MAKING PHASE EQUILIBRIUM MORE USER-FRIENDLY

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I believe phase equilibrium thermodynamics is the most conceptually difficult undergraduate chemical engineering class. Even students who perform calculations satisfactorily seem confused over the meaning of what they have learned.

Phase equilibrium is the single undergraduate chemical engineering class in which abstract concepts are presented to the near exclusion of practical applications. Table 1 gives examples of practical or physically intuitive subject matter found in classes that students typically consider abstract, theoretical, or mathematical. These actually contain some balance of theory and practice, giving students a point of reference to physical processes and equipment. Calculations such as bubble and dew points are needed for practical design, of course, but most phase equilibrium courses do not connect these to real processes or equipment. Practical applications of the material are taught as part of unit operations, mass transfer, or distillation courses.

Students frequently have more intuition about the physical meaning of abstract quantities in classes other than phase equilibrium. Heat transfer students could define the Prandtl number as $C_p\mu / k$, give a physical interpretation for all three variables, and potentially recognize related facts. For example, "The Prandtl number could be derived by applying the Buckingham Pi theorem to a heat transfer problem," or "Larger Prandtl numbers result in larger convective heat transfer coefficients." They know that the Prandtl number for liquid water at 100 atm and 150°C is unlikely to be 100 or 0.01.

When phase equilibrium students define chemical potential, it is typically in terms of other abstract concepts—free energy, standard states, fugacity, and activity. They are unlikely to know whether a certain chemical potential is positive or negative, nor what practical significance its sign would have. Without doing a calculation, how many phase equilibrium students know whether the fugacity of liquid water at 100 atm and 150°C is closest to 5 atm, 50 atm, or 500 atm? Most are at a complete loss when asked to apply abstract quantities such as activity coefficients to practical questions, *e.g.*, "Is ethanol more likely to form an azeotrope with n-hexane or n-octane?" Lacking qualitative understanding, their only approach for answering this question is detailed quantitative calculation.

STRATEGIES FOR BUILDING INTUITION

Prausnitz, et al.,[1] describes the phase equilibrium problem as a three-step process. First, a real problem is translated into an abstract mathematical problem. Second, the mathematical problem is solved. In the final step, the mathematical solution is translated back into physically meaningful

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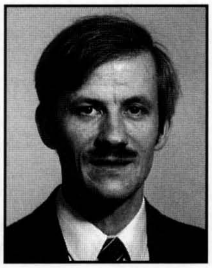

TABLE 1
Content of "Theoretical" ChE Classes

Class	Theoretical Concepts	Practical Concepts
Fluid Mechanics	Shear stress tensor, Dimensional Analysis	Pumps, Valves, Piping
Mass Transfer	Fluxes of all sorts	Packed absorption towers
Transport Phenomena	Partial differential equations, Dimensionless Greek variables	Viscometers, Heat transfer with free convection, Wetted wall columns
Phase Equilibrium	Chemical potential fugacity, activity	Bubble and Dew Points, Flash, Solubilities

TABLE 2

Common Intuition about Chemical Engineering Data

- High moleclar weight compounds have high boiling points
- A substance with a density order of magnitude less than water is probably a gas
- A Reynolds number in the laminar range for flow of water in typical process piping is not typical
- Convective heat transfer coefficients are very low for gases as compared to liquids

TABLE 3

Uncommon Intuition about Phase Equilibrium Data

- The fugacity of a liquid is approximately its vapor pressure, as long as the pressure is not extremely high
- The fugacity of a component in an ideal gas mixture is its partial pressure
- Substances we consider noncondensible gases have fugacity coefficients larger than one; liquids and condensible vapors have fugacity coefficients smaller than one
- Substances with large differences in boiling points are unlikely to form azeotropes; substances with very close boiling points are almost certain to form them
- Activity coefficients larger than approximately seven indicate that liquid-liquid phase separation is possible
- The dilute component in either of two nearly immiscible phases obeys Henry's Law up to its solubility limit

terms. Typically, this step consists of transforming highly abstract variables into physically significant ones.

Chemical Potential ➔ Fugacity ➔ Activity ➔ Composition

Each transformation results in a less abstract variable than the previous step. Students do not seem to recognize this, perhaps because we do not teach it explicitly. Instead, they see chemical potential, fugacity, and activity as equally nebulous and abstract concepts upon which a rote series of mathematical operations will hopefully produce a physically meaningful variable such as composition, pressure, or temperature.

One of my principal goals in teaching phase equilibrium thermodynamics is to help students develop an intuitive understanding of the topic. I point out to them in the beginning that this class deals with techniques for generating data to use in other classes to the nearly total exclusion of applications. Since students will not be able to rely on processes or equipment to provide intuition, I emphasize understanding the data and its significance. This type of intuition about data, rather than equipment, occurs in other classes as the Prandtl number example above and as similar examples in Table 2 indicate.

To promote this, I emphasize calculation and use of data having an obvious physical interpretation, *e.g.,* temperature, pressure, volume, vapor pressure, composition, and enthalpy. When concepts such as free energy, chemical potential, fugacity, and activity are presented, the focus is partly on their use in solving for the more physical variables. Whenever possible, I encourage students to examine how the abstract variables affect the physical variables, and thus to develop some intuition about the significance of the abstract variables. Examples are given in Table 3; these are sometimes present, but not frequently emphasized, in phase equilibrium texts.

More so than in many chemical engineering classes, phase equilibrium data are most useful and understandable when presented graphically. This is evident from observations given in Table 4 of how frequently graphical material is presented in textbooks.

Thermodynamics and unit operations texts contain more graphs and a higher proportion of figures that are graphs, as opposed to schematic diagrams and other drawings. Within each text, the chapters more

TABLE 4

Comparison of Graphical Figure Use in ChE Textbooks

Textbook	*Graph Figures*	*Non-graph Figures*	*Pages*[b]	*Graphs per 100 pages*	*Percent Graph Figures*
Introduction to Chemical Engineering Thermodynamics[2] (Chapters 10-15)	107 (57)	44 (11)	568 (199)	19 (29)	71 (84)
Chemical and Process Thermodynamics[3] (Chapters 9-13)	116 (62)	60 (6)	541 (253)	21 (25)	66 (91)
Transport Phenomena[4]	69	105	711	10	40
Elementary Principles of Chemical Processes[5] (Chapter 6)	17 (8)	15 (0)	587 (71)	3 (11)	53 (100)
Momentum, Heat, and Mass Transfer[6] (Chapters 35, 37-40)	159 (63)	106 (19)	773 (143)	21 (44)	60 (77)

[a] Graph figures include all two- and three-dimensional coordinate plots and nomographs. Any figure that included both graphical and nongraphical information was treated as a graph figure. Only numbered, captioned figures in text and examples were counted; figures with problems and in appendices were excluded.

[b] Pages include all text, examples, questions, and problems but exclude appendices.

closely related to phase equilibrium have a higher proportion of graphs than the text as a whole, as indicated by the numbers in parentheses in Table 4.

Furthermore, many students have a visual learning style. These students may struggle with equations and textual information, especially in an abstract context, and it is crucial that they see data presented graphically and also learn how to prepare data in a format that is most comprehensible to them. Hence, students need to make the connection between calculations and equations discussed in class and graphical presentation of phase equilibrium data. To assure they are capable of both understanding and generating graphical data, I assign a significant number of computer problems requiring this, as explained in further detail later in this article. Computer spreadsheets have been previously suggested[7,8] for use in solving phase equilibrium and equation-of-state calculations, and they are well suited both for the calculations and for subsequent graphical presentation. One recent text[9] includes a number of example spreadsheets that may be used for applications similar to those described in this article, although I prefer to have students write their own spreadsheets.

DETAILS OF PHASE DIAGRAM COMPUTER ASSIGNMENT

As an illustration of such assignments, consider the construction of a binary Pxy diagram for an ideal solution at some constant temperature. Figure 1 is an example generated by repetitive dew point pressure and bubble point pressure calculations. Taking liquid mole fraction x_1 as the independent variable, and assuming component vapor pressures P_1^{sat} and P_2^{sat} are known, Eqs. (1-3) allow calculation of all dependent variables in the problem. To generate the diagram, allow x_1 to vary over the range 0.0 to 1.0. These calculations are easily done using computer spreadsheet software.

$$x_2 = 1 - x_1 \tag{1}$$

$$P = x_1 P_1^{sat} + x_2 P_2^{sat} \tag{2}$$

$$y_1 = \frac{x_1 P_1^{sat}}{P} \tag{3}$$

Figure 2 shows the general organization of this spreadsheet. The upper rows contain headings and constants such as the vapor pressures. The middle rows are used for calculations. The leftmost column is initially filled with values between 0 and 1 at intervals of 0.01, or a suitable small increment. (This should be done using spreadsheet commands or formulas; occasionally, a student will attempt to enter the numbers manually and become frustrated that using the computer apparently makes solving the problem too time-consuming.) Fill the remaining three columns in the middle rows of the spreadsheet with formulas given by Eqs. (1-3). If these formulas are entered correctly in the first of the middle rows, a single copy/paste command generates the entire table through the remaining middle rows.

There may be one complication in producing a graph from these results. In a conventional Pxy diagram, pressure is taken as the vertical coordinate twice. With liquid composition as the horizontal coordinate, a bubble point curve is produced, then with vapor composition as the horizontal coordinate, a dew point curve is produced. To do this on the spreadsheet, a single y-coordinate must be paired with two different x-coordinates. At one time, few spreadsheet packages included this capability, but many recent versions (including Microsoft Excel) now allow it. If using an older package without this

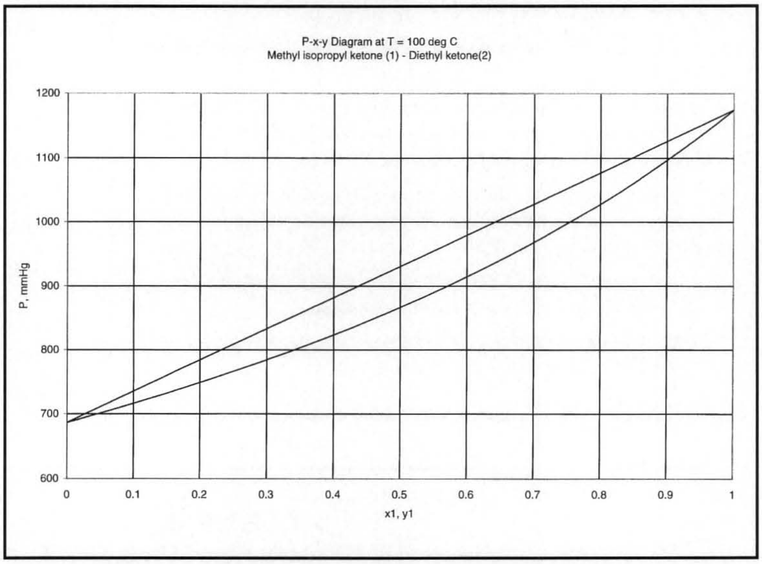

Figure 1. *Pxy diagram prepared using spreadsheet.*

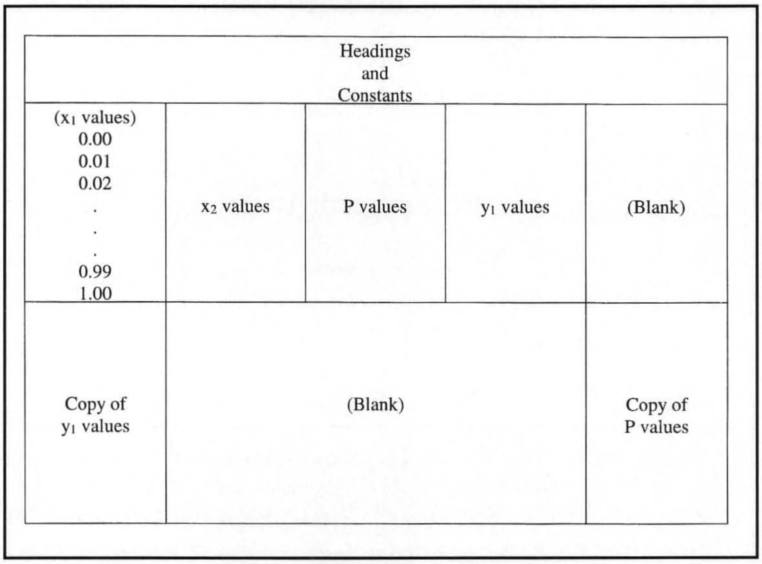

Figure 2. *General structure of spreadsheet for Pxy diagram.*

capability, set up the lower rows of Figure 2 as shown, then define the first column as the x-coordinate for graphing and each of the two columns containing pressure values as separate y-coordinates. The lower rows of Figure 2 can be omitted when using current versions of Excel and other spreadsheets that allow multiple xy pairs to be graphed.

ADDITIONAL COMPUTER ASSIGNMENTS

Table 5 lists other thermodynamic data graphs prepared using computer spreadsheets. A very brief discussion of each follows. Many were prepared by students as homework assignments using techniques similar to those outlined for the Pxy diagram. Copies of these assignments are available upon request. Some graphs were not assigned but were generated by the instructor and presented during class discussion.

TABLE 5
Graphs Prepared Using Spreadsheets for Phase Equilibrium Class

Binary phase diagrams for ideal solutions
- Pxy[a]
- Txy[b]
- xy[a]

Fugacity versus pressure
- Numerical integration of PV data[b]
- Generalized viral coefficient[b]
- Redlich-Kwong equation of state[b]

Volumetric properties of binary nonideal solutions
- Excess volume[a]
- Partial molar excess volumes[a]

Activity coefficients in binary solutions versus composition
- Margules[a]
- Van Laar[b]
- Wilson[a]

Infinite dilution activity versus temperature
- Wilson[a]

Phase diagram for nonideal azeotrope forming binary mixture
- Pxy[b]
- Txy[b]
- xy[a]

Excess free energy of homogeneous azeotrope forming binary mixture versus composition
- Experimental data[a]
- Margules equation (fit to azeotrope data)[a]
- Margules equation (best fit to VLE data)[a]
- Wilson equation (literature constants)[b]

Excess free energy of heterogeneous azeotrope forming binary mixture versus composition
- Experimental data[a]
- Margules equation (best fit to VLE data)[a]
- Margules equation (best fit to LLE solubility data)[a]

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[a] Prepared by students as homework assignment

[b] Prepared by instructor for class discussion

The same spreadsheet data used to produce a Pxy diagram as described above could be used to plot an xy diagram at constant temperature. Pxy and Txy are the predominant representations of VLE data in phase equilibrium classes, but xy is probably the most frequently used format of the phase equilibrium data in other classes, *e.g.*, distillation, absorption, mass transfer.

Using the method described above, generating Pxy data for an ideal binary system at constant temperature does not require trial and error. Calculation of a single Txy datum for an ideal binary system at constant pressure requires iteration or trial and error since the vapor pressures are functions of temperature. But generating a Txy diagram for such a system —the locus of dew and bubble point temperatures for all possible compositions— does not require trial and error. Taking temperature as the independent variable rather than liquid composition, all other variables can be calculated directly by Eqs. (1-3). Selecting a range of temperatures in increments between the pure-component boiling points generates the diagram. Plotting y versus x instead of T versus y and T versus x produces an xy diagram at constant pressure from the same data.

For nonideal binary mixtures, activity coefficients are functions of liquid composition and possibly temperature. Pxy and xy diagrams at constant temperature are generated in a straightforward fashion without iteration since temperature is fixed and liquid composition is taken as the independent variable for generating the table as described above.

Iteration cannot be avoided when generating Txy and xy diagrams at constant pressure for nonideal binaries. To find activity coefficients and vapor pressures, liquid composition and temperature are needed. Only one can be assumed. Direct calculation of liquid composition from vapor pressure, as in the ideal case, is not possible. If temperature is used as the independent variable, as suggested for the ideal case, a unique composition may not result because azeotropes are possible. I recommend using liquid mole fraction as the independent variable ranging from 0 to 1, as in the Pxy diagrams. Iteration can be performed by circular recalculation on the spreadsheet. Unfortunately, spreadsheets vary significantly in their implementation of circular recalculation, even from version to version, and it is difficult to give a "recipe" that works in all cases. Often, particular rearrangements of equations or ordering of the columns is necessary. No matter what package was being used, however, I have always been able to find some method that eventually worked.

Thermodynamics textbooks commonly contain graphs of excess and partial excess properties such as volume and enthalpy for binary solutions. In the volumetric properties assignment, students generate similar graphs for ethanol-water using density data as a function of composition taken from

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handbooks.[10,11] By doing this assignment, students can develop a better intuitive understanding of the meaning of such excess property data because they see where the data came from. Additionally, the magnitude of the variation of activity coefficient with pressure is related to the partial molar excess volume. Using these results, students can prove to themselves why activity coefficients are typically assumed pressure-independent.

Before using activity coefficients in VLE calculations, students prepare a few plots of activity coefficient versus composition or of infinite dilution activity coefficient versus temperature. When they produce graphs similar to those in the textbook, students reinforce their concept of what "shape" these functions should have. Also, by plotting results from several different equations on one graph, students see that it makes little difference which correlation is chosen in most cases. For subsequent VLE and LLE calculations, they typically use the Margules equation because it is the most simple mathematically.

In conjunction with VLE phase diagrams, students produce plots of excess free energy functions. These plots can be used to determine constants in an activity coefficient correlation. For example, a plot of G^E/RTx_1x_2 versus x_1 can be used to determine Margules equation parameters by a straight-line fit. When constants determined by several methods are used to plot an xy diagram, students learn the fit of the data is as important as which equation is used.

Phase separation and LLE are analyzed with graphs of free energy of mixing versus liquid composition. For LLE, it is the shape of these curves—convex or concave—that is the determining factor in phase stability. As with the VLE data, students generate plots of these functions from experimental data points and, by fitting activity coefficient correlations in various ways, compare the results.

Phase equilibrium and chemical reaction equilibrium are often taught in one course. I have also successfully used computer spreadsheet assignments or demonstrations for class discussion in the reaction equilibrium portion of the course.

It is a fundamental belief of mine that students will choose to use the computer and specific software in cases where it makes a problem easier to solve. When I assigned these problems, I did not require the use of specific software. (In fact, I did not require the use of a computer at all, but with the availability of computing resources and the students' general familiarity with computers, no hand-plotted solutions have been submitted in about ten years!) I typically discussed how to structure a spreadsheet for the assignment and frequently had the students work through a hand calculation for a single data point as an in-class exercise.

The majority of students "follow the path of least resistance" and complete the assignment using the standard spreadsheet package, currently Microsoft Excel. The specific choice of spreadsheet has little effect. Students have solved the problems using Quattro Pro, Lotus 1-2-3, SuperCalc, and the Smart Spreadsheet in past years. Moreover, it is unnecessary to use a spreadsheet, as a few students have demonstrated by solving the problems using programming languages (FORTRAN, C), graphics packages, and math solvers (Mathcad, Maple). All students eventually gravitated to spreadsheets by the end of the class, however. The only warning I give to students who use nonstandard computer software is that I may not be able to assist them with computer-related problems if they are using a package with which I am unfamiliar.

CONCLUSIONS

In teaching phase equilibrium thermodynamics, I have attempted to promote understanding and intuition of the course material. Initial explanation that the goals of the class relate mainly to data handling and generation, unlike other chemical engineering classes, prevents confusing expectations from developing. Meaning and consequences of data are emphasized, particularly for abstract quantities such as activity coefficients for which interpretation is not necessarily explicit. Widespread presentation and students' use of graphical data is made convenient using computer spreadsheet software.

ACKNOWLEDGMENTS

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