1

Integrated Computer-aided Methods and Tools as Educational Modules

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1.1
Introduction

The CAPE community has been developing computer-aided methods and tools for several decades and these days it is common practice in teaching as well as in industrial problem solving to use one or more pieces of currently available software. Students are trained to solve process-product engineering problems with state-of-the-art software, which they also later use during their professional career. Process simulators and their use in process design education has become a standard tool for process design courses everywhere. While these tools are able to provide excellent training in analysis of problems that are well-defined and have sufficient information to completely solve the problem, it is questionable if they are also suitable for solving open-ended problems (Doherty et al. 2000), such as those related to process-product design. Also, use of these tools in process-product design encourages the use of the inefficient trial and error solution approach as opposed to a systematic generate and test approach where additional tools for synthesis and design may be used together with process simulators.

As computer-aided design becomes more prevalent in the process industry, according to Finlayson and Rosendall (2000), it is essential that graduating engineers know the capabilities of the computer-aided systems that are available as well as the scepticism to interpret the results wisely. At the same time, advances in computer-aided design and simulation tools and reduced computing costs have allowed new uses of computing in chemical engineering education. Indeed, chemical process industries remain one of the strongest segments of the world-wide economy due to the cost effectiveness of well-designed chemical processes as well as to innovative chemistry (Doherty et al. 2000).
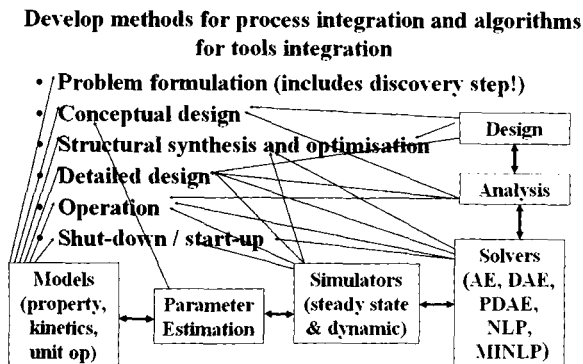
Process simulators (ASPEN+, PRO-II, gPROMS, ChemCad, ProSim, etc.) together with modeling and simulation software (Mathematica, Maple, MATLAB, etc.) have become standard computer-aided tools in chemical process design, process control

and, chemical process-operation modeling. As industries face major new challenges because of increased global competition, greater regulatory measures, uncertainties in prices for energy, raw materials and products, etc., it becomes more and more important to consider integrated solution approaches. Similar to process integration, tools and/or problem integration imply the solution of more than one problem simultaneously or use of more than one tool in the solution of the problem. Also, the introduction of new courses such as product design has led to new challenges in fields such as applied thermodynamics (Abildskov and Kontogeorgis 2004), which also requires new software.

This chapter highlights the use of a system viewpoint within an integrated approach to the solution of chemical engineering problems. As noted by Edgar and Rawlings (2004), the chemical engineer leverages knowledge of molecular processes across multiple length scales to synthesize and manipulate complex systems that encompass both processes and products. Several computer-aided educational modules that encourage the development of this viewpoint, are presented in this chapter. First, a brief overview of the integrated approach to CAPE is given, followed by a short presentation of an integrated computer-aided system that has been used as a basis for the development of a number of computer-aided education modules. Three examples of these educational modules are presented together with references of where other modules can be found. In conclusion, uses of these modules in courses are discussed.

1.2
Integrated Approach to CAPE

An integrated approach to CAPE, also known as concurrent engineering, simply means the solution of two or more problems in a single step, for example, make decisions in the early stages of design that also select the control structure and guarantee acceptable environmental impact. In this way, it is similar to process integration where two or more operations are performed through a single operation, for example, a heat exchanger combining a cooling operation with a heating operation. Application of the integrated approach, however, also needs an integration of tools. As illustrated through Fig. 1.1, most CAPE problems (synthesis, design, and analysis) are multitask by nature and require a number of different tools. To achieve integration of tools, it is necessary to establish the workflow and data flow with respect to the solution steps and the tools that would be needed in each of the steps. Tools integration, therefore, avoids duplication of work while providing efficient data transfer from one tool to another. Through a computer-aided framework that includes a collection of tools (and their associated subtools such as databases, models, solvers, etc.) and allows access of the tools according to specific workflow and data flow, typical chemical engineering problems can be solved in an integrated manner. More details on tools integration can be found in Fraga et al. (2002).

**Develop methods for process integration and algorithms
for tools integration**

• /**Problem formulation (includes discovery step!)**
• / **Conceptual design**
• / **Structural synthesis and optimisation**
• / **Detailed design**
• / **Operation**
• / **Shut-down / start-up**

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Models          Parameter        Simulators        Solvers
(property,      Estimation       (steady state     (AE, DAE,
kinetics,                        & dynamic)        PDAE,
unit op)                                           NLP,
                                                   MINLP)
```

Design
Analysis
Solvers

1.2.1
Integrated Computer-aided System

An integrated computer-aided system (ICAS) (Gani 2001) combines computational tools for modeling, simulation (including property prediction), synthesis/design, control and analysis in a single integrated system. These computational tools are presented as toolboxes. During the solution of a problem, the student moves from one toolbox to another in order to solve problems, which require tools from more than one toolbox. Typically, problems in process synthesis, process design, and process control require the use of more than one tool. For example, in process design/synthesis, one option is to define the system input stream, to analyze the mixture (use of analysis tools), to generate flow sheet alternatives (synthesis/design tools), to evaluate the alternatives (simulation and analysis tools), and finally, to optimize the flow sheet (design tools). Each toolbox has a number of tools associated with it and are connected to the necessary tools from other toolboxes. Figure 1.2 illustrates the architecture of ICAS.

ICAS has been developed specifically to solve problems in an integrated manner, which can be used to develop educational modules for different types of product-process engineering problems. It is currently used to solve industrial problems as well as research and teaching. In this chapter, only the teaching related features will be highlighted. As shown in Fig. 1.2, ICAS consists of a simulator (with steady state and dynamic simulation engines) having the same features as other process simulators. ICAS, however, also has tools that "add to the system" and "toolboxes" that help to solve some of the tasks typically found in different CAPE related problems (for example, designselection of solvents, synthesis of process flow sheets, environmental impact analysis, model parameter estimation, etc.). The "add to the system" helps to introduce new compounds into the database, new unit operation models into the simulation model library, and new property models into the property model library in an integrated manner and requiring no additional programming. Once all these additions are introduced to the system, all tools within ICAS will be able to use them. In this way, the "add to the system" and "toolboxes" help to define the problem
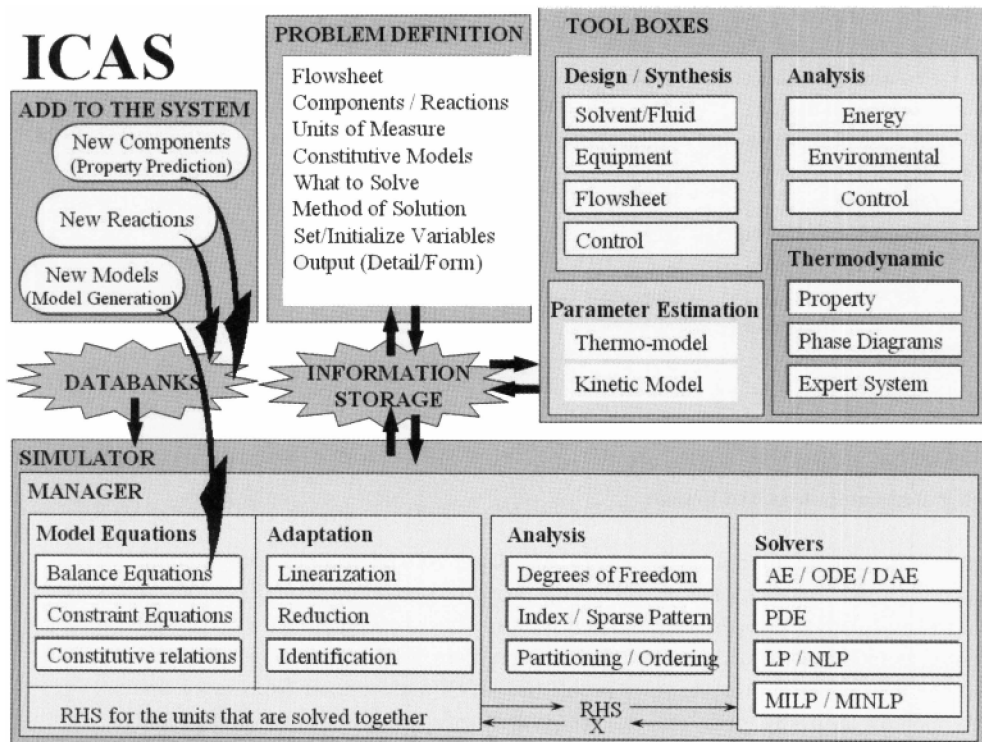
Figure 1.2 Multidisciplinary tools for nature process-product design problems

where most of the time is spent in software-based solution of problems. Often, the problems are not defined correctly or consistently, resulting in failure of the numerical solver. The different features of ICAS help to guide the students into defining/formulating the problem correctly so that the numerical solver does fail, if a solution for the formulated problem exists.

1.3
Educational Modules

Three computer-aided educational modules involving property prediction (suitable for a course on thermodynamics or product design), extractive distillation-based separation (suitable for courses on separation processes, distillation, or process design), and model derivation and solution (suitable for courses on modeling, simulation and/or numerical methods) are presented. The objective of these educational modules is to highlight the solution strategies for typical chemical engineering problems (traditional as well as new) where software may be used (with clearly defined objectives) in some or all the solution steps (tasks). At the same time, it is emphasized that

the software is just an efficient calculator (that is, it provides answers when asked) but it does not work as an engineer. Also, in addition to the above calculator service, the software plus the workflow and data flow provide insights to improve the solution efficiency (of the overall problem) and therefore, the productivity of the user (student).

1.3.1
Computer-aided Property Estimation

This computer–aided teaching module introduces the students to the workflow, data flow and the tools needed to perform phase equilibrium calculations (saturation point calculation and generation of various types of phase diagrams: vapor–liquid, liquid–liquid or solid–liquid). The students learn the importance of the property model selection, the need for property databases, the need for additional property models, the model equations, and finally, the important calculation steps for solving the problem. In this way, the students are able to appreciate not only the property related calculations but also understand their influence in other problems, such as process simulation and design. Two problems are presented here:

● Analyze the properties of a chemical called chemical fentanyl.
● Evaluate the binary mixture of ethanol–water.

The first problem could easily come from the product analysis step of a chemical product design problem, while the second problem could come from a bioprocess (downstream separation of a fermentation product or solvent based separation by distillation or even a solvent based crystallization process). In order to progress further in the process-product design problem, the pure component properties as well as the mixture properties need to be evaluated.

1.3.1.1
Analysis of Fentanyl

Here, we wish to analyze the properties of fentanyl (CAS number 000437-38-7) in terms of its state at the normal conditions of temperature and pressure, if it is toxic and its solubility properties in water and other solvents. The pure component properties that would be needed are: normal boiling point (T_b), normal melting point (T_m), the heat of fusion (ΔH_f), the heat of vaporization (ΔH_{vap}), the vapor pressure (P^{sat}), the Hildebrand solubility parameter (δ_s), the octanol–water partition coefficient (log K_{ow}) and a measure of toxicity (LC_{50}).

The following steps (workflow) could be performed:

1. Check databases to find properties of fentanyl (properties such as T_b, T_m, ΔH_f, (H_{vap}, P^{sat}, δ_s, log K_{ow} and LC_{50}).
2. If the properties cannot be found in the databases, use a property estimation package.
   a. Generate the needed properties through a property model by giving the molecular structural information.

3. Analyze the properties (estimated or retrieved from database).
   a. What is the state (solid, liquid or gas) at the normal condition of temperature and pressure?
   b. Is it a hazardous compound?
   c. Are there known solvents for fentanyl?
   d. How can solubility of fentanyl in solvents be quickly checked?

The methods and tools that are needed to perform the workflow shown above are the following: a fairly large database of pure component properties, a software package for prediction of pure component properties (with its resident model parameter tables), a software package for solvent search, a software package for solubility calculations (requires property models for mixture properties as well as algorithms for saturation point calculations). ICAS provides all the above in a single integrated system. Uses of ICAS (Gani 2001) for each of the above steps are highlighted below (information on all the ICAS tools can be found at www.capec.kt.dtu.dk/Software/ICAS-and-its-Tools/or in Gani (2001)):

Step 1: Search of the CAPEC database (Nielsen et al. 2001) in ICAS finds fentanyl but having only the molecular weight (336.48) and the normal melting point (360.65 K). This means all other properties need to be estimated. Databases in most process simulators will not have this compound or its properties.

Step 2: To generate the properties, the ProPred toolbox within ICAS is used. ProPred needs the molecular structure of the molecule (as a 2D drawing, as a 2D/3D mol.file or as a SMILES string). The CAPEC database has the SMILES string, from which ProPred is able to draw the molecule, identify the needed groups and estimate the properties (in the case of fentanyl, since all the group parameters were not available, it also needed to create the groups, which is an option available in ProPred). Table 1.1 gives the SMILES string for fentanyl, the 2D drawing of the molecule and the properties estimated by ProPred.

Step 3: Analyze fentanyl in terms of the generated properties.
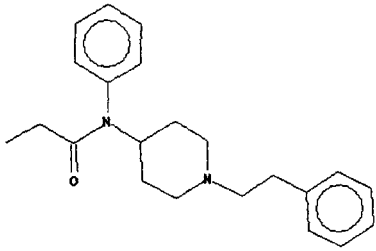   Step 3a: At the normal condition of 300 K and 1 atm, fentanyl is solid.
   Step 3b: It is hazardous as indicated by the $-\log (LC_{50})$ value. A high value (higher than 3) indicates a highly toxic compound. LC_{50} is the aqueous concentration causing 50 % mortality in fathead minnow after 96 hours.
   Step 3c: The CAPEC database does not list any known solvents for fentanyl. However, as the Hildebrand solubility parameter is known (δ_S at 298 K), it can be used to obtain some idea of which compounds could be good solvents. A search of the database for compounds having similar δ_S (at 298 K) shows that hydrocarbons are likely to be good solvents while fentanyl will have very low solubility in water.
   Step 3d: To estimate the solubility, the needed properties can be seen from the following equation (condition for solid–liquid equilibrium where only one compound exists in the solid phase):

$$1 = x_S \gamma_S \, \exp \left[\Delta H_f / (R T_m) \{ (T - T_m) \} \right] \tag{1}$$

Table 1.1 Estimated properties of fentanyl

Estimated properties of fentanyl	
SMILES string	CCC(=O)N(c1ccccc1)C2CCN(CCc3ccccc3)CC2
2D molecular structure	
T_b	703.47 K (estimated with created groups[a])
T_m	360.65 K
ΔH_f	44.66 kJ mol^{-1} (estimated with created groups)
ΔH_{vap} at 298 K	42.16 kJ mol^{-1}
δ_S at 298 K	20.78 MPa$^{1/2}$ (estimated with created groups)
Log K_{ow}	3.85
$-$Log (LC$_{50}$)	7.32
P^{sat} at 300 K	Fentanyl is solid at this temperature

a "Estimated with created groups" means that the need group parameters were not available and therefore, ProPred automatically generated the missing group parameters to estimate the needed properties.

where x_s is the saturation composition of solid s in solution, γ_s is the liquid activity coefficient of the solid compound in solution, R is the universal gas constant and T is the temperature at which solubility is to be calculated. From Eq. (1), it becomes clear that to estimate the solubility of fentanyl in a solvent, we need to estimate its liquid activity coefficient in the solvent (for which a property model is necessary) as well as the heats of fusion and melting point of fentanyl. A quick estimate may be obtained by setting $\gamma_s = 1$ (assuming ideal liquid). Note that if a liquid activity coefficient model such as UNIFAC (Hansen et al. 1991; Kang et al. 2002) is used, it will require the corresponding group interaction parameters, which for fentanyl are not available. Also, since γ_s is dependent on composition as well as temperature, an iterative solution technique would be necessary. The SoluCalc toolbox in ICAS, which has been specially developed for estimating solid solubility in solvents, can be used for this purpose. Figure 1.3 shows the calculated fentanyl saturation curve in hexane (solvent). Note that the students have the option to directly calculate the temperature versus composition diagram through ICAS utility toolbox, or, develop their own binary SLE phase diagram software using the property model (as a model object) from ICAS through modeling/simulation software (such as EXCEL, MATLAB, etc.).
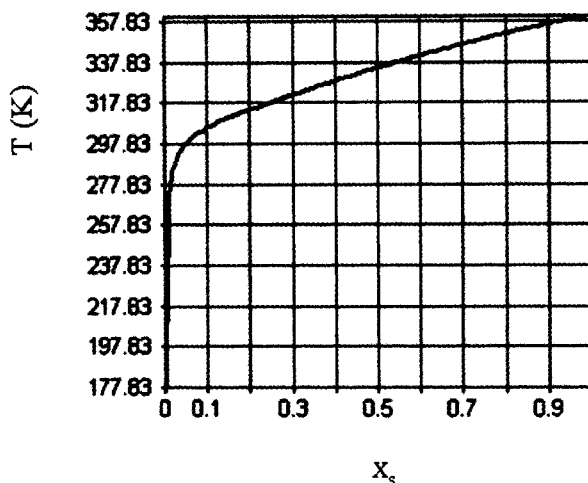
Figure 1.3 Estimated saturation solubility curve for fentanyl in hexane

The above workflow could be repeated for any new chemical being considered as a product, provided the needed property variables can be identified and their values measured or estimated through appropriate property models. Solving this type of problems with process simulators is not efficient and in most cases probably not also possible. Having all the necessary tools available in an integrated manner saves time and provides valuable insights to the problem and its solution.

1.3.1.2
Evaluation of Ethanol–Water Mixture

Here, we wish to evaluate the ethanol–water mixture with respect to its separation from a biofermentation reactor. Depending on the mixture characteristics, different separation schemes may be generated. Here, however, we will first look at the vapor–liquid equilibrium and confirm that it is indeed a minimum boiling azeotrope. Then we will introduce a solvent, for example benzene or ethylene glycol, to the system and evaluate the ternary mixture (in terms of ternary azeotrope and liquid–liquid miscibility). The methods and tools needed to perform these tasks (calculations) are available in most commercial simulators but they are not necessarily organized for an integrated approach. In this example, however, we will break down the problem into multiple tasks in order to understand the problem, to highlight the importance of property model selection, the need for accurate pure component properties (in this case, vapor pressure) as well as the associated workflow (calculation steps or tasks) and data flow.

Since ethanol–water is a nonideal mixture for which vapor–liquid (and possibly vapor–liquid–liquid when a ternary system is considered), equilibrium needs to be calculated, the properties, calculation methods and tools that are needed, are linked to the equilibrium model used. That is, if we select the equilibrium model as a two-model gamma–phi type, we may select an activity coefficient model for the liquid

phase and the ideal gas model (equation of state) for the vapor phase. Neglecting the Poynting correction factor, the vapor–liquid equilibrium is represented by:

$$y_i = x_i \gamma_i P_i^{sat}/P \tag{2}$$

In the above equation, y_i is the vapor phase composition of component i, x_i is the corresponding equilibrium liquid phase composition, γ_i is the liquid phase activity coefficient of component i, P_i^{sat} is the vapor pressure of component i at the equilibrium temperature and P is the corresponding system pressure. Since γ_i is a function of composition and temperature and P_i^{sat} is a function of temperature, an iterative solution scheme needs to be devised to obtain the equilibrium temperature and the corresponding vapor composition for given liquid composition and pressure. Repeating the calculations for different values of liquid composition within the limit zero to one and keeping the pressure fixed at the original value, generates the entire so-called PT-xy diagram. Now consider the following three options:

- Given models for γ_i (for example, UNIFAC) and P_i^{sat} (for example, the Antoine correlation), develop a computer program to generate the phase diagram. In principle, any modeling software (EXCEL, MATLAB, etc.) can be used to develop the software with the ICAS supplied property model object.
- Given a program to calculate the saturation temperature and vapor composition for specified liquid composition and pressure (and for a selected set of property models), repeat the calculations to generate the phase diagram. In principle, any modeling software (EXCEL, MATLAB, etc.) can be used to develop the software with the ICAS supplied property-utility object.
- Given software with built-in models and calculation options, select the appropriate model and calculation option to generate the needed phase diagram. In principle, any process simulator and/or ICAS utility toolbox may be used. If, however, the compounds are not ethanol and water, then the available options in the software need to be checked.

All three options will give the required solution, while the first option will be time-consuming, the student will gain more insight on the needed workflow and data flow than the last option, which will be efficient in terms of problem solution but will provide little insight. An interesting approach could be to get the students to use all options, that is, use the first option at the beginning and use the last option when they are experienced in phase equilibrium calculations.

This example also provides insights on property model selection (assuming an ideal system, which is usually the default selection for many software, the azeotrope will not be found) and accuracy of the needed properties (that is, the predicted azeotrope location may be highly sensitive to the accuracy of the vapor pressure model). Also, the parameters of the liquid activity coefficient model are important as they may give different values of the location of the azeotrope.

Having analyzed the binary system, the next step is to analyze the mixture when a third component (for example, a solvent) is introduced. What happens to the azeotrope? Are there still a vapor and a liquid phase in equilibrium? If not, is there an

additional liquid phase? If yes, how to calculate the phase compositions and is there also a ternary azeotrope?

As in the case of the binary mixture calculations, most commercial simulators also provide options to perform the calculations so that the above questions can be answered. The important points, however, are the following: Have the correct property model selections been made? What are the workflow and data flow? Are the results acceptable? Again, by breaking down the problem into multiple tasks, the students will gain more insights to the solution of the problem. In terms of calculations, in addition to the vapor–liquid equilibrium, the liquid–liquid equilibrium also needs to be computed:

$$x_{1i}\gamma_{1i} = x_{2i}\gamma_{2i} \tag{3}$$

The subscript 1 and 2 in the above equation indicates liquid phase 1 and liquid phase 2, respectively. The same liquid phase activity coefficient model will now be used in Eq. (2) and (3). However, the liquid composition from Eq. (2) needs to be checked for phase stability and if found unstable, Eqs. (2) and (3) will need to be solved simultaneously. The following calculation steps (workflow) could be used:

- Use Eq. (3) to identify any binary pair (there are 3 binary pairs in the ternary mixture), which splits into two liquid phases:
  - Check also if this is the vapor–liquid azeotrope point (for a vapor–liquid–liquid system, one pair will satisfy this condition).
  - For the binary system showing both an azeotrope as well as liquid–liquid phase split, add incremental amounts of the third component and perform the vapor––liquid–liquid calculations until there is only one liquid phase (note that for each calculation, the pressure is fixed at a constant value but the temperature is also calculated). The ethanol–water system with benzene as the solvent will show a vapor–liquid–liquid ternary system with the benzene–water pair showing the binary liquid–liquid phase split.
- If none of the binary pairs split into two liquid phases, there will only be a vapor in equilibrium with liquid and the calculations for the binary mixture can be repeated in the same way as before. The ethanol–water system with ethylene glycol as the solvent will show only a vapor–liquid system.

The three options listed above for the binary mixture calculations can also be repeated now for the ternary mixture calculations. Again, initially, it is better for the students to develop their own calculation program but later, they can use standard software (process simulator and/or ICAS utility toolbox).

Further extension to this problem could be considered by adding an inorganic salt to the ethanol–water mixture (to study the salting-in or salting-out effect). Here, again the workflow will basically remain the same but the data flow will be significantly different because of the different property models and their corresponding property parameters.

The above modules will prepare the students to solve all types of phase equilibrium problems in a systematic way, even when not all data and/or property model parameters are available. One advantage of allowing the students to develop their

own software is that in the case of new compounds or systems, they will be better prepared to perform the necessary tasks. Note that since developing their software will not need much programming effort, they will actually concentrate on learning the calculations involved in each task.

1.3.2
Separation of Azeotropic Mixtures

The second computer-aided educational module introduces the students to aspects of design and simulation of solvent-based extractive distillation. The students use the phase diagrams that they have learned to generate. The main feature of this module is that it encourages the students to make the design decisions based on simple thermodynamic calculations rather than use the simulator on a trial and error basis to find the solution. That is, all the important design decisions are made through the generated phase diagrams and thermodynamic insights (for example, sequencing of distillation columns, selection of solvents, design of individual columns, etc.), which also generates an initial estimate for a detailed simulation of the process. In the final step, the initial estimate is passed to the simulator and the solution is obtained without too many iterations (by the rigorous model solver). Therefore, the student spends less time with the simulator and more time generating information (knowledge) that can be used for problem solution.

1.3.2.1
Problem Description
The problem which we will consider is the separation of a binary mixture of acetone and chloroform into high purity products. As this binary mixture forms an azeotrope (to be verified), solvent-based extractive distillation is an option. Benzene is a well known solvent that has been reported as a suitable solvent. Benzene, however, is not acceptable for environmental, health and safety (EHS) reasons and an alternative solvent needs to be found and verified.

1.3.2.2
Problem Solution
The following steps provide a solution to this binary mixture problem.

Step 1: Perform a mixture analysis and verify that an azeotrope exists and check for its dependence on pressure. Make decisions/choice of property model and calculation steps. An ideal system cannot be assumed since the binary mixture forms an azeotrope. A VLE-based phase diagram (using Eq. (2)) needs to be generated. Figures 1.4a and 1.4b show the binary azeotropes as a function of pressure (ICAS utility toolbox is used to generate these diagrams).

Step 2: Find solvents that perform as well as benzene but without the negative EHS properties of benzene. Using the ProCAMD tool in ICAS, a large number of candidate solvents are generated. The problem definition is as follows: find solvents that
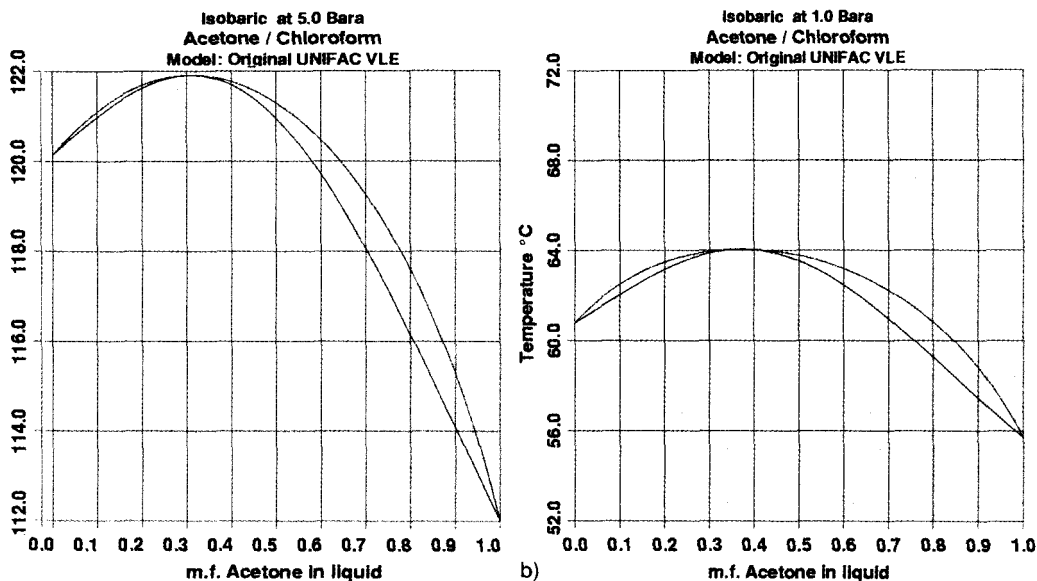
Figure 1.4 Acetone-chloroform VLE calculated at 5 bar (a). Acetone-chloroform VLE calculated at 1 bar (b)

are acyclic organic compounds having 320 K $< T_b <$ 420 K, $T_m <$ 250 K, that is more selective to chloroform than acetone (selectivity $>$ 1.7), is totally miscible with acetone-chloroform (therefore a vapor–liquid system) and does not form azeotrope with either acetone or chloroform.

The solution statistics from ProCAMD is shown in Fig. 1.5. It can be noted that 5614 candidate molecules were generated, out of which 59 satisfied all constraints. From these 59 molecular structures, 133 isomers were generated and a more refined property estimation was made to identify 111 compounds that satisfied all constraints. Note that to identify the solvents, pure component properties (T_b, T_m) as well
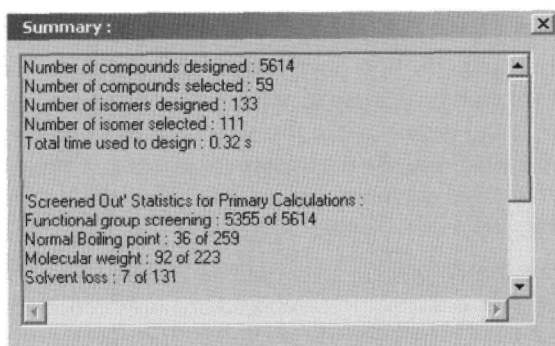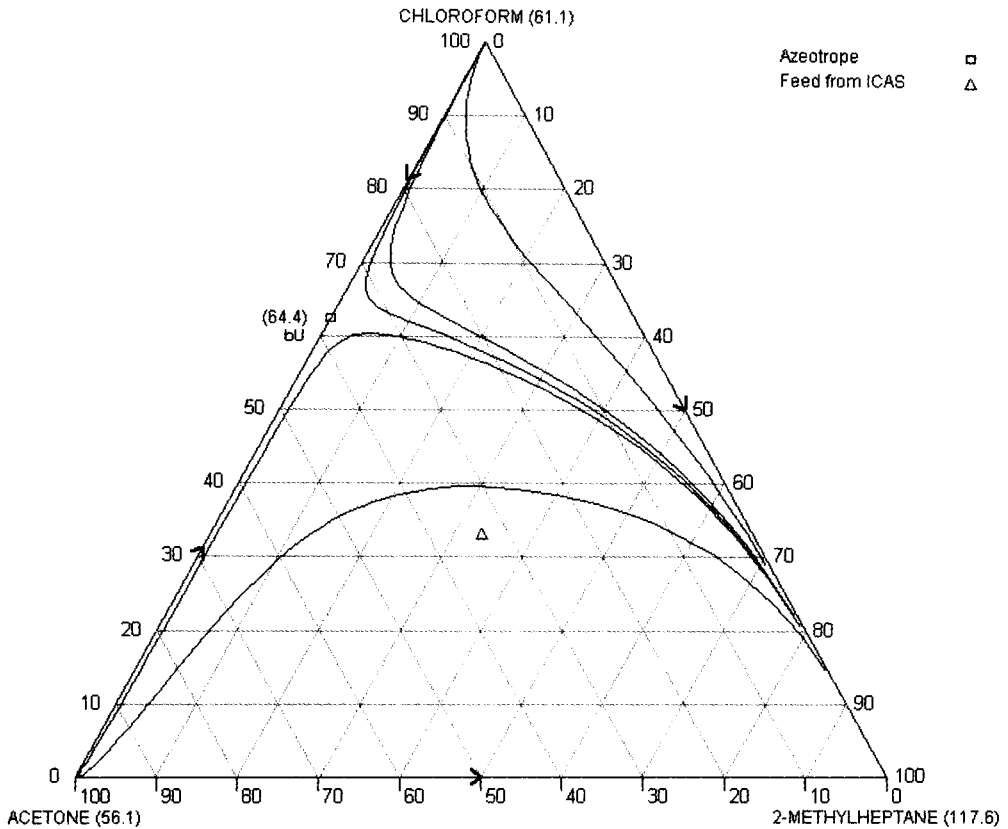

Figure 1.5 Solution statistics from ProCamd for the solvent selection/design task

CHLOROFORM (61.1)

Azeotrope □
Feed from ICAS △

ACETONE (56.1)

2-METHYLHEPTANE (117.6)

Figure 1.6 Calculated distillation boundaries for the acetone-chloroform solvent

as phase equilibrium calculations (selectivity, azeotrope calculation and liquid miscibility) needed to be performed. Therefore, an integrated system capable of doing these steps automatically for the user is very useful for this type of problems. Two of the alternatives found are methyl-n-pentyl-ether and 2-methylheptane.

Step 3: Analyze the alternative solvent candidates in terms of distillation boundaries. For this step, the PDS tool in ICAS is used. PDS performs, among others calculations of distillation boundaries, residue curves and distillation column design for a specified ternary system (reacting or nonreacting). This problem is nonreacting and the distillation boundaries calculated through PDS are shown in Fig. 1.6.

Step 4: Generate the process flow sheet and design the corresponding distillation columns. This can be done interactively. Design the first distillation column with the feed mixture and the fresh solvent added. The combination of the feed mixture and solvent places the total feed in the region where acetone can be obtained as the top product, and a mixture of mainly solvent and chloroform will be obtained as the bot-
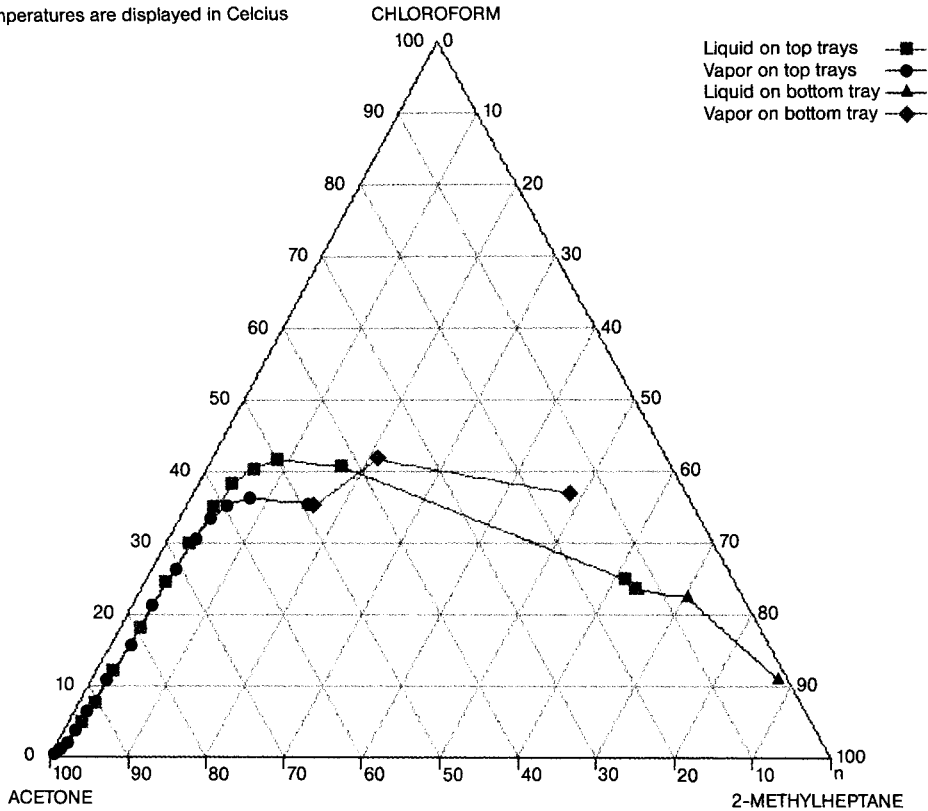
Figure 1.7 Design of the distillation column that is consistent with the distillation boundaries

tom product. This feed will then be sent to a second column, from where the chloroform will be obtained as a top product and the solvent will be recovered and recycled. PDS and ICAS-SIM (steady state simulation engine) can be used interactively to design the first column (number of stages, feed location, product purity, reflux ratio, etc.) and verified through steady state simulation. Then the second column is added and the procedure repeated, which also generates the total flow sheet. Figure 1.7 shows an output from PDS, highlighting the design calculations for the distillation column.

Step 5: Perform simulation and optimization to determine the optimal design of the separation process. In this case, all solvents can also be included in the same calculations and the optimization problem will find the optimal flow rate for each of the solvents. The flow sheet used in problem formulation and the sample simulation of the flow sheet are shown in Figs. 1.8a and 1.8b. This last step can be performed with the steady state simulation engine of ICAS or with any process simulator. ICAS has a

a)
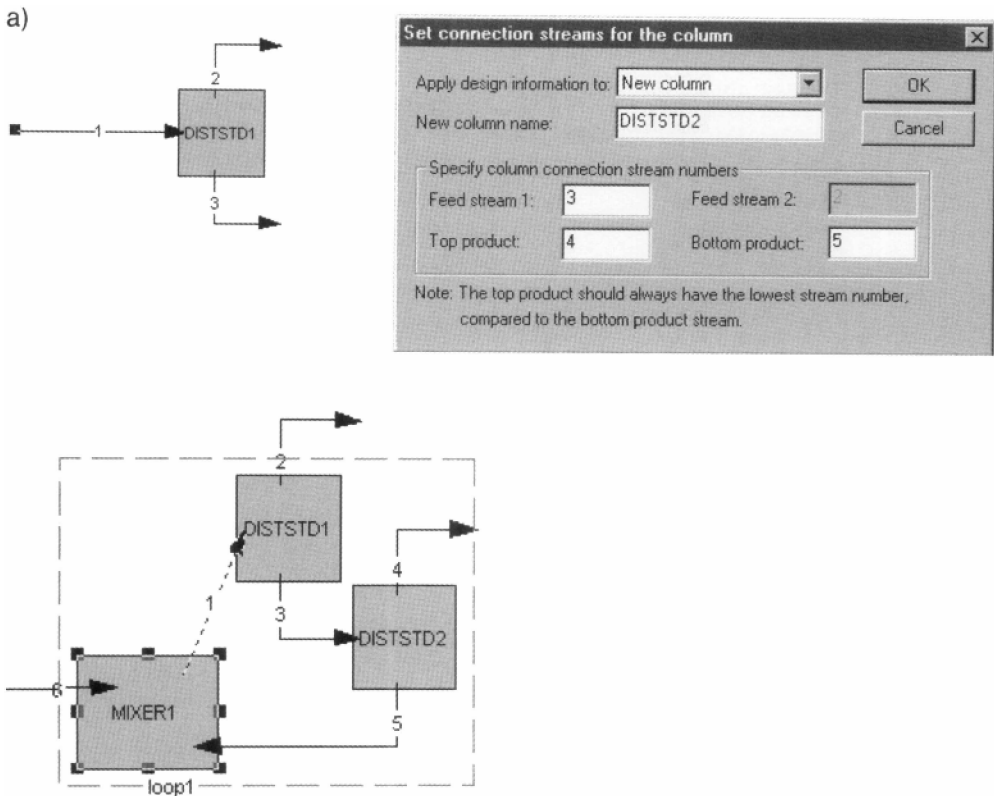
Figure 1.8a Generation of flow sheet (synthesis and design) with PDS-ICAS (a).

direct interface for the PRO-II steady state simulator. This means that any flow sheet synthesized and designed can be directly simulated in PRO-II without adding any further information in PRO-II.

Several variations of the problem are possible. For example, provide a binary azeotropic mixture that has significant pressure dependence so that the solvent-based separation can be compared with pressure-swing distillation. If a solvent that introduces a phase split is selected or specified, then at least one distillation column will have vapor–liquid–liquid phase equilibrium and the design calculations will have to be consistent with the resulting distillation boundaries. Also, a reacting system may be introduced. Basically, the tasks (steps in workflow) shown above would be similar in all cases but the data flow would be different because of specific choices of the models used to perform the tasks. If the student is given the calculation steps (workflow) and a corresponding set of integrated tools, the students will not only be able to solve these problems without too much difficulties but also gain valuable insights with each solution step.

b)

STREAM NUMBER	1	2	3	4
TEMPERATURE (K)	350.00000	332.04270	373.15131	342.63881
PRESSURE (atm)	1.00000	1.00000	1.00000	1.00000
ENTHALPY(K/Kmole)	-27615.86917	-24505.51626	-26910.01571	-14287.60495
ENTROPY(1/Kmole)	41.50294	35.62145	44.69363	37.41181
U-ENERGY(K/Kmole)	-27616.02699	-24532.76285	-26910.18654	-14315.72103
DENS. (Kmole/m^3)	6.33628	0.03670	5.85403	0.03557
VAPOUR FRACTION	0.00000	1.00000	0.00000	1.00000
LIQUID FRACTION	1.00000	0.00000	1.00000	0.00000
--------(Kmole/hr)--				
ACETONE	10.00039	9.05476	0.94563	0.94524
CHLOROFORM	10.98840	0.85620	10.13220	9.14408
2-METHYLHEPTANE	89.89447	0.06853	89.82593	0.93118
TOTAL	110.88325	9.97949	100.90376	11.02051

| STREAM NUMBER	5	6
TEMPERATURE (K)	389.00747	350.00000
PRESSURE (atm)	1.00000	1.00000
ENTHALPY(K/Kmole)	-27545.64659	-19114.10880
ENTROPY(1/Kmole)	47.80138	36.69383
U-ENERGY(K/Kmole)	-27545.83081	-19142.82893
DENS. (Kmole/m^3)	5.42829	0.03482
VAPOUR FRACTION	0.00000	1.00000
LIQUID FRACTION	1.00000	0.00000
--------(Kmole/hr)--		
ACETONE	0.00039	10.00000
CHLOROFORM	0.98811	10.00000
2-METHYLHEPTANE	88.89475	1.00000
TOTAL	89.88325	21.00000

Figure 1.8b Verification by simulation of the generated process flow sheet (b)

1.3.3
Integrated Computer-aided Modeling

The third educational module deals with modeling issues. Here, the importance of model analysis before attempting to solve the model equations is emphasized together with model reuse in an external modeling/simulation environment. The degrees of freedom, the ordering of equations, the method of solution are all interrelated and through a computer-aided modeling toolbox, the students are encouraged to use these features whenever they have to solve problems represented by a set of equations. As shown in Fig. 1.9, the objective is to transform the model equations into a program code that can be used by other simulation engines and/or solvers. At the same time, the programming effort should be a minimum. But, before going to the solution phase, the model equations must be thoroughly analyzed. Although the modeling/simulation problems in most cases can be solved through a number of existing programs (MATLAB, Maple, Mathematica, etc.), in the current example, the use of ICAS-MoT is highlighted for the reasons given above.
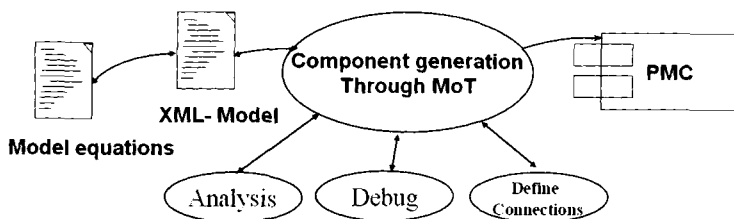
Figure 1.9 Import of model equations to MoT and after transformation and analysis, export to a process modeling component (or external simulation engine)

The use of MoT, a tool in ICAS, as an educational tool will be highlighted through a simple reactor modeling exercise.

1.3.3.1
Modeling Problem Description
The series reactions:

$$2A \xrightarrow[\text{(1)}]{k_{1a}} B \xrightarrow[\text{(2)}]{k_{2b}} 3C \tag{4}$$

are catalyzed by H_2SO_4. All reactions are first order in the reactant concentration. The reactions are carried out in a semi-batch reactor that has a heat exchanger inside with $UA = 35\,000$ cal h^{-1} K and ambient temperature of 298 K (see Fig. 1.10). Pure A enters at a concentration of 4 mol dm^{-3}, a volumetric flow rate of 240 dm^3 h^{-1}, and a temperature of 305 K. Initially there is a total of 100 dm^3 in the reactor, which contains 1.0 mol dm^{-3} of A and 1.0 mol dm^{-3} of the catalyst H_2SO_4. The reaction rate is independent of the catalyst concentration. The initial temperature of the reactor is 290 K.

The objective of this exercise is to highlight the basic features of ICAS-MoT and at the same time, the modeling steps needed to obtain the dynamic evolution of all concentrations in the semi-batch reactor for the given operating conditions.
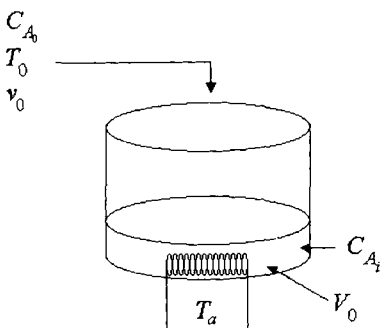
Figure 1.10 Semi-batch reactor scheme

1.3.3.2
Description of the Mathematical Model

Mole Balances

$$\frac{dC_A}{dt} = r_A + \frac{(C_{A0} - C_A)}{V} v_0 \tag{5}$$

$$\frac{dC_B}{dt} = r_B - \frac{C_B}{V} v_0 \tag{6}$$

$$\frac{dC_C}{dt} = r_C - \frac{C_C}{V} v_0 \tag{7}$$

where the rate laws are:

$$-r_{1A} = k_{1A} C_A \tag{8}$$

$$-r_{2B} = k_{2B} C_B \tag{9}$$

and the kinetic constants are Arrenhius-type

$$k_{1a} = k_{1A} \exp\left\{ \left(\frac{E_{1A}}{R}\right) \left[\frac{1}{T_{1A}} - \frac{1}{T}\right] \right\} \tag{10}$$

$$k_{2b} = k_{2B} \exp\left\{ \left(\frac{E_{2B}}{R}\right) \left[\frac{1}{T_{2B}} - \frac{1}{T}\right] \right\} \tag{11}$$

The relative rates are obtained using the stoichiometry (liquid phase) for the reaction series (Eq. (4)):

$$-r_{2B} = \frac{r_{2C}}{3} \tag{12}$$

$$r_{2C} = -3r_{2B} \tag{13}$$

So that the net rates are as follows:

$$r_A = r_{1A} = -k_{1A} C_A \tag{14}$$

$$r_B = r_{1B} + r_{2B} = \frac{-r_{1A}}{2} + r_{2B} = \frac{k_{1A} C_A}{2} - k_{2B} C_B \tag{15}$$

$$r_C = 3k_{2B} C_B \tag{16}$$

$$N_i = C_i V \tag{17}$$

$$V = V_0 + v_0 t \tag{18}$$

$$N_{H_2SO_4} = \left(C_{H_2SO_4,0}\right) V_0 = \frac{1\,\text{mol}}{\text{dm}^3} \times 100\,\text{dm}^3 = 100\,\text{mol} \tag{19}$$

$$F_{A_0} = \frac{4\,\text{mol}}{\text{dm}^3} \times 240\,\frac{\text{dm}^3}{\text{h}} = 960\,\frac{\text{mol}}{\text{h}} \tag{20}$$

Energy Balance

$$
\frac{dT}{dt} = \frac{UA(T_a - T) - \sum\limits_{i=1}^{NC} F_{i0} Cp_i(T - T_0) + \sum\limits_{i=1}^{NR} \Delta H_{Rx_{i,j}} r_{i,j} V}{\sum\limits_{i=1}^{NC} N_i Cp_i} \tag{21}
$$

is equivalent to

$$
\frac{dT}{dt} = \frac{UA(T_a - T) - F_{A0} Cp_A(T - T_0) + \left[\left(\Delta H_{Rx_{1A}}\right)\left(r_{1A}\right) + \left(\Delta H_{Rx_{2R}}\right)\left(r_{2B}\right)\right]V}{\left[C_A Cp_A + C_B Cp_B + C_C Cp_C\right]V + N_{H_2SO_4} Cp_{H_2SO_4}} \tag{22}
$$

Summarizing, the process model is given by: four ordinary differential equations (Eqs. (4–6, 22)) and fourteen algebraic equations (Eqs. (8–20); note that Eq. (14) is actually two equations). This differential-algebraic system can be solved simultaneously using ICAS-MoT. The data for this problem can be found in Table 1.2.

Table 1.2 Data for the differential-algebraic system

Variable	Value	Units	Description	MoT-variable
C_{A_0}	4.0	mol dm^{-3}	Initial concentration of compound A	CA0
$C_{H_2SO_4,0}$	1.0	mol dm^{-3}	Initial catalyst concentration	CH2SO40
v_0	240.0	dm^3 h^{-1}	Initial flow rate	vo
V_0	100.0	dm^3	Initial reactor volume	V0
UA	35˚000.0	cal h^{-1} K	Heat transfer coefficient	UA
T_a	298.0	K	Ambient temperature	Ta
T_0	305.0	K	Inlet Temperature	T0
T_{1A}	320	K	Reaction temperature (reaction 1)	T1A0
T_{2B}	300	K	Reaction temperature (reaction 2)	T2B0
k_{1A}	1.25	h^{-1}	Kinetic reaction constant(reaction 1)	k1A0
k_{2B}	0.08	h^{-1}	Kinetic reaction constant (reaction 2)	k2B0
E_{1A}	9500.0	cal mol^{-1}	Activation energy (reaction 1)	E1A
E_{2B}	7000.0	cal mol^{-1}	Activation energy (reaction 2)	E2B
Cp_A	30.0	cal mol^{-1} K	Thermal heat capacity of compound A	CpA
Cp_B	60.0	cal mol^{-1} K	Thermal heat capacity of compound B	CpB
Cp_C	20.0	cal mol^{-1} K	Thermal heat capacity of compound C	CpC
$Cp_{H_2SO_4}$	35.0	cal mol^{-1} K	Thermal heat capacity of catalyst	CpH2SO4
ΔH_{Rx1A}	−6500.00	cal mol^{-1}	Reaction enthalpy (reaction 1)	DHRx1A
ΔH_{Rx2B}	+8000.00	cal mol^{-1}	Reaction enthalpy (reaction 2)	DHRx2B
R	1.987	cal mol^{-1} K	Universal gas constant	R

1.3.3.3
Modeling Steps in MoT

The model developer does not need to write any programming codes to enter the model equations. Models are entered (imported) as text files or XML files, which are then internally translated.

Step 1: Type the model equations in MoT or transfer a text file or an XML file. In Fig. 1.11, the model (Eqs. (4–22)) has been typed into MoT.

```
#***********************************************
#*Nonisothermal Multiple Reaction         *
#*                                         *
#*CAPEC, Department of Chemical Engineering*
#*Technical University of Denmark          *
#*MSC, April, 2004                         *
#***********************************************

#The series reactions:
#              k1A        K2B
#         2A ------> B ------> 3C
#              (1)        (2)

#*************
#Solution    *
#*************

#Kinetic
  k1A = k1A0*exp((E1A/R)*(1/T1A0 - 1/T))
  k2B = k2B0*exp((E2B/R)*(1/T2B0 - 1/T))

#Rate Laws
  r1A = -k1A*CA
  r2B = -k2B*CB
  rA = r1A
  rB = k1A*CA/2-k2B*CB
  rC = 3*k2B*CB

#Reactor volume
  V = V0 + vo*t

  FA0 = CA0*vo
  Cpmix = CA*CpA + CB*CpB + CC*CpC

#Mol balances
  dCA = rA + (CA0 - CA)*vo/V
  dCB = rB - CB*vo/V
  dCC = rC - CC*vo/V

#Energy Balance
  dT = (UA*(Ta-T) - FA0*CpA*(T-T0) + (DHRx1A*r1A +
        DHRx2B*r2B)*V)/(Cpmix*V + CH2SO40*V0*CpH2SO4)
```
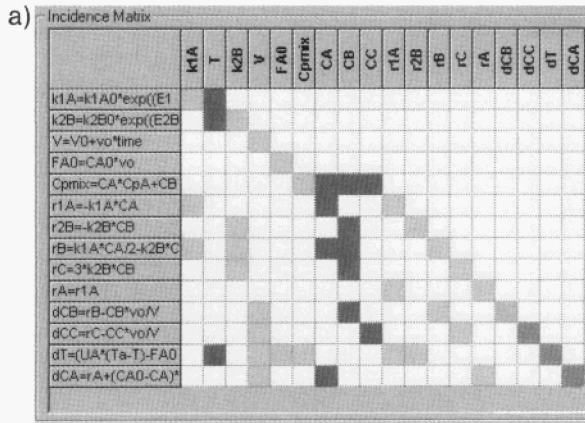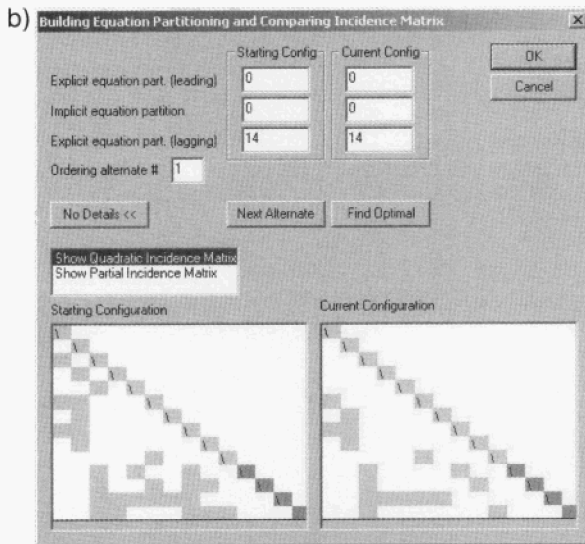
Figure 1.11 MoT model

a)

Incidence Matrix

	k1A	T	k2B	V	FA0	Cpmix	CA	CB	CC	r1A	r2B	rB	rC	rA	dCB	dCC	dT	dCA
k1A=k1A0*exp((E1		■																
k2B=k2B0*exp((E2B																		
V=V0+vo*time																		
FA0=CA0*vo																		
Cpmix=CA*CpA+CB							■											
r1A=-k1A*CA																		
r2B=-k2B*CB								■										
rB=k1A*CA/2-k2B*C								■										
rC=3*k2B*CB																		
rA=r1A																		
dCB=rB-CB*vo/V																		
dCC=rC-CC*vo/V																		
dT=(UA*(Ta-T)-FA0		■																
dCA=rA+(CA0-CA)*																		

Figure 1.12a Incidence matrix (a). Equation partitioning and incidence matrix comparison (b)

b)

Building Equation Partitioning and Comparing Incidence Matrix

	Starting Config	Current Config
Explicit equation part. (leading)	0	0
Implicit equation partition	0	0
Explicit equation part. (lagging)	14	14

Ordering alternate # 1

No Details <<   Next Alternate   Find Optimal

OK   Cancel

Show Quadratic Incidence Matrix
Show Partial Incidence Matrix

Starting Configuration   Current Configuration

Step 2: Model translation. MoT translates the imported model, lists all the equations and variables found in the translated model. It has built-in knowledge to distinguish between algebraic equations (explicit and implicit), ordinary differential equations and partial differential equations. The variables are classified as parameters, known, unknown (implicit), unknown (explicit), dependent and dependent prime (used for differential equations only). MoT automatically identifies the unknown (implicit), unknown (explicit) and dependent equations. The user needs to classify the known variables as either parameters (which could then be selected for model parameter estimation) or known variables (which could be used as design variables for optimization). Also, the user needs to link the dependent variables to the dependent prime (that is, in dy/dt, y is the dependent variable and dy is the dependent prime).

Step 3: Incidence matrix analysis. As the variables are assigned, MoT is able to generate a corresponding incidence matrix (equations are placed in rows and variables in columns) and order the equations as near as possible to a lower tridiagonal form. Also, unless the degrees of freedom are matched (that is, a square matrix of equations and unknown variables and the known variables equal the degrees of freedom), MoT does not allow the solver to be called. A sample of the incidence matrix is shown in Figs. 1.12a and 1.12b.

Step 5: Define the independent variable. In this case, the independent variable is time t. MoT is now able to find the 14 algebraic equations and 4 ordinary differential equations and is therefore ready to start the solver. However, before the solver is called, the initial values for the dependent variables need to be specified together with the parameters and the known variables.

Step 6: Set variable values. Figure 1.13 shows the specified values for the variables.

Model Solution
Step 7: Select variables for output. The user may select the variables whose values can be stored and visualized as the numerical solver progresses towards the solution.

	Dependent	Dependent Prime	Unknown	Explicit	Known	Parameter
T	298					
CA	1					
CB	0					
CC	0					
dCA		0				
dCB		0				
dCC		0				
dT		0				
k1A			0			
k2B			0			
r1A			0			
r2B			0			
rA			0			
rB			0			
rC			0			
V			0			
FA0			0			
Cpmix			0			
k1A0					1.25	
E1A					9500	
R					1.987	
T1A0					320	
k2B0					0.08	
E2B					7000	
T2B0					300	
V0					100	
vo					240	
CA0					4	
CpA					30	
CpB					60	
CpC					20	
UA					35000	
Ta					298	
T0					305	
DHRx1A					-6500	
DHRx2B					8000	

Figure 1.13 Initial condition and values of known variables

a)

b)
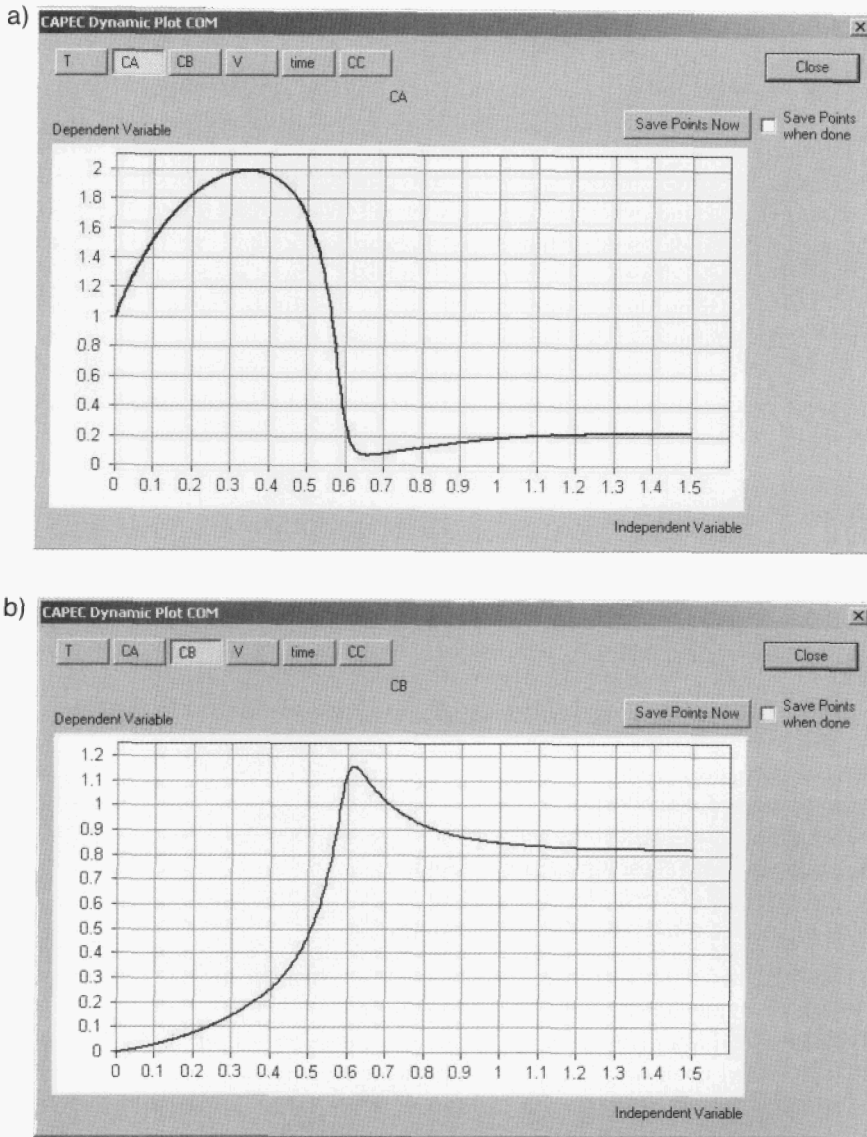
Figure 1.14 Component A: dynamic concentration motion. Component B: dynamic concentration motion

Step 8: Select the solver. In this case, dynamic option and forward integration with the BDF method is chosen and an end-time of 1.5 hours may be specified.

Step 9: Simulation results. As the numerical solver integrates, the selected variables values from Step 7 will be shown in dynamic plots and their values will be stored in files for later use. Figures 1.14a and 1.14b shows two samples of the dynamic plots.

Step 10: Saving the MoT file for reuse as well as export to other simulation engines. When the user is satisfied with the model and its solution, the MoT file can be saved for use within the ICAS simulation engine, for use from EXCEL or for use from any external simulation engine (with or without the CAPE-OPEN interface).

Further expansion of the exercise includes providing experimental data and regressing the kinetic model parameters and process optimization. Other exercises may also be developed where the generated model object is used to simulate the reactor, which is part of a process flow sheet. The same procedure can also be repeated to generate model objects for new property models, kinetic models and unit operation models. Using these model objects and a simulation environment such as EXCEL, the student can develop their own process simulator. For process design tasks involving new chemical products, this option is very practical and useful as the available process simulators do not have the chemicals and/or the models to handle them.

1.3.4
Other Educational Modules

A number of ICAS-based educational modules have been developed and can be downloaded from the following address: www.capec.kt.dtu.dk/Software/ICAS-Tutorials/ICAS-Tutorials-Workshops.

These tutorials cover problems related to:

- computer-aided property estimation
- computer-aided modeling
- computer-aided product design
- computer-aided separation process design
- computer-aided batch process modeling
- integrated computer-aided process engineering.

The objective of all these exercises is to highlight a systematic solution procedure and the use of an integrated set of methods and tools.

Other useful information can be found in the document from CACHE Corporation (2004) on *Computing through the curriculum: an integrated approach for chemical engineering* (www.che.utexas.edu/cache/newsletters/fall2003_computing.pdf). See also *Strategies for creative problem solving* by Fogler and LeBlanc (www.che.utexas.edu/cache/strategies.html); *The frontiers in chemical engineering education* (web.mit.edu/che-curriculum/); the EURECHA Web site at (www.capec.kt.dtu.dk/eurecha/); the EFCE working party on Education (www.efce.org/wpe.html).

1.4
Conclusion

The educational modules are documents containing the problem definition together with a detailed step by step solution strategy where the calculations for each step are highlighted with possible use of specific software (data flow and workflow). They can be used by the teacher to highlight an algorithm or methodology or technique (theory). They can also be used by the student to learn how to apply the theory (algorithms/methods) to solve problems.

Through the education modules, some of the important issues (including the danger of misuse) related to the use of computers in chemical engineering education have been highlighted. They have been prepared such that the user is in charge of the navigation and decisions while the computer does the calculations, data transfer, code generation, etc., which it is supposed to perform very efficiently. One of the principal experiences from the use of the presented educational modules has been that once the students understood the main ideas and got familiar with the workflow and data flow, they are able to tackle a wide range of similar problems without much help and in a very short time. In this way, they also learn to appreciate that the computer-aided tools are there to help them but they are the ones who need to make the right decisions and drive the use of the software in the appropriate direction. Finally, it was found that the students were able to appreciate the concepts better, were able to solve more challenging problems in a shorter time, resulting, thereby, an increase in productivity. They were able to use the same methods and tools also for problem solution in other courses. The feedbacks from the students have also helped to improve the software as well as the workflow and data flow of the educational modules. Finally, we would like to emphasize that software should not be used as a replacement of the process-product engineer; it should be used to do what it was designed for, with the user always in charge of directing it.

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