Pure Component Equations

Fitting of Pure Component Equation Parameters

DDBSP – Dortmund Data Bank Software Package

DDBST
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SOFTWARE & SEPARATION
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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

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 $\eta = E\exp\left[A\left(\frac{C-T}{T-D}\right)^{\frac{1}{3}}+B\left(\frac{C-T}{T-D}\right)^{\frac{4}{3}}\right]$ 5. Extended Andrade $\eta = e^{A+\frac{B}{T}+CT+DT^2+ET^3}$ 6. Polynomial in 1/T $\eta = A+\frac{B}{T}+\frac{C}{T^2}+\frac{D}{T^3}+\frac{E}{T^4}$
Vapor Viscosity T[K] η [mPa s]	1. DIPPR 102 $\eta = \frac{A\,T^{B}}{1+\frac{C}{T}+\frac{D}{T^2}}$ 2. Polynomial $\eta = A+B\cdot T+CT^2+DT^3+ET^4$

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

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-Coon Constants for EOS $\alpha=T_r^{\left(c_3\cdot\left(c_2-1\right)\right)}\cdot\exp\left(c_1\cdot\left(1-T_r^{\left(c_2\cdot c_3\right)}\right)\right)$ (c₁, c₂, c₃ 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 $\alpha=\exp\left(c_1\cdot\left(1-T_r\right)+c_2\cdot\left(1-\sqrt{T_r}\right)^2\right)$ 4. Stryjek-Vera Constants for EOS $\kappa=\kappa_0+\kappa_1\left(1+\sqrt{T_r}\right)\left(0.7-T_r\right)$ $\alpha=\left(1+\kappa\left(1-\sqrt{T_r}\right)\right)^2$ 5. Stryjek-Vera-2 Constants for EOS $\kappa=\kappa_0+\left[\kappa_1+\kappa_2\left(\kappa_3-T_r^{0.5}\right)\left(1-T_r^{0.5}\right)\right]\left(1+T_r^{0.5}\right)\left(0.7-T_r\right)$ $\alpha=\left(1+\kappa\left(1-T_r^{0.5}\right)\right)^2$ 6. 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]	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 $\tau=1-\frac{T}{T_c}$

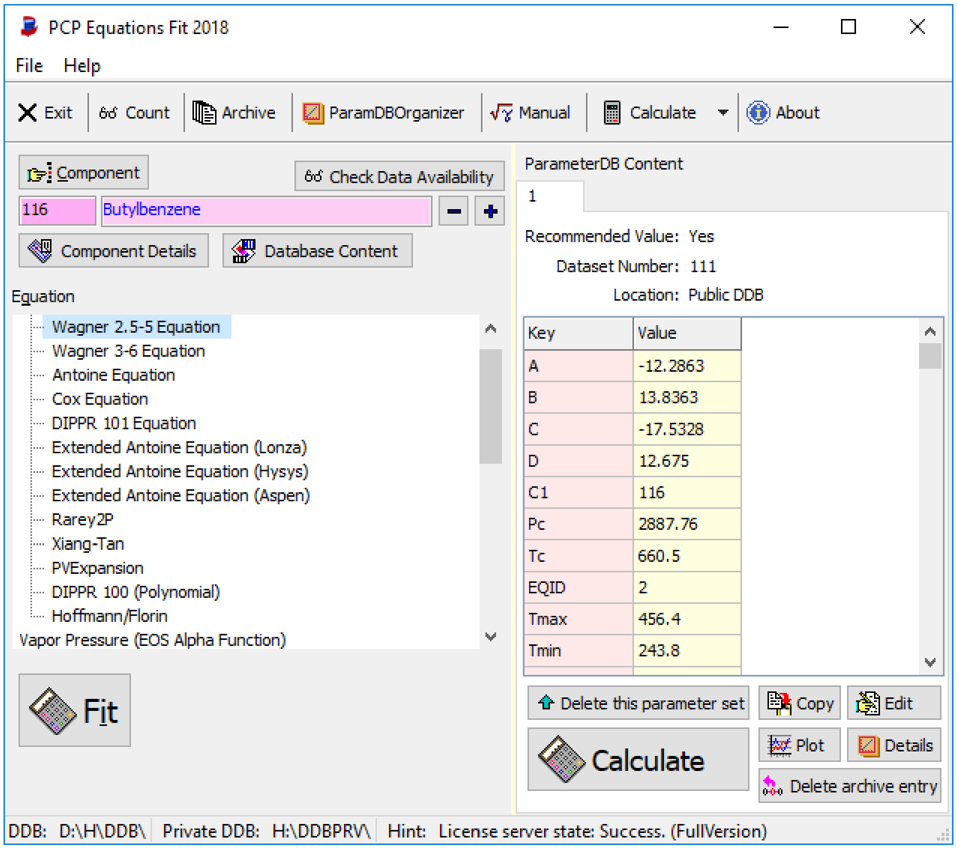
Property	***Equation***
Ideal Gas Heat Capacity T [K] c_p [J/mol K]	1. Polynomial $c_P = A + BT + CT^2 + DT^3 + ET^4$ 2. Aly-Lee, DIPPR 107 $c_p = a_0 + a_1 \left(\dfrac{\frac{a_2}{T}}{\sinh \frac{a_2}{T}} \right)^2 + a_3 \left(\dfrac{\frac{a_4}{T}}{\cosh \frac{a_4}{T}} \right)^2$ 3. PPDS 2 $C_P = R\left(B + (C - B)\, y^2 \left[1 + (y-1)\left(D + Ey + Fy^2 + Gy^3\right)\right]\right)$ with $y = \dfrac{T}{A+T}$ 4. Shomate $c_P = A + B\,T + C\,T^2 + D\,T^3 + \dfrac{E}{T^2}$ 5. Wilhoit $\dfrac{c_P}{R} = A + \left(\dfrac{B}{T^2}\right) \cdot \exp\left(\dfrac{-C}{T}\right) + D \cdot y^2 + \left(E - \dfrac{F}{(T-H)^2}\right) \cdot y^8$ with $y = \dfrac{T-G}{T+F}$
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]	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) $T_{reduced}=100 \quad T_R=\frac{T}{T_{reduced}}$ $C=c_0+c_1T_R$ $B=b_0+b_1T_R+b_2T_R^2+b_3T_R^3+b_4T_R^4$ $\rho=\frac{\rho_{ref}}{1-C\ln\left[\frac{B+P}{B+P_{ref}}\right]}$ 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 $\tau=1-\frac{T}{T_c}$ 5. 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]	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 $T_r=\frac{T}{T_c}$ 5. PPDS 14 $\sigma=A\cdot\tau^B\cdot\left(1+C\cdot\tau\right)$ with $\tau=1-\frac{T}{T_c}$

Property	***Equation***
Second Virial Coefficient T [K] B_{ii} [cm³/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 $H_{Vap}=A\left(1-\frac{T}{T_C}\right)^{B+C\left(\frac{T}{T_C}\right)+D\left(\frac{T}{T_C}\right)^2+E\left(\frac{T}{T_C}\right)^3}$ 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 $\tau=1-\frac{T}{T_c}$ 4. Pitzer/Carruth/Kobayashi $H_{vap}=A\cdot\tau^{\frac{1}{3}}+B\cdot\tau^{\frac{2}{3}}+C\cdot\tau$ 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


PCP Equations Fit 2018
File
Help
Exit
Count
Archive
ParamDBOrganizer
Manual
Calculate
About
Component
Check Data Availability
Component Details
Database Content
Equation
Wagner 2.5-5 Equation
Wagner 3-6 Equation
Antoine Equation
Cox Equation
DIPPR 101 Equation
Extended Antoine Equation (Lonza)
Extended Antoine Equation (Hysys)
Extended Antoine Equation (Aspen)
Rarey2P
Xiang-Tan
PVExpansion
DIPPR 100 (Polynomial)
Hoffmann/Florin
Vapor Pressure (EOS Alpha Function)
Fit
ParameterDB Content
1
Delete this parameter set
Copy
Edit
Plot
Details
Calculate
Delete archive entry

116 Butylbenzene

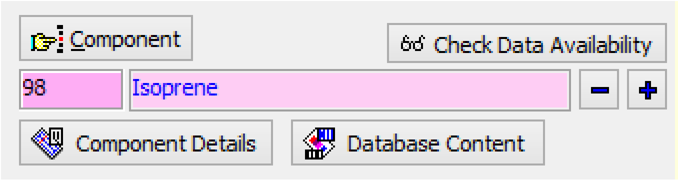
Recommended Value: Yes
Dataset Number: 111
Location: Public DDB

Key	Value
A	-12.2863
B	13.8363
C	-17.5328
D	12.675
C1	116
Pc	2887.76
Tc	660.5
EQID	2
Tmax	456.4
Tmin	243.8

DDB: D:\H\DDB\ Private DDB: H:\DDBPRV\ Hint: License server state: Success. (FullVersion)

Figure 1 Main PCPEquationFit Dialog

The program's start dialog contains three major parts:


Component
Check Data Availability
Component Details
Database Content

98 Isoprene

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.

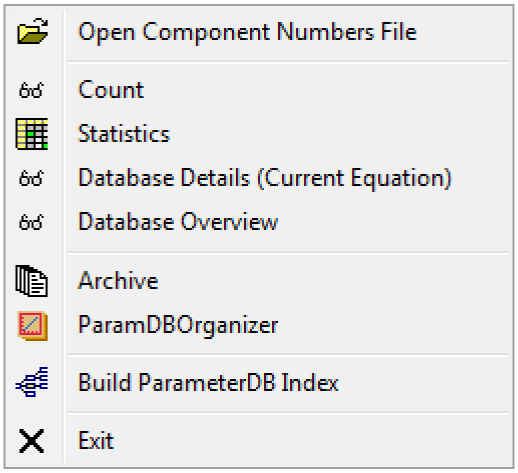
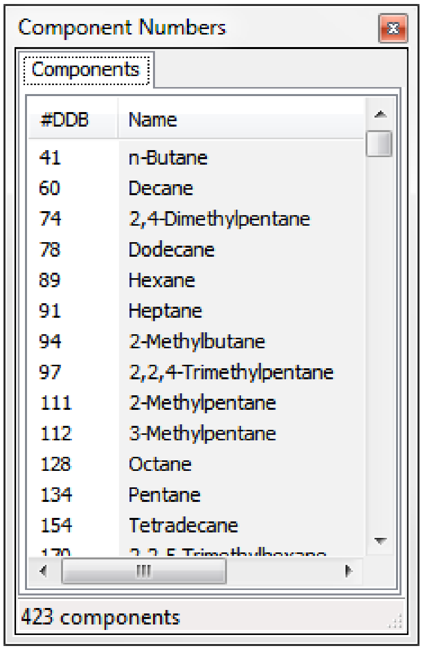

Open Component Numbers File
Count
Statistics
Database Details (Current Equation)
Database Overview
Archive
ParamDBOrganizer
Build ParameterDB Index
Exit

Figure 2: File menu

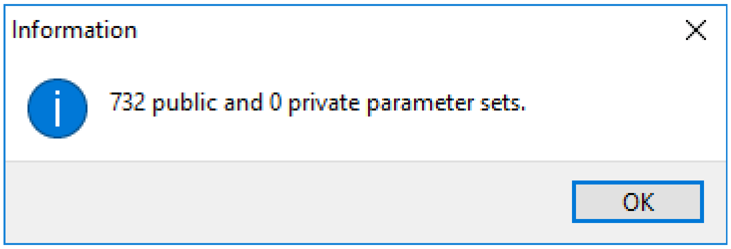

Component Numbers
Components

#DDB	Name
41	n-Butane
60	Decane
74	2,4-Dimethylpentane
78	Dodecane
89	Hexane
91	Heptane
94	2-Methylbutane
97	2,2,4-Trimethylpentane
111	2-Methylpentane
112	3-Methylpentane
128	Octane
134	Pentane
154	Tetradecane

423 components

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

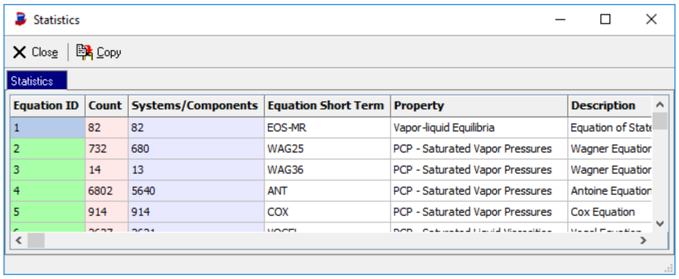
- **Count**
  Count shows the number of available parameter data sets for the current model.


Information
OK

732 public and 0 private parameter sets.

Figure 3: Parameter Data Set Count

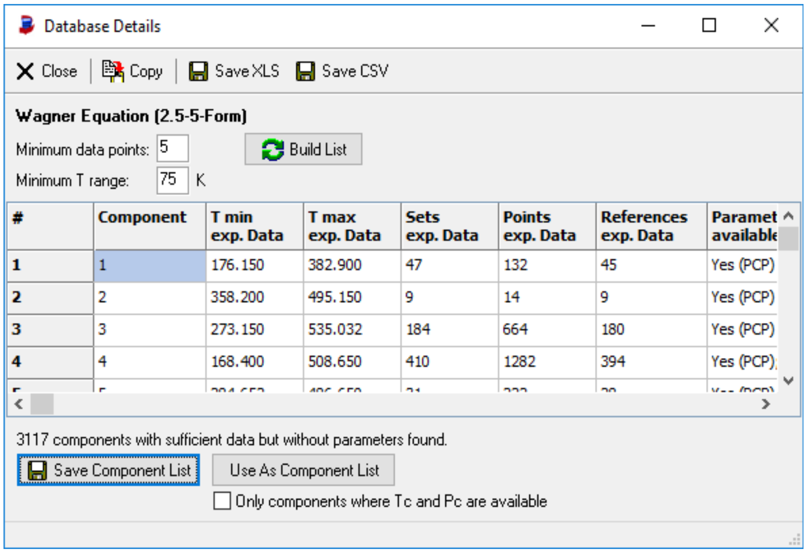
- **Statistics**
  Statistics creates a table with an overview over all equations


Statistics
Close
Copy
Statistics

Equation ID	Count	Systems/Components	Equation Short Term	Property	Description
1	82	82	EOS-MR	Vapor-liquid Equilibria	Equation of Stat
2	732	680	WAG25	PCP - Saturated Vapor Pressures	Wagner Equatio
3	14	13	WAG36	PCP - Saturated Vapor Pressures	Wagner Equatio
4	6802	5640	ANT	PCP - Saturated Vapor Pressures	Antoine Equatio
5	914	914	COX	PCP - Saturated Vapor Pressures	Cox Equation

Figure 4: Statistics

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



Wagner Equation (2.5-5-Form)

Minimum data points: 5

Minimum T range: 75 K

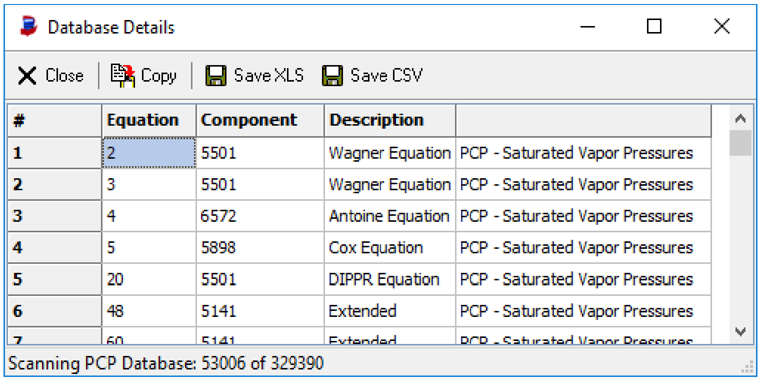
#	Component	T min exp. Data	T max exp. Data	Sets exp. Data	Points exp. Data	References exp. Data	Paramet available
1	1	176.150	382.900	47	132	45	Yes (PCP)
2	2	358.200	495.150	9	14	9	Yes (PCP)
3	3	273.150	535.032	184	664	180	Yes (PCP)
4	4	168.400	508.650	410	1282	394	Yes (PCP)

3117 components with sufficient data but without parameters found.

☐ Only components where Tc and Pc are available

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.



#	Equation	Component	Description	
1	2	5501	Wagner Equation	PCP - Saturated Vapor Pressures
2	3	5501	Wagner Equation	PCP - Saturated Vapor Pressures
3	4	6572	Antoine Equation	PCP - Saturated Vapor Pressures
4	5	5898	Cox Equation	PCP - Saturated Vapor Pressures
5	20	5501	DIPPR Equation	PCP - Saturated Vapor Pressures
6	48	5141	Extended	PCP - Saturated Vapor Pressures

Scanning PCP Database: 53006 of 329390

Figure 6: Database Overview

- **Archive**
  See chapter "Fit Archive" on page 27.
- **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

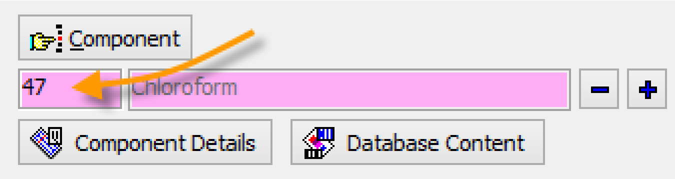
The help menu contains a button which brings this PDF help up and an "About" button which shows some information about the program.

Manual
About

Figure 7: Help menu

3.4 Component Selection

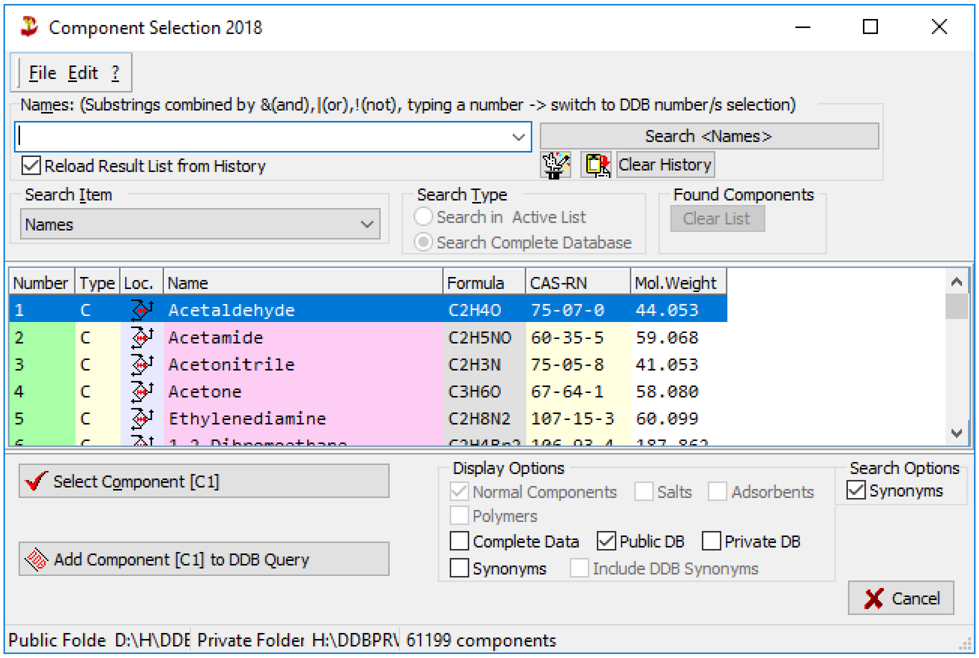
DDB component numbers can be typed directly in the component field.


Component
47
Chloroform
−
+
Component Details
Database Content

After a *Return* the component name is added.

The buttons − + allow to navigate through the DDB component list.

The button Component calls the component selection dialog


Component Selection 2018
File Edit ?
Search <Names>
Clear History
Clear List
Select Component [C1]
Add Component [C1] to DDB Query
Cancel

Names: (Substrings combined by &(and),|(or),!(not), typing a number -> switch to DDB number/s selection)

☑ Reload Result List from History

Search Item: Names

Search Type: ○ Search in Active List ● Search Complete Database

Found Components

Number	Type	Loc.	Name	Formula	CAS-RN	Mol.Weight
1	C		Acetaldehyde	C2H4O	75-07-0	44.053
2	C		Acetamide	C2H5NO	60-35-5	59.068
3	C		Acetonitrile	C2H3N	75-05-8	41.053
4	C		Acetone	C3H6O	67-64-1	58.080
5	C		Ethylenediamine	C2H8N2	107-15-3	60.099

Display Options: ☑ Normal Components ☐ Salts ☐ Adsorbents ☐ Polymers ☐ Complete Data ☑ Public DB ☐ Private DB ☐ Synonyms ☐ Include DDB Synonyms

Search Options: ☑ Synonyms

Public Folde D:\H\DDE Private Folder H:\DDBPR\ 61199 components

Figure 8 Component Selection

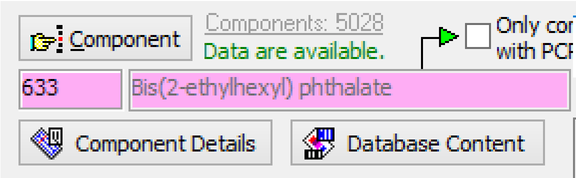
which is described in details in other documents.

3.5 Check Data Availability

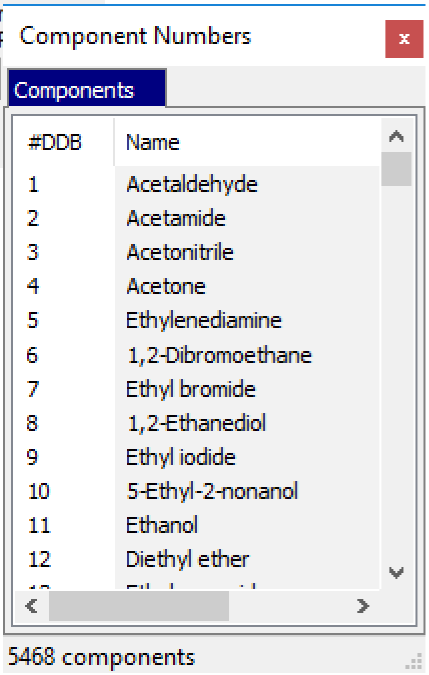
Check Data Availability

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.



633 Bis(2-ethylhexyl) phthalate



#DDB	Name
1	Acetaldehyde
2	Acetamide
3	Acetonitrile
4	Acetone
5	Ethylenediamine
6	1,2-Dibromoethane
7	Ethyl bromide
8	1,2-Ethanediol
9	Ethyl iodide
10	5-Ethyl-2-nonanol
11	Ethanol
12	Diethyl ether

5468 components

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.

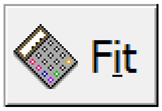
The "Data are available" line indicates that there are enough data points for the specific equation. This number is normally set to <number of parameters + 1>.

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.

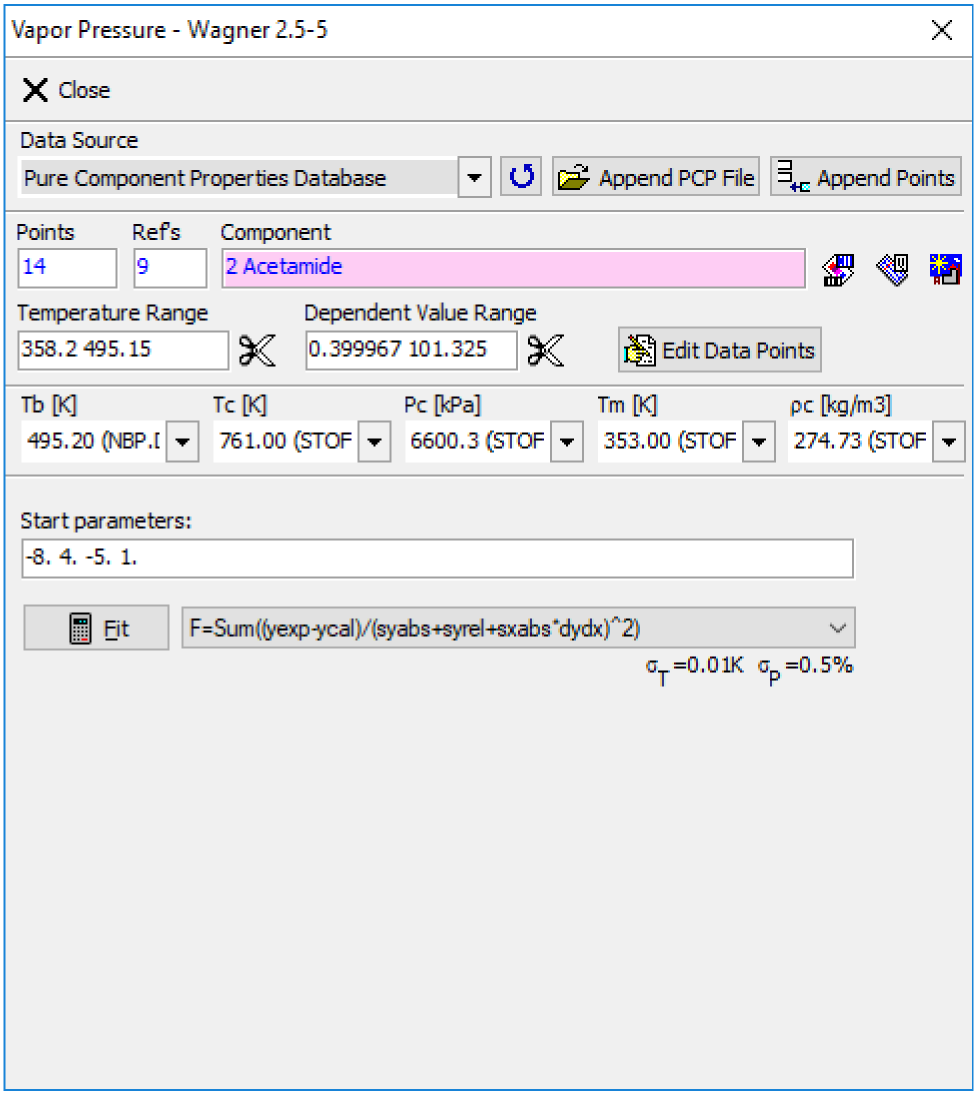
A detailed description of all component selection features is available in the "Component Management" documentation.

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.


Vapor Pressure - Wagner 2.5-5
Close
Append PCP File
Append Points
Edit Data Points
Fit

Data Source: Pure Component Properties Database

Points: 14

Ref's: 9

Component: 2 Acetamide

Temperature Range: 358.2 495.15

Dependent Value Range: 0.399967 101.325

Tb [K]	Tc [K]	Pc [kPa]	Tm [K]	ρc [kg/m3]
495.20 (NBP.I	761.00 (STOF	6600.3 (STOF	353.00 (STOF	274.73 (STOF

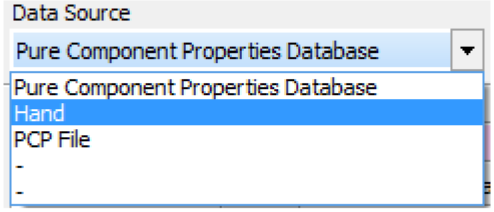
Start parameters: -8. 4. -5. 1.

F=Sum((yexp-ycal)/(syabs+syrel+sxabs*dydx)^2)

σ_T=0.01K σ_p=0.5%

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


Data Source
Pure Component Properties Database
Pure Component Properties Database
Hand
PCP File
-
-

1. Database
2. Input by hand
3. Reading from file
4. 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.

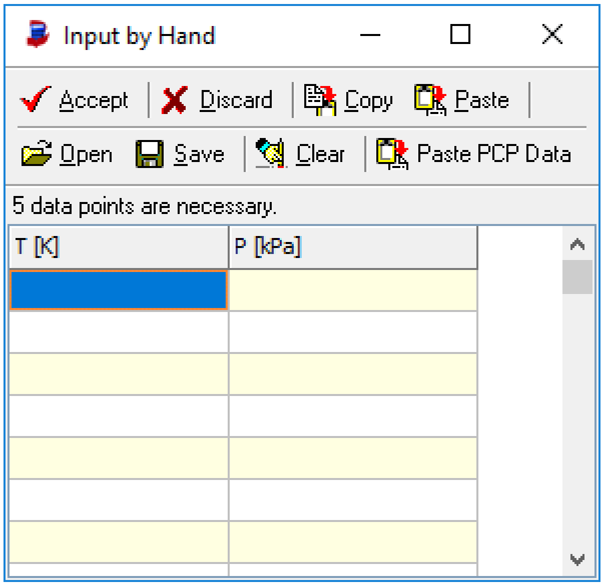
The temperature and pressure range are also displayed. These limits are editable and can be used to cut points by increasing the lower limit or decreasing the upper limit. The knife button ✂ will actually throw the points outside the given ranges away. The “Edit Data Points” allows to modify the data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

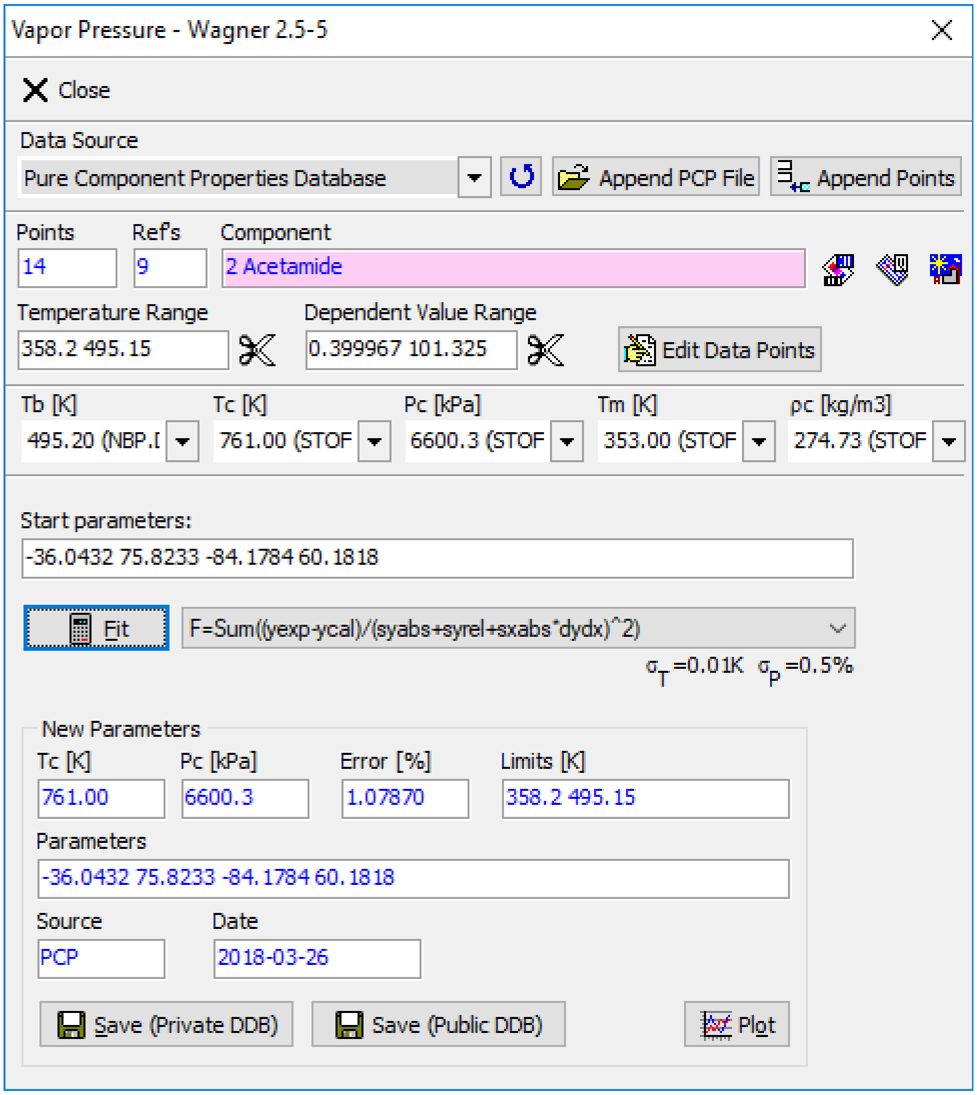


5 data points are necessary.

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:


Vapor Pressure - Wagner 2.5-5

Data Source: Pure Component Properties Database
Points: 14
Ref's: 9
Component: 2 Acetamide
Temperature Range: 358.2 495.15
Dependent Value Range: 0.399967 101.325
Tb [K]: 495.20 (NBP.I
Tc [K]: 761.00 (STOF
Pc [kPa]: 6600.3 (STOF
Tm [K]: 353.00 (STOF
ρc [kg/m3]: 274.73 (STOF
Start parameters: -36.0432 75.8233 -84.1784 60.1818
F=Sum((yexp-ycal)/(syabs+syrel+sxabs*dydx)^2)
σ_T=0.01K σ_P=0.5%

New Parameters
Tc [K]: 761.00
Pc [kPa]: 6600.3
Error [%]: 1.07870
Limits [K]: 358.2 495.15
Parameters: -36.0432 75.8233 -84.1784 60.1818
Source: PCP
Date: 2018-03-26

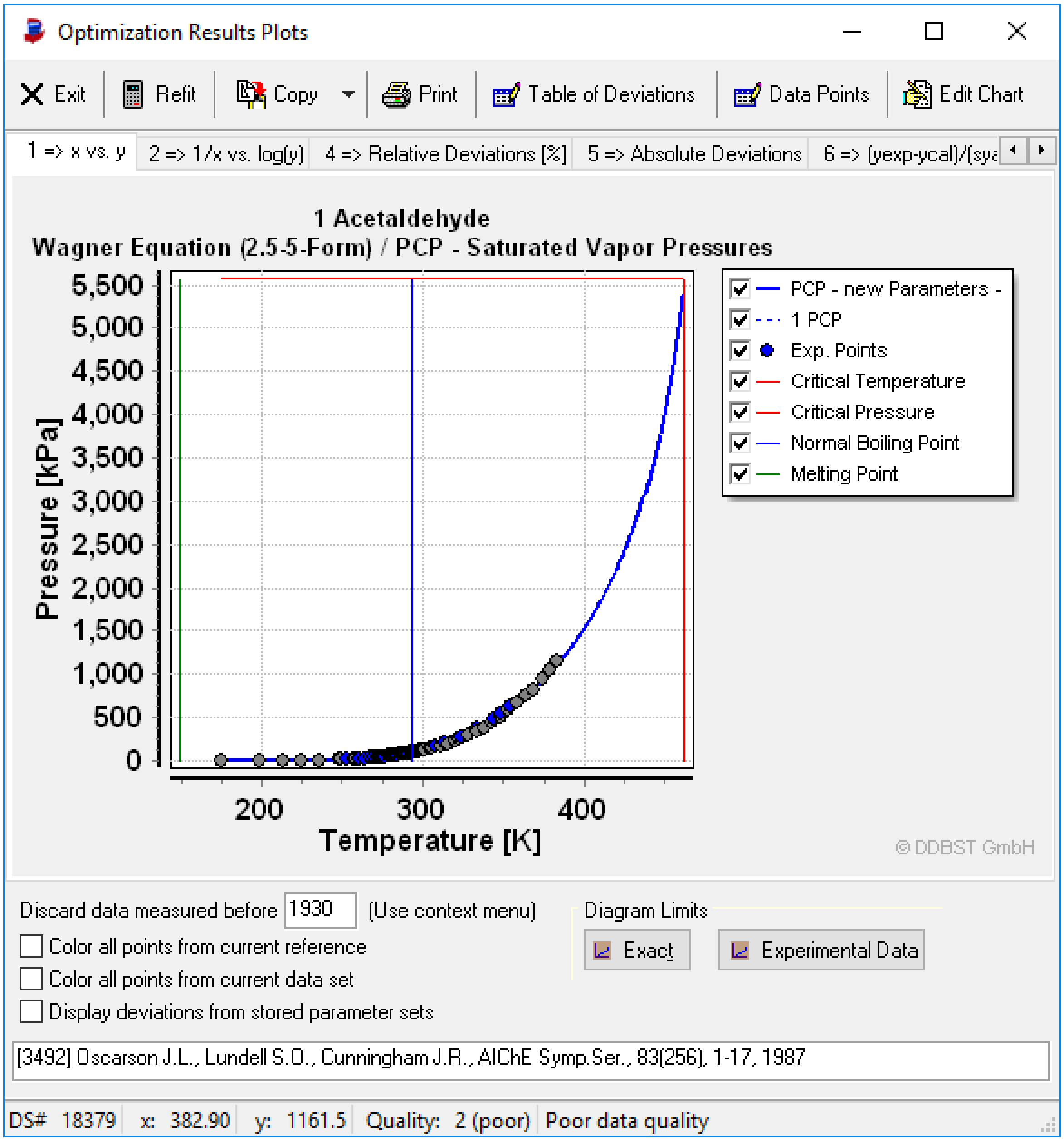
Figure 11 Fit Result

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.


Optimization Results Plots
Exit
Refit
Copy
Print
Table of Deviations
Data Points
Edit Chart
1 => x vs. y
2 => 1/x vs. log(y)
4 => Relative Deviations [%]
5 => Absolute Deviations
6 => (yexp-ycal)/(sy
1 Acetaldehyde
Wagner Equation (2.5-5-Form) / PCP - Saturated Vapor Pressures
Pressure [kPa]
5,500
5,000
4,500
4,000
3,500
3,000
2,500
2,000
1,500
1,000
500
0
200
300
400
Temperature [K]
☑ PCP - new Parameters -
☑ 1 PCP
☑ Exp. Points
☑ Critical Temperature
☑ Critical Pressure
☑ Normal Boiling Point
☑ Melting Point
© DDBST GmbH
Diagram Limits
Exact
Experimental Data

Discard data measured before 1930 (Use context menu)

☐ Color all points from current reference

☐ Color all points from current data set

☐ Display deviations from stored parameter sets

[3492] Oscarson J.L., Lundell S.O., Cunningham J.R., AIChE Symp.Ser., 83(256), 1-17, 1987

DS# 18379 x: 382.90 y: 1161.5 Quality: 2 (poor) Poor data quality

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 "Experimental Data" button adjusts the diagram so that the experimental data are filling the chart window.

Diagram Limits
Exact
Experimental Data

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. The "Exact" button restores the original diagram so that all data are shown.

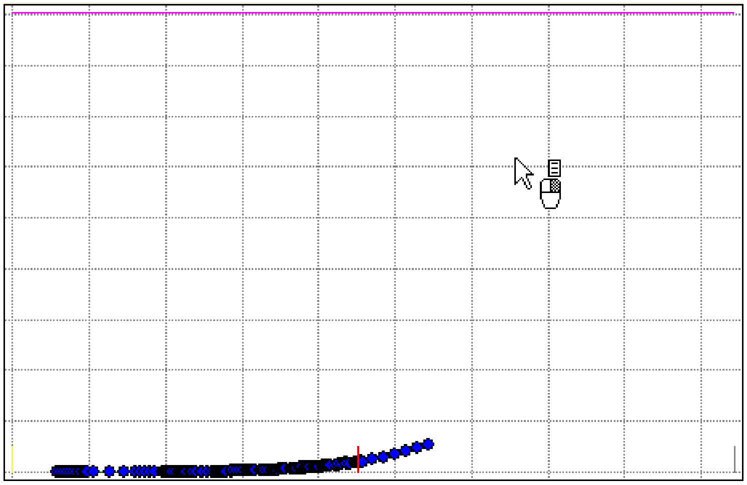


Figure 13: "Exact"

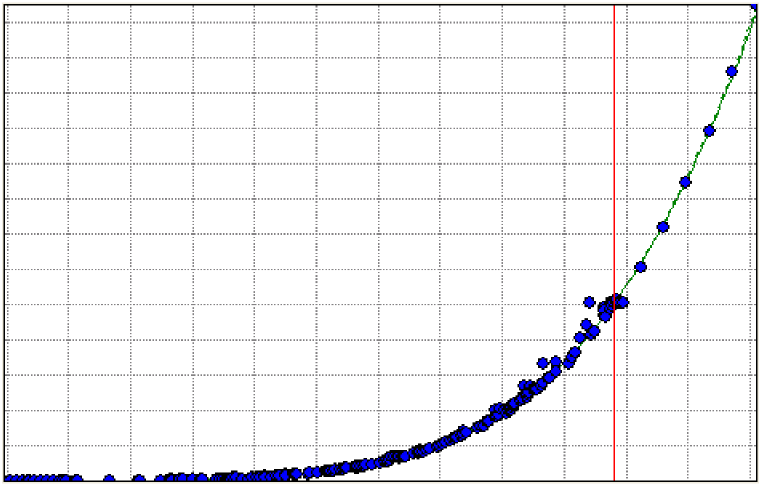


Figure 14: "Experimental Data"

Through a context menu on the plot it is possible to

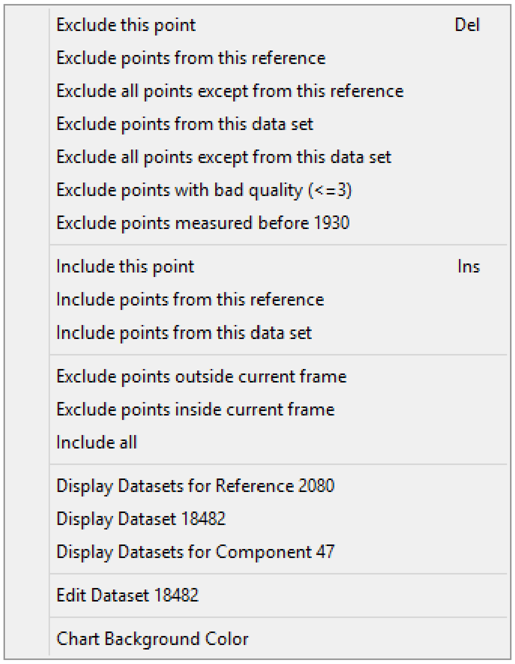
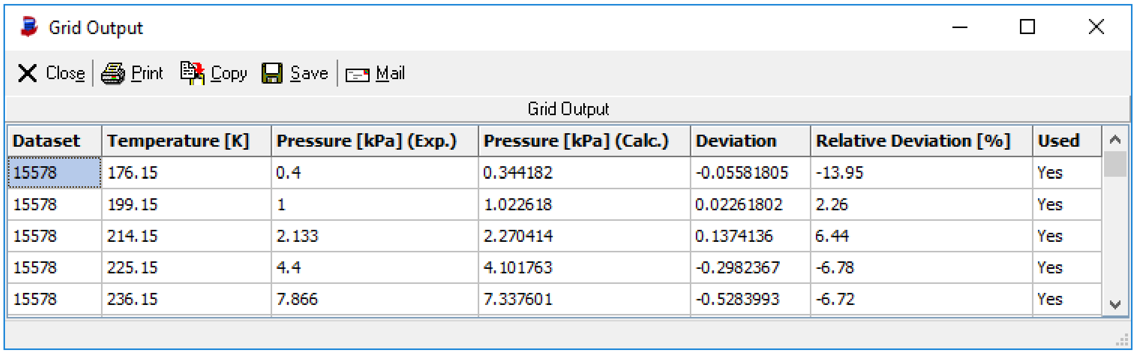

Exclude this point Del
Exclude points from this reference
Exclude all points except from this reference
Exclude points from this data set
Exclude all points except from this data set
Exclude points with bad quality (<=3)
Exclude points measured before 1930
Include this point Ins
Include points from this reference
Include points from this data set
Exclude points outside current frame
Exclude points inside current frame
Include all
Display Datasets for Reference 2080
Display Dataset 18482
Display Datasets for Component 47
Edit Dataset 18482
Chart Background Color

Figure 15 Plot Context Menu

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

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.

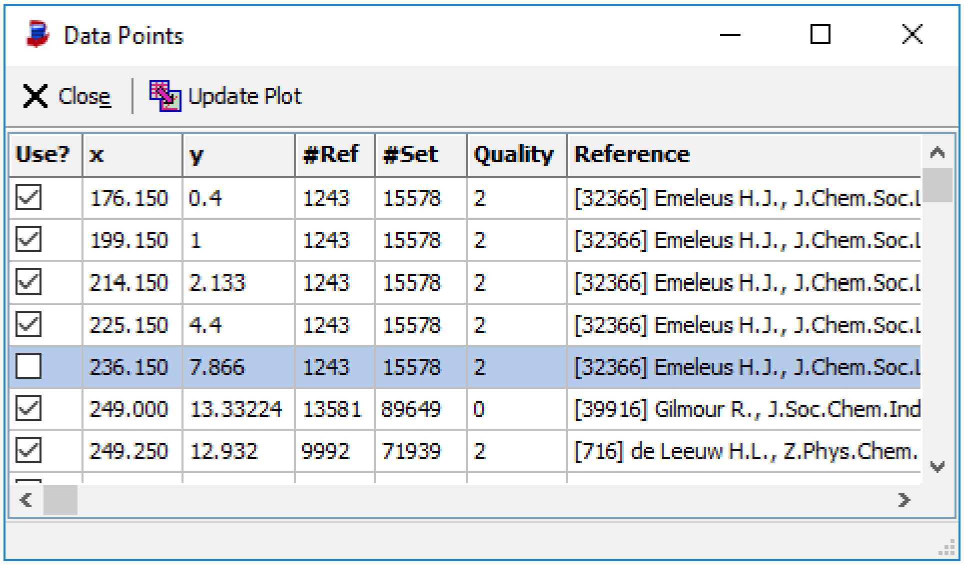

Grid Output
Close
Print
Copy
Save
Mail
Grid Output

Dataset	Temperature [K]	Pressure [kPa] (Exp.)	Pressure [kPa] (Calc.)	Deviation	Relative Deviation [%]	Used
15578	176.15	0.4	0.344182	-0.05581805	-13.95	Yes
15578	199.15	1	1.022618	0.02261802	2.26	Yes
15578	214.15	2.133	2.270414	0.1374136	6.44	Yes
15578	225.15	4.4	4.101763	-0.2982367	-6.78	Yes
15578	236.15	7.866	7.337601	-0.5283993	-6.72	Yes

Figure 16 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.

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.

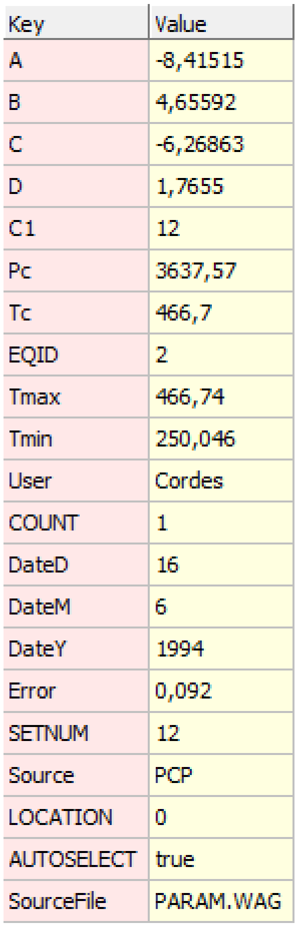


Use?	x	y	#Ref	#Set	Quality	Reference
☑	176.150	0.4	1243	15578	2	[32366] Emeleus H.J., J.Chem.Soc.L
☑	199.150	1	1243	15578	2	[32366] Emeleus H.J., J.Chem.Soc.L
☑	214.150	2.133	1243	15578	2	[32366] Emeleus H.J., J.Chem.Soc.L
☑	225.150	4.4	1243	15578	2	[32366] Emeleus H.J., J.Chem.Soc.L
☐	236.150	7.866	1243	15578	2	[32366] Emeleus H.J., J.Chem.Soc.L
☑	249.000	13.33224	13581	89649	0	[39916] Gilmour R., J.Soc.Chem.Ind
☑	249.250	12.932	9992	71939	2	[716] de Leeuw H.L., Z.Phys.Chem.

Figure 17: Data Points Selection

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.

4 Understanding the ParameterDDB Data Set Display



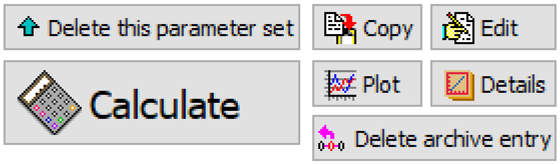
Key	Value
A	-8,41515
B	4,65592
C	-6,26863
D	1,7655
C1	12
Pc	3637,57
Tc	466,7
EQID	2
Tmax	466,74
Tmin	250,046
User	Cordes
COUNT	1
DateD	16
DateM	6
DateY	1994
Error	0,092
SETNUM	12
Source	PCP
LOCATION	0
AUTOSELECT	true
SourceFile	PARAM.WAG

Figure 18 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.

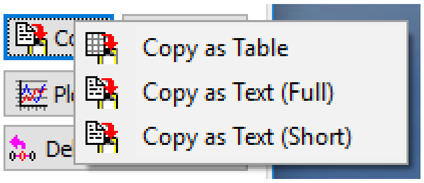
1. The keys “A”, “B”, “C”, “D” and so on are the parameters of the equations.
2. “C1” is the DDB component number. Its name can be found in the component editor.
3. “Pc”, “Tc” are critical temperature and pressure. Other possible entries are e.g. “Tb”.
4. “EQID” is the internal equation number.
5. “Tmax” 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


Delete this parameter set
Copy
Edit
Calculate
Plot
Details
Delete archive entry

5.1 Copy

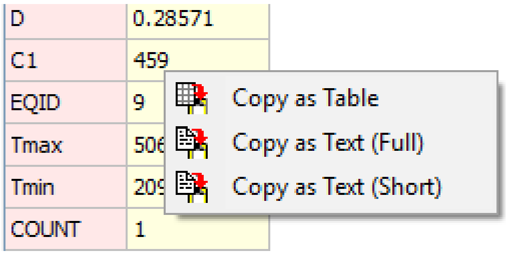
The data set grid will be copied to the windows clipboard as it is displayed in Figure 18 (source) and Figure 19 (destination).

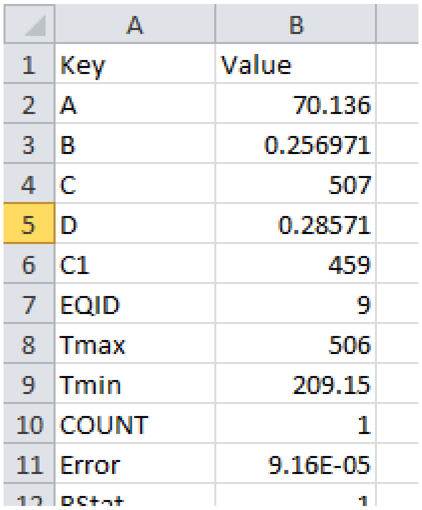

Copy as Table
Copy as Text (Full)
Copy as Text (Short)

Three formats are supported:

1. "Copy as Table" with key and value separated by tab. This is useful for pasting the content into a spreadsheet.
2. "Copy as Text (Full)" with key and value separated by the equation sign ("="). This is a useful format for pasting into text processors.
3. "Copy as Text (Short) with key and value separated by the equation sign ("=") but limited to parameters and validity limits. This is a useful format for pasting into mails.

The Copy function are also available in a context menu of the parameter grid.


D
0.28571
C1
459
EQID
9
Tmax
506
Tmin
209
COUNT
1
Copy as Table
Copy as Text (Full)
Copy as Text (Short)



	A	B
1	Key	Value
2	A	70.136
3	B	0.256971
4	C	507
5	D	0.28571
6	C1	459
7	EQID	9
8	Tmax	506
9	Tmin	209.15
10	COUNT	1
11	Error	9.16E-05

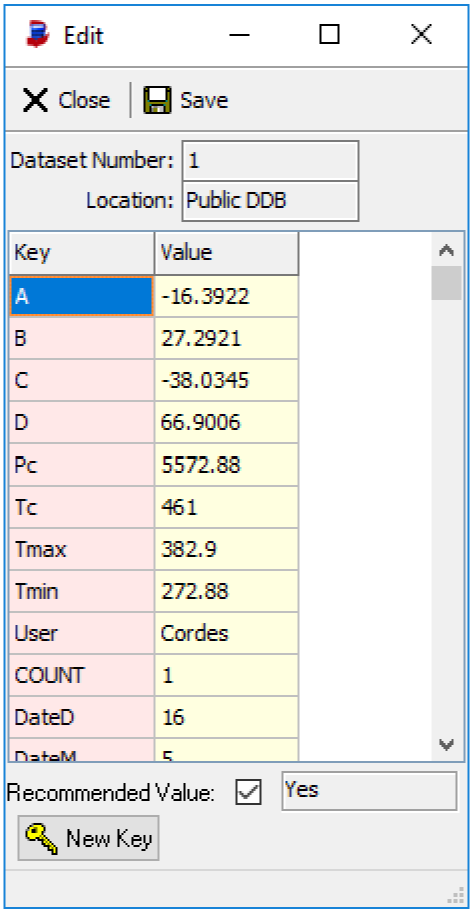
Figure 19 Data set pasted in spreadsheet

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 (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.



Dataset Number: 1
Location: Public DDB

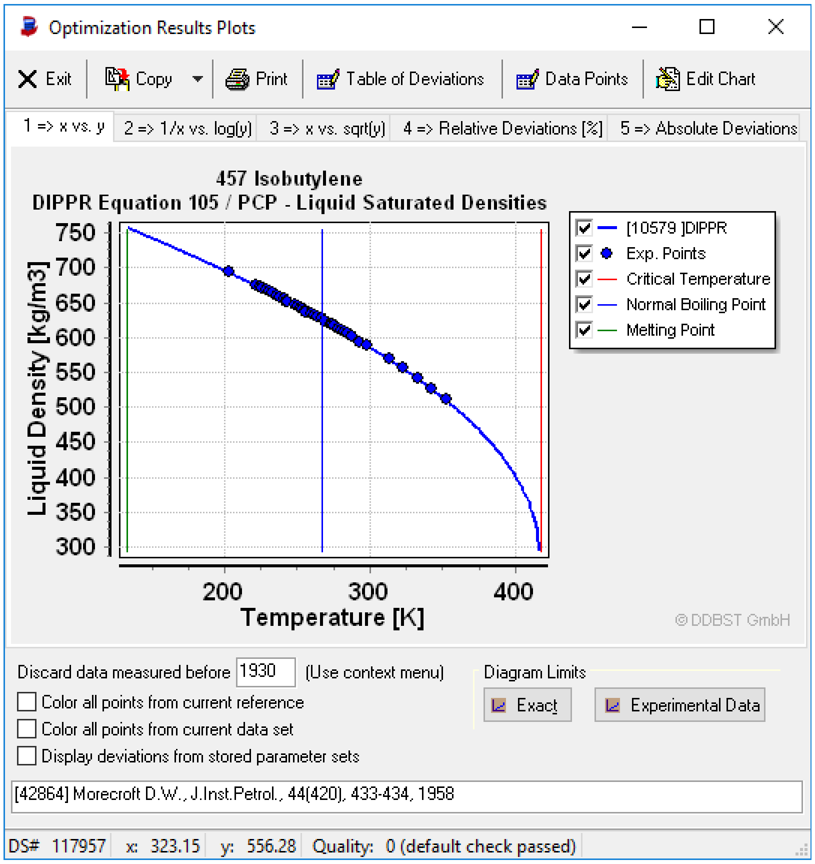
Key	Value
A	-16.3922
B	27.2921
C	-38.0345
D	66.9006
Pc	5572.88
Tc	461
Tmax	382.9
Tmin	272.88
User	Cordes
COUNT	1
DateD	16
DateM	5

Recommended Value: ☑ Yes

Figure 20: Data set editor

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.


Optimization Results Plots
Exit
Copy
Print
Table of Deviations
Data Points
Edit Chart
1 => x vs. y
2 => 1/x vs. log(y)
3 => x vs. sqrt(y)
4 => Relative Deviations [%]
5 => Absolute Deviations
457 Isobutylene
DIPPR Equation 105 / PCP - Liquid Saturated Densities
Liquid Density [kg/m3]
750
700
650
600
550
500
450
400
350
300
200
300
400
Temperature [K]
☑ [10579]DIPPR
☑ Exp. Points
☑ Critical Temperature
☑ Normal Boiling Point
☑ Melting Point
© DDBST GmbH
Diagram Limits
Exact
Experimental Data

Discard data measured before 1930 (Use context menu)

☐ Color all points from current reference

☐ Color all points from current data set

☐ Display deviations from stored parameter sets

[42864] Morecroft D.W., J.Inst.Petrol., 44(420), 433-434, 1958

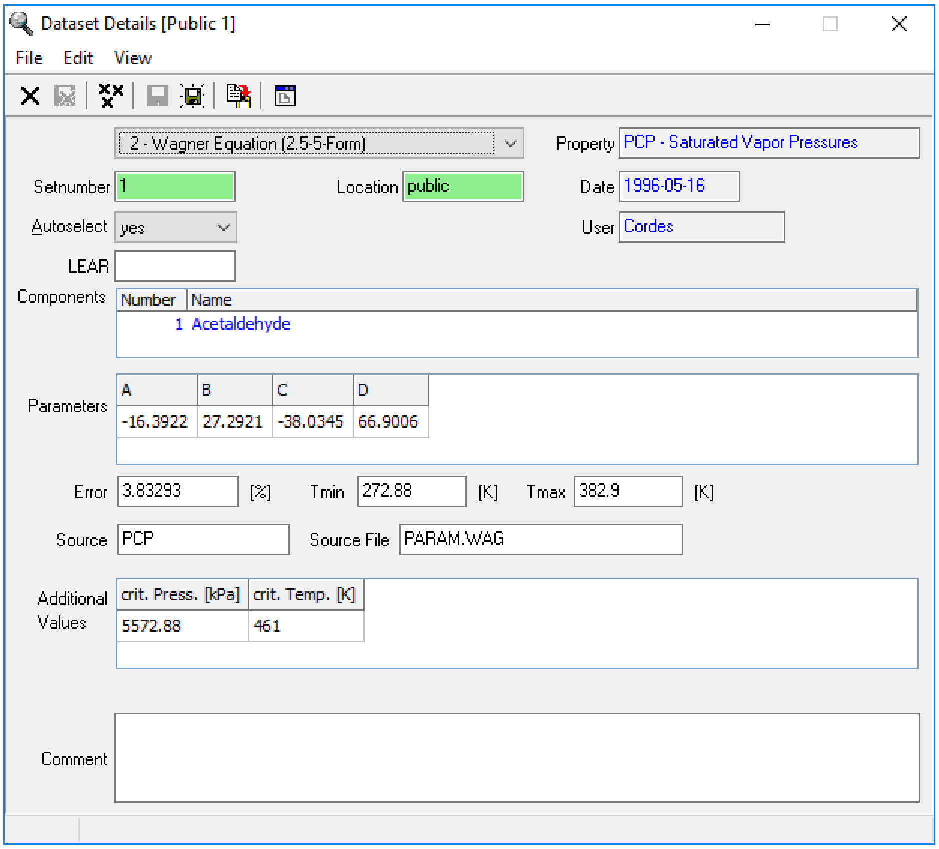
DS# 117957 x: 323.15 y: 556.28 Quality: 0 (default check passed)

Figure 21: Plot output

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”.



2 - Wagner Equation (2.5-5-Form)

Property: PCP - Saturated Vapor Pressures

Setnumber: 1

Location: public

Date: 1996-05-16

Autoselect: yes

User: Cordes

LEAR:

Components

Number	Name
1	Acetaldehyde

Parameters

A	B	C	D
-16.3922	27.2921	-38.0345	66.9006

Error: 3.83293 [%] Tmin: 272.88 [K] Tmax: 382.9 [K]

Source: PCP

Source File: PARAM.WAG

Additional Values

crit. Press. [kPa]	crit. Temp. [K]
5572.88	461

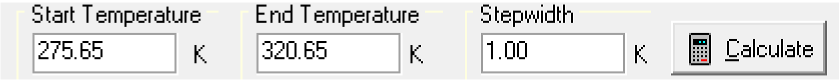
Comment:

Figure 22 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

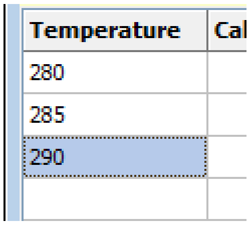


Start Temperature: 275.65 K

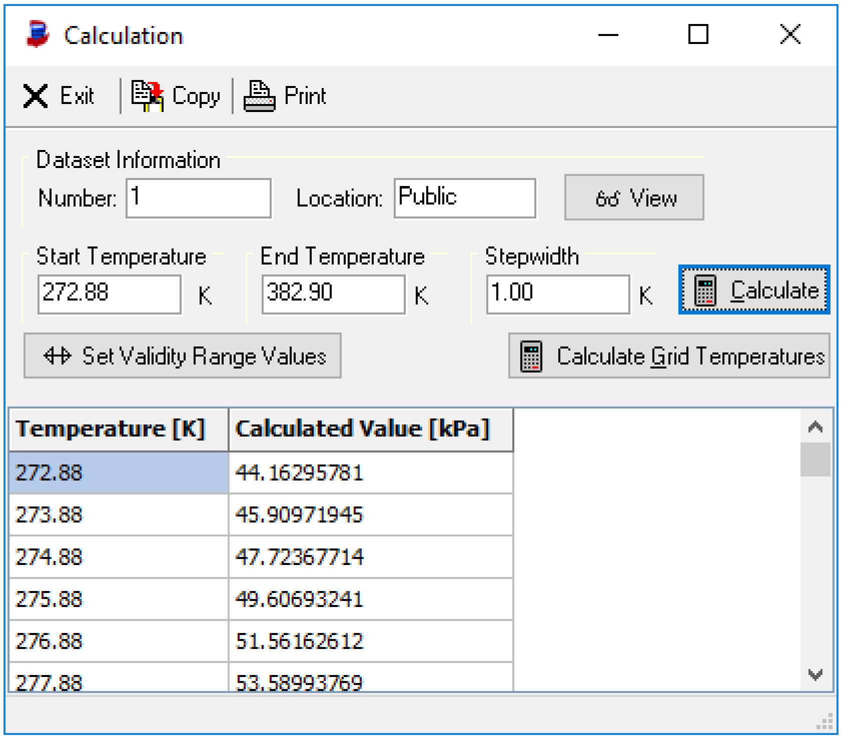
End Temperature: 320.65 K

Stepwidth: 1.00 K

or single values typed in the data grid.



Temperature	Cal
280	
285	
290	



Dataset Information

Number: 1

Location: Public

Start Temperature: 272.88 K

End Temperature: 382.90 K

Stepwidth: 1.00 K

Temperature [K]	Calculated Value [kPa]
272.88	44.16295781
273.88	45.90971945
274.88	47.72367714
275.88	49.60693241
276.88	51.56162612
277.88	53.58993769

Figure 23: Calculate properties with stored parameters

6 Fit Archive

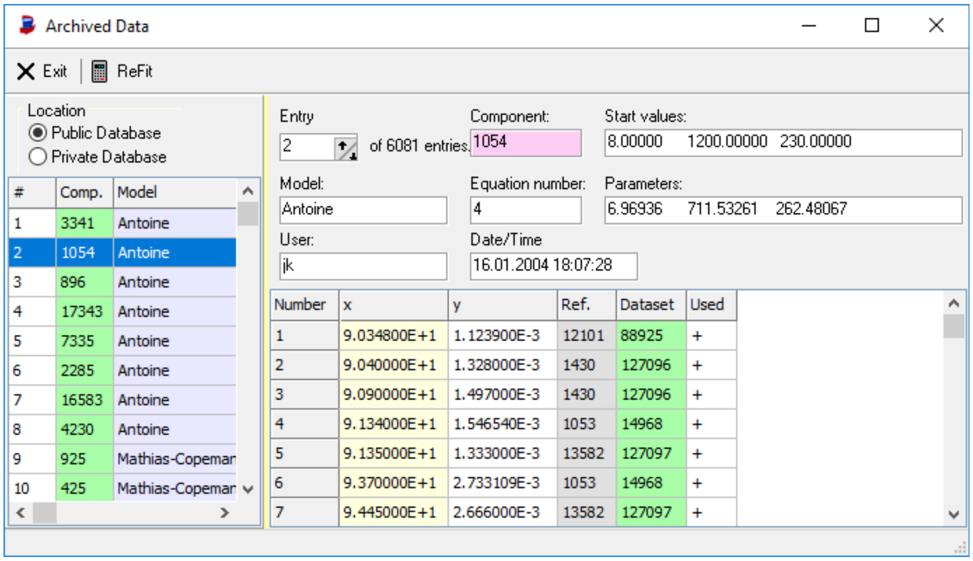
PCPEquationFit stores a history of fitted parameters and used data sets. This archive is accessible through the tool bar button Archive .

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 24) 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 data set 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 25).


Archived Data
Exit
ReFit

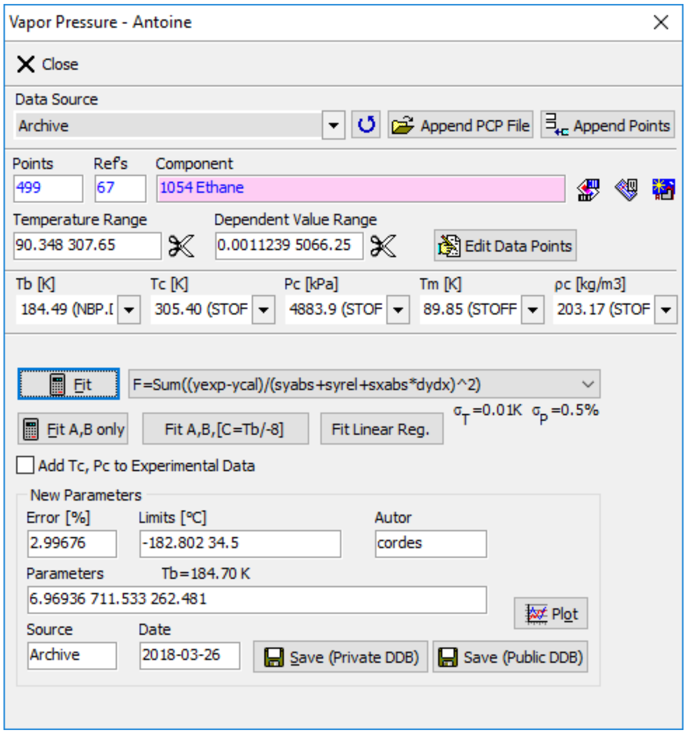
Location
● Public Database
○ Private Database

#	Comp.	Model
1	3341	Antoine
2	1054	Antoine
3	896	Antoine
4	17343	Antoine
5	7335	Antoine
6	2285	Antoine
7	16583	Antoine
8	4230	Antoine
9	925	Mathias-Copeman
10	425	Mathias-Copeman

Entry: 2 of 6081 entries
Component: 1054
Start values: 8.00000 1200.00000 230.00000
Model: Antoine
Equation number: 4
Parameters: 6.96936 711.53261 262.48067
User: jk
Date/Time: 16.01.2004 18:07:28

Number	x	y	Ref.	Dataset	Used
1	9.034800E+1	1.123900E-3	12101	88925	+
2	9.040000E+1	1.328000E-3	1430	127096	+
3	9.090000E+1	1.497000E-3	1430	127096	+
4	9.134000E+1	1.546540E-3	1053	14968	+
5	9.135000E+1	1.333000E-3	13582	127097	+
6	9.370000E+1	2.733109E-3	1053	14968	+
7	9.445000E+1	2.666000E-3	13582	127097	+

Figure 24 Fit archive

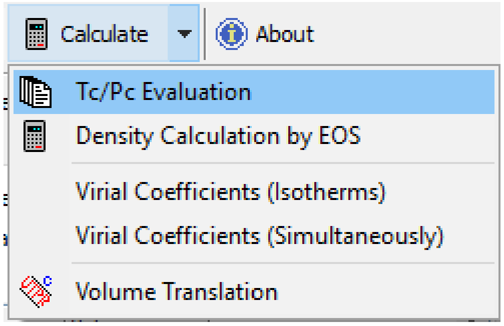

Vapor Pressure - Antoine
Close
Append PCP File
Append Points
Edit Data Points
Fit
Fit A,B only
Fit A,B,[C=Tb/-8]
Fit Linear Reg.
Plot
Save (Private DDB)
Save (Public DDB)

Data Source: Archive
Points: 499
Refs: 67
Component: 1054 Ethane
Temperature Range: 90.348 307.65
Dependent Value Range: 0.0011239 5066.25
Tb [K]: 184.49 (NBP.I
Tc [K]: 305.40 (STOF
Pc [kPa]: 4883.9 (STOF
Tm [K]: 89.85 (STOFF
ρc [kg/m3]: 203.17 (STOF
F=Sum((yexp-ycal)/(syabs+syrel+sxabs*dydx)^2)
σ_T=0.01K σ_P=0.5%
☐ Add Tc, Pc to Experimental Data

New Parameters
Error [%]: 2.99676
Limits [°C]: -182.802 34.5
Autor: cordes
Parameters: 6.96936 711.533 262.481
Tb=184.70 K
Source: Archive
Date: 2018-03-26

Figure 25 Refit with archived data

7 T_c/P_c Evaluation


Calculate
About
Tc/Pc Evaluation
Density Calculation by EOS
Virial Coefficients (Isotherms)
Virial Coefficients (Simultaneously)
Volume Translation

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.

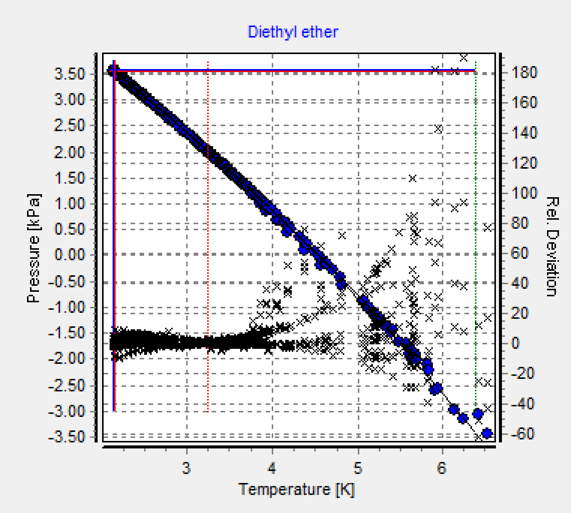
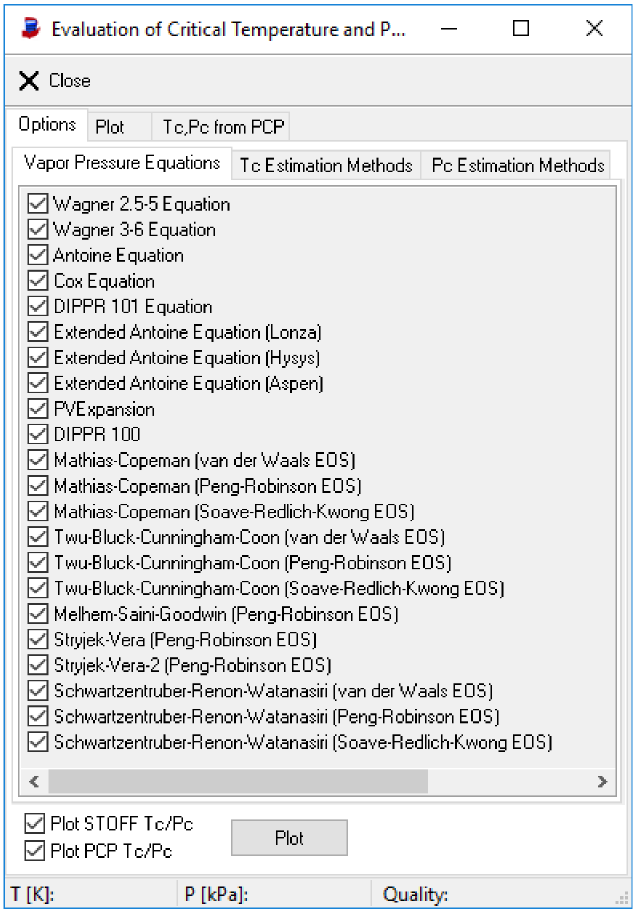


Figure 26 Critical Data Evaluation - Plot

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


Evaluation of Critical Temperature and P...
Close
Options
Plot
Tc,Pc from PCP
Vapor Pressure Equations
Tc Estimation Methods
Pc Estimation Methods
Plot
T [K]:
P [kPa]:
Quality:

☑ Wagner 2.5-5 Equation
☑ Wagner 3-6 Equation
☑ Antoine Equation
☑ Cox Equation
☑ DIPPR 101 Equation
☑ Extended Antoine Equation (Lonza)
☑ Extended Antoine Equation (Hysys)
☑ Extended Antoine Equation (Aspen)
☑ PVExpansion
☑ DIPPR 100
☑ Mathias-Copeman (van der Waals EOS)
☑ Mathias-Copeman (Peng-Robinson EOS)
☑ Mathias-Copeman (Soave-Redlich-Kwong EOS)
☑ Twu-Bluck-Cunningham-Coon (van der Waals EOS)
☑ Twu-Bluck-Cunningham-Coon (Peng-Robinson EOS)
☑ Twu-Bluck-Cunningham-Coon (Soave-Redlich-Kwong EOS)
☑ Melhem-Saini-Goodwin (Peng-Robinson EOS)
☑ Stryjek-Vera (Peng-Robinson EOS)
☑ Stryjek-Vera-2 (Peng-Robinson EOS)
☑ Schwartzentruber-Renon-Watanasiri (van der Waals EOS)
☑ Schwartzentruber-Renon-Watanasiri (Peng-Robinson EOS)
☑ Schwartzentruber-Renon-Watanasiri (Soave-Redlich-Kwong EOS)

☑ Plot STOFF Tc/Pc
☑ Plot PCP Tc/Pc

Figure 27 Critical Data Evaluation - Vapor Pressure Equations

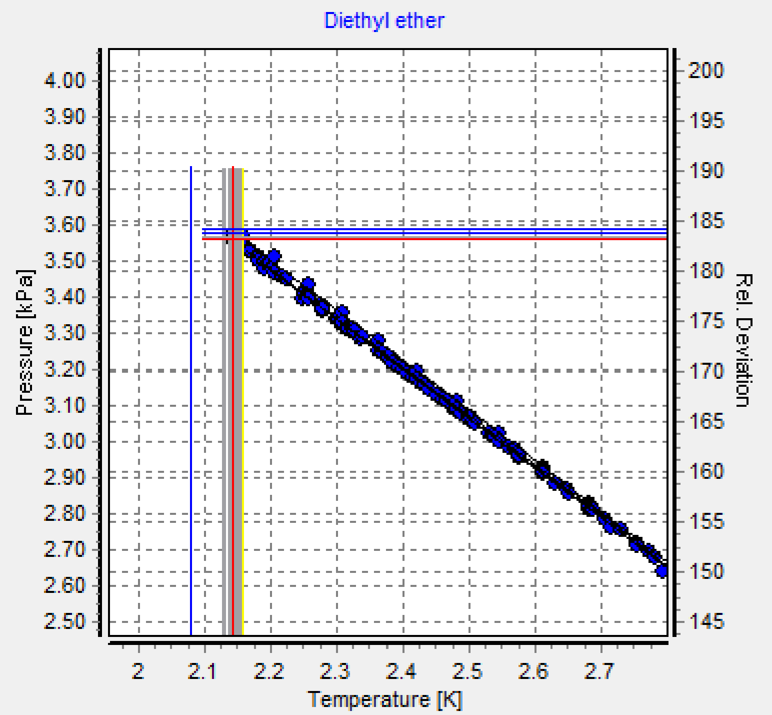


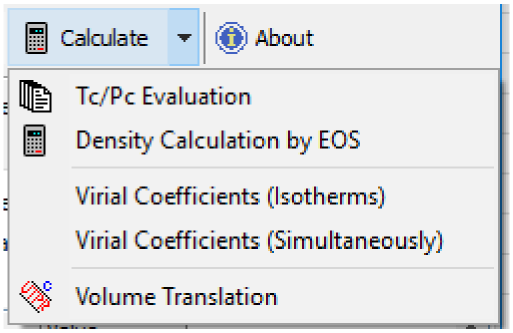
Figure 28: Zoomed in for Critical Point

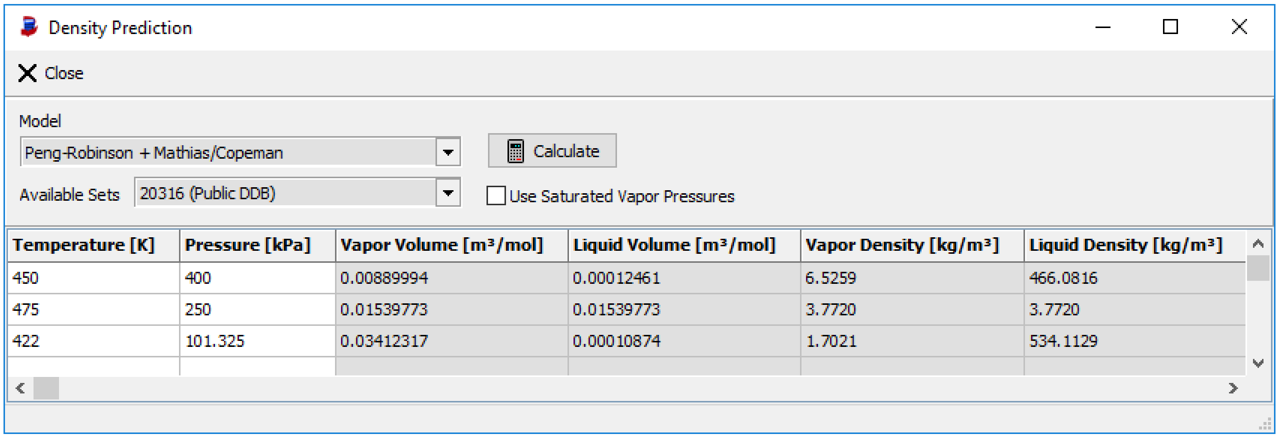
The resulting diagram shows all experimental, calculated, and estimated data points in a Temperature vs. Pressure plot. Deviations are shown in the same diagram with its scale on the diagram's right side.

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


Calculate
About
Tc/Pc Evaluation
Density Calculation by EOS
Virial Coefficients (Isotherms)
Virial Coefficients (Simultaneously)
Volume Translation


Density Prediction
Close
Calculate

Model: Peng-Robinson + Mathias/Copeman

Available Sets: 20316 (Public DDB)

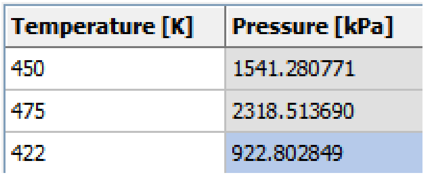
☐ Use Saturated Vapor Pressures

Temperature [K]	Pressure [kPa]	Vapor Volume [m³/mol]	Liquid Volume [m³/mol]	Vapor Density [kg/m³]	Liquid Density [kg/m³]
450	400	0.00889994	0.00012461	6.5259	466.0816
475	250	0.01539773	0.01539773	3.7720	3.7720
422	101.325	0.03412317	0.00010874	1.7021	534.1129

Figure 29: Density Prediction

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.



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

Figure 30: 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 data sets 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 ¾ 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 ½ 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 $\frac{Compressibility\ Factor-1}{Density}$ 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

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

and the third virial coefficient

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

The equation evolved up to the third virial coefficient

$$z = 1 + B * d + C * d^2$$

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

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

Because virial coefficients are normally shown in molar units (B [cm^3*mol^{-1}], C[cm^6*mol^{-2}]) and densities in [$kg*m^3$] the ordinate shows $\frac{Compressibility\ Factor - 1}{Density}$ in [cm^3*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.

$$F = \sum_i \left(z_i - zcalc_i \right)^2 \overset{!}{=} Min$$

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 $zcalc_i$ for the experimental density ρ_i

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

with

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

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 [cm^3*mol^{-1}] and the third in [cm^6*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 `PmaxB`

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 PmaxB is the maximum pressure where the equation with only B yields a real solution.

$$PmaxB = -\frac{R \cdot B}{4 \cdot B}$$

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 data sets, especially for non-isothermal data (see previous chapter 32 “Isotherms“ for isothermal data). Additionally the program allows to select data sets 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 PρT space to the Pρ (pressure against density) plain. The virial equation is drawn as a series of isothermal P=f(ρ) 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

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

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

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

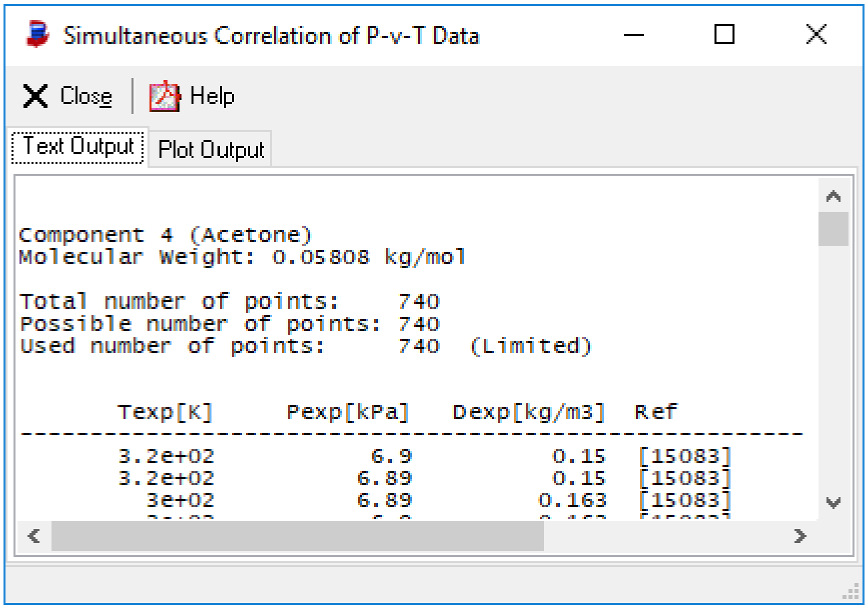
$b_2[m^3\cdot mol^{-1}\cdot K]$

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

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

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⇒cm).

9.2.4 Short Tutorial

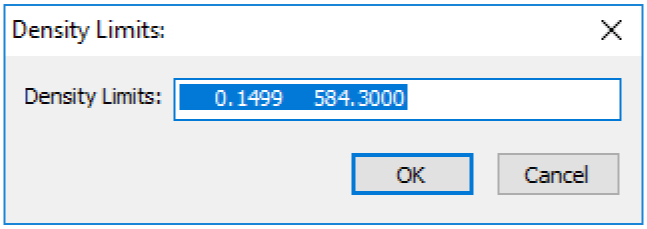


```
Component 4 (Acetone)
Molecular Weight: 0.05808 kg/mol

Total number of points:    740
Possible number of points: 740
Used number of points:     740   (Limited)


       Texp[K]      Pexp[kPa]   Dexp[kg/m3]  Ref
-------------------------------------------------------
       3.2e+02           6.9          0.15  [15083]
       3.2e+02          6.89          0.15  [15083]
         3e+02          6.89         0.163  [15083]
```

Figure 31: Start Screen

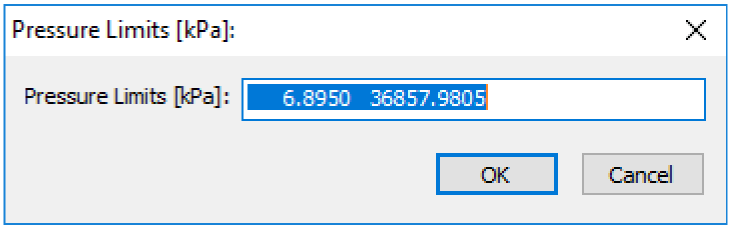
Start Screen, Figure 31, shows the start screen. The PVT data are either obtained from the DDB pure component properties database if a component is selected or loaded from a PCP interface file which has been created by another program.

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.



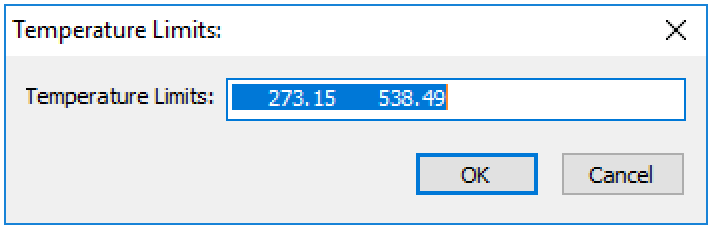
Density Limits: 0.1499 584.3000

Figure 32: Density Limits



Pressure Limits [kPa]: 6.8950 36857.9805

Figure 33: Pressure Limits



Temperature Limits: 273.15 538.49

Figure 34: 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 35) 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.

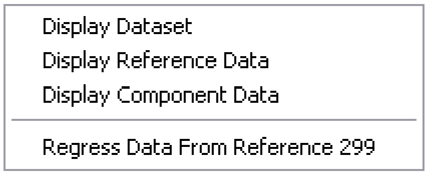

Display Dataset
Display Reference Data
Display Component Data
Regress Data From Reference 299

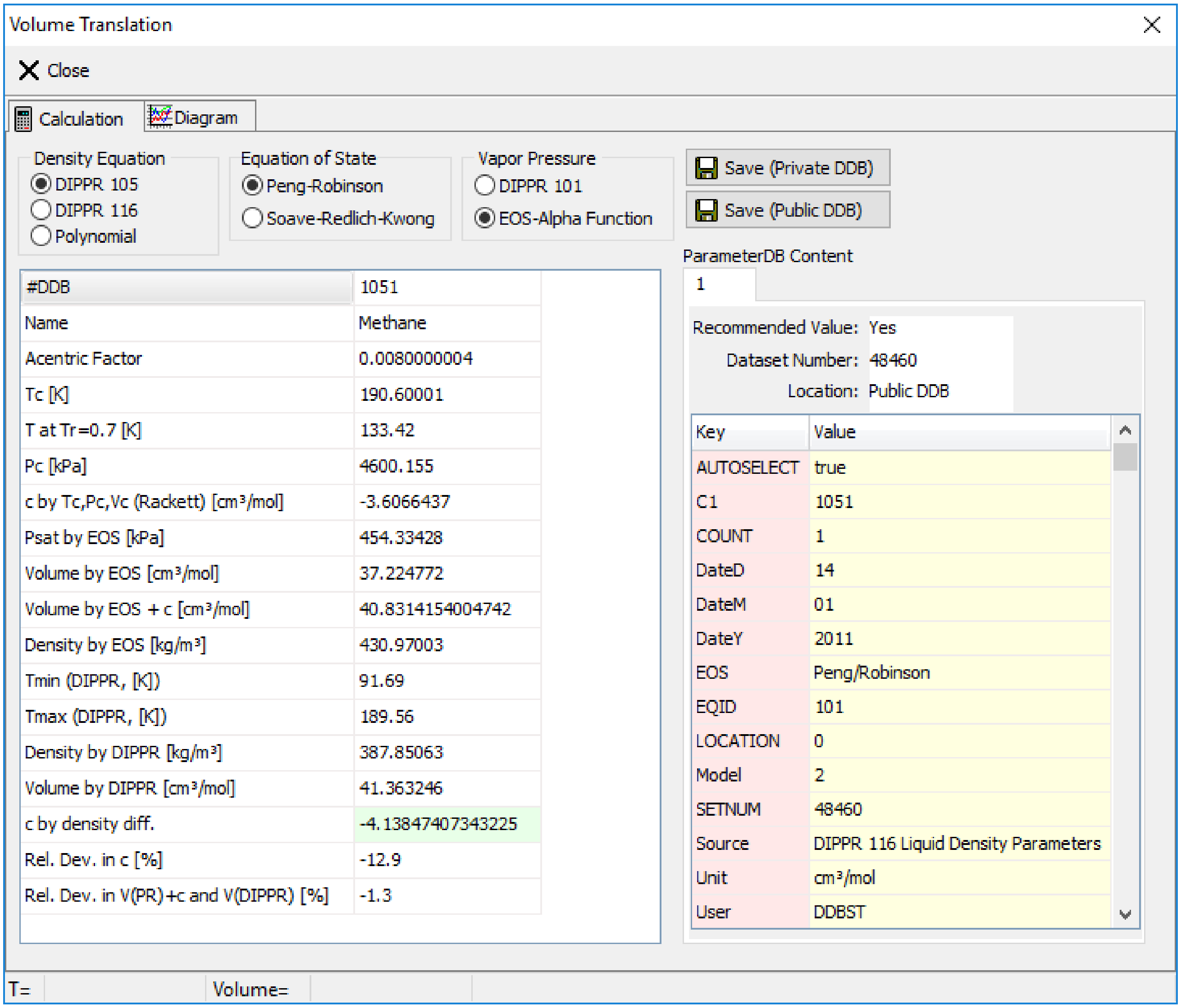
Figure 35

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

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.



Density Equation
● DIPPR 105
○ DIPPR 116
○ Polynomial

Equation of State
● Peng-Robinson
○ Soave-Redlich-Kwong

Vapor Pressure
○ DIPPR 101
● EOS-Alpha Function

#DDB	1051
Name	Methane
Acentric Factor	0.0080000004
Tc [K]	190.60001
T at Tr=0.7 [K]	133.42
Pc [kPa]	4600.155
c by Tc,Pc,Vc (Rackett) [cm³/mol]	-3.6066437
Psat by EOS [kPa]	454.33428
Volume by EOS [cm³/mol]	37.224772
Volume by EOS + c [cm³/mol]	40.8314154004742
Density by EOS [kg/m³]	430.97003
Tmin (DIPPR, [K])	91.69
Tmax (DIPPR, [K])	189.56
Density by DIPPR [kg/m³]	387.85063
Volume by DIPPR [cm³/mol]	41.363246
c by density diff.	-4.13847407343225
Rel. Dev. in c [%]	-12.9
Rel. Dev. in V(PR)+c and V(DIPPR) [%]	-1.3

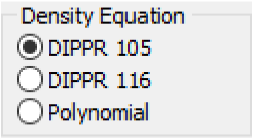
ParameterDB Content
1

Recommended Value: Yes
Dataset Number: 48460
Location: Public DDB

Key	Value
AUTOSELECT	true
C1	1051
COUNT	1
DateD	14
DateM	01
DateY	2011
EOS	Peng/Robinson
EQID	101
LOCATION	0
Model	2
SETNUM	48460
Source	DIPPR 116 Liquid Density Parameters
Unit	cm³/mol
User	DDBST

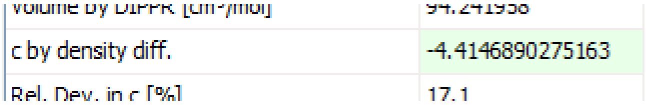
T=
Volume=

Figure 36: Volume Translation - Calculation



Density Equation
● DIPPR 105
○ DIPPR 116
○ Polynomial

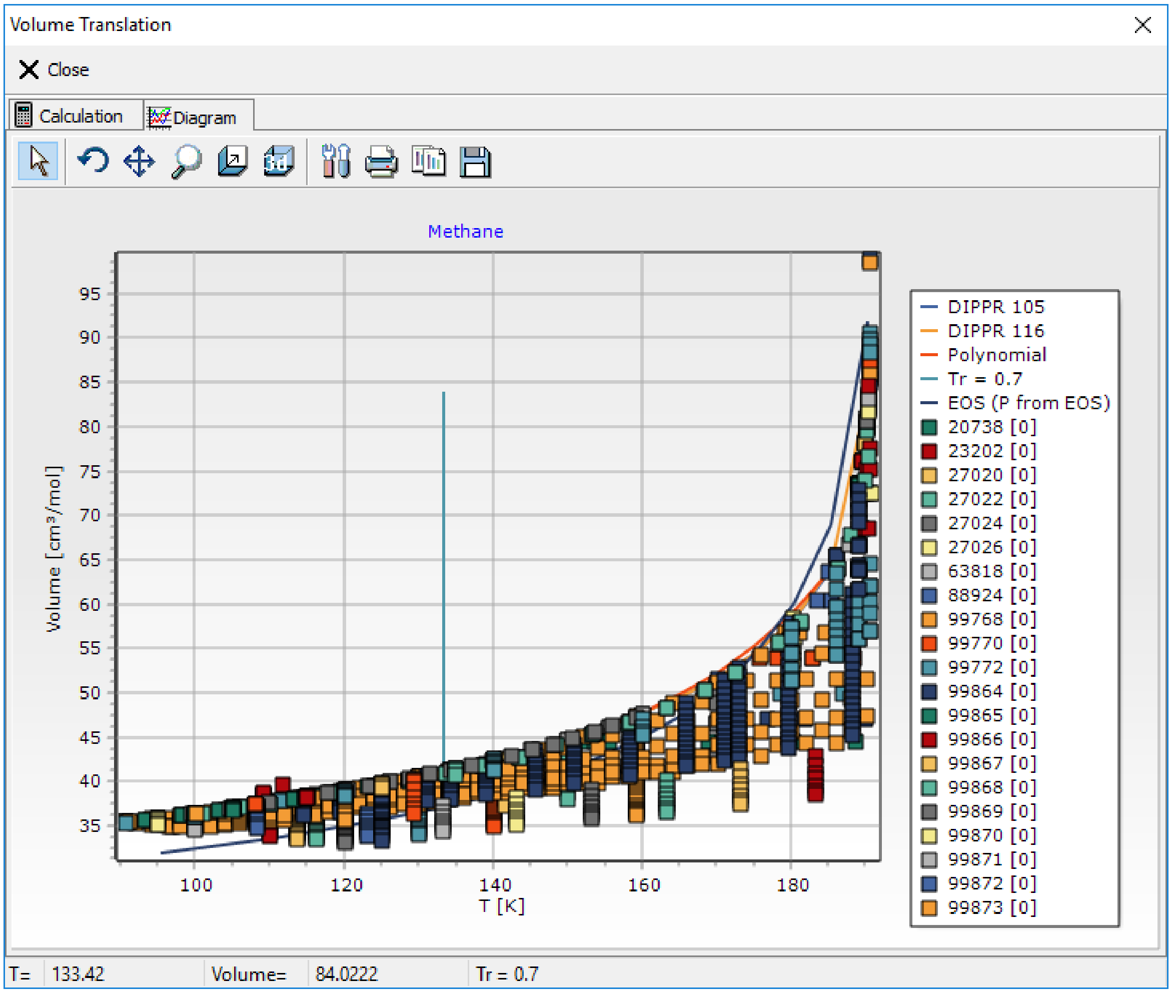
In this dialog the volumes calculated by the equations DIPPR 105, DIPPR 116, or Polynomial. The left table shows the calculation result with the volume translation value c in light green.



c by density diff.	-4.4146890275163
Rel. Dev. in c [%]	17.1

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

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


Volume Translation
Close
Calculation
Diagram
Methane
Volume [cm³/mol]
95
90
85
80
75
70
65
60
55
50
45
40
35
100
120
140
160
180
T [K]
DIPPR 105
DIPPR 116
Polynomial
Tr = 0.7
EOS (P from EOS)
20738 [0]
23202 [0]
27020 [0]
27022 [0]
27024 [0]
27026 [0]
63818 [0]
88924 [0]
99768 [0]
99770 [0]
99772 [0]
99864 [0]
99865 [0]
99866 [0]
99867 [0]
99868 [0]
99869 [0]
99870 [0]
99871 [0]
99872 [0]
99873 [0]

T= 133.42 Volume= 84.0222 Tr = 0.7

Figure 37: Volume Translation - Diagram

11 Simultaneous Regression of α Function Parameters

A simultaneous fitting tool for α parameters is available for Mathias-Copeman constants for Soave-Redlich-Kwong (used in PSRK) and for Twu-Bluck-Cunningham-Coon constants (used in VTPR).

The fitting routine supports the simultaneous fit of parameters to vapor pressures, heats of vaporization, second virial coefficients, and liquid heat capacities.

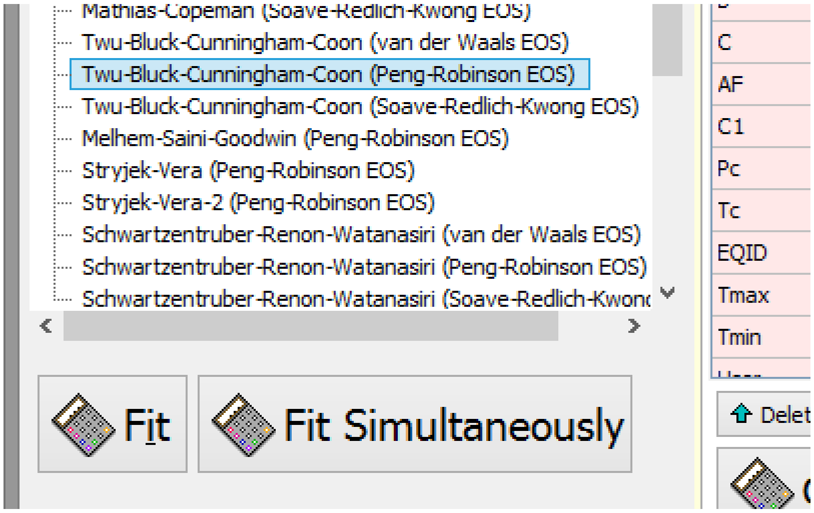
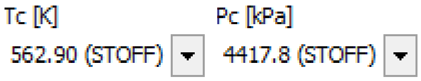

Mathias-Copeman (Soave-Redlich-Kwong EOS)
Twu-Bluck-Cunningham-Coon (van der Waals EOS)
Twu-Bluck-Cunningham-Coon (Peng-Robinson EOS)
Twu-Bluck-Cunningham-Coon (Soave-Redlich-Kwong EOS)
Melhem-Saini-Goodwin (Peng-Robinson EOS)
Stryjek-Vera (Peng-Robinson EOS)
Stryjek-Vera-2 (Peng-Robinson EOS)
Schwartzentruber-Renon-Watanasiri (van der Waals EOS)
Schwartzentruber-Renon-Watanasiri (Peng-Robinson EOS)
Schwartzentruber-Renon-Watanasiri (Soave-Redlich-Kwonç
C
AF
C1
Pc
Tc
EQID
Tmax
Tmin
Fit
Fit Simultaneously
Delet

Figure 38: Start simultaneous fit

The calculation dialog allows

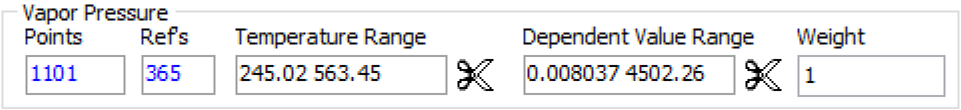
1. selecting or editing the appropriate critical temperature and pressure



Tc [K] 562.90 (STOFF)

Pc [kPa] 4417.8 (STOFF)

2. setting weights for the different properties
3. setting temperature and property ranges (cutting data points)

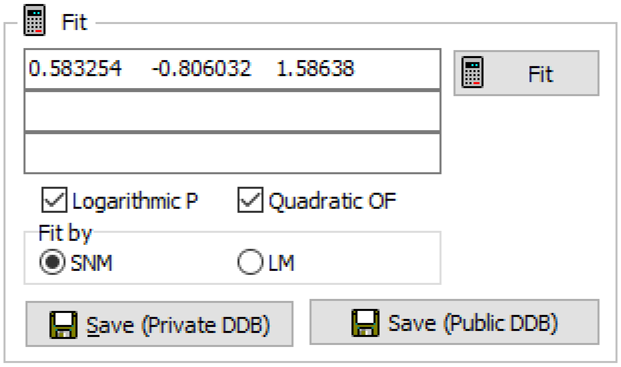


Vapor Pressure

Points	Ref's	Temperature Range	Dependent Value Range	Weight
1101	365	245.02 563.45	0.008037 4502.26	1

4. selecting the objective function with regard to the pressure (logarithmic or not) and with regard to all properties (quadratic or linear)
5. selecting the optimization routine (Simplex-Nelder-Mead or Levenberg-Marquardt)
6. plotting the calculated properties together with experimental data from the PCPDDB.

The found parameters can be stored in the public (from DDBST) or private data bank (for custom parameters).



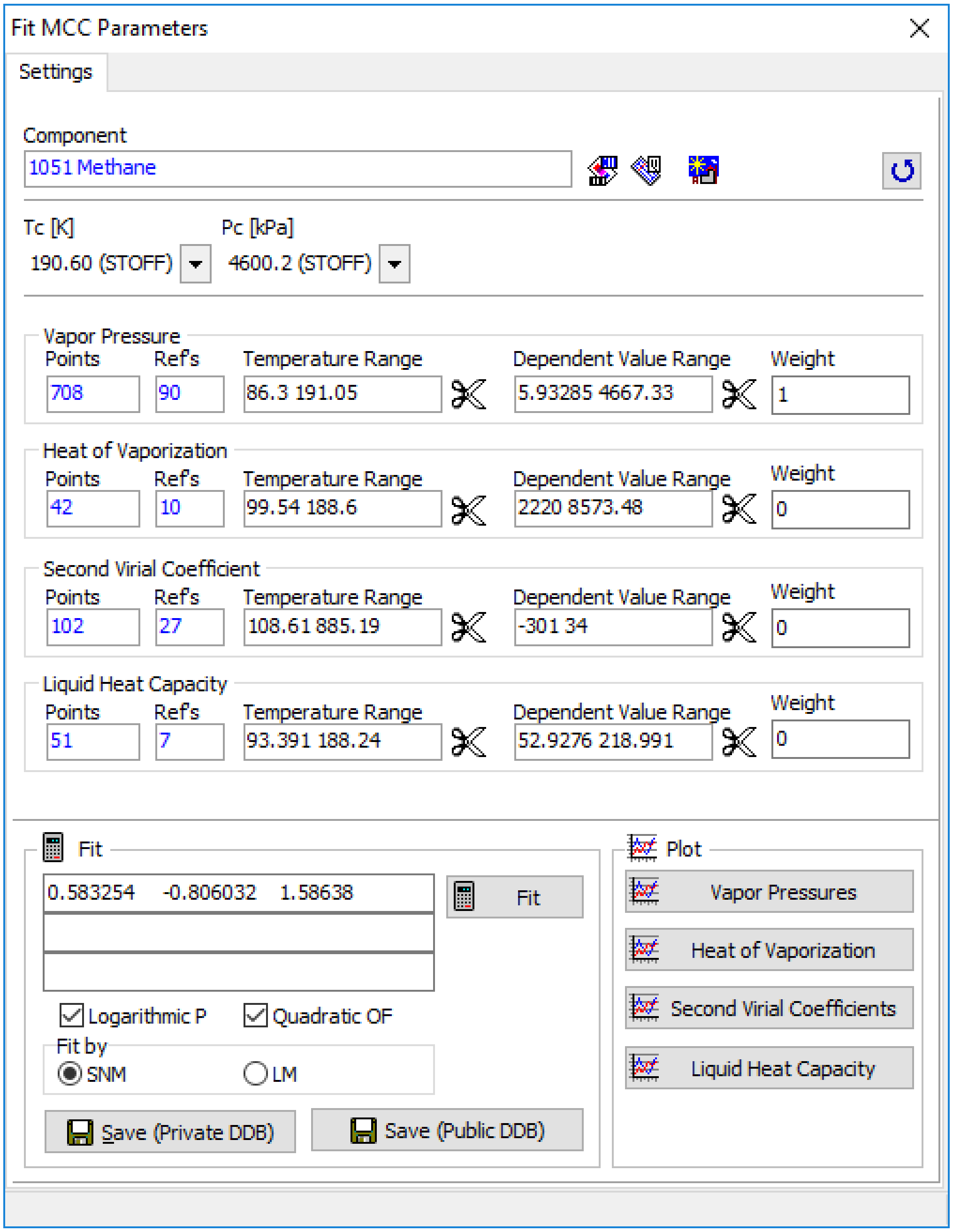
Fit

0.583254 -0.806032 1.58638

☑ Logarithmic P ☑ Quadratic OF

Fit by: ● SNM ○ LM

Fit
Save (Private DDB)
Save (Public DDB)


Fit MCC Parameters
Settings
Fit
Plot
Vapor Pressures
Heat of Vaporization
Second Virial Coefficients
Liquid Heat Capacity
Save (Private DDB)
Save (Public DDB)

Component: 1051 Methane

Tc [K]: 190.60 (STOFF)

Pc [kPa]: 4600.2 (STOFF)

	Points	Ref's	Temperature Range	Dependent Value Range	Weight
Vapor Pressure	708	90	86.3 191.05	5.93285 4667.33	1
Heat of Vaporization	42	10	99.54 188.6	2220 8573.48	0
Second Virial Coefficient	102	27	108.61 885.19	-301 34	0
Liquid Heat Capacity	51	7	93.391 188.24	52.9276 218.991	0

Fit: 0.583254 -0.806032 1.58638

☑ Logarithmic P ☑ Quadratic OF

Fit by: ● SNM ○ LM

Figure 39: Settings for simultaneous fitting