

## ChemSep Tutorial: Phase Equilibrium Calculations

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In this document we illustrate the use of *ChemSep* by considering its use to solve some example problems posed in thermodynamics textbooks. The examples considered below are:

- 1. Estimating K-values from the Peng-Robinson Equation of State (this is Example 10.2 in *Introductory Chemical Engineering Thermodynamics*, by J.R. Elliott and C.T. Lira (Prentice-Hall, 1999).
- 2. Creating a phase diagram for methanol-benzene (this is Example 10.8 in the same book).

## Tutorial 1: K-values from the Peng-Robinson Equation of State

The bubble point pressure of an equimolar mixture of nitrogen(1) and methane(2) at a temperature of 100 K is to be calculated using the Peng-Robinson equation

We begin by starting *ChemSep* and selecting nitrogen and methane from the databank.

🕂 ChemSep v6.17					
File Edit Solve Analysi	is Databanks Tools Help				
🗋 🚅 🖬 🕨 🥰 🧇	→ × IJ T E Ø				
Title	✓ Components				
Components	Select Components				
X Operation				1.	
	Component databank: c:\chemse	pl\pcd\lite.pcd		rowse	Advanced search
Coocifications					Sort
	Find				
	Components in databank:	Se	elected components in s	simulation:	
Solve options					
Paths	Name	Lomponent(s):	Identifier	L#	File Loc.
	Air	bba 🗠	Methane	1	c:\chemsepl\pcd\ 11
	Argon		Nitrogen	905	c:\chemsepl\pcd\ /
	Carbon tetrachloride				
	Water	Add the compo	ound(s) selected on the	left to the li	st of compound(s) on the right
	Ammonia	Substitute			
	Nitrogen				
	Oxygen				
	Hydrogen				
	Chloroform				
	Methane	TOP UP			
	Methanol	- Down			
	Ethylene				
	Acetic acid				
	Ethyl chloride	Add New			
	Ethane				
			•		• • •
Changed Not converg	ed				///

Next select the **Operation** tab and choose **Flash** 



The next step is to select the appropriate thermodynamic models. It is beyond the scope of this tutorial to explain *how* to choose appropriate models (it must suffice to note that the proper selection of thermodynamic models is of central importance in phase equilibrium calculations).

The screen shot below shows the models selected for this exercise.

🕂 ChemSep v6.11				
File Edit Solve Analysis Databanks Tools Help				
<u>B</u> 🕒 🕒 🥭 🔶	XITE	Z		
	× Thermodynamics	V Physical properties		
✓ Operation	-Select Thermodynam	ic Models		
	K-Value	EOS 💌		
Specifications     Secults	Equation of state	<b>_</b>		
- Units Solve options	Activity coefficient	Soave-RK API-SRK		
Paths	Vapour pressure	SRK-UMR PR-UMR		
	Enthalpy	-		

No enthalpy model is needed for this exercise (we are not interested in that calculation this time), but we selected the Peng-Robinson model there as well.

The next step is to specify the composition of the mixture. This is done in the feed panel:

🕂 ChemSep v6.11					
File Edit Solve Analysis Databanks Tools Help					
🔥 🕞 🕒 🍣 🔶					
Title	✓ Feeds				
Components	Feed Stream(s) Specifications				
✓ Operation					
	Insert Remove Molar flows				
E Specifications					
	Feed: 1				
Units	Name Feed1				
- Solve options	Stage 1				
E Paths	State T & p				
	Pressure (MPa) 0.411900				
	Vapour fraction (-)				
	Temperature (K) 100.000				
	Flowrates (kmol/s):				
	Nitrogen 0.500000				
	Methane 0.500000				
	Total flowrate 1.00000				

The feed panel asks for component flows, but what matters to us is the composition and not the flows. Accordingly, we simply set the component flows equal to the corresponding mole fractions.

Note that the feed pressure and temperature are not that important in this calculation. We will set the pressure at which the calculation is to be done in the Flash Specifications panel.

The first task is to select the type of flash calculation that we wish to perform. There are several different flash types available in ChemSep. To determine the bubble point pressure we need to specify the temperature and vapor flow as indicated by the image below.

ChemSen v6.11				
Cite Edit, Calue Analusia Databanka Tanla Usla				
File Eult Solve Analysis	Databanks Tools	пер		
Title	🗹 Analysis 🗙	Flash specs		
Components	Elash specification	· · · · · · · · · · · · · · · · · · ·		
🛛 🛶 🗸 Operation	r idan specification	•		
🗄 √ Properties	Flash type	Pressure & heat duty		
Feeds				
🖃 🗙 Specifications	Pressure	Pressure & vapour flow Pa)		
🚽 🚽 🗸 Analysis		Pressure & liquid flow		
K Flash specs	Temperature	Pressure & heat duty		
E X Besults	remperatore	Temperature & vapour flow		
		Temperature & liquid flow		
Calua antiana	Vapor Now	Temperature & heat duty hol/sj		
Solve options		Vapour now & near duty		
- Paths	Liquid flow	Liquid riow & near duty (whol/s)		

We now set the temperature (to the desired value of 100 K) and the vapor flow to zero (corresponding to a bubble point calculation).

f ChemSep v6.11				
File Edit Solve Analysis Databanks Tools Help				
Title	🖌 Analysis 🖌 Flash specs			
	Flash specifications			
Properties     Feeds	Flash type Temperature & vapour flow			
Specifications	Pressure (MPa)			
	Temperature 100.000 (K)			
- Units	Vapor flow 0.000000 (kmol/s)			
Paths	Liquid flow (kmol/s)			
	Heat duty (J/s)			

The problem specifications now are complete and we can proceed to solve the problem. First we save the file (using the **File** menu – note that the file name appears on the blue bar at the top of the ChemSep window) and then click on the green arrow head icon to start the calculations.

🕂 ChemSep - Tutorial_01.sep - Flash
File Edit Solve Analysis Databanks Tools Help
Title Save the current input and run the simulator without performing any checks
Components     Flash specifications

This will bring up the solve window – which very soon (this is an easy problem) looks like this:

RunForm		
EQS parameters missing - set to zero		
Beading specifications		
Checking Component Data		
Nitrogen		
* Missing Hboil		
Methane		
* Missing Hboil		
Determining feed conditions		
Solving TP flash		
Reading flash specifications		
Solving TV flash		
Iteration Error		
Iteration Elloi		
1 43		
720E-06		
2 2.3201E-11		
Convergence obtained in 2 iterations		
Time 15 milliseconds		
FixMem driver done		
Process ended		
		•
•		Þ
	Done	

Click on **Done** to close the window and bring up the results panel.

f ChemSep - Tutorial_0	D1.sep - Flash		
File Edit Solve Analysis	5 Databanks Tools Help		
<u>B</u> 🕒 🕞 🧶 🦣			
Title	Tables Rating		
Components	Tables	1	
🗸 Operation			
Properties	Select table: Streams 💌 XL Edit Copy Font Print		
Thermodynamic:			
Physical properti			
Feedo	Stream Feed1 Top Bottom		
Analysis	Pressure (MPa)         0.411900         0.426958         0.426958           Vapour fraction (-)         0.0484042         1.00000         0.000000           Temperature (K)         100.000         100.000         100.000           Enthalpy (J/kmol)         -1.270E+07         -6.029E+06         -1.294E+07           Entropy (J/kmol/K)         -143590         -43616.0         -100034		
Tables Rating Units	Mole flows (kmol/s)         0.500000         0.000000         0.500000           Nitrogen         0.500000         0.000000         0.500000           Methane         0.500000         0.000000         0.500000		
- Solve options	Total molar flow 1.00000 0.000000 1.00000		
- Paths	Mole fractions (-) Nitrogen 0.500000 0.946231 0.500000 Methane 0.500000 0.0537690 0.500000		
	Mass + lows (kg/s)         14.0070         0.000000         14.0070           Nitrogen         14.0070         0.000000         14.0070           Methane         8.02150         0.000000         8.02150		
	Total mass flow 22.0285 0.000000 22.0285		
	Mass fractions (-) Nitrogen 0.635858 0.968484 0.635858	-	
Saved Converged 2 i	iterations C:\ChemSep_\Sep_Files\StandardTest\Flash\Tutorial_01.sep		

We from this screen shot that the bubble point pressure has been estimated to be 0.427 MPa (Elliott and Lira report that the pressure is close to 0.428 Mpa but their calculation is not converged as tightly as is the one here).

The K-values at the specified temperature (and calculated pressure) can be found in another table:

Tables Select table: K-Values	▼ XL Edit Copy Font Print
K-Values Nitrogen Methane	1.89246 0.107538

The K-values given by Elliott and Lira are  $K_1 = 1.890$  and  $K_2 = 0.1073$  (remember that their calculation is not fully converged).

## Tutorial 2: Phase Diagram for Methanol – Benzene from a Cubic Equation of State

Our second example (which happens to be Example 10.8 in Eliiott and Lira) concerns the creation of a phase diagram for Methanol and Benzene at atmospheric pressure.

We start by selecting methanol and benzene on the **components** panel. Then select **Flash** as before on the **Operation** panel. Use the following **thermodynamic model**:

🕂 ChemSep v6.11		- U ×
File Edit Solve Analysi:	is Databanks Tools Help	
<u>B</u> 🕒 📄 🍣 🔶		
Title	✓ Thermodynamics ✓ Physical properties ✓ Reactions	
Components	Select Thermodynamic Models	[
Feeds	K-Value EOS 🔽 Show enthalpy/exergy settings:	
🕀 🗙 Specifications	Foundation of states Principal	
⊕ × Results		
- Units - Solve options	Activity coefficient	
Paths		
	Vapour pressure	
	Enthalpy Peng-Bobinson	
	Enter Thermodynamic Model Parameters (when required)	
	Peng Robinson  Peng Robinson	
	Reset i · i k·ii	
	Methanol - Benzene *	
	Save	
	Correlation	
Changed Not converge	ed	1.

Note the bottom half of this page where we can enter model parameters as required. In this case the interaction parameter is 0.084 and that value must be typed in the space occupied by the \* in the image above (the \* will be assumed to be zero in this case – but be warned that a \* means the default value is taken and that is not always zero).

The feed composition is not so important here because, in order to create a phase diagram, we need to perform many calculations at different compositions. In this case, however, we start with a "mixture" that is pure benzene (component 2):

ed Stream(s) Specification	s
InsertF	Temove Molar flows
Feed:	1
Name	Feed1
Stage	1
State	Т&р
Pressure (kPa)	101.325
Vapour fraction (-)	
Temperature (K)	300.000
Flowrates (kmol/s):	
Methanol	0.000000
Benzene	1.00000
Total flowrate	1.00000
Enter the details o	f each feed stream

Specify the pressure at which the phase diagram is to be determined (on the **Flash Specifications** panel) and the vapor flow (here set to zero to indicate that we are doing a bubble point calculation).

Flash specification	ns	
Flash type	Pressure & vapour flow	•
Pressure	101.325	(kPa)
Temperature		(K)
Vapor flow	0.000000	(kmol/s)
Liquid flow		(kmol/s)
Heat duty		(J/s)

Save the file (under the **File**) menu and Solve it (click on the green arrow head icon and then click on **Done** in the calculation window) to bring up the results page:

🕂 ChemSep - Themo_Tuto	rial_02.sep - Flash					- U ×
<u>File E</u> dit <u>S</u> olve <u>A</u> nalysis [	<u>D</u> atabanks <u>T</u> ools <u>H</u> elp					
<u>B</u> 🕒 🕒 🍣 🔶	XUTE					
Title Components Operation Properties Thermodynamic:	ables Rating Tables Select table: Streams	Y	XL Edit	Сору	Font Print	
Reactions	Stream	Feed1	Тор	Bottom		<b>_</b>
Analysis Flash specs	Pressure (kPa) Vapour fraction (-) Temperature (K) Enthalpy (J/kmol) Entropy (J/kmol/K)	101.325 0.00000 300.000 -3.235E+07 -91858.5	101.325 1.00000 352.815 4.7064E+06 14753.4	101.325 0.000000 352.815 -2.560E+07 -71161.6		
Rating Units	Mole flows (kmol/s) Methanol Benzene	0.000000 1.00000	0.000000	0.000000 1.00000		
- Solve options	Total molar flow	1.00000	0.000000	1.00000		
	Mole fractions (-) Methanol Benzene	0.000000 1.00000	0.000000 1.00000	0.000000 1.00000		
	Mass flows (kg/s) Methanol Benzene	0.000000 78.1140	0.000000	0.000000 78.1140		
	Total mass flow	78.1140	0.000000	78.1140		
	Mass fractions (-) Methanol	0.000000	0.000000	0.000000		<b>•</b>
	1					Þ
Saved Converged 1 iter	ations C:\ChemSep_\Sep_Files	\StandardTest\Flash\`	Themo_Tutorial_0	2.sep		1.

This page tells us that (according to the PR EOS), benzene boils at a temperature of 352.8 K. This is close to the experimental value of 353.25 K).

To prepare a Txy diagram we need to carry out many such calculations at different feed compositions. *ChemSep* has a parametric study option that can make it quite easy to carry out many similar calculations.

Go to Analysis (on the main menu bar) and select parametric study.



This brings up the following screen:

f Parametric Study
Select input variables
Number of steps 🚺 🔽 Use old results 🔽 Automatic 🔽 Keep sep-files 🔽 Restore original
Add Delete Reset
Name Variable Units Value Start/Valuelist End
Select result variables
Add Delete Reset
Name
Current Value
Results
Run Plot Copy data XL Graph Edit Plot
Close

Click on Add and select Feed component 1 flow as shown below.

-Select inp Number	ut variables of steps 1 🔲 Use old results 1	🗸 Automatic 🧮 Keep sep-files 🔽 Restr	ore original
Add Name	Feed1 stage=F1N Feed1 temperature (K)=F1T Feed1 pressure (kPa)=F1P Feed1 vapour fraction=F1VF Feed1 component 1 flow (kmol/s)=F1F1 Feed1 total flow (kmol/s)=F1FT Flash type=FY Flash type=FY	Delete     Reset     Start/Valuelist     End	

Repeat this step and select **Feed component 1 flow** a second time (there will be warning that you should not select the same variable twice). Clear this warning because this is exactly what you must do at this stage. The top portion of the screen now looks like this:

elect input var Number of ste	riables eps 1 🛛	Use old results	🔽 Automatic 🛛	🗖 Keep sep-files	: 🔽 Restore original
Add			De	elete F	Reset
Name	Variable	Units	Value	Start/Valuelist	End
Feed1 comp	one F1F1	kmol/s	0	0	0
Feed1 comp	one F1F1	kmol/s	0	0	0

It does not, of course, make sense to vary the same variable more than once at the same time; we are now going to change the second one. Click on the box above where you can read **F1F1** (which means Flow 1, component 1). Retype the string so that it reads **F1F2** (for Flow 1, component 2).

In addition, change the start and end values of both variables as shown in the image below:

lumber of steps	51	Use old results	🔽 Automatic	Keep sep-files	E 🔽 Restore origi
vdd			<b>•</b> [	Delete F	Reset
Name	Variable	Units	Value	Start/Valuelist	End
Feed1 compone	F1F1	kmol/s	1	1	0
Feed1 compone	F1F2	kmol/s	0	0	1

Now, when the parametric study is run it will vary the amount of methanol in the feed (from one to zero) and the amount of benzene in the feed (from 0 to 1) in such a way that the total amount remains the same (1).

The next step is to select the results variables. For a Txy diagram we need the temperature and the mole fraction of methanol in the vapor phase. Use the drop down list in the center part of the Parametric study window to select these variables and so that this part of the window appears as shown below:

\dd			De De	lete	Reset	
Name	Feed1 compone	Stream Top vap	Stream Top tem			
Variable	F1F1	TOPSY(#)	TOPST			
Units	kmol/s		К			
Current Value	0	0	352.8151			

The # sign must be replaced by the number for methanol (1 in this case). Click on that box and replace the # sign by 1:

\dd			•	Del	ete	Reset	1
Name	Feed1 compone	Stream Top yap	Stream	Top temr			_
Variable	F1F1	TOPSY(1)	TOPST	roptoni			
Units	kmol/s		К				
Current Value	0	0	352.815	51			
	-	-					

We are almost ready to run the parametric study. First, select the number of steps we want to cover the range of mole fractions. Enter this number in the space provided near the top of the window.

E	[ Parametric Study				<u>_ 0 ×</u>	
	Select input variables					
	Number of steps 51	🔲 Use old results	🔽 Automatic	🔲 Keep sep-files	Restore original	

Now click **Run** (near the foot of the window). *ChemSep* will now run through a series of closely related problems as it varies the specified variables (feed mole fractions in this case) over the specified range (0-1 and 1-0 in this case). When completed you will see the window look something like this:

elect input variat						
Number of steps	51	Use old results	V Automatic	: 🗌 Кеер	sep-files 🔽	Restore origin
Add			•	Delete	Reset	
Name	Variable	Units	Value	Start/V	aluelist End	
Feed1 compone	e F1F1	kmol/s	1	1	0	
Feed1 compone	e F1F2	kmol/s	0	0	1	
elect result varial	bles					
	5103					
Add			• _	Delete	Reset	
Name	Feed1 compor	ne Stream Top va	ap Stream Top	temp		
Variable	F1F1	TOPSY(1)	TOPST			
Units	kmol/s		K			
Current Value	0	0	352.8151			
esults						
Run	Plot	Copy dat	∍ XLG	raph	Edit Plot	
Step	Feed1 compor	ne Stream Top va	ap Stream Top	temp 🔺		
Units	kmol/s		K			
1	1	1	337.7835			
2	0.98	0.902747	335.6954			
3	0.96	0.837537	334.242			
4	0.94	0.793191	333.2435			
-	0.92	0.762627	332.5641			
5	0.0	0 741311	332,1057	-		
5 6	0.9	0.141011				

We can plot the results in several different ways using either the plotting capabilities built into *ChemSep* or by using an alternative software package.

First, we show how to display the Txy diagram using the plotting capabilities built into *ChemSep*. If we click on the the **Plot** button *ChemSep* will plot the parametric study results using the first variable that was varied on the X axis (that would be the mole fraction of methanol here) and *all* other variables on the y-axis (that includes both the mole fraction of methanol in the vapor and the temperature). Consequently the diagram will not be exactly what we want to see (which is why we don't show it here). Instead of clicking on **Plot** we suggest that you click on the **Edit Plot** button ; this will bring up the panel shown below.

€ ChemSep - Thermo_Tuto	orial_02.sep							<u>_ 0 ×</u>
File Edit Solve Analysis D	atabanks Tools Help							
🗅 🚅 🖬 🕨 🍠 🔶 🔶	× UT E 🖉							
Title Components Operation	ables Graphs Rating							
Properties	Select graph:			▼ Displa	iy XL	Сору	data 🔽	Graph settings
Physical properti	Plot	,	1	1	,	,	,	
Feeds	Title	Labels	Stages	Axis color	Commands	Box	Labels box	Import data
- √ Specifications	Parametric Study	Un	Vertical	Black		Un	Ult	
Analysis	Axes	[a	1=	let to the	10	la u	li ni i	
√ Flash specs	Little	Start	1.2	0.2	Small tics	Girid Off	Logarithmic Off	Scientific not
🖻 🗸 Results	v1 Stream Ton	-0.2 v-70 56302	423 3781	100	0	Off	Off	Off
- Lables Rating	x2				0	Off	Off	Off
Units	ψ2				0	Off	Off	Off
Solve options Paths	Add set Reset set:	s Calc.	Dev's	Save graph	Auto A	kis 🔽 Ai	uto colors	Black 💌
	Delete set Save sets	Exp	port	Delete graph	Oversize	0.2 🔽 A	uto points 🛛	Diamond 💌
	Data sets							
	Label Plot X Plot	Y Xaxis	Yaxis Unit	s >Units 4	Color Poin	ts Thickne	Style 1st	stiLast si
	2 Stream PS1 PS2	81	yi kmo	1/5 K	Green +	Normal	Solid 1	51
		Information o	on how to plo	each data se	t			
Saved Converged 1 iter	ations C:\ChemSep	_\Sep_Files\Tl	hermo_Tutori	al_02.sep				//

Note the lowest part of this panel headed **Data sets**. *ChemSep* uses the labels PSx (where x is a number) to refer to the columns of results obtained in the Parametric Study. As already noted above *ChemSep* is programmed to display PS2 (the mole fraction of methanol in the vapor) as a function of PS1 AND PS3 (temperature) as a function of PS1. We need to change these settings. Click in the Plot X and Plot Y cells and retype the entries so that this section appears as shown below.

	Data sets									
		Label	Plot X	Plot Y						
	1	Stream	PS1	PS3						
	2	PS2	PS2	PS3						
1.1										

Next, set the axis limits (the quick way is to click on **Auto Axis** but we would recommend adjusting at least the x-axis limits to vary from 0-1). The plot and axis titles can also be changed (click in the appropriate cells and type the names that you prefer). In the screen shot below we show that the plot title was removed, The axis labels were changed to better represent the variable names, the

data set labels were deleted, the default plot colors were changed and the plotting of points was suppressed (leaving only the line joining the points).

	Select graph: Display XL Copy data 🔽 Graph settings											
	Plot Title		Labels	Stages	- A>	is color	Comma	ands	Зох	Labels	box In	nport data
			On	Vertica	il Bi	ack			On	Off	•	
Г	Axes											
		Title	Start	End	Ti	c interval	Small ti	ics	Grid	Logarit	thmic S	cientific not
	x1	Mole fraction	n 0	1	0.	2	0		Dff	Off	0	Iff
	γ <b>1</b>	Temperature	325	360	5		0		Dff	Off	0	Iff
	x2						0		Dff	Off	0	Iff
	γ2						0		Dff	Off	0	Iff
	Add set	Reset set	s Ca	lc.Dev's	Sa	ve graph	A	uto Axi:		uto color	s Bla	ck 💌
	Delete set	Save sets	:	Export	Del	ete graph		ersize	0.2 🔽 A	luto point	s Dia	mond 💌
Γ.	Data sets											
	Label F	lot X Plo	t Y Xaxi	s Y axis	Units >	Units (	Color	Point	5 Thickne	Style	1st st	(Last s
	1 F	PS1 PS3	×1	y1	kmol/s	E	Blue	No Po	ir Normal	Solid	1	51
	2 F	PS2 PS3	×1	y1	kmol/s	K F	Red	No Po	ir Normal	Solid	1	51

Finally, we click on the **Display** button near the top of this panel to bring up the Txy diagram in a separate window.



It is also possible to add actual experimental data to this plot, detailed instructions on how to do this can be found on the *ChemSep* web site:

www.chemsep.com/downloads/source/VLE\_Data/howto\_vle/howto\_vle.html

Another option is to use some other package that can create plots such as a spreadsheet program. Click on the **Copy Data** button, open a spreadsheet program and paste the data into an open worksheet. Here we use **OpenOfficeCalc** (free from <u>www.openoffice.org</u>) to illustrate.

撞 Untitled1 - OpenOffice.org Calc										
<u>File Edit View Insert Format Iools Data Window H</u> elp										
j 🗟 • 🥔 🖬 📨   🔐   🚔 🔗   🚏 颸   🗶 🖆 🛱 • 🛷   🦘 • 🕐 •   💩 抖 👬   🥭 🖌   👭 🥢 🖄 🎟 🔍   🖓 💂										
In ▼ B I U = Ξ ≡ ⊞   10 % \$2 km + + + + + + + + + + + + + + + + + +										
B2 $f_{(x)} \Sigma = $ Step										
	A	В	С	D	E	F	G	Н	I	
1										
2		Step	Feed1 comp@	Stream Top 🦻	Stream Top te	emperature (K)				
3		Units	kmol/s		K					
4			1 0	0	352.82					
5			2 0.02	0.09	350.18					
6			3 0.04	0.17	347.88					
7			4 0.06	0.24	345.86					
8			5 0.08	0.29	344.09					
9			6 0.1	0.34	342.52					
10			7 0.12	0.38	341.13					
11			8 0.14	0.41	339.9					

Column C contains the mole fraction of methanol in the liquid, column D has the vapor mole fraction and the temperature is in column E.

Now we can use the plotting capabilities of *OpenOfficeCalc* to create the Txy diagram shown below.

## **Txy Diagram for Methanol - Benzene**

