TECHVIEW

SOFTWARE

An Eye for the Abstract

Perla B. Balbuena

Usually macroscopic concepts are introduced by making connections to everyday experience. This, however, is not always possible. For example, one of the problems that frequently arises in studying the macroscopic behavior of materials is the characterization of the phases present under a given set of conditions. A pure substance, such as water, under some given conditions of pressure P, density ρ (molecules per unit volume), and temperature T, may exist as a liquid, vapor, or solid, or as a mixture of phases. A set made of any pairing of the P, T, and ρ variables constitutes a complete set of independent variables; the expression that relates them is the equation of state. The equilibrium state points (that is, the conditions of pressure, temperature, and density at which any substance exists as a single phase or as a mixture of phases) are usually identified by displaying two-dimensional (2D) phase diagrams. For a pure substance, these are projections on the P-T, P-ρ, and T-ρ planes of three-dimensional (3D) surfaces known as P-ρ-T diagrams. It helps enormously, however, to have access to the full 3D view because one can better interpret the evolution of the system when the macroscopic variables are changed.

Phase
Kenneth R. Jolls *et al.*
Iowa State University.
Available free of charge
at ftp://isua.iastate.edu

When the system consists of a mixture containing two chemical species, the composition (x) must be added to fully represent the equilibrium states, and the phase diagram becomes tetra-dimensional, now represented by P-T-ρ-x. This increases the difficulty in conceptualizing the system. However, carefully designed software and appropriate computer hardware can help the student visualize and grasp these phenomena.

K. R. Jolls, in collaboration with graduate students K. S. Tian and R. Campero, has developed a computer program called Phase (*1*) that permits the display of 3D phase diagrams corresponding to a collection of binary, ternary, and quaternary mixtures. Previous examples of Jolls's thermodynamic visualizations have been published in several related articles (*2–7*) and textbooks (*8–10*). Phase is the first software product to come from his group that deals only with the properties of mixtures. It is a powerful tool for teaching chemical thermodynamics, allowing one to perceive changes in phase diagrams when temperature, pressure, or composition are altered, as well as to visualize the appearance, disappearance, and coexistence of phases. The phase equilibria have been calculated with the Peng-Robinson (P-R) equation of state (*11*), which is an empirical equation with parameters adjusted to fit experimental phase-equilibrium data. The mixing rules used to extend the description to multicomponent systems are those implemented in ASPEN PLUS (*12*), a process simulation program used for the design and control of equipment in the chemical industry. Although quantitative predictions are limited to specific property ranges, the P-R equation provides a qualitative description of phase behavior that is valid over a wider range of conditions and resulting phases.

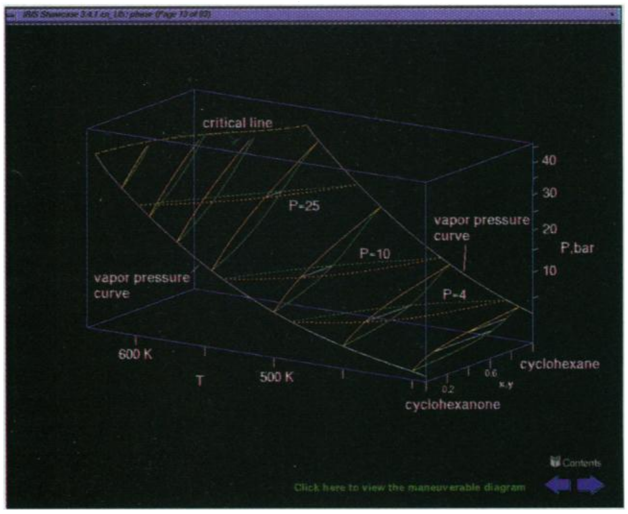

Fig. 1. Vapor-liquid equilibria for a binary mixture. This figure can be further inspected in subsequent movable images.

Phase combines resources from the Showcase feature of Silicon Graphics IRIS workstations with the Silicon Graphics Open Inventor software to generate movable tutorial images in a slide-show format. Color and transparency are used to characterize phases and chemical components in the diagrams. Text slides and fixed and movable images can be zoomed and rotated, thus permitting a detailed visualization. All together, there are 108 sequentially arranged slides in the program. The mixture systems have been selected to highlight the main characteristics of binary, ternary, and quaternary phase diagrams involving vapor-liquid and liquid-liquid equilibria. Unfortunately, the software does not permit one to make further calculations for visualizing regions outside the limits of the displayed diagrams; in this sense, the software lacks flexibility. However, the examples selected cover the most common features of phase equilibrium in mixtures containing vapor and liquid phases that are needed for a qualitative understanding. Two or three pages of text precede each image and describe the details of the thermodynamic principles and numerical procedures used to generate the curves and surfaces. Suggestions are also provided for the best way to manipulate variables in movable images to capture other perspectives and to obtain the best interpretation of the diagrams.

There are three main sections describing binary, ternary, and quaternary systems. Each section begins with the simplest case, followed by systems of increasing complexity. First, the vapor-liquid equilibrium (VLE) for the binary system, cyclohexanone-cyclohexane, is examined on 2D projections for a wide range of temperatures and pressures. This description is followed by both fixed and movable images of a 3D P-T-x-y diagram, where one axis is used to display both x and y mole fractions in the liquid and vapor phase, respectively. This diagram (Fig. 1) can be zoomed and rotated to recover the 2D projections. Dew points (the temperature at which the first drop of liquid forms from a vapor mixture at a given pressure) and bubble points (the temperature at which the first bubble of vapor forms at a given pressure) are plotted by the software for varying temperatures and pressures. The resulting dew and bubble curves are identified with different colors, and typical tie lines connecting states of coexisting phases are indicated. The second system in the tutorial sequence is cyclopentane/acetone, which forms a constantly boiling mixture (azeotrope). It is also visualized on a 3D P-T-x-y diagram that can be rotated, tilted, and sectioned. These features give an excellent illustration of binary azeotropy and its evolution under changes of pressure, temperature, and composition.

P-x_1-x_2-x_3 (isothermal) and T-x_1-x_2-x_3 (isobaric) prisms represent equilibria in ternary systems. Ternary VLE is illustrated for the benzene/acetone/*n*-pentane system. Movable images of the isothermal and iso-

---

The author is in the Department of Chemical Engineering, University of South Carolina, Columbia, SC 29208, USA. E-mail: balbuena@engr.sc.edu

baric prisms show regions containing dew- and bubble-point surfaces. It is also possible to add constant-pressure or constant-temperature sectioning planes, and to convert 3D diagrams into 2D projections, or vice versa. Color features are combined to show regions of homogeneous phases and the boundaries where phase transitions take place. A thermodynamically infeasible region is illustrated for *n*-pentane/nitrobenzene/*i*-butane, a system that exhibits liquid-liquid immiscibility and three-phase VLLE (vapor-liquid-liquid equilibrium) behavior. Other important phenomena, such as the location of critical points, can be observed by further image manipulation because the movable drawings may be viewed from all angles.

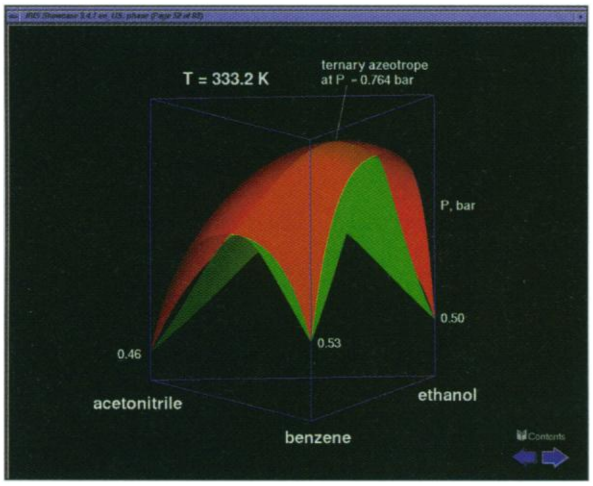

Fig. 2. Isothermal phase diagram for a ternary mixture displaying a maximum-pressure ternary azeotrope.

The final topic addressed by Phase concerning ternary mixtures includes analyses of systems that exhibit maximum-pressure (minimum-temperature) ternary azeotropes. The drawing in Fig. 2 introduces the concept of ternary azeotropy with a view of an isothermal prism for the acetonitrile/benzene/ethanol system. This is followed by a movable image comprising two views of the same diagram, as illustrated in Fig. 3. The isothermal prisms are intersected by constant-pressure planes, where the position (pressure) of the planes can be modified using a slide control at the bottom of the screen. The diagram on the right in Fig. 3 illustrates the possibility of simultaneously viewing the same image from two angles. Using buttons at the upper left, the right image can be switched to a 2D view to show the intersecting plane from above and display the bubble and dew curves at the selected pressure. In a similar manner, the minimum-temperature azeotropic phenomenon corresponding to Figs. 2 and 3 also is displayed in a pair of isobaric prisms.

Quaternary systems, which require a five-dimensional display, are represented in a tetrahedral space at fixed temperature and pressure, where the pure components are located at the vertices, the six binary sub-mixtures are located along the edges of the tetrahedron, and the four ternary subsystems lie on the faces. First, the tutorial gives a useful introduction to reading tetrahedral diagrams. Its graphical display illustrates how to locate a quaternary composition point inside the tetrahedron. Next, the benzene/acetone/*n*-pentane/*n*-butane system is used as an example of a completely miscible, nonazeotropic, quaternary mixture. Dashed tie lines connect saturated coexisting state points, both for selected quaternary compositions (white lines) and also for the binary sub-mixtures (blue lines).

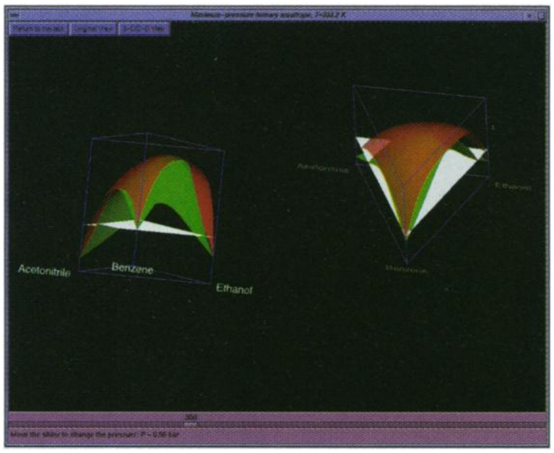

Fig. 3. Further views obtained by freezing movable images of the diagram shown in Fig. 2. The position of the constant-pressure plane can be changed with a slider. The right-hand diagram can be displayed in a 2D view with buttons at the top of the screen.

In a final example, acetonitrile/benzene/ethanol/acetone illustrates the complexity of a four-component system that forms binary azeotropes for three of the six possible pairs and forms a ternary azeotrope over a range of fixed temperatures and pressures. The focus in this case is to demonstrate how using a sequence of diagrams can clarify this complexity and to show how understanding the lower-order equilibria (binary and ternary) can give insights into the phase behavior of the full quaternary system. Representing the evolution of these isothermal-isobaric quaternary phase diagrams when the pressure or temperature, or both, changes is a computational challenge. The tutorial describes some alternative features that are not yet incorporated into the software, such as displaying an animated series of isothermal tetrahedrons, each at a given pressure. This modification requires the manipulation of even larger data sets, which goes along with the requirements for increased memory and computing power. However, considering the rapid advances in computer technology, it should be possible to provide more robust quaternary phase diagrams than is feasible at present.

In conclusion, Phase is a useful tool for teaching the principles of complex multicomponent phase equilibria. One can imagine several ways to extend its range of applications, for example, by beginning the tutorial with pure substances, by adding examples of systems that exhibit solid phases, and by illustrating the relationship between intermolecular forces and macroscopic phase behavior. Jolls and another student, E. Cochran, are currently working on a new version of the software that contains additional features such as animation and a numerical display of the properties of the equilibrium phases. Undoubtedly it will remain true to the philosophy of Phase: that the best way to teach abstract concepts is with visually attractive and scientifically accurate images.

The current version of Phase runs on Silicon Graphics IRIS workstations and is available without cost via FTP. The file "phase1.tar" can be retrieved from the site ftp://isua.iastate.edu, user name "anonymous.jolls," password "yourusername@your.e-mail.host." Downloading instructions and documention may be obtained by writing to jolls@eng.iastate.edu. Development and maintenance of Phase is supported by the General Electric Foundation.

References and Notes

1. K. S. Tian, thesis, Iowa State University, Ames (1997).
2. K. R. Jolls and G. P. Willers, *Cryogenics* **18**, 6, 329 (1978).
3. K. R. Jolls, J. Burnet, J. T. Haseman, *Chem. Eng. Educ.*, XVII, 112 (1983).
4. K. Jolls, *J. Chem. Educ.* **61**, 5, 393 (1984).
5. ———, *Chem. Eng. Prog.* **85**, 2 (1989).
6. ———, in *Proceedings of the Gibbs Symposium*, D. Caldi and G. Mostow, Eds. (American Math Society, Providence, RI, 1990) p. 293.
7. K. R. Jolls and D. C. Coy, *Phys. Today* **45**, 96 (1992).
8. M. Modell and J. W. Tester, *Thermodynamics and Its Applications* (Prentice Hall, Upper Saddle River, NJ, 1997).
9. B. Kyle, *Chemical and Process Thermodynamics* (Prentice Hall, Upper Saddle River, NJ, ed. 3, 1998).
10. S. M. Walas, *Phase Equilibria in Chemical Engineering* (Butterworth-Heinemann, Newton, MA, 1985).
11. D.-Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam.* **15**, 59 (1976).
12. ASPEN PLUS is a product of Aspen Technology, Inc., Cambridge, MA.