental and estimated critical T_c and P_c are shown as horizontal and vertical line. The intersections give a hint where the correct critical point lies.

8 Density Prediction by Equation of State



This dialog

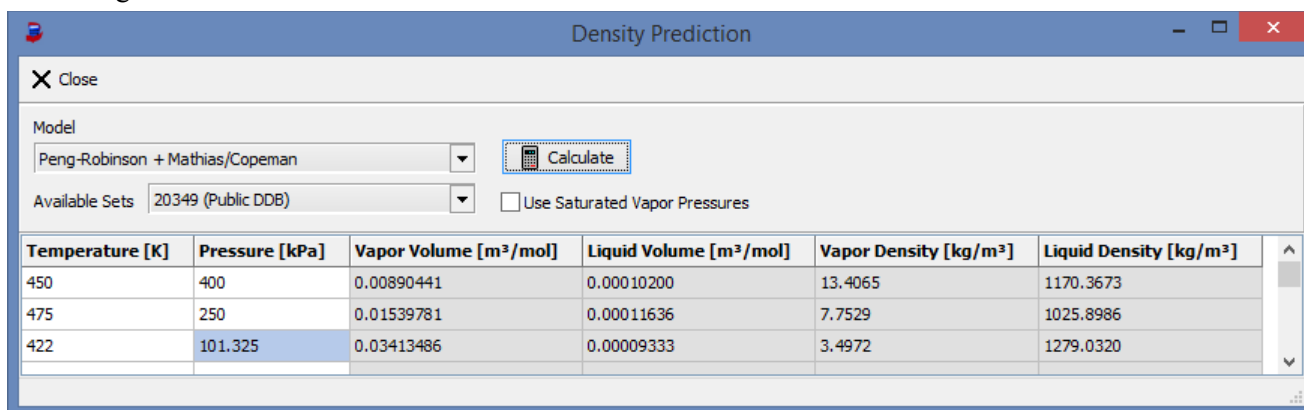


Figure 25: Density Prediction

can be used to calculate liquid and vapor densities and volumes of pure components by equation of states. The supported equations of state are the same which can be used to regress α function parameters in the main dialog and the regressed α function parameters are used also for this density calculation.

Input for the calculation by the equation of state are temperatures and pressures. The pressure can either be given directly or the saturated vapor pressure can be used. The saturated vapor pressure would be determined by the equation of state.

Temperature [K]	Pressure [kPa]
450	1541.280771
475	2318.513690
422	922.802849

Figure 26: Using saturated vapor pressures

9 Virial Coefficients

Original Author: Romana Laznickova

9.1 Isotherms

9.1.1 Rationale

The sub program ISOTHERM calculates second and third virial coefficients from qualified isothermal gas-phase PVT-data. The program also allows to compare the datasets and judge their quality.

9.1.2 Application Flow

The program allows either to load a pure component properties file containing PVT data or searches the datasets itself after a component has been selected.

The data from this list are sorted by temperature and data points measured at the same temperatures are collected and combined in isotherms.

These isotherms are searched for applicable data. For the calculation of virial coefficients only data up to $\frac{3}{4}$ of the critical density are used. Near the critical isotherm, at reduced temperatures between $T_r=0.95$ and $T_r=1.2$, only data with densities up to $\frac{1}{2}$ of the critical density are used. If an isotherm has at least two data points in the specified range it will be used to regress the second and third virial coefficients.

The virial coefficients are regressed by an optimizing algorithm which minimizes the sum of the squared errors of the compressibility factor. The quality of the optimization can be judged by the absolute and relative deviation in the compressibility factor and the density of the regressed virial equation from the experimental values. The regression quality is also characterized by the numbers square root from the mean squared error of the compressibility factor and the density. Additionally the program determines a maximum pressure (PmaxB), which gives a real density value for a virial equation made up only with the second coefficient B.

The results are listed on screen giving an overview over all temperatures. Regression results are given for all temperatures where experimental data points have been available. The experimental datasets are listed together with the regressed second and third virial coefficients, the maximum pressure (PmaxB), the absolute and relative density deviation and both characterization numbers.

9.1.3 Description of the Graphics Output

The main chart is the display of $\frac{\text{Compressibility Factor} - 1}{\text{Density}}$ against the density. The virial equation build with B and C is a straight line in this case. The axis intercept on the y-axis is the second virial coefficient B and slope of the straight line is the third virial coefficient C. This projection allows evaluating the quality of the optimization in a very clear way. For isotherms where B and C have been obtained a calculated line is included.

There are four other charts which display differences between the experimental values and the correlation:

1. Absolute deviation in the density,
 2. Relative deviation in the density,
 3. Absolute deviation in the compressibility factor,
 4. Relative deviation in the compressibility factor
- against the density.

The chart also includes the critical density.

9.1.4 Mathematical and Physical Relations

9.1.4.1 Display of Compressibility Factor-1 against Density

This presentation is based on the relation for second virial coefficient

$$B = \lim_{d \rightarrow 0} \left(\frac{z-1}{d} \right)$$

and the third virial coefficient

$$C = \lim_{d \rightarrow 0} \left(\frac{\partial \left(\frac{z-1}{d} \right)}{\partial d} \right)$$

The equation evolved up to the third virial coefficient

$$z = 1 + B \cdot d + C \cdot d^2$$

is a straight line in the presentation of $\frac{\text{Compressibility Factor} - 1}{\text{Density}}$ against *density*.

$$\frac{z-1}{\rho} = B + C \cdot \rho$$

Because virial coefficients are normally shown in molar units (B [cm³*mol⁻¹], C[cm⁶*mol⁻²]) and densities in [kg*m³] the ordinate shows $\frac{\text{Compressibility Factor} - 1}{\text{Density}}$ in [cm³*mol⁻¹] and the abscissa shows densities in [kg*m⁻³]. If the third virial coefficient shall be determined graphically from this presentation it is necessary to convert both units.

9.1.4.2 Optimization

The optimization routine searches for a combination of the second and third virial coefficients where the sum of squares of errors of the compressibility factor is minimal.

$$F = \sum_i (z_i - z_{calc,i})^2 \stackrel{!}{=} \text{Min}$$

i runs over all experimental data points for a specified isotherm. The compressibility factor z_i is calculated from the measured temperature T, pressure P_i, and density ρ_i.

$$z_i = \frac{P_i \cdot M}{\rho_i \cdot R \cdot T}$$

The virial equation calculates the compressibility factor z_{calc,i} for the experimental density ρ_i

$$z_{calc,i} = 1 + B' \cdot \rho_i + C' \cdot \rho_i^2$$

with

$$B' = \frac{B}{M} \quad \text{and} \quad C' = \frac{C}{M^2} \quad \text{Equation 8}$$

The minimum of the objective function $F=F(B',C')$ is determined mathematically exact. The necessary condition for a minimum is the existence of a combination of the second and third virial coefficients that the partial derivations of the objective function by B' and C' are zero.

$$\frac{\partial F}{\partial B'}=0 \quad \text{and} \quad \frac{\partial F}{\partial C'}=0$$

These conditions lead to linear equation system.

$$\sum_i \frac{P_i \cdot M}{R \cdot T} - \rho_i - B' \cdot \sum_i \rho_i^2 - C' \cdot \sum_i \rho_i^3 = 0$$

$$\sum_i \frac{P_i \cdot M \cdot \rho}{R \cdot T} - \rho_i^2 - B' \cdot \sum_i \rho_i^3 - C' \cdot \sum_i \rho_i^4 = 0$$

This equation system is solved by the Gauß-Jordan method. The results are the second and third virial coefficients B' and C' in mass units. These values are converted by equations (8) into molar units. The program displays the second virial coefficient in [cm³*mol⁻¹] and the third in [cm⁶*mol⁻²].

9.1.4.3 Evaluation of the Optimization Quality

The goodness of the optimization can be evaluated by the difference between the experimental values and the calculated values.

- absolute deviation in the density

$$\rho_i - \rho_{calc,i}$$

- relative deviation in the density

$$\frac{\rho_i - \rho_{calc,i}}{\rho_i} \cdot 100.$$

- absolute deviation in the compressibility factor

$$z_i - z_{calc,i}$$

- relative deviation in the compressibility factor

$$\frac{z_i - z_{calc,i}}{z_i} \cdot 100.$$

These deviations are determined for all experimental values.

Additional quality numbers are square root from the mean squared error of the compressibility factor

$$\sqrt{\sum_i \frac{(z_i - z_{calc,i})^2}{n}}$$

and the square root from the mean squared error of the density

$$\sqrt{\sum_i \frac{(\rho_i - \rho_{calc,i})^2}{n}}$$

These number are obtained only from the experimental values used in the optimization. n is the number of these values.

9.1.4.4 Pressure P_{maxB}

A virial equation with only B is quadratic against the density. If the second virial coefficient is negative, it depends on the pressure if the quadratic equation yields real solutions for the density. The pressure P_{maxB} is the maximum pressure where the equation with only B yields a real solution.

$$P_{maxB} = -\frac{R \cdot B}{4 \cdot B}$$

9.1.5 Practical Tips

This program only calculates virial coefficients from measured values in a reasonable range, despite this statement it is still necessary to carefully evaluate the results.

- Experimental values might be distributed only in a narrow range which might lead to an arbitrary result depending on scattering.
- If the densities are very small the experimental error will increase.

9.1.6 Gas Constant, Molar Mass, Critical Density

This program uses the gas constant $R = 8.3144 \frac{J}{K \cdot mol}$. The molar mass and the critical density are taken from the DDB file STOFF.

9.2 All Data Simultaneously

9.2.1 Rationale

The simultaneous correlation can be used for the evaluation of PVT datasets, especially for non-isothermal data (see previous chapter 30 “Isotherms“ for isothermal data). Additionally the program allows to select datasets and interpolation between different data. The implemented virial equation regresses the second and third virial coefficient and uses a two-parameter temperature relation. Therefore the correlation needs at least four points in a system.

9.2.2 Problem Description

The correlation is a three-dimensional problem. T_i , P_i , ρ_i are lying on a surface. This surface has to be described by the virial equation with second and third coefficient and a two-parameter temperature function. Because it is hard to obtain meaningful three-dimensional graphical displays the program uses a projection of the $P\rho T$ space to the $P\rho$ (pressure against density) plain. The virial equation is drawn as a series of isothermal $P=f(\rho)$ curves.

9.2.3 Regression

The objective function is

$$F = \sum_i \left(z_i - z_{calc,i} \right)^2 \rightarrow Min \quad \text{with} \quad z = \frac{P_i \cdot M}{\rho \cdot R \cdot T_i}$$

The virial equation is

$$z_{calc,i} = 1 + B_i \cdot \left(\frac{\rho_i}{M} \right) + C_i \cdot \left(\frac{\rho_i}{M} \right)^2 \quad \text{with } M \text{ [kg/mol], } B \text{ [m}^3\text{/mol], } C \text{ [m}^6\text{*mol}^{-2}\text{]}$$

The two-parameter temperature dependence for the second virial coefficient B is

$$B_i = \frac{b_1}{T_i^{0.5}} + \frac{b_2}{T_i}$$

Two-parameter temperature dependence for the third virial coefficient C is

$$C_i = \frac{c_1}{T_i^{1.2}} + \frac{c_2}{T_i^{10}}$$

The exact mathematical solution ($\frac{\partial F}{\partial b_1} = 0, \frac{\partial F}{\partial b_2} = 0, \frac{\partial F}{\partial c_1} = 0, \frac{\partial F}{\partial c_2} = 0$) leads to the linear equation system:

$$A_{11} \cdot x_1 + A_{12} \cdot x_2 + A_{13} \cdot x_3 + A_{14} \cdot x_4 = D_1$$

$$A_{21} \cdot x_1 + A_{22} \cdot x_2 + A_{23} \cdot x_3 + A_{24} \cdot x_4 = D_1$$

$$A_{31} \cdot x_1 + A_{32} \cdot x_2 + A_{33} \cdot x_3 + A_{34} \cdot x_4 = D_1$$

$$A_{41} \cdot x_1 + A_{42} \cdot x_2 + A_{43} \cdot x_3 + A_{44} \cdot x_4 = D_1$$

with

$$b_1 = x_1, b_2 = x_2, c_1 = x_3, c_2 = x_4$$

$$A_{11} = \frac{1}{M^2} \cdot \sum_i \frac{\rho_i^2}{T_i} \quad A_{12} = \frac{1}{M^2} \cdot \sum_i \frac{\rho_i^2}{T_i^{1.5}} \quad A_{13} = \frac{1}{M^3} \cdot \sum_i \frac{\rho_i^3}{T_i^{1.7}} \quad A_{14} = \frac{1}{M^3} \cdot \sum_i \frac{\rho_i^3}{T_i^{10.5}}$$

$$A_{21} = \frac{1}{M^2} \cdot \sum_i \frac{\rho_i^2}{T_i^{1.5}} \quad A_{22} = \frac{1}{M^2} \cdot \sum_i \frac{\rho_i^2}{T_i^2} \quad A_{23} = \frac{1}{M^3} \cdot \sum_i \frac{\rho_i^3}{T_i^{2.2}} \quad A_{24} = \frac{1}{M^3} \cdot \sum_i \frac{\rho_i^3}{T_i^{11}} \quad 7$$

$$A_{31} = \frac{1}{M^3} \cdot \sum_i \frac{\rho_i^3}{T_i^{1.7}} \quad A_{32} = \frac{1}{M^3} \cdot \sum_i \frac{\rho_i^3}{T_i^{12.2}} \quad A_{33} = \frac{1}{M^4} \cdot \sum_i \frac{\rho_i^4}{T_i^{2.4}} \quad A_{34} = \frac{1}{M^4} \cdot \sum_i \frac{\rho_i^4}{T_i^{11.2}}$$

$$A_{41} = \frac{1}{M^3} \cdot \sum_i \frac{\rho_i^3}{T_i^{10.5}} \quad A_{42} = \frac{1}{M^3} \cdot \sum_i \frac{\rho_i^3}{T_i^{11}} \quad A_{43} = \frac{1}{M^4} \cdot \sum_i \frac{\rho_i^4}{T_i^{11.2}} \quad A_{44} = \frac{1}{M^4} \cdot \sum_i \frac{\rho_i^4}{T_i^{20}}$$

$$D_1 = \sum_i \left(\frac{P_i}{R \cdot T_i^{1.5}} - \frac{\rho_i}{T_i^{0.5} \cdot M} \right)$$

$$D_2 = \sum_i \left(\frac{P_i}{R \cdot T_i^2} - \frac{\rho_i}{T_i^{0.5} \cdot M} \right)$$

$$D_3 = \sum_i \left(\frac{P_i}{M \cdot R \cdot T_i^{2.2}} - \frac{\rho_i^2}{T_i^{1.2} \cdot M} \right)$$

$$D_4 = \sum_i \left(\frac{P_i}{M \cdot R \cdot T_i^{11}} - \frac{\rho_i^2}{T_i^{10} \cdot M} \right)$$

This equation system is solved by the Gauß-Jordan method. The results are

$$b_1 [m^3 \cdot mol^{-1} \cdot K^{0.5}]$$

$$b_2 [m^3 \cdot mol^{-1} \cdot K]$$

$$c_1 [m^6 \cdot mol^{-2} \cdot K^{1.2}]$$

$$c_2 [m^6 \cdot mol^{-2} \cdot K^{10}]$$

On screen the values are multiplied by 10^6 for b_1 and b_2 , and 10^{12} for c_1 and c_2 ($m \Rightarrow cm$).

9.2.4 Short Tutorial

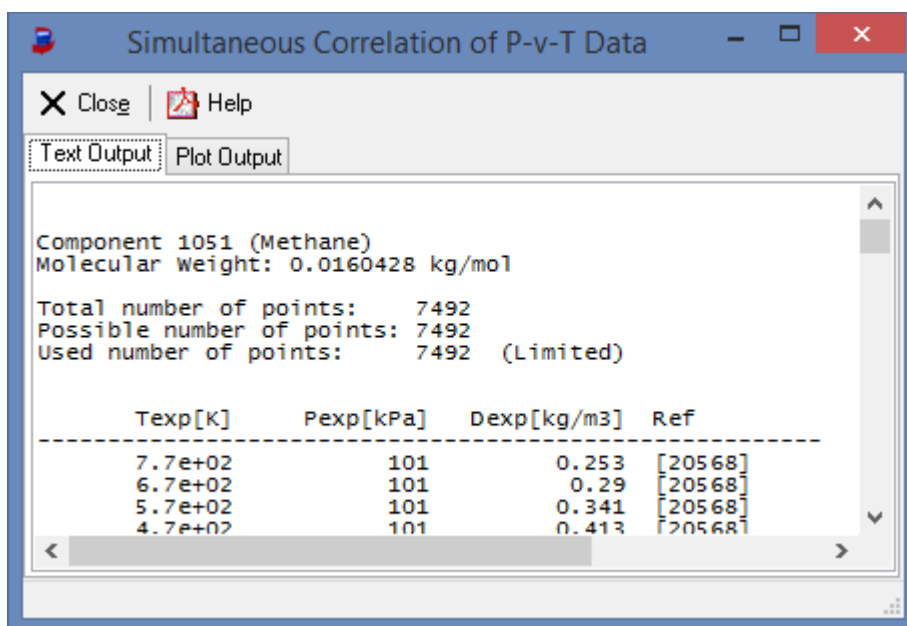


Figure 27: Start Screen

Start Screen Figure 27 shows the start screen of SIMULTAN. The PVT data are either obtained from the DDB pure component properties database if a component is selected or loaded from a PCP interface file which has been created by another program.

After selecting a component or loading a file the program display the ranges in density, pressure, and temperature and allows here to set new limits.

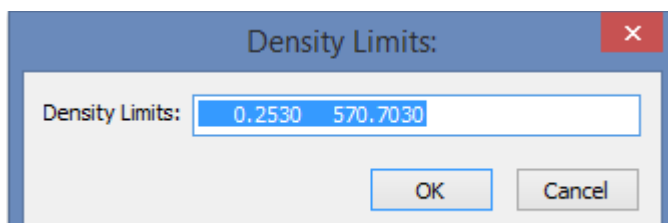


Figure 28: Density Limits

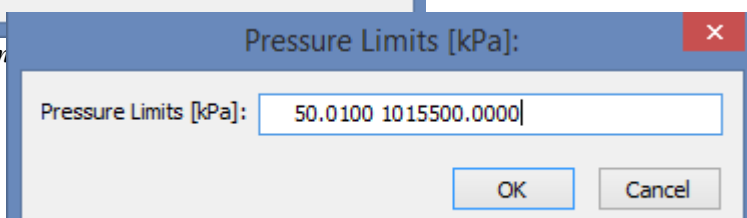


Figure 29: Pressure Limits

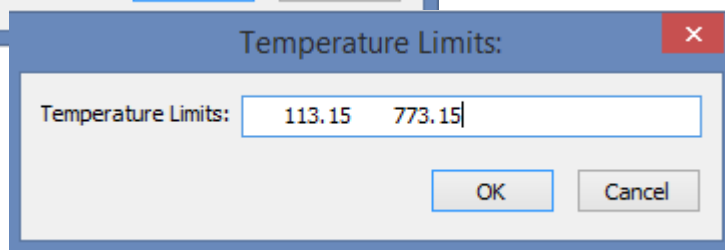


Figure 30: Temperature Limits

After these dialogs the program immediately regresses the virial coefficients and display a result. The result list gives

1. name of component with its molecular weight,
2. number of points given and used,
3. the experimental values either from file or database,
4. used temperature, pressure, and density limits,
5. the regressed b_1 , b_2 , c_2 , c_3 values,
6. examples if the B and C at 353 K,
7. a table with experimental and calculated data,
8. error numbers for specifying the quality of the regression.

The plot output displays six charts.

1. normal plot (no isotherms)
2. B against T
3. C against T
4. relative compressibility factor deviation
5. compressibility factor deviation
6. relative density deviation

7. density deviation
8. normal plot: P against molar density

The plot output has a context menu (see Figure 31) which allows to display the experimental data in the database retrieval program or all the data coming from a single reference or some component details.

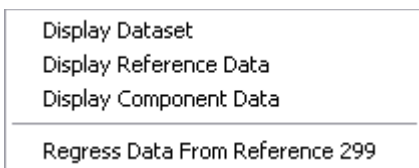


Figure 31

Additionally it allows to select data from a single reference for correlation. In this case the program recorrelates b_1 , b_2 , c_1 , c_2 only from this reference's datasets.

The chart contains some additional lines which are the critical density, 0.5 and 0.75 of the critical density, a zero line and the critical pressure, if the ordinate shows pressure values.

10 Volume Translation

VTPR uses a volume translation based on the difference between the experimental volume and the volume calculated by the Peng-Robinson equation of state at $T=T_c*0.7$. This temperature is normally quite close to the normal boiling point. PSRK normally does not use a volume translation for the Redlich-Kwong EOS but it can use such a correction, in principle.

In this dialog

The screenshot shows the 'Volume Translation' dialog box. It has a 'Close' button and two tabs: 'Calculation' and 'Diagram'. The 'Calculation' tab is active, showing three sections of radio buttons: 'Density Equation' (DIPPR 105 selected), 'Equation of State' (Peng-Robinson selected), and 'Vapor Pressure' (EOS-Alpha Function selected). There are 'Save (Private DDB)' and 'Save (Public DDB)' buttons. Below these is a table of calculated parameters for Chloroform. The 'ParameterDB Content' section on the right shows a table of stored values for various parameters.

#DDB	47
Name	Chloroform
Acentric Factor	0.21600001
Tc [K]	536.40002
T at Tr=0.7 [K]	375.48002
Pc [kPa]	5471.55
c by Tc,Pc,Vc (Rackett) [cm ³ /mol]	-10.384743
Psat by EOS [kPa]	331.50463
Volume by EOS [cm ³ /mol]	84.185399
Volume by EOS + c [cm ³ /mol]	94.5701420642906
Density by EOS [kg/m ³]	1418.0254
Tmin (DIPPR, [K])	203.15
Tmax (DIPPR, [K])	535.95
Density by DIPPR [kg/m ³]	1325.1174
Volume by DIPPR [cm ³ /mol]	90.087893
c by density diff.	-5.90249451690433
Rel. Dev. in c [%]	75.9
Rel. Dev. in V(PR)+c and V(DIPPR) [%]	5.0

Key	Value
C1	47
COUNT	1
DateD	14
DateM	0
DateY	2011
EOS	Peng/Robinson
EQID	101
LOCATION	0
Model	2
SETNUM	47924
Source	DIPPR 105 Liquid Density Parameters
Unit	cm ³ /mol
c	-5.90275

the volumes calculated by the equations DIPPR 105, DIPPR 116, and Polynomial are used as source for the experimental volume. The left table shows the calculation result with the volume translation value c in light green.

The right table shows the already stored values in the parameter data bank.

The “Diagram” page shows the different calculated volume ($1/\rho$) curves, a vertical line at $T_c*0.7$ and experimental values from the pure component property data base.

