Residue Curves
Contour Lines
Azeotropic Points

Calculation of Residue Curves, Border Lines, Singular Points, Contour Lines, Azeotropic Points

DDBSP - Dortmund Data Bank Software Package

DDBST

Dortmund Data Bank
Software & Separation
Technology

Contents

Introduction

The knowledge of the real behavior of the pure compounds and their mixtures is of great importance for the development and design of chemical processes. Since the greatest parts of the costs are caused by the separation step, reliable information about the phase equilibrium behavior is especially important. For the synthesis of distillation processes, besides the knowledge about azeotropic points, also information about the residue curves, borderlines, and contour lines are of interest to fully understand the separation process[1].

The program "ResidueCurves" as part of the DDB software package is a powerful tool for the calculation of topology maps for ternary systems. By means of these maps, the process engineer is able to evaluate the feasibility and estimate the costs of the investigated separation process.

Topology Maps

Besides the characteristic of the pure components and possible azeotropes (stable, unstable or saddle points) also borderlines and residue curves are shown on the resulting diagrams.

Border Lines

Borderlines divide a mixture into distillation regions which always contain a stable and an unstable point. In a three-dimensional projection, they form either a ridge or a valley which cannot be overcome by rectification processes.

Residue Curves

Starting from singular points, residue curves always end in singular stable points, no matter if they are pure components or azeotropes. They show the concentration gradient by open evaporation and can be expressed by the following differential:

$$\frac{dx}{d\xi} = x_i - y_i$$

The possibility to integrate in both directions allows the calculation of a residual curve from any initial concentration. The description of an unknown curvature with known starting values by the help of a differential equation assumes an explicit function which is able to calculate the system state at a later date from the actual state. Here, the approach following Runge-Kutta-Gill [2,3] as fourth order Runge-Kutta method is applied. It is known as numerically stable and leads to a good description of the curvature.

Contour Lines

Contour lines, often called isolines or isopleths, are line of constant properties, e.g., same pressure, same temperature, or same separation factors at different compositions. Typically, several contour lines for different constant are include in one diagram.

Azeotropic Points

Azeotropic points are essential for separation processes because they prohibit easy separation through single-column evaporation.

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[1] J.D. Seader, J. Ernest, Henley, Separation Process Principles, Wiley & Sons, New York, 1997
[2] S. Gill, Proc. Cambridge Philos. Soc. 47 (1951) 96-108.
[3] A. Ralston, H.S. Wilf, Mathematical Methods for Digital Computers, Wiley, New York, 1960

Overview

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.

Now the different tasks like the determination of the topology or mixing gaps and the calculation of the residual curves can be performed. In the results window, by left-clicking with the mouse inside the composition space, a new residue curve is generated. Shift-clicking deletes the closest curve. The resulting diagram can be viewed as a three-dimensional plot. Also, 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

Component Selection

A new calculation is started by adding three components to the component list. This can be done either by directly typing the DDB numbers (1) or by clicking the "Add Component" – button (2).
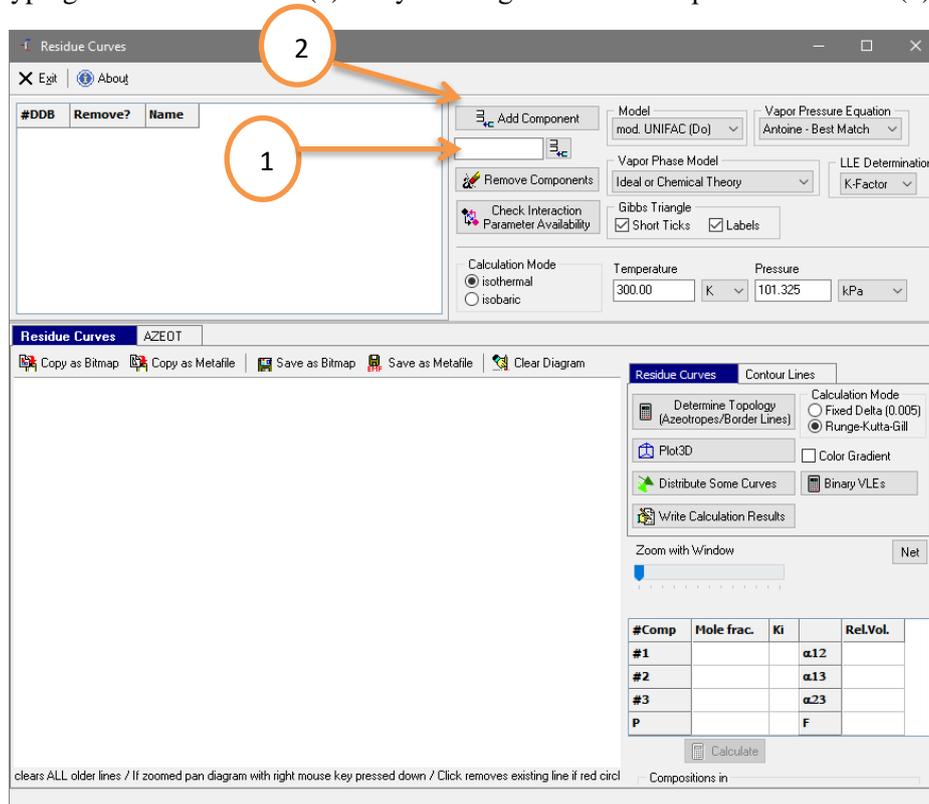

"Add Component" will bring up the "Component Selection" dialog which allows searching for the desired component by several properties (like name, formula or CAS number).
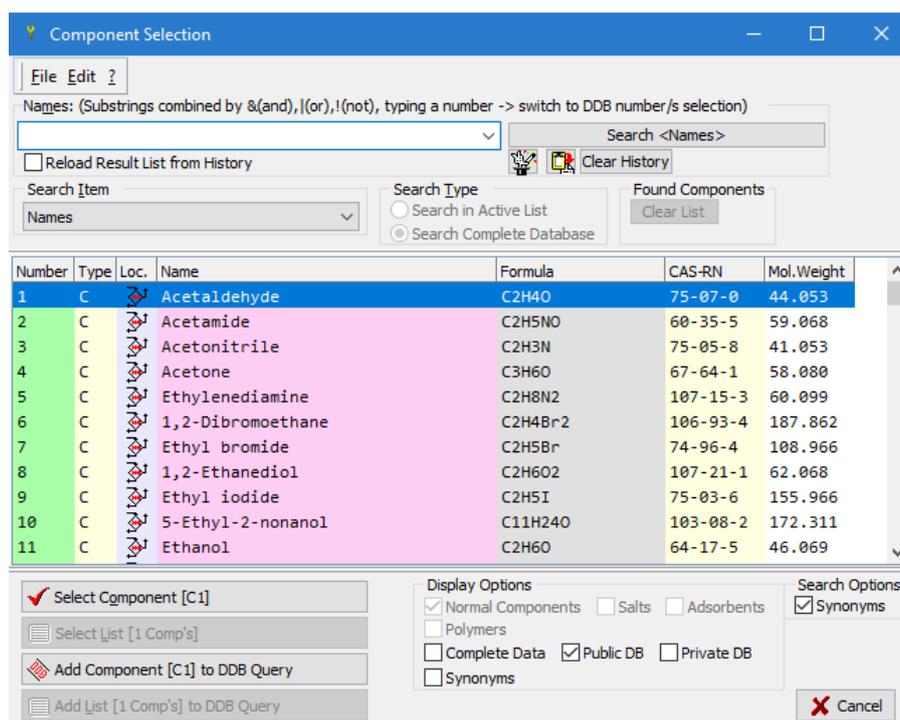
Except for the first option where all components are set automatically, the procedure must be repeated until all desired components are specified. When the third component is added, the Gibbs Triangle is initialized.

Model Selection

Now the mixture model, vapor pressure equation and vapor phase model have to be selected from the according drop-down menus on the upper right side.
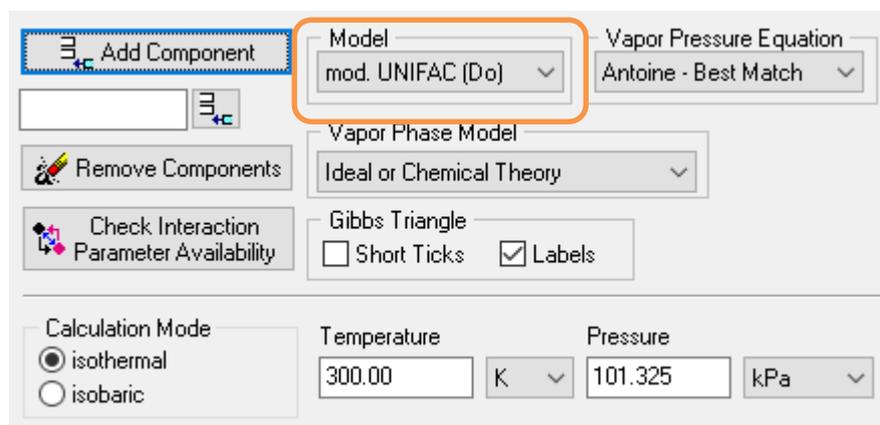
There are two different approaches for calculating liquid phase non-ideality, g^E based and equation of state based models:

g^E- models with fitted interaction parameters

- o   NRTL
- o   UNIQUAC
- o   Wilson

Group contribution g^E models

- o   original UNIFAC
- o   modified UNIFAC (Dortmund)
- o   modified UNIFAC (Lyngby)
- o   NIST-modified UNIFAC

Equation of state group contribution models

- o   PSRK
- o   VTPR

COSMO-based models

- o   COSMO-RS(Ol)
- o   COSMO-SAC
- o   COSMO-SAC2010
- o   COSMO-SAC2013

Group contribution methods have the advantage that all available group interaction parameters[4] are stored in the DDB. The calculation for several systems can be performed without the need of fitting model parameters. The mixture property estimation model must be given. If a g^E-model is selected, system specific binary interaction parameters for all component pairs have to be entered.
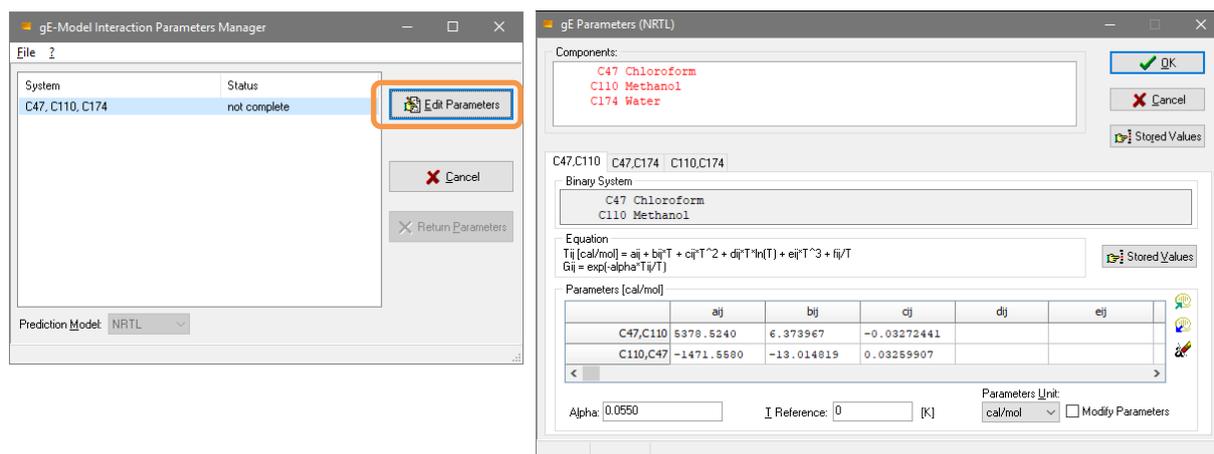
"Edit Parameters" opens a dialog where the parameters can be entered or loaded from the parameter data bank.

Vapor Pressure Equation

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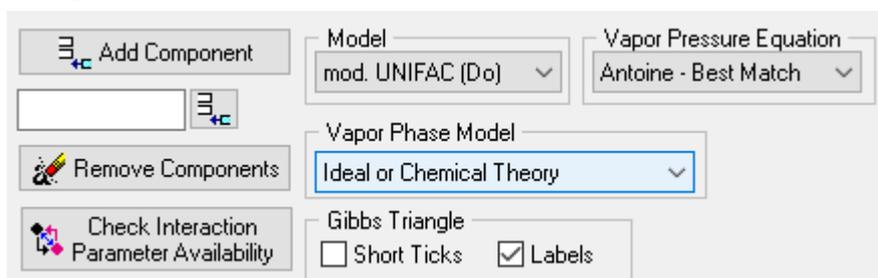
[4] The most current development of the UNIFAC group contribution methods is available from the UNIFAC consortium. Please visit the consortium web pages (www.unifac.org) for detailed information.

Concerning the vapor pressure, the following equations can be chosen:

- o Antoine – Best Match
- o Antoine – Low
- o DIPPR 101
- o Wagner 25
- o Wagner 36
- o Cox

Vapor Phase Model

For the vapor phase model, there are two main choices. The vapor phase can be calculated as ideal mixture. If the real vapor phase behavior should be taken into account a method has to be selected. Possible choices are:

- o Peng-Robinson EOS with quadratic mixing rule
- o Redlich-Kwong EOS with quadratic mixing rule
- o Soave-Redlich-Kwong EOS with quadratic mixing rule
- o Hayden-O'Connell method
- o VPA (vapor phase association, also for HF)

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.

The last common setting is choosing the values for temperature or pressure.

Temperature [K]	Pressure [kPa]
300.00	101.325

For Residue Curves only:

The Runge-Kutta-Gill method for the numerical solution of the differential equation is used. The other option uses a constant step width and is normally slower and not that precise.
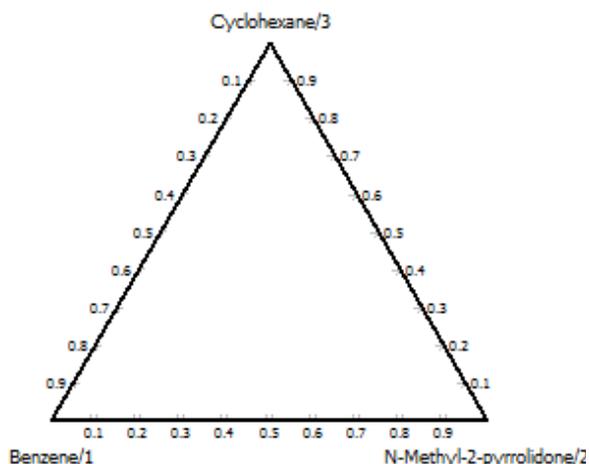
Calculation Mode
○ Fixed Delta (0.005)
⦿ Runge-Kutta-Gill

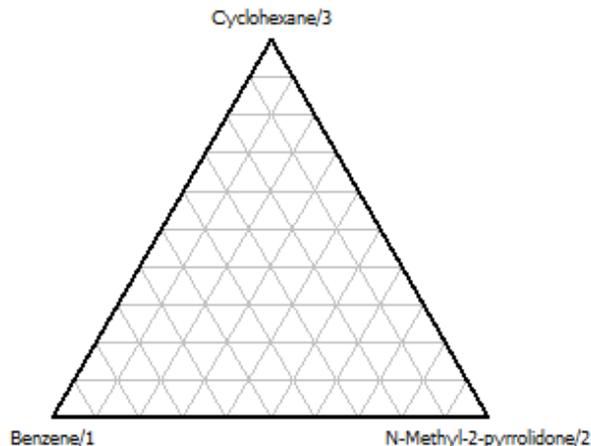**Options for Drawing the Gibbs' Triangle**

Gibbs Triangle
☐ Short Ticks   ☑ Labels

These two options change the look of the Gibbs' Triangle:
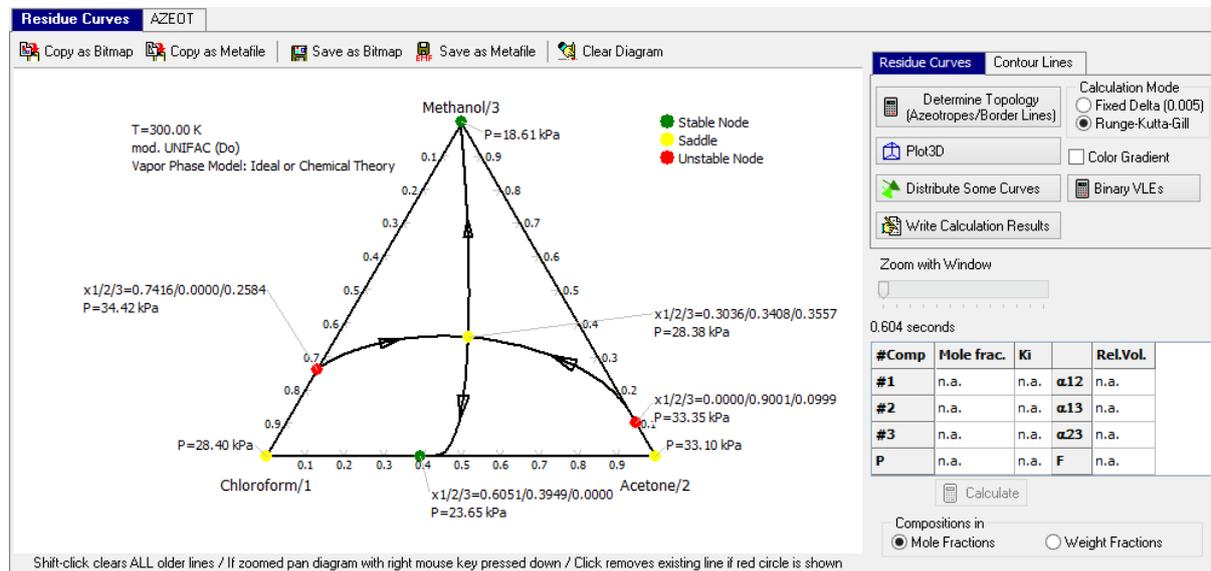
Short Ticks; Show Labels	Long Ticks; No Labels

Residue Curve Calculations

Having set the boundary conditions, the topology of the system can be calculated by clicking the button "Determine Topology (Azeotropes / Borderlines)".

At first, a search for binary and ternary azeotropes is performed. Together with the required pure component properties at the selected calculation conditions, the program determines the topology of the investigated system (i. e. whether a component is an absolute high boiler, absolute low boiler or saddle). The resulting topology is automatically displayed in the result window.

The selected calculation conditions can be seen at the upper left corner of the result window. Pure components as well as binary and ternary azeotropic points are colored according to their characteristics. For each point, the temperature (if running an isobaric calculation) or the pressure (if running an isothermal calculation) and in case of azeotropes also the composition is shown. And finally, the borderlines which divide the mixture into (four) distillation regions are colored black.

Residue curves are added by left-clicking inside the triangle. All older curves are deleted by shift-clicking on the curve; single curves can be removed by left-clicking very close to that line. 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 and the corresponding temperature (if running an isobaric calculation) or pressure (if running an isothermal calculation) is shown in the grid on the right-hand side. Additional values are the K-factors and the separation factors.

The program then calculates the residual curves starting from that point.

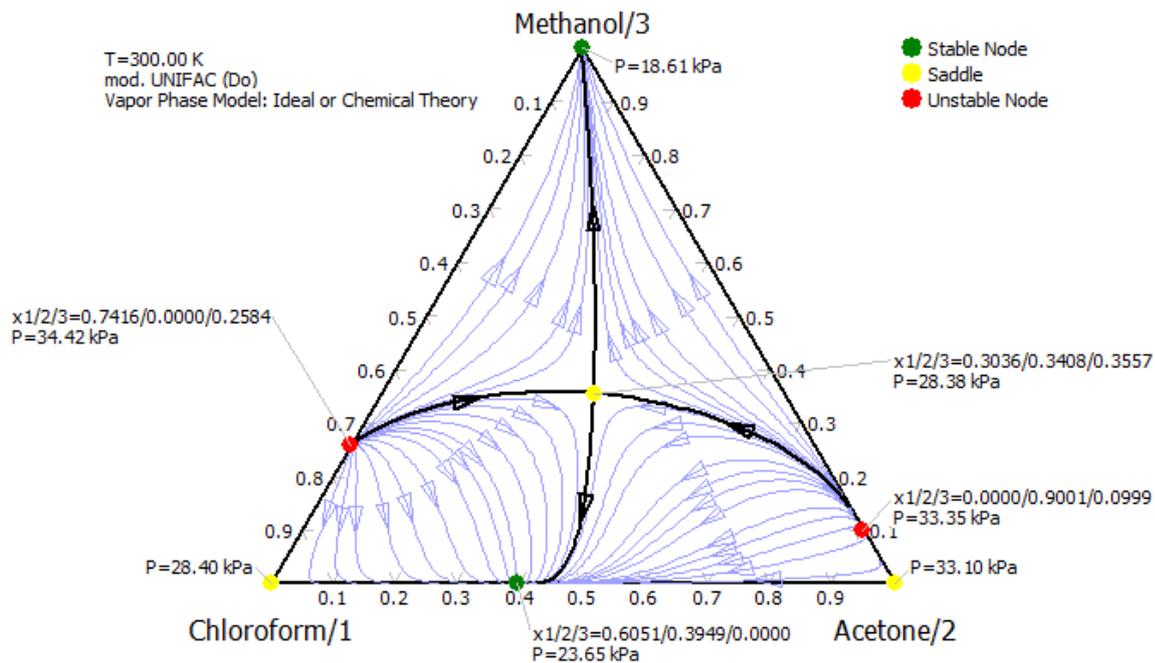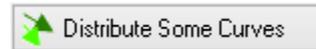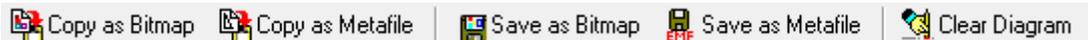The button "Distribute some curves" can be used to add some uniformly distributed residual curves.

**Figure 1:** Result of "Distribute Some Curves"

To store the results, the plot can be copied to the clipboard either as bitmap or as metafile or saved as bitmap and metafile respectively.
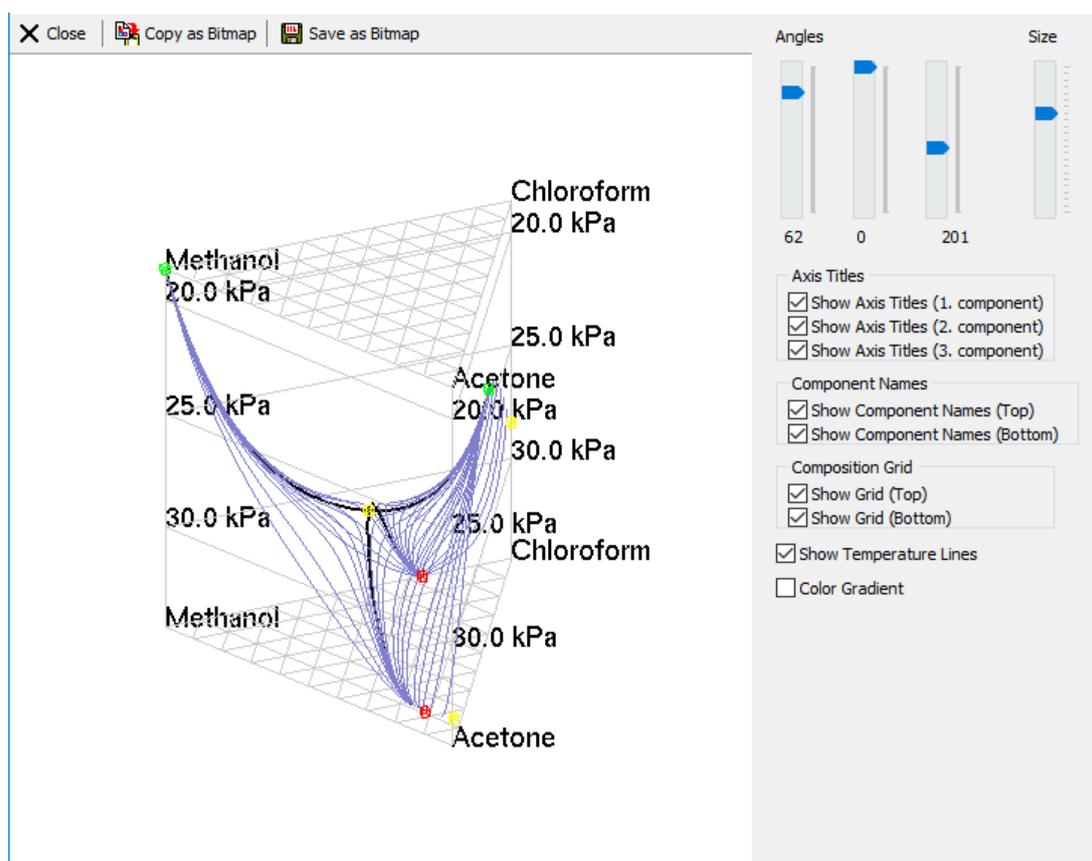

And the calculation results can be saved as plain text to a file.

To get a better impression about the topology, the "Plot3D" – button uses OpenGL for the visualization in a three-dimensional space. Here, the temperature (if running an isobaric calculation) or the pressure (if running an isothermal calculation) is plotted on the z-axis.
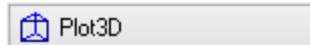
The diagram can be rotated with the left mouse key pressed down and moved with the right mouse key pressed down. The sliders on the right-hand side also allow free rotation of the plot. Pressing the little buttons above the sliders enables an auto-rotate mode along the respective axis. The grid may be switched on or off and smooth the lines using the check boxes. Azeotropes and pure components are represented by little cubes. The color is the same as in the 2D Plot. The time to display the 3D – plot varies a bit with the amount of data to display.

The option "Color Gradient" changes the colors of the residual curves and show high pressure or temperature values in red and low values in blue.
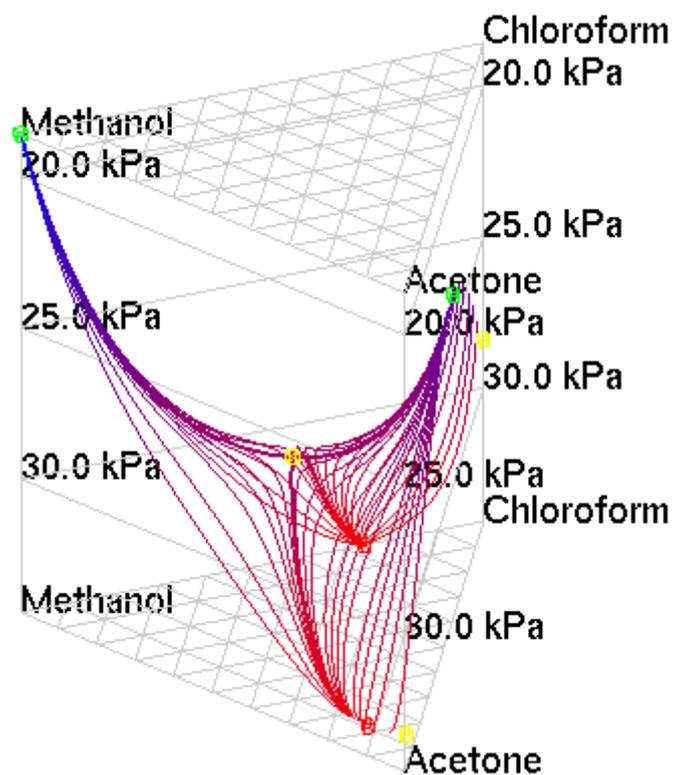

 "Clear Diagram" finally clears the diagram without deleting the components and settings and removing the components from the component list is the precondition to set up a new system.
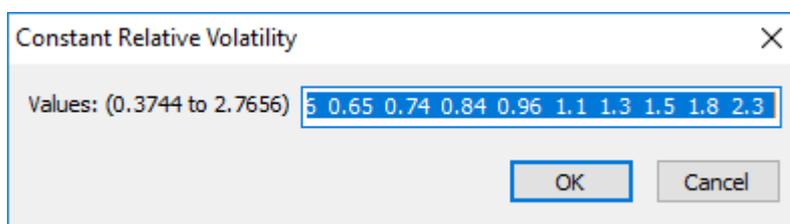
Contour Line Calculation

The program supports the calculation of contour lines for the properties

- Separation factor of two components (1-2, 1-3, 2-3)
- K factors for the three components
- Pressure
- Temperature
- $F = |1 - \alpha_{12}| + |1 - \alpha_{13}| + |1 - \alpha_{23}|$
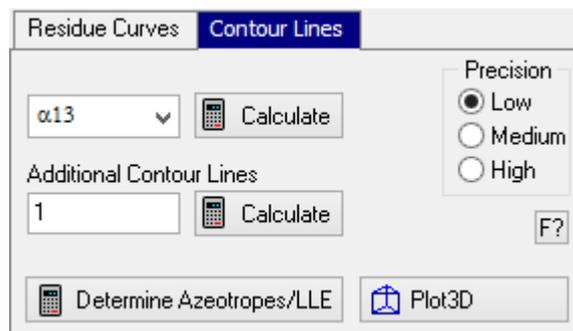
The program supports the calculation of multiple lines with a constant value. In this mode, the program determines the minimum and maximum values and displays a uniformly distributed list of values which can be edited.

The "Additional Contour Lines" edit field allows adding further single contour lines, if needed.

The "Precision" selection alters some iteration parameters. A calculation with a low precision is much quicker but much less precise and will probably also overlook some lines. It is recommended to use high precision and only switch to lower precision on very slow workstations.

A typical result for a system of two components forming a binary azeotrope where a third component is used as an entrainer to change the separation factors away from unity in order to break the azeotrope is the mixture of Cyclohexane and Benzene where NMP can be used as third component in the separation process.
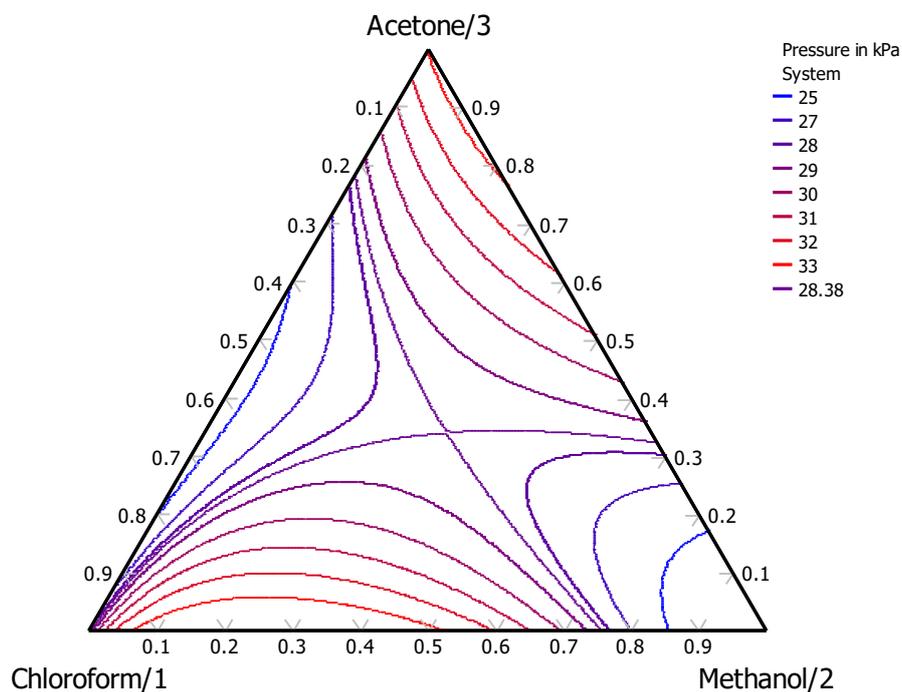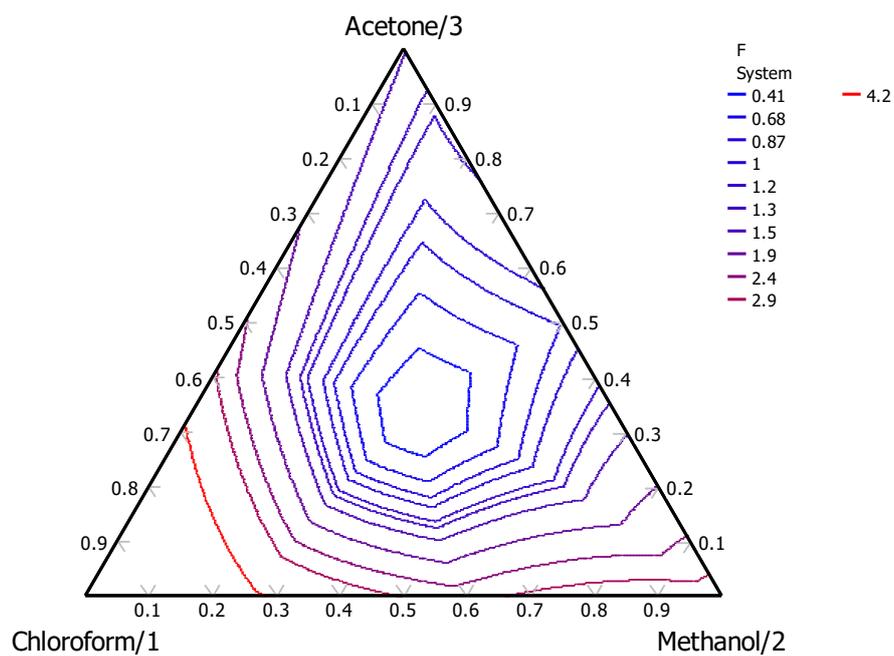
A typical K factor diagram:
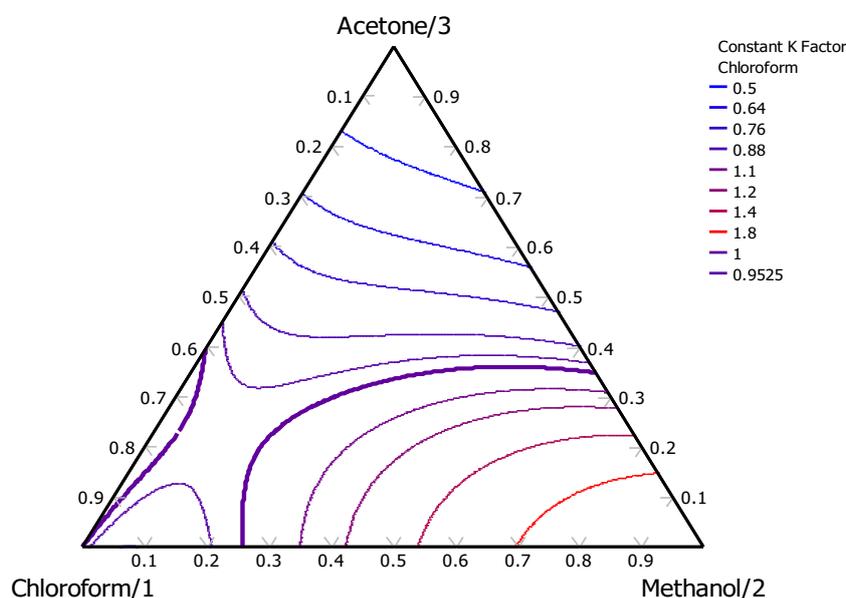
A typical relative volatility diagram:
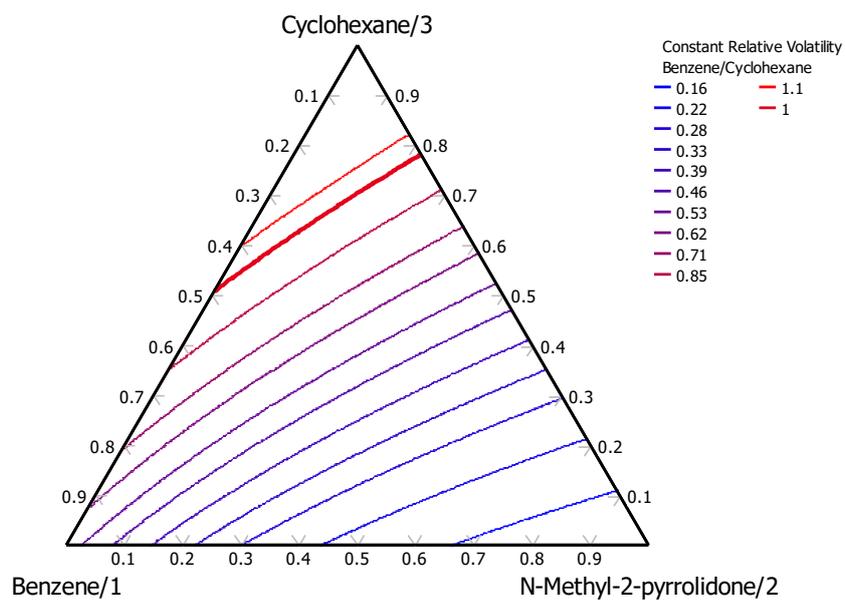
A typical diagram with constant pressures is

and a diagram with sum of differences of separation factors to one is

This diagram draw "circles" around the ternary azeotropic point.

Prediction of Azeotropic Points

The prediction of azeotropic points uses the same component and model specification as the calculation of residue curves and contour lines does. The only additional information needed are temperature or pressure ranges.

The program calculates azeotropic points for the specified mixtures and for all sub systems starting with all binary mixtures.

The result is presented as text and as table both having their specific advantages. Binary and ternary azeotropes can also be plotted.