

# ChemSep Case Book: Handling Missing Components

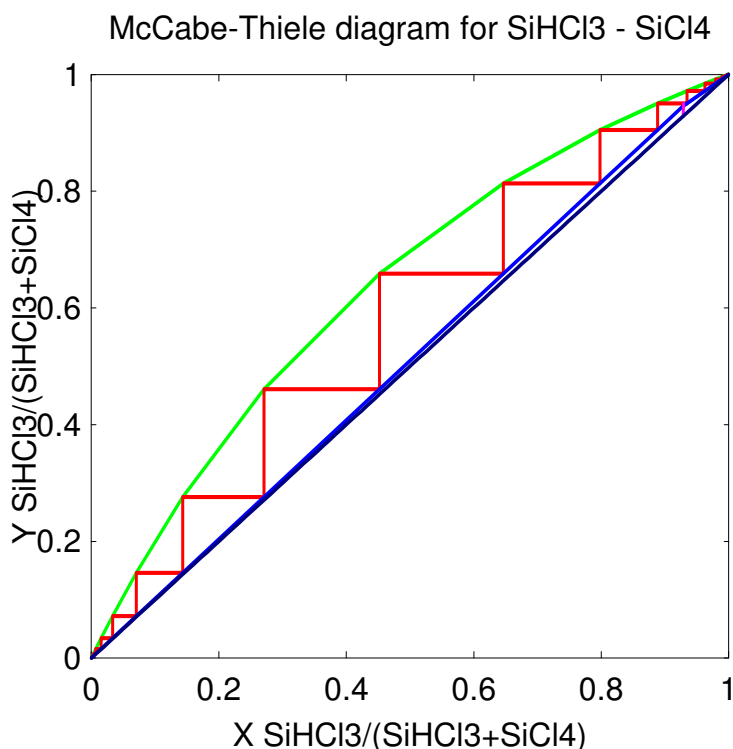
Ross Taylor and Harry Kooijman

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 <sub>2</sub> Cl <sub>2</sub>	2 mol%
SiHCl <sub>3</sub>	91 mol%
SiCl <sub>4</sub>	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.



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](http://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.

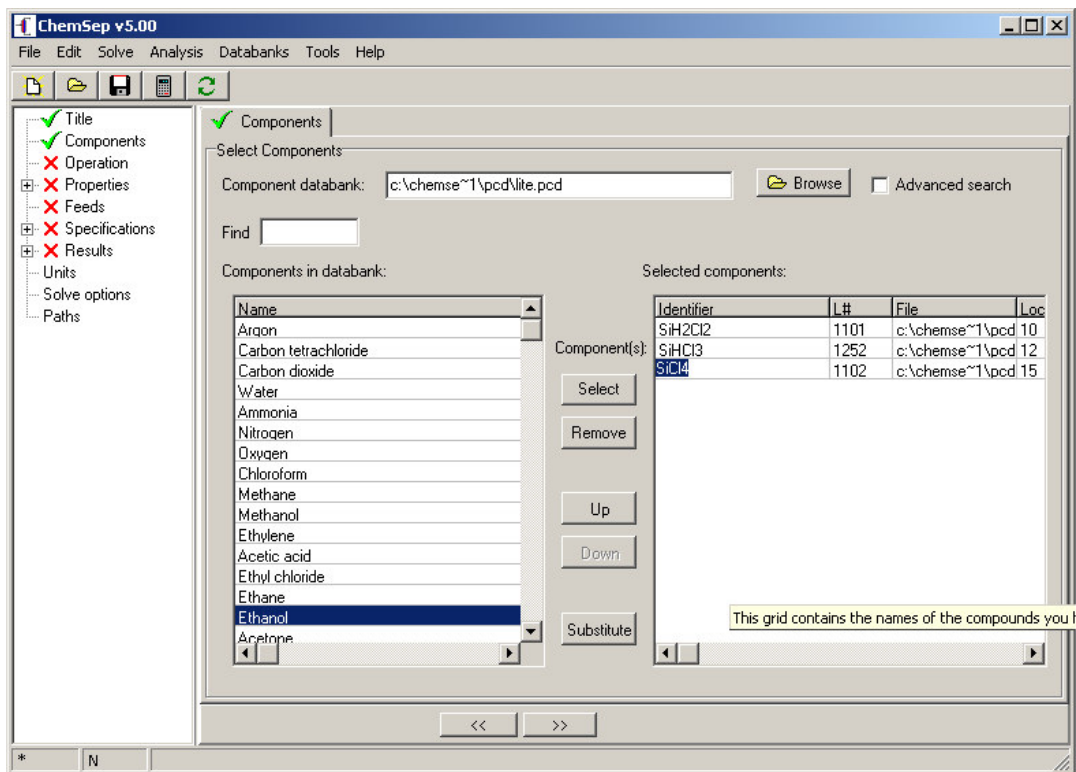
*Export:* Simulation results may be saved in a variety of formats such as text, html and csv. Tables and graphs may be sent directly to Excel, (see the buttons *XL Table* and *XL Graph* that sends the data directly to Excel where it can be plotted as shown below for an example from Seader and Henley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

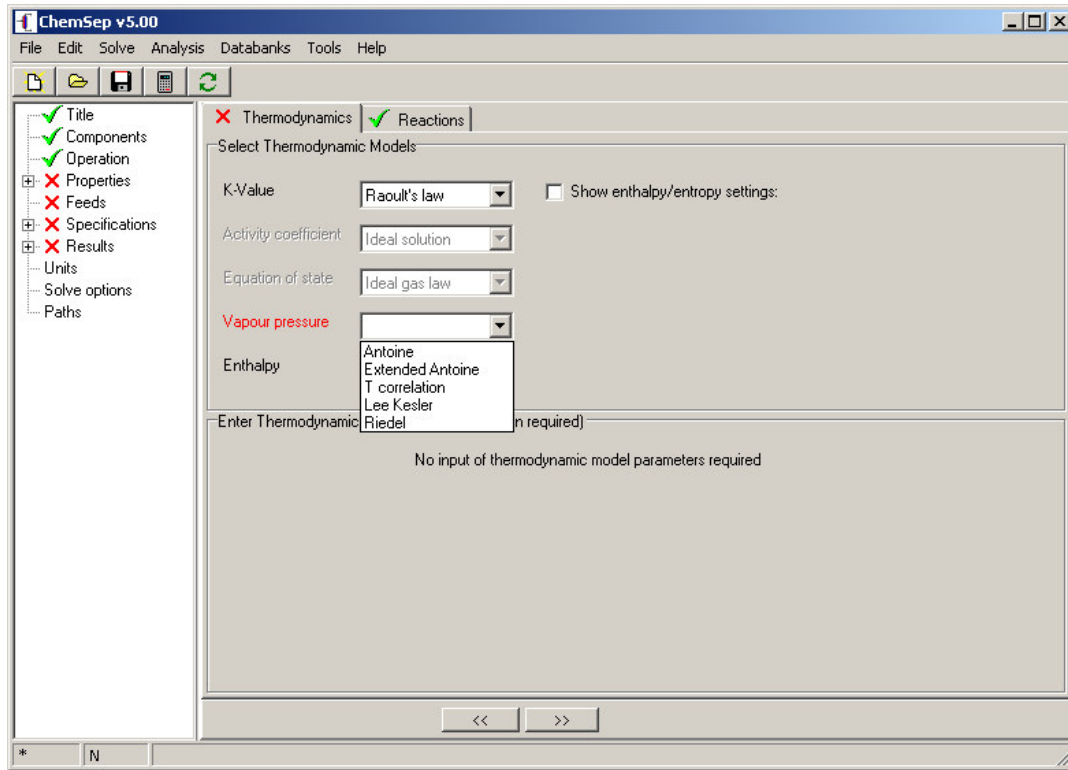
## Separation of Silicon Chlorides

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.



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.



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:

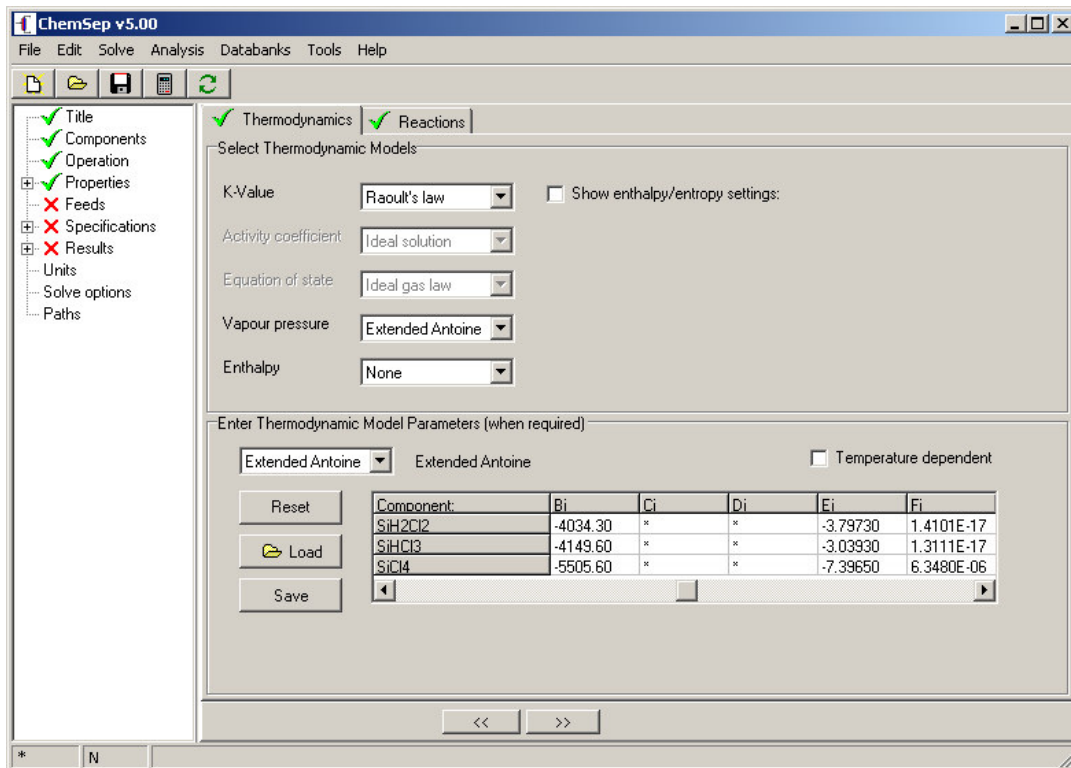
$$\ln P_{sat} = A - \frac{B}{T + C}$$

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](http://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.

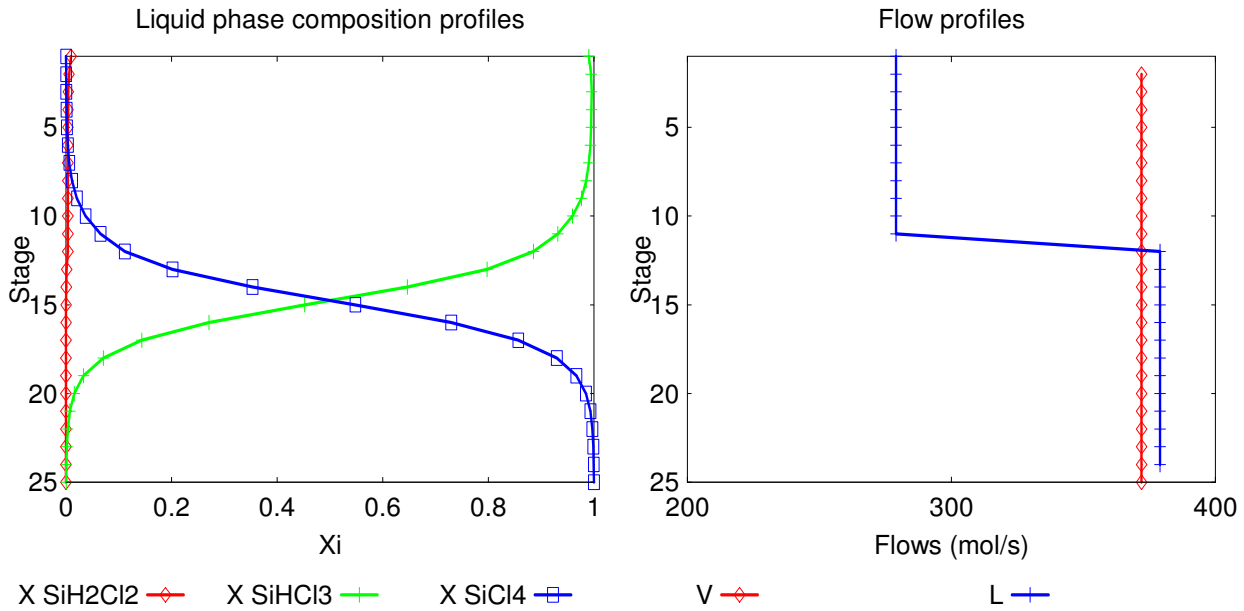


Loading parameters for extended Antoine equation.

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

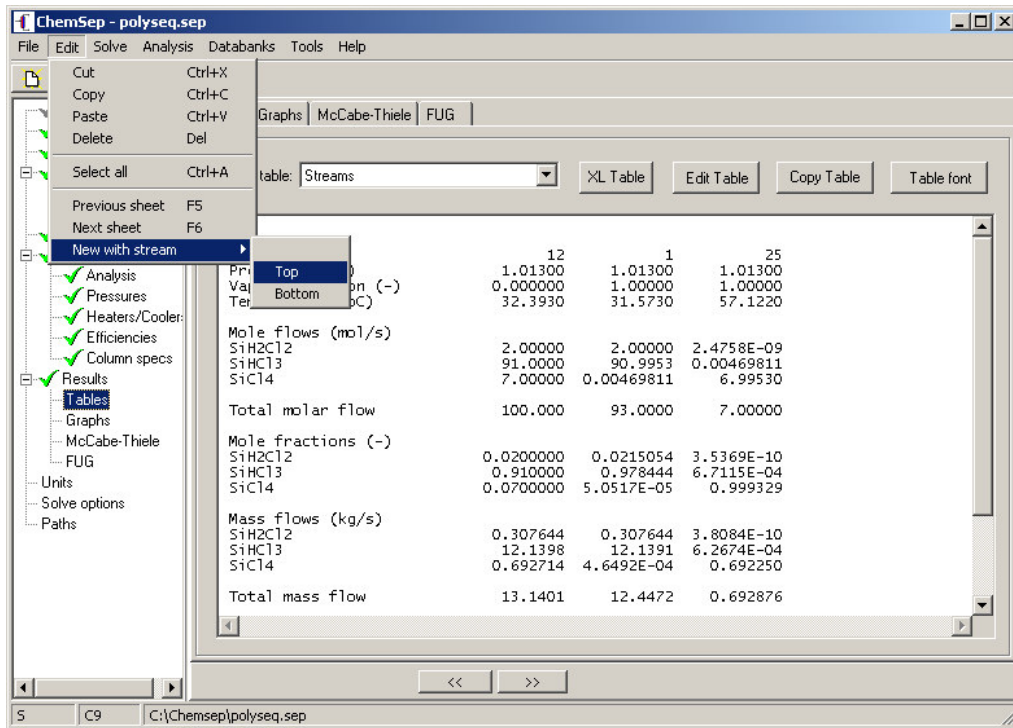
- Number of stages: 25 equilibrium stages
- Feed stage: 12
- Feed and column pressure: 1.2 atm
- Reflux ratio: 3
- Bottoms flow rate: 7 (arbitrary units)

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.



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