ChemSep Case Book: Handling Missing Components

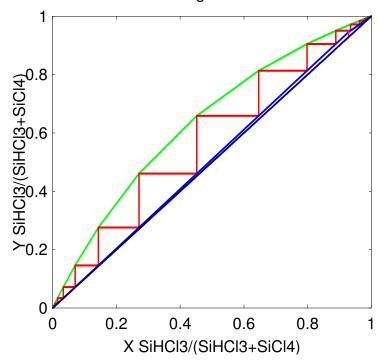
Ross Taylor and Harry Kooijman

In their book *Conceptual Design of Distillation Systems* M.F. Doherty and M.F. Malone (McGraw-Hill, 2001) describe a process for the manufacture of polysilcon (used in processes for making solid-state electronic devices and optical fibres). In their illustration they show a flowsheet for a plant that has a stream with the following composition

SiH ₂ Cl ₂	2 mol%
SiHCl ₃	91 mol%
SiCl ₄	7 mol%

This mixture is to be separated by distillation. These separations must be carried out to very high purities (at least 99.9 mol%).

During the Fall 2004 semester we used this mixture as the basis of an in-class exercise for students to design simple column sequences using *ChemSep*. The McCabe-Thiele diagram shown below is for one possible column that produces silicon tetrachloride as bottom product.



McCabe-Thiele diagram for SiHCl3 - SiCl4

Now, any *ChemSep* user reading this article might well ask how is this possible since none of these compounds is available in the *ChemSep* databank. In fact, it is possible to model the separation of many (but not all) systems that contain compounds that are not included in the databank. The purpose of this article is to show how.

Just in case you are new to *ChemSep*...

ChemSep is a program for performing multicomponent separation process calculations. *ChemSep* was created specifically for use in courses on thermodynamics and/or separation processes. *ChemSep* integrates flash, the classic equilibrium stage column model and a **nonequilibrium** or **rate-based** column model in one easy-to-use program. Kooijman and Taylor (CACHE News, Fall 2004) described in detail *ChemSep* Release 5 for Windows.

On January 1, 2005 we made freely available a version of *ChemSep* with limited functionality at www.chemsep.org. *ChemSep-Lite* retains many of the capabilities of the full version of *ChemSep* including:

Graphical User Interface: ChemSep-Lite includes the graphical user interface for Windows developed for ChemSep 5.0. The novice is taken through the problem solving process in a natural way. *ChemSep* checks your input, lets you know when each phase of problem setup is complete, and flags potential sources of difficulty before running a simulation.

Thermodynamic Property Models: ChemSep includes almost all of the most widely used thermodynamic models: 7 K-value models including DECHEMA (modified Raoult's law), Equation of State, and Chao-Seader; 10 Activity coefficient models including UNIFAC; and 8 equations of state including Peng-Robinson and Hayden-O'Connell (with chemical theory).

Powerful plotting capabilities: ChemSep has extensive support for plotting almost any kind of column profile including composition, flow, temperature, pressure, K-values, and more. The plots are completely configurable. *ChemSep* uses the Open Source package Gnuplot (for Windows) to display a plot in its own separate window. Except where noted, the plots that appear in this article were created with Gnuplot and pasted directly into the word processor used to create this article. Users can design their own plots and include them in the pull-down plot selection list for future use.

McCabe-Thiele Diagrams are a standard feature in *ChemSep* (even for multicomponent systems such as the one shown above).

Tabular Output can be viewed in *ChemSep*, or sent directly to text editor such as Notepad or spreadsheet program such as Excel.

Export: Simulation results may be saved in a variety of formats such as text, html and csv. Tables and graphs may be sent directly to Excel, (see the buttons *XL Table* and *XL Graph* that sends the data directly to Excel where it can be plotted as shown below for an example from Seader and Henley (1998).

The main limitations of *ChemSep-Lite* are: no more than 5 components in a simulation, no more than 50 stages in a column simulation, and no nonequilibrium model.

Another and potentially more important drawback may well be the fact that *ChemSep-Lite* comes with a databank of only 53 common compounds. However, if the VLE of the system you wish to model is adequately described by either Raoult's law or by the DECHEMA model (Raoult's law modified by the inclusion of an activity coefficient) and one has vapor pressure model parameters and activity coefficient model parameters available, then it is possible to model your system using *ChemSep-Lite*. We note in passing that the techniques described here can also be used with the full *ChemSep* 5.0 for Windows.

Separation of Silicon Chlorides

The first step of any simulation is to tell *ChemSep* what compounds are involved. *In this case* it does not matter what compounds are selected; pick any three compounds from the databank (the actual compounds selected here were methanol, acetic acid, and ethanol). Click on the component *Identifier* in the selected component list on the right and type in the string that you will use to identify the compounds actually involved. In this case we use their formulae as shown in the Figure below.

🕂 ChemSep v5.00					
File Edit Solve Analysis Databanks Tools He)				
Title Components					
Components Select Components					
Contraction	L L with HD				Advanced search
Keeds Component databank:	c:\chemse~1\pcd\lite.pc	a		P DIOWSE	Advanced search
Units Components in databan		S	elected components		
Solve options					
Paths	<u> </u>		Identifier	L#	File Loc
Argon		c ()	SiH2Cl2	1101	c:\chemse~1\pcd 10
Carbon tetrachloride Carbon dioxide		Component(s):	Sift(13	1252	c:\chemse~1\pcd 12
Water		Select		1102	c:\chemse~1\pcd 15
Ammonia					
Nitrogen		Remove			
Oxygen					
Chloroform					
Methane		1			
Methanol		Up			
Ethylene		Down			
Acetic acid Ethyl chloride		DOWN			
Ethyl Chloride					
Ethanol			This grid	d contains the r	ames of the compounds you
Agetope	▼	Substitute			
	Þ		•		Þ
		>>			
* N					

Replacement of the compound identifier.

The next step is to select appropriate thermodynamic models. This is a mixture that can be considered to be ideal; thus we will use Raoult's law for the K-values and None for the enthalpy model (thereby forcing *ChemSep* to consider all the enthalpies equal and leading to constant molar flows in the column). We must also select a vapor pressure model from the list of those available in *ChemSep* (see figure below). Note that we may also use an activity coefficient model if we have parameters available.

f ChemSep v5.00			X
File Edit Solve Analysi	s Databanks Tools	Help	
<u> </u>	<u>2</u>		
Title	× Thermodynamics	✓ Reactions	
	Select Thermodynam	ic Models	
X Feeds	K-Value	Raoult's law Show enthalpy/entropy settings:	
🕀 🗙 Results	Activity coefficient	Ideal solution	
Units	Equation of state	Ideal gas law	
Solve options			
- Paths	Vapour pressure	•	
		Antoine	
	Enthalpy	Extended Antoine T correlation	
		Lee Kesler	
	Enter Thermodynami	c Riedeln required)	
		No input of thermodynamic model parameters required	
		<< >>>	
* N			///

Selection of thermodynamic models

The Antoine equation cannot be used here since that option requires the model parameters be available in the databank. The same is true of the Lee-Kesler and Riedel equations. However, the Extended Antoine equation allows the user to enter parameters from the keyboard.

The Extended Antoine Equation incorporated in *ChemSep*'s thermodynamic routines is:

$$\ln P_{sat} = A + \frac{B}{T+C} + DT + E \ln T + FT^{G}$$

where A to G are the parameters in the model. T is the temperature and P_{sat} is the vapor pressure. ChemSep requires the temperature to be specified in Kelvin and returns the vapor pressure in Pascals. This equation includes as special cases the Antoine equation:

$$\ln P_{sat} = A - \frac{B}{T+C}$$

and the equation used by DIPPR to correlate vapor pressures:

$$\ln P_{sat} = A + \frac{B}{T} + C \ln T + DT^{E}$$

It is possible to find parameters for the standard Antoine equation for many compounds in the NIST databank

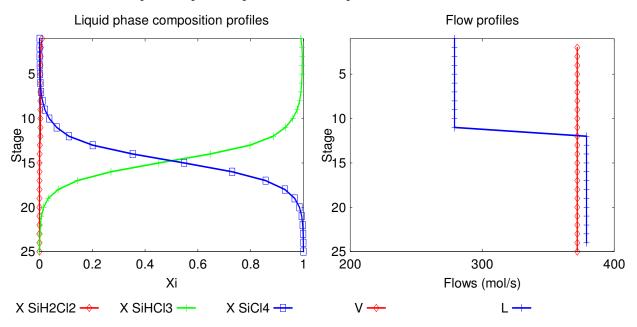
(www.nist.gov) (although the form of the Antoine equation differs from that given above thereby emphasizing the need possibly to convert any parameters from the literature that may be in different units or which use a different form of the equation (log rather than ln, for example). However, the NIST databank contains Antoine equation parameters for only two of the three compounds involved here. Thus, we need an alternative source of model parameters. Fortunately, the DIPPR databank contains Antoine parameters for all three of these compounds. These parameters can be entered into the spreadsheet for the extended Antoine equation as shown below.

f ChemSep v5.00							_0	×
File Edit Solve Analysi	s Databanks Tools	Help						
<u> </u>	<u>2</u>							
✓ Title ✓ Components	✓ Thermodynamics ⊢Select Thermodynam							
 ✓ Operation ⊕ ✓ Properties ★ Feeds 	K-Value	Raoult's law	🔲 Show er	ithalpy/entro	opy settings:			
	Activity coefficient	Ideal solution						
- Units - Solve options	Equation of state	Ideal gas law 💌						
- Paths	Vapour pressure	Extended Antoine						
	Enthalpy	None						
Enter Thermodynamic Model Parameters (when required)								
	Extended Antoin	e 💌 Extended Antoine				🔲 Tempera	ture dependent	
	Reset	Component:	Bi	l Ci	Di	Ei	Fi	
		SiH2Cl2	-4034.30	×	×	-3.79730	1.4101E-17	
	🕞 Load	SiHCl3	-4149.60	×	×	-3.03930	1.3111E-17	
		SiCl4	-5505.60	×	×	-7.39650	6.3480E-06	
	Save	•					Þ	
		<<	>>					
* N								1.

Loading parameters for extended Antoine equation.

The remaining steps require completing the specification of the column configuration and key operation specifications. In the example shown here we specified:

Number of stages: 25 equilibrium stages Feed stage: 12 Feed and column pressure: 1.2 atm Reflux ratio: 3 Bottoms flow rate: 7 (arbitrary units)



Below we show the liquid composition profiles and flow profiles for this column.

Liquid composition and flow profiles in the silicon chlorides distillation column.

From the stream table shown below we see that this column produces a bottoms stream that is 99.99% silicon tetrachloride. The overhead product needs to be distilled in a second column in order to obtain pure trichlorosilane. *ChemSep* will create a new case file from the currently loaded file that retains all the components and thermodynamic properties of the existing case and one of the product streams as the feed. The figure below shows the creation of a new file from the top product stream.

ChemSep - polyseq File Edit Solve Analy	and the second second	abanks Tools Help					<u>-0×</u>
Cut Copy Paste Delete	Ctrl+X Ctrl+C Ctrl+V Del	Graphs McCabe-Thiele) FUG				
Select all Previous sheet	Ctrl+A F5	table: Streams	•	XL Table	Edit Table	Copy Table	Table font
Next sheet New with stream Analysis Pressures Heaters/Cooler	F V	Top) /a Bottom C)	12 1.01300 0.000000 32.3930	1 1.01300 1.00000 31.5730	25 1.01300 1.00000 57.1220		4
Efficiencies Column specs	P of of of	Mole flows (mol/s) 5iH2Cl2 5iHCl3 5iCl4 Fotal molar flow	2.00000 91.0000 7.00000 100.000	2.00000 90.9953 0.00469811 93.0000	2.4758E-09 0.00469811 6.99530 7.00000		
Graphs McCabe-Thiele FUG Units Solve options	010101	Mole fractions (-) SiH2Cl2 SiHCl3 SiCl4	0.0200000 0.910000 0.0700000	0.0215054 0.978444 5.0517E-05	3.5369E-10 6.7115E-04 0.999329		
- Paths		Mass flows (kg/s) SiH2Cl2 SiHCl3 SiCl4	0.307644 12.1398 0.692714	0.307644 12.1391 4.6492E-04	3.8084E-10 6.2674E-04 0.692250		
	1	Fotal mass flow	13.1401	12.4472	0.692876		•
			_ «] »				
S C9 C:\C	hemsep\p	polyseq.sep					11

We leave the completion of this design as an exercise for our readers.