User Guide for

Multiflash for Windows

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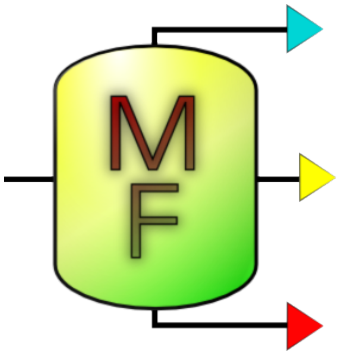

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Contents

Contents iii

Introduction

Introduction to Multiflash 3
The Multiflash user interface 3
Results output 5
Phase labelling 7
Flash calculations available in Multiflash 8
Bubble and dew point flash calculations 9
Model files 10
Specifying a model 10
Configuring Multiflash 12
Specifying default units 12
Specifying units during a session 13
Specifying folder locations 14

Using Multiflash

Defining fluids 17
Defining a standard fluid 17
Defining a petroleum fraction 18
Editing petroleum fraction data 20
Viewing pure component properties 20
Editing pure component properties 23
Editing temperature-dependent properties 24
Defining a fluid using a PVT analysis 25
Defining a fluid using a black oil analysis 28
Defining a fluid from distillation data 30
Adding a user-defined component 33
Applying the freeze-out model 36
Blending fluids 36
Blending example: petroleum fluids 38
Blending example: asphaltenic crudes 41
Blending example: waxy crudes 45
Stream types 49
Exploring the effect of user-defined pseudocomponents 52
Characterizing multiple fluids 55
Using mud numerical cleaning 58
Using the delumping tool 60
Basic flash calculations 62
Performing single flash calculations 63
Calculating bubble and dew points 64
Other preconfigured calculations 65
Performing a fixed phase flash calculation 65
Using the tolerance calculation tool 67
Calculating pure component properties 68
The phase envelope plotter 71
Plotting phase boundaries 71
Scaling the phase plot 74
Using initial values for the phase plotter 75
Plotting property boundaries 75

Generating other plot types 77
Plot tools 78
Working with PVT lab tests 79
Entering PVT lab test data 80
Validating data using the PVT lab tests 82
Simulating an experiment using the PVT lab tests 84
Tuning a model using the PVT lab tests 87
Multistage Separator Flash 91
Working with hydrates 93
Specifying the hydrate model 93
Calculating hydrate formation at a given pressure and temperature 95
Calculating hydrate formation and dissociation 98
Determining maximum allowable water content 104
Adding inhibitors with the inhibitor calculator 107
Salt calculator 109
Calculating inhibitor amounts required to suppress hydrate formation 110
Looking at the effect of inhibitors 112
Scale precipitation 116
Working with asphaltenes 121
Preparing for asphaltene calculations 121
Water and asphaltene calculations 122
Specifying the asphaltene model 123
Tuning the asphaltene model 124
Looking at the effect of input data on the asphaltene model 126
Looking at the effect of n-paraffins on the asphaltene model 132
Calculating asphaltene precipitation conditions 135
Calculations with no asphaltene precipitation data 137
Looking at the effect of gas injection 140
Working with waxes 143
Specifying the wax model 143
Tuning the wax model 145
Calculating the wax appearance temperature 147
Calculating wax precipitation 149
Plotting the wax phase envelope 151
Working with mixed solids 155
Looking at the effect of multiple solids formation 155
Calculate the APE with a wax phase present 157
Calculate the APE with hydrates and a wax phase present 160
Working with mercury species 163
Distribution of mercury species 163
Specifying the mercury model 163
Calculating mercury partitioning and dropout 164
Working with binary interaction parameters 171
Viewing binary interaction parameter values 171
Editing binary interaction parameter values 173
Looking at the effect of binary interaction parameters 174
Working with polar systems 177
Comparing the polar models 177
Exploring liquid-liquid equilibria 178
Identifying azeotropes 179
Identifying a eutectic point 181
Exchanging data with other programs 183
Exporting PIPESIM PVT files 183
Exporting OLGA files 185
Exporting PROSPER PVT files 187
Exporting a CAPE-OPEN property package 189
Exporting a Multiflash legacy file 189

Importing PVTsim files 190
PVT table file viewer 190
Example Excel spreadsheets 191
UNIFACFIT.xls 191
Using the spreadsheet 192
VLEFIT.xls 193
Using the spreadsheet 193

Multiflash Reference

Phases and components 197
Phase diagram: A brief description 197
Phase descriptors and key components 198
Key components 199
Components 200
Component properties 200
Enthalpy and entropy definition 203
Activity model enthalpy 204
Multiflash models 206
Models and component data requirements 206
Tuning models 209
Equation of state models 211
Equations of state available in Multiflash 211
Differences between the PR model in Multiflash and Aspen Hysys 215
Advanced equation of state options 216
The Peneloux density correction 216
Fitting the vapour pressure curve 216
Mixing rules 216
CSMA and GERG-2008 reference fluids 216
Activity coefficient models 218
Liquid activity coefficient models available in Multiflash 218
Solid phase models 220
Solid freeze-out model 220
Scaling 220
Hydrate formation and inhibition models 220
Hydrate model 220
Nucleation model 222
Ice modelling 223
Inhibitor modelling 223
Phases for hydrate modelling 223
Wax precipitation model 224
Asphaltene flocculation model 225
Combined solids model 225
Transport property models 226
Viscosity 226
Thermal conductivity 227
Surface tension 228
Diffusion coefficient 229
Binary interaction parameters 230
Temperature dependence 230
Units 230
BIPs and models 231
BIPs for CSMA and GERG mixing rule 231
BIPs available in Multiflash 232
Petroleum fluids 233
PVT laboratory analysis 233

True boiling point distillation data 233
D86 distillation data 233
Characterization 234
Data validation in PVT experiments 234
Constant mass expansion 234
Differential liberation 235
Constant volume depletion 235
Separator test 235
How the blending method works 236
Differences between blending and characterizing multiple fluids 236
Troubleshooting 237
Models 237
Input conditions 237
BIPs 238
PVT analysis 238
Flash calculations 239
Components 240
PVT analysis 241
Errors and warning messages 241
Technical support 242
About Multiflash 242
Glossary 245
Index 249

Introduction

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Introduction to Multiflash

Multiflash is a powerful and versatile system for modelling physical properties and phase equilibria. It can be used as a stand-alone program or in conjunction with other software.

Multiflash can provide:

- All the thermodynamic and transport properties needed for engineering studies.
- Comprehensive fluid characterisation and model tuning for petroleum fluids.
- Flash calculations to determine the phases present at specified conditions and their type, composition and amounts.
- Complete phase envelopes, showing phase boundaries and critical points.
- Modelling solids formation, including pure solids, halide scales, hydrates, waxes and asphaltenes.

Multiflash has a comprehensive set of configurable options, making it easy to specify all aspects of a study. Each configuration can be saved for future use with Multiflash or other compatible applications.

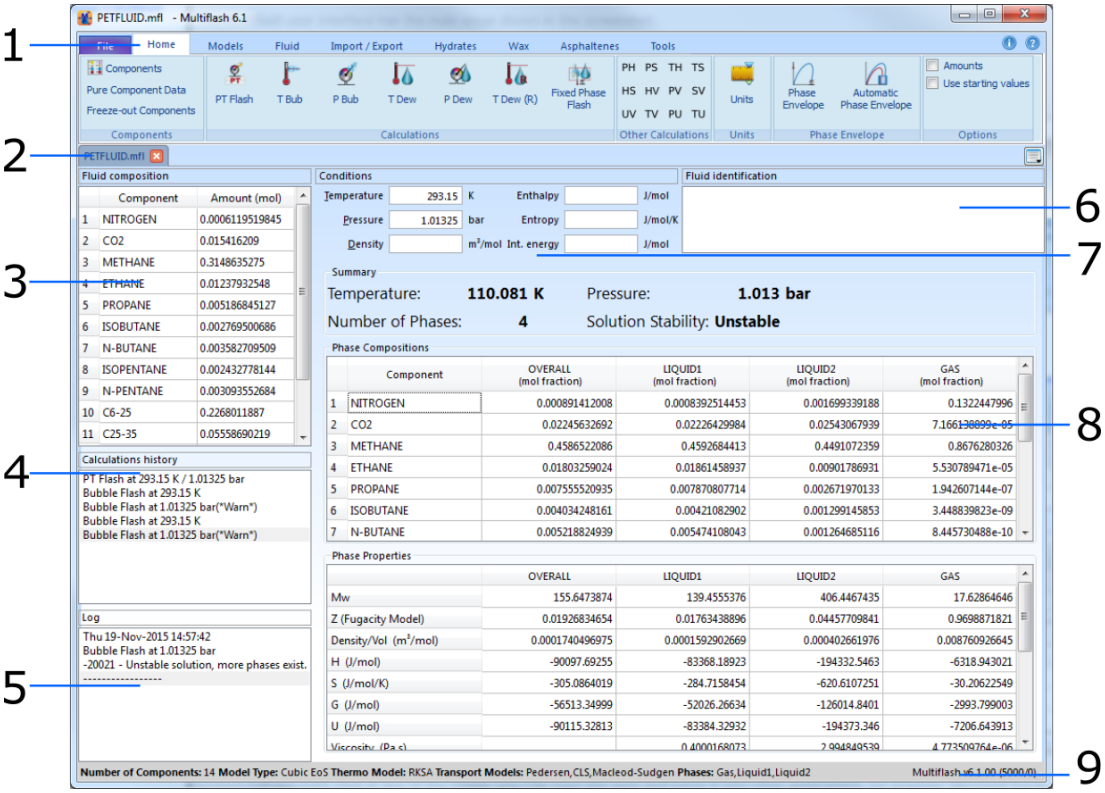
Multiflash can be accessed using:

- A graphical user interface.
- An add-in for Microsoft Excel.
- An interface for use with any application that is CAPE-OPEN enabled.
- Any software that can call a Windows DLL. We provide support for applications written in various programming languages, including C++, Visual Basic and Fortran. Linux applications can also be supported.

Separate documentation is available for each of these interfaces.

The Multiflash user interface

The Multiflash user interface has the main areas shown in the screenshot.



Item	Description
1	The ribbon provides access to all functions available through the user interface. Related functions are grouped on each ribbon.
2	Each tab contains a separate Multiflash problem. The current tab is the one on which all functions are performed.
3	The **Fluid composition** panel shows the name and amount of each component that comprises the fluid under investigation. You must enter a fluid composition before any calculation can be made. You can edit the amount of a component at any time by clicking on the value and then typing the new amount in the units specified in the column header.
4	The **Calculations history** panel shows each calculation performed on the fluid. If you click on any calculation, the results of that calculation appear in the **Results** area. **Tip:** Right click on any result in this list and you can export the result in a single operation to the clipboard, ready to be pasted in **Excel**
5	The **Log** panel shows warning and error messages, labelled with a time stamp and the calculation used. If, at any time, your calculation fails, use the messages shown here to help you diagnose the problem with your calculation. You can clear the error messages by right-clicking within the **Log** panel, and selecting **Clear Errors**.
6	The **Fluid identification** panel is for adding comments and notes. This can be useful for future reference, for example, to identify the study and the source of the fluid data. Any text that you enter is saved as part of the .mfl file and shown when the file is reloaded.

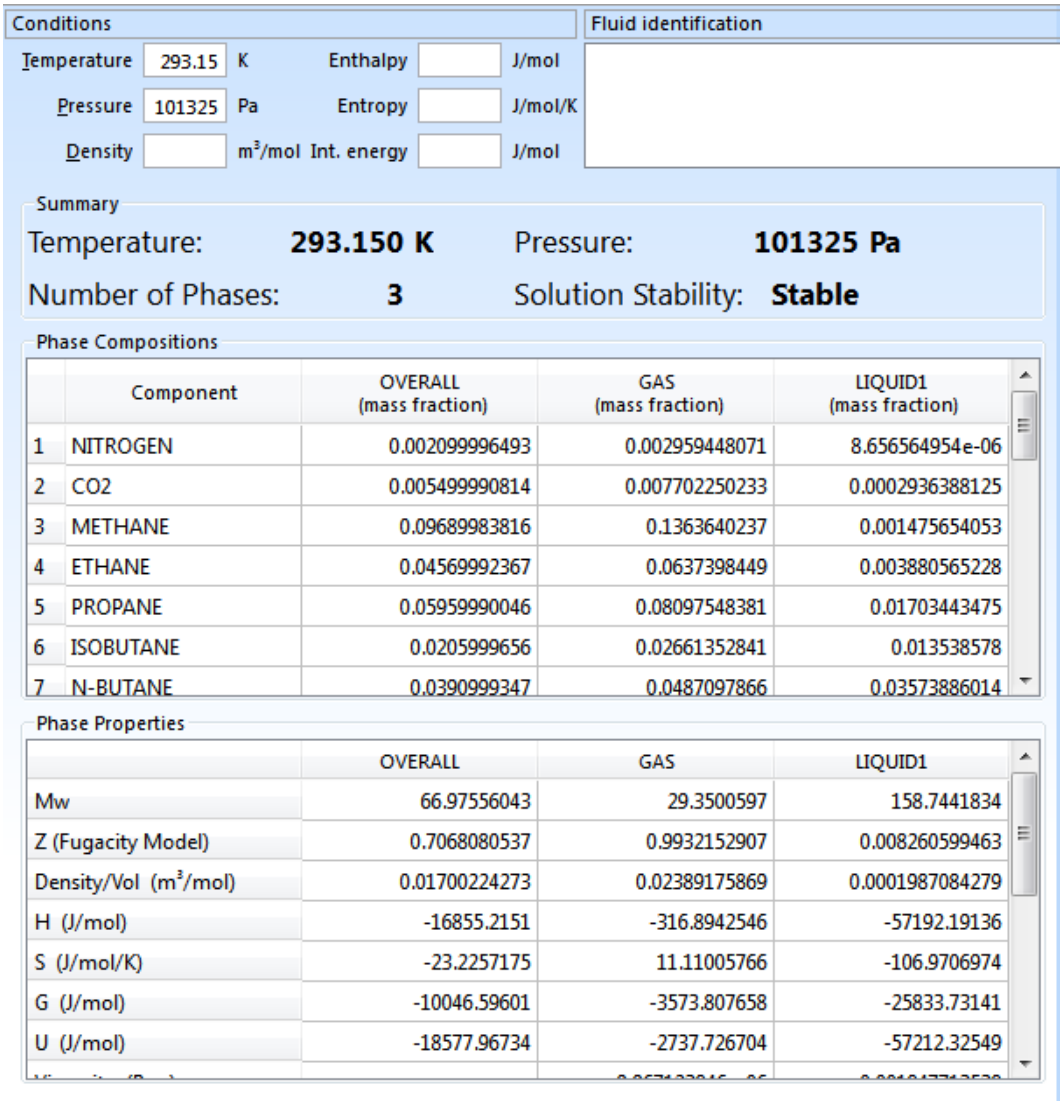
Item	Description
7	The **Conditions** panel is where you specify the initial conditions for Multiflash calculations. The conditions required depend on the calculation. Only the conditions required for your chosen calculation are used, so you can have values for other conditions, foe example, if you are going to perform a series of different flash calculations. You can specify the units used for input and output values.
8	The **Results** area shows all the values generated by the most recent Multiflash calculation. These generally consist of a summary together with the phase fractions, composition and properties, see *Results output*. If you right-click in any of the tables, you can copy the data and paste it into other applications, for example, Microsoft Excel.
9	The **Status Bar** area displays information about the loaded model: Number of components, main model type, transport property models and phases.

You can rearrange or combine the panels (2-7) into tabbed groups by holding down the left mouse button on the panel title bar and dragging to your preferred location. Valid locations are identified by a colour change or rectangular outline on the background of the main Multiflash window, depending on your current style setting. Your changes are valid only for the current session.

Results output

The results of every calculation are displayed in the **Results** area. The output will vary slightly, depending on the type of calculation and the level of physical property output specified, but will be in the style shown in the screenshot.

Tip: If, at any time, your calculation fails, use the messages shown in the **Log** panel to help you diagnose the problem with your calculation.



The **Results** area provides the information shown in the following table.

Item	Description
Temperature	The temperature of your calculated result.
Pressure	The pressure of your calculated result.
Number of Phases	The number of phases found for your calculated result.

Item	Description
Solution Stability	The stability of your calculated result, which is one of the following values: **Note:** Multiflash can only check for the stability of a solution with respect to the formation of another phase of a type already specified. For example, if you have only defined two liquid phases, the possible formation of a vapour or solid phase cannot be checked. ■ Stable: No further phases (out of the list provided) will form. ■ Unstable: Further phases might form if more phases are specified in the problem. For example, if only vapour and one liquid phase are specified but in fact the true solution is vapour-liquid-liquid, you must include an additional phase descriptor in your model definition. **Note:** The results of a hydrate nucleation calculation are always labelled unstable because this is not an equilibrium point. ■ Marginally Stable: Although the solution is stable, changing the conditions slightly might result in the formation or disappearance of a phase, for example, near the critical point.
Phase Compositions	The table shows each component and its amount in each phase. For a point calculated on a phase boundary, the amounts for the zero phase represent those at the initial phase appearance. The last line shows the total for each phase. If you check **Total Amounts**, the amount of each phase and each component is shown absolute amounts instead of fractions.
Phase Properties	The properties that appear here provide the property values for the whole fluid, and each phase. For a point calculated on a phase boundary, the property values for the zero phase represent those at the initial phase appearance.

Phase labelling

The list of phases displayed after a flash calculation shows the phase label for each phase. At low pressures there is usually a clear distinction between a gas phase and a liquid phase. This is not the case in the 'dense phase' region above the vapour-liquid phase envelope, where the phase present is supercritical. In such cases there is no physical distinction between a gas and a liquid, and the phase label assigned by Multiflash is arbitrary.

The criterion used to label a supercritical phase gas or liquid is:

- A phase is labelled as gas if $VT^2 > V_c T_c^2$, where V_c and T_c are the pseudo-critical temperature and volume, otherwise the phase is labelled as liquid.

Note: The pseudo-critical properties are model-dependent and do not correspond to the true critical properties for a mixture.

One consequence of this is that the phase name might change with slight alterations in your initial conditions. A change in the phase label does not affect the correctness of the results or phase properties, it is only the label attached to the phase that is ambiguous.

These conditions only apply to equation of state type models that can represent both gas and liquid phases. Phase properties, such as density and enthalpy, are not affected by the label attached to the phase since, by definition, the phase is supercritical and there is only one solution for the volume of the equation of state model.

Flash calculations available in Multiflash

The following flashes can be calculated in Multiflash and are available from the Main ribbon. The table shows the required input values for each flash calculation. The input values are taken from the Conditions area of the main window. If the calculation has a shortcut, the icon is shown.

Flash name	Description	Required input
PT Flash 	Isothermal flash, a calculation of the equilibrium conditions of a given mixture at specified pressure and temperature. You can determine the number and type of phases present and the properties of those phases. It is the most widely applicable and the most reliable of the flash calculations.	Temperature Pressure
T Bub 	Bubble point at fixed temperature.	Temperature
P Bub 	Bubble point at fixed pressure.	Pressure
T Dew 	Dew point at fixed temperature.	Temperature
P Dew 	Dew point at fixed pressure.	Pressure
T Dew (R) 	Retrograde dew point at fixed temperature. This enables you to do the calculation without using the fixed phase fraction flash.	Temperature
PH Flash	Isenthalpic flash at fixed pressure and enthalpy. This is useful for studying flow through valves or pipelines.	Pressure Enthalpy
TH Flash	Isenthalpic flash at fixed temperature and enthalpy.	Temperature Enthalpy
PS Flash	Isentropic flash at fixed pressure and entropy. This is used for adiabatic and reversible processes, for example, a turbo expander.	Pressure Entropy
TS Flash	Isentropic flash at fixed temperature and entropy. This is used for adiabatic and reversible processes.	Temperature Entropy

Flash name	Description	Required input
HS Flash	Isentropic flash at fixed enthalpy and entropy. This is used for adiabatic and reversible processes, for example, turbine calculations.	Enthalpy Entropy
PV Flash	Isochoric flash at fixed pressure and volume. This is used for closed systems, for example, to find the temperature of a container for which the volume and pressure are known.	Pressure Density‡
SV Flash	Isochoric flash at fixed entropy and volume. This is used for closed systems.	Entropy Density‡
TV Flash	Isochoric flash at fixed temperature and volume. This is used for closed systems, for example, to find the pressure of a container for which the volume and temperature are known.	Temperature Density‡
UV Flash	Isochoric flash at fixed internal energy and volume. This is used for closed systems.	Internal energy Volume
HV Flash	Isochoric flash at fixed enthalpy and volume.	Enthalpy Volume
PU Flash	Flash at fixed pressure and internal energy.	Internal energy Pressure
TU Flash	Flash at fixed temperature and internal energy.	Internal energy Temperature
Fixed Phase Flash 	Flash at a specified temperature or pressure, with a specified fraction of one of the phases. This has many applications, for example, to find the freezing point of a phase, or the point at which mercury precipitates.	Pressure or temperature Phase fraction

‡Multiflash calculates the volume of your system from the measured density of your fluid and the fluid composition that you have entered, providing greater flexibility in the calculations that you can do.

Bubble and dew point flash calculations

In a simple two phase system, a dew point is the first point at which liquid appears. In a multiphase situation, there can be a dew point for each liquid phase.

The standard Multiflash dew point calculation returns the primary normal dew point, defined as follows:

- The temperature (at a fixed pressure) at which the first liquid phase appears as the temperature is reduced.
- The lowest pressure (at a fixed temperature) at which the first liquid phase appears.

In most oil and gas systems there is also a retrograde dew point, corresponding to condensation of liquid from a gas phase as the pressure is reduced. The retrograde dew point pressure (at fixed temperature) is

the pressure at which a liquid phase appears as the pressure is reduced. The retrograde dew point can be calculated using the fixed phase flash calculation, setting the fixed amount of the phase to zero.

The bubble point is the first point at which gas appears as the pressure is reduced at fixed temperature or the temperature is increased at fixed pressure.

The bubble point calculation returns the bubble point, defined as follows:

- The temperature (at a fixed pressure) at which the first bubble of vapour is formed as the temperature is increased.
- The pressure (at a fixed temperature) at which the first bubble of vapour is formed as the pressure is decreased.

Depending on the temperature or pressure specified, and where this is in relation to the phase envelope and critical point, a dew point or bubble point calculation might not have a solution.

Model files

Multiflash uses model files to store model and calculation details. Model files have the suffix .mfl.

Model files can contain any combination of the following:

- Model definition
- Fluid definition (components and amounts)
- Experimental conditions
- Modified model parameters (from tuning models)
- Experimental data entered for the fluid.

When you save a file, all information about the current state of the Multiflash experiment is saved, enabling you to return to that state when you reload the file.

You can save a model file at any time, by selecting **Save** on the **File** menu.

You can load a model file at any time, by selecting **Open** on the **File** menu.

Multiflash comes with a number of model files, stored in the MFL Files folder of the Multiflash installation. They are used for examples within the help, but also as useful starting points for calculations, for example, refrigerants.

Specifying a model

Your choice of model is critical to the success of the calculations that you perform with Multiflash. You should review the available models and their suitability for your required calculations before you specify your model.

You can specify your model in the following ways:

- Use one of the predefined models available from the ribbons. This method is recommended for general use, when there are no special requirements for your calculations. Choosing the model sets up the default options automatically.
- Load a previously saved model from file.

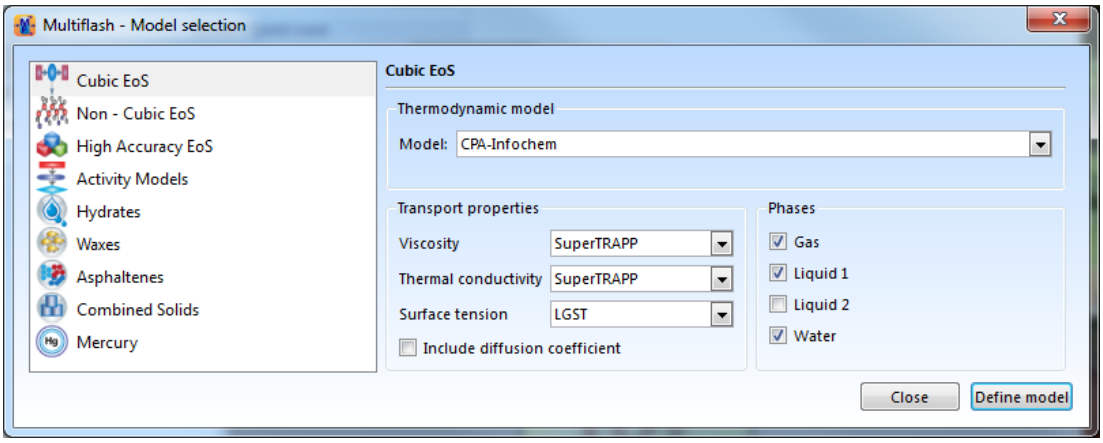
- Specify a model manually. This method is required when you have a specific requirement, for example, to add or remove phases from a calculation.

The predefined models are chosen by clicking the appropriate icon on the ribbons. General models are on the **Models** ribbon, and specialised models are available on the **Hydrates**, **Wax**, and **Asphaltenes** ribbons.

Tip: You can modify the options for a model at any time by clicking Select Model on the Models ribbon, and then adjusting the options as required.

To specify a model manually:

1. On the **Models** ribbon, click **Select Model**.



2. In the list, select the category of model that you want.
3. If available, choose your thermodynamic model.
4. If required, adjust the transport property options.
5. Check the box for each phase that you want to consider in your calculations.

   Tip: Specify only the phases that you need. Each phase added increases the calculation time.
6. Click **Define Model**, and then, on the message, click **OK**.

Tip: You can save your model definition in a file so that you do not need to respecify it each time that you want to use it. To do so, on the **File** menu, click **Save**, and give the file a descriptive name to help you identify it.

Configuring Multiflash

Specifying default units

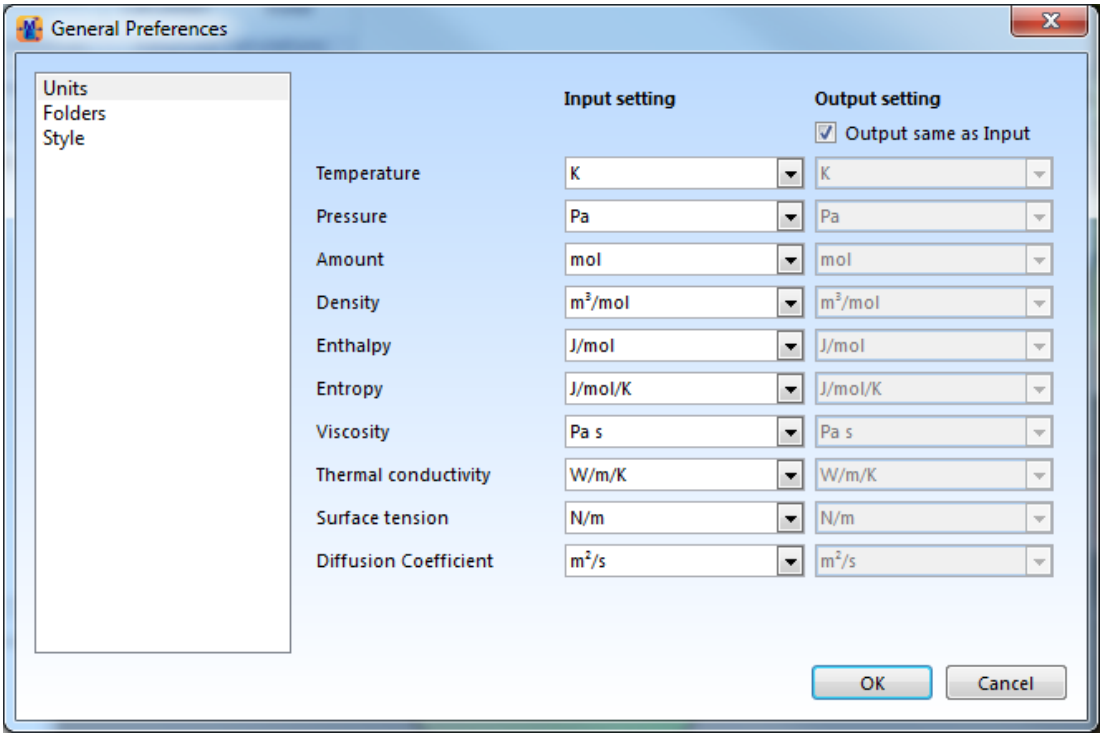
The default input and output units are SI units, but you can specify any available combination of units as your default values. You can specify different units for the input and output property values. The default units that you specify take effect at the beginning of each Multiflash session.

Note: If you create your own .mfl file and include numeric values without specifying the units, those values are not recalculated when the default units change. The values are assumed to be in the current default unit.

If you want to change the units used during a session, see *Specifying units during a session*.

To specify default units:

1. On the **Tools** ribbon, click **Preferences**.



2. To specify a unit for any input property, in that property's row, select the required unit from the list in the **Input setting** column.
3. To specify a unit for any output property, in that property's row, select the required unit from the list in the **Output setting** column.

   Tip: If you want to match the input and output units, check **Output same as Input**.
4. Click **OK**.

Result: The default units that you specify take effect at the beginning of the next Multiflash session.

Specifying units during a session

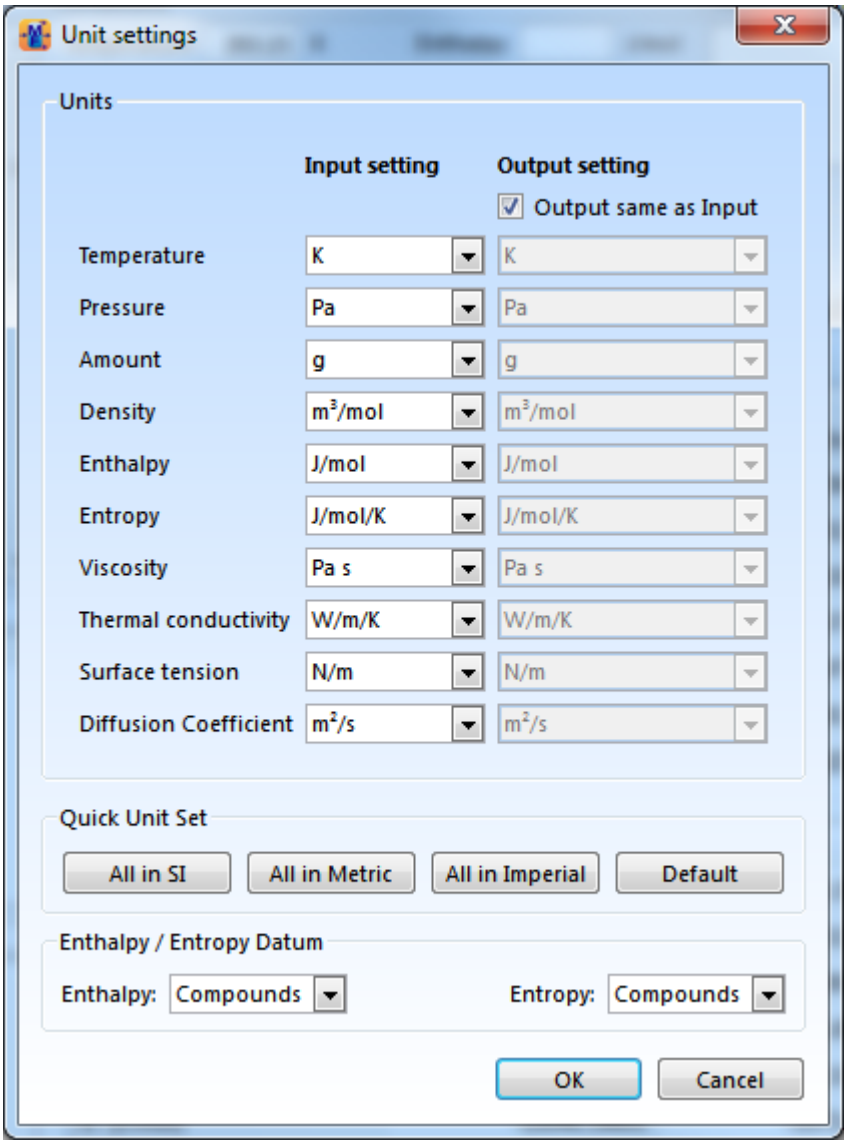
You can change the units used for your property values at any time within a Multiflash session. You can specify different units for the input and output property values. If you save a problem setup, the current unit definitions for your session are also saved.

If you want to change the default units that every session uses, see *Specifying default units*.

To change units:

1. On the **Home** ribbon, click **Units**.

   Tip: The Unit settings dialog box can be also accessed by clicking the **Units** button, when it appears on a dialog box, for example, the Tolerance Calculation dialog box.



2. To specify a unit for any input property, in that property's row, select the required unit from the list in the **Input setting** column.
3. To specify a unit for any output property, in that property's row, select the required unit from the list in the **Output setting** column.

Tip: If you want the same units for all input and output properties, check **Output same as Input**. Alternatively, you can use the **Quick Unit Set** buttons to specify a predefined unit set.

4. From the **Enthalpy** and **Entropy** lists, specify your required reference state for enthalpy calculations.

   Tip: See *Enthalpy and entropy definition* for details of the available reference states.

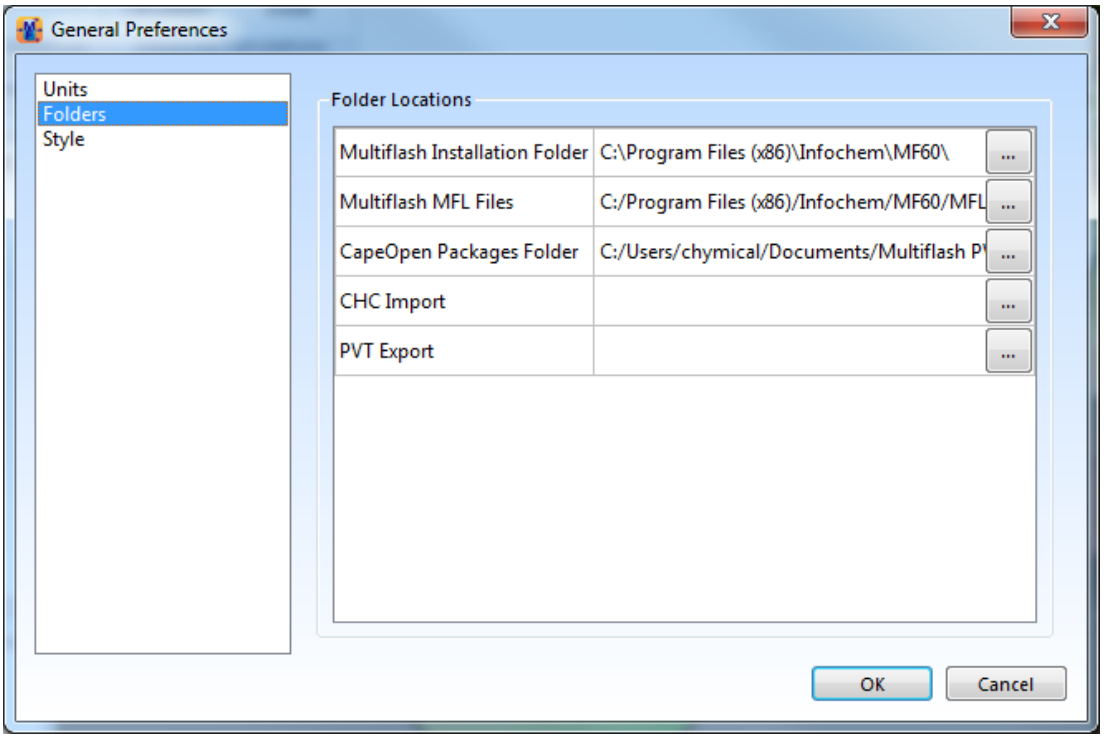
5. Click **OK**.

Specifying folder locations

Multiflash enables you to specify default folder locations for the various files used in Multiflash. This is useful when you regularly use specific locations.

To specify default folders:

1. On the **Tools** ribbon, click **Preferences**, and then click **Folders**.



2. To specify a folder location, click Browse  on the row of the file type, select your folder, and then click **Select Folder**.
3. Click **OK**.

Result: Multiflash uses the specified location as the default for that file type.

Using Multiflash

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Defining fluids

In Multiflash, a fluid is the mixture of components on which you carry out calculations. The definition of your fluid is therefore critical to the successful use of Multiflash.

A fluid can be defined in several ways:

- As a mixture of standard components.
- As a set of petroleum fractions.
- As a mixture of standard components and petroleum fractions.
- As a petroleum fluid characterised by a comprehensive PVT laboratory analysis.
- As a petroleum fluid characterised from limited data (black oil analysis).
- As a petroleum fluid characterised from experimental distillation data.
- As a blend of previously characterised petroleum fluids.

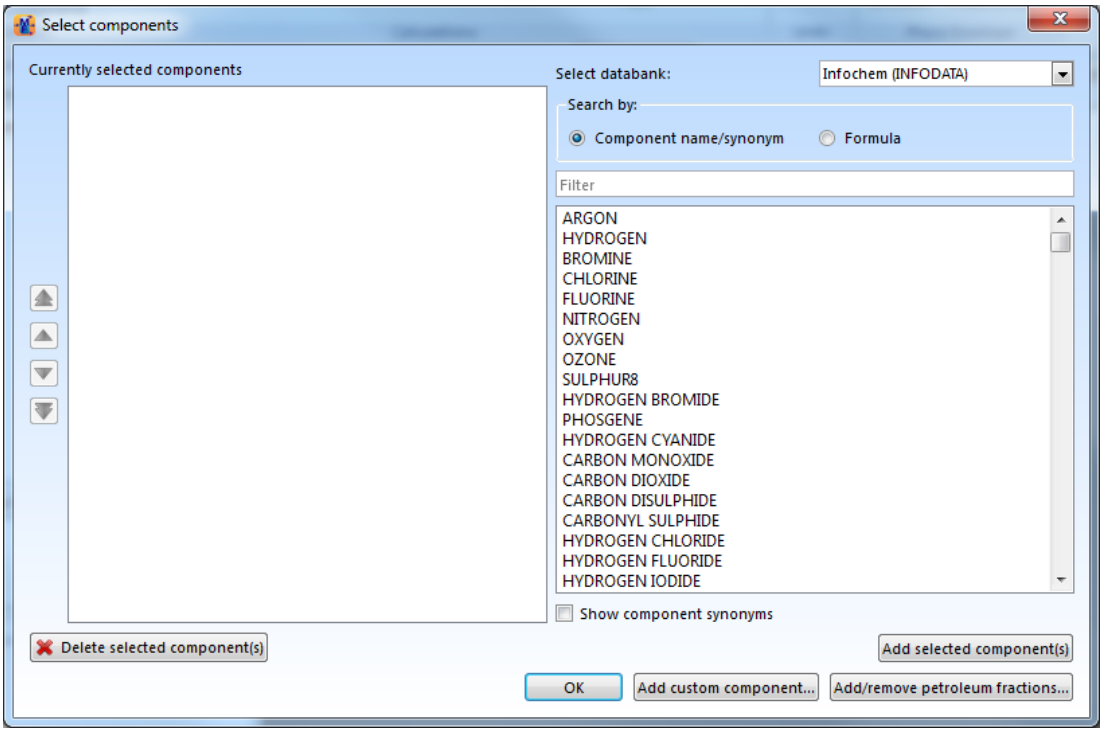
Defining a standard fluid

A standard fluid comprises standard components available in Multiflash. You can specify a maximum of 200 components in a standard fluid.

You can add or remove components from your fluid at any time. One reason for doing so would be to add water or another component for a tolerance or saturation calculation.

To define a standard fluid:

1. On the **Home** ribbon, click **Components**.



2. Select the databank from which you want to take component properties.
3. If required, filter the component list as shown in the table.

To filter by	Do this
Name	Select **Component name/synonym**, and start entering the name above the component list. The text that you enter is interpreted as a substring filter, so the component list contains only those names that contain the text string that you enter. **Tip:** If you want to see all synonyms of the components in the list, check **Show component synonyms**.
Chemical formula	Select **Formula**, enter the chemical formula, for example, C6H14, and then click **Search**. You must use upper case letters for the elements. You can use the asterisk (*) to represent any number for an element. Your search formula must include the letter of each element in the component. For example, C*H*O* finds only components that contain carbon, hydrogen and oxygen; it will not find any ethanolamines, because they contain nitrogen.

4. Scroll through the list and click on the components that you want to add.

   Tip: You can select multiple components by holding down the Ctrl key while you make selections. Contiguous selections can be made by clicking the first component, and then holding down the Shift key while you click the component at the end of a set.

5. Click **Add selected components**.

   Result: The selected components appear in the **Currently selected components** list.

6. If required, you can also add a user-defined component or petroleum fraction.
7. If you need to remove one or more components, select them in the **Currently selected components** list, and then click **Delete selected components**.
8. Click **OK**.
9. In the Multiflash window, specify the amounts of each component, by clicking in the **Amount** column, and entering the required amount.

   Tip: To enter mole fractions or mass fractions, select an appropriate unit to use, and then enter values that sum to one.

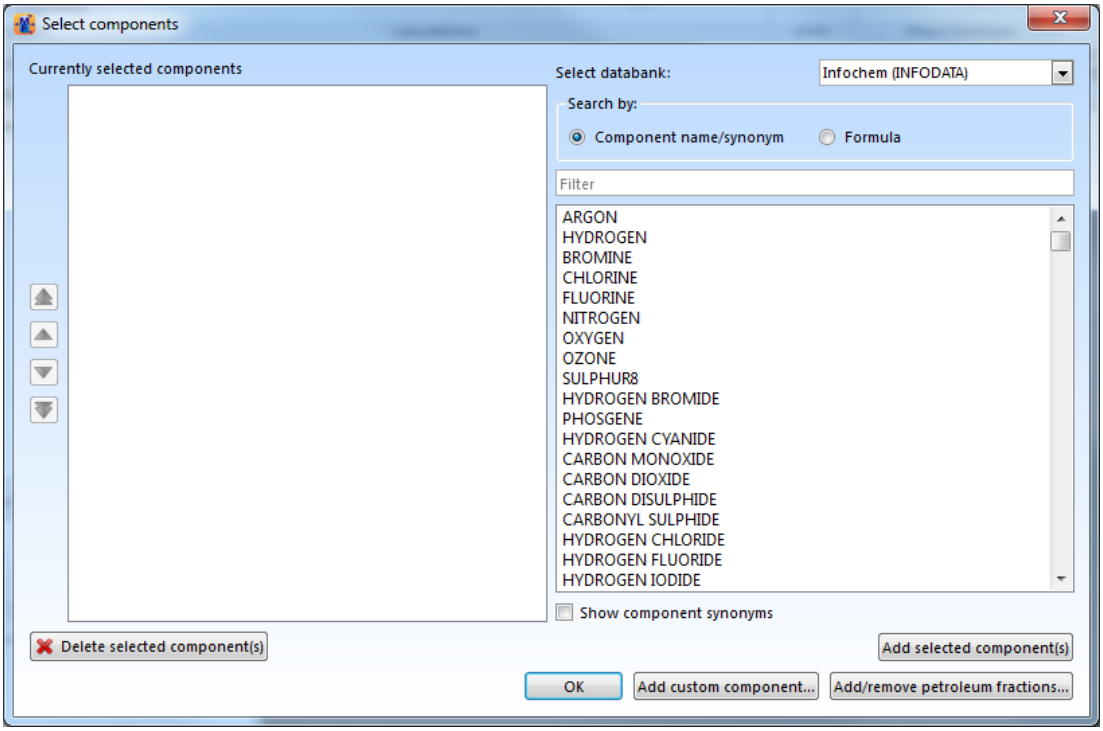
Result: Your fluid is fully defined and ready for calculations.

Defining a petroleum fraction

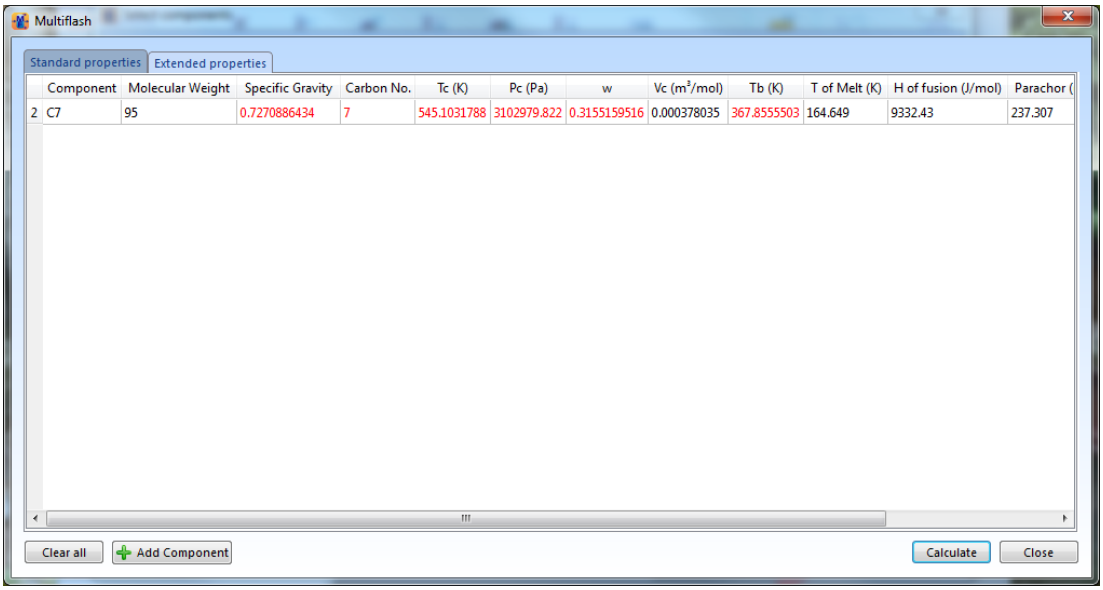
You might have data about petroleum fractions in your fluid; for example, data from other process simulation software. If so, you can create a petroleum fraction using that data. You can specify a maximum of 100 petroleum fractions.

To define a petroleum fraction:

1. On the **Home** ribbon, click **Components**.



2. Select the databank from which you want to take component properties.
3. Click **Add/remove petroleum fractions**.



The window displays any existing petroleum fractions. User-specified values are displayed as red; those calculated by Multiflash are black.

4. For each fraction that you want to add, click **Add Component**, and then do the following:
   - In the new row, click the **Component** cell, and then enter a name.
   - Click in the **Carbon No.** cell, and then enter the carbon number of the fraction.

- For each property for which you have a value, click in the appropriate cell and then enter the value, using the units shown at the top of the column.

  Tip: If required, you can change the input units used by clicking 

on the **Home** ribbon prior to entering your data.

  Note: You need not enter any properties; physical properties that you do not enter are calculated by Multiflash using the industry standard correlations of petroleum fractions, as recommended by *Riazi, M.R. and Al-Sahhaf, T.A., Fluid Phase Equilibria 117 217 1996*.

Tip: You can enter multiple fractions by pasting data from an Excel spreadsheet. To do so, click **Add Component** multiple times, to add as many new rows as you have fractions to add, copy the data from your spreadsheet, right-click in the top left corner of the area to which you want to add data, and then click Paste. If you have missing data, you must leave blank cells in your spreadsheet, as appropriate, to ensure that data are copied into the correct cell.

5. Click **Calculate**.

   Result: Any properties for which you do not supply a value are calculated by Multiflash and appear in the table.

6. Click **Close**.

Editing petroleum fraction data

After you have carried out some calculations, you might want to change the petroleum fraction definition. For example, you might want to see how a different data input set alters a phase envelope.

To edit or replace a petroleum fraction definition:

1. On the **Home** ribbon, click **Components**.
2. Click **Add/remove petroleum fractions**.
3. Delete the value for any data you want to recalculate.
4. Modify or add values as required.
5. Click **Calculate**, and then click **OK**.

   Result: The physical properties of the fraction are recalculated and loaded into the fluid model.

Tip: If you want to change a single property of a petroleum fraction without recalculating any other properties that depend on it, on the **Home** ribbon, click **Pure Component Data**, and modify the value on that table instead. This is useful when you want to determine the sensitivity of a calculation to that property alone. If you change the molecular weight of a petroleum fraction this way, the critical properties of the fraction are not recalculated.

Viewing pure component properties

You can view the stored properties of any pure component, including the equations used to calculate temperature-dependent properties. You can also evaluate individual temperature-dependent properties at temperatures that you specify.

Tip: You can calculate the values of any property for a pure component at specific conditions, by specifying a fluid with a single component and using the full range of Multiflash calculations.

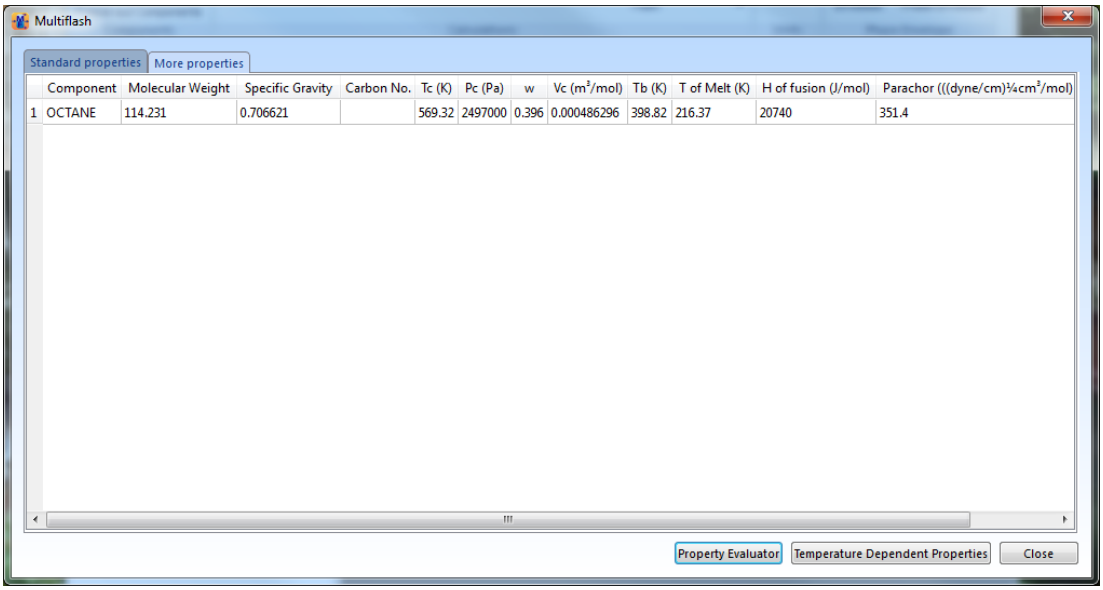
The following procedure uses the file octane.mfl as an example.

To view pure component properties:

1. On the **File** menu, click **Open**, and open the file octane.mfl.

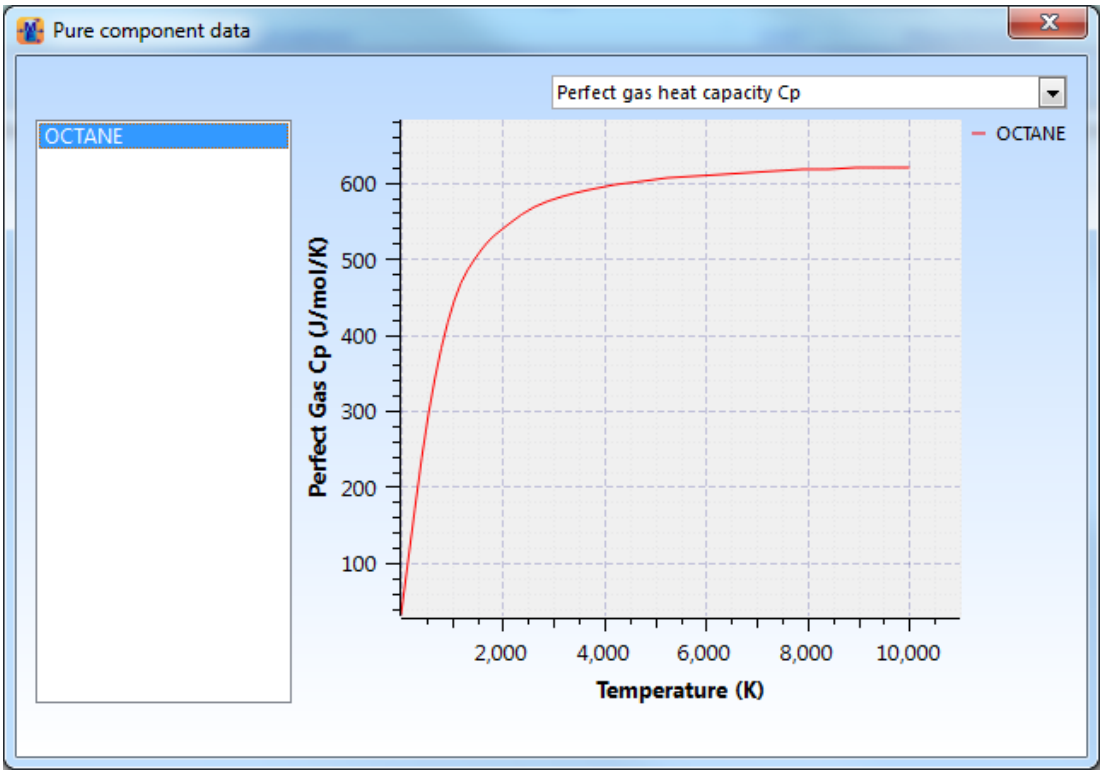
   Tip: By default, the example files are in the MFL Files folder of the Multiflash installation.

2. On the **Home** ribbon, click **Pure Component Data**.



3. View the constant properties of the component on the **Standard properties** or **More properties** tab.

4. To view a temperature-dependent property, click **Temperature Dependent Properties**, click the component whose property you want to view, and then choose the required property from the list.



5. To see the coefficients for the equation used to calculate a temperature-dependent property, click

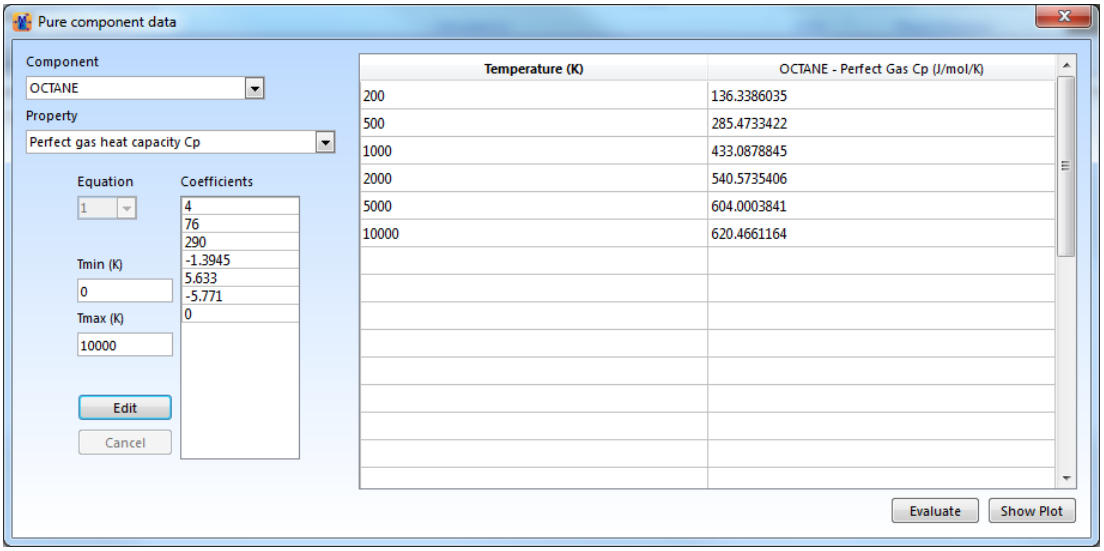
Property Evaluator, and then do the following:

- In the **Component** list, choose your component.
- In the **Property** list, choose the property whose coefficients you want to see.

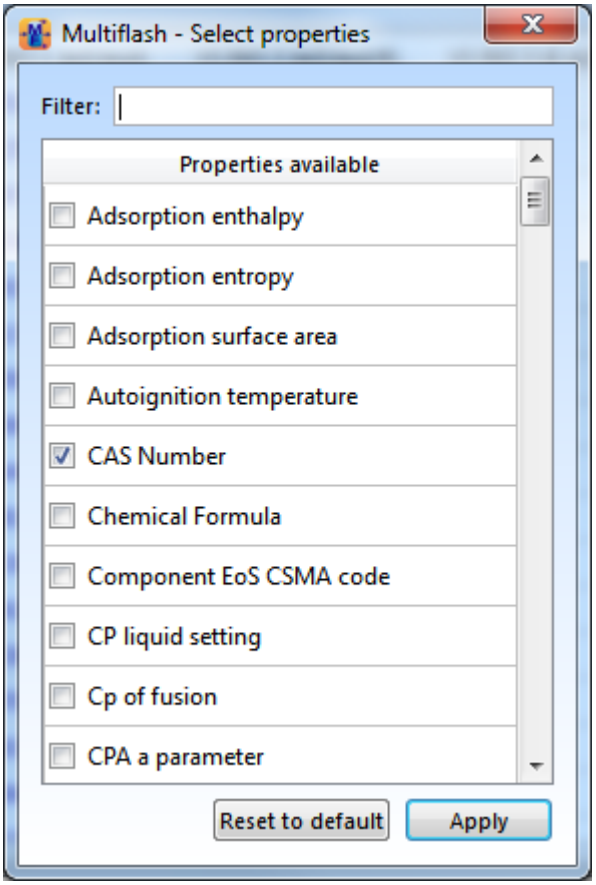
Result: The coefficients are displayed in the **Coefficients** table, and the valid temperature limits in the **Tmin** and **Tmax** fields. The equation number is the number of the property equation in the *Models and Physical Properties User Guide* that is being used to calculate the property.

6. To evaluate a temperature-dependent property at specified temperatures, click **Property Evaluator**, and then do the following:
   - In the **Component** list, choose your component.
   - In the **Property** list, choose the property that you want to evaluate.
   - In the **Temperature** column, enter the temperatures at which you want to evaluate the property.
   - Click **Evaluate**.

   Tip: Click **Show Plot**, to see a graph of the data points.



7. When in the **More Properties** tab, clicking **Select Display Properties...** allows you to select which properties should be visible.



Type in the **Filter** to quickly find the desired property.

Editing pure component properties

You can edit the stored properties of any pure component, including the equations used to calculate temperature-dependent properties.

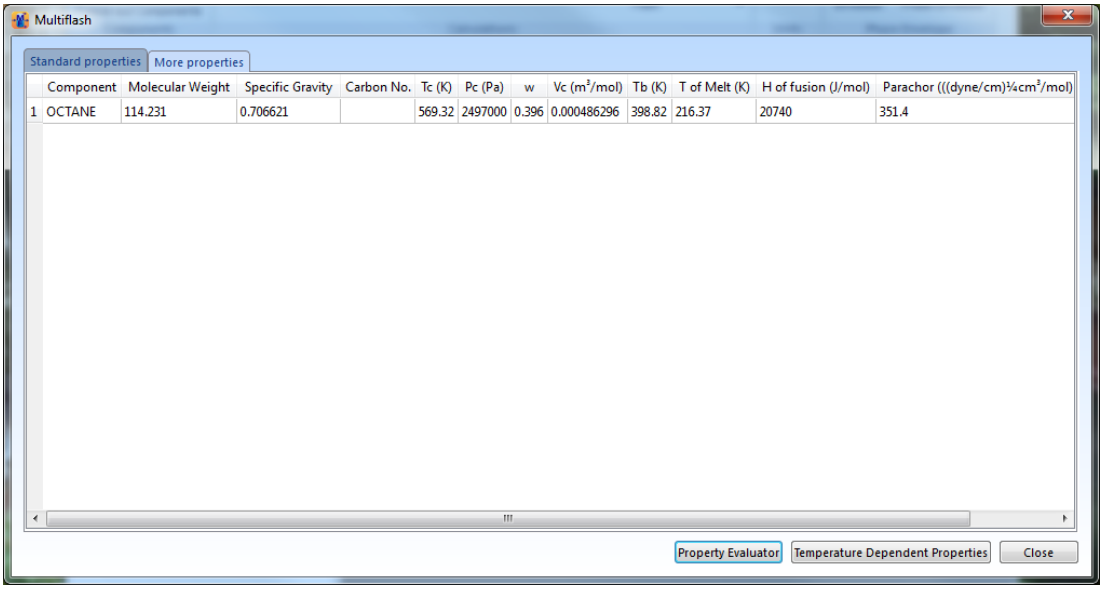
The following procedure uses the file octane.mfl as an example.

To edit a constant property for a pure component:

1. On the **File** menu, click **Open**, and open the file octane.mfl.

   Tip: By default, the example files are in the MFL Files folder of the Multiflash installation.

2. On the **Home** ribbon, click **Pure Component Data**.



3. Click in the cell of the property whose value you want to modify, and then enter the new value.

   Result: The new value appears in red.

Editing temperature-dependent properties

Multiflash uses one of several equations for the evaluation of any given temperature-dependent property. The equations for each property are described in the *Models and Physical Properties User Guide*. If you want to change the equation that is being used, or have fitted your own data to the equation being used, you can enter the new coefficients and temperature range.

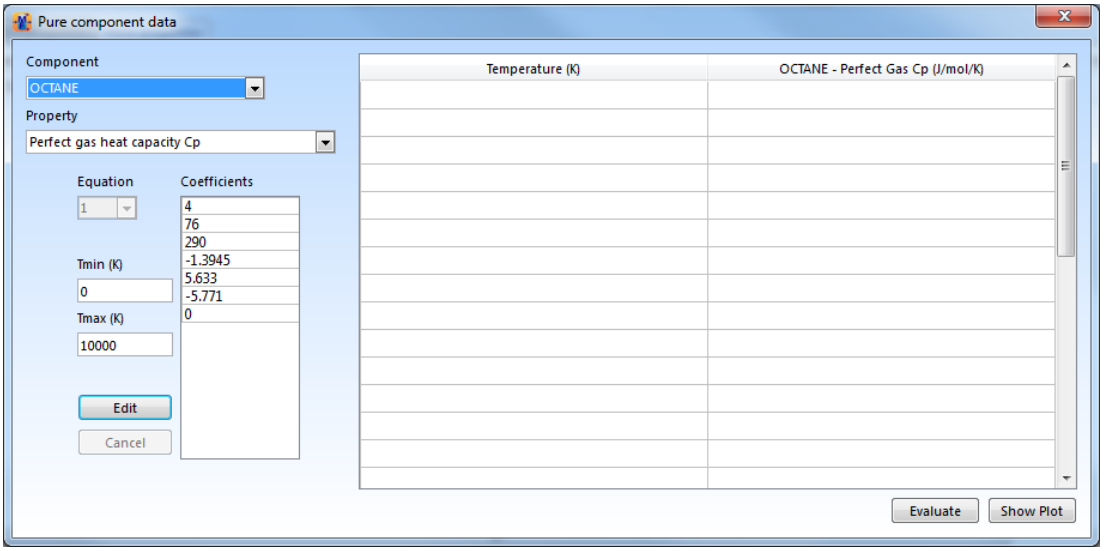
The following procedure uses the file octane.mfl as an example.

To edit a temperature-dependent property for a pure component:

1. On the **File** menu, click **Open**, and open the file octane.mfl.

   Tip: By default, the example files are in the MFL Files folder of the Multiflash installation.

2. On the **Home** ribbon, click **Pure Component Data**.
3. Click **Property Evaluator**.



4. Select your component, and then, from the **Property** list, select the property whose equation you want to modify.
5. Click **Edit**, and then choose the equation number that you are using.

   Note: The equation number is the number of the equation in the *Models and Physical Properties User Guide* that you are using for the property.
6. Enter the equation's coefficients and temperature range.
7. Click **Commit**.

   Example: You fit your perfect gas heat capacity data using the DIPPR equation 100, which is equation 5 in the *Models and Physical Properties User Guide*. To enter your data, click **Edit**, select 5 from the **Equation** list, click in each position in the **Coefficients** list to add your five fitted coefficient values, enter the minimum and maximum temperature for which your data is valid, and then click **Commit**.

Defining a fluid using a PVT analysis

If you have a PVT laboratory analysis of your fluid, you can use the information to create a compositional fluid model for use in Multiflash calculations. Multiflash calls this process characterization.

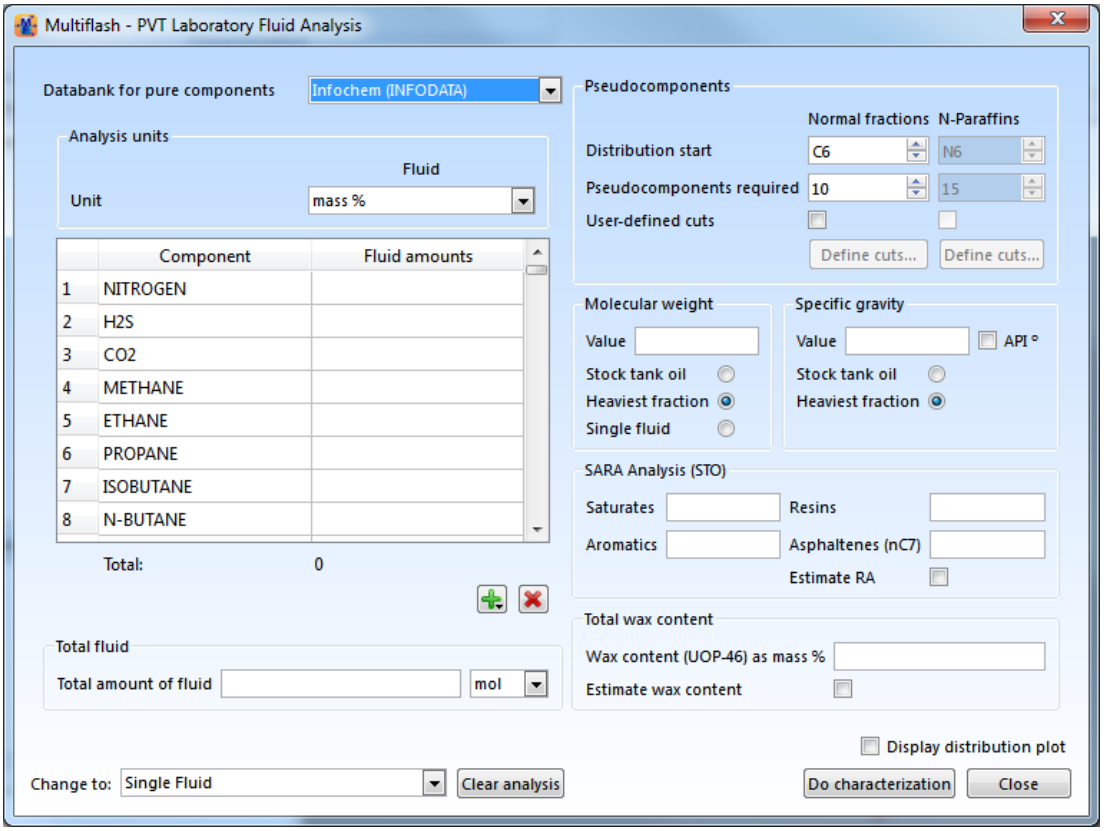
Tip: If you already have a characterized fluid, you can use the **Change to** list to select a different fluid type, modify the values, and then recharacterize the fluid.

To define a fluid using a PVT analysis:

1. On the **Fluid** ribbon, click **PVT Analysis**.
2. Choose the analysis type according to the type of PVT analysis report you have, as shown in the table.

   The example screenshot shows the dialog box for a single fluid.

For report containing	Choose
A recombined reservoir fluid analysis	Single Fluid
A separator gas and separator liquid analysis	Gas and liquid
A recombined reservoir fluid analysis plus an analysis of the n-paraffin distribution measured for the STO	Single Fluid and N-Paraffins (STO)
A recombined reservoir fluid analysis plus an analysis of the n-paraffin distribution described as the fraction of each individual SCN above C6 which is n-paraffin	Single Fluid and N-Paraffins (fractions)
A separator gas and separator liquid analysis plus an analysis of the n-paraffin distribution in the liquid phase measured for the STO	Gas, Liquid and N-Paraffins (STO)
A separator gas and separator liquid analysis plus an analysis of the n-paraffin distribution in the liquid phase described as the fraction of each individual SCN above C6 which is n-paraffin	Gas, Liquid and N-Paraffins (fractions)



3. Choose the databank from which you want to take properties of real components.
4. Specify the analysis units.

   Important: Use units that match the PVT analysis.

   Restriction: After values are entered in the component list, if you change the analysis units, the values are not converted to reflect the new unit choice.
5. For each component in your PVT report, enter the amounts in the component list.

   Tips:

   - The component list is filled automatically with a typical list of PVT reported components. If some of your reported components are not present in the list, you can overwrite the name of a listed component that is not in your report.
   - If you put your report data into Microsoft Excel, you can cut and paste the information directly into the component list.
6. For a gas and liquid fluid, enter the recombination GOR and units.
7. If you want to specify the total amount of fluid, enter the required amount and units.

   If the amount is left blank, the amount generated depends on the way the composition is entered. For example, if the composition is entered in mass units and the sum is 100 then 100 g of fluid is generated.
8. In the **Pseudocomponents** panel, specify the start SCN and number of pseudocomponents (maximum of 200) for the normal fractions.

   Example: If you set **Distribution start** to C10, and **Pseudocomponents required** to 5, the components C6, C7, C8 and C9, if present, are represented by individual pseudocomponents, and the

remaining normal alkanes are grouped, or lumped, into five pseudocomponents that depend on the actual composition of the fluid, with the last pseudocomponent being a plus fraction.

Tip: You can specify your own lumped ranges by checking **User-defined cuts**, clicking **Define cuts**, and then entering the SCN values at which you want the groups to start.

9. If required, specify the start SCN and number of pseudocomponents (maximum of 200) for the n-paraffin fractions.

   Requirement: If you are modelling a system that might include a wax phase, you must specify n-paraffin pseudocomponents if your PVT analysis does not include measured n-paraffin values.

   Restriction: For a PVT analysis without measured n-paraffin values, the n-paraffin settings are only enabled if you have entered a wax content value or checked **Estimate wax content**.

10. Specify the molecular weight and specific gravity, using the guidelines in the table.

    Note: The specific gravity (SG) can be entered relative to water at 60ºF and 1 atm, or check API to use the API gravity. You can convert from API gravity to SG using the following formula:

    SG = 141.5/(API + 131.5)

Specify the value as	when
Stock Tank Oil	You have a reliable measurement of the values.
Heaviest SCN Heaviest fraction	You have no other reliable values, because this value is usually calculated, not measured.
Single fluid	You have the SG of the original reservoir fluid.
Leave blank	You have no values to use. In this case, Multiflash provides an estimate of the value based on the fluid distribution you have supplied.

11. If you are using the asphaltene model, do one of the following. We recommend that you use the first available option:

    - If you have a full SARA analysis, enter the values.
    - If you have the resin and asphaltene ratio, enter the values.
    - To have the resin/asphaltene ratio estimated by Multiflash, check **Estimate RA**.

    Note: Do not enter these values when you use other models. They might produce results with the asphaltene and resin components but will not give the correct phase behaviour.

12. If you are specifying a wax phase calculation, specify a total wax content by doing one of the following:

    - Enter your measured value for wax content as mass %, if available.
    - To have the value estimated by Multiflash, check **Estimate wax content**.

    Note: You do not enter wax content for a PVT analysis with measured n-paraffin values.

13. Click **Do characterization**.

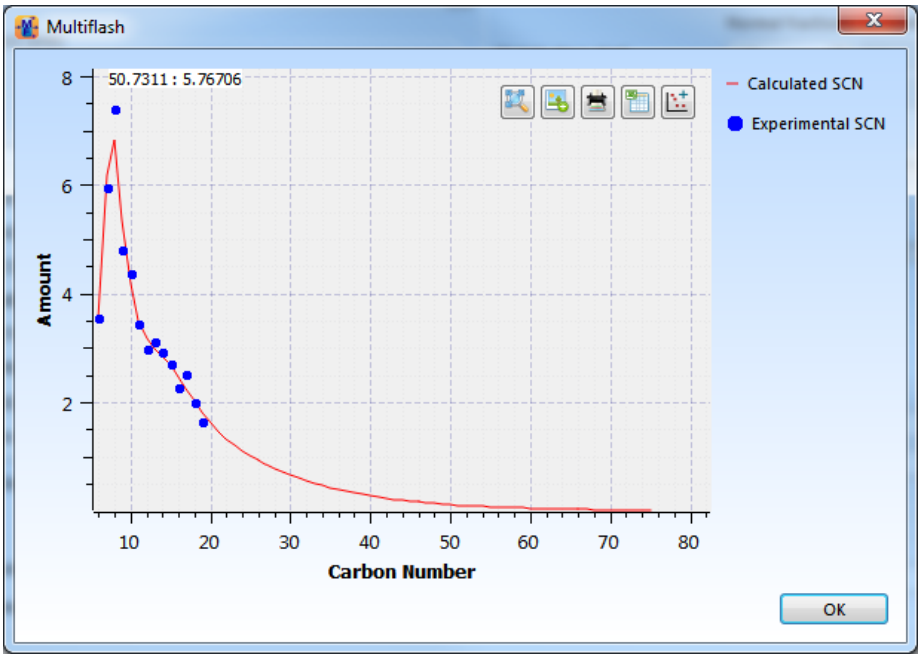
    Result: If the inputs provided are consistent with the requirement of the fluid characterisation in Multiflash, you see a message to indicate that the characterisation has been successfully completed.

14. Click **Close**.

Result: The Fluid Composition list is updated to include all the calculated components, pseudo-components and amounts. The pseudocomponent names correspond to the type and range of

pseudocomponent. For example, C21-35 is a pseudocomponent that contains the normal fractions C21 to C35. The n-paraffin pseudocomponents are prefixed with N, for example N15-27, and the remaining non-n-pseudocomponents with I, for example, I13-19.

Tip: To get some detail of the performance of the PVT analysis distribution, check the **Display distribution plot** option. After the characterisation is successful a plot will be shown:

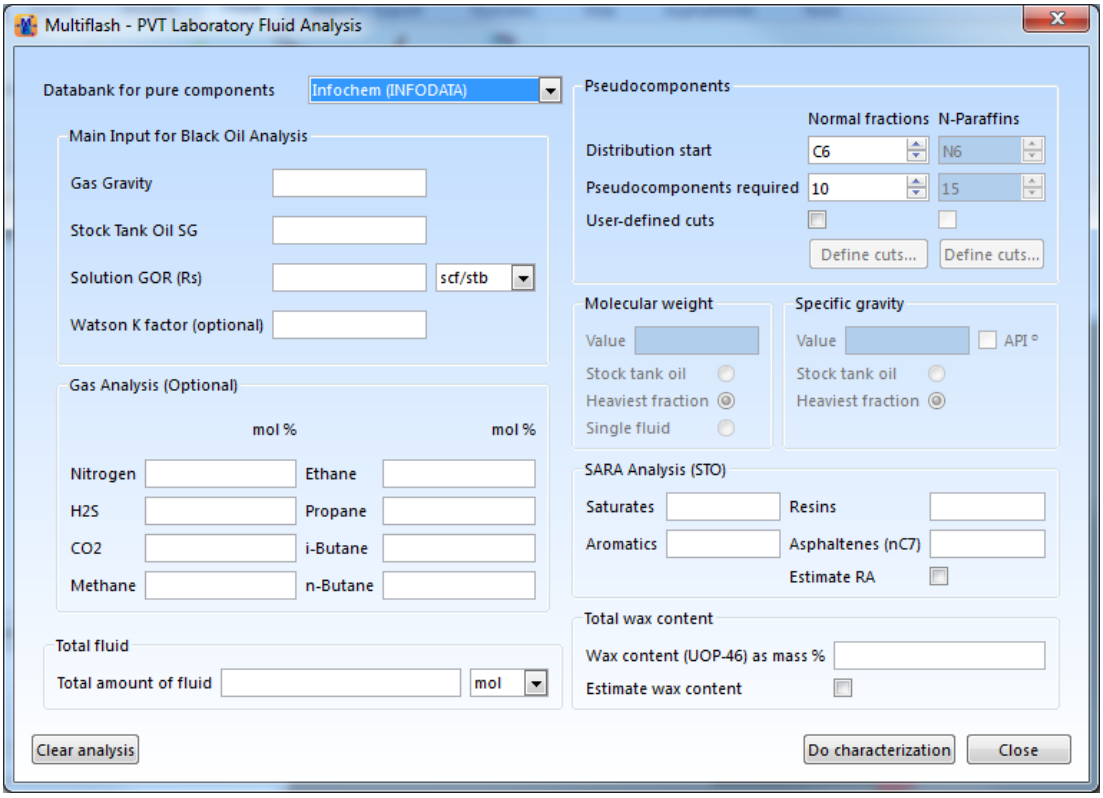


Defining a fluid using a black oil analysis

A black oil analysis enables you to define a fluid when you have only limited compositional data; for example, a compositional analysis is not available or the data is generated from another application.

To define a fluid using a black oil analysis:

1. On the **Fluid** ribbon, click **PVT Laboratory analysis**.
2. Click **Black oil**.



3. Choose the databank from which you want to take properties of real components.
4. Enter the required data.

Item	Description
Gas Gravity	The MW of the gas divided by the MW of air (28.964).
Stock Tank Oil SG	The specific gravity relative to water at 60ºF.
Solution GOR	The amount of gas relative to oil at standard conditions, often referred to as R_s.

5. Optionally, you can provide additional information if it is available.

Item	Description
Watson K-factor	$K_w = (T_b)^{1/3} / SG$ where T_b is the boiling point in ºR
Gas Analysis	The gas analysis need not be complete; only the mole percentages of the components named on the form can be entered, and they need not sum to 100%.

6. If you want to specify the total amount of fluid, enter the required amount and units.

   If the amount is left blank, the amount generated depends on the way the composition is entered. For example, if the composition is entered in mass units and the sum is 100 then 100 g of fluid is generated.

7. In the **Pseudocomponents** panel, specify the start SCN and number of pseudocomponents (maximum of 200) for the normal fractions.

   Example: If you set **Distribution start** to C10, and **Pseudocomponents required** to 5, the components C6, C7, C8 and C9, if present, are represented by individual pseudocomponents, and the remaining normal alkanes are grouped, or lumped, into five pseudocomponents that depend on the actual composition of the fluid, with the last pseudocomponent being a plus fraction.

   Tip: You can specify your own lumped ranges by checking **User-defined cuts**, clicking **Define cuts**, and then entering the SCN values at which you want the groups to start.

8. If required, specify the start SCN and number of pseudocomponents (maximum of 200) for the n-paraffin fractions.

   Requirement: If you are modelling a system that might include a wax phase, you must specify n-paraffin pseudocomponents if your PVT analysis does not include measured n-paraffin values.

   Restriction: For a PVT analysis without measured n-paraffin values, the n-paraffin settings are only enabled if you have entered a wax content value or checked **Estimate wax content**.

9. If you are using the asphaltene model, do one of the following. We recommend that you use the first available option:

   - If you have a full SARA analysis, enter the values.
   - If you have the resin and asphaltene ratio, enter the values.
   - To have the resin/asphaltene ratio estimated by Multiflash, check **Estimate RA**.

   Note: Do not enter these values when you use other models. They might produce results with the asphaltene and resin components but will not give the correct phase behaviour.

10. If you are specifying a wax phase calculation, specify a total wax content by doing one of the following:

    - Enter your measured value for wax content as mass %, if available.
    - To have the value estimated by Multiflash, check **Estimate wax content**.

    Note: You do not enter wax content for a PVT analysis with measured n-paraffin values.

11. Click **Do characterization**.

    Result: If the inputs provided are consistent with the requirement of the fluid characterisation in Multiflash, you see a message to indicate that the characterisation has been successfully completed.

12. Click **Close**.

Result: The Fluid Composition list is updated to include all the calculated components, pseudocomponents and amounts. The pseudocomponent names correspond to the type and range of pseudocomponent. For example, C21-35 is a pseudocomponent that contains the normal fractions C21 to C35. When you calculate N-paraffin pseudocomponents, the fraction names begin with N, for example N15-27, and the remaining pseudocomponent names (the non-N fractions) begin with I, for example, I13-19.

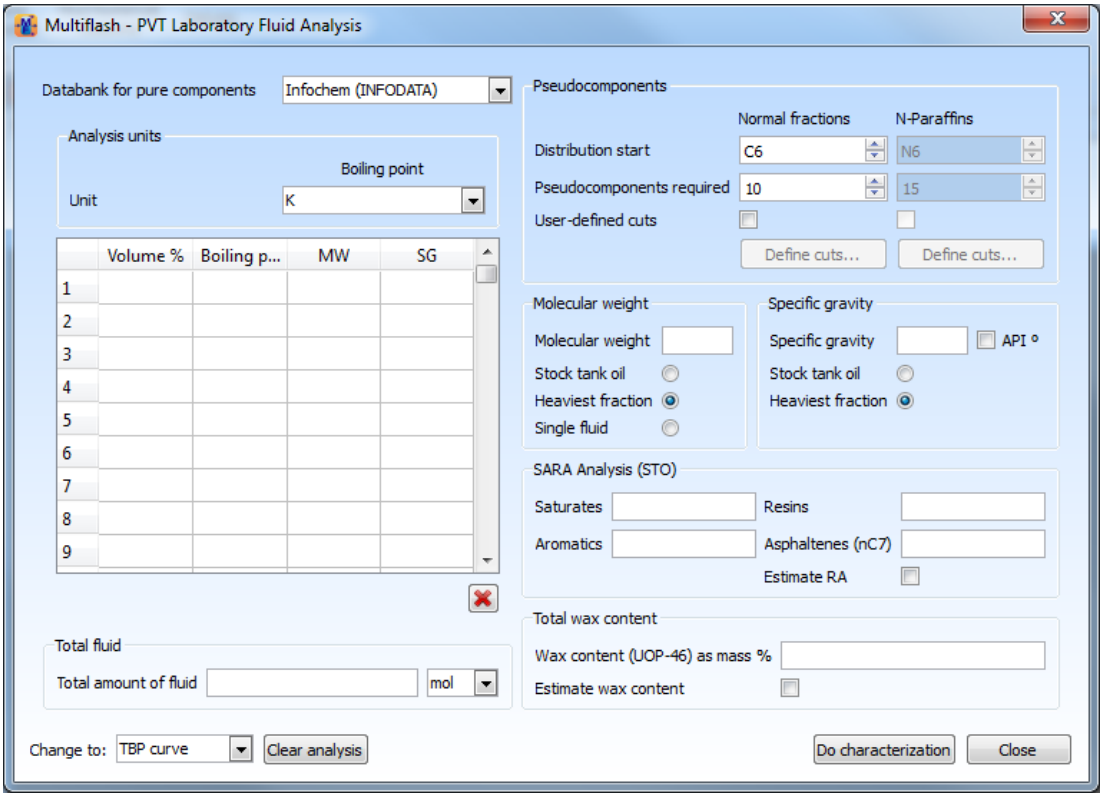
Defining a fluid from distillation data

If your PVT analysis data, instead of a detailed SCN/Composition report, is based on distillation data, such as a true boiling point (TBP) curve or a D86 analysis, you can enter this and convert the data to fixed carbon number fractions.

To define a fluid using a PVT analysis:

1. On the **Fluid** ribbon, click **PVT Analysis**.
2. Choose the analysis type according to the type of distillation data you have, as shown in the table.

For report containing	Choose
True boiling point (TBP) data	TBP
D86 data	D86



3. Choose the databank from which you want to take properties of real components.
4. Specify the temperature units.
5. Enter your data by clicking in the appropriate cell, and then entering the value.

   Tip: You can enter your data by pasting data from an Excel spreadsheet. To do so, copy the data from your spreadsheet, right-click in the top left corner of the area to which you want to add data, and then click Paste. If you have missing data, you must leave blank cells in your spreadsheet, as appropriate, to ensure that data are copied into the correct cell.

Item	Description
Volume %	Cumulative percentage distilled by volume
Boiling point	Upper boiling point of fraction

Item	Description
MW	Measured molecular weight of fraction. This is optional, and not applicable for D86 data.
SG	Measured specific gravity of fraction. This is optional, and not applicable for D86 data.

6. If you want to specify the total amount of fluid, enter the required amount and units.

   If the amount is left blank, the amount generated depends on the way the composition is entered. For example, if the composition is entered in mass units and the sum is 100 then 100 g of fluid is generated.

7. In the **Pseudocomponents** panel, specify the start SCN and number of pseudocomponents (maximum of 200) for the normal fractions.

   Example: If you set **Distribution start** to C10, and **Pseudocomponents required** to 5, the components C6, C7, C8 and C9, if present, are represented by individual pseudocomponents, and the remaining normal alkanes are grouped, or lumped, into five pseudocomponents that depend on the actual composition of the fluid, with the last pseudocomponent being a plus fraction.

   Tip: You can specify your own lumped ranges by checking **User-defined cuts**, clicking **Define cuts**, and then entering the SCN values at which you want the groups to start.

8. If required, specify the start SCN and number of pseudocomponents (maximum of 200) for the n-paraffin fractions.

   Requirement: If you are modelling a system that might include a wax phase, you must specify n-paraffin pseudocomponents if your PVT analysis does not include measured n-paraffin values.

   Restriction: For a PVT analysis without measured n-paraffin values, the n-paraffin settings are only enabled if you have entered a wax content value or checked **Estimate wax content**.

9. Specify the molecular weight and specific gravity, using the guidelines in the table.

   Note: The specific gravity (SG) can be entered relative to water at 60ºF and 1 atm, or check API to use the API gravity. You can convert from API gravity to SG using the following formula:

   SG = 141.5/(API + 131.5)

Specify the value as	when
Stock Tank Oil	You have a reliable measurement of the values.
Heaviest SCN Heaviest fraction	You have no other reliable values, because this value is usually calculated, not measured.
Single fluid	You have the SG of the original reservoir fluid.
Leave blank	You have no values to use. In this case, Multiflash provides an estimate of the value based on the fluid distribution you have supplied.

10. If you are using the asphaltene model, do one of the following. We recommend that you use the first available option:

- If you have a full SARA analysis, enter the values.
- If you have the resin and asphaltene ratio, enter the values.
- To have the resin/asphaltene ratio estimated by Multiflash, check **Estimate RA**.

Note: Do not enter these values when you use other models. They might produce results with the asphaltene and resin components but will not give the correct phase behaviour.

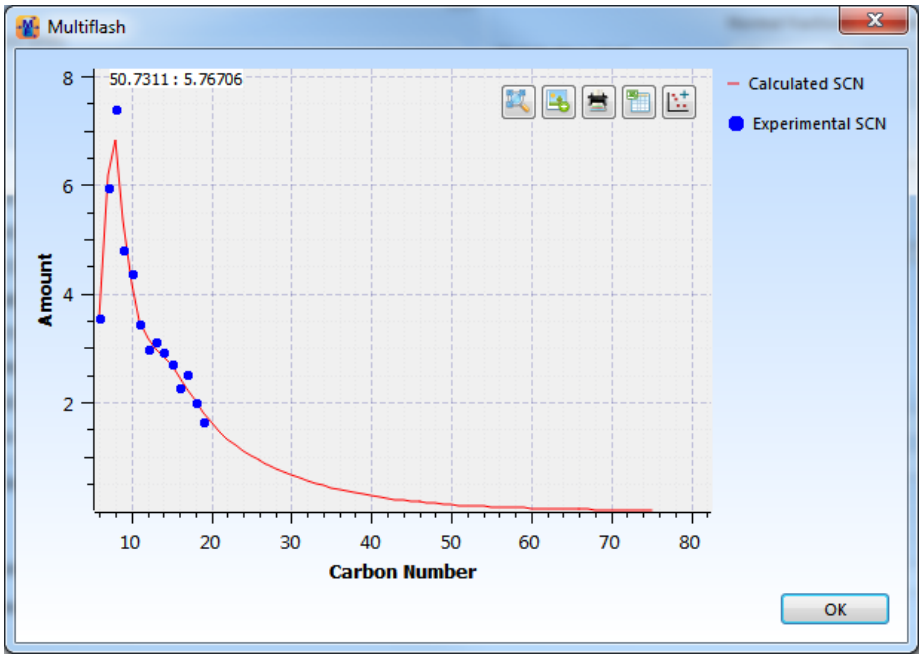
11. If you are specifying a wax phase calculation, specify a total wax content by doing one of the following:
    - Enter your measured value for wax content as mass %, if available.
    - To have the value estimated by Multiflash, check **Estimate wax content**.

    Note: You do not enter wax content for a PVT analysis with measured n-paraffin values.
12. Click **Do characterization**.

    Result: If the inputs provided are consistent with the requirement of the fluid characterisation in Multiflash, you see a message to indicate that the characterisation has been successfully completed.
13. Click **Close**.

Result: The Fluid Composition list is updated to include all the calculated pseudocomponents and amounts. The pseudocomponent names correspond to the type and range of pseudocomponent. For example, C21-35 is a pseudocomponent that contains the normal fractions C21 to C35. When you calculate N-paraffin pseudocomponents, the fraction names begin with N, for example N15-27, and the remaining pseudocomponent names (the non-N fractions) begin with I, for example, I13-19.

Tip: To get some detail of the performance of the PVT analysis distribution, check the **Display distribution plot** option. After the characterisation is successful a plot will be shown:



Adding a user-defined component

You can add a user-defined component if the component that you require is not available in the databanks.

Note: A component in this context is a pure chemical compound or element. To define a petroleum fraction, see *Defining a petroleum fraction*.

When you add a component, you must enter a minimum set of data before you can use the component in Multiflash calculations:

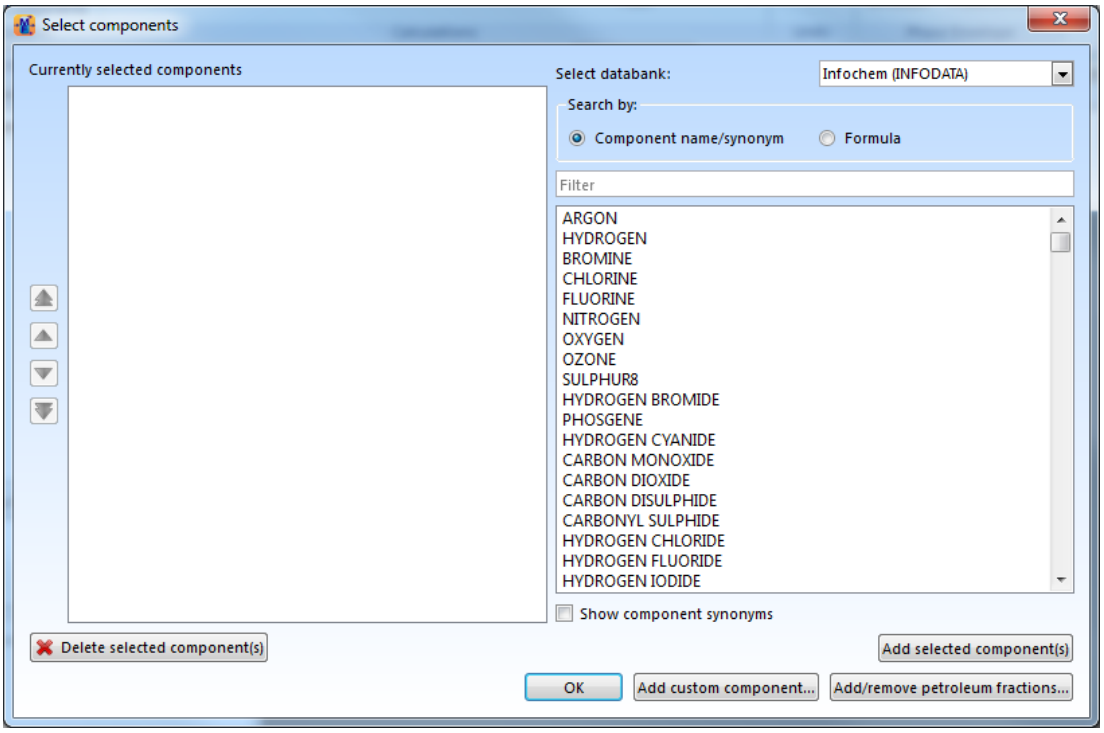
- Molecular weight
- Critical temperature
- Critical pressure
- Acentric factor
- Perfect gas heat capacity.

The minimum data requirement for each model is listed in *Models and component data requirements*.

Requirement: You must have fitted the perfect gas heat capacity data for your component using one of the available equations specified in the *Models and Physical Properties User Guide*, and have the equation coefficients and valid temperature range ready for entry into the component definition.

To add a user-defined component:

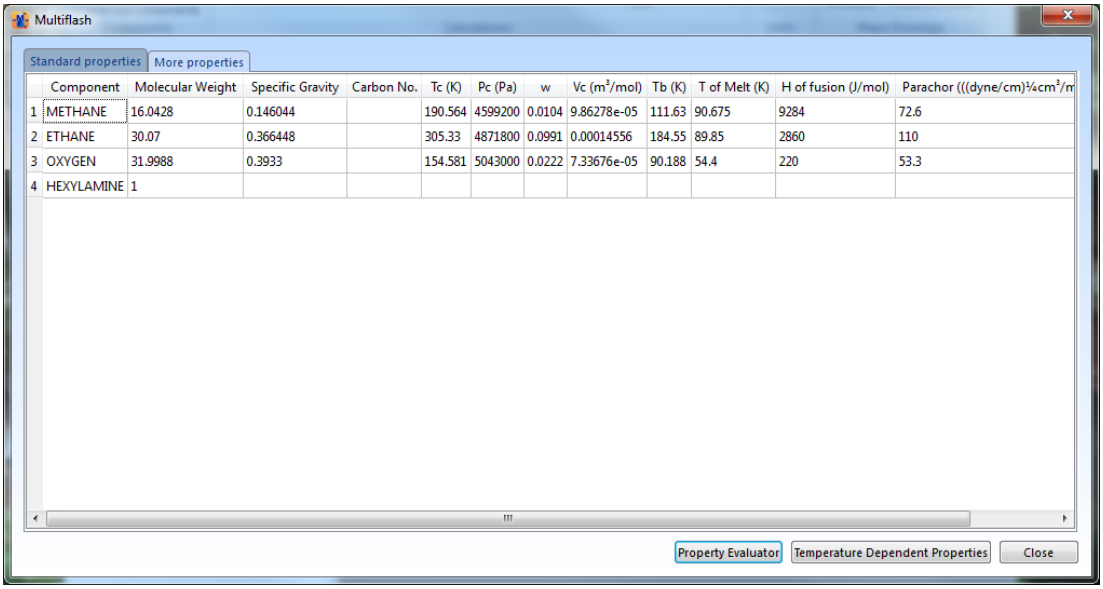
1. On the **Home** ribbon, click **Components**.



2. Click **Add custom component**, enter the component name, and then click **OK**.

   Result: The component is added to the **Currently selected components** list.

3. Click **OK**.
4. On the **Home** ribbon, click **Pure Component Data**.

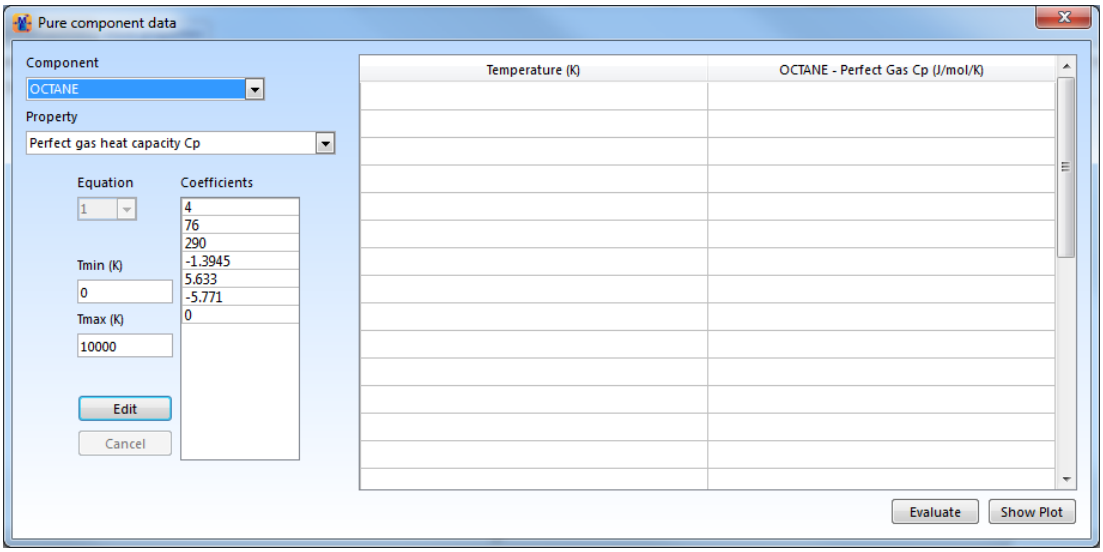


5. In the row of your added component, enter values for the following properties by clicking in the appropriate cell:

   Note: These are the minimum required constant values. You should review the requirements for the models that you want to use and also enter any additional values that are needed.

   - Molecular weight
   - Critical temperature, T_c
   - Critical pressure, P_c
   - Acentric factor, ω

6. Click **Property Evaluator**.



7. Select your added component, and then, from the **Property** list, select "Perfect gas heat capacity Cp".

8. Click **Edit**, and then choose the equation number that you are using.

   Note: The equation number is the number of the perfect gas heat capacity equation in the *Models and Physical Properties User Guide* to which you fitted your data.

9. Enter the coefficients and temperature range.
10. Click **Commit**.

    Example: You fit your perfect gas heat capacity data using the DIPPR equation 100, which is equation 5 in the *Models and Physical Properties User Guide*. To enter your data, click **Edit**, select 5 from the **Equation** list, click in each position in the **Coefficients** list to add your five fitted coefficient values, enter the minimum and maximum temperature for which your data is valid, and then click **Commit**.
11. If the models that you want to use require additional temperature dependent properties, enter the data for each property in the same way as for the perfect gas heat capacity.
12. Close the Pure component data window, and then click **Close**.

Applying the freeze-out model

The freeze-out model is used to find solid pure components. You can apply the freeze-out model to any pure solid component, for example, water or CO_2. It can be used in conjunction with any model set for the fluid phases, but most commonly with one of the cubic equations of state.

You can apply the freeze-out model after your fluid is specified.

Restriction: You can have a maximum of 20 phases in a calculation. This includes the phases defined in the model, in addition to the phases added by the freeze-out model.

To apply the freeze-out model to fluid components:

1. On the **Home** ribbon, click **Freeze-out Components**.
2. In the Freeze-out Components dialog box, check the box next to each component to which you want to apply the model, and then click **Add/Remove**.

   Tip: Clear a check box if you no longer want the model applied to a component.
3. On the message, click **OK**, and then click **Close**.

Result: The solid phase is created, and given the component name, prefixed by SOLID, for example, SOLIDEICOSANE (except in the case of water, where the solid phase name is ICE).

Blending fluids

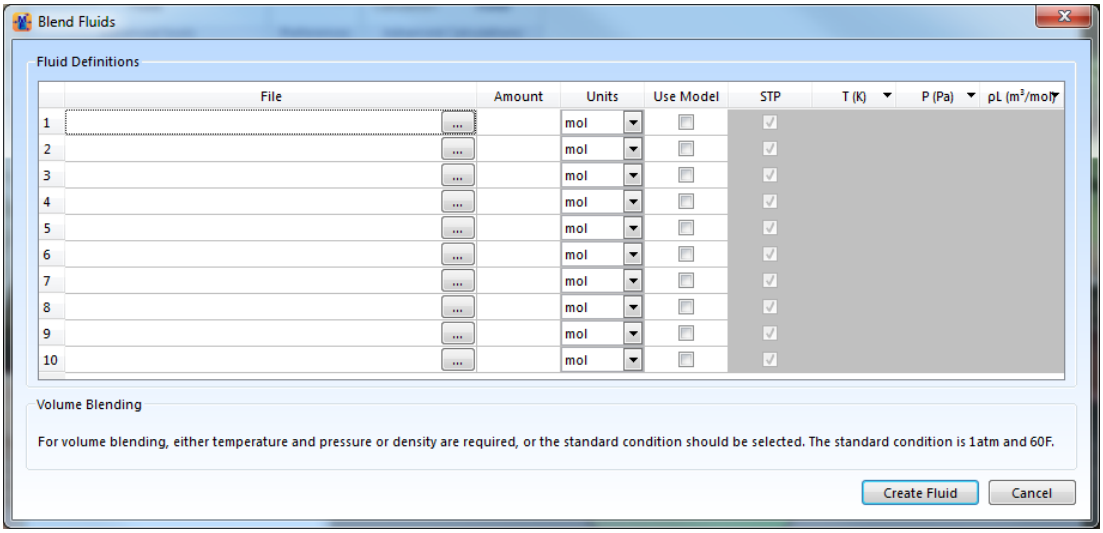
You can blend existing, characterised fluids to create a new fluid that is characterised by its own set of components and pseudocomponents. The properties and relative amounts of the blended fluid's pseudo-components are automatically calculated by Multiflash.

Creating a blended fluid is useful for any situation when two or more fluids mix, for example when pipes intersect.

Prerequisite: You must have at least two Multiflash project (.mfl) files available that contain characterised fluids.

To create a blended fluid:

1. On the **Tools** ribbon, click **Blend Fluids**, and then, on the message, do one of the following:
   - Click **Yes**, to create a new fluid.
   - Click **No**, to use the current .mfl file. This option overwrites any existing information in the current .mfl file.



2. For each existing fluid that you want to blend, in the **File** column, click Browse ..., select the experiment file that contains the fluid, and then click **Open**.
3. In the **Amount** and **Units** columns, specify the amount and units for each fluid in the blend.
4. If you select a volume unit for a fluid, you must also specify parameters as shown in the table, so that Multiflash can use the fluid density in the blending calculation.

Parameters	Density calculation
STP checked	Multiflash calculates the fluid density at standard conditions (1 atm and 60°F), using the model defined in the .mfl file for the fluid. If no model is defined, Wilson correlation is used to estimate the K values, and then the fluid is flashed at the standard conditions to find the fluid density.
STP cleared Temperature‡ Pressure‡	Multiflash calculates the fluid density at the given temperature and pressure, using the model defined in the .mfl file for the fluid. If no model is defined, Wilson correlation is used to estimate the K values, and then the fluid is flashed at the given temperature and pressure to find the fluid density.
STP cleared Density‡	The density entered is used in the blending calculation.
‡You can only enter a value after STP is cleared.	

5. If you want to use one of your stored models for the blended fluid, check **Use Model** in the row of the appropriate fluid.

   Note: If one or more of the source fluids are asphaltenic, the parameters of the asphaltene models for each of those fluids are averaged to give a prediction of asphaltene precipitation in the blend.

However, to obtain this prediction you must select a model definition from one of the asphaltenic fluids, otherwise the asphaltene model parameters are lost.

Result: The model, phases, and all saved utility information, for example, matching, PVT analysis, and salinity calculator, are taken from the selected fluid and used for the blended fluid.

6. Click **Create Fluid**.

What else can I do?

1. After you have defined the blended fluid, you can use it just like any other Multiflash fluid, and the fluid definition can be saved at any time.
2. If you have suitable data about the properties of the fluid, for example, measurements taken after a pipe intersection, you can use the Multiflash PVT lab tests to refine your model.
3. Follow the blended fluid examples to see some applications of the blending process.

Blending example: petroleum fluids

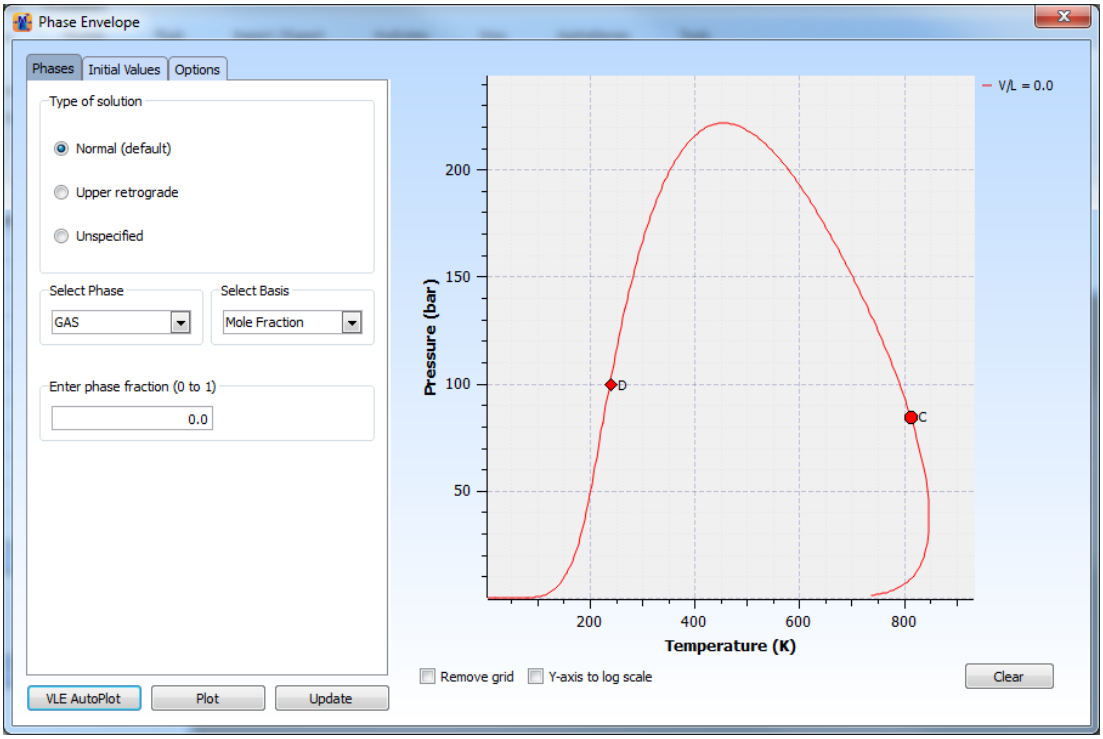
This example uses two standard Multiflash examples of petroleum fluid models. Petfluid.mfl is an oil for which a PVT analysis is provided and which is characterised by five pseudocomponents. Blackoil.mfl is an oil for which no analysis exists, the properties of which have been estimated by the Multiflash black-oil input option, characterised by fifteen pseudocomponents.

The fluids are loaded in turn, and the phase envelope plotted. A series of blends are created, and the phase envelope for each is plotted for comparison with the source fluids.

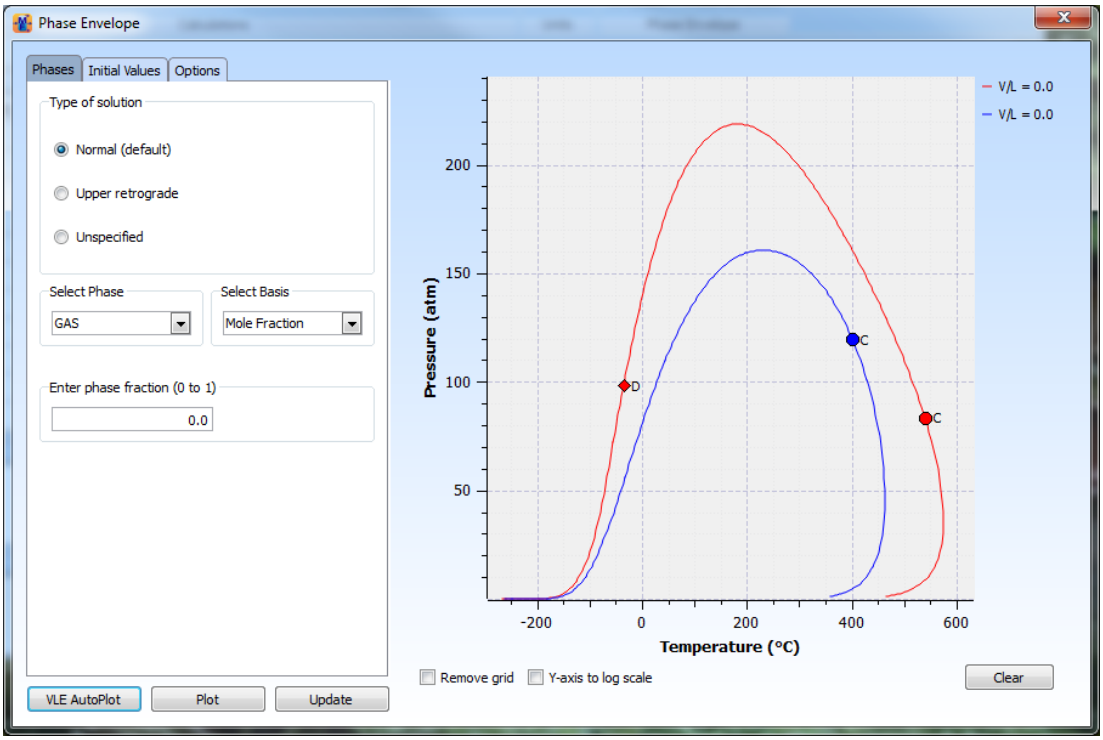
Try it yourself:

1. On the **File** menu, click **Open** and load the file petfluid.mfl.
2. On the **Home** ribbon, click 

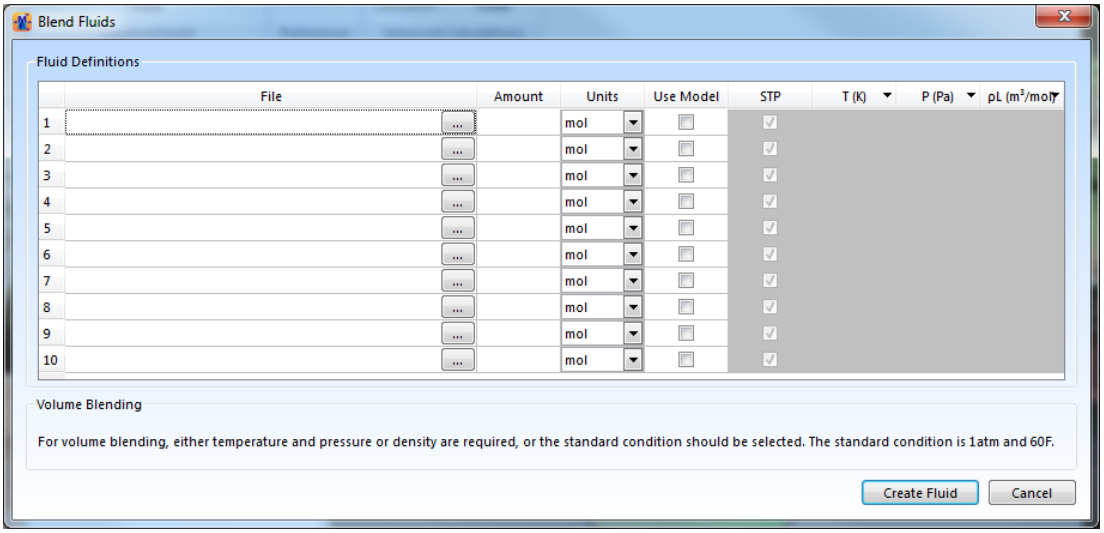
, and then click **VLE AutoPlot**.



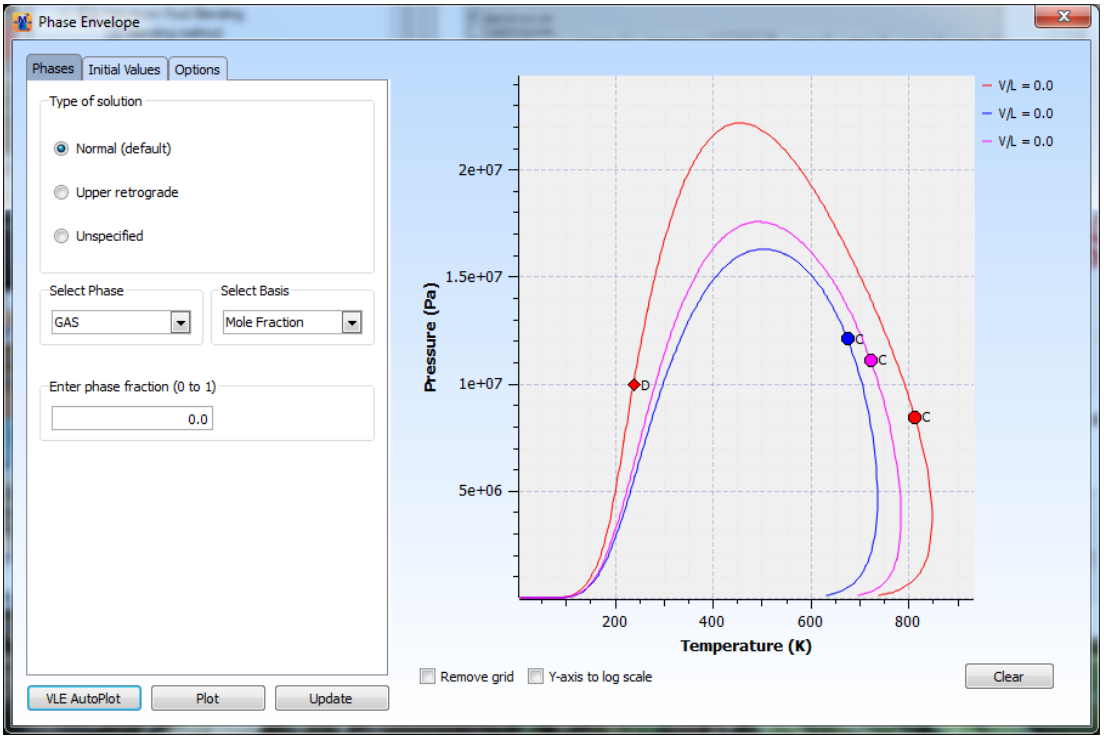
3. Leave the Phase Envelope window open, and load the file blackoil.mfl.
4. On the Phase Envelope window, click **VLE AutoPlot**.



5. On the **Tools** ribbon, click **Blend Fluids**, and then click **Yes** on the message.



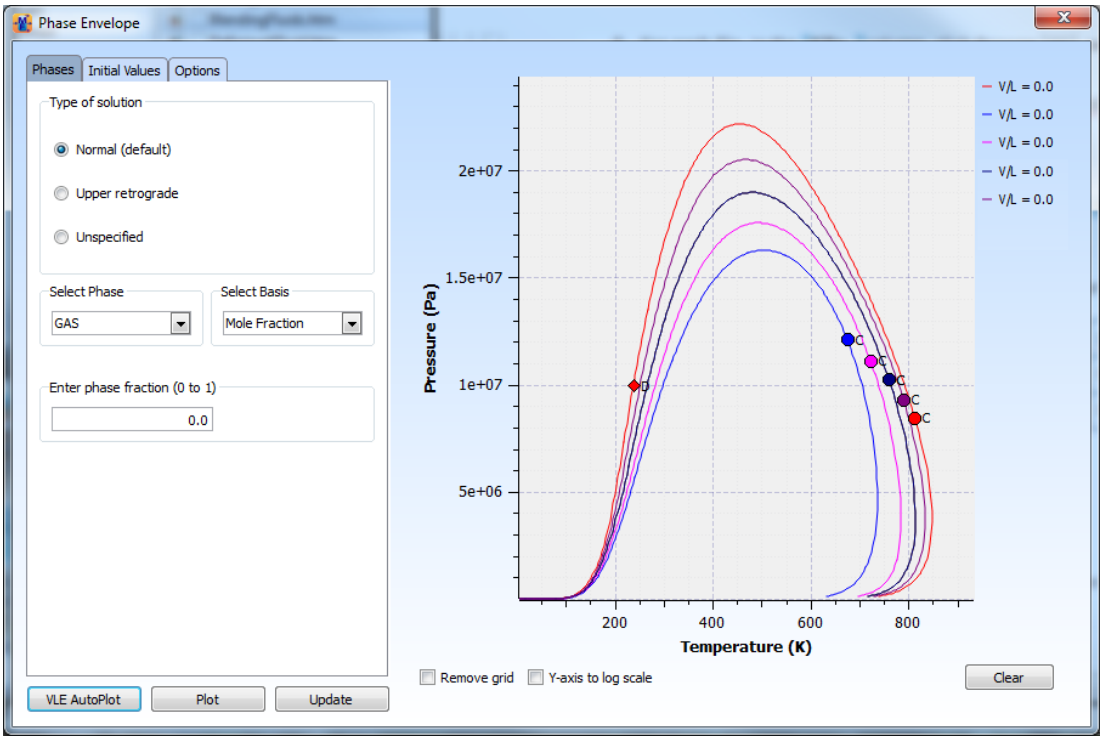
6. For each example file, in the **File** column, click Browse ..., select the file, and then click **Open**.
7. In the **Amount** column, specify 0.25 moles of petfluid.mfl and 0.75 moles of blackoil.mfl.
8. In the blackoil.mfl row, check **Use Model**.
9. Click **Create Fluid**, and then, on the message, click **OK**.
10. On the Phase Envelope window, click **VLE AutoPlot**.



11. Repeat steps 7-10, using the mole fractions shown in the table.

Blend number	petfluid.mfl (mol)	blackoil.mfl (mol)
2	0.5	0.5

Blend number	petfluid.mfl (mol)	blackoil.mfl (mol)
3	0.75	0.25



As expected, the phase envelopes of the blends move between the two outlying envelopes of the original fluids, depending on the blending proportions.

Blending example: asphaltenic crudes

This example uses two standard Multiflash examples of asphaltenic fluids, asphex2.mfl and asphex3.mfl.

The fluids are loaded in turn, and the bubble point line and asphaltene phase envelope (APE) plotted. A 50:50 blend is created, and the bubble point line and APE are plotted for comparison to the source fluids.

The result is characteristic of an asphaltenic oil where asphaltene precipitation occurs when the temperature falls within the asphaltene boundary.

Try it yourself:

1. On the **File** menu, click **Open**, and open the file asphex2.mfl.
2. On the **Home** ribbon, click 

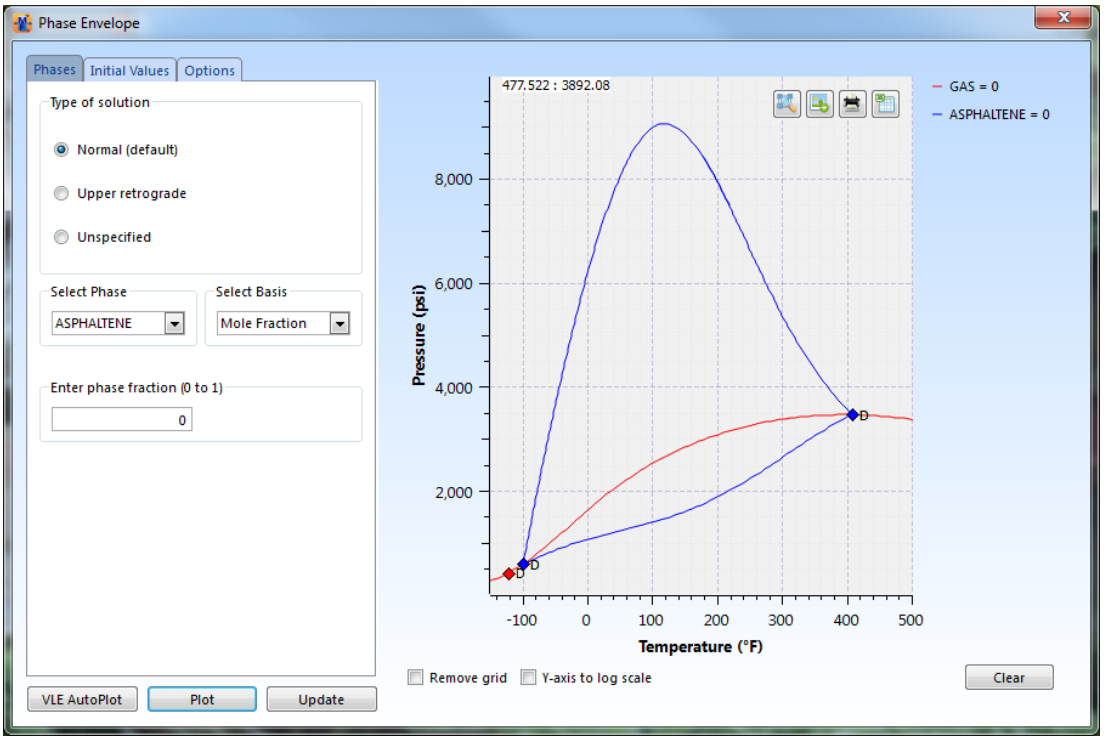
.
3. Click **Plot**, click **Yes** on the plotting limit message, and then click **No**.
4. Enter the data shown in the table.

   Rationale: These values are based on prior knowledge of the fluid. If you are using your own fluid, you should use values that result in a successful APE plot.

Phase tab			Initial values tab			Options tab	
Item	**Value**		**Item**	**Value**		**Item**	**Value**
Type of solution	Normal		Pressure	8500		X-axis Minimum	-150
Select Phase	Asphaltene		Start off from	Pressure		X-axis Maximum	500
Select Basis	Mole Fraction		Initial value to	Decrease			
Enter phase fraction	0						

5. Click **Plot**.

   Note: Multiflash asks if you want more points to be plotted. Click **Yes**, until the asphaltene boundary becomes complete.

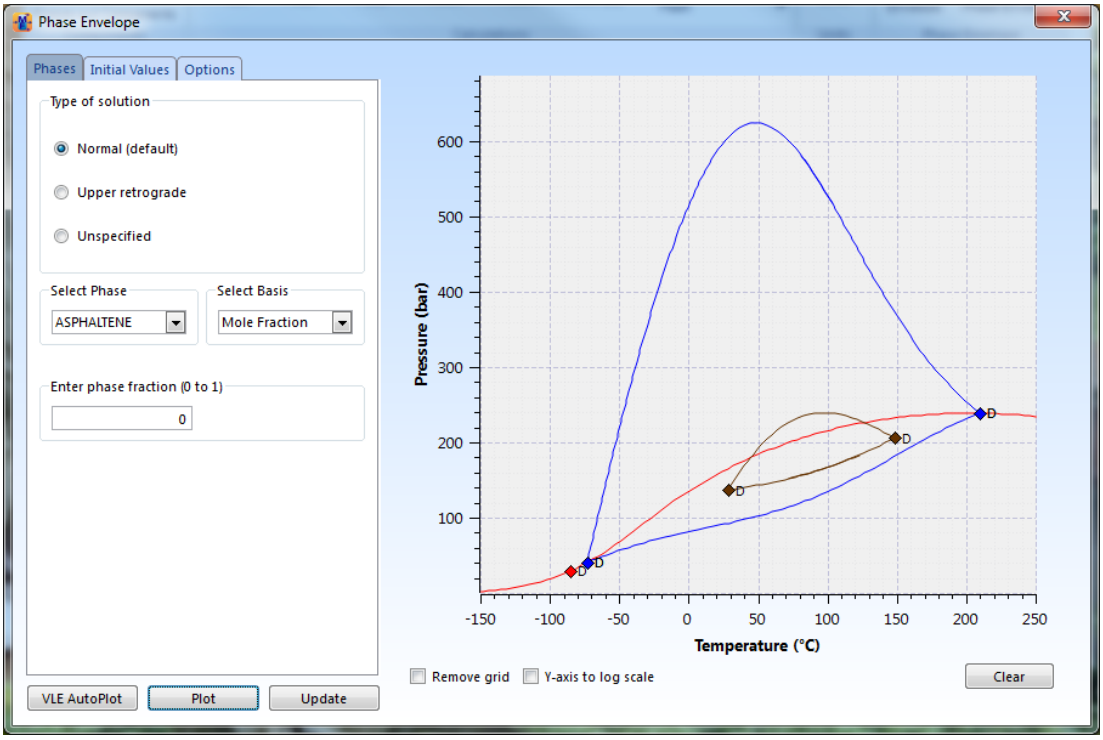


6. Repeat steps 1-5, using the file asphex3.mfl, and the values in the table for the APE plot.

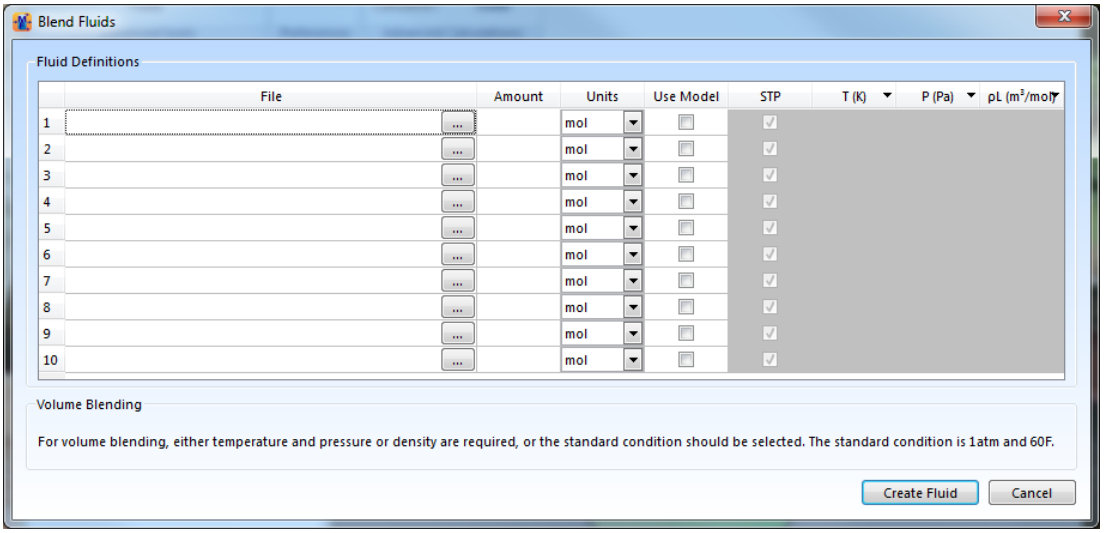
   Tip: Remember to set the initial value to **Increase** for the bubble line plot.

Phase tab			Initial values tab			Options tab	
Item	**Value**		**Item**	**Value**		**Item**	**Value**

Phase tab			Initial values tab			Options tab	
Type of solution	Normal		Pressure	150		X-axis Minimum	-150
Select Phase	Asphaltene		Start off from	Pressure		X-axis Maximum	250
Select Basis	Mole Fraction		Initial value to	Increase			
Enter phase fraction	0						



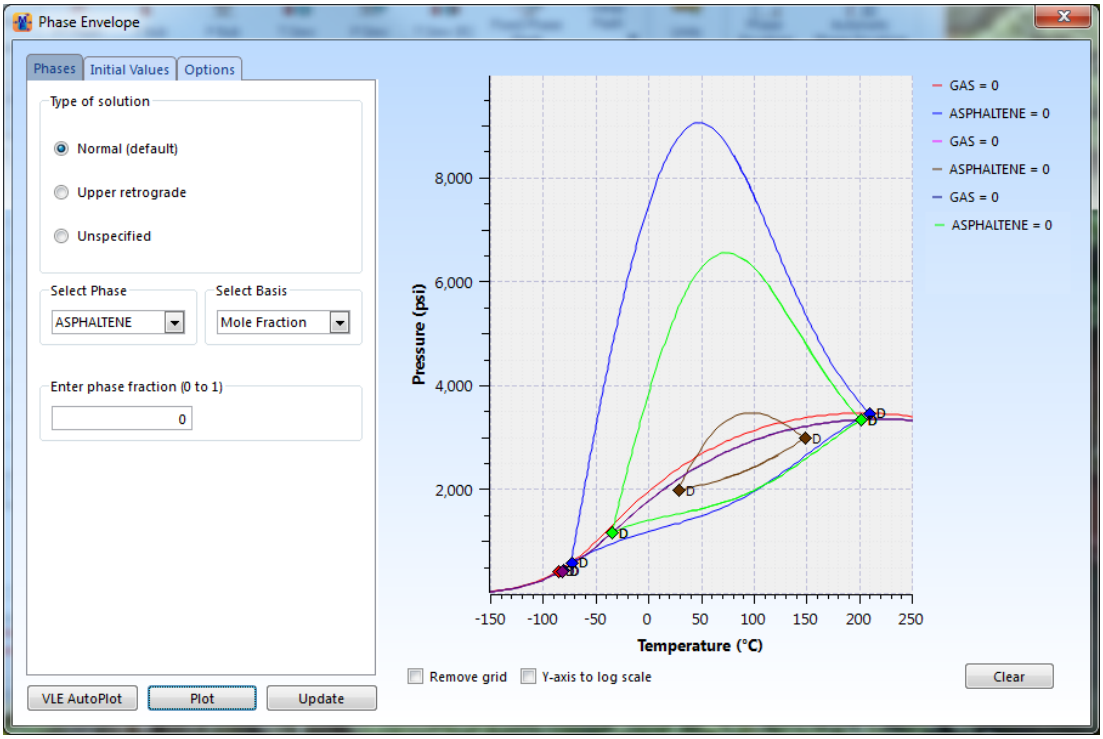
7. On the **Tools** ribbon, click **Blend Fluids**, and then click **Yes** on the message.



8. For each example file, in the **File** column, click Browse ..., select the file, and then click **Open**.
9. In the **Amount** column, specify 0.5 moles of each fluid.
10. In the asphex2.mfl row, check **Use Model**.
11. Set the temperature units to °C and the pressure units to psi.
12. Click **Create Fluid**, and then, on the message, click **OK**.
13. On the **Home** ribbon, click Units, and ensure that **Output same as Input** is checked.
14. Repeat steps 1-5, using the blended fluid, and the values in the table for the APE plot.

Tip: Remember to set the initial value to **Increase** for the bubble line plot.

Phase tab			Initial values tab			Options tab	
Item	**Value**		**Item**	**Value**		**Item**	**Value**
Type of solution	Normal		Pressure	6500		X-axis Minimum	-150
Select Phase	Asphaltene		Start off from	Pressure		X-axis Maximum	250
Select Basis	Mole Fraction		Initial value to	Decrease			
Enter phase fraction	0						



The bubble point line is intermediate between those of the two original oils. The properties of the resins and asphaltenes in the blend are calculated from those of the original oils using simple averaging rules; in this case the predicted asphaltene line of the blend is closer to that of asphex2.mfl. The predicted behaviour is highly speculative; there are no data in the public domain that can be used to support any model for the blending of asphaltenic crudes. For engineering calculations, these predictions must be treated with caution.

Blending example: waxy crudes

This example uses two standard Multiflash examples of waxy crudes. Waxycondensate.mfl is a condensate crude with an n-paraffin distribution estimated from the total wax content; waxycrude.mfl has a measured n-paraffin distribution. The latter is much heavier and waxier, because its n-paraffin carbon numbers go to much higher molecular weights—nC80+ as opposed to nC62+.

The fluids are loaded in turn, and the fluid phase envelope and wax line plotted. A 25:75 blend is created, and the fluid phase envelope and wax line are plotted for comparison with the source fluids.

Try it yourself:

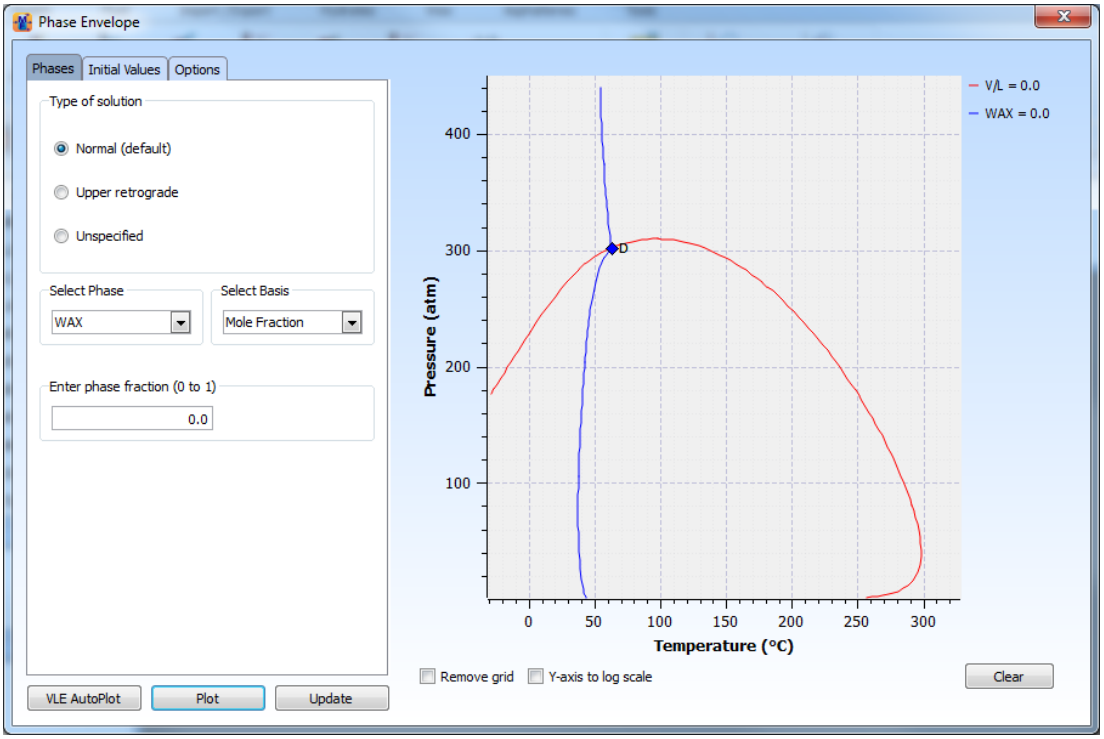
1. On the **File** menu, click **Open**, and open the file waxycondensate.mfl.
2. On the **Home** ribbon, click 

, and set the input and output pressure to atm.
3. On the **Home** ribbon, click 

, and then click **VLE AutoPlot**.
4. Enter the data shown in the table.

Phase tab			Initial values tab			Options tab	
Item	**Value**		**Item**	**Value**		**Item**	**Value**
Type of solution	Normal		Pressure	1		Y-axis Minimum	450
Select Phase	Wax		Start off from	Pressure			
Select Basis	Mole Fraction		Initial value to	Increase			
Enter phase fraction	0						

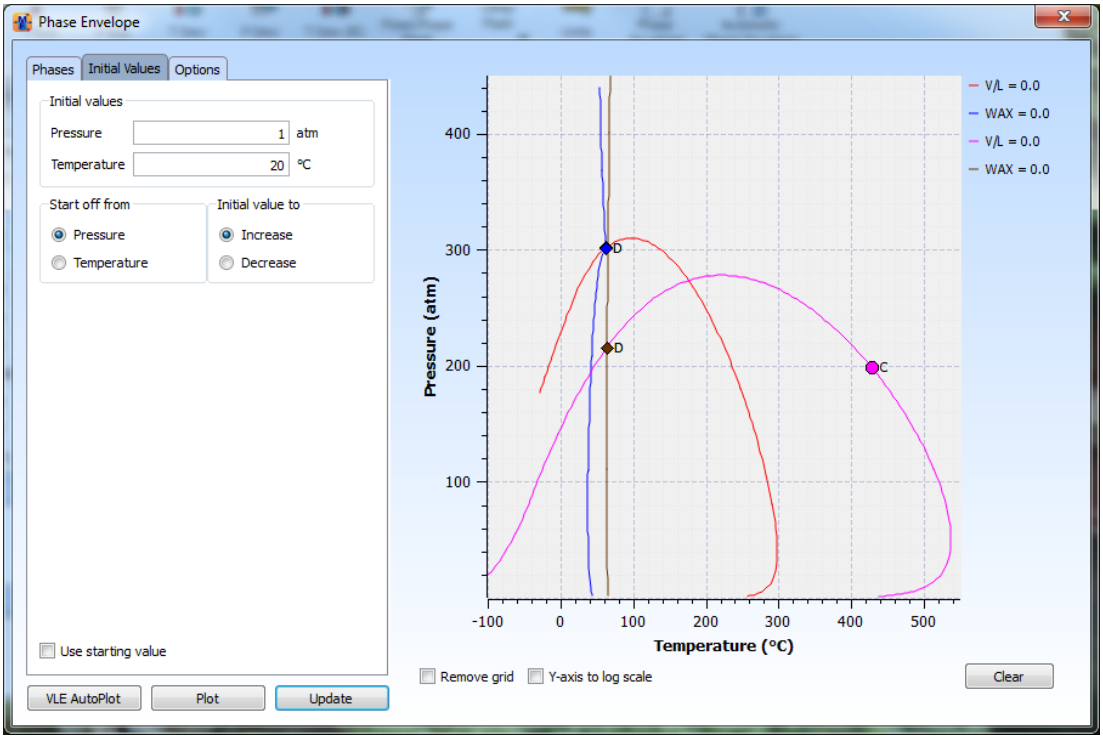
5. Click **Plot**.



6. Repeat the plots using the file waxycrude.mfl, and the values in the table for the wax phase boundary plot.

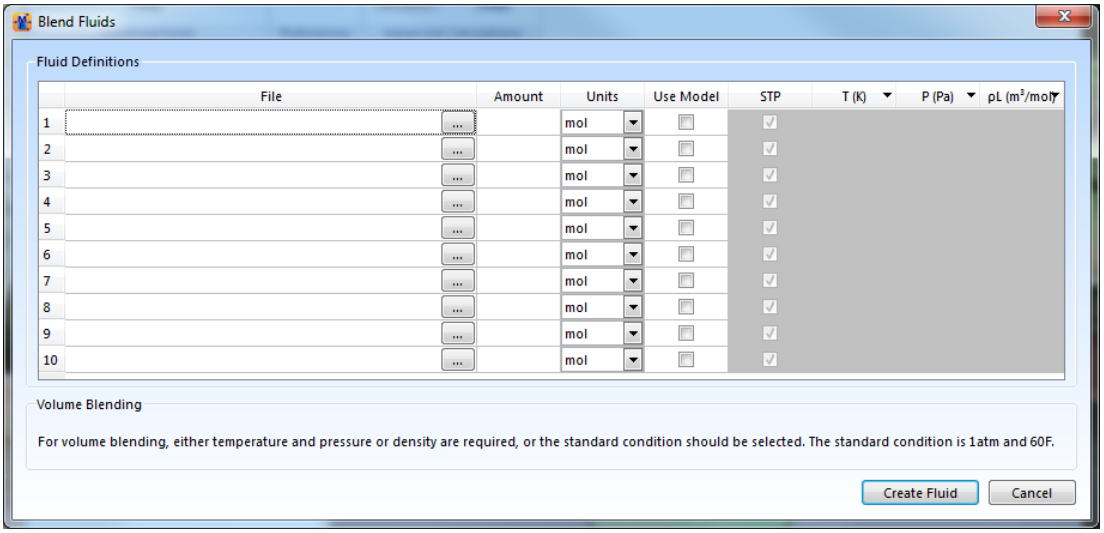
Phase tab			Initial values tab			Options tab	
Item	**Value**		**Item**	**Value**		**Item**	**Value**
Type of solution	Normal		Pressure	1		X-axis Minimum	-100

Phase tab			Initial values tab			Options tab	
Select Phase	Wax		Start off from	Pressure		X-axis Maximum	550
Select Basis	Mole Fraction		Initial value to	Increase		Y-axis Maximum	450
Enter phase fraction	0						



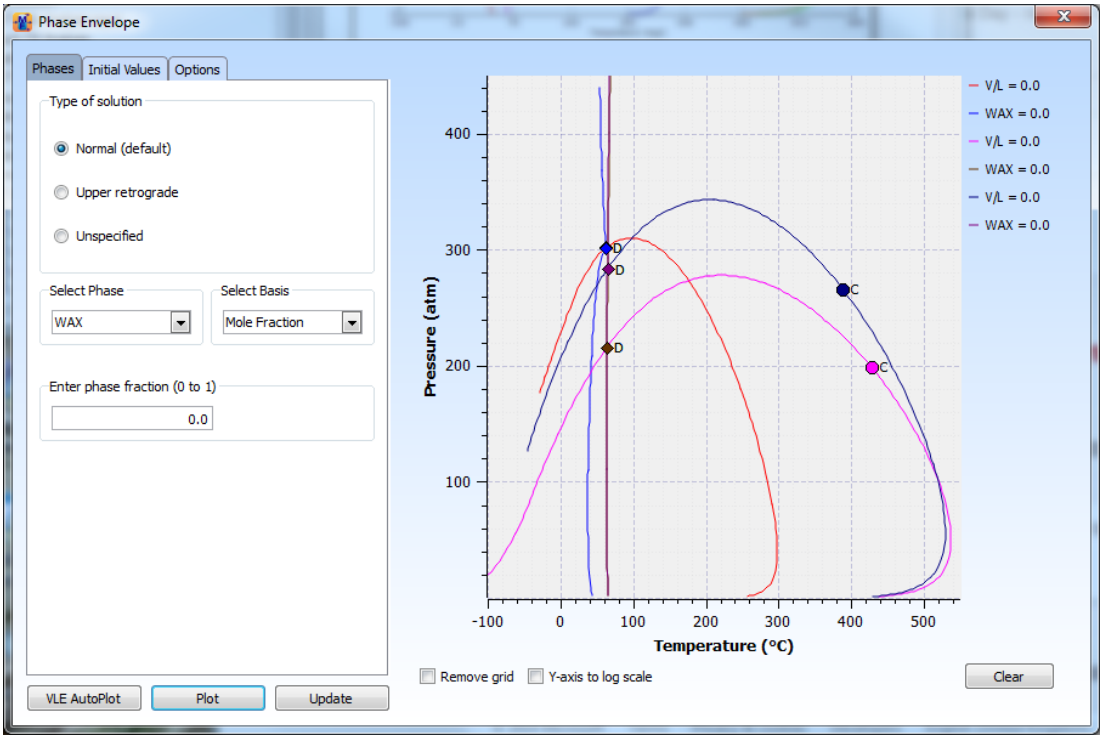
The wax line occurs at a higher temperature for waxycrude.mfl because the fluid contains heavier n-paraffin components.

7. On the **Tools** ribbon, click **Blend Fluids**, and then click **Yes** on the message.



8. For each example file, in the **File** column, click Browse ..., select the file, and then click **Open**.
9. In the **Amount** column, specify 0.25 mole for waxycondensate.mfl and 0.75 mole for waxycrude.mfl.
10. In the waxycrude.mfl row, check **Use Model**.
11. Set the temperature units to °C and the pressure units to atm.
12. Click **Create Fluid**, and then, on the message, click **OK**.
13. On the **Home** ribbon, click Units, and ensure that **Output same as Input** is checked.
14. Repeat the plots using the blended fluid, and the values in the table for the wax phase boundary plot.

Phase tab			Initial values tab			Options tab	
Item	**Value**		**Item**	**Value**		**Item**	**Value**
Type of solution	Normal		Pressure	1		X-axis Minimum	-100
Select Phase	Wax		Start off from	Pressure		X-axis Maximum	550
Select Basis	Mole Fraction		Initial value to	Increase		Y-axis Maximum	450
Enter phase fraction	0						



As expected, the vapour-liquid phase envelope for the blended crude has mixed effects from both crudes. The waxy oil is much heavier and has a much stronger effect on the phase envelope of the blended crude at the higher temperature end, whereas the waxy condensate has a greater contribution at lower temperature end. However, the blended wax line is almost identical to that of waxycrude.mfl because the heavier n-paraffins in waxycrude.mfl continue to dominate the point of wax precipitation in the blended mixture.

Stream types

It is possible to define a number of stream types in Multiflash. Each stream type consists of a subset of all the defined components and may be associated with its own set of models. The stream type concept is useful in the Multiflash GUI to be able to specify a separate composition for each stream. This method is used when creating fluids using the Same Pseudos method "Characterizing multiple fluids" on page 55. It is primarily intended to support process simulation applications where different sets of components (with different models) may be present in different unit operations or sections of a flowsheet.

A simple example, shown in the Multiflash Excel manual, is to describe a mainly hydrocarbon stream containing some water and glycol using a cubic equation of state for high and low pressure separator flashes but to change to an activity model to look at glycol regeneration from the recombined water streams.

We will describe how to set up stream types in the Multiflash GUI.

Initially we have defined an input stream containing 4 hydrocarbons, water and MEG and supplied a composition.

Component	Composition (mol)
Methane	60
Ethane	20
Propane	5
n-Butane	1
Water	10

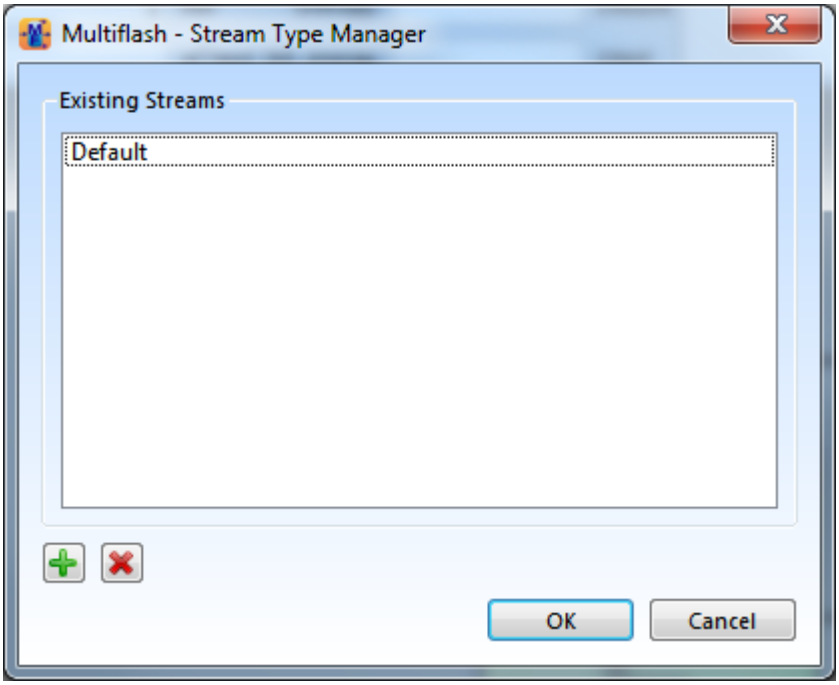
MEG 5

Select the default RKSA model for this mixture. This will be the default or original stream.

A new stream type can be created for example to use the CPA model for pure water.

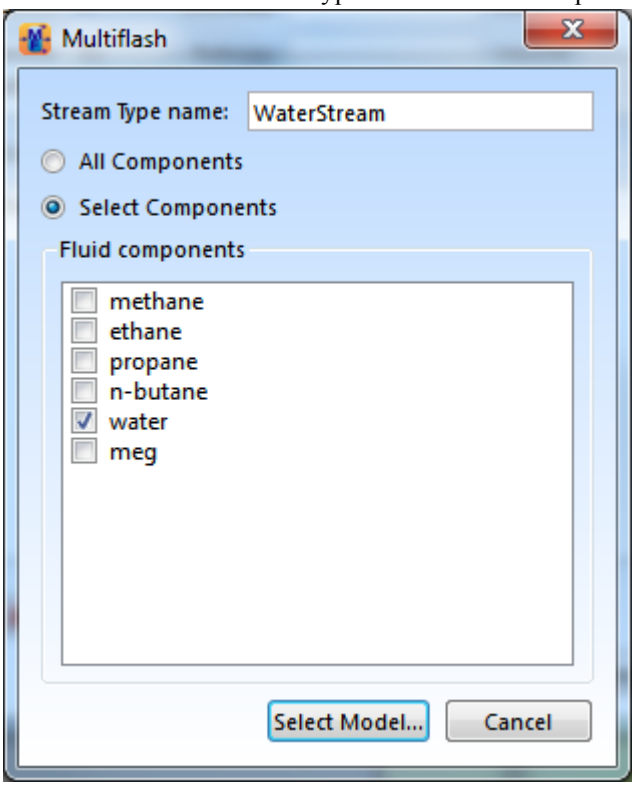
To create a new stream type:

1. Click [] under Tools->Stream Types:



2. Click + button.

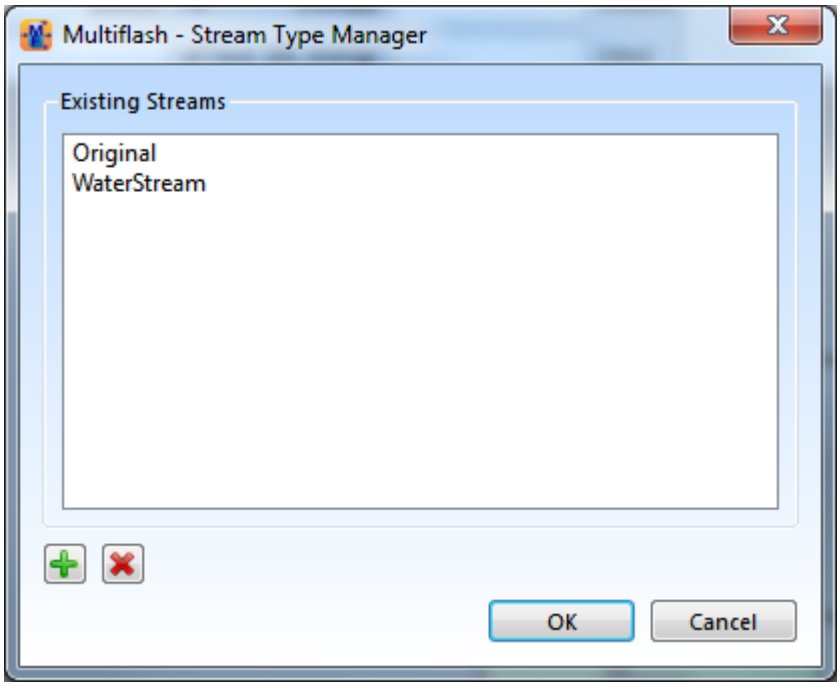
3. Enter a name for the stream type and select the components required (water only in our example)



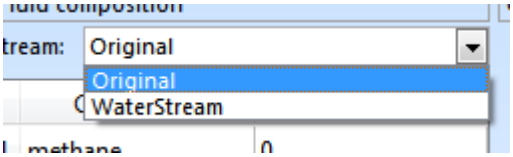
4. Click **Select Model...**. The model normal selection dialog will appear. Select the CPA model.

Result:

Two Streams appear now in the Stream Types tool:



The main window of Multiflash shows two streams that can be quickly selected.



When selecting the WaterStream, only water will show in the composition list, allowing to make some water properties calculations with CPA only.

Note:

While a stream is active, some operations will only use/affect that stream:

- Flash calculations
- Phase envelope
- Defining a model
- add/remove components
- Edit binary interaction parameters

Other operations will remove all the existing streams:

- Fluid characterisation
- Fluid blending

Exploring the effect of user-defined pseudocomponents

By default, the carbon number cuts, SCN, are defined by Multiflash. However, you can specify your own SCN values. This can be useful if you need to specify the SCN lower boundary cuts to match a previous characterisation from Multiflash or any other package. For further information on user-defined cuts, see *Defining a fluid using a PVT analysis*.

Try it yourself:

1. On the **File** menu, click **Open**, and open the file pvt_anal2.mfl.
2. On the **Fluid** ribbon, click **PVT Analysis**.
3. Modify the values shown in the table, click **Do characterization** , and then click **OK**.

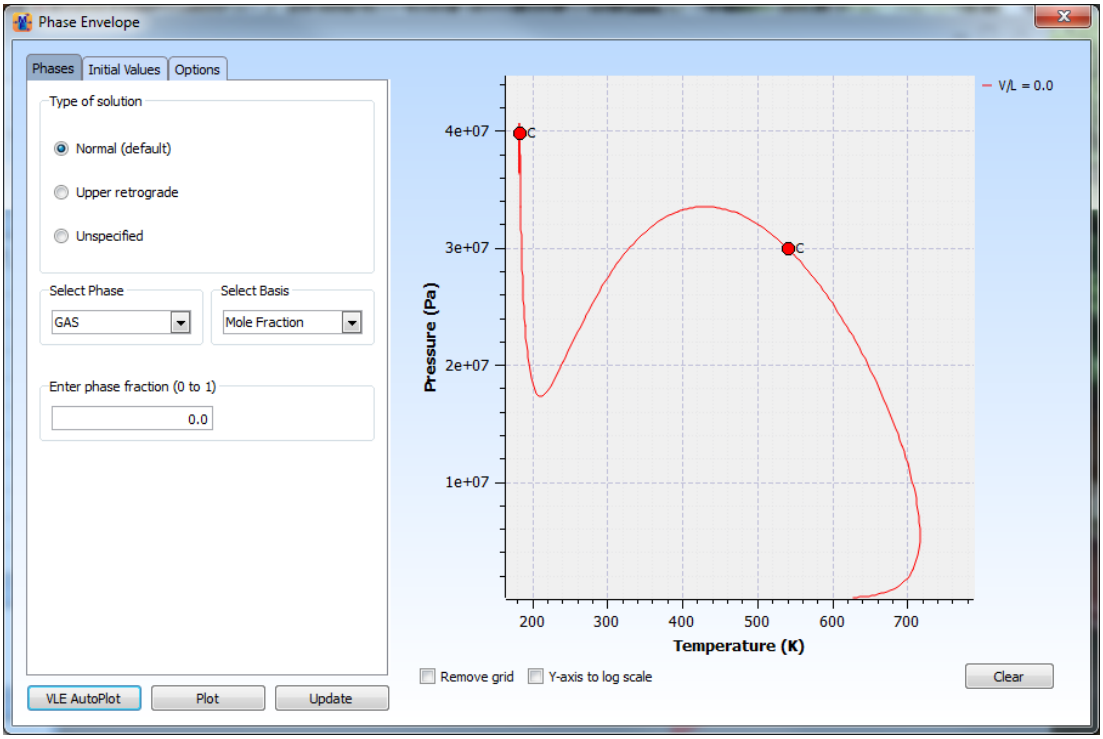
Item	Value
Normal fractions - Distribution start	C6
Normal fractions - Pseudocomponents required	5

   Result: The five pseudocomponents are included in the fluid composition:

   - C6-12, C13-17, C18-26, C27-40, C41+

4. On the **Home** ribbon, click 

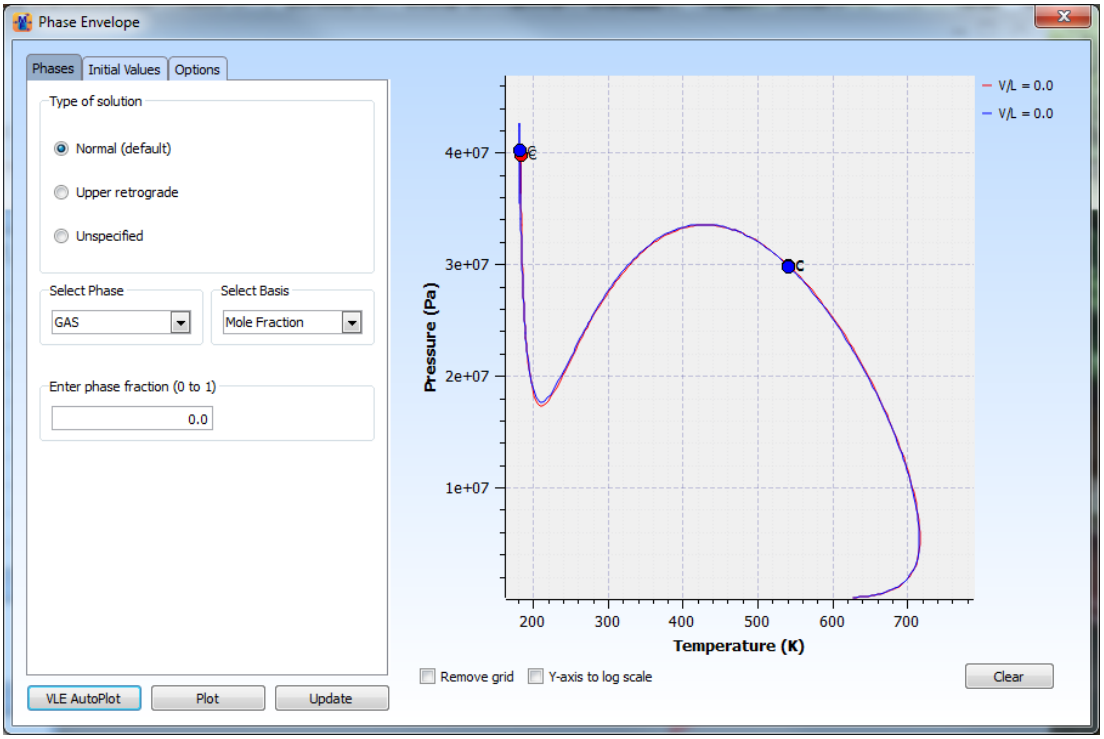
, and then click **VLE AutoPlot**.



5. On the **Fluid** ribbon, click **PVT Analysis**.
6. Check **User-defined cuts**, and then click **Define cuts**.
7. In the Define Cuts dialog box, enter the following values, one on each line, and then click **OK**:
   - 6, 10, 20, 30, 40
8. Click **Do characterization**, and then click **OK**.

   Result: The five pseudocomponents are included in the fluid composition:
   - C6-9, C10-19, C20-29, C30-39, C40+
9. On the **Home** ribbon, click 

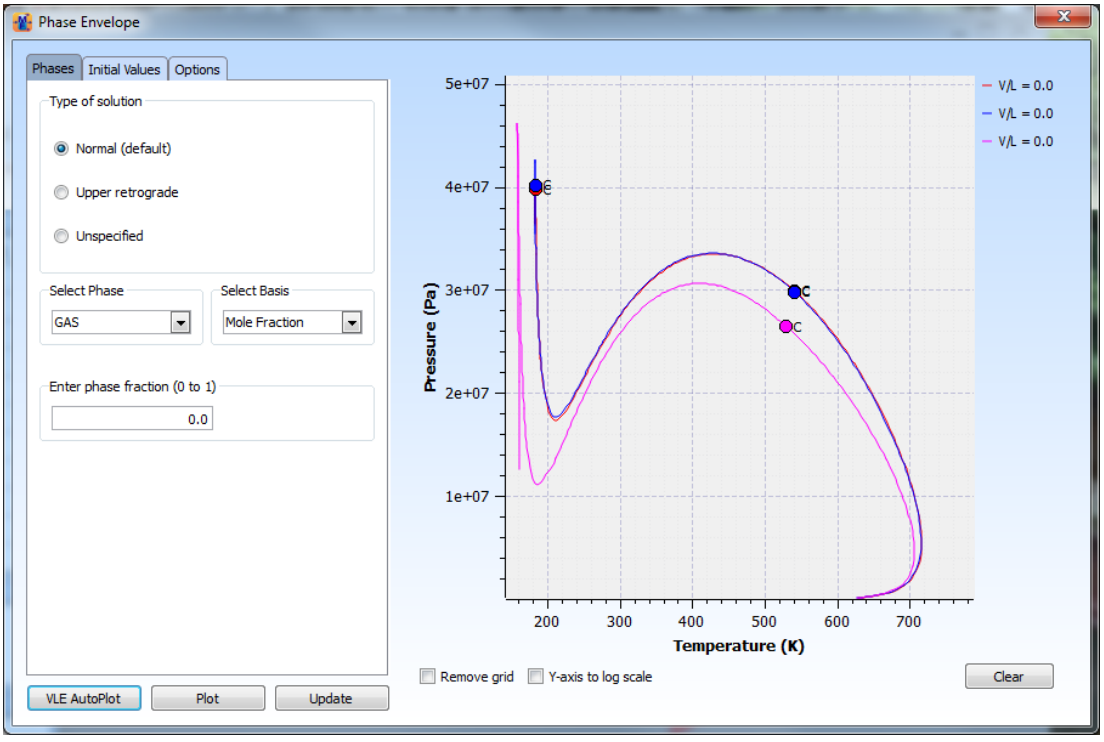
, and then click **VLE AutoPlot**.



For these user defined SCNs, the phase envelope is virtually identical to the original.

10. Create the following distribution, and plot again:

    - 6, 30, 35, 37, 40



You can see that the modified pseudocomponents distort the phase envelope.

Characterizing multiple fluids

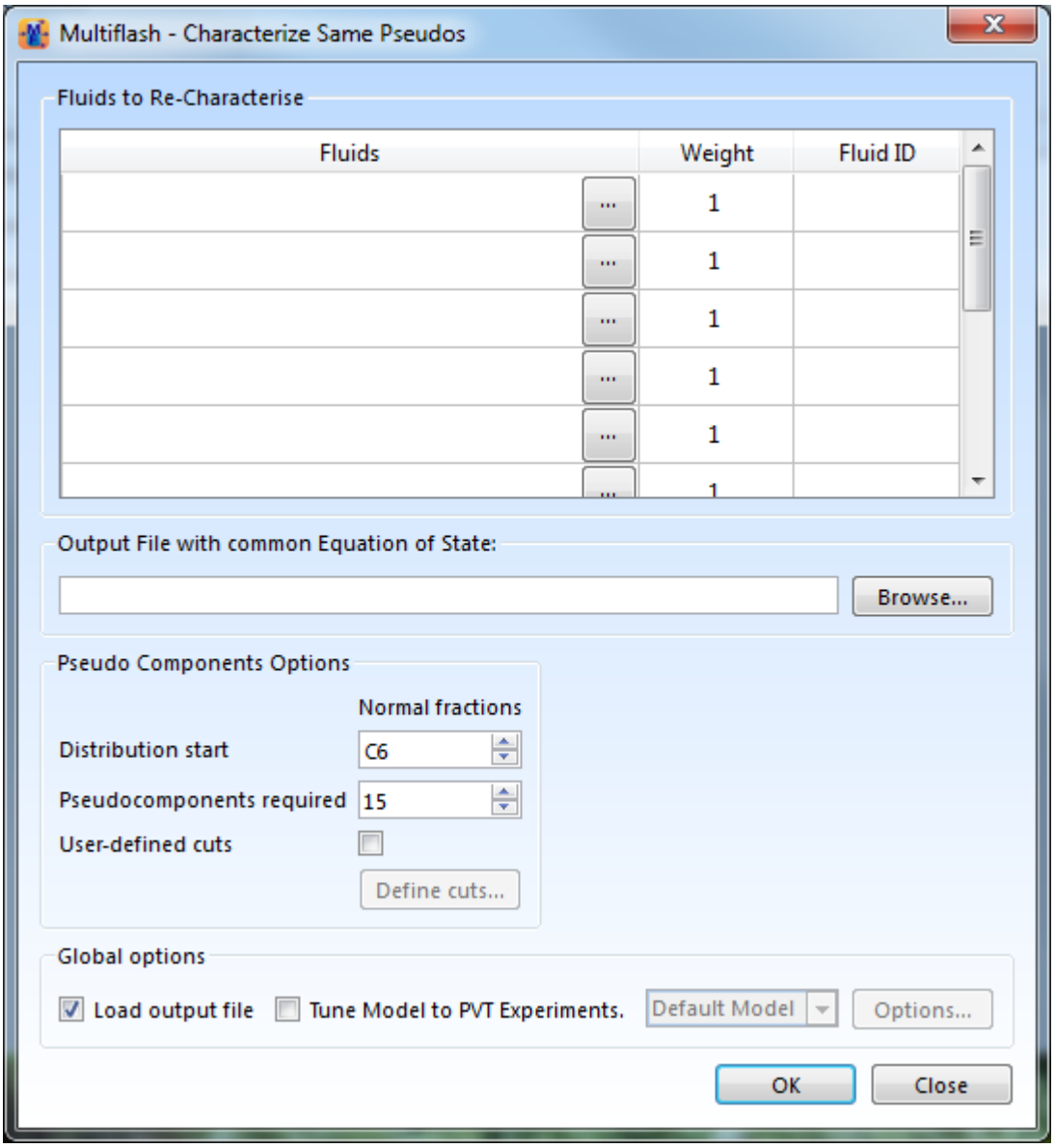
Multiflash enables you to characterize multiple reservoir fluids with the same set of pseudocomponents. This can be useful, for example, when you are processing multiple fluids simultaneously.

Each fluid is first characterised in terms of the single carbon number (SCN) fractions. You can weight each fluid's contribution to obtain common SCN properties and a representative composition. These common properties are then used to decide on the common carbon number ranges in each of the required pseudocomponents and their properties. The composition in each fluid is then lumped into the same set of pseudocomponents.

Requirement: You must have two or more files with fluids defined, and each fluid must have SCN fractions.

To characterize multiple fluids:

1. On the **Fluid** ribbon, click Same Pseudos.



2. Select the databank from which you want to take component properties.
3. For each fluid that you want to characterize, use ... to add the file.

   Tip: If you want to add more than ten files, right-click any row, and select **Add New Fluid**.
4. Enter a name for the output file.

   Note: The output file is a multiple stream file that contains all the input fluids.
5. In the **Pseudo Components Options** panel, specify the start SCN and number of pseudo-components (maximum of 200) for the normal fractions.

Example: If you set **Distribution start** to C10, and **Pseudocomponents required** to 5, the components C6, C7, C8 and C9, if present, are represented by individual components, and the remaining normal alkanes are grouped into five fractions that depend on the actual composition of the fluid, with the last pseudocomponent being a plus fraction.

Tip: You can specify your own group ranges by checking **User-defined cuts**, clicking **Define cuts**, and then entering the SCN values at which you want the groups to start.

6. If you want to load the output file automatically after the calculation, check **Load output file**.
7. If one of your input files contains PVT experiments that you want to use to tune the common properties, check **Tune Model to PVT Experiments**.
8. To modify the default tuning options, click **Options**, and do the following:
   - For each property that you want to vary in the tuning calculation, check the box next to the property name.
   - In **% Change**, enter the range within which the property value can vary. The range is a percentage amount above or below the current value of the property.

   The modifiable properties are described in the following table. To view the properties that are modifiable when you tune a model using a specific experiment type, see *Tuning models*.

Property	Description
T_c	Critical temperature of the petroleum fractions in the mixture.
P_c	Critical pressure of the petroleum fractions in the mixture.
Acentric factor	Acentric factor (ω) of the petroleum fractions in the mixture.
BIPs	Binary interaction parameters for the petroleum fractions with methane, ethane and propane.
Volume shift	The Peneloux parameters of the petroleum fractions, used to correct liquid density predictions. **Tip:** You can cut and paste the data to a spreadsheet.
Viscosity	The following petroleum fraction properties are modified in viscosity fitting: ■ V_c (critical volume) for the LBC viscosity model ■ T_c (critical temperature) for the Supertrapp viscosity model ■ MW (molecular weight) for the Pedersen model ■ T_b (boiling point) for the Twu viscosity model
LBC A parameters	The model parameters in the LBC viscosity model.

9. Click **OK**.

Result: Your fluids are characterized with the same set of pseudocomponents and output to the file of your choice.

Tip: When you open the file in Multiflash, you can view and perform calculations on each fluid separately, by selecting the fluid from the **Stream** list in the **Fluid Composition** area.

Using mud numerical cleaning

Oil-based muds (OBM) are widely used in offshore drilling, mainly because their use results in substantial cost savings. Bottomhole samples collected in wellbore systems under these circumstances are likely to be contaminated with the OBM as these tend to be highly soluble in the hydrocarbon fluids. No experimental method exists to estimate the composition of the clean reservoir fluid.

Numerical methods have been designed to estimate the level of mud contamination and composition of the clean reservoir fluid based on the expected semi-logarithmic dependence of the composition of the natural reservoir fluids on carbon number. PVT laboratories analyse the composition of the mud filtrate and provide an estimate of the level of mud contamination in samples. The contamination is normally quoted as the weight fraction of mud in the stock tank oil that results from a single stage flash of the contaminated sample.

Multiflash contains a procedure which uses the compositions of the contaminated fluid and the mud, together with the quoted level of mud contamination in the stock tank oil, to estimate the composition of the clean reservoir fluid. This is achieved by performing molar, mass and volume balances on the single carbon number (SCN) fractions.

Requirement: You must have created Multiflash files for the contaminated fluid and mud filtrate, using the PVT analysis reports.

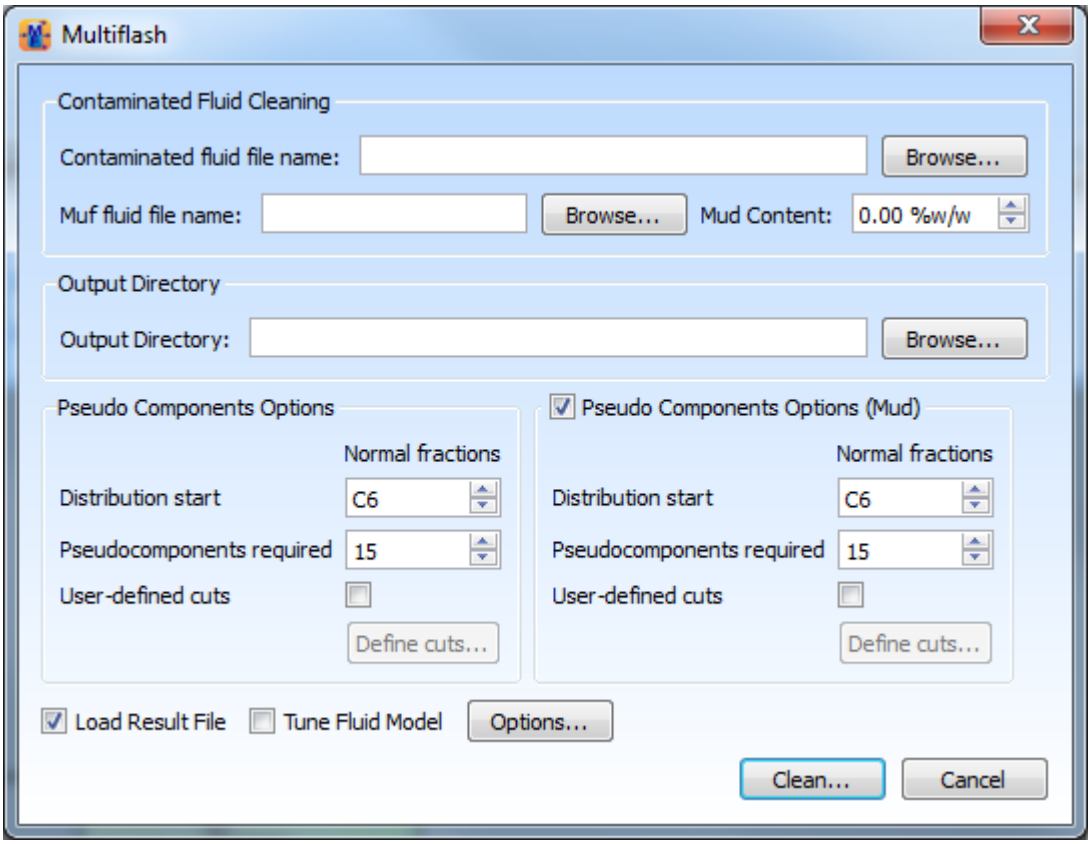
Tips:

- The model specified in the contaminated fluid file is the one used for the numerical cleaning.
- If you want to use PVT experiment data to tune the model after cleaning, ensure that the PVT experiment data is included in your contaminated fluid file.
- When you create the mud filtrate fluid, you must enter each mud SCN petroleum fraction separately, using the add petroleum fractions feature of the Select Components dialog box, see *Defining a petroleum fraction*. Use the molecular weight and specific gravity values for each SCN if these are provided in the PVT report. If these are not given, enter the carbon number of each mud SCN, and allow Multiflash to estimate all other properties.

To perform mud numerical cleaning:

1. On the **Fluid** ribbon, click 

.



2. Enter the full path to the file names for your contaminated fluid and mud filtrate, using the **Browse** button if required.
3. For the mud filtrate, enter the mud content as the weight % of mud in the stock tank oil resulting from the single stage flash of the contaminated fluid.
4. Enter a location for the output file, using the **Browse** button if required.

   Note: The output file has the same name as the contaminated fluid file, appended by "_Clean".
5. In the **Pseudo Components Options** panel, specify the start SCN and number of pseudo-components (maximum of 200) for the normal fractions.

   Example: If you set **Distribution start** to C10, and **Pseudocomponents required** to 5, the components C6, C7, C8 and C9, if present, are represented by individual components, and the remaining SCN fractions are grouped into five fractions that depend on the actual composition of the fluid, with the last pseudocomponent being a plus fraction.

   Tip: You can specify your own group ranges by checking **User-defined cuts**, clicking **Define cuts**, and then entering the SCN values at which you want the groups to start.
6. If you want to include the mud SCNs in the pseudocomponents analysis, check **Pseudo Components Options (Mud)**, and then specify the start SCN and number of pseudocomponents (maximum of 200) for the normal fractions.
7. If you want to load the output file automatically after the calculation, check **Load Result File**.

8. If your contaminated fluid file contains PVT experiments that you want to use to tune the model after the fluid is cleaned, check **Tune Fluid Model**.
9. To modify the default tuning options, click **Options**, and do the following:
   - For each property that you want to vary in the tuning calculation, check the box next to the property name.
   - In **% Change**, enter the range within which the property value can vary. The range is a percentage amount above or below the current value of the property.

   The modifiable properties are described in the following table. To view the properties that are modifiable when you tune a model using a specific experiment type, see *Tuning models*.

Property	Description
T_c	Critical temperature of the petroleum fractions in the mixture.
P_c	Critical pressure of the petroleum fractions in the mixture.
Acentric factor	Acentric factor (ω) of the petroleum fractions in the mixture.
BIPs	Binary interaction parameters for the petroleum fractions with methane, ethane and propane.
Volume shift	The Peneloux parameters of the petroleum fractions, used to correct liquid density predictions. **Tip:** You can cut and paste the data to a spreadsheet.
Viscosity	The following petroleum fraction properties are modified in viscosity fitting: ■ V_c (critical volume) for the LBC viscosity model ■ T_c (critical temperature) for the Supertrapp viscosity model ■ MW (molecular weight) for the Pedersen model ■ T_b (boiling point) for the Twu viscosity model
LBC A parameters	The model parameters in the LBC viscosity model.

10. Click **Clean**.

Result: Your contaminated fluid is cleaned as specified. The output file contains the specified pseudocomponents, with the mud pseudocomponents identifed by the prepended letter M. If you selected the tuning option, your non-mud component properties are modified to fit the PVT experimental data that you provided. The fluid, minus the mud pseudocomponents, can now be used in further Multiflash calculations.

Using the delumping tool

You use the delumping tool to recharacterize a fluid that has been imported from another software package. The delumping tool can be used with any previously characterized fluid. It can also handle fluids where asphaltenes and waxes are present. With waxes, the n-paraffin components are also delumped.

Tip: If the fluid is characterized in Multiflash, you can also use the delumping tool. However, all the PVT analysis inputs are stored, so it is easy to re-characterize the fluid by clicking **PVT Analysis** on the **Fluid ribbon**, and using the **Change to** list on the PVT Laboratory Fluid Analysis dialog box.

Requirement: You must have your fluid file open, and a model defined.

To use the delumping tool:

1. On the **Fluid ribbon**, click 

.

   Result: The PVT Laboratory Fluid Analysis dialog box appears.

   Note: Any model tuning or modified parameters that were in your original fluid file are lost after delumping.

2. Use the PVT Laboratory Fluid Analysis dialog box to recharacterize your fluid, using all the features of Multiflash.

Basic flash calculations

In a flash calculation the overall composition and any two of the following variables are fixed:

- Temperature (T)
- Pressure (P)
- Volume (V)
- Enthalpy (H)
- Entropy (S)
- Internal energy (U)
- Amount of a phase

The flash calculation enables you to determine, subject to the constraints imposed (the two fixed quantities), the number and type of phases present and the composition and properties of those phases. This is based on the thermodynamic principles that at equilibrium:

- The fugacities of each component in all phases are equal.
- The temperature of all phases is the same.
- The pressure of all phases is the same.

The calculations available in Multiflash can be divided into these categories:

- Single flash calculations, where any two quantities, excluding phase amount, are specified, and the amounts and compositions of all phases at equilibrium are calculated.
- Fixed phase calculations, where one of the fixed quantities is the amount of one phase. Bubble and dew point calculations, where the first gas or liquid appears at a fixed temperature or pressure, are a special case of these calculations, where the gas phase (for bubble point) or liquid phase (for dew point) is set to 0.
- Phase envelope or sequential flash calculations to follow a phase boundary or to simulate a laboratory procedure.

Tip: If you need to carry out many single calculations and generate tabular output, use the Multiflash Excel interface. See the separate document *Multiflash Excel Interface User Guide* for details.

The general approach to a Multiflash calculation is as follows:

1. Define the fluid by specifying the components and their amount.
2. Specify the model to use, including the required phases.
3. If required, change the units of measurement for the calculation.
4. Specify any input conditions required for the calculation.
5. Perform the calculation.

Performing single flash calculations

A single flash calculation is where any two quantities, excluding phase amount, are specified, and the amounts and compositions of all phases at equilibrium are calculated.

You can perform a flash calculation after you have specified your fluid and model.

Note: Fixed phase calculations are described in separate topics.

To perform a flash calculation:

1. In the **Conditions** area, enter the two values that you want fixed for the calculation, as shown in the table.

Flash type	Required fixed conditions
PT	Pressure, temperature
PH	Pressure, enthalpy
TH	Temperature, enthalpy
PS	Pressure, entropy
TS	Temperature, entropy
HS	Enthalpy, entropy
PV	Pressure, density‡
SV	Entropy, density‡
UV	Internal energy, density‡
HV	Enthalpy, density‡
TV	Temperature, density‡
PU	Pressure, internal energy
TU	Temperature, internal energy

‡Multiflash calculates the volume of your system from the measured density of your fluid and the fluid composition that you have entered, providing greater flexibility in the calculations that you can do.

2. On the **Home** ribbon, take one of these actions:

   - To perform a PT flash, click PT Flash 

.

     Tip: If you have plotted a phase boundary, you can right-click anywhere on the plot to perform a PT flash calculation at the pressure and temperature shown in the upper left corner of the plot.

   - To perform any other type of single flash, click **Other Flash** and then choose from the list.

Result: If the input conditions lead to a valid solution, the flash results appear in the **Results** area.

Calculating bubble and dew points

Multiflash provides a set of convenient, preconfigured calculations for determining bubble and dew points. Individual calculations can be either at fixed temperature or fixed pressure.

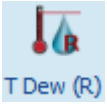
Note: If you want to generate the phase envelope, use the phase envelope plotter rather than a series of individual calculations.

Tip: If you want to find a retrograde dew point or the dew point for a second liquid phase, you should use the fixed phase flash calculator. For example, to find the dew point for water when your fluid has two or more liquid phases, you must use a fixed phase fraction flash and look for the temperature or pressure where there is a zero amount of the water phase.

You can perform a bubble or dew point calculation after you have specified your fluid and model.

To calculate a single bubble or dew point:

1. In the **Conditions** area, enter the pressure or temperature that you want fixed for the calculation.
2. On the **Home** ribbon, click the required calculation icon.

Icon	Calculation type
	Bubble point at fixed temperature
	Bubble point at fixed pressure
	Dew point at fixed temperature
	Dew point at fixed pressure
	Retrograde dew point at fixed temperature

Result: If the input conditions lead to a valid solution, the flash results appear in the **Results** area.

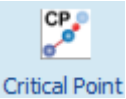
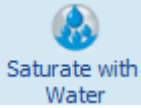
If you find a situation where you get failures for dew and bubble point calculations, or the solutions are not in the region you expect, then it is worth carrying out some isothermal (P,T) flashes or plotting the phase diagram to see those areas where solutions are likely: Solutions only exist at a phase boundary. In general, there is no solution to bubble or dew point problems at pressures above the cricondenbar or temperatures above the cricondentherm.

Initial Estimates: If the flash fails and you are certain that a solution should exist, you can instruct Multiflash to use values from the Conditions area as initial estimates.

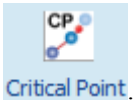
For example, for a bubble point calculation at constant temperature you can click the **Use starting values** option in the Home tab. This will use the pressure in the conditions area as initial guess.

Other preconfigured calculations

In addition to the common flash calculations, Multiflash provides the following preconfigured calculations on the **Tools** ribbon:

Icon	Calculation type
	Critical point of the fluid.
	The amount of water to add before a distinct water phase can form. This calculation is the equivalent of using the tolerance calculation with the water phase defined with a zero molar phase fraction (see *Using the tolerance calculation tool*).

Requirement: You can perform the calculations after you have specified your fluid and model. For the saturation calculation, you must ensure that water is a component in your fluid, with an amount of zero.

To perform a critical point calculation, on the **Tools** ribbon, click  .

To perform a water saturation calculation:

1. In the Conditions area, enter the required temperature and pressure for your calculation.
2. On the **Tools** ribbon, click  .

   Result: The Tolerance Result dialog box displays how much water is required to saturate your fluid.
3. In the **Tolerance Result** dialog box, do one of the following:
   - To add the calculated amount of water to your fluid, click **Yes**.
   - To leave your fluid composition unchanged, click **No**.

   Result: The flash calculation results appear in the **Results** area and, if requested, the calculated amount of water is added to your fluid composition.
4. Check **Total Amounts**.
5. Scroll through the **Phase Compositions** list, to see the composition of the saturated fluid.

Performing a fixed phase flash calculation

A fixed phase flash calculation is one in which the amount of one phase is fixed, with pressure or temperature as the other fixed variable.

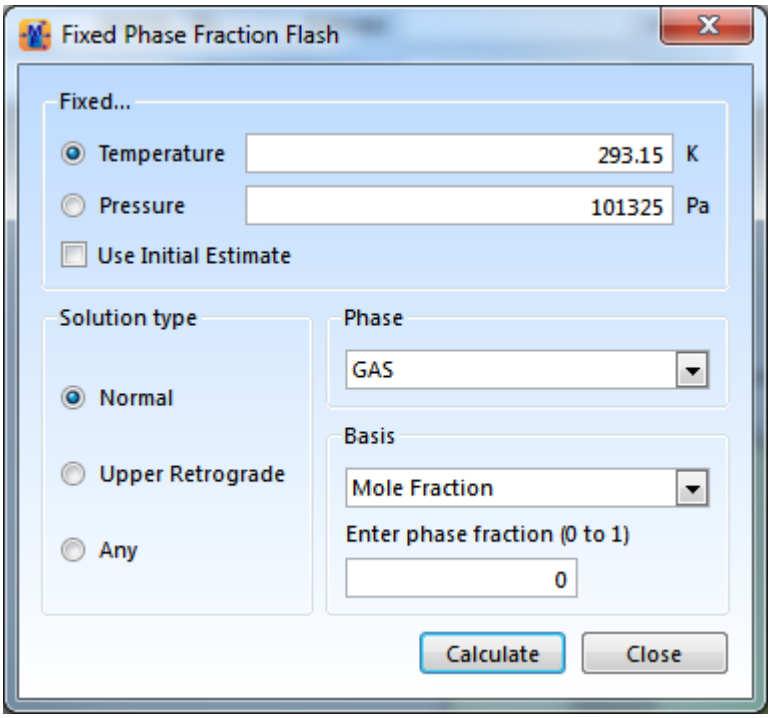
The fixed phase flash calculation can be used to explore the phase space of a specified phase. Unlike the bubble and dew point calculations, it enables you to explore conditions away from the phase boundary.

You can perform a fixed phase flash calculation after you have specified your fluid and model.

To perform a fixed phase flash calculation:

1. On the **Home** ribbon, click Fixed Phase Flash 

.



2. Select whether to fix the pressure or temperature, and enter the required value.
3. From the **Phase** list, choose the phase that you want to fix.

   Note: The phases available depend on the model settings that you specified.
4. From the **Basis** list, choose the purpose of the calculation, as shown in the table.

Basis	Description
Mole Fraction	Specify the phase fraction in moles. We recommend this for phase boundary plots.
Mass Fraction	Specify the phase fraction by mass.
Volume Fraction	Specify the phase fraction by volume.
Nucleation	Use for hydrate formation calculations when you have specified the phase as hydrate. Only present if nucleation model loaded.

5. Enter the fraction of the phase that you want to fix, or a value for the property that you chose as the basis.

   Requirement: The fraction must be between 0 and 1.

   Tip: To search for a point on the phase boundary, set the phase fraction of the appropriate phase to 0.

6. For the Mole, Mass, or Fraction Volume calculation basis, choose a solution type, using the following guidelines.

Solution type	Use for
Normal	Systems with normal dew and bubble points.
Upper Retrograde	Gas condensate systems that are likely to exhibit retrograde condensation. In these systems, there are two dew points, the upper one being the retrograde dew point.
Any	Finding the nearest solution to the starting point, making no distinction between normal and retrograde behaviour. One example of using this is when you calculate an asphaltene phase boundary above the bubble point.

7. Tick the box **Use Initial Estimate** to use a value as initial guess for finding temperature in fixed pressure flashes and vice versa.
8. Click **Calculate**.

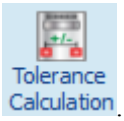
Tip: If your calculation fails or the solutions are not in the region you expect, try carrying out some isothermal PT flashes or plotting the phase envelope to establish the likely areas of the phase diagram where solutions exist.

Using the tolerance calculation tool

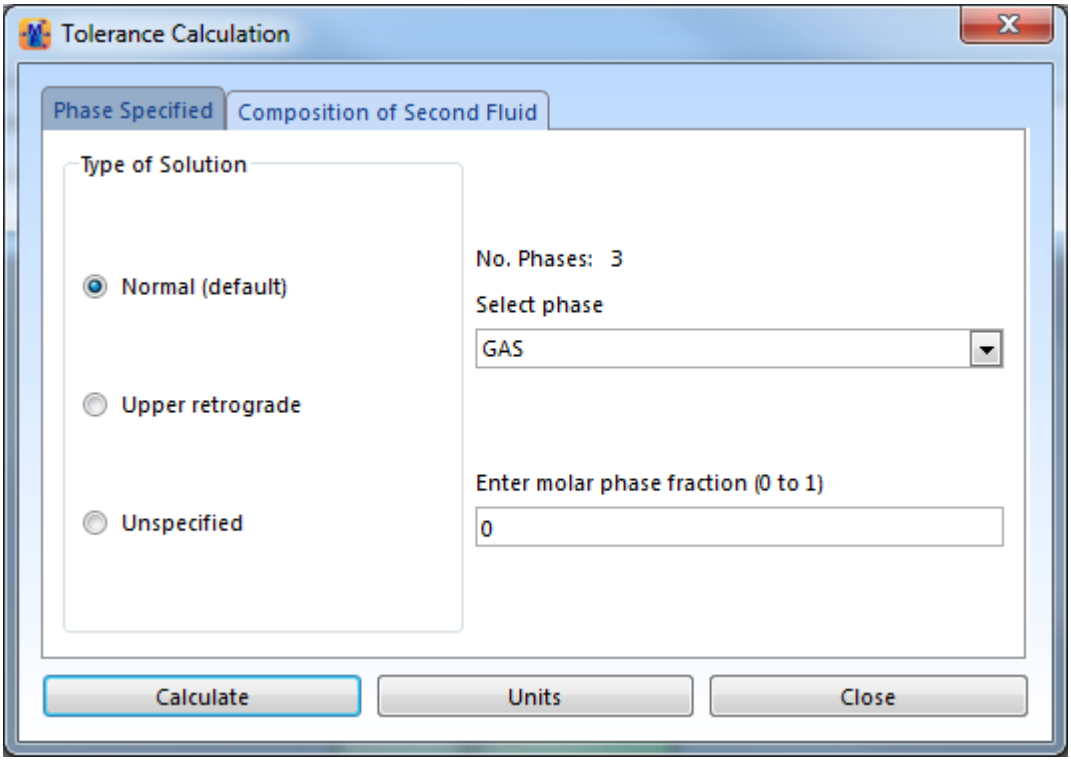
Tolerance calculations are used to determine the amount of a component or mixture that must be added to an existing fluid to achieve a given phase split. A typical application is to determine how much inhibitor is required to suppress hydrate formation. Tolerance calculations are carried out at fixed temperature and pressure and for a fixed phase fraction specified in moles.

Requirement: You can perform a tolerance calculation after you have specified your fluid and model. If there are components in the added mixture that are not present in the original fluid, you must first add those components, with zero amount, to your fluid.

To perform a tolerance calculation:

1. In the Conditions area, enter the required temperature and pressure for your calculation.
2. On the **Tools** ribbon, click 

.



3. From the **Select phase** list, choose the phase that you are interested in, and then enter the required phase fraction.
4. On the **Composition of Second Fluid** tab, enter the composition of the fluid that you are adding.

   Tip: Multiflash normalises the amounts to 1.0 before the calculation is performed, so you need not enter normalised values.
5. Click **Calculate**.

   Result: The **Tolerance Result** dialog box displays the amount of fluid added.
6. In the **Tolerance Result** dialog box, do one of the following:
   - To add the calculated component amounts to your fluid, click **Yes**.
   - To leave your fluid composition unchanged, click **No**.

   Result: The flash calculation results appear in the **Results** area and, if requested, the calculated amount of your second fluid is added to your fluid composition.
7. On the Tolerance Calculation dialog box, click **Close**.
8. Check **Total Amounts**.
9. Scroll through the **Phase Compositions** list, to see the distribution of added components that satisfies the conditions you set.

Tip: You can try a worked example in *Determining maximum allowable water content*.

Calculating pure component properties

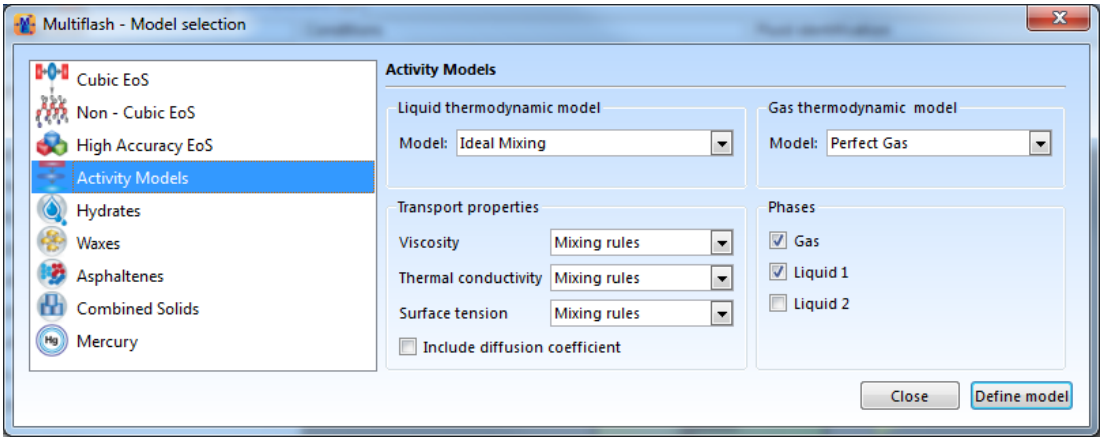
You can use Multiflash to obtain the properties of a pure component, by defining a fluid that contains only the component of interest. The model to use depends on which properties you want:

- Select the ideal gas and ideal solution models if you want the properties as set in the pure component databank. When you select this model set, all properties are taken from the databank correlations, except liquid C_p, which is calculated from the vapour phase model and the enthalpy of vaporisation.
- Select any other model set to have properties calculated using the model set definitions. When you select any non-ideal model, only the pure component properties needed for that model set are taken from the databank. Other properties are calculated using the model set definitions, which include models for the transport properties.

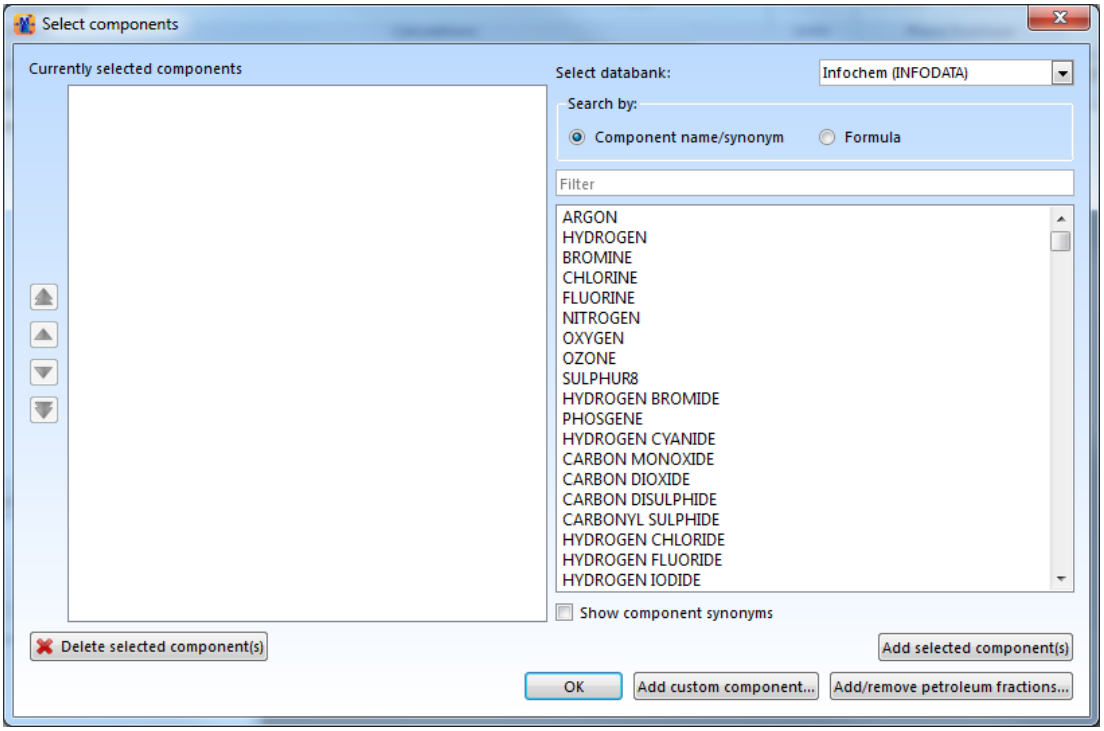
Tip: If you just want to know the stored values for the temperature independent properties or the correlation coefficients of a temperature dependent property, you can view the pure component data.

To calculate pure component properties:

1. On the **File** menu, click **New problem**.
2. On the **Models** ribbon, click **Select Model**, and then choose Activity Models.



3. Click **Define Model**, and then, on the message, click **OK**.
4. On the **Home** ribbon, click **Components**.



5. Select the databank from which you want to take component properties.
6. Scroll through the list and click on the component whose properties you want to calculate.
7. Click **Add selected components**, and then click **OK**.
8. In the Multiflash window, specify the amount of the component, by clicking in the **Amount** column, and entering the required amount.

   Tip: The amount is not important, because it is a pure component, so just enter 1.
9. To obtain the component properties, perform flash calculations at appropriate temperatures and pressures, and view the properties in the **Phase Properties** area.

   Tip: To obtain liquid-vapour equilibrium for pure components, use either the dew point or the bubble point tools. This is because the vapour-liquid coexistence region is just a line on the P-T plane, and standard P-T flashes are not suitable to find phase coexistence.

What else can I do?

1. Follow the above procedure for octane, then perform a bubble point calculation at 400K using 

. In the **Phase Properties** area, you can scroll through and see the properties for octane at the flash conditions.
2. If you want to evaluate a temperature-dependent property at several temperatures, on the **Home** ribbon, click **Pure Component Data**, and then click **Property Evaluator**. For further details, see *Viewing pure component data*.

The phase envelope plotter

The phase envelope plotter is a convenient way to determine the phase boundaries and the phases you might expect to be present under given temperature and pressure conditions.

The plotter can trace any phase boundary on pressure-temperature coordinates and works with any Multiflash model.

Note: Some models, such as activity coefficient models, are valid only at low pressures and will not produce closed phase boundaries.

The plotter can trace the following items:

- Any selected phase boundary on the basis of mole, mass or volume fraction.
- Constant enthalpy, entropy, volume or free energy boundaries.
- A generalisation of the plotting facility, so that for any chosen phase boundary or constant property, you can plot any phase amount or property against another phase amount or property.

After you have generated your plots, you can do the following:

- Print your plot.
- Export the plot data to Microsoft Excel.
- right-click anywhere on the plot and perform a PT Flash calculation.
- Add points to the plot
- click on the legend item and change the characteristics of the curve (or points) such as colour, line thickness, etc.

The above plot operation can be done for any plot in the Multiflash application.

Plotting phase boundaries

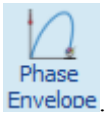
The phase envelope plotter enables you to plot phase boundaries for any phase.

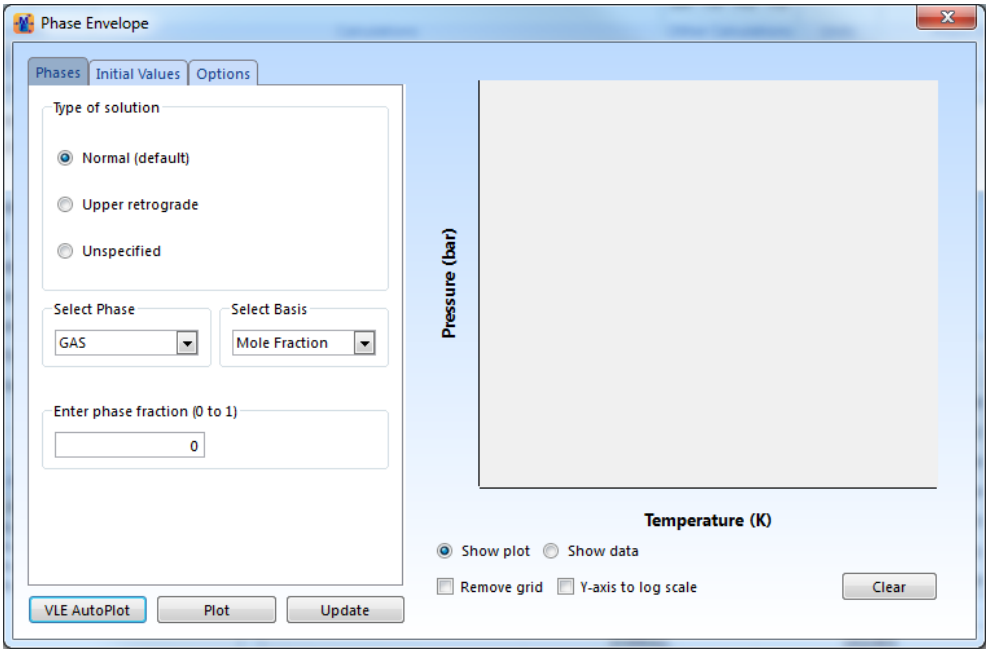
You can use the phase envelope plotter after you have specified your fluid and model.

Tip: On the **Home** ribbon, click 

to plot all available phase envelopes automatically at any stage. However, the resultant plot does not enable you to use any other features of the phase envelope plotter.

To use the phase envelope plotter:

1. On the **Home** ribbon, click 
.



2. If you want to plot the vapour-liquid envelope, click **VLE AutoPlot**.

   Note: None of the settings on the **Phase** tab or **Initial Values** tab are used by this option.

   Result: The phase envelope is plotted. You can now plot other phase boundaries and they are all shown on the same plot until you click **Clear**.

3. Choose a solution type, using the following guidelines.

Solution type	Use for
Normal	Systems with normal dew and bubble points.
Upper Retrograde	Gas condensate systems that are likely to exhibit retrograde condensation. In these systems, there are two dew points, the upper one being the retrograde dew point.
Unspecified	Finding the nearest solution to the starting point, making no distinction between normal and retrograde behaviour. One example of using this is when you calculate an asphaltene phase boundary above the bubble point.

4. From the **Select Phase** list, choose the phase whose boundary you want to plot.

   Note: The phases available depend on the model settings that you specified.

5. From the **Select Basis** list, choose the purpose of the calculation, as shown in the table.

Basis	Description
Mole Fraction	Specify the phase fraction in moles. We recommend this for phase boundary plots.
Mass Fraction	Specify the phase fraction by mass.
Volume Fraction	Specify the phase fraction by volume.
Nucleation	Use for hydrate formation calculations when you have specified the phase as hydrate, and your hydrate model includes a nucleation phase.
Enthalpy Entropy Volume Internal energy	Plot an iso curve for the specified property and value. See *Plotting property boundaries* for further details.

6. Enter the fraction of the phase that you want to fix.

   Requirement: A phase fraction must be between 0 and 1.

   Tip: To search for a phase boundary, set the phase fraction to 0, with the basis as mole fraction.

7. If required, use the **Initial Values** tab to adjust the initial conditions for the calculation.

   Note: You do not usually need to adjust these values for well-defined systems.

8. If required, use the **Options** tab to specify your axis ranges.

   Requirement: The axes must be pressure and temperature for a phase envelope.

   Note: You do not usually need to adjust these values for standard phase plots.

9. Click **Plot**.

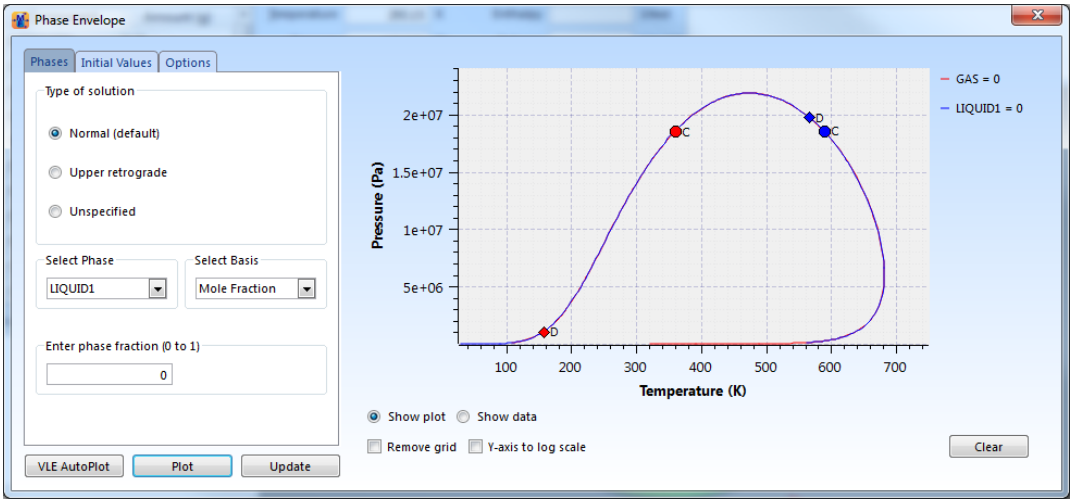
   Note: You might see the message, "Plotting has reached limit. Would you like to plot more points?" You can click **Yes** to enable the plotter to complete more of the phase envelope.

10. Optionally you can click **Show data** to view and copy the values used to generate the plot. These include all the calculated properties, like Enthalpy, Entropy, etc.

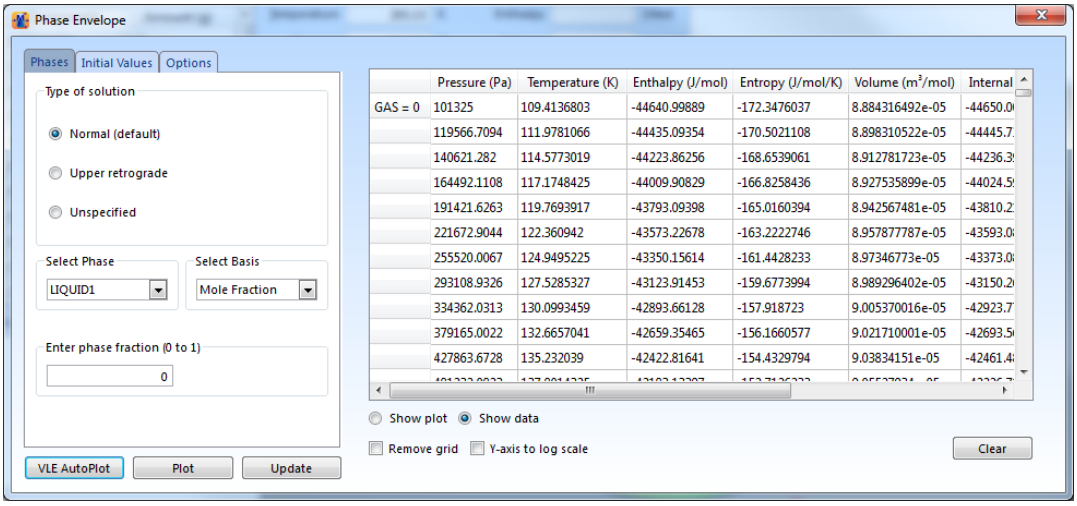
Tip: If Multiflash fails to find a phase boundary, provide a starting value using the **Initial Values** tab.

Try it yourself:

Using the example file pvt_anal2.mfl, plot the normal gas phase mole fraction 0, and then the normal liquid1 phase mole fraction 0.



click **Show data**



If you now click **VLE AutoPlot**, you can see that the automatic phase envelope plot correctly traces the phase boundaries.

Scaling the phase plot

Main ribbon > Phase Envelope

You can scale the axes of your phase plot to enhance the view of multiple plots, or to view a portion of the plot in greater detail.

In addition to scaling the axes, you can modify the display in the following ways:

- On the plot, hold down the left mouse button while you draw a rectangle around the area that you want to expand, and then release the mouse button.
- To fit all currently plotted items within the display area, click **fit to view** .

To scale the axes:

1. In the Phase Envelope window, click the **Options** tab.
2. Enter your required values for the minimum and maximum of each axis.

   You need only enter those values that you want as minimum or maximum values. If you omit a value, Multiflash plots to a sensible value for the displayed plots.

   Result: The next time you click **Plot**, the plot is drawn with your chosen axis values.

   Tip: If you are rescaling an existing plot, click **Update** to redraw the plot with your chosen axis ranges.

Using initial values for the phase plotter

Main ribbon > Phase Envelope

The **Initial Values** tab on the phase plotter enables you to set a pressure or temperature value for the start of the phase boundary or property plot. These values are not used when you click **VLE Autoplot**.

For many situations, you do not need to modify the default setting of pressure increasing from 1 atm. However, there is not always a solution for a particular boundary at this pressure. For example, when you plot the phase boundary for a solid, a good strategy is to start from a high pressure and decrease it.

To specify initial values:

1. In the Phase Envelope window, click the **Initial Values** tab.
2. In the **Initial values** panel, enter your starting value for pressure or temperature.
3. In the **Start off from** panel, specify whether you are starting with a pressure or temperature.
4. In the **Initial value to** panel, specify whether the starting value should increase or decrease as Multiflash searches for the phase boundary.

Result: When you next click **Plot**, Multiflash uses your initial value as a start point for calculations.

Tip: If Multiflash still fails to find a phase boundary, provide starting values for both the temperature and pressure. To do so, enter both values, and then check **Use starting value**. When you next click **Plot**, Multiflash uses your values as the starting point for calculations, and this might make it possible to trace the phase boundary.

Plotting property boundaries

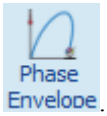
The phase envelope plotter enables you to plot an iso curve for the following properties:

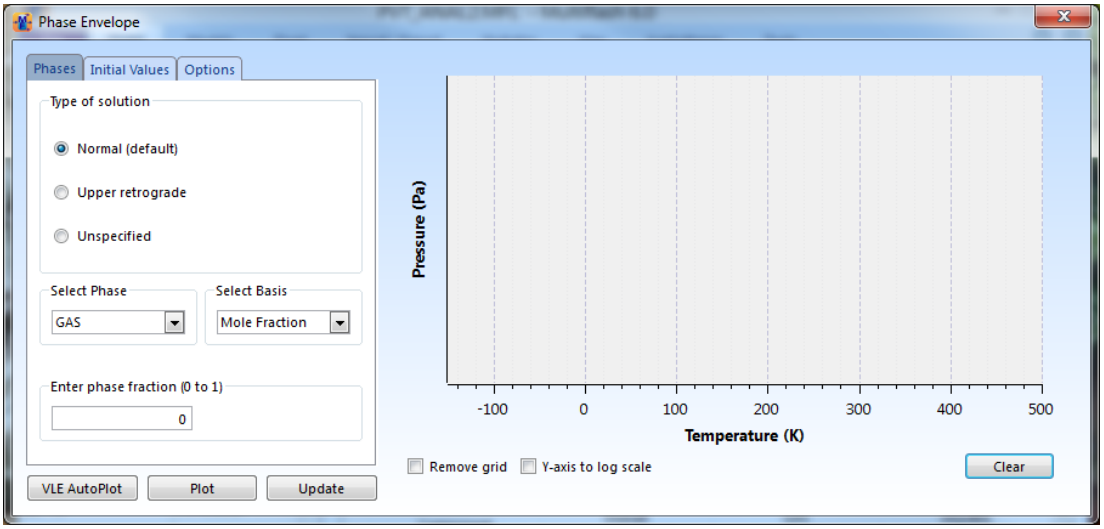
- Enthalpy
- Entropy
- Volume
- Internal energy

The property that you plot is the total for all phases present in the system.

You can use the phase envelope plotter to trace a property boundary after you have specified your fluid and model.

To generate a property boundary:

1. On the **Home** ribbon, click 
.



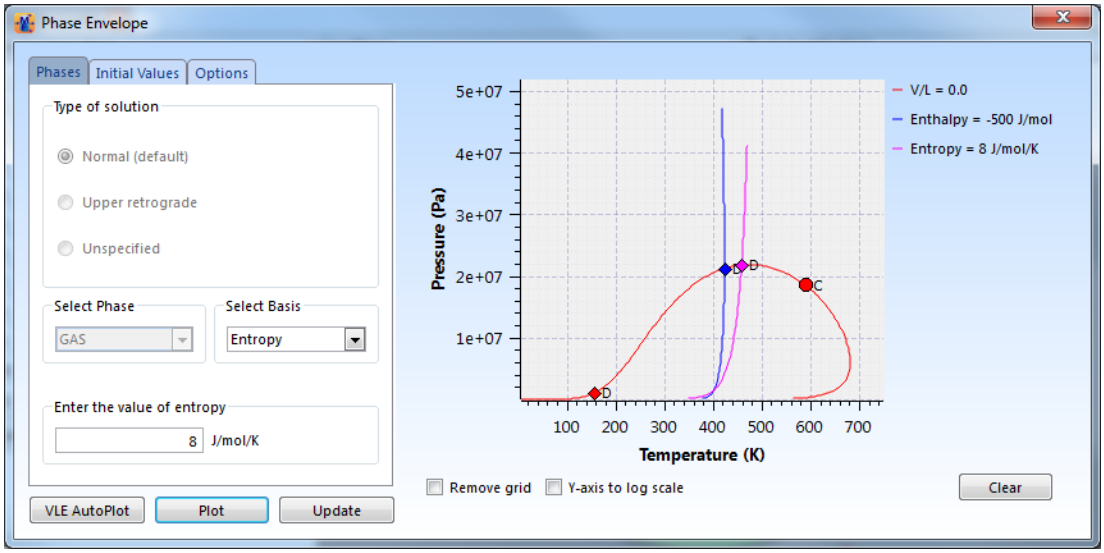
2. From the **Select Basis** list, choose the purpose of the calculation, as shown in the table.

Basis	Description
Enthalpy	Plot the isenthalpic curve for your specified value. Selecting this option disables the solution type and phase options because the property line plotted is the total for all the phases present.
Entropy	Plot the isentropic curve for your specified value. Selecting this option disables the solution type and phase options because the property line plotted is the total for all the phases present.
Volume	Plot the isochoric curve for your specified value. Selecting this option disables the solution type and phase options because the property line plotted is the total for all the phases present.
Internal Energy	Plot the constant internal energy curve for your specified value. Selecting this option disables the solution type and phase options because the property line plotted is the total for all the phases present.
Mole Fraction Mass Fraction Volume Fraction Nucleation	Plot a phase boundary. See *Plotting phase boundaries* for further details.

3. Enter the value for the property whose iso curve you want to plot.
4. Click **Plot**.

Try it yourself:

Using the example file pvt_anal2.mfl, click **VLE AutoPlot**, then plot the isenthalpic curve at -500 J mol^{-1}, and the isentropic curve at 8 J mol^{-1} K^{-1}.



Generating other plot types

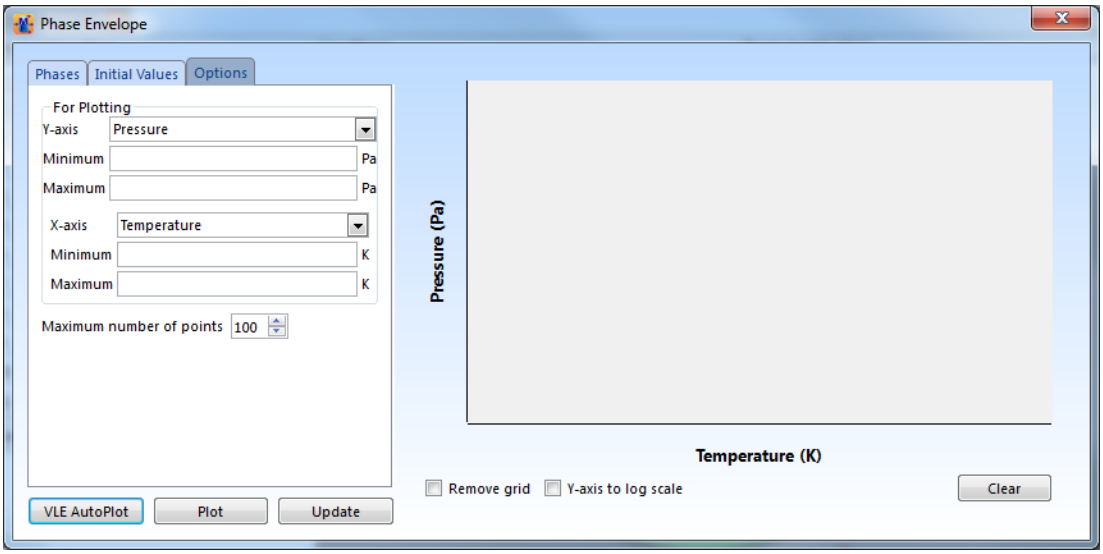
The phase envelope plotter enables you to plot any two properties or phases against each other. The values of your chosen variables are those found at the appropriate points along the phase boundary or iso property that you specify on the Phases tab. Alternatively, you can use the **VLE AutoPlot** button to plot values along vapour-liquid equilibrium phase envelope.

You can use the phase envelope plotter after you have specified your fluid and model.

To generate a user-defined plot:

1. On the **Home** ribbon, click 

, and then click the **Options** tab.



2. Choose the variables that you want to plot on the x-axis and y-axis.

   Note: When you change the property of an axis, any existing plots are cleared.

3. On the **Phases** and **Initial Values** tabs, specify the phase or property boundary along which you want to plot your chosen variables.

   See *Plotting phase boundaries* and *Plotting property boundaries* for full details of this step.

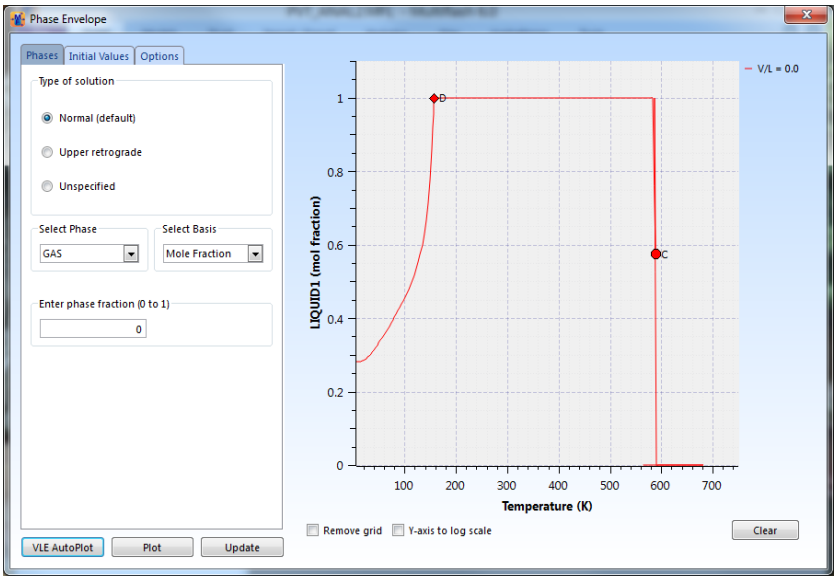
4. Click **Plot**.

Example:

Use the example file pvt_anal2.mfl to plot mole fraction of the liquid1 phase vs temperature along the vapour-liquid equilibrium phase envelope.

1. On the **File** menu, click **Open**, and open the file pvt_anal2.mfl.
2. On the **Home** ribbon, click 

, and then click the **Options** tab
3. From the **Y-axis** list, choose LIQUID1.
4. Click **VLE AutoPlot**.



You can see that along the VLE boundary, the mole fraction of the liquid changes abruptly from 1 to 0, as expected, when the critical temperature is passed.

Plot tools

Exporting phase plot data

You can export the plot and data points from the phase envelope window, by clicking on the tools available when the cursor is inside the plot axes.

Tool	Description
	Redraws the plot so that all current plots fit on the display.

Tool	Description
	Copies the plot to the clipboard so that you can import it into other applications.
	Prints the plot to your chosen printer.
	Exports the plot, and the data used to generate each displayed plot, to Microsoft Excel. This feature is supported for Microsoft Excel version 97 and later. **Tip:** You can also call all Multiflash functions directly from an Excel spreadsheet. Refer to the *Multiflash Excel Manual*.

Modify Plot

The plots can be modified in a number of ways. You can add used defined data by using the Add User Data tool.

 Add user data to plot. Useful to make quick comparisons of calculated data and experimental data.

Working with PVT lab tests

The PVT lab tests enable you to do the following:

- Validate the experimental data that you enter.
- Simulate the experiments with your chosen model and fluid characterization, and compare with the experimental data.
- Tune your chosen model by modifying model parameters to better fit experimental data, when the properties calculated for your fluid do not correspond to known or measured values for that property. You can use the PVT lab tests when the mixture includes petroleum fractions.

  Note: Multiflash provides other model tuning techniques. The asphaltene precipitation point is matched by adjusting the model parameters rather than the fluid properties, and this is described in *Tuning the asphaltene model*. The wax appearance temperature is matched by adjusting n-paraffin component properties, and is described in *Tuning the wax model*.

The experiments that you can simulate with the PVT lab tests, and their associated experimental properties, are shown in the table.

PVT lab test	Experimental properties
Constant-mass expansion (CME)	Pressure Liquid density Gas density Relative volume Liquid volume fraction Y-Factor Compressibility factor Compressibility Saturation pressure Saturation temperature

PVT lab test	Experimental properties
Differential liberation (DLE)	Pressure Liquid density Compressibility factor Solution gas-oil ratio Gas volume formation factor Oil volume formation factor Gas specific gravity Saturation pressure Saturation temperature Gas compositions
Constant volume depletion (CVD)	Pressure Liquid density Gas density Liquid volume fraction Compressibility factor Two-phase Z-factor Moles of depleted gas % cumulative moles of depleted gas Gas viscosity Saturation pressure Saturation temperature Gas compositions
Separator test	Temperature Pressure Liquid density Gas-oil ratio Oil volume formation factor Gas specific gravity Gas compositions
Viscosity	Gas or liquid viscosity
Saturation	Bubble point or dew point data GOR data

Separate from the PVT Experiments, the Multistage flash tool is an enhanced version of the Separator test that can do:

- GOR matching by combining 2 streams
- Water cut matching
- Pressure conditions optimization to maximise stock tank yelds

Entering PVT lab test data

You enter the data for each experiment type in the same way.

Requirement: Your fluid must contain one or more petroleum fractions.

You can enter more than one set of experimental data, for different experiment types or for the same experiment type.

To enter experimental data:

1. On the **Fluid** ribbon, click **PVT Lab Tests**.
2. Click , and then, from the **Type** list, select the required test, using the table as a guide.

Experiment type	Use for
CME	Constant-mass expansion data.
CVD	Constant-volume depletion data.
DLE	Differential liberation experiment data.
Separator test	Separator test data, with or without bubble point data.
Viscosity	Gas or liquid viscosity data.
Saturation	Bubble point or dew point data.

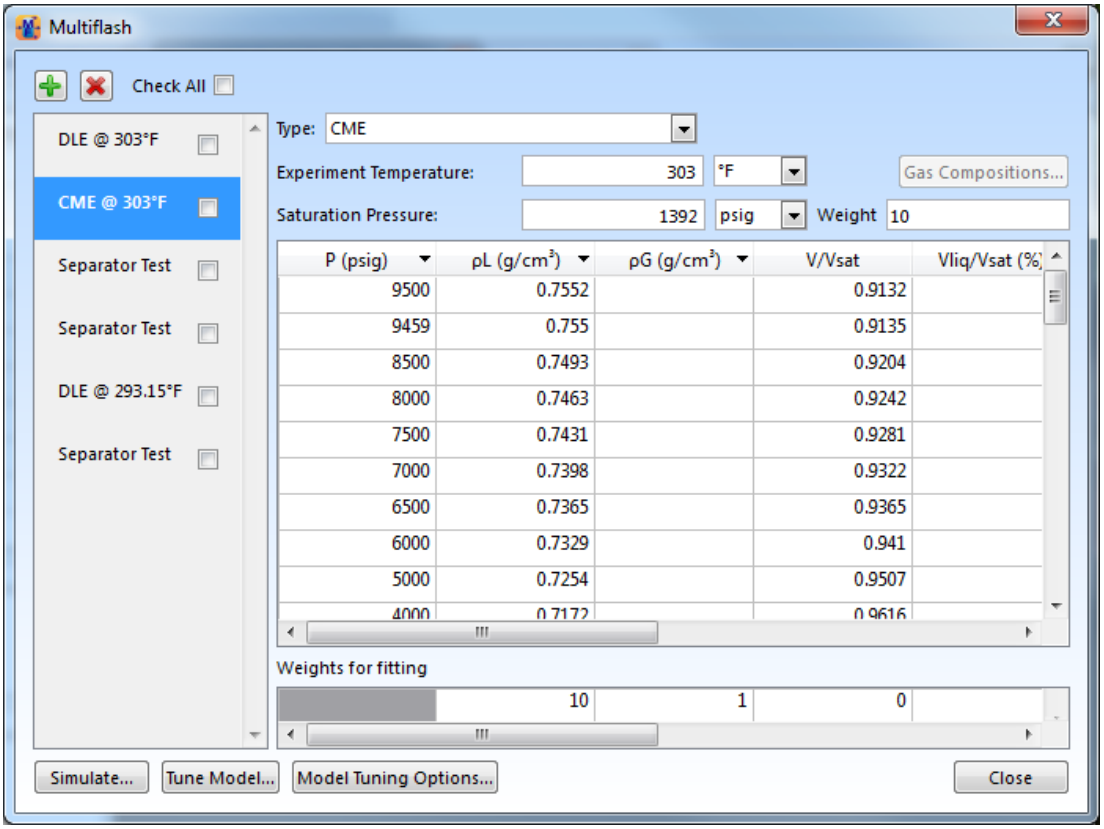
3. Enter the data that you have for your chosen experiment, by clicking in each cell, and then entering the value.

   Tips:

   - Remember to set the correct units for your data, by clicking the column title and then choosing the units type.
   - You can cut and paste data from a spreadsheet. You must ensure that you leave space in the spreadsheet for missing data. For example, in the screenshot below, your spreadsheet would have a blank column between the last two data columns.

   Note: For the separator test, the first line must contain the saturation point data.

   The screenshot shows CME data.



4. If you have experimental gas compositions for your experiment, click **Gas Compositions**, and enter the values for each component at each temperature for which you have data.
5. To add further experimental data for other experiments, repeat steps 2 to 5.
6. Click **Close**.
7. On the **File** menu, click **Save**.

You can now proceed to validate your data.

Tip: You can remove an experiment by highlighting the experiment name, and then clicking .

Validating data using the PVT lab tests

The PVT lab tests enable you to validate experimental data for the following experiment types:

- CME
- CVD
- DLE
- Separator test

You should use the PVT lab tests as part of a coordinated treatment of your data to include the following steps:

1. Validate the experimental data for your test using the Sample QC function.
2. Simulate your experiment to see how your current model and fluid characterization predict the experimental data.
3. Tune your model to optimize the prediction of experimental data.

Requirements:

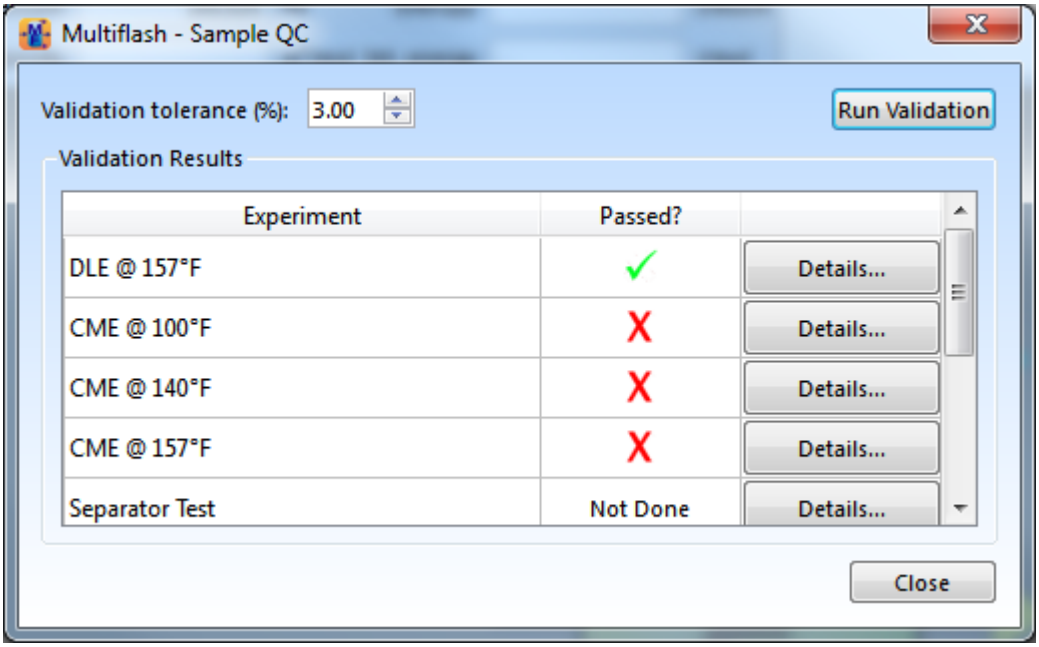
- Your fluid must contain one or more petroleum fractions.
- You must have entered one or more sets of experimental data into PVT lab tests.

To validate experimental data:

1. On the **Fluid** ribbon, click 

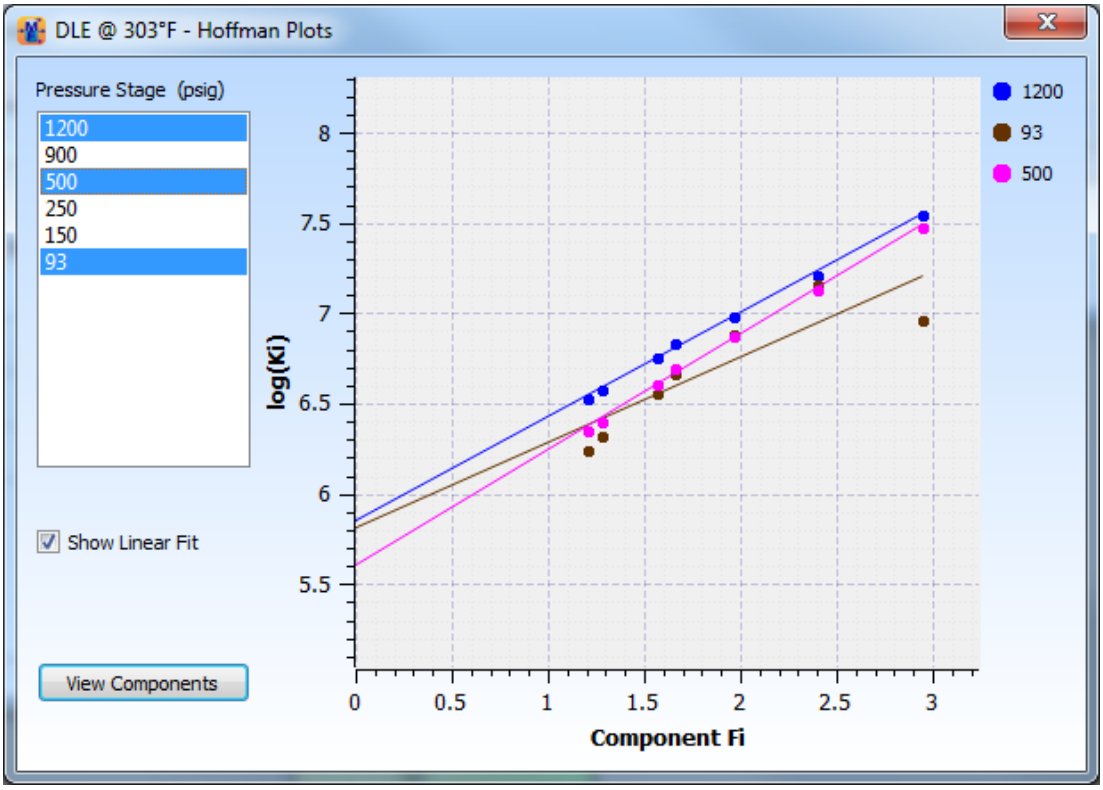
.
2. Select a validation tolerance. The default is 3.0 %.
3. Click **run validation**.
4. **Result:** The entered data for each experiment is evaluated, and the summary appears, with the following key for results.

Pass notifier	Description
✓	The data are consistent with the experiment type. If sufficient data exists for the separator test, DLE or CVD, Hoffman Plots are generated and are available.
X	The data are inconsistent with the experiment type. Click **Details** to view inconsistent data, highlighted in red.
Not done	Usually, this means that there was insufficient data to perform a validation. Additional information might be available if you click **Details**.



5. If a Hoffman plot is available for your experiment type, and you want to view them, on the row for that experiment, click **Hoffman Plots**, and then view the data, using the features shown in the table.

Plot feature	Description
Pressure stage	Click a pressure value to plot the data for that pressure. Click again to remove the plot.
Show Linear Fit	Check **Show Linear Fit** to fit a straight line to the data.
View Components	Click **View Components** to show the component names associated with each value of F_i.



You can now use the PVT lab test dialog box to perform simulations and tune your model, using the validated data.

Simulating an experiment using the PVT lab tests

The PVT lab tests enable you to simulate an experiment, and compare the simulation with your entered experimental data. You can also simulate any of the tests without experimental data to compare.

You should use the PVT lab tests as part of a coordinated treatment of your data to include the following steps:

1. Validate the experimental data for your test using the Sample QC function.
2. Simulate your experiment to see how your current model and fluid characterization predict the experimental data.
3. Tune your model to optimize the prediction of experimental data.

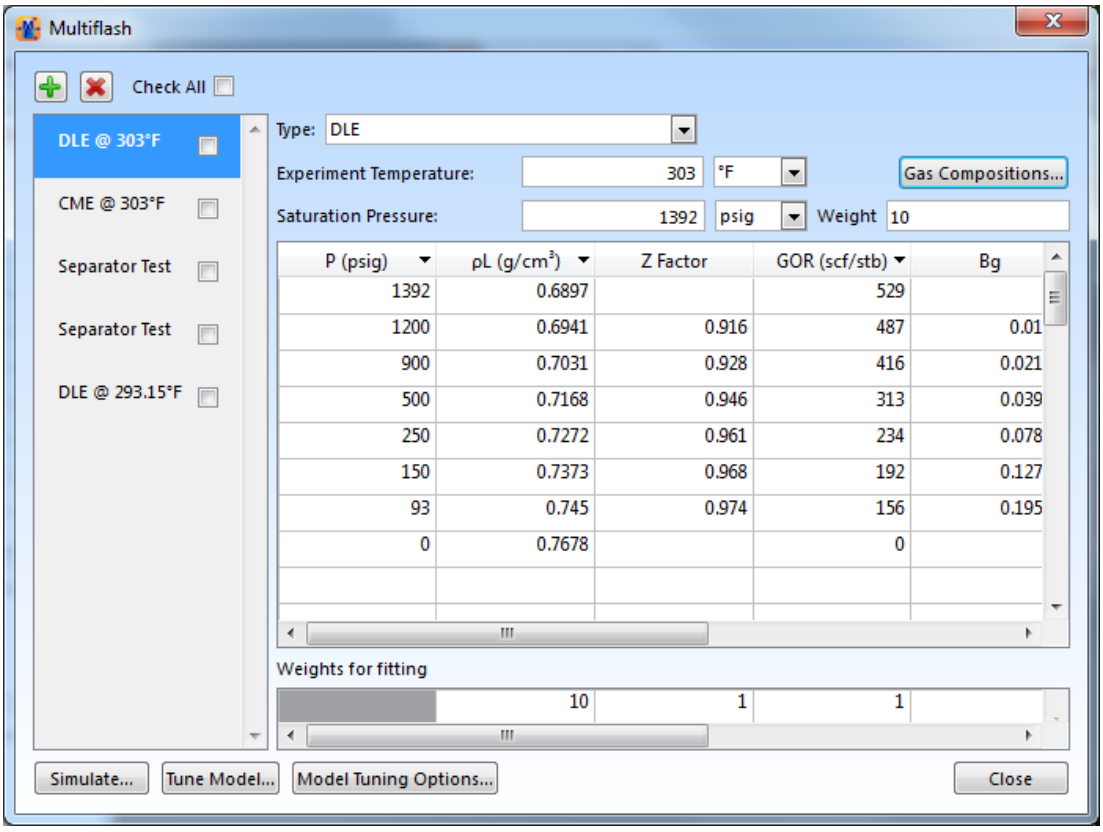
Requirements:

- Your fluid must contain one or more petroleum fractions.
- You must have entered one or more sets of experimental data into PVT lab tests.

To simulate an experiment that has experimental data:

1. On the **Fluid** ribbon, click **PVT Lab Tests**.
2. In the list on the left hand side, highlight the experiment that you want to simulate.

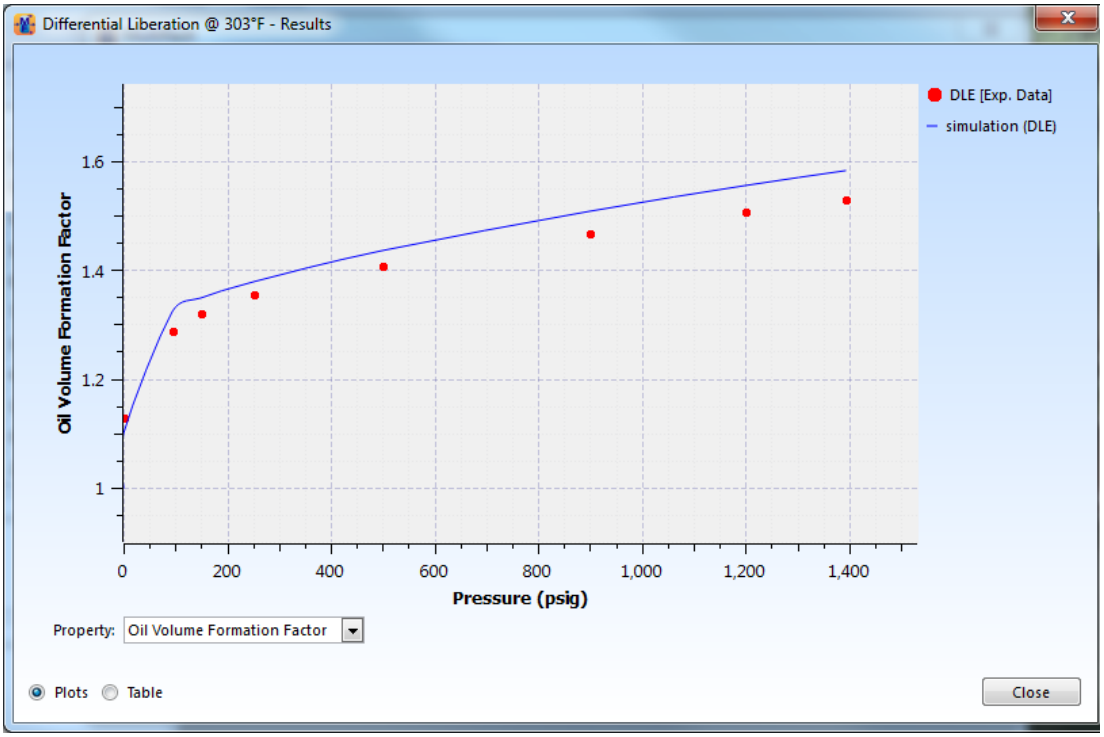
   Tip: The check boxes in the list apply only to the tuning function. In the screenshot, the DLE @ 303°F experiment is the one undergoing simulation.



3. Click **Simulate**.

   Result: The displayed plots show the experimental data, and the result of the simulation, shown as a curve. You can view all the data using the features shown in the table.

Plot feature	Description
Vertical axis	Choose which parameter to plot on the graph. The available parameters vary, depending on which experiment you simulate. The horizontal axis is always pressure.
Plots	Select **Plots** to view the plots.
Table	Select **Table** to view the experimental and simulated data points in a table. You can also view the calculated gas and liquid compositions for the simulation, at each pressure. **Tip:** You can cut and paste the data to a spreadsheet.



4. If you feel that the simulation could be improved, you can now tune your model.

To simulate an experiment without experimental data:

1. On the **Fluid** ribbon, click **PVT Lab Tests**.
2. Click , and then, from the **Type** list, select the required test, using the table as a guide.

Experiment type	Use for
CME	Constant-mass expansion data.
CVD	Constant-volume depletion data.
DLE	Differential liberation experiment data.
Viscosity	Gas or liquid viscosity data.

3. Enter some representative data appropriate for the experiment.

Example: For a CME experiment, you can enter a value for the experiment temperature, and a few values for the pressure range over which to simulate the experiment.

4. Click **Simulate**.

   Result: The displayed plots show the result of the simulation, shown as a curve. You can view all the data in the same way as for a simulation with experimental data.

Tuning a model using the PVT lab tests

The PVT lab tests enable you to refine your chosen model and fluid characterization by modifying model parameters and pseudocomponent properties to better fit experimental data, when the properties calculated for your fluid do not correspond to known or measured values for that property.

You should use the PVT lab tests as part of a coordinated treatment of your data to include the following steps:

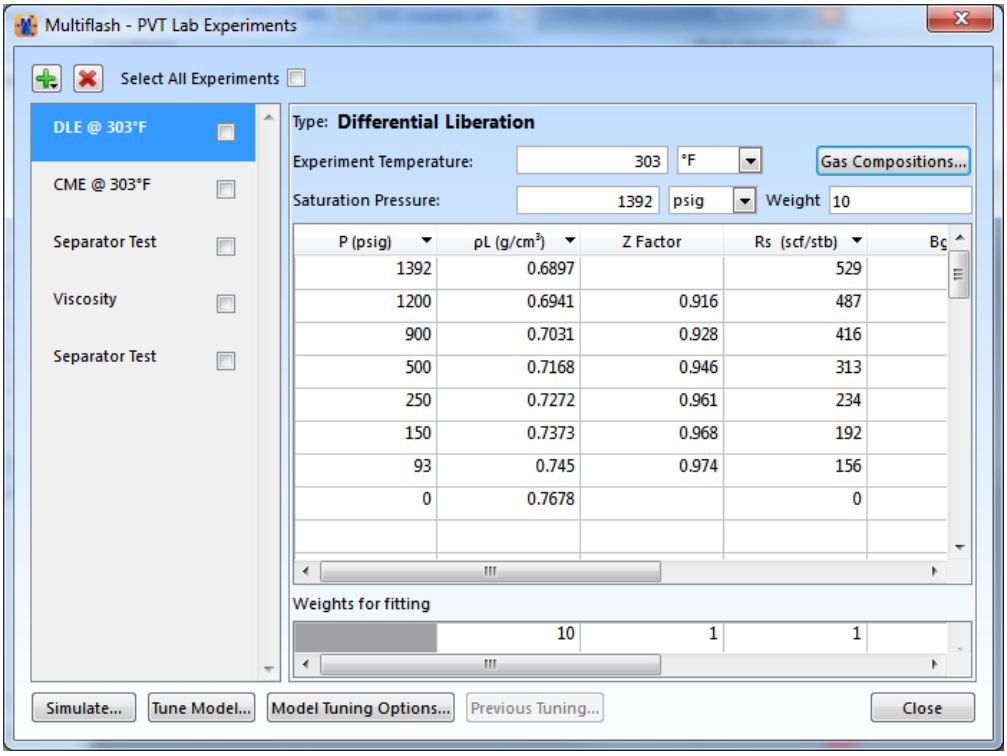
1. Validate the experimental data for your test using the Sample QC function.
2. Simulate your experiment to see how your current model and fluid characterization predict the experimental data.
3. Tune your model to optimize the prediction of experimental data.

Requirements:

- Your fluid must contain one or more petroleum fractions.
- You must have entered one or more sets of experimental data into PVT lab tests.

To tune your model:

1. On the **Fluid** ribbon, click **PVT Lab Tests**.



2. Check the box next to each experiment that you want to include in the tuning process.
3. To prioritise your preference for fitting the data, in the **Weights for fitting** area, click in each cell whose weighting you want to adjust, and enter your required value.
4. To modify the default tuning options, click **Model Tuning Options**, and do the following:
   - For each property that you want to vary in the tuning calculation, check the box next to the property name.
   - In **% Change**, enter the range within which the property value can vary. The range is a percentage amount above or below the current value of the property.

   The modifiable properties are described in the following table. To view the properties that are modifiable when you tune a model using a specific experiment type, see *Tuning models*.

Property	Description
T_c	Critical temperature of the petroleum fractions in the mixture.
P_c	Critical pressure of the petroleum fractions in the mixture.
Acentric factor	Acentric factor (ω) of the petroleum fractions in the mixture.
BIPs	Binary interaction parameters for the petroleum fractions with methane, ethane and propane.
Volume shift	The Peneloux parameters of the petroleum fractions, used to correct liquid density predictions. **Tip:** You can cut and paste the data to a spreadsheet.

Property	Description
Viscosity	The following petroleum fraction properties are modified in viscosity fitting: ■ V_c (critical volume) for the LBC viscosity model ■ T_c (critical temperature) for the Supertrapp viscosity model ■ MW (molecular weight) for the Pedersen model ■ T_b (boiling point) for the Twu viscosity model
LBC A parameters	The model parameters in the LBC viscosity model.

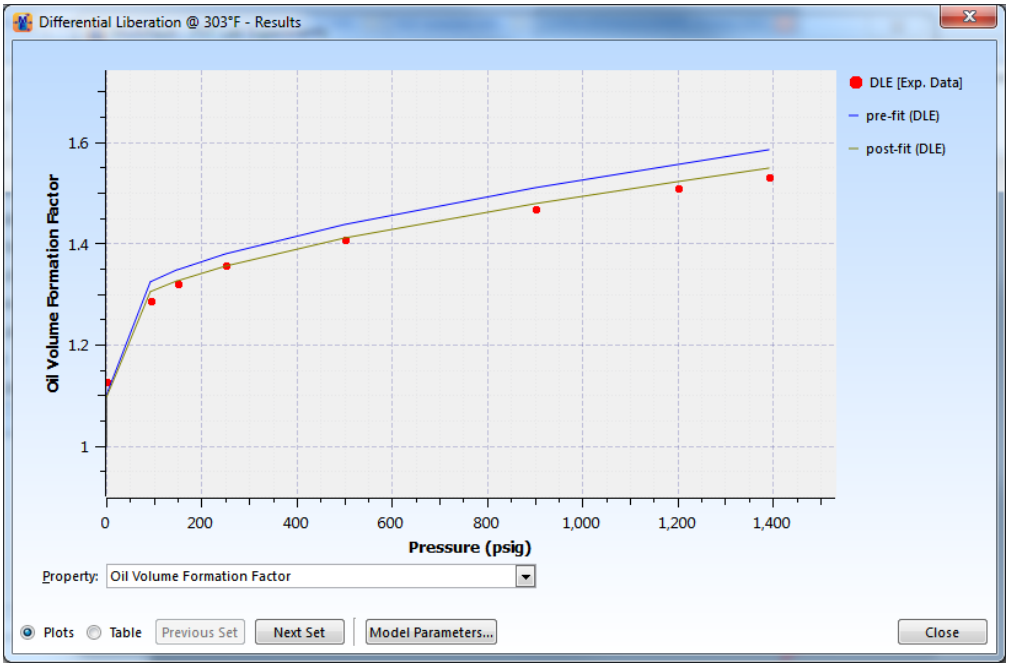
5. Click **Tune Model**.

   Result: The model parameters are adjusted, within the ranges specified, to optimise the fit to the experimental data entered.

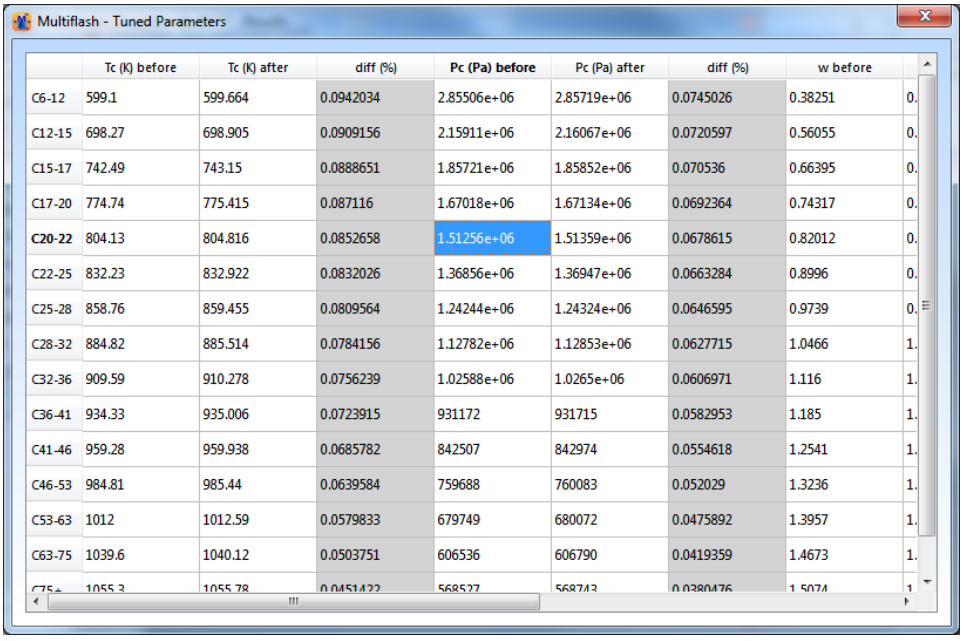
   Tip: If the tuning fails, try modifying the variables adjusted and their allowed ranges, using the **Model Tuning Options** button, then tune the model again.

   Result: The displayed plots show the experimental data, and the pre-fit and post-fit simulations. The example here demonstrates that the model tuning has improved the fit to the experimental values for the oil volume formation factor. You can view all the data using the features shown in the table.

Plot feature	Description
Vertical axis	Choose which parameter to plot on the graph. The available parameters vary, depending on which experiment you simulate. The horizontal axis is always pressure.
Plots	Select **Plots** to view the plots.
Table	Select **Table** to view the experimental and simulated data points in a table. You can also view the calculated gas and liquid compositions for the simulation, at each pressure. **Tip:** You can cut and paste the data to a spreadsheet.
Previous Set Next Set	If you tuned the model with more than one experiment data set, you can view the results of each set in turn by clicking **Next Set** or **Previous Set**. The current set is identified by the graph key at the upper right corner of the plot.
Model Parameters	View which pure component parameters have changed and by much .



6. If you want to view the modified pseudocomponent properties, click **Model Parameters...** and a dialog will appear with a report of changed properties.

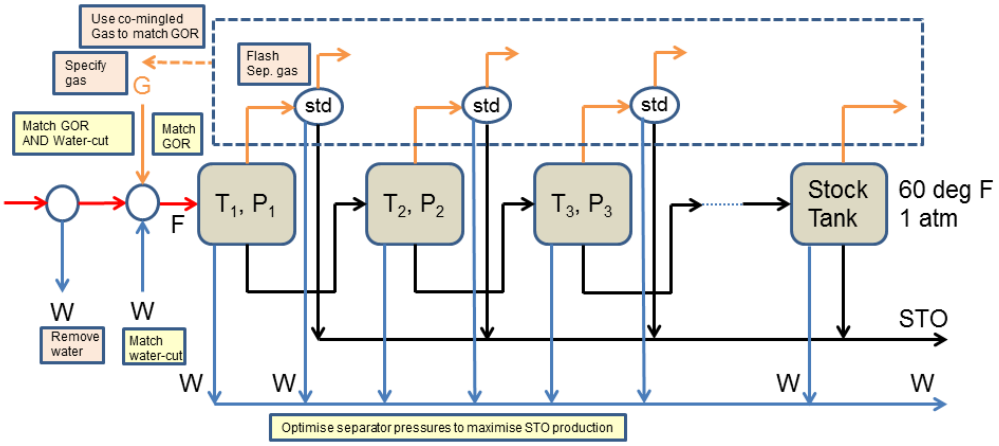


	Tc (K) before	Tc (K) after	diff (%)	Pc (Pa) before	Pc (Pa) after	diff (%)	w before	
C6-12	599.1	599.664	0.0942034	2.85506e+06	2.85719e+06	0.0745026	0.38251	0.
C12-15	698.27	698.905	0.0909156	2.15911e+06	2.16067e+06	0.0720597	0.56055	0.
C15-17	742.49	743.15	0.0888651	1.85721e+06	1.85852e+06	0.070536	0.66395	0.
C17-20	774.74	775.415	0.087116	1.67018e+06	1.67134e+06	0.0692364	0.74317	0.
C20-22	804.13	804.816	0.0852658	1.51256e+06	1.51359e+06	0.0678615	0.82012	0.
C22-25	832.23	832.922	0.0832026	1.36856e+06	1.36947e+06	0.0663284	0.8996	0.
C25-28	858.76	859.455	0.0809564	1.24244e+06	1.24324e+06	0.0646595	0.9739	0.
C28-32	884.82	885.514	0.0784156	1.12782e+06	1.12853e+06	0.0627715	1.0466	1.
C32-36	909.59	910.278	0.0756239	1.02588e+06	1.0265e+06	0.0606971	1.116	1.
C36-41	934.33	935.006	0.0723915	931172	931715	0.0582953	1.185	1.
C41-46	959.28	959.938	0.0685782	842507	842974	0.0554618	1.2541	1.
C46-53	984.81	985.44	0.0639584	759688	760083	0.052029	1.3236	1.
C53-63	1012	1012.59	0.0579833	679749	680072	0.0475892	1.3957	1.
C63-75	1039.6	1040.12	0.0503751	606536	606790	0.0419359	1.4673	1.
C75+	1055.3	1055.78	0.0451422	568527	568743	0.0380476	1.5074	1

7. If you are satisfied with the revised model, and want to retain the changes for further calculations, on the main Multiflash window, on the **File** menu, click **Save**.

   Result: When you subsequently load the experiment file, the tuned model is used for all your calculations. The parameters stored in the component databases are not modified; all modifications are stored in the experiment file.

Multistage Separator Flash

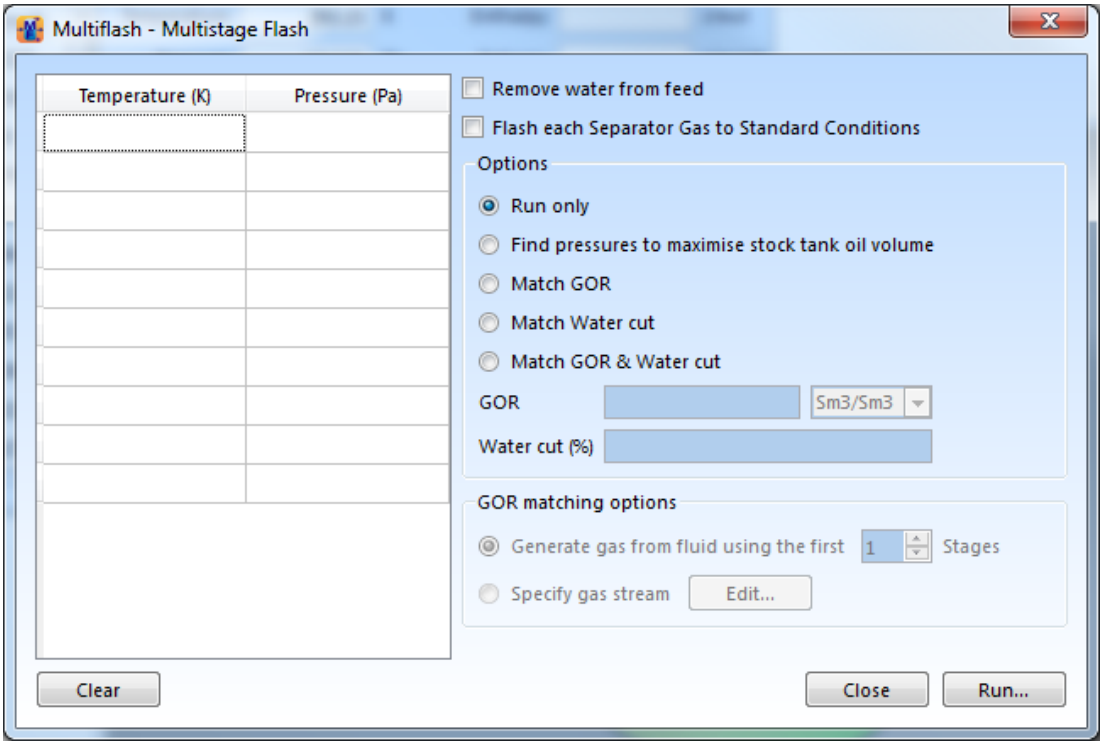


Given a feed stream, the multistage separation module can be used to perform the following calculations for a specified set of separators (up to a maximum of 10, including the stock tank) where the feed to the downstream separator is the liquid product from the upstream separator as shown in the above figure:

- Simulate the separators with the supplied conditions of temperature and pressure and report results
- At the supplied temperatures for the separators, find the corresponding pressures which maximise the stock tank oil volume and report results. **Note**: an initial set of temperatures/pressures is needed.
- Match a given gas oil ratio (GOR) at the supplied temperatures and pressures of the separators by combining the feed stream with a supplied/calculated gas stream and report results
- Match a given water-cut at the supplied temperatures and pressures of the separators by adding water to the feed stream and report results
- Match GOR and water-cut simultaneously at the supplied temperatures and pressures of the separators by combining the feed stream with a supplied/calculated gas stream and water and report results

The calculations assume that the last separator is at standard conditions. If this is not the case, internally, the calculations will add a separator stage at standard conditions. The standard conditions of temperature and pressure are 60 F and 1 atmosphere respectively.

The tool can be accessed from the **Tools** tab.



Options

The following options are provided to extend the calculations:

- If you have a stream which contains water and you wish to carry out the calculations without water, simply check **Remove water from feed**.
- By default, the gas from each separator is assumed to be single gas phase at the standard conditions of 60 F and 1 atm. If you wish to flash each gas stream to standard conditions and account for any precipitated oil and/or water, check **Flash each separator gas to standard conditions**
- For GOR matching, two further options are provided for the gas stream which is to be combined with the feed stream:
    - If you wish to specify this stream, check **Specify gas stream**
    - If you wish the module to calculate this gas stream, you have the option of using the co-mingled gas from the first specified stages of separators. Check **Generate gas from fluid using the first … stages** and supply the number of stages required.

Working with hydrates

Note: You can only perform hydrate calculations if your Multiflash licence includes the hydrates option.

Natural gas hydrates are solid, ice-like compounds of water and the light components of natural gas. Some heavier hydrocarbons found in gas condensates and oils are also known to form hydrates if smaller molecules, such as methane or nitrogen, are present to stabilise the structure. Hydrates can form at temperatures above the ice point and are therefore a serious concern in oil and gas processing operations. The phase behaviour of systems involving hydrates can be very complex; up to seven phases must be considered, even without considering the possibility of scale formation. The behaviour is particularly complex if there is significant mutual solubility between phases, for example, when inhibitors or CO_2 are present.

Multiflash offers a powerful set of thermodynamic models and calculation techniques for modelling hydrates. In principle, hydrate calculations with Multiflash are no different from flash calculations for fluid phases alone. Multiflash treats fluid and solid phases on the same basis and the full range of flashes can be carried out for fluids with hydrates. The models used in Multiflash hydrate calculations are described briefly in the reference section of this help file. For a more detailed description, refer to the *Models and Physical Properties User Guide*.

In addition to applying all the available flash calculations to a hydrate system, Multiflash enables you to perform the following types of hydrate calculation:

- Prediction of hydrate formation at a specific temperature and pressure.
- Hydrate formation and dissociation temperature at a given pressure.
- Hydrate formation and dissociation pressure at a given temperature.
- Hydrate phase boundaries for formation and dissociation.
- Minimum water content for hydrate formation.
- The effect of inhibitors, including salt inhibition, on hydrate formation and dissociation.
- Dosage calculations of the amount of inhibitor required to suppress hydrate formation under specified conditions.
- Prediction of scale precipitation.

Requirement: You must include water explicitly in your fluid to perform hydrate calculations. The amount of water may influence the results of the calculations, particularly when inhibitors or water-soluble gases are present or the fluid is under-saturated with water.

Specifying the hydrate model

To ensure that reliable results are obtained for hydrate calculations, you must specify the hydrate model appropriately for the problem you are trying to solve.

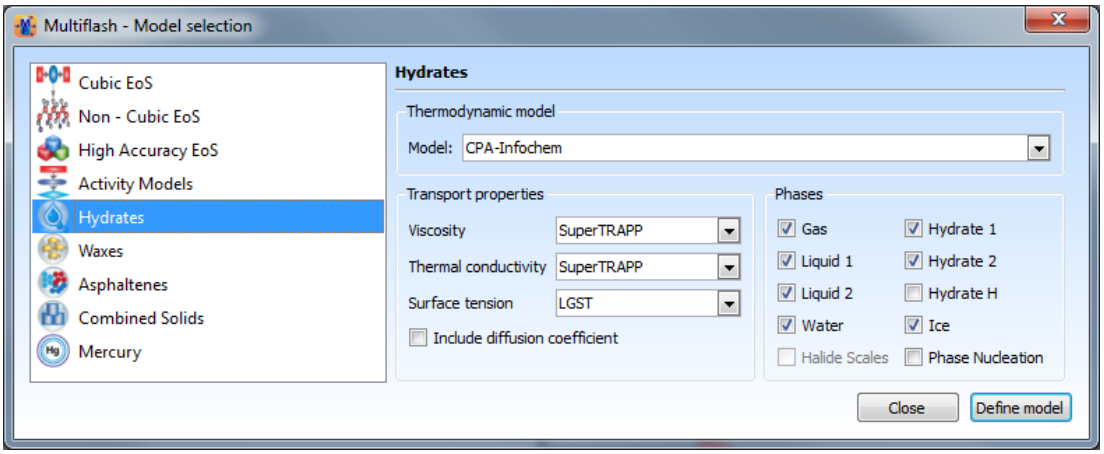
For many basic types of hydrate calculation, you do not need to specify the model manually. Instead, you can use the preconfigured model setups, available from the Hydrates ribbon:

Model setup	Use for
CPA Infochem	These calculations with no salts present: ■ Standard flash calculations ■ Hydrate dissociation ■ Hydrate structure types I and II only ■ Hydrate inhibition
CPA + Electrolytes	These calculations with salts present: ■ Standard flash calculations ■ Hydrate dissociation ■ Hydrate structure types I and II only ■ Hydrate inhibition

If you want to perform other types of calculation, or change the transport property models, you must specify the model manually.

To specify the hydrate model for other calculation types:

1. On the **Models** ribbon, select Select Model.
2. From the model list, select **Hydrates**.



The image shows the default settings for the hydrates model.

3. Choose the model and phases required for your particular calculation, as shown in the following table.

Calculation type	Model	Additional non-default phase required‡
Some components form structure H hydrates (no salts present).	CPA-Infochem	Hydrate H
Hydrate formation (no salts present)	CPA-Infochem	Phase Nucleation
Some components form structure H hydrates (salts present).	CPA-Infochem + electrolyte	Hydrate H
Hydrate formation (salts present)	CPA-Infochem + electrolyte	Phase Nucleation
Salt precipitation (scale formation)	CPA-Infochem + electrolyte	Halide Scales

‡Required phases are additive. For example, if you want to calculate formation of structure H hydrates, you should select the additional phases for both calculation types, Hydrate H and Phase Nucleation.

4. If required, choose an alternative model for your transport properties.
5. Click **Define Model**.
6. On the success message, click **OK**.

Calculating hydrate formation at a given pressure and temperature

Problem:

Will hydrates form at a given temperature and pressure?

Approach:

1. Define your fluid.
2. Specify the hydrate model.
3. Perform a PT flash calculation at your required temperature and pressure, and check the results for the presence of a hydrate phase.

For the following example, you can use the file hydrate.mfl, which describes a gas condensate, if you do not want to enter the model and component data manually.

Try it yourself:

1. If you are using our example file, on the **File** menu, click **Open**, open the file hydrate.mfl, and then proceed to step 7.

   Tip: By default, the example files are in the MFL Files folder of the Multiflash installation.

2. On the **Home** ribbon, click **Units**, ensure that the input and output pressure units are MPa, the input and output temperature units are K, the amount input units are mol, and the amount output units are g, and then click **OK**.
3. Click **Components**.
4. Enter the fluid components shown in the following table, and then click **OK**.

Component	Amount (mol)
Methane	85.93
Ethane	6.75
Propane	3.13
Isobutane	0.71
Butane	0.88
Pentane	0.57
Carbon dioxide	1.31
Nitrogen	0.72
Water	10

5. In the **Fluid composition** panel, enter the amounts for each component, as shown in the previous table.
6. On the **Hydrates** ribbon, click **CPA Infochem**, and then click **OK** on the message.

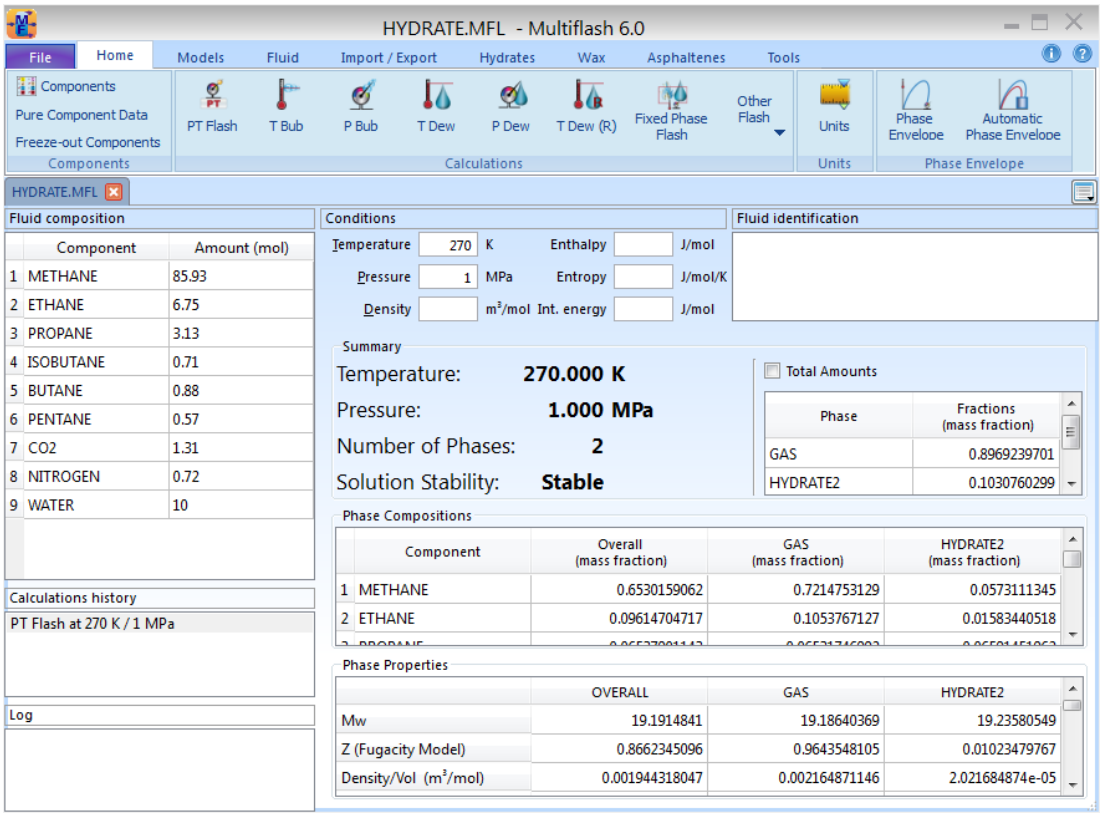
   This automatically specifies the hydrates model with default settings.

7. In the **Conditions** area, enter the temperature as 270 K and the pressure as 1 MPa.
8. On the Home ribbon, click 

.

Results:

Hydrate2 is formed at the specified conditions. The output shows the amount of hydrate and gas phases formed.



FAQ:

Q: Why don't I get any hydrate formation with my own fluid?

A: Every system has its own properties and behaviour. There are several things you can try to obtain a hydrate formation prediction.

1. Try the calculation again with a different quantity of water.
2. Check that you are using the appropriate hydrate phase in your calculation. By default, the HYDRATE H phase is not included in your model. You can find a list of typical hydrate-forming components and their hydrate phase type in *Hydrate formation and inhibition models*.
3. Generate the hydrate phase boundary so that you can see the areas of temperature and pressure where your hydrate is likely to form, and then repeat the PT flash calculation with appropriate temperature and pressure values. To do so, click Phase Envelope 

, select the appropriate hydrate phase, select the basis as mole fraction, set the phase fraction to 0, and then click Plot.

If you are still unsuccessful, it is likely that your system does not form hydrates.

Q: Why is the calculation sensitive to the amount of water, and how do I know whether the amount I have used is correct to give reliable results for my system?

A: At equilibrium conditions, water distribution among the different phases is determined by the model used, and depends on the current temperature, pressure and global fluid composition. Ideally, you should use the amount of water expected in the total global fluid composition of the system that you are modelling. Only in this case can the software estimate a rigorous phase distribution.

If you use too small an amount of water, you might find the water distributed among the fluid phases, rather than forming a hydrate phase. If you use too large an amount of water, you might find that a hydrate phase is predicted to form too readily.

What else can I do?

1. To support your PT flash calculation, you should consider plotting the phase envelope for your system to obtain an overview of its behaviour under different conditions.
2. You can add inhibitors and explore the effect on hydrate formation.

Calculating hydrate formation and dissociation

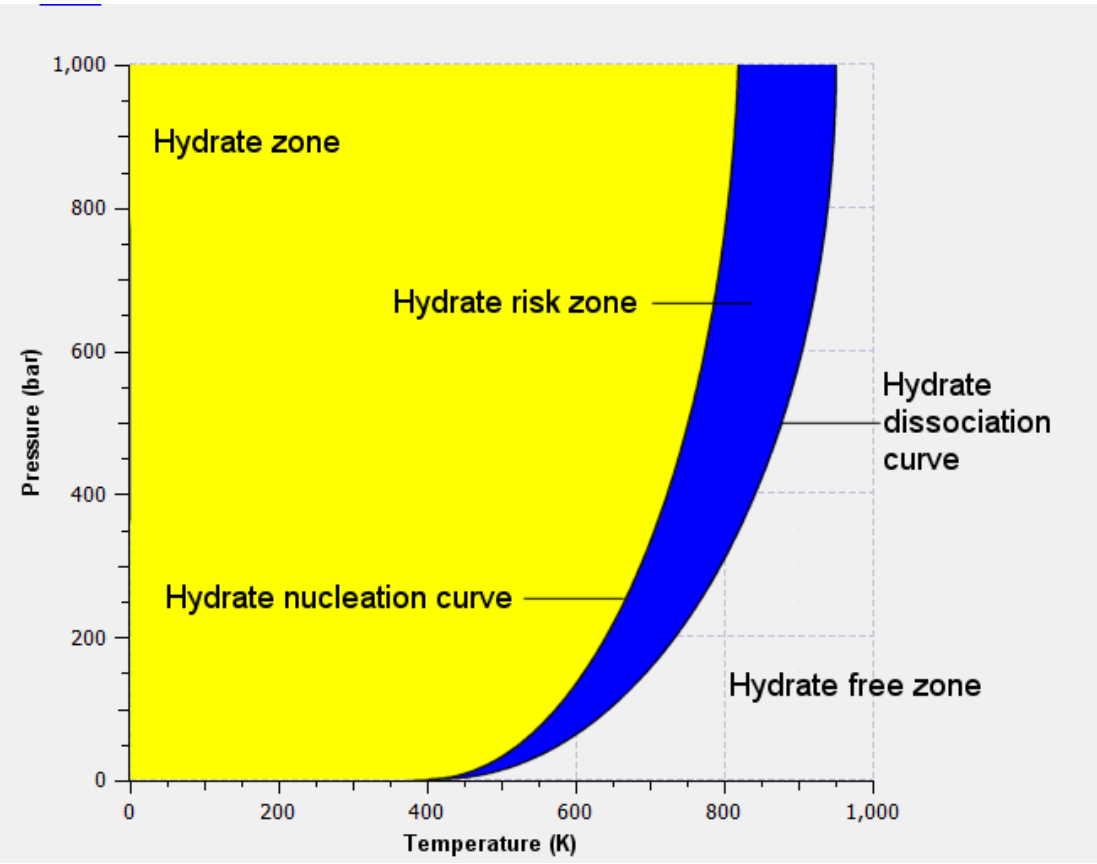
Problem:

What are the hydrate formation and dissociation temperatures at fixed pressure, and the formation and dissociation pressures at fixed temperature?

The hydrate dissociation temperature is the temperature below which hydrates can form. The hydrate dissociation calculation is an example of a fixed phase fraction flash.

The hydrate nucleation temperature is the temperature at which the nucleation of hydrates occurs and hydrates can form. It is not strictly a PT flash calculation; rather, it is based on the stochastic behaviour of how hydrate crystals form, and provides an estimate of the conditions that cause the hydrate crystals to go from a meta-stable state and start to form.

Between the dissociation and nucleation temperatures is the area of hydrate risk where hydrates may or may not form, depending on the time scale and kinetics of the formation process. The formation and dissociation temperatures vary with pressure, as shown in the image. The hydrate dissociation curve is also known as the equilibrium hydrate formation curve.



Approach:

1. Define your fluid.
2. Specify the hydrate model with nucleation, so that you can calculate hydrate formation.
3. Perform fixed phase flash calculations at your required temperature and pressure.

For the following example, you can use the file hydrate.mfl, which describes a gas condensate, if you do not want to enter the model and component data manually.

Try it yourself:

1. If you are using our example file, on the **File** menu, click **Open**, open the file hydrate.mfl, and then proceed to step 7.

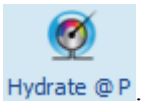
   Tip: By default, the example files are in the MFL Files folder of the Multiflash installation.
2. On the **Home** ribbon, click **Units**, ensure that the input and output pressure units are MPa, the input and output temperature units are K, the amount input units are mol, and the amount output units are g, and then click **OK**.
3. Click **Components**.
4. Enter the fluid components shown in the following table, and then click **OK**.

Component	Amount (mol)
Methane	85.93
Ethane	6.75
Propane	3.13
Isobutane	0.71
Butane	0.88
Pentane	0.57
Carbon dioxide	1.31
Nitrogen	0.72
Water	10

5. In the **Fluid composition** panel, enter the amounts for each component, as shown in the previous table.
6. On the **Hydrates** ribbon, click **CPA Infochem**, and then click **OK** on the message.

   This automatically specifies the hydrates model with default settings.
7. On the **Models** ribbon, click **Select Model**.
8. Check **Phase Nucleation**.
9. Click **Define model**, and then click **OK** on the message.

   Rationale: You must specify phase nucleation when you are calculating formation of hydrates.
10. Click the **Hydrates** ribbon.
11. In the **Conditions** area, enter the temperature as 270 K and the pressure as 1 MPa.

12. To calculate the dissociation temperature at a pressure of 1 MPa, click 

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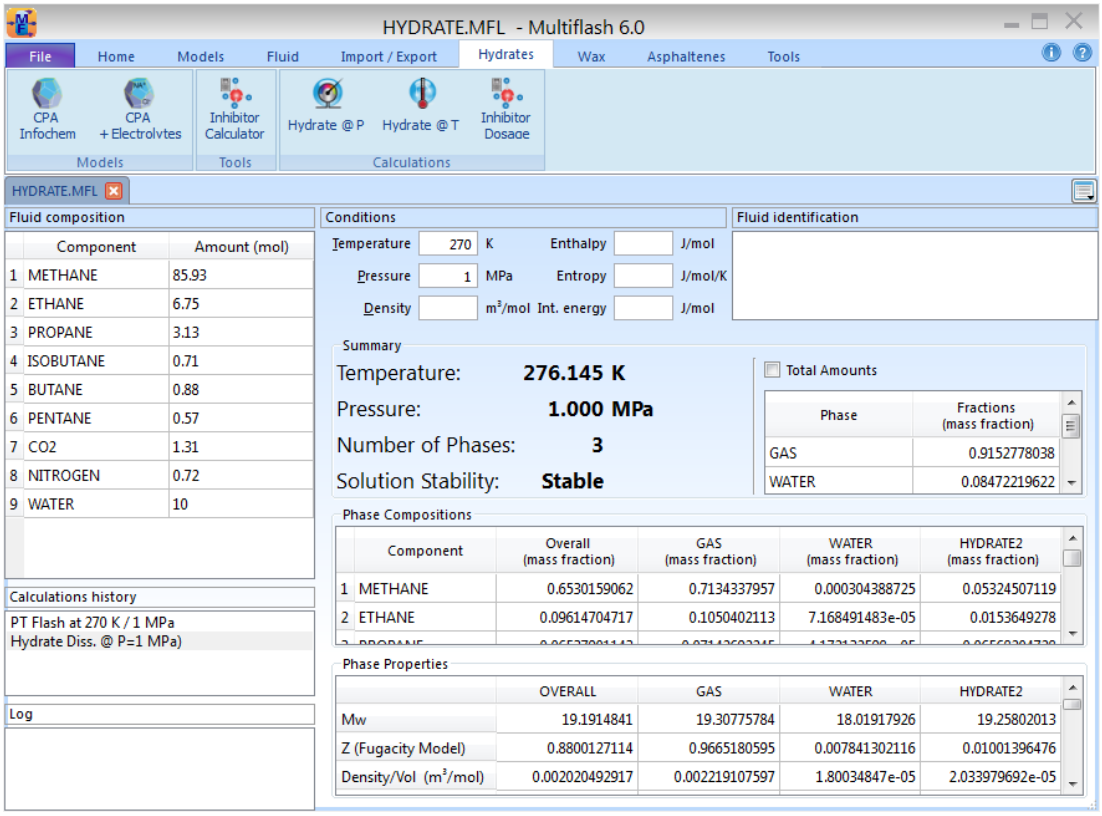
Note: This shortcut performs a fixed phase flash at the specified pressure, and searches for the most stable hydrate phase.

Result: HYDRATE2 is the most stable hydrate phase at the specified pressure, and the dissociation temperature at 1 MPa is 276.15 K.

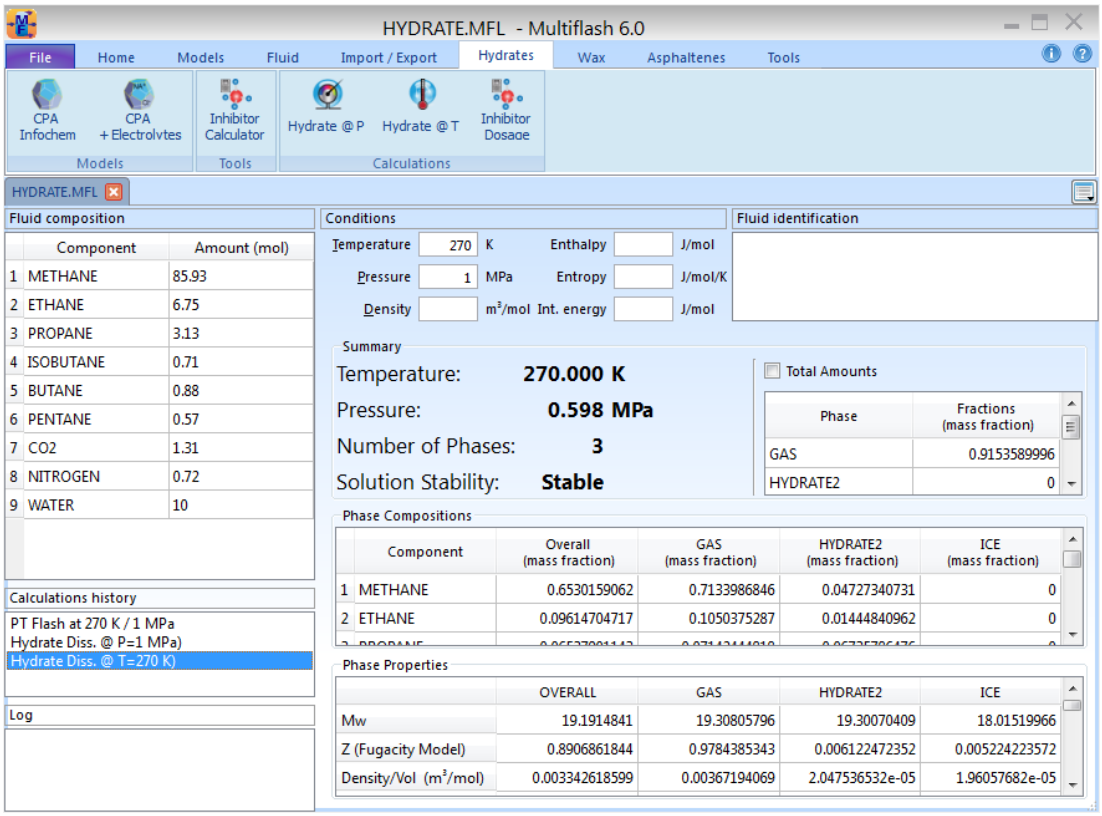


13. To calculate the dissociation pressure at a temperature of 270 K, click 

.

Note: This shortcut performs a fixed phase flash at the specified temperature, and searches for the most stable hydrate phase.

Result: HYDRATE2 is the most stable hydrate phase at the specified temperature, and the dissociation pressure at 270 K is 0.598 MPa.



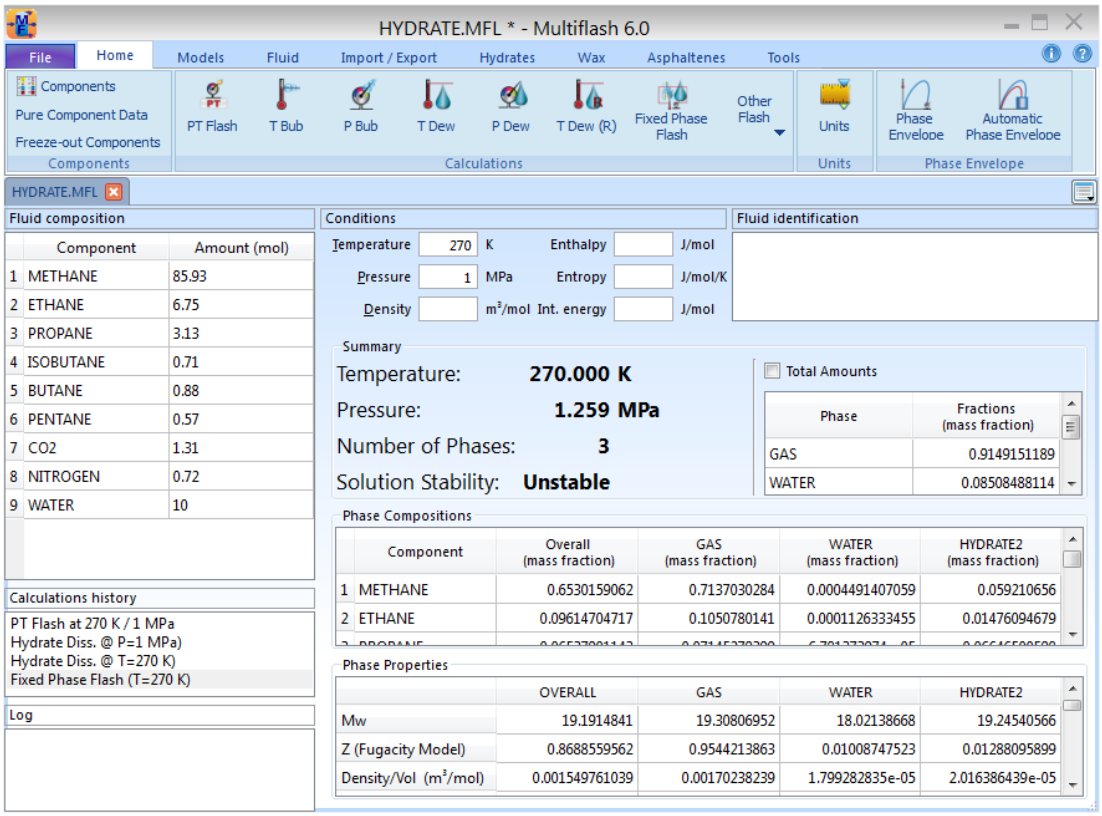
14. On the **Home** ribbon, click 

.

15. To calculate the hydrate formation pressure at 270 K, in the Fixed Phase Fraction Flash dialog box, enter the following values, and then click **Calculate**.

Item	Value
Temperature	270
Phase	Hydrate2
Basis	Nucleation

Result: The hydrate formation pressure at 270 K is 1.26 MPa. The nucleation calculation is, in the thermodynamic sense, inherently unstable, as reported.



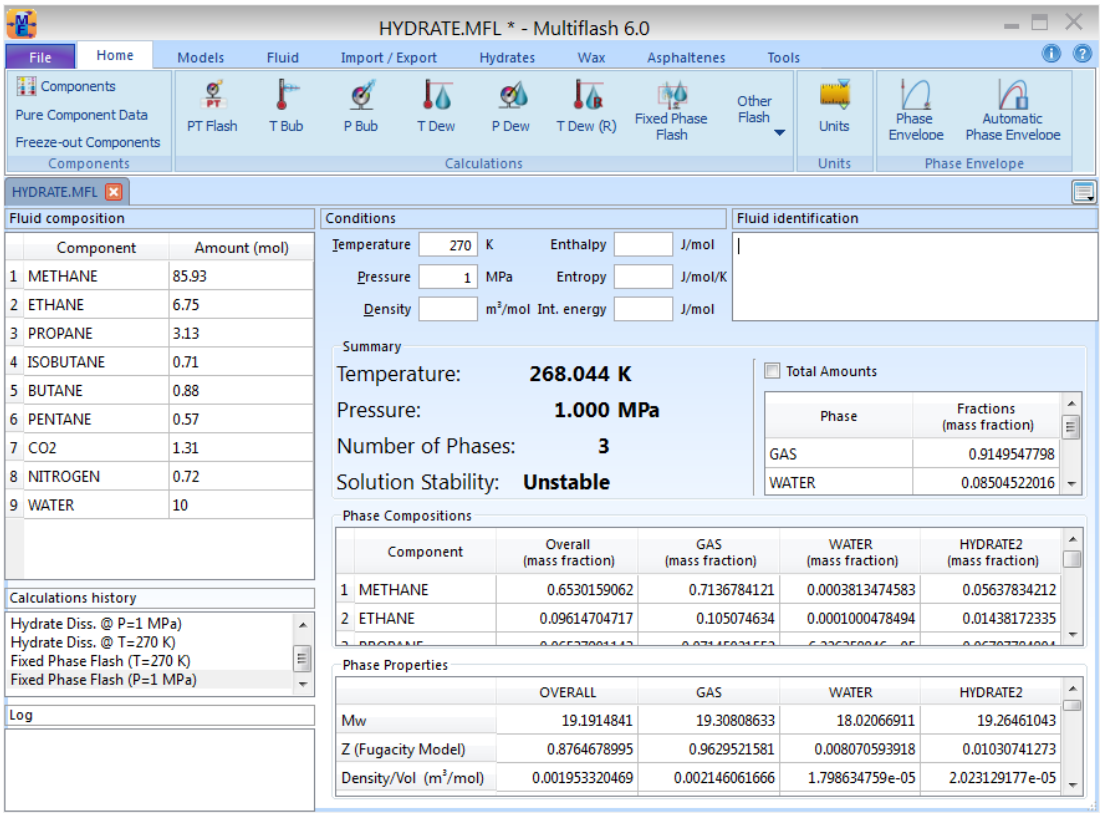
16. On the **Home** ribbon, click 

.

17. To calculate the hydrate formation temperature at 1 MPa, in the Fixed Phase Fraction Flash dialog box, enter the following values, and then click **Calculate**.

Item	Value
Pressure	1
Phase	Hydrate2
Basis	Nucleation

Result: The hydrate formation temperature at 1 MPa is 268 K. The nucleation calculation is, in the thermodynamic sense, inherently unstable, as reported.



Results:

Fixed	Hydrate formation value	Hydrate dissociation value
Temperature (270 K)	1.26 MPa	0.598 MPa
Pressure (1 MPa)	268.04 K	276.15 K

FAQ:

Q: When I try to calculate the hydrate formation temperature, I get an error message like this:

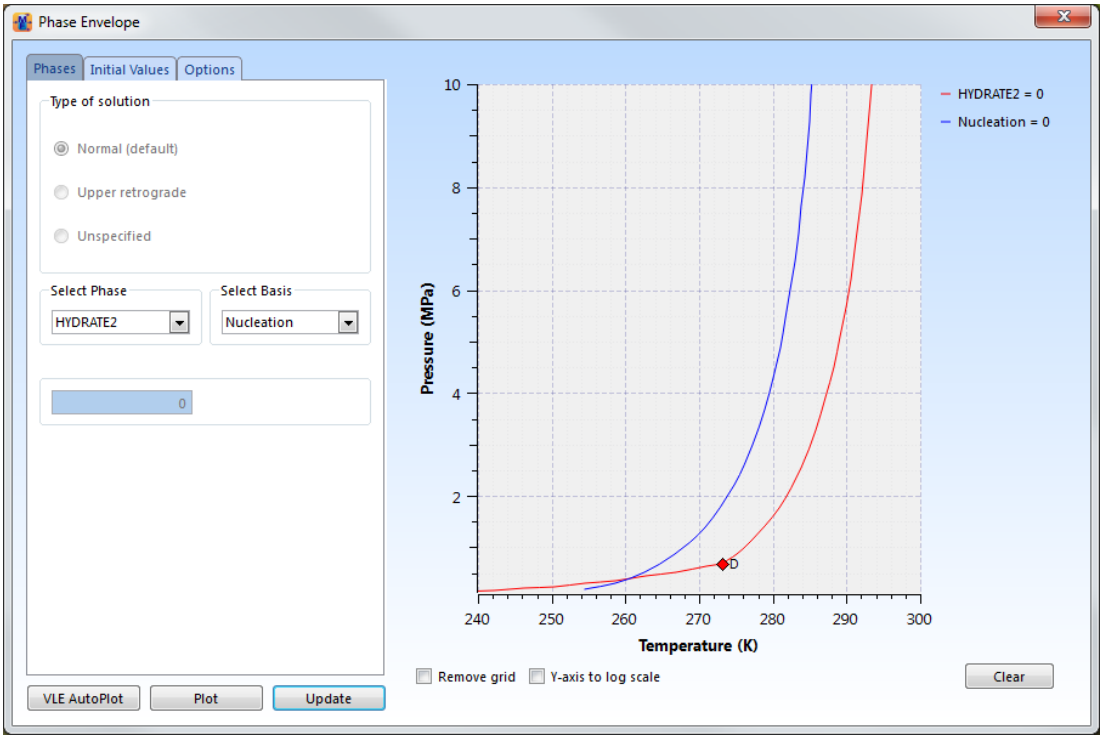
20292 - Cannot find converged point - max. iterations
20024 - Cannot find starting point for calculation - there may be no solution

A: For hydrate formation calculations, this is most often because there is no hydrate phase at the specified conditions. You can confirm this by plotting the phase boundaries for hydrate formation and dissociation, as outlined next.

What else can I do?

To support your calculations, you should consider plotting the phase boundaries for hydrate formation and dissociation, to obtain an overview of behaviour under different conditions. To do so, on the Main ribbon, click 

, choose your hydrate phase, and then plot mole fraction (value 0) and nucleation in turn.



Determining maximum allowable water content

Problem:

What is the maximum amount of water that can be present in my fluid at a given pressure and temperature before hydrates can form?

The tolerance calculation combines two mixtures in different ratios until a specified condition is met. The following example finds the maximum water content for the mixture at 270 K and 1 MPa before hydrates will form. The initial water content is zero, and this is increased until the initial formation of hydrate.

Approach:

1. Define your fluid.
2. Specify the hydrate model.
3. Perform a tolerance calculation at your required temperature and pressure.

Try it yourself:

1. If you are using our example file, on the **File** menu, click **Open**, open the file hydrate.mfl, and then proceed to step 7.

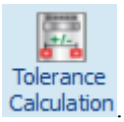
   Tip: By default, the example files are in the MFL Files folder of the Multiflash installation.
2. On the **Home** ribbon, click **Units**, ensure that the input and output pressure units are MPa, the input and output temperature units are K, the amount input units are mol, and the amount output units are g, and then click **OK**.
3. Click **Components**.
4. Enter the fluid components shown in the following table, and then click **OK**.

Component	Amount (mol)
Methane	85.93
Ethane	6.75
Propane	3.13
Isobutane	0.71
Butane	0.88
Pentane	0.57
Carbon dioxide	1.31
Nitrogen	0.72
Water	0

5. In the **Fluid composition** panel, enter the amounts for each component, as shown in the previous table.
6. On the **Hydrates** ribbon, click **CPA Infochem**, and then click **OK** on the message.

   This automatically specifies the hydrates model with default settings.
7. If you are using our example file, in the **Fluid composition** panel, set the amount of water to 0.
8. In the **Conditions** area, ensure that the following values are entered.

Condition	Value
Temperature	270 K
Pressure	1 MPa

9. On the **Tools** ribbon, click 

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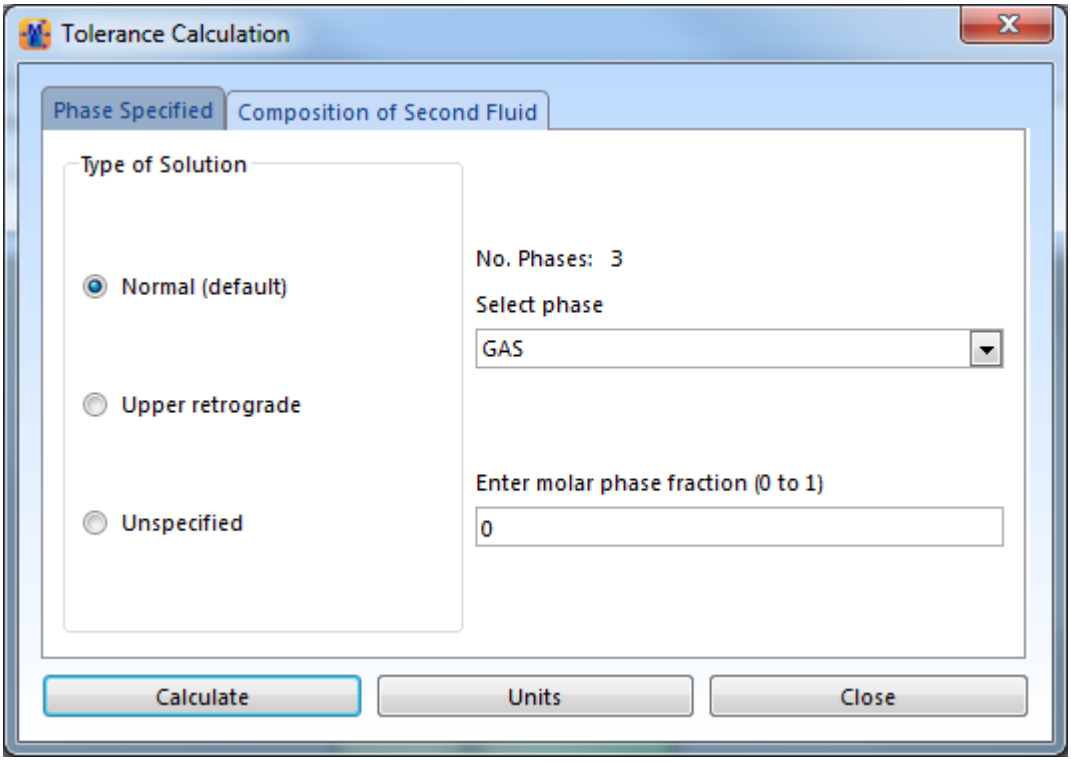


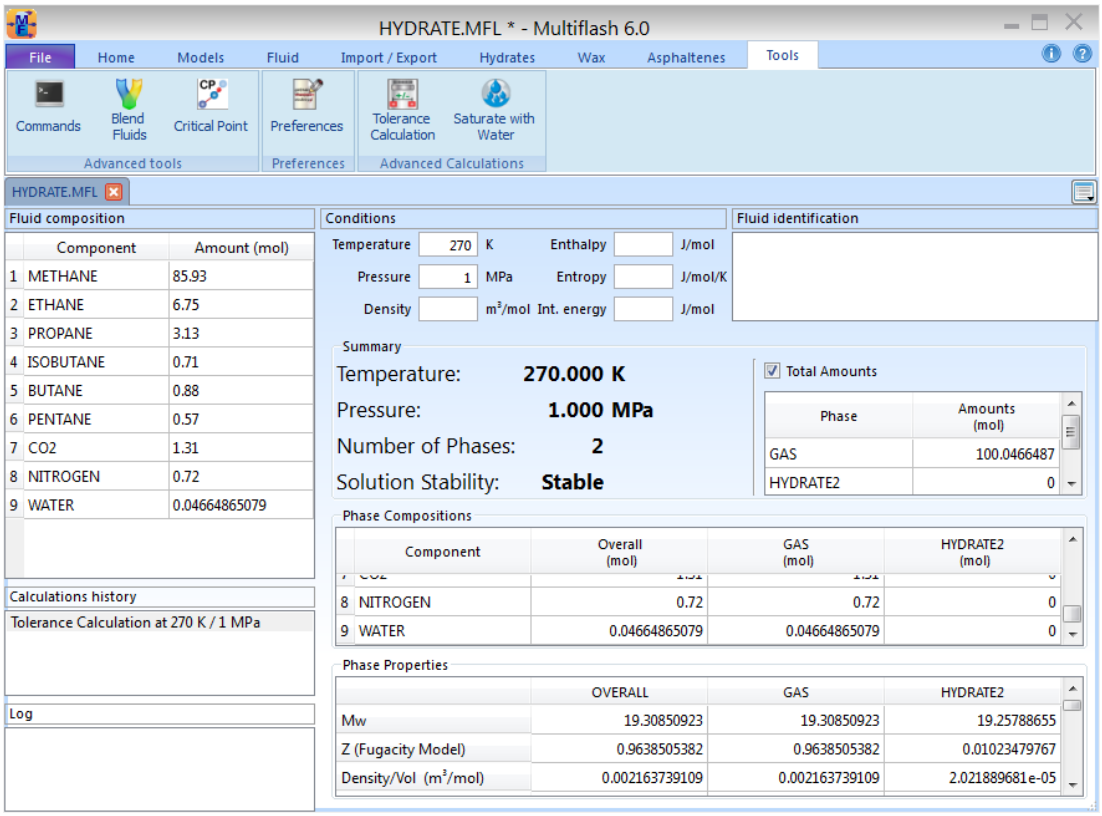
10. From the **Select phase** list, choose HYDRATE2, and then ensure that the molar phase fraction is set to 0.

    Rationale: The example file specifies a fluid that forms structure II hydrates.

11. On the **Composition of Second Fluid** tab, set the amount of water to 1.
12. Click **Calculate**, and then, in the **Tolerance Result** dialog, click **Yes**.

    Result: The calculated amount of water is added to your fluid.

13. Click **Close**.
14. Check **Total Amounts**.
15. Scroll to the end of the **Phase Compositions** list, to see the maximum amount of water that can be added to the original water-free stream to meet the condition of zero hydrate phase at the chosen P and T.



FAQ:

My calculation failed, where did I go wrong?

The tolerance calculation is a fixed phase calculation and might not have solution. if the calculation fails, check that the specified temperature and pressure are within the hydrate phase envelope when the system is saturated with water.

Adding inhibitors with the inhibitor calculator

Thermodynamic hydrate inhibitors decrease the temperature or increase the pressure at which hydrates will form from a given gas mixture. In Multiflash, the CPA-based hydrate model includes parameters for water with methanol, ethanol, MEG, DEG, TEG and salts.

To investigate the effect of an inhibitor, you include the inhibitor in the list of components for your fluid. You can add inhibitors using either of the following methods:

- Add it to the list of components in your fluid and specify the amount in the total mixture just as for any other component.
- Use the inhibitor calculator to calculate the amount of inhibitor or inhibitors to be added to the amount of water present in the fluid in order to reach a user-defined inhibitor concentration.

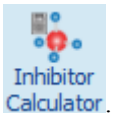
  Note: The inhibitor partitions between the different fluid phases present at equilibrium, and the amount in a particular phase depends on the conditions and the amounts of other components. For example, methanol will typically be present to a significant extent in the oil and gas phases, as well as in the aqueous phase.

The inhibitor calculator is included to simplify the addition of common inhibitors. The concentration can be specified in mass, molar or volume units. When you use the inhibitor calculator, the components that you specify are added automatically to the components list, along with the calculated amounts.

You can add components from both types of inhibitor (alcohols and salts) to the same fluid. Also simultaneously if required.

After you have added your chosen inhibitors, you can perform the full range of Multiflash calculations on your fluid.

To add alcohols and glycols:

1. On the **Hydrates** ribbon, click 
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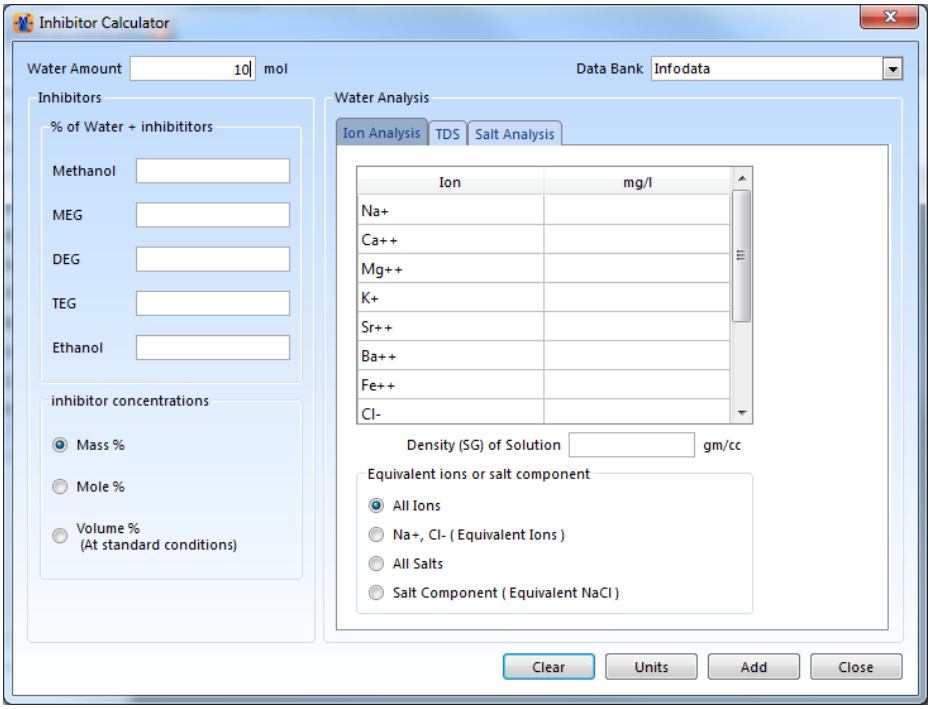


2. Select a databank for the pure component properties.
3. Enter the amount of water to which the inhibitor is added.

   Note: If you have already defined water in your fluid, the amount is shown in the **Water Amount** field.

   Tip: You can change the units used for the water by clicking **Units**.
4. Specify the units to use for inhibitor concentration.

   Note: The inhibitors are added to your fluid in the selected input unit for the fluid, even if the inhibitor concentration is specified in other units.
5. For each inhibitor that you want to add, enter the required concentration as a percentage of the total amount of water plus inhibitors.

   Restriction: The total percentages of all inhibitors must sum to less than 100.

   Example: If you have 10 mol of water, and specify 10% methanol and 10% MEG, in mole % units, the calculator adds 1.25 mol of each of the inhibitors (a total amount of 12.5 mol of the three components).

6. Click **Add**.

   Result: The inhibitors and amounts displayed in the Inhibitor Amounts dialog box are added to the components of your fluid.

7. Remove the Inhibitor Amounts dialog box, and then click **Close**.

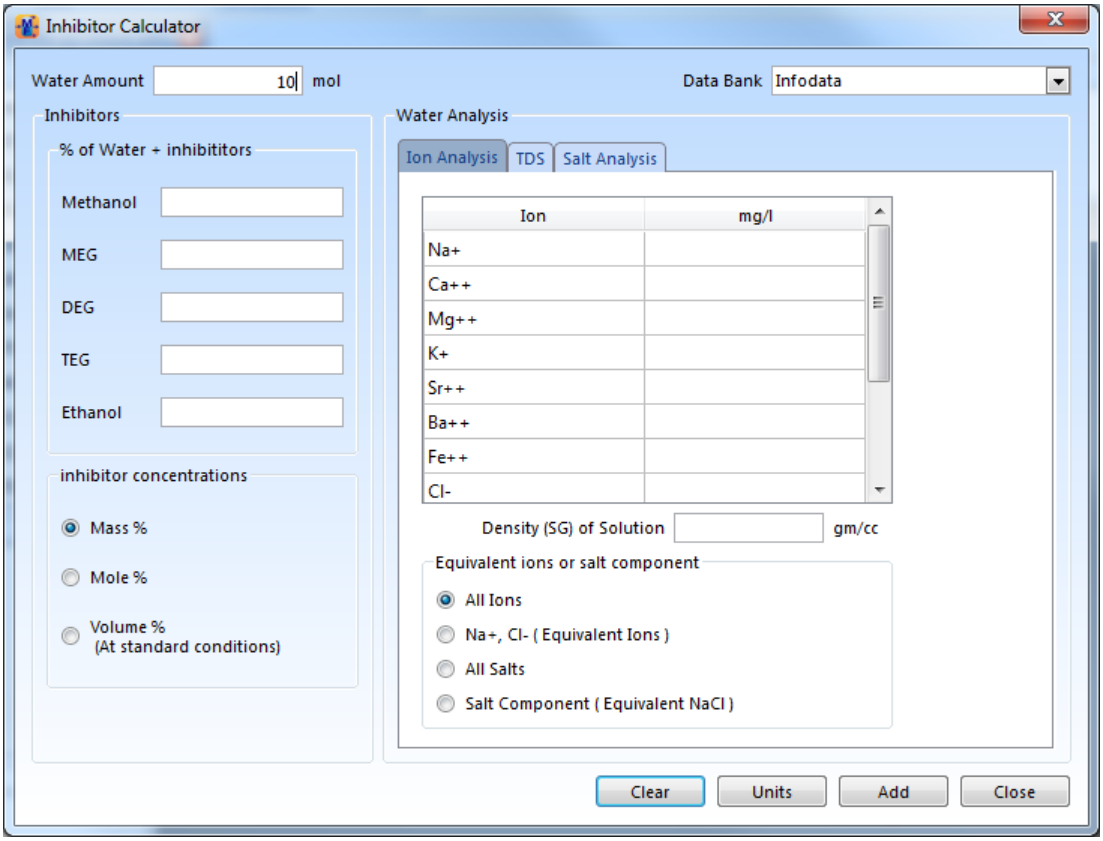
Salt calculator

Although you can include the ions in your component list by selecting them from INFODATA, it is easier to use the inhibitor calculator to specify the concentration of various salts in water using commonly-reported laboratory measurements.

When you add ions, the electrolyte model can only be selected as part of the hydrate model. The model selection is made on the **Hydrates** tab, using **CPA + Electrolytes**.

To add salts and ions:

1. On the Hydrates ribbon, click Inhibitor Calculator, and then click the **Salts/Ions** tab.



2. Select a databank for the pure component properties.
3. Enter the amount of water to which the inhibitor is added.

   Note: If you have already defined water in your fluid, the amount is shown in the **Water Amount** field.

   Tip: You can change the units used for the water by clicking **Units**.

4. Click the tab for the analysis type that you have, and proceed as shown in the table.

Note: The inhibitors are added to your fluid in the selected input unit for the fluid, even if the inhibitor concentration is specified in other units.

Analysis type	Procedure
Ion Analysis	1. Enter the amounts of each ion, in mg/l. 2. If you have a solution density measurement, enter the value, in gm/cc. **Restriction:** You must enter both positive and negative ions. 3. Choose whether to include the effect of ions other than Na^+, K^+, Ca^{2+}, Cl^- and Br^- as an equivalent amount of all those ions, or as equivalent Na^+ and Cl^- ions only.
Total dissolved solids (TDS)	1. Enter the total dissolved solid, in mg/l. 2. If you have a solution density measurement, enter the value, in gm/cc.
Salt Analysis	1. Choose the salt analysis units. 2. Enter the amounts of each salt. 3. Choose whether to include the effect of ions other than Na^+, K^+, Ca^{2+}, Cl^- and Br^- as an equivalent amount of all those ions, or as equivalent Na^+ and Cl^- ions only.

5. Click **Add**.

   Note: If you enter values on more than one analysis option, the amount of salt to be added will be taken from the visible tab.

   Result: The inhibitors and amounts displayed in the Inhibitor Amounts dialog box are added to the components of your fluid.

6. Remove the Inhibitor Amounts dialog box, and then click **Close**.

Calculating inhibitor amounts required to suppress hydrate formation

Problem:

How much inhibitor do I need to suppress hydrate formation at a given temperature and pressure?

Approach:

1. Define your fluid.
2. Specify the hydrate model.
3. Use the inhibitor dosage tool to calculate the required amount of a single inhibitor.

For the following example, you can use the file hydrate.mfl, which describes a gas condensate, if you do not want to enter the model and component data manually.

Try it yourself:

1. If you are using our example file, on the **File** menu, click **Open**, open the file hydrate.mfl, and then proceed to step 7.

   Tip: By default, the example files are in the MFL Files folder of the Multiflash installation.

2. On the **Home** ribbon, click **Units**, ensure that the input and output pressure units are MPa, the input and output temperature units are K, the amount input units are mol, and the amount output units are g, and then click **OK**.
3. Click **Components**.
4. Enter the fluid components shown in the following table, and then click **OK**.

Component	Amount (mol)
Methane	85.93
Ethane	6.75
Propane	3.13
Isobutane	0.71
Butane	0.88
Pentane	0.57
Carbon dioxide	1.31
Nitrogen	0.72
Water	10

5. In the **Fluid composition** panel, enter the amounts for each component, as shown in the previous table.
6. On the **Hydrates** ribbon, click **CPA Infochem**, and then click **OK** on the message.

   This automatically specifies the hydrates model with default settings.

7. In the **Conditions** area, enter the temperature as 270 K and the pressure as 1 MPa.

   Rationale: We know from the same example fluid that, at this temperature and pressure, hydrates form. See *Calculating hydrate formation at a given pressure and temperature*.

8. We will be using methanol as an inhibitor.

   Tip: If you have a fluid that already contains an amount of your inhibitor, you need not set the amount to 0; the inhibitor dosage tool takes account of the existing amount , and adds only the extra amount of inhibitor required.

9. On the **Hydrates** ribbon, click 

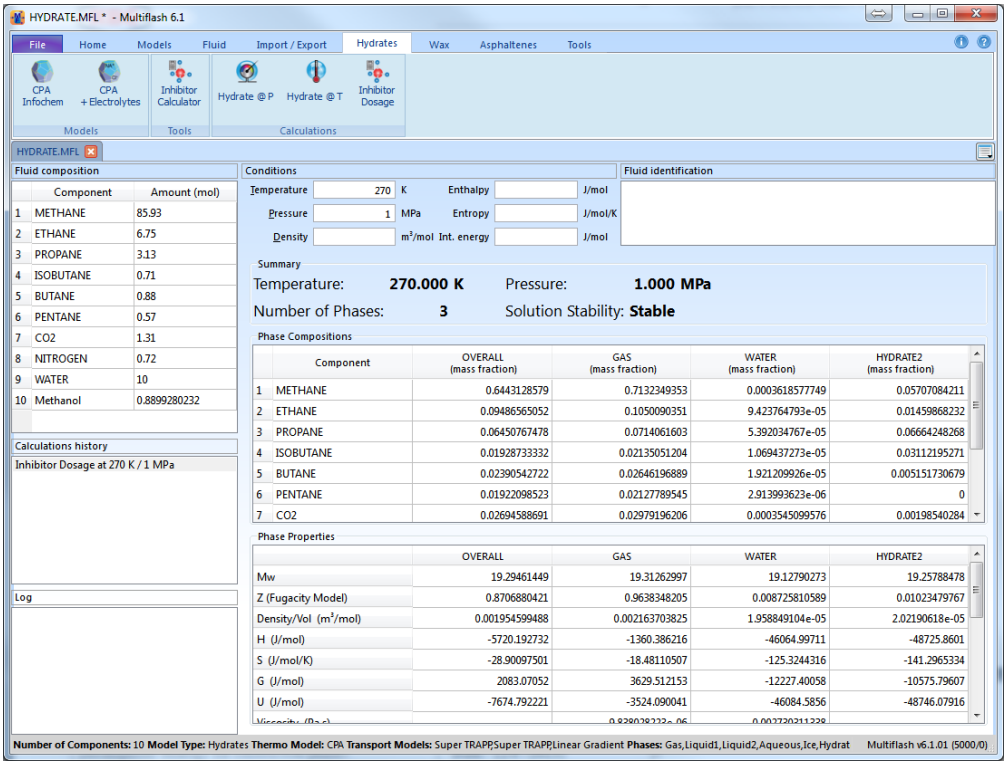
.
10. In the Calculate Inhibitor Amount dialog box, enter 1 for the amount of Methanol.
    Tip If the inhibitor is not pure, you can specify its concentration in water as mass, mol or volume fractions.

11. Click **Calculate**, and then, on the Tolerance Result dialog box, click OK.

    Result: The required inhibitor amount is displayed and you can add it to the composition. The value is also reported as % weight of total fluid and % weight of water in initial fluid.

12. Click **Yes** or **No**, if you want to add to the composition or not, respectively.

13. Scroll to the end of the **Phase Compositions** list, to see the amount of methanol required to meet the condition of zero hydrate phase at the chosen P and T.



FAQ:

Why has Multiflash calculated a negative amount of inhibitor to add?

If the amount of inhibitor currently specified in your fluid exceeds the required amount to suppress hydrate formation at the specified conditions, Multiflash calculates a negative amount of the inhibitor, meaning that the current amount of hydrate inhibitor can be reduced by the amount shown.

What else can I do?

After the inhibitors are added to the system, you can check the hydrate phase boundary to see the hydrate inhibition effect and the partitioning of the inhibitors among the fluid phases by performing a flash calculation at a given T and P. You can find a worked example in *Looking at the effect of inhibitors*.

Looking at the effect of inhibitors

Problem:

What is the effect on hydrate dissociation of adding an inhibitor?

Approach:

1. Define your fluid.
2. Calculate the hydrate phase boundary.
3. Add your inhibitor.
4. Calculate the hydrate phase boundary and compare it with the previous boundary.

For the following example, you can use the file hydrate.mfl, which describes a gas condensate, if you do not want to enter the model and component data manually.

Try it yourself:

1. If you are using our example file, on the **File** menu, click **Open**, open the file hydrate.mfl, and then proceed to step 7.

   Tip: By default, the example files are in the MFL Files folder of the Multiflash installation.
2. On the **Home** ribbon, click **Units**, ensure that the input and output pressure units are MPa, the input and output temperature units are K, the amount input units are mol, and the amount output units are g, and then click **OK**.
3. Click **Components**.
4. Enter the fluid components shown in the following table, and then click **OK**.

Component	Amount (mol)
Methane	85.93
Ethane	6.75
Propane	3.13
Isobutane	0.71
Butane	0.88
Pentane	0.57
Carbon dioxide	1.31
Nitrogen	0.72
Water	10

5. In the **Fluid composition** panel, enter the amounts for each component, as shown in the previous table.
6. On the **Hydrates** ribbon, click **CPA Infochem**, and then click **OK** on the message.

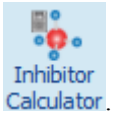
   This automatically specifies the hydrates model with default settings.
7. On the **Home** ribbon, click 

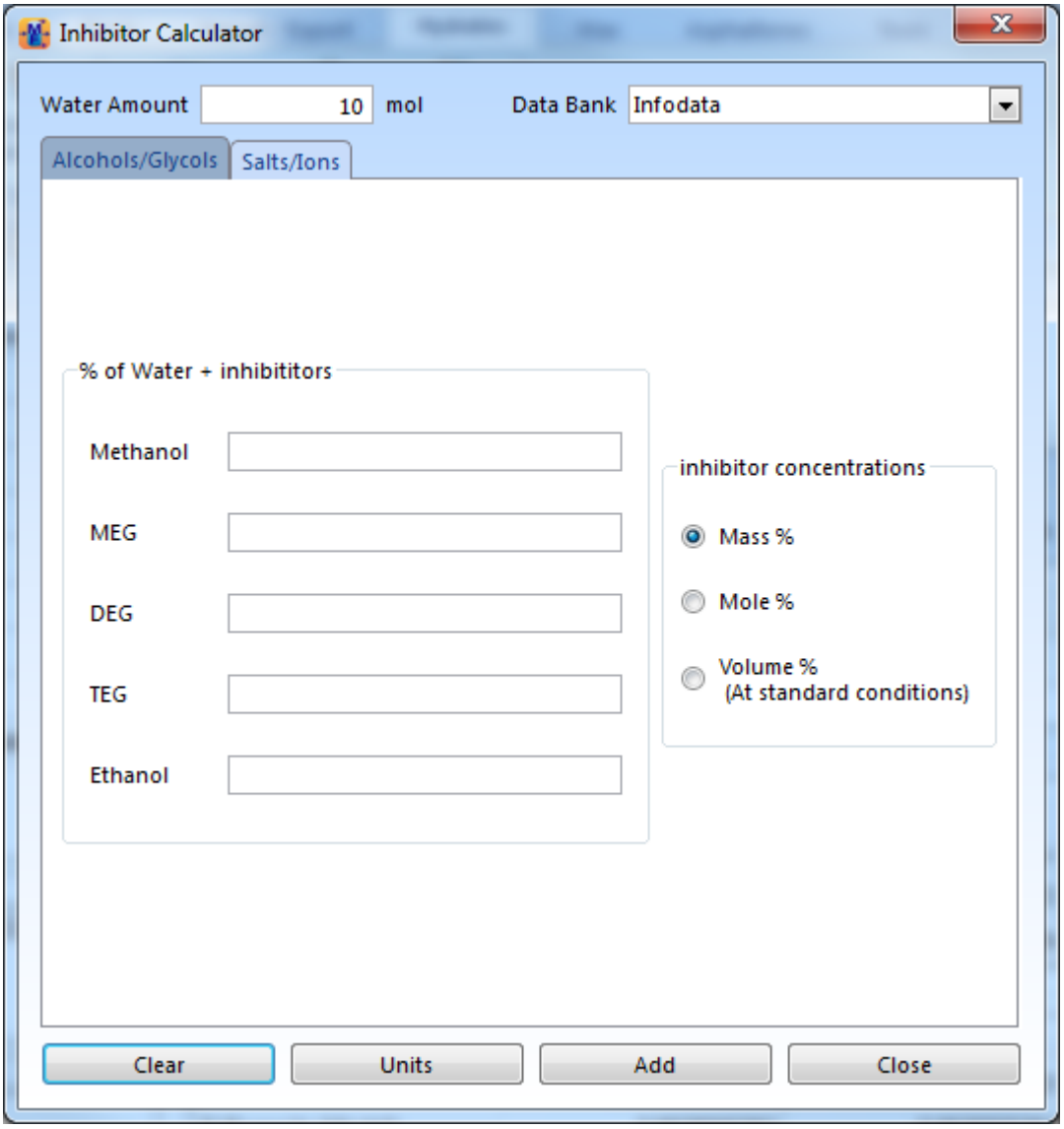
.
8. In the Phase Envelope dialog box, on the Phases tab, set the values shown in the table.

Item	Value
Type of solution	Normal
Select Phase	Hydrate2
Select Basis	Mole fraction
Phase fraction	0

9. Click **Plot**, and then click **No** in the message.
10. Remove the Phase Envelope dialog box.

    Important: Do not clear the plot because you will compare this later.

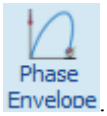
11. On the **Hydrates** ribbon, click 
.



12. In the Methanol field, enter 10.

    Tip: For your own calculations, you can specify the inhibitor concentration as mass %, mole % or volume %. This example has units of mass %.

13. Click **Add**, remove the Inhibitor Amounts dialog box, and then click **Close**.

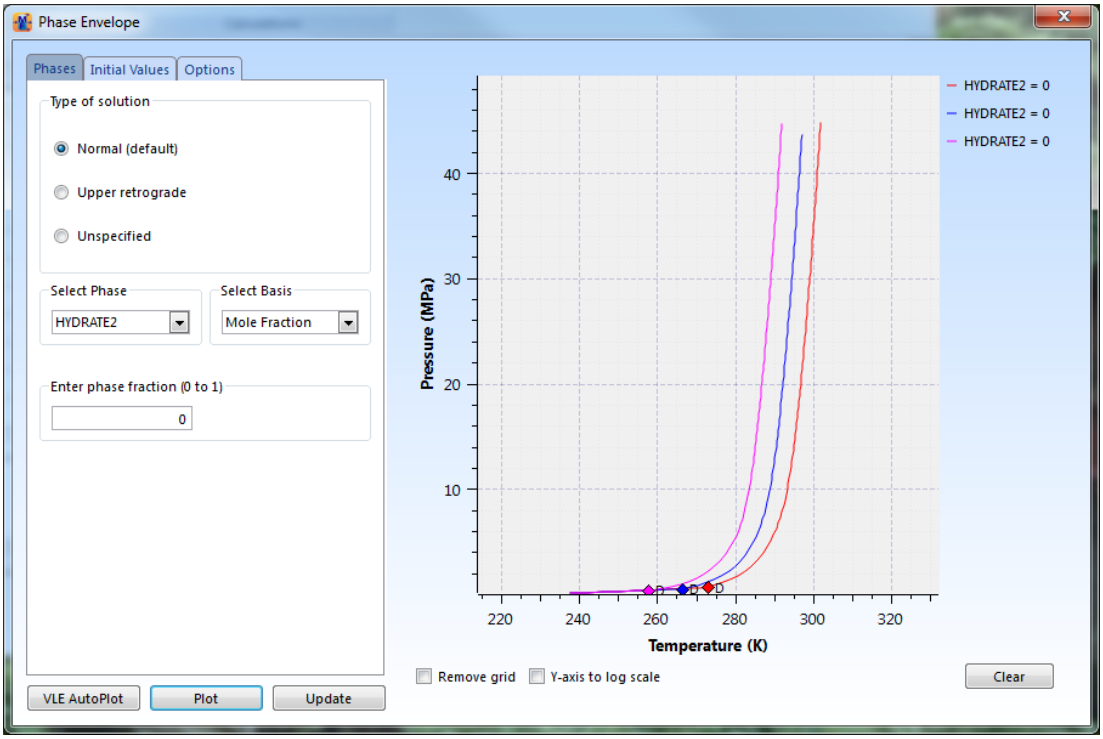
14. On the **Home** ribbon, click 

.

15. Enter the same values as previously, and then click Plot.

16. Repeat the addition of inhibitor, using 20% methanol.

17. Plot the phase boundary again.



As more inhibitor is added, you can see that, for a given pressure, the hydrate dissociation temperature is reduced.

FAQ:

Anything to add here?

What else can I do?

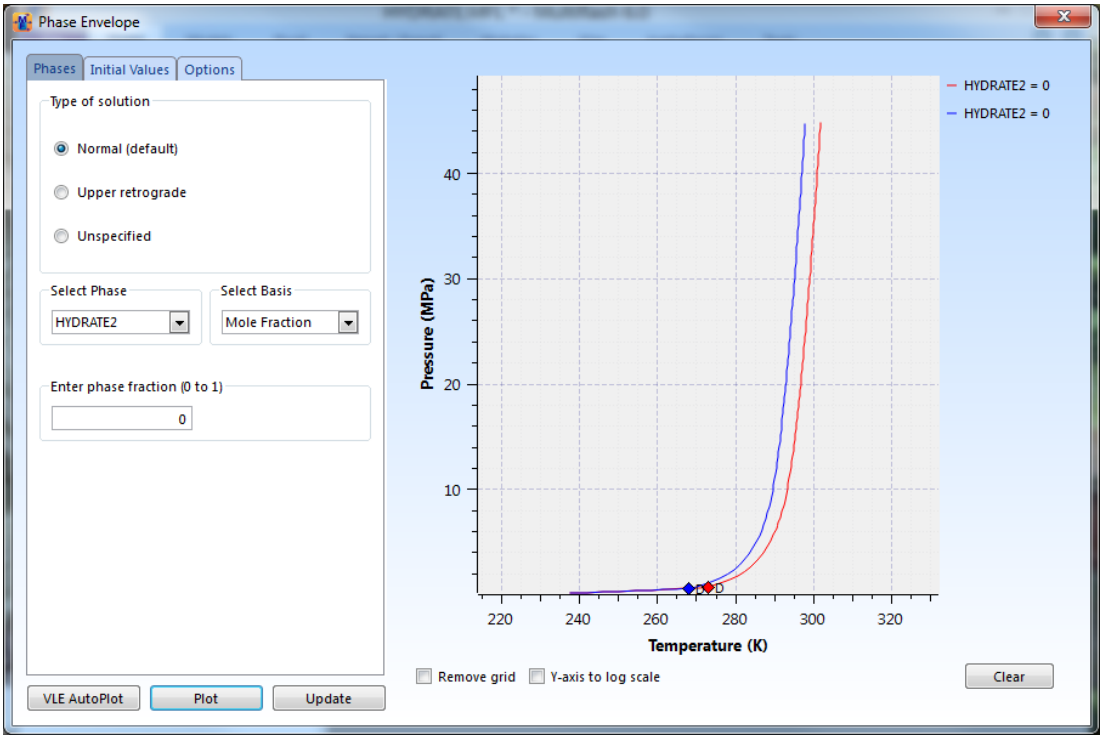
1. Perform a series of fixed phase flashes or boundary plots, varying the inhibitor type and amount, to see the trends in inhibitor effect.

2. You can see the effect of salts on the hydrate dissociation by following the procedure above, but using a salt solution as the inhibitor instead of methanol. Enter the following salt analysis data into the inhibitor calculator, to add salts to your fluid, and then plot the phase boundary as before.

   Tip: Do not forget to change the hydrate model to CPA + Electrolytes.

Salt	Mass % in Solution
NaCl	6.993
$CaCl_2$	0.735
$MgCl_2$	0.186
KCl	0.066
$SrCl_2$	0.099
$BaCl_2$	0.036

You should obtain these phase boundary plots if you use the hydrate.mfl file:



3. If your fluid has only a trace amount of water, it might be more effective to dehydrate your system to inhibit hydrate formation rather than add inhibitor. To investigate this, perform a maximum water content calculation to see if it is more effective to remove the excess water or add your inhibitor.

Scale precipitation

Problem:

Is there any scale precipitation in my hydrate system?

Salt injection represents a powerful hydrate inhibition strategy. However, salts themselves can also introduce problems, for example, scale formation. Given the presence of salts in the mixture, Multiflash can determine whether there is any scale precipitation at given conditions, or, for a given amount of salts in the mixture, the conditions at which there might be scale precipitation.

Note: The salt precipitation model is a simple model to predict the salt precipitation together with hydrate formation and inhibitition. The model is not suitable for comprehensive water analysis.

Approach:

1. Define your fluid.
2. Specify scale precipitation calculations in your model.
3. Perform a standard flash or fixed phase flash to calculate the phases in your fluid.

For the following example, you can use the file scaling.mfl, which describes a gas condensate, if you do not want to enter the model and component data manually.

Try it yourself:

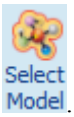
1. If you are using our example file, on the **File** menu, click **Open**, open the file scaling.mfl, and then proceed to step 11.

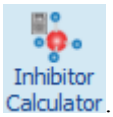
   Tip: By default, the example files are in the MFL Files folder of the Multiflash installation.
2. On the **Home** ribbon, click **Units**, ensure that the input and output pressure units are MPa, the input and output temperature units are K, the amount input units are mol, and the amount output units are g, and then click **OK**.
3. Click **Components**.
4. Enter the fluid components shown in the following table, and then click **OK**.

Component	Amount (mol)
Methane	85.93
Ethane	6.75
Propane	3.13
Isobutane	0.71
Butane	0.88
Pentane	0.57
Carbon dioxide	1.31
Nitrogen	0.72
Water	10

5. In the **Fluid composition** panel, enter the amounts for each component, as shown in the previous table.
6. On the **Hydrates** ribbon, click **CPA + Electrolytes**, and then click **OK** on the message.

   This automatically specifies the hydrates model with default settings for calculations including salts.

7. On the **Models** ribbon, click 

.
8. In the **Phases** panel, check **Halide Scales**.
9. Click **Define Model**.
10. On the success message, click **OK**.
11. On the **Hydrates** ribbon, click 

.
12. Select the **Salts/Ions** tab, and then the **Salt Analysis** tab, and enter the salt analysis shown in the table.

Salt	Mass % in Solution
NaCl	6.993
$CaCl_2$	0.735
$MgCl_2$	0.186
KCl	0.066
$SrCl_2$	0.099
$BaCl_2$	0.036

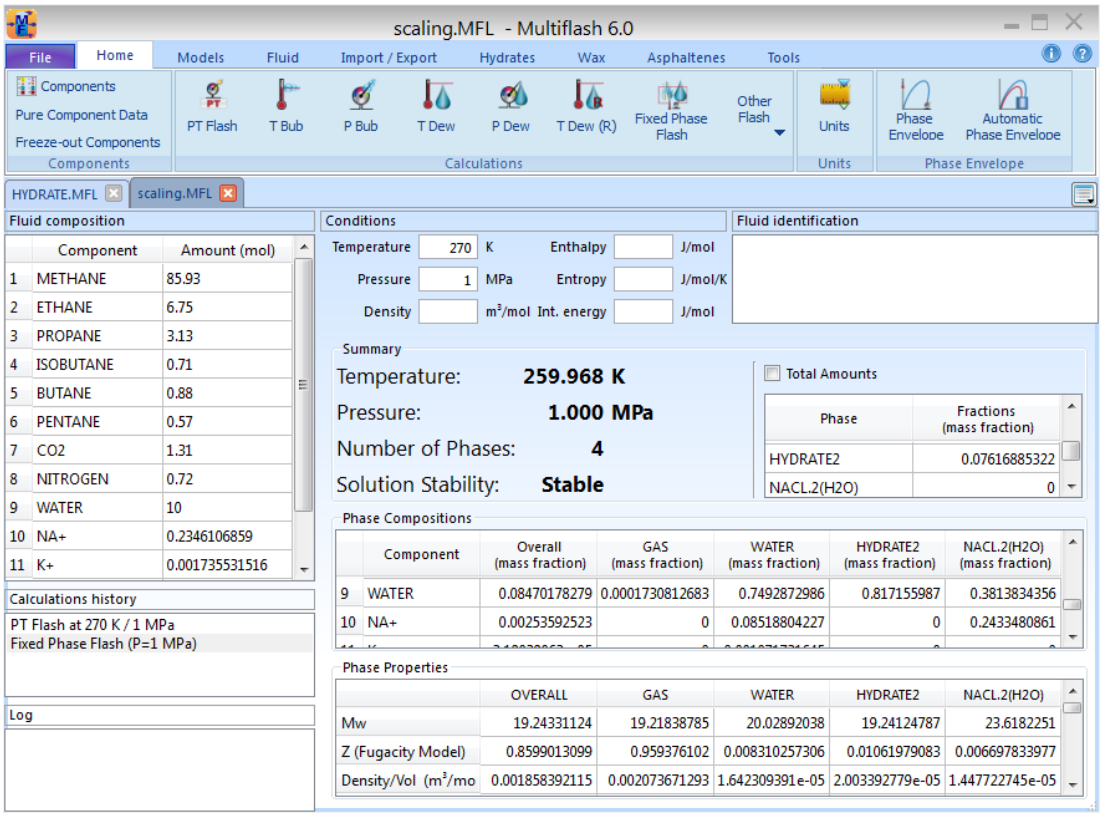
13. Click **Add**, close the Inhibitor Amounts message, and then click **Close**.
14. In the **Conditions** area, enter the temperature as 270 K and the pressure as 1 MPa.
15. On the **Home** ribbon, click 

.

    Result: Under the current conditions, the temperature is too high for any scale precipitation.
16. To calculate the temperature at which Nacl.2(H_20) precipitation occurs at a pressure of 1 MPa, in the Fixed Phase Fraction Flash dialog box, enter the following values, and then click **Calculate**.

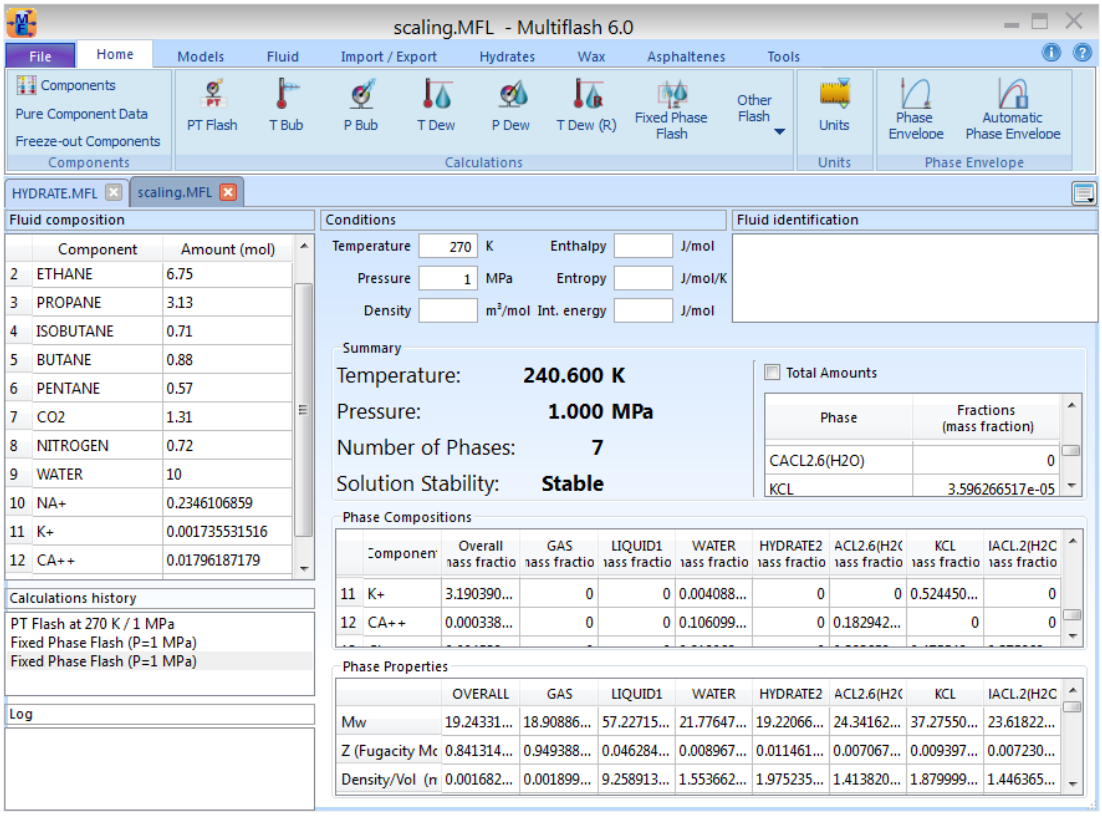
Item	Value
Pressure	1
Phase	NACL.2(H20)
Basis	Mole Fraction
Enter phase fraction	0

    Result: The Nacl.2(H_20) precipitation temperature at 1 MPa is 259.9 K.



17. Repeat the calculation for the precipitation of $CaCl_2.6(H_2O)$.

Result: The $CaCl_2.6(H_2O)$ precipitation temperature at 1 MPa is 240.6 K. At this temperature, precipitation of KCL and Nacl.2(H_20) also occurs.



FAQ:

Anything to add here?

What else can I do?

A realistic scenario occurs if the salt concentration is higher, for example, 30 wt% equivalent of NaCl. A flash at a temperature higher than hydrate dissociation conditions shows NaCl formation, whereas at a temperature where a hydrate phase is present, NaCl.2(H2O) forms. You can do this as follows:

1. Using the scaling.mfl file, modify the salt analysis in the inhibitor calculator so that only 30 wt % of NaCl is present.
2. Do a fixed phase flash at a pressure of 1 MPa to find the hydrate dissociation temperature (260.7 K).
3. Do a PT flash at a pressure of 1 MPa and 280 K and see NaCl formation.
4. Do a PT flash at a pressure of 1 MPa and 250 K and see NaCl.2(H_2O) formation.

Working with asphaltenes

One of the major problems for the oil industry is the precipitation of heavy organics during production, transportation and refining or processing of crude oil. Asphaltenes are polar,organic compounds that are stabilised in crude oil by the presence of resins. If the oil is diluted by light hydrocarbons, the concentration of resins goes down and a point may be reached where the asphaltene is no longer stabilised and it flocculates to form a solid deposit.

Because the stabilising action of the resins works through the mechanism of polar interactions, their effect becomes weaker as the temperature rises, meaning that flocculation occurs more readily as the temperature increases. However, as the temperature increases further, the asphaltene solubility in the oil increases as well. Thus, depending on the temperature and the composition of the oil, it is possible to find cases where flocculation both increases and decreases with increasing temperature.

The asphaltene model is intended for use in predicting the asphaltene phase behaviour of live oils, and the generation of the model parameters is based on asphaltene studies of live fluids. However, live oil asphaltene studies can be expensive, particularly with the requirement to obtain and transport bottom hole samples. We have investigated whether titration measurements on dead oils can also be used to generate the model parameters. To date, we have only been able to obtain limited samples of titration data and have traced only one oil, in the public domain, where there is information on both asphaltenes in the live oil and reported titration on the associated stock tank oil (STO), enabling us to compare results. However, we understand that some of our users have applied this approach successfully, and the procedure for using titration data has been automated.

The asphaltene model is complex, and to ensure reliable results we recommend that you follow the procedure we suggest in *Preparing for asphaltene calculations*, until you are familiar with the model and the behaviour of your particular fluid.

The asphaltene model in Multiflash is primarily intended for calculating asphaltene precipitation from live oils. We are aware that many users have only titration data for dead (STO) oils, so we also provide a method for using titration data to set the asphaltene model parameters.

Preparing for asphaltene calculations

To ensure that reliable results are obtained for asphaltene calculations, you must prepare the asphaltene model, using the following steps:

1. Specify the asphaltene model.
2. Characterise your fluid.
3. Tune the model and optimize the asphaltene model parameters.

The ideal input data for the fluid characterization and tuning are:

- A compositional analysis of the live oil.
- The amount of asphaltene in the oil and the ratio of resin to asphaltene, often determined from the SARA analysis of a stock tank oil. You do not need a full analysis, the weight % (wt%) of resins and asphaltenes in the stock tank oil is sufficient, because the wt% of saturates and aromatics are only used to normalise the wt% of resins and asphaltenes.

  Note: The wt% of asphaltenes is taken to be that precipitated by n-heptane. Some laboratories report the value precipitated by n-pentane. The conversion of values between n-pentane and n-heptane precipitation varies from oil to oil and laboratory to laboratory. In general, we have found

that the wt% asphaltene precipitated by n-pentane is approximately twice that precipitated by n-heptane. However, ratios can vary between 1.3 and 2.7.

- At least two asphaltene precipitation onset (AOP) data at two different temperatures.
- At least one bubble point.

If you do not have the complete data set, we have developed correlations to assign the required parameters. The following table provides a summary of the options available to you if you do not have the ideal input data set available.

Description of missing data	Alternative
Fluid characterization	
You only have the wt% of asphaltene in the oil.	In the PVT Laboratory Fluid Analysis dialog box, enter your asphaltene value in the **SARA Analysis** panel, and check **Estimate RA** before you characterize your fluid.
You have no information on the amount of asphaltene in the oil	In the PVT Laboratory Fluid Analysis dialog box, check **Estimate RA** before you characterize your fluid.
Asphaltene model tuning	
You have only one AOP temperature.	Use the reservoir saturation pressure as a second AOP at the reservoir temperature, provided that no asphaltene precipitation is found experimentally at the reservoir condition. If the reservoir saturation pressure has not been measured, you can enter the reservoir temperature and a bubble point measurement.
You have no AOP data.	You can use asphaltene onset titration data, or the reservoir condition. **Note:** The titration data used is the amount of n-heptane required to initiate asphaltene precipitation, measured as the ratio by weight of n-heptane to oil.
You have no titration, reservoir or AOP data	Enter a bubble point. In this case, Multiflash assumes that the reservoir temperature is the same as the bubble point temperature and estimates the reservoir pressure as 2.5 times the bubble point.
You have no experimental data	Multiflash generates model parameters from correlations based on data held in the database.

Water and asphaltene calculations

The asphaltene phase is modelled as a liquid, so the presence of a water phase makes the calculations more complex, especially for phase boundaries. If you need to include water in your calculations, you must not include water within the fluid characterisation and model tuning, because the experimental measurements from which the asphaltene model is derived are done in a water-free environment.

To include water as a component in your fluid, ensure that you do the following in order:

1. Specify the water phase as part of your model definition.
2. Do not add a water component to your fluid prior to characterization and tuning.
3. Characterize the fluid.
4. Tune the model.
5. Add the water component to your fluid.

Specifying the asphaltene model

For most calculations, you do not need to specify the model manually. Instead, you can use the preconfigured model setup, by clicking 

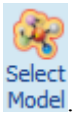
on the **Asphaltenes** ribbon.

If you want to use non-default options, you must specify the model manually.

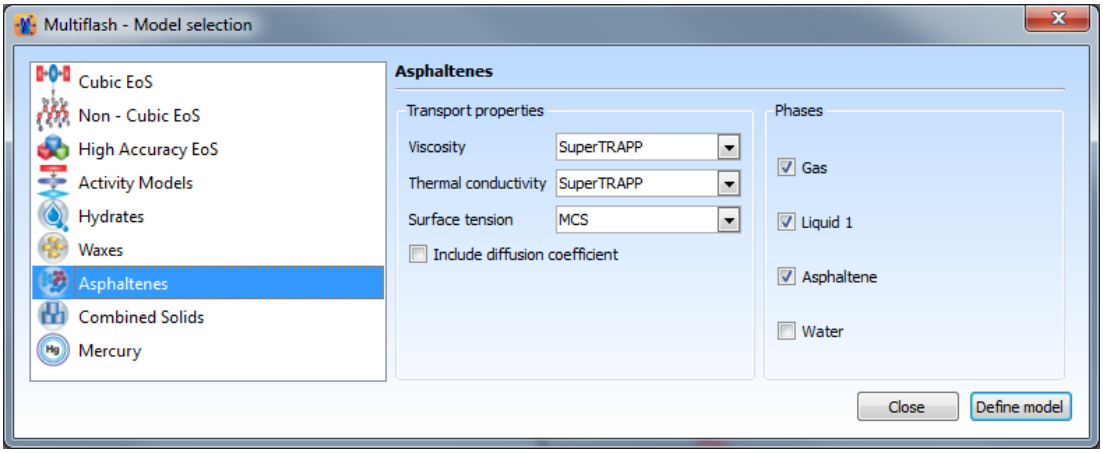
To specify the asphaltene model:

1. If you are using our example file, on the **File** menu, click **Open**, and open the file asphex.mfl.

   Tip: By default, the example files are in the MFL Files folder of the Multiflash installation.

2. On the **Models** ribbon, select 

.
3. From the model list, select **Asphaltenes**.



   The image shows the default settings for the asphaltenes model. The example file settings differ from the default values.

4. Modify the options as required.

   Tip: Choose the transport properties to best describe the fluid phase. They do not take into account the asphaltenes.

5. Click **Define Model**.
6. On the success message, click **OK**.
7. If you are using our example file, proceed to step 9.
8. On the **Fluid** ribbon, click **PVT Analysis**, and then enter your fluid components, amounts and

properties, as described in *Defining a fluid using a PVT analysis*, ensuring that you enter the values shown in the table.

Requirement: If you want to include water in your fluid, do not add the water component until after the model has been tuned.

Item	Value
Pseudocomponents Normal fractions - Distribution start	C6
Pseudocomponents Normal fractions - Pseudocomponents requred	15
Molecular weight	Your experimental value, if available.
Specific gravity	Your experimental value, if available.
SARA Analysis	Your experimental values, if available. If you do not have an analysis, or have only a partial analysis that does not include the resin/asphaltene ratio, check **Estimate RA**.

9. Click **Do characterization**, and then click **OK** on the message.

   Result: After successful characterization, your fluid composition changes to include the asphaltene component, Asphaltene, and the resin components (fractions with an "R" prefix, for example, R36-48).

10. Tune your model, as described in *Tuning the asphaltene model*.
11. If required, add your water component and amount.

Your model is now ready to use in asphaltene calculations.

FAQ

Why am I getting a warning message when I try to characterize my fluid?

The asphaltene model in Multiflash was developed based on experimental data where the resin/asphaltene (R/A) ratio was always greater than 2.5. If your ratio is below 2, you see a warning message. If the characterization is subsequently unsuccessful, you can do one of the following:

- Increase the resin/asphaltene ratio manually.
- Delete the resin amount from the SARA analysis and check **Estimate RA**. When you do this, Multiflash generates a suitable set of resin pseudocomponents, using a default ratio.

Tuning the asphaltene model

After you have specified the model and characterized the fluid, as described in *Specifying the asphaltene model*, you can tune the asphaltene model, using available experimental data.

Multiflash tunes the model in two stages, in the order shown:

1. Tune the pseudocomponent properties by matching to the experimental data.
2. Tune the asphaltene model parameters by matching to asphaltene data.

Multiflash can use a variety of experimental data for tuning the pseudocomponent properties. We recommend bubble point matching, especially for light oils. You can omit the tuning of pseudocomponent properties, but any subsequent calculations are less reliable.

Tip: If you want to tune the pseudocomponent properties using experimental data other than bubble point data, refer to *Using the PVT lab tests*. In this case, you do not need to enter bubble point data in the following tuning procedure.

You should always tune the asphaltene model parameters, using the best available experimental data, as discussed in *Preparing for asphaltene calculations*. We recommend that you do not use the default asphaltene model parameters, even if you have no asphaltene data. For cases with no measured asphaltene data, use the reservoir condition as a minimum to tune the model parameters.

Note: When you tune the model with bubble point data using the 

tool, only the acentric factor is varied. If you want greater flexibility in the tuning, tune using the saturation test in the PVT lab tests.

To tune the asphaltene model:

1. Ensure that you have characterized your fluid, as described in *Specifying the asphaltene model*.
2. On the **Asphaltenes** ribbon, click 

.
3. Enter your experimental data, as shown in the table.

   Tip: Use the best available data set that you have. In the table, the data sets are in descending order of choice.

   Note: If you have no experimental data, Multiflash generates model parameters from correlations based on data held in the database. We recommend that you do not proceed without experimental data.

Available data	Do this
At least two asphaltene precipitation onset (AOP) data points and at least one bubble point.	1. On the **AOP Data** tab, enter the available AOP data points. 2. Check **Bubble point data**, and then enter the available data points.
One AOP data point, reservoir condition and at least one bubble point.	**Restriction:** Do not use this method if asphaltene precipitation is found experimentally at the reservoir condition. 1. On the **AOP Data** tab, enter the AOP data point. 2. On the **AOP Data** tab, enter the reservoir conditions as a second AOP data point. 3. Check **Bubble point data**, and then enter the available data points.

Available data	Do this
Asphaltene onset titration data and at least one bubble point.	1. On the **C7 Titration** tab, enter the titration value. 2. Check **Bubble point data**, and then enter the available data points.
Reservoir condition and at least one bubble point.	1. On the **Reservoir T/P** tab, enter the reservoir temperature and saturation pressure. 2. Check **Bubble point data**, and then enter the available data points. **Note:** Using the reservoir condition, based on the screening procedure suggested by de Boer et al (SPE 24987, 1992), assumes that the asphaltene is nearly saturated at the reservoir condition.
Reservoir temperature and at least one bubble point.	1. On the **Reservoir T/P** tab, enter the reservoir temperature. 2. Check **Bubble point data**, and then enter the available data points.
At least one bubble point.	1. Check **Bubble point data**, and then enter the available data points. If more than one bubble point is entered, only the first one is used to estimate the reservoir conditions. Multiflash assumes that the reservoir temperature is the same as the bubble point temperature, and estimates the reservoir pressure as 2.5 times that of the bubble point.

4. Click **Match**.
5. In the Match Asphaltene Data message, click **OK**.

Result: Multiflash displays a plot of the matched data.

To see the effect of the different levels of data used to tune the asphaltene model, see *Looking at the effect of input data on the asphaltene model*.

Note: If all the three asphaltene data sets mentioned above are available, the most adequate data would be the AOP data, followed by the titration data and finally the reservoir conditions. Only the data used for matching is saved in the .mfl file after matching.

» Tuning with incomplete titration data

Looking at the effect of input data on the asphaltene model

Problem:

What is the effect on asphaltene calculations of different levels of experimental data?

Approach:

1. Define and characterise your fluid.
2. Using the match asphaltene data tool, enter bubble point data to tune the pseudocomponent properties, and plot the asphaltene phase envelope (APE) to see the default parameter boundary.
3. Enter some experimental data and use the match asphaltene data tool.

4. Plot the APE.
5. Repeat steps 3 and 4 for different levels of experimental data.
6. Compare the phase boundaries.

The example compares the effect on the APE of the following types of asphaltene data:

- Reservoir conditions (pressure and temperature).
- Asphaltene upper onset data at two different temperatures.

For advice on coping with incomplete data, see *Tuning the asphaltene model*.

For the following example, use the file asphex.mfl to ensure that you can reproduce the plots.

Try it yourself:

1. On the **File** menu, click **Open**, and open the file asphex.mfl.
2. On the **Fluid** ribbon, click **PVT Analysis**.
3. Click **Do characterization**, and then click **OK** on the message.
4. On the **Asphaltenes** ribbon, click 

.
5. On the dialog box, check **Bubble point data**, and enter the values shown in the table.

Temperature (°F)	Pressure (psi)
48	2105
120	2640
150	2825
180	2980
210	3120
241	3235

6. Click **Match**, click **OK** on the message, close the matching plot, and then click **Close**.

   Result: The pseudocomponent properties are adjusted to fit the bubble point data, and in the absence of asphaltene data, Multiflash estimates a reservoir condition and uses that to adjust the asphaltene model parameters.

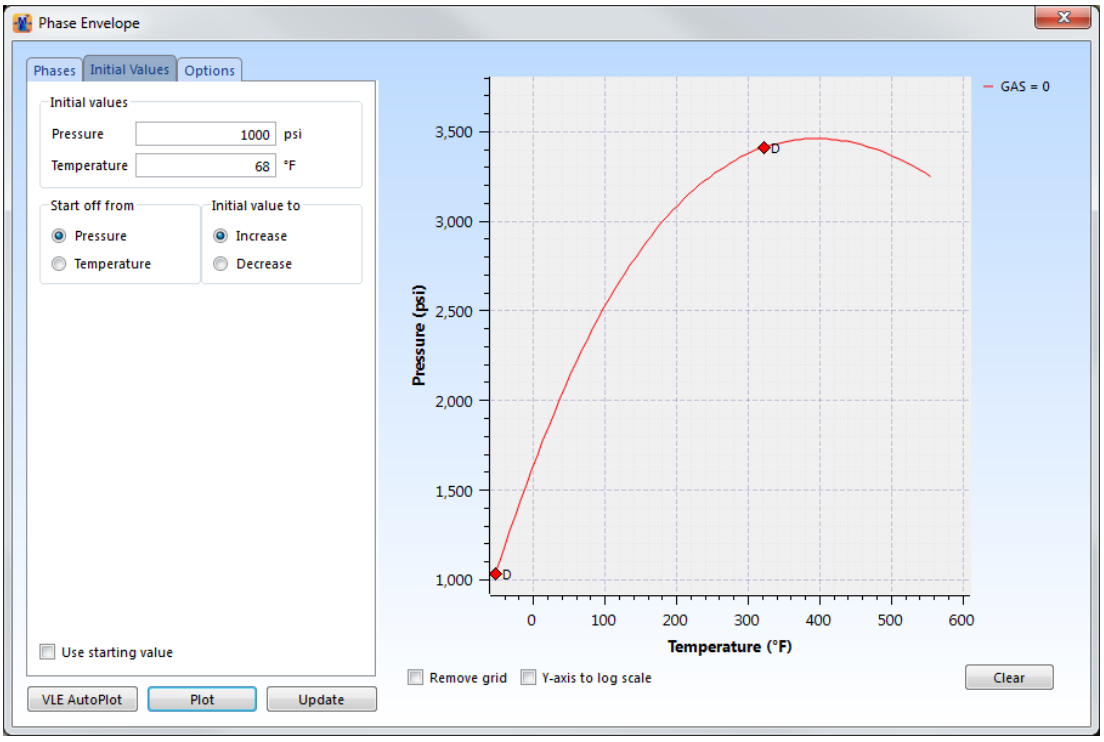
7. On the **Home** ribbon, click 

.
8. To identify a starting point for the APE, generate the bubble point line by entering the data shown in the table, and then clicking **Plot**.

   Rationale: Points on the phase envelope that are labelled D identify a point of discontinuity, and represent a point of overlap with another phase envelope. In this case, the APE crosses the bubble point line, and provides a starting point for the APE calculation.

Alternative: To identify if a particular region has an asphaltene phase,right click on the plot and perform a PT flash. The results area lists all phases which are present at these conditions. If an asphaltene phase is present, you can use the flash pressure as a starting point.

Phase tab			Initial values tab	
Item	**Value**		**Item**	**Value**
Type of solution	Normal		Pressure	1000
Select Phase	Gas		Start off from	Pressure
Select Basis	Mole Fraction		Initial value to	Increase
Enter phase fraction	0			

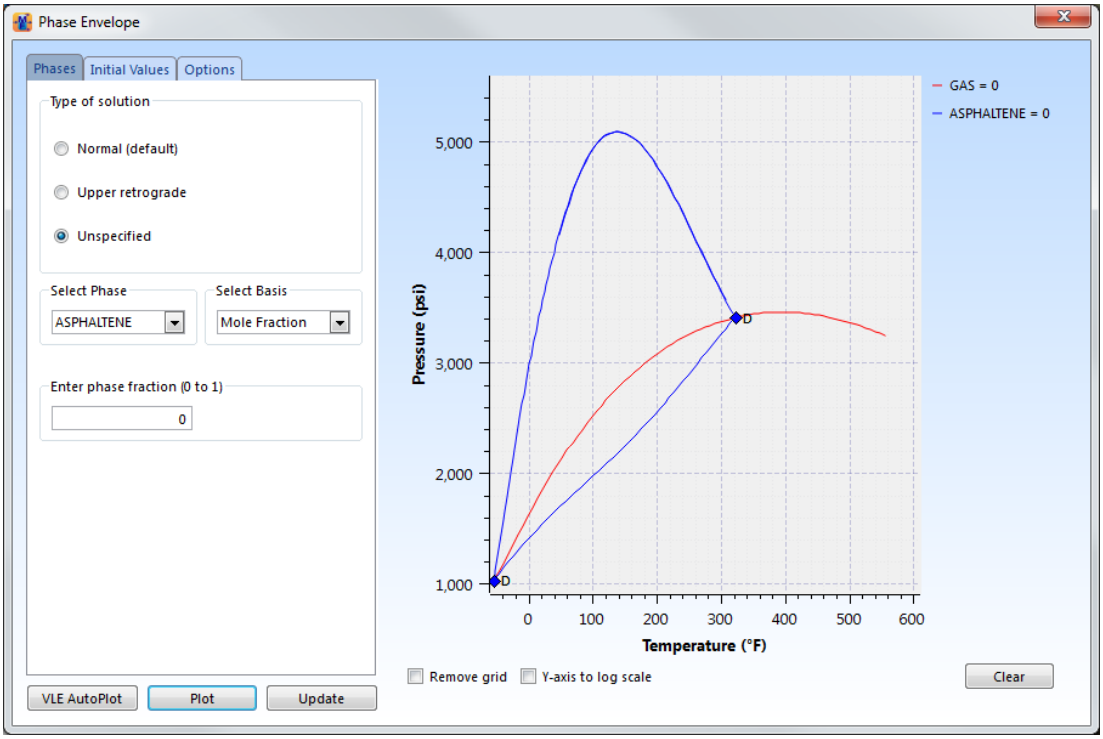


Result: The discontinuity for our example is about 3500 psi.

9. To plot the APE, modify the items shown in the table, and then click **Plot**.

   Note: Multiflash asks if you want more points to be plotted. Click **Yes**, until the asphaltene boundary becomes complete.

Phase tab			Initial values tab	
Item	**Value**		**Item**	**Value**
Type of solution	Unspecified		Pressure	3500
Select Phase	Asphaltene			



Result: The APE is shown in blue.

10. Close the plot window.

    Do not click **Clear**; you will compare further plots.

11. On the **Asphaltenes** ribbon, click 

.

12. On the **Reservoir T/P** tab, enter the reservoir conditions shown in the table.

Temperature (°F)	Pressure (psi)
241	8500

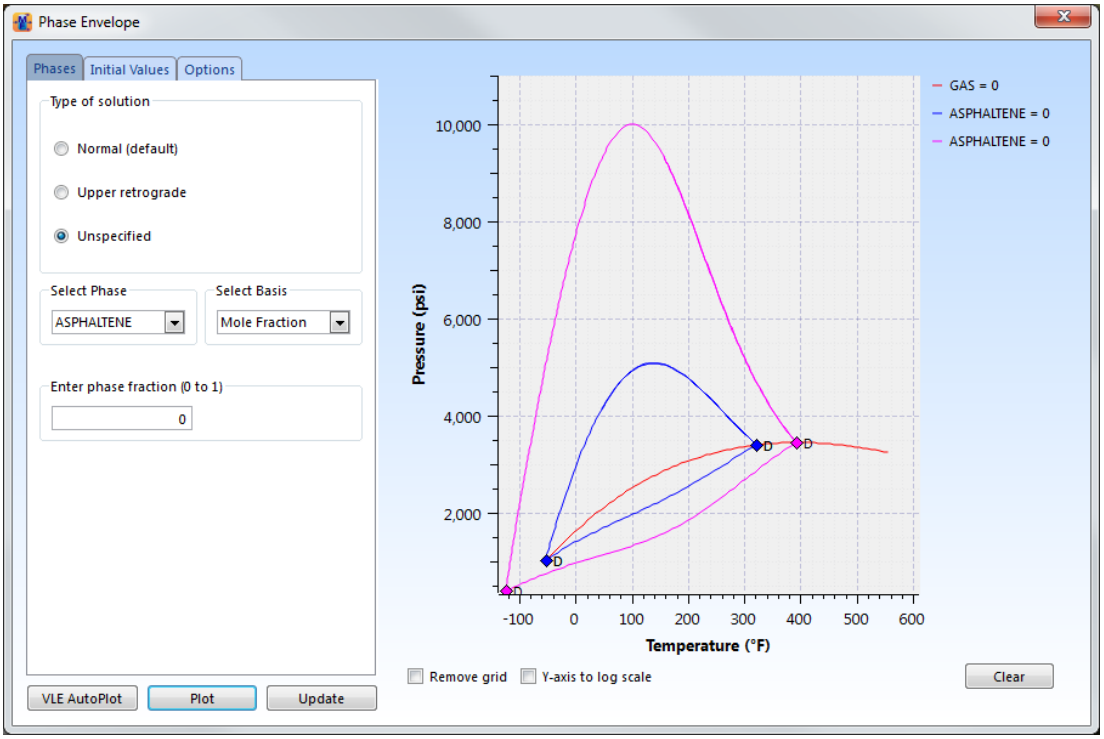
13. Click **Match**, click **OK** on the message, close the matching plot, and then click **Close**.

    Result: The pseudocomponent properties are adjusted to fit the existing bubble point data, and the reservoir condition is used to adjust the asphaltene model parameters.

14. On the **Home** ribbon, click 

, and then click **Plot**.

    Note: Multiflash asks if you want more points to be plotted. Click **Yes**, until the asphaltene boundary becomes complete.



Result: By taking into account the specific reservoir conditions, Multiflash makes a conservative prediction of the APE (pink line) in comparison to that predicted by the bubble point data (blue line).

15. Close the plot window.

    Do not click **Clear**; you will compare further plots.

16. On the **Asphaltenes** ribbon, click 

.

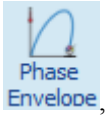
17. On the **AOP Data** tab, enter the onset data shown in the table.

Temperature (°F)	Pressure (psi)
241	6921
120	9150

18. Click **Match**, click **OK** on the message, close the matching plot, and then click **Close**.

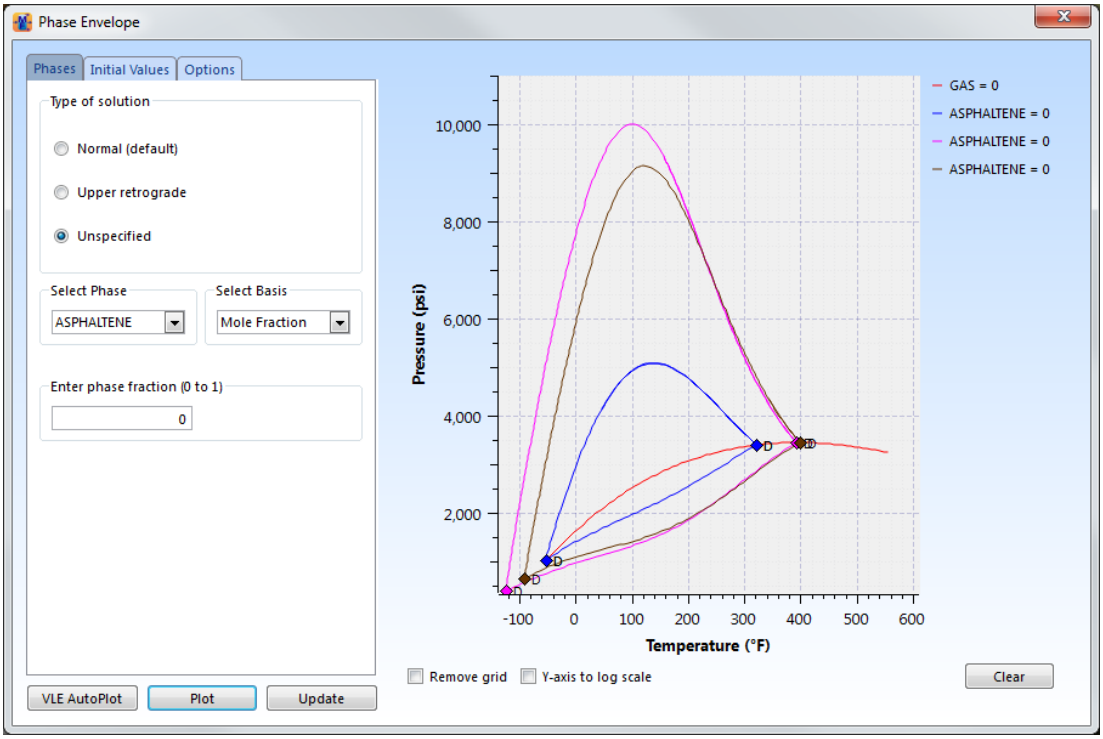
    Note: When you have entered data on more than one of the tabs, the data used for matching is taken from the tab that is currently visible.

    Result: The pseudocomponent properties are adjusted to fit the existing bubble point data, and the AOP data is used to adjust the asphaltene model parameters.

19. On the **Home** ribbon, click 

, and then click **Plot**.

    Note: Multiflash asks if you want more points to be plotted. Click **Yes**, until the asphaltene boundary becomes complete.



Result: By using comprehensive AOP and bubble point data, Multiflash produces the most robust estimation of the APE (brown line). It is less conservative than the APE implied by the reservoir conditions (pink line), yet not as liberal as the one derived from bubble point data alone (blue line).

20. Close the plot window.

FAQ:

Anything to add here?

What else can I do?

1. You can explore how robust the calculation is, for example by looking at one or more of these situations:
   - Substitute one of the AOP data points by the reservoir condition, to see the effect of having only one AOP point.
   - Compare the calculations that you have just done with the equivalent calculation, using just one bubble point to tune the pseudocomponent properties.
   - Repeat the calculations with no bubble point data, to see the effect of using the default pseudocomponent properties.
2. Explore the effect of different levels of SARA analysis, by doing the following two comparison characterizations, and then plotting the APE as before:
   - Remove all SARA analysis values from your fluid, except for the asphaltene value, and check **Estmate RA**. Multiflash estimates the wt% of asphaltene, and calculates the resin to asphaltene ratio.
   - Remove all SARA analysis values from your fluid, and check **Estmate RA**. Multiflash estimates the asphaltene content and calculates the resin to asphaltene ratio.
3. Look at the effect of including n-paraffin pseudocomponents, see *Looking at the effect of n-paraffins on the asphaltene model*.

Looking at the effect of n-paraffins on the asphaltene model

Problem:

What is the effect on asphaltene calculations of including n-paraffin pseudocomponents in the fluid characterization?

Approach:

1. Define and characterize your fluid without n-paraffins.
2. Using the match asphaltene data tool, enter bubble point data to tune the pseudocomponent properties, and plot the asphaltene phase envelope (APE).
3. Recharacterize the fluid with n-paraffins and repeat the steps to plot the APE.

Try it yourself:

1. On the **File** menu, click **Open**, and open the file asphex.mfl.
2. On the **Fluid** ribbon, click **PVT Analysis**.
3. Click **Do characterization**, and then click **OK** on the message.
4. On the **Asphaltenes** ribbon, click 

.
5. On the dialog box, check **Bubble point data**, and enter the values shown in the table.

Temperature (°F)	Pressure (psi)
48	2105
120	2640
150	2825
180	2980
210	3120
241	3235

6. Click **Match**, click **OK** on the message, close the matching plot, and then click **Close**.

   Result: The pseudocomponent properties are adjusted to fit the bubble point data, and in the absence of asphaltene data, Multiflash estimates a reservoir condition and uses that to adjust the asphaltene model parameters.

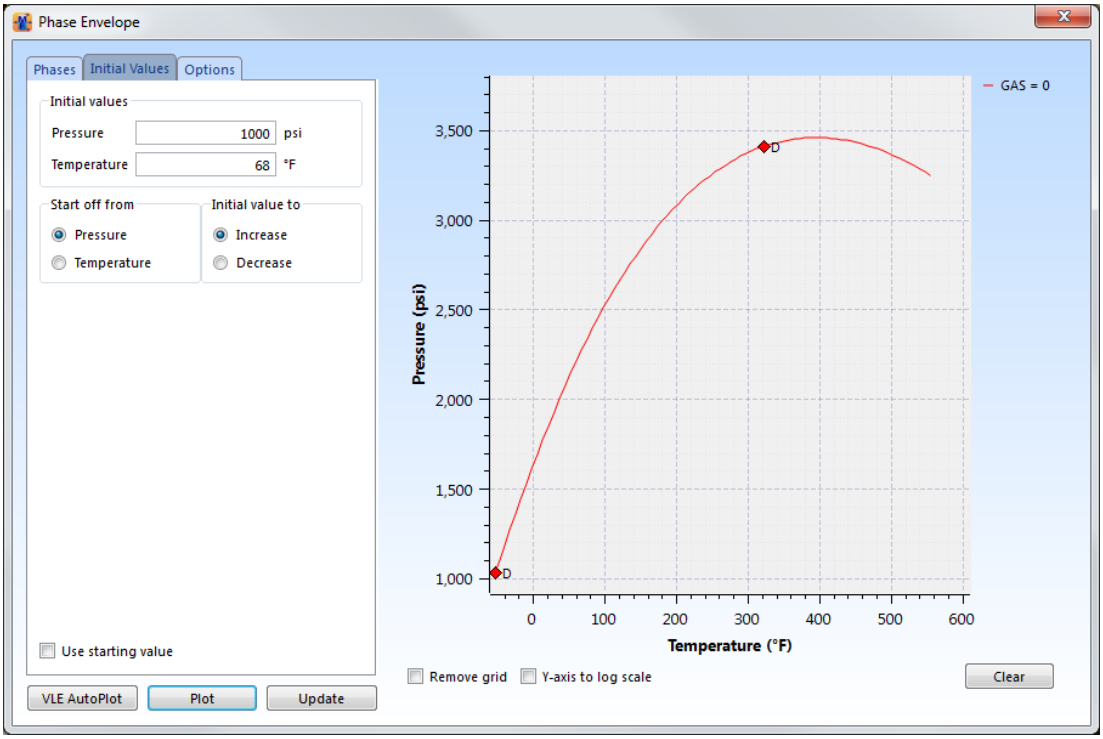
7. On the **Home** ribbon, click 

.
8. To identify a starting point for the APE, generate the bubble point line by entering the data shown in the table, and then clicking **Plot**.

Rationale: Points on the phase envelope that are labelled D identify a point of discontinuity, and represent a point of overlap with another phase envelope. In this case, the APE crosses the bubble point line, and provides a starting point for the APE calculation.

Alternative: To identify if a particular region has an asphaltene phase,right click on the plot and perform a PT flash. The results area lists all phases which are present at these conditions. If an asphaltene phase is present, you can use the flash pressure as a starting point.

Phase tab			Initial values tab	
Item	**Value**		**Item**	**Value**
Type of solution	Normal		Pressure	1000
Select Phase	Gas		Start off from	Pressure
Select Basis	Mole Fraction		Initial value to	Increase
Enter phase fraction	0			



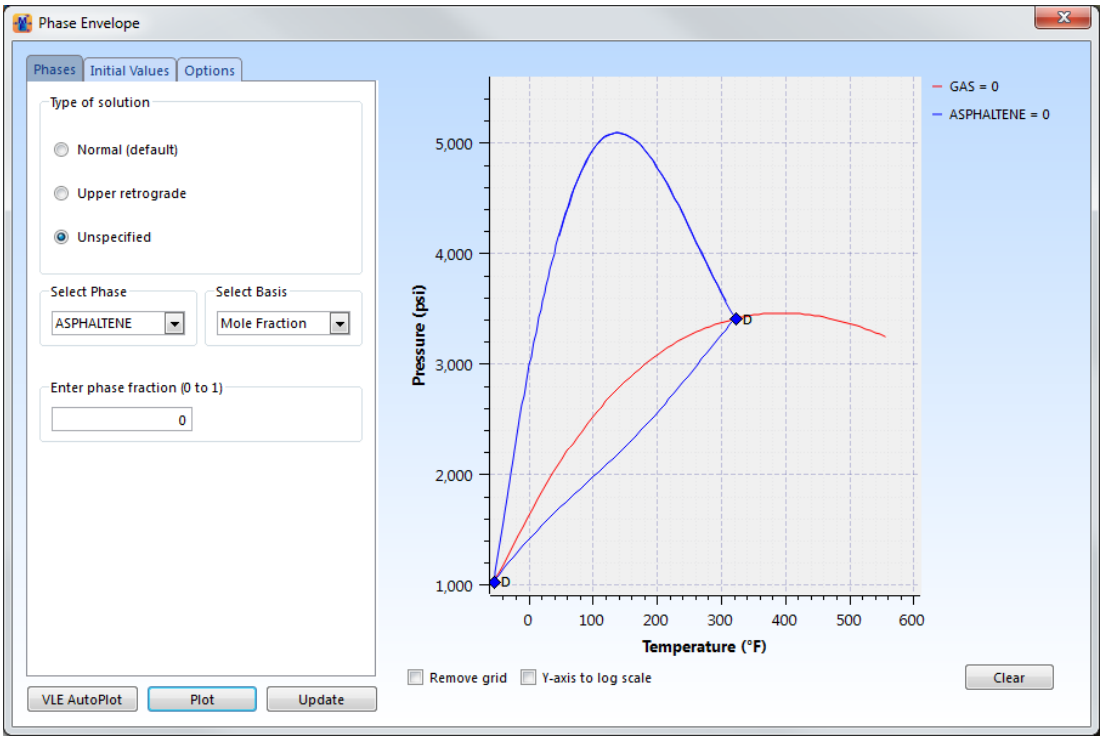
Result: The discontinuity for our example is about 3500 psi.

9. To plot the APE, modify the items shown in the table, and then click **Plot**.

Note: Multiflash asks if you want more points to be plotted. Click **Yes**, until the asphaltene boundary becomes complete.

Phase tab			Initial values tab	
Item	**Value**		**Item**	**Value**
Type of solution	Unspecified		Pressure	3500

Phase tab			Initial values tab	
Select Phase	Asphaltene			



Result: The APE is shown in blue.

10. Close the plot window.

    Do not click **Clear**; you will compare further plots.

11. On the **Fluid** ribbon, click **PVT Analysis**.
12. Check **Estimate wax content**.
13. For the N-paraffin pseudocomponents, enter the values shown in the table.

Item	Value
Distribution start	N6
Pseudocomponents required	15

14. Click **Do characterization**.
15. On the **Asphaltenes** ribbon, click 

.
16. Click **Match**, click **OK** on the message, close the matching plot, and then click **Close**.

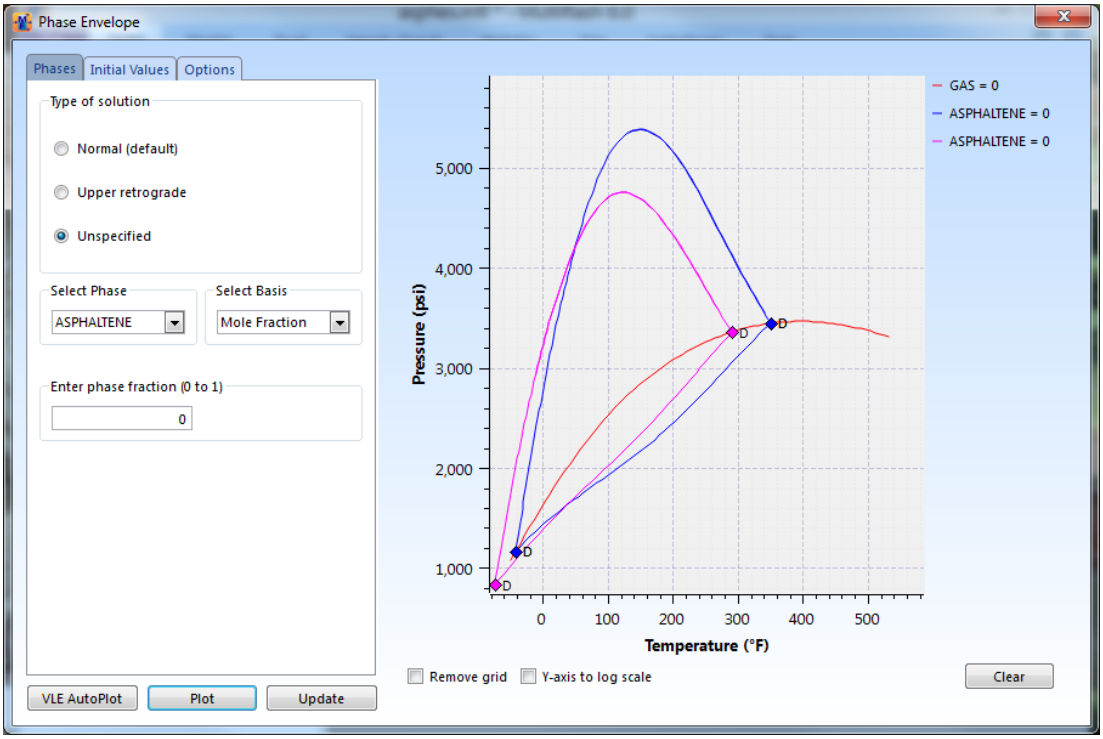
    Result: The pseudocomponent properties are adjusted to fit the existing bubble point data.

17. On the **Home** ribbon, click 

.

18. From the **Select Phase** list, choose Asphaltenes, and then click **Plot**.

    Note: Multiflash asks if you want more points to be plotted. Click **Yes**, until the asphaltene boundary becomes complete.



    Result: The plot shows that the presence of n-paraffins shifts the APE slightly to lower temperature.

FAQ:

Anything to add here?

What else can I do?

1. Look at the effect of different levels of asphaltene data on the calculations, see *Looking at the effect of input data on the asphaltene model*.

Calculating asphaltene precipitation conditions

You can carry out asphaltene precipitation calculations after the asphaltene model has been tuned. You can use the full range of flash calculations available, such as:

- A PT flash calculation to see if, and how much, asphaltene is present under specific conditions.
- A fixed phase flash calculation to find the pressure at which asphaltene will start to precipitate at any given temperature, or the temperature at which asphaltene will start to precipitate at any given pressure.

However, a direct way to visualise asphaltene precipitation as a function of pressure is to use the asphaltene precipitation curve tool.

For the following example, use the file asphexBP.mfl to ensure that you can reproduce the plots.

To plot the asphaltene precipitation curve:

1. On the **File** menu, click **Open**, and open the file asphexBP.mfl.

   This file is the asphex.mfl file after tuning the asphaltene model with bubble point data.

   #### Show me what you did to the asphex file:

   1. On the **Fluid** ribbon, click **PVT Analysis**.
   2. Click **Do characterization**, and then click **OK** on the message.
   3. On the **Asphaltenes** ribbon, click 

.
   4. On the dialog box, check **Bubble point data**, and enter the values shown in the table.

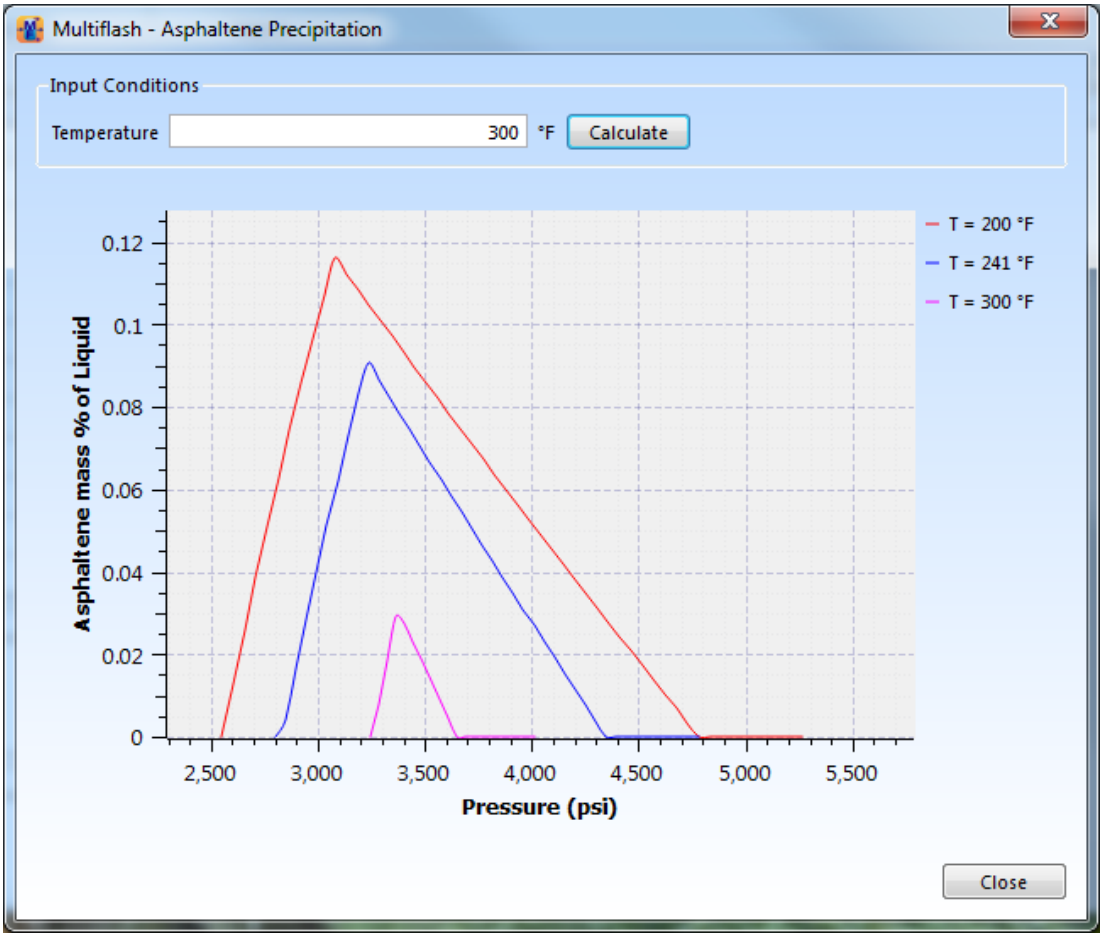
Temperature (°F)	Pressure (psi)
48	2105
120	2640
150	2825
180	2980
210	3120
241	3235

   5. Click **Match**, click **OK** on the message, close the matching plot, and then click **Close**.

      Result: The pseudocomponent properties are adjusted to fit the bubble point data, and in the absence of asphaltene data, Multiflash estimates a reservoir condition and uses that to adjust the asphaltene model parameters.

2. Click 

.
3. Enter each of the following temperatures in turn, and click **Calculate**:
   - 200
   - 241
   - 300



Tip: You can use the 

tool to find the upper pressure limit of precipitation at a specific temperature. To do so, enter the temperature in the **Conditions** area, and then click 

. The calculated pressure appears in the **Results** area. For example, entering 241 °F gives the result 4347.67 psi for the system used in this procedure.

Calculations with no asphaltene precipitation data

If you are starting from the position where you have no information on specific precipitation conditions, you should use the phase boundary plot to get an overall picture. Under these circumstances, it can be difficult to find convergence or even starting values. We recommend that you follow the procedure below to maximise your chances of producing a plot. The procedure is illustrated using the asphexBP.mfl file.

Alternative: For other fluids, you might need to set the pressure to decrease or to plot the upper and lower boundaries separately, or specify temperature rather than pressure. The method for each of these is similar to the procedure shown. We have found asphaltene boundaries most difficult to plot for very light oils.

To plot the asphaltene phase boundary:

1. On the **File** menu, click **Open**, and open the file asphexBP.mfl.

   This file is the asphex.mfl file after tuning the asphaltene model with bubble point data.

   #### Show me what you did to the asphex file:

   1. On the **Fluid** ribbon, click **PVT Analysis**.
   2. Click **Do characterization**, and then click **OK** on the message.
   3. On the **Asphaltenes** ribbon, click 

.
   4. On the dialog box, check **Bubble point data**, and enter the values shown in the table.

Temperature (°F)	Pressure (psi)
48	2105
120	2640
150	2825
180	2980
210	3120
241	3235

   5. Click **Match**, click **OK** on the message, close the matching plot, and then click **Close**.

      Result: The pseudocomponent properties are adjusted to fit the bubble point data, and in the absence of asphaltene data, Multiflash estimates a reservoir condition and uses that to adjust the asphaltene model parameters.

2. On the **Home** ribbon, click 

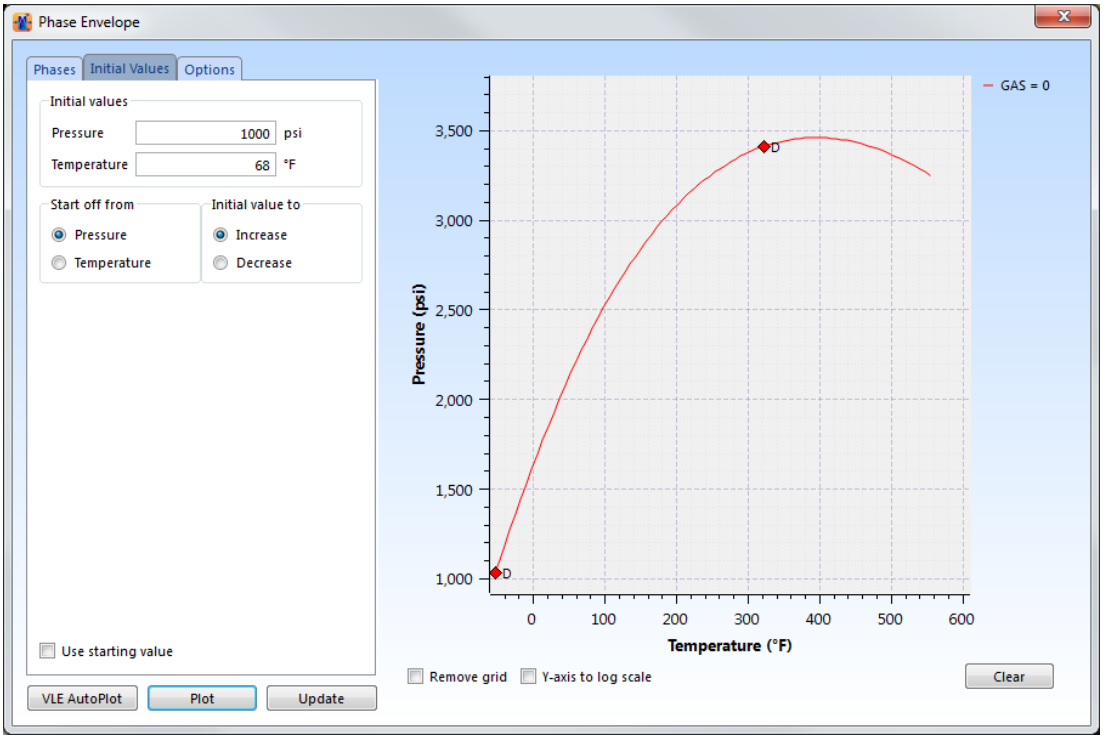
.
3. To identify a starting point for the APE, generate the bubble point line by entering the data shown in the table, and then clicking **Plot**.

   Rationale: Points on the phase envelope that are labelled D identify a point of discontinuity, and represent a point of overlap with another phase envelope. In this case, the APE crosses the bubble point line, and provides a starting point for the APE calculation.

   Alternative: To identify if a particular region has an asphaltene phase,right click on the plot and perform a PT flash. The results area lists all phases which are present at these conditions. If an asphaltene phase is present, you can use the flash pressure as a starting point.

Phase tab			Initial values tab	
Item	**Value**		**Item**	**Value**
Type of solution	Normal		Pressure	1000
Select Phase	Gas		Start off from	Pressure

Phase tab			Initial values tab	
Select Basis	Mole Fraction		Initial value to	Increase
Enter phase fraction	0			

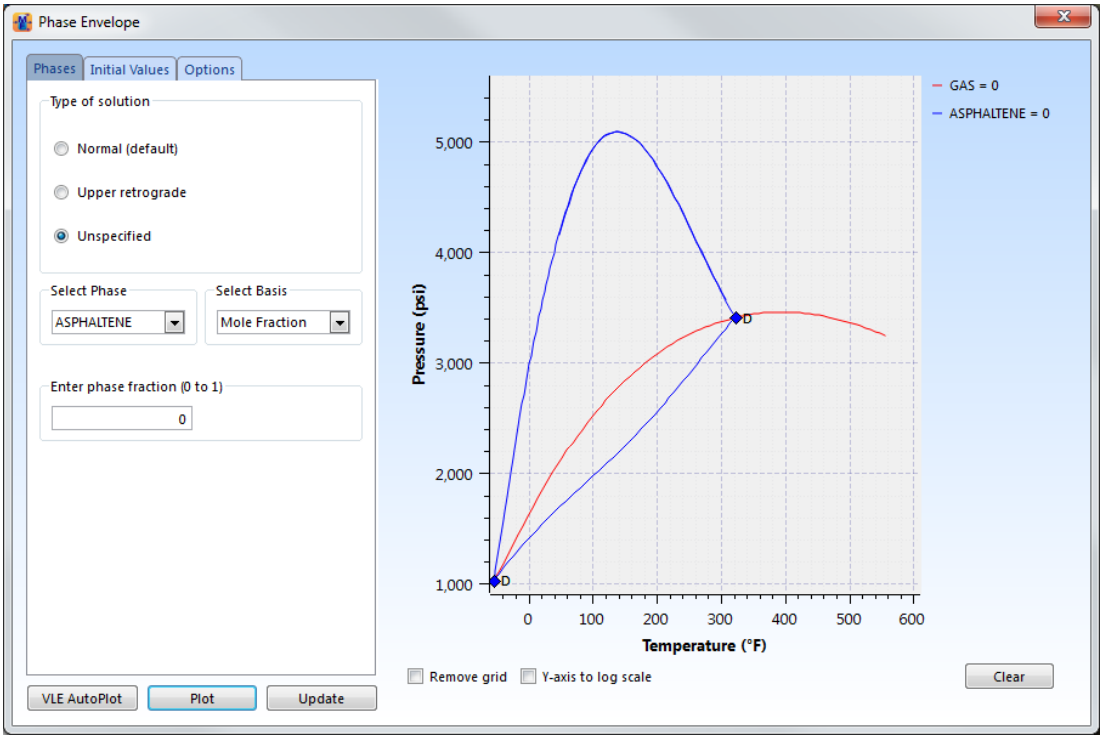


Result: The discontinuity for our example is about 3500 psi.

4. To plot the APE, modify the items shown in the table, and then click **Plot**.

Note: Multiflash asks if you want more points to be plotted. Click **Yes**, until the asphaltene boundary becomes complete.

Phase tab			Initial values tab	
Item	**Value**		**Item**	**Value**
Type of solution	Unspecified		Pressure	3500
Select Phase	Asphaltene			



Result: The APE is shown in blue.

5. Close the plot window.

Looking at the effect of gas injection

Problem:

How does the asphaltene phase envelope (APE) change when gas is injected into a reservoir?

Approach:

1. Characterize your fluid and tune the asphaltene model as usual.
2. Plot the APE to see the shape without gas injection.
3. Add gas to your fluid.

   Restriction: You must not use the PVT Analysis GOR option to add the injection gas to the reservoir fluid. Any re-characterisation resets the pseudocomponent properties and model parameters to the default values and, as you now have a different fluid, the values of bubble point and reservoir conditions used for matching are no longer valid.
4. Plot the APE again to see how the gas injection modifies the envelope.

Tip: If you have a complex injection gas and want to study the effect of different gas injection rates, then we suggest that you use an Excel spreadsheet, or use the blending procedure in Multiflash to blend the injection gas stream and the reservoir fluid.

For the following example, use the file asphmatch.mfl to ensure that you can reproduce the plots. This file contains an asphaltene fluid with the model parameters tuned using bubble points and the reservoir condition.

Try it yourself:

1. On the **File** menu, click **Open**, and open the file asphmatch.mfl.
2. On the **Home** ribbon, click 

.
3. Enter the data shown in the table.

   Rationale: These values are based on prior knowledge from *Looking at the effect of input data on the asphaltene model*. If you are using your own fluid, you should use values that result in a successful APE plot.

Phase tab			Initial values tab	
Item	**Value**		**Item**	**Value**
Type of solution	Unspecified		Pressure	3400
Select Phase	Asphaltene		Start off from	Pressure
Select Basis	Mole Fraction		Initial value to	Increase
Enter phase fraction	0			

4.
5. Click **Plot**.

   Note: Multiflash asks if you want more points to be plotted. Click **Yes**, until the asphaltene boundary becomes complete.

   Result: The APE with no added gas is displayed.
6. Close the plot window.

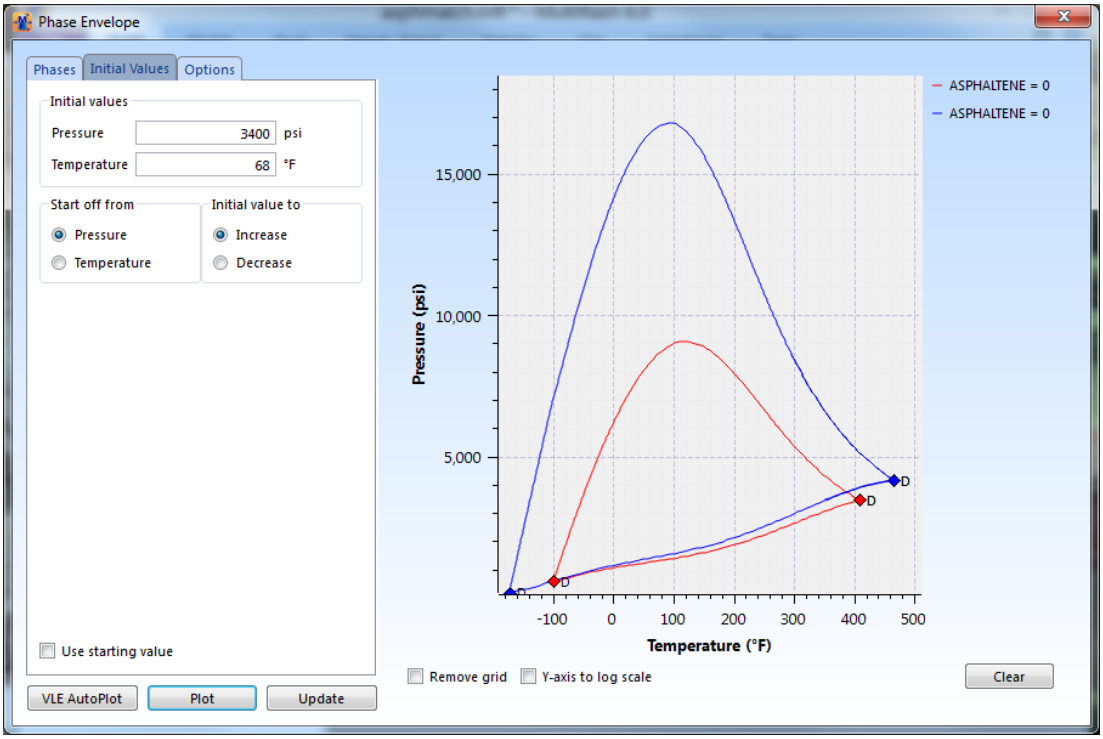
   Do not click **Clear**; you will compare the APE with another one.
7. On the Multiflash main window, change the amount of methane from 8.32 to 12.

   Note: For your own fluid, enter a suitable additional amount of gas.
8. On the **Home** ribbon, click 

.
9. Click **Plot**.

   Note: Multiflash asks if you want more points to be plotted. Click **Yes**, until the asphaltene boundary becomes complete.

   Result: The APE with added gas is plotted. The injected gas destabilises the asphaltene and hydrocarbon fluid. This results in the fluid bubble point line shifting to higher pressure and the APE expanding to reflect the wider range of temperature and pressure over which the asphaltene phase can appear.



What else can I do?

Use the blending procedure in Multiflash to blend the injection gas stream and the reservoir fluid. The reservoir fluid with bubblepoints matched and asphaltene model tuned should be selected for the model definition in the blending form, so that the asphaltene model parameters are based on the original reservoir fluid. To reproduce the above example, proceed as follows:

1. Create a .mfl file that contains only methane.
2. On the Blend Fluids tool, add the asphmatch.mfl file and your methane file.
3. Change the units to grams for both files, and enter the amount of 100 for asphmatch.mfl, and 3.68 for your methane file.
4. On the asphex.mfl line, check **Use Model**.
5. Click **Create Fluid**, to create the fluid.

   Note: If asphaltene precipitation data are available for the blended mixtures, the data should be matched after blending.
6. Now plot the asphaltene phase envelope.

   Result: The APE is the same as the injected gas APE in the procedure above.

Working with waxes

Waxes are complex mixtures of solid hydrocarbons that precipitate out of crude oils if the temperature is low enough. Under conditions of interest to the oil industry, waxes consist mainly of normal paraffins, with iso-paraffins and naphthenes also present. Waxes are thought to consist of many crystals, each of which is a solid solution of n-paraffins within a narrow range of molecular weight.

The wax appearance temperature (WAT), also called the cloud point, is the temperature at which wax crystals appear as the fluid is cooled at a specified pressure. An experimental measurement of the WAT requires a detectable, non-zero, amount of wax to be formed. The WAT is very sensitive to small amounts of heavy alkanes in the mixture, so very different WAT values can be obtained, depending on the criteria for detectability.

The two most common experimental techniques are Cross Polar Microscopy (CPM) and Differential Scanning Calorimetry (DSC). CPM is more sensitive than DSC and usually detects the presence of a smaller amount of wax. Hence the WAT measured by CPM is usually higher than the measurement by DSC. After reviewing the WAT measurements in our database, we have developed guidelines for detectability limits for the two techniques and these are included in the WAT calculator.

Recommendation: For calculations, use positive amounts of precipitated wax to identify the WAT, rather than the strict thermodynamic interpretation of zero percent, the onset of wax phase formation. The suggested default values are 0.045 wt% (0.015 mol%) for reproducing CPM measurements, and 0.3 wt% (0.1 mol%) for DSC. The wt% or mol% of wax is related to the oil plus wax phases.

Note: The WAT predicted by thermodynamic models, using 0 wt% of wax, should be higher than the measured value. A lower predicted temperature can indicate that the heavy n-paraffins are lost in the samples used for measuring the n-paraffins. In such a situation, you should check the wax content or the measured n-paraffin values. It must be emphasised that these figures are guidelines and might not apply in all cases.

A paper by *Erickson et al. SPE 26604, (1993)* compares the results of measuring WAT using three different experimental techniques. For twelve oils, where there were measurements made by at least two different techniques, there was only one case of complete agreement between two methods. Otherwise, the minimum difference between techniques was 8 ºF, the maximum difference was 55 ºF, and the average difference was 24 ºF. The accuracy of WAT measurements has improved in recent years, but WAT is still difficult to measure; it is realistic when assessing results to assume that experimental error in WAT values may amount to several degrees.

Recommendation: The best data for model validation and comparison are the measured amounts of wax precipitated at temperatures below the WAT, which together comprise the wax precipitation curve. Below the WAT, the measurements by different techniques are more consistent and reliable. A measurement close to the WAT requires a finite amount of precipitated wax to detect the WAT, which gives rise to uncertainty in the measurement.

Specifying the wax model

The Coutinho wax model is a solid solution model that requires information on the normal paraffins in the fluid. Predictions from the model are largely governed by the n-paraffin distribution. If no experimental data are available for the n-paraffin distribution, it can be estimated from the total wax content. If the n-paraffin distribution or wax content are unavailable, Multiflash uses an empirical correlation to estimate the total wax content, from which the n-paraffin distribution can be calculated.

Techniques for measuring the total wax content vary, but the total wax content used in the fluid characterization in Multiflash is equivalent to the total amount (in mass) of C20+ n-paraffins (relative to STO) that is determined using the industrial standard UOP Method 46.

Restriction: The n-paraffin distribution estimate is valid only for oils, not waxy condensates.

For most calculations, you do not need to specify the model manually. Instead, you can use the preconfigured model setup, by clicking 

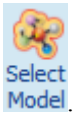
on the **Wax** ribbon.

If you want to use non-default options, you must specify the model manually.

To specify non-default options for the wax model:

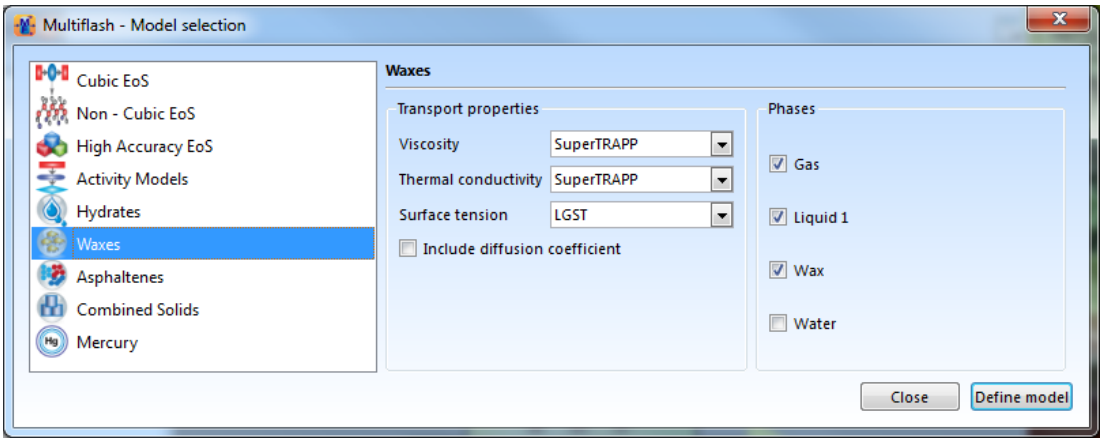
1. If you are using our example file, on the **File** menu, click **Open**, and open the file wax.mfl.

   Tip: By default, the example files are in the MFL Files folder of the Multiflash installation.

2. On the **Models** ribbon, select 

.

3. From the model list, select **Waxes**.



   The image shows the default settings for the wax model.

4. Modify the transport properties and included phases as required.
5. Click **Define Model**.
6. On the success message, click **OK**.
7. If you are using our example file, proceed to step 10.
8. On the **Fluid** ribbon, click **PVT Analysis**, and then enter your fluid components, amounts and properties, as described in *Defining a fluid using a PVT analysis*, ensuring that you enter the values shown in the table.

Item	Value
Pseudocomponents Normal fractions - Distribution start	C6
Pseudocomponents Normal fractions - Pseudocomponents required	15
Pseudocomponents N-Paraffins - Distribution start	N6

Item	Value
Pseudocomponents N-Paraffins - Pseudocomponents required	15
Molecular weight	Your experimental value, if available.
Specific gravity	Your experimental value, if available.
Total wax content	Your experimental value, if available. If you do not have a value, check **Estimate wax content**.

9. Click **Do characterization**, and then click **OK** on the message.

   Result: After successful characterization, your fluid composition changes to include the n-paraffin components, identified by an N prefix, for example, N16-19, and the non-n-paraffin pseudo-components, identified by an I prefix, for example, I6-22. The number after the prefix indicates the carbon number range for the pseudocomponent.

10. If you have experimental data for wax precipitation, tune your model, as described in *Tuning the wax model*.

Your model is now ready to use in wax calculations.

FAQ:

What is a good default for the number of n-paraffin pseudocomponents?

For wax appearance calculations, the exact distribution of n-paraffin components is not critical. In such cases, you would typically start the pseudocomponent distribution at N6 and use on the order of 10 pseudo components. For wax precipitation calculations, the distribution is critical, and you would start the pseudocomponent distribution at N90, with a single pseudocomponent. This ensures that every component below N90 is represented individually.

Tuning the wax model

After you have specified the model and characterized the fluid, as described in *Specifying the wax model*, you can tune the wax model, using available experimental data. Tuning the model works by adjusting the default melting temperature and enthalpy of fusion of the n-paraffin petroleum fractions to best fit the experimental data.

Recommendation: To reproduce experimental data, you should tune the model before performing any calculations.

Multiflash uses experimental data for the wax percentage at a stated temperature and pressure. The data can be any of the following:

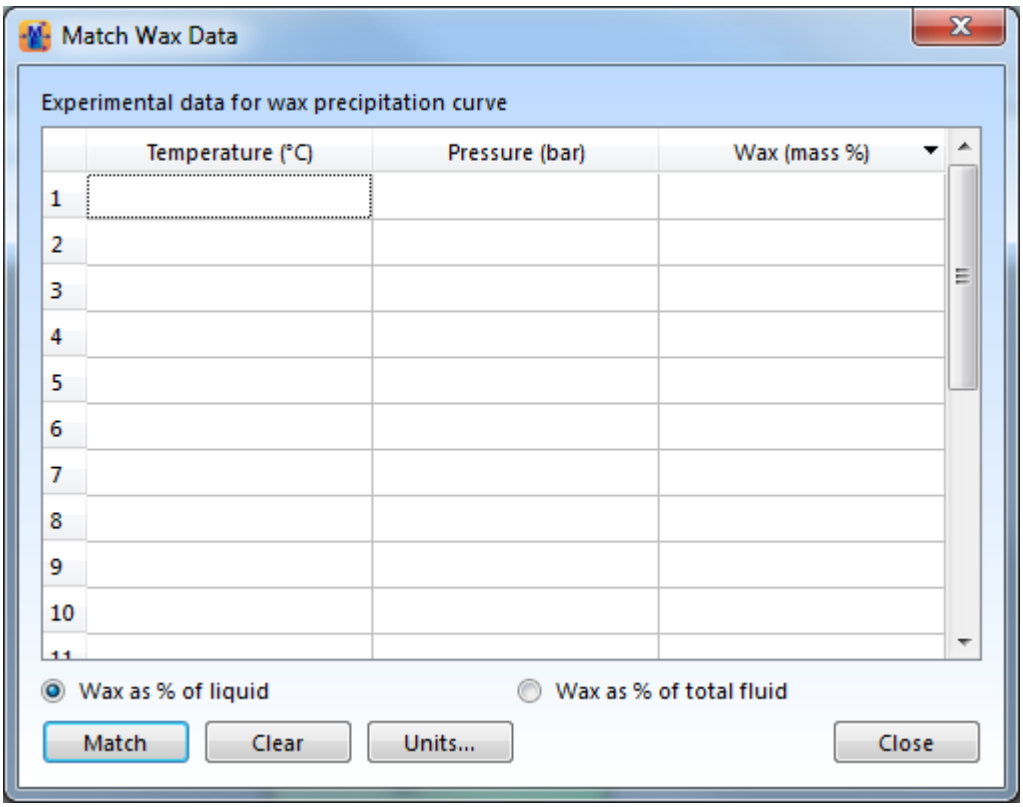
- A set of wax precipitation data at a fixed pressure or temperature.
- The wax appearance temperature (WAT).

Important: The two most common experimental techniques are Cross Polar Microscopy (CPM) and Differential Scanning Calorimetry (DSC). CPM is more sensitive than DSC and usually detects the presence of a smaller amount of wax. Hence the WAT measured by CPM is usually higher than the measurement by DSC.

To tune the wax model:

1. Ensure that you have characterized your fluid, as described in *Specifying the wax model*.
2. On the **Wax**ribbon, click 

.



3. Specify how your wax amount is expressed:
   - As percentage of liquid, usually for a dead oil.
   - As a percentage of total fluid, usually for a live oil.

   Tip: If you are entering WAT data with the amount of wax as zero, it does not matter which option you choose. The options are equivalent for a dead oil.
4. Enter your experimental data.

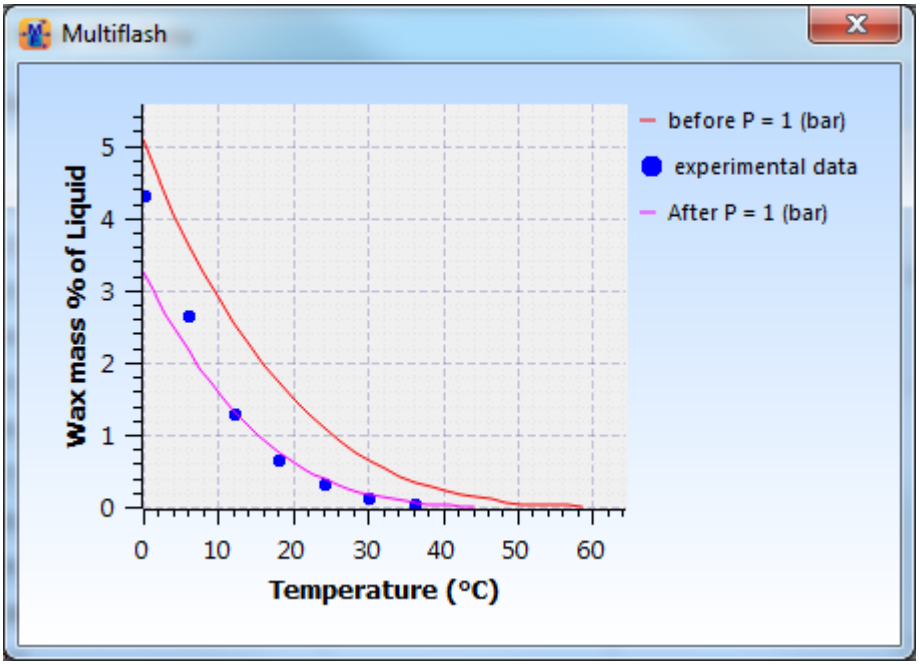
   Note: If you are using WAT data, you can give the amount of wax as zero mass (or mole) %. However, we recommend 0.045 mass% for CPM or 0.3 mass% for DSC.

   Recommendation: For calculations, use positive amounts of precipitated wax to identify the WAT, rather than the strict thermodynamic interpretation of zero percent, the onset of wax phase formation. The suggested default values are 0.045 wt% (0.015 mol%) for reproducing CPM measurements, and 0.3 wt% (0.1 mol%) for DSC. The wt% or mol% of wax is related to the oil plus wax phases.

   Note: The WAT predicted by thermodynamic models, using 0 wt% of wax, should be higher than the measured value. A lower predicted temperature can indicate that the heavy n-paraffins are lost in the samples used for measuring the n-paraffins. In such a situation, you should check the wax content or the measured n-paraffin values. It must be emphasised that these figures are guidelines and might not apply in all cases.

5. Click **Match**.

   Result: A plot of the experimental data appears, and the melting temperature and enthalpy of fusion of the n-paraffin petroleum fractions are modified.



6. Close the plot, and then click **Close**.
7. If you want to use the tuned model for calculations, save the file.

   Tip: Save the file with an appropriate name, so that you can identify it at a later date. You might want to save several tuned models to compare results. To reset the model to its pre-tuned state, recharacterize the fluid.

Calculating the wax appearance temperature

The calculation of the wax appearance temperature (WAT), also known as the cloud point, is an example of a fixed phase fraction flash. Multiflash provides a convenient method of performing the calculation.

Recommendation: For calculations, use positive amounts of precipitated wax to identify the WAT, rather than the strict thermodynamic interpretation of zero percent, the onset of wax phase formation. The suggested default values are 0.045 wt% (0.015 mol%) for reproducing CPM measurements, and 0.3 wt% (0.1 mol%) for DSC. The wt% or mol% of wax is related to the oil plus wax phases.

Note: The WAT predicted by thermodynamic models, using 0 wt% of wax, should be higher than the measured value. A lower predicted temperature can indicate that the heavy n-paraffins are lost in the samples used for measuring the n-paraffins. In such a situation, you should check the wax content or the measured n-paraffin values. It must be emphasised that these figures are guidelines and might not apply in all cases.

Requirement: You must have an n-paraffin distribution defined in your fluid before you can calculate a WAT.

In general, comparing predicted WATs with measured values is not straightforward, because there is uncertainty over how much wax is precipitated at the measured WAT. With a well-measured n-paraffin distribution, the wax model is purely predictive and can provide you with the thermodynamic upper boundary for the wax phase. However, when you want to reproduce the experimental data, you should tune the model before performing any calculations.

To calculate the wax appearance temperature:

1. In the **Conditions** area, enter the pressure at which you want to calculate the WAT.
2. On the **Wax** ribbon, click 

.
3. Choose a method for determining the WAT.

   Tip: The default wax percentage values for the CPM and DSC methods are a recommended start point if you have no available information. If you have experimental data, or want to experiment with the calculation to get improved results, use the user-defined option to provide alternative values.
4. If you are using the user-defined method, enter a value for the amount of precipitated wax to identify the WAT, and choose the units for the value.
5. Click **Calculate**.

What else can I do?

Use the file wax.mfl to practice the following suggestions. The file contains a fluid with a reported experimental WAT measured at 1 bar, based on two different measurement techniques.

1. Explore the effect of different tuning methods. Calculate the WAT with no tuning using zero wax, and with the recommended values for wax; tuning with zero wax at the experimental WAT; and tuning with the recommended values for wax at the experimental WAT. The results you should discover are tabulated below.

WAT origin	CPM method	DSC method
Experimental (ºC)	53	40
Calculated with no tuning and zero wax[1,2] (ºC)	58.6	58.6
Calculated with no tuning and default wax[3] (ºC)	49.5	37.7
Calculated with tuning and zero wax[1,4] (ºC)	62.5	61.4
Calculated with tuning and default wax[3,4] (ºC)	53	40

[1]Wax percentage of 0 used for WAT calculation.

[2]For this calculation, there is no distinction between CPM and DSC methods.

[3]Wax percentage of 0.045 wt% (0.015 mol%) for CPM WAT, and 0.3 wt% (0.1 mol%) for DSC WAT.

[4]CPM tuning on one point: 53 ºC, 1 atm, 0.045 wt% wax. DSC tuning on one point: 40 ºC, 1 atm, 0.3 wt% wax.

   From these results, you can see that the recommendation to use positive amounts of wax is justified. Without tuning, the default amount of wax in the WAT calculation differentiates between the different experimental values for the CPM and DSC methods, and provides a reasonable prediction of the WAT for each method. With tuning, the default amount of wax in the WAT calcu-

lation reproduces the experimental values perfectly, as expected, because you are tuning to the single measured point.

2. You can vary the n-paraffin distribution to explore the effect on the predicted WAT and the wax precipitation curves.

   One suggestion is to extend the heavy end of the n-paraffin distribution as far as possible, to establish a more comprehensive distribution and minimise grouping. You can do this by setting the start of the n-paraffin distribution to N90, and only splitting into 1 n-paraffin. If you do this, you are warned that the distribution has been extended as far as possible, and the highest n-paraffin will be lower than the N90 specified. In the case of the example file wax.mfl, the heaviest fraction is N76+.

   The WAT values are shown in the table.

WAT origin	CPM method	DSC method
Experimental WAT (ºC)	53	40
Calculated with no tuning and zero wax[1,2] (ºC)	58.4	58.4
Calculated with no tuning and default wax[3] (ºC)	46.4	35.1
Calculated with tuning and zero wax[1,4] (ºC)	66.5	65.6
Calculated with tuning and default wax[3,4] (ºC)	53	40

[1]Wax percentage of 0 used for WAT calculation.

[2]For this calculation, there is no distinction between CPM and DSC methods.

[3]Wax percentage of 0.045 wt% (0.015 mol%) for CPM WAT, and 0.3 wt% (0.1 mol%) for DSC WAT.

[4]CPM tuning on one point: 53 ºC, 1 atm, 0.045 wt% wax. DSC tuning on one point: 40 ºC, 1 atm, 0.3 wt% wax.

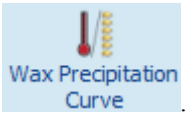
   Using the recommended wax percentage for both CPM and DSC, the predicted WATs for an untuned model are lower than the measured data, indicating that the percentage is only a rough guide for comparison. Extending the n-paraffin distribution does not necessarily increase the WAT, as there are competing effects from both the properties of the new heaviest n-paraffin and the solubility of the reduced amount of this fraction.

Calculating wax precipitation

As with other phases, the amount and composition of the wax phase are determined as part of any flash calculation. However, because of the uncertainty of the WAT from experimental techniques, and the sensitivity of WAT calculations to the characterisation of the heaviest fractions, a better picture of wax precipitation can be derived from a calculation of the wax precipitated as a function of temperature at a given pressure. Multiflash automates this calculation for you.

Requirement: You must have an n-paraffin distribution calculated defined in your fluid before you can calculate a wax precipitation curve.

To calculate the wax precipitation curve:

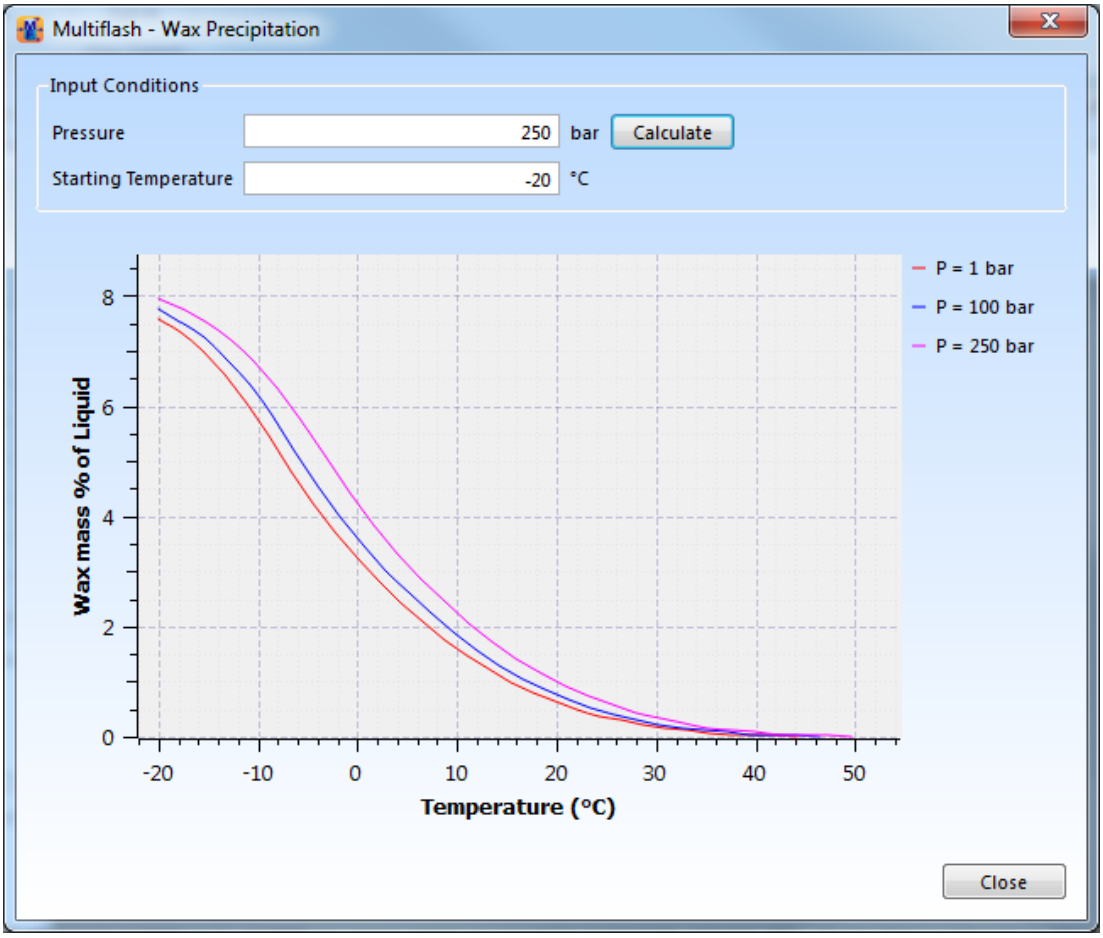
1. On the **Wax** ribbon, click 

.
2. Enter the pressure at which you want to calculate the wax precipitation curve.
3. If required, enter a starting temperature.

   Tip: If you do not enter a temperature, the default start temperature is 0 °C. The end temperature is the calculated WAT for zero percent wax.
4. Click **Calculate**.
5. If required, repeat the calculation at additional pressures.

Example

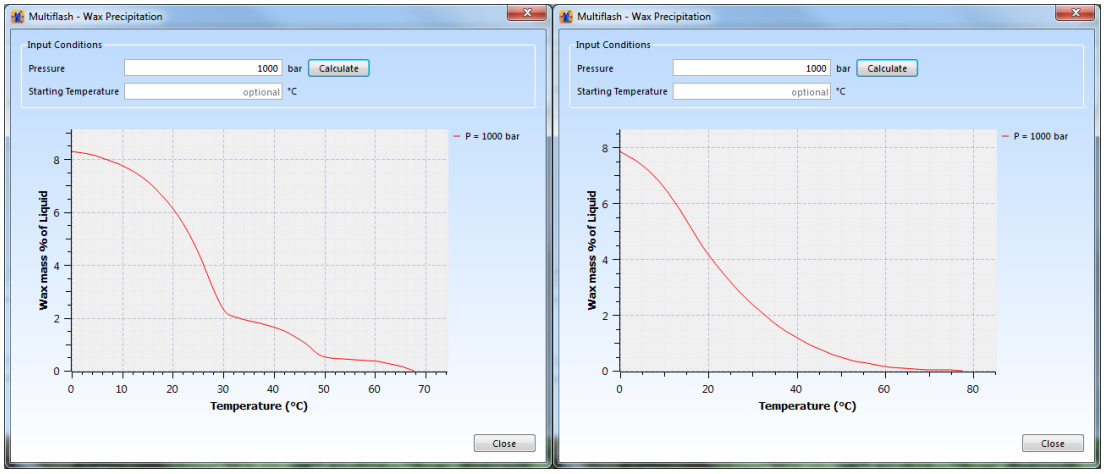
The wax precipitation curve below was generated using the file wax.mfl.



FAQ:

How can I evaluate how many pseudocomponents I need for calculating the wax precipitation curve?

The most effective way to evaluate the number of pseudocomponents is to look at the calculated wax precipitation curve and make sure the physical behaviour is correct. The curve should be continuous, with a gradual decay. For example, in the following plots, the left hand plot was done after characterizing starting at N6, with 4 pseudocomponents. You can see the curve is uneven. The right hand plot was done after characterizing starting at N6, with 16 pseudocomponents. The curve decays evenly.



Plotting the wax phase envelope

Problem:

What do I need to do to get a good wax phase envelope plot?

Approach:

1. Tune your model, if you have available experimental data.
2. In the phase envelope calculation, calculate a non-zero phase fraction to use that complements the technique used in the wax measurements used for tuning.

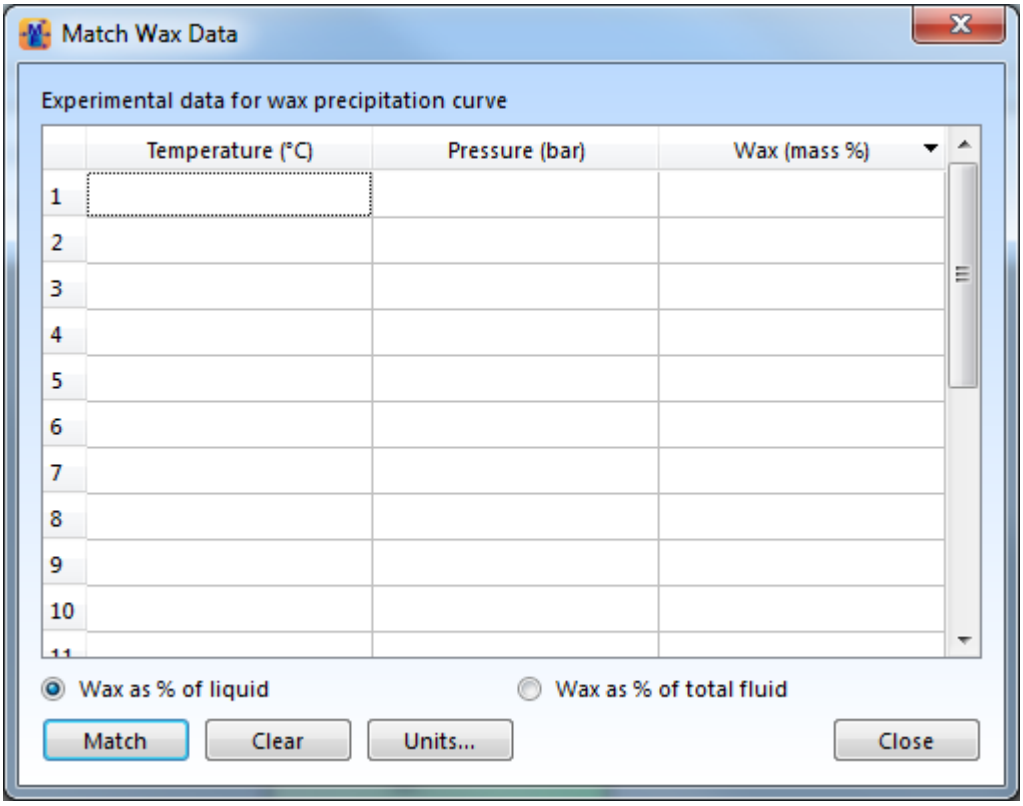
   Note: The non-zero phase fraction in the phase envelope plot is the wax % of the total fluid, not the % of liquid as it is in the WAT calculations for the CPM and DSC methods. Therefore, if the fluid has a gas phase, the wax % value must be adjusted to account for the total fluid, if this has not already been done, and then converted to a mass fraction by dividing by 100.

   Tip: For a live oil, the amount of wax is defined with respect to the total fluid, which varies with pressure. In such a case it can be better to choose a zero mass fraction for the plot.
3. Perform a phase envelope calculation in the usual way.

Try it yourself:

1. On the **File** menu, click **Open**, and open the file wax.mfl.
2. On the **Wax**ribbon, click 

.



3. Enter the experimental WAT data , as shown in the table, and then click **Match**.

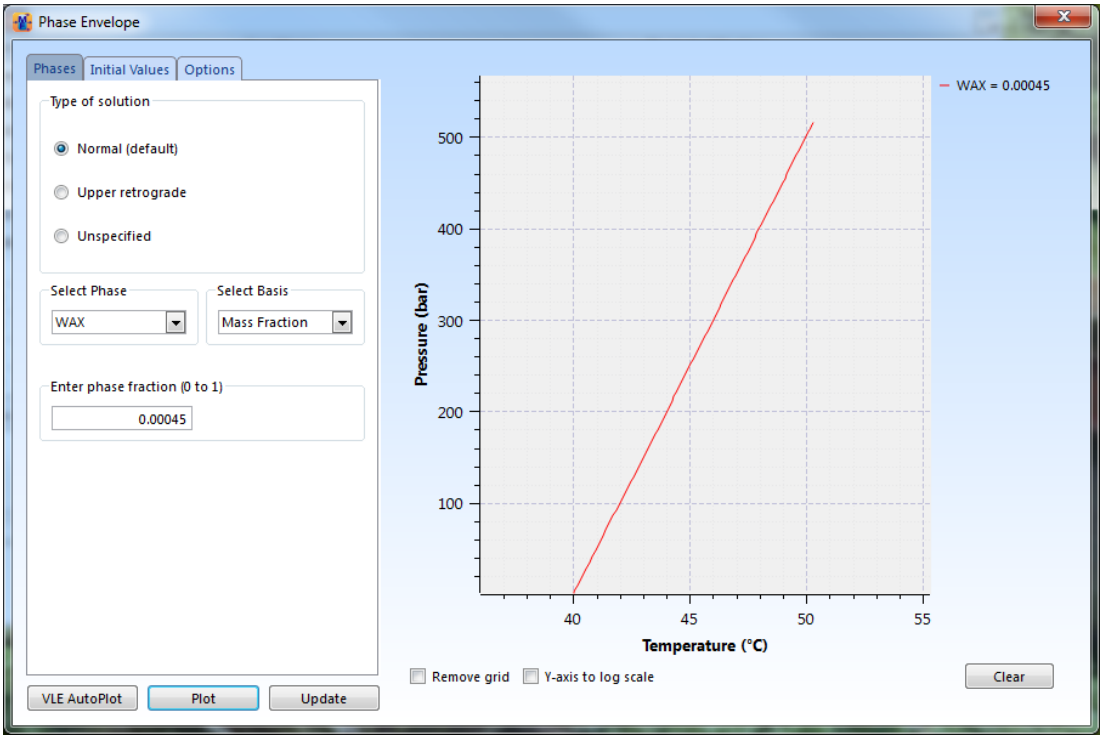
Temperature (°C)	Pressure (bar)	Fraction (mass %)
40	1	0.045*
*Experimental data measured using CPM.		

4. When the match plot appears, close the plot, and then click **Close**.
5. On the **Home** ribbon, click 

.
6. On the **Phases** tab, enter the phase details shown in the table, and then click **Plot**.

   Note: The phase fraction is 0.00045 because the fluid defined in wax.mfl is a dead oil, and the experimental data was a CPM measurement.

Select Phase	Select Basis	Enter phase fraction
Wax	Mass fraction	0.00045



You can see that the phase envelope for this dead oil is linear.

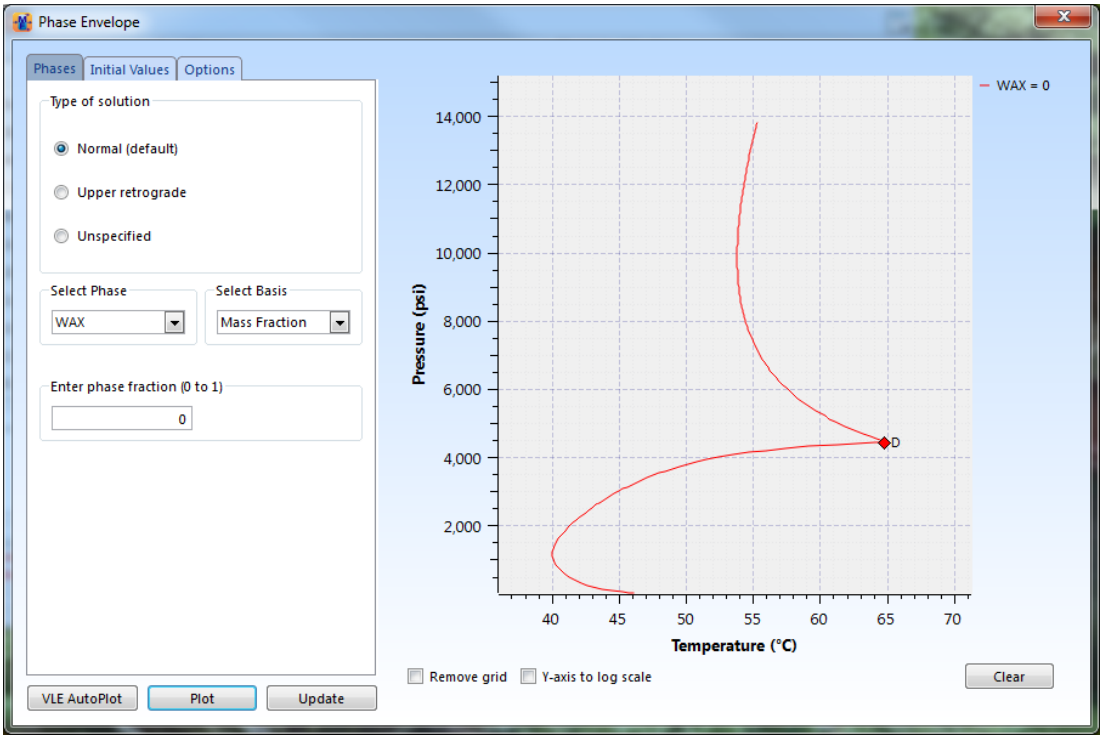
FAQ:

Anything to add here?

What else can I do?

1. Repeat the phase envelope plot, using the live oil example file waxycondensate.mfl and the data in the table.

Temperature (°C)	Pressure (bar)	Fraction (mass %)
0	1	4.33
6	1	2.657
12	1	1.296
18	1	0.657
24	1	0.336
30	1	0.143
36	1	0.045



The wax boundary for a live oil has a distinctly different shape. The D marks the point where the wax boundary crosses the bubble point line.

Working with mixed solids

For some fluids there is the possibility that hydrates, waxes and asphaltenes can form at the same time. The formation of any one will affect the overall composition of the fluid and therefore affect the formation of the other solids. Multiflash enables you to explore this possibility using the combined solids model.

The particular model options for each solid have been chosen to provide the best model whilst ensuring compatibility. The common fluid phase model is RKSA. The hydrate models use RKSAINFO as the fluid model, combined with the electrolyte salt model. The wax model is the Coutinho model and the asphaltene model is the standard Infochem model.

The combined solids option is only designed to look at solids formation. If you want to study more complex problems, such as hydrate inhibition, you should choose a dedicated model set appropriate to your problem.

Note: If you choose only a single type of solid phase in the combined solids option you are asked to use the model for that type of solid instead, for example, the hydrate model if only hydrate phases are chosen.

Looking at the effect of multiple solids formation

Problem:

What is the effect on asphaltene formation when other solids are also formed?

Approach:

1. Plot the APE of your asphaltene fluid, using the same strategy as in *Calculating asphaltene precipitation conditions*.
2. Add an n-paraffin distribution to your fluid and recharacterize it.
3. Change to the combined solids model and add a wax phase.
4. Match the modified model to the asphaltene data.
5. Plot the APE of your fluid again to see the effect of wax on the asphaltene phase.
6. Add hydrate phases to the model and match the modified model to the asphaltene data.
7. Plot the APE of your fluid again to see the effect of hydrates on the asphaltene phase.

The example input file is combsolid.mfl. This includes an oil composition to C20+, which has a molecular weight of 81, 12.04 wt% resin and 0.7 wt% asphaltene. The fluid is characterised from C6 with 15 fractions.

The asphaltene model parameters are already matched with a bubble point of 120 F and 2650 psia and an asphaltene precipitation point of 120 F and 8750 psia. The example file is therefore ready for the initial APE plot.

Try it yourself:

1. On the **File** menu, click **Open**, and open the file combsolid.mfl.
2. On the **Home** ribbon, click 

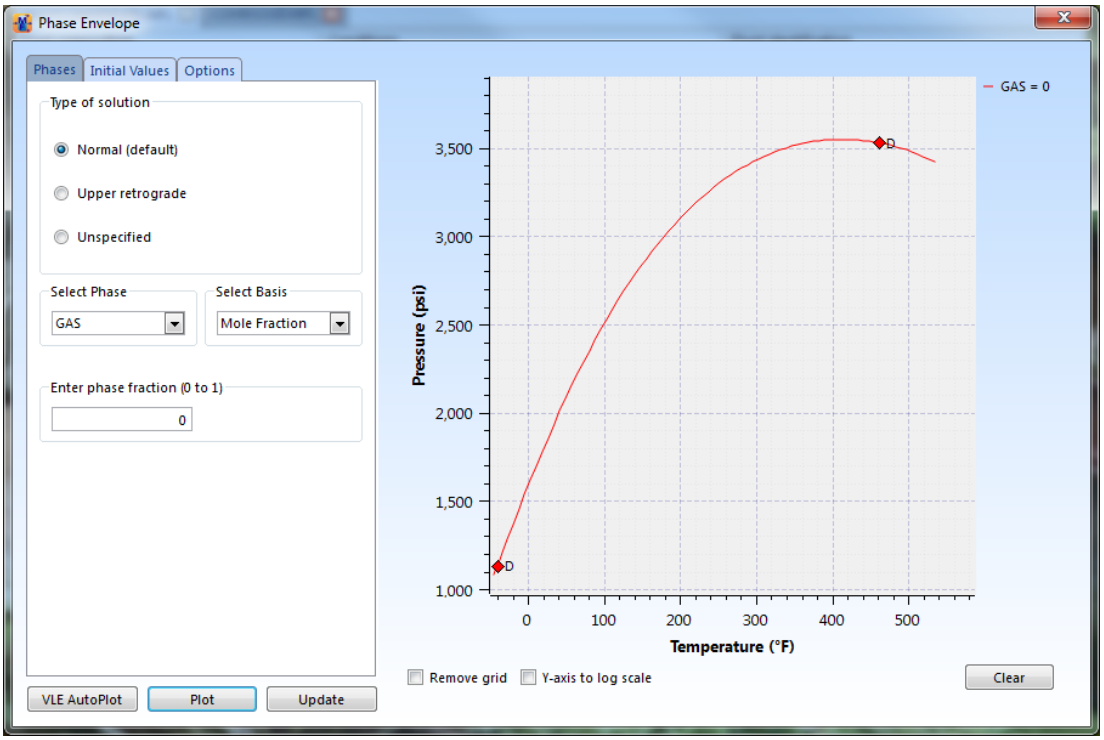
.
3. To identify a starting point for the APE, generate the bubble point line by entering the data

shown in the table, and then clicking **Plot**.

Rationale: Points on the phase envelope that are labelled D identify a point of discontinuity, and represent a point of overlap with another phase envelope. In this case, the APE crosses the bubble point line, and provides a starting point for the APE calculation.

Alternative: To identify if a particular region has an asphaltene phase,right click on the plot and perform a PT flash. The results area lists all phases which are present at these conditions. If an asphaltene phase is present, you can use the flash pressure as a starting point.

Phase tab			Initial values tab	
Item	**Value**		**Item**	**Value**
Type of solution	Normal		Pressure	1000
Select Phase	Gas		Start off from	Pressure
Select Basis	Mole Fraction		Initial value to	Increase
Enter phase fraction	0			



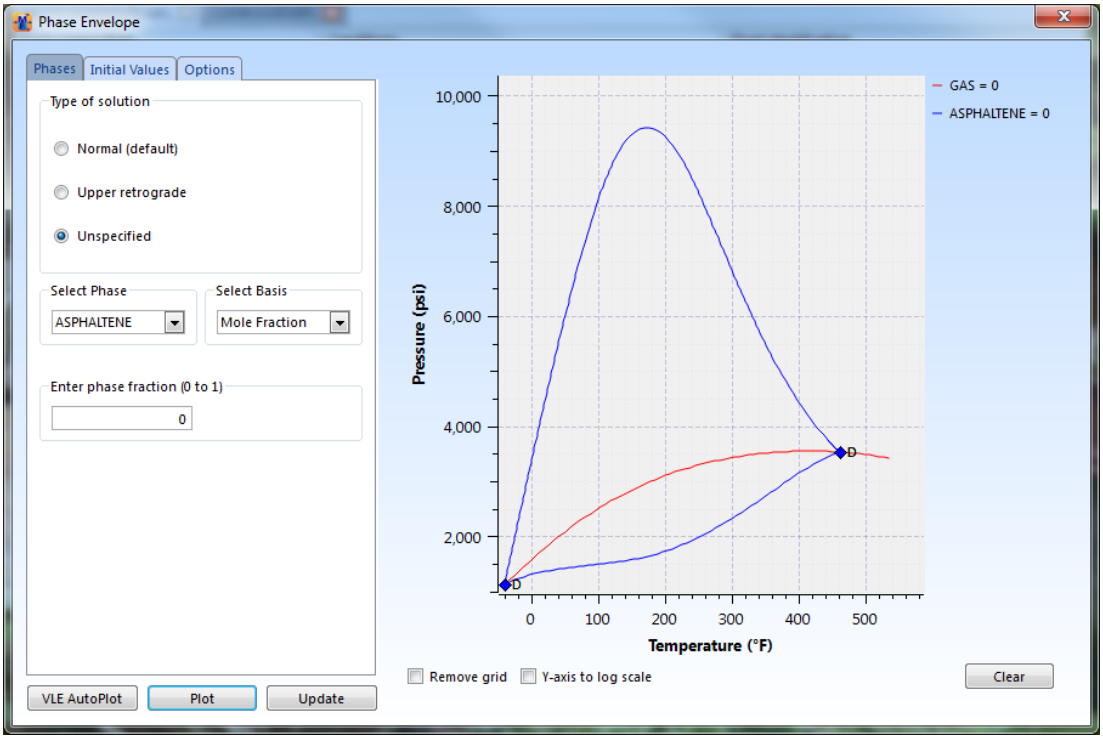
Result: The discontinuity for our example is about 3500 psi.

4. To plot the APE, modify the items shown in the table, and then click **Plot**.

   Note: Multiflash asks if you want more points to be plotted. Click **Yes**, until the asphaltene boundary becomes complete.

Phase tab			Initial values tab	
Item	**Value**		**Item**	**Value**

Phase tab			Initial values tab	
Type of solution	Unspecified		Pressure	3500
Select Phase	Asphaltene			



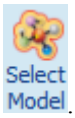
Result: The APE is shown in blue.

5. Close the plot window.

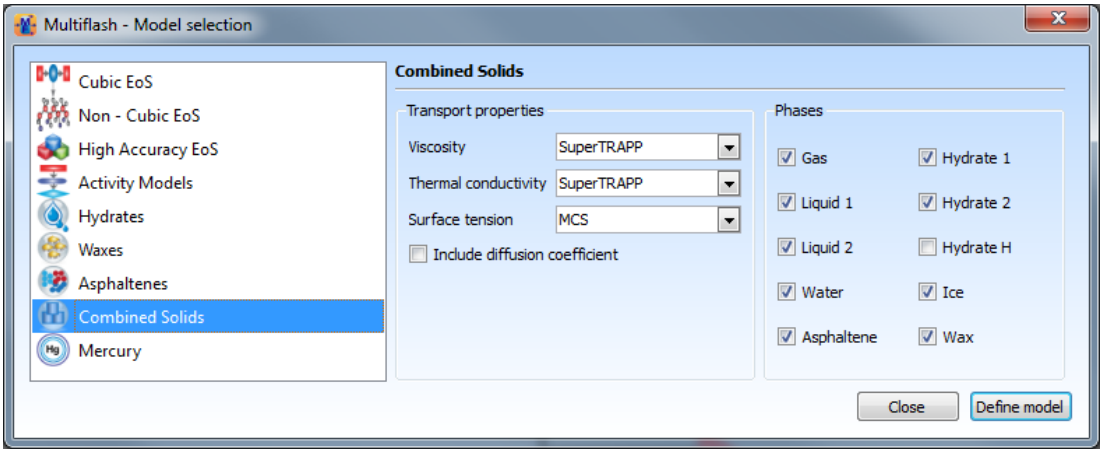
   Do not click **Clear**; you will compare further plots.

Calculate the APE with a wax phase present

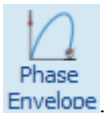
To see the effect of simultaneous wax and asphaltene precipitation, you must re-characterise the fluid with an n-paraffin distribution, in order to apply the Coutinho wax model. The following procedure continues from the previous one and covers steps 2 to 5 of the general approach outlined above.

1. On the **Fluid** ribbon, click **PVT Analysis**.
2. On the PVT Laboratory Fluid Analysis dialog box, check **Estimate wax content**.
3. In the **Pseudocomponents** panel, enter 15 for the number of n-paraffin pseudocomponents required, and then click **Do Characterization**.
4. Click **Close**.
5. On the **Models** ribbon, click 

.
6. From the Models list, select **Combined Solids**.



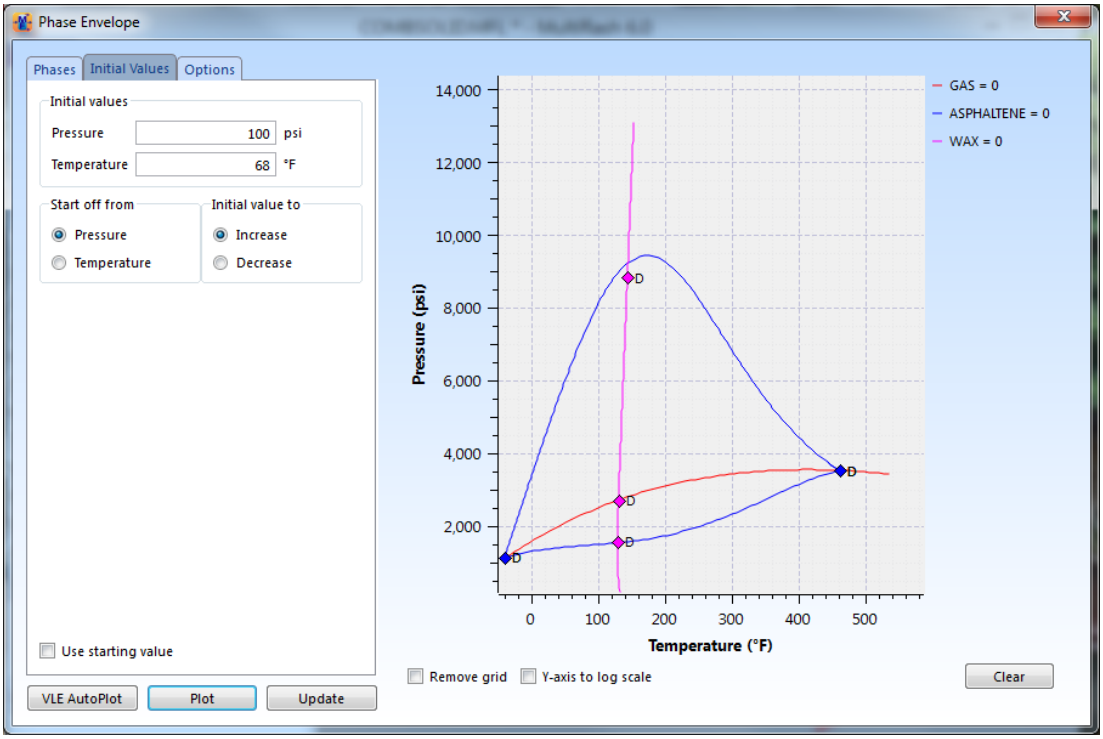
7. Clear the water, ice and hydrates check boxes, and then click Define Model.
8. On the **Asphaltenes** ribbon, click 

.
9. Click **Match**, click **OK** on the message, close the matching plot, and then click **Close**.
10. On the **Home** ribbon, click 

.
11. Generate the wax phase boundary by entering the data shown in the table, and then clicking **Plot**.

    Tip: Click **Yes** at the end of the first plot iteration, so that the wax line extends above the asphaltene envelope.

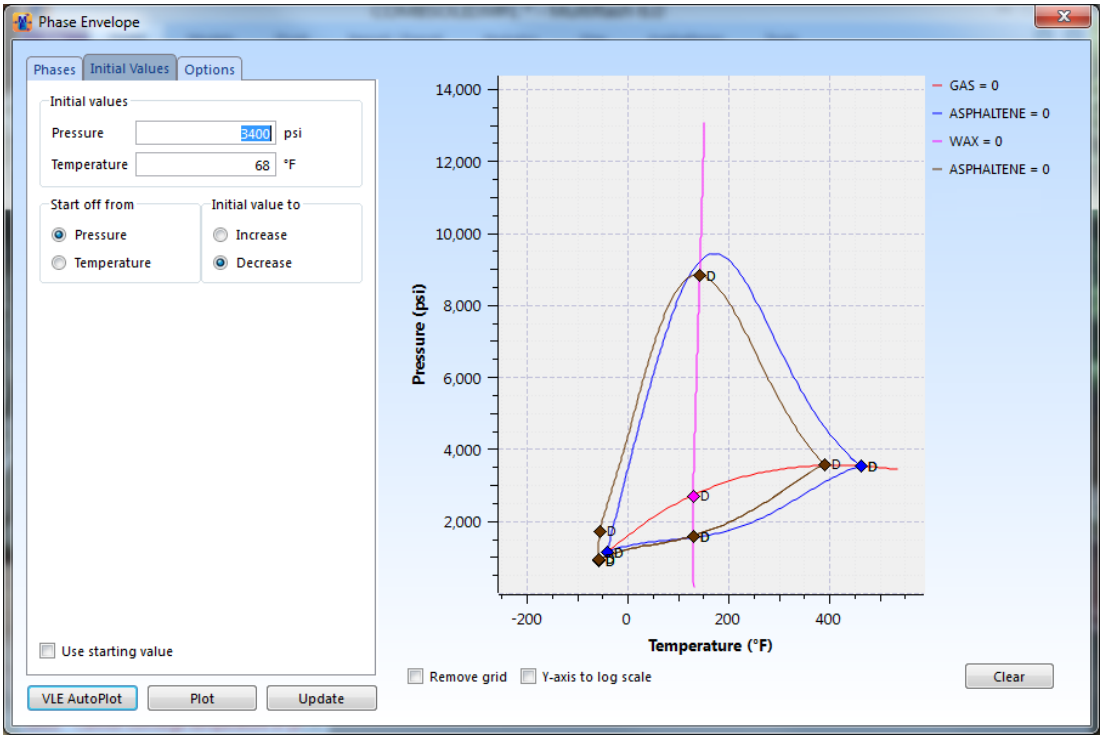
Phase tab			Initial values tab	
Item	**Value**		**Item**	**Value**
Type of solution	Normal		Pressure	100
Select Phase	Wax		Start off from	Pressure
Select Basis	Mole Fraction		Initial value to	Increase
Enter phase fraction	0			



12. Generate the modified asphaltene phase boundary by entering the data shown in the table, and then clicking **Plot**.

    Tip: Click **Yes** at the end of each plot iteration, until the asphaltene envelope becomes complete.

Phase tab			Initial values tab	
Item	**Value**		**Item**	**Value**
Type of solution	Unspecified		Pressure	3400
Select Phase	Asphaltene		Start off from	Pressure
Select Basis	Mole Fraction		Initial value to	Decrease
Enter phase fraction	0			



Changing the resin distribution and removing some of the n-paraffins has the effect of stabilising the asphaltene slightly.

13. Close the plot window.

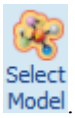
    Do not click **Clear**; you will compare further plots.

Calculate the APE with hydrates and a wax phase present

To study the effect of hydrate formation on the asphaltene and wax, we can retain the fluid characterisation used for wax and asphaltene, but need to add water. The following procedure continues from the previous one and covers steps 6 and 7 of the general approach outlined above.

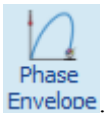
1. On the **Home** ribbon, click **Components**.
2. In the component list, select Water, click **Add selected component** and then click **OK**.

   Note: Do not add an amount for water at this stage. You are changing the model and must therefore re-match the asphaltene parameters, which is best done in the absence of water.

3. On the **Models** ribbon, click 

.
4. In the Phases panel, check **Water**, **Ice**, **Hydrate 1** and **Hydrate 2**.
5. Click **Define Model**, and then click **OK** on the message.
6. On the **Asphaltenes** ribbon, click 

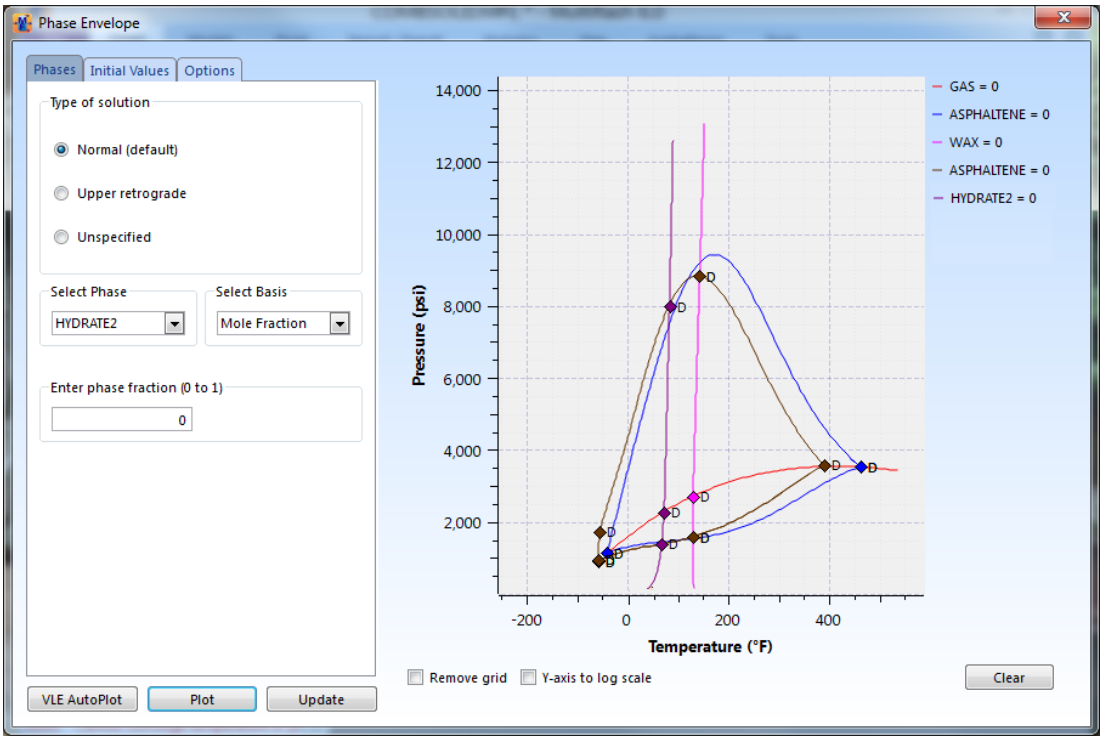
.
7. Click **Match**, click **OK** on the message, close the matching plot, and then click **Close**.
8. In the main Multiflash window, in the **Component** list, enter the value of 10 for the amount of water.

9. On the **Home** ribbon, click 
.

10. Generate the hydrate phase boundary by entering the data shown in the table, and then clicking **Plot**.

    Tip: Click **Yes** at the end of the first plot iteration, so that the hydrate line extends above the asphaltene envelope.

Phase tab			Initial values tab	
Item	**Value**		**Item**	**Value**
Type of solution	Normal		Pressure	100
Select Phase	Hydrate2		Start off from	Pressure
Select Basis	Mole Fraction		Initial value to	Increase
Enter phase fraction	0			

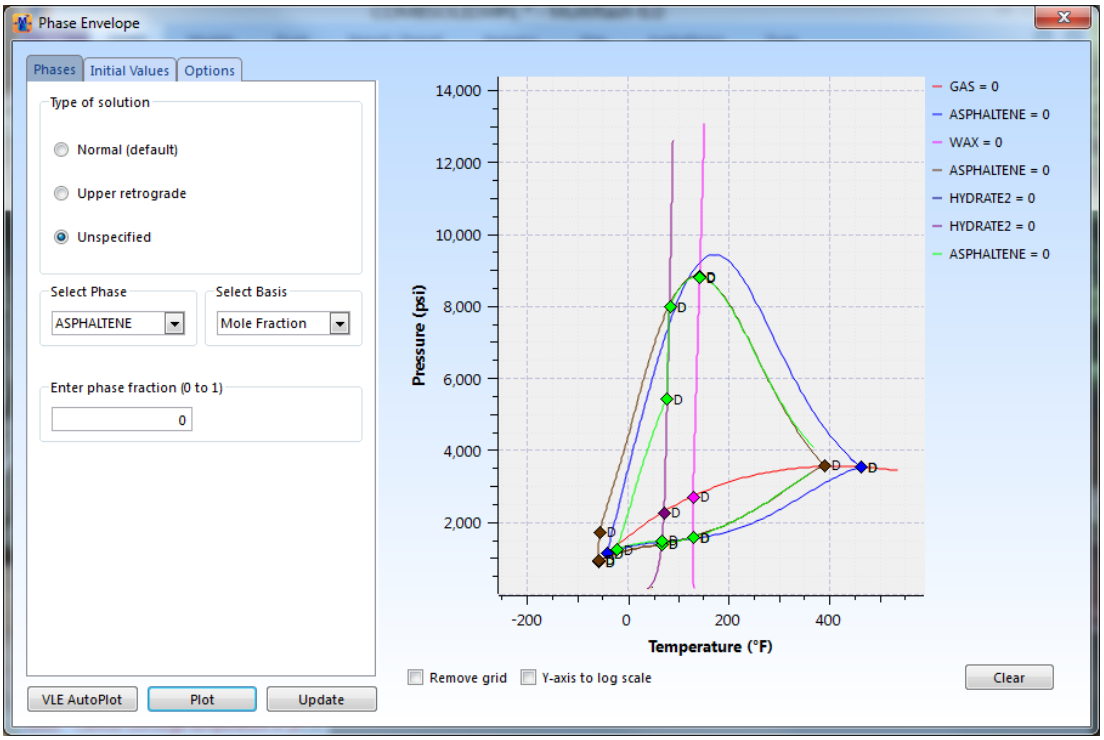


11. Generate the modified asphaltene phase boundary by entering the data shown in the table, and then clicking **Plot**.

    Tip: Click **Yes** at the end of each plot iteration, until the asphaltene envelope becomes complete.

Phase tab			Initial values tab	
Item	**Value**		**Item**	**Value**
Type of solution	Unspecified		Pressure	3400

Phase tab			Initial values tab	
Select Phase	Asphaltene		Start off from	Pressure
Select Basis	Mole Fraction		Initial value to	Decrease
Enter phase fraction	0			



The wax boundary is not affected by the addition of water or the formation of hydrate, which occurs at lower temperatures. However, the effect on the upper APE is significant. As the hydrate is formed, the low density gas hydrate formers are removed from the fluid and the upper asphaltene onset point comes down to lower pressures. This is in effect the reverse of gas injection and the asphaltene is stabilised.

Working with mercury species

Note: You can only perform mercury calculations if your Multiflash licence includes the mercury option.

Multiflash includes a mercury model for prediction of the solubility of mercury in natural gases and condensates, and the distribution of mercury between gas, condensate and water phases. The mercury model is available in combination with RKSA, PR78A or CPA-Infochem fluid models.

The mercury model can be used for any flash calculation such as P,S or P,H. The model can also be used for mercury partitioning in a gas dehydrator.

In condensates and petroleum liquids, organomercury compounds are significant and may be the predominant form of mercury, although it is generally agreed that mercury in natural gas is mostly in elemental form. Dimethylmercury and diphenylmercury represent light and heavy organomercury compounds, respectively. The mercury model in Multiflash is based on data for solubility both in hydrocarbons and in water, including data which is not available in the public domain.

The mercury model was originally developed based on the RKSA equation of state. This is our recommendation for the fluid phase model. However PR78A and CPA can be chosen for compatibility with fluid characterisation based on these models.

Distribution of mercury species

Multiflash can model elemental mercury, dimethylmercury and diphenylmercury, but the model cannot predict how much of a measured total mercury content is elemental mercury, and how much is organomercury.

For a given total mercury content in a gas stream, we assume that all the mercury is elemental mercury, because elemental mercury is much more volatile than the two organomercury components. However, if the measured total mercury content is for a separator liquid stream, it is difficult to predict the quantity of each of the three mercury components. Assuming that all mercury is elemental can lead to an over-estimate of the amount of mercury in the evolved gas phase when the separator liquid is further processed.

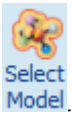
One way of solving this problem is to assume some distribution between the three mercury species in the separator liquid. An equimolar distribution of the organomercury species is assumed if no information is available. If a measurement of the total mercury content for the evolved gas phase is available, the amount of elemental mercury in the assumed distribution for the separator liquid can be adjusted to match the measurement for the gas phase.

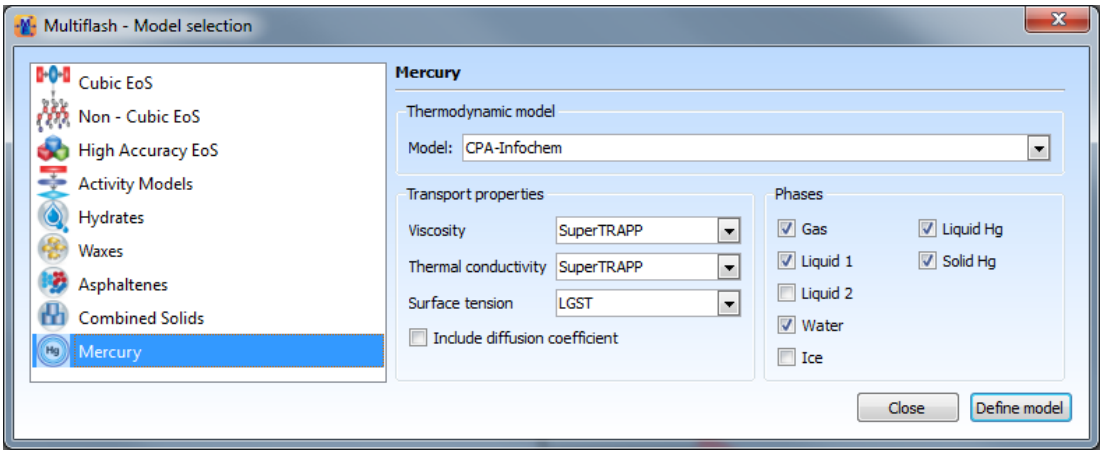
The approach outlined is not very accurate, and is not based on observations, but gives the best estimate of mercury distribution between the species, based on the available information. It also provides agreement with the measured total mercury content in both the separator liquid and the evolved gas.

Specifying the mercury model

To ensure that reliable results are obtained for mercury calculations, you must specify the model appropriately for the problem you are trying to solve.

To specify the mercury model:

1. On the **Models** ribbon, select 
.
2. From the model list, select **Mercury**.



   The image shows the default settings for the mercury model.
3. Choose the model and phases required for your particular calculation.

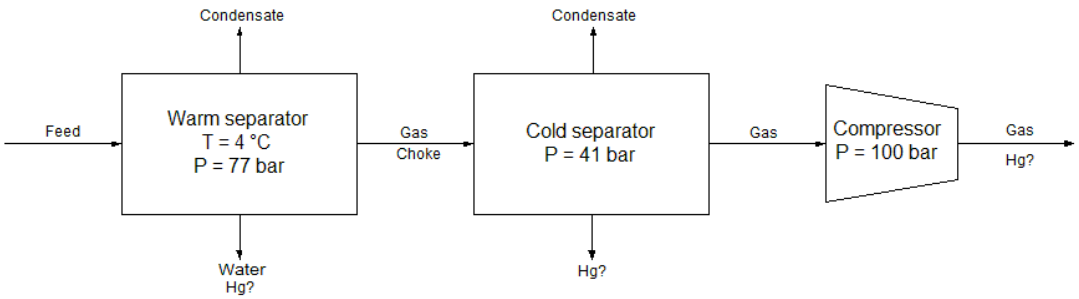
   Note: Specify a second hydrocarbon liquid phase (Liquid2) only if you anticipate the formation of multiple hydrocarbon liquid phases.
4. If required, choose an alternative model for your transport properties.
5. Click **Define Model**.
6. On the success message, click **OK**.

Calculating mercury partitioning and dropout

Problem:

How can I use Multiflash to simulate mercury partitioning and dropout?

We are using the following separator process for the example. The feed gas goes through a warm separator; the exiting gas enters a cold separator; and the final exiting gas is compressed for export.



Approach:

1. Specify your fluid and model.
2. Perform a PT flash at the warm separator conditions.
3. Copy the gas phase composition to the fluid composition list.
4. Perform a PH flash to simulate the choke down to the cold separator pressure, and see if mercury drops out as a liquid.
5. Perform a PT flash below the freezing point of mercury to see if more mercury drops out as the mercury solidifies.
6. Copy the gas phase composition from the PH flash to the fluid composition list.
7. Perform a fixed phase flash at the compressor pressure to determine the temperature at which the mercury drops out.
8. As a comparison, repeat steps 6 and 7 for the gas phase composition from the PT flash below the freezing point of mercury.

The file for this example is Hg_Example.mfl, and uses RKSA as the fluid model. The initial conditions for the warm separator are already specified. In this particular example we have only specified mercury, but the principle is the same if the components dimethyl- and diphenylmercury are also present.

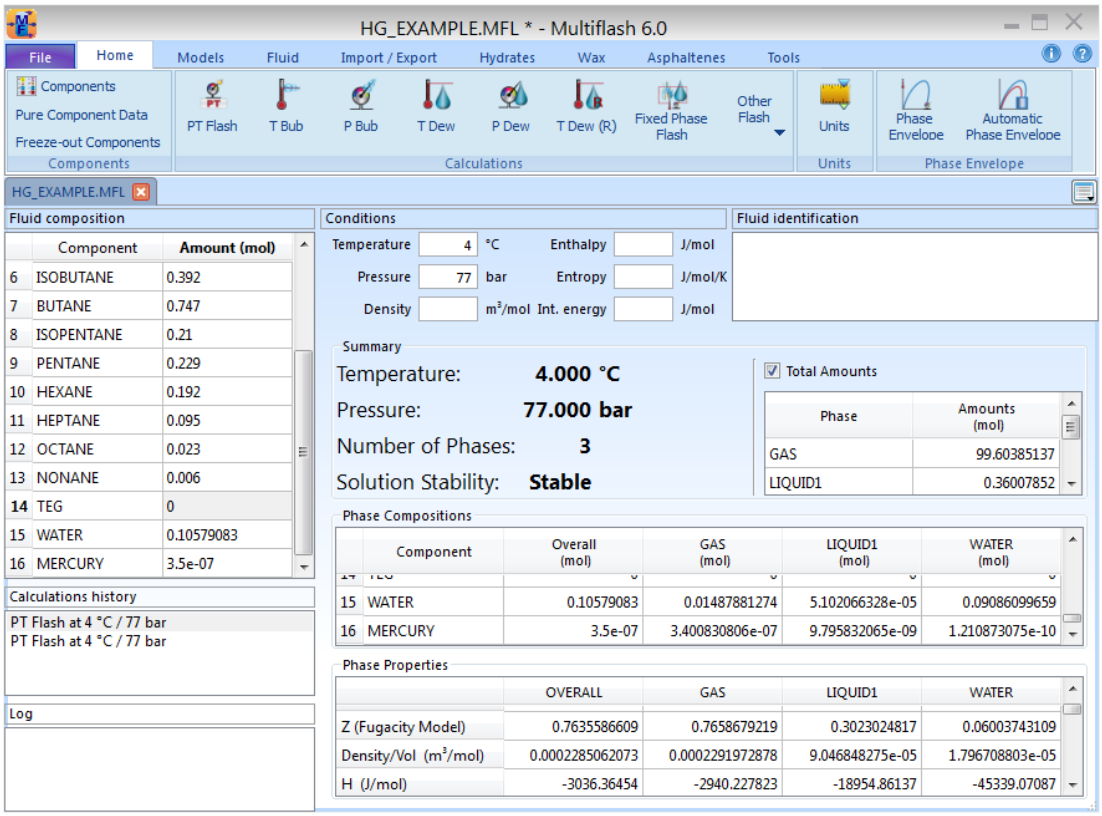
Note: If the mercury model is used in an Excel spreadsheet or a third party simulator, you can set the streams to merge and recycle automatically. However, in the Multiflash GUI, you must use the output composition from one calculation as the input for successive calculations.

Try it yourself:

1. On the **File** menu, click **Open**, and open the file hg_example.mfl.
2. On the **Home** ribbon, click 

.

   Result: The mercury partitions among the fluid phases (Gas, Liquid1 and Water). We have checked **Total Amounts** to display the moles of each component in the phase for clarity.



3. In the **Phase Compositions** area, click **GAS (mol)**, to highlight the column, then right-click anywhere in the column and select **Copy**.

   Rationale: The gas phase is the input stream for the second stage of the process.

4. In the **Fluid composition** area, right-click the first value in the Amount column, and then select **Paste**.

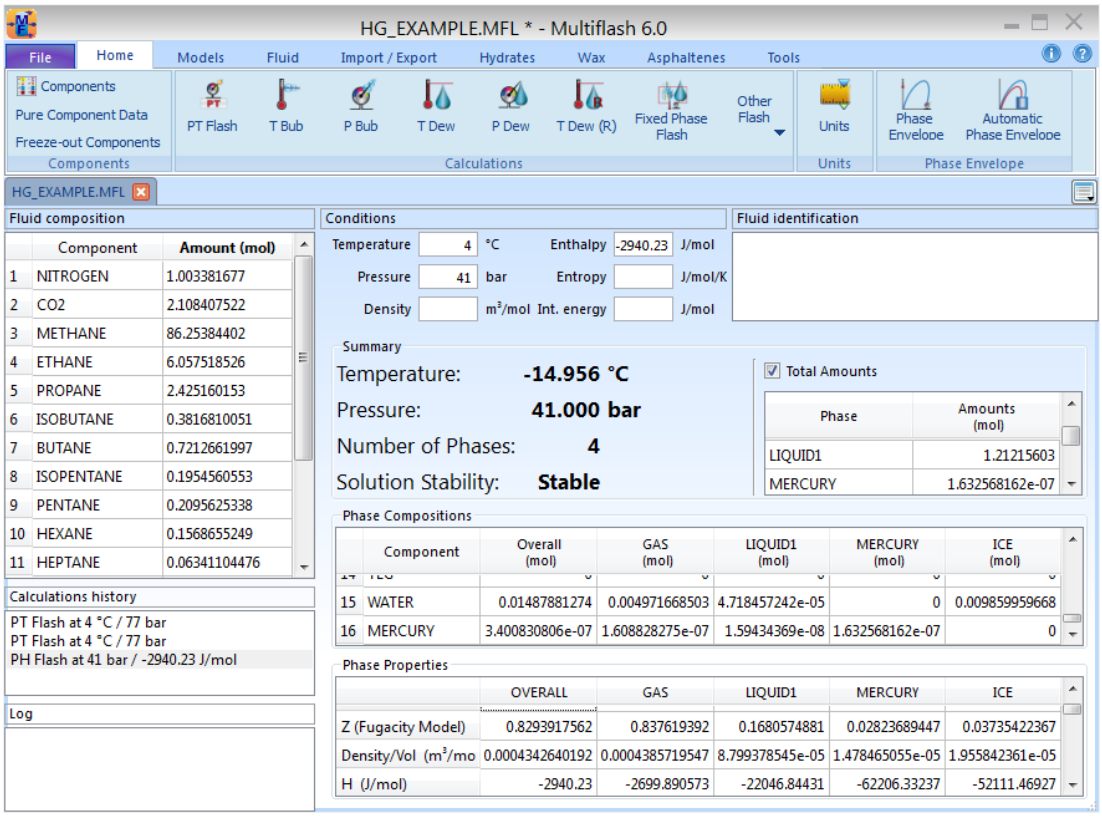
5. In the **Conditions** area, enter the conditions for a PH flash, as shown in the table.

   Rationale: This simulates the choke between the separators.

Condition	Value
Pressure	41 bar
Enthalpy‡	-2940.23 J mol^{-1}
‡Calculated by Multiflash as part of the PT flash, available from the **Phase Properties** area.	

6. On the **Home** ribbon, click **Other Flash**, and then select **PH Flash**.

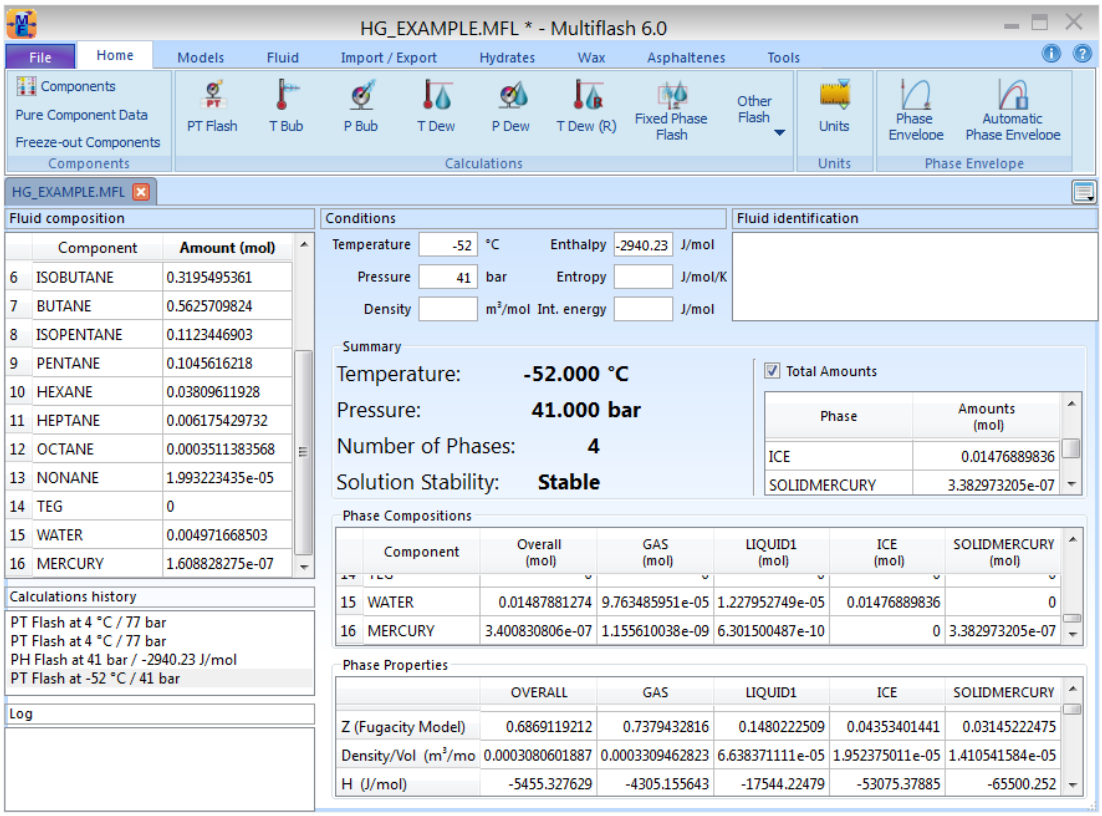
   Result: The reduction in pressure from 77 bar to 41 bar results in a temperature drop to -15 °C. Under these conditions the separator is cold enough for a separate liquid mercury phase to form. We have checked **Total Amounts** to display the moles of each component in the phases for clarity.



7. In the **Conditions** area, enter -52 °C in the **Temperature** field, and then click 

.

   Result: At this temperature, solid mercury forms and approximately twice as much mercury drops out of the gas phase compared with the original choke temperature.



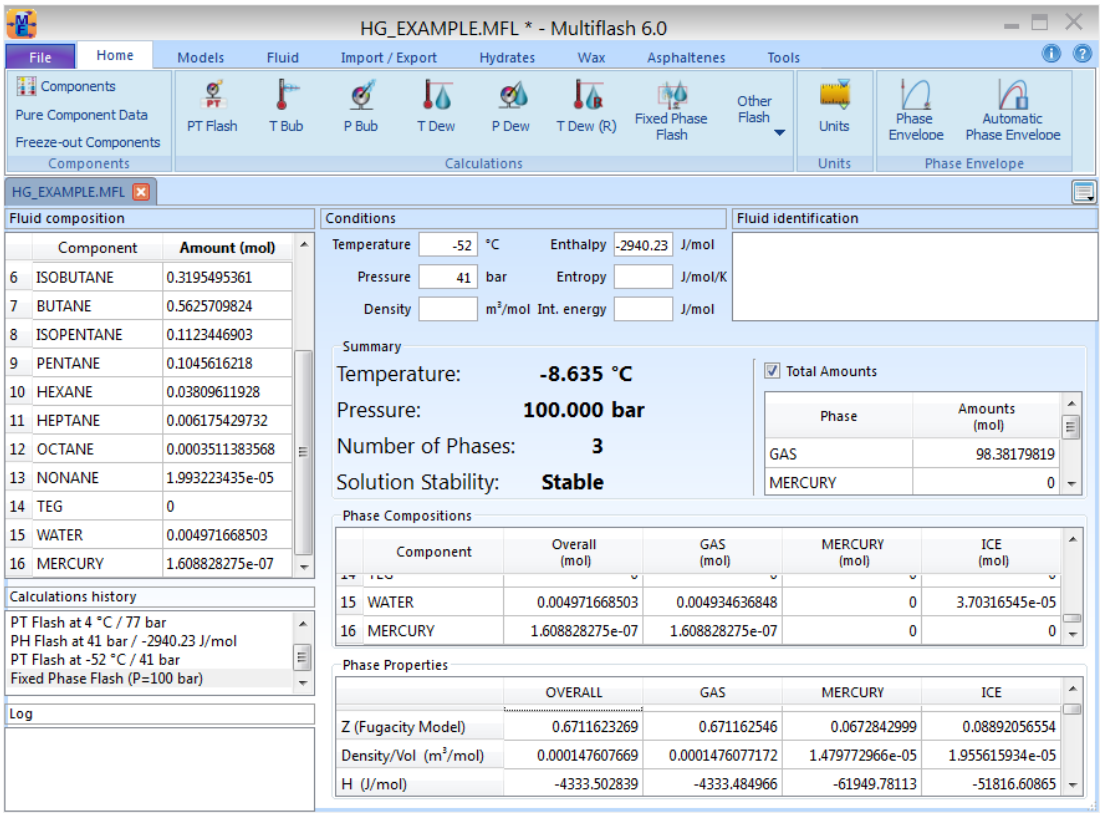
8. In the **Calculations history** area, click the PH flash calculation.
9. Copy the gas phase composition to the **Amount** column, in the same way as before.
10. On the **Home** ribbon, click 

.
11. In the Fixed Phase Fraction Flash dialog box, enter the values shown in the table, and then click **Calculate**.

    Rationale: This calculation determines at which temperature mercury starts to drop out when the gas from the cold separator is compressed to 100 bar for export.

Item	Value
Pressure	100
Solution type	Normal
Phase	Mercury
Basis	Mole fraction
Enter phase fraction	0

    Result: Using the gas output from the cold separator at -15 °C and 100 bar, the liquid mercury begins to drop out at -8.7 °C.



FAQ:

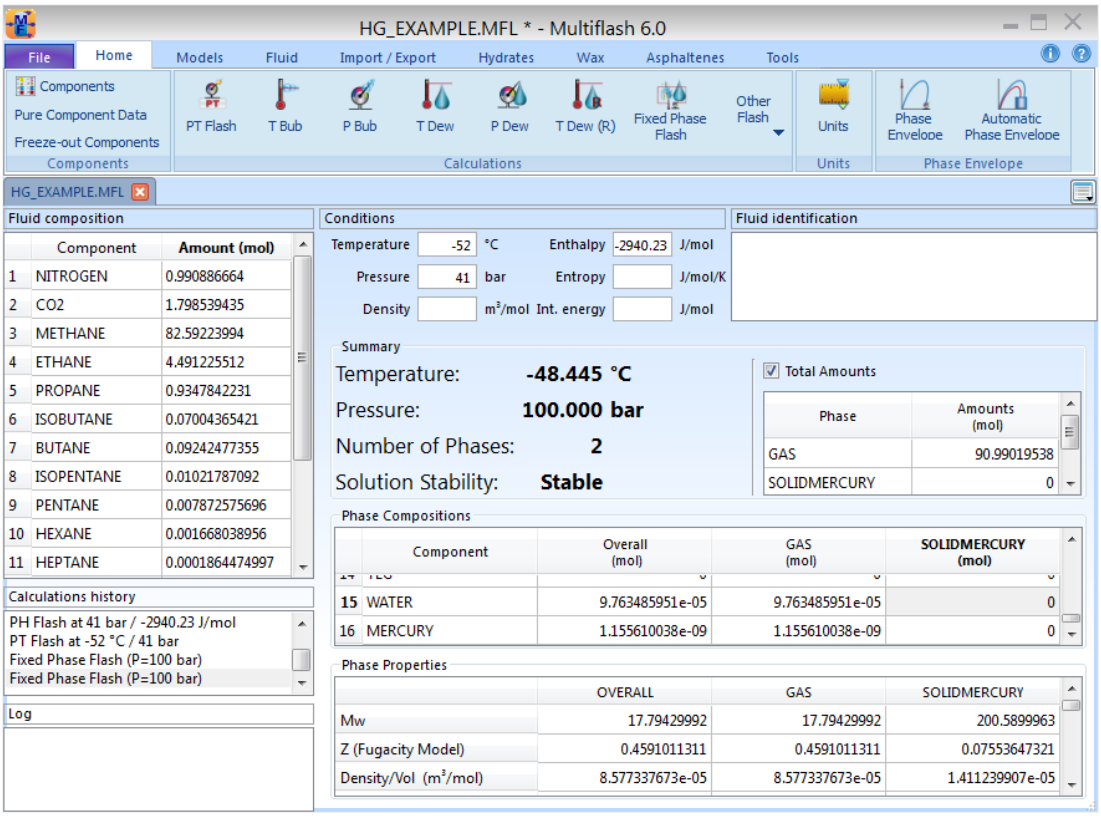
Anything to add here?

What else can I do?

1. Repeat the final fixed phase flash, this time using the gas phase composition from the PT Flash at -52 °C.

   Tip: You must set the phase to SolidMercury.

   Rationale: This compares the efficiency of varying the cold separator conditions. You can do this for any chosen conditions to optimise the amount of mercury removed.



Result: In this case, mercury will not drop out until the temperature is below -48 °C at 100 bar, at which point solid mercury begins to form. This is because of the lower amount of mercury in the gas stream from the cold separator at -52 °C, compared to the gas stream from the cold separator at -15 °C.

2. TEG is included in the component list for the above example, but was present at zero concentration in the calculations. If you add TEG (0.3 moles), you can repeat the calculations, but starting with a PT flash at 10 degC and 110 bar to simulate a simple dehydrator step, rather than the warm separator. You can then see the mercury partitioning into the aqueous TEG phase and the consequent effects. If you follow through the calculations, you can compare the mercury distribution with the system without TEG.

Working with binary interaction parameters

Binary interaction parameters (BIPs) are adjustable factors used to modify the predictions from a model so that they reproduce as closely as possible the experimental data. BIPs are usually generated by fitting experimental VLE or LLE data to the model in question.

The more a BIP varies from its default value, the greater the adjustment required to make the underlying model fit the measured data. For some models, BIPs have some physical significance, but they are usually treated as empirical adjustment factors. Different models require different numbers of BIPs.

Multiflash enables you to view and edit the BIPs for the model that you are using. It also provides the flexibility to have BIPs defined as constant or temperature-dependent parameters. You can also use your own BIP files in place of those supplied with Multiflash.

Viewing binary interaction parameter values

You can view the values of any binary interaction parameters (BIPs) used in Multiflash calculations, whether from the supplied databanks or those entered by a user. A BIP dataset is assigned when the model is defined. The number of BIP datasets listed depends on the model that you are using.

Within Multiflash, the BIP dataset name is formed from the following elements:

- The acronym of the model name, for example, RKS.
- LLE, for LLE versions of a model.
- BIP.
- If there is more than one set of BIPs for a model, an integer indicating the number of BIP datasets.

Example names:

RKSBIP, PRBIP, PR78BIP, PR78ABIP, RKSABIP, RKSAINFOBIP (for RKSA + Infochem mixing rule), CPABIP1, PCSBIP-1, PCS-SBIP-1, LKBIP, LKPBIP, WILSONBIP2, NRTLBIP3, UNIQUACBIP2, NRTLLLEBIP3, UNIQUACLLEBIP2.

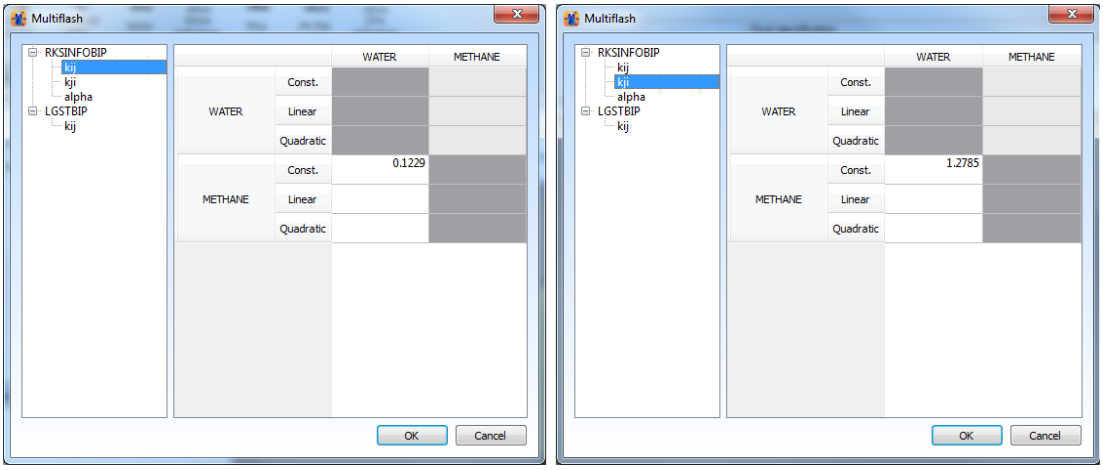
Note: Some models, for example, PSRK and the UNIFAC variants, are based on group contributions, so BIPs are calculated automatically from the groups that form the component molecules. A few other models have no BIPs or non-modifiable BIPs, for example, Steam Tables and CO2 high-accuracy. In all these cases, no BIP datasets are shown.

You can view BIPs when you have a fluid and model specified.

To view BIP values:

1. Define your model and fluid.
2. On the **Models** ribbon, click 

.



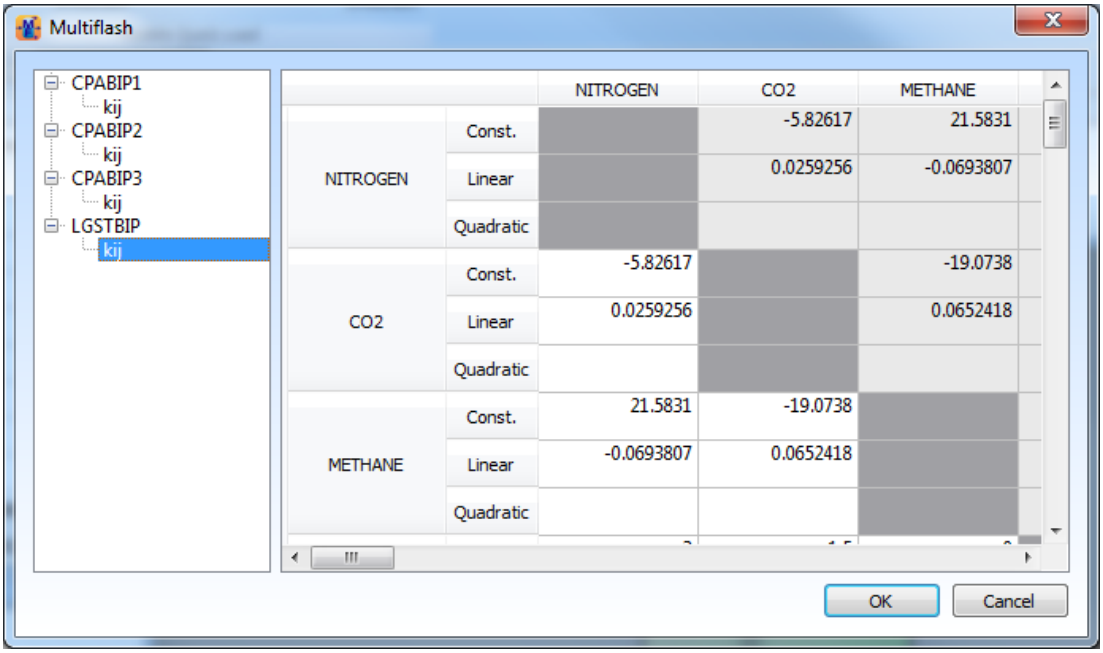
Result: The BIP sets for each currently specified model are listed.

For asymmetric parameters, the indices i and j refer to column and row, respectively. For example, in the screenshot to the left, the water-methane asymmetric parameter (k_{ij}) is 0.1229, and in the screenshot to the right, the methane-water asymmetric parameter (k_{ji}) is 1.2785. In the grid of values, a symmetric value is displayed in both halves of the grid.

In the screenshots above, the BIPs are asymmetric and defined as constant, temperature-independent values.

In the following screenshot, the symmetric BIPs of the LGST model are defined as temperature-dependent values with a linear expression of the form:

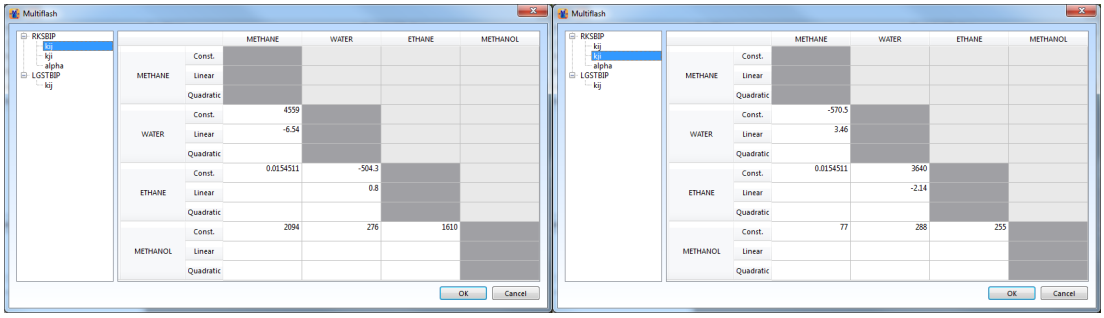
BIP = Constant + Linear x T



In a third example we consider a mixture of water, methanol, methane, and ethane, with the RKS-HVP model. The HVP mixing rule can work with two different types of BIPs:

- VDW-like parameters, which are symmetrical, dimensionless, and are equal to those used in the classical mixing rule of the RKS equation.
- NRTL and HVP-like parameters, which are composed of symmetrical and asymmetrical BIPs.

When different types of BIP are used, both symmetric and asymetric BIP values are shown in the asymmetric k_{ij} and k_{ji} tables. In the screenshot, only the pair methane-ethane has VDW-like parameters, indicated by the identical constant value in both tables for that pair.



Editing binary interaction parameter values

You can add or replace the BIP values used in your calculations. The BIP values stored in the database supplied by Multiflash are not overwritten; any changes are stored with the calculation when you save the .mfl file.

Tip: If you want to use a different set of BIP values regularly, consider using your own BIP file.

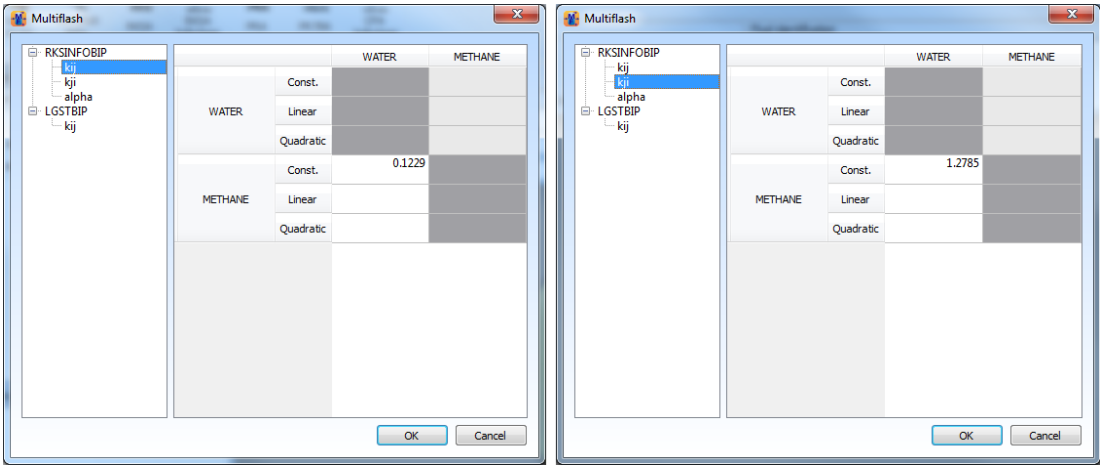
If you change the model, your modified BIP values are retained if the new model uses the same BIP data set. For example, if you change the number of phases or use a different transport property model, you need not enter your BIP values again.

Requirement: You must ensure that the BIP values you supply conform to the model definition used in Multiflash and that you have specified and supplied BIP values in the correct units.

To edit the binary interaction parameter values:

1. On the **Models** ribbon, click 

.



Result: The BIP sets for each currently specified model are listed.

For asymmetric parameters, the indices i and j refer to column and row, respectively. For example, in the screenshot to the left, the water-methane asymmetric parameter (k_{ij}) is 0.1229, and in the

screenshot to the right, the methane-water asymmetric parameter (k_{ji}) is 1.2785. In the grid of values, a symmetric value is displayed in both halves of the grid.

2. For each value that you want to add or modify, choose the parameter from the list on the left, click in the appropriate cell of the grid, and then enter the value.

   Tip: You edit the value of a symmetric parameter in the lower half of the grid.

3. Click **OK**.

   Tip: If you want to retain the values that you have entered, and use them at a later date, save your current system before you change to a model that uses a different BIP dataset. For example, if you want to overwrite the standard BIPs every time you run Multiflash, define the model and components and then use the BIPSet window to enter the values and then save the file. Use this file as the starting point for your calculations with the modified BIP values.

Looking at the effect of binary interaction parameters

Problem:

What is the effect on calculations of the binary interaction parameters (BIPs)?

Approach:

1. Define your fluid.
2. Select an activity model.
3. Perform a flash calculation.
4. Add BIPs, and repeat the flash calculation.
5. Repeat steps 2-4 for other activity models.

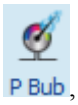
In this example, you will use the BIP values reported for the CCl_4-Hexane system, shown in the table, for the listed activity models.

Model	BIP values‡ (J mol^{-1})
Wilson E	266.61, 461.91
UNIQAC VLE	208.5, -12.84
NRTL VLE	276.8, 284.9, .3
‡Reported for CCl_4-Hexane	

Try it yourself:

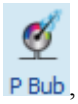
1. On the **File** menu, click **New problem**.
2. On the **Home** ribbon, click **Components**.
3. Scroll through the list, double-click on the components hexane and carbon tetrachloride, and then click **OK**.

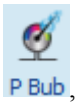
4. On the **Home** ribbon, click 

, set the pressure to bar and the temperature to Kelvin, and then click **OK**.
5. In the **Conditions** area, set the pressure to 1 bar.
6. In the **Amount** column, specify 0.325 mole carbon tetrachloride and 0.675 mole hexane.
7. On the **Models** ribbon, click **Select Model**, click Activity Models, choose Wilson-E from the list, click **Define model**, and then click **OK** on the message.
8. On the **Home** ribbon, click 

, and make a note of the temperature and CCl_4 gas fraction.
9. On the **Models** ribbon, click 

.
10. Enter the BIP values for the model, and then click **OK**.

    Tip: Remember that for asymmetric parameters, the indices i and j refer to column and row, respectively.
11. On the **Home** ribbon, click 

, and make a note of the temperature and CCl_4 gas fraction.
12. Repeat steps 7 to 11 for the UNIQUAC-VLE and NRTL-VLE models.
13. On the **Models** ribbon, click **Select Model**, choose UNIFAC-VLE from the list, click **Define model**, and then click **OK** on the message.
14. On the **Home** ribbon, click 

, and make a note of the temperature and CCl_4 gas fraction.
15. Repeat the calculation one more time, using the UNIFAC-VLE model, which generates its own BIPs from group contributions.

Method	Temperature (K)	CCl_4 vapour (mole fraction)
Experimental	342.8	0.286
Wilson E	344.3	0.270
Wilson E + BIPs	342.7	0.289
UNIQUAC-VLE	344.2	0.271
UNIQUAC-VLE + BIPs	342.8	0.288
NRTL-VLE	344.0	0.273
NRTL-VLE + BIPs	342.7	0.287
UNIFAC-VLE	343.4	0.279

You can see from the results the importance of using interaction parameters for non-ideal systems. All the calculations were carried out with the ideal model for the vapour phase. For this system, using the Virial (HOC) or RK model for the vapour phase model does not give significant differences. However, for some components, such as acetic acid which may dimerise, using the Virial (HOC) model would be beneficial.

What else can I do?

You could enter different BIPs for this system and examine the sensitivity of the results to these variations.

Working with polar systems

Polar mixtures are usually non-ideal, and we recommend using an activity coefficient model, such as Wilson-E, NRTL, UNIQUAC or UNIFAC, to predict phase behaviour for such systems. Binary interaction parameters (BIPs) are usually needed to obtain accurate results; however, the UNIFAC BIPs are generated from group structures.

Before you carry out phase equilibrium calculations for polar systems using an activity coefficient model, we recommend that you check the availability of BIPs for your system. To do this, use the following list in order of priority :

1. If you have your own BIPs available for any particular activity model, then this is the model you should use.
2. Load an activity model and check that BIPs are available for all your system components.
3. Look up interaction parameters for the binary pairs where none are available in Multiflash.

   Tip: A good source of experimental data and BIPs is the "Chemistry Data Series", Vol I - XIV, published by Dechema.
4. Fit experimental data to a Multiflash activity model to calculate BIPs.

   This is useful if you have access to good quality VLE data for the component pairs in your system for which BIPs are unavailable. We have provided the example spreadsheet vlefit.xls so that you can do this using the Excel interface.
5. Generate data from UNIFAC and fit this to a Multiflash activity model to calculate BIPs.

   This is the last method of choice, and should be used only when you have exhausted the other options. We have provided the example spreadsheet unifacfit.xls so that you can do this using the Excel interface.

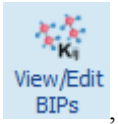
Comparing the polar models

You can use Multiflash to see how well the different models and different sets of parameters represent experimental data. Depending on the relative importance to your application of accurate temperature or phase composition, you can choose the appropriate flash calculation.

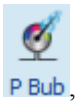
This example compares results from the Wilson E and UNIFAC models, attempting to reproduce an experimental point from acetone - water data by Kojima et al, Kagaku Kogaku 32, 149 (1968), with an initial molar ratio of acetone:water of 0.4:0.6. The file aceth2o.mfl is used, which has the Wilson E model already selected.

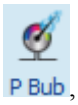
Try it yourself:

1. On the **File** menu, click **Open**, and open the file aceth2o.mfl.

   Tip: By default, the example files are in the MFL Files folder of the Multiflash installation.
2. On the **Models** ribbon, click 

, and verify that BIP values are available for the component pair.

3. On the **Home** ribbon, click 

, and make a note of the temperature and acetone gas fraction.
4. On the **Models** ribbon, click **Select Model**, choose UNIFAC-VLE from the list, click **Define model**, and then click **OK** on the message.
5. On the **Home** ribbon, click 

, and make a note of the temperature and acetone gas fraction.

Method	Temperature (°C)	Acetone vapour mole fraction
Experimental	60.39	0.8426
Wilson E	61.4	0.821
UNIFAC	60.87	0.824

Both methods give a reasonable prediction, compared to the experimental result.

What else can I do?

You can repeat the calculation, using the other activity models to compare results.

Exploring liquid-liquid equilibria

Problem:

How do I model liquid-liquid equilibria in a polar system?

Many non-ideal polar systems exhibit liquid-liquid equilibria. To model these systems, you must choose an activity model capable of predicting two liquid phases. Two suitable models are UNIQUAC LLE and NRTL LLE.

To obtain realistic results, you should have suitable BIPs. The following example uses a butanol-water mixture, for which Multiflash has available BIPs in the models mentioned.

Approach:

1. Define your fluid.
2. Select an activity model.
3. Verify that BIPs are available, or add your own BIPs.
4. Specify your conditions.
5. Perform your chosen calculation.

Try it yourself:

1. On the **File** menu, click **New problem**.
2. On the **Home** ribbon, click **Components**.
3. Scroll through the list, double-click on the components butanol and water, and then click **OK**.

4. On the **Home** ribbon, click 

, set the pressure to Pascal and the temperature to Kelvin, and then click **OK**.
5. In the **Conditions** area, set the temperature to 298.15 K and the pressure to 1e5 Pa.
6. In the **Amount** column, specify 0.5 mole butanol and 0.5 mole water.
7. On the **Models** ribbon, click **Select Model**, click Activity Models, choose UNIQUAC-LLE from the **Liquid thermodynamic model** list, check **Liquid 2**, click **Define model**, and then click **OK** on the message.

   Rationale: If you anticipate that two liquid phases might form, ensure that you have two liquid phases specified, otherwise Multiflash generates warning messages when a second phase is calculated, and the phase results are invalid.
8. On the **Home** ribbon, click 

.

   Result: The system is a single liquid phase.
9. In the **Amount** column, specify 0.3 mole butanol and 0.7 mole water.
10. On the **Home** ribbon, click 

.

    Result: The system now comprises two liquid phases.

FAQ:

Why do I see a warning message about additional phases or mismatched phases?

You have not specified enough phases for the calculation. This is most often because you have only one liquid phase specified in your model. Return to your model definition and ensure that both liquid phases are selected.

What else can I do?

1. Try using different activity models.
2. Look at the effect of different BIPs.
3. Investigate the system as a VLLE. Remember to ensure that the gas phase and both liquid phases are selected in the model you use.

   Tip: It is often better to use the LLE variant of a model for VLLE calculations.

Identifying azeotropes

Problem:

How do I find an azeotrope?

You can identify the azeotrope for a binary mixture either by plotting the gas and liquid phase fractions of one component against each other, or by plotting the bubble and dew point temperatures for a series of mole fractions of one component.

Approach:

1. Specify your fluid and use an activity model.
2. Perform a series of flash calculations at fixed pressure, varying the mole fraction of the components, and keeping the total amount constant.

   Tip: Use the Excel interface to reduce your effort.
3. Plot the results to identify the azeotropic point.

You can use the following procedure when you have specified your fluid and activity model.

Try it yourself:

1. If you are using our example file, on the **File** menu, click **Open** and then open the file AzeotropeExample.mfl.
2. To use the spreadsheet AzeotropeExample.xls, do the following:
   - In cell A1, enter the line

     include "filename.mfl";

     where filename is the full path to your saved fluid and model, for example, C:\Program Files (x86)\Infochem\MF61\MFL Files\AzeotropeExample.mfl.
   - In cell B11, enter the pressure at which you want to do the calculations.
   - If required, modify the column titles to match your fluid.
3. For each manual calculation, do the following:
   - In the **Conditions** area, enter the pressure that you want fixed for the calculations.
   - In the **Fluid composition** area, set the mole fraction amounts in the **Amount** column.
   - On the **Home** ribbon, click 

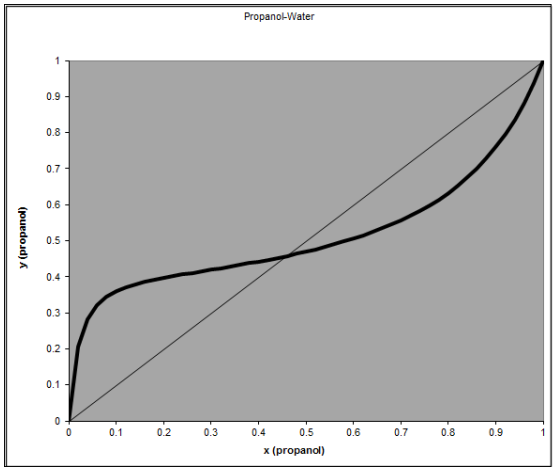
and 

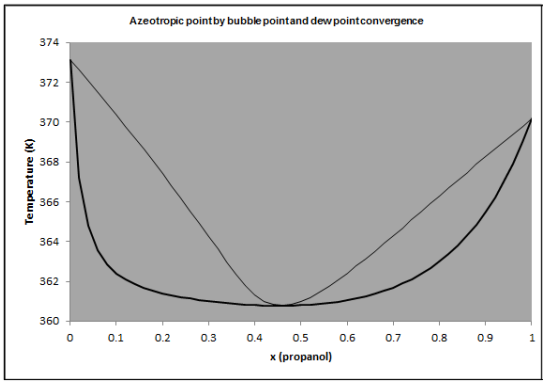
tools as required, and record the relevant data.

Plot type	Data to record
Gas vs liquid fractions	■ Gas mole fraction ■ Liquid mole fraction ■ Bubble point temperature
Bubble and dew point temperature vs mol fraction	■ Gas mole fraction ■ Dew point temperature ■ Bubble point temperature

Result: If you used the spreadsheet, the flash calculations are done automatically, using the mole fractions entered in columns A and B, and graphs are plotted automatically. For manual calculations, you must create plots using your own spreadsheet or other application.

The following plots were produced using our example files. The plots were generated using the Wilson-E model, by making a series of bubble point and dew point calculations at 1 bar at varying composition of the liquid phase. The azeotrope is at a mole fraction of 0.46 propanol.





FAQ:

Anything to add here?

What else can I do?

1. Repeat the calculation at different pressures to see the effect on the azeotropic point.
2. See what happens when you add a third component to the fluid.

Identifying a eutectic point

Problem:

How do I find a eutectic point?

You can identify the eutectic point by plotting the predicted temperature versus composition for all components. The intersection of all the temperature lines is the eutectic point.

Approach:

1. Specify your fluid and use the NRTL-VLE model.
2. Apply the freeze-out model to each component.
3. Perform a series of fixed phase flash calculations at fixed pressure, varying the mole fraction of the components, and keeping the total amount constant, to identify the temperature at which your components solidify.

   Tip: Use the Excel interface to reduce your effort.
4. Plot the results to identify the eutectic point.

You can use the following procedure when you have specified your fluid and the NRTL-VLE model.

Try it yourself:

1. If you are using our example file, on the **File** menu, click **Open** and then open the file EutecticExample.mfl.
2. On the **Home** ribbon, click **Freeze-out Components**.
3. Check each component, click **Add/Remove**, click **OK** on the message, and then click **Close**.
4. On the **File** menu, click **Save as**, and save the system using a new name.

5. To use the spreadsheet EutecticExample.xls, do the following:
   - In cell A1, enter the line

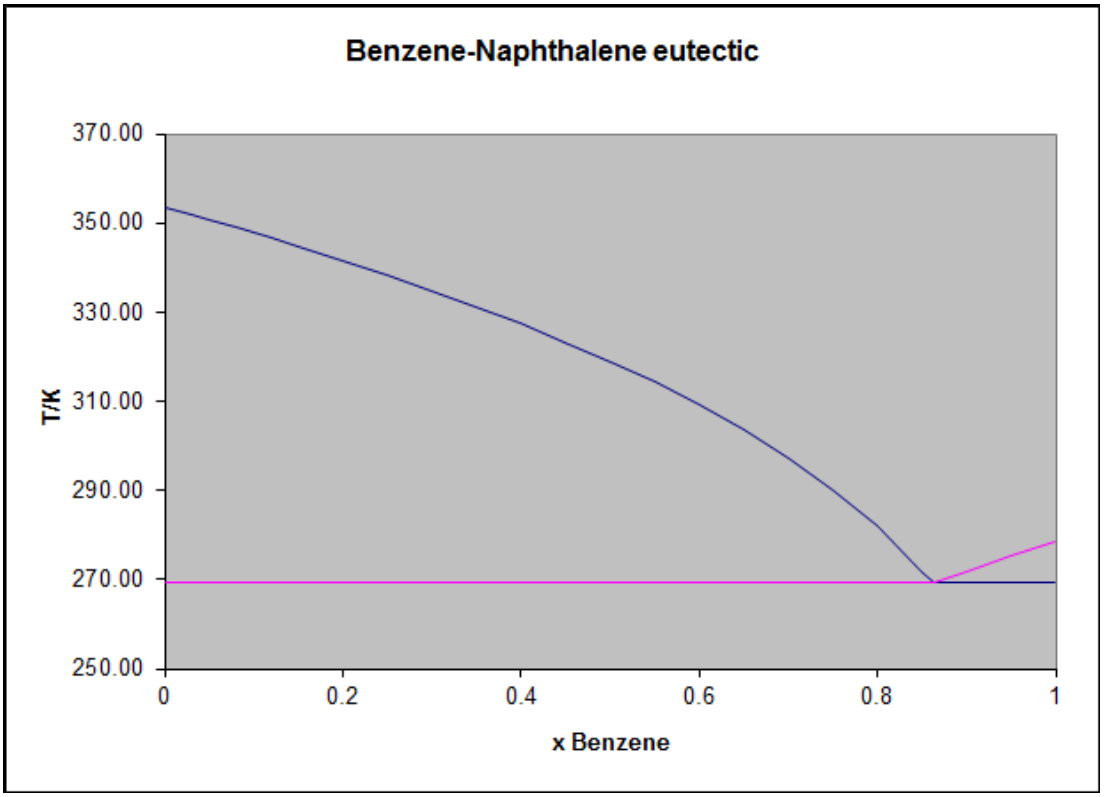
     include "filename.mfl";

     where filename is the full path to your saved fluid and model, for example, C:\Program Files (x86)\Infochem\MF61\MFL Files\AzeotropeExampleFreeze.mfl.
   - In cell B6, enter the pressure at which you want to do the calculations.
   - If required, modify the column titles to match your fluid.
6. For each manual calculation, do the following:
   - In the **Fluid composition** area, set the mole fraction amounts in the **Amount** column.
   - On the **Home** ribbon, click 

.
   - Select **Pressure**, and enter the required pressure.
   - From the **Phase** list, choose the solid component for which you want to calculate the melting point, for example, SOLIDBENZENE.
   - From the Basis list, choose Mole Fraction, and enter 0 for the phase fraction.
   - Click **Calculate**.
   - Record the calculated temperature and starting mole fractions of the components.

Result: If you used the spreadsheet, the flash calculations are done automatically, using the mole fractions entered in columns A and B, and the graph is plotted automatically. For manual calculations, you must create a plot using your own spreadsheet or other application.

The following plot was produced using our example files. The plot was generated using the NRTL-VLE model, by making a series of fixed phase flash calculations at 1 bar at varying composition of the two components. The eutectic point is predicted to be at 269.2 K and a mole fraction of benzene of 0.862.



Exchanging data with other programs

In addition to using Multiflash to do stand-alone calculations, you can export property data files for use by other application programs. Multiflash can also import files from PVTSim to perform calculations.

The table shows the applications to which Multiflash can export data.

Application	Description
PIPESIM PVT	PIPESIM is a general purpose simulator for modelling fluid flow in oil and gas wells, flow lines and pipeline systems. It is a product of Schlumberger Information Systems.
OLGA	OLGA is a general purpose transient simulator for modelling fluid flow in flow lines and pipeline systems. It is a product licensed by the Schlumberger.
Prosper PVT	Prosper is a well performance, design and optimisation program for modelling well configurations for the oil and gas industry. It is a product of Petroleum Experts.
CAPE-OPEN	CAPE-OPEN (CO) is a set of standards for interfacing process modelling software components, developed specifically for the design and operation of chemical processes. Infochem/KBC has been an active participant in developing and testing the CO standards.
Multiflash legacy file applications	A number of software packages use older versions of Multiflash as their PVT engine. Multiflash provides an export option that generates a .mfl file that is compatible with versions 4.3 and 4.4 of Multiflash.

Exporting PIPESIM PVT files

Multiflash exports a file containing all the physical property data required by PIPESIM. The data consists of a set of flash calculations performed at a series of pressure and temperature values. The information stored includes the following:

- Stream composition.
- For each grid point: liquid volume fraction; water cut volume fraction; liquid density; gas density; gas compressibility factor; gas molecular weight; liquid viscosity; total enthalpy; total entropy; liquid heat capacity; gas heat capacity; and liquid surface tension.
- Details of the version of the BIP correlations and the viscosity model used.

  Note: BIPs specified by the user in Multiflash are not stored.

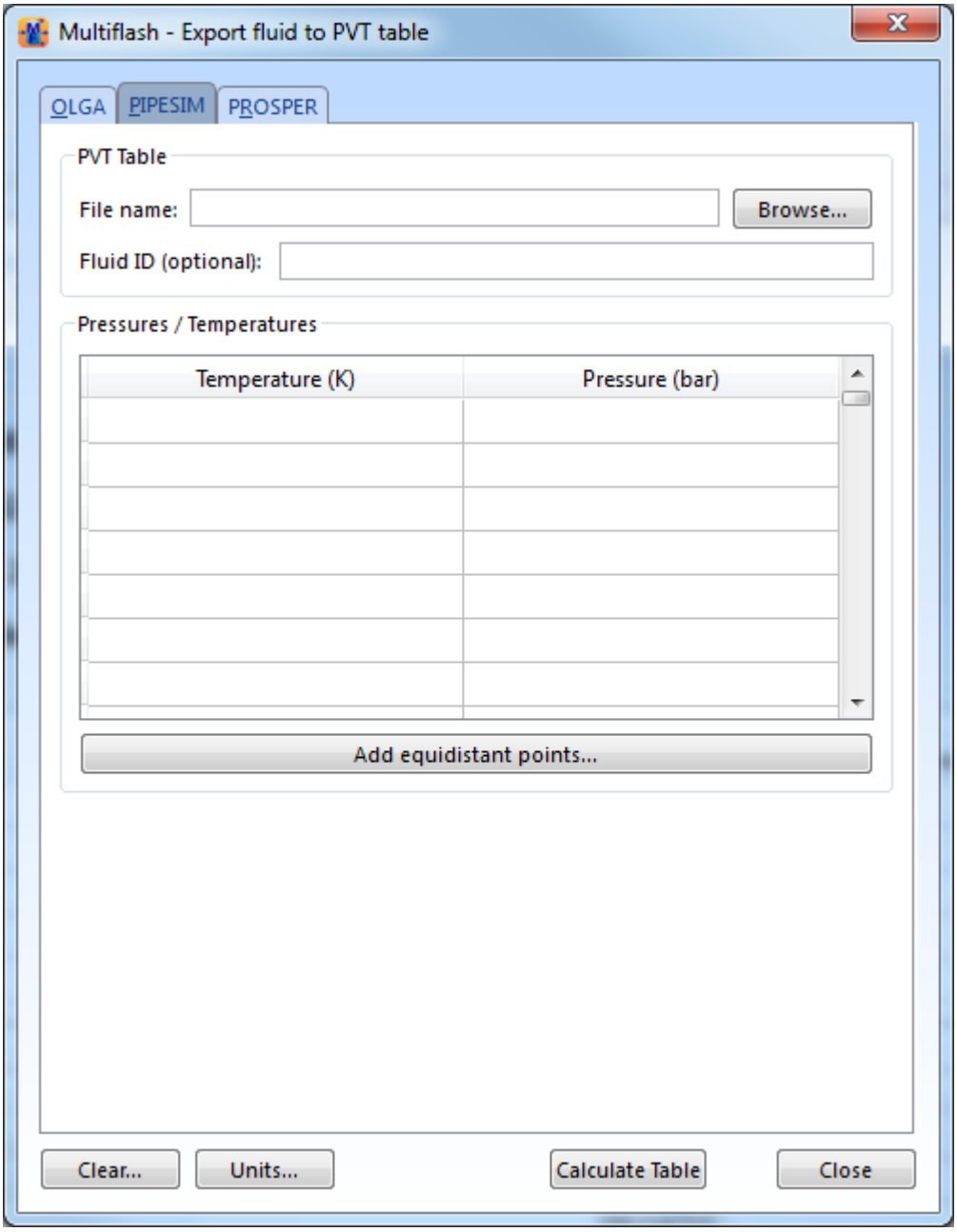
For a complete definition of PIPESIM PVT files, see the PIPESIM manual.

To generate the export file:

1. Specify your model and fluid composition in the usual way.

   Requirement: The model specified for your fluid must include models for surface tension and viscosity.

2. On the **Import/Export** ribbon, click **PVT Tables**.
3. Click the **PIPESIM** tab.



4. Enter an export file name, by typing or using the **Browse** button.

   Tip: Use a file extension of .pvt. If you do not use the the Browse button, the file is saved in the folder specified for PVT export files.

5. Optionally, specify a fluid ID.
6. For each temperature and pressure at which you want to generate data for the export file, enter the

values into the table.

Note: The values are used to generate a grid of points comprising each temperature at each pressure. For example, when you enter three temperatures and four pressures, you generate twelve points.

Tip: Use **Add equidistant points** to generate a regular grid of points. Enter a start and end value for each variable, and the number of points to generate for each variable. For example, enter 50, 250, 5 for temperature (°C), and 10, 100, 10 for pressure (bar), to generate 50 sets of data, the five temperatures 50, 100, 150, 200 and 250 °C, each at a pressure of 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 bar.

7. If required, click **Units** to change the temperature and pressure units used.

   Restriction: You cannot specify the units for the output data. Multiflash outputs the data with the units required by PIPESIM.

8. Click **Calculate Table**.
9. If required, the **Clear** button can be used to restart the data input.

Exporting OLGA files

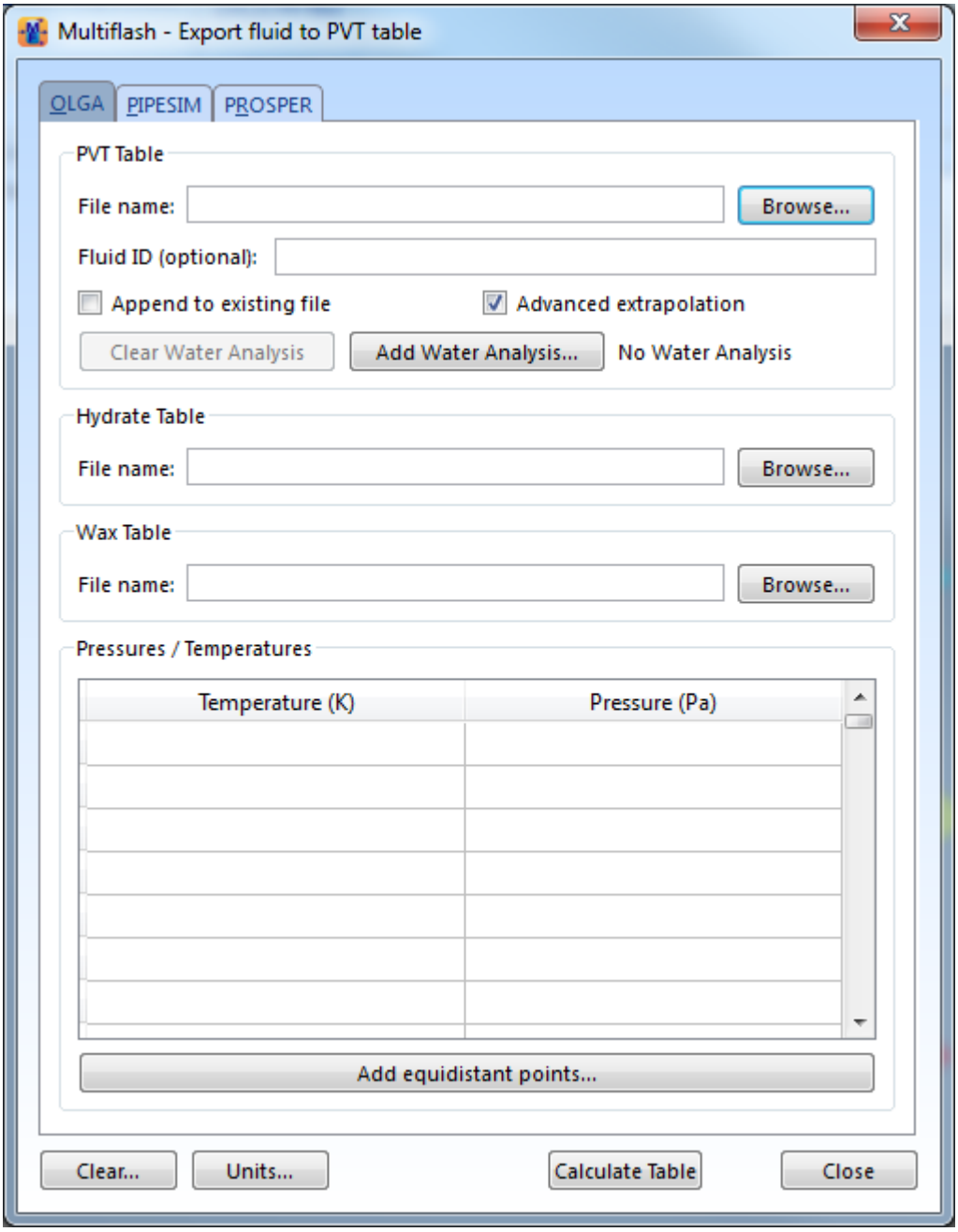
Multiflash exports a file containing all the physical property data required by OLGA. The format of the exported file is keyword-based and the data consists of a set of flash calculations performed at a series of pressure and temperature values. The information exported includes all the properties required by OLGA for either two-phase or three-phase problems.

To generate the export file:

1. Specify your model and fluid composition in the usual way.

   Requirement: The model specified for your fluid must include models for surface tension and viscosity.

2. On the **Import/Export** ribbon, click **PVT Tables**.
3. Click the **OLGA** tab.



4. Enter an export file name, by typing or using the **Browse** button.

   Tip: Use a file extension of .tab. If you do not use the the Browse button, the file is saved in the folder specified for PVT export files.

   Tip: The option *Append to existing file* can be used to append a new PVT table to a file that already has previously calculated OLGA PVT tables.

5. Optionally, specify a fluid ID.

   Tip: If you do not enter an ID, Multiflash generates one automatically. The ID must start with a letter.

6. Before generating the OLGA table, the fluid can be modified and a Water Analysis can be added. This follows the same procedure as the Inhibitor calculator. Several tables can be generated using different compositions for the aqueous phase without modifying the original composition.

7. The OLGA flow simulator relies on the fact that tables contain properties for non existing phases. Since Multiflash 6.1 a new extrapolation method is available, which is enabled by default. If you prefer to use the old method, uncheck the **Advanced Extrapolation** option. The new advanced extrapolation method directly extrapolates from the point where the phase exists to ensure continuity of the property values. The previous method did not fully ensure continuity for some fluids with sudden property changes at the phase boundaries.
8. To output an OLGA hydrate file, which defines the boundary of the hydrate forming region, enter a file name for the **Hydrate Table** by typing or using the **Browse** button.

   Tip: Use a file extension of .hyd. If you do not use the the Browse button, the file is saved in the folder specified for PVT export files.

   Requirement: You must have specified the hydrate model and one or more hydrate phases to output a hydrate file.
9. To output an OLGA wax file, which defines the paraffin wax precipitation, enter a file name for the **Wax Table** by typing or using the **Browse** button.

   Tip: Use a file extension of .wax. If you do not use the the Browse button, the file is saved in the folder specified for PVT export files.

   Requirement: You must have specified the wax model and wax phase to output a wax file.
10. For each temperature and pressure at which you want to generate data for the export file, enter the values into the table.

    Note: The values are used to generate a grid of points comprising each temperature at each pressure. For example, when you enter three temperatures and four pressures, you generate twelve points.

    Tip: Use **Add equidistant points** to generate a regular grid of points. Enter a start and end value for each variable, and the number of points to generate for each variable. For example, enter 50, 250, 5 for temperature (°C), and 10, 100, 10 for pressure (bar), to generate 50 sets of data, the five temperatures 50, 100, 150, 200 and 250 °C, each at a pressure of 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 bar.
11. If required, click **Units** to change the temperature and pressure units used.

    Restriction: You cannot specify the units for the output data. Multiflash outputs the data with the units required by OLGA.
12. Click **Calculate Table**.
13. When the OLGA table is created, you have the option to load it in the PVT table viewer for inspection.
14. If required, the **Clear** button can be used to restart the data input.

Exporting PROSPER PVT files

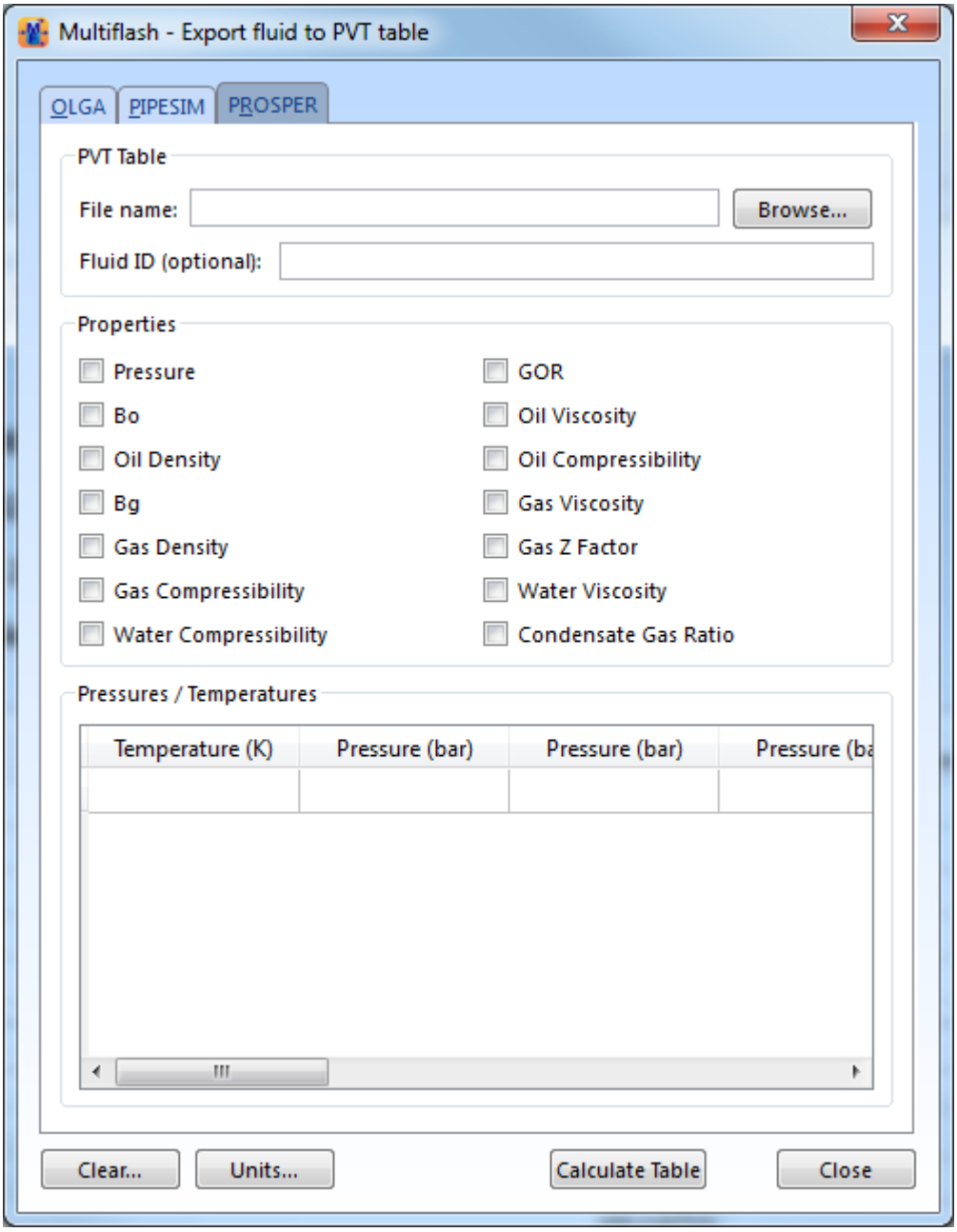
Multiflash exports a file containing all the physical property data required by PROSPER. The data consists of a set of flash calculations performed at a series of pressure and temperature values. For a complete definition of the PVT files please see the PROSPER manual.

To generate the export file:

1. Specify your model and fluid composition in the usual way.

   Requirement: The model specified for your fluid must include models for surface tension and viscosity.

2. On the **Import/Export** ribbon, click **PVT Tables**.
3. Click the **PROSPER** tab.



4. Enter an export file name, by typing or using the **Browse** button.

   Tip: Use a file extension of .pvt. If you do not use the the Browse button, the file is saved in the folder specified for PVT export files.

5. Optionally, specify a fluid ID.
6. For each property that you want to include in the export file, check the property's box.

7. For each temperature at which you want to generate data for the export file, enter the values into the table, and up to nine pressure values for each temperature.

   Tip: Each time you enter a temperature, a blank line is added to the table.

8. If required, click **Units** to change the temperature and pressure units used.

   Restriction: You cannot specify the units for the output data. Multiflash outputs the data with the units required by PROSPER.

9. Click **Calculate Table**.
10. If required, the **Clear** button can be used to restart the data input.

Exporting a CAPE-OPEN property package

Multiflash can export a CAPE-OPEN (CO) property package for use with the Multiflash CAPE-OPEN module.

To export the CO property package:

1. Specify your model and fluid in the usual way.
2. On the **Import/Export** ribbon, click **CapeOpen Package**.
3. Optionally, enter a fluid description.
4. Enter a name for the package.
5. Click **OK**.

Result: The package is saved in the folder specified for CAPE-OPEN packages.

Exporting a Multiflash legacy file

A number of software packages use older versions of Multiflash as their PVT engine. Multiflash provides an export option that generates a .mfl file that is compatible with versions 4.3 and 4.4 of Multiflash. This enables you to use the latest features of Multiflash to characterize your fluids and tune models, and then export those results for use in other packages.

The export tool has a number of restrictions because of the differences between the current and legacy file formats:

- Only the current stream is exported.
- The viscosity tuning is lost, because from Multiflash 6.0 the viscosity tuning method is different.
- PVT experiment data is not exported.
- If the fluid exported has a model that is unsupported in older versions of Multiflash, you will get an error when the file is opened using previous versions of Multiflash.

To generate the export file:

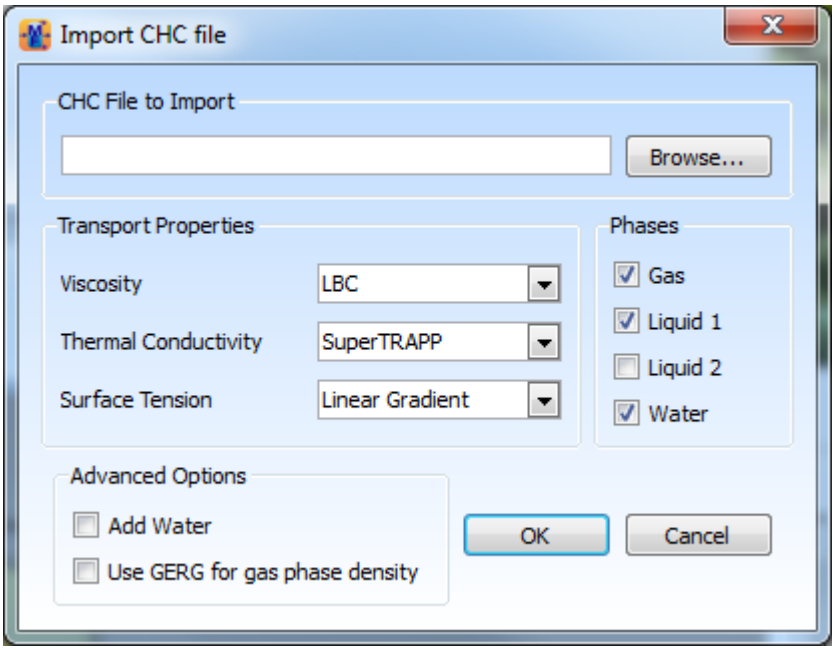
1. On the **Import/Export** ribbon, click **Export 4.3/4.4 MFL**.
2. On the message that summarises the restrictions, click **Yes**.
3. Enter a name for the new file, and then click **OK**.

Importing PVTsim files

PVTsim is a general thermodynamic properties package of Calsep. You can import the files generated by PVTsim (.chc files) into Multiflash to perform thermodynamic calculations.

To import a PVTsim file:

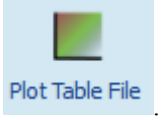
1. On the **Import/Export** ribbon, click **Import PVTSim CHC/CTM files**.



2. Click **Browse**, navigate to the file that you want to import, and then click **Open**.
3. Specify the transport properties and phases that you want to include for your model in Multiflash.
4. If you want to include water in your fluid, and it is not included in the .chc file that you are importing, check **Add Water**.
5. To use the GERG 2008 model to calculate the vapour phase density, check **Use GERG for gas phase density**.
6. Click **OK**.

PVT table file viewer

Multiflash exports a file containing all the physical property data required by OLGA. The generated file can be inspected for problems in the continuity of the property values along the pressure/temperature plane.

The PVT file viewer can be invoked by going to the **Import / Export** tab and clicking the Plot Table file button 

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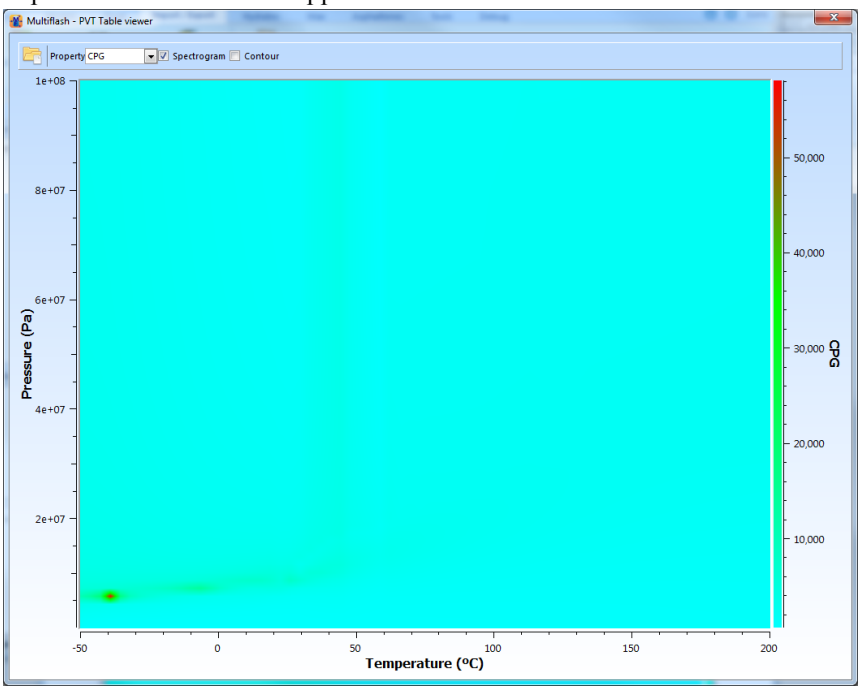
Using the PVT file viewer:

- Open a .tab file by clicking on the open file button
  A plot similar to this will appear:



- you can select which property to view by clicking the combo box.
  Tip: put the mouse over the plot to view the values of temperature, pressure and current property.

Example Excel spreadsheets

For any large set of flash calculations involving model comparison, or evaluation of the impact of operating conditions on the overall production design, the best approach is to use the Multiflash Excel functions. The details on how to use the functions are discussed in the *Multiflash Excel manual*. Example calculations are generating tables of pure component data, using linked flashes, and recycles for simple flowsheet calculations.

Example Excel files referred to are available in the MFL Files folder of your Multiflash installation, by default C:\Program Files\Infochem\MF61\ for 32-bit systems and C:\Program Files (x86)\Infochem\MF61\ for 64-bit systems.

Note: Some users want to fit their own experimental data for components not included in their version of Multiflash. To help users to do this, we have available a series of spreadsheets for fitting pure component data. They are not issued with the standard installation but we supply them on request.

UNIFACFIT.xls

What does it do?

This spreadsheet enables you to generate binary interaction parameters (BIPs) for activity models if UNIFAC group structures are available for your chosen components. The BIP values are adjusted so that predicted values fit the UNIFAC values.

How does it do it?

1. UNIFAC is used to calculate the phase equilibria of the binary pair.
2. You use the Excel solver tool to fit the data and generate BIPs for the binary pair. You can minimise the sum of squares of the differences between given and predicted temperature or pressure, or the differences in gas composition.

Why is it useful?

There are times when you want to use an activity model that has no stored BIPs for one or more binary pairs in your fluid. This spreadsheet is useful when you do not have the time to search for experimental data for the missing pairs, or are unable to find any.

Using the spreadsheet

The spreadsheet has several worksheets.

UNIFAC

This is the worksheet where you generate the phase equilibria data (liquid and gas phase compositions and temperature or pressure) that you are going to fit.

You specify, by entering information in the appropriate red cells:

- The databank to act as the source of pure component data, either Infodata or DIPPR if you have it.
- The names of the two components for your binary pair.
- Whether you wish to generate data for an isotherm or isobar and your chosen temperature or pressure.

The required data is generated by the Multiflash functions when the calculation in the spreadsheet is updated. It includes both column headings and plots. The composition range is fixed and the units are SI. There is no need to change these, although you can if you want.

You can see the status of the data generation in the spreadsheet. This should be OK if the UNIFAC group structures are available for your chosen components. An error status of –13201 means that the structures are missing for one or both components.

After the data is generated, select the worksheet for the model you want to use, WilsonE, UNIQUAC VLE or NRTL VLE.

Activity model worksheets

All the model worksheets function in a similar manner. The component names, conditions, temperature or pressure, and phase equilibria data are copied automatically from the UNIFAC worksheet. You then enter an initial guess for the BIPs (a useful default is to start with 0.0 for both) and use the Excel Solver tool to start the fitting procedure. The calculated BIPs appear in the cells used for the initial guesses and in the cells reporting the fitted BIPs. The equilibrium data are plotted for comparison with the UNIFAC generated data, enabling you to decide easily whether the solution is acceptable.

If the solution is not acceptable you can try one or more of the following:

- Start with a different initial estimate for the BIPs.
- Use a different criterion for minimisation. The default setting is to minimise the sum of squares of the differences between given and predicted temperature or pressure. You can also minimise differences in gas composition by changing the target cell in Excel Solver.

- Change the constraints on the values for BIPs when fitting. We have set limits on the values the BIPs can take as part of the Excel Solver tool.

After you have generated acceptable BIPs, you can store them in the Multiflash .mfl file that you are using for your fluid calculations.

VLEFIT.xls

What does it do?

This spreadsheet enables you to generate binary interaction parameters (BIPs) for activity models by adjusting the BIP values so that predicted values fit experimental data.

How does it do it?

1. Enter your experimental phase equilibria data for the binary pair.
2. You use the Excel solver tool to fit the data and generate BIPs for the binary pair. You can minimise the sum of squares of the differences between given and predicted temperature or pressure, or the differences in gas composition.

Why is it useful?

There are times when you want to use an activity model that has no stored BIPs for one or more binary pairs in your fluid. This spreadsheet is useful when you do not have the time to search for experimental data for the missing pairs, or are unable to find any, but you do have experimental equilibrium data for the required binary pairs.

Using the spreadsheet

The spreadsheet has several worksheets.

Experimental

This is the worksheet where you enter the phase equilibria data (liquid and gas phase compositions and temperature or pressure) that you are going to fit.

You specify, by entering information in the appropriate red cells:

- The databank to act as the source of pure component data, either Infodata or DIPPR if you have it.
- The names of the two components for your binary pair.
- Whether you wish to generate data for an isotherm or isobar and your chosen temperature or pressure.
- The choice of temperature and pressure units, from the list in blue below the temperature and pressure input values.
- Your experimental data.

  Note: If you have more data points than we have used, and are familiar with Excel, you can extend the range, remembering to change the cell references in the dependent activity model worksheets. Otherwise you should limit the data by choosing suitable points from the data available. If you have fewer data points, or missing data, enter #N/A in the cells which would otherwise be empty.

After you enter the data, select the worksheet for the model you want to use, WilsonE, UNIQUAC VLE or NRTL VLE.

Activity model worksheets

All the model worksheets function in a similar manner. The component names, conditions, temperature or pressure, and phase equilibria data are copied automatically from the experimental worksheet. You then enter an initial guess for the BIPs (a useful default is to start with 0.0 for both) and use the Excel Solver tool to start the fitting procedure. The calculated BIPs appear in the cells used for the initial guesses and in the cells reporting the fitted BIPs. The equilibrium data are plotted for comparison with the experimental data, enabling you to decide easily whether the solution is acceptable.

Note: If you have not used #N/A for missing data, the plots for x, y will not be relevant and should be ignored.

If the solution is not acceptable you can try one or more of the following:

- Start with a different initial estimate for the BIPs.
- Use a different criterion for minimisation. The default setting is to minimise the sum of squares of the differences between given and predicted temperature or pressure. You can also minimise differences in gas composition by changing the target cell in Excel Solver.
- Change the constraints on the values for BIPs when fitting. We have set limits on the values the BIPs can take as part of the Excel Solver tool.

After you have generated acceptable BIPs, you can store them in the Multiflash .mfl file that you are using for your fluid calculations.

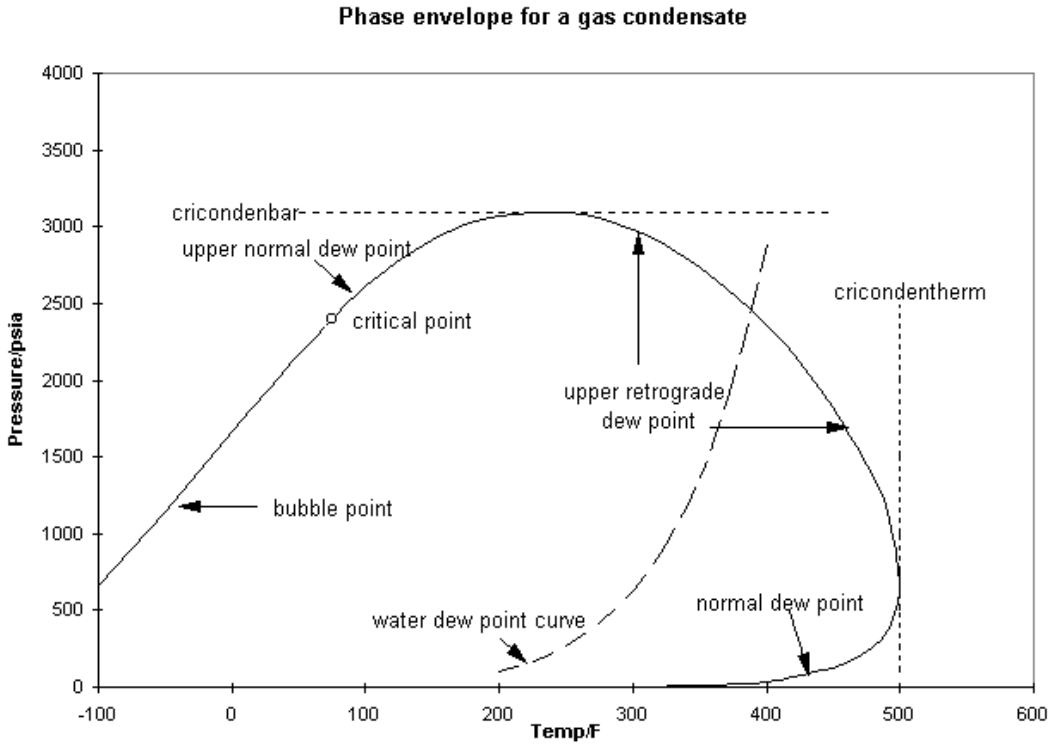
Multiflash Reference

Blank
by
design

Phases and components

Phase diagram: A brief description

A typical phase diagram for a gas condensate is shown below.



Feature	Description
Critical point	The point where the gas and liquid phases become identical, having the same density and composition. It is also possible to have a liquid-liquid critical point, where two liquid phases become identical.
Cricondentherm	The maximum temperature at which a two phase mixture can exist.
Cricondenbar	The maximum pressure at which a two phase mixture can exist.
Bubble point	If the pressure is reduced along an isotherm from the liquid or dense gas region (to the left of the critical point) it reaches its bubble point, where the light components no longer remain dissolved in the heavier liquid components and separate off as a gas.

Feature	Description
Retrograde dew point	In gas condensates the gaseous components are in excess and the heavier liquid components in the minority. In this case, as the pressure is reduced (to the right of the critical point) the liquids drop out of the gas phase at the retrograde dew point and the amount of liquid increases as the pressure decreases. This is known as retrograde condensation. The phase envelope shown above has a large retrograde region. At 300°F, for example, there are two dew points; one at 2.5 psia (the normal dew point) and one at 2977 psia (the retrograde dew point).
Normal dew point.	As the pressure is reduced further from the retrograde dew point, the liquid components evaporate again and the liquid disappears at the normal dew point.

Phase descriptors and key components

Multiflash can handle up to twenty phases at any time. An individual calculation will consider the possibility of all specified phases, but the maximum which can exist together at equilibrium is limited to seven.

The phase types that are included in the current version of Multiflash are:

- Vapour
- Liquid
- Pure solid
- Fixed composition solid
- Hydrate
- Wax
- Asphaltene

More than one of all these types can coexist, except for vapour. However, the software and models are structured such that it would not be sensible to define more than one wax or asphaltene phase. To identify each phase uniquely, they are assigned names and, in some cases, key components.

The default set of names used for the different phases is shown in the table. The phase names are used to identify the different phases when carrying out fixed phase flashes and to identify the phases in the Multi-flash output. You can create phases with any name, not just the standard list shown. For example, if you load a problem file that was not created in the Multiflash GUI, you might see other names.

Phase name	Description
GAS	Vapour phase
LIQUID1	First liquid phase
LIQUID2	Second liquid phase
WATER	Liquid phase with key component water
ICE	Solid phase with freeze-out model used for water

Phase name	Description
HYDRATE1	Hydrate phase, structure 1
HYDRATE2	Hydrate phase, structure 2
HYDRATEH	Hydrate phase, structure H
WAX	Wax phase
ASPHALTENE	Asphaltene phase with key component asphaltene
SOLIDNAME	If you apply the freeze-out model to any component other than water, the default phase name is generated by adding the prefix “SOLID” to the component name, for example, SOLIDDECANE.
NaCl, $NaCl.2H_2O$, KCl, $CaCl_2.2H_2O$, $CaCl_2.4H_2O$, $CaCl_2.6H_2O$, NaBr, $NaBr.2H_2O$, KBr and $CaBr_2.6H_2O$.	These are fixed composition phases included automatically when the **Halide Scales** option is selected in the hydrates model.

A supercritical phase (often termed dense phase) represented by equation of state models cannot be assigned an unambiguous phase type. This means that there is no way to distinguish between a gas phase and a liquid phase. The rule used in Multiflash is that a supercritical phase is labelled as GAS if

$VT^2 > V_c T_c^2$

where V_c is the pseudo-critical volume and T_c is the pseudo-critical temperature.

Key components

A key component helps to identify a particular phase. A key component can be specified in these ways:

- The key component is present in the phase to the maximum amount relative to the total mixture composition.
- The key component is present in the phase in the minimum relative concentration.

A key component is only required when a flash calculation must identify a phase uniquely, for example, when searching for a particular phase fraction. In Multiflash version 4.4 and later, multiple key components can be specified for each phase.

The phases defined by the Multiflash GUI include key components automatically. WATER is defined with aqueous components as key components and the other two liquid phases (LIQUID1 and LIQUID2) with aqueous components as a minimum key component. The aqueous key components are:

- Water
- Methanol
- Ethanol
- MEG
- DEG
- TEG

- Glycol
- Propylene glycol
- Propylene glycol monomethyl ether
- Dipropylene glycol
- Dipropylene glycol monomethyl ether

Non-aqueous phases can also have the special key component * (asterisk). This denotes a phase that has negligible amounts of the positive key components of all the other phase descriptors.

If you perform a calculation that requires a key component, for example, a fixed phase fraction flash, for a phase without a specified key component, you receive an error message.

To prevent potential problems, specify at least one key component for one of two non-aqueous liquids, using the Commands window from the **Tools** ribbon. See the *Command Reference Manual* for full details.

Example: The following command sets heptane as the key component (present in highest concentration) for the phase liquid1:

```
keys liquid1 heptane;
```

Another possibility is to use the following specifications for selecting the lightest and heaviest liquid phases:

```
keys liquid1 heaviest;
keys liquid2 lightest;
```

Whilst the latter might appear convenient, the rule is that the key component should be present in the phase to the maximum amount relative to the total mixture composition. If you have a mixture rich in methane, when the first liquid forms, it might have more methane than the heaviest component and thus be labelled liquid2. For the same reason, when specifying a liquid in terms of a specific component, it is often more useful to choose one in the middle of the component range rather than the heaviest hydrocarbon.

Another occasion when you need to be particularly careful in your choice of key components is when using an Excel spreadsheet to carry out linked flashes or recycles, where the composition of your streams can change significantly, thus changing the phase labelling without an actual phase change.

Components

Multiflash uses the following types of component:

- Normal component – A pure compound such as hydrocarbons, petrochemicals and chemicals which may exist as gas, liquid or solid depending on conditions of temperature and pressure.
- Petroleum fraction – A mixture of hydrocarbons, whose aggregate properties are characterised by standard tests, the results of which may be found in PVT laboratory reports.
- Pseudocomponent – An aggregated group of SCN petroleum fractions. Multiflash uses pseudocomponents to simplify the model of the fluid under investigation.

Component properties

The physical properties of normal components are stored in databanks. If you have a component that is not present in the databank, you must enter it as a user-defined component with a minimum set of properties for the component, depending on the models that you are using.

The physical properties of petroleum fractions and pseudocomponents are either entered by you, or estimated by Multiflash using the industry standard correlations of petroleum fraction recommended by Riazi and Al-Sahhaf *(Riazi, M.R. and Al-Sahhaf, T.A., Fluid Phase Equilibria 117 217 1996)*.

Multiflash provides two databanks, INFODATA and DIPPR^{TM}.

INFODATA is the Infochem fluids databank, which contains data on several hundred compounds and is always supplied as part of Multiflash. INFODATA contains only a limited range of components, mainly suitable for oil and gas applications. Although every effort has been made to ensure that the data stored are correct, we do not offer INFODATA as a quality assured databank.

DIPPR, produced under the auspices of AIChE, currently has data for around 2000 compounds, and is extended annually. DIPPR is offered as an optional module for Multiflash. The databank contains a broad range of components, including hydrocarbons, petrochemicals, chemicals and some metals. The correlations used in Multiflash are the recommended set for each property and component. Questions concerning quality codes and sources of data for the DIPPR databank should be referred to Infochem.

Both INFODATA and DIPPR store data for each temperature-dependent property (for example, vapour pressure) of a component as a function of temperature. Both databanks contain information on the upper and lower temperature limits for the correlation used for each component. Extrapolation routines are included in Multiflash so that pure component properties from either databank behave reasonably beyond the temperature limits of the stored correlation.

Properties which are not temperature-dependent are stored as constant values.

The properties available in DIPPR and INFODATA are shown in the table, together with properties that are estimated for petroleum fractions and pseudocomponents. Some properties might be missing for individual components. Both databanks, in addition to the properties listed, also contain the UNIFAC or PSRK group structures, where applicable.

Component properties available in Multiflash

Property	In INFODATA	In DIPPR	Estimated for petroleum fractions
Constant properties[1]			
Carbon number	N	N	Y
Molecular weight[2]	Y	Y	Y
Critical temperature[2]	Y	Y	Y
Critical pressure[2]	Y	Y	Y
Acentric factor[2]	Y	Y	Y
Critical volume	Y	Y	Y
Critical compressibility factor	Y	Y	N
Melting point	Y	Y	Y
Triple point temperature	Y	Y	N
Triple point pressure	Y	Y	N
Normal boiling point (at 1 atm)	Y	Y	Y
Liquid molar volume at 298.15K	Y	Y	N

Property	In INFODATA	In DIPPR	Estimated for petroleum fractions
Solubility parameter at 298.15K	Y	Y	N
Refractive index	Y	Y	N
Lower flammability limit	Y	Y	N
Upper flammability limit	Y	Y	N
Autoignition temperature	Y	Y	N
Flash point	Y	Y	N
Standard ideal gas enthalpy of formation at 298.15K	Y	Y	Y
Standard ideal gas Gibbs energy of formation at 298.15K	Y	Y	N
Standard ideal gas entropy at 298.15K	Y	Y	N
Heat capacity change on fusion	Y	Y	Y
Volume change on fusion	Y	Y	N
Enthalpy of fusion at melting point	Y	Y	Y
Entropy of fusion at melting point	Y	Y	Y
Standard net enthalpy of combustion at 298.15K	Y	Y	N
Radius of gyration	Y	Y	N
Parachor	Y	Y	Y
Dipole moment	Y	Y	Y
van der Waals area (UNIQUAC q)	Y	Y	N
van der Waals volume (UNIQUAC r)	Y	Y	N
Polarizability[3]	Y	N	N
Quadrupole moment[3]	Y	N	N
PC-SAFT model parameters[3]	Y	N	N
Entropy of formation[3]	Y	N	Y
Specific gravity[3]	Y	N	Y
Isobaric expansivity[3]	Y	N	N
Temperature dependent properties			

Property	In INFODATA	In DIPPR	Estimated for petroleum fractions
Solid density	Y	Y	N
Liquid density	Y	Y	Y
Vapour pressure	Y	Y	Y
Enthalpy change on evaporation (latent heat)	Y	Y	Y
Solid heat capacity	Y	Y	N
Liquid heat capacity	Y	Y	Y
Ideal gas heat capacity[2]	Y	Y	Y
Second virial coefficient	Y	Y	N
Liquid viscosity	Y	Y	Y
Vapour viscosity	Y	Y	Y
Liquid thermal conductivity	Y	Y	Y
Vapour thermal conductivity	Y	Y	Y
Surface tension	Y	Y	Y
Relative permittivity (dielectric constant)[3]	Y	N	N
Identity properties			
TYPE[4]	Y	Y	N
CAS number	Y	Y	N
FORMULA	Y	Y	N
FAMILY code[5]	Y	Y	N

[1] There are also some model-specific parameters.

[2] These properties are the minimum required for successful modelling. Most models require additional properties.

[3] These properties are available for a small proportion of the components in the databank.

[4] Normal databank components are TYPE 1, petroleum fractions are usually TYPE 12.

[5] Deprecated since DIPPR 2013.

Enthalpy and entropy definition

In Multiflash the enthalpy is calculated as:

$H = H_{ref} + H_{pg} + H_{res}$

Similarly, entropy is calculated as:

$S = S_{ref} + S_{pg} + S_{res}$

In both cases, suffixes represent the following:

- ref - the arbitrary value in a reference state to be defined.
- pg - the perfect gas contribution, which is calculated by integrating the equation for the perfect gas heat capacity.
- res - the residual value, which is calculated from the thermodynamic model specified for thermal properties.

The absolute value of enthalpy has no physical meaning but enthalpy differences are measurable quantities, therefore H_{ref} can be assigned an arbitrary value. The absolute value of entropy can be argued to have a physical interpretation, but in practise only entropy differences are experimentally accessible, so S_{ref} can also be assigned an arbitrary value.

Multiflash provides the reference types shown in the following table.

Reference type	Description
Compound	The enthalpy or entropy of each pure component is set to zero in the perfect gas state at 298.15K and 1 atm. This is the default reference state.
Elements	The enthalpy or entropy of each element is set to zero in the perfect gas state at 298.15K and 1 atm. This produces values that are much larger numerically than the 'compound' reference state, but differences between two states are the same. **Requirement:** You must use this reference type when calculating chemical reaction equilibria, because it is the elemental entities that are conserved rather than the molecular entities.
Standard‡	The reference value is chosen so that the entropy of each component in the perfect gas state at 298.15K and 1 atm is equal to the standard entropy of that component. The standard entropy is relative to a zero value at absolute zero. You can use this reference type in chemical reaction analysis for entropy, because the results are equivalent to the 'elements' reference type.
‡This can only be used for entropy calculation.	

If calculated values for a component differ between Multiflash and other software, the most likely cause is the different choice of reference state. However, enthalpy differences between two states should not differ significantly.

Activity model enthalpy

For activity methods, the default route for calculating the enthalpy is as described above. However, there are two additional methods by which the enthalpy of each component can be calculated. We recommend that these methods be used only if the consequences and implications are well-understood.

Notes:

- To select the enthalpy setting using the GUI go to the **Pure component** proprieties tool and in the **More Properties** tab select the "CP Liquid setting" property from the **Select Display Properties**

tool.

Liquid enthalpy based on saturated liquid heat capacity

The data stored for each pure component will normally include a correlation for the saturated liquid heat capacity (C_p) as a function of temperature. The enthalpy can be calculated based on the liquid C_p correlation instead of the perfect gas C_p correlation as usual.

With this option for the liquid phase, the pure component enthalpy at the reference state, 298.15K and 1 atm, is calculated with the existing procedure described above. Then the total enthalpy of pure components at the system temperature is calculated by adding the integral of the liquid C_p from the reference temperature to the given temperature plus the enthalpy change on evaporation at 298.15K, the Poynting correction, and the excess enthalpy calculated from the activity coefficient models.

Notes:

- The Poynting correction is disabled for low density components such as N_2 and O_2. This ensures a more correct description of mixtures of these components with denser ones such as water.
- The Poynting correction has been modified to give zero correction to the enthalpy and entropy at saturation pressure.

The enthalpy for the gas phase is calculated by the default method. The consequence is that the liquid heat capacity is based on the stored correlation for the liquid phase so it might be expected to be more accurate than the value calculated by the default method, which is based on the perfect gas heat capacity. However, the enthalpy difference between gas and liquid is no longer based on the databank correlation for enthalpy change on evaporation.

Gas and liquid enthalpy based on saturated liquid heat capacity

With this option, the liquid phase enthalpy is calculated as described above. The gas phase enthalpy is calculated by subtracting the enthalpy change on evaporation from the liquid phase value.

This procedure provides liquid phase enthalpy and C_p based on the databank correlation for liquid C_p. The enthalpy difference between gas and liquid is based on the correlation for the enthalpy change on evaporation. However, the gas phase enthalpy is no longer based on the perfect gas heat capacity and would, therefore, be expected to be less accurate than in the default method.

To use this option, set the Cp liquid setting to 2. This has to be done for all components, otherwise the results obtained will be invalid.

Multiflash models

A Multiflash model is a mathematical description of how one or more thermodynamic or transport properties of a fluid or solid depend on pressure, temperature and composition.

The key calculation carried out in Multiflash is the determination of phase equilibrium. This is based on the fundamental relationship that, at equilibrium, the fugacity of a component is equal in all phases. For a simple vapour-liquid system,

where

is the fugacity of component in the vapour phase,

is the fugacity of component in the liquid phase.

The models used in Multiflash to represent the fugacities in terms of temperature, pressure and composition fall into two groups: equation of state (EoS) methods and activity coefficient methods.

All thermodynamic properties for any fluid phase can be derived from an EoS.

For an activity coefficient method, the vapour phase properties are derived from an equation of state, whereas the liquid properties are determined from a combination of models which include a representation of the excess properties.

Liquid activity models are based on the following equation for the fugacity of component in the mixture,

In an ideal solution the liquid fugacity of each component is directly proportional to the mole fraction of the component, that is, the activity coefficient is equal to 1.

The ideal solution assumes that all molecules interact with the same intermolecular potential. This assumption is reasonable for molecules of a similar size and similar type. However, most real mixtures deviate significantly from ideality and the activity coefficient is different from unity.

Multiflash can also be used to calculate the phase equilibrium of systems containing solid phases. A solid phase can be either of the following:

- A fluid component that freezes.
- A specific solid phase such as a hydrate, wax or asphaltene.

The transport properties of a phase (viscosity, thermal conductivity and surface tension) are generally derived from semi-empirical models.

For a full description of all models in Multiflash, see the *Models and Physical Properties User Guide*.

Models and component data requirements

A basic minimum data set for any component should include the following:

- Molecular weight
- Critical temperature
- Critical pressure
- Acentric factor
- Perfect gas heat capacity.

The following table lists the data required, in addition to the above, for each model.

Model	Additional data required
Thermodynamic models	
RKS	None
RKSAPI	None
RKSA	Vapour pressure Saturated liquid density
RKSAINFO	As RKSA
RKS-HVP	None
PR, PR78	None
PR-HVP	None
PRA, PR78A	As RKSA
PSRK	As RKSA plus UNIFAC subgroup structures
LK, LKP	None
BWRS	Critical volume (VCRIT)
CSMA or GERG-2008	None
CPA	As RKSA plus association parameters (ASSBE, ASSEP, ASSGA) for associating components.
PC-SAFT	PC-SAFT parameters (SAFTEK, SAFTSIGMA, SAFTM, SAFTKAPPA, SAFTEPSILON, SAFTFF). Critical properties and the acentric factor are used to generate starting values for flash calculations, but do not affect the computed results from PC-SAFT. SAFTKAPPA, SAFTEPSILON and SAFTFF are only needed for associating components.
Ideal mixing	Vapour pressure Saturated liquid density Enthalpy of evaporation
NRTL	As Ideal mixing
Wilson E	As Ideal mixing
UNIQUAC	As Ideal mixing plus UNIQUAC surface and volume parameters (UNIQQ, UNIQR).
UNIFAC	As Ideal mixing plus UNIFAC subgroup structures (UNIFAC).

Model	Additional data required
Dortmund Modified UNIFAC	As Ideal mixing plus UNIFAC subgroup structures (UNIFAC).
Regular Solution	As Ideal mixing plus solubility parameter (SOLUPAR) and molar volume at 25°C (V25).
Flory-Huggins	As Ideal mixing plus solubility parameter (SOLUPAR) and molar volume at 25°C (V25).
Perfect gas	None
RK	None
Hayden O'Connell	Radius of gyration (RADGYR), dipole moment (DIPOLEMOMENT), Hayden-O'Connell association parameter (HOCASS).
Pure solid freeze-out	Melting point (TMELT), enthalpy of fusion (HMELT), heat capacity change on fusion (CPMELT), volume of fusion (VMELT).
Hydrate	Potential parameters (HYD1, HYD2, HYD3), cavity occupation code (HYDOC).
Wax	Melting point (TMELT), enthalpy of fusion (HMELT), heat capacity change on fusion (CPMELT), volume of fusion (VMELT).
Asphaltene	Vapour pressure Saturated liquid density
Mercury partitioning model	As specified fluid model
Transport properties	
Pedersen	None
Twu	Boiling point (TBOIL) Vapour pressure Saturated liquid density
LBC Lohrenz-Bray-Clarke	Critical volume (VCRIT) or model specific VC (VCLBC) Specific gravity (SG) Dipole moment (DIPOLEMOMENT)
CLS Chung-Lee-Starling	Critical volume (VCRIT) Dipole moment (DIPOLEMOMENT)
SuperTRAPP models	Critical volume (VCRIT) Dipole moment (DIPOLEMOMENT)
Macleod-Sugden (MCS and MCSA)	Parachor (PARACHOR)

Model	Additional data required
Costald	Saturated liquid density
Liquid viscosity mixing rule	Liquid viscosity
Vapour viscosity mixing rule	Vapour viscosity
Liquid thermal conductivity mixing rule	Liquid thermal conductivity
Vapour thermal conductivity mixing rule	Vapour thermal conductivity
Surface tension mixing rule	Surface tension
Linear Gradient Theory	Saturated liquid surface tension (STENSION)
Diffusivity – Fuller's method	Chemical formula (FORMULA) UNIFAC subgroup structures (UNIFAC).
Diffusivity - Hayduk-Minhas method	Critical molar volume (VCRIT), normal boiling point (TBOIL), parachor (PARACHOR) dipole moment (DIPOLEMOMENT), saturated liquid density, chemical formula (FORMULA), UNIFAC subgroup structures (UNIFAC).

Tuning models

Sometimes the properties calculated for a fluid do not correspond to known or measured values for that property. If the fluid contains petroleum fractions, you can refine the model used for your fluid to better fit experimental values.

Model tuning works by adjusting the petroleum fraction properties so that the model used matches experimental data more closely. The petroleum fraction properties that are adjusted depend on the type of experimental data used. For further information, refer to the *Models and Physical Properties User Guide*.

The experiment types that you can use for tuning a model are shown in the following table.

Experiment type	Description	Property values modified
Saturation (Dew and bubble point)	The dew point is the first point at which liquid appears. The bubble point is the first point at which gas appears.	If the RKSA, PRA, PR78A, or CPA models are used, the vapour pressure of each of the fractions is modified. The modifications are defined by two Mathias Copeman parameters. For other equation of state models, the acentric factor of the fractions is adjusted to match the experimental data.
Viscosity	You can use data for total hydrocarbon liquid viscosity or the stock tank oil viscosity.	Each viscosity model will modify different model specific properties: Pedersen (Mw), superTRAPP (Mw), LBC (Vc) and Twu (Tb).
Constant-mass expansion (CME)	The CME experiment provides information about the relative amounts of gas and liquid phase at a fixed temperature over a range of pressure. It also provides volumetric and compressibility data.	The critical temperature, critical pressure, Z_c, Peneloux volume shift, triple point pressure, and volume at 25°C for each fraction.
Constant-volume depletion (CVD)	The CVD experiment provides information about the relative amounts and volumes of gas and liquid in a reservoir during the process of gas extraction.	The critical temperature, critical pressure, Z_c, Peneloux volume shift, triple point pressure, and volume at 25°C for each fraction.
Differential liberation (DLE)	The DLE experiment provides information about the amount and volume of gas released during the extraction of oil from a reservoir. It also provides volumetric data.	The critical temperature, critical pressure, Z_c, Peneloux volume shift, triple point pressure, and volume at 25°C for each fraction.
Separator test	The separator test provides information about the relative amount of gas and liquid and their compositions at each of several stages of a separation.	The critical temperature, critical pressure, Z_c, Peneloux volume shift, triple point pressure, and volume at 25°C for each fraction.
Asphaltene matching	You can use data for bubble points, upper onset, titration or reservoir conditions.	Asphaltene matching adjusts the asphaltene model parameters, not the petroleum fraction properties.
Wax precipitation	You can use data for wax as percentage of liquid or the total fluid.	The melting point and enthalpy of melting of each n-paraffin fraction. The enthalpy of fusion, entropy of fusion and melting point of pure components.

Equation of state models

An equation of state (EoS) describes the pressure, volume and temperature (PVT) behaviour of pure components and mixtures. Each EoS has different terms to represent the attractive and repulsive forces between molecules. Any thermodynamic property, such as fugacity coefficients and enthalpies, can be calculated from an EoS relative to the ideal gas properties of the same mixture under the same conditions.

An EoS describes any system more accurately when binary interaction parameters (BIPs) have been derived from the regression of experimental phase equilibrium data. BIPs are adjustable parameters that are used to alter the predictions from a model until these reproduce as closely as possible the experimental data.

An EoS can be used over a wide range of temperature and pressure, including the subcritical and supercritical regions. They are frequently used for ideal or slightly non-ideal systems such as those related to the oil and gas industry, where modelling of hydrocarbon systems containing low density gases, such as H_2S, CO_2 and N_2, is the norm.

EoS methods are not generally useful for highly non-ideal chemical systems, for example, alcohol-water. For this type of system, at low pressure an activity coefficient approach is preferable, but at higher pressure you can use an EoS with excess Gibbs energy mixing rules, such as RKSA(Infochem).

The thermal properties of any fluid phase can be derived from an EoS. However, one property which is often poorly represented by the simpler equations of state is the liquid density. Multiflash offers enhanced versions of both the Redlich-Kwong-Soave (RKS) and Peng-Robinson (PR) cubic equations of state, where the EoS parameters can be fitted to reproduce both the pure component saturated vapour pressure, using a databank correlation, and the saturated liquid density at 298K or Tr=0.7 (Peneloux method). These are referred to in Multiflash as the advanced version of the particular EoS.

Equations of state available in Multiflash

Multiflash provides you with a comprehensive set of equations of state (EoS) to use in your PVT calculations.

Name	Notes	Recommended for
Ideal gas	This model is normally used in conjunction with an activity coefficient method when the latter is used to model the liquid phase.	Gases at low pressure.
Peng-Robinson (PR)	A cubic EoS. There is some evidence that this method provides improved volumes (densities) compared to RKS. An advanced version is available, which includes the ability to match stored values for liquid density and saturated vapour pressure, and a choice of mixing rule.	The advanced version is suitable for most applications.

Name	Notes	Recommended for
Peng-Robinson 1978 (PR78)	The 1978 revised version of the Peng-Robinson equation has a different treatment for the parameter κ. This model removes a defect in the original equation where heavy components with higher acentric factors become more volatile than components with lower acentric factors. For any mixture containing components with acentric factors greater than 0.49, the PR78 equation gives different results to the PR model and must therefore be treated as a different model. An advanced version is available, which includes the ability to match stored values for liquid density and saturated vapour pressure, and a choice of mixing rule.	The advanced version is suitable for most applications.
Redlich-Kwong (RK)	A cubic EoS. The "a" and "b" parameters are expressed explicitly in terms of the critical temperature and pressure.	This model is normally used in conjunction with an activity coefficient method, when the latter is used to model the liquid phase.
Redlich-Kwong-Soave (RKS)	A cubic EoS. There is some evidence that this method provides improved fugacities compared to PR and PR78. An advanced version is available which includes the ability to match stored values for liquid density and saturated vapour pressure, and a choice of mixing rule.	The advanced version is suitable for most applications that contain non-polar components. The API version is applicable to petroleum systems and mixtures containing hydrogen.
Cubic plus association (CPA)	A cubic EoS. This model contains the RKS (advanced) EoS plus an additional term, based on Wertheim's theory, that represents the effect of chemical association. For non-polar components, CPA reduces to the RKS (advanced) EoS. The CPA model also uses the Peneloux density correction to match the liquid density calculated from the equation of state to that stored in the chosen physical property data system. The volume shift is a linear function of temperature, set to match the saturated liquid density at two different temperatures. For low density gases, a constant volume shift is used, fitted to the gas's liquid density at a reduced temperature of 0.7.	Hydrate calculations and other fluids containing water, methanol, ethanol, MEG, DEG, TEG and salts.

Name	Notes	Recommended for
PSRK	A cubic EoS. This model contains the RKS (advanced) EoS with vapour pressure fitting, the Peneloux volume correction and the PSRK type mixing rules. The excess Gibbs energy is provided by the PSRK variant of the UNIFAC method. This is the same as the normal VLE UNIFAC model, except that the group table has been extended to include a large number of common low density gases.	Fluids with polar liquids.
Zudkevitch-Joffe (ZJ)	A cubic EoS. A variant of the original RK EoS. The “a” and “b” parameters are defined by simultaneously solving the equations of fugacity coefficients along the saturation line and the equation of pressure for both vapour and liquid phase. Suitable BIPs are required in order to use the model effectively, as the default BIPs in our databank are not regressed against any experimental data.	Improved predictions on enthalpy departures of saturated and compressed liquids, both pure and mixtures with suitable BIPs.
Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT)	This incorporates current ideas of how to model accurately the detailed thermodynamics of fluids within the framework of an EoS. The Multiflash version includes an implementation of the association term of PC-SAFT, which follows the same general structure as the association term in the CPA model. We also include the dipolar and quadrupolar terms when the dipole moment and quadrupole moments are available.	Polymer systems; most polar and non-polar systems.
PC-SAFT simplified	A version of PC-SAFT with simplified mixing rules, as proposed by researchers at the Danish Technical University. The same pure component parameters can be used for this model variant, but the model interaction parameters will be different.	Polymer systems; most polar and non-polar systems.
Lee-Kesler (LK) and Lee-Kesler-Plöcker (LKP)	These are 3-parameter corresponding states methods, based on interpolating the reduced properties of a mixture between those of two reference substances. The methods predict fugacity coefficients, thermal properties and volumetric properties of a mixture. However, they are rather slow and complex compared to the cubic equations of state and are not particularly recommended for phase equilibrium calculations.	Accurate predictions for density and enthalpy; non-polar or mildly polar mixtures, such as hydrocarbons and low density gases.

Name	Notes	Recommended for
Benedict-Webb-Rubin-Starling (BWRS)	An 11-parameter non-cubic equation of state. For methane, ethane, ethylene, propane, propylene, iso-butane, n-butane, iso-pentane, n-pentane, hexane, heptane, octane, carbon dioxide, hydrogen sulphide and carbon dioxide, the pure component parameters are set to values recommended by Starling in his book *'Fluid Thermodynamic Properties for Light Petroleum Systems', Gulf Publishing Co., Houston, 1973*. For other substances, the pure component parameters are estimated using correlations developed by Starling and Han, which are given in the same book. Given suitable interaction parameters, the model gives reasonable vapour-liquid phase equilibrium predictions, but we do not provide many BIPs in our databank. Owing to its complexity, it requires more computing time than the cubic equations of state.	Reproducing calculations based on this method; accurate volumetric and thermal property predictions for low density gases and hydrocarbons.
Multi-reference fluid corresponding states (CSMA)	Based on a collection of very accurate equations of state for a number of reference fluids. It provides accurate values of thermodynamic properties for any of the reference fluids and uses a 1-fluid corresponding states approach to estimate mixture properties. It is formulated so that mixture properties will reduce to the pure component values as the mixture composition approaches each of the pure component limits. You can also include the GERG-2008 gas model. Substances that are not reference fluids are included using a generalised equation of state.	Any mixture of the reference fluids; the GERG-2008 recommended uses, if included.
GERG-2008	An industry-standard high-accuracy model for mixtures of natural gas components. The model includes appropriate BIPs for all components in the GERG reference list. The model performs best for mixtures that do not involve strong specific interactions, and for any of the pure reference substances. The mixture model is applicable to systems that do not contain free water. The GERG-2004/2008 model is a well-verified standard. It is probably the best model for natural gas mixtures containing the GERG reference components. The model is fully described in *The GERG-2004 wide-range equation of state for natural gases and other mixtures, O. Kunz, R. Klimeck, W. Wagner, M. Jaeschke, GERG Technical Monograph 15 (2007).*	Acid gas injection; natural gas pipelines and processes; CO_2 transport and carbon sequestration; water/steam systems; air; instrument calibration and multi-phase meters.

Name	Notes	Recommended for
GERG-2008 (Infochem extension)	GERG-2008 has been extended to provide a pseudo reference EoS for petroleum fractions or components for which the high accuracy equations of state are not available. For a component or a peseudocomponent in a mixture with no high accuracy EoS, a four-parameter corresponding-states principle (CSP) model proposed by Sun and Ely(2005) is used to generalize the universal technical EoS. This CSP model implemented in Multiflash is in the form of the Helmholtz free energy, and the two non-spherical fluids of propane and octane are used as the reference fluids for non-polar or weakly polar components. For the details of the method, refer to *A corresponding states model for generalized engineering equations of state, L. Sun, J.F. Ely, International Journal of Thermophysics, Vol. 26, No. 3 (2005).*	Modelling the fluid phase behaviour of low density condensates containing small amounts of residuals, or a mixture with some components for which the high accuracy equations of state are not available.
Carbon dioxide high accuracy	The model comprises the reference EoS of Span & Wagner and high-accuracy models for the transport properties of carbon dioxide.	Any fluid where the carbon dioxide properties are critical to the calculation.
COSTALD	A corresponding states method for estimating the density of liquid mixtures. The COSTALD method can provide very accurate volumes for pure substances and simple mixtures, such as LNG. It is not generally recommended for heavy hydrocarbon mixtures with dissolved gases. **Note:** This model is not accessible from the user interface. For details of how to use the model, refer to the *Multiflash Command Manual*.	Liquids on the saturation line and compressed liquids up to a reduced temperature of 0.9.

Differences between the PR model in Multiflash and Aspen Hysys

The Peng-Robinson (PR) and PR78 equation of state (EoS) models implemented in Multiflash are based on the original publications by Peng and Robinson (1976, 1978). By default, the PR model is used for all phase properties: fugacities, density and thermal properties.

Based on information in Aspen Hysys documentation, in the standard PR model, the fugacity coefficients of components in a mixture are obtained from the PR78 EoS. This means that if the components in Multiflash have the same critical properties, acentric factors and BIPs as in Hysys, the calculated phase equilibrium (phase amounts and compositions) at given pressure and temperature should be very similar. However, the volumetric properties (density) and thermal properties (enthalpy, entropy) might differ. This is because the Hysys model uses a version of the COSTALD model to obtain the liquid density at subcritical conditions. Thermal properties are evaluated from the Lee-Kesler model.

The recommended version of the PR model in Multiflash is PRA78A. Amongst other features, this model allows the use of a volume-shift adjustment that considerably improves density predictions compared to the original PR or PR78 models. To obtain a match between Hysys PR liquid densities and PRA78A for

systems including petroleum fractions, we recommend that you use volume matching (using the CME PVT lab test) to adjust the volume shift parameters to match densities from Hysys.

You can specify that the LK model should be used in Multiflash to calculate thermal properties. You should contact Infochem technical support for assistance if you want to do this. Absolute values of enthalpy and entropy in Multiflash and Hysys will probably differ irrespective of the model used. This is because the enthalpy and entropy zero points are different. Enthalpy and entropy differences should, however, be comparable.

Advanced equation of state options

The advanced implementation of both the Peng-Robinson and the Redlich-Kwong-Soave equations of state (PRA, PR78A and RKSA models) contain additional non-standard features. These include the ability to match stored values for the liquid density and the saturated vapour pressure, and a choice of mixing rule.

The Peneloux density correction

The Peneloux density correction is a correlation used to match the density calculated from the equation of state (EoS) to that stored in the chosen physical property data system. For low density gases, the density is matched at a reduced temperature of 0.7 and the volume correction is assumed constant. In Multiflash, for liquid components the volume shift is treated as a linear function of temperature; the density is matched at 290.7 K and 315.7 K so as to reproduce the density and thermal expansivity of liquids over a range of temperatures centred on ambient. However, a third term is available, and you can enter all three coefficients as pure component properties. Refer to the *Models and Physical Properties User Guide* for further details.

Fitting the vapour pressure curve

For each component, the EoS a parameter is fitted by linear regression to the vapour pressure over a range of reduced temperatures corresponding to the stored data. Up to five coefficients are used, but fewer coefficients are fitted if there are insufficient data or if the extrapolation to low temperatures is unrealistic. If there is no vapour pressure equation for a component, the standard expression for each equation of state is used.

Mixing rules

The standard mixing rule for the cubic equations of state is the van der Waals 1-fluid mixing rule. This is a simple recipe for obtaining the properties of a mixture by combining the pure-component properties. It is a widely used and highly effective method for many non-polar mixtures encountered in the oil and gas industries.

For highly non-ideal systems, it is often useful to use a Gibbs energy excess model, for example, UNIQUAC or NRTL, as part of the mixing rule for the EoS. Refer to the *Models and Physical Properties User Guide* for further details.

CSMA and GERG-2008 reference fluids

The following substances are included in the CSMA model:

acetone	fluorine	propane	R134A
ammonia	helium	propylene	R14

argon	heptane	sulphur dioxide	R141B
benzene	cyclohexane	SF6	R142B
iso-butane	iso-hexane	toluene	R143A
n-butane	n-hexane	water	R152A
1-butene	hydrogen	xenon	R161
iso-butene	hydrogen sulphide	R11	R218
cis-2-butene	krypton	R113	R22
trans-2-butene	methanol	R114	R227EA
carbon dioxide	neon	R115	R23
carbon monoxide	nitrogen	R116	R236EA
carbonyl sulphide	nitrogen trifluoride	R12	R236FA
decane	nonane	R123	R245FA
DME	octane	R1234YF	R32
dodecane	oxygen	R1234ZE	R365MFC
ethane	iso-pentane	R124	R41
ethanol	neo-pentane	R125	RC318
ethylene	n-pentane	R13	

The equations of state are taken from various sources and do not all have the same quality or range of applicability.

The following substances are included in the GERG-2008 model:

methane	n-pentane	argon
nitrogen	isopentane	oxygen
carbon dioxide	hexane	hydrogen
ethane	heptane	carbon monoxide
propane	octane	water
n-butane	nonane	helium
isobutane	decane	H_2S

Activity coefficient models

Activity coefficient models are usually used to model any combination of polar and non-polar compounds, including those exhibiting very strong non-ideality. An activity model comprises a liquid model and a gas model.

The gas phase model used for sub-critical point mixtures is pressure-dependent, as shown in the table.

For pressure (bar)	Use this model
3-5	Ideal
5-10	HOC. The implementation of the HOC model in Multiflash allows the vapour phase association of substances such as acetic acid to be represented.
10-20	Redlich-Kwong or other EoS.

If the mixture contains one or more components above their critical point, such as dissolved gases, the properties of such components, for example, vapour pressure, are extrapolated.

To obtain accurate predictions from the liquid activity coefficient models, except UNIFAC, you must use BIPs. If these are not available in the BIP data set for your system then you must supply them for the missing values, matching the model used and using the correct units. The BIPs in Multiflash are in standard SI units, J mol^{-1}, except for Wilson A, where the BIPs are dimensionless. You can supply BIPs in other units, provided the units are specified correctly.

Liquid activity coefficient models available in Multiflash

A number of activity coefficient equations are available in Multiflash. Full details of each model are in the *Models and Physical Properties User Guide*.

Name	Notes	Recommended for
Ideal solution	The ideal solution model is used when the mixture is ideal, that is, when there are no mixing effects.	Ideal mixtures Pure component properties (from the physical property databank)
Wilson E	If no BIPs are included for your particular mixture you must supply them in the correct units to obtain accurate predictions.	VLE
Wilson A	A simplified form of the Wilson E model. To obtain accurate predictions you must supply dimensionless BIP values.	VLE

Name	Notes	Recommended for
NRTL equation	If no BIPs are included for your particular mixture you must supply them in the correct units to obtain accurate predictions. If you do not specify a value for the third adjustable parameter, α_{ij}, it is automatically set to 0.3 if the VLE version of NRTL is specified, or to 0.2 if the LLE version is specified. **Note:** The α parameter is symmetric, so only α_{ij} values need be supplied.	VLE, LLE, VLLE Use NRTL-VLE for azeotropic systems.
UNIQUAC equation	If no BIPs are included for your particular mixture you must supply them in the correct units to obtain accurate predictions.	VLE, LLE, VLLE
Regular Solution theory	The theory is applicable to systems that exhibit negligible entropies and volumes of mixing. However, it has been largely superseded by equations of state.	VLE for non-polar or slightly polar components
Flory-Huggins	The Multiflash implementation of Flory-Huggins theory includes a correction term. The Multiflash expression reduces to the standard Flory-Huggins theory if all interaction parameters are set to zero. However, to obtain reasonable results, the interaction parameters should be adjusted to better fit the data. It has been to some extent superseded by other models, such as PC-SAFT, but still offers the advantages of speed and simplicity.	Long chain molecules and polymer systems
UNIFAC method	Similar to UNIQUAC but the interaction parameters are predicted based on the molecular group structure of the components in the mixture. The model is completely predictive and does not require BIPs. Not suitable for mixtures that contain low density gases.	VLE, LLE, VLLE
Dortmund Modified UNIFAC	The two binary parameters between components are treated as quadratic functions of temperature. This is better able to represent the simultaneous VLE, LLE and excess enthalpies of polar mixtures than the original UNIFAC method. Not suitable for mixtures that contain low density gases.	VLE, LLE, VLLE of polar mixtures

Solid phase models

Multiflash can be used to calculate the phase equilibrium of systems containing solid phases, either mixed or pure. These can be when a normal fluid component freezes or a specific solid phase, such as a hydrate.

Solid freeze-out model

This model is used to calculate the thermodynamic properties of pure solid phases formed by freezing one or more of the components in the fluid mixture. It can be applied to any component, for example, water, carbon dioxide or methane in natural gases. It can also be used to model eutectic systems.

Scaling

In its general form, the freeze-out model can be applied to any solid phase of fixed composition. The model can, for example, be applied to hydrated salts such as monoethylene glycol (MEG) monohydrate, or to crystalline mineral salts. The model is available as part of the hydrates module, where it can be applied to halide scales.

Hydrate formation and inhibition models

Natural gas hydrates are solid, ice-like compounds of water and the light components of natural gas. They form at temperatures above the ice point and are therefore a serious concern in oil and gas processing operations. The phase behaviour of systems involving hydrates can be very complex because up to seven phases must normally be considered. The behaviour is particularly complex if there is significant mutual solubility between phases, for example, when inhibitors or CO_2 are present.

With the Multiflash recommended hydrate model and nucleation model, the hydrate dissociation and formation boundaries can be predicted. Between these two boundaries is the area of potential hydrate formation.

Hydrate model

The recommended hydrate model is the CPA-Infochem equation of state for the fluid phases plus the van der Waals and Platteeuw model for the hydrate phases. The CPA-Infochem model is based on the advanced RKS equation of state with additional association terms for describing the chemical association among the polar components such as water and methanol. The model also represents the inhibition effects and partitioning between phases of the common hydrate inhibitors methanol, ethanol, MEG, DEG, TEG and salts.

Two sets of BIPs are required, one for the equation of state, and the other for the association terms. The required binary interaction parameters by CPA for hydrocarbons, low density gases, water and inhibitors are available from the BIP databanks, INFOBIPS and the BIP correlations of OILANDGAS.

The thermodynamic hydrate model consists of lattice parameters for the empty hydrate and parameters for the interaction of gas molecules with water in the hydrate. There are different parameter values for each hydrate structure, I, II and H for gas hydrate formers. The hydrate must be associated with a liquid phase model that is used to obtain the properties of water. This must be the same model that is used for water as a fluid phase.

Note: In the Multiflash interface, the hydrate structure types are labelled as Hydrate 1, Hydrate 2 and Hydrate H, and are referred to using that terminology when discussing the use of Multiflash.

The main features of the model are:

- The description of hydrate phase behaviour uses a thermodynamically consistent set of models for all phases present. The vapour pressures of pure water and sublimation pressures of ice are very accurately reproduced.
- The following natural gas hydrate formers are included:

methane	ethane	propane
isobutane	butane	nitrogen
carbon dioxide	hydrogen sulphide	

- The following hydrate formers that are not usually present in natural gas but which form hydrate structure I or II are also included:

sulphur hexafluoride	ethylene	propylene
cyclopropane	oxygen	argon
krypton	xenon	THF

- Parameters are provided for the following compounds that form hydrate structure II in the presence of small 'help-gases' such as methane or nitrogen. These compounds might be present in condensate and oil systems:

cyclopentane	benzene	neopentane

- Parameters are provided for the following compounds that form hydrate structure H in the presence of small 'help-gases' such as methane or nitrogen. The formation temperatures are significantly higher (about 10 K) than pure methane or nitrogen hydrate. In practice, structure II hydrates usually form before structure H hydrates but, if there is enough water, structure H can also form. These compounds might be present in condensate and oil systems:

isopentane	neohexane	2,3-dimethylbutane
2,2,3-trimethylbutane	2,2-dimethylpentane	3,3-dimethylpentane
methylcyclopentane	methylcyclohexane	cis-1,2-dimethyl-cyclohexane
2,3-dimethyl-1-butene	3,3-dimethyl-1-butene	cycloheptene
cis-cyclooctene	adamantane	ethylcyclopentane
1,1-dimethylcyclohexane	ethylcyclohexane	cyclohexane
cycloheptane	cyclooctane	

- The thermal properties (enthalpies and entropies) of the hydrates and ice are included, allowing isenthalpic and isentropic flashes involving these phases.
- Calculations can be made for any possible combination of phases including cases without free water. No modification of the phase models is required to do this.
- The properties of the hydrates have been established by investigating data for natural gas components in both simple and mixed hydrates to obtain reliable predictions of structure I, structure II and structure H hydrates.

- The properties of the empty hydrate lattices have been investigated and the most reliable values have been adopted.
- Accurate prediction of the solubility of gases in water by the fluid model is achieved. This is particularly important for carbon dioxide and hydrogen sulphide, which are relatively soluble in water.
- Correct thermodynamic calculations of the most stable hydrate structure have been made.

The model is used to calculate the conditions (temperature or pressure) corresponding to the experimental determination of the hydrate dissociation point. This is equivalent to the conditions where the first very small quantity of hydrate appears after a sufficiently long time: the thermodynamic formation point. Before the thermodynamic formation point is reached, hydrate cannot form - this point is also called the stability limit. Beyond the stability limit hydrate can form, but might not do so for a long time.

The model has been tested on a wide selection of open literature and proprietary experimental data. In most cases the hydrate dissociation temperature is predicted to within ±1 K.

Hydrates in water sub-saturated systems

Hydrates can form even in systems where there is no free water present. Our hydrate model is capable of predicting this phenomenon, although the data available for validating the results are very limited. What we have noticed is that, for systems with very little water and at high pressures, the predicted hydrate dissociation temperatures using RKSAINFO and CPA tend to diverge with increasing pressure, with CPA predicting lower hydrate dissociation temperatures than RKSAINFO. There are no data presently available to confirm which is correct. However, for any water sub-saturated system, hydrate models must be extrapolated. In general, the thermodynamic principle of CPA provides more physically realistic extrapolation than RKSAINFO.

Nucleation model

The nucleation model was developed in collaboration with BP as part of the EUCHARIS joint industry project. This model is an extension of the existing thermodynamic model for hydrates. To extend the nucleation model for use with Multiflash, the following enhancements to the nucleation model were made:

- The model was extended to cover the homogeneous nucleation of ice and fitted to available ice nucleation data.
- The model was generalised to cover, in principle, nucleation from any liquid or gas phase.
- A correction for heterogeneous nucleation was included that was matched to available hydrate nucleation data.
- An improved expression was adopted for fluid diffusion rates.
- More robust numerical methods were introduced into the program.

The nucleation model can be used to predict the nucleation of any hydrate phases and provides an estimate of the temperature or pressure at which hydrates can be realistically expected to form. The model is based on the statistical theory of nucleation in multicomponent systems. Although there are limitations and approximations involved in this approach, it has the major benefit that a practical nucleation model can be incorporated within the framework of a traditional thermodynamic hydrate modelling package.

Comparisons of model predictions with experimental data have been made where possible. In general, measurements of hydrate nucleation result in an experimental error of ± 2º C and predictions are usually within this error band.

With the combination of the hydrate model and the nucleation model, it is possible to predict the hydrate risk area which lies between the dissociation and formation boundaries.

Note: The nucleation model considers only the nucleation of the specified phase. At low pressures, this can lead to predictions that the hydrate nucleation temperature is higher than the dissociation temperature. However, this is not a real situation as ice is not being considered except for nucleation.

Ice modelling

Ice is treated as a pure solid phase. The Infochem/KBC freeze-out model is used to model the ice phase within the hydrate model. As with the hydrate phase, you must associate the solid phase model with a liquid phase model that is used to obtain the properties of water. This must be the same liquid model that is associated with the hydrate phase.

Inhibitor modelling

Thermodynamic hydrate inhibitors decrease the temperature or increase the pressure at which hydrates will form from a given gas mixture.

The CPA-based hydrate model includes parameters for water with methanol, ethanol, MEG, DEG, TEG and salts. The RKSAINFO-based model also includes parameters for the less-common inhibitors isopropanol, propylene glycol and glycerol.

The treatment of hydrate inhibition has the following features:

- The model can explicitly represent all the effects of inhibitors, including the depression of the hydrate formation temperature, the depression of the freezing point of water, the reduction in the vapour pressure of water (the dehydrating effect) and the partitioning of water and inhibitor between the oil, gas and aqueous phases.
- The model has been developed using all available data for mixtures of water with methanol, ethanol, MEG, DEG and TEG. This involves representing simultaneously hydrate dissociation temperatures, depression of freezing point data and vapour-liquid equilibrium data. The model can be used to predict the amount of inhibitor required to suppress hydrate formation, see *Calculating inhibitor amounts required to suppress hydrate formation*.
- An electrolyte model is available in Multiflash, and a salinity calculator tool is provided as part of the inhibitor calculator, allowing the salt composition to be entered in a variety of ways, see *Adding inhibitors with the inhibitor calculator*. The electrolyte model includes the ions Na^+, K^+, Ca^{2+}, Cl^- and Br^-, and the salinity calculator can be used to convert a water analysis that includes other ions into an equivalent amount of Na^+, K^+, Ca^{2+}, Cl^- and Br^-, or salt pseudo-component.
- The solubility of hydrocarbons and low density gases in water/inhibitor mixtures has also been represented.

Phases for hydrate modelling

In most cases, six phase descriptors (PDs) are required for hydrate modelling: gas, hydrocarbon liquid, aqueous liquid, hydrate I, hydrate II and ice. At high pressures and low temperatures the “gas” phase may become liquid-like and a second non-aqueous liquid PD is needed. This is also the case if there is a significant amount of CO_2 or H_2S present. When considering structure H hydrates, an additional phase descriptor is needed for hydrate H.

In most practical cases a natural gas contains propane and the stable hydrate structure will be hydrate II, although for very lean gases at higher pressures hydrate I may be the most stable form. Key components are defined to distinguish between the hydrocarbon and aqueous liquid phases.

The phase names used in the hydrate models are: GAS, LIQUID1, LIQUID2, Water, Ice, HYDRATE1, HYDRATE2 and HYDRATEH. You can apply phase nucleation to both hydrates and ice, defined by the hydrate model. If phase nucleation is selected, this means that the nucleation model is defined and can be used to predict the nucleation of any of the hydrate phases or ice.

In contrast to the thermodynamic hydrate model, which allows all possible phases to be present when carrying out calculations, the nucleation model considers only the nucleation of the specified phase. At low pressures this can lead to predictions that the hydrate nucleation temperature is higher than the dissociation temperature. However, this is not a real situation as ice is not being considered except for nucleation.

If halide scales are considered, further phase descriptors are required. These must represent the correct fixed composition of the scale, these are: NaCl, $NaCl.2H_2O$, KCl, $CaCl_2.2H_2O$, $CaCl_2.4H_2O$, $CaCl_2.6H_2O$, NaBr, $NaBr.2H_2O$, KBr, $CaBr_2.6(H_2O)$.

The addition of these phase descriptors is done automatically by Multiflash when the **Halide Scales** option is selected.

Wax precipitation model

Waxes are complex mixtures of solid hydrocarbons that precipitate out of crude oils if the temperature is low enough. Under conditions of interest to the oil industry, waxes consist mainly of normal paraffins, with iso-paraffins and naphthenes also present. Waxes are thought to consist of many crystals, each of which is a solid solution of n-paraffins within a narrow range of molecular weight.

The wax model in Multiflash was developed by Coutinho.

The main features of the model are:

- It represents wax as a solid solution.
- It gives good predictions of waxing behaviour, both wax appearance temperature (WAT) and the amount of wax precipitated at different temperatures.
- It is applicable to both live and dead oils.
- It requires that the normal paraffins are explicitly present in the fluid model, as these are the wax forming components. You must either enter the measured n-paraffin concentrations or use the Multiflash PVT analysis to estimate the n-paraffin distribution.
- The composition of the wax phase is determined by the known thermal properties (normal melting point, enthalpy of fusion) of the n-paraffins, combined with their solution behaviour in both oil and wax phases.
- In principle the wax model can be used in conjunction with any conventional cubic equations of state. The default option in the Multiflash implementation is RKSA.

There are two versions of the model, the Wilson and UNIQUAC variants. The default version is the Wilson model, which approximates the wax as a single solid solution. This approach is relatively simple to apply and gives a good representation of the data, so it is recommended for general engineering use. The more complex UNIQUAC variant models the tendency of waxes to split into several separate solid solution phases. The UNIQUAC variant is activated by configuration files that can be supplied by Infochem if you want to simulate the detailed physical chemistry of wax precipitation.

With a limited experimental data set, we cannot make any definitive statements concerning the accuracy of the model in predicting the WAT. However, Coutinho's model provides a much improved prediction of the amount of wax precipitated as a function of temperature, compared with other published thermodynamic models.

Asphaltene flocculation model

The Multiflash asphaltene model is a variant of CPA, where the association term is used to describe the association of asphaltene molecules and their solvation by resin molecules. The interactions between asphaltenes and asphaltenes with resins are characterised by two temperature-dependent association constants: K_{AA} and K_{AR}. The remaining components are described by the van der Waals 1-fluid mixing rule, with the usual binary interaction parameters k_{ij}, so the asphaltene model is completely compatible with existing engineering approaches that work well for describing vapour-liquid equilibria. The model is a computationally-efficient way of incorporating complex chemical effects into a cubic equation of state.

The parameters for the model were initially developed from a study of nearly thirty sets of experimental measurements of asphaltene precipitation, which include both proprietary and public domain data.

The CPA-based asphaltene model in Multiflash is compared to a PC-SAFT approach from the literature in a paper by Zhang, X., Pedrosa, N. and Moorwood, T., *Modeling asphaltene phase behaviour: Comparison of methods for flow assurance studies, Energy Fuels, 26 (5), 2011*.

Combined solids model

The combined solids model enables you to specify any combination of wax, hydrate and asphaltene solid phases. The fluid phase model is RKSA-Infochem and the effect of salts on hydrates is represented by the electrolyte model.

Transport property models

For each of the transport properties, Multiflash offers several approaches to obtaining values for mixtures.

Viscosity

Name	Notes	Recommended for
SuperTRAPP Model	A predictive extended corresponding states model that uses propane as a reference fluid. The Infochem implementation of the SuperTRAPP model includes modifications to ensure that the viscosity of aqueous solutions of methanol, ethanol, MEG, DEG and TEG, or salts and ions, are predicted reasonably well. Overall, the SuperTRAPP method is the most versatile for viscosity predictions and its performance is generally better than the other methods available in Multiflash. **Reference:** *The corresponding-states principle: Dense Fluids, Huber, M. L. & Hanley, H.J.M.*, in *Transport properties of Fluids: Their correlation, Prediction and Estimation, J. Millat, J. H. Dymond & C. A. Nieto (Eds.), Cambridge University Press, (1996).*	Petroleum fluids and well-defined components over the entire phase range from the dilute gas to the dense fluid. The default viscosity model for use with equations of state.
Pedersen model	A predictive corresponding states model originally developed for oil and gas systems. It is based on accurate correlations for the viscosity and density of the reference substance methane. The model is applicable to both gas and liquid phases. The Infochem implementation of the Pedersen model includes modifications to ensure that the viscosity of liquid water, methanol, ethanol, MEG, DEG and TEG, and aqueous solutions of these components or salts, are predicted reasonably well. **Reference:** *Properties of Oils and Natural Gases, Pedersen, Fredenslund and Thomassen, Gulf Publishing Co., (1989).*	General oil and gas applications.
Twu Model	This is a predictive model suitable for oils. It is based on a correlation of the API monograph for kinematic viscosity, plus a mixing rule for blending oils. It is only applicable to liquids. **Reference:** *Twu, Generalised method for predicting viscosities of petroleum fractions, AIChE Journal,* ***32****, 2091, (1986).*	Liquid phase oils only.

Name	Notes	Recommended for
Lohrenz-Bray-Clark method	The LBC model is a predictive model which relates gas and liquid densities to a fourth degree polynomial in reduced density. In Multiflash the fluid densities are derived from any chosen equation of state, rather than the correlations proposed by *Lohrenz et al*. This has the advantage that there is no discontinuity in the dense phase region when moving between liquid-like and gas-like regions. Multiflash also allows two variants of the LBC model. The first uses the original LBC method to estimate the critical volume of petroleum fractions and takes the critical volume of other components from the chosen data source. The second variant fits the critical volume of each component to reproduce the liquid viscosity at the boiling point.	Fluids that contain the standard components found in oil and gas processing.
Liquid viscosity mixing rule	This method obtains the liquid mixture viscosity by applying a simple mixing rule to the pure component saturated liquid viscosities generated from a databank. Each component in the mixture must have a liquid viscosity correlation stored in the databank. This method is always used in conjunction with the vapour viscosity mixing rule.	Fluids whose components each have a liquid viscosity correlation stored in the databank.
Vapour viscosity mixing rule	The viscosity of a gas mixture at low density is calculated from the databank correlations for the zero pressure gas viscosities of the pure components. Each component in the mixture must have a vapour viscosity correlation stored in the databank. This method is always used in conjunction with the liquid viscosity mixing rule.	Fluids whose components each have a vapour viscosity correlation stored in the databank.

Thermal conductivity

Name	Notes	Recommended for
SuperTRAPP thermal conductivity method	The SuperTRAPP method is an extended corresponding states model that uses propane as a reference fluid. It is applicable to both gas and liquid phases. The model can be used for petroleum fluids and well-defined components. The thermal conductivity is defined as the sum of internal and translational contributions. The latter are divided into three contributions: dilute gas, residual and critical enhancement. The Multiflash model does not include a critical enhancement term. For pure substances, this can result in under-prediction of the thermal conductivity near the critical region. However, for a mixture the critical enhancement is usually negligible. The performance of the Super TRAPP method is generally better than the Chung-Lee-Starling method.	Petroleum fluids and well-defined components over the entire phase range from the dilute gas to the dense fluid. The default thermal conductivity model for use with equations of state.

Name	Notes	Recommended for
Chung-Lee-Starling thermal conductivity method	The CLS model is a predictive model for both gas and liquid mixture thermal conductivities. It requires the critical properties, T_c, V_c and ω for non-polar components. For polar and associating fluids, the dipole moment and an association parameter are also required. Association parameters for water, acetic acid and the lower alcohols are provided. The fluid density is required as part of the calculation and this quantity can be obtained from any of the thermodynamic models in Multiflash.	Oil and gas processing and polar mixtures.
Liquid thermal conductivity mixing rule	This method obtains the liquid mixture thermal conductivity by applying a simple mixing rule to the pure component saturated liquid thermal conductivities generated from a databank. Each component in the mixture must have a liquid thermal conductivity correlation stored in the databank. This method is always used in conjunction with the vapour thermal conductivity mixing rule.	Fluids whose components each have a liquid thermal conductivity correlation stored in the databank.
Vapour thermal conductivity mixing rule	The thermal conductivity of a gas mixture at low density is calculated from the correlations for zero density gas thermal conductivity of the pure components at the same temperature. Each component in the mixture must have a liquid thermal conductivity correlation stored in the databank. This method is always used in conjunction with the liquid thermal conductivity mixing rule.	Fluids whose components each have a vapour thermal conductivity correlation stored in the databank.

Surface tension

Name	Notes	Recommended for
Linear gradient theory model (LGST)	The model uses the properties of the phases in equilibrium to determine the interfacial tension. The key property is the density gradient that exists across the interface. With this model, you can estimate the interfacial tension between liquid-gas and liquid-liquid phases. **Reference:** *Zuo, Y. X. and Stenby, E. H., A Linear Gradient Theory Model for Calculating Interfacial Tensions of Mixtures, Journal of Colloid & Interface Science,* ***182****, 12, Elsevier (1996).*	Use in combination with any EoS-based fluid model, except for LKP, CSMA and the asphaltene model.
Macleod-Sugden surface tension model (MCS)	The model predicts the liquid-vapour surface tension of a mixture based on the pure component parachors stored in a databank. In the Multiflash implementation the vapour phase is described by the ideal gas equation. **Reference:** *Properties of Oils and Natural Gases, Pedersen, Fredenslund and Thomassen, Gulf Publishing Co., (1989).*	Fluids with standard components found in oil and gas processing.

Name	Notes	Recommended for
Macleod-Sugden 2-phase variant (MCSA)	The model predicts the liquid-vapour surface tension of a mixture based on the pure component parachors stored in a databank. In the Multiflash implementation the vapour phase is described by the selected model for the gas phase, and therefore is more accurate than the 1-phase variant. **Reference:** *Properties of Oils and Natural Gases, Pedersen, Fredenslund and Thomassen, Gulf Publishing Co., (1989).*	Fluids with standard components found in oil and gas processing.
Surface tension mixing rule	The surface tension for a liquid mixture is calculated from the correlations for the surface tension of the pure saturated liquids at the same temperature and pressure using a power law model.	Fluids with standard components found in oil and gas processing.

Diffusion coefficient

Name	Notes	Recommended for
Fuller method	The Fuller method calculates gas phase diffusion coefficients. It is an empirical modification of Chapman-Enskog theory.	Any model in Multiflash.
Hayduk-Minhas method	The Hayduk-Minhas method calculates liquid phase diffusion coefficients. It consists of a number of empirical correlations for different classes of mixture.	Any model in Multiflash.

Binary interaction parameters

Binary interaction parameters (BIPs) are adjustable factors used to modify the predictions from a model so that they reproduce as closely as possible the experimental data. BIPs are usually generated by fitting experimental VLE or LLE data to the model in question.

In general, the fitting procedure may be based on both binary and multi-component phase equilibria information, the former being the most common.

For the UNIFAC and PSRK models, BIPs are predicted by group contribution methods and BIPs apply between pairs of groups that form the components. Therefore, the group interaction parameters are usually regressed simultaneously from large sets of experimental binary data.

Temperature dependence

In most of the open literature sources, the reported BIPs are temperature-independent, that is, constant values. However, you can also enter temperature-dependent BIPs with either a linear or a quadratic dependence.

Note: We do not recommend using temperature-dependent values for the NRTL α parameter.

Units

The BIPs for most equation of state models are dimensionless. For activity models, and the two CPA association parameters, the BIPs have default units of J mol^{-1}.

Important: If BIPs from external sources are used in Multiflash, you must either change the BIP units in Multiflash to match the input values, or convert the external BIP values to J mol^{-1}.

The following table shows the available units and the actual input functions for the activity model BIPs.

BIP unit	Input function
J mol^{-1}	$A_{ij}=a + bT + cT^2$
cal mol^{-1}	$A_{ij}/4.184=a + bT + cT^2$
K	$A_{ij}/R=a + bT + cT^2$
Dimensionless	$A_{ij}/RT=a + b/T + cT$
Aspen	$A_{ij}/RT=a + b/T + cT$

The DECHEMA Data Series (CDS) for activity model VLE and LLE BIPs uses the K and cal mol^{-1} units.

The Aspen format allows you to transfer the BIP values for the NRTL equation from Aspen Plus without further change.

For the NRTL equation, the a parameter is defined as follows:

- All formats except Aspen, $a_{ij}= a + bT + cT^2$
- Aspen format, $a_{ij}= a + b(T-273.15) + c(T-273.15)^2$

BIPs and models

The more a BIP varies from its default value, the greater the adjustment required to make the underlying model fit the measured data. For some models, BIPs have some physical significance, but they are usually treated as empirical adjustment factors. Different models require different numbers of BIPs.

The cubic equations of state (RKS, RKSA, PR, PR78, PRA, PR78A, ZJ) require only a single BIP that can be either a constant, or a linear or quadratic function of temperature. When there is no available parameter value, the default value is zero. A BIP will usually have a small positive or negative value and the magnitude is usually much less than 1. For the models LK, LKP and CSMA, the default value of the interaction parameter is 1.

When non-standard mixing rules are used, for example, when using RKSA(Infochem), the number of BIPs increases. For the excess Gibbs energy type mixing rules (MHV2-type and Huron-Vidal-type), the number of BIPs is determined by the activity coefficient model used to describe the liquid phase. For the RKSA-Infochem mixing rule or the Huron-Vidal-Pedersen (HVP), three sets of BIPs are needed.

Note: The HVP mixing rule can work with two different types of BIP set. For information on how to specify which BIP set is used, see the *Models and Physical Properties User Guide*.

PC-SAFT requires two symmetric BIP sets, in addition to the pure component model parameters. The default value for both sets is zero.

CPA uses the same interaction parameters as RKSA, with the addition of three association parameters that describe cross association and self association. For non-associating binaries, the CPA and RKSA BIPs are the same. When one or both of the components can associate, the BIPs can be different.

Activity models generally reduce to the ideal mixing model when all BIPs are zero (the default value). The Wilson A, Wilson E and UNIQUAC models require two BIPs. NRTL requires two binary energy interaction parameters and a non-randomness factor, α. With the exception of α, these BIPs can take a wide range of numerical values and more that one set may adequately represent the same experimental data.

Note: The BIPs for the activity models are asymmetric and you must define the binary pair of components i and j in the correct order to agree with the fitted or reported BIPs.

The NRTL α parameter defaults to 0.3 for VLE calculations and 0.2 for LLE calculations. Values derived from fitting to experimental data will vary but are unlikely to be much greater than 0.6.

The Regular Solution and Flory Huggins models both use a single symmetric BIP with a default value of zero.

BIPs for CSMA and GERG mixing rule

For the CSMA with GERG mixing rule or GERG-2008 models, there are two BIPs for improving the critical temperature and volume of the mixture. There is also a weighting factor for the binary high accuracy departure functions for modelling the mixing behaviour.

The default names for the three BIPs with the GERG-2008 model are GERGBIP, GERGBIP-2 and GERGBIP-3. For GERGBIP and GERGBIP-2, each pair of components can potentially have three parameter coefficients. The first two are symmetric and represent the constant and linear (in temperature) interactions. The third value is asymmetric, where the coefficient between X and Y is the reciprocal of that between Y and X.

GERGBIP-3 is the weighting factor of the binary high accuracy departure functions. By default, it is set to zero. If the mixing rule has the departure function equation available for the binary system, a non-zero value will be displayed.

BIPs available in Multiflash

Our main BIP databanks are applicable to oil and gas processing operations. The user does not need to change the BIP databank. It will be automatically selected following the rules below:

INFOBIPS contains all the BIPs for the cubic equation of state models PR, PRA, PR78, PR78A, PRA-HVP, RKS, RKSA, RKSA-HVP, RKSA (Infochem) and CPA for hydrocarbons, water, methanol, glycols, H_2S, CO_2 and N_2. It also includes BIPS for Wilson-E and the VLE variants of NRTL and UNIQUAC, based on the data reported in the Dechema Chemistry Data Series. Other BIPs are also included for models such as CSMA, GERG-2008, BWRS and LKP. These values are generally for particular mixtures not covered in the standard correlations.

OILANDGAS contains BIP correlations that can be used to estimate BIPs for the PR and RKS variants, CPA and LKP models for hydrocarbon and low density gas mixtures that include petroleum fractions.

INFOLLBIPS stores BIPs for use with the LLE variants of NRTL and UNIQUAC.

INFODATA and our version of DIPPR are used for the UNIFAC model, whose BIPs are predicted from group contributions. The data records for pure components in INFODATA contain information on UNIFAC groups, where applicable, enabling the BIPs to be generated. Groups for use with the PSRK and Dortmund Modified UNIFAC models are also stored as part of the pure component UNIFAC record. Where the groups vary, Multiflash applies the correct group structure to match the chosen model. The DIPPR databank includes the same group information.

Note: When using the PSRK EoS, you may see a warning message if the UNIFAC group contributions are missing for any component in your system.

You can have two BIP banks in force for any problem. When an equation of state model is defined, Multiflash first searches INFOBIPS and then OILANDGAS. If any BIPs are still missing, they are set to default values. The VLE variants of the activity methods only access INFOBIPS, but the LLE variants access INFOLLBIPS, followed by INFOBIPS.

Petroleum fluids

Petroleum fluids are typically complex mixtures consisting of many thousands of hydrocarbon components. It is not practical to identify all these components by analytical methods. Even if it were possible to carry out an analysis it would not be feasible to model the physical properties of the fluid by including all the identified components.

The practical approach adopted in the oil and gas industry is to base the model of a fluid on limited compositional analysis and other standard tests.

PVT laboratory analysis

A PVT laboratory analysis is a compositional analysis of the fluid, usually carried out by gas chromatography. The gas and liquid from a separator test or bottom-hole sample are analysed separately and the results are usually recombined to give a reservoir fluid composition.

The analysis usually comprises the following:

- The lighter hydrocarbons are individually identified, along with some inorganic compounds, such as nitrogen, CO_2 and H_2S.
- The analysis for hydrocarbons with more than six or seven carbon atoms is generally reported as single carbon number fractions (SCNs), which represent compounds in boiling point ranges. For example, a C9 SCN contains all hydrocarbons that boil between the normal boiling point of n-octane + 0.5 ºC, and the normal boiling point of n-nonane + 0.5 ºC.
- The analysis stops at a carbon number that is reported as a plus fraction, for example, C22+. The plus fraction contains all the material in the heavy end of the fluid and often represents a substantial proportion of the fluid.
- Optionally, an analysis of the n-paraffin content.

True boiling point distillation data

True boiling point (TBP) data usually comprise the following items for each measured fraction:

- Cumulative percentage distilled by volume
- Fraction boiling point
- Measured molecular weight of fraction (optional)
- Measured specific gravity of fraction (optional)

Example: The fraction from 0% to 10% by volume has a molecular weight of 136 and a specific gravity of 0.782. The TBP of 165.6 °C corresponds to 0% distilled off and 176.7 °C corresponds to 10% distilled off, so the first fraction is that which distils between 165.6°C and 176.7°C.

D86 distillation data

D86 is a standard analytical procedure that provides only cumulative and boiling point data for each fraction. The oil sample is placed in a single vessel and progressively heated to drive off gas. Multiflash converts D86 data into equivalent TBP data using the method of *Riazi and Daubert, Analytical Correlations Interconvert Distillation Curve Types, Oil & Gas Journal, 84, 50, 1986*.

Characterization

Characterization is the use of the information from a PVT laboratory analysis report to construct a compositional fluid model in Multiflash. Characterizing a petroleum fluid is an essential pre-requisite to studying the phase behaviour and other properties of the fluid.

The objectives of the Multiflash characterization procedure can be summarised as:

- Make optimum use of measured data.
- Construct a compositional model that is not restricted to a particular thermodynamic model.
- Ensure that phase behaviour calculations are not sensitive to the number of pseudocomponents.
- Achieve high fidelity based on compositional information.
- Allow model tuning to reproduce reliable experimental measurements.

Data validation in PVT experiments

Multiflash provides a data consistency and validation scheme for PVT experimental data. The quality of the data is analyzed using the following criteria to assess the quality of the data:

- Expected trends in experimental properties.
- Internal consistency between experimental properties.
- Hoffman plots after deriving liquid phase composition from experimental data in depletion experiments.
- Relationship amongst the experimental properties implied by the overall mass balance.

Constant mass expansion

The constant mass expansion experiment provides information about the relative amounts of gas and liquid phase at a fixed temperature over a range of pressure. It also provides volumetric and compressibility data.

The following checks are carried out:

- Relative volume is inversely proportional to pressure.
- At saturation point, relative volume is unity.
- Y factor is proportional to pressure.
- Y factor is consistent with the pressure, saturation pressure and relative volume.
- Single phase liquid density is proportional to pressure.
- Single phase density is consistent with the Z factor.
- Compressibility is consistent with the relative volume in single phase region.

Differential liberation

The differential liberation experiment provides information about the amount and volume of gas released during the extraction of oil from a reservoir. It also provides volumetric data.

The following checks are carried out, where P_b is the bubble point pressure of the oil at the experiment temperature:

- For $P > P_b$
  - Oil volume formation factor is inversely proportional to pressure.
  - Liquid density is proportional to pressure.
  - Solution gas oil ratio is constant at its value at the bubble point pressure.
- For $P < P_b$
  - Oil volume formation factor is proportional to pressure.
  - Liquid density is inversely proportional to pressure.
  - Solution gas oil ratio is proportional to pressure.
- Gas volume formation factor is inversely proportional to pressure.
- If appropriate data exist, material balance calculations to obtain liquid compositions at each stage and develop diagnostic Hoffman plots.

Constant volume depletion

The constant volume depletion experiment provides information about the relative amounts and volumes of gas and liquid in a reservoir during the process of gas extraction.

The following checks are carried out:

- Moles of cumulative depleted gas is inversely proportional to pressure
- Gas density is consistent with the gas Z factor
- If appropriate data exist, material balance calculations to obtain liquid compositions at each stage and develop diagnostic Hoffman plots.

Separator test

The separator test provides information about the relative amount of gas and liquid and their compositions at each of several stages of a separation.

The following checks are carried out:

- Overall mass balance over the entire set of separators.
- If appropriate data exist, material balance calculations to obtain liquid compositions at each stage and develop diagnostic Hoffman plots.

How the blending method works

The blending method is a way to combine previously defined fluids within Multiflash. It works for any type of fluid that can be represented in Multiflash and saved in a .mfl file, although it works best if the fluids and the pseudo-component distributions are similar.

Note: Volume blending requires a density value. If you use volume blending, we recommend that the fluid model is defined in the original .mfl files, so that the density can be calculated at the standard or the given condition, if the density is not specified.

The blending method works as follows:

1. Identify the pure components from each fluid used, and add them together in the correct proportions.
2. Identify the dominant pseudo-components from each fluid used, and add them to the new mixture.

   The dominant pseudo-components are those with the highest concentrations in the mixture for each range of molecular weight and also those that occupy the extreme positions of the molecular weight distribution.
3. For the remaining pseudo-components from each fluid used, add them to the most physically similar dominant pseudo-component, and average the physical properties of the resulting blended pseudo-components.

The method has the following advantages:

- It is automatic and requires no user intervention.
- The properties of the blend change smoothly with changing blend ratios. The properties of the unblended fluids also change smoothly as small amounts of other fluids are added, that is, the method shows correct limiting behaviour.
- The method of averaging the properties of the blended pseudo-components is exactly the same as that used in the PVT analysis procedure to create the pseudo-components used to represent the properties of the original petroleum fluids.
- The method handles waxy and asphaltenic crudes, thereby predicting the likely wax or asphaltene formation from the fluid blend.

Differences between blending and characterizing multiple fluids

The blending tool and the same pseudos tool perform a similar function, but there are important differences:

- The blending tool produces a single fluid, whereas the same pseudos tool produce a fluid for each input fluid.
- Blending uses the lumped components without considering the original characterization, and therefore maintains a plus fraction for each fluid.
- Blending does not make use of PVT Experimental data, therefore you cannot perform model tuning after blending.

Troubleshooting

Models

Model is not available

If a model on a Select Model Set tab is greyed out this usually means that it is an optional add-on and has not been licensed. The optional models include:

- Hydrates
- Wax
- Asphaltenes
- Mercury
- PC-SAFT
- CSMA (includes IAPWS-95 and CO2 High accuracy model)

Groups not available for UNIFAC model

The UNIFAC model generates the binary interaction parameters (BIPs) from group contributions. Although the majority of components in both the INFODATA and DIPPR databanks can be constructed from UNIFAC groups, there are exceptions, for example, complex cyclic components.

If some BIPs cannot be generated you see a warning dialog box.

In the **Log** panel you see a warning message:

*** WARNING -13201 ***
Missing UNIFAC structure for one or more components

If you define the model first this warning message will not be generated until you have defined components and tried to carry out a calculation.

Tip: If you do encounter a situation where standard UNIFAC groups are missing, particularly for low density gases, you should try loading the PSRK model. PSRK uses a variant of UNIFAC with additional structural groups.

If there are missing groups then you should note that because UNIFAC is the liquid phase model, if you try to carry out flashes involving the liquid phase, for example, dew and bubble point calculations, the flash will fail. However, the gas phase for the UNIFAC VLE model is defined with a separate gas phase model and isothermal flashes will apparently work, with the stream being reported as all gas.

It is possible to add user-defined UNIFAC groups, although there are no specific menu options. You would have to enter commands through the command box. Information on the commands can be found in the *Multiflash Command Reference Manual*.

Input conditions

Check units

It is always possible to make mistakes when entering numerical values. You should therefore check carefully, particularly if you feel the results appear unusual, that

- the values for the input conditions are correct
- they are in the correct units and that
- if they are fixed quantities for the flash calculation chosen, they appear correctly in the output

Another problem relating to units may occur if the input conditions are set in a problem setup file, but the input units are not specifically defined. In this case, when the file is loaded, it will be assumed that the values correspond to the units currently set in Multiflash. If this is not your intention it will clearly lead to an incorrect result in your terms, but may not be reported as an error in Multiflash.

BIPs

Components not defined for a BIP set

If you load a file of BIPs that contains values for components that are not in your current fluid, you see a warning message for each missing pair:

*** WARNING -223 ***
One or more components in this BIP set are not currently defined

If you know the reason for the warning, you can ignore it, for example, when BIPs for components that are not yet specified are in the loaded file.

BIP units

We cannot stress often enough that to obtain correct results the BIPs entered must match the Multiflash definition and be in the correct units. A good source of phase equilibrium data and BIPs is the Dechema Chemistry Data Series, which is in several volumes:

Dechema Chemistry Data Series (CDS)
ISSN 0840-9645
Volume I to XVI
Publisher: Dechema

Their standard convention is to report activity model BIPs for VLE in cal/mol. Either these need to be converted to J mol^{-1} for use in Multiflash or the units for BIPs must be changed to cal/mol. Similarly, the LLE BIPs for UNIQUAC and NRTL either need to be multiplied by the gas constant R (8.314 $JK^{-1}mol^{-1}$) for use in Multiflash or the BIP units must be set to K.

PVT analysis

Inconsistency warning for fluid characterization

Not all the PVT analyses we have tested are well reproduced by the PVT characterisation fitting method. If this happens, it may be due to the inconsistency between the SCN distribution and the information for the molecular weight and/or specific gravity for the plus fraction or STO or total fluid. If you do see a warning related to the inconsistency, use the phase envelope tracer to see how the phase envelope is affected by characterising the fluid with and without the information for the molecular weight and/or specific gravity.

Water in the fluid

Defining a water cut using the PVT analysis form alters the amount of water in the overall stream but without changing the amounts of any components which are not hydrocarbons and are not in the list of discrete components. It can therefore affect the composition of an aqueous phase defined elsewhere in the program.

Flash calculations

General

This is the most difficult area for which to give general guidance. Multiflash is capable of handling complex mixtures which may exhibit multiphase phase equilibrium.

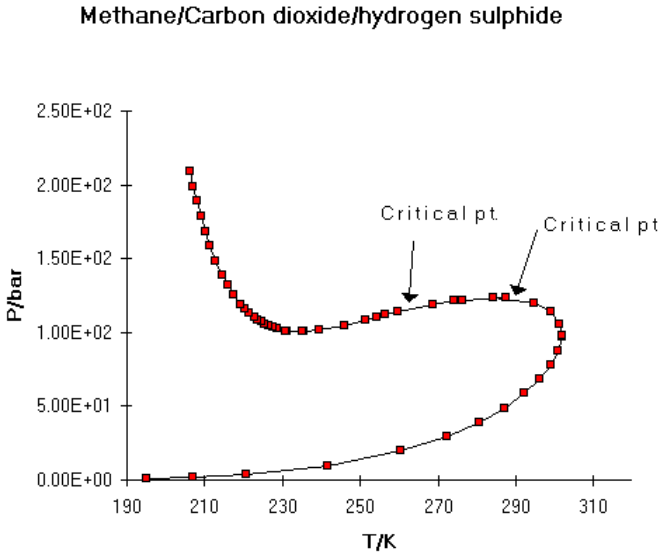
Some flash calculations gave a unique solution. These include (P,T), (P,H), (P,S), (T,V), (U,V) and (S,V). In principle, these flash calculations should always have a solution. However, in practise, the range of conditions for which a solution can be found depends on the models used. For example, if the volume specified for a flash is smaller than the b parameter for a cubic equation of state it is not possible to solve any flash that includes the volume.

Dew and bubble point calculations (and fixed phase fraction flashes in general) are common cases of flashes that may have no solution, a single solution or multiple solutions. When one of these calculations fails it will produce output similar to the following in the main output window:

*** ERROR 20292 ***
Cannot find converged point - max. iterations
*** ERROR 20024 ***
Cannot find starting point for calculation - there may be no solution.
*** ERROR 344 ***
The flash calculation has not converged

The difficulty is to assess the reason for the error and how best to investigate the cause and take corrective action. An error may be reported when there is genuinely no solution to the problem posed. The error above, for example, resulted from asking for a bubble point at a pressure above the cricondenbar for the gas condensate discussed earlier. As you can see from the phase diagram presented there is no bubble point at this pressure as it is above the pressure at which the two phase mixture will exist. In general you will not be able to solve bubble or dew point problems at pressures above the cricondenbar or temperatures above the cricondentherm.

Another type of phase envelope where problems can arise is shown below



As you can see the phase envelope turns up at low temperatures and high pressures. This is also typical of phase envelopes with a significant amount of hydrogen where you may not find a solution for the bubble point at low temperatures.

Insufficient phases specified

If you have set up a problem with only one gas and one liquid phase defined, you might see a warning

message above a vapour-liquid or single liquid phase solution. Two different warnings will be given depending on the problem:

*** WARNING -20001 ***
Unstable solution, more phases exist.

*** WARNING -20006 ***
Type of phases present do not agree with phase descriptors.

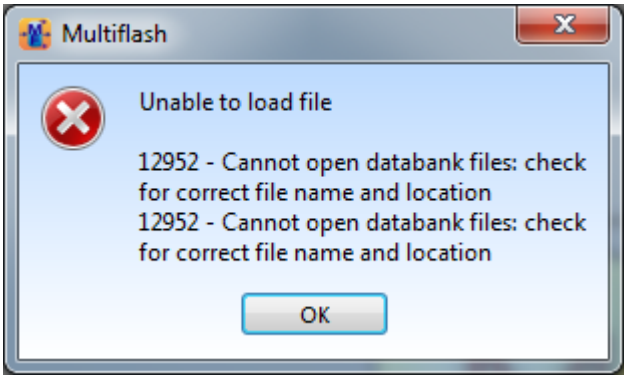
These warnings indicate that you should consider looking for another liquid phase, and therefore define a second liquid phase descriptor for this.

Components

Databank not found

All licensed databanks will be placed in the installation folder. However, it is possible that the files may have been moved or overwritten. If a databank cannot be found then the following warning message will appear when you use the Select Component dialog box.

If you attempt to load a Multiflash problem file that defines the databank and the databank cannot be found a message similar to the following will appear.



The path used by Multiflash to find databank files is set in the Preferences Window under Folders. Initially this will be the installation folder but you can change the path if you have moved the databank to another location.

Databank not licensed

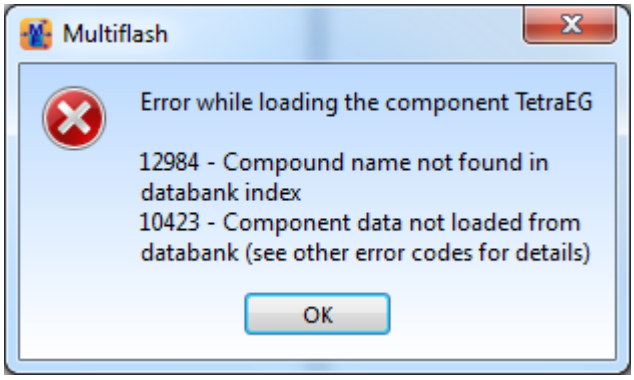
If you have not licensed DIPPR then warnings will appear.

If you have an earlier version of DIPPR and try to run Multiflash with the latest version, then following error message will appear.

The only corrective action is to substitute INFODATA as the data source or extend your licence.

Component cannot be found

The component you need may not be stored in the selected databank. The error message is self-explan-atory



Before you accept this, however, it is worth checking

- That you have spelt the name correctly
- That a formula or substring search cannot identify the component under another name
- That formula searches are specified in standard chemical nomenclature

If a component is not present in the INFODATA databank you should try the DIPPR databank if you have a license. If you are planning a study and find that a component is missing please check with Infochem. We may be able to locate the required data.

Tip: If the component you cannot find in the databank is present only in small or trace amounts it may be possible to substitute a similar compound without significant error. However, this will clearly depend on the particular calculation and application

Too many components in the mixture

The maximum number of components in a mixture in the current version of the software is 200. If you try to select more components you will be warned that the limit has been reached.

Tip: If you have some components of similar type and size in your mixture, preferably present in small amounts, then it may be worth combining them to reduce the overall number of components. This is particularly useful when dealing with natural gases and gas condensates that have been analysed in great detail.

PVT analysis

Sensitivity to characterisation

Not all the PVT analyses we have tested are well reproduced by the PVT characterisation fitting method. If this happens, it may be due to the inconsistency between the SCN distribution and the information for the molecular weight and/or specific gravity for the plus fraction or STO or total fluid. If you do see a warning related to the inconsistency, use the phase envelope tracer to see how the phase envelope is affected by characterising the fluid with and without the information for the molecular weight and/or specific gravity.

Errors and warning messages

Errors are usually associated with Multiflash output, indicating that a solution cannot be found or that the results may be invalid. Error messages and warning messages are displayed in the results window. Each error and warning has a unique identification number. Errors are denoted by positive numbers and

warnings by negative numbers. The error number is followed by a single line description of the problem. For example:

```
Dew point at fixed T:
*** ERROR   20292 ***
Cannot find converged point - max. iterations
*** ERROR   20024 ***
Cannot find starting point for calculation - there may be no solution.
*** ERROR    344 ***
The flash calculation has not converged
```

When several errors are reported, as above, it is the first error that is closest to the fundamental problem. For more information on each error code see Multiflash Error Codes Manual that is distributed the Multiflash. The information on the module in which the error occurred and the subprogram name is intended for use by Infochem technical support.

Warning messages should be checked carefully. In many cases they may be ignored if the cause is understood.

Technical support

To report bugs found in Multiflash, or if you need further assistance, contact us at:

Infochem/KBC Advanced Technologies ltd
42-50 Hersham Road
Walton on Thames
Surrey
KT12 1RZ
UK
Tel: +44 (0) 1932 242 424
e-mail: software@kbcat.com

About Multiflash

The About option  provides information about the Multiflash software and your license. It is particularly useful when reporting any problems to Infochem's technical support team.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Multiflash version 6.0.15 (May 2015)
Serial number: 999/5
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Expiry Date: 31 January 2016
Installation directory: C:\Program Files (x86)\Infochem\MF60
Contact information
Website: http://www.kbcat.com/technology/infochem-software
Email: software@kbcat.com
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OK

Continue
to the next
section

Glossary

A

AIChE

American Institute of Chemical Engineers

APE

Asphaltene phase envelope

azeotrope

A mixture of components that has the same composition in the liquid and vapour phase, and which boils at a constant temperature.

B

BIP

Binary interaction parameter

C

characterization

The use of the information from a PVT laboratory report to construct a compositional fluid model in Multiflash.

CME

The CME experiment provides information about the relative amounts of gas and liquid phase at a fixed temperature over a range of pressure. It also provides volumetric and compressibility data.

CPM

Cross Polar Microscopy, a technique used to measure wax appearance temperature.

cricondenbar

The maximum pressure at which a two phase mixture can exist.

cricondentherm

The maximum temperature at which a two phase mixture can exist.

critical point

The point on a phase diagram at which both the liquid and gas phases of a substance have the same density, and are therefore indistinguishable.

CVD

The CVD experiment provides information about the relative amounts and volumes of gas and liquid in a reservoir during the process of gas extraction.

D

delumping

The process of decomposing the pseudocomponents of a fluid in preparation for a new characterization.

DLE

The DLE experiment provides information about the amount and volume of gas released during the extraction of oil from a reservoir. It also provides volumetric data.

DSC

Differential Scanning Calorimetry, a technique used to measure wax appearance temperature.

E

EoS

Equation of State

eutectic

A eutectic system is a mixture of chemical compounds or elements that has a single composition that solidifies at a lower temperature than any other composition. This composition is known as the eutectic composition, and the temperature is known as the eutectic temperature. On a phase diagram, the intersection of the eutectic temperature and the eutectic composition gives the eutectic point.

G

GOR

The ratio of volumetric flow of produced gas to the volumetric flow of crude oil for crude oil and gas mixture sample. It is always specified at standard temperature and pressure conditions.

H

HOC

Hayden and O'Connell gas phase model, a second virial coefficient model.

Hoffmam-Standing plot

The Hoffman-Standing plot is a useful tool for checking equilibrium conditions of gas and liquid components.

Hoffman plot

The Hoffman-Standing plot is a useful tool for checking equilibrium conditions of gas and liquid components.

L

LLE

Liquid-liquid equilibrium

M

My Term

My definition

O

OBM

Oil-based mud

P

petroleum fraction

A complex mixture of hydrocarbons, whose aggregate properties are characterised by standard tests, the results of which may be found in PVT laboratory reports.

plus fraction

The highest number SCN fraction in a fluid, for example C30+. This fraction contains all the material in the heavy end of the fluid and often represents a substantial proportion of the fluid.

pseudocomponent

In Multiflash, a set of petroleum SCN fractions that are aggregated together.

PVT laboratory analysis

A compositional analysis of a fluid, usually carried out by gas chromatography.

R

retrograde dew point

The point where liquids drop out of the gas phase and the amount of liquid increases as the pressure decreases. This physical phenomenon is known as retrograde condensation.

RK

Redlich-Kwong equation of state

S

SARA analysis

A Saturates, Aromatics, Resins and Asphaltenes analysis. This is the industry standard fractionation method for dividing crude oils into four components according to their polarizability

and polarity. The analysis is usually expressed in mass % relative to the stabilised oil. Within Multiflash, the SARA analysis is used to characterise resin and asphaltene components that are used by the asphaltene model.

SCN

Single carbon number. The analysis for hydrocarbons with more than 6 or 7 carbon atoms is generally reported as single carbon number fractions, which represent compounds in boiling point ranges. For example, a C9 SCN contains all hydrocarbons that boil between the normal boiling point of n-octane + 0.5ºC and the normal boiling point of n-nonane + 0.5ºC.

STO

Standard tank oil

T

total wax content

The total amount (in mass) of C20+ n-paraffins (relative to Stock Tank Oil), determined using the industrial standard UOP Method 46, where the wax is precipitated by addition of a polar solvent such as acetone.

V

VLE

Vapour-liquid equilibrium

VLLE

vapour-liquid-liquid equilibrium

W

WAT

Wax appearance temperature, the theoretical onset of wax formation. Complex mixtures of solid hydrocarbons can freeze out of crude oils if the temperature is low enough. Waxes are mainly formed from normal paraffins, but iso-paraffins and naphthenes are also present.

Index

.

.mfl files 10

A

Activity coefficient models 218
Adding a user-defined component 33
Adding inhibitors 107
Adding water 65
Applying the freeze-out model 36
Aspen Hysys 215
Asphaltenes
  definition 121
  effect of input data 126
  effect of n-paraffins 132
  effect of other solids 155
  flocculation model 225
  gas injection 140
  incomplete data 121
  model 121
  precipitation 135
  preparing for calculations 121
  specifying the model 123
  tuning the model 124
  with water 121
Automatic phase envelope 71
Azeotropes
  identifying 179
  spreadsheet example 179

B

Basic flash calculations 62
Binary interaction parameters 171, 232
  databanks 232
  displaying values 171
  editing 173
  effect on calculations 174
  model requirements 231
  temperature dependence 230
  units 230
  viewing 171
BIP set
  names 171
BIPs See Binary interaction parameters
Black oil analysis 28
Blending
  asphaltenes 41
  fluids 36
  method 236
  petroleum fluids 38
  waxes 45
Blending fluids 36
Bubble point
  calculating 64
  calculation 9

C

Calculating hydrate dissociation 98
Calculating hydrate formation 95, 98
Calculating mercury partitioning 164
Calculating pure component properties 68
Calculating wax precipitation 149
CAPE-OPEN
  exporting data 189
  interface 3
Changing folder locations 14
Changing units 12-13
Characterization 234
Characterizing fluids 234
Characterizing multiple fluids 55
Choosing a model 10
Choosing default units 12
Choosing session units 13
Chung-Lee-Starling See Models, Chung-Lee-Starling (CLS) thermal conductivity
Cloud point 143
CLS See Models, Chung-Lee-Starling (CLS) thermal conductivity
CME See Constant-mass expansion

Combined solids 155
Combined solids model 225
Components 240
properties 200
Troubleshooting 240
types 200
user-defined 33
Constant-mass expansion
experimental properties 79
validating experimental data 82
Constant-volume depletion
experimental properties 80
validating experimental data 82
Coutinho wax model 143
Critical point
calculating 65
Cross polar microscopy 143, 146-147
CSMA reference fluids 216

D

D86 See D86 data
D86 analysis 30
D86 data 233
Data exchange See Exchanging data
Databank 201
DIPPR 201
INFODATA 201
Defining a fluid from distillation data 30
Defining a fluid using a black oil analysis 28
Defining a petroleum fraction 18
Defining a standard fluid 17
Defining fluids 17
black oil analysis 28
from D86 30
from distillation data 30
from TBP 30
petroleum fraction 18
PVT analysis 25
solid components 36
standard 17
user-defined component 33
Delumping tool 60
Dew point
calculating 64
calculation 9
retrograde 9
Differential liberation
experimental properties 80
validating experimental data 82
Differential scanning calorimetry 143, 146-147
Diffusion coefficient 229
Distillation
D86 233
true boiling point (TBP) 233
DLE See Differential liberation
Dortmund modified UNIFAC model 219

E

Editing petroleum fraction data 20
Editing pure component properties 23
Editing temperature-dependent properties 24
Enthalpy
definition 203
in activity models 204
reference types 203
Entropy
definition 203
reference types 203
Equation of state models 211, 216, See also Models, equation of state
Equilibrium hydrate formation curve 98
Errors 241
Messages 241
Eutectic point
identifying 181
spreadsheet example 181

Example spreadsheets
BIP generation using Excel solver tool 193
UNIFAC BIP generation 191
Excel
BIP generation using Excel solver tool example 193
example spreadsheets 191
Multiflash functions 191
UNIFAC BIP generation example 191
Exchanging data
CAPE-OPEN 189
export types 183
import types 183
Multiflash legacy file 189
OLGA 185, 190
PIPESIM 183
PROSPER 187
PVTsim 190
Exporting data See Exchanging data

F

Files
CAPE-OPEN 189
mfl 10
model 10
Multiflash legacy export 189
OLGA PVT file 185, 190
PIPESIM PVT file 183
Prosper PVT file 187
PVTsim 190
Fixed phase flash 65
Flash calculations
available calculations 8
bubble point 9, 64
definition 62
dew point 9, 64
fixed phase 65
performing 63-65
single 63
Flory Huggins model 219
Fluids 17
blending 36
characterizing 234
defining 17-18, 25, 28, 30, 33, 36, See also Defining fluids
delumping 60
multiple 55
recharacterizing 60
Folder locations 14
Freeze-out model 36
Fuller diffusion coefficient model 229

G

Gas injection 140
GERG-2008 reference fluids 216

H

Halide scales 220
Halides
scaling 220
Hayduk Minhas diffusion coefficient method 229
Hydrates 110
calculation types 93
definition 93
dissociation 98
formation 95, 98
hydrate model 220
inhibitor model 223
maximum water content before formation 104
nucleation model 222
nucleation temperature 98
phases 223
scale precipitation 116
specifying model 93
suppressing formation 110
water sub-saturated systems 222

Hysys 215

I

Ice model 223
Ideal solution model 218
Inhibition
  hydrate 110
  model for hydrate inhibition 223
Inhibitor
  calculator 107
  dosage 110
  effect on hydrate dissociation 112
Inhibitor calculator 107
Inhibitor dosage 110
Inhibitor effects 112
Interface
  CAPE-OPEN 3
  Microsoft Excel 3
Iso curves 75

K

Key components 199
  aqueous 199
  example 199

L

LBC model See Lohrentz-Bray-Clark model
LGST See Linear gradient theory
Linear gradient theory 228
Liquid-liquid equilibria 178
Liquid thermal conductivity mixing rule 228
Liquid viscosity mixing rule 227
LLE See Liquid-liquid equilibria
Lohrentz-Bray-Clark model 227

M

Macleod-Sugden
  surface tension model 228-229
Match asphaltene data 124
Matching
  GOR 91
  Water Cut 91
MCS See Macleod-Sugden, surface tension model
MCSA See Macleod-Sugden, surface tension model
Mercury
  distribution 163
  dropout 164
  model 163
  partitioning 164
  species 163
  specifying the model 163
Mercury calculations 163
mfl files 10
Microsoft Excel
  interface 3
Mixed solids 155
Mixing rules 216
  liquid thermal conductivity 228
  Liquid viscosity 227
  surface tension 229
  vapour thermal conductivity 228
  Vapour viscosity 227
Model files 10
Model tuning
  PVT lab tests 79, 87
Models
  activity coefficient 218
  asphaltene flocculation 225
  available equation of state 211
  BIPs 231
  choosing 10
  Chung-Lee-Starling (CLS) thermal conductivity 228
  combined solids 225
  component data requirements 206
  Coutinho 224

diffusion coefficient 229
Dortmund modified UNIFAC 219
equation of state 211
equation of state advanced options 216
Flory-Huggins 219
freeze-out 36
Fuller diffusion coefficient 229
Hayduk Minhas diffusion coefficient 229
hydrate model 220
hydrate nucleation model 222
ice 223
ideal solution 218
inhibitor model 223
linear gradient theory 228
linear gradient theory surface tension 228
liquid thermal conductivity mixing rule 228
Liquid viscosity mixing rule 227
Lohrentz-Bray-Clark (LBC) 227
Macleod-Sugden surface tension 228-229
minimum data required 206
mixed solids 155
mixing rules 216
NRTL 219
overview 206
Pedersen viscosity 226
Peneloux density correction 216
Peng-Robinson 215
regular solution 219
scaling 220
solid freeze-out 220
solid phase 220
specifying 10
SuperTRAPP thermal conductivity 227
SuperTRAPP viscosity 226
surface tension 228
surface tension mixing rule 229
thermal conductivity 227
transport property 226
tuning 79, 209
Twu viscosity 226
UNIFAC 219
UNIQUAC 219
vapour thermal conductivity mixing rule 228
Vapour viscosity mixing rule 227
viscosity 226
Wax 224
Wilson A 218
Wilson E 218
Mud numerical cleaning 58
Multiflash
Excel functions 191
export legacy file format 189
folder locations 14
Overview 3
results 5
units 12-13
user interface 3

N

NRTL model 219
Nucleation model 222
Numerical cleaning 58

O

OBM
numerical cleaning 58
Oil-based muds
numerical cleaning 58
OLGA
exporting PVT file 185
Organomercury compounds 163

P

Pedersen model 226

Peng-Robinson
differences from Aspen Hysys 215
Petroleum fluids 233
Petroleum fractions
defining 18
editing data 20
Phase descriptors 198
default names 198
supercritical phase 198
Phase diagram 197, See also Phase envelope
Phase envelope 75, 77, 239, See also Plots
diagram 197
initial values 75
plotter 71, 75
plotting 71
scaling the plot 74
Phase envelope plotter 71
Phases 239
Example of a phase envelope 239
hydrate model 223
PIPESIM
exporting PVT file 183
Plots See also Phase envelope
exporting data 78
initial values 75
iso curves 75
modify 78
printing 78
property boundaries 75
scaling 74
user-defined 77
Plotting iso curves 75
Plotting phase boundaries 71
Plotting property boundaries 75
Polar models
comparing 177
Polar systems 177
Properties
calculating 68
databanks 200
Prosper
PVT file 187
Pseudocomponents
effect of user-defined 52
Pure component properties 20, 23
Pure components
calculating properties 68
editing properties 23
viewing properties 20
PVT analysis 233
defining a fluid 25
distillation data 233
PVT experiments
data validation 234
Multistage Flash 91
PVT lab tests
entering data 80
experiment types 79
model tuning 79
overview 79
simulating an experiment 84
tuning a model 87
validating experimental data 82
PVTsim
importing data 190

R

Recharacterizing fluids 60
Reference fluids 216
Regular solution model 219
Retrograde dew point 9

S

Salt calculator 109
Salt injection 116
Saturate with water 65

Saturation 65
PVT lab test 80
Scale precipitation 116
Scaling 220
Scaling phase plots 74
Separator test
experimental properties 80
validating experimental data 82
Simulating an experiment 84
Single flash calculations 63
Solid phase models 220
Solids
mixed 155
Specifying a model 10
Specifying default units 12
Specifying folder locations 14
Specifying session units 13
Specifying the hydrate model 93
Spreadsheets See Excel
Stream types 49
Supercritical phase 198
SuperTRAPP model
thermal conductivity 227
viscosity 226
Surface tension 228
Surface tension mixing rule 229

T

TBP See True boiling point data
TBP curve 30
Temperature dependence
binary interaction parameters 230
Thermal conductivity models 227
Tolerance calculation 67, 104
Tools
automatic phase envelope 71
blend fluids 36
critical point 65
delump 60
inhibitor dosage 110
match asphaltene data 124
mud numerical cleaning 58
preferences 12
same pseudos 55
saturate with water 65
tolerance calculation 67
Transport properties
Models 226
True boiling point data 233
Tuning a model 87
Tuning models 79, 209, See also Models, tuning
Twu model 226

U

UNIFAC
Dortmund modified 219
UNIFAC model 219
UNIQUAC model 219
Units 13
BIPs 230
changing 12-13
DECHEMA data series (CDS) 230
default units 12
specifying default units 12
specifying session units 13
User-defined components
adding 33
User-defined plots 77
User-defined pseudocomponents 52

V

Vapour thermal conductivity mixing rule 228
Vapour viscosity mixing rule 227
Viewing pure component properties 20
Viscosity
models 226
PVT lab test 80

VLE autoplot 71, 77

W

Warnings 240-241
Additional phases 240
Wax
calculating WAT 147
cloud point 143, 147
Coutinho model 143
Coutinho Model 224
definition 143
plotting the wax phase envelope 151
precipitation 149, 224
precipitation curve 149
specifying the model 143
tuning the model 145
wax appearance temperature 143, 146-147
Wax appearance temperature 143, 146-147
calculating 147
Wax precipitation curve 149
Wilson A model 218
Wilson E model 218