

Residual Curves

Tutorial & Documentation

DDBSP - Dortmund Data Bank Software Package



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Introduction

ResidualCurves calculates the concentration of a three-component system by open evaporation. The resulting residual curves resemble the concentration profiles in a packed distillation column at infinite reflux. This type of calculation is based on phase equilibrium models.

The resulting diagrams, called *residue curve maps* are helpful for the understanding and the design of distillation columns.

Overview of the Program

This program is closely linked to the Dortmund Data Bank (DDB). Therefore, all specifications of components and parameters are referring to the DDB.

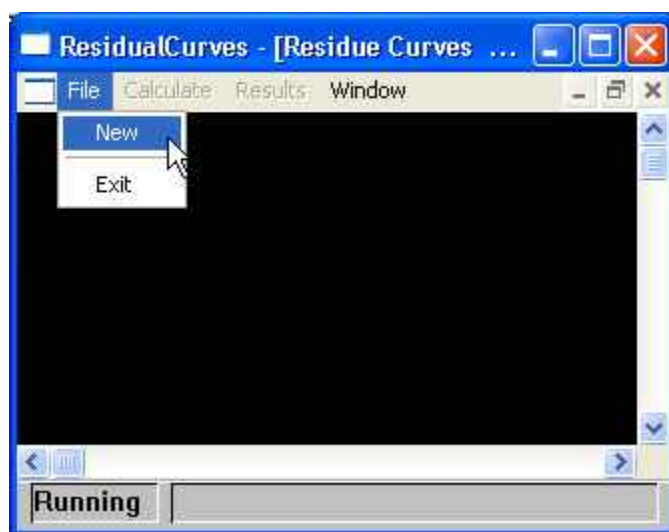
The calculation procedure starts fairly sequential. In brief, a new calculation is started by specifying the components, the calculation settings, and the models for the liquid and vapor phase. After that, azeotropes have to be calculated and the topology of the resulting map is determined. At this point, the results can be viewed and the program now operates interactively.

In the results window, by left-clicking with the mouse inside the composition space, a new residue curve is generated. Right-clicking deletes the closest curve. The resulting diagram can be viewed as a three dimensional plot (depending on the calculation settings). Also, binary or ternary VLE-Plots and a log file with the most important calculated parameters and data can be generated. Results and specifications can be saved in an editable text file.

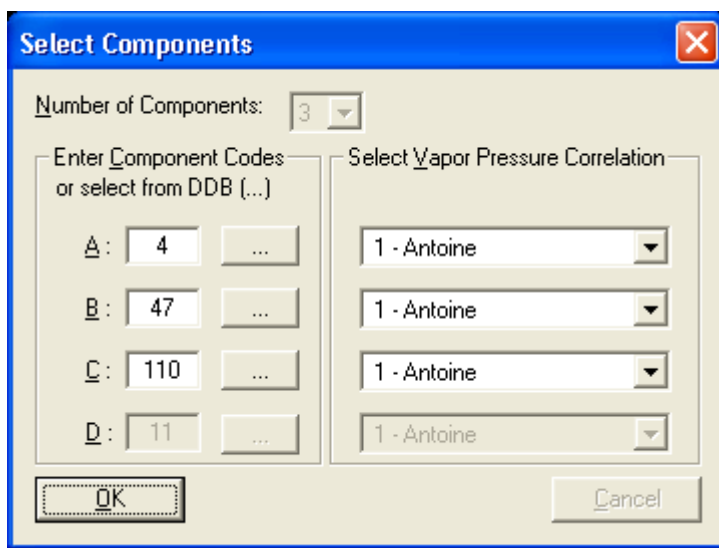
Short Tutorial – Step by Step to First Results


Creating a New System

A new calculation is started by selecting the *File* menu entry *New*.




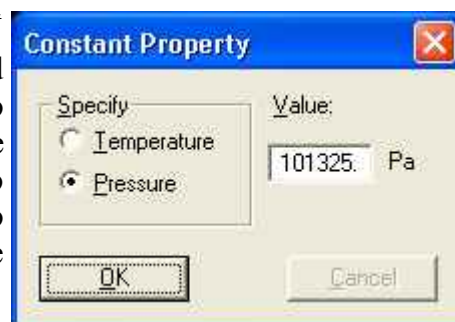
This guide helps through the necessary specification steps. This process can't be stopped or canceled.



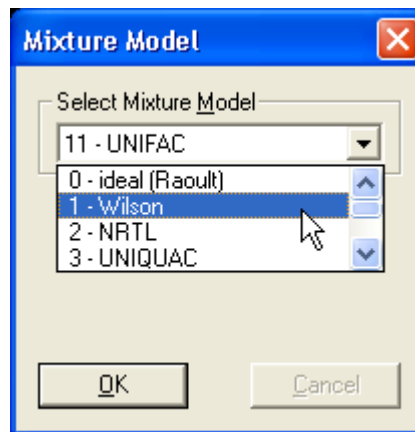
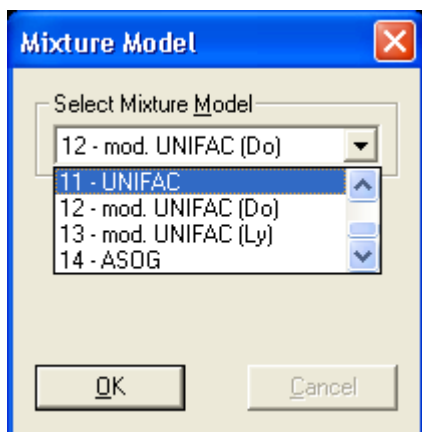
First the system definition dialog is displayed. A component can be selected either by entering the DDB-Component code (e. g. 4 for acetone) or by hitting the corresponding ellipse-button . The latter will open the compound selection dialog which allows to search for the desired component by several properties (like name, formula or CAS number). The component selection is described briefly in the *Dortmund Data Bank* documentation.

All three components must be selected for the *ResidualCurves* calculations. The selection procedure must be repeated until all desired components are specified.

When clicking the OK button  in the *Select Components* dialog the next dialog *Constant Property* is displayed where either a constant pressure or a constant temperature has to be entered. This is the most important setting. Usually, the pressure is set to a fixed value, because this corresponds closely to the conditions found in a distillation column. When switching to isothermal conditions be sure to specify a reasonable temperature in the field *Value*.



The next dialog is the *Mixture Model* selection. There are two different approaches for calculating liquid phase non-ideality. g^E -Models are identified by one-digit



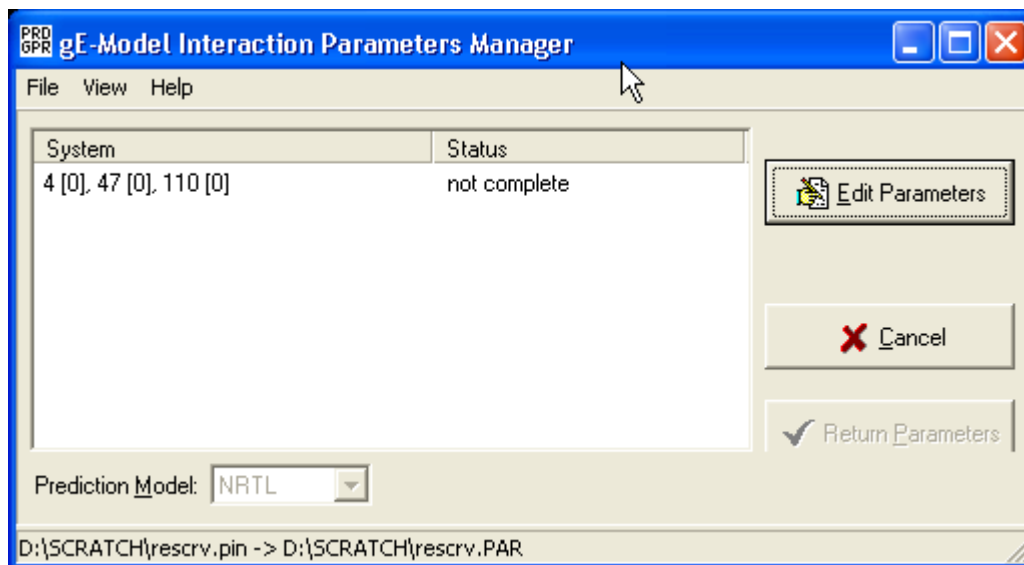
numbers, while group contribution models carry two-digit numbers in front of the model name. Group contribution methods have the advantage that all the available group interaction parameters¹ are stored


¹ The most current developments in the development of the UNIFAC group contribution methods is available from the UNIFAC consortium. Please visit the [consortium web pages](http://www.unifac.org) (www.unifac.org) for detailed information.

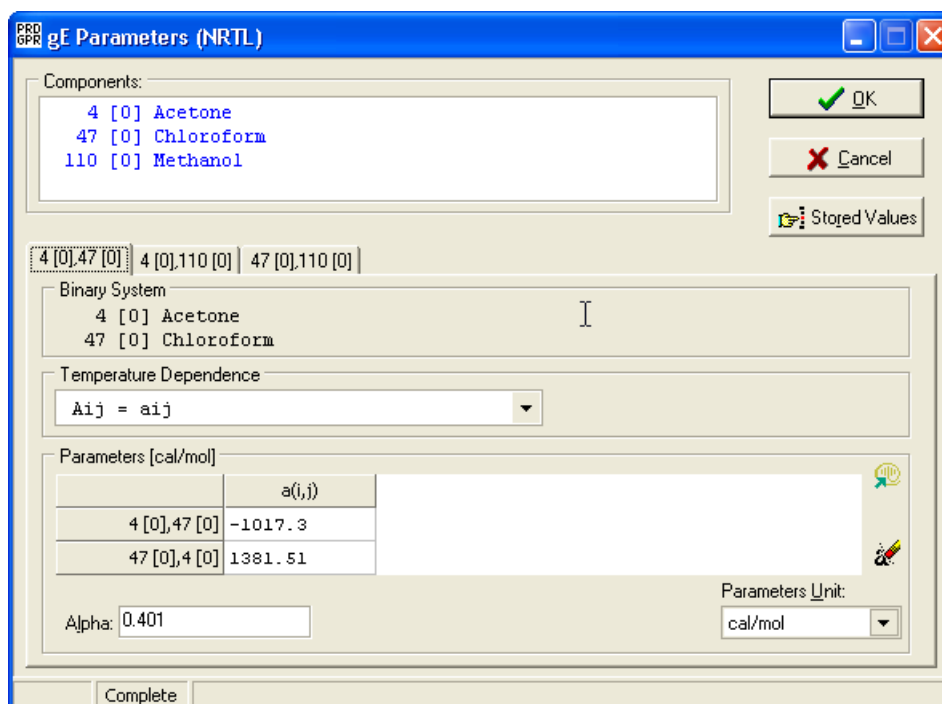
in the DDB, so calculations for several systems can be performed without the need of fitting of model parameters.

The mixture property estimation model must be given. Default is *mod. UNIFAC (Dortmund)*.

If a g^E -model is selected system specific binary interaction parameters for all component pairs have to be entered.

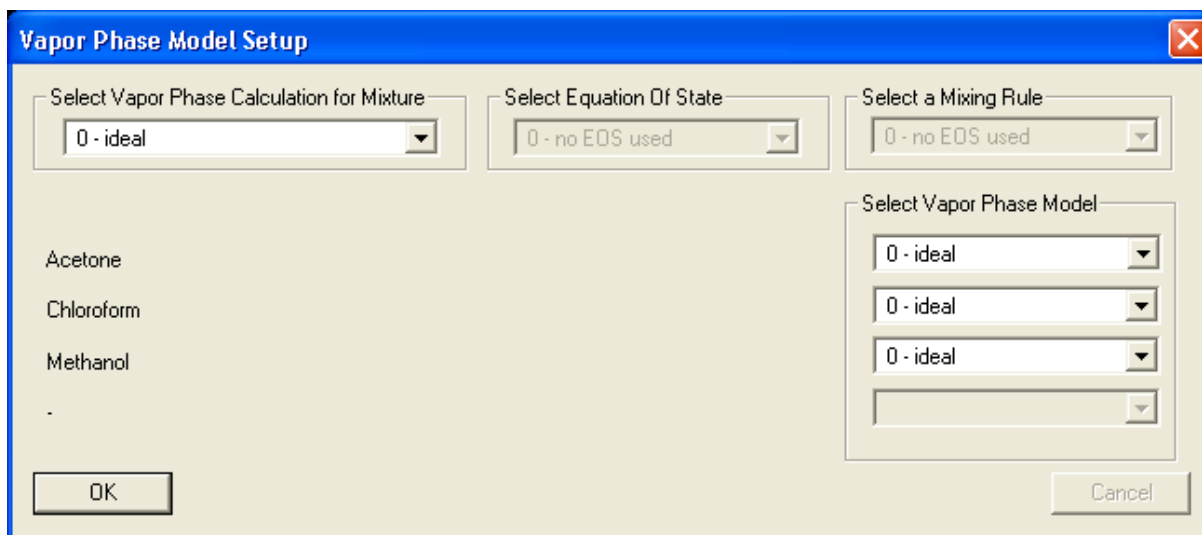


The  Edit Parameters opens a dialog where the parameters can be entered or loaded from the parameter data bank.



The next step is the specification of the vapor phase model.

The different settings have to be selected from drop-down menus. The four menus are



Vapor phase calculation settings for mixture:

- 0 - ideal
- 1 - Tsonopoulos approx.
- 2 - Vetere approx.
- 3 - Dauber-Danner corr.
- 8 - cubic EOS
- 9 - enter Virial Coefficients manually
- 10 - Chemical Theory

Vapor phase model settings for single components:

- 0 - ideal
- 1 - Tsonopoulos approx.
- 2 - Vetere approx.
- 3 - Dauber-Danner corr.
- 9 - enter Bij manually
- 10 - Chemical Theory

There are two main choices. The vapor phase can be calculated as ideal mixture. In this case only the vapor pressure correlation to be used for each component has to be specified. Because of its widespread use and the availability of parameters from the DDB for most components, the use of the Antoine correlation is strongly recommended and selected by default.

If the real vapor phase behavior should be taken into account a method has to be selected. Possible choices are Tsonopoulos, Vetere, Daubert-Danner, cubic equations of state (EOS), direct input of virial coefficients or chemical theory.

Unless strongly associating compounds such as carboxylic acids are present in the mixture, or high pressure calculations are performed, it is recommended to use ideal behavior of the vapor phase. If carboxylic acids are present, chemical theory is automatically selected for these components and mixture calculation. All other components are then treated as ideal gases in the vapor phase.



If "cubic EOS" is selected it is necessary to specify the type of EOS and the type of the mixing rule.

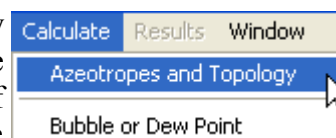
0 - no EOS used	1 - quadratic
1 - van der Waals	2 - Huron Vidal
2 - Redlich Kwong	3 - Tochigi
3 - Soave Redlich Kwong	4 - modified Huron Vidal sec
4 - Peng Robinson	5 - predictive Soave Redlich
5 - Peng Robinson Stryjek Vera	6 - Michelsen

This completes the setup procedure.

Now, the program can calculate the properties for the binary subsystems, i. e. the VL(L)E and the presence of azeotropic points. The results may be displayed using the *Calculate – Binary VLE* menu entry (see section *Calculations* below). At this point, bubble or dew point calculations (*Calculate – Bubble or Dew Point*) at arbitrary pressures, temperatures, and compositions can be performed.

Calculations

Calculate Use the *Calculate* menu to start different calculations. To actually calculate residue curves a search for binary and ternary azeotropes has to be done first. With this information, the program determines the topology of the system (i. e. whether a component is an absolute high boiler, absolute low boiler or saddle). After the topology has been determined, new curves from this menu can be added or a number of curves using predefined patterns for the starting points can be distributed.



For a quick look at some binary VL(L)E or for performing some bubble or dew point calculations searching for azeotropes first is not necessary.

Azeotropes and Topology	Selecting <i>Azeotropes and Topology</i> starts the search for azeotropes and calculates the topology of the system. This is a prerequisite for the residue curve calculation. Entries marked with * are only selectable, after the azeotropic search has been completed.
Bubble or Dew Point	The entry <i>Bubble or Dew Point</i> allows to calculate arbitrary bubble and dew points within the selected system.
Binary VLE	The menu entry <i>Binary VLE</i> allows to calculate the vapor-liquid equilibrium of all binary subsystems.
Ternary VLE *	Using <i>Ternary VLE</i> allows to calculate a ternary bubble point surface of the (sub-) system.
Add Curve *	With <i>Add Curve</i> the starting composition of a new curve by entering mole fractions can be specified.
Distribute Some Curves *	With <i>Distribute Some Curves</i> multiple curves can be calculated at once. The starting points are distributed following predefined patterns.
Add Border Lines *	<i>Add Border Lines</i> will calculate all boundary residue curves that separate different distillation regions.

Azeotropes and Topology

After selecting *Azeotropes and Topology* the programs NTAZDHOM and NTAZDHET are called. They search for azeotropic points in the selected systems. The calculation can take some seconds.

Bubble or Dew Point

Select Calculation Type		Conditions	
<input type="radio"/> isothermal	<input checked="" type="radio"/> bubble point	Temperature: 326.875 K	
<input checked="" type="radio"/> isobaric	<input type="radio"/> dew point	Pressure: 101325.00 Pa	

Compositions		
	liquid phase (x)	vapor phase (y)
Acetone	0.333	0.333
Chloroform	0.333	0.333
Methanol	0.333	0.333
- only 3 components selected -	0.000	0.000
sum:	1.000	1.000

This dialog allows to calculate vapor phase compositions from liquid phase compositions (bubble point) or reverse (dew point) at different conditions.

Binary VLE

After selecting *Binary VLE* a list of the possible subsystems is presented.

Select Binary Subsystem

- Acetone - Chloroform
- Acetone - Methanol
- Chloroform - Methanol
- only 3 components present
- only 3 components present
- only 3 components present

The result is the graphical output shown below. It contains a description of the settings and always an x/y – plot of the system. Depending on the choice for the fixed property either an x/T (in the isobaric case) or an x/P – plot is displayed.

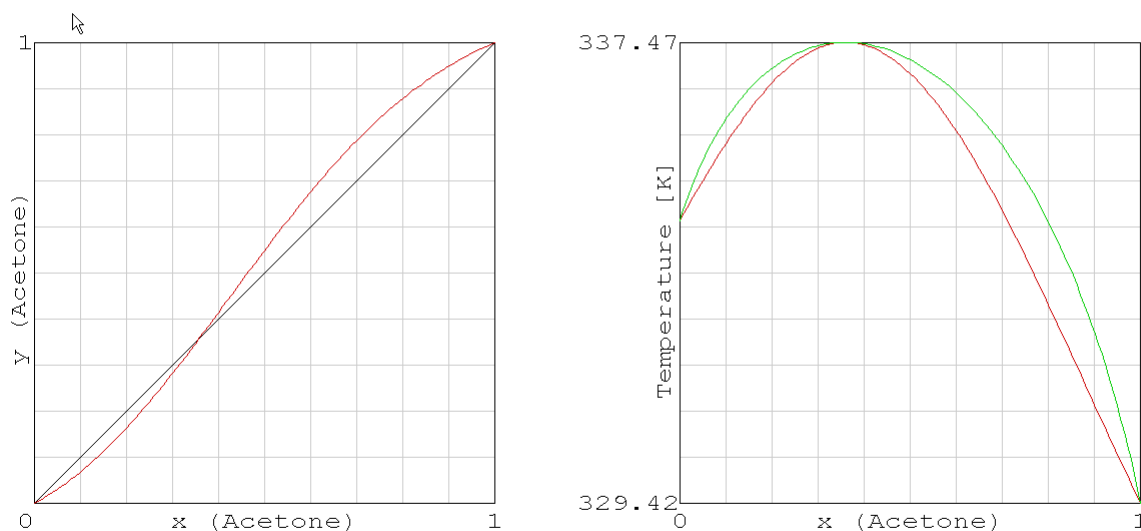
This plot is opened as a separate window.

VLE PLOT

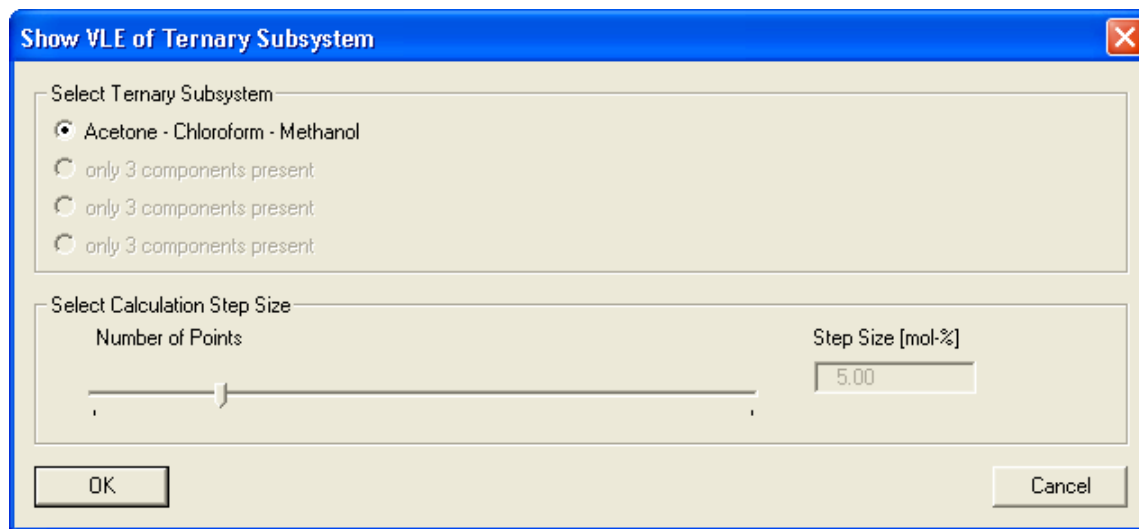
(1) [329.42K] (4) Acetone
(2) [334.35K] (47) Chloroform

Pressure: 101.33 kPa

liquid phase activity coefficients : MOD UNIFAC (DO)
vapor phase fugacity coefficients : IDEAL VAPOR PHASE

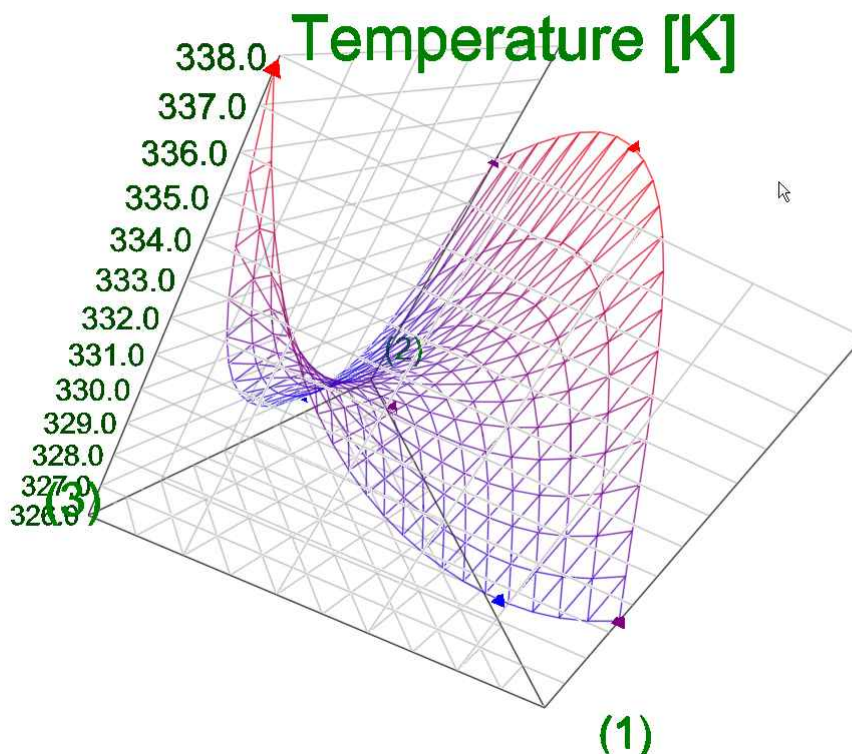
**Ternary VLE**

The *Show VLE of Ternary Subsystem* dialog is displayed. It is possible to edit the grid size. This can be done by using the slider below *Number of Points*. The resulting step size is displayed right from the slider.



After the calculation (which may take some time if small step sizes have been specified) a separate program (PLOT3D) is launched to display the results like this:

(1) [329.42K] Acetone (4)
 (2) [334.35K] Chloroform (47)
 (3) [337.72K] Methanol (110)
 (1) - (2) [337.47K]
 (1) - (3) [328.59K]
 (2) - (3) [326.86K]
 (1) - (2) - (3) [330.72K]
 Pressure: 101.325kPa



The viewer program needs some time to load the data points (some seconds up to a minute for steps of 1 mole %). The color of the surface represents the boiling temperature or pressure, with red meaning high temperature or low pressure, and blue standing for low temperature resp. high pressure.

Add Curve

Selecting this entry allows to specify a starting point for a residue curve by entering mole fractions. If the 2D-output window is opened the calculation progress is visible on-screen. This happens every time a new curve is being calculated.

Distribute Some Curves

Using some predefined patterns (simplex, angle bisection or topology dependent) a variable number of curves is distributed. In most cases it is easier to use the interactive input (see section *Viewing Residue Curve Maps*).

Add Border Lines

This feature is extremely useful for adding the residue curves separating the distillation regions. These have a different color and can not be deleted.

Viewing Residue Curve Maps

Results

There are three main options available specifying the presentation of the calculation results.

The fourth option allows to display a text file summarizing the calculation details (settings, pure component properties, azeotropes, etc.).

Display 2D Plot

Display 2D Plot displays the triangle plot internally. This plot has to be used to add residual curves or distillation lines

Display 3D Plot

Display 3D Plot displays a freely rotatable graphic using an external program (PLOT3D).

Display List

Display List calls the registered text editor to show calculation specifications and some important results.

The *Display 2D Plot* is most important function because it is the most convenient place to add residue curves. The most important settings and the pure components involved are listed. A triangular representation of the composition space is appended. When the mouse pointer is moved over the triangle, the current position in terms of mole fractions is displayed in the order of the components. The colored points are the azeotropic points, with red standing for a stable node, blue for an unstable node and violet for any saddle. The boiling point of the azeotropes is listed on the right hand side of the triangular plot.

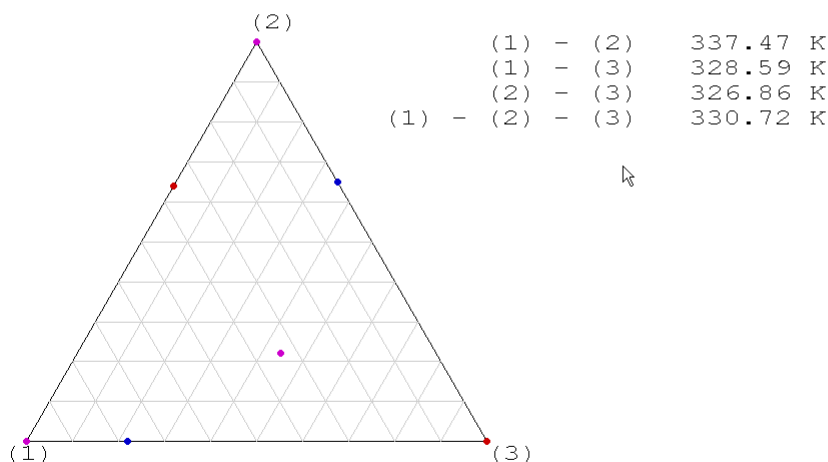
RESIDUE CURVE MAP

```
(1) [329.42K] ( 4) Acetone
(2) [334.35K] ( 47) Chloroform
(3) [337.72K] ( 110) Methanol
```

Pressure: 101.325 kPa

```
liquid phase activity coefficients : MOD UNIFAC (DO)
vapor phase fugacity coefficients : IDEAL VAPOR PHASE
```

Mouse Position :



Residual curves are added by *left-clicking* inside the triangle. Curves are deleted by *right-clicking* on the curve. The curve closest to the cursor is deleted, so it is not necessary to hit the curve directly. If the mouse cursor is inside the triangle, its position in mole fractions is shown below the mouse position line. The program then calculates the residual curves starting from that point.

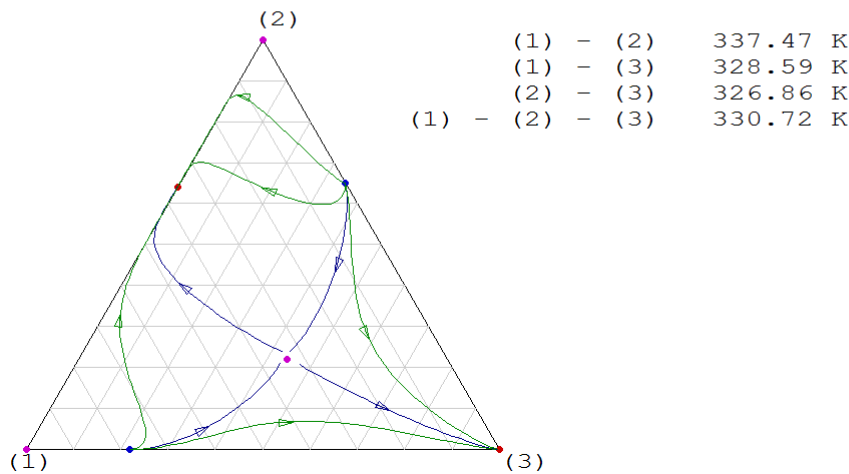
RESIDUE CURVE MAP

(1) [329.42K] (4) Acetone
 (2) [334.35K] (47) Chloroform
 (3) [337.72K] (110) Methanol

Pressure: 101.325 kPa

liquid phase activity coefficients : MOD UNIFAC (DO)
 vapor phase fugacity coefficients : IDEAL VAPOR PHASE

Mouse Position :



The *3D Plot* is used as additional information. Here, the temperature (if running an isobaric calculation) or the pressure (if running an isothermal calculation) is plotted on the z-axis. The sliders on the right hand side allow free rotation of the plot. Pressing the little buttons above the sliders enables an auto-rotate mode along the respective axis. The grid may be switched on or off and smooth the lines using the check boxes. Azeotropes and pure components are represented by little pyramids. The color is the same, as in the *2D Plot*.

(1) [329.42K] Acetone (4)
 (2) [334.35K] Chloroform (47)
 (3) [337.72K] Methanol (110)
 (1) - (2) [337.47K]
 (1) - (3) [328.59K]
 (2) - (3) [326.86K]
 (1) - (2) - (3) [330.72K]
 Pressure: 101.325kPa

