

A Thermodynamics Teaching Aid for Undergraduate Engineers*

K. GIDH

M. E. HANYAK, JR.

Bucknell University, Chemical Engineering Department, Lewisburg, PA 17837, U.S.A.

The feasibility of using Mathematica to develop a thermodynamics teaching/learning tool is explored here. The desired characteristics of the teaching/learning tool are the ability to generate plots, to view the equations and to modify them easily, to operate the software using minimal commands, and to port the software. The software is designed using the 'Notebook' capabilities of Mathematica. Thermodynamic properties are implemented for a point calculation as well as for a plot, in accordance with the software design. The software is tested, using different system mixtures, to assess its efficiency and limitations in serving as a teaching/learning tool.

SUMMARY OF EDUCATIONAL ASPECTS OF THE PAPER

1. The paper discusses material for a course in: thermodynamics
2. Students of the following departments are taught in the course: Chemical Engineering.
3. Level of the courses: junior.
4. Mode of presentation: computer lab.
5. Is the material presented in a regular or in an elective course?: regular course.
6. Class hours required to cover the materials: 4-6 hours per week.
7. Student homework and revision hours required for the materials: 4-6 hours per week.
8. Description of the novel aspects presented in the paper: Comparison of equation of state models for different homogeneous mixtures and vapor-liquid equilibrium.
9. The standard text recommended for the course, in addition to authors' notes: J. M. Smith and H. C. Van Ness, *Introduction to Chemical Engineering Thermodynamics*, McGraw-Hill.
10. The material is/is not covered in the text. The discussion in the text is different in the following aspects:
Material is covered in a broad sense in the textbook. The Mathematica-based software package allows students to experiment with specific application of the models based on Soave-Redlich-Kwong equation of state.

NOMENCLATURE

Variables

P	total pressure of the system, kPa
T	absolute temperature of the system, K
V	molar volume of the system, m ³ /kgmol
n	number of components in the system
z_i	mole fraction of component i in the system
a	attraction parameter in the equation of state
α	temperature-dependence factor in a
b	co-volume in the equation of state
k_{ij}, l_{ij}	parameters of the mixing rule
T_{ri}	reduced temperature of component i , K
ϕ_i	fugacity coefficient of component i in a mixture
ϕ	fugacity coefficient of the system
Z	compressibility factor of the system
V_f	molar vapor fraction of the system
L_f	molar liquid fraction of the system
x_i	mole fraction of component i in the liquid phase
y_i	mole fraction of component i in the vapor phase
K_i	equilibrium coefficient for component i
P_{s_i}	saturation pressure of pure component i

* Paper accepted 4 January 1993.

Constants

R	universal gas constant, $\text{m}^3 \text{kPa}/\text{kgmol K}$
T_{ci}	critical temperature of component i , K
P_{ci}	critical pressure of component i , kPa
p_{1i}, p_{2i}, p_{3i}	polar parameters
ω_i	acentric factor
$k^{(0)}_{ij}, k^{(1)}_{ij}, k^{(2)}_{ij}$	temperature-dependence parameters for k_{ij}
$l^{(0)}_{ij}, l^{(1)}_{ij}, l^{(2)}_{ij}$	temperature-dependence parameters for l_{ij}
κ_{ij}	Kronecker delta $\{\kappa_{i,j} = 1 \text{ for } i = j; \kappa_{i,j} = 0 \text{ for } i \neq j\}$
$Vpa_{1i}, Vpa_{2i}, Vpa_{3i}, Vpa_{4i}, Vpa_{5i}, Vpa_{6i}, Vpa_{7i}$	Antoine correlation constants

Subscripts

i, j	component indices
c	critical property
r	reduced property
L	liquid phase
V	vapor phase

Superscript

—	partial molar property of component i
---	---

Abbreviations

PVT	pressure–volume–temperature diagram
PH	pressure–enthalpy diagram
PS	pressure–entropy diagram
$P\phi$	pressure–fugacity coefficient diagram
TXY	temperature–composition diagram
PXY	pressure–composition diagram
HXY	enthalpy–composition diagram

INTRODUCTION

THIS PAPER discusses the feasibility of using Mathematica [1] to develop a thermodynamic teaching/learning tool. The teaching of thermodynamics has always involved property models and the study of diagrams. Computer programs have been largely used to educate the user about these aspects of thermodynamics. Several property prediction and process simulation programs have been developed: Flowtran, a process simulator developed by Monsanto [2]; Calorimetry and Thermodynamics, a tutorial designed to illustrate some aspects of thermodynamics [3]; Aspen Plus, a process simulator developed by Aspen Technologies [4]; TTPGL, a thermodynamic property calculator to estimate thermodynamic and transport properties [5]; BUTS (Bucknell University Thermodynamics System), a property prediction pack-

age [6] and Ekilib, a ‘user-friendly’ program for vapor–liquid equilibrium [7].

Although the many programs available for calculation of various aspects of equilibrium thermodynamics have been in use for educational purposes quite prevalently, not many of them are geared as a teaching/learning tool. The high-tech simulation programs such as Flowtran and Aspen Plus can be difficult for a novice to use as they require long hours of studying technical manuals and rarely have any on-line help facilities. Academic programs, written by students and research groups, are frequently hostile to the user, do not detect errors easily and hardly have any graphics capabilities since the usual programming language is FORTRAN. Moreover, in all these programs the actual thermodynamics model is hidden from the user and cannot be modified without recompilation.

An effective teaching/learning tool should not only perform the necessary thermodynamic calculations but also allow the user to ‘experiment’ by changing the models. Moreover, it should have the necessary graphics capabilities universally available on almost all computer systems. A software tool that meets the requirements of providing a good user interface, graphics and portability is Mathematica.

The numerous advantage of using Mathematica over FORTRAN-based teaching/learning tools are its portability, high functionality, standard mathematical algorithms and most of all, its notebook format (currently available on Macintosh and NEXT computers). Notebooks are ideally suited for teaching/learning purposes, since they allow the user to see and understand the equations involved in a particular calculation. The information can be structured in the same way as in a book, defining chapters, sections, subsections, and so on. The immediate feedback that notebooks provide allows the user to do calculations interactively. This feature of notebooks is ideal for teaching/learning purposes.

This article explores the feasibility of using Mathematica to teach the undergraduate chemical engineer about the application of thermodynamics to the design process and to make the learning process more effective by providing graphic capabilities and by making the software tool more interactive. Thus, the primary issues to be resolved are:

1. How to perform the thermodynamic calculations using equations of state (EOS), which relate temperature, pressure, and molar volume of fluid mixtures.
2. How to use Mathematica to set up and solve these equations.
3. How best to utilize the graphic capabilities of Mathematica as a teaching/learning tool.
4. How effectively does Mathematica serve in developing a thermodynamic teaching/learning tool.

FUNCTIONAL REQUIREMENTS

The Aspen modification of the Soave-Redlich-Kwong (SRK) equation of state [8] can be used to calculate the thermodynamic properties of fluids and fluid mixtures, such as molar volume, molar enthalpy, molar entropy, and vapor-liquid equilibrium temperature. The Aspen modification of the SRK EOS, applicable to polar as well as non-polar chemical components, has been validated and implemented in the process simulator Aspen Plus as of 1987. This new cubic EOS is flexible and relatively straightforward to use. It is competitive with the best activity-coefficient models for phase equilibrium, and can be readily extrapolated. It also offers facilities for calculating other properties, such as enthalpies and entropies. In short, this cubic EOS provides a general way to estimate properties of state, over a wide temperature and pressure range for liquid-liquid equilibrium (LLE), vapor-liquid equilibrium (VLE) and vapor-liquid-liquid equilibrium (VLLE) systems.

Molar volume and molar fugacity coefficients for pure substances and mixtures, vapor-liquid equilibrium temperature, pressure, and vapor fraction for binary and multicomponent mixtures, all calculated using the Aspen modification of the SRK EOS, are the focus of this article. Gidh [9] describes in detail the application of Mathematica to a larger range of thermodynamic properties.

Homogeneous fluid property calculations

Usually an EOS approach to calculate fluid properties is a two-step procedure. First, the mixture compressibility factor of the given fluid is determined at the specified conditions of temperature, pressure, fluid composition, and phase state. Typically, this calculation is iterative; that is, it requires a numerical algorithm such as Newton's method. The fluid property, such as enthalpy or fugacity coefficient, is then calculated directly using a derived expression from the EOS.

An alternate way to calculate fluid properties is to solve the cubic equations of state analytically, using a software program such as Mathematica. This method is used here to perform all the fluid property calculations given in Gidh [9]. Two algorithms for molar volume and fugacity coefficient are described in the following sections.

Molar volume

The necessary equations for determining molar volume are listed in Fig. 1. The Aspen cubic EOS shown in Fig. 1 is similar to other cubic EOS. It gives an accurate description of the *PVT* behavior of fluids over wide ranges of temperature and pressure and is sufficiently general to apply to liquids as well as gases and vapors. In the EOS of Fig. 1, parameters a and b are positive constants, a is the attraction parameter and b is the covolume parameter. When they are zero, the EOS reduces the ideal gas equation. For mixtures, a linear mixing rule is used to calculate b , and a non-quadratic

mixing rule is used to calculate a , as shown in Fig. 1. Here the binary interaction parameters, k_{ij} and l_{ij} , are temperature-dependence parameters used in calculating a and b . When a mixture contains only one component, the temperature dependence of a and b reduces to the pure component case. When the components are supercritical, this dependence is determined by another set of equations as shown in Fig. 1 where c and d are pure-component parameters for supercritical temperatures. The acentric factor ω , which is a measure of deviation from the law of corresponding states; and, p_{1i} , p_{2i} and p_{3i} , are polar parameters that represent the polarity of the components.

The various constants and variables in the set of equations are listed in Fig. 1. Degrees of freedom analysis on the equations and variables determines that $(n + 3)$ variables need to be specified to calculate the molar volume. For these degrees of freedom, the composition of all the n number of components in the mixture must be specified and must add up to one. Also the number of components in the mixture, n , must be specified. In addition to the overall composition and the number of components, if the temperature and pressure of the mixture are also specified, then all the degrees of freedom are satisfied. The various constants: critical temperatures and pressures, acentric factors and polar parameters p_{1i} , p_{2i} and p_{3i} , are available from tables for pure components and the binary parameters k_{ij} and l_{ij} are determined by regressing experimental VLE, LLE, or VLLE data [8]. For a mixture containing only a pure component (i.e. $n = 1$ and $z_1 = 1.0$), the degrees of freedom reduces to two, so only temperature and pressure need to be specified.

Like other cubic EOS, Aspen cubic EOS has three volume roots as illustrated in Fig. 1., of which two may be complex. Physically meaningful values of V are always real, positive, and greater than the constant b . When $T > T_c$, solution for V at any positive value of P yields only one real positive root. This fact is also true when $T = T_c$, except at the critical pressure there are three roots all equal to the critical volume. For $T < T_c$, there is but one real positive root at high pressures, $P > P_c$, but for a range of lower pressures three real positive roots exist. Here, the middle root is of no physical significance; the smallest root is a liquid or liquid-like volume of the mixture, and the largest root is vapor or vapor-like volume of the mixture. For a pure-component mixture, the saturated liquid and saturated vapor volumes are given by the smallest and the largest roots when P is the saturation or vapor pressure.

Fugacity coefficient of component i in mixture

The necessary equations for determining the fugacity coefficient of component i in a mixture are listed in Fig. 2. This coefficient is fundamental in modelling phase equilibrium. The fugacity coefficient ϕ_i of component i in the mixture, for all components, is calculated from the expression

given in Fig. 2. This expression is derived by solving the integral in Eq. 1 using the Aspen cubic EOS.

$$\ln \phi_i = \int_0^P (\bar{Z}_i - 1) \frac{dP}{P} \quad (\text{const. } T, \bar{z}) \quad (1)$$

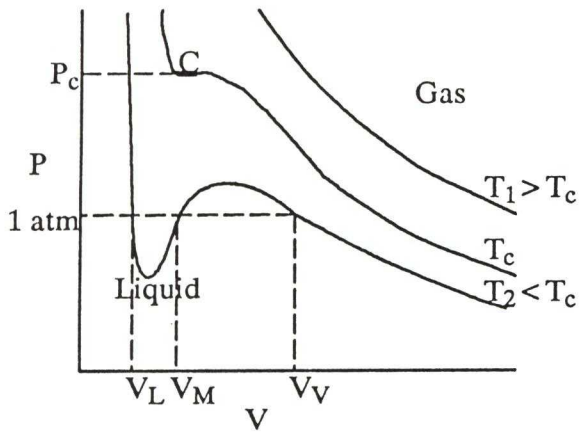
$$\bar{Z}_i = \frac{P\bar{V}_i}{RT} \quad (2)$$

The molar volume, parameters a , b , l_{ij} , etc. are calculated as shown previously in Fig. 1. The fugacity coefficient of the mixture ϕ is related to the fugacity coefficient of component i in the mixture by the equation given in Fig. 2.

The various constants and variables in the set of equations are listed in Fig. 2. Degrees of freedom analysis on the equations and variables determines

PVT diagram using cubic EOS (fixed composition \bar{z})

Assumptions



1. homogeneous phase (i.e., vapor or liquid)
2. ASPEN SRK E.O.S.

Mathematical Model

{ subscript i denotes n no. of equations;
subscripts ij denote n² no. of equations }

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

Mixture variables:

$$a = \sum_{i=1}^n \sum_{j=1}^n a_{ij} z_i z_j$$

$$b = \sum_{i=1}^n b_i z_i$$

$$a_{ij} = (a_i a_j)^{\frac{1}{2}} [1 - k_{ij} - l_{ij} (z_i - z_j)]$$

$$k_{ij} = k_{ij}^{(0)} + k_{ij}^{(1)} T + \frac{k_{ij}^{(2)}}{T}$$

$$l_{ij} = l_{ij}^{(0)} + l_{ij}^{(1)} T + \frac{l_{ij}^{(2)}}{T}$$

Pure component i :

{ for $i = 1, 2, \dots, n$ }

$$a_i = a_i a_{ci}$$

$$a_i = \left[1 + m_i \left(1 - T_n^{\frac{1}{2}} \right) - p_{1i} (1 - T_n) (1 + p_{2i} T_n + p_{3i} T_n^2) \right]^2$$

$$\begin{aligned}
 d_i &= 1 + \frac{m_i}{2} - p_{1i}(1 + p_{2i} + p_{3i}) \\
 c_i &= 1 - \frac{1}{d_i} \\
 a_i &= e^{2c_i} \left(1 - r_{ci}^{d_i} \right) \\
 a_{ci} &= 0.42748 \frac{(RT_{ci})^2}{P_{ci}} \\
 m_i &= 0.48508 + 1.55171 \omega_i - 0.15613 \omega_i^2 \\
 b_i &= 0.08664 \frac{RT_{ci}}{P_{ci}} \\
 T_{ri} &= \frac{T}{T_{ci}}
 \end{aligned}
 \quad \left. \vphantom{\begin{aligned} d_i \\ c_i \\ a_i \\ a_{ci} \\ m_i \\ b_i \\ T_{ri} \end{aligned}} \right\} \text{for supercritical components}$$

variables: $a_{ij}, k_{ij}, l_{ij}, z_i, b_i, a_i, \alpha_i, a_{ci}, m_i, c_i, d_i, T_{ri}, T, P, V, a, b, n$

constants: $R, p_{1i}, p_{2i}, p_{3i}, T_{ci}, P_{ci}, \omega_i, k^{(0)}_{ij}, k^{(1)}_{ij}, k^{(2)}_{ij}, l^{(0)}_{ij}, l^{(1)}_{ij}, l^{(2)}_{ij}$

Degrees of Freedom analysis:

$$\begin{aligned}
 \text{no. of variables} &= 3n^2 + 9n + 6 \\
 \text{no. of equations} &= \underline{3n^2 + 8n + 3} \\
 \text{D.O.F.} &= \underline{\quad\quad\quad} n + 3
 \end{aligned}$$

Fig. 1. Mathematical model for the molar volume calculation.

that $(n + 3)$ variables need to be specified to calculate the fugacity coefficient of component i in mixture. For these degrees of freedom, the composition of all the n number of components in the mixture must be specified and must add up to one. Also the number of components in the mixture, n , must be specified. In addition to the overall composition and the number of components, if the temperature and pressure of the mixture are also specified, then all the degrees of freedom are satisfied. The various constants: critical temperatures and pressures, acentric factors and polar parameters p_{1i} , p_{2i} and p_{3i} , are available from tables for pure components, and the binary parameters l_{ij} are determined by regressing experimental VLE, LLE or VLLE data. For a mixture containing only a pure component (i.e. $n = 1$ and $z_1 = 1.0$), the degrees of freedom are equal to two, so only temperature and pressure need to be specified.

If liquid and vapor molar volumes exist at the specified conditions, then liquid and vapor fugacities of component i in the mixture exist. For a pure-component mixture, the saturated liquid and saturated vapor fugacities of the pure compound

are given when P is the saturation of vapor pressure.

Vapor-liquid equilibrium property calculations

The general mathematical model for a general vapor-liquid equilibrium system (VLE) is shown in Fig. 3. For a closed system having vapor and liquid phases in equilibrium, the overall material balance gives the sum of the molar vapor and liquid fraction equal to one. A component material balance gives the overall mole fraction of each compound in the system as molar average of the mole fractions of that compound in the two phases. The mole fraction of a component in the vapor phase is directly proportional to the mole fraction of that component in the liquid phase. The proportionality factor called a K -value is determined by the ratio between the fugacity coefficient of component i in the mixture in the liquid phase and the fugacity coefficient of component i in the mixture in the vapor phase. The fugacity coefficient of component i in the mixture for the two phases can be determined by an algorithm derived from the model in Fig. 2. The constraint on the VLE system of equations is that the sum of the mole fractions of all

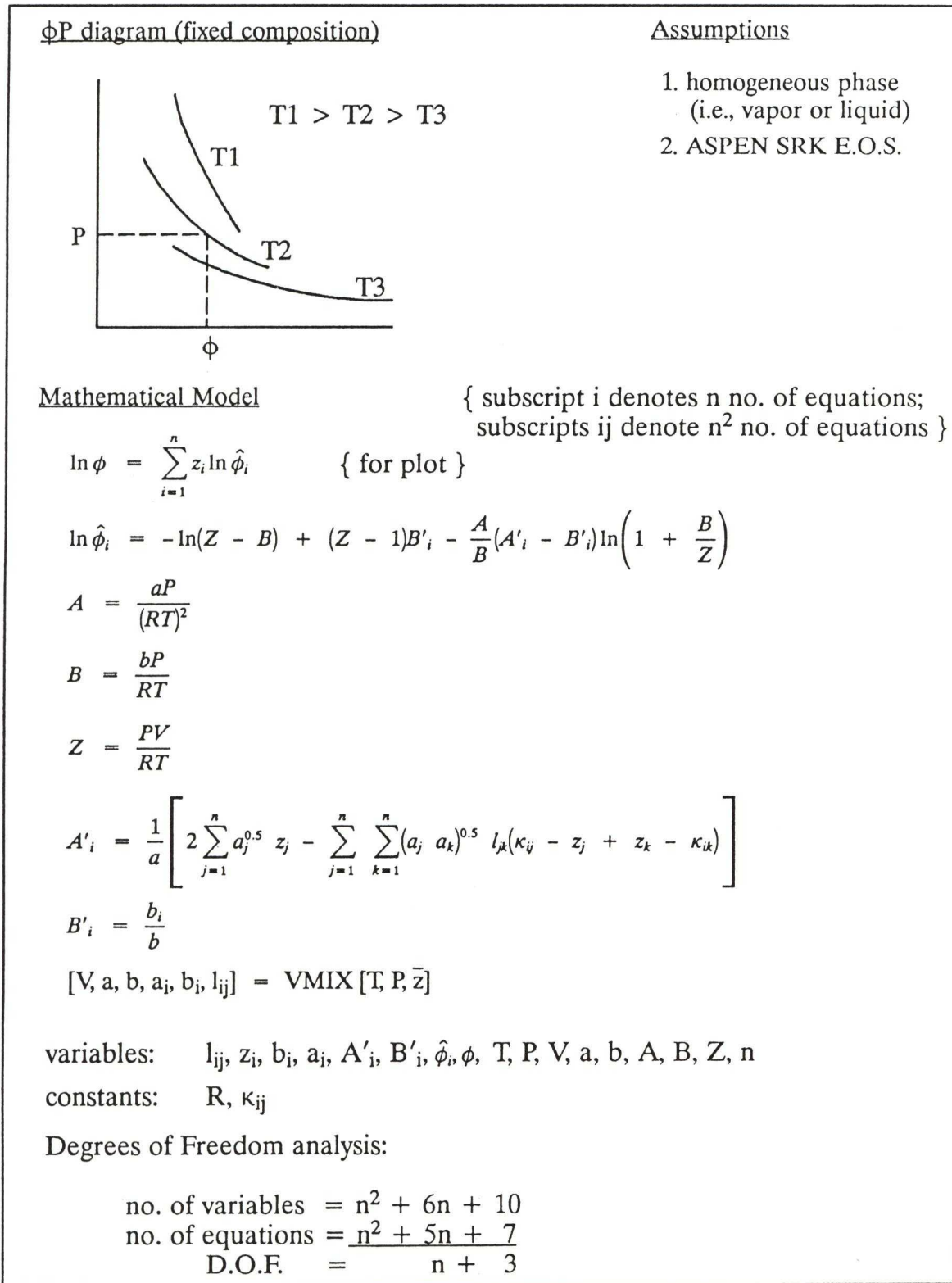


Fig. 2. Mathematical model for the fugacity coefficient of component *i* in mixture calculation.

components in each phase must equal one. Degrees of freedom analysis on the equations and variables listed in Fig. 3 determines that $(n + 3)$ variables need to be specified to calculate a vapor-liquid equilibrium property (temperature, pressure or vapor fraction).

The equilibrium distribution coefficients, *K*-values in Fig. 3, can be defined in three ways:

1. ϕ_{iL} and ϕ_{iV} from EOS
2. ϕ_{iV} from EOS; ϕ_{iL} from activity coefficients
3. $\phi_{iV} = 1.0$ ideal gas; $\phi_{iL} = P_{s_i}/P$ Raoult's law

This article focuses on Methods 1 and 3 as they are commonly used in design calculations. Method 1, based on an EOS, offers internal consistency as one of its advantages. Also, it is valid over a wide range of temperatures and pressures, including ones in the mixture critical region. The presence of supercritical components poses no special problems. The method is therefore attractive for K -value calculations, including ones involving high pressures.

For the general model of Fig. 3, the equations

can be solved either sequentially or simultaneously. The sequential solution involves an iteration within an iteration [10]. The inner loop converges the K -values using a numerical technique such as the Wegstein method. The outer loop converges an unknown variable (either temperature or vapor fraction) using a numerical technique such as the secant or Newton's method. The simultaneous solution converges all unknown variables using the Newton-Raphson method [10]. A simultaneous solution approach requires fewer iterations than a

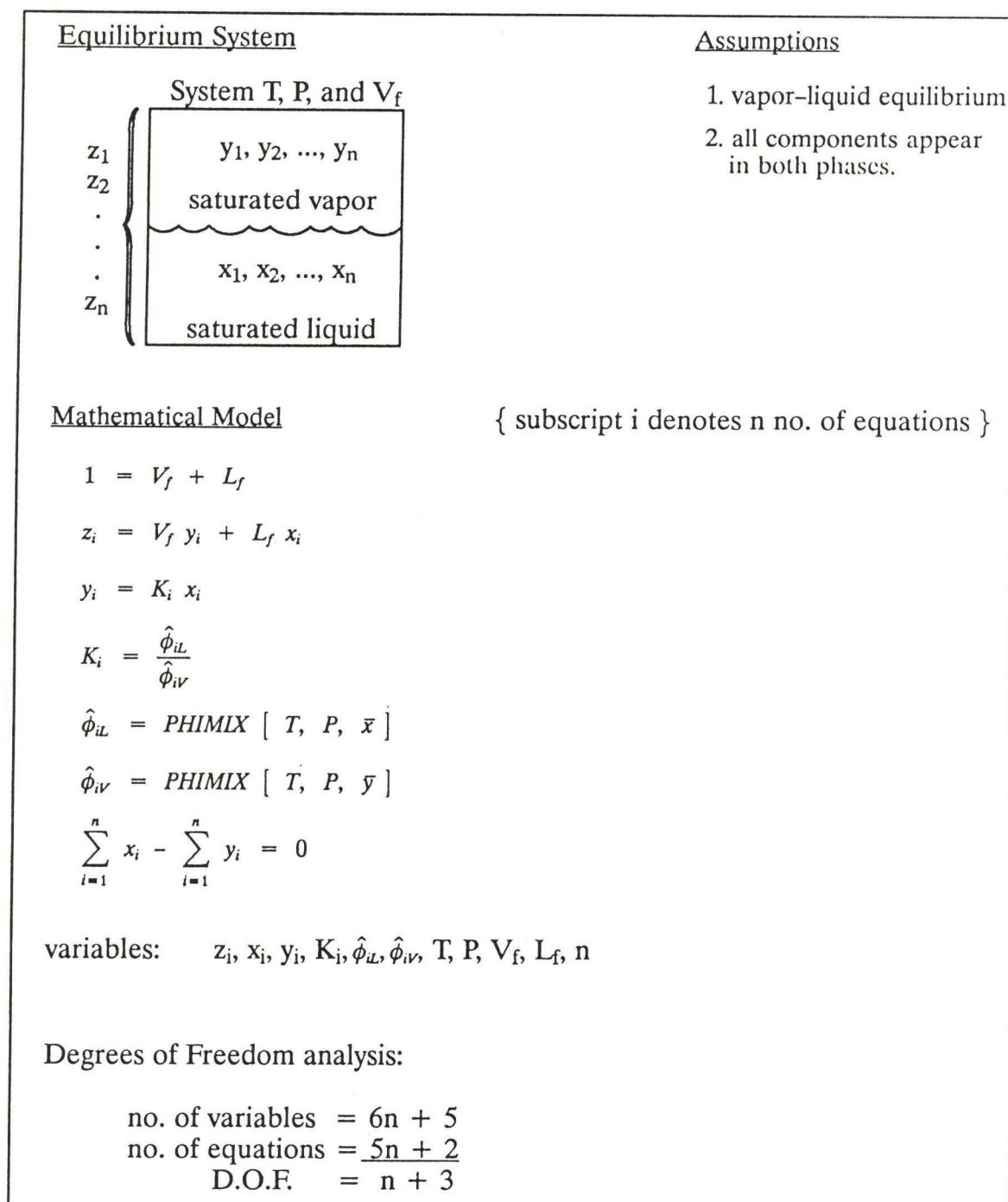


Fig. 3. General mathematical model for the vapor-liquid equilibrium calculations.

sequential solution approach, but, a sequential solution approach is more stable.

In the following sections, mathematical models and algorithms are developed for the calculation of the vapor–liquid equilibrium properties using Raoult’s law and using the equation of state approach. For both these approaches, the simultaneous method is used for convergence in the mathematical algorithms because the simultaneous method requires less number of iterations to converge to the correct solution, and it is supported by a built-in function in Mathematica called **FIND-ROOT**.

Vapor–liquid equilibrium property calculations using Raoult’s law

The necessary equations for determining vapor–liquid equilibrium properties using Raoult’s law are listed in Fig. 4. The proportionality factor, the *K*-value, is determined by the ratio between the saturation pressure of that pure component and the total pressure. The saturation pressure of each component is determined from Antoine’s equation.

The set of equations listed in Fig. 4 are solved for the vapor–liquid equilibrium properties using the simultaneous method. The various constants and variables in the set of equations are listed in

<u>Equilibrium System</u>	<u>Assumptions</u>
<div style="text-align: center; margin-bottom: 10px;">System T, P, and V_f</div> <div style="display: flex; align-items: center;"> <div style="margin-right: 10px;"> z_1 z_2 \cdot \cdot \cdot z_n </div> <div style="border: 1px solid black; padding: 10px; width: 200px;"> <div style="text-align: center; margin-bottom: 10px;">y_1, y_2, \dots, y_n</div> <div style="text-align: center; margin-bottom: 10px;">saturated vapor</div> <hr style="border: none; border-top: 1px dashed black; margin: 5px 0;"/> <div style="text-align: center; margin-bottom: 10px;">x_1, x_2, \dots, x_n</div> <div style="text-align: center;">saturated liquid</div> </div> </div>	<ol style="list-style-type: none"> 1. vapor–liquid equilibrium 2. all components appear in both phases. 3. Raoult’s law 4. Antoine equation
<p><u>Mathematical Model</u> { subscript i denotes n no. of equations }</p> <p>$1 = V_f + L_f$</p> <p>$z_i = V_f y_i + L_f x_i$</p> <p>$y_i = K_i x_i$</p> <p>$K_i = \frac{P_{s_i}}{P}$</p> <p>$\ln P_{s_i} = V_{pa_{1i}} + \frac{V_{pa_{2i}}}{T + V_{pa_{3i}}} + V_{pa_{4i}}T + V_{pa_{5i}} \ln T + V_{pa_{6i}}T^{V_{pa_{7i}}}$</p> <p>$\sum_{i=1}^n x_i - \sum_{i=1}^n y_i = 0$</p> <p>variables: $z_i, x_i, y_i, K_i, P_{s_i}, T, P, V_f, L_f, n$</p> <p>constants: $V_{pa_{1i}}, V_{pa_{2i}}, V_{pa_{3i}}, V_{pa_{4i}}, V_{pa_{5i}}, V_{pa_{6i}}, V_{pa_{7i}}$</p> <p>Degrees of Freedom analysis:</p> <p style="margin-left: 40px;">no. of variables = $5n + 5$</p> <p style="margin-left: 40px;">no. of equations = $4n + 2$</p> <p style="margin-left: 40px;">D.O.F. = $n + 3$</p>	

Fig. 4. Mathematical model for the vapor–liquid equilibrium calculations using Raoult’s law.

Fig. 4. These equations can be solved in one of three ways: for either the vapor–liquid equilibrium temperatures, pressure or vapor fraction. Also these equations can be solved together with the molar volume and the molar enthalpy equations to generate the HXY diagram for binary mixtures. While determining the vapor–liquid equilibrium properties, supercritical components are not considered in this work because the Antoine's equation is only valid at subcritical conditions. The vapor–liquid equilibrium calculations for temperature, pressure and vapor fractions and the HXY diagram are solved and described by Gidh [9]. Here, only the vapor–liquid equilibrium temperature calculation is described.

Degrees of freedom analysis on the equations and variables listed in Fig. 4 determines that $(n + 3)$ variables need to be specified to calculate the vapor–liquid equilibrium temperature. For these degrees of freedom, the overall composition of all the n number of components in the system must be specified and must add up to one. Also the number of components in the system, n , must be specified. In addition to the overall composition and the number of components, if the pressure and vapor fraction of the system are also specified, then all the degrees of freedom are satisfied. The equations can be solved simultaneously in two ways: an iteration can be performed to solve for all the $(4n + 2)$ unknown variables in the $(4n + 2)$ equations, or the equations can be reduced algebraically to $(2n + 2)$ equations by eliminating dependent variables and then iterating on the remaining $(2n + 2)$ unknown variables (vapor–liquid equilibrium temperature and mole fractions of the liquid and vapor phases). The various constants in the Antoine's equation are available from tables for pure components.

For a mixture containing only a pure component (i.e. $n = 1$ and $z_1 = 1.0$), the degrees of freedom reduces to two (vapor fraction and pressure). This fact is contrary to the value obtained by using the Gibbs–Duhem equation for a known pure component, which gives the degrees of freedom as one (pressure). The model in Fig. 4 breaks down for a known pure component because specifying the vapor fraction gives only the liquid fraction which is independent of specifying the pressure which gives only the temperature. Therefore, to determine the vapor–liquid equilibrium temperature of a known pure component, only pressure needs to be specified.

Vapor–liquid equilibrium property calculations using Aspen cubic EOS

The necessary equations for determining vapor–liquid equilibrium properties using Aspen cubic EOS are listed in Fig. 5. The proportionality factor called a K -value is determined by the ratio between the fugacity coefficient of component i in the mixture in the liquid phase and the fugacity coefficient of component i in the mixture in the vapor phase. The rest of the equations are for calculating

the molar volume and the fugacity coefficient of component i in the mixture for all components in the liquid and vapor phase.

The set of equations listed in Fig. 5 are solved for the vapor–liquid equilibrium properties using the simultaneous method. The various constants and variables in the set of equations are listed in Fig. 5. There are three ways to solve the equations, that is, to solve for either vapor–liquid equilibrium temperature, pressure or vapor fraction. All three ways are solved and described by Gidh [9]. Here, only the vapor–liquid equilibrium temperature calculation is described.

Degrees of freedom analysis on the equations and variables listed in Fig. 5 determines that $(n + 3)$ variables need to be specified to calculate the vapor–liquid equilibrium temperature. For these degrees of freedom, the overall composition of all the n number of components in the mixture must be specified and must add up to one. Also the number of components in the system, n , must be specified. In addition to the overall composition and the number of components, if the pressure and vapor fraction of the system are also specified, then all the degrees of freedom are satisfied. The equations can be solved simultaneously in two ways: an iteration can be performed to solve for all the $(4n^2 + 17n + 14)$ unknown variables in the $(4n^2 + 17n + 14)$ equations, or the equations can be reduced algebraically to $(5n + 4)$ equations by eliminating dependent variables and then iterating on the remaining $(5n + 4)$ unknown variables (vapor–liquid equilibrium temperature, mole fractions of the liquid and vapor phases, and liquid and vapor molar volumes).

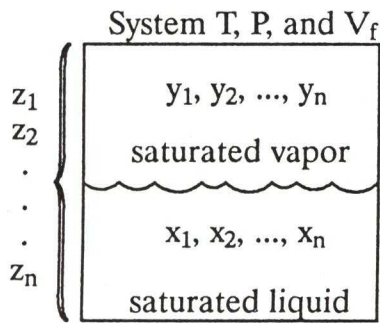
For a mixture containing only a pure component (i.e. $n = 1$ and $z_1 = 1.0$), the degrees of freedom reduces to two (vapor fraction and pressure). This fact is contrary to the value obtained by using the Gibbs–Duhem equation for a known pure component, which gives the degrees of freedom as one (pressure). The model in Fig. 5 breaks down for a known pure component because specifying the vapor fraction gives only the liquid fraction which is independent of specifying the pressure which gives only the temperature. Therefore, to determine the vapor–liquid equilibrium temperature of a known pure component, only pressure needs to be specified.

SOFTWARE DESIGN

Once the functional requirements are listed, the next step in the software development process is to design the software. Certain design objectives are set which are followed throughout the software development process. Since this software is to be used as a teaching/learning tool, the various objectives for the software design are as follows:

- to maximize readability, allowing the user to see equations that are used in performing calculations;

Equilibrium System



Assumptions

1. vapor-liquid equilibrium
2. all components appear in both phases.
3. ASPEN SRK E.O.S.

Mathematical Model

{ subscript i denotes n no. of equations;
subscripts ij denote n² no. of equations }

$$1 = V_f + L_f$$

$$z_i = V_f y_i + L_f x_i$$

$$y_i = K_i x_i$$

$$K_i = \frac{\hat{\phi}_{iL}}{\hat{\phi}_{iV}}$$

$$\sum_{i=1}^n x_i - \sum_{i=1}^n y_i = 0$$

$$a_{ci} = 0.42748 \frac{(RT_{ci})^2}{P_{ci}}$$

$$b_i = 0.08664 \frac{RT_{ci}}{P_{ci}}$$

$$m_i = 0.48508 + 1.55171 \omega_i - 0.15613 \omega_i^2$$

$$k_{ij} = k_{ij}^{(0)} + k_{ij}^{(1)}T + \frac{k_{ij}^{(2)}}{T}$$

$$l_{ij} = l_{ij}^{(0)} + l_{ij}^{(1)}T + \frac{l_{ij}^{(2)}}{T}$$

$$a_i = a_i a_{ci}$$

$$\alpha_i = \left[1 + m_i \left(1 - T_{ri}^{\frac{1}{2}} \right) - p_{1i}(1 - T_{ri}) (1 + p_{2i}T_{ri} + p_{3i}T_{ri}^2) \right]^2$$

Fig. 5. (Part 1 of 3)

$$d_i = 1 + \frac{m_i}{2} - p_{1i}(1 + p_{2i} + p_{3i})$$

$$c_i = 1 - \frac{1}{d_i}$$

$$a_i = e^{2c_i} (1 - r_n^{d_i})$$

$$T_n = \frac{T}{T_{ci}}$$

for supercritical
components

Molar volume of the saturated liquid

$$P = \frac{RT}{(V_L - b_L)} - \frac{a_L}{V_L(V_L + b_L)}$$

$$a_L = \sum_{i=1}^n \sum_{j=1}^n a_{ijL} x_i x_j$$

$$b_L = \sum_{i=1}^n b_i x_i$$

$$a_{ijL} = (a_i a_j)^{\frac{1}{2}} [1 - k_{ij} - l_{ij} (x_i - x_j)]$$

Molar volume of the saturated vapor

$$P = \frac{RT}{(V_V - b_V)} - \frac{a_V}{V_V(V_V + b_V)}$$

$$a_V = \sum_{i=1}^n \sum_{j=1}^n a_{ijV} y_i y_j$$

$$b_V = \sum_{i=1}^n b_i y_i$$

$$a_{ijV} = (a_i a_j)^{\frac{1}{2}} [1 - k_{ij} - l_{ij} (y_i - y_j)]$$

Fugacity coefficient of component i in mixture of the saturated liquid

$$\ln \hat{\phi}_{iL} = -\ln(Z_L - B_L) + (Z_L - 1)B'_{iL} - \frac{A_L}{B_L} (A'_{iL} - B'_{iL}) \ln \left(1 + \frac{B_L}{Z_L} \right)$$

$$A_L = a_L \frac{P}{(RT)^2}$$

Fig. 5. (Part 2 of 3)

$$B_L = b_L \frac{P}{RT}$$

$$Z_L = \frac{PV_L}{RT}$$

$$A'_{iL} = \frac{1}{a_L} \left[2 \sum_{j=1}^n a_j^{0.5} x_j - \sum_{j=1}^n \sum_{k=1}^n (a_j a_k)^{0.5} l_{jk} (\kappa_{ij} - x_j + x_k - \kappa_{ik}) \right]$$

$$B'_{iL} = \frac{b_i}{b_L}$$

Fugacity coefficient of component i in mixture of the saturated vapor

$$\ln \hat{\phi}_{iV} = -\ln(Z_V - B_V) + (Z_V - 1)B'_{iV} - \frac{A_V}{B_V}(A'_{iV} - B'_{iV}) \ln \left(1 + \frac{B_V}{Z_V} \right)$$

$$A_V = a_V \frac{P}{(RT)^2}$$

$$B_V = b_V \frac{P}{RT}$$

$$Z_V = \frac{PV_V}{RT}$$

$$A'_{iV} = \frac{1}{a_V} \left[2 \sum_{j=1}^n a_j^{0.5} y_j - \sum_{j=1}^n \sum_{k=1}^n (a_j a_k)^{0.5} l_{jk} (\kappa_{ij} - y_j + y_k - \kappa_{ik}) \right]$$

$$B'_{iV} = \frac{b_i}{b_V}$$

variables: $a_{ijL}, a_{ijV}, k_{ij}, l_{ij}, a_{ci}, a_i, b_i, B'_{iL}, B'_{iV}, A'_{iL}, A'_{iV}, z_i, x_i, y_i, K_i, \hat{\phi}_{iL}, \hat{\phi}_{iV}, \alpha_i, c_i, d_i, m_i, T_{ri}, Z_L, Z_V, B_L, B_V, A_L, A_V, V_L, V_V, b_L, b_V, a_L, a_V, V_f, L_f, T, P, n$

constants: $R, T_{ci}, P_{ci}, \omega_i, k_{ij}^{(0)}, k_{ij}^{(1)}, k_{ij}^{(2)}, l_{ij}^{(0)}, l_{ij}^{(1)}, l_{ij}^{(2)}, p_{1i}, p_{2i}, p_{3i}, \kappa_{ij}$

Degrees of Freedom analysis:

$$\text{no. of variables} = 4n^2 + 18n + 17$$

$$\text{no. of equations} = \frac{4n^2 + 17n + 14}{n + 3}$$

$$\text{D.O.F.} = n + 3$$

Fig. 5. Mathematical model for the vapor-liquid equilibrium calculations using the Aspen SRK equation of state.

- to maximize flexibility, allowing the user to experiment by modifying the equations;
- to be able to generate thermodynamic plots;
- to have a logical structure;
- to minimize the need for the user to memorize commands.

An effective teaching/learning tool should have the ability to allow the user to see the equations used during computation. Moreover these equations should be presented in an easy-to-comprehend form so that the user can understand the relationship between the various equations. Therefore, the equations should be sectioned on the basis of the calculations they perform. To enhance the creativity and learning of the user, the software design should be flexible enough to allow modification of the equations, to get different results, without recompiling the whole program. Moreover, the software design should support the capability of generating plots which can be used to relate the different results to give a good overview. The software should also possess the capability to mix graphics (plots), text (explanatory comments) and input (equations) to explain a certain topic. Minimization of the number of commands required to operate the software reduces the learning time for the user. If the software has a direct visual interface (e.g. icons, pull-down menus) then the need to memorize commands can be reduced.

To meet the design objectives set earlier, a dynamic 'textbook' format is essential. Mathematica has all the aforementioned capabilities which can be used to meet the design objectives for an effective teaching/learning tool. The software can be designed using the 'Notebook' capabilities of Mathematica currently available on Macintosh and NEXT computers. A 'Notebook' stores 'alive' information like graphics commands to generate plots and input commands to give results or textual information. The information in Mathematica 'Notebooks' is organized into units called cells. These cells can be grouped hierarchically, and can have different characteristics, depending on their contents and functions. Since Mathematica is an interpreter, input in the form of equations can be modified without the need for recompilation. Also, Mathematica on the Macintosh or NEXT computers uses the direct visual capabilities available on these computers.

Figure 6 shows an initial table of contents for the software. All the sections in the software are listed here in the order of usage, distinguished by their individual cell brackets on the right. The first section of the table of contents is used to define the system mixture. The various constants used in the thermodynamic calculations are given in this section. The second section is used to define the independent variables, e.g. temperature, pressure, composition and vapor fraction in the equations for the thermodynamic calculations. The remaining sections are used to calculate the various thermodynamic properties outlined earlier in this article.

Each major section shown in the initial table of contents is further subdivided into various subsections to enhance modularity and readability. Figure 7 shows the second-level table of contents in the 'Define the System Mixture' section. Each of these subsections are used to define a certain set of constants. For example, the 'Antoine Correlation Constants' subsection contains values of all the constants in the Antoine equations for the current system mixture, as illustrated in Fig. 8 for a binary mixture of hexane and octane. When the values for the constants are not available, default values are given with the provision for the user to change them.

Each section for calculating a thermodynamic property contains an 'Equations' subsection listing the necessary equations and a 'Results' subsection to generate the results in a predefined format. The section where a thermodynamic diagram is to be generated also contains a 'Diagram' subsection. Figure 9 shows the various subsections in the molar volume section. All the necessary equations used in the molar volume calculations are coded in the subsection 'Equations'. Results of the molar volume calculations are generated through the 'Results' subsection and the PVT diagram is generated by the 'PVT diagram' subsection. Some thermodynamic property calculations require results from other thermodynamic property calculations. The software is so designed that the equations generating the previously calculated results need not be repeated.

SOFTWARE IMPLEMENTATION

The implementation of the software is carried out in accordance with a top-down design approach. The software is sectioned, based on the various thermodynamic calculations to be performed as described earlier. The various sections, such as 'How to Use Mathematica Notebook', 'Define the System Mixture', 'Define the Independent Variables', at the uppermost level of the software are listed in Fig. 6.

The implementation of the various sections in the software uses the cell concept in the Macintosh notebook format. Each section has a group of cells containing text (header cell marked with \boxtimes) and related input commands. As a default, a hexane-octane mixture is considered and various constants are supplied in the software, and thermodynamic calculations are based on the Aspen SRK EOS as described earlier. The implementation of all the sections listed in Fig. 6 is given in Gidh [9] and some of the characteristic sections are described below.

Define the System Mixture

Before the user can perform any thermodynamic calculations, certain constants of a mixture need to be specified. These constants are defined for a default mixture of hexane-octane in the

Bucknell University Thermodynamics Teaching-Aid

By
Kedar Gidh
Chemical Engineering Department
Bucknell University
August 1991

- ☒ How to use Mathematica notebook (double click on the cell bracket to start →
- ☒ Define the System Mixture
- ☒ Define the Independent Variables
- ☒ Molar Volume
- ☒ Molar Enthalpy
- ☒ Molar Entropy
- ☒ Fugacity Coefficient of Component i in Mixture
- ☒ VLE Temperature (using Raoult's law)
- ☒ VLE Pressure (using Raoult's law)
- ☒ VLE Vapor Fraction (using Raoult's law)
- ☒ HXY diagram
- ☒ VLE Temperature (using ASPEN SRK equation of state)
- ☒ VLE Pressure (using ASPEN SRK equation of state)
- ☒ VLE Vapor Fraction (using ASPEN SRK equation of state)

Fig. 6. Initial table of contents showing various sections in the software.

'Define the System Mixture' section and categorized into subsections as listed in Fig. 7. As shown in Fig. 10, the general format of a subsection has a header cell (marked with ■) with text describing the overall cell's contents (outermost cell bracket) and an input cell containing definitions and explanatory comments, with text enclosed in

(*..*) brackets, and executable commands. As a convention, variable names ending with i denote vector variables and those ending with ij denote matrix variables.

All the subsections described above are implemented as initialization cells, i.e. the assignment of the values to the various variables is done auto-

■ Define the System Mixture	}}
■ Pure-component physical properties	}}
■ Pure-component polar parameters	}}
■ Mixture binary interaction parameters	}}
■ Enthalpy and Entropy constants	}}
■ Antoine Correlation constants	}}

Fig. 7. Table of contents showing the subsections in the 'Define the System Mixture' section.

■ Antoine Correlation constants	}}
VPa1i = { 4.7641224 10 ¹ , -1.2428626 10 ² }	}}
VPa2i = {-5.1832881 10 ³ , -1.5641240 10 ³ }	}}
VPa3i = {-3.8703409, -6.0739229 10 ¹ }	}}
VPa4i = {-1.1802620 10 ⁻³ , -8.6680807 10 ⁻² }	}}
VPa5i = {-4.6871710 2.6971140 10 ¹ }	}}
VPa6i = { }	}}
VPa7i = { 5., 2.};	}}

Fig. 8. Subsection 'Antoine Correlation Constants' containing various constants in Antoine equation.

■ Molar Volume	}}
■ Equations	}}
■ Results	}}
■ PVT diagram	}}

Fig. 9. Table of contents showing various subsections in the 'Molar Volume' section.

matically at the start of the program. If desired, the user may change these values while doing the thermodynamic calculations by simply editing the values and then executing that input cell. The various subsections in the 'Define the System Mixture' section are grouped together as an evaluation group, i.e. when any one of the subsections is executed by the user, all the other subsections are also automatically executed. This is done so that the user can edit one or more subsections and then execute all of them together at one time.

Define the independent variables

Degrees of freedom in thermodynamic calculations shown in the Functional Requirements section of this paper are satisfied by various independent variables. The next section in the software is for defining these independent variables. Default values are given which are automatically assigned to the independent variables at the start of the program, and which can be later changed by the user at any time.

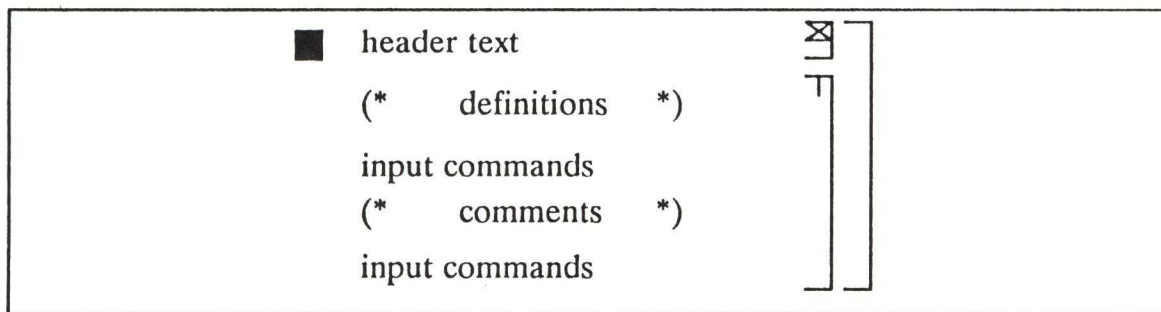


Fig. 10. Illustration of a subsection in 'Define the System Mixture' section.

Molar volume

Molar volume calculations are performed using the Aspen SRK EOS as described in the Functional Requirements section of this paper. The 'Equations' subsection consists of a header cell and two input cells. The first input cell begins with definitions followed by input commands. The necessary equations for molar volume calculations are implemented as functions, using ":=", so that these equations can also be used during other fluid property calculations, without repeating them. Double assignments are used so that results from equations in the form of functions can be used later without re-evaluating the equations.

The user can experiment with the equations in the first input cell but the second input cell is closed, to prevent the user from making any changes. Both of the input cells are also initialization cells so that the equations, in the form of functions, are read at the start of the program and can later be used at any time.

Since the equations in the 'Molar Volume' section are in the form of functions, the actual execution of these equations takes place in the reverse order, that is, the last equation calls on the equation above it which calls on the equation above it, and so on, until the first equation is called. When the first equation is called, it calculates the value of its defining variable which subsequently is used to calculate the value of the variable in the next equation and so on, until the value of the variable in the last equation is calculated.

Once the correct molar volume roots are generated, results are printed out in a formatted manner. The 'Results' subsection has a header cell and a closed input cell. After the heading and the independent variables are printed, the molar volume of the current system mixture and the corresponding compressibility factor are printed.

The third subsection in the molar volume calculation section is for generating a PVT diagram. This subsection has a header cell and two input cells. The first input cell calls the function *frhs* which is defined in the 'Equations' subsection. This input cell is closed. The second input cell uses function *PLOT* for generating the PVT diagram. The size of the plots generated can be changed dynamically using a mouse button. Also values of the

coordinates from the diagrams can be read using the mouse button.

VLE temperature (using Raoult's law)

As a first attempt to perform vapor-liquid equilibrium calculations, the simplified case of Raoult's law is implemented, as described earlier. Of the three vapor-liquid equilibrium calculations, the implementation of VLE temperature calculations is described here. The implementation of VLE pressure and vapor fraction calculations is similar and is described by Gidh [9]. All three vapor-liquid calculations are implemented in Gidh [9].

The 'Equations' subsection consists of a header cell and an input cell. In the input cell, the necessary equations for vapor-liquid equilibrium temperature calculations are implemented. To keep the execution of the three VLE calculations independent from each other, VLE temperature, pressure and vapor fraction are given variable names in lower case and only two out of these three variables are defined during any VLE calculation.

The VLEset of equations contains the necessary equations in symbolic form which have to be solved simultaneously. These equations have values for any constants and defined variables. Before the list of equations assigned to variable VLEset can be solved numerically, some initial estimates are generated. Function *FINDROOT* is then used to solve the VLEset of equations.

The 'TXY Diagram' subsection contains three input cells. In the first input cell, the coordinates for the saturated liquid and vapor curves are generated. The second input cell contains the commands for plotting the TXY diagram. The third input cell clears an assigned value. The first and third input cells are closed cells. All of the three input cells are grouped together as an evaluation group, i.e. when any one of the cells is executed by the user, all the other cells are also automatically executed.

VLE temperature (using Aspen SRK equation of state)

The 'VLE Temperature (using Aspen SRK equation of state)' section is divided into two subsections, namely, 'Equations' and 'Results'. The 'TXY diagram' section, using Aspen SRK equation

of state, is not implemented because the execution of a point calculation itself takes a considerable amount of time as described later in the Utilization section of this paper.

The 'Equations' subsection consists of a header cell and an input cell. In the input cell, the necessary equations for vapor-liquid equilibrium temperature calculations using Aspen SRK equation of state are implemented. The 'Results' subsection has a header cell and a closed input cell. After the heading and the independent variables are printed, the vapor-liquid equilibrium temperature, the mole fractions of the components in the liquid and vapor phases, and the molar volumes of the liquid and vapor phases are printed.

UTILIZATION

Once the software has been implemented, it is ready for testing. In this section, various aspects of the software are tested using different kinds of system mixtures. The testing procedure tries to determine the efficiency and the limitations of the Mathematica software in handling varied system mixtures, by calculating the various thermodynamic properties, and by generating the various thermodynamic diagrams.

The results obtained by using the Bucknell University Thermodynamic Teaching-Aid (BUTT), implemented in Mathematica, are com-

pared with a standard thermodynamics software package, Aspen Plus [4], for speed and accuracy. Aspen Plus is a process simulator, developed by Aspen Technologies, Inc., which is now in use and which has been successfully validated.

Test cases

The software should be tested for its capability to handle system mixtures having ideality/non-ideality, different number of components, different overall compositions, and condensible/non-condensable components. The various system mixtures selected as test cases are listed below:

- octane;
- hexane-octane;
- isopropanol-water;
- hexane-octane-nitrogen;
- isobutylene-butadiene-isobutane-butane;
- isobutylene-butadiene-isobutane-butane-butanol.

Hexane-octane is an ideal mixture, isobutylene-butadiene-isobutane-butane is a less ideal mixture, and isopropanol-water is a highly non-ideal mixture. Hexane-octane-nitrogen mixture contains a non-condensable component (nitrogen). Isobutylene-butadiene-isobutane-butane-butanol mixture contains four components with one in trace amount (butanol).

The Mathematica software BUTT is tested for its ability to perform fluid property calculations

Table 1. Molar volume calculation results

Mixture (overall comp. in parenthesis)	Indp. Variables P = 101.325kPa	Molar Volume (m ³ /kgmol)			Time (sec)	
		BUTT	ASPEN PLUS	% Diff.*	BUTT†	ASPEN PLUS‡
Octane(1)	T = 300K	0.19078	0.1915162	0.38	5	22
	T = 600K	48.6697	48.67410	0.01	6	18
Hexane(0.5) Octane(0.5)	T = 300K	0.169376	0.1707721	0.82	8	25
	T = 600K	48.8102	48.81110	0.00	10	26
Isopropanol(0.5) Water(0.5)	T = 300K	0.0575186	0.05735281	0.29	10	22
		0.0570434#	0.0568929#	0.26	10	20
	T = 600K	49.1056	49.11057	0.01	8	19
		49.0969#	49.10285#	0.01	10	19
Isobutylene(0.2) Butadiene(0.3) Isobutane(0.25) Butane(0.25)	T = 200K	0.0882373	0.0882463	0.01	41	21
	T = 600K	49.1229	49.12603	0.01	70	20
Isobutylene(0.2) Butadiene(0.3) Isobutane(0.25) Butane(0.24) Butanol(0.01)	T = 200K	0.0882342	0.0882463	0.01	85	25
	T = 600K	49.1214	49.12603	0.01	157	22

$$* \% \text{ Diff.} = \frac{\text{BUTT} - \text{Aspen Plus}}{\text{Aspen Plus}} \times 100$$

† Calculations performed on a Macintosh IIci, with Motorola 68030 chip having a clock speed of 25 MHz

‡ Calculations performed on an Apollo DN4500, with Motorola 68030 chip having a clock speed of 33 MHz.

Results obtained using binary interaction parameters.

(molar volume, molar enthalpy, molar entropy, and fugacity coefficient), vapor-liquid equilibrium calculations (temperature, pressure, and vapor fraction) using both Raoult's law and Aspen SRK equation of state, and to generate the related thermodynamic diagrams (PVT, PH, PS, P ϕ , TXY, PXY, and HXY). The fluid property calculations are performed at a subcritical temperature and a supercritical temperature. The software is also tested for its utilization of binary interaction parameters during various calculations.

All results obtained from the various test cases using BUTT are listed and compared with the results obtained on using Aspen Plus [9]. Here, only the results of molar volume, fugacity coefficient of component *i* in the mixture, and VLE temperature using Raoult's law and Aspen SRK equation of state are considered.

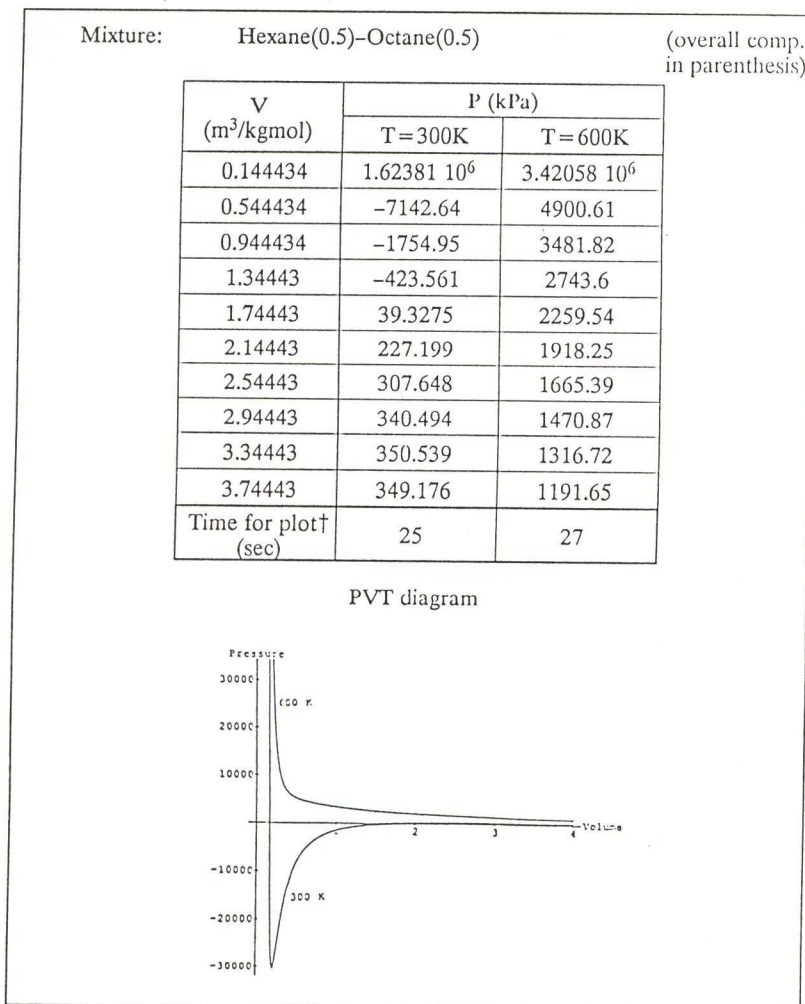
Molar volume

Table 1 shows the results of the molar volume calculations using various system mixtures at a subcritical temperature and a supercritical tem-

perature. The results from BUTT agree within 1% of the results obtained from Aspen Plus (using SYSOP3) [4]. The results from BUTT are obtained by solving the cubic equation of state for volume analytically [11], whereas the results from Aspen Plus are obtained by solving the cubic equation of state for volume numerically. Thus, the results from BUTT may have less round-off error, compared to the results from Aspen Plus.

The time taken by BUTT to perform molar volume calculations for one-component or two-component mixtures on a Macintosh IIfx, having a Motorola 68030 chip of clock speed 25 MHz and a Motorola 68882 co-processor [12], is observed to be less than that taken by Aspen Plus on an HP/Apollo DN4500, having a Motorola 68030 chip of clock speed 33 MHz and a Motorola 68882 co-processor. The two computer speeds are roughly identical. But for more than two component mixtures, the time taken by BUTT is more than that of Aspen Plus. It is also observed that the time taken by BUTT doubles as the number of components in the mixture is increased by one, for example, the

Table 2. PVT diagram and table for hexane-octane mixture



time taken to do molar volume calculation for a one-component mixture is around 5 s but for a two-component mixture is around 10 s. Thus BUTT is not efficient as a teaching/learning tool for mixtures having more than two components. Although Aspen Plus takes less execution time for calculations, it takes a long time (6 min) to generate a complete report file because the code has to be compiled and linked each time it is executed, and so Aspen Plus takes more time to give the results.

The PVT plots and tables for the various mixtures are shown by Gidh [9]. The PVT plot and table for hexane–octane mixture is shown in Table 2. Isotherms are plotted for a subcritical temperature and a supercritical temperature by varying the volume to calculate the values for pressure. Sample points for each isotherm are listed in the table. The time taken for generating each isotherm is also shown. It is observed that the time taken to generate an isotherm for a PVT diagram approximately doubles as the number of components in the mixture is increased by one [9].

Fugacity coefficient of component *i* in mixture

Table 3 shows the results of the fugacity coefficient using various system mixtures at a subcritical temperature and a supercritical temperature. The results agree within 6% of those obtained from Aspen Plus (using SYSOP3) in most cases. The difference between the results may be attributed to the different methods by which the molar volume calculations are performed, as described earlier, because molar volume is subsequently used in determining the fugacity coefficients.

The time taken by BUTT to perform fugacity coefficient calculations follows a trend similar to that described for the molar volume calculations and ranges from under 10 s for a one-component mixture to about 80 min in some cases for a five-component mixture. Fugacity coefficient calculations take longer than the molar volume calculations using BUTT, for the same system mixture, because more equations need to be solved for the fugacity coefficient calculations.

The $P\phi$ plots are generated for the mixture rather

Table 3. Fugacity coefficient of component *i* in mixture calculation results

Mixture (overall comp. in parenthesis)	Indp. Variables P= 101.325kPa	Fugacity Coefficient of component <i>i</i> in mixture			Time (sec)	
		BUTT	ASPEN PLUS	% Diff.*	BUTT†	ASPEN PLUS‡
Octane(1)	T = 300K	0.0201142	0.020532	2.04	6	22
	T = 600K	0.988649	0.9886	0.01	6	18
Hexane(0.5) Octane(0.5)	T = 300K	0.21049 0.0201164	0.2107 0.020537	0.10 2.05	32	25
	T = 600K	0.994065 0.988855	0.9939 0.9888	0.02 0.00	48	26
Isopropanol(0.5) Water(0.5)	T = 300K	0.106081 0.14956	0.081378 0.1408	30.35 6.22	33	22
		0.0991102# 0.0698906#	0.083146# 0.059204#	19.20 18.06	34	20
	T = 600K	0.99673 0.998085	0.9968 0.9980	0.01 0.01	41	19
		0.996569# 0.997896#	0.9967# 0.9977#	0.01 0.02	44	19
Isobutylene(0.2) Butadiene(0.3) Isobutane(0.25) Butane(0.25)	T = 200K	0.0262879 0.00735818 0.0383283	0.027085 0.0074039 0.040420	2.94 0.62 5.12	803	21
		0.0185401	0.019420	4.53		
		T = 600K	0.997894 0.997653 0.997917 0.997604	0.9978 0.9976 0.9979 0.9975	0.01 0.01 0.00 0.01	1478
	T = 200K	0.0263196 0.00730249 0.0385698 0.0185901 1.2089 10 ⁻⁶	0.027117 0.0073464 0.040681 0.019475 1.2775 10 ⁻⁶	2.94 0.60 5.19 9.54 5.36	2555	25
T = 600K		0.997895 0.997653 0.997917 0.997603 0.994712	0.9978 0.9976 0.9979 0.9975 0.9947	0.01 0.01 0.00 0.01 0.00	4977	22

change the assignment for variable phi from

```
phi = Exp[ Sum[ Zi[[i]] Log[ phi[[i]] ], (i, nc) ], ]
```

to

```
phi = phi[[i]]
```

for component i

than for the individual components because for multicomponent mixtures more than one plot would have to be generated. A user can generate a $P\phi$ plot for any desired component in a mixture by slightly modifying the existing code as shown above.

VLE temperature (using Raoult's law)

Table 4 shows the results of VLE temperature calculations using Raoult's law for various system mixtures. The results agree within 1% of those obtained from Aspen Plus (using SYSOP0). The results from BUTT are obtained by simultaneously solving the equations set for VLE temperature and mole fractions in the two phases, whereas the results from Aspen Plus are obtained by sequentially solving the equations set. The simultaneous solution is obtained using function **FINDROOT** which uses the Newton-Raphson method for convergence [10]. For the system mixtures containing a non-condensable component, the mole fraction of the non-condensable component in the liquid phase is almost equal to zero which agrees with the physical behavior of the non-condensable component.

During the generation of the results from BUTT, it is observed that the solution to the equations set depends largely on the initial estimates. For the system mixture containing a single component, octane, an initial estimate away from the correct solution leads to an incorrect solution. But when the initial estimates are close to the correct solution, values converge to the correct solution. Also, the time for convergence reduces when the initial estimates are close to the correct solution, so the time taken to converge using initial estimates close to the correct solution for a one-component mixture is about 6 s. For system mixtures containing more than two components, the equations set has to be reduced algebraically to get the correct solution, because the function **FINDROOT** is not able to handle a large number of equations. The time taken to converge using a reduced set of VLE equations for a three-component mixture is about 13 s. Thus the time indicated for calculating the VLE temperature using the various system mixtures is not a true representative of the complexity of the calculations involved.

The TXY plots and tables for the binary mixtures are shown by Gidh [9]. TXY plots are not shown for other mixtures because TXY plots cannot be generated for non-binary mixtures. The TXY plot and table for hexane-octane mixture is shown in Table 5. The TXY plot is generated at a fixed pressure by varying the overall composition from zero to one to calculate the VLE temperature at vapor fractions equal to zero and one.

VLE temperature (using Aspen SRK equation of state)

Table 6 shows the results of the VLE temperature calculations using Aspen SRK equations of state for various system mixtures. The results agree within 1% of those obtained from Aspen Plus (using SYSOP3). The results from BUTT are obtained by simultaneously solving the equations set for VLE temperature and mole fractions in the two phases, whereas the results from Aspen Plus are obtained by sequentially solving the equations set. The simultaneous solution is obtained using function **FINDROOT** which uses the Newton-Raphson method for convergence [10].

During the generation of the results from BUTT, it is observed that the solution to the equations set is extremely sensitive to the initial estimates. Correct solutions can only be achieved if the initial estimates are almost the same as the correct solution. This fact is because the reduced equations set for VLE calculations using Aspen SRK equation of state is very unstable due to the complex nature of the reduced equations. The time taken to converge using a reduced set of VLE equations for a two-component mixture is more than 3 min. For system mixtures containing more than two components, the equations set does not converge to the correct solution in spite of giving the correct solution as the initial estimates because of memory overload problems.

In general, the time taken to do a VLE calculation is less using Raoult's law than using the Aspen SRK equation of state, for the same mixture, as summarized in Table 7. VLE calculations using Raoult's law take less time because the equations in its VLE equations set are less complex.

CONCLUSIONS

Some of the desired characteristics in a thermodynamics teaching/learning tool are the ability to generate plots, to view the equations and to modify them easily, to operate the software using a minimum set of commands, and for the software to be portable. A thermodynamics teaching/learning tool has been developed using Mathematica which has the above mentioned features.

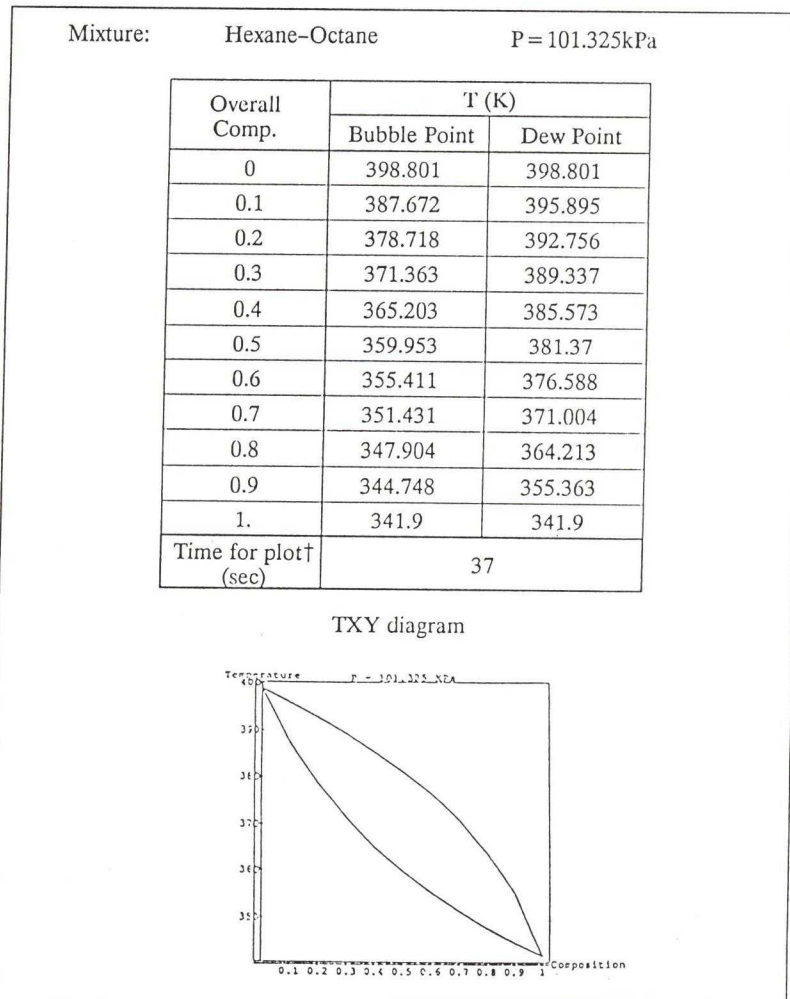
The implementation of the software allows for the calculations of molar volume, molar enthalpy, molar entropy, fugacity coefficient of component i in the mixture, vapor-liquid equilibrium temperature, pressure, and vapor fraction (using Raoult's law and Aspen Soave-Redlich-Kwong equation of state) and the generation of PVT, PH, PS, $P\phi$, TXY, PXY and HXY diagrams.

Certain conclusions can be reached based on the implementation and utilization of the software

Table 4. VLE temperature calculation results, using Raoult's law

Mixture (overall comp. in parenthesis)	Indp. Variables P = 101.325kPa	VLE Temperature (K) & mole fracs. in liq. and vap. phases			Time (sec)	
		BUTT	ASPEN PLUS	% Diff.*	BUTT†	ASPEN PLUS‡
Octane(1)	$V_f = 0.5$	398.801	398.7996	0.00	6	21
		1.	1.	0.00		
		1.	1.	0.00		
Hexane(0.5) Octane(0.5)	$V_f = 0.5$	371.175	371.2518	0.02	15	29
		0.302816	0.30273	0.03		
		0.697184	0.69727	0.01		
		0.697184	0.69727	0.01		
		0.302816	0.30273	0.03		
Isopropanol(0.5) Water(0.5)	$V_f = 0.5$	364.058	364.1683	0.03	13	23
		0.41664	0.41802	0.33		
		0.58336	0.58198	0.24		
		0.58336	0.58198	0.24		
		0.41664	0.41802	0.33		
Hexane(0.45) Octane(0.45) Nitrogen(0.1)	$V_f = 0.5$	362.341	362.4289	0.02	13	25
		0.319132	0.31888	0.08		
		0.680868	0.68101	0.02		
		0.	$0.113 \cdot 10^{-3}$	0.00		
		0.580868	0.58112	0.04		
		0.219132	0.21899	0.07		
		0.2	0.19989	0.06		

Table 5. TXY diagram and table for hexane-octane mixture



which uses Mathematica in its development as a teaching/learning tool. These are:

- Using the simultaneous approach in performing vapor–liquid equilibrium calculations improves the accuracy of the results and the readability of the equations used, but, makes the solution highly unstable for a large equations set.
- A large VLE equations set can be reduced algebraically to generate a solution, but by doing so the readability of the equations is reduced.
- Mathematica is convenient to write the code for the software but is not efficient in performing the calculations because of the large amounts of time it takes for large mixtures.
- The generation of fluid property thermodynamics plots (except PVT diagrams) is difficult for mixtures containing more than two components because the time taken to perform a point calculation is itself very high.
- The time for a VLE plot using Aspen SRK EOS would be approximately 20 min (based on the time for a point calculation) thus making it less effective for teaching/learning purposes.

- Thermodynamic calculations can be performed in less than 60 s on a Macintosh IICI for a system mixture containing not more than three components, which is a reasonable response time for the teaching/learning process.
- The time taken for a fluid property calculation using BUTT doubles as the number of components in the mixture is increased by one.
- The use of binary interaction parameters increases the accuracy of the results but takes a longer time than the results generated without using binary interaction parameters.
- The solution to the VLE equations set is extremely sensitive to the initial estimates. For a quick solution the initial estimates must be close to the correct solution. It is difficult to get solution for VLE calculations (using Aspen SRK EOS) for mixtures containing more than two components in spite of providing close initial estimates, because of memory limitations.

Overall, Mathematica is successful only to a limited extent in developing a thermodynamic teaching/learning tool using its available functions.

Table 6. VLE temperature calculation results, using Aspen SRK equation of state

Mixture (overall comp. in parenthesis)	Indp. Variables P = 101.325kPa	VLE Temperature (K) & mole fracs. in liq. and vap. phases			Time (sec)	
		BUTT	ASPEN PLUS	% Diff.*	BUTT†	ASPEN PLUS‡
Octane(1)	V _f =0	398.766	398.5479	0.05	27	22
		1.	1.	0.00		
		1.	1.	0.00		
	V _f =0.5	398.766	398.5452	0.06	27	20
		1.	1.	0.00		
		1.	1.	0.00		
	V _f =1	398.766	398.5480	0.05	27	23
		1.	1.	0.00		
		1.	1.	0.00		
Hexane(0.5) Octane(0.5)	V _f =0	360.602	360.6944	0.03	250	22
		0.5	0.5	0.00		
		0.5	0.5	0.00		
		0.84359	0.84142	0.26		
		0.15641	0.15858	1.37		
	V _f =0.5	371.493	371.4342	0.02	175	23
		0.310341	0.31185	0.48		
		0.689659	0.68815	0.22		
		0.689659	0.68815	0.22		
		0.310341	0.31185	0.48		
	V _f =1	381.234	381.0517	0.05	190	24
		0.179071	0.18091	1.02		
		0.820929	0.81909	0.22		
		0.5	0.5	0.00		
		0.5	0.5	0.00		
Isopropanol(0.5) Water(0.5)	V _f =0	344.262	346.5875	0.67	194	22
		0.5	0.5	0.00		
		0.5	0.5	0.00		
		0.444933	0.41753	6.56		
		0.555067	0.58247	4.70		

Table 6 (cont.)

Mixture (overall comp. in parenthesis)	Indp. Variables P= 101.325kPa	VLE Temperature (K) & mole fracs. in liq. and vap. phases			Time (sec)		
		BUTT	ASPEN PLUS	% Diff.*	BUTT†	ASPEN PLUS‡	
Isopropanol(0.5) Water(0.5)	$V_f=0$	351.682#	353.9145#	0.63	657	21	
		0.5#	0.5#	0.00			
		0.5#	0.5#	0.00			
		0.568381#	0.59507#	4.49			
	$V_f=0.5$	0.431619#	0.40493#	6.59	256	25	
		344.287	346.7051	0.70			
		0.552674	0.57379	3.68			
		0.447326	0.42621	4.96			
		$V_f=1$	0.552674	0.57379	3.68	611	23
			351.924#	354.2478#	0.66		
			0.459991#	0.43216#	6.44		
			0.540009#	0.56784#	4.90		
	$V_f=1$		0.540009#	0.56784#	4.90	245	26
			0.552674#	0.43216#	6.44		
			345.165	348.1815	0.87		
			0.688577	0.71886	4.21		
		$V_f=1$	0.311423	0.28114	10.77	615	28
			0.5	0.5	0.00		
			0.5	0.5	0.00		
			352.415#	355.7774#	6.95		
	0.397159#		0.14901#	166.53			
0.602841#	0.85099#		29.16				
0.5#	0.5#		0.00				
0.5#	0.5#		0.00				

Table 7. Time taken to perform VLE calculations, using Raoult's law and Aspen SRK EOS.

Mixture (overall comp. in parenthesis)	VLE property	Time (sec) using BUTT	
		Raoult's law	ASPEN SRK EOS
Hexane(0.5) Octane(0.5)	Temperature	15	175 - 250
	Pressure	10	65 - 85
	Vapor Fraction	6	60 - 70
Isopropanol(0.5) Water(0.5)	Temperature	13	194 - 256
	Pressure	9	71 - 87
	Vapor Fraction	4	94 - 116

This fact may be attributed to the functional capability of Mathematica which makes it useful for performing only specific calculations and not

useful for performing calculations in a more general sense.

REFERENCES

1. S. Wolfram, Mathematica, version 1.2, computer software, Wolfram Research Inc. (1988).
2. J. D. Seader, W. D. Seider and A. C. Pauls, Flowtran, version 2, computer software, Monsanto (1977).
3. Calorimetry and thermodynamics, computer software, Educational Materials and Equipment (1983).
4. Aspen Plus, Version 8, computer software, Aspen Technologies (1988).

5. A. K. Shyu, D. H. Chen and C. L. Yaws, A transport and thermodynamic properties package for personal computers, *CACHE News* no. 24, April (1986).
6. M. E. Hanyak, Bucknell University Thermodynamics System, computer software, Bucknell University, Lewisburg, Pennsylvania (1987).
7. F. A. D. Silva, L. A. Baez and E. A. Muller, A user-friendly program for vapor-liquid equilibrium, *Chem. Engng Ed.*, **XXV** (1), 24-32 (1991).
8. J. Schwartzentruer, H. Renon and S. Watanasiri, *K*-values for non-ideal systems: an easier way, *Chem. Engng.*, March, 118-124 (1990).
9. K. Gidh, Bucknell University thermodynamics teaching aid, M.S. thesis, Bucknell University, Lewisburg, Pennsylvania (1991).
10. C. J. King, *Separation Processes*, 2nd edn. 781-784, McGraw-Hill, New York (1980).
11. W. H. Beyer, *CRC Standard Mathematical Tables*, 26th edn, p. 9, CRC Press, Inc., Florida (1981).
12. Datapro Research Group, *Datapro Reports on Microcomputers*, **1**, p. CM11-060MM-107, McGraw-Hill Inc., New Jersey (1991).

Kedar Gidh is an applications programmer with Computer-Aided Engineering Design Center at Bucknell University. Mr Gidh received a MSChE from Bucknell University in 1991. His current interests encompass computer-aided design in chemical engineering. He is an associate member of AIChE and Sigma Xi.

Michael E. Hanyak received his BS at Penn State, MS at Carnegie-Mellon and Ph.D. at the University of Pennsylvania. After working at Air Products for three years on developing a steady-state process simulator for cryogenic systems, Dr Hanyak moved to Bucknell in 1974. His chemical engineering interests are in computer-aided design and thermodynamics. He is a member of AIChE and Sigma Xi.