Pure Component Equations

Fitting of Pure Component Equations

DDBSP - Dortmund Data Bank Software Package

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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.

List of Equations

Property	*Equation*
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 $\eta = E\exp\left[A\left(\frac{C-T}{T-D}\right)^{\frac{1}{3}}+B\left(\frac{C-T}{T-D}\right)^{\frac{4}{3}}\right]$
Vapor Viscosity T[K] η [mPa s]	1. DIPPR 102 $\eta = \frac{A\,T^{B}}{1+\frac{C}{T}+\frac{D}{T^{2}}}$

Property	*Equation*
Saturated Vapor Pressure T [K] P [kPa]	1. Antoine $P=10^{A-\frac{B}{T+C}}$ (▶Other Units: T [°C], P [mmHg]) 2. Wagner 2,5 $P=\exp\left(\ln P_c+\frac{A(1-T_r)+B(1-T_r)^{1.5}+C(1-T_r)^{2.5}+D(1-T_r)^5}{T_r}\right)$ 3. Wagner 3,6 $P=\exp\left(\ln P_c+\frac{A(1-T_r)+B(1-T_r)^{1.5}+C(1-T_r)^3+D(1-T_r)^6}{T_r}\right)$ 4. Cox $P=\exp\left[\ln 101.325+e^{A+B\left(\frac{T}{T_B}\right)+C\left(\frac{T}{T_B}\right)^2}\left(1-\frac{T_B}{T}\right)\right]$ 5. DIPPR 101 $P=e^{A+\frac{B}{T}+C\ln T+DT^E}$ (▶Other Units: P [Pa]) 6. Extended Antoine $P=\exp\left(A-\frac{B}{T+C}+DT+ET^2+F\ln(T)\right)$ 7. Extended Antoine (Aspen) $P=\exp\left(A-\frac{B}{T+C}+DT+E\ln(T)+F\,T^G\right)$ (in preparation) 8. Short Antoine (Aspen) $P=e^{A-\frac{B}{T}+CT}$ (in preparation) 9. Rarey2P $P=P_{atm}10^{\left[(4.1012+A)\left(\frac{T-B}{T-\frac{B}{8}}\right)\right]}$ $B\approx T_b$ $-1<A<+1$

Property	*Equation*
Saturated Vapor Pressure by EOS T [K] P [kPa]	1. Mathias-Copeman Constants for EOS $\alpha=\left(1+m\cdot\left(1-\sqrt{T_r}\right)\right)^2$ $m=c_1+c_2\cdot\left(1-\sqrt{T_r}\right)+c_3\cdot\left(1-\sqrt{T_r}\right)^2$ 2. Twu-Bluck-Cunningham-Cool Constants for EOS $\alpha=T_r^{\left(c_3\cdot\left(c_2-1\right)\right)}\cdot\exp\left(c_1\cdot\left(1-T_r^{\left(c_2\cdot c_3\right)}\right)\right)$ (c_1,c_2,c_3 used in DDB programs) $\alpha=T_r^{\left(N\cdot\left(M-1\right)\right)}\cdot\exp\left(L\cdot\left(1-T_r^{\left(M\cdot N\right)}\right)\right)$ (L,M,N like original authors) 3. Melhem-Saini-Goodwin Constants for EOS $\alpha=\exp\left(c_1\cdot\left(1-T_r\right)+c_2\cdot\left(1-\sqrt{T_r}\right)^2\right)$
Liquid Heat Capacity T [K] c_p [J/mol K]	1. Polynomial $c_P=A+BT+CT^2+DT^3+ET^4$ 2. PPDS 15 $c_p=R\left(\frac{A}{\tau}+C\tau+D\tau^2+E\tau^3+F\tau^4\right)$ with $\tau=1-\frac{T}{T_c}$
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 $c_p=a_0+a_1\left(\frac{\frac{a_2}{T}}{\sinh\frac{a_2}{T}}\right)^2+a_3\left(\frac{\frac{a_4}{T}}{\cosh\frac{a_4}{T}}\right)^2$ 3. PPDS 2 $C_P=R\left(B+\left(C-B\right)y^2\left[1+\left(y-1\right)\left(D+Ey+Fy^2+Gy^3\right)\right]\right)$ with $y=\frac{T}{A+T}$ 4. Shomate $c_P=A+BT+CT^2+DT^3+\frac{E}{T^2}$

Property	***Equation***
Liquid Density T [K] ρ [kg/m³]	1. DIPPR 105 $\rho = \frac{A}{B^{1+\left(1-\frac{T}{C}\right)^{D}}}$ 2. Polynomial $\rho = A + B \cdot T + CT^2 + DT^3 + ET^4$ 3. Tait (pressure-dependent data) $P_{ref} = max(f(T), 1.01325)\,MPa$ (Wagner-Equation) $\rho_{ref} = f(T)\frac{kg}{m^3}$ (DIPPR 105-Equation) $T_{reduced} = 100 \quad T_R = \frac{T}{T_{reduced}}$ $C = c_0 + c_1 T$ $B = b_0 + b_1 + b_2 T + b_2 T^2 + b_3 T^3 + b_4 T^4$ $\rho = \frac{\rho_{ref}}{1 - C \ln\left[\frac{B+P}{B+P_{ref}}\right]}$ 4. 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 $\tau = 1 - \frac{T}{T_c}$
Surface Tension T [K] σ [N/m]	1. Polynomial $\sigma = A + BT + CT^2 + DT^3 + ET^4$ 2. Short DIPPR 106 $\sigma = A(1-T_R)^n$ with $T_R = \frac{T}{T_c}$ 3. $\sigma = A(T - T_C)^B$ 4. Full DIPPR 106 $\sigma = A\left(1 - T_r\right)^{B + CT_r + DT_r^2 + ET_r^3}$ with $T_r = \frac{T}{T_c}$
Second Virial Coefficient T [K] B_{ii} [cm³/mol]	1. Polynomial $B_{ii} = A + BT + CT^2 + DT^3 + ET^4$ 2. $B_{ii} = \frac{A}{\sqrt{T}} + \frac{B}{T}$ 3. DIPPR 104 $B_{ii} = A + \frac{B}{T} + \frac{C}{T^3} + \frac{D}{T^8} + \frac{E}{T^9}$

Property	*Equation*
Heat of Vaporization T [K] H_{vap} [J/mol]	1. DIPPR 106 $H_{Vap}=A\left(1-\frac{T}{T_C}\right)^{B+C\left(\frac{T}{T_C}\right)+D\left(\frac{T}{T_C}\right)^2+E\left(\frac{T}{T_C}\right)^3}$ 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

Using the program

Initial Dialog

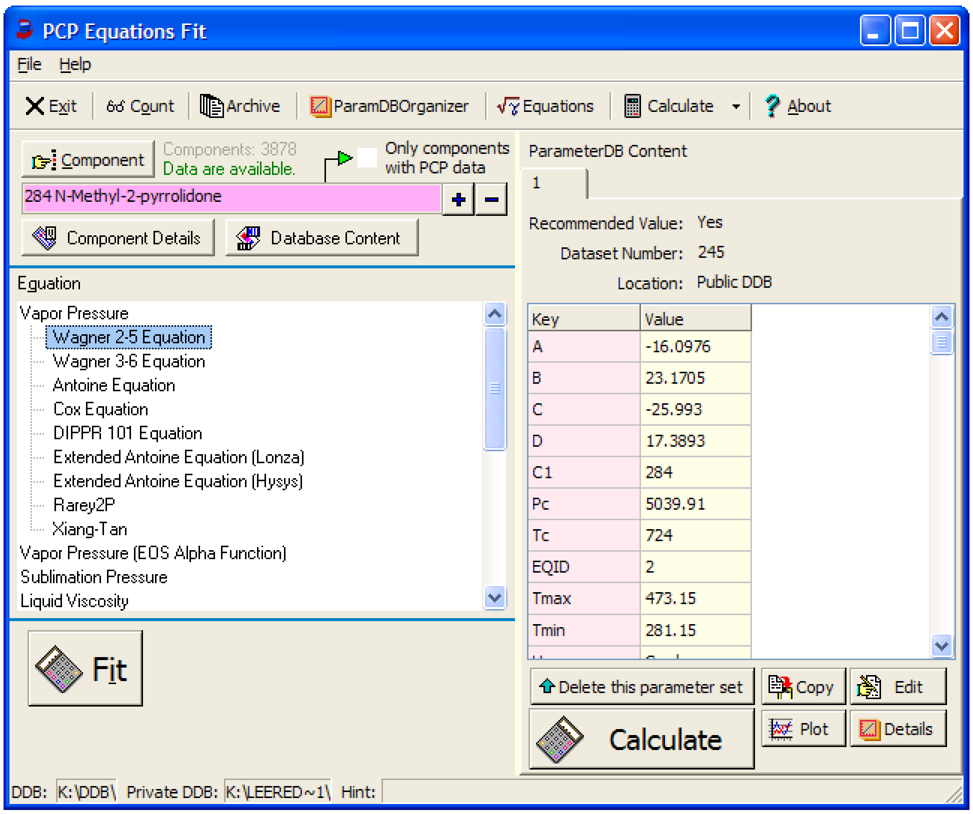

Figure 1 Main PCPEquationFit Dialog

The program's start dialog contains three major parts:

1. The components area allows to
   1. select components
   2. display component details with the component editor
   3. display the content of the Dortmund Data Bank for the selected component
   4. see, 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.

Component Selection

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

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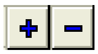
After a *Return* the component name is added.

The buttons  allow to navigate through the DDB component list.

The button  calls the component selection dialog

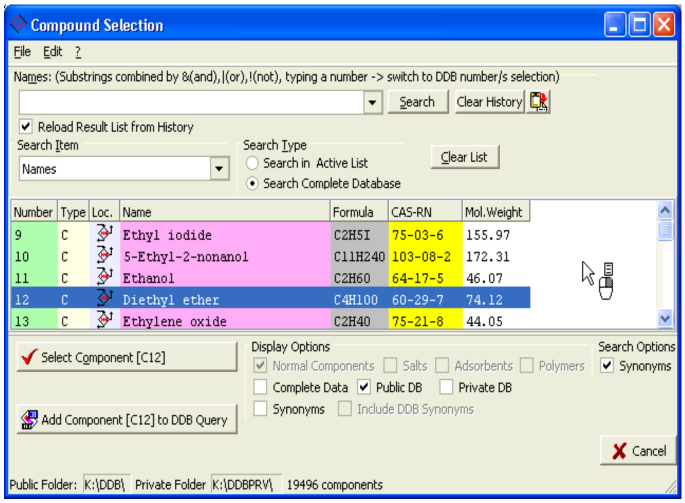


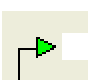
Figure 2 Component Selection

which is described in details in other documents.

The information lines Components: 6368 Data are available. show for how many components the Dortmund Data Bank contains experimental data sets (in the case of saturated vapor pressures there are 6368 data sets available).

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 checkbox  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.

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 equation for saturated vapor pressures.

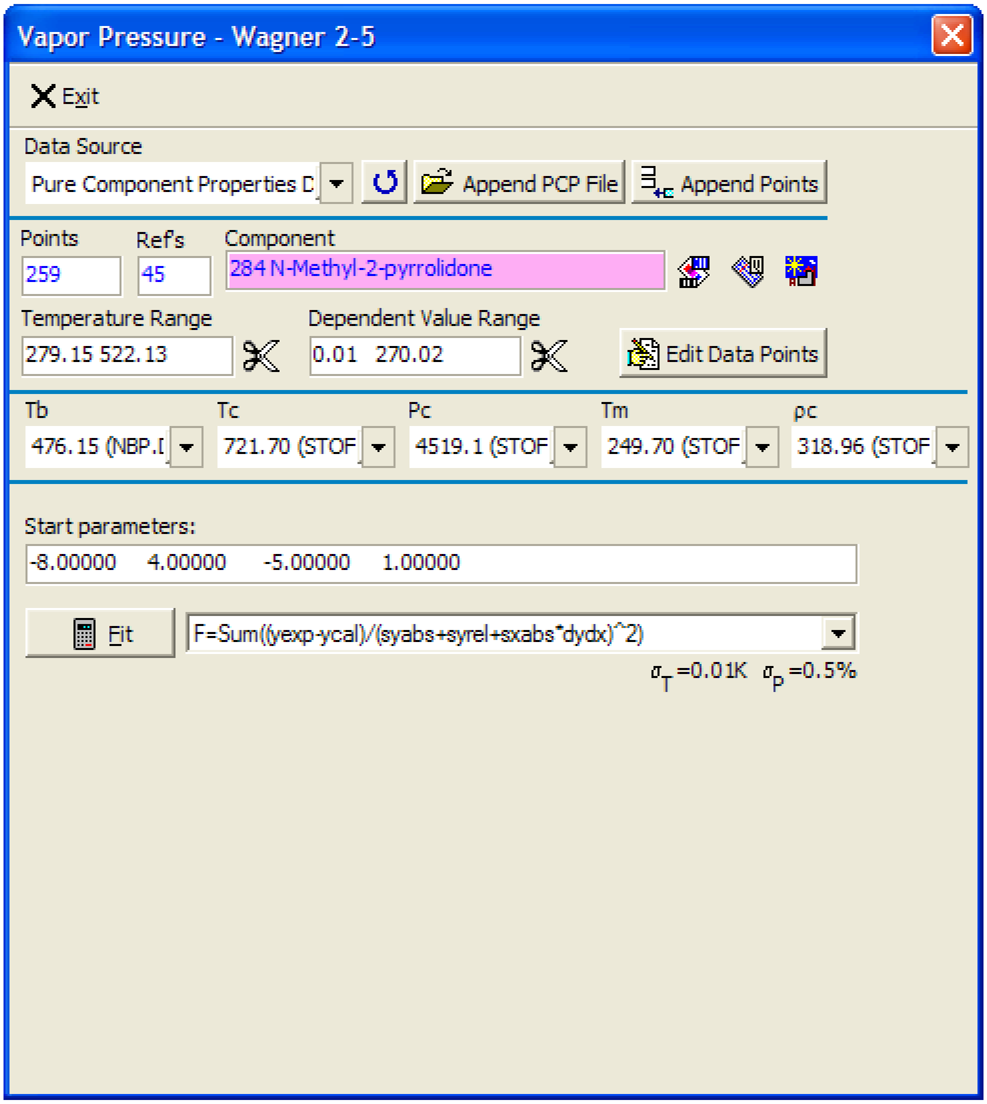
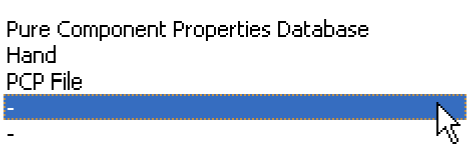


Figure 3 Fit Dialog for Wager 2-5 equation

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



1. Input by hand
2. Reading from file
3. Calculated data or stored data points (here marked as '-')

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 buttons 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.

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.

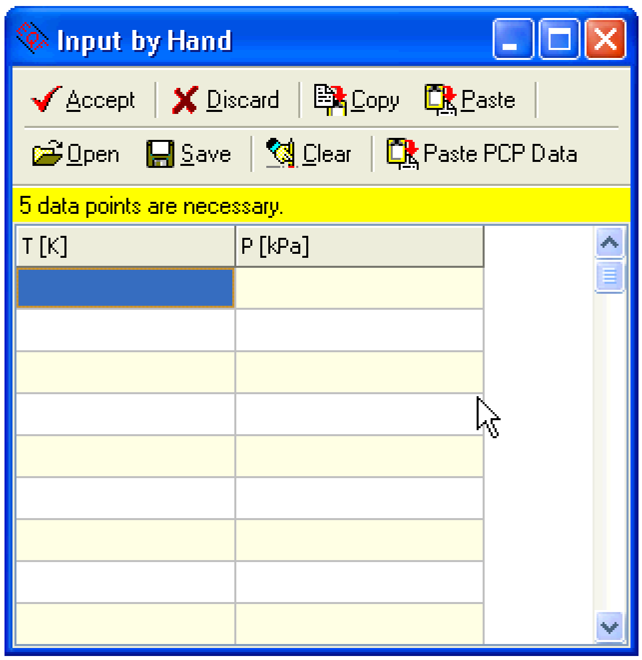


Figure 4 Input by Hand

Fit Results

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

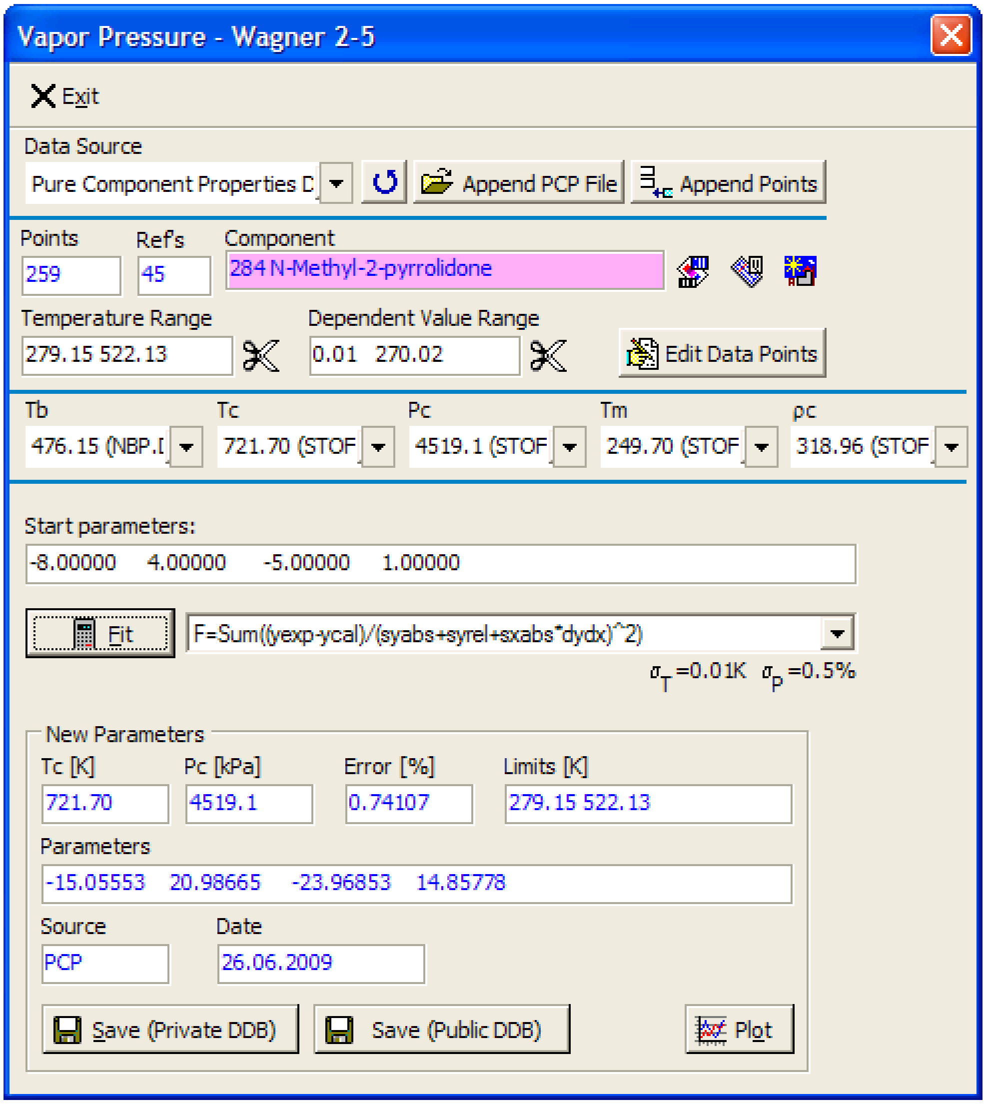


Figure 5 Fit Result

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.

Plot

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

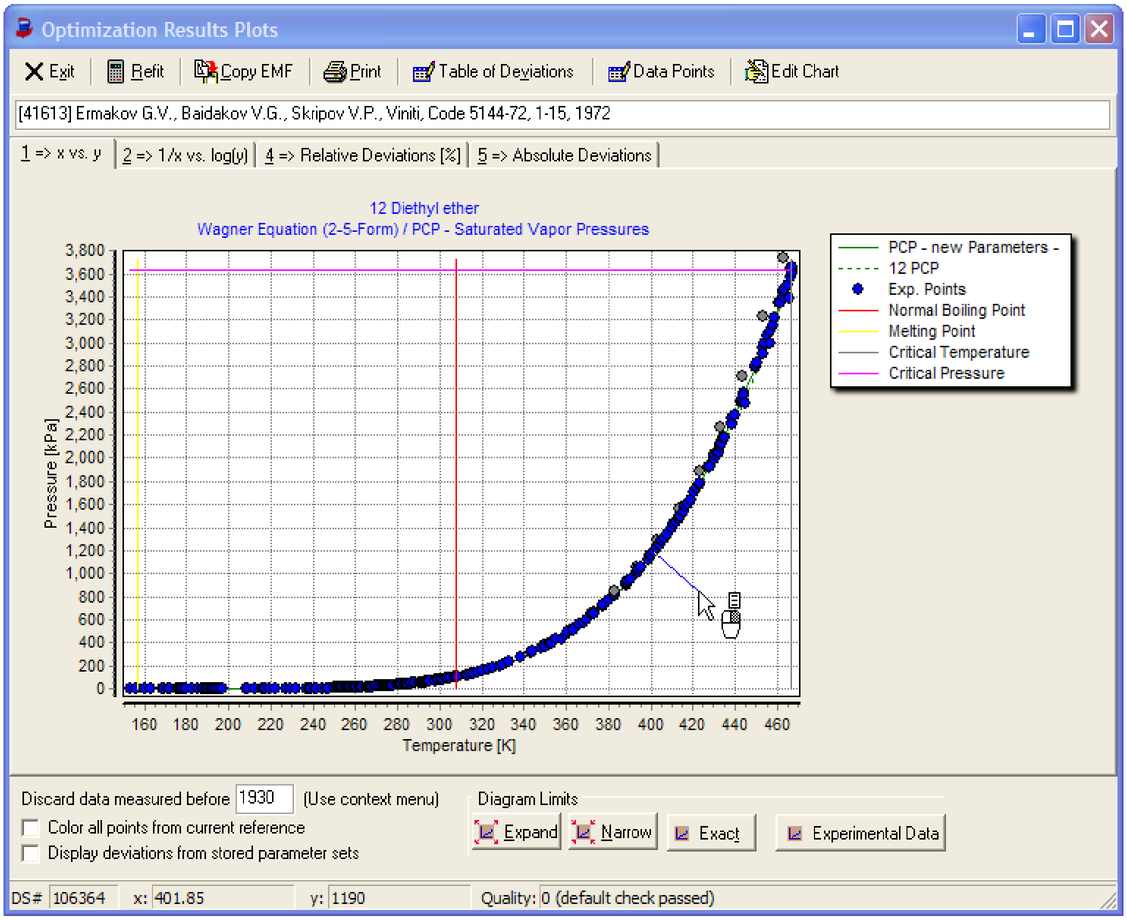
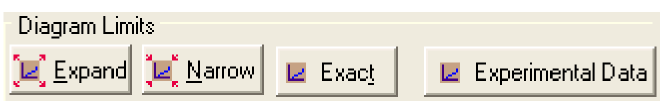


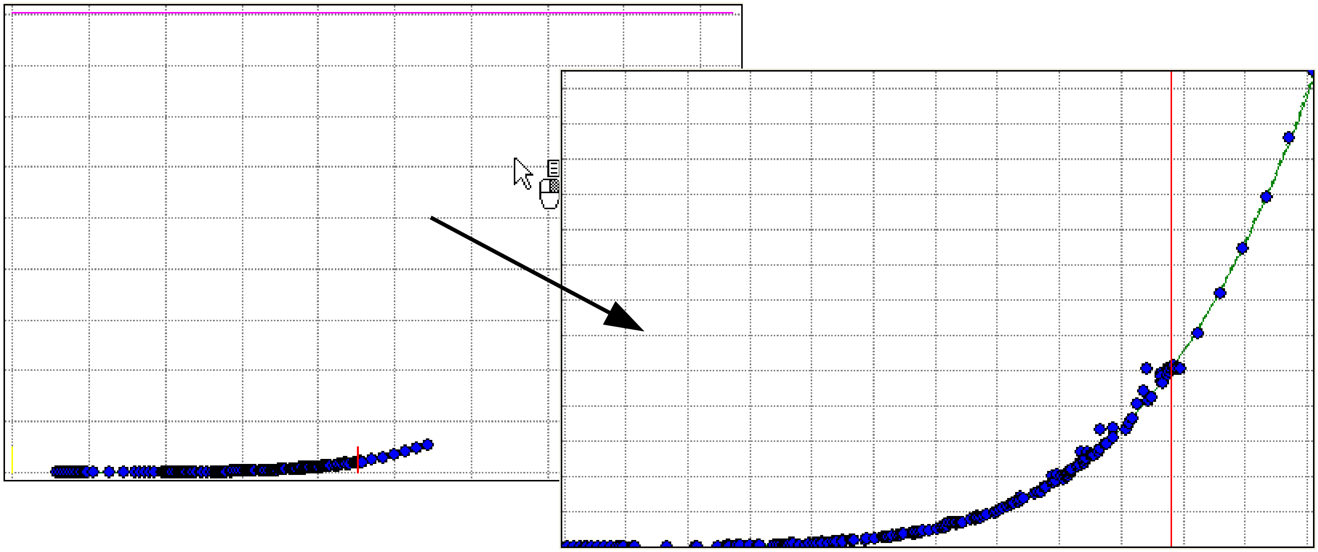
Figure 6 Plot of Fit

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

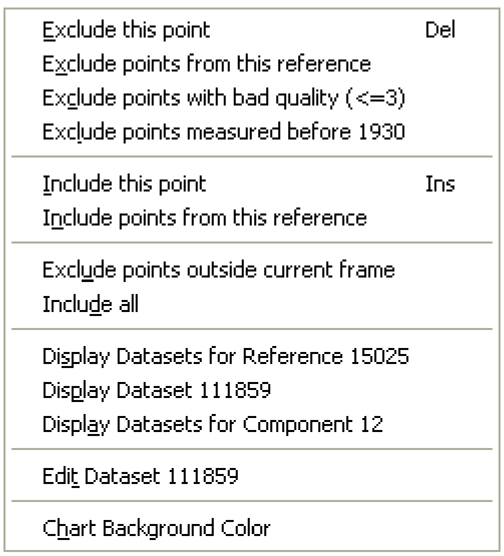


Figure 7 Plot Context Menu

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

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.

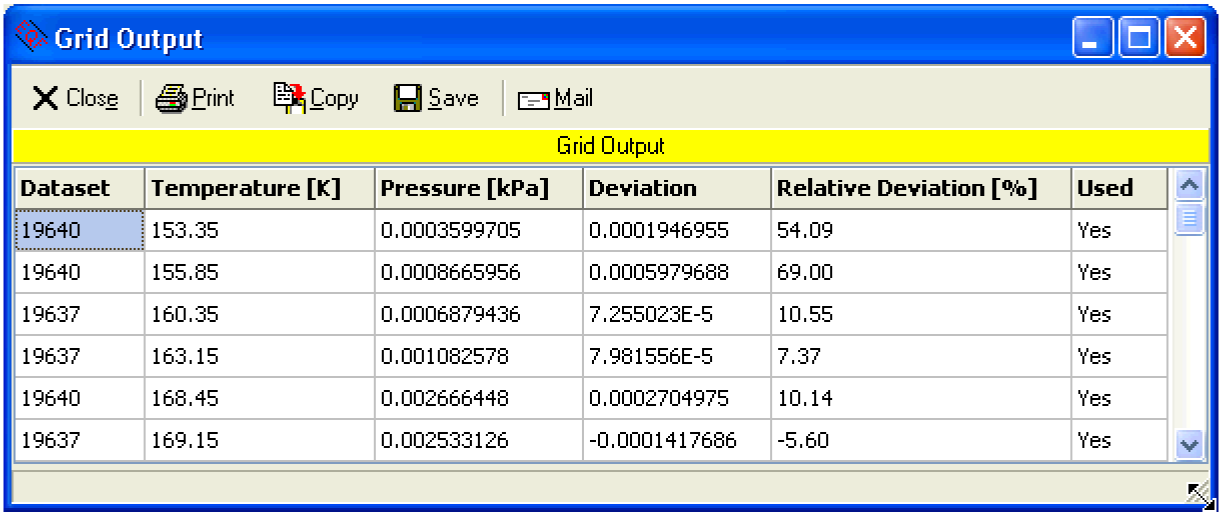


Figure 8 Table of Deviations

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

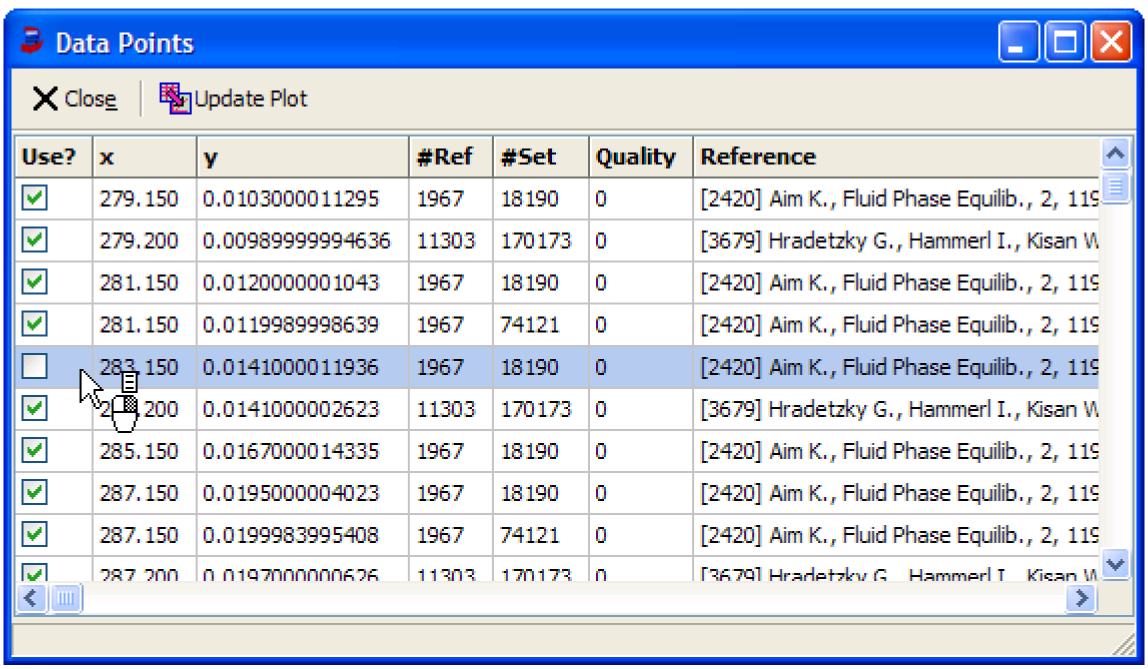


Figure 9: Data Points Selection

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 Refit . This will return us to the fit dialog allowing to store the modified parameters.

Understanding the ParameterDDB Dataset Display

Recommended Value: Yes
Dataset Number: 12
Location: Public DDB

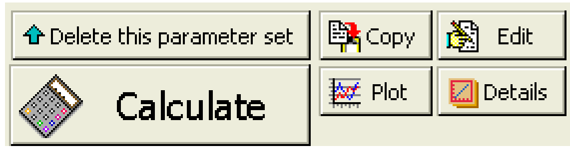
Key	Value
A	-8.41515
B	4.65592
C	-6.26863
D	1.7655
C1	12
Pc	3637.57
Tc	466.7
EQID	2
Tmax	466.74
Tmin	250.046
User	Cordes
COUNT	1
DateD	16
DateM	6
DateY	1994
Error	0.092
SETNUM	12
Source	PCP
LOCATION	0
AUTOSELECT	true
SourceFile	PARAM.WAG

Figure 10 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.

Working with a Parameter Data Set



Copy

The dataset grid will be copied to the windows clipboard as it is displayed in Figure 10 (source) and Figure 11 (destination).

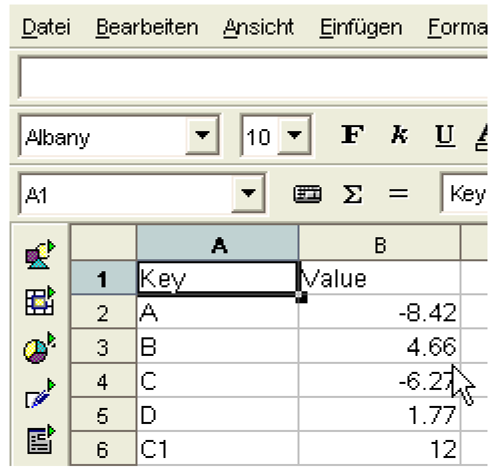


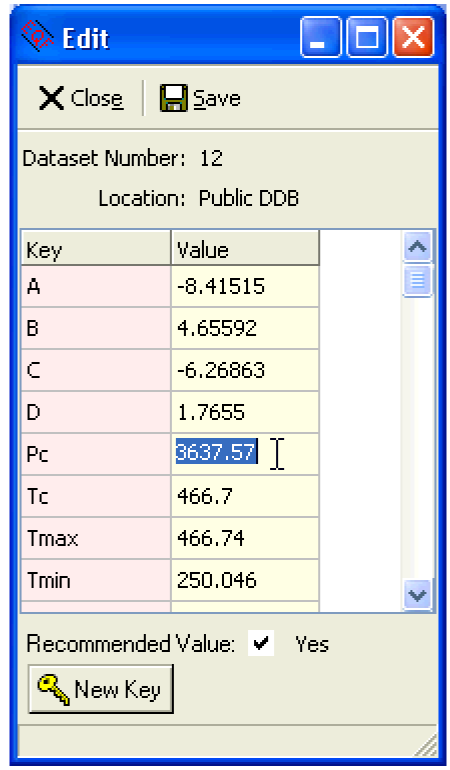
Figure 11 Data set pasted in spreadsheet program

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 (New Key) 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.



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.

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".

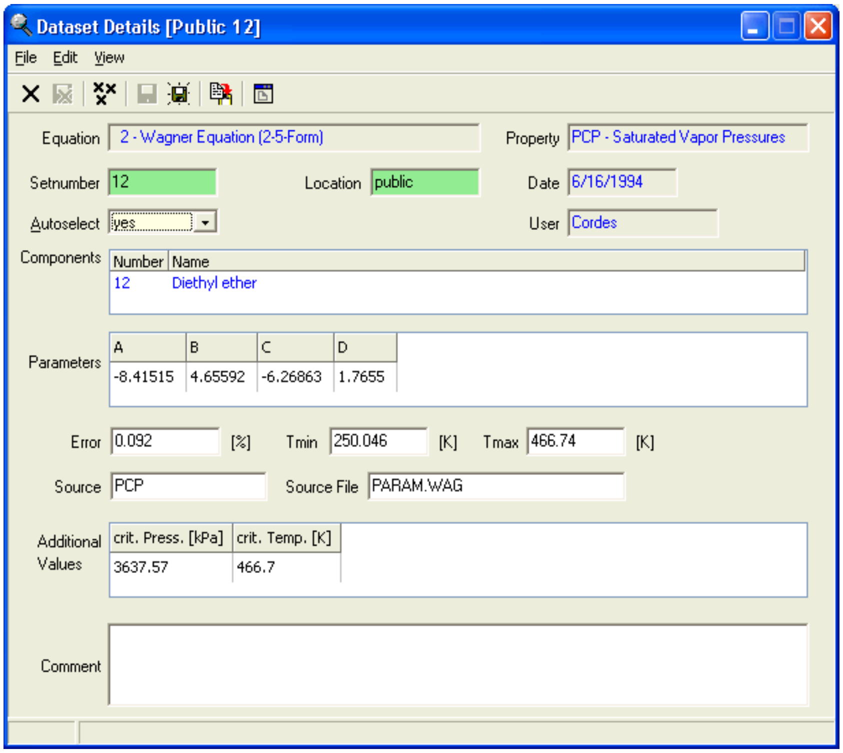


Figure 12 Data set details

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 13) 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 14).

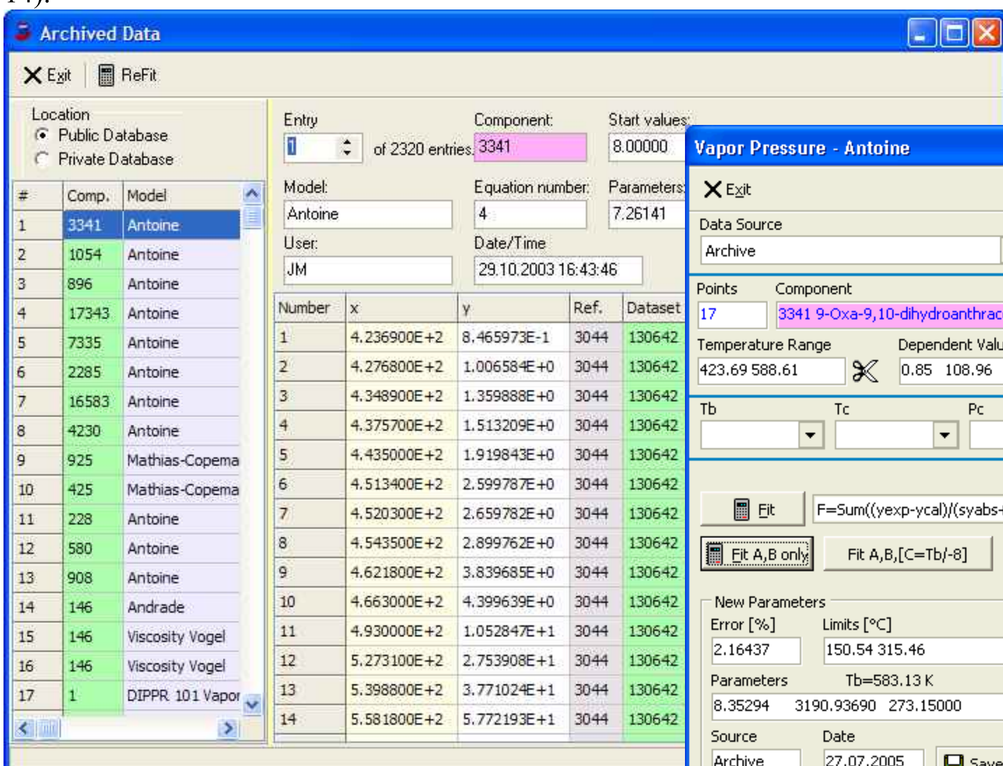


Figure 13 Fit Archive

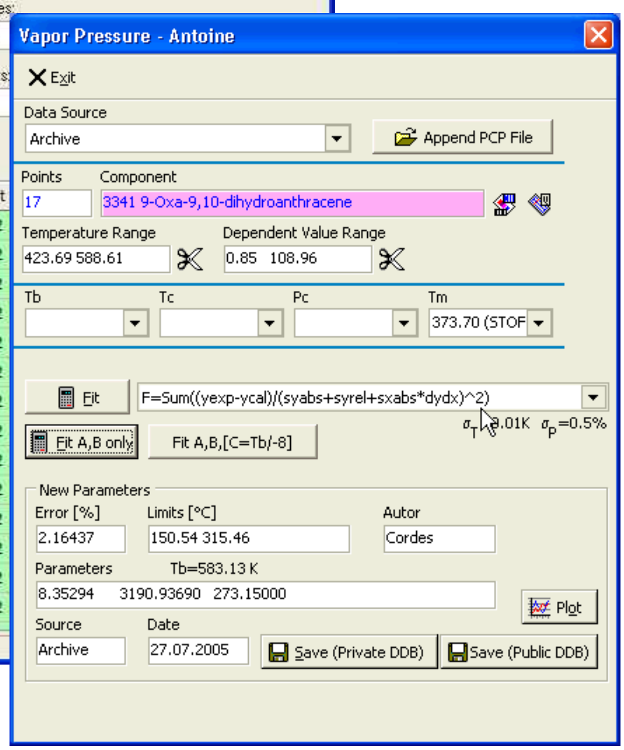
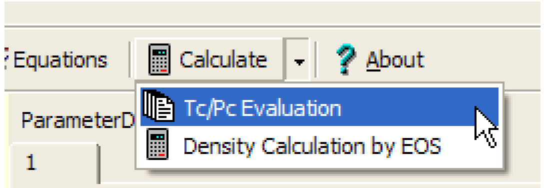


Figure 14 Refit with archived data

Tc/Pc Evaluation



PCPEquationFit allows with this function to evaluate 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.

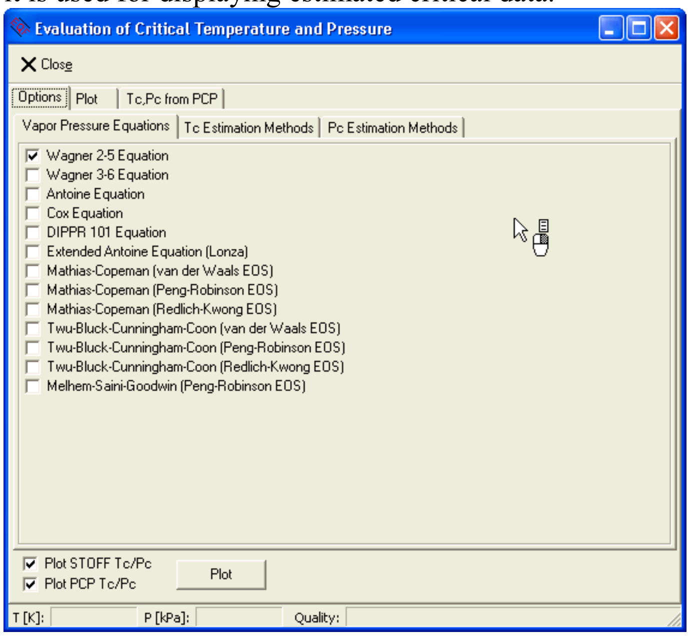


Figure 15 Critical Data Evaluation - Vapor Pressure Equations

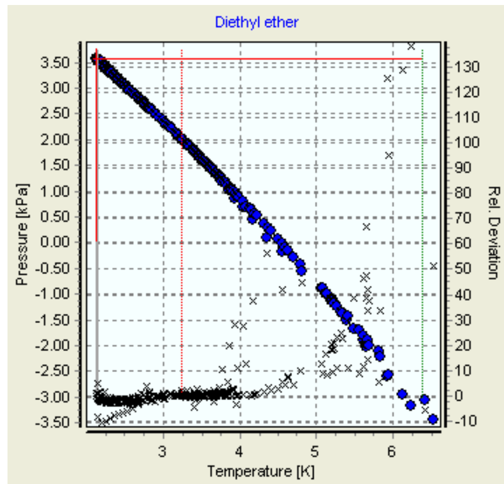
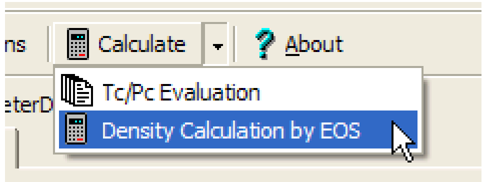
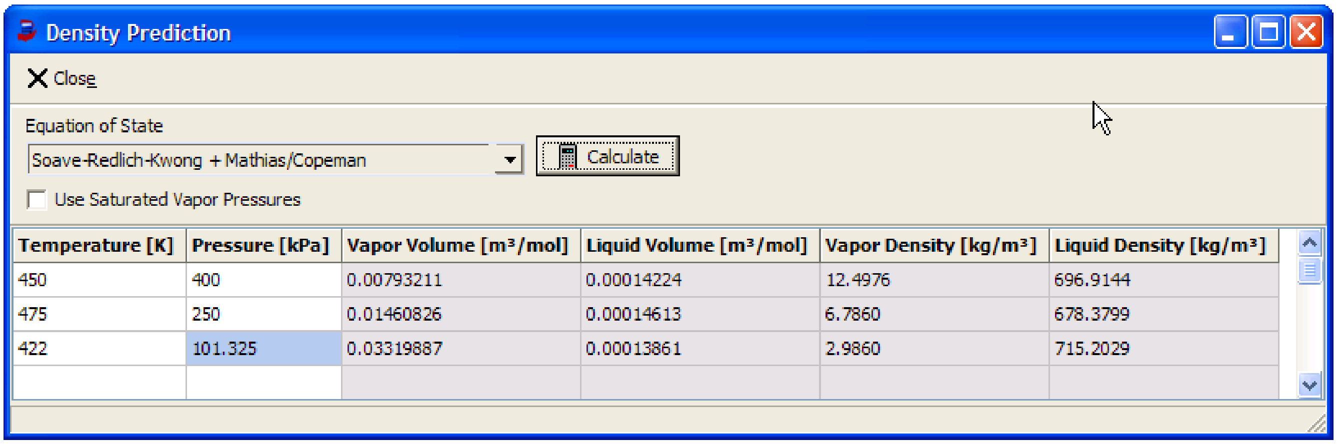


Figure 16 Critical Data Evaluation - Plot

Density Prediction by Equation of State



This dialog



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.

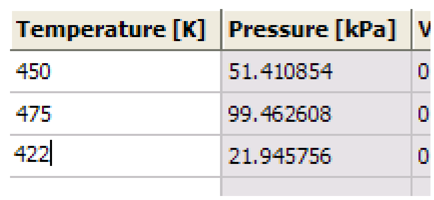


Figure 17: Using saturated vapor pressures