Thermodynamic Models & Physical Properties

When building a simulation, it is important to ensure that the properties of pure components and mixtures are being estimated appropriately. In fact, selecting the proper method for estimating properties is one of the most important steps that will affect the rest of the simulation. There for, it is important to carefully consider our choice of methods to estimate the different properties.

In Aspen Plus, the estimation methods are stored in what is called a "Property Method". A property method is a collection of estimation methods to calculate several thermodynamic (fugacity, enthalpy, entropy, Gibbs free energy, and volume) and transport (viscosity, thermal conductivity, diffusion coefficient, and surface tension). In addition, Aspen Plus stores a large database of interaction parameters that are used with mixing rules to estimate mixtures properties.

Property Method Selection

Property methods can be selected from the Data Browser, under the Properties folder as shown in Figure 13. To assist you in the selection process, the Specifications sheet (under the Properties folder) groups the different methods into groups according to Process type. For example, if you select the OIL-GAS process type, you will be given three options for the Base method: Peng-Robinson, Soave-Redlich-Kwong, and Perturbed Chain methods. These are the most commonly used methods with hydrocarbon systems such as those involved in the oil and gas industries.

When you select a property method, you are in effect selecting a number of estimation equations for the different properties. You can see for example, to the right hand side of the Property methods & models box, what equations are being used. For example, when you select the Peng-Robinson equation, you can see that the equation of state (EOS) selection is set to ESPR (equation of state Peng-Robinson) which is given by:

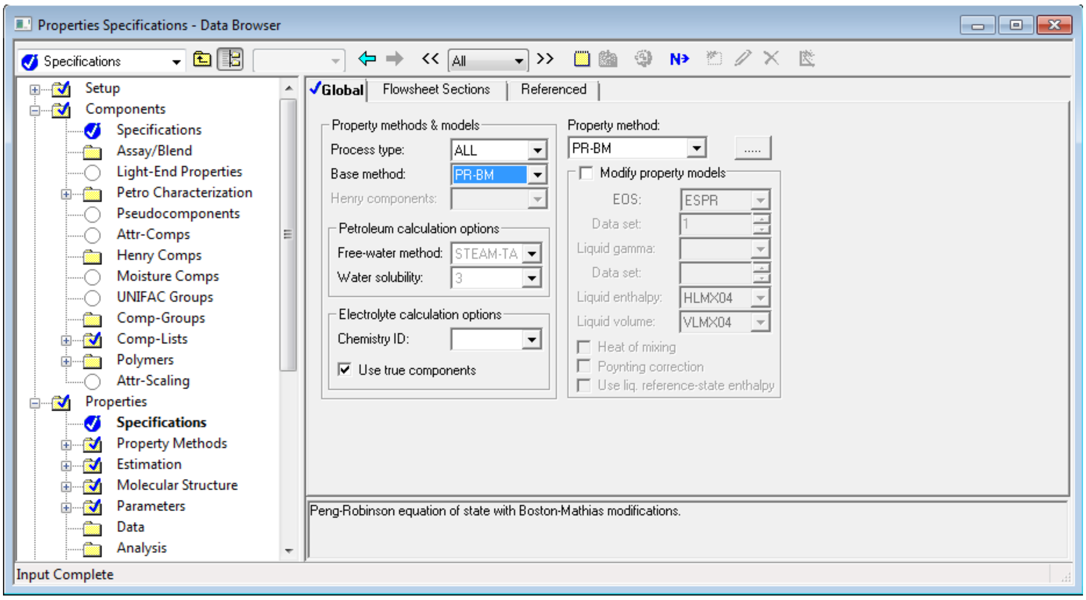
$$P = \frac{RT}{(c + V_m) - b} - \frac{a}{(V_m + c)(V_m + c + b) + b(V_m + c - b)}$$

Where a, b, and c are component specific parameters. The values of these parameters are stored in Aspen Plus database for pure components or calculated using mixing rules for mixtures.

You can examine the whole set of estimations equations for each property method by clicking on the Property Methods folder and selecting the method of interest (PR-BM in this case). For example, the diffusion coefficients in liquids (called DL) are estimated using DL01 model, which is the name for the Wilke-Change model given by:

$$D_{ij}^{l} = \frac{\left(D_{ij}^{\infty,l}\eta_j^{l}\right)^{x_j}\left(D_{ji}^{\infty,l}\eta_i^{l}\right)^{x_i}}{\eta^{l}}$$

and so on.



Process type: ALL
Base method: PR-BM
Henry components:
Free-water method: STEAM-TA
Water solubility: 3
Chemistry ID:
☑ Use true components
Property method: PR-BM
☐ Modify property models
EOS: ESPR
Data set: 1
Liquid gamma:
Data set:
Liquid enthalpy: HLMX04
Liquid volume: VLMX04

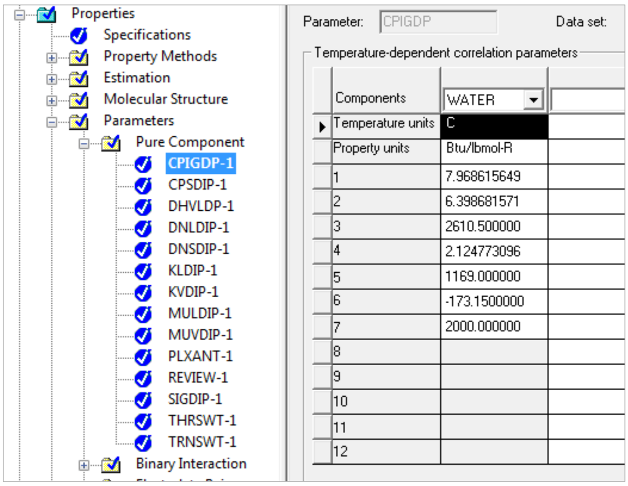
Peng-Robinson equation of state with Boston-Mathias modifications.

Input Complete

Figure 13. Selecting a property method.

Determining How Properties are Estimated

When you select a component to be included in the simulation, many properties for this component will be loaded. A large number of the properties are loaded under the Parameters subfolder in the Properties folder. If you expand the Parameters subfolder, you will see that it consists of subfolders for Pure Component (where properties for the component itself, like heat capacity, heat of formation, etc are stored as shown in the snapshot to the right), Binary Interaction (where interaction parameters of the component with other loaded components are stored for different calculations), Electrolyte Pair (for electrolytic interaction parameters), and so on.



Parameter: CPIGDP
Data set:

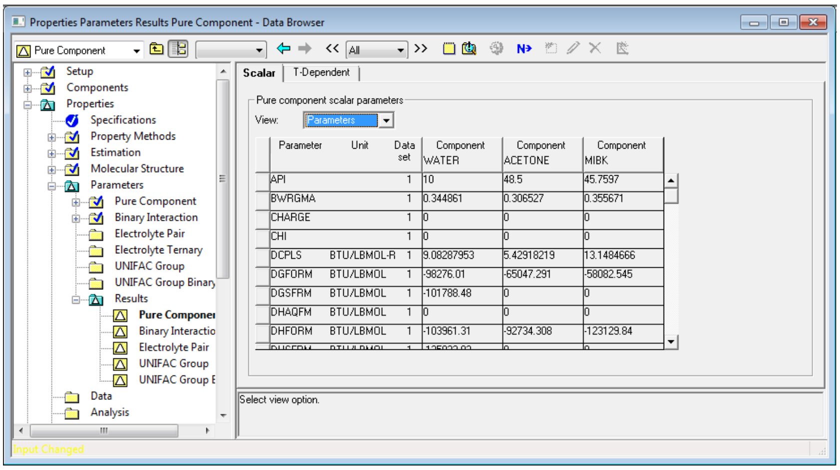
Components	WATER
Temperature units	C
Property units	Btu/lbmol-R
1	7.968615649
2	6.398681571
3	2610.500000
4	2.124773096
5	1169.000000
6	-173.1500000
7	2000.000000
8	
9	
10	
11	
12	

Let us examine the Pure Component folder. As you can see in the snapshot above, the properties are denoted by a short name. For example, CPIGDP property is a short hand notation for the ideal gas heat capacity for the DIPPR database. If you are not familiar with the notation, you can check its meaning by going to the “Pure Component Databank Parameters” topic in the Help. If you click on CPIGDP page, you will see a list of parameters numbers from 1 to 7 and the units in which the independent variable (temperature in this case) and the parameter itself are given. In order to determine what correlations are these parameters are used with, go the THRSWT (thermo switch) page. In this page, a number is used to refer to the correlation that will be applied for some of the properties. To understand what the numbers mean, you need to check the “Pure Component Temperature-Dependent Properties” topic in the help. For the CPIGDP, the correlation number is stored in row number 7. For water, for example, the correlation used is number 107. If you search under “General Pure Component Ideal Gas Heat Capacity”, you will find that 107 refers to DIPPR 107 correlation, which is given by:

$$C_p^{*,ig} = C_{1i} + C_{2i}\left(\frac{C_{3i}/T}{\sinh(C_{3i}/T)}\right)^2 + C_{4i}\left(\frac{C_{5i}/T}{\cosh(C_{5i}/T)}\right)^2 \; ; \quad \text{for } C_{6i} \le T \le C_{7i}$$

View Component Properties

If you are interested in view all properties of pure components, you can use Aspen Plus “Retrieve Parameter Results…” from the Tools menu. This option allows you to extract all properties of pure components used by Aspen Plus, even the ones not displayed by default. Once you activate the Retrieve Parameter Results option, you can navigate in the Data Browser to the Properties>Parameters>Results folder, where the results for pure components, binary interaction parameters, and others are shown (see Figure 14).



Pure component scalar parameters

View: Parameters

Parameter	Unit	Data set	Component WATER	Component ACETONE	Component MIBK
API		1	10	48.5	45.7597
BWRGMA		1	0.344861	0.306527	0.355671
CHARGE		1	0	0	0
CHI		1	0	0	0
DCPLS	BTU/LBMOL-R	1	9.08287953	5.42918219	13.1484666
DGFORM	BTU/LBMOL	1	-98276.01	-65047.291	-58082.545
DGSFRM	BTU/LBMOL	1	-101788.48	0	0
DHAQFM	BTU/LBMOL	1	0	0	0
DHFORM	BTU/LBMOL	1	-103961.31	-92734.308	-123129.84

Select view option.

Figure 14. Retrieving components properties.

Phase Equilibrium Calculations

One of the key calculations performed in process simulations is phase equilibrium calculations. As you have learned in different courses, the basic principle of several unit operations (such as flash tanks, distillation columns, extraction…) is based on multi-phase equilibrium. Phase equilibrium is calculated using the fugacity (which is a measure of the tendency of a component to leave its phase). Equilibrium is achieved when the fugacity of the component is equal in all phases. The fugacity of component i in liquid phase is given by:

$$f_i^L = \phi_{i,L} x_i P$$

and in the vapor phase:

$$f_i^V = \phi_{i,V} y_i P$$

where ϕ_i is the fugacity coefficient. At equilibrium $f_i^L = f_i^V$. Of course, for pure components the fugacities simply reduce to $\phi_i^o P$, since x_i and y_i are both 1. The question here is how to calculate the fugacities, and the answer is: it depends on the system. In general, there are four choices:

1. **Ideal model:** as you already know, an ideal system is a system composed of ideal gases and liquids. And ideal gas follows the ideal gas law ($PV = NRT$) and has a fugacity of 1. An ideal liquid has an activity coefficient (γ) of 1. Ideal behavior can be assumed for vacuum/low pressure or very high temperature operations, for gases, and when very small interactions (or interactions that cancel each other) in liquids. Interactions are negligible when molecules of similar size and character are mixed together in the liquid phase.

   In Aspen Plus, ideal behavior is modeled using the IDEAL property method. This method sets the activity coefficient for the liquid phase to 1, the EOS to the ideal gas law, and estimates the molar volume of liquids using the Rackett model. You can also use Henry’s law with the ideal model by designating relevant components as Henry’s components.

   As a general rule of thumb, when you have systems involving material such as water, organic acids, amines, alcohols, esters, ketones, aldehydes, and/or ethers, then you are dealing with polar molecules and there is a very good chance that the system deviates considerably from ideality. Think, for example, of water/alcohol mixtures.
2. **Equations of state models:** an equation of state (EOS) is a PVT relation used to predict thermodynamic properties. You might remember some of the equations of state that you have learned in the thermodynamics course such as the cubic and the virial EOS’s. In Aspen Plus, there are several equations of state used for different applications. For example, there the Peng-Robinson EOS (and its variations) and the Soave-Redlich-Kwong EOS (and its variations), which belong to the cubic EOS. Other forms of EOS include those derived from statistical thermodynamics such as the Sanchez-Lacombe and SAFT. Another form of the EOS models is the steam tables (provided as a Base model in Aspen Plus).

3. **Activity coefficient models:** For non-ideal liquid solutions, the fugacity of the components in the solution deviates from that of the pure component. The ratio of the fugacity in solution to that of pure component is defined as the activity:

$$a_i = \frac{f_i}{f_i^o}$$

The activity can be calculated from the activity coefficient (γ) as follows:

$$a_{i,L} = \gamma_{i,L} x_i$$

In general, the activity coefficient is greater than unity. What this means is that the fugacity of a component in mixture is higher than that of pure component. Thus, the same liquid will have higher tendency to vaporize when in mixture than in its pure state. This can be attributed to the increased repulsion between molecules with mixtures. In few cases, the activity coefficient will be less than unity, indicating increased attraction between molecules and less tendency to vaporize.

In Aspen Plus, there are several activity coefficient models. Among the most commonly used is the NRTL, which can be applied to polar mixtures. Other models include: Wilson, Van Laar, UNIFAC, UNIQUAC, Flory Huggins, Electrolyte NRTL, and Scatchard Hildebrand models. In these models, the activity coefficient approach is used to calculate the liquid properties, while the vapor phase properties are calculated using an equation of state.

4. **Other Models:** There are still many other property models available through Aspen Plus. These models are classified as "Vapor Pressure and Liquid Fugacity Models" and have found applications in specific processes. Among these models are the API sour model (developed for sour water treatment applications), Chao-Seader and Grayson-Streed models (applicable to heavy hydrocarbon systems), and Kent-Eisenberg model (for amine sweetening units).

The question now is how to select a model. In general, different industries tend to accumulate experience on which model best fits its system. For example, from experience we now that the PR and the SRK models fit the oil and gas processing systems very well. Thus, these two models have been used extensively for such systems. Other systems require specialize models due to high non-ideality, for example, the amine sweetening unit in gas processing. You can always check the Help files for more recommendations about the use of property packages.

As a general guideline you can refer to the chart in Figure 15. The main criterion here is the present of polar compounds (water, alcohol, acids…). If this is the case, then non-ideality is expected and we refer to the activity coefficient models. Also, be aware of any non-condensable components (CO_2, N_2, O_2…) which require special treatment using Henry's law.

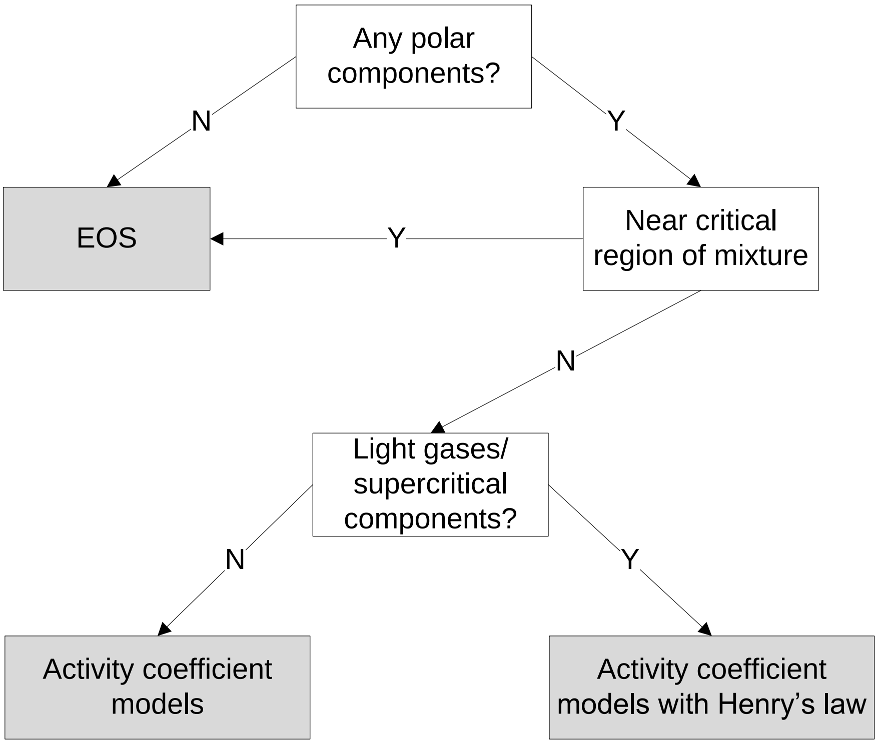
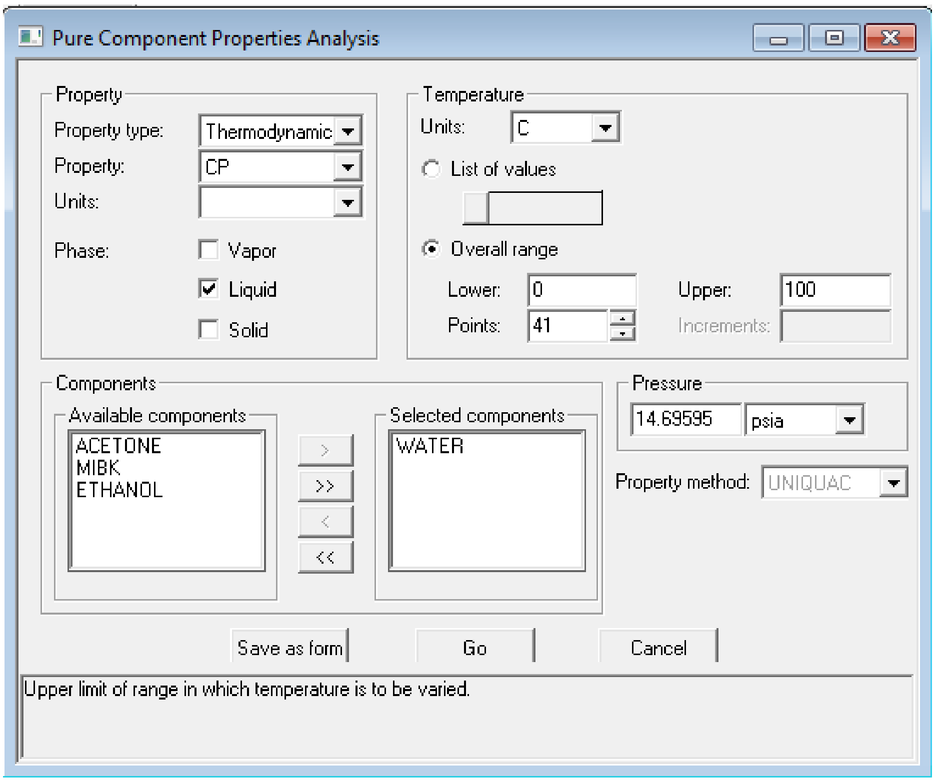


Figure 15. Selecting a property method.

Presenting Physical Properties

You can view many properties for pure components as well as mixtures once you have successfully run a simulation. This can be done by the Tools>Analysis menu item. Here you can obtain thermodynamic and transport properties of pure components in your simulation and plot them as a function of temperature. In addition, you can plot binary systems phase diagram (such as *Txy* and *Pxy* diagrams) for the components in your simulation based on the property method you select. Ternary phase equilibrium diagrams can be obtained as well using the Ternary item in the menu.

For example, if you are interested in seeing how the heat capacity of water changes with temperature for the UNIQUAC model at 1 atm, go to Tools>Analysis>Property>Pure…. This will open the dialog box shown in Figure 16. To plot the heat capacity, select CP from the Property dropdown menu (note that the heat capacity is a thermodynamic property). Next, choose the component(s) of interest (water in this case), and the temperature range and pressure on which you want to plot the data. Now, if you click Go, you will get a table and a plot for C_p (in the units you specify under Units) versus temperature. Notice also that the dialog will give you the option to select the phase for which you want to determine C_p.



Property type: Thermodynamic
Property: CP
Units:
Phase: ☐ Vapor ☑ Liquid ☐ Solid

Units: C
○ List of values
● Overall range
Lower: 0
Upper: 100
Points: 41
Increments:

Available components: ACETONE, MIBK, ETHANOL
Selected components: WATER

Pressure: 14.69595 psia
Property method: UNIQUAC

Upper limit of range in which temperature is to be varied.

Figure 16. Obtaining pure component properties.

For this specific example, the plot of C_p versus temperature is shown in Figure 17. If you refer to the original dialog window, you will see that you can present the data for multiple phases and components. Also, notice that the same data plotted in Figure 17 will be given as a table in case you are interested in numerical values.

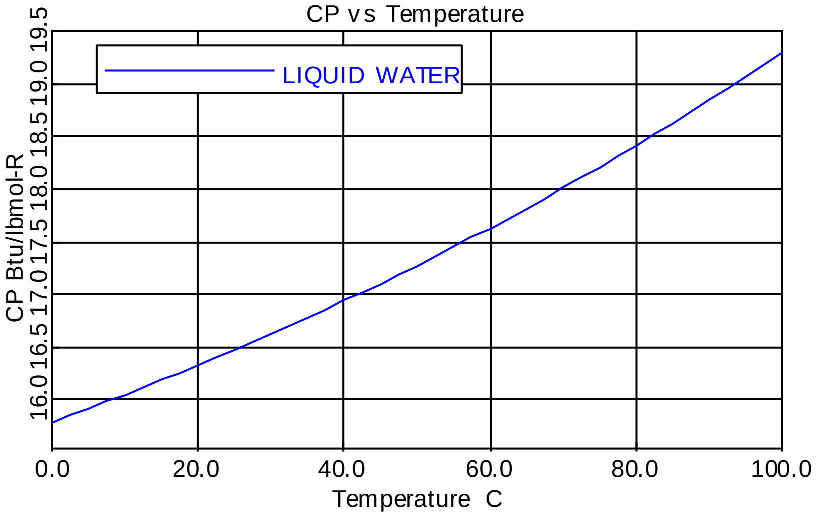
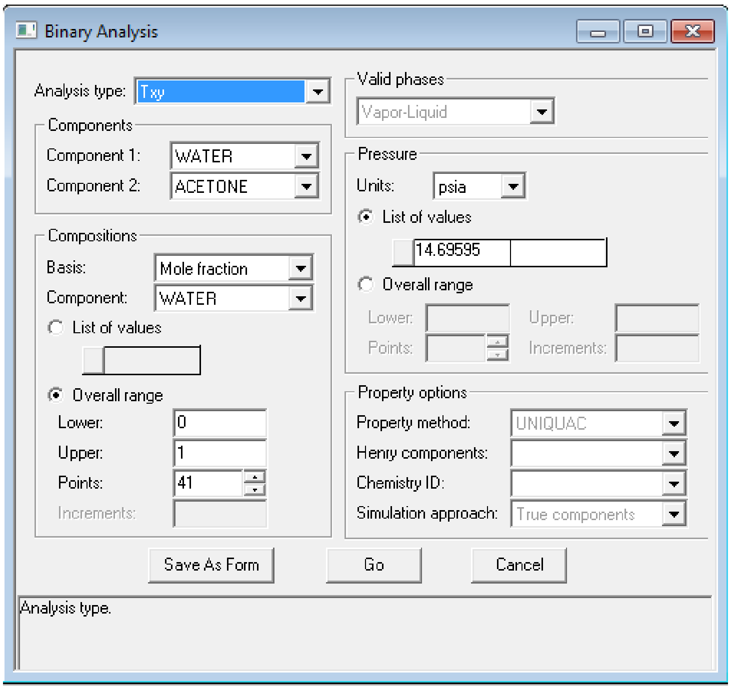


Figure 17. Heat capacity data for water obtained using the Pure Component data in Aspen Plus.

Similarly, you can obtain data for binary mixtures. For example, if you are interested in obtained a *Txy* diagram for water-ethanol, you can obtain this from the Tools>Analysis>Property>Binary…and select Txy from the Analysis type dropdown menu as shown in Figure 18. After specifying the components, composition range, and pressure, click Go. This will give you the well-known water-ethanol Txy diagram shown in Figure 19.


Binary Analysis

Analysis type: Txy

Components
Component 1: WATER
Component 2: ACETONE

Compositions
Basis: Mole fraction
Component: WATER
○ List of values
● Overall range
Lower: 0
Upper: 1
Points: 41
Increments:

Valid phases: Vapor-Liquid

Pressure
Units: psia
● List of values
14.69595
○ Overall range
Lower:
Upper:
Points:
Increments:

Property options
Property method: UNIQUAC
Henry components:
Chemistry ID:
Simulation approach: True components

Analysis type.

Figure 18. Binary mixtures properties.

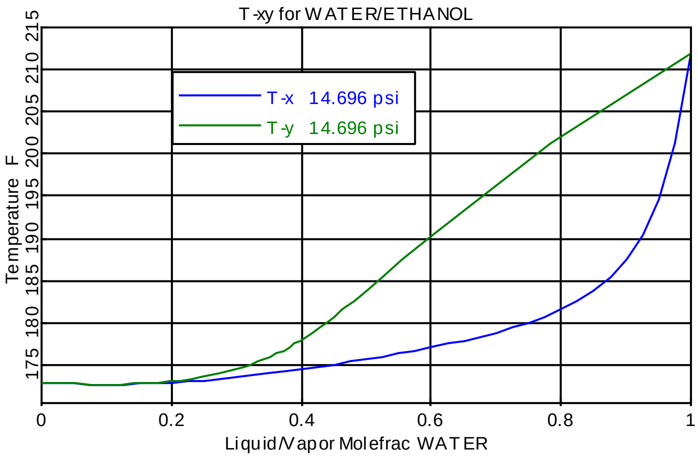
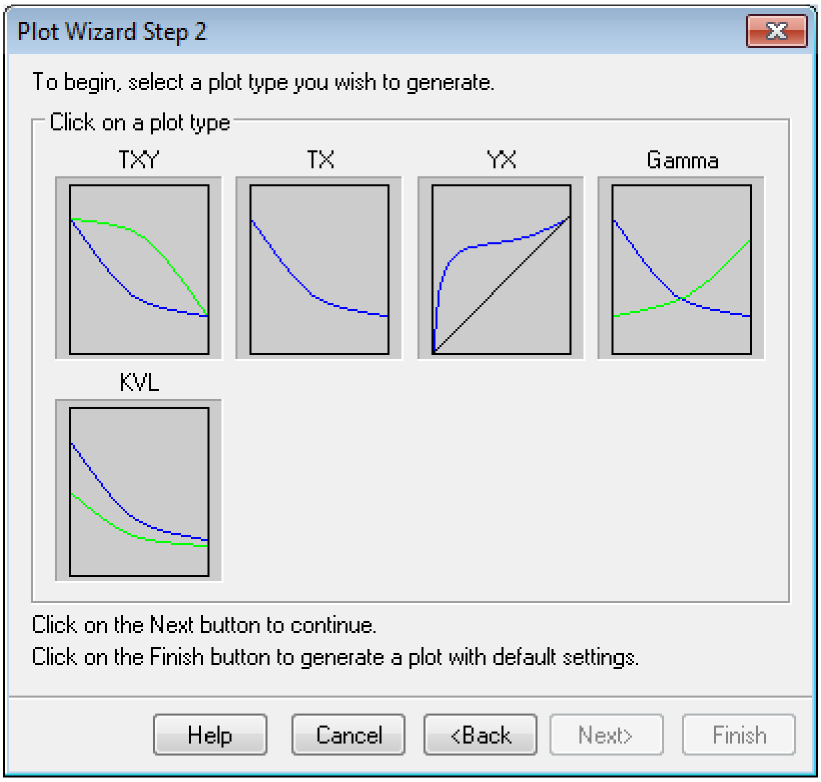


Figure 19. *Txy* diagram for water-ethanol system.

Other options for plotting can be obtained from the Plot Wizard option in the Plot menu or from some windows only when you are viewing certain pages. For example, when you generated the *Txy* diagram above, the data table for the numeric data was presented in the Binary Analysis window. In this window, you can click on the Plot Wizard button, which will open a new dialog window. Once you hit Next, you will be presented with the window shown in Figure 20. Here you can see that you have several options for plotting including the *Txy*, *Tx*, *yx*, activity coefficient, distribution coefficient, and others. If you are interested in the *yx* diagram, you can select it and hit Next. This will bring up a new window with the some options such as the component for which you want to plot. Select ethanol and click finish. This will bring up the plot shown in Figure 21.

Using the Plot Wizard you can plot many figures for both pure components and mixtures. The Plot Wizard is also functional when we are doing data regression, as we will learn later.



Plot Wizard Step 2

To begin, select a plot type you wish to generate.

Click on the Next button to continue.
Click on the Finish button to generate a plot with default settings.

Figure 20. Plot Wizard window.

Estimating Parameters

In some cases, Aspen Plus values for certain components' parameters do not fit will with experimental data or not known. For example, you might have the values for the heat capacity of a certain substance, but Aspen Plus does not have the parameters to predict the heat capacity. Or, in other cases, Aspen Plus might have the parameters, but the predictions do not compare well with the experimental data. In such cases we can resort to either entering the parameters manually, if we know the parameters from other sources (literature), use data regression of the experimental data and let Aspen Plus obtain or modify the parameters of interest, or let Aspen Plus determine the properties based on the structure and some physical known properties.

The second option is refer to as data regression, where the parameters are estimated based on experimental data. In the following sections we will demonstrate how to use data regression to fit experimental (or literature data).

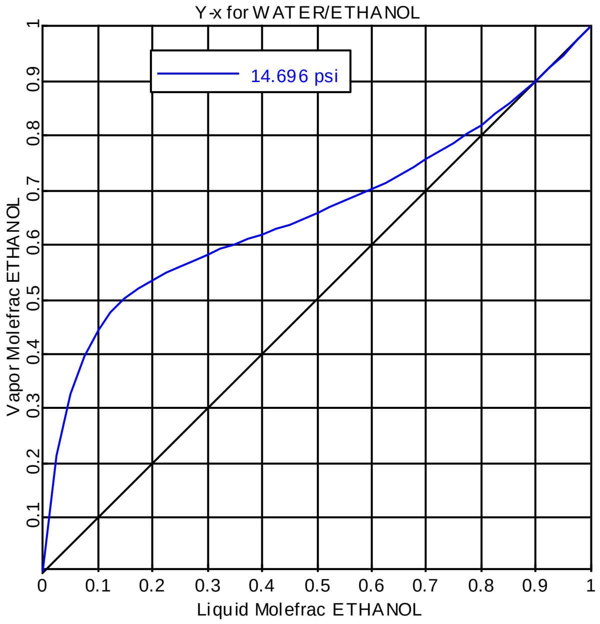
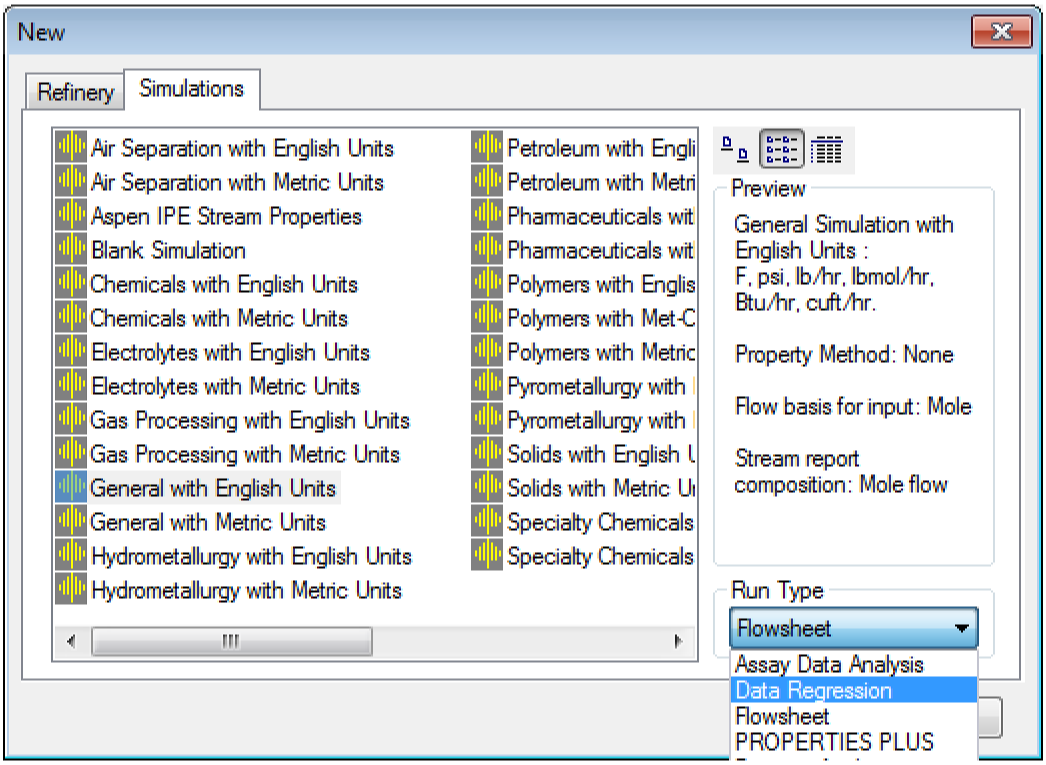


Figure 21. Ethanol equilibrium *yx* data for water-ethanol system.

Data Regression

To perform data regression, we first need to declare the simulation type as "Data Regression". This can be done either when we open a new Aspen Plus file through the New dialog window shown in Figure 21. Alternatively, an existing run can be changed to Data Regression by Setup folder in the Data Browser. Once you create a Data Regression run, you will notice that the Properties folder in the Data Browser has two new folder called "Data" and "Regression".

In the Data folder, we can enter the data of the property we need to determine the parameters for. In the Regression folder, we can define the regression that we need to perform. Let us take a simple example of estimating the density for H_2SO_4. While Aspen Plus gives good prediction of this property, we will assume that the data is not satisfactory and use literature data to do the fitting. The data to be used is shown in Table **1** which was taken from Perry's Handbook (8th ed., p. 2-113) for the density of pure liquid sulfuric acid at different temperatures. The original data was given in g/cm^3 units and converted to cm^3/mol using the molecular weight of H_2SO_4. This is necessary since the correlation used to predict liquid densities in Aspen Plus gives the molar volume and not the mass density.



General Simulation with English Units : F, psi, lb/hr, lbmol/hr, Btu/hr, cuft/hr.

Property Method: None

Flow basis for input: Mole

Stream report composition: Mole flow

Run Type: Flowsheet

Figure 22. Changing the run type to Data Regression.

Now, we need to enter the data into Aspen Plus (make sure you opened a Data Regression run, added H_2SO_4 as a component, and use a proper property package such as NRTL). Next, in the Data Browser window, select the Properties folder, the click on the Data subfolder. Click on the New… button, give the data a name (such as VDATA) and select PURE-COMP for the type. Hit OK. In the Setup page that just opened, select VL (liquid molar volume) for the property and select H_2SO_4 for the component. Set the pressure to 1 atm, which is the pressure at which the data is given. On the Data tab of the same page, copy and paste the temperature and V_L data as show in Table 1 (always check the units). Now the data has been entered and ready to be used. The next step will be to do the regression.

T (°C)	ρ (g/cm^3)	V_L (cm^3/mol)
0	1.8517	0.018895
10	1.8409	0.018785
15	1.8357	0.018732
20	1.8305	0.018679
25	1.8255	0.018628
30	1.8205	0.018577
40	1.8107	0.018477
50	1.8013	0.018381
60	1.7922	0.018288

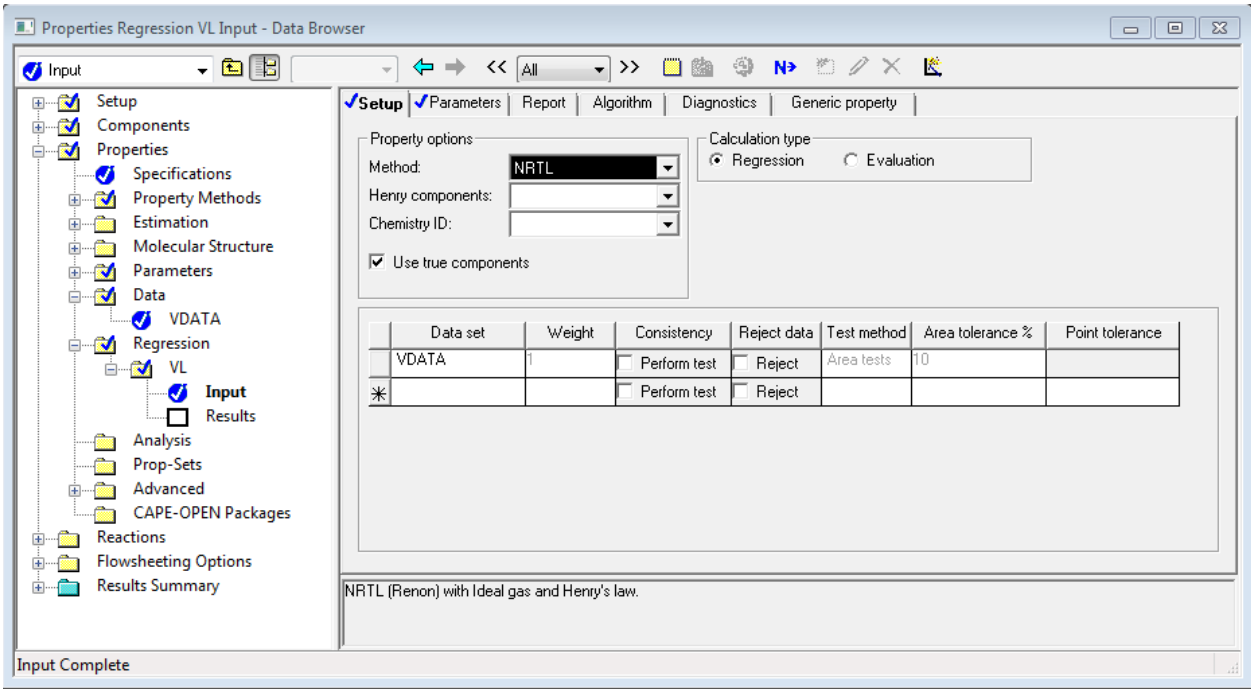
Table 1. H_2SO_4 density as a function of temperature.

In order to regress the data, we need to know what model is used to describe the molar volume of H_2SO_4. As discussed before, many of the correlations used to estimate pure components properties are given in the THRSWT page under the Pure Component folder. If you do not see the THRSWT page, you can generate using the Tools>Retrieve Parameter Results… menu. The second row of the THRSWT table gives the correlation used to liquid molar volume. For H_2SO_4, the data correlation used is the DIPPR with the DNLDIP parameter. Under the "General Pure Component Liquid Molar Volume" topic in the Help, you can see that the DIPPR model is given by:

$$\rho_i^{*l} = C_{1i}/C_{2i}^{(1+(1-\frac{T}{C_{3i}}))^{C_{4i}}} \quad ; \quad \text{for } C_{6i} \le T \le C_{7i}$$

with the DNLDIP parameters indicating the $C_{1i}\ldots C_{7i}$. For H_2SO_4, these parameters are given by: 1.4986×10^{-3}, 0.2653, 924.0, 0.2713, 0.0, 10.3 ^{o}C, and 336.9 ^{o}C. If you compare the results for molar volumes of H_2SO_4 using these values (from the Tools>Analysis>Property>Pure… menu) you will see that the results give a good match to the data in Table 1. However, if we want to improve our predictions, we can use the data to get new parameters for $C_{1i}\ldots C_{7i}$.

Now we are ready to perform data regression. In the Data Browser, go to the Properties/Regression folder. Click on the New… button and type in a name for this regression case (such as VL). In the Setup page select the Property method you want to use (NRTL), and select the data (VDATA) as your Data set. Your window should look like that in Figure 23.



Property options

Method: NRTL

Henry components:

Chemistry ID:

☑ Use true components

Calculation type

● Regression ○ Evaluation

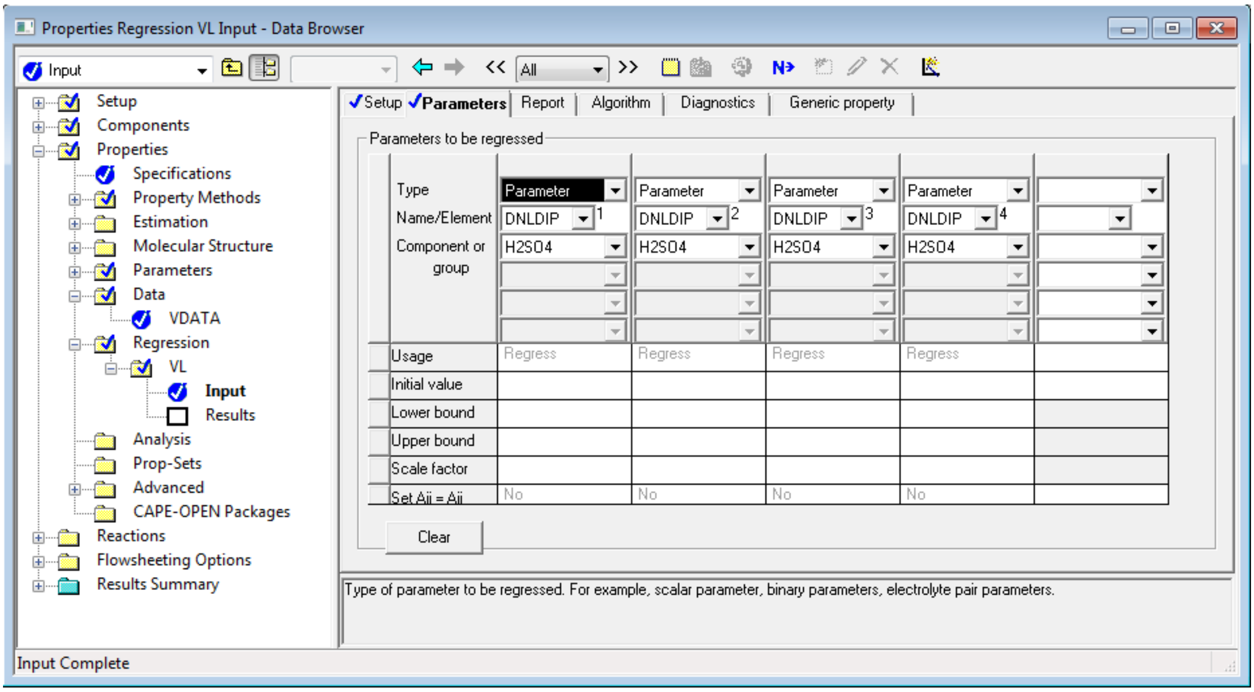
	Data set	Weight	Consistency	Reject data	Test method	Area tolerance %	Point tolerance
	VDATA	1	☐ Perform test	☐ Reject	Area tests	10	
*			☐ Perform test	☐ Reject			

NRTL (Renon) with Ideal gas and Henry's law.

Input Complete

Figure 23. Data Regression form.

Next, click on the Parameters tab. In this tab we will tell Aspen Plus what parameters to regress. As we saw earlier, the parameters of interest are the DNLDIP (from 1 to 4, since 5 to 7 are either zero or not included in the correlation). To input the parameters, select Parameter (since we are dealing with pure component and not mixtures), select the DNLDIP from the Name and type 1 in the field to the right of the name, and select H_2SO_4 for the Component. Now, repeat this step in the column to the right with 2 from the Element number, then 3, and finally 4 as shown in Figure 24.



Parameters to be regressed

	1	2	3	4	
Type	Parameter	Parameter	Parameter	Parameter	
Name/Element	DNLDIP	DNLDIP	DNLDIP	DNLDIP	
Component or group	H2SO4	H2SO4	H2SO4	H2SO4	
Usage	Regress	Regress	Regress	Regress	
Initial value					
Lower bound					
Upper bound					
Scale factor					
Set Aij = Aji	No	No	No	No	

Type of parameter to be regressed. For example, scalar parameter, binary parameters, electrolyte pair parameters.

Figure 24. Selecting the parameters to regress.

Once all data has been entered, you can run the simulation. Once the simulation has successfully run, the results of regression will be given in the Results page under the VL Regression case. If you check the values for the DNLDIP parameters you will see that the new values are different from the ones in Aspen Plus database, as shown in Table 2. To compare the results before and after regression, the VL data and the estimations obtained with the database constants and the regression constants are shown in Figure 25. It is clear that the prediction with the new constants more closely matches the data. The different between the original data and the estimation with the database is 1.25×10^{-4}, while that of the regression is 3.55×10^{-5}; almost an order-of-magnitude lower. However, we have to keep in mind that the regression was done with data in the temperature range of 0 to 60 ^{o}C, thus the constants obtained will be valid on this range. The original constant, however, we valid for a broader range from, roughly, 10 to 336 ^{o}C, as indicated by the DNLDIP constants 6 and 7.

Para.	**DB**	**Reg.**
C_{1i}	0.0015	0.0042
C_{5i}	0.2653	0.0095
C_{3i}	924.0	10164.0
C_{4i}	0.2713	-1.1127

Table 2. Regression results.

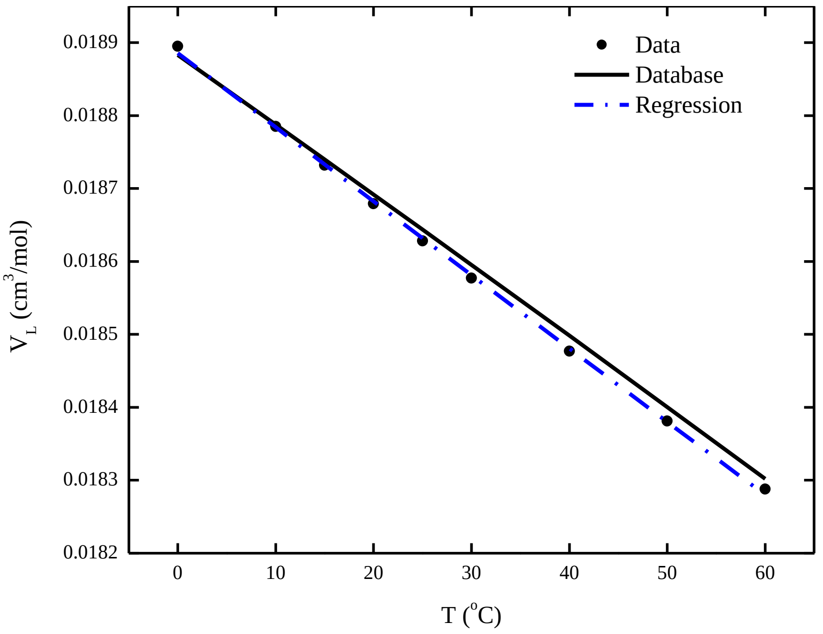


Figure 25. Comparison of H_2SO_4 data with database and regression results.

Data Regression of Mixture Properties

An important application of data regression in Aspen Plus is to obtain data for mixtures. A common example is obtaining the binary parameters from VLE data. As mentioned earlier, there are cases where parameters for some systems have not been measured, or the parameters were measured but do not give a satisfactory predictions. In such cases we can use data regression to make or improve such predictions.

For example, consider the ethanol-water system. This is a non-ideal system due to the interactions between the two molecules. The proper method to model this system will be an activity coefficient model such as the NRTL. However, for the sake of demonstration, let us assume we want to use an EOS like the Peng-Robinson (PR) equation to model this mixture. If you try to plot the *Txy* diagram for this mixture using the PR equation in Aspen Plus (from the `Tools>Analysis>Property>Binary…` menu), you will notice that the results obtained is does not make sense, as shown in Figure 26. If you try to look at the PR interaction parameters for ethanol-water, you will see that there is none. However, if we have experimental data, we can generate the interaction parameters using data regression.

To perform data regression we need first to obtain experimental data for our system, then determine what parameters can be regressed, and finally perform the regression. Experimental data for ethanol-water has been published in literature. The data in Table 3 gives *Txy* data (in mole fraction water) of ethanol-water system at 1 atm (*Ind. Eng. Chem.*, **41**(12):2905). We will use this data to find the binary parameters for the PR EOS. Our next task is to investigate the PR model and determine which parameters to regress.

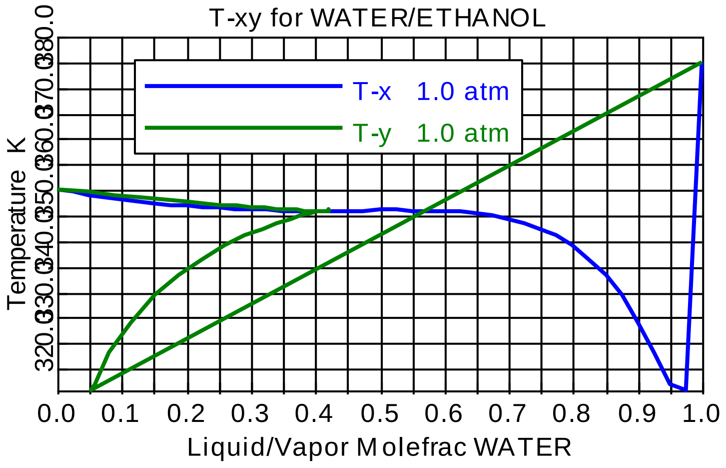


Figure 26. *Txy* diagram for ethanol-water system using the Peng-Robinson EOS.

Details about the PR model are given in Aspen Plus Help. As you have already studied, the PR EOS is given by:

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)}$$

Table 3. Ethanol-water VLE data at 1 atm.

T (°C)	X_{H2O}	Y_{H2O}	T (°C)	X_{H2O}	Y_{H2O}	T (°C)	X_{H2O}	Y_{H2O}
100.0	1.0	1	86.4	0.90	0.57	79.9	0.5	0.343
98.4	0.995	0.935	85.5	0.88	0.54	79.5	0.45	0.322
97.1	0.99	0.89	84.8	0.86	0.518	79.1	0.4	0.302
94.9	0.98	0.825	84.1	0.84	0.5	78.8	0.35	0.275
93.5	0.97	0.769	83.6	0.82	0.487	78.7	0.3	0.245
91.8	0.96	0.727	83.2	0.80	0.475	78.5	0.25	0.213
90.6	0.95	0.69	82.3	0.75	0.449	78.4	0.2	0.172
89.5	0.94	0.66	81.7	0.7	0.425	78.3	0.15	0.145
88.5	0.93	0.633	81.2	0.65	0.405	78.2	0.1	0.102
87.7	0.92	0.608	80.7	0.6	0.386	78.3	0.05	0.058
86.9	0.91	0.585	80.2	0.55	0.365	78.3	0	0

The equation contains two parameters a, and b. Each parameter is given by mixing rules. For example, the parameter b for a mixture is given by the simple mixing rule of:

$$b = \sum_i x_i b_i$$

where b_i is a component specific property (*i.e.*, does not depend on the interactions.) Therefore, there is no need for regression here. The parameter a, on the other hand, is given by:

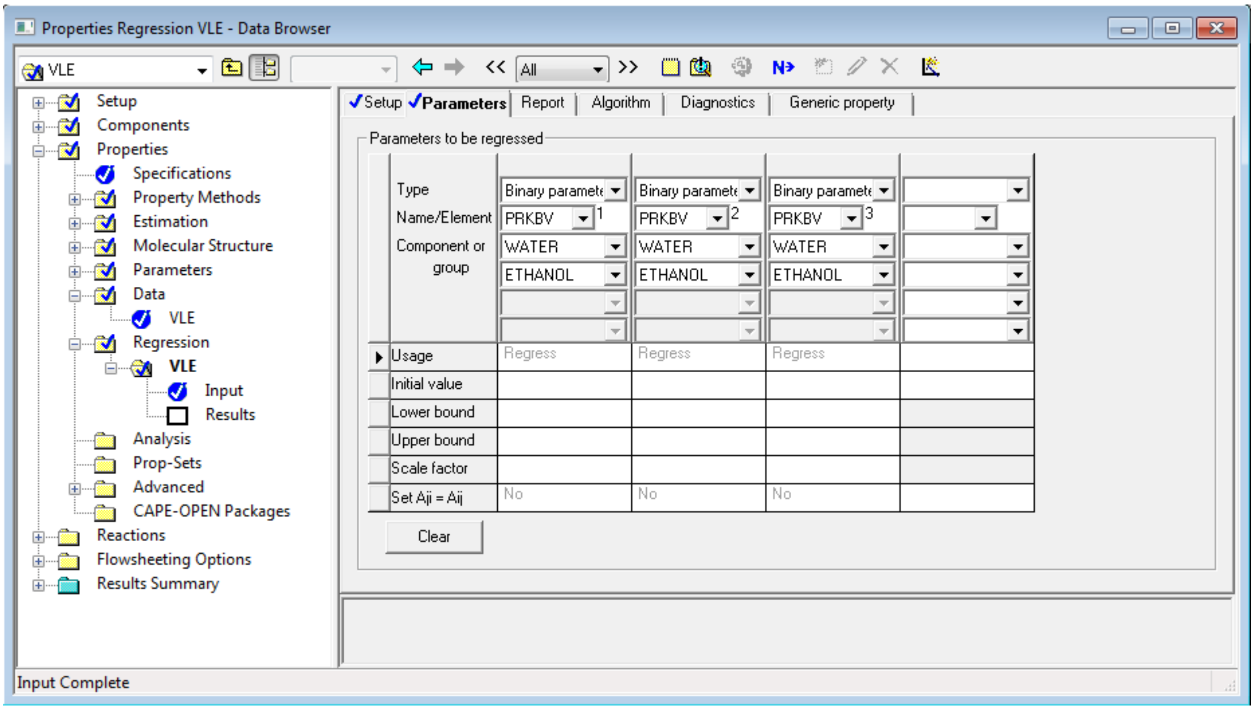
$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - k_{ij})$$

where a_i is a pure component property and is a function of the temperature, critical properties, and acentric factor (ω_i), and k_{ij} is an interaction parameter given by:

$$k_{ij} = k_{ij}^{(1)} + k_{ij}^{(2)} T + \frac{k_{ij}^{(3)}}{T}$$

where k_{ij}'s are binary interaction constants. Therefore, if we want to fit the data we can choose k_{ij}'s as our fitting parameters. It is also acceptable to choose ω_i as a fitting parameter. We will only fit the k_{ij}'s in this example.

To perform the regression, open a new run and change its type to Data Regression. Select ethanol and water as components, and select PENG-ROB as property method. Retrieve the parameters from the `Tools` menu and check the binary interaction parameters for PR EOS (located under the PRKBV page). There should be not parameters for this system. Next, create a new data set (call VLE) and set its type to MIXTURE. Select the components of interest, set the Data type to TXY, pressure to 1 atm, and the Basis to Mole fraction. Next, copy and paste the data in the Data tab (make sure you select the proper units and components).



Type	Binary paramete	Binary paramete	Binary paramete	
Name/Element	PRKBV 1	PRKBV 2	PRKBV 3	
Component or group	WATER	WATER	WATER	
	ETHANOL	ETHANOL	ETHANOL	
Usage	Regress	Regress	Regress	
Initial value				
Lower bound				
Upper bound				
Scale factor				
Set Aji = Aij	No	No	No	

Figure 27. Data regression input form.

The next step is to create the regression case. This can be done as in the previous example with binary parameters. The parameter of interest here is the PRKBV 1, 2, and 3. You should have a window similar to that in Figure 28

.

Once all input has been provided, run the simulation. Once the simulation is completed, check out PRKBV page under the Binary Interaction folder. You will notice now that the values of the k_{ij}'s are now reported in the page as: kaij ($k_{ij}^{(1)}$) = -25.9, kbij ($k_{ij}^{(2)}$) = 0.03459, and kcij ($k_{ij}^{(3)}$) = 4801.4. The results for regression and how it compares to experimental data can be investigated from the Plot Wizard menu. These are shown in Figure 28.

.

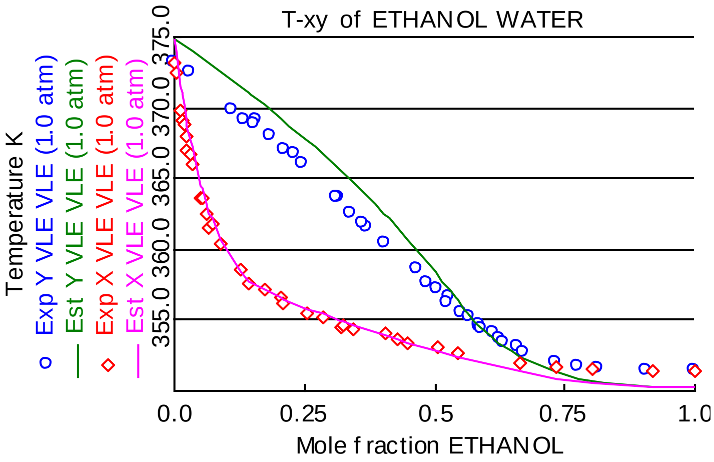


Figure 28. Data regression of ethanol-water system using PR EOS.

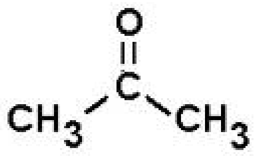
Two observations can be made from Figure 28. The PR EOS predictions improved considerable when interaction parameters where used. The model now predicts the general behavior of equilibrium and the presence of azeotrope above 0.75 mole fraction. It is also evident from the plot that the model does not fit very well the experimental data, and there are some obvious deviation especially in the vapor composition curve and compositions above the azeotrope.

Defining New Components

Although Aspen Plus has a large databank of components covering a wide range of oil, gas, chemical, and petrochemical applications, sometimes you might need to use a component that is not present in the database. In such case, you can define a new component and let Aspen Plus predict its properties based on some characteristic properties and chemical structure.

In general, the properties can be either entered directly, estimated using property estimation techniques, or regressed from experimental data. Inputting the parameters directly is straightforward, as will be demonstrated later, and data regression has already been demonstrated.

Property estimation relies mainly on the group contribution methods. These methods look at the chemical structures and see what chemical groups present, then use a formula to estimate certain thermodynamic and physical properties. For example, the well-known Joback method presents equation that can predict many properties including the boiling point,



melting point, critical temperature and pressure, and others. Consider, for example, acetone which has the chemical structure shown to the right. Acetone has three functional groups: C=O, CH_3, and CH_3. According to Joback model, the boiling point of a molecule can be estimated using the following relation:

$$T_b = 198 + \sum G_i$$

where G_i is the contribution for group i. The contribution for the different groups is tabulated and can be easily found. For example, for C=O, the value of G_i is 76.75 and for CH_3 it is 23.58 (Poling et al., *The Properties of Gases & Liquids.* 5th ed., 2001). Thus, T_b for acetone using the above equation is 321.91 K (or 48.76 ^oC). The boiling point for acetone is 56.53 ^oC, which means that the estimated value is almost 14% lower than the true one.

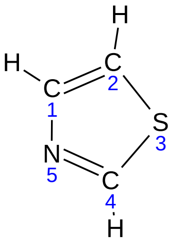
Other properties, such as freezing point, critical temperature, pressure, and volume, heat of formation, heat capacity, and others. Some of these properties are then used to calculate other properties. For example, the acentric factor used in the equations of estimate can be estimated using the critical temperature and pressure and the vapor pressure of the compound.

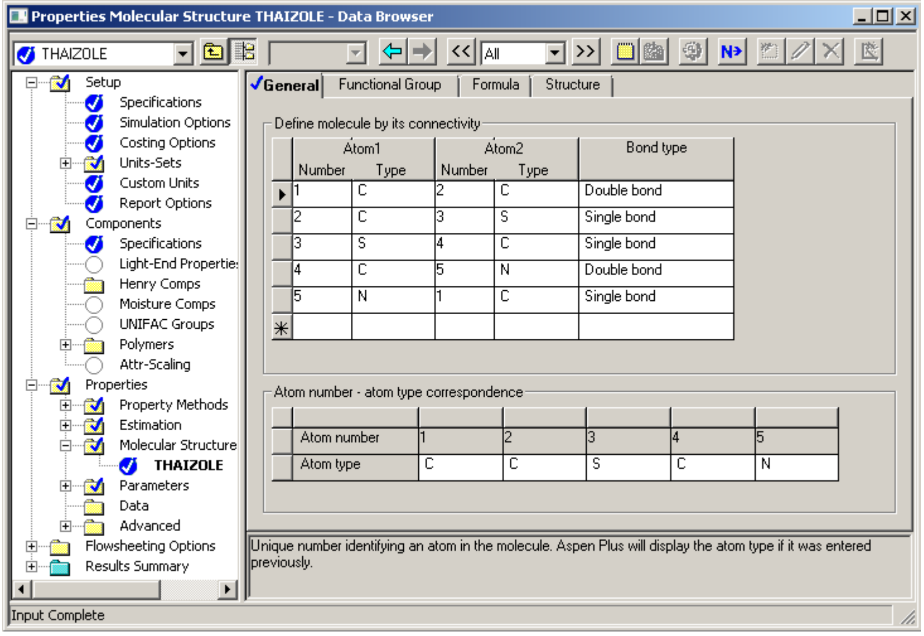
To demonstrate these ideas, consider the thiazole ring component. Some of the known component properties are shown in Table 4. In addition to the structure, we have some fixed properties (MW, T_b) and a temperature dependent property (vapor pressure).

To define a new component, go to the **Components | Specifications** page and type in the component name under the component ID. Since this component is not defined in the database, you will see that the Component name remains empty. Next, we need to define the molecular structure. The easiest way to do so is to draw the structure using the Molecule Editor which can be accessed from the **Properties | Molecular Structure | Thaizole** page, under the Structure tab. Once you draw the structure click on the Calculate Bonds button.

Alternatively, you can you input the structure in the General tab according to a numbering scheme. To number a structure, number all main atoms (not including the hydrogen atoms) in a successive manner, as shown in Table 4. Notice that we started with a carbon atom, giving it number 1, then numbers the rest of the ring in a clockwise manner. Once we number all atoms, we can now identify the bond. For example, atom 1 (a carbon) is connected to atom 2 (another carbon) with double bond. Atom 2 is connected to atom 3 (a sulfur) in a single bond. And so on. In both methods, you will end up with the window shown in Figure 29.

Table 4. Properties of thiazole

Molecular structure	
Molecular weight	85
Normal boiling point (^oC)	116.5
Vapor pressure (mmHg) (T given in ^oC for the range 69 – 118 ^oC)	$16.445 - \dfrac{3281.0}{T + 216.255}$



Define molecule by its connectivity

Atom1 Number	Atom1 Type	Atom2 Number	Atom2 Type	Bond type
1	C	2	C	Double bond
2	C	3	S	Single bond
3	S	4	C	Single bond
4	C	5	N	Double bond
5	N	1	C	Single bond

Atom number - atom type correspondence

Atom number	1	2	3	4	5
Atom type	C	C	S	C	N

Unique number identifying an atom in the molecule. Aspen Plus will display the atom type if it was entered previously.

Input Complete

Figure 29. Chemical structure of thiazole defined in the Molecular Structure page.

Next, we define the other properties given in Table 4. The first two properties, T_B and MW, are scalar (constant). To input the properties go to **Properties | Parameters | Pure Components** and click the New… button. Select Scalar in the dialog that appears, and give it a name TBMW, then click OK. In the Input page, select TB for the Parameters, C for units, and thiazole for the component. Now, enter the boiling point (116.5 ^oC). Next, enter the MW (85) in the same manner.

The final property is the vapor pressure. Notice that the vapor pressure is not a constant, but depends on the temperature. In fact, the formula given is Antoine's equation. To input the vapor pressure, go back to the **Properties | Parameters | Pure Components** and click the New… button. Select T-dependent correlation and click on the Liquid vapor pressure. Finally select PLXANT (which stands for extended

Antoine equation for liquid vapor pressure). In the Input sheet that opens, select thaizole, set the units to ^{o}C and mmHg, and set the parameters as follows: 1 = 16.445, 2 = -3281.0, 3 = 216.225, 8 = 69, and 9 = 118 ^{o}C. The last two parameters are the temperature range in which the equation is defined.

Now we are ready to run the simulation and investigate the results. Hit F5, click Next if asked to. The simulation might gives some warnings from the binary parameters estimation. Again, there are two types of properties that has been estimated. To view the results, go to **Properties | Estimation | Results** sheet. Under Pure Component tab, you will find all estimated properties. Properties that depends on temperature are present on the T-Dependent tab.

Once you complete the run, you now have a new component defined that you can use in you simulation. To do so, you first need to save this file as backup file, for example thiazole.bkp, which you can import into any simulation through the File>Import… menu.

Exercise 1: Using Aspen Plus Help

1 . Use Aspen Plus Help to select a suitable property method for the following processes:

a) A process in which large rocks of a phosphate is crushed, grinded, sieved, and washed to produce a final product. ....

b) Burning coal to produce electric power. ....

c) A plant to produce styrene. ....

d) Most parts of an oil refinery. ....

2. What does the following parameters stand for:

a) CPSXP: ....

b) KVDIP: ....

c) HFUS: ....

d) NATOM: ....

e) TPT: ....

3. Write down the general equations used to estimate the following:

a) Liquid volume of water.

....

b) Liquid volume of ethylene glycol.

....

c) Solid heat capacity of ethylene glycol.

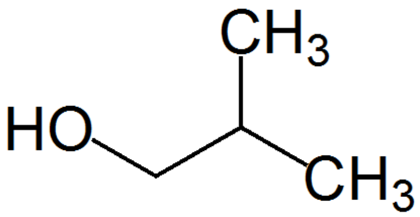
....

d) Solid heat capacity of silver nitrate.

....

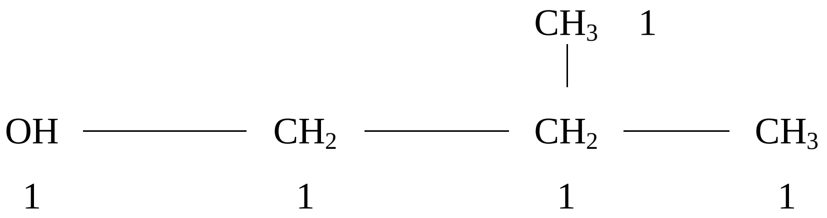
Exercise 2: New Components Based on Properties

Create a Property estimation simulation to define the component isobutyl alcohol based on its chemical structure:



Questions:

1. Indicate below how did you number the atoms?



$$\begin{array}{ccccccc} & & & & CH_3 & 1 & \\ & & & & | & & \\ OH & \text{———} & CH_2 & \text{———} & CH_2 & \text{———} & CH_3 \\ 1 & & 1 & & 1 & & 1 \end{array}$$

   Fill out the structure using your numbering scheme.

2. Using Aspen Plus Help, what are the functional groups (defined by its number) present in this molecule using the Lydersen method? An example is already given for the $–CH_3$ group.

Group	Group Number	Occurrence
$–CH_3$	100	2

3. Setup the your simulation to estimate the boiling point (T_B), surface tension (σ) at 20 ^oC, and heat of vaporization (ΔH_v) at 227 ^oC. Try different methods until you get the closest match to the literature value.

Property	Literature	Estimation	Difference
TB (^oC)	107.9		
σ at 20 ^oC (dyne/cm)	23.0		
ΔH_v at 227 ^oC (J/mol)	42,780.0		

Exercise 3: New Component Based on Experimental Data

Therminol 59 is a heat transfer fluid used for a wide range of temperatures (-50 to 600 ^{o}F). The component, however, it is not included into the database. The company that provides this fluid, called Solutia has provided the attached specification booklet with a lot of information about this component. In this exercise, do the following:

Therminol 59

1. Create a data regression simulation and configure to be valid only for the liquid-phase.
2. Set the property method to Wilson-LR
3. Input the properties for: boiling point, critical temperature, critical pressure and MW.
4. Input the data for liquid heat capacity, liquid thermal conductivity, liquid viscosity, and molar liquid volume.
5. Create regression for the data above using the Racket model for the molar liquid volume, and the DIPPR model for the other three.
6. Configure your simulation to estimate all missing parameters.

Questions:

1. Create plots for liquid molar volume, liquid viscosity, and liquid thermal conductivity versus temperature for the temperature range of Therminol 59 use. Create the plots on the same graph.

Exercise 4: VLE Data Regression

VLE data for ethanol-ethyl acetate (EtOH-ETOAC) has been published in literature. We want to use these data to estimate the binary interaction parameters for this system. Start a data regression simulation and use the data provided in the attached Excel sheet to estimate the first two binary parameters of EtOH-ETOAC for the Wilson, NRTL, and UNIQUAC models.

VLE Data

Questions

1. Fill out the table below using the original interaction parameters from the database, and that obtained from the regression.

Model	**Wilson**		**NRTL**		**UNIQUAC**	
	DB	**Reg.**	**DB**	**Reg.**	**DB**	**Reg.**
$a_{\text{ETOH-ETOAC}}$						
$a_{\text{ETOAC-ETOH}}$						
$b_{\text{ETOH-ETOAC}}$						
$b_{\text{ETOAC-ETOH}}$						

2. Prepare one plot that compares the *Txy* data at 1 atm with the three regression results.

3. Check out the Consistency tests tab in the regression results to make sure the experimental data is consistent. Also, use the Sum of Squares tab in the regression results to determine which model gives the closest fit to the experimental data.