

# CalculateX3

Calculation of Ternary Phase Equilibrium Diagrams

**DDBSP** - Dortmund Data Bank Software Package



DDBST Software & Separation Technology GmbH

Marie-Curie-Straße 10

D-26129 Oldenburg

Tel.: +49 441 36 18 19 0

Fax: +49 441 36 18 19 10

[support@ddbst.com](mailto:support@ddbst.com)

[www.ddbst.com](http://www.ddbst.com)

|          |                                       |           |
|----------|---------------------------------------|-----------|
| <b>1</b> | <b>Introduction .....</b>             | <b>3</b>  |
| <b>2</b> | <b>Overview.....</b>                  | <b>3</b>  |
| 2.1      | Component Selection .....             | 4         |
| <b>3</b> | <b>Calculation .....</b>              | <b>4</b>  |
| <b>4</b> | <b>Calculation Settings .....</b>     | <b>4</b>  |
| 4.1      | Calculation Step Width .....          | 5         |
| 4.2      | Temperature .....                     | 5         |
| 4.3      | Pressure .....                        | 5         |
| 4.4      | Activity Coefficient Models .....     | 5         |
| 4.5      | Adding Experimental Data .....        | 5         |
| 4.6      | VLE Output.....                       | 6         |
| <b>5</b> | <b>Calculated Data .....</b>          | <b>6</b>  |
| 5.1      | Typical Results .....                 | 7         |
| 5.1.1    | Solid-Liquid Equilibria .....         | 7         |
| 5.1.2    | Vapor-Liquid Equilibria.....          | 8         |
| 5.1.3    | Excess enthalpies .....               | 9         |
| 5.1.4    | Activity Coefficients .....           | 10        |
| 5.1.5    | Activities.....                       | 11        |
| 5.2      | Rotating and sizing the diagram ..... | 12        |
| 5.3      | Copying and saving the diagram .....  | 13        |
| <b>6</b> | <b>Contour Lines .....</b>            | <b>13</b> |
| <b>7</b> | <b>Limitations .....</b>              | <b>14</b> |
| 7.1      | Solid-Liquid Equilibria .....         | 14        |
| 7.2      | Vapor-Liquid Equilibria .....         | 14        |
| 7.3      | Models.....                           | 14        |
| <b>8</b> | <b>Literature .....</b>               | <b>15</b> |

## 1 Introduction

Vapor-liquid and solid-liquid phase equilibria as well as mixing enthalpies for ternary systems are quite difficult to visualize in an easily comprehensible manner. The program CalculateX3 has been implemented to solve this problem and deliver insight in the phase behavior of ternary systems.

CalculateX3 uses the activity coefficient models UNIFAC<sup>1,2,3,4,5</sup> and modified UNIFAC (Dortmund)<sup>6,7,8,9,10</sup> and the group contribution equations of state PSRK<sup>11</sup> and VTPR<sup>12,13</sup> to estimate the phase equilibria and mixing enthalpies.

The program is part of the DDBSP (Dortmund Data Bank Software Package) Part 1.5 “Mixture Data Bank Add On – Prediction Methods”.

## 2 Overview

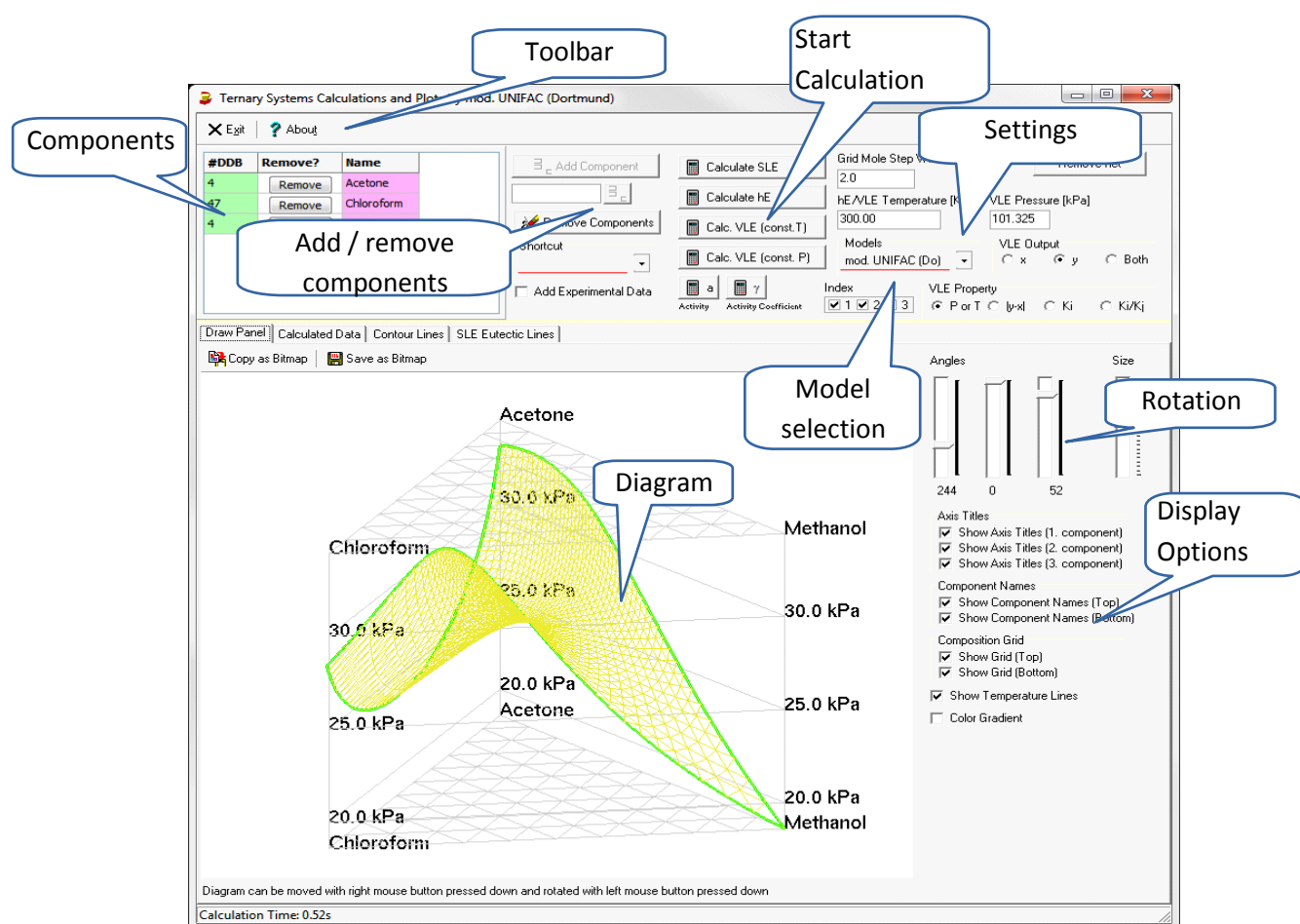


Figure 1: Main window.

## 2.1 Component Selection

The program allows the selection of three components either by the standard DDB component selection program using the “add component” button or by typing the DDB component numbers directly in the edit field .

Single components can be removed by selecting the “Remove” button of its line. The complete list can be removed by selecting the “Remove Components” button. The components can be sorted with the mouse by dragging a component to another line.

| #DDB | Remove?                               | Name        |
|------|---------------------------------------|-------------|
| 176  | <input type="button" value="Remove"/> | p-Xylene    |
| 154  | <input type="button" value="Remove"/> | Tetradecane |
| 175  | <input type="button" value="Remove"/> | m-Xylene    |

| #DDB | Remove?                               | Name        |
|------|---------------------------------------|-------------|
| 154  | <input type="button" value="Remove"/> | Tetradecane |
| 176  | <input type="button" value="Remove"/> | p-Xylene    |
| 175  | <input type="button" value="Remove"/> | m-Xylene    |

The shortcut list box contains some typical systems for both solid-liquid equilibria and heats of mixing.

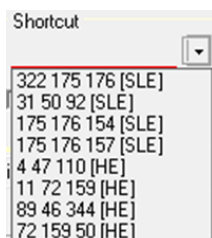


Figure 2: Shortcut list box.

## 3 Calculation

The calculation can be started by the four calculation buttons for  $h^E$ , SLE, VLE, and  $\gamma$ . The SLE calculation is the slowest because the program has to iterate a lot especially for finding the binary eutectic points and the ternary eutectic lines.

## 4 Calculation Settings

|                                     |                                       |
|-------------------------------------|---------------------------------------|
| Grid Mole Step Width [mole-%]       | <input type="button" value="Remove"/> |
| <input type="text" value="2.0"/>    |                                       |
| $h^E$ /VLE Temperature [K]          | VLE Pressure [kPa]                    |
| <input type="text" value="300.00"/> | <input type="text" value="101.325"/>  |

Figure 3: Calculation settings.

## 4.1 Calculation Step Width

The “Grid Mole Step Width” determines the resolution of the calculation grid. The smaller the step width is set the better the result will be – but the screen resolution limit will make results in very high resolutions looking strange.

## 4.2 Temperature

The temperature setting is only used for  $h^E$ , isothermal VLE, and  $\gamma$  calculations because the temperature is the SLE calculation result.

## 4.3 Pressure

The pressure is only used for isobaric VLE calculations.

## 4.4 Activity Coefficient Models

Currently only two models are supported:

- original UNIFAC
- modified UNIFAC (Dortmund)

Both models have been selected because they are still in development mainly through the UNIFAC consortium (<http://www.unifac.org/>) founded by Prof. Gmehling.

The  $g^E$  models UNIQUAC, Wilson, and NRTL will be supported in future revisions. Support for COSMO models (COSMO-RS(OI) and COSMO-SAC) is also planned.

## 4.5 Adding Experimental Data

It is possible to add experimental data if VLE, HE, ACT, or SLE data banks are available. The experimental data are displayed as small boxes.

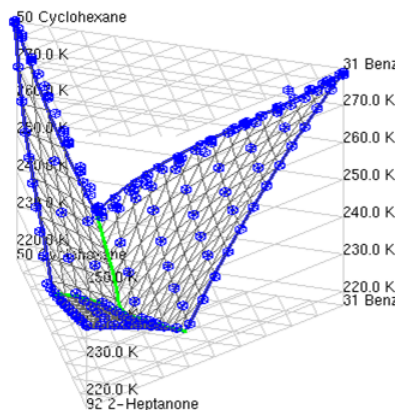


Figure 4: Added experimental data.

If multiple VLE data sets with matching (constant temperature or pressure) experimental data are shown a selection dialog which allows including or excluding single data sets.

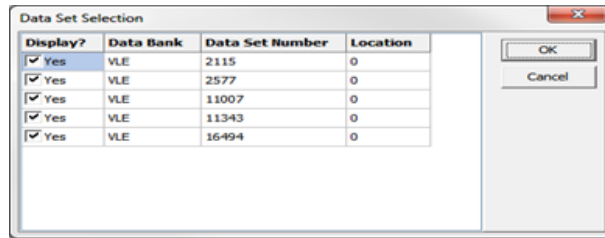
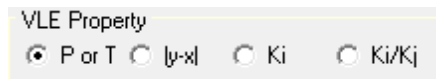


Figure 5: Data set selection.

## 4.6 VLE Output

VLE output can be the standard pressure or temperature planes (P for isothermal calculations, T for isobaric) or a deviation diagram of the absolute differences between liquid and vapor composition. Additional options are the display of K factors and the fraction between K factors (separation factor).



The second setting determines whether the liquid or the vapor composition or both should be used.



## 5 Calculated Data

The program calculates the entire component range from 0..1 for all components with the specified step size. The raw data are displayed in a table.

| Draw Panel   Calculated Data   Contour Lines   SLE Eutectic Lines |              |              |              |          |
|---|--------------|--------------|--------------|----------|
| Copy Grid   |              |              |              |          |
| #   | x1 [mol/mol] | x2 [mol/mol] | x3 [mol/mol] | T [K]    |
| 672   | 0.1400       | 0.6400       | 0.2200       | 329.2587 |
| 673   | 0.1400       | 0.6600       | 0.2000       | 329.3767 |
| 674   | 0.1400       | 0.6800       | 0.1800       | 329.5300 |
| 675   | 0.1400       | 0.7000       | 0.1600       | 329.7272 |
| 676   | 0.1400       | 0.7200       | 0.1400       | 329.9795 |
| 677   | 0.1400       | 0.7400       | 0.1200       | 330.3029 |

Figure 6: Calculated data.

The data table can be copied to the Windows clipboard.

## 5.1 Typical Results

### 5.1.1 Solid-Liquid Equilibria

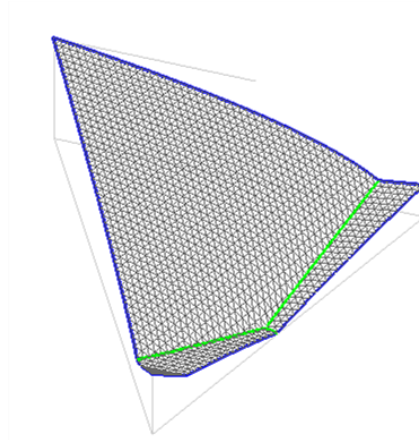


Figure 7: *m*-xylene – *p*-xylene - tetrachloromethane

Figure 7 shows a typical result where all labels and legends have been omitted. The mole fractions (resolution 2 mole-%) of the three components are displayed as a triangle as used typically in liquid-liquid equilibrium diagrams. The height of the lines are the melting points of the mixture at the given composition.

The blue lines are the binary SLE curves and the green lines are the eutectic curves for the ternary system. All three blue lines have minimums representing the eutectic point of the binary system. The three green lines start from the binary eutectic points and meet each other in the eutectic point of the ternary system representing normally the lowest melting point. The gray net represents the melting points of the mixture at the given composition.

#### 5.1.1.1 SLE Eutectic Lines

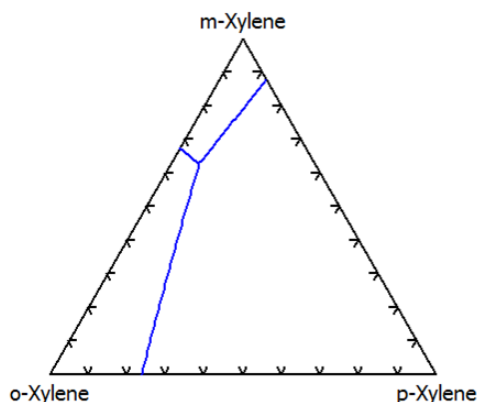


Figure 8: Eutectic lines.

This diagram is a projection of the 3D diagram to the 2D plane. It shows the eutectic lines only in a Gibbs' triangle.

### 5.1.2 Vapor-Liquid Equilibria

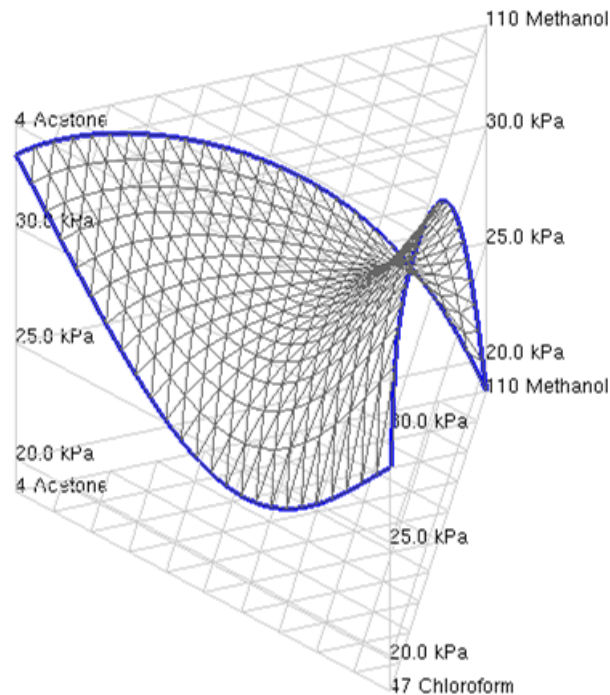
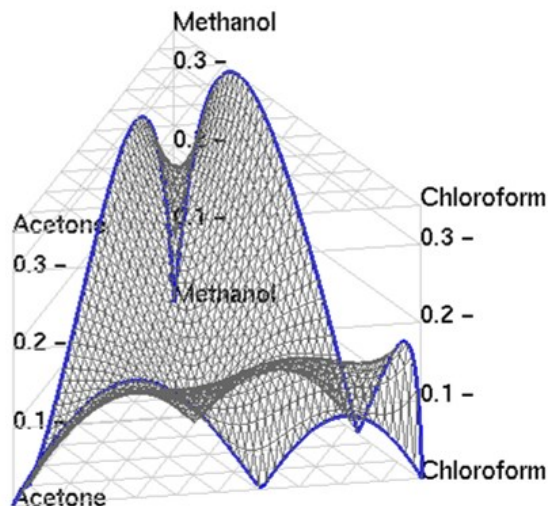


Figure 9: Methanol – acetone - chloroform

Figure 9 shows a not so typical result for a system building azeotropes in both the binary and ternary area. This is an example for a saddle-point azeotrope and it can be easily seen from the diagram why this name has been chosen. In these diagrams all labels and legends are shown and the resolution is 5 mole-%. Acetone and chloroform form a pressure minimum azeotrope, whereas chloroform and methanol as well as acetone and methanol form a pressure maximum azeotrope.

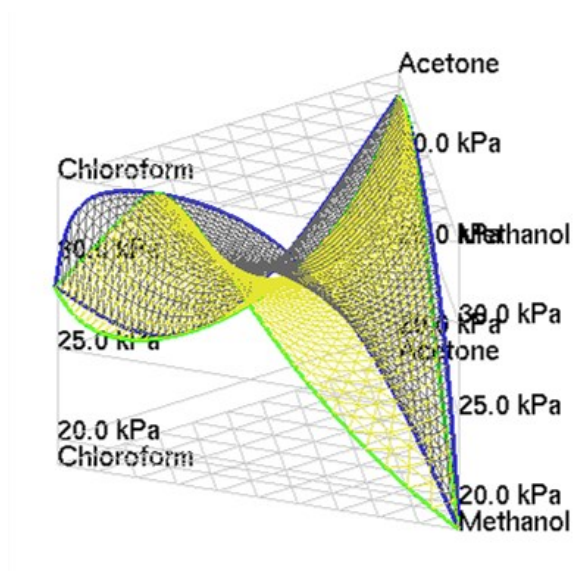
The deviation diagram (deviation between vapor and liquid compositions)





**Figure 10:** Deviation diagram.

shows the azeotropic point as 0 values touching the bottom. If both vapor and liquid composition are selected, two planes are shown.

**Figure 11:** Vapor and liquid composition planes.

### 5.1.3 Excess enthalpies

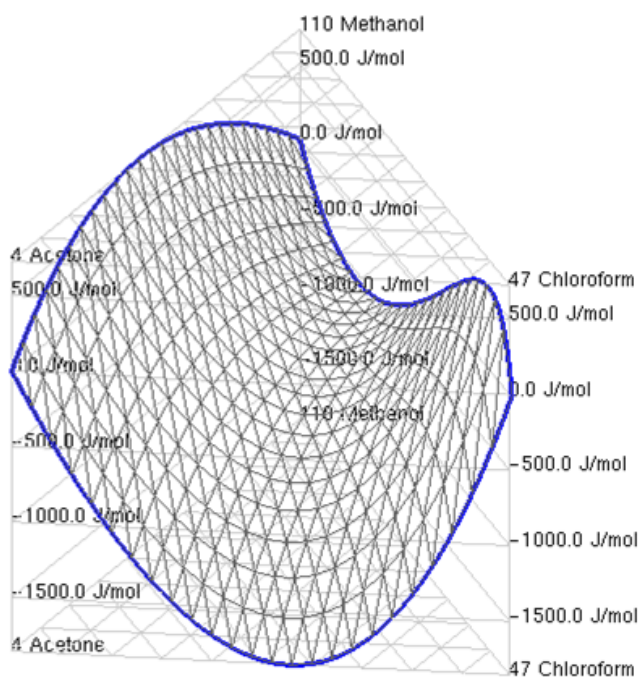
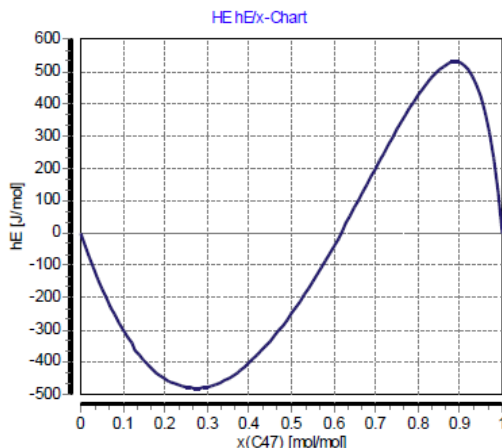
**Figure 12:** Excess enthalpies of the system methanol – acetone – chloroform.

Figure 12 shows the same system as already used for the VLE calculation. The blue lines are the excess enthalpies of the binary systems. The binary system acetone - chloroform has strong negative excess enthalpies. A negative value denotes that mixing is exothermic. The excess enthalpies of the system methanol - acetone are strong positive. This positive value indicates that mixing is endothermic. The  $h^E$  has a quite similar shape as the VLE diagram but it doesn't build a saddle.

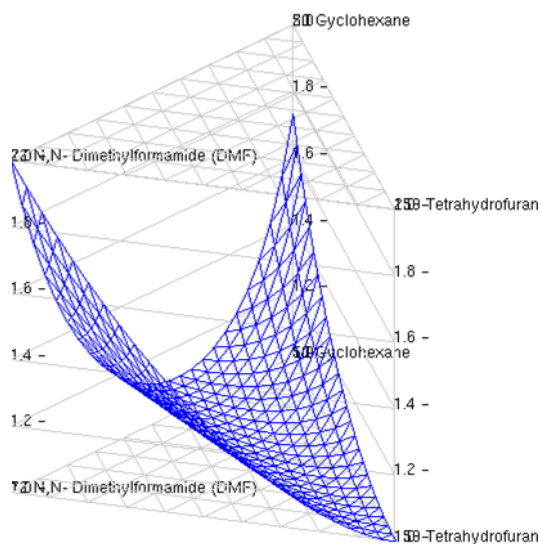


**Figure 13:** Excess enthalpies of the system Chloroform – methanol.

The system Chloroform/Methanol has both a positive and a negative excess enthalpy depending on the composition of the mixture.

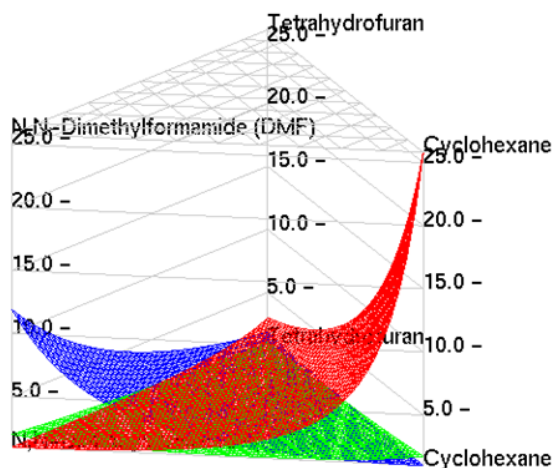
### 5.1.4 Activity Coefficients

The activity coefficient calculation needs one further setting. It has to be determined for which component the  $\gamma$  shall be shown.



**Figure 14:** System DMF – THF – cyclohexane.

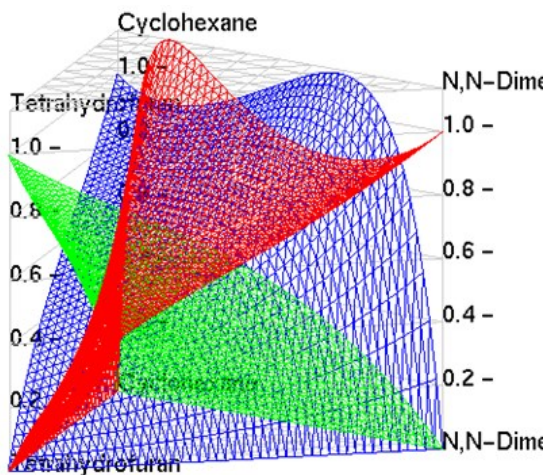
Figure 14 shows the activity coefficient plane of cyclohexane in the ternary system cyclohexane - tetrahydrofuran - N,N-dimethylformamide. In this calculation only the calculated net for the complete compositions is shown and the binary lines are not emphasized. The diagram with all three activity coefficients are look like this:



**Figure 15:** Activity coefficients for the ternary system DMF – THF – cyclohexane.

### 5.1.5 Activities

Activities are defined as  $sa_i = x_i * \gamma_i$ . The activity calculation has also one further setting. It has to be determined for which component the activity shall be shown.

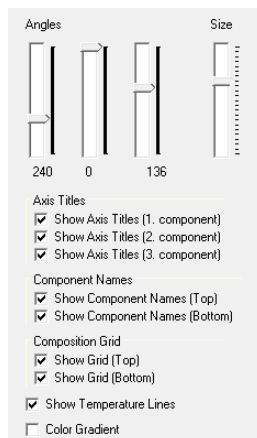


**Figure 16:** Activities for the ternary system DMS – THF – cyclohexane.

## 5.2 Rotating and sizing the diagram

Rotating can also be done directly by the mouse. If the mouse is moved over the diagram – and the left mouse key is pressed down – the diagram will be rotated around the x axis when the mouse cursor is moved up and down, and around the y axis when the mouse cursor is moved to the left or right.

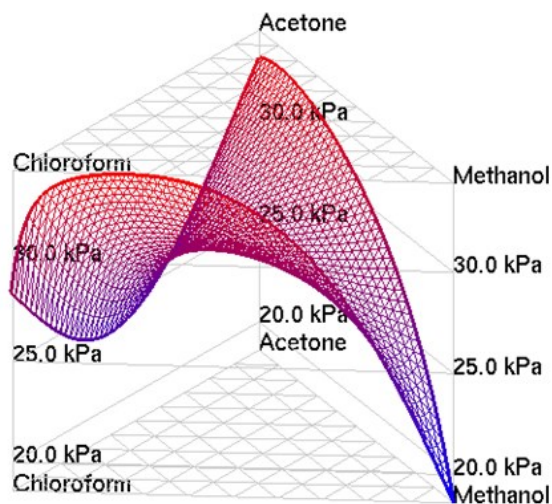
With the right key pressed down the chart can be moved. The check boxes below the sliders allow switching on and off labels and legends in the diagram.



**Figure 17:** Rotating and sizing options.

The three sliders below the “Angles” title on this panel sitting at the right side of the diagram also allow rotating the diagram in all three directions in space. The “Size” slider enlarges or reduces the size of the diagram.

Color gradient replaces the normal single color by a gradient from blue for low values to red for high values. A typical example is this:



**Figure 18:** Color gradients.

### 5.3 Copying and saving the diagram

The diagram can be copied to the clipboard using the tool bar button “Copy as bitmap”. “Save as bitmap” saves the diagram to a file.

## 6 Contour Lines

Contour lines (or isolines) are lines representing a constant property. These properties are the melting temperature in case of solid-liquid equilibria, in case of an isothermal or isobaric vapor-liquid equilibrium the pressure or the temperature, the enthalpy in case of heats of mixing and the activity coefficient in case of activity coefficients.

A contour line diagram is a 2D projection of the 3D diagram. It has the same triangle for the compositions (mole fractions) of the three components but it displays the value of the calculation in a flat diagram. The lines are colored with respect to its value in the range of available values. Red lines are close to the maximum value and blue lines are close to the minimum value.

The program displays the minimum and the maximum value of the calculated property. The “Calculated values range” contains a list of property values. The count is calculated by the “Grid step width”. A value of 1 % would lead to 51 entries a value of 2 % to 26 entries and so on. The “Draw values” button displays all these values.

If only some lines are needed, their constant properties can be added in the “Some Lines” edit line and calculated by the “Draw some lines” button.

The data grid shows the values where the mouse cursor is located inside the diagram.

Single lines can be calculated either by typing a single value into the “Some lines” edit line or by clicking with the left mouse key inside the diagram.

A live calculation (direct drawing of lines when the mouse is moved) is done when the Control key (Ctrl, Strg, etc.) is pressed. This can become slow if the resolution is high.

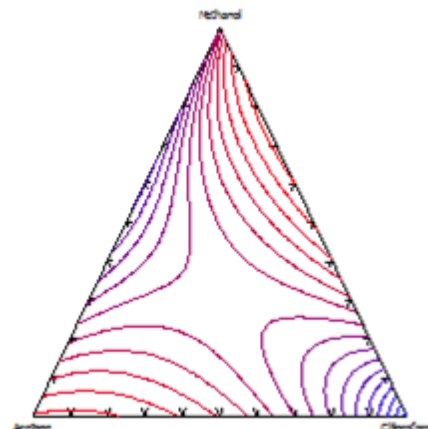
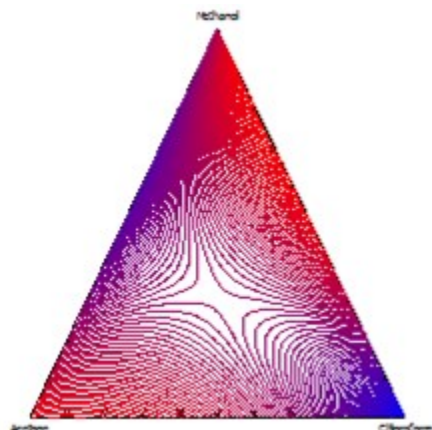
Minimum Value P [kPa]

Maximum Value P [kPa]

Calculated Values Range

Some Lines

| #Comp          | Mole frac.   |
|----------------|--------------|
| #1             | n.a.         |
| #2             | n.a.         |
| #3             | n.a.         |
| <b>Propert</b> | <b>Value</b> |
| P [kPa]        | 30.7994      |



## Limitations

The precision is determined by the resolution of the given composition. The algorithm uses the calculated values from the standard calculation and interpolates to the concrete value. This leads to artifacts in cases where isolines meet or cross and the slope is low.

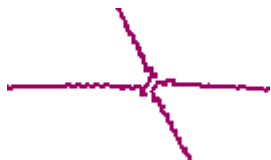


Figure 19: 1 mol% resolution.



Figure 20: 2 mol% resolution

## 7 Limitations

### 7.1 Solid-Liquid Equilibria

Only eutectic systems can be calculated correctly. A prerequisite for the calculation are the availability of the melting temperature ( $T_m$ ) and the melting enthalpy ( $H_m$ ) for every single component.  $T_m$  and  $H_m$  are both taken from the DDB basic component file.

### 7.2 Vapor-Liquid Equilibria

The vapor phase is calculated ideally and no test on liquid-liquid equilibrium is performed. If the vapor phase is strongly non-ideal or if miscibility gaps are present, the calculation will give wrong results.

The calculation needs the saturated vapor pressures for all pure components. The parameters are calculated with the Antoine equation for which the parameters are taken from the ParameterDB, a part of the Dortmund Data Bank.

### 7.3 Models

Both models are group contribution methods. The calculation needs the list of groups for every component which is taken from the DDB basic component file. The model specific group interaction parameters are provided through a DDB specific parameter file.

This parameter file and the list of groups exist in two versions. There's a relatively small list of groups and parameters which have been published in the freely accessible literature and there's an extended list of groups and parameters provided by the UNIFAC consortium (<http://www.unifac.org/>). This – by the factor of two – extended list is only available for members of that consortium. The consortium list contains not only many new parameters for new groups but also a lot of revised parameters.



## 8 Literature

---

- <sup>1</sup> Fredenslund A., Gmehling J., Michelsen M.L., Rasmussen P., Prausnitz J.M., "Computerized Design of Multicomponent Distillation Columns Using the UNIFAC Group Contribution Method for Calculation of Activity Coefficients", Ind.Eng.Chem. Process Des.Dev., 16(4), p450-462, 1977
- <sup>2</sup> Gmehling J., Rasmussen P., Fredenslund A., "Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension. 2", Ind.Eng.Chem. Process Des.Dev., 21(1), 118-127, 1982
- <sup>3</sup> Macedo E.A., Weidlich U., Gmehling J., Rasmussen P., "Vapor-Liquid Equilibria by UNIFAC Group-Contribution. Revision and Extension. 3", Ind.Eng.Chem. Process Des.Dev., 22(4), 676-678, 1983
- <sup>4</sup> Tiegs D., Gmehling J., Rasmussen P., Fredenslund A., "Vapor-Liquid Equilibria by UNIFAC Group Contribution. 4. Revision and Extension", Ind.Eng.Chem.Res., 26(1), 159-161, 1987
- <sup>5</sup> Wittig R., Lohmann J., Gmehling J., "Vapor-Liquid Equilibria by UNIFAC Group Contribution. 6. Revision and Extension", Ind.Eng.Chem.Res., 42(1), 183-188, 2003
- <sup>6</sup> Weidlich U., Gmehling J., "A Modified UNIFAC Model. 1. Prediction of VLE,  $h^E$ , and  $\gamma^\infty$ ", Ind.Eng.Chem.Res., 26(7), p1372-1381, 1987
- <sup>7</sup> Gmehling J., Li J., Schiller M., "A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties", Ind.Eng.Chem.Res., 32(1), 178-193, 1993
- <sup>8</sup> Gmehling J., Lohmann J., Jakob A., Li J., Joh R., "A Modified UNIFAC (Dortmund) Model. 3. Revision and Extension", Ind.Eng.Chem.Res., 37(12), 4876-4882, 1998
- <sup>9</sup> Gmehling J., Wittig R., Lohmann J., Joh R., "A Modified UNIFAC (Dortmund) Model. 4. Revision and Extension", Ind.Eng.Chem.Res., 41(6), 1678-1688, 2002
- <sup>10</sup> Jakob A., Grensemann H., Lohmann J., Gmehling J., "Further Development of Modified UNIFAC (Dortmund): Revision and Extension 5", Ind.Eng.Chem.Res., 45(23), 7924-7933, 2006
- <sup>11</sup> Holderbaum T., Gmehling J., PSRK: A Group-Contribution Equation of State based on UNIFAC. Fluid Phase Equilib. 1991, 70, 251.
- <sup>12</sup> Ahlers J., Gmehling J., Development of a universal group contribution equation of state. I. Prediction of liquid densities for pure compounds with a volume translated Peng-Robinson equation of state. Fluid Phase Equilib. 2001, 191, 177.
- <sup>13</sup> Schmid B., Gmehling J., Revised parameters and typical results of the VTPR group contribution equation of state. Fluid Phase Equilib. 2012, 317, 110-126.