RAPID DETERMINATION OF VAPOR-LIQUID EQUILIBRIA

— An Undergraduate Laboratory Exercise —

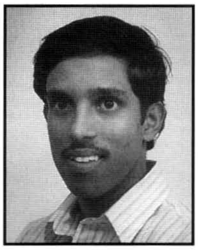
SCOTT W. CAMPBELL, VENKAT R. BHETHANABOTLA
University of South Florida • Tampa, FL 33620-5350

Because of its role in the design of staged separation processes, phase equilibria is given considerable attention in the undergraduate chemical engineering curriculum. Owing to the continued importance of distillation, vapor-liquid equilibrium receives the most emphasis. Often, classroom instruction on this topic (typically in a second thermodynamics course) is supplemented by a laboratory exercise in which students measure vapor-liquid equilibria for a binary mixture. Generally, a classical approach is followed in which a mixture is charged either to a static cell maintained at constant temperature or to a boiling still operated at constant pressure. After allowing time for the liquid and vapor phases to equilibrate, temperature and pressure are recorded and samples of both phases are taken for composition determination.

The determination of composition requires time-consuming analytical techniques such as gas chromatography and refractive index measurement. In a three-hour laboratory period, students may have time to take only one or two data points over the entire mixture composition range between the two pure components. This may allow them to compare their measurements to published results, but it gives them no experience in the treatment of data. Of particular importance in the context of vapor-liquid equilibrium is the process of data reduction, which includes selecting an activity coefficient model to represent the data, fitting the model to the data, and testing whether the selected model is appropriate.

For mixtures at pressures below several bars, the total pressure method is an alternative to the classical approaches of measuring vapor-liquid equilibria. Here, the equilibrium pressure P of a binary vapor-liquid mixture is measured as a function of liquid-phase mole fraction x_1 at constant temperature. Vapor-phase mole fractions y_1 are not measured but are derived from the P-x_1 data.

***Scott Campbell** received his BE in chemical engineering from Youngstown State University and his MS and PhD from Northwestern University. He has been at the University of South Florida since 1986, and his research is in the areas of phase equilibria and physical property measurement.*



***Venkat Bhethanabotla** received his BS in chemical engineering from Osmania University (India) and his PhD from Penn State. He has been teaching at the University of South Florida since the fall of 1987. His research interests are in computer simulation and statistical mechanics and in physical property measurement.*

The total pressure method and the reduction of total pressure data were examined in a series of papers by Van Ness and coworkers[1-5] who found that the technique was capable of yielding precise pressures and accurate vapor-phase compositions. Moreover, they described a method[1] by which liquid-phase compositions could be precisely determined without sampling and analysis. The result was a rapid technique that allows determination of an equilibrium state every fifteen to twenty minutes. With this method, it is possible for students to obtain a number of data points sufficient for meaningful data reduction.

Over the past several years, students in our phase and chemical equilibria course have measured vapor-liquid equilibria with a total pressure apparatus. We believe this exercise provides a valuable supplement to classroom instruction and that the details are worthy of dissemination. Our aim here is to describe the total pressure method and how we have implemented it as an undergraduate laboratory experiment.

Since an understanding of the data reduction procedure is essential to the full appreciation of the method, it will be described first. This subject has been considered in detail by Abbott and Van Ness,[4] so only a brief summary will be given here.

DATA REDUCTION

A typical vapor-liquid isotherm for a binary system is shown in Figure 1. A single equilibrium state at this temperature (illustrated by the tie-line shown in the figure) is characterized by values of the equilibrium pressure P, the liquid-phase mole fraction x_1, and the vapor-phase mole fraction y_1. A collection of data for such states, if sufficient in number, would define the entire isotherm shown in this figure.

For simplicity, we will assume that the vapor phase is an ideal gas and that the Poynting corrections to the pure liquid fugacities are negligible. These assumptions may be relaxed without changing the fundamental approach to data reduction. According to thermodynamic theory, the equilibrium state described by a tie-line is one in which the component fugacities are the same in both phases. Under the assumptions indicated above, the equations representing a tie-line are

$$\gamma_1 x_1 P_1^{sat} = y_1 P \qquad (1)$$

and

$$\gamma_2 x_2 P_2^{sat} = y_2 P \qquad (2)$$

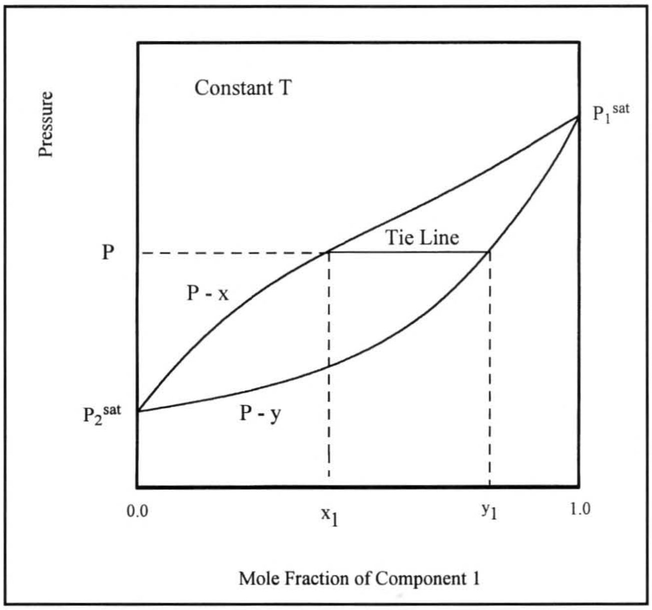


Figure 1. *Pressure vs. liquid phase mole fraction x_1 of component 1, and vapor phase mole fraction y_1 of component 1 for a binary system at constant temperature.*

Our aim here is to describe the total pressure method and how we have implemented it as an undergraduate laboratory experiment.

where $y_2 = 1-y_1$ and $x_2 = 1-x_1$. In Eqs. (1) and (2), P_1^{sat} and P_2^{sat} are the vapor pressures of pure species 1 and 2 at the temperature of the experiment, and γ_1 and γ_2 are the liquid-phase activity coefficients of species 1 and 2. Generally, the activity coefficient is a function of temperature, pressure, and liquid-phase mole fraction. At low pressure, however, the pressure dependence is negligible and, since the experiment has been done under isothermal conditions, the activity coefficients may be regarded as functions only of x_1.

In a classical experiment, both pressure P and vapor-phase mole fraction y_1 are measured as a function of x_1 at constant temperature. Data reduction involves fitting an activity coefficient model to values of γ_1 and γ_2 that have been calculated from these data via Eqs. (1) and (2). Once obtained, this model may be substituted into the same two equations to calculate vapor-phase mole fraction y_1 and pressure P at each experimental value of x_1. These calculated values are then compared to the measured values of P and y_1 to assess the suitability of the selected model.

Data taken by the total pressure method consist only of pressure P as a function of x_1 at constant temperature. Hence, a total pressure apparatus can completely define the curve labeled P-x in Figure 1, but not the curve labeled P-y. Since vapor-phase compositions are not measured, values of the activity coefficients cannot be calculated and the data reduction procedure described above cannot be applied.

Two means of treating total pressure data have been described in the literature. The first[6] is based on integration of the coexistence equation and does not require that a model for the activity coefficients be assumed a priori. The second approach, based on ideas put forth by Barker,[7] requires that a model be assumed. Since we wish to emphasize the role of modeling in the representation of vapor-liquid equilibria, Barker's method is the preferred approach and is described here.

To fix ideas, we assume the availability of n sets of equilibrium pressure P and liquid-phase mole fraction x_1 measured at constant T. These should include the pure component vapor pressures P_1^{sat} and P_2^{sat} measured at $x_1=1$ and $x_1=0$, respectively. Our goals are to select an activity coefficient model, to obtain values for the model parameters using the P-x_1 data, to calculate the vapor-phase composition for each experimental liquid-phase composition, and to assess the suitability of the selected model.

Equations (1) and (2) may be rearranged into a form more suitable for reduction of total pressure data:

$$P = \gamma_1 x_1 P_1^{sat} + \gamma_2 x_2 P_2^{sat} \tag{3}$$

and

$$y_1 = \gamma_1 x_1 P_1^{sat} / P \tag{4}$$

The first step in application of Barker's method is to select an activity coefficient model, which we will represent by

$$\gamma_1 = f_1(x_1, A, B, \ldots) \qquad \text{and} \qquad \gamma_2 = f_2(x_1, A, B, \ldots) \tag{5}$$

Equation (5) emphasizes that the activity coefficients are functions of liquid-phase composition and depend parametrically on some number of adjustable constants A, B, ... that are obtained from fitting the model to experimental data. The model for γ_1 and γ_2, of course, must satisfy the Gibbs-Duhem equation.

The activity coefficient model may be selected from among a number of popular models such as the Margules, van Laar, Wilson, NRTL, and UNIQUAC equations. For highly nonideal systems, it may be necessary to use more flexible models, such as those suggested by Abbott and Van Ness[4] or by Campbell.[8]

Once a model is selected, it is substituted into Eq. (3) and values for parameters A, B, ... are obtained by minimizing an objective function OF given by

$$OF = \sum_{i=1}^{n} \left(P_{i,exp} - P_{i,calc} \right)^2 \tag{6}$$

where $P_{i,exp}$ are the measured pressures and $P_{i,calc}$ are pressures calculated from the model via Eq. (3).

The suitability of the selected activity coefficient model can be assessed by examining a plot of the pressure residuals $P_{i,exp} - P_{i,calc}$ versus x_1. If the residuals scatter randomly around zero to within the precision of the apparatus, the model is adequate. If not, a different model must be assumed and the procedure repeated.

It is evident from this discussion that Barker's method does not require measured values of the vapor-phase composition for its implementation. Once data reduction is complete, however, values of y_1 can be computed for each experimental value of x_1 from Eq. (4). Abbott and Van Ness[4] found that calculated vapor-phase mole fractions will be accurate if the selected activity coefficient model provides an adequate representation of the equilibrium pressures. In fact, upon applying classical procedures and Barker's method to the same complete sets of P-x_1-y_1 data, they found that vapor-phase compositions calculated from Barker's method were *at least* as reliable as those computed from classical approaches, even though the latter used the experimentally determined vapor-phase compositions in data reduction.

TOTAL PRESSURE APPARATUS

The apparatus we use in our undergraduate laboratory is based on the design suggested by Gibbs and Van Ness.[1] A schematic diagram is shown in Figure 2. Each of the two pure components comprising the binary system under examination is stored in its own piston injector. The injectors are equipped with scales that allow the volume of liquid pumped from an injector into the equilibrium cell to be determined to within 0.001 cm^3.

The overall composition of the mixture in the equilibrium cell is computed from the cumulative volumes of liquids pumped from the two piston-injectors. Since the liquids stored in the injectors are only lightly compressed, liquid volumes are converted to moles using saturated liquid densities at room temperature. Bourdon tube gauges are placed on each injector so that the operator may ensure (by slightly compressing the liquids) that no vapor space exists within the piston-injectors or charging lines. Use of the Bourdon tube gauges also facilitates using the same charging pressure for each addition of liquid so as to minimize any small but systematic effects of pressure on the liquid densities.

The details of the equilibrium cell F are shown in Figure 3. Our cell is made from Pyrex and has an internal volume of about 130 cm^3. It is suspended in a water bath in which the temperature is controlled (typically at 30 °C) by a heater-circulator. The contents of the equilibrium cell are agitated using a submersible stirrer.

The pressure inside the equilibrium cell is measured to 0.001 kPa resolution using a Baratron pressure gauge. The pressure gauge and the lines between the cell and pressure gauge are wrapped with heating tape and are maintained at 60°C with a proportional controller so as to prevent condensation of the equilibrium cell contents within them.

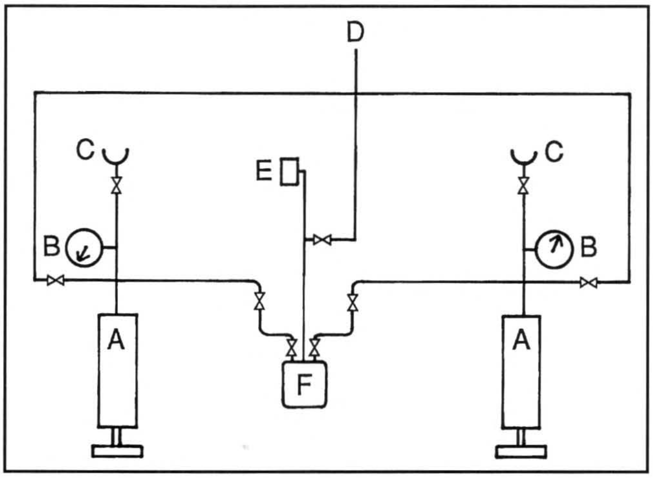


***Figure 2.** Schematic of total pressure apparatus. A-piston injector; B-Bourdon gauge; C-fill tube; D-vacuum line; E-Baratron pressure gauge; F-equilibrium cell*

PROCEDURE

Before starting a run it is important to degas both pure liquids since measurement of vapor pressure is highly sensitive to the presence of dissolved air. We degas liquids by simple vacuum distillation. Here, a glass bulb with a stopcock is partially filled with one of the pure liquids and is connected to a vacuum pump via a liquid nitrogen trap. A sequence of shaking the bulb followed by opening the stopcock to evacuate the vapor space is performed. It is usually found that ten or so repetitions of this sequence are enough to degas the liquid. Van Ness and Abbott[9] describe a simple "click" test that we use to test for sufficient degassing.

Once both pure liquids have been degassed, the entire apparatus is evacuated and the liquids are charged to their respective piston injectors through the fill tubes. Next, the equilibrium cell is isolated from the vacuum line and a portion of the contents of the piston injector storing the first component are metered into the equilibrium cell. After allowing time for equilibration, the pressure (which is the vapor pressure of the pure first component) is recorded. A measured amount of the second component is then metered into the cell and the total pressure is recorded after equilibration (typically fifteen to twenty minutes, as evidenced by constancy of pressure within the equilibrium cell). This procedure is repeated until approximately one-half of the composition range is covered. In a three-hour lab period, a group of students can be expected to obtain five or six data points over this range.

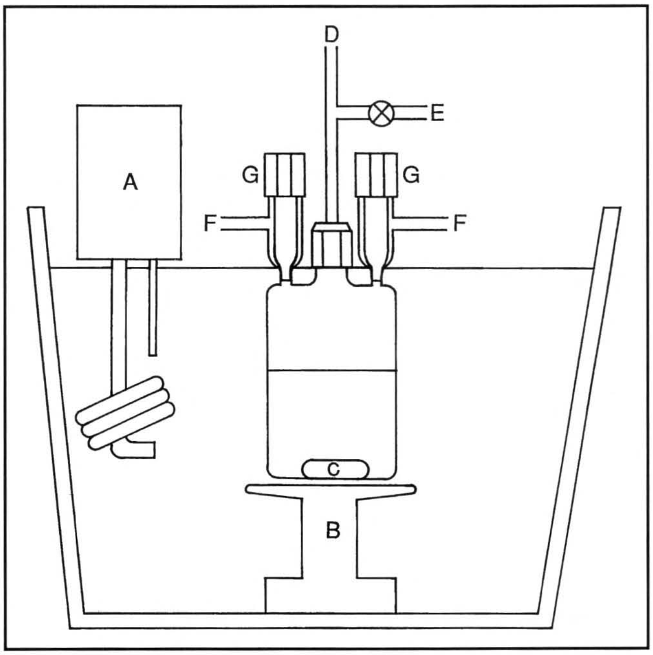


Figure 3. *Schematic of equilibrium cell. A-heater-circulator; B-submersible stirrer; C-stirring bar; D-line to Baratron gauge; E-vacuum line; F-line to piston-injector; G-Teflon valves*

At this point, the equilibrium cell is evacuated, but the remaining pure liquids are left in the piston-injectors. The next day, a second group of students repeats the procedure described above except that they begin the run by first charging the *second* component to the equilibrium cell. Furthermore, they are instructed to finish their run at or near the last composition examined by the group that worked on the previous day. This provides a check of the internal consistency between the two runs. The two laboratory groups are instructed to share their results so that each group has a complete isotherm to analyze.

One point about the procedure described above requires additional discussion. The volumes of liquids charged to the equilibrium cell from the piston-injectors are sufficient to provide overall composition within the equilibrium cell, but not the liquid-phase composition. At the low pressures examined in our laboratory (typically less than 300 torr and always less than one atmosphere), however, the density of the vapor phase is very small compared to that of the liquid. As a result, the difference between the overall cell composition and the liquid-phase composition is small (0.001 or less in mole fraction) and may be neglected. It is possible to correct the overall cell composition to liquid-phase composition, as we do in our research, by making appropriate modifications to the data reduction program. Details are described elsewhere.[10] But whether this modification is made or not, students should be encouraged to examine the effect of assuming these two compositions to be equal.

SAMPLE RESULTS

It is probably inappropriate in an undergraduate course to require that the students write their own nonlinear regression program to fit an activity coefficient model to their data. Fortunately, an instructor in an earlier course in our curriculum requires the students to purchase a software package (TKSolver) for solving equations. TKSolver contains a library that has, among other tools, a nonlinear regression subroutine based on the Nelder-Mead flexible polyhedron search. We have written the code that applies this search technique to reduction of total pressure data and supply it on diskette to each group of students.

Only the very basic parts of the data reduction procedure are included in this code, and students are encouraged to modify it to allow use of different activity coefficient models or to produce the various graphs and tables that are asked for in the laboratory handout. Students that later elect to make measurements as part of an independent study project can modify the code to account for vapor-phase nonidealities and to correct the overall compositions to the liquid-phase compositions.

Some plots prepared from results taken from student laboratory reports are shown in Figures 4-6. These particular groups measured total pressures for the methanol-water system at 35°C and used the 4-suffix Margules equation (3 adjustable parameters) as a model for the liquid-phase activity coefficients. Figure 4 shows a graph comparing students' P-x_1 data to that calculated from the model and also to data taken from the literature.[11] Figure 5 compares vapor-phase mole fractions derived from their P-x_1 data to directly measured values obtained from the literature. The agreement is typical of the results that the students obtain in this laboratory exercise.

The suitability of the model can be assessed by examining the pressure residuals as shown in Figure 6. Curves that represent the precision of the apparatus are also shown and were calculated from estimated uncertainties in temperature bath reading, piston-injector scale reading, and calibration of the pressure gauge. While this plot indicates that the 4-suffix Margules model provides a reasonable fit to the data, the residuals exceed the precision of the apparatus at low methanol concentrations. This, along with the nonrandom scatter of the residuals, indicates that a more sophisticated model is appropriate for this system. Figure 7 shows the residuals resulting from application of the 5-suffix Margules equation (one additional parameter) to the same set of data. The residuals are more nearly random and fall within the precision of the apparatus.

OTHER CONSIDERATIONS

The apparatus described here was not built with undergraduate instruction in mind. Rather, we use it for our research on vapor-liquid equilibria of mixtures for which hydrogen bonding is important. Due to our unique lab structure at the University of South Florida, in which individual laboratory exercises are not part of a laboratory course but are tied directly to classroom lectures on the same concepts, scheduling is not difficult: the apparatus is used for research during the first eight weeks and last four weeks of the semester and is used for undergraduate labs during the intervening three weeks.

One might wonder, however, if the expense of such an apparatus would be justified for exclusive use in the undergraduate curriculum. The most expensive part of the apparatus is the pressure measurement system ($6000), followed by the heater-circulator ($1000) and the vacuum pump ($1000). The piston-injectors we use are manufactured by Ruska and are quite expensive, but we have also used less expensive injectors that are available for approximately $1000 each. The supporting equipment, including the water bath, submersible stirrer, temperature controller for the pressure sensor, and heating tape can be obtained for less that $1000, as can the valves, glassware, fittings, and lines. All in all, the apparatus can be constructed for perhaps $12,000. This is not out of line with costs of other laboratory exercises and is particularly less expensive than those that require equipment for composition analysis.

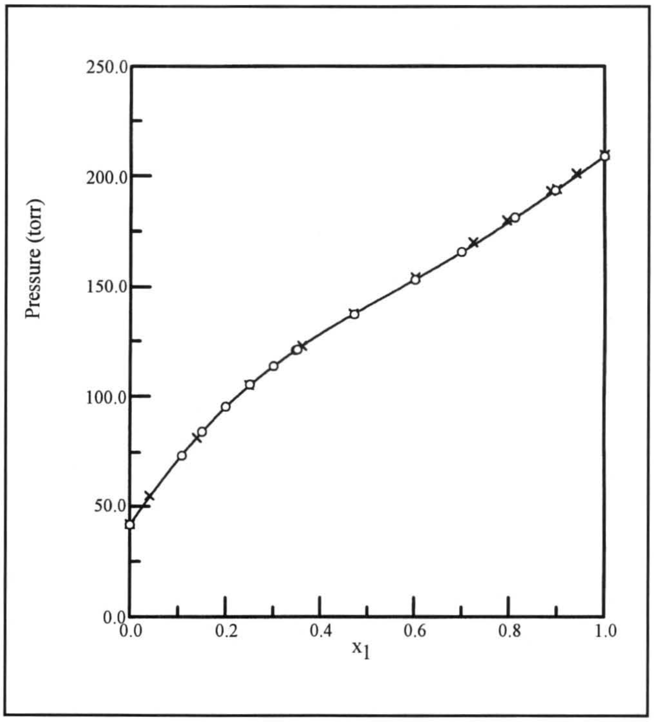


Figure 4. *Pressure vs. liquid-phase mole fraction x_1 for methanol (1) + water (2) at 35°C (o=student data; x=literature results;[11] line represents fit of 4-suffix Margules model to student data.*

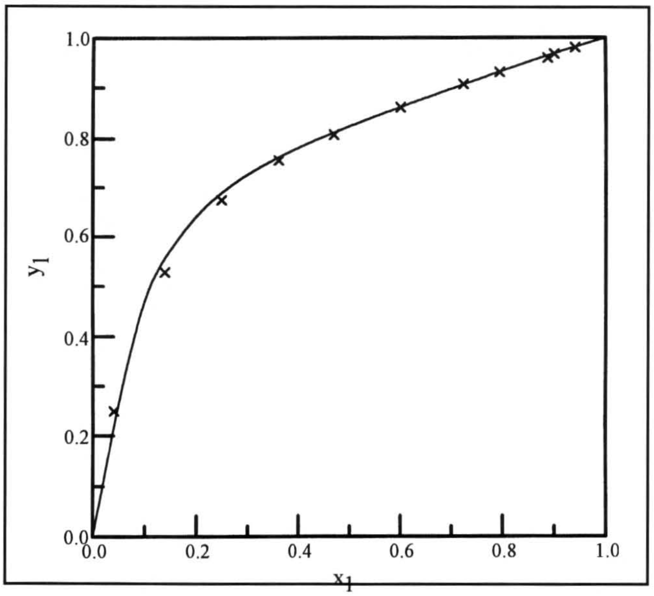


Figure 5. *Vapor-phase mole fraction y_1 vs. liquid-phase mole fraction x_1 for methanol (1) + water (2) at 35°C (x=literature results;[11] line represents results derived from fit of 4-suffix Margules model to student P-x_1 data).*

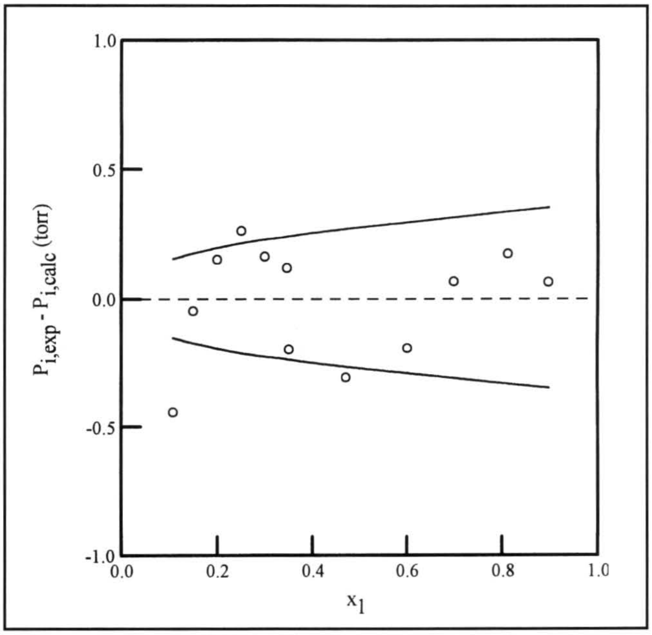


Figure 6. *Pressure residuals $P_{i,exp}$ - $P_{i,calc}$ vs. liquid-phase mole fraction x_1 of methanol resulting from selection of the 4-suffix Margules equation. Solid lines represent the precision of the apparatus.*

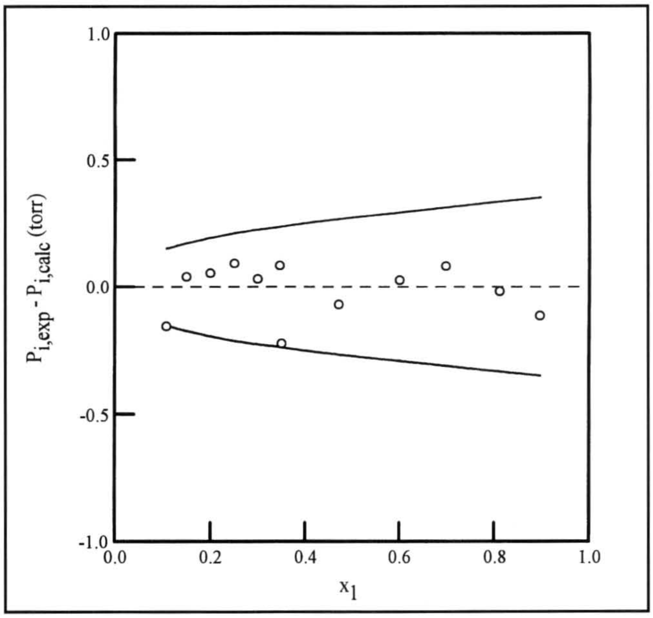


Figure 7. *Pressure residuals $P_{i,exp}$ - $P_{i,calc}$ vs. liquid-phase mole fraction x_1 of methanol resulting from selection of the 5-suffix Margules equation.*

CONCLUSIONS

We believe the apparatus and procedure described here have greatly enhanced our students' understanding of vapor-liquid equilibrium. In addition to the obvious benefits of gaining experience in making precise measurements on a research-grade apparatus, the students are exposed to model selection and to fitting a model to their own data. Furthermore, they see first-hand the difference between precision (how smooth their data are) and accuracy (reflected by agreement with literature data within the combined experimental error of the two studies). Finally, the indirect approach of obtaining vapor-phase compositions from total pressure data emphasizes the practical application of thermodynamic theory, particularly its utility in extracting maximum information from experimental data.

ACKNOWLEDGMENT

It should be obvious from the text that this laboratory exercise is based on the work of Hendrick C. Van Ness and his colleagues. Our goal here is simply to illustrate how the methods they developed may be incorporated into the undergraduate chemical engineering curriculum. We would like to thank Professor Van Ness for his helpful comments over several years and for generously donating equipment that comprises part of our apparatus.

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