

Getting started with Simulis® Thermodynamics

Use Case 9: Create a compound
that is not available in databases

Software & Services In Process Simulation

We guide You to efficiency








ProSim

Introduction

This document presents the different steps to follow to create a new compound that is not present in databases and to determine its properties.

The steps are the following:

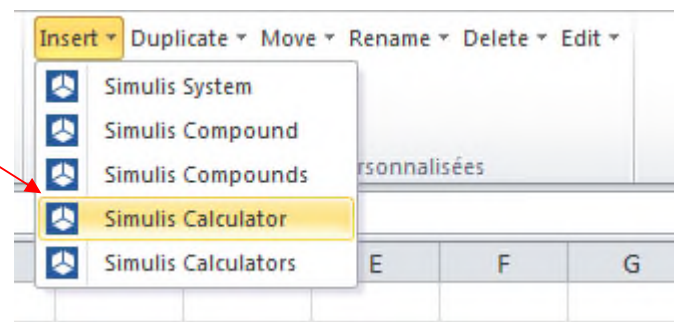
-  Step 1: Add a new compound
-  Step 2: Enter the SMILES of the compound
-  Step 3: Determine constant properties
-  Step 4: Decomposition into functional sub-groups
-  Step 5: Temperature dependent properties

Step 1: Add a new compound

ACCESS THE THERMODYNAMIC CALCULATOR EDITOR:

- If you are using Simulis Thermodynamics in Excel:

Create the calculator object in a spreadsheet



- If you are using Simulis Thermodynamics within another ProSim environment (ProSimPlus, BatchReactor, BatchColumn etc...):

Click on the thermodynamic icon to open the calculator editor:



or



Simulis Thermodynamics is a « software component » that you can integrate into different applications: ProSim software, Excel, Matlab, your own software, etc...

Step 1: Add a new compound

Thermodynamic calculator editor

CALCULATOR

FILE

- Open...
- Save as...

PACKAGE

SERVICES

- Calculate
- Export as a PSF file
- Diagrams
- Residue...
- Export as a PVT file
- Stream...
- Sigma profiles

MODIFICATIONS

CONFIGURATION

Name

Comments

Calculator type

Native

Show the expert mode

This window helps you to define the context of your thermodynamic calculator

COMPOUNDS MODEL PARAMETERS

#	IUPAC Name	CAS Registry Number®
1	[New compound]	

COMPOUNDS

FILE

- Open...
- Save as...
- Publish...

PACKAGE

EDIT

- Import compounds...
- Edit this compound...
- Create a new compound
- Remove all the compounds
- Clone this compound
- Update the compounds
- Delete the selection

SERVICES

- Create a pseudo-compound...
- Temperature dependent properties...
- Editor array
- Compare with the original
- Compare the compounds

ORDER

Move this compound up

Ok Cancel

CAS Registry Numbers® are the intellectual property of the American Chemical Society; and are used by ProSim SA with the express permission of ACS. CAS Registry Numbers® have not been verified by ACS and may be inaccurate.

Create a new compound and edit this compound (Double-click or right-click on the [New compound] added)

Step 1: Add a new compound

1. Enter known information and properties of the new compound:

- Name
- CAS Registry number
- Chemical formula
- Etc.

2. Enter the SMILES of the compound
Allows estimation of complementary properties from group contribution methods

Compound Editor

COMPOUND

FILE

- Open...
- Save as...

TOOLS

- Select a compound...
- Copy
- Paste
- PDF Export (Print)
- Excel Export
- Import
- Export
- Pseudo-compound...
- Properties prediction...

VIEW

- Create a view
- Delete this view
- Modify this view

MODIFICATIONS

- Undo
- Redo

Name: [New compound]
ID: [0BF5600E-F83C-4B98-8D83-7996E3213064]
Original ID:
Original location: \\

About properties...

Properties	Value
Identification	
IUPAC name	[New compound]
Specific name	<unknown>
CAS registry number	<unknown>
Chemical family	<unknown>
Chemical formulae	<unknown>
Smiles	
Set identifier	
Intrinsic number (ProSim specific)	0
Synonyms	
Compound comments	
Cosmo file	<unknown>
Group contribution model	
Atomic	
Molecular weight	
Dipole moment	
Van der Waals volume	<unknown>
Van der Waals area	<unknown>
Modified Van der Waals area	<unknown>
Spro and Prausnitz molar surfa...	<unknown>
Van der Waals radius	
Solubility parameter in (cal/cm ³) ^{1/2}	<unknown>
Radius of gyration	
Diffusion volume	
Born radius	

Import a mol file... Clear

Ok Cancel

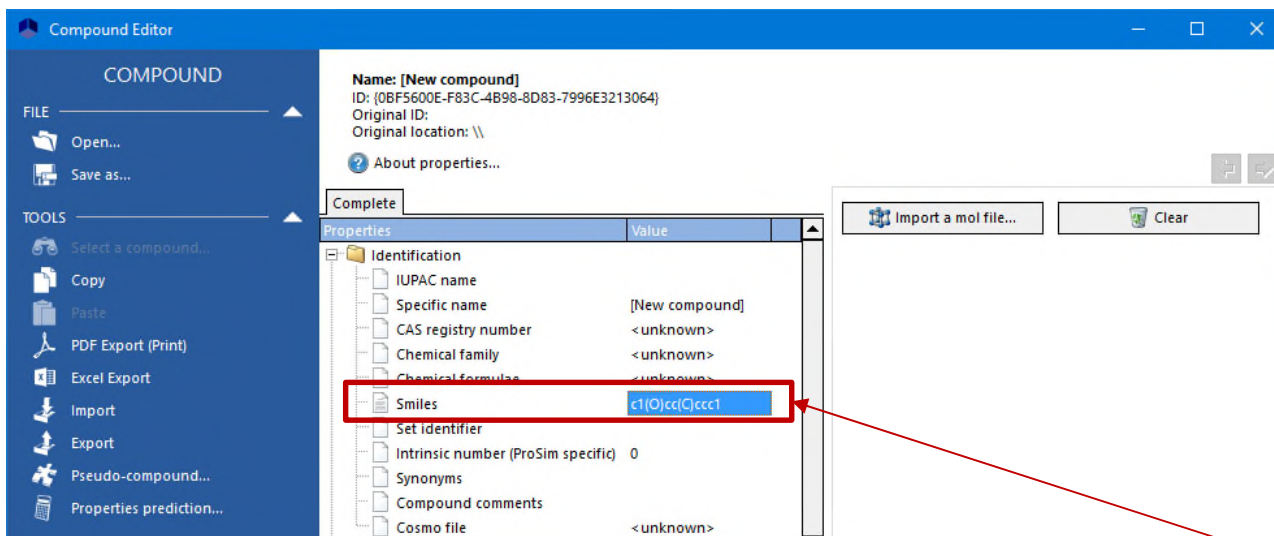
Step 2: Enter the SMILES of the compound

SMILES: **S**implified **M**olecular **I**nterface **L**ine **E**nter **S**pecification

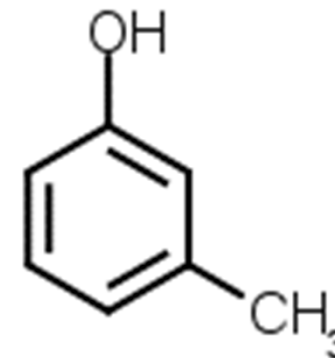
Weininger, J. Chem. Inf. Comput. Sci., 28 (1988)

Specification in form of a line notation for describing the structure of chemical species using short ASCII strings

https://en.wikipedia.org/wiki/Simplified_molecular-input_line-entry_system

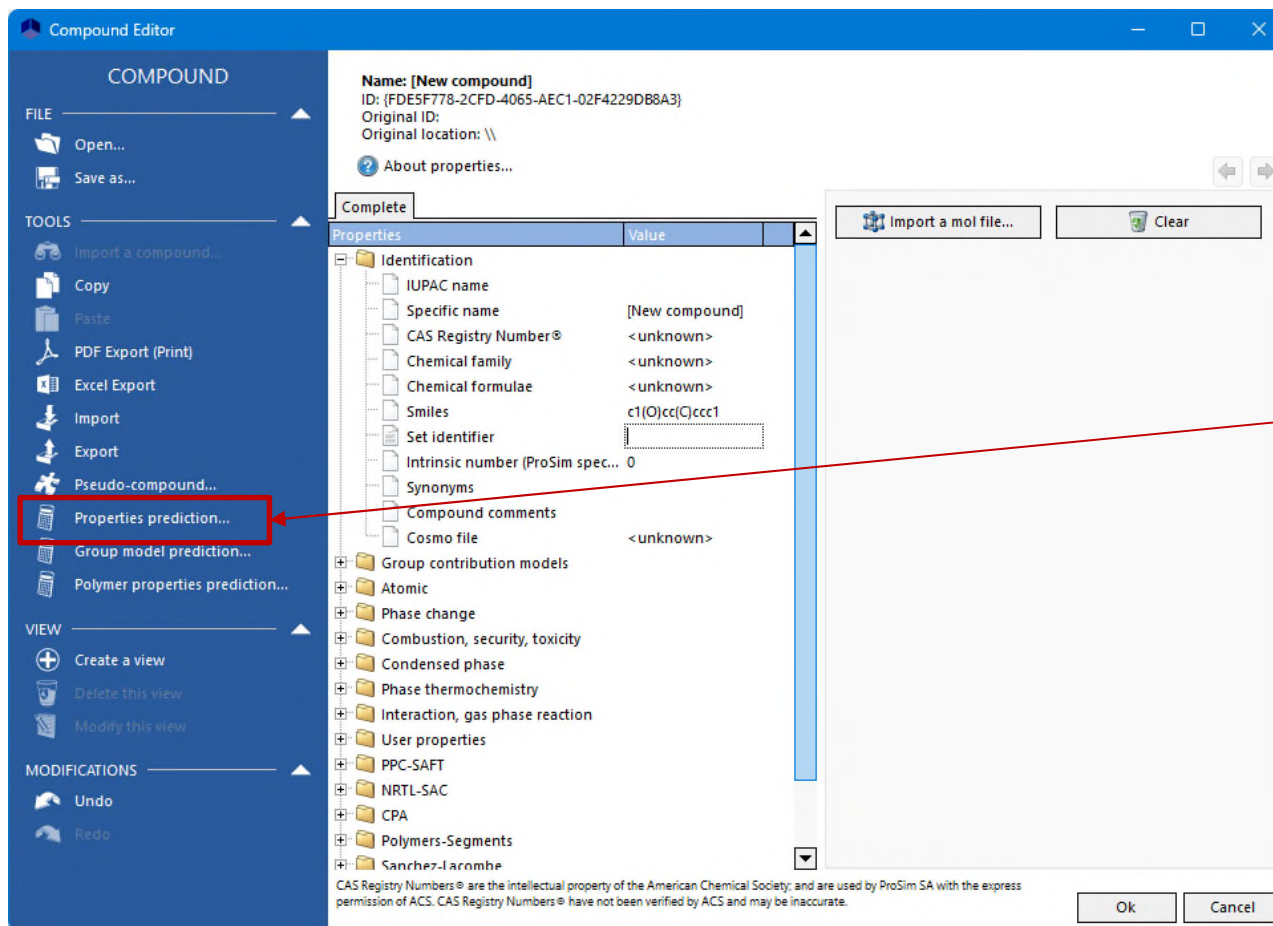


Example:



c1(O)cc(C)ccc1

Step 3: Determine constant properties



Click on
"Properties prediction..."

Step 3: Determine constant properties

1. Select all
(or only properties to be estimated)

2. Select predictive models
or keep automatic selection

5. Select all
(or only properties to be used)


Constant property prediction

Use a prediction system to calculate the properties of a compound.

☒ Select all

Property	Model	Current value	Overwrite	Predicted value
<input checked="" type="checkbox"/> Molecular weight	Automatic	108.140 g/mol	<input checked="" type="checkbox"/>	108.140 g/mol
<input checked="" type="checkbox"/> Normal boiling point	Automatic	468.921 K	<input checked="" type="checkbox"/>	468.921 K
<input checked="" type="checkbox"/> Critical temperature	Automatic	695.009 K	<input checked="" type="checkbox"/>	695.009 K
<input checked="" type="checkbox"/> Critical pressure	Automatic	49.5058 bar	<input checked="" type="checkbox"/>	49.5058 bar
<input checked="" type="checkbox"/> Critical volume	Automatic	352.050 cm ³ /mol	<input checked="" type="checkbox"/>	352.050 cm ³ /mol
<input checked="" type="checkbox"/> Enthalpy of fusion (melting point)	Automatic	13.7280 kJ/mol	<input checked="" type="checkbox"/>	13.7280 kJ/mol
<input checked="" type="checkbox"/> Normal melting point	Automatic	302.838 K	<input checked="" type="checkbox"/>	302.838 K
<input checked="" type="checkbox"/> Acentric factor	Automatic	0.490502	<input checked="" type="checkbox"/>	0.490502
<input checked="" type="checkbox"/> Enthalpy of vaporization (Tb)	Automatic	46.7646 kJ/mol	<input checked="" type="checkbox"/>	46.7646 kJ/mol
<input checked="" type="checkbox"/> Flash Point	Automatic	366.668 K	<input checked="" type="checkbox"/>	366.668 K
<input checked="" type="checkbox"/> Standard state enthalpy of formation at 25°C	Automatic	-127.850 kJ/mol	<input checked="" type="checkbox"/>	-127.850 kJ/mol
<input checked="" type="checkbox"/> Standard state Gibbs energy of formation at 25°C	Automatic	-36.4073 kJ/mol	<input checked="" type="checkbox"/>	-36.4073 kJ/mol
<input checked="" type="checkbox"/> Octanol-Water partition coefficient	Automatic	2.12490	<input checked="" type="checkbox"/>	2.12490
<input checked="" type="checkbox"/> Autoignition temperature	Automatic	1229.20 K	<input checked="" type="checkbox"/>	1229.20 K
<input checked="" type="checkbox"/> Translation volume parameter - cubic equation state	Automatic	18.6838 cm ³ /mol	<input checked="" type="checkbox"/>	18.6838 cm ³ /mol
<input checked="" type="checkbox"/> ULPDHS solvation number at infinite dilution	Automatic	0.00000	<input checked="" type="checkbox"/>	0.00000
<input checked="" type="checkbox"/> Hydrocarbon-water secondary interaction parameter (Kabad Automatic	Automatic	4.51981E+007 atm.	<input checked="" type="checkbox"/>	4.90970E+007 atm.(cm ³ /mol) ²

☒ Select all

☐ Use the predicted values in the calculations 

6. Use

3. Allows to use for the
calculations predicted values
instead of current values



Access to the help: description
of all estimation methods

Step 3: Determine constant properties

Constant properties have been estimated by predictive methods from the SMILES of the molecule

The screenshot shows the 'Compound Editor' window. On the left is a sidebar with 'COMPOUND', 'TOOLS', 'VIEW', and 'MODIFICATIONS' sections. The 'TOOLS' section has 'Import' highlighted. The main area displays compound information and a 'Properties' table. A red arrow points from the text above to the 'Properties' table header.

Compound Information:

- Name: [New compound]
- ID: {0BF5600E-F83C-4B98-8D83-7996E3213064}
- Original ID:
- Original location: \\\
- About properties...

Properties Table:

Properties	Value
Phase change	
Normal melting point	302.838435110524 K
Normal boiling point	468.92078230197 K
Enthalpy of fusion (melting point)	13.728 kJ/mol
Triple point temperature	
Triple point pressure	
Physical state at 25°C	< unknown >
Physical state in aqueous solution at 25°C	< unknown >
Diffusion coefficient	
Enthalpy of vaporization (boiling point)	46.7646 kJ/mol
Octanol-Water partition coefficient	2.1249
soil sorption coefficient (Koc@20°C)	
Liquid vapor calculation type	< unknown >
Acentric factor	0.49050183415645
Modified acentric factor	< unknown >
Critical temperature	695.008879515091 K
Critical pressure	49.5058297081625 bar
Critical volume	352.0495 cm ³ /mol
Critical compressibility factor	< unknown >
Critical density	
Heat of sublimation at the triple point	
Combustion, security, toxicity	
Condensed phase	
Phase thermochemistry	
Interaction, gas phase reaction	

On the right, there is a panel with 'Import a mol file...' and 'Clear' buttons, and 'Ok' and 'Cancel' buttons at the bottom.

Step 4: Decomposition into functional sub-groups

The use of a predictive thermodynamic model based on group contribution (UNIFACs, PPR78...) requires the knowledge of molecule decompositions in functional sub-groups

The screenshot displays the 'Compound Editor' software interface. On the left is a sidebar with a 'TOOLS' section containing various options. The 'Group model prediction...' option is highlighted with a red rectangle. An arrow points from this option to a dialog box titled 'Group contribution models prediction'. This dialog box contains a list of models for prediction, each with a checkbox and an 'Overwrite' checkbox. The models listed are:

Model	Current value	Overwrite
<input type="checkbox"/> PPR78		<input type="checkbox"/>
<input type="checkbox"/> GC-PPC-SAFT		<input type="checkbox"/>
<input type="checkbox"/> UNIFAC original		<input type="checkbox"/>
<input type="checkbox"/> UNIFAC modified (Dortmund) 1993		<input type="checkbox"/>
<input type="checkbox"/> UNIFAC modified (Dortmund)		<input type="checkbox"/>
<input type="checkbox"/> UNIFAC modified (Larsen)		<input type="checkbox"/>
<input type="checkbox"/> UNIFAC modified (Nist)		<input type="checkbox"/>
<input type="checkbox"/> UNIFAC LLE		<input type="checkbox"/>
<input type="checkbox"/> NRTL PR		<input type="checkbox"/>
<input type="checkbox"/> UNIFAC PSRK		<input type="checkbox"/>
<input type="checkbox"/> UNIFAC VTPR		<input type="checkbox"/>
<input type="checkbox"/> UNIFAC UMRPRU		<input type="checkbox"/>

At the bottom of the dialog box are buttons for 'Predict', 'Use', and 'Cancel'. The background shows the 'Properties' table of the 'New compound' with fields like IUPAC name, CAS Registry Number, and Smiles.

Step 3: Determine constant properties

1. Select all
(or only some models)

3. Select all
(or only some models)

Group contribution models prediction

Use a prediction system to estimate decompositions of the group contribution models of a compound.

☒ Select all

Model	Current value	Overwrite	Predicted value
<input checked="" type="checkbox"/> PPR78		<input checked="" type="checkbox"/>	
<input checked="" type="checkbox"/> GC-PPC-SAFT		<input checked="" type="checkbox"/>	[CHa](1, 0) 4 [Ca](1, 0) 2 [a-CH3](3, 0) 1 [OHa1_mCre:
<input checked="" type="checkbox"/> UNIFAC original		<input checked="" type="checkbox"/>	[ACOH] 1 [ACH] 4 [ACCH3] 1
<input checked="" type="checkbox"/> UNIFAC modified (Dortmund) 1993		<input checked="" type="checkbox"/>	[ACH] 4 [ACOH] 1 [ACCH3] 1
<input checked="" type="checkbox"/> UNIFAC modified (Dortmund)		<input checked="" type="checkbox"/>	[ACOH] 1 [ACH] 4 [ACCH3] 1
<input checked="" type="checkbox"/> UNIFAC modified (Larsen)		<input checked="" type="checkbox"/>	
<input checked="" type="checkbox"/> UNIFAC modified (Nist)		<input checked="" type="checkbox"/>	[ACOH] 1 [ACH] 4 [ACCH3] 1
<input checked="" type="checkbox"/> UNIFAC LLE		<input checked="" type="checkbox"/>	[ACOH] 1 [ACH] 4 [ACCH3] 1
<input checked="" type="checkbox"/> NRTL PR		<input checked="" type="checkbox"/>	
<input checked="" type="checkbox"/> UNIFAC PSRK		<input checked="" type="checkbox"/>	[ACOH] 1 [ACH] 4 [ACCH3] 1
<input checked="" type="checkbox"/> UNIFAC VTPR		<input checked="" type="checkbox"/>	[ACOH] 1 [ACH] 4 [ACCH3] 1
<input checked="" type="checkbox"/> UNIFAC UMRPRU		<input checked="" type="checkbox"/>	[ACOH] 1 [ACH] 4 [ACCH3] 1

Predict ? Use Cancel

2. Click on the button allowing automatic decomposition of the molecule from its SMILES

4. Use



The automatic decomposition can fail if the molecule cannot be decomposed in the sub-groups available in the chosen group contribution model

Step 5: Temperature dependent properties

For temperature dependent properties, choose a correlation if it is known...

The screenshot shows the 'Compound Editor' window. On the left is a sidebar with 'COMPOUND', 'FILE', 'TOOLS', 'VIEW', and 'MODIFICATIONS' sections. The main area displays 'Properties' for a new compound. Under 'Temperature dependent properties', the 'Correlation' sub-folder is selected. A list of correlations is shown, including '<unknown>', 'Equation # 99', 'Equation # 100', 'Equation # 101', 'Equation # 115', 'Equation # 118', 'Lee-Kesler', and 'Riedel-Plank-Miller'. The 'Regression' button is located at the bottom right of the window.

... or click on the "Regression" button

Step 5: Temperature dependent properties

If experimental data is available:

[New compound]

IDENTIFICATION

PROPERTY ▲

Vapor pressure

Correlation to use :
Equation # 99

DATA ▲

Paste data from clipboard

Insert a new line

Delete the current line

Prediction...

IDENTIFICATION ▲

Calculate now

Copy table to clipboard

Show/Hide graph window

OPTIONS ▲

Numerical parameters...

Use this parameters identification tool to obtain the coefficients intervening in the mathematical equation that represents the evolution of the property according to temperature.

Default units :

Temperature	K	▲
Pressure	bar	▲
Percentage	%	▲

Formula (click for a larger view) :

$$\ln(Y) = A - \frac{B}{T + C}$$

Experimental and calculated points :

Used	Temperature	Vapor pressure (exp.)	Vapor pressure (calc.)	Absolute error	Relative error
<input checked="" type="checkbox"/>					

Identification results :

A	B	C	Criterion
			Mean relative error
			Max. relative error
			Mean absolute error
			Max. absolute error

Set as initialization coefficients

Correlation expressed in mmHg

Use Cancel

1. Select the units for the temperature and the property to be regressed

2. Copy/paste the table of experimental values temperature/property (e. g. from Excel)



Do not use "CTRL + V" to paste experimental values but the "Paste data from clipboard" button

Step 5: Temperature dependent properties

If no experimental data is available:

[New compound]

IDENTIFICATION

PROPERTY ▲

Vapor pressure

Correlation to use :

Equation # 99

DATA ▲

Paste data from clipboard

Insert a new line

Delete the current line

Prediction...

IDENTIFICATION ▲

Calculate now

Copy table to clipboard

Show/Hide graph window

OPTIONS ▲

Numerical parameters...

Use this parameters identification tool to obtain the coefficients intervening in the mathematical equation that represents the evolution of the property according to temperature.

Default units :

Temperature	K	▲
Pressure	bar	▲
Percentage	%	▼

Formula (click for a larger view) :

$$\ln(Y) = A - \frac{B}{T + C}$$

Experimental and calculated points :

Used	Temperature	Vapor pressure (exp.)	Vapor pressure (calc.)	Absolute error	Relative error
<input checked="" type="checkbox"/>					

Identification results :

A		Criterion	
B		Mean relative error	
C		Max. relative error	
		Mean absolute error	
		Max. absolute error	

☒ Set as initialization coefficients

Correlation expressed in mmHg

Use Cancel

Click on the "Prediction..." button (only available if the SMILES has been provided)

Step 5: Temperature dependent properties

Generation of pseudo-experimental data estimated by predictive methods from the SMILES



Access the help file:
description of all estimation
methods

Temperature dependent properties prediction

Use a prediction system to calculate the temperature dependent properties of a compound.

Predictive model: Riedel, 1954

Specify the temperature interval

Property	Unit	Initial	Final	Step	Points
Temperature	K	300	700	10	41

Ok Cancel

Give the temperature range for the selected property
(e. g., for vapor pressure,
from the normal melting temperature to the critical temperature)
and the step of calculation to generate the expected number of
points

Step 5: Temperature dependent properties

2. Select the correlation to be used for the regression

[New compound]

IDENTIFICATION

PROPERTY

Vapor pressure

Correlation to use: **Equation # 101**

DATA

Paste data from clipboard

Insert a new line

Delete the content line

Prediction...

IDENTIFICATION

Calculate now

Copy table to clipboard

Show/Hide graph window

OPTIONS

Numerical parameters...

Use this parameters identification tool to obtain the coefficients intervening in the mathematical equation that represents the evolution of the property according to temperature.

Default units:

Temperature	K
Pressure	bar
Percentage	%

Formula (click for a larger view):

$$\ln(Y) = A + \frac{B}{T} + C \cdot \ln(T) + D \cdot T^E$$

Experimental and calculated points:

Used	Temperature	Vapor pressure (exp.)	Vapor pressure (calc.)	Absolute error	Relative error
<input checked="" type="checkbox"/>	300 K	0.000429074 bar	0.000429059 bar	1.47365E-008	0.0034345 %
<input checked="" type="checkbox"/>	310 K	0.000900784 bar	0.000900758 bar	2.5492E-008	0.00282998 %
<input checked="" type="checkbox"/>	320 K	0.001793 bar	0.00179296 bar	4.13853E-008	0.00230816 %
<input checked="" type="checkbox"/>	330 K	0.00340107 bar	0.00340101 bar	6.32513E-008	0.00185975 %
<input checked="" type="checkbox"/>	340 K	0.00617538 bar	0.00617529 bar	9.11866E-008	0.00147661 %
<input checked="" type="checkbox"/>	350 K	0.0107756 bar	0.0107755 bar	1.2409E-007	0.00115158 %
<input checked="" type="checkbox"/>	360 K	0.0181328 bar	0.0181327 bar	1.59258E-007	0.000878282 %
<input checked="" type="checkbox"/>	370 K	0.0295184 bar	0.0295182 bar	1.9218E-007	0.00065105 %
<input checked="" type="checkbox"/>	380 K	0.0466156 bar	0.0466154 bar	2.16673E-007	0.000464808 %
<input checked="" type="checkbox"/>	390 K	0.071592 bar	0.0715917 bar	2.2551E-007	0.000314993 %
<input checked="" type="checkbox"/>	400 K	0.107168 bar	0.107168 bar	2.11633E-007	0.000197477 %
<input checked="" type="checkbox"/>	410 K	0.15668 bar	0.15668 bar	1.70016E-007	0.000108512 %
<input checked="" type="checkbox"/>	420 K	0.22413 bar	0.22413 bar	1.00119E-007	4.46702E-005 %
<input checked="" type="checkbox"/>	430 K	0.314229 bar	0.314229 bar	8.81533E-009	2.80539E-006 %
<input checked="" type="checkbox"/>	440 K	0.43242 bar	0.43242 bar	-8.64392E-008	-1.99896E-005 %
<input checked="" type="checkbox"/>	450 K	0.58489 bar	0.58489 bar	-1.54505E-007	-2.6416E-005 %

Identification results:

	Value	Criterion	Value
A	73.4914		5.95516E-006
B	-9014.65	Mean relative error	5.45978E-004 %
C	-6.95778	Max. relative error	3.43450E-003 %
D	2.96263E-018	Mean absolute error	3.48250E-005 bar
E	6.00000	Max. absolute error	-4.34823E-004 bar

Set as initialization coefficients

Correlation expressed in Pa

Use Cancel

1. Data generated by the prediction tool

3. Click on "Calculate"

4. Verify the results of the regression, then click on "Use"

Step 5: Temperature dependent properties

Results of the regression of a temperature dependent property

The screenshot displays the Compound Editor interface. On the left is a sidebar with 'COMPOUND' and 'TOOLS' sections. The main area shows a tree view of properties under 'Temperature dependent properties', with 'Vapor pressure' expanded and 'Correlation' selected. A table on the right shows the regression results for Equation # 101. A red arrow points from the 'Results of the regression of a temperature dependent property' text to the 'Correlation' row in the tree view.

Property	Value
Equation # 101	
TMin	300 K
TMax	700 K
Coef A	73.491385515002
Coef B	-9014.6548525658
Coef C	-6.9577840475961
Coef D	2.962630543296E-018
Coef E	6

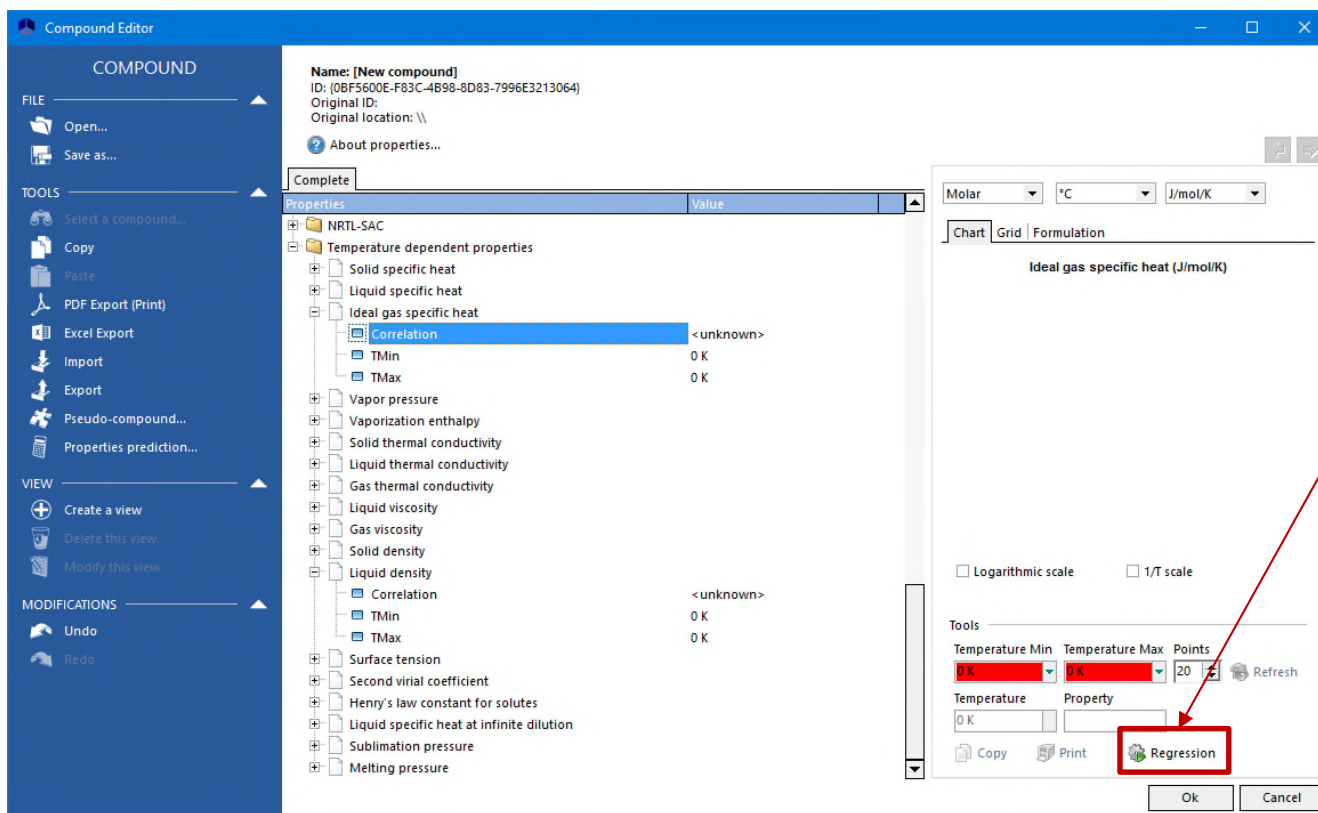
On the right, a 'Formulation' dialog box shows the equation:

$$\ln(Y) = A + \frac{B}{T} + C \cdot \ln(T) + D \cdot T^E$$

The Y unit is: Pa. The dialog also includes 'Tools' for Temperature Min (300 K), Temperature Max (700 K), and Points (20). The Temperature Property is set to 300 K, and the Property value is 4.29059E-004 bar. Buttons for Copy, Print, Regression, Ok, and Cancel are at the bottom.

Step 5: Temperature dependent properties

Renew the operation for the other temperature dependent properties (with a correlation, by regression from experimental data or estimated with the knowledge of the SMILES)



For the selected property, click on “Regression”. Generation of pseudo-experimental data from the SMILES is available for the following properties:

- Vapor pressure
- Ideal gas specific heat
- Liquid density
- Liquid viscosity
- Surface tension

Conclusion

The properties of a compound that is not available in databases:

- Constant
- Decomposition in functional sub-groups
- Temperature dependent

can be given by the user or estimated with predictive methods from the knowledge of the SMILES of the molecule.

The required properties to create a compound depend on the type of thermodynamic calculation (equilibrium, transport properties...) and the choice of the thermodynamic model to represent the studied system (cf. help on thermodynamic models to know required pure component properties according to the chosen model)

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