



Simplified apparatus for vapor-liquid equilibrium
by Trudy Ann Scholten

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

Knowledge of the equilibrium behavior of liquid and vapor phases is necessary for proper sizing and design of distillation systems. A novel vapor-liquid equilibrium still was designed to be easy to construct, operate, and clean, while yielding thermodynamically consistent data. The still was constructed and tested using two binary systems. These systems were chosen based on their thermodynamic characteristics, p-Xylene/m-xylene at 635 mmHg, with a temperature range of 129.5°C to 133.0°C, was chosen to represent a thermodynamically ideal system. Benzene/isopropyl alcohol at 640 mmHg, with a temperature range of 67.5°C to 77.9°C, was chosen to represent a nonideal, azeotropic system. Data collected for the p-xylene/m-xylene system was seen to be ideal. Three forms of the Gibbs-Duhem equation were used to evaluate the thermodynamic consistency of the data collected for the benzene/isopropyl alcohol system. The results of these tests indicate that the still design produces consistent data. Wilson parameters obtained from experimental data were seen to be slightly superior to those obtained from literature data.

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APPROVAL

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This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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Latin Symbols

a_{12}, a_{21}	Temperature-dependent Wilson parameters
A, B, C	Antoine coefficients
c	Constant of integration
G_{12}, G_{21}	Wilson parameters
h^{α}	Enthalpy of liquid phase
h^{β}	Enthalpy of vapor phase
Δh	Change in enthalpy
P	Total pressure
P°	Vapor pressure
p_i	Partial pressure of component i
Q	Function for combining binary system data
R	Universal gas constant
T	Absolute temperature (K)
t	Temperature ($^{\circ}\text{C}$)
v^{α}	Specific molar volume of liquid phase
v^{β}	Specific molar volume of vapor phase
x_i	Liquid fraction of component i
y_i	Vapor fraction of component i

Greek Symbols

γ_i	Activity coefficient of component i
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Subscripts

p	<i>p</i> -xylene
b	benzene

ABSTRACT

Knowledge of the equilibrium behavior of liquid and vapor phases is necessary for proper sizing and design of distillation systems. A novel vapor-liquid equilibrium still was designed to be easy to construct, operate, and clean, while yielding thermodynamically consistent data. The still was constructed and tested using two binary systems. These systems were chosen based on their thermodynamic characteristics. *p*-Xylene/*m*-xylene at 635 mmHg, with a temperature range of 129.5°C to 133.0°C, was chosen to represent a thermodynamically ideal system. Benzene/isopropyl alcohol at 640 mmHg, with a temperature range of 67.5°C to 77.9°C, was chosen to represent a non-ideal, azeotropic system. Data collected for the *p*-xylene/*m*-xylene system was seen to be ideal. Three forms of the Gibbs-Duhem equation were used to evaluate the thermodynamic consistency of the data collected for the benzene/isopropyl alcohol system. The results of these tests indicate that the still design produces consistent data. Wilson parameters obtained from experimental data were seen to be slightly superior to those obtained from literature data.

INTRODUCTION

Knowledge of the equilibrium behavior of liquid and vapor phases is necessary for proper sizing and design of distillation systems [1]. For example, it is absolutely essential to be aware of the presence of any azeotropes or pinch points, as normal rectification cannot efficiently separate the components in these systems [2]. Very few systems exist that may be described accurately with purely theoretical calculations. The remaining systems must be evaluated experimentally. In addition, in extractive and azeotropic distillation, the addition of a solvent or azeotropic agent can dramatically change the equilibrium behavior of the system. In these cases, some systems are susceptible to polymerization. Therefore, it would be especially useful to have a still to obtain vapor-liquid-equilibrium data that is easy to construct, operate, and clean, yet yields consistent data.

Purpose of Research

The purpose of this research was to create a novel VLE still that produces accurate data, is inexpensive to construct, as well as easy to operate and clean. Many existing stills

were evaluated and most favorable aspects combined in the creation of this still. Once this design was achieved, the still was then constructed and tested for thermodynamic consistency, using two systems, *p*-xylene/*m*-xylene and benzene/isopropyl alcohol. These systems were chosen based on their thermodynamic characteristics. The system *p*-xylene/*m*-xylene was chosen to represent a thermodynamically ideal system, while benzene/isopropyl alcohol was chosen to represent a non-ideal, azeotropic system.

Methods of Obtaining Experimental VLE Data

Equilibrium relations may be determined experimentally in several ways. These may be classified as follows [3]:

- 1) Distillation method
- 2) Static method
- 3) Dew and Bubble point method
- 4) Flow method
- 5) Circulation method

The distillation method involves distilling a small amount from a large charge in a boiling flask. By using a large charge, the liquid fraction remains essentially constant, thus approximating an equilibrium condition. Although very simple, this method is seldom used, as it requires a large amount of initial liquid charge and is subject to considerable error [3].

The static method charges a binary mixture to a closed, heated chamber and mixes until equilibrium is established between the liquid and vapor phases. Since small changes in pressure or volume can have significant effects on the system, it is very difficult to

remove samples for analysis without disturbing equilibrium. This method is generally used only at high pressures, since at low to moderate pressures there are easier methods to remove accurate samples.

Using the dew and bubble point method, the dew and bubble point pressures of a mixture of known composition are measured, yielding a pair of points for each composition. Given enough pairs of this type, a vapor (dew point) curve and a liquid (bubble point) curve may be drawn by connecting these points, yielding a P-x-y diagram. An example of this type of graph is shown in Figure 1. This method is generally only applied to light (low molecular weight) hydrocarbons.

The flow method continuously feeds a steady stream of known composition to an equilibrium chamber where it is heated to boiling. After the liquid and vapor streams exiting the equilibrium chamber reach steady state, as evidenced by their temperature and pressure remaining constant, samples are taken and analyzed. This method may yield very precise results, but requires fairly complicated equipment. Further drawbacks include the possibility of long equilibration times and large liquid volume requirements.

Finally, the circulation method is the most widely used method. It is the basis of the experimental still described later in this paper. In the circulation method, vapors coming off a boiling mixture in the liquid chamber are condensed, and this condensate is returned to the liquid chamber, creating a continuous cycle (see Figure 2) [3]. A pseudo-equilibrium steady state is eventually achieved, indicated by the temperature and pressure remaining constant.

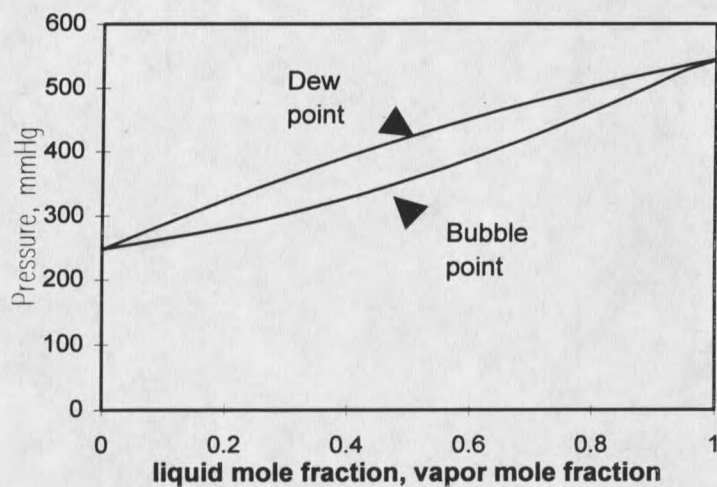


Figure 1: Sample pressure-liquid mole fraction-vapor mole fraction diagram ethanol/propanol, 70°C [16].

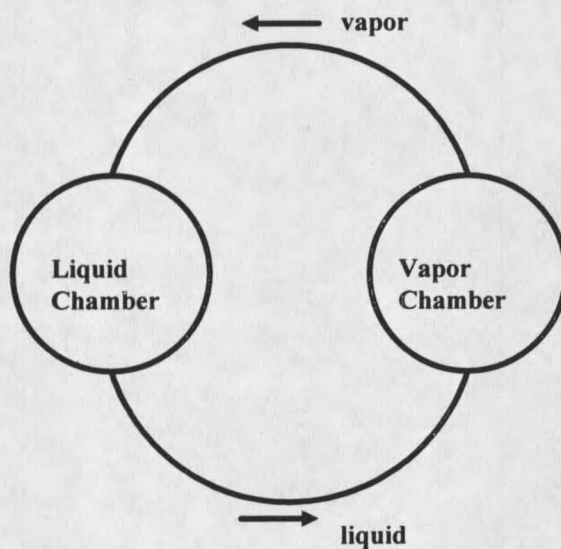


Figure 2: Schematic of circulation method for vapor-liquid equilibrium measurement[3]

Circulation-Type Stills

The first circulation-type vapor-liquid equilibrium (VLE) still to be used successfully was the Othmer still shown in Figure 3 [4]. Operation of the Othmer still begins with a liquid charge heated to boiling in chamber A. Vapors coming off this liquid travel through the vapor tube, past the thermowell, to the condenser. Condensate is collected below the condenser in chamber B, and returned to the boiling liquid via the connecting tube. This design is still widely used today. However, in its unmodified form, the Othmer still has several potential sources of error. The only temperature measurement is of the vapor directly above the liquid. This may be inaccurate, due to condensation on the thermowell. The still contains a fairly large vapor space, and partial condensation may occur on the walls of this vapor space, resulting in more than one theoretical stage. This may lead to incorrect vapor samples, since the vapor composition measured may be a mixture of the vapor coming off the liquid in the flask and the vapor coming off the condensate on the walls. No mechanical mixing of the boiling liquid exists, creating the possibility of concentration gradients in the liquid, possibly producing inaccurate liquid samples. Another concern about the accuracy of the Othmer still is the possibility of mixing between the liquid phase and the returning condensate in the sampling loop if liquid levels are not adjusted correctly. Finally, the amount of condensate required implies a long equilibration time for accurate results.

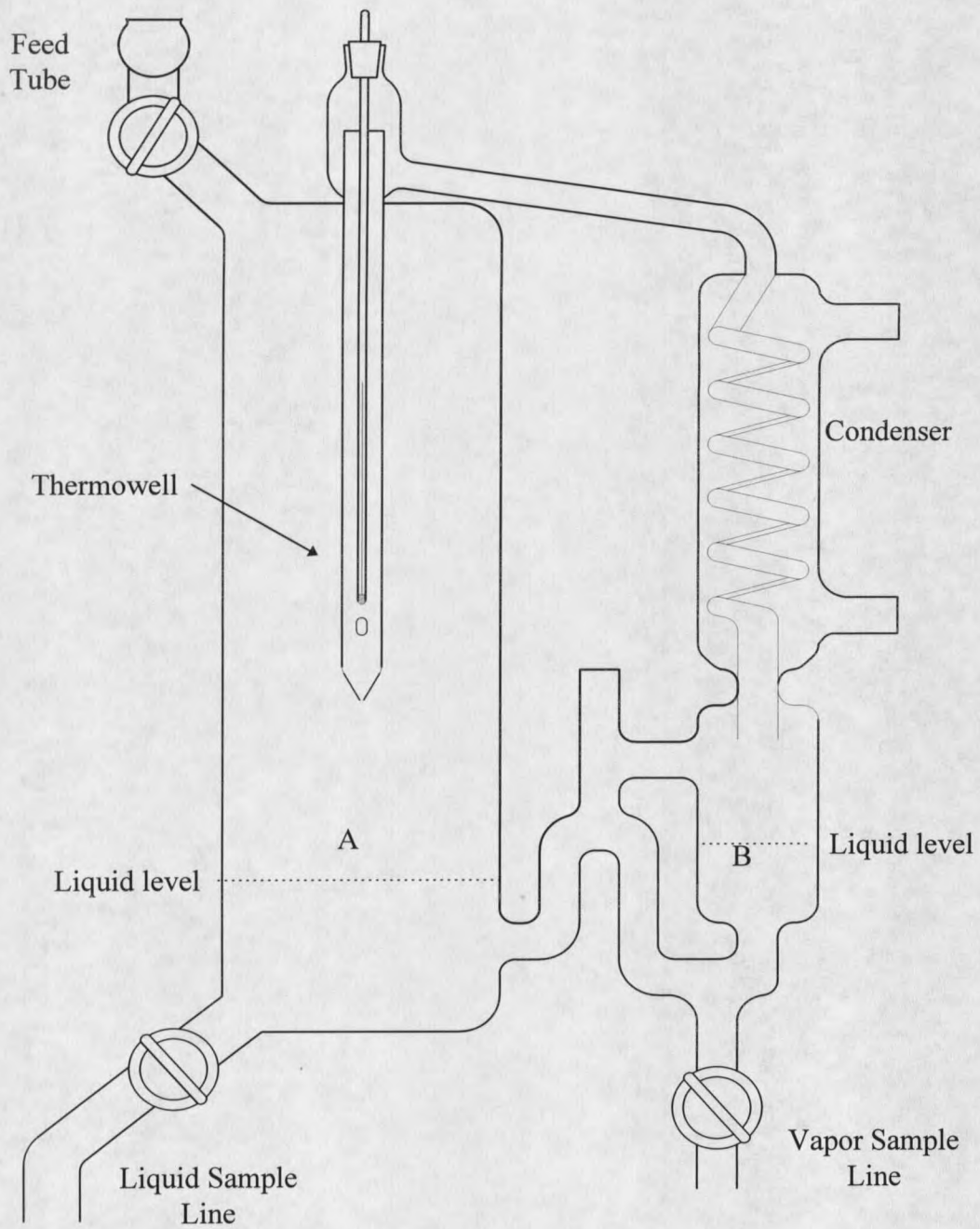


Figure 3: Othmer VLE still [4].

A number of alternative designs are also in use today. Possibly the most common of these is the Stage and Muller still shown in Figure 4 [5], which has been produced commercially. Although this still is generally considered to be quite accurate, it is a fairly complicated design. In this design, liquid is boiled in chamber A. A mixture of vapor and entrained liquid rises through P to the vapor space, V. The vapor space is surrounded by an evacuated jacket, intended to reduce condensation on the walls. The liquid and vapor phases are separated in the vapor space, and returned to A. The two solenoid actuators control the glass ball valves. These valves control the flow path of the returning streams. Liquid samples are collected in chamber E, while vapor condensate samples are collected in chamber F. The number of small tubes in the still result in a difficult cleaning problem. This is considered to be a major drawback of this type of still.

The Kortüm still (Figure 5) is a modification of the Othmer still [3]. The liquid is heated in chamber A by circulating fluid in the jacket of the chamber, as well as by a platinum resistance heater in the liquid. Vapor leaves the top of chamber A and is condensed as it flows towards chamber B. The funnel N is positionable, and can be placed such that liquid flows directly back to chamber A, or into chamber C for sampling. Liquid samples are taken through the capillary tube V, fitted with a rubber bulb. This design has the advantage of being able to take vapor samples from chamber C without interrupting the circulation. Drawbacks of this design include inaccurate temperature measurement, complicated construction, and the possibility of flashing part of the liquid sample during removal from the boiling flask.

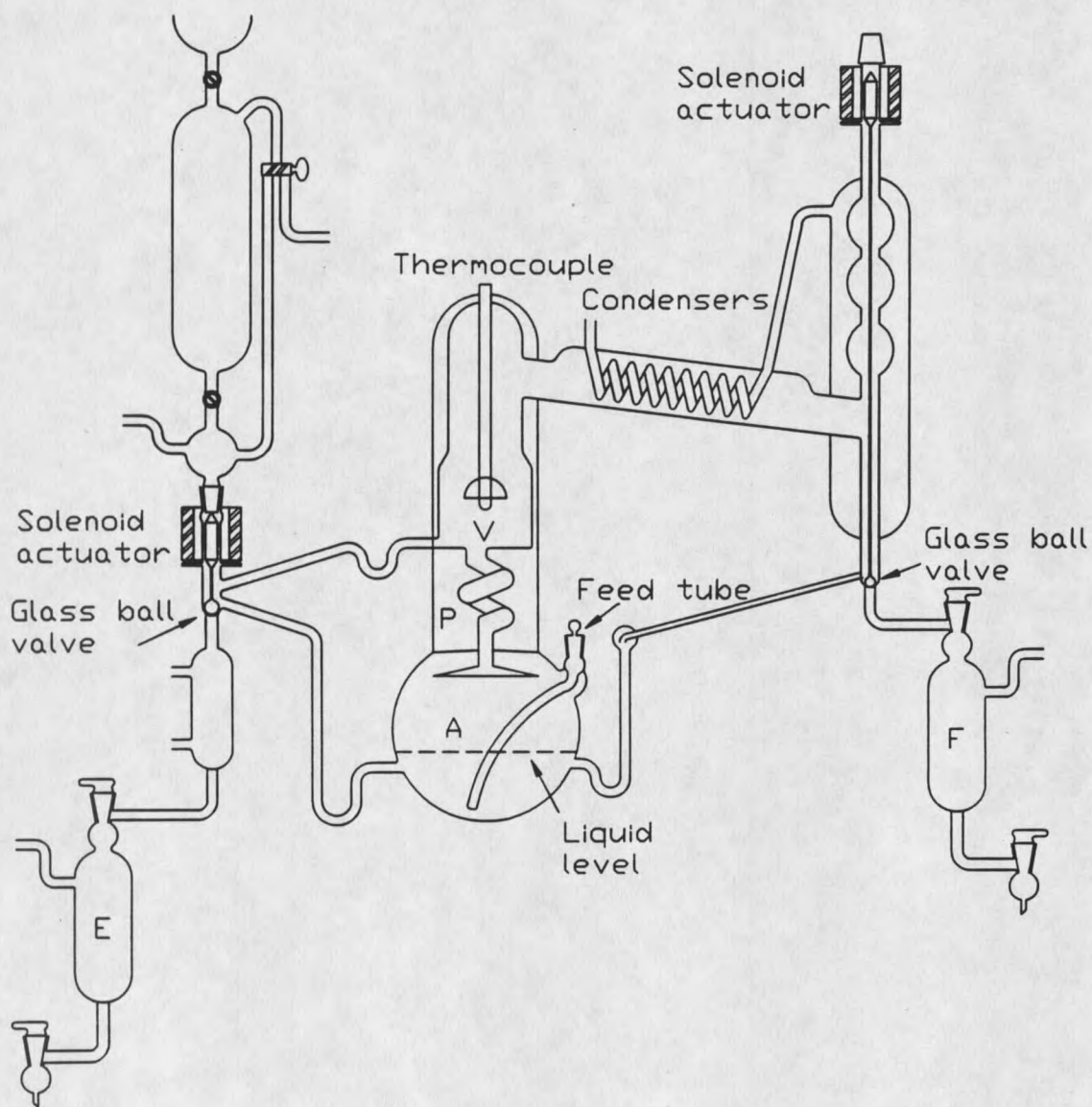


Figure 4: Stage-Müller VLE still [5].

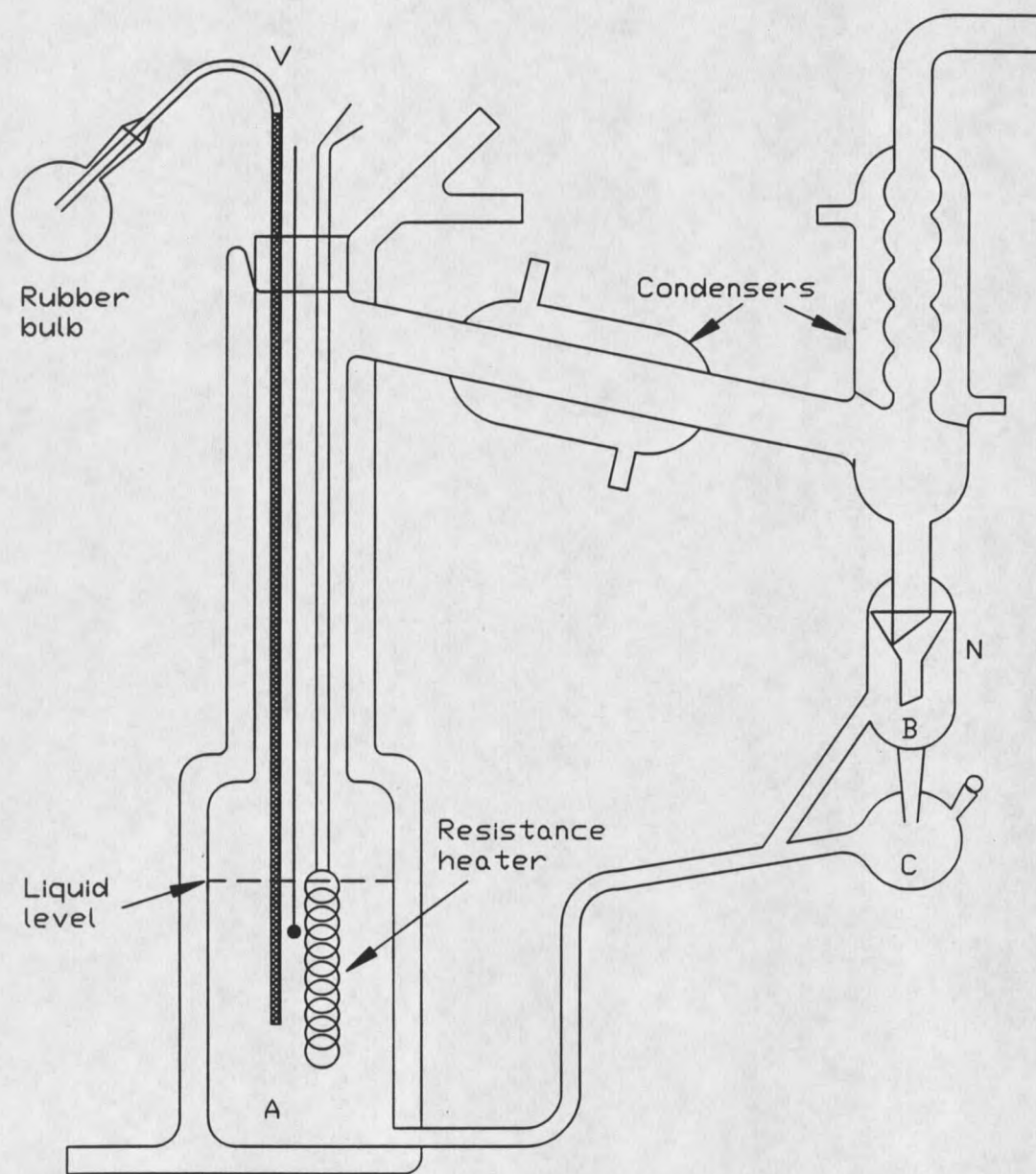


Figure 5: Kortüm VLE still [3].

The Jones still, shown in Figure 6 [3], is a fairly uncomplicated design. The liquid chamber A is heated by electrical wire wrapped around the vessel. This heating continues to the start of the condenser, where vapors are cooled for collection in receiver B. The condensate is completely vaporized in section V by electrical wire wrapped around the glass tube. The vaporized condensate is then returned to the liquid chamber where it is bubbled through the liquid sample. The bubbling vapor provides the only mixing in this chamber. This design yields very precise results [3], and is easily constructed. However, operation of this still can be difficult. Heating rates must be adjusted such that sufficient vapor circulates to ensure adequate mixing, while keeping this circulation below the maximum capacity of the vaporizer (V). Exceeding this capacity results in liquid holdup in the vapor return line.

Figure 7 illustrates the Williams still [3], a specialized design for use at low pressures (0.1 to 1 mmHg). In this design, liquid is heated in vessel A, which is insulated to reduce heat loss. The vapors are condensed and collected in tube B. The desired pressure is measured and maintained through the opening at M. The accuracy of this still is reported to be quite good [3]. Disadvantages of this design include the lack of any stirring mechanism in vessel A, the lack of any temperature measurement, and the absence of any method for liquid sampling.

The final still design discussed here is the Fowler-Norris still (Figure 8) [3]. Liquid is boiled in chamber A with an internal heater H, and a mixture of the liquid and vapor rises through P. From P, the mixture enters the equilibrium chamber R. The mix-

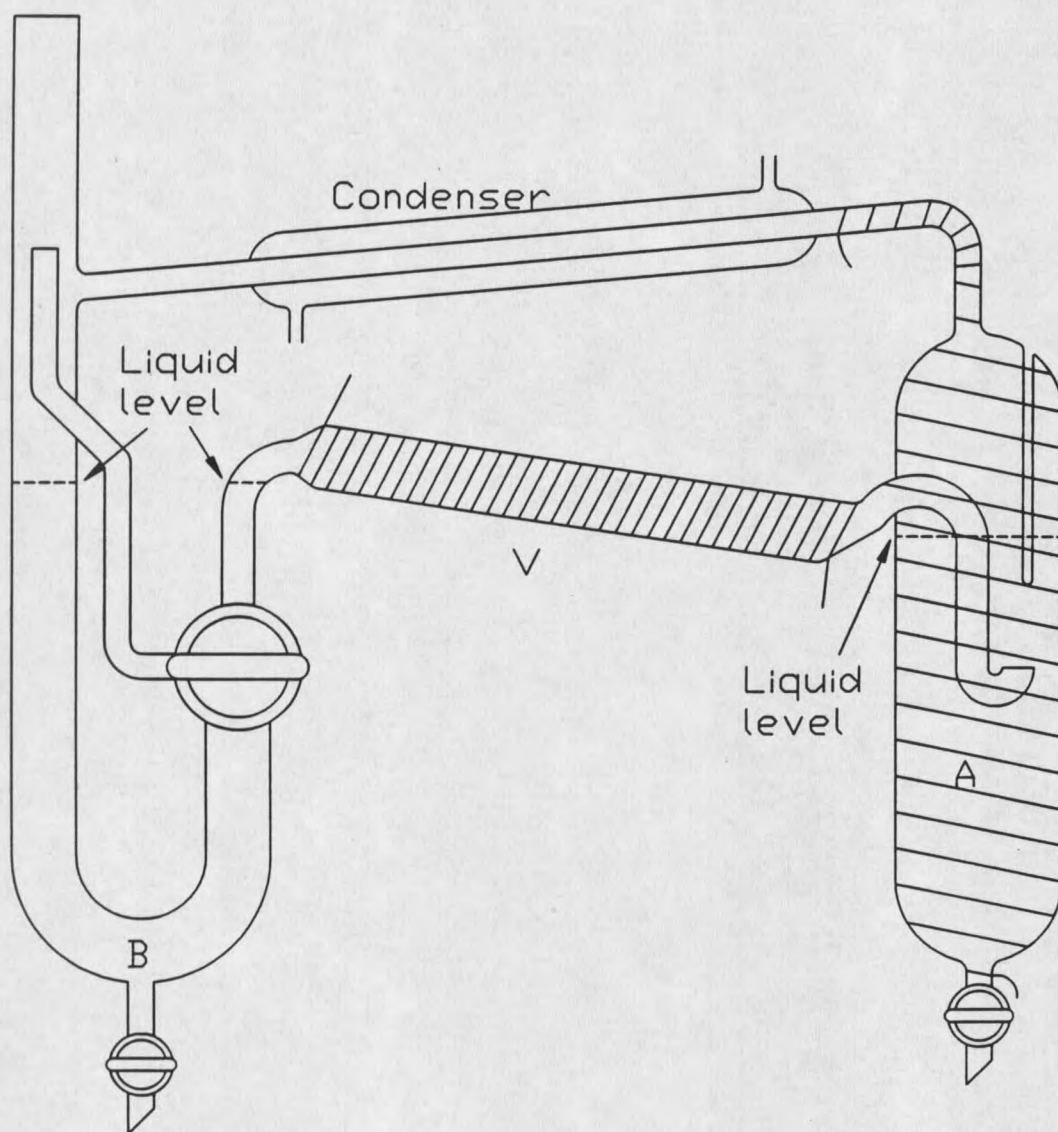


Figure 6: Jones VLE still [3].

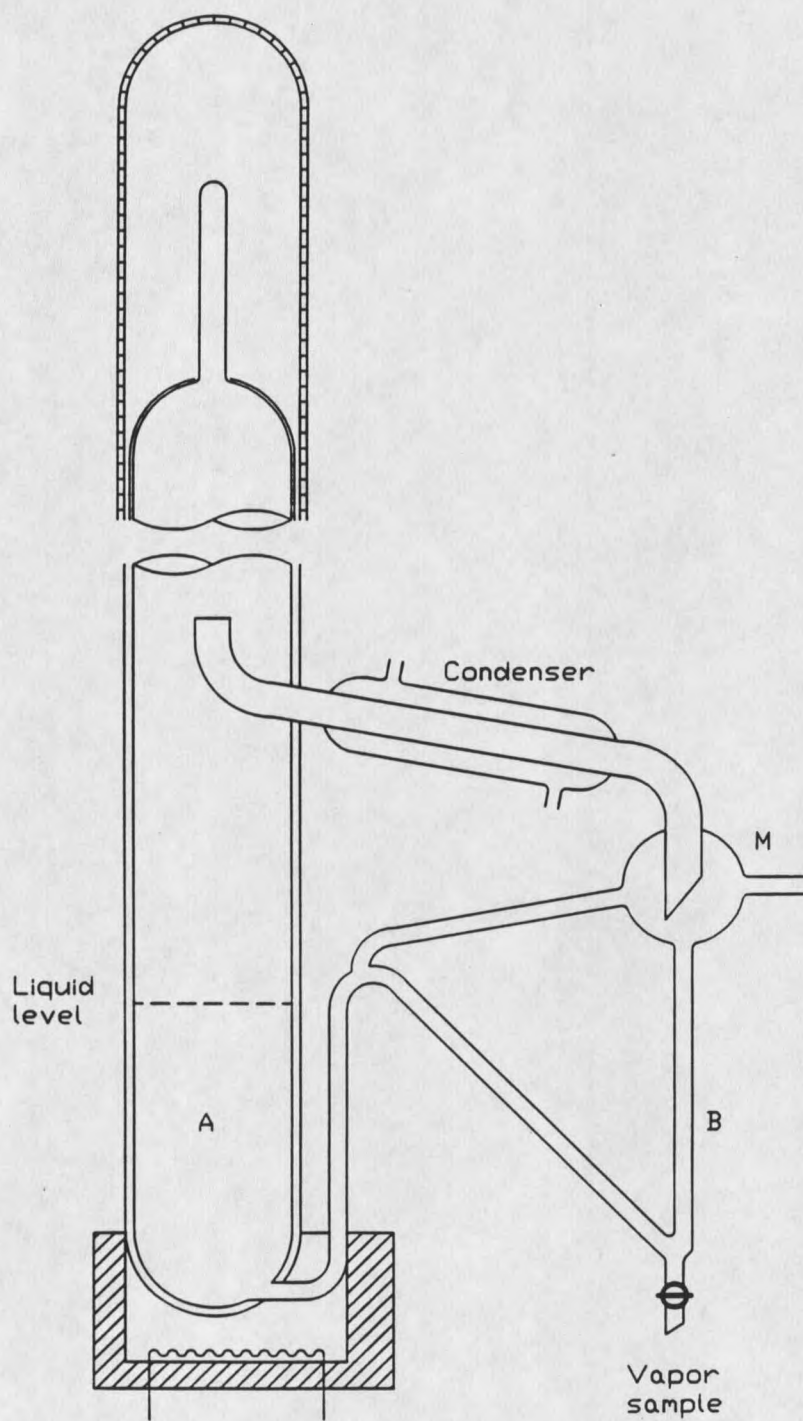


Figure 7: Williams VLE still [3].

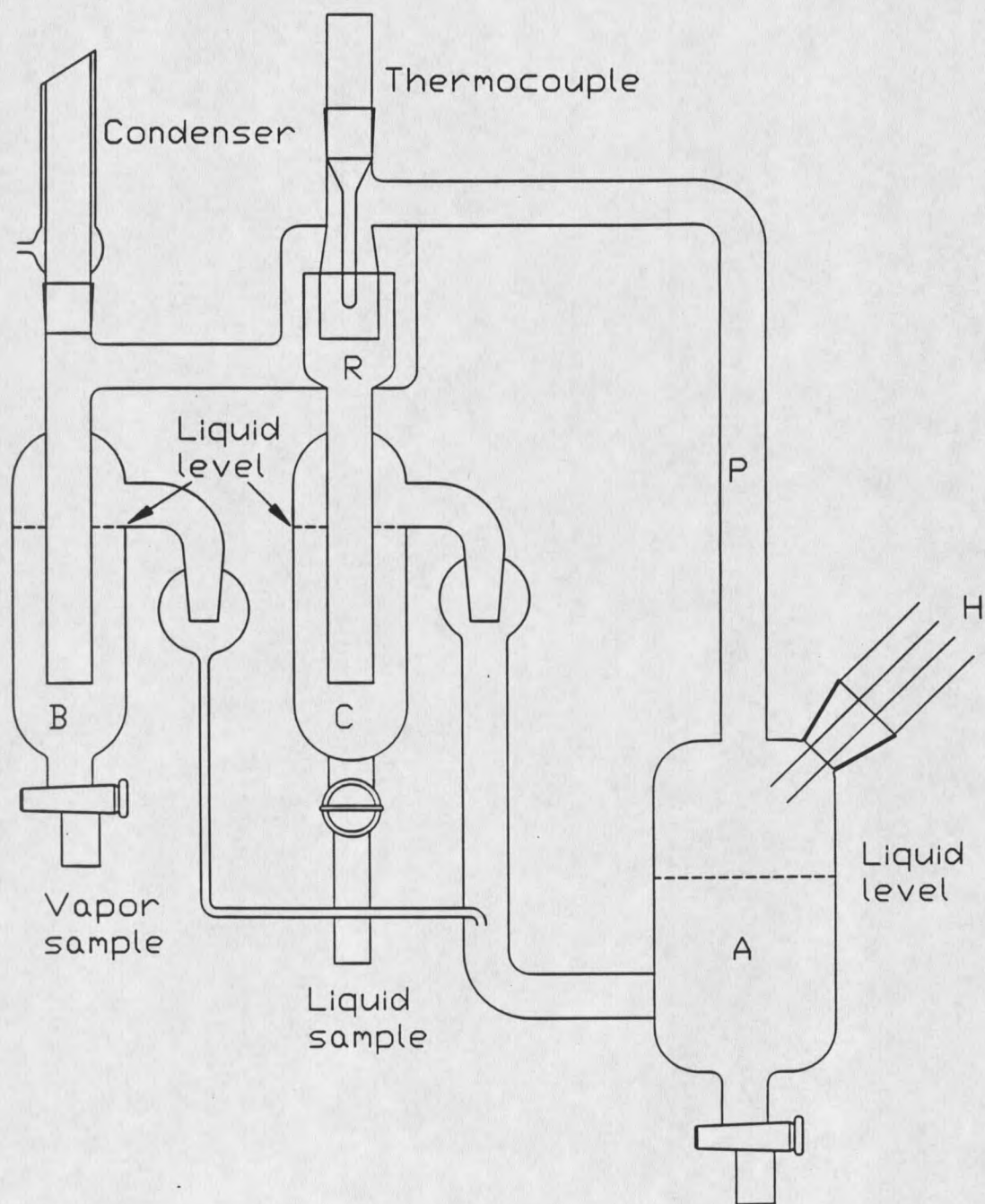


Figure 8: Fowler-Norris VLE still [3]

ture is then separated and the liquid flows down to chamber C. The vapor flows to the condenser, and the condensate is collected in chamber B. As these chambers fill, the overflow is recycled back to chamber A. Although operation of this still is not complicated, a long time is required to reach equilibrium. Advantages of this design include the precise measurement of liquid temperature, as well as sampling of truly equilibrium liquid.

Many other stills have been proposed, but are not discussed in detail here. These include those proposed by Hess, et al [6], Hiaki, et al [7], Raal, et al [8], Seker, et al [9], and Zemp, et al [10]. Most of these are relatively complicated designs that are actually modifications of the stills discussed here. Table 1 provides a short summary of these stills, as well as those discussed previously. Included on the table are advantages and disadvantages of each still, as well approximate equilibration times, where available.

Table 1: Advantages and disadvantages of various VLE still designs (adapted from Hala, et al[3])

Still	Advantages	Disadvantages	Approximate Equilibration Time
Othmer	simple to construct and operate	inaccurate temperature measurement, possibility of temperature gradients and ineffective mixing, data not entirely consistent	30-60 min.
Stage-Müller	precise, remove sample during circulation, commercially available	complicated construction and operation, difficult cleaning	Not Available
Kortum	remove sample during circulation	measurement of temperature not accurate, complicated construction and operation	30-60 min.
Jones	relatively precise	operation difficult	15-40 min.
Williams	simple construction and operation	no temperature measurement, no liquid sample	Not Available
Fowler-Norris	simple operation, sampling of true equilibrium liquid, precise measurement of boiling point	long period to attain steady state	2-3 hours
Hess	simple operation, high pressure operation possible	complicated construction, no mixing of liquid	45-60 min.
Hiaki	no contamination of samples, isothermal operation	complicated construction, difficult cleaning	Not available
Raal	stirring of condensate, accurate vapor temperature measurement, adiabatic operation	complicated construction, difficult cleaning, long equilibration time	1-2 hours
Seker	simple construction, can be modified for high pressure operation	temperatures must be closely adjusted, cleaning difficult	45-75 min.
Zemp	recirculation of both phases, accurate temperature measurement, isothermal or isobaric operation	difficult construction and operation	Not Available

THERMODYNAMICS

Evaluating the reliability and accuracy of a vapor-liquid equilibrium still requires an understanding of the thermodynamics of solutions. The equations used to describe multicomponent systems may be used to verify the consistency of experimental data, thus providing a measuring tool for comparing stills.

For a single component, two phase system, the Clapeyron equation establishes a relation among temperature, pressure, volume change, and enthalpy change at equilibrium [11]:

$$\frac{dP}{dT} = \frac{h^{\alpha} - h^{\beta}}{(v^{\alpha} - v^{\beta})T} \quad (1)$$

where P is pressure, T is temperature, h is enthalpy, v is specific molar volume, α specifies the liquid phase, and β specifies the vapor phase. For a system in which the vapor specific molar volume (v^{β}) is much larger than the liquid specific molar volume (v^{α}), this equation can be simplified, assuming ideal gas behavior, to the Clausius-Clapeyron equation [11]:

$$\frac{dP^{\circ}}{dT} = \frac{P^{\circ} \Delta h}{RT^2} \quad (2)$$

where P° is vapor pressure and R is the universal gas constant. If this equation is then integrated with the assumption of constant Δh , it becomes:

$$\ln P^\circ = c - \frac{\Delta h}{RT} \quad (3)$$

where c is an integration constant. For ranges of temperature over which Δh can be considered constant, this equation may be used to evaluate vapor pressure data. Over this range, a plot of $\ln P^\circ$ versus $1/T$ should be linear. The Antoine equation is a modification of this, customized for individual compounds:

$$\log P^\circ = A - \frac{B}{C+t} \quad (4)$$

A , B , and C are empirical constants, tabulated in the literature for numerous organic and inorganic compounds [12,13].

For an ideal system, the relationship between composition (expressed as mole fractions, x and y for liquid and vapor phases respectively), pressure, and vapor pressure (shown above to be a function of temperature) is as follows:

$$p_i = Py_i = P_i^\circ x_i \quad (5)$$

where p_i is the partial pressure of component i . The activity coefficient, γ , is a correction factor that is used to correct for the non-ideal behavior of systems. At low pressures,

$$p_i = Py_i = P_i^\circ x_i \gamma_i \quad (6)$$

The Gibbs-Duhem equation provides a mathematical condition for equilibrium, valid at constant temperature and pressure [11].

$$\left[\sum x_i d \ln \gamma_i = 0 \right]_{T,P} \quad (7)$$

This equation must be true if equilibrium is established. It also provides a basis for thermodynamic consistency tests of vapor-liquid equilibrium data.

The first test inspired by this equation is a point-by-point graphical test. In terms of the activity coefficient, the Gibbs-Duhem equation may be expressed:

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} = 0 \quad (8)$$

This test is performed by plotting the natural log of the activity coefficients versus x_1 , and determining a slope for each curve at each point [11]. Figure 9 shows a typical plot of this type. For a detailed example of this method, see Appendix A.

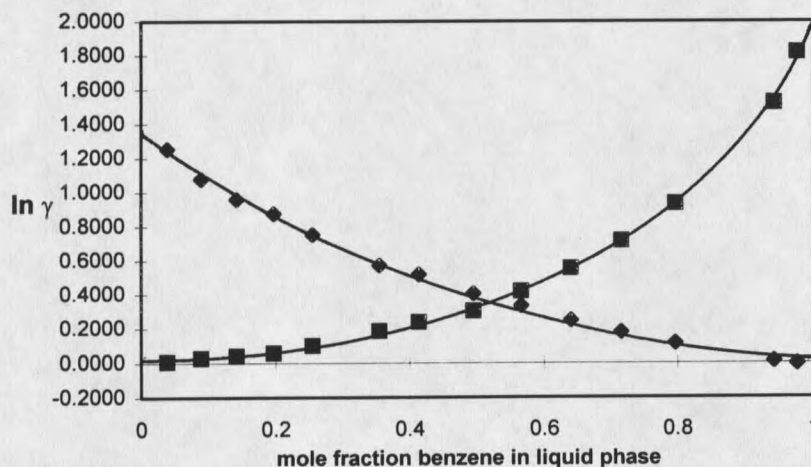


Figure 9: Consistency test plot using activity coefficients, benzene (1)/isopropyl alcohol (2) [16]

A similar test may be performed without calculating activity coefficients [11,14].

For a binary system at low pressures, the Gibbs-Duhem equation may be written:

$$\frac{x_1}{p_1} \frac{dp_1}{dx_1} + \frac{x_2}{p_2} \frac{dp_2}{dx_1} = 0 \quad (9)$$

This test is performed as the last test, plotting partial pressure versus x_1 . Figure 10 shows a plot of this variety: Appendix B details the test method.

It is often more desirable to test a set of data rather than each individual point. This may be accomplished through the use of an objective function Q , defined as [11]:

$$Q = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (10)$$

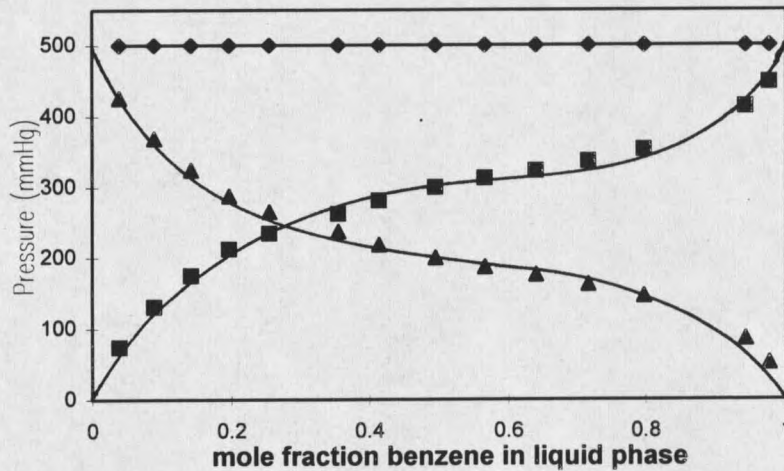


Figure 10: Consistency test plot using partial pressures, benzene (1)/isopropyl alcohol (2) [16].

Differentiating equation 10 with respect to x_1 at constant T and P gives:

$$\frac{dQ}{dx_1} = x_1 \frac{d \ln \gamma_1}{dx_1} + \ln \gamma_1 + x_2 \frac{d \ln \gamma_2}{dx_1} + \ln \gamma_2 \frac{dx_2}{dx_1} \quad (11)$$

From the Gibbs-Duhem equation (equation 5) and the relation between x_1 and x_2 , this equation may be simplified to:

$$dQ = \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1 \quad (12)$$

If this result is integrated from $x_1=0$ to $x_1=1$, the result is:

$$0 = \int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 \quad (13)$$

This test is performed by plotting $\ln(\gamma_1/\gamma_2)$ versus x_1 and comparing positive and negative areas of the plot (Figure 11). Ideally, thermodynamically consistent data will yield equal positive and negative areas. This method has however, been shown to be imperfect [15]. Appendix C details the method used.

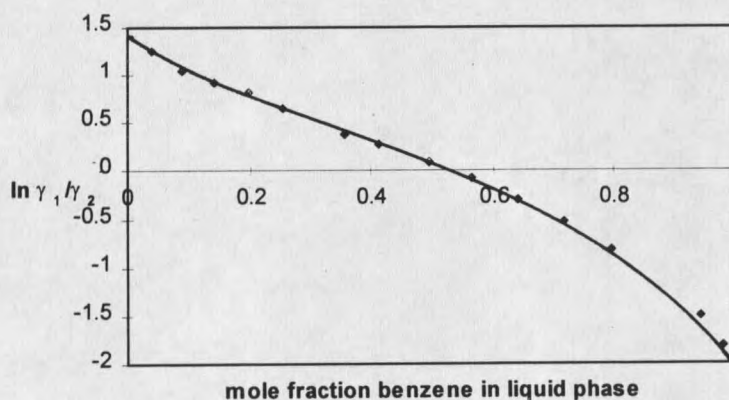


Figure 11: Area consistency test plot using activity coefficients, benzene(1)/isopropyl alcohol (2) [16].

The Wilson equation is used to correlate experimental data [11]. The Wilson equation was developed through the consideration of molecular behavior, and unlike other equations of this type, includes temperature dependence. Since the data collected here is not isothermal, the Wilson equation was considered to be the best option because of the inherent temperature dependence. The Wilson equation is an empirical model that satisfies the Gibbs-Duhem equation and allows the researcher to relate x and γ using empirically derived values, G_{12} , G_{21} , a_{12} , and a_{21} :

$$\begin{aligned}\ln \gamma_1 &= -\ln(x_1 + x_2 G_{12}) + x_2 \left(\frac{G_{12}}{x_1 + x_2 G_{12}} - \frac{G_{21}}{x_2 + x_1 G_{21}} \right) \\ \ln \gamma_2 &= -\ln(x_2 + x_1 G_{21}) - x_1 \left(\frac{G_{12}}{x_1 + x_2 G_{12}} - \frac{G_{21}}{x_2 + x_1 G_{21}} \right) \\ G_{12} &= \frac{v_2}{v_1} \exp\left(-\frac{a_{12}}{RT}\right) \\ G_{21} &= \frac{v_1}{v_2} \exp\left(-\frac{a_{21}}{RT}\right)\end{aligned}\tag{14}$$

where v_1 and v_2 are liquid specific molar volumes of the pure components at the absolute temperature T . G_{12} and G_{21} may be solved for directly with isothermal data, while solving first for a_{12} and a_{21} accounts for temperature variations. Hirata et al [16] tested four computational techniques for optimizing the Wilson parameters, including:

- 1) non-linear least squares
- 2) gradient search
- 3) pattern search
- 4) complex search

ChemCAD[®], a commercial process simulation software package, was used here to calculate temperature-dependent Wilson parameters (a_{12} and a_{21}), as well as for determination of liquid specific molar volumes (v_1 and v_2). ChemCAD[®] uses a pattern search to optimize Wilson parameters.

EXPERIMENTAL STILL DESIGN

The purpose of this research was to create a novel VLE still that produces accurate data, and is inexpensive to construct as well as easy to operate and clean. Many existing stills were evaluated and the favorable aspects combined in the creation of this new still. Figure 12 shows the still design produced by this research. The liquid chamber and vapor space are constructed of pyrex glass, the vapor space adapter from the liquid chamber to the condenser being the only custom piece. Using commercially available glassware for all pieces except the vapor space adapter minimizes cost. The liquid chamber is a 500 milliliter round-bottomed flask with four necks, each a 24/40 ground glass connection. The modularity of the design allows for easy assembly, operation, and cleaning. For difficult cleaning situations, such as polymerization of the liquid, it is relatively inexpensive to simply replace the flask. The liquid phase is mixed using a magnetic stir bar, or for more viscous systems, an overhead stirrer. During operation, the liquid chamber is immersed in a constant-temperature oil bath, kept at a temperature slightly above that of the boiling liquid. The vapor space is wrapped in electrical heat tape and insulation. The vapors in this space are heated to approximately three to five degrees above the liquid

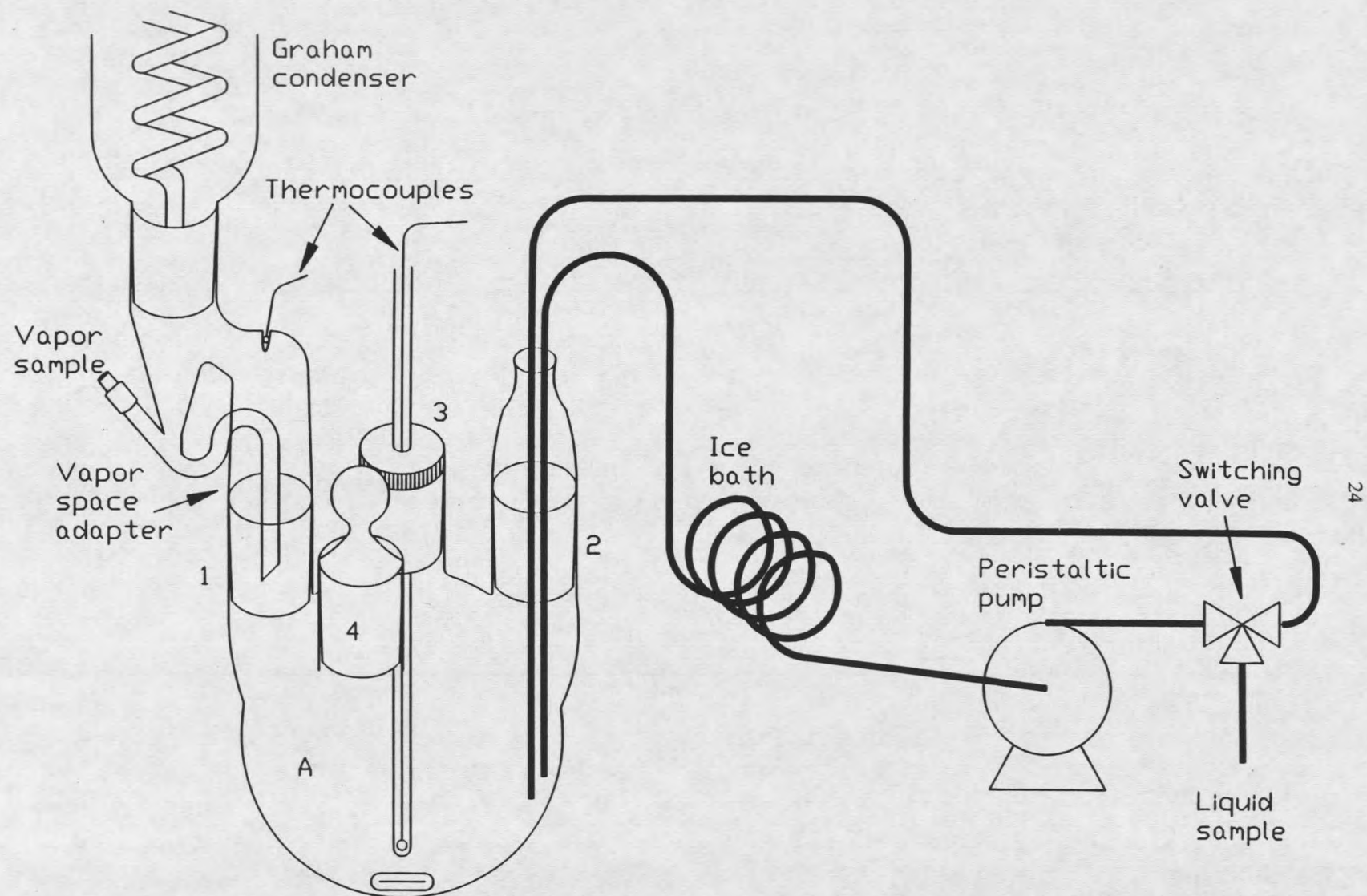


Figure 12. Experimental design for VLE still.

temperature to avoid condensation on the walls of the vapor space adapter. All ground-glass joints are fitted with Teflon[®] sleeves to ensure good seals and to prevent freezing of the joints.

The vapor space adapter attaches directly to the round-bottomed flask at the first side neck (1) of the round bottomed flask (A). This adapter includes a side arm, extending from the condensate loop, fitted with a rubber septum for sampling the condensate. The condensate collects in the bottom portion of the "s"-shaped tube, which is constructed of thick-walled six millimeter pyrex glass tubing. In addition to allowing sample withdrawal without disrupting equilibrium, this design minimizes the amount of condensate holdup. Therefore, this reduces the time necessary to reach equilibrium. The condensate flows through this loop back to the flask. The end of the tube is positioned to prevent contact with the flask walls. This minimizes the possibility of vaporization of the condensate and the creation of a second distillation stage.

For these experiments, a Graham condenser with cooling fluid at 4°C was used to ensure complete condensation of the vapors. This type of condenser consists of a glass coil in a jacket. Cooling fluid circulates shell side, while the vapors are condensed tube side, in the coil. The condenser is connected above the vapor space adapter.

A liquid sample loop attaches to the second position (2) on the round-bottomed flask. The loop is constructed of 1/16" 316 stainless steel and Viton[®] tubing. The liquid line passes through an ice bath immediately after exiting the liquid chamber (A), to ensure minimal damage to the Viton[®] tubing or valve due to heat or solvation. This also

minimizes sample loss to evaporation. Cooling of this liquid does not cause any composition changes, since it is not in contact with any other phase. Fluid is pumped through this line by a peristaltic pump (Masterflex® L/S variable-speed drive). Use of this type of pump decreases the risk of contamination, since there is no direct contact between the fluid and the pump head. A small section of Viton® tubing replaces the stainless steel tubing through the pump head. Immediately after the pump, the liquid passes through a switching valve (Rheodyne® model number 7030). When the switching valve is set in the "run" position, the liquid circulates through the sampling line and returns to the liquid chamber (A). In the "sample" position, the liquid is diverted to a second tube, from which a sample may be collected.

The third neck on the flask is occupied by the thermowell. A Teflon® adapter ensures a good seal on this neck. The thermocouple used here, as well as in the vapor space, is a type K thermocouple manufactured by Omega Engineering. Temperatures are read from a 10-channel display device, also manufactured by Omega Engineering (model number MDSS41-TC-GN).

The remaining neck is used for a glass stopper or an overhead stirrer, if required. When an overhead stirrer is used, it is placed in the center neck (3), and the thermowell in the fourth neck (4). If magnetic stirring is used, the thermowell is placed in the center position, while a glass stopper is placed in the remaining side position (4). This stopper may be used for easy addition of liquid to the flask. When the stopper is not present, liquid may be added by briefly removing either the thermowell or the liquid sample loop.

EXPERIMENTAL PROCEDURES

Two different types of experiments were performed. The first was a timed test, intended to determine the amount of time necessary for equilibrium to be established. The second was to collect vapor and liquid compositions at a series of different points.

The timed test began with placing a charge of approximately 200 milliliters in the round bottomed flask. The charge contained a mixture of the two components in the system (benzene/isopropyl alcohol or *p*-xylene/*m*-xylene). The still was assembled and submerged in a hot oil bath as far as possible without the neck tops being under oil. Once the liquid in the still was heated to reflux, timing began. Vapor samples were collected every five minutes from the start of refluxing to 30 minutes, then every ten minutes until two hours had elapsed. Liquid samples were not collected during this experiment, since no significant change in liquid composition occurs.

The second experiment began with a charge of about 100 milliliters of a pure component being placed in the flask. Again the still was assembled and submerged in the hot oil bath. The pure component was heated and allowed to reflux for approximately 20 minutes. Temperature and pressure were recorded. These measurements were then used to

evaluate the accuracy of the thermocouple. Table 2 shows these measurements, as well as purity and source of the components that were used. After these measurements were taken, small amounts of the second component in the system were added through the stoppered neck on the flask. The mixture was allowed to reflux for at least one hour, to ensure equilibrium had been attained. After equilibrium was established, samples were collected. Vapor samples were obtained by inserting a syringe needle through the septum on the vapor space adapter and removing a small amount of condensate (approximately 0.25 milliliter). Minimal flashing of the sample occurs from the vacuum in the syringe since the condensate is cool. Samples were diluted in methylene chloride for analysis. Liquid samples were collected by turning the switching valve to the "sample" position, letting a few drops fall into an empty waste beaker to flush out the line, then collecting one or two drops in a vial of methylene chloride. All samples were capped immediately to minimize the effects of evaporation.

All samples were analyzed by gas chromatograph (see Appendices D and E for specific methods). Accuracy of analysis was ensured by preparing solutions of known composition for use as standards. Appendices G and I report the results obtained from these standards.

Table 2: Boiling point measurements, purity and source of pure components.

Component	Pressure mmHg	Measured Temperature	Calculated Temperature	Purity	Source
Benzene	639.8	74.6 °C	74.6 °C	99.9+%	Aldrich Chemical Company
Isopropyl alcohol	638.5	78.1 °C	78.0 °C	99.5%	Aldrich Chemical Company
<i>m</i> -Xylene	642.8	133.0 °C	133.0 °C	99%	Aldrich Chemical Company
<i>p</i> -xylene	640.1	132.8 °C	132.8 °C	99+%	Aldrich Chemical Company

RESULTS & DISCUSSION

Results obtained for the system *p*-xylene/*m*-xylene are shown in Tables 3 and 4, and in Figures 13 and 14. Table 3 contains the results from the equilibration time test. These results are plotted, vapor fraction as a function of time, in Figure 13. Table 4 tabulates the results of the equilibrium tests, and these results are plotted, liquid fraction versus vapor fraction, in Figure 14. Raw experimental data for the *p*-xylene/*m*-xylene system are shown in Appendices G and H.

Results obtained for the system benzene/isopropyl alcohol are shown in Tables 5 and 6, and in Figures 15 and 16. Table 5 contains the results from the equilibration time test. These results are plotted, vapor fraction as a function of time, in Figure 15. Table 6 tabulates the results of the equilibrium tests, and these results are plotted, liquid fraction versus vapor fraction, in Figure 16. Raw experimental data for the benzene/isopropyl alcohol system may be found in Appendices I and J.

Literature data for the system *p*-xylene/*m*-xylene are tabulated in Table 7 [17]. Literature data for the system benzene/isopropyl alcohol are tabulated in Table 8 [16].

Table 3: Time versus composition data - *p*-xylene/*m*-xylene system

vapor mole		vapor mole	
Time (min.)	fraction - <i>p</i> -xylene	Time (min.)	fraction - <i>p</i> -xylene
5	0.21	60	0.204
10	0.205	70	0.204
15	0.204	80	0.204
20	0.204	90	0.204
25	0.204	100	0.204
30	0.204	110	0.204
40	0.204	120	0.204
50	0.204		

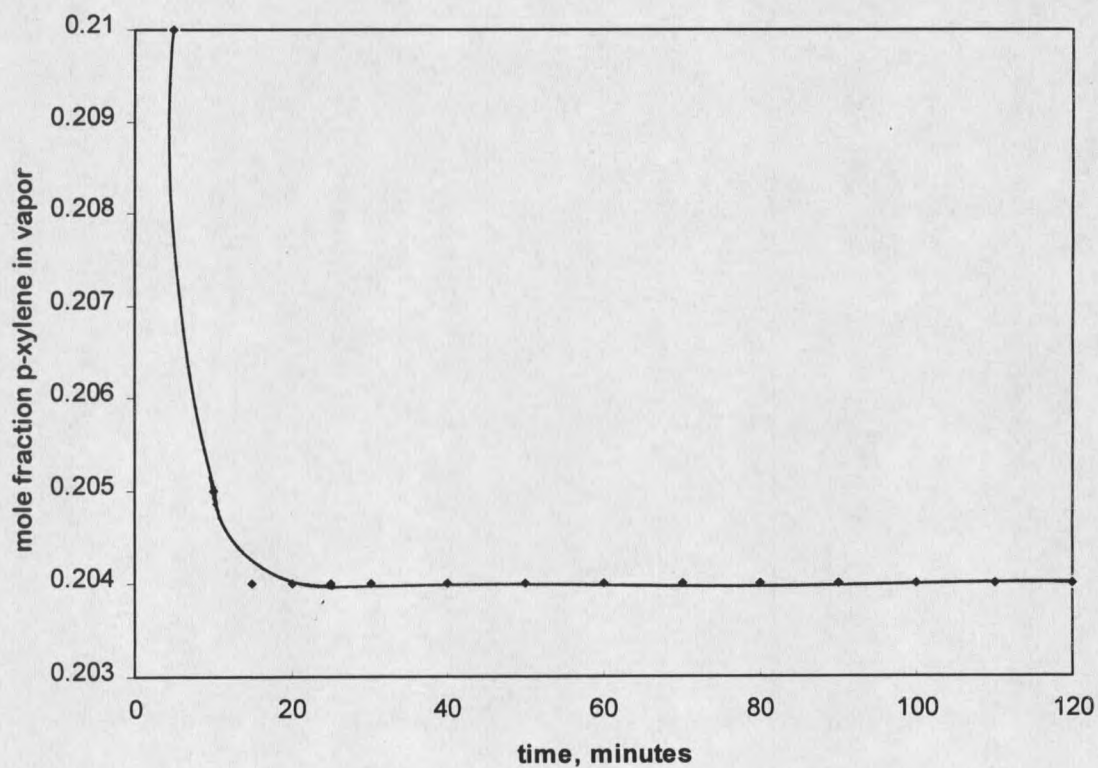
Figure 13. Time versus vapor composition *p*-xylene/*m*-xylene system

Table 4. Composition data - *p*-xylene/*m*-xylene system

liquid mole fraction <i>p</i> -xylene	vapor mole fraction <i>p</i> -xylene	Temperature °C	Pressure mmHg
0.000	0.000		
0.008	0.008	132.2	642.8
0.032	0.033	131.9	642.8
0.044	0.045	132.6	638.0
0.078	0.080	132.5	638.0
0.134	0.137	132.5	638.0
0.167	0.169	131.9	638.0
0.177	0.180	132.7	638.1
0.188	0.192	132.5	638.0
0.284	0.287	132.5	638.1
0.355	0.360	132.2	642.8
0.449	0.452	132.4	638.1
0.544	0.549	132.5	638.1
0.805	0.809	130.1	612.0
0.900	0.901	129.6	612.0
0.935	0.935	133.0	645.7
0.945	0.946	129.5	612.0
0.982	0.982	130.0	612.0
1.000	1.000		

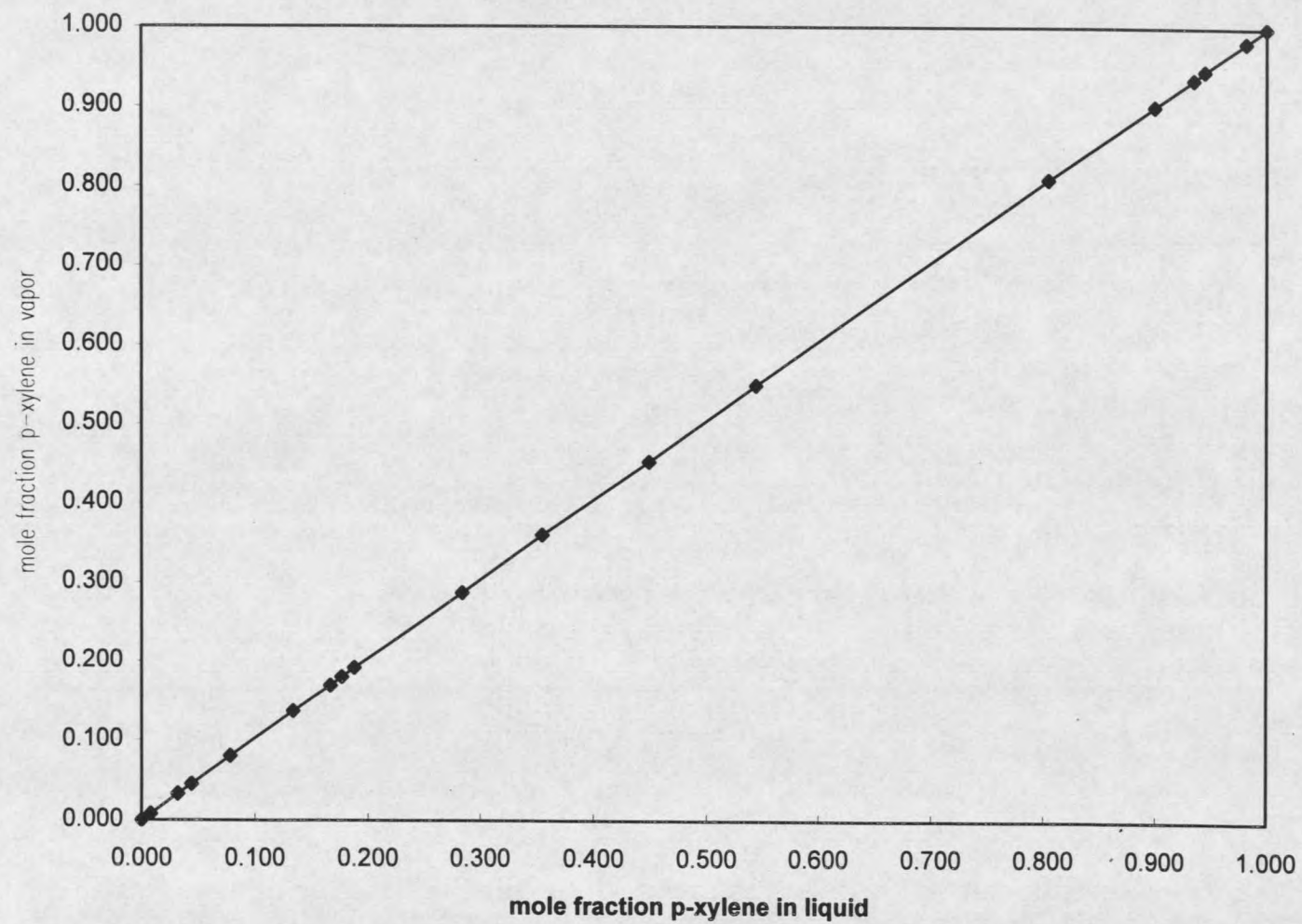


Figure 14: Equilibrium curve- *p*-xylene:*m*-xylene system

Table 5: Time versus composition data - benzene/isopropyl alcohol

Time (min.)	vapor mole fraction benzene	Time (min.)	vapor mole fraction benzene
5	0.387	60	0.385
10	0.387	70	0.385
15	0.386	80	0.385
20	0.386	90	0.385
25	0.385	100	0.385
30	0.385	110	0.385
40	0.385	120	0.385
50	0.385		

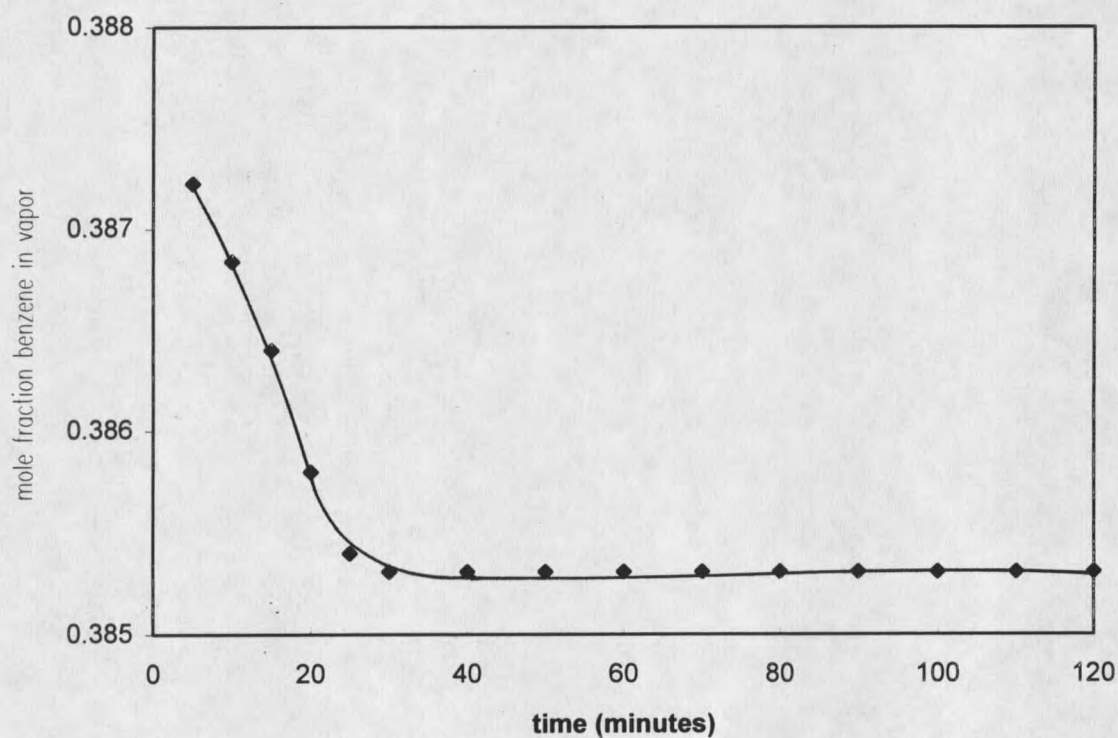


Figure 15: Time versus vapor composition benzene/isopropyl alcohol system

Table 6. Composition data - benzene/isopropyl alcohol

liquid mole fraction benzene	vapor mole fraction benzene	Temperature °C	Pressure mmHg
0.000	0.000		
0.018	0.051	77.9	640.5
0.037	0.104	76.9	640.5
0.074	0.192	75.1	640.5
0.099	0.246	74.1	641.2
0.184	0.385	71.2	641.2
0.300	0.494	68.8	641.2
0.392	0.534	67.9	641.3
0.524	0.564	67.5	641.5
0.618	0.589	67.8	639.7
0.718	0.622	68.6	639.7
0.778	0.658	69.2	639.6
0.828	0.697	69.7	639.7
0.938	0.822	71.0	638.9
0.988	0.898	71.7	638.9
1.000	1.000		638.9

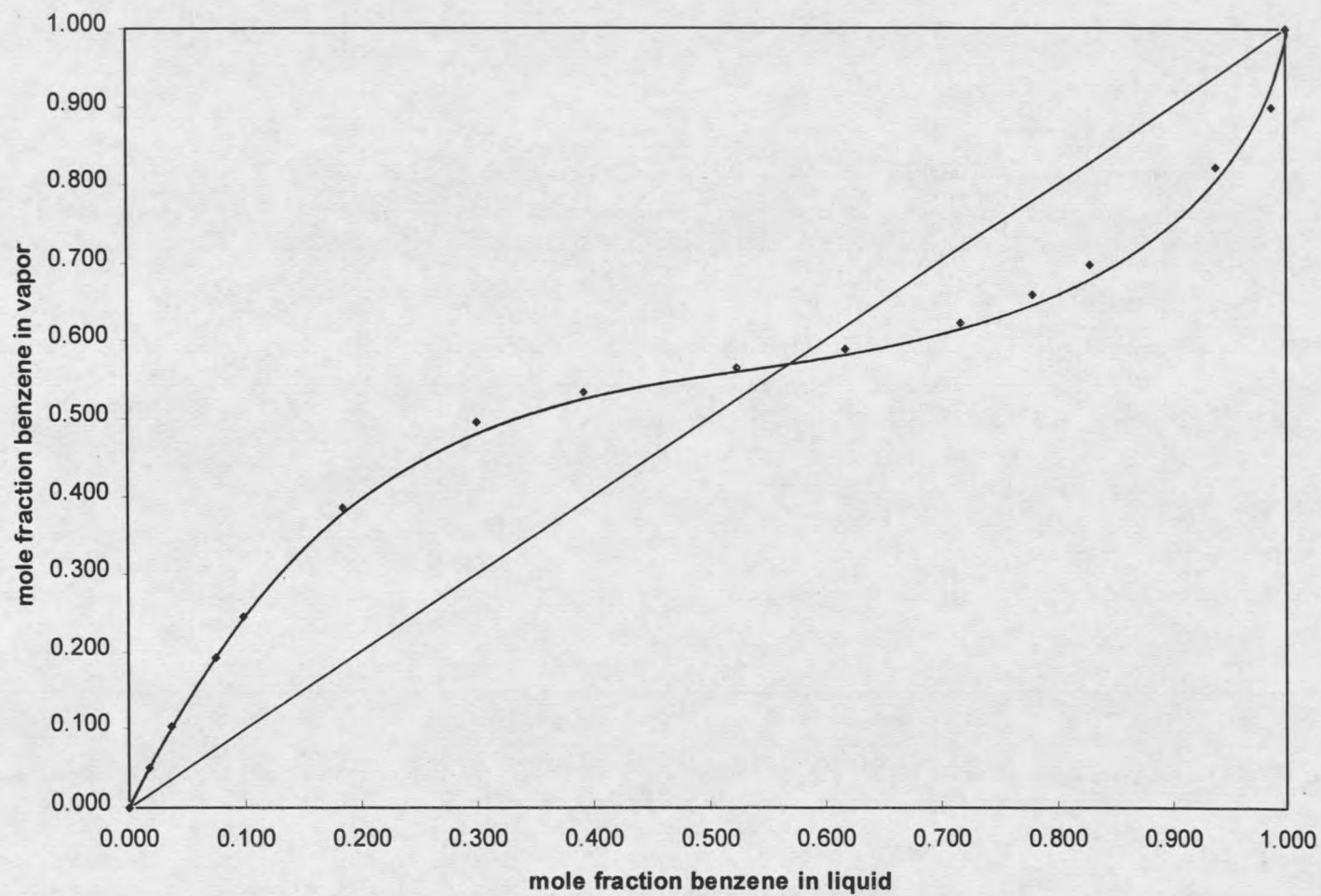


Figure 16: Equilibrium curve - benzene/isopropyl alcohol system

Table 7: Literature data, *p*-xylene/*m*-xylene [17].

x_p	y_p	T (°C)	P (mmHg)
0.0	0.0	139.1	760.0
0.1000	0.1018	139.03	760.0
0.2000	0.2032	138.95	760.0
0.3000	0.3042	138.88	760.0
0.4000	0.4043	138.80	760.0
0.5000	0.5058	138.73	760.0
0.6000	0.6048	138.65	760.0
0.7000	0.7042	138.58	760.0
0.8000	0.8032	138.50	760.0
0.9000	0.9018	138.43	760.0
1.0000	1.0000	138.35	760.0

Table 8: Literature data, benzene/isopropyl alcohol [16].

x_b	y_b	T (°C)	P (mmHg)
0.039	0.148	69.50	500.00
0.089	0.262	67.10	500.00
0.142	0.350	65.40	500.00
0.197	0.424	63.90	500.00
0.255	0.469	62.90	500.00
0.355	0.525	61.80	500.00
0.414	0.563	61.00	500.00
0.495	0.600	60.90	500.00
0.566	0.626	60.30	500.00
0.640	0.647	60.20	500.00
0.716	0.674	60.10	500.00
0.797	0.707	60.30	500.00
0.942	0.828	63.00	500.00
0.976	0.896	64.70	500.00

Time tests were performed to determine the length of time necessary for the establishment of equilibrium. The results of these tests are shown in Table 3 and Figure 13 for the system p-xylene/m-xylene, and in Table 4 and Figure 14 for the system benzene/isopropyl alcohol. For both systems tested, it appears that equilibrium is fully established in 30 minutes. Experimental data points were taken after an equilibration time of at least one hour to ensure equilibrium at all points.

As discussed in the thermodynamics section, several consistency tests are available to evaluate VLE data. These tests were applied to the experimental data as well as to the literature data. Not all tests were performed on all data sets, however. The reasons for this are discussed in each case.

The point-by point consistency test using activity coefficients was applied to the literature and experimental data for the system benzene/isopropyl alcohol. Table 9 shows the values of the Antoine coefficients that were used for these calculations. Table 10 contains the results of the calculations for the literature data, taken from Hirata, et al [16], at a pressure of 500 mmHg. The graph that was used to determine slopes is shown in Figure 17. The literature data was determined to be fairly consistent based on this test.

Table 9. Antoine coefficients [12].

Compound	A	B	C
benzene	6.90565	1211.033	220.790
isopropyl alcohol	8.11778	1580.92	219.61
m-xylene	7.00908	1462.266	215.11
p-xylene	6.99052	1453.430	215.31

Table 10. Consistency test using activity coefficients, literature data [16], benzene/isopropyl alcohol, 500 mmHg.

x_b	γ_b	γ_i	$d\ln\gamma_b/dx_b$	$d\ln\gamma_i/dx_b$	$x_b d\ln\gamma_b/dx_b$	$x_i d\ln\gamma_i/dx_b$
0.039	3.502	1.006				
0.089	2.943	1.027	-3.48	0.18	-0.31	0.17
0.142	2.610	1.041	-2.27	0.15	-0.32	0.13
0.197	2.399	1.059	-1.53	0.23	-0.30	0.19
0.255	2.122	1.105	-2.11	0.94	-0.54	0.70
0.355	1.773	1.205	-1.80	1.55	-0.64	1.00
0.414	1.677	1.270	-0.95	1.37	-0.39	0.81
0.495	1.500	1.355	-1.38	1.76	-0.68	0.89
0.566	1.398	1.519	-0.99	4.40	-0.56	1.91
0.64	1.282	1.738	-1.17	6.39	-0.75	2.30
0.716	1.198	2.044	-0.89	6.02	-0.64	1.71
0.797	1.121	2.545	-0.82	6.64	-0.65	1.35
0.942	1.011	4.575	-0.71	4.85	-0.67	0.28
0.976	0.996	6.158	-0.44	4.37	-0.43	0.10

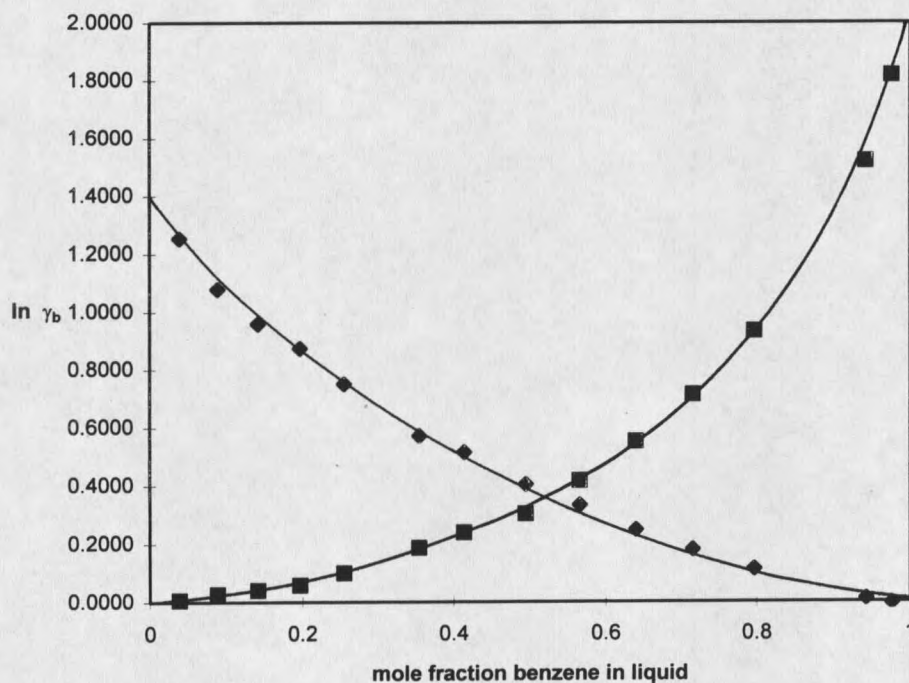


Figure 17. Consistency test using activity coefficients, literature data [16], benzene/isopropyl alcohol, 500 mmHg.

At most points the error is seen to be fairly small. There are a few points from the benzene fraction of 0.566 to 0.797 where the error is much greater, but as a whole the data seems to satisfy this test fairly well. The experimental data was slightly less satisfactory. Table 11 shows the results of the calculations for the experimental data, taken at 640 mmHg. Figure 18 shows the graph used in these calculations. The error was again seen to be much greater than normal near the benzene fraction of 0.5, and the endpoints seemed to be inconsistent. For consistent data, the signs of the slopes will always be opposite, but at the endpoints in the experimental data this was not the case. Possible reasons for this inconsistency include analytical error and instrumentation error (thermocouple or barometer). The analytical error was estimated to be approximately ± 0.003 weight fraction. The barometer is specified to be accurate to ± 0.2 mmHg, while the thermocouple is specified at $\pm 0.2^\circ\text{C}$. Given these values, the error introduced to the activity coefficient calculation was estimated to be approximately 5% (see Appendix F). This may account for a significant portion of the inconsistency observed in this test.

The activity coefficient point-by-point method was not applied to experimental data for the p-xylene/m-xylene system, since all activity coefficients were found to be equal to unity. This is expected for an ideal system such as this, so the results from this test would be inconclusive for the p-xylene/m-xylene system.

The point-by-point consistency test using partial pressures was applied to all data sets. Results for the p-xylene/m-xylene system are shown in Tables 12 and 13 as well as Figures 19 and 20. Table 12 shows the calculated results for the literature data [17]; these

Table 11. Consistency test using activity coefficients, experimental data,
benzene/isopropyl alcohol, 640 mmHg.

x	γ_1	γ_2	$d\ln\gamma_1/dx_1$	$d\ln\gamma_2/dx_1$	$x_1 d\ln\gamma_1/dx_1$	$x_2 d\ln\gamma_2/dx_1$
0.018	2.575	0.972			0	0
0.037	2.591	0.977	0.319	0.090	0.012	0.087
0.074	2.563	0.990	-0.297	0.154	-0.022	0.142
0.099	2.533	0.992	-0.474	0.029	-0.047	0.026
0.184	2.340	1.016	-0.929	0.171	-0.171	0.140
0.300	1.992	1.088	-1.388	0.633	-0.417	0.443
0.392	1.700	1.203	-1.729	2.512	-0.678	1.527
0.524	1.357	1.460	-1.701	6.417	-0.892	3.052
0.618	1.191	1.690	-1.392	5.748	-0.861	2.194
0.718	1.053	2.031	-1.235	5.711	-0.887	1.610
0.779	1.006	2.283	-0.738	3.240	-0.575	0.716
0.828	0.986	2.532	-0.426	2.655	-0.353	0.457
0.938	0.983	3.927	-0.028	3.505	-0.026	0.216
0.988	0.997	11.430	0.293	13.932	0.290	0.163

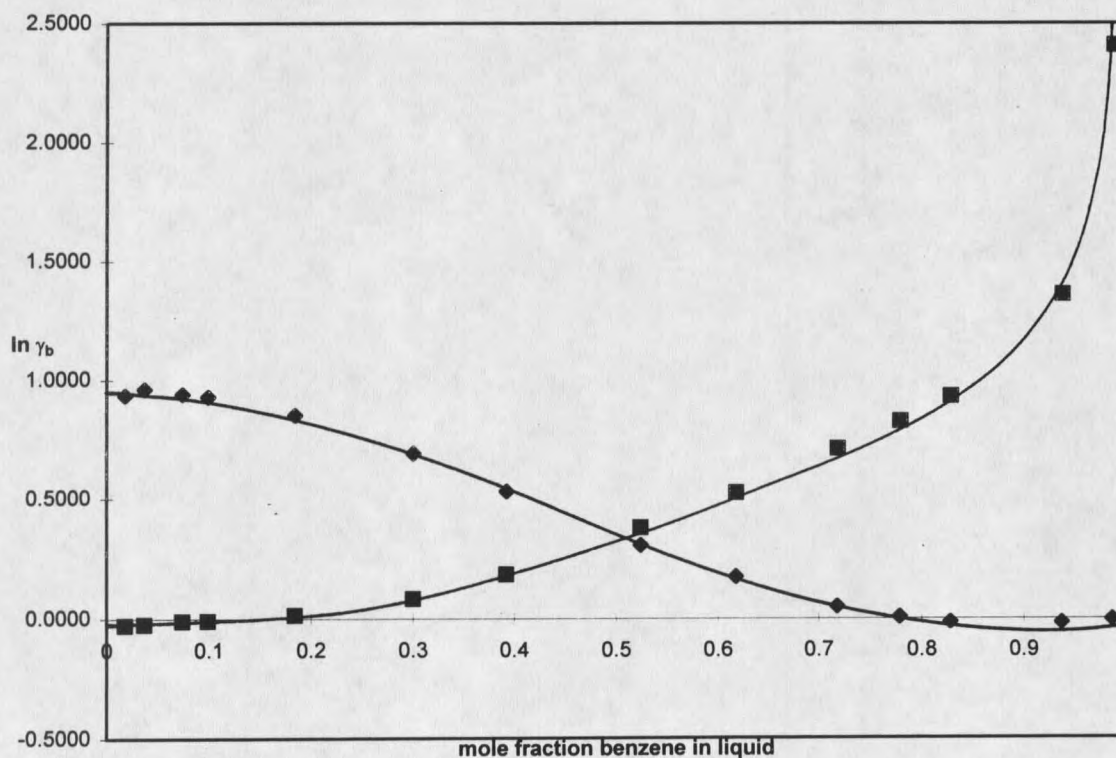


Figure 18. Consistency test using activity coefficients, experimental data, benzene/
isopropyl alcohol, 640 mmHg.

Table 12: Consistency test using partial pressures, literature data, *p*-xylene/*m*-xylene, 760 mmHg [17].

X_p	p_1	p_2	dp_1/dx_1	dp_2/dx_1	x_1/p_1	x_1/p_2	dp_2/dx_1
0.100	77.4	682.6					
0.200	154.4	605.6	770.6	-770.6	1.00	-1.02	
0.300	231.2	528.8	767.6	-767.6	1.00	-1.02	
0.400	307.3	452.7	760.8	-760.8	0.99	-1.01	
0.500	383.8	376.2	765.3	-765.3	1.00	-1.02	
0.600	459.6	300.4	758.5	-758.5	0.99	-1.01	
0.700	535.2	224.8	755.4	-755.4	0.99	-1.01	
0.800	610.4	149.6	752.4	-752.4	0.99	-1.01	
0.900	685.4	74.6	749.4	-749.4	0.98	-1.00	
1.000	760.0	0.0	746.3	-746.3			

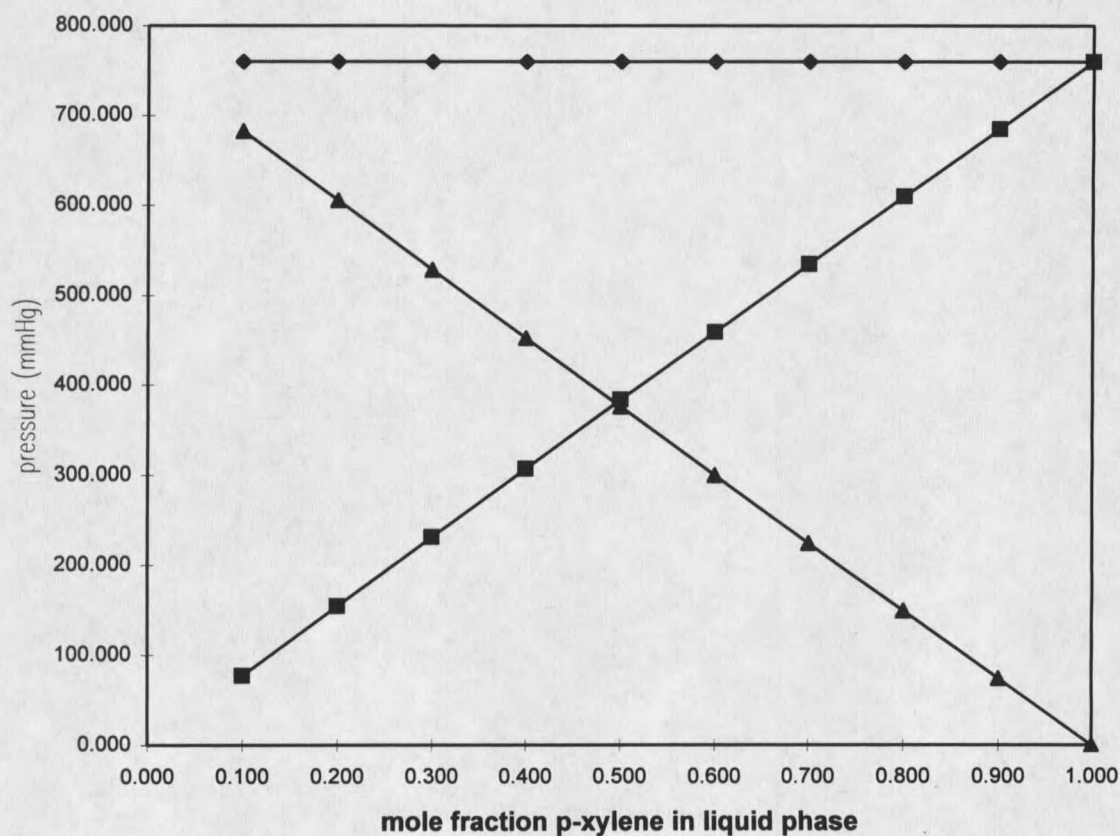


Figure 19. Consistency test using partial pressures, literature data [17], *p*-xylene/*m*-xylene, 760 mmHg.

Table 13. Consistency test using partial pressures, experimental data,
p-xylene/*m*-xylene, 635 mmHg.

x_p	p_p	p_m	dp_p/dx_p	dp_m/dx_p	x_p/p_p	dp_p/dx_p	x_p/p_m	dp_m/dx_p
0.008	5.3	629.7						
0.032	21.0	614.0	648.6	-648.6	1.00		-1.02	
0.044	28.6	606.4	654.5	-654.5	1.01		-1.03	
0.078	50.9	584.1	649.8	-649.8	1.00		-1.03	
0.134	86.8	548.2	646.6	-646.6	1.00		-1.02	
0.167	107.6	527.4	633.8	-633.8	0.98		-1.00	
0.177	114.5	520.5	653.4	-653.4	1.01		-1.03	
0.188	121.8	513.2	700.9	-700.9	1.08		-1.11	
0.284	182.5	452.5	633.1	-633.1	0.98		-1.00	
0.355	226.2	408.8	616.0	-616.0	0.97		-0.97	
0.449	287.1	347.9	622.1	-622.1	0.97		-0.98	
0.544	348.6	286.4	648.0	-648.0	1.01		-1.03	
0.805	513.5	121.5	632.0	-632.0	0.99		-1.01	
0.900	571.9	63.1	617.5	-617.5	0.97		-0.98	
0.935	593.7	41.3	625.9	-625.9	0.99		-0.99	
0.945	600.4	34.6	669.4	-669.4	1.05		-1.07	
0.982	623.6	11.4	623.5	-623.5	0.98		-1.00	

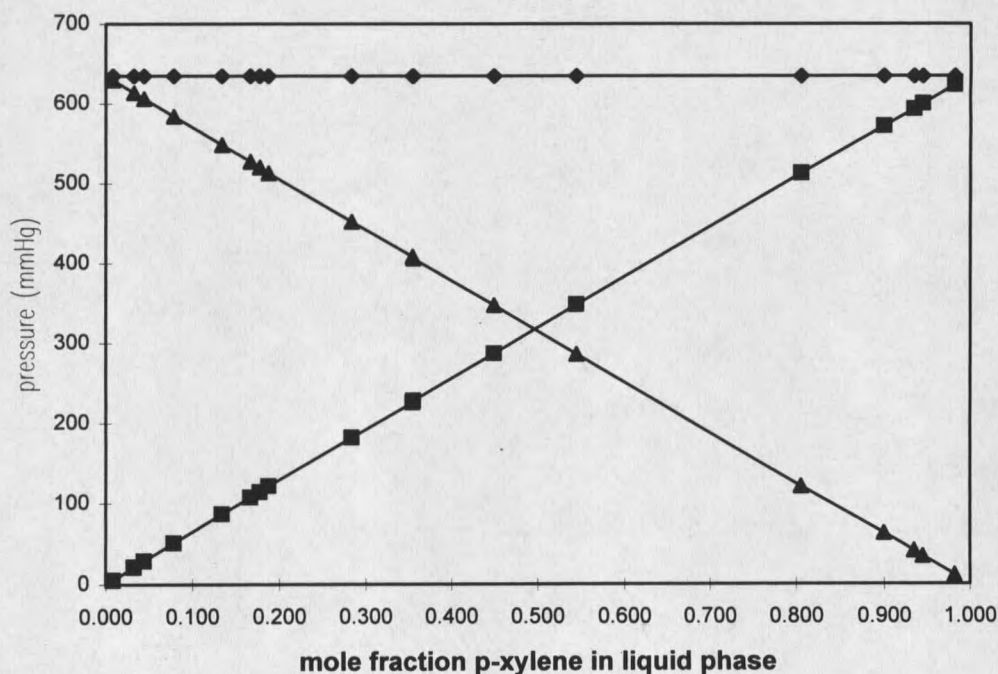


Figure 20. Consistency test using partial pressures, experimental data,
p-xylene/*m*-xylene, 635 mmHg.

results are shown graphically in Figure 19. Table 13 contains the calculations on the experimental data, while Figure 20 displays the resulting graph. The literature data was collected at 760 mmHg, while the experimental data was collected at 635 mmHg. The literature data satisfied the test well, as did the experimental data. Based on the results of this test, the data of both sets are judged to be consistent.

Results for the benzene/isopropyl alcohol system literature data [16] are displayed in Table 14 and graphed in Figure 21. The experimental data is similarly shown in Table 15 and graphed in Figure 22. Neither the literature data nor the experimental data appear to satisfy this test well. At most points the equation is not well-satisfied. However, the experimental data appears to be very similar to the literature data in terms of the magnitude of error.

Possible sources of error in the partial pressure test include inaccurate pressure measurements and analytical error. Error in the pressure measurement should be on the order of 0.2 mmHg, as specified by the manufacturer of the barometer used (Princo model number 453X). This should not significantly affect the results of this test. Analytical error is estimated to be on the order of 0.02 mole fraction. Again, this should not significantly affect the results of this test. Combined error from these two sources would be 0.004 mmHg in the calculated partial pressures. This is considerably less than the error introduced by graphical determination of the slopes, estimated to be approximately 5% of the slope. Of considerably more concern is the method itself. The Gibbs-Duhem equation is valid for constant temperature and pressure. Although the pressure is essentially

Table 14: Consistency test using partial pressures, literature data [16],
benzene/isopropyl alcohol, 500 mmHg.

X_b	p_b	p_i	dp_b/dx_b	dp_i/dx_b	x_b/p_b	dp_b/dx_b	x_b/p_i	dp_i/dx_b
0.039	74.0	426.0						
0.089	131.0	369.0	1140	-1140	0.77		-2.81	
0.142	175.0	325.0	830.19	-830.19	0.67		-2.19	
0.197	212.0	288.0	672.73	-672.73	0.63		-1.88	
0.255	234.5	265.5	387.93	-387.93	0.42		-1.09	
0.355	262.5	237.5	280.00	-280.00	0.38		-0.76	
0.414	281.5	218.5	322.03	-322.03	0.47		-0.86	
0.495	300.0	200.0	228.40	-228.40	0.38		-0.58	
0.566	313.0	187.0	183.10	-183.10	0.33		-0.42	
0.64	323.5	176.5	141.89	-141.89	0.28		-0.29	
0.716	337.0	163.0	177.63	-177.63	0.38		-0.31	
0.797	353.5	146.5	203.70	-203.70	0.46		-0.28	
0.942	414.0	86.0	417.24	-417.24	0.95		-0.28	
0.976	448.0	52.0	1000	-1000	2.18		-0.46	

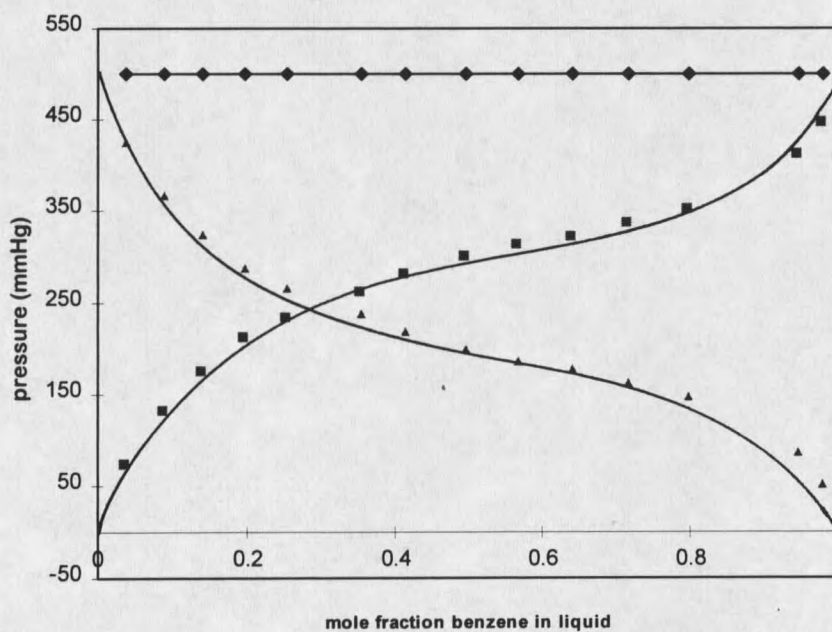


Figure 21. Consistency test using partial pressures, literature data [16],
benzene/isopropyl alcohol, 500 mmHg.

Table 15. Consistency test using partial pressures, experimental data,
benzene/isopropyl alcohol, 640 mmHg.

x_b	p_b	p_i	dp_b/x_b	dp_i/x_b	$x_b p_b$	dp_b/x_b	$x_i p_i$	dp_i/x_b
0.018	32.5	608.0						
0.037	66.6	573.9	1741.3	-1741.3	0.98		-2.92	
0.074	123.1	518.1	1546.2	-1527.1	0.93		-2.72	
0.099	157.8	483.4	1383.7	-1383.7	0.87		-2.58	
0.184	247.1	394.1	1046.5	-1046.5	0.79		-2.17	
0.300	316.6	324.7	599.9	-599.9	0.57		-1.29	
0.392	342.3	299.2	280.2	-278.0	0.32		-0.56	
0.524	360.7	279.0	139.0	-152.6	0.20		-0.26	
0.618	377.0	262.7	173.0	-173.0	0.28		-0.25	
0.718	397.5	242.1	206.0	-207.0	0.37		-0.24	
0.779	420.7	219.0	378.3	-376.7	0.70		-0.38	
0.828	445.0	193.9	501.8	-518.2	0.93		-0.46	
0.938	525.0	113.9	722.2	-722.2	1.29		-0.39	
0.988	574.0	64.9	983.0	-983.0	1.69		-0.18	

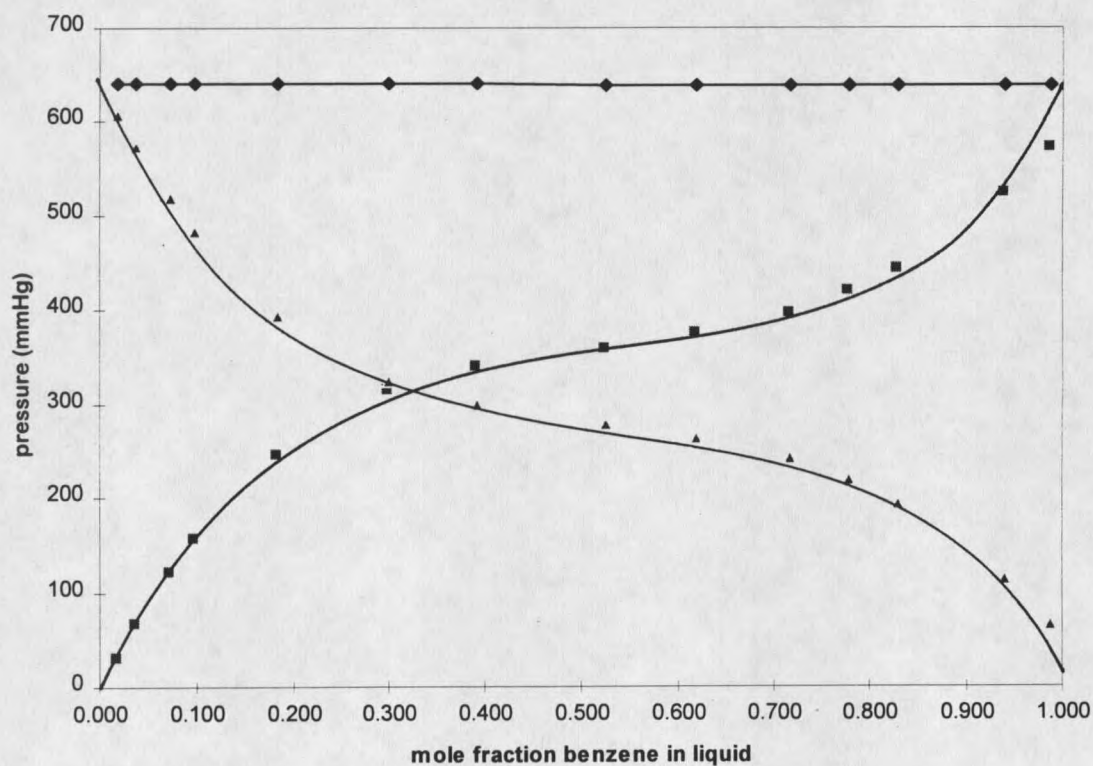


Figure 22. Consistency test using partial pressures, experimental data,
benzene/isopropyl alcohol, 640 mmHg.

constant, the temperature of the benzene/isopropyl alcohol system varies from 67 to 78 °C. This amount of variation may be enough to cast significant doubt on the accuracy of the method. For the *p*-xylene/*m*-xylene system, the temperature variation is only about three degrees, and thus the method is much more applicable to that system.

The test used on sets of data, the Redlich-Kister test, also uses activity coefficients, and so results are reported only for the benzene/isopropyl alcohol system. For the literature data, shown in Table 16 and in Figure 23, the results are fairly consistent. The positive area calculated is 0.341, while the calculated negative area is 0.372. The experimental data set shows similar results, with a positive area of 0.376 and a negative area of 0.339. These results are shown in Table 17 and Figure 24. Based on the results of this test, both sets of data are judged to be consistent.

The most significant source of error for this method is the temperature measurement. Temperature measurements are used to calculate vapor pressures, which are then used in the calculation of the activity coefficients. Inaccuracies in the absolute pressure measurement are not significant, since the pressure term is effectively canceled by using the ratio of γ_1 to γ_2 . Inaccuracies in analysis may similarly be canceled out, depending on the type of error introduced. If the analysis is consistently off by a constant factor then the error will cancel out. An example of this type of error is when the measured fraction of one component is consistently 99% of the actual composition. If the error is not consistent, or is not off by a constant factor, the inaccuracy will not be negligible. An example of this

Table 16. Area consistency test, literature data [16],
benzene/isopropyl alcohol, 500 mmHg.

x_b	$\ln \gamma_b/\gamma_i$	x_b	$\ln \gamma_b/\gamma_i$
0.039	1.247	0.495	0.101
0.089	1.052	0.566	-0.083
0.142	0.919	0.64	-0.304
0.197	0.818	0.716	-0.534
0.255	0.653	0.797	-0.820
0.355	0.386	0.942	-1.510
0.414	0.278	0.976	-1.822

Positive area = 0.341	Negative area = 0.372
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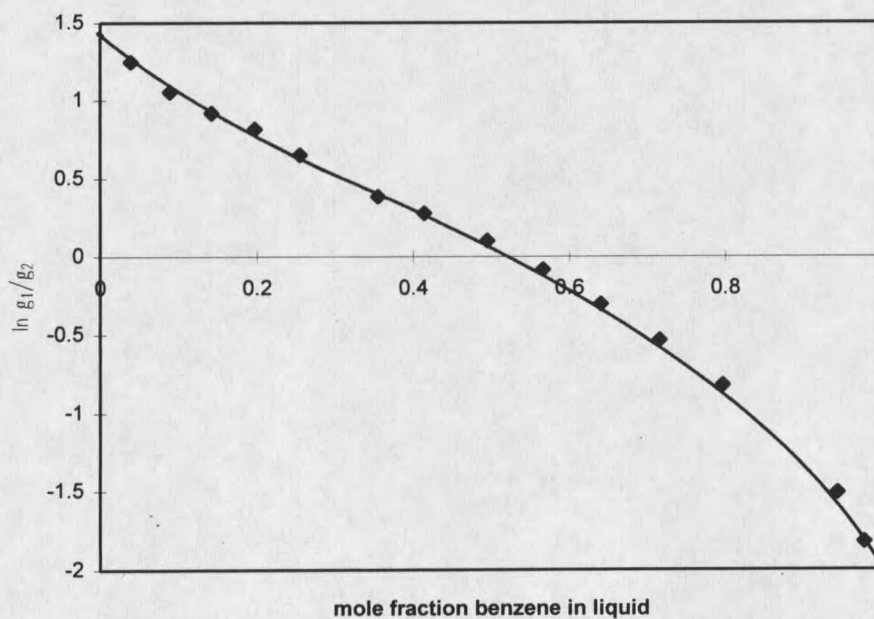


Figure 23. Area consistency test, literature data [16], benzene/isopropyl alcohol

Table 17. Area Consistency test, experimental data, benzene/isopropyl alcohol, 640 mmHg.

x_b	$\ln \gamma_b/\gamma_i$	x_b	$\ln \gamma_b/\gamma_i$
0.018	0.974	0.524	-0.073
0.037	0.976	0.618	-0.350
0.074	0.951	0.718	-0.657
0.099	0.938	0.779	-0.819
0.184	0.835	0.828	-0.943
0.300	0.605	0.938	-1.385
0.392	0.346	0.988	-2.439

Positive area = 0.376

Negative area = 0.339

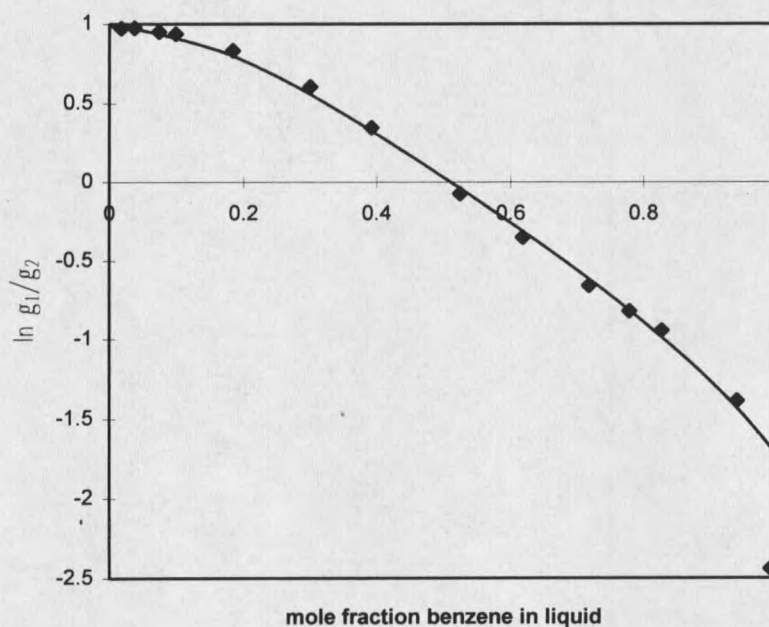


Figure 24. Area consistency test, experimental data, benzene/isopropyl alcohol

error is when the measured benzene fraction is consistently 0.002 higher than the actual fraction.

Wilson parameters were optimized using ChemCAD® for the benzene/isopropyl alcohol system. The data reported by Hirata, et al [16] includes optimized Wilson parameters, but these parameters are not temperature-dependent. Experimental data as well as the data from Hirata were input to ChemCAD®. Results are tabulated in Table 18. Liquid densities were obtained from the ChemCAD® databank and converted to liquid specific molar volumes. Values of this property for the temperature range of 60° to 80°C are shown in Figure 25. Figure 26 plots the liquid and vapor fractions obtained from the Wilson equation using each set of parameters in Table 18. Appendix K shows how these results were calculated. Figure 26 indicates that the values of the Wilson parameters calculated by ChemCAD® for both the literature data and the experimental data provide a good fit for the experimental data. Since the Wilson equation satisfies the Gibbs-Duhem equation, finding values of the Wilson parameters that fit the data well indicates thermodynamic consistency.

Table 18. Wilson parameters for benzene/isopropyl alcohol system

Data Set	Wilson Parameters	
	a_{12}	a_{21}
Literature [16], calculated by ChemCAD®	211.00	1096.00
Experimental, calculated by ChemCAD®	337.08	802.85

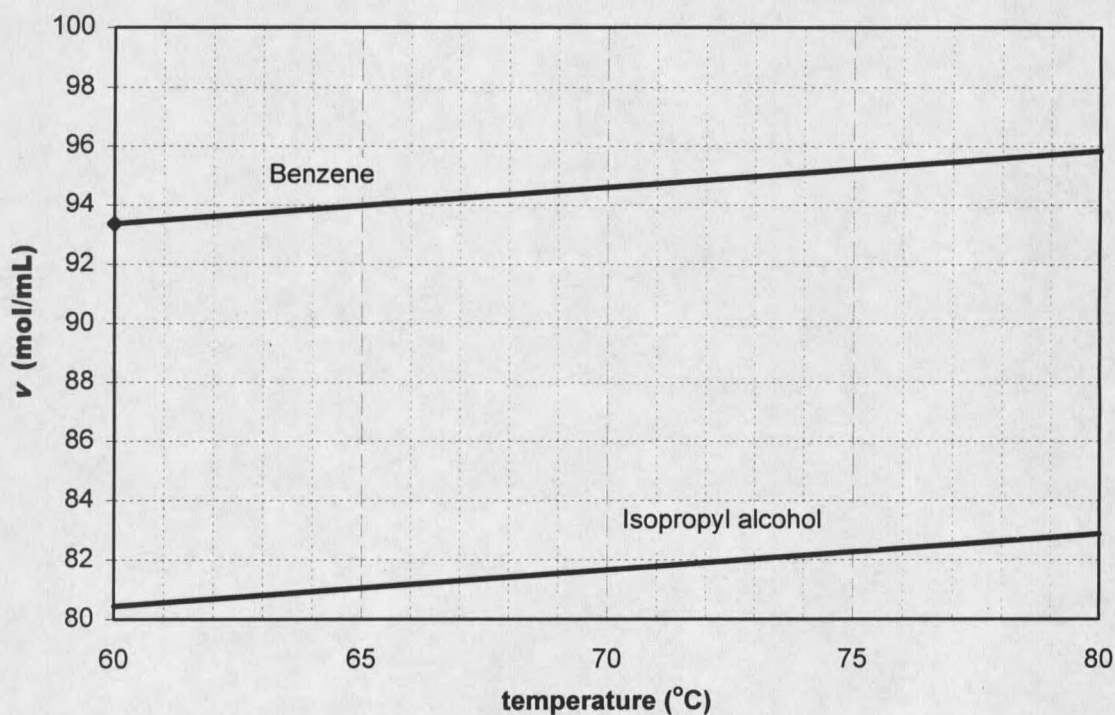


Figure 25. Specific molar volumes of isopropyl alcohol and benzene over the temperature range 60-80°C.

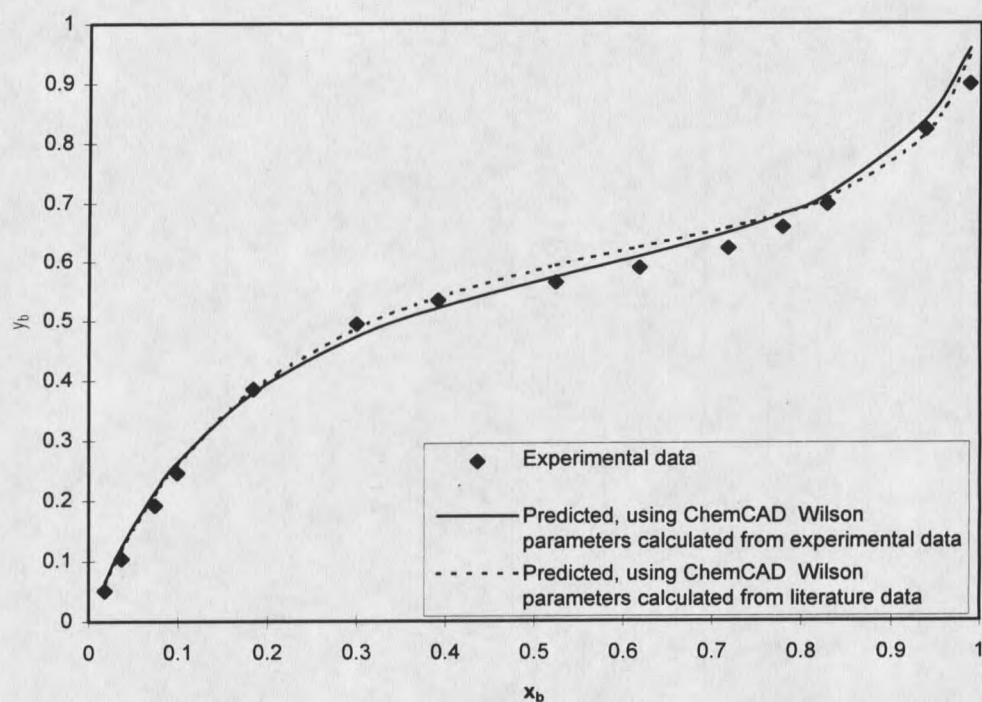


Figure 26. Equilibrium curves predicted from Wilson parameters, plotted with experimental data, benzene/isopropyl alcohol

CONCLUSIONS

The experimental VLE still design was tested on two systems. The first system was ideal, *p*-xylene/*m*-xylene. Two consistency tests were applied to the data obtained for this system. The Redlich-Kister test indicated thermodynamic consistency for the experimental and literature data for this system, as did the point-by-point partial pressure test. The second system was a highly non-ideal azeotropic system, benzene/isopropyl alcohol. Four consistency tests were applied to this system. Two of these tests were point-by-point consistency tests. The first, using activity coefficients, did not indicate thermodynamic consistency for either the experimental or literature data. The second point-by-point test, using partial pressures, showed better consistency for the literature data than the experimental data. The final two tests applied to the benzene/isopropyl alcohol system are intended to test sets of data rather than individual points. The Redlich-Kister test was fairly well-satisfied for both sets, literature and experimental. Wilson parameters were optimized for each set of data. Although the parameters obtained for each set were not identical, they each represent their respective data sets fairly well. The Wilson

equation was derived to satisfy the Gibbs-Duhem equation, so the existence of parameters that cause the data to be well-fit indicates thermodynamic consistency.

Based on these results, it is concluded that the VLE still designed and tested here provides overall consistent data for the systems tested. Although the point-by-point consistency tests were not always well-satisfied, these tests are inherently more prone to error than the overall tests.

For both systems, it was seen that the still should be run for a minimum of 45 minutes at each data point to ensure the establishment of equilibrium.

RECOMMENDATIONS

This still design has been shown to be a suitable choice for the collection of vapor-liquid equilibrium data. This design is especially appropriate for systems with the potential for polymerization or other reactions, due to the ease of cleaning. Future modifications that may be considered include a liquid sampling loop that can handle systems with two liquid phases and a more accurate temperature measurement device. The liquid sampling loop modification would allow the collection of vapor-liquid-liquid equilibrium data, useful for the design of extraction and extractive distillation processes. Since temperature measurement is considered to be the largest source of error in the current setup, improved performance may be achieved by converting to a more accurate measurement device.

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APPENDICES

APPENDIX A

Example of Point-by-Point Consistency Test Using Activity Coefficients

Consider the data set:

Table 19. Benzene/isopropyl alcohol data[16]

x	y	t	P
0.039	0.148	69.5	500
0.089	0.262	67.1	500
0.142	0.350	65.4	500
0.197	0.424	63.9	500
0.255	0.469	62.9	500
0.355	0.525	61.8	500
0.414	0.563	61.0	500
0.495	0.600	60.9	500
0.566	0.626	60.3	500
0.640	0.647	60.2	500
0.716	0.674	60.3	500
0.797	0.707	60.3	500
0.942	0.828	63.0	500
0.976	0.896	64.7	500

For the data point $x = 0.142$:

1. Calculate the vapor pressure of the pure components at the experimental temperature, using the Antoine equation.

$$P_i^o = 10^{\left(A - \frac{B}{C+t}\right)}$$

For the data shown above, the system is benzene (1) and isopropyl alcohol (2), which have the Antoine constants [12]:

1	A = 6.90565	B = 1211.033	C = 220.79
2	A = 6.6604	B = 813.055	C = 132.93

Yielding the following equations:

$$P_1^o = 10^{\left(6.90565 - \frac{1211.033}{220.79+65.4}\right)} = 472.2 \text{ mmHg}$$

$$P_2^o = 10^{\left(6.6604 - \frac{813.055}{132.93+65.4}\right)} = 363.8 \text{ mmHg}$$

2. Calculate the experimental activity coefficients at each point using the equation:

$$\gamma_i^{\text{exp}} = \frac{y_i P}{x_i P_i^o}$$

For the example data point, this gives:

$$\gamma_1^{\text{exp}} = \frac{0.35 * 500 \text{ mmHg}}{0.142 * 472.2 \text{ mmHg}} = 2.61$$

$$\gamma_2^{\text{exp}} = \frac{(1 - 0.350) * 500 \text{ mmHg}}{(1 - 0.142) * 363.8 \text{ mmHg}} = 1.04$$

3. Graph $\ln \gamma_1$ and $\ln \gamma_2$ versus x_1 .

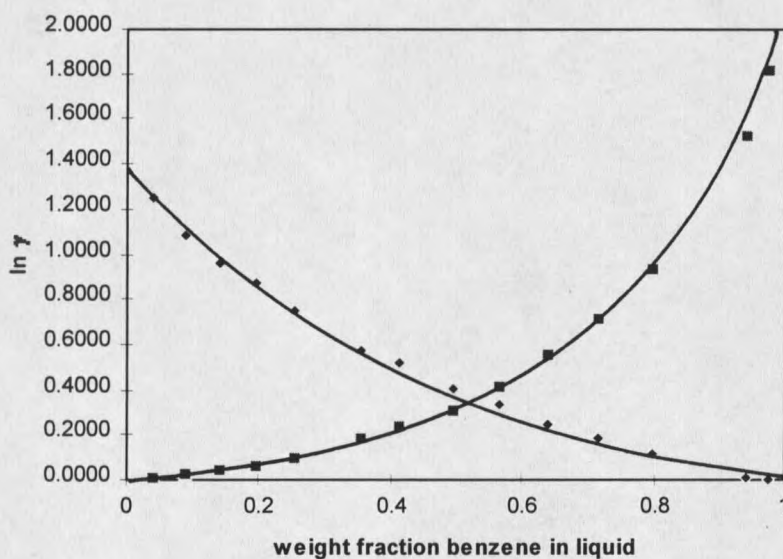


Figure 27. Activity coefficient consistency test, benzene/isopropyl alcohol, 500 mmHg.

4. Graphically determine slopes at each point, and use the following equation to determine thermodynamic consistency. A consistent point will cause this equation to be reasonably well satisfied.

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} = 0$$

For the example data point, this gives:

From the graph in number 3:

$$\frac{d \ln \gamma_1}{dx_1} = -2.27$$

$$\frac{d \ln \gamma_2}{dx_1} = 0.15$$

so,

$$\begin{aligned} & 0.142 \times (-2.27) + (1 - 0.142) \times (0.15) \\ & = -0.32 + 0.13 = -0.19 \end{aligned}$$

APPENDIX B

Example of Point-by-Point Consistency Test Using Partial Pressures

This is a point-by-point consistency test, so calculations for one data point will be shown.

Consider the data set:

Table 20. Benzene/isopropyl alcohol data [16]

x	y	t	P
0.039	0.148	69.5	500
0.089	0.262	67.1	500
0.142	0.350	65.4	500
0.197	0.424	63.9	500
0.255	0.469	62.9	500
0.355	0.525	61.8	500
0.414	0.563	61.0	500
0.495	0.600	60.9	500
0.566	0.626	60.3	500
0.640	0.647	60.2	500
0.716	0.674	60.3	500
0.797	0.707	60.3	500
0.942	0.828	63.0	500
0.976	0.896	64.7	500

For the data point $x = 0.142$:

1. Calculate experimental partial pressures using the following equation:

$$p_i = y_i P$$

This gives the following results:

$$p_1 = 0.350 * 500 \text{ mmHg} = 175.0 \text{ mmHg}$$

$$p_2 = (1 - 0.350) * 500 \text{ mmHg} = 325 \text{ mmHg}$$

2. Graph p_1 and p_2 versus x_1 .

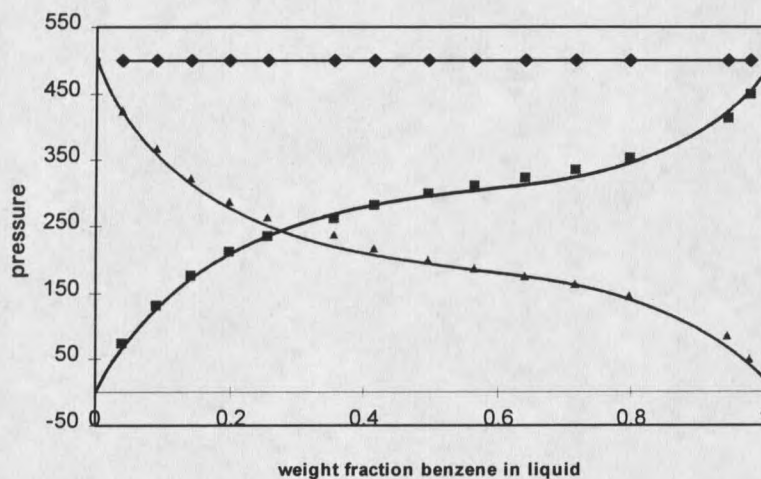


Figure 28. Partial pressure consistency test, benzene/isopropyl alcohol, 500 mmHg.

3. Graphically determine slopes at each point, and use the following equation to determine thermodynamic consistency. A consistent point will cause this equation to be reasonably well satisfied.

$$\frac{x_1}{p_1} \frac{dp_1}{dx_1} + \frac{x_2}{p_2} \frac{dp_2}{dx_1} = 0$$

For the example data point, from the graph in number 2:

$$\frac{dp_1}{dx_1} = 830.2$$

$$\frac{dp_2}{dx_1} = -830.2$$

So:

$$\frac{0.142}{175.0} \times 830.2 + \frac{(1-0.142)}{325.0} \times (-830.2)$$

$$= 0.67 - 2.19 = -1.52$$

APPENDIX C
Example of Area Consistency Test

Consider the data set:

Table 21. Benzene/isopropyl alcohol data [16]

x	y	t	P
0.039	0.148	69.5	500
0.089	0.262	67.1	500
0.142	0.350	65.4	500
0.197	0.424	63.9	500
0.255	0.469	62.9	500
0.355	0.525	61.8	500
0.414	0.563	61.0	500
0.495	0.600	60.9	500
0.566	0.626	60.3	500
0.640	0.647	60.2	500
0.716	0.674	60.3	500
0.797	0.707	60.3	500
0.942	0.828	63.0	500
0.976	0.896	64.7	500

1. Calculate the vapor pressure of the pure components at the experimental temperature, using the Antoine equation.

$$P_i^o = 10^{\left(A - \frac{B}{C+t}\right)}$$

For the data shown above, the system is benzene (1) and isopropyl alcohol (2), which have the Antoine constants [12]:

1	A = 6.90565	B = 1211.033	C = 220.79
2	A = 6.6604	B = 813.055	C = 132.93

Yielding the following equations at $x = 0.142$:

$$P_1^o = 10^{\left(6.90565 - \frac{1211.033}{220.79 + 65.4}\right)} = 472.2 \text{ mmHg}$$

$$P_2^o = 10^{\left(6.6604 - \frac{813.055}{132.93 + 65.4}\right)} = 363.8 \text{ mmHg}$$

2. Calculate the experimental activity coefficients at each point using the equation:

$$\gamma_i^{\text{exp}} = \frac{y_i P}{x_i P_i^o}$$

For the data point $x = 0.142$, this gives:

$$\gamma_1^{\text{exp}} = \frac{0.35 * 500 \text{ mmHg}}{0.142 * 472.2 \text{ mmHg}} = 2.61$$

$$\gamma_2^{\text{exp}} = \frac{(1 - 0.350) * 500 \text{ mmHg}}{(1 - 0.142) * 363.8 \text{ mmHg}} = 1.04$$

3. Graph $\ln(\gamma_1/\gamma_2)$ versus x_1 .

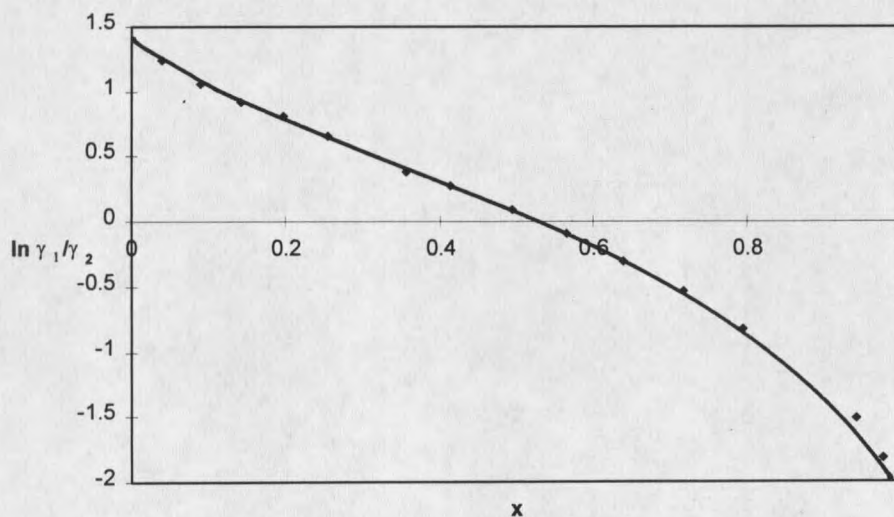


Figure 29. Area consistency test, benzene/isopropyl alcohol, 500 mmHg.

4. Determine positive and negative areas and compare. A consistent set of data will have equal areas. Areas here were approximated using the trapezoidal rule:

$$Area = \frac{(x_2 - x_1) \times (y_1 + y_2)}{2},$$

where *Area* is the area between the axis and the line formed by the graph, (x_1, y_1) and (x_2, y_2) are points on the graph.

For the segment from $x = 0.142$ to $x = 0.197$,

$$(x_1, y_1) = (0.142, 0.919)$$

$$(x_2, y_2) = (0.197, 0.818)$$

So, the area becomes:

$$Area = \frac{(0.197 - 0.142) \times (0.919 + 0.818)}{2} = 0.0478$$

APPENDIX D

Analytical Method: Benzene / Isopropyl Alcohol

All samples were diluted approximately 100:1 in methylene chloride.
All temperatures given in degrees C.

Instrument: Hewlett-Packard 6890 gas chromatograph
with: Autosampler
Split/splitless capillary inlet
Flame ionization detector (FID)

Settings: 10 μ l syringe, 1 μ l injection
Hydrogen carrier gas

Column: J & W Scientific DB5MS ((5 % phenyl)-methylpolysiloxane)
30 m x 0.32 mm x 0.5 μ m

Inlet: 250°
2.1 psi initial head pressure
split ratio = 62.5
0.8 ml/min column flow, constant flow

Oven:	initial temp.	45°		initial time:	5 min.	
	ramp 1:	5°/min.	final temp.:	60°	final time:	0 min.

Detector: 250°

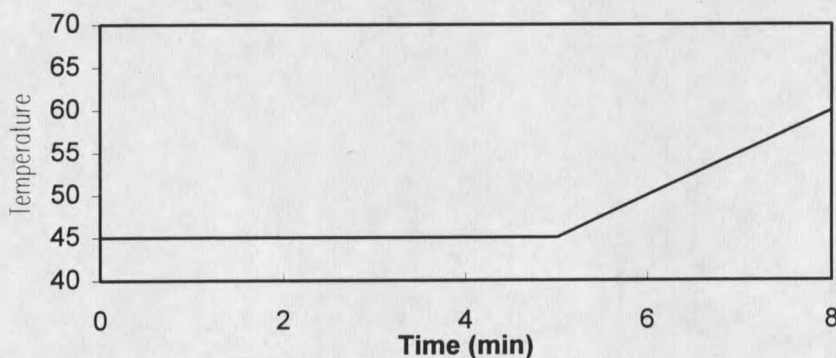


Figure 30. Temperature profile, benzene/isopropyl alcohol analytical method.

APPENDIX E

Analytical Method: *p*-Xylene / *m*-Xylene

All samples were diluted approximately 100:1 in methylene chloride. All temperatures given in degrees C.

Instrument: Hewlett-Packard 6890 gas chromatograph
with: Autosampler
Split/splitless capillary inlet
Flame ionization detector (FID)

Settings: 10 μ l syringe, 1 μ l injection
Hydrogen carrier gas

Column: Hewlett-Packard HP20-M (polyethylene glycol)
50 m x 0.25 mm x 0.5 μ m

Inlet: 220°
31 psi head pressure
split ratio = 60
1.0 ml/min column flow, constant flow

Oven: initial temp. 50° initial time: 10 min.

Detector: 250°

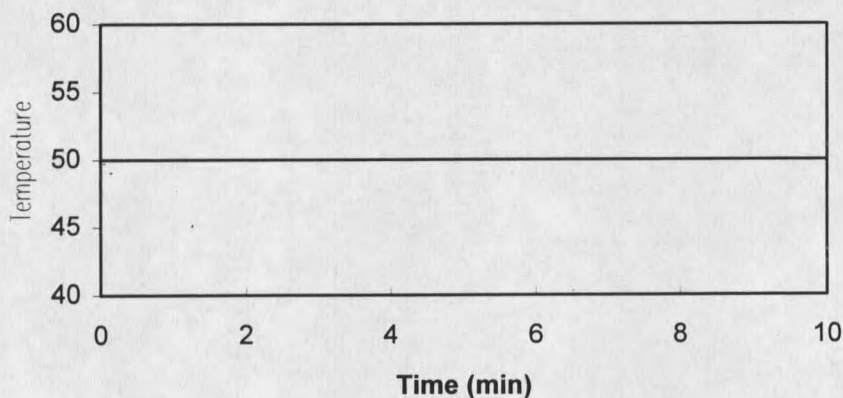


Figure 31. Temperature profile, *p*-xylene/*m*-xylene analytical method.

APPENDIX F

Error Analysis

Error in the calculation of activity coefficients was estimated by combined the maximum error in each component of the calculation. The equation used to calculate activity coefficients was:

$$\gamma_i = \frac{P y_i}{P_i^\circ x_i}$$

Error in each variable was as follows:

Table 22. Error sources.

Source of Error	Error	Variable(s) affected
Barometer	± 0.2 mmHg	P
Analytical	± 0.01	x, y
Thermocouple	$\pm 0.2^\circ\text{C}$	P°

Analytical error was determined by the use of standards, while barometer and thermocouple error are manufacturer specifications.

With these errors, a sample point was analyzed for the benzene/isopropyl alcohol system:

Measured values:

$$T = 71.2^\circ\text{C}$$

$$P = 641.2 \text{ mmHg}$$

$$x = 0.227$$

$$y = 0.449$$

Calculated using measured values:

$$P^\circ = 573.0 \text{ mmHg}$$

$$\gamma = \frac{641.2 \text{ mmHg} \times 0.449}{573.0 \text{ mmHg} \times 0.227} = 2.21$$

Partial derivatives are calculated:

$$\frac{\partial \gamma}{\partial P} = \frac{y}{P^o x} = \frac{0.449}{573 \times 0.227} = 0.00345$$

$$\frac{\partial \gamma}{\partial y} = \frac{P}{P^o x} = \frac{641.2}{573 \times 0.227} = 4.930$$

$$\frac{\partial \gamma}{\partial P^o} = \frac{-Py}{(P^o)^2 x} = \frac{-641.2 \times 0.449}{573^2 \times 0.227} = 0.00386$$

$$\frac{\partial \gamma}{\partial x} = \frac{-Py}{P^o x^2} = \frac{-641.2 \times 0.449}{573 \times (0.227)^2} = 9.751$$

Error is calculated from these derivatives:

$$\begin{aligned} \text{Error}(\gamma) &= \left[\left(\frac{\partial \gamma}{\partial P} \right)^2 \text{Error}(P)^2 + \left(\frac{\partial \gamma}{\partial y} \right)^2 \text{Error}(y)^2 + \left(\frac{\partial \gamma}{\partial P^o} \right)^2 \text{Error}(P^o)^2 + \left(\frac{\partial \gamma}{\partial x} \right)^2 \text{Error}(x)^2 \right]^{1/2} \\ &= \left[(0.00345)^2 (0.2)^2 + (4.930)^2 (0.01)^2 + (0.00386)^2 (4)^2 + (9.751)^2 (0.01)^2 \right]^{1/2} \\ &= \left[4.761 \times 10^{-7} + 2.430 \times 10^{-3} + 2.384 \times 10^{-4} + 9.508 \times 10^{-3} \right]^{1/2} \\ &= 0.110 \end{aligned}$$

So, for this point,

$$\gamma = 2.21 \pm 0.11$$

which corresponds to an error of approximately 5 %:

$$\frac{0.11}{2.21} = 5\%$$

APPENDIX G
p-Xylene/*m*-Xylene standard data

Table 23. Standard data, *p*-xylene/*m*-xylene.

standard number	weight <i>p</i> -xylene	weight <i>m</i> -xylene	actual wt% <i>p</i> -xylene	actual wt% <i>m</i> -xylene	area <i>p</i> -xylene	area <i>m</i> -xylene	area % <i>p</i> -xylene	area % <i>m</i> -xylene
xst110	2.9522	0.74	79.96%	20.04%	1054.929	265.693	79.88%	20.12%
	2.9522	0.74	79.96%	20.04%	711.811	178.786	79.93%	20.07%
	2.9522	0.74	79.96%	20.04%	990.607	249.604	79.87%	20.13%
xst111	3.5661	0.0323	99.10%	0.90%	702.498	7.234	98.98%	1.02%
	3.5661	0.0323	99.10%	0.90%	682.034	7.048	98.98%	1.02%
	3.5661	0.0323	99.10%	0.90%	669.297	6.847	98.99%	1.01%
xst112	1.952	1.6976	53.49%	46.51%	366.042	318.547	53.47%	46.53%
	1.952	1.6976	53.49%	46.51%	337.208	293.522	53.46%	46.54%
	1.952	1.6976	53.49%	46.51%	356.429	310.066	53.48%	46.52%
xst113	2.446	0.9552	71.92%	28.08%	317.652	124.437	71.85%	28.15%
	2.446	0.9552	71.92%	28.08%	311.787	122.083	71.86%	28.14%
	2.446	0.9552	71.92%	28.08%	319.016	125.048	71.84%	28.16%
xst114	0.7977	2.6086	23.42%	76.58%	283.667	924.579	23.48%	76.52%
	0.7977	2.6086	23.42%	76.58%	258.568	842.256	23.49%	76.51%
	0.7977	2.6086	23.42%	76.58%	276.485	901.352	23.47%	76.53%

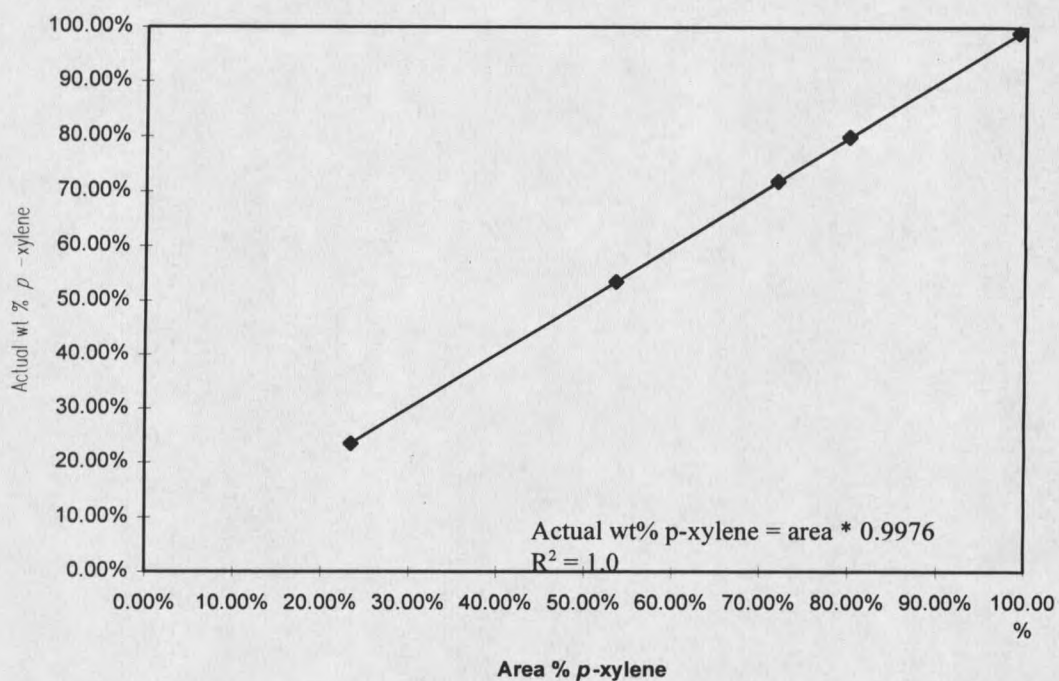


Figure 32. Standard curve - *p*-xylene/*m*-xylene analysis

APPENDIX H
p-Xylene/*m*-Xylene experimental data

Table 24. Time test, *p*-xylene/*m*-xylene.

Run #	xr47		area % <i>p</i> -xylene			area % <i>p</i> -xylene	
time (min)	<i>p</i> -xylene	<i>m</i> -xylene		time (min)	<i>p</i> -xylene	<i>m</i> -xylene	
5	344.505	1301.114	0.209347	50	177.4567	694.2014	0.203585
5	343.203	1296.086	0.209361	50	179.2152	701.0567	0.203591
5	433.169	1623.671	0.210599	60	207.9235	813.493	0.203564
5	399.6141	1498.639	0.210517	60	210.0517	822.1847	0.203492
10	324.5715	1261.286	0.204666	60	357.3633	1398.89	0.20348
10	342.4245	1329.371	0.204824	60	364.4003	1426.223	0.203505
10	127.4126	494.6246	0.204831	70	193.7602	757.1771	0.203757
10	109.2396	423.9239	0.20489	70	195.0454	762.5849	0.203675
15	188.4474	734.3178	0.20422	70	258.9635	1012.292	0.203707
15	183.0024	712.9407	0.204257	70	265.0337	1036.244	0.203672
15	215.9069	839.4114	0.204589	80	226.6353	885.3594	0.20381
15	219.1346	852.5056	0.204485	80	220.996	863.5928	0.20376
20	233.4251	910.3453	0.204084	80	233.1849	911.518	0.203708
20	255.1977	994.8654	0.204148	90	213.3693	834.5947	0.203604
20	218.1739	851.3947	0.203983	90	217.9358	852.1916	0.203654
20	213.6053	832.9423	0.204105	90	273.0654	1067.498	0.203694
25	284.9492	1111.431	0.204063	90	270.708	1058.084	0.203725
25	273.763	1067.58	0.204096	100	274.228	1071.311	0.203805
25	268.3401	1046.078	0.204151	100	282.8591	1106.174	0.203637
25	292.2204	1139.501	0.204104	100	118.9957	464.841	0.203817
30	435.4211	1698.19	0.204077	100	118.2311	461.743	0.203856
30	404.0791	1576.376	0.204033	110	209.6512	820.4435	0.203526
30	376.8437	1469.985	0.204049	110	203.9904	797.8799	0.20361
40	254.437	993.8275	0.203833	110	170.6627	667.3844	0.203643
40	243.2047	949.6062	0.203892	110	169.9239	664.6196	0.203613
40	281.6729	1100.101	0.203849	120	175.5653	686.5227	0.203651
40	270.7798	1057.414	0.203871	120	181.8227	710.9699	0.203656
50	301.1964	1178.653	0.203532	120	160.4553	627.7867	0.203561
50	310.5299	1214.573	0.203612	120	160.6063	628.2056	0.203605

Table 25. VLE Data, *p*-xylene/*m*-xylene.

Run #	area counts - liquid		area counts - vapor		fractions - liquid		fractions - vapor		Rel. vol.	T	P
	<i>p</i> -xylene	<i>m</i> -xylene	<i>p</i> -xylene	<i>m</i> -xylene	<i>p</i> -xylene	<i>m</i> -xylene	<i>p</i> -xylene	<i>m</i> -xylene			
xr43	7.14	857.61	10.65	1259.37	0.008	0.992	0.008	0.992	1.02	132.2	642.8
	6.62	796.72	6.09	716.52	0.008	0.992	0.008	0.992	1.02		
	5.78	695.05	5.44	637.78	0.008	0.992	0.008	0.992	1.03		
xr44	32.19	959.73	45.18	1319.53	0.032	0.968	0.033	0.967	1.02	131.9	642.8
	30.74	914.89	44.86	1309.33	0.033	0.967	0.033	0.967	1.02		
	38.71	1152.38	82.28	2401.14	0.033	0.967	0.033	0.967	1.02		
xr8	41.26	892.92	78.19	1654.48	0.044	0.956	0.045	0.955	1.02	132.6	638
	62.08	1343.98	83.25	1759.35	0.044	0.956	0.045	0.955	1.02		
xr9	382.92	4508.40	323.16	3712.00	0.078	0.922	0.080	0.920	1.02	132.5	638
	135.22	1591.84	286.14	3287.64	0.078	0.922	0.080	0.920	1.02		
xr10	308.84	1996.88	344.79	2176.37	0.134	0.866	0.137	0.863	1.02	132.5	638
	604.07	3905.16	385.12	2431.32	0.134	0.866	0.137	0.863	1.02		
xr45	108.48	542.35	197.20	966.67	0.167	0.833	0.169	0.831	1.02	131.9	642.7
	107.08	534.94	189.71	929.64	0.167	0.833	0.169	0.831	1.02		
	126.86	633.55	255.46	1252.00	0.167	0.833	0.169	0.831	1.02		
xr32	90.36	419.34	202.79	921.63	0.177	0.823	0.180	0.820	1.02	132.7	638.1
	90.22	418.29	198.75	903.61	0.177	0.823	0.180	0.820	1.02		
	78.17	362.82	145.27	660.19	0.177	0.823	0.180	0.820	1.02		
xr11	747.52	3236.28	454.64	1916.05	0.188	0.812	0.192	0.808	1.03	132.5	638
	440.94	1908.04	515.50	2173.55	0.188	0.812	0.192	0.808	1.03		
xr33	171.97	434.39	409.94	1016.15	0.284	0.716	0.287	0.713	1.02	132.5	638.1
	123.98	313.35	401.95	996.74	0.283	0.717	0.287	0.713	1.02		
	147.54	373.03	307.24	758.42	0.283	0.717	0.288	0.712	1.02		
xr34	275.13	500.92	497.13	898.33	0.355	0.645	0.356	0.644	1.01	132.4	638.1
	288.14	524.17	458.74	829.52	0.355	0.645	0.356	0.644	1.01		
	232.99	424.22	418.62	757.13	0.355	0.645	0.356	0.644	1.01		

Table 25. (Continued)

Run #	area counts - liquid		area counts - vapor		fractions - liquid		fractions - vapor		Rel. vol.	T	P
	<i>p</i> -xylene	<i>m</i> -xylene	<i>p</i> -xylene	<i>m</i> -xylene	<i>p</i> -xylene	<i>m</i> -xylene	<i>p</i> -xylene	<i>m</i> -xylene			
xr46	329.61	598.81	600.10	1067.99	0.355	0.645	0.360	0.640	1.02	132.2	642.8
	329.57	598.14	611.49	1088.26	0.355	0.645	0.360	0.640	1.02		
	69.52	126.19	583.98	1039.41	0.355	0.645	0.360	0.640	1.02		
xr35	326.64	400.45	516.62	626.18	0.449	0.551	0.452	0.548	1.01	132.4	638.1
	265.16	325.13	686.22	833.02	0.449	0.551	0.452	0.548	1.01		
	297.25	364.48	450.05	546.14	0.449	0.551	0.452	0.548	1.01		
xr36	154.98	129.76	371.98	305.53	0.544	0.456	0.549	0.451	1.02	132.5	638.1
	408.20	345.54	383.21	320.48	0.542	0.458	0.545	0.455	1.01		
xr41	371.51	89.97	1287.88	304.87	0.805	0.195	0.809	0.191	1.02	130.1	612
	614.49	149.54	1476.92	349.04	0.804	0.196	0.809	0.191	1.03		
	553.54	134.84	1384.41	327.71	0.804	0.196	0.809	0.191	1.03		
xr40	300.55	33.48	1664.65	183.53	0.900	0.100	0.901	0.099	1.01	129.6	612
	298.35	33.22	1386.50	152.79	0.900	0.100	0.901	0.099	1.01		
	319.82	35.58	370.45	40.70	0.900	0.100	0.901	0.099	1.01		
xr18	937.96	65.69	1418.46	98.62	0.935	0.065	0.935	0.065	1.01	133	645.7
	1069.49	74.88	1441.73	100.16	0.935	0.065	0.935	0.065	1.01		
xr39	110.49	6.48	1502.52	86.53	0.945	0.055	0.946	0.054	1.02	129.5	612
	383.15	22.69	1576.96	91.02	0.944	0.056	0.945	0.055	1.03		
xr38	302.00	5.60	1541.45	28.09	0.982	0.018	0.982	0.018	1.02	130	612
	331.56	6.18	1443.76	26.47	0.982	0.018	0.982	0.018	1.02		

APPENDIX I
Benzene/Isopropyl alcohol standard data

Table 26. Standard data, benzene/isopropyl alcohol.

Standard number	weight benzene	weight ipa	actual wt% benzene	actual wt % ipa	area benzene	area ipa	area % benzene	area % ipa
xst115	0.9802	2.9898	32.78%	67.22%	54.880	98.758	35.72%	64.28%
			32.78%	67.22%	55.185	101.314	35.26%	64.74%
			32.78%	67.22%	52.850	96.069	35.49%	64.51%
xst116	2.0131	3.5581	56.58%	43.42%	75.185	47.576	61.24%	38.76%
			56.58%	43.42%	71.489	46.237	60.72%	39.28%
			56.58%	43.42%	78.542	48.501	61.82%	38.18%
xst117	3.07	3.6863	83.28%	16.72%	84.157	9.194	90.15%	9.85%
			83.28%	16.72%	87.272	10.024	89.70%	10.30%
			83.28%	16.72%	92.249	11.255	89.13%	10.87%
xst 120	0.2454	3.3235	7.38%	92.62%	8.427	97.007	7.99%	92.01%
			7.38%	92.62%	10.258	117.078	8.06%	91.94%
			7.38%	92.62%	8.550	98.520	7.99%	92.01%
xst121	0.9363	3.4651	27.02%	72.98%	24.182	58.493	29.25%	70.75%
			27.02%	72.98%	25.186	61.525	29.05%	70.95%
			27.02%	72.98%	34.216	81.726	29.51%	70.49%
xst122	1.751	3.4505	50.75%	49.25%	62.189	51.021	54.93%	45.07%
			50.75%	49.25%	65.542	53.552	55.03%	44.97%
			50.75%	49.25%	72.086	59.541	54.77%	45.23%
xst123	3.1517	3.6841	85.55%	14.45%	98.552	8.752	91.84%	8.16%
			85.55%	14.45%	100.254	8.226	92.42%	7.58%
			85.55%	14.45%	105.186	9.054	92.07%	7.93%
xst124	3.3251	3.5249	94.33%	5.67%	110.250	2.451	97.82%	2.18%
			94.33%	5.67%	102.584	2.065	98.03%	1.97%
			94.33%	5.67%	115.186	2.752	97.67%	2.33%

Regression Information:

$$\text{Actual wt\% benzene} = \text{Area \% benzene} * 0.9371$$

$$r^2 = 0.998$$

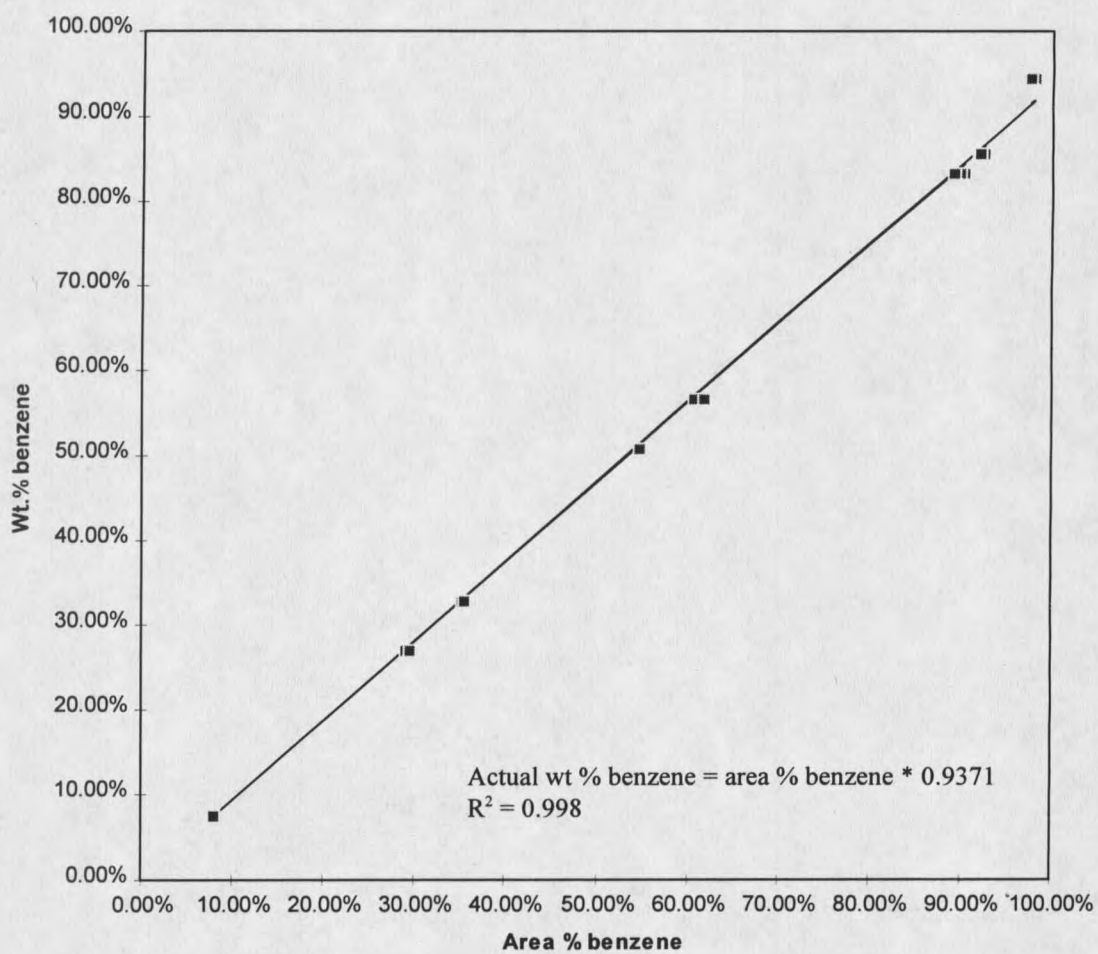


Figure 33. Standard curve - benzene/ isopropyl alcohol analysis.

APPENDIX J

Table 27. Time Test, benzene/isopropyl alcohol

Time (min)	area counts - vapor		mole fraction vapor benzene	Time (min)	area counts - vapor		mole fraction vapor benzene
	benzene	ipa			benzene	ipa	
			0				
5	7.272935	7.856471	0.387	60	26.07193	28.39303	0.385
5	5.778348	6.244753	0.387	60	24.32513	26.47889	0.385
5	8.027729	8.66989	0.387	60	25.22657	27.48346	0.385
10	12.6487	13.61994	0.387	70	39.08011	42.57068	0.385
10	12.7487	13.78285	0.387	70	37.33331	40.72041	0.385
10	12.9487	14.01095	0.386	70	38.23474	41.64219	0.385
15	11.74692	12.73391	0.386	80	39.40534	42.87208	0.385
15	12.21692	13.2605	0.386	80	37.65854	41.00914	0.385
15	11.80692	12.79661	0.386	80	38.55998	42.0026	0.385
20	26.47945	28.74584	0.386	90	38.46701	41.90695	0.385
20	25.51705	27.72644	0.385	90	36.72021	40.0576	0.385
20	26.33156	28.61953	0.385	90	37.62165	40.99276	0.385
25	45.15826	49.17646	0.385	100	22.76826	24.77133	0.385
25	31.86513	34.74705	0.385	100	21.02146	22.86063	0.385
25	42.8919	46.71616	0.385	100	21.9229	23.81571	0.385
30	26.16051	28.46201	0.385	110	22.17568	24.08721	0.385
30	26.63051	28.96041	0.385	110	20.42888	22.18984	0.385
30	26.22051	28.48437	0.385	110	21.33032	23.20421	0.385
40	28.10165	30.52399	0.385	120	23.43997	25.48117	0.385
40	27.33865	29.69522	0.385	120	21.69317	23.58226	0.385
40	27.36755	29.77181	0.385	120	22.5946	24.56219	0.385
50	27.10228	29.52829	0.385				
50	25.35548	27.63747	0.385				
50	26.25691	28.60086	0.385				

Table 28. VLE Data, benzene/isopropyl alcohol.

Run #	area counts - liquid		area counts - vapor		mass fraction	mass fraction	mole fractions	mole fraction	T	P
	benzene	ipa	benzene	ipa	liquid benzene	vapor benzene	liquid benzene	vapor benzene		
xr 50					0	0	0	0	78.1	638.5
xr51	5.16857	202.9349	12.04587	160.8183	0.023	0.065	0.018	0.051	77.9	640.5
	6.2587	247.6386	12.5487	167.5313	0.023	0.065	0.018	0.051		
	5.84975	230.989	11.58492	154.6644	0.023	0.065	0.018	0.051		
xr52	7.81548	143.7087	25.15648	154.6486	0.048	0.131	0.038	0.104	76.9	640.5
	8.1547	149.9461	24.81795	152.5675	0.048	0.131	0.037	0.104		
	8.00548	147.2023	24.99851	153.6775	0.048	0.131	0.037	0.104		
	10.51698	94.20497	25.18555	74.81773	0.094	0.236	0.074	0.192		
xr53	9.95586	89.1788	24.81975	73.73107	0.094	0.236	0.073	0.192	75.1	640.5
	11.57486	103.6809	23.78941	70.67027	0.094	0.236	0.074	0.192		
	6.46268	41.99145	36.79758	78.98685	0.125	0.298	0.099	0.246		
xr54	6.22348	40.43724	37.12282	79.68498	0.125	0.298	0.100	0.246	74.1	641.2 ⁸⁰
	6.27466	40.76978	36.18449	77.67082	0.125	0.298	0.099	0.246		
	10.24329	32.10141	20.48574	22.3004	0.227	0.449	0.184	0.385		
xr60	10.50662	32.92665	19.89316	21.65533	0.227	0.449	0.183	0.385	71.2	641.2
	10.69906	33.52974	21.15744	23.0316	0.227	0.449	0.182	0.385		
	9.28046	15.02575	27.90354	18.84763	0.358	0.559	0.300	0.494		
xr61	10.84912	17.56553	26.59769	17.96558	0.358	0.559	0.302	0.494	68.8	641.2
	10.49206	16.98743	33.34495	22.52307	0.358	0.559	0.298	0.494		
	29.2885	30.63028	32.12255	18.18628	0.458	0.598	0.394	0.534		
xr62	22.39856	23.4247	32.78973	18.564	0.458	0.598	0.393	0.534	67.9	641.3
	26.45776	27.66986	29.06582	16.4557	0.458	0.598	0.389	0.534		
	32.92044	19.48608	16.50855	8.160999	0.589	0.627	0.524	0.564		
xr63	39.14392	23.16985	16.26935	8.042751	0.589	0.627	0.523	0.564	67.5	641.5
	45.41858	26.88391	16.32053	8.068052	0.589	0.627	0.525	0.564		
	25.88169	9.855418	18.19908	8.009439	0.679	0.651	0.619	0.589		
xr64	26.12548	9.948249	17.94799	7.898932	0.679	0.651	0.617	0.589	67.8	639.7
	25.22156	9.604048	18.00179	7.92261	0.679	0.651	0.618	0.589		

Table 28. (Continued)

Run #	area counts - liquid		area counts - vapor		mass fraction liquid	mass fraction vapor	mole fractions liquid	mole fraction vapor	T	P
	benzene	ipa	benzene	ipa	benzene	benzene	benzene	benzene		
xr65	36.77685	8.098918	31.97269	11.99521	0.768	0.681	0.718	0.622	68.6	639.7
	37.30608	8.215464	31.53657	11.83159	0.768	0.681	0.720	0.622		
	36.59318	8.05847	30.47612	11.43374	0.768	0.681	0.716	0.622		
xr59	27.99261	3.980443	36.6193	11.41661	0.820	0.714	0.779	0.658	69.2	639.6
	28.18313	4.007535	36.32812	11.32583	0.820	0.714	0.778	0.658		
	24.4862	3.481846	33.43107	10.42263	0.820	0.714	0.778	0.658		
xr58	20.47735	1.789045	26.12684	6.543897	0.862	0.749	0.828	0.697	69.7	639.7
	20.59417	1.799251	25.84259	6.472699	0.862	0.749	0.829	0.697		
	18.3364	1.601997	23.02517	5.767031	0.862	0.749	0.828	0.697		
xr57	37.99637	0.438184	29.08442	2.710541	0.952	0.857	0.938	0.822	71	638.9
	37.76665	0.445211	28.79963	2.684	0.952	0.857	0.941	0.822		
	33.67355	0.448421	25.97611	2.42086	0.952	0.857	0.937	0.822		
xr56	51.31543	0.94934	59.27757	1.124961	0.991	0.920	0.988	0.898	71.7	638.9
	50.73307	0.96765	58.69627	1.113929	0.991	0.920	0.988	0.898		
	44.93897	1.036327	52.91438	1.004201	0.991	0.920	0.988	0.898		
xr55					1	1	1.000	1	74.6	639.8

APPENDIX K

Calculations from Wilson Parameters

Compositions were calculated from the optimized Wilson parameters using a spreadsheet trial and error method. A sample of the spreadsheet is shown on the following page. At the top of the page values are listed for the Wilson parameters, Antoine coefficients, as well as regression information for molar volumes. Below these values, 15 columns are used to calculate vapor compositions. The first column contains liquid compositions. Column 2 contains temperature values. This is the column that must be optimized by trial and error. Columns 3 through 8 calculate molar volumes, Wilson parameters, and activity coefficients. Column 9 contains the pressure at which the data is being evaluated. Columns 10 through 13 calculate saturation pressures and partial pressures, while column 14 calculates an experimental total pressure. Column 15 calculates vapor compositions. In the method, values in column 2 are adjusted such that the values in column 9 and column 14 are equal. That is, the temperature is adjusted until the experimental total pressure is equal to the actual pressure. The sample shown on the next page shows the steps taken for one data point. The first line is the experimental temperature, which is used as a starting point for the procedure.

Figure 29. Spreadsheet for calculations using Wilson parameters.

Wilson parameters				component 1 = benzene component 2 = isopropyl alcohol										
a_{12}	337.08													
a_{21}	802.85													
Molar volume information				Antoine coefficients										
v_1	0.12413	85.9084		$a_1=$ 6.90565	$a_2=$ 8.11778									
v_2	0.12158	73.1450		$b_1=$ 1211.033	$b_2=$ 1580.92									
				$c_1=$ 220.79	$c_2=$ 219.61									
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
x	t	v_1	v_2	G_{12}	G_{21}	γ_1	γ_2	P	P°_1	P°_2	p_1	p_2	P^{exp}	y_1
0.184	71.2	94.747	81.802	0.5274	0.3581	2.35	1.04	640	572.97	480.30	248.23	408.92	657.150	0.388
0.184	70	94.598	81.656	0.5264	0.3567	2.36	1.04	640	550.83	456.03	239.15	388.30	627.444	0.374
0.184	70.5	94.660	81.717	0.5268	0.3573	2.36	1.04	640	559.97	466.01	242.90	396.78	639.681	0.380
0.184	70.6	94.672	81.729	0.5269	0.3574	2.36	1.04	640	561.82	468.03	243.66	398.50	642.152	0.381
0.184	70.55	94.666	81.723	0.5269	0.3573	2.36	1.04	640	560.89	467.02	243.28	397.64	640.916	0.380
0.184	70.54	94.665	81.722	0.5269	0.3573	2.36	1.04	640	560.71	466.82	243.20	397.47	640.669	0.380
0.184	70.51	94.661	81.718	0.5268	0.3573	2.36	1.04	640	560.16	466.22	242.98	396.95	639.928	0.380
0.184	70.52	94.662	81.719	0.5268	0.3573	2.36	1.04	640	560.34	466.42	243.05	397.12	640.175	0.380
0.184	70.515	94.662	81.719	0.5268	0.3573	2.36	1.04	640	560.25	466.32	243.01	397.04	640.051	0.380
0.184	70.512	94.661	81.718	0.5268	0.3573	2.36	1.04	640	560.19	466.26	242.99	396.99	639.977	0.380
0.184	70.513	94.661	81.719	0.5268	0.3573	2.36	1.04	640	560.21	466.28	243.00	397.00	640.002	0.380

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