

## What's New in ChemSep 6.2

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There are several important changes to **ChemSep™**

1. **New feed-stage model**
2. **New relative volatility model**
3. **New convergence methods and other solve options**
4. New physical property data manager with new estimation methods and plotting capabilities
5. Physical properties for streams and stages
6. A configurable Tool bar
7. Automatic backup of sep files
8. Binary physical property diagrams
9. Copy & paste plots as EMF so they can be imported into MS Word and Open-Office Writer

**The items in bold represent changes to ChemSep that could affect your simulation results. Please read this document carefully.**

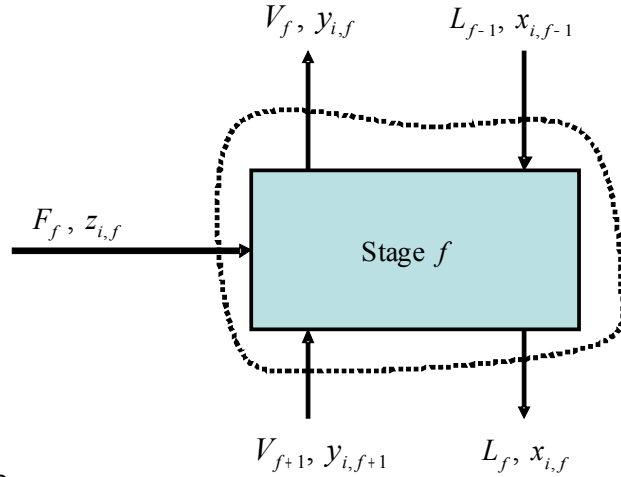
### **New Feed Stage Model in ChemSep**

The feed stage model for the equilibrium stage model in **ChemSep** has been changed in two ways:

1. All feeds are flashed twice, the first time to determine its initial phase state (and enthalpy) at the specified feed conditions, and a second time at the pressure on the feed stage inside the column to determine the phase(s) of the feed once it enters the column. For example, a feed that is a saturated liquid before it enters the column will undergo a partial vaporization if the pressure in the column is lower than the external feed pressure (and this would normally be the case although many simulations are done assuming that the column and feed pressures are equal).
2. The vapor portion of a two-phase feed now will go up to the stage above the designated feed stage.

In order to explain the changes it is helpful to describe the old feed-stage model that was part of the equilibrium stage model. The old model is most easily understood with the help of Figure 1. In the old model all of the feed to stage  $f$  is brought into contact with the liquid from the stage above and the vapor from the stage below. Figure 2 shows an equivalent model that shows this split explicitly.

**Old Feed Stage Model**



Stage mass balance

$$V_{f+1}y_{i,f+1} + L_{f-1}x_{i,f-1} = F_f z_{i,f} + V_f y_{i,f} + L_f x_{i,f}$$

Figure 1: Old feed-stage model in **ChemSep**.

**Equivalent Feed Stage Model**

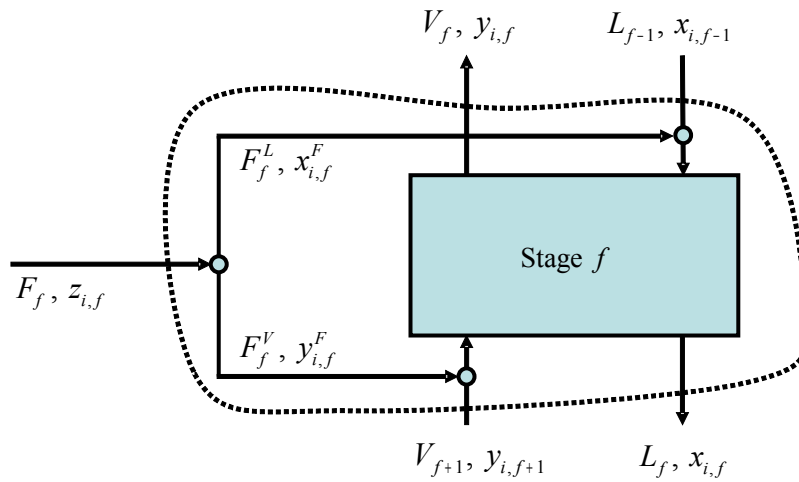


Figure 2: Equivalent old feed-stage model in **ChemSep**.

Notice how the vapor and liquid parts of the feed are diverted to mix with streams entering the same stage, and that, in effect, the vapor goes below the stage so that it can enter with the vapor from below. Note also that the feed split is contained entirely within the control volume for the feed stage as indicated by the broken line. Thus, the equations that model the stage in Figure 2 are identical to those that model the stage in Figure 1.

This is a very literal interpretation of the equilibrium stage model. It is an adequate model of how the feed to a real column behaves only if the feed stream is either all liquid or all vapor (and in the latter case the feed stage number would be off by one). It is not an adequate model for two-phase feeds where the vapor and liquid portions of a feed stream become part of the vapor and liquid on two *different* stages.

The new model in **ChemSep** is shown in Figure 3 where we see that only the liquid portion of a feed to stage  $f$  is brought into contact with the liquid from the stage above and with the vapor from the stage below. The vapor portion of a two phase feeds goes to the stage above. Figure 3 shows the default model for all feeds in the equilibrium stage model of **ChemSep**. **It is important to note that the “new” model shown in Figure 3 has always been the feed stage model for the nonequilibrium stage model**

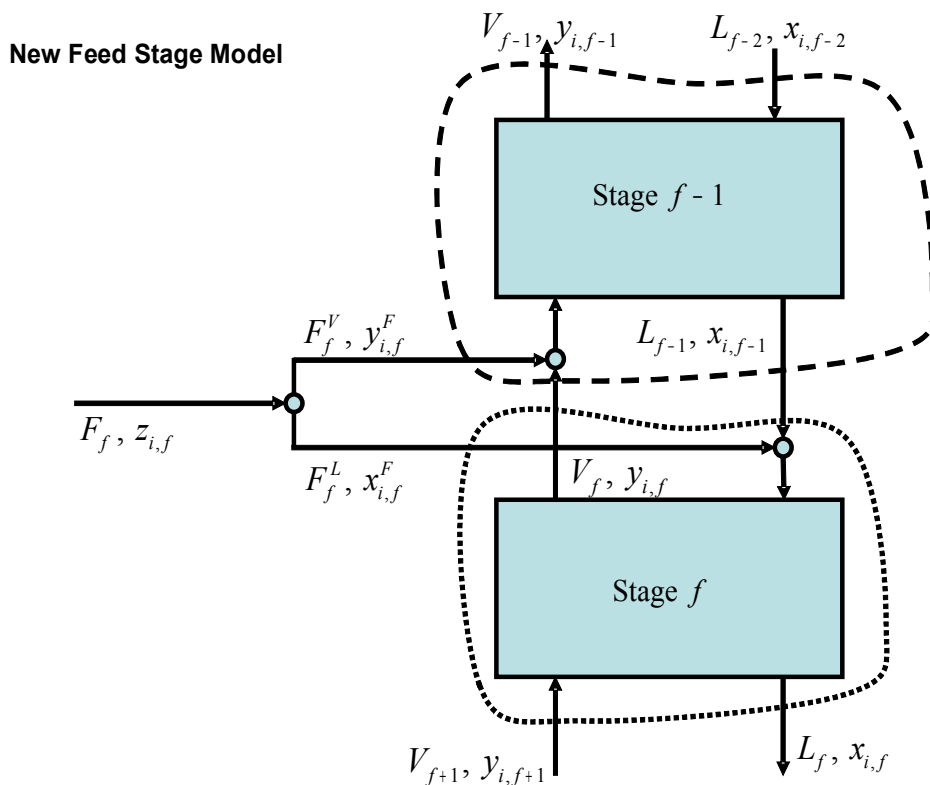


Figure 3: Feed-stage model in **ChemSep** Version 6.17 et seq.

The model shown in Figure 3 may not properly model the feeds to the top and bottom stages of simple absorption and stripping columns. In the (perhaps unlikely) case that there is some vapor in a feed at the top of a column or liquid in the feed below the column then it is possible for portions of such feeds to bypass the column entirely. These cases are depicted in Figures 4 and 5 respectively.

**Model for top stage  
(if not condenser)**

Stage mass balance

$$V_1' + L_1 = F_1^L + V_2$$

Stage + Feed zone balance

$$V_1 + L_1 = F_1 + V_2$$

Feed mixing point

$$V_1 = F_1^V + V_1'$$

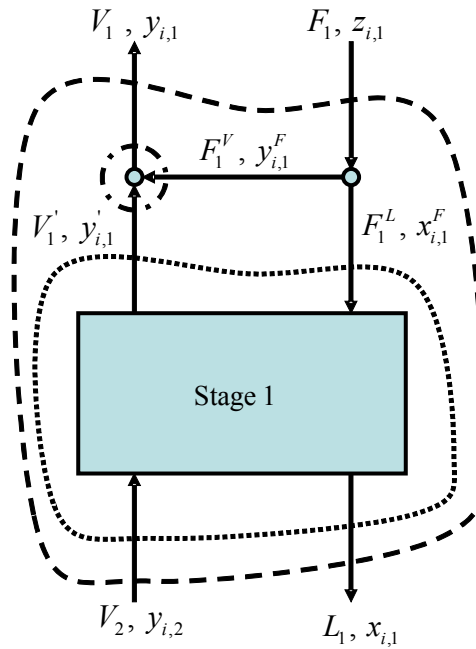


Figure 4: Feed-stage model for the top stage.

The default model in *ChemSep* is that feeds to the bottom stage are from “below” and that feeds to the top stage are from “above”. Note that in both cases the mole fractions used in the equilibrium equations are those indicated by the primes in Figures 4 and 5. The mole fractions used in the material balances are the unprimed mole fractions in the streams in the material balance for the combined equilibrium stage and feed zone.

**Model for last stage  
(if not reboiler)**

Stage mass balance

$$V_s + L_s' = F_s^V + L_{s-1}$$

Stage + Feed zone balance

$$V_s + L_s = F_s + L_{s-1}$$

Liquid mixing point

$$L_s = F_s^L + L_s'$$

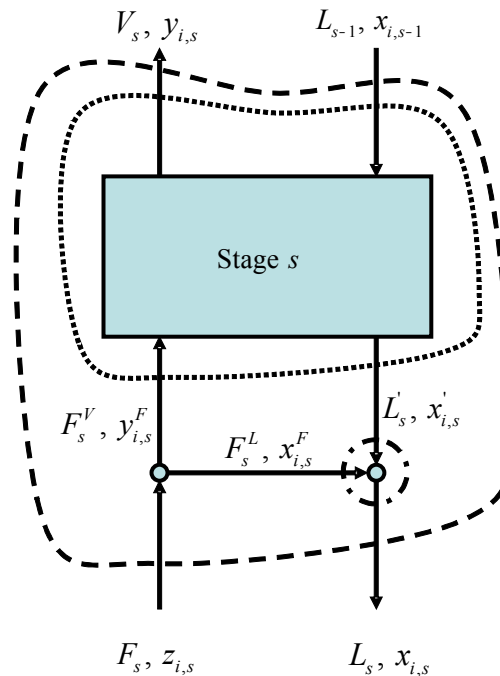


Figure 5: Feed-stage model for the last stage.

A particularly interesting (and probably very rare) situation that was impossible to model with older versions of ChemSep would have been an absorption column with two feeds to the lowest stage, only one of which is “below” the stage, the other being “to” the lowest stage. This situation is depicted in Figure 6.

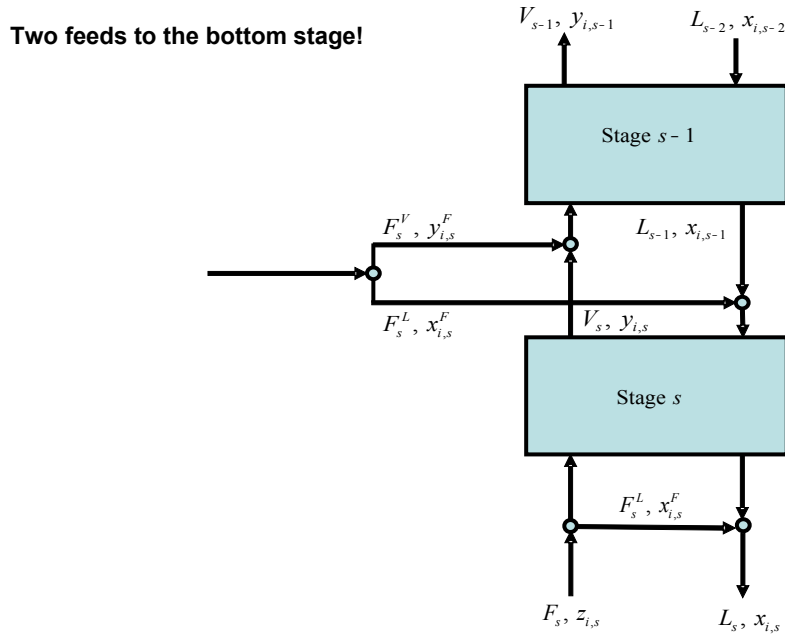


Figure 6: Two two-phase feeds to lowest stage

The older version of *ChemSep* would have assumed that both feeds were from below and it was not possible for the user to change this while maintaining the second feed as a single stream. In the new version we can send both feeds to the last stage but designate only one as “below” the stage. How, you might ask, does *ChemSep* know which of the two feeds is from below the column? The answer is that you must specify which feed is below. A screen shot of part the new feed panel can be seen in Figure 7. Note the new entry for two-phase feeds with three available options: **Split**, **Not-split**, and **Split-below**. The default is “Split” and represents the model in Figure 3 except for feeds to the bottom of a column for which the default is “Split-below” (as depicted in Figure 5). To add a second feed “to” the last stage that is not from below the column it is necessary to choose either the “Split” or “Not-split” options. The “Not-split” option should be selected if the old feed stage model shown in Figure 1 is desired.

Feed:	1
Name	Feed1
Stage	5
Two-phase feed	Split
State	Split
Pressure [atm]	Not-split
Vapour fraction [-]	Split-below
Temperature [oF]	
Flowrates [kmol/h]:	
A	64.0001
B	36.0000
Total flowrate	100.000

Figure 7: Feed specification panel

## New Relative Volatility Model

In versions of **ChemSep** older than Version 6.2 the relative volatility model for VLE had no temperature dependence. Thus, the temperatures provided in the output were entirely without any meaning (in fact the temperature was more or less constant over the height of such a model column). This was not realistic and in Version 6.2 we have provided a new implementation of the relative volatility VLE model.

The relative volatility is defined by:

$$\alpha_{i,r} = \frac{K_i}{K_r}$$

where the subscript  $r$  refers to the reference compound and the second part of the above equation is valid when the K-values are given by Raoult's law.

In the new version of the relative volatility model we assume that the K-value of the reference compound is given by Raoult's law:

$$K_r = \frac{P_{sat,r}}{P}$$

The K-values of all compounds (including that of the reference compound) may, therefore, be obtained from:

$$K_i = \alpha_{i,r} \frac{P_{sat,r}}{P}$$

The values of the relative volatilities are specified as before; the reference compound is automatically taken to the compound that has a specified relative volatility of one. If none of the relative volatilities are entered as equal to one then the relative volatilities are calculated from the ratios of the volatilities that are entered and the reference compound is assumed to be the last.

The inclusion of a temperature dependence in the model means that it is also possible to estimate enthalpies from the Ideal Enthalpy model (more complicated and realistic models are reset back to the Ideal model because there is no basis for the estimation of fugacity and activity coefficients with this VLE model). It is also possible to retain the constant enthalpy model (identified in the model selection panel as None).

**The user will see no changes to composition profiles obtained with this model unless the Ideal enthalpy model is selected.** However, a temperature profile will now be available and enthalpies, entropies and other physical properties are estimated using the calculated temperature and composition, and the specified pressure.

**Note that the relative volatility model should not be used in nonequilibrium simulations.**

## New Solve Options in ChemSep

*ChemSep* uses Newton's method to solve all of the model equations at the same time. Convergence is not assured using this method and whether or not a solution is found depends largely on the quality of the initial guess of the unknown variables (flow rates, temperatures and mole fractions in the equilibrium stage model and, in addition, pressures and mass transfer rates in the nonequilibrium model).

### Accuracy

First, and perhaps most importantly, there is a very significant change in the convergence criterion. In older versions of *ChemSep* the default tolerance (accuracy in the Solve Options tab panel shown in Figure 8 below – although the cell in to which a number is typed is hidden in this image) was  $10^{-3}$  except for flash calculations where the default tolerance was  $10^{-6}$ . In versions of *ChemSep* after 6.17 all the model equations are scaled and the default tolerance now is  $10^{-6}$  for all types of calculation. This means that if you load an old sep file in which the tolerance is set to  $10^{-3}$  it might not be converged when the current version says it is.

**It is essential that you review the tolerance in any old sep file and reduce it as described above.**

### New Algorithm Options

*ChemSep* now includes several different approaches to solving the model equations, all based on Newton's method, but now automatically incorporating various “tricks” that we have found helpful in our own use of the program. The options are shown in the partial screen shot (from **Solve Option**) shown below. In the drop down list next to **Method** (look in the top left corner) we can see a list of methods:

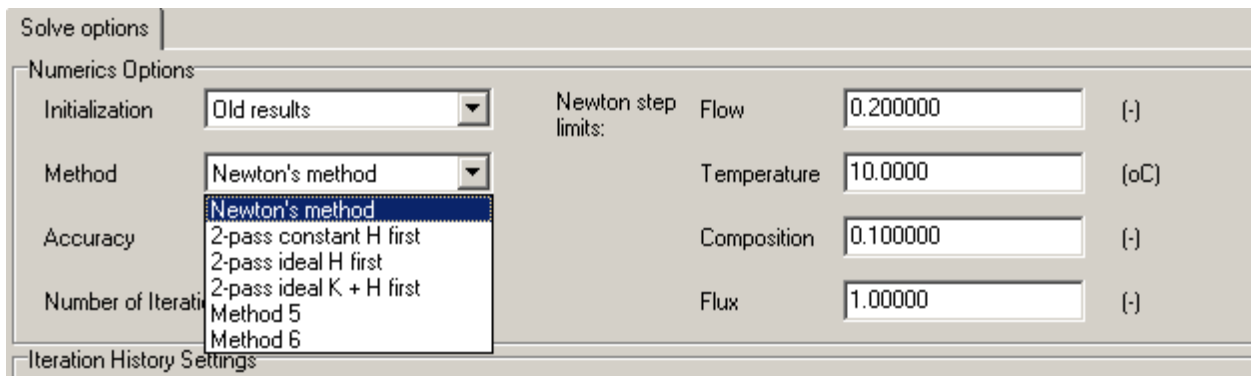


Figure 8: Part of Solve Options tab sheet showing new algorithms and control options

#### **Method 1: Newton's method**

Newton's method is the default setting and will be the method used unless you select something else from the drop-down list shown above. Newton's method will be successful 90% of the time; however, it is those cases that Newton's method fails to solve that demand 90% of the users time.

Experienced users of simulation programs will know that problems involving mixtures that are thermodynamically ideal usually are very easy to solve. Thus, methods 2 to 4 in the above list exploit this fact in different ways.

#### **Method 2: 2-pass constant H first**

Distillation is a process in which one often assumes that the molar flows are constant from stage to stage. The practical consequence of this assumption is that the energy balances for each stage can be ignored. The calculations are much simpler and convergence often is very rapid.

Thus, in this option *ChemSep* first attempts to solve a problem with constant enthalpies (for each phase). This is done by resetting the enthalpy model to **None**; once that problem has converged the program automatically resets the enthalpy model to be whatever was initially selected and the simulation re-run using the solution to the constant H-model as the starting point.

### **Method 3: 2-pass ideal-H first**

The approach taken here is very similar to that of method 2. Rather than select **None** as the enthalpy model, in this version of our algorithm, the enthalpy model used in the first pass is **Ideal**.

### **Method 4: 2-pass ideal K+H first**

In this third version of the 2-pass Newton method, the first problem is solved using ideal enthalpies *and* ideal K-values (in practice this means the Raoult's law-like **Wilson K-value model**).

## **Recommendations**

Newton's method should be the first choice (it is the default setting) until it has been shown not to work. In the event of failure then one of the alternative options can be tried (but not all of these methods will allow every problem to be solved). Method 2 can be useful for hard-to-converge distillation-type models. It is less useful for hard-to-converge reboiled absorbers and strippers. One of the alternatives might work better for those applications. Our experience is that Method 4 is perhaps the best for these applications. Methods 2-4 should not be used for liquid-liquid extraction operations where the enthalpy model plays little or no role and where the concept of ideal K-values would mean that two liquids phases would not be able to co-exist.

## **Newton Step Limits**

The upper right hand side of the **Solve Options** panel shows the step limits that our program applies in order to stop the variables from changing too much between iterations.

The **Flow** limit represents the maximum allowed percentage change in the vapor and liquid flow rates between iterations. We prefer to keep this to 0.5 or less to prevent overly large changes to the flow rates between iterations. A smaller number can be useful in nonequilibrium simulations because the column flow dynamics calculations are somewhat sensitive to the actual flow rates in the column (this is not an issue in equilibrium stage calculations because there are no equipment calculations carried out during the simulation and so it is only the relative flows that matter in such cases).

The **Temperature** limit is the number of degrees by which the temperature is allowed to change between iterations. The default setting is 10K, but sometimes we will set this lower (it is most likely that we would do this in column simulations at "high" pressure).

The **Mole fraction** limit is the maximum amount by which mole fractions are allowed to change between iterations. Mole fractions are not allowed to become negative, however. *ChemSep* uses a strategy whereby any step large enough to make a mole fraction negative (or greater than one) is automatically reduced so as to take half the step from the current value to zero (or one if the calculated step would take the mole fraction out of range in the other direction, so to speak).

*ChemSep* users that have made use of this feature before might observe that there is a new option in this section; the 4<sup>th</sup> line shows **Flux** which allows us to limit changes to the mass transfer rates between iterations. This option is only used in the Nonequilibrium model, of course, but our experience is that it can make all the difference between success and failure. In particular, we find that setting the flux limit becomes more and more important as the column pressure increases. At very high pressure (relative to the critical point of the mixture) we find that success is more likely when the flux limit is set to 0.1 (the default is 1.0 and that value is usually sufficient at low and moderate pressures).



# Pure Component Databank Manager

New in *ChemSep* 6.2 is a completely new pure component physical property databank manager:

1. Import data directly from the NIST Chemistry Web Book (<http://webbook.nist.gov/chemistry/>)
2. Import data from DIPPR source file (not provided with *ChemSep*)
3. Estimate missing property data from UNIFAC structural information
4. Estimate property data from boiling point and specific gravity
5. Automatically display temperature dependent physical property data in tabular or graphical form
6. Fit temperature dependent property data
7. Export data in a variety of file formats including DIPPR text format, *ChemSep* binary format etc.
8. Allow unit conversions when data is entered from the keyboard
9. Undo/Redo ALL changes

The screen shot below shows the correlation for the ideal gas heat capacity of benzene. The plot shows data points imported from (in this case) the DIPPR source file. Right-mouse-button clicking on the plot brings up the menu shown far center-right that permits the plot to be customized. The plot can be copied directly to Microsoft Word or OpenOffice Writer (the program used to create this document).

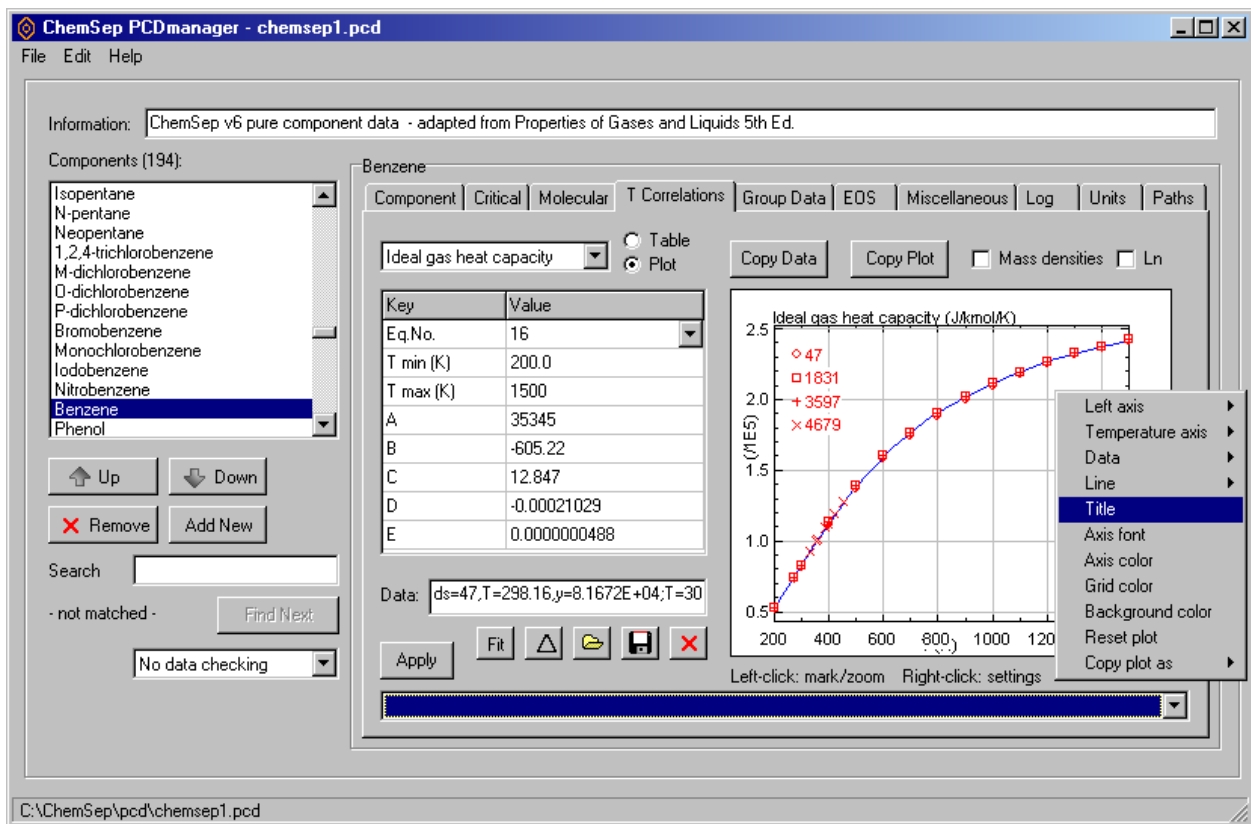


Figure 9: Screen shot of ChemSep PCDManager, the new physical properties data manager in *ChemSep*

## Buttons and Bows

Well, no bows, but we do have more buttons! Lots more buttons. The screenshot below shows the button bar with some of the newly available buttons. From left to right the buttons show: New file, Open file, Save current file, Run current file, Reload currently open file, Previous Input/Output Panel, Next input/output panel, Liquid mole fraction profiles, Vapor and liquid flow profiles, Temperature profile, Efficiency profile (appears here in grey because this was an equilibrium stage simulation), McCabe-Thiele diagram.

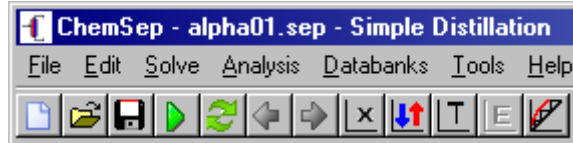


Figure 10: Button bar in ChemSep 6.2

The button bar can be configured by the *ChemSep* user; click on **Tools** and then on **Configure Tools** to bring up the window shown below. The lower left half of this panel shows the buttons that have been selected to appear on the button bar. The list on the lower right half shows available buttons. Buttons can be selected, removed, and their order changed using the grey buttons in the lower center section.

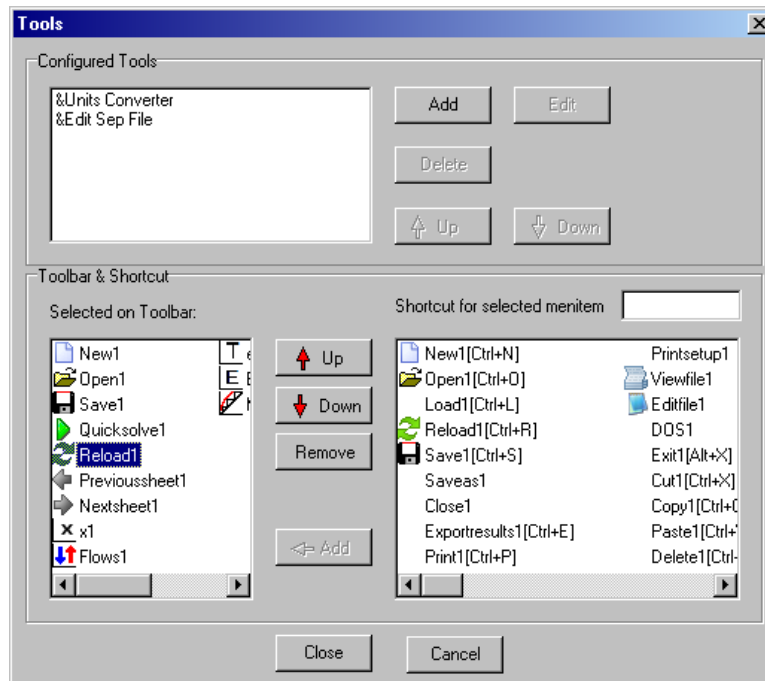


Figure 11: Tool configuration panel

## Automatic backup of sep files

*ChemSep* now by default makes backup files of each simulation file. You can switch this feature off in the Interface Settings under Tools. *ChemSep* can also be configured to keep more than one backup file.

## Binary physical property diagrams

*ChemSep* can now create physical property diagrams for binary mixtures. On the **Analysis** menu is the **Property Diagram** option. Figure 12 shows a binary property diagram with the Fick liquid diffusivity for ethanol and water at two temperatures, together with experimental data from literature. *ChemSep* can prepare such diagrams for many different physical properties including density, viscosity, thermal conductivity, and surface tension but also activity and fugacity coefficients, vapour pressures, or heat capacities. They can be drawn at constant temperature and pressure or at vapour-liquid equilibrium T or P.

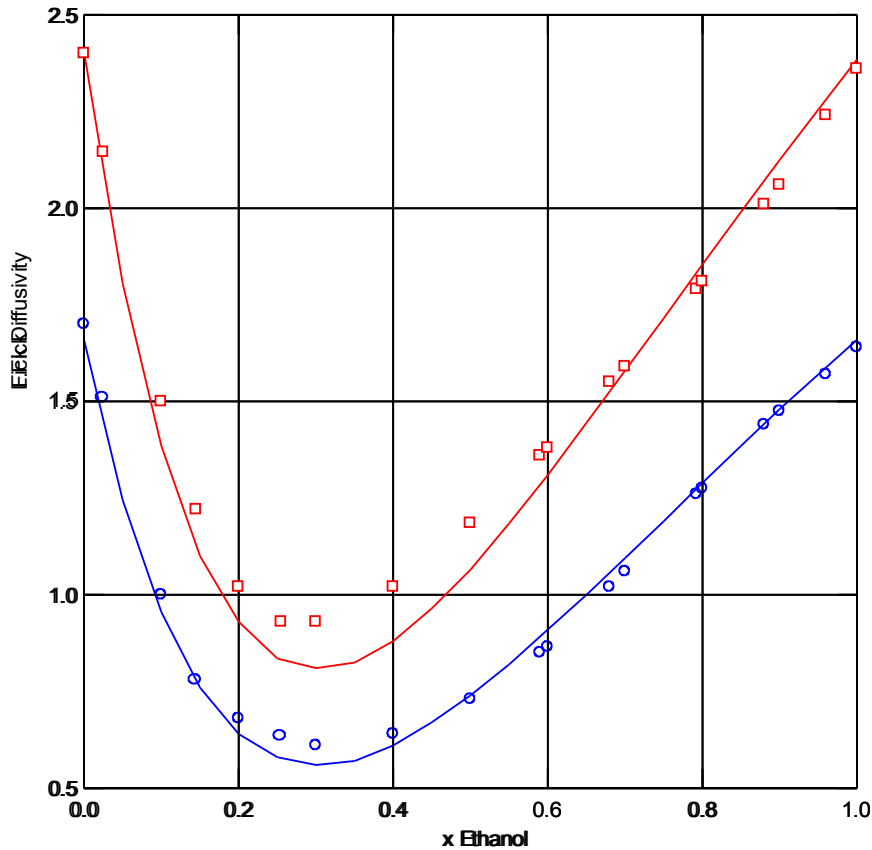


Figure 12: Binary property diagram in *ChemSep* showing Ethanol-Water diffusivity at 40 (blue line and points) and 58 degrees Celcius( red line and points), at 1 atm. Lines are calculated with the Kooijman diffusion model and the Kooijman-Taylor Vignes Maxwell-Stefan mixing model.

## Copy and Paste using EMF pictures

Any plot in *ChemSep* can be copied and pasted as MS Windows [Enhanced Metafile](#) (EMF) allowing quick inclusion of plots into reports and technical documentation. These plots can be scaled to any size without loss of detail and require less space in the report than bitmaps; Figure 12 is an example.