

If the pressure of a system is increased isothermally, eventually solid phases will appear; these are not shown in Figs. 13.13 and Fig. 13.14.

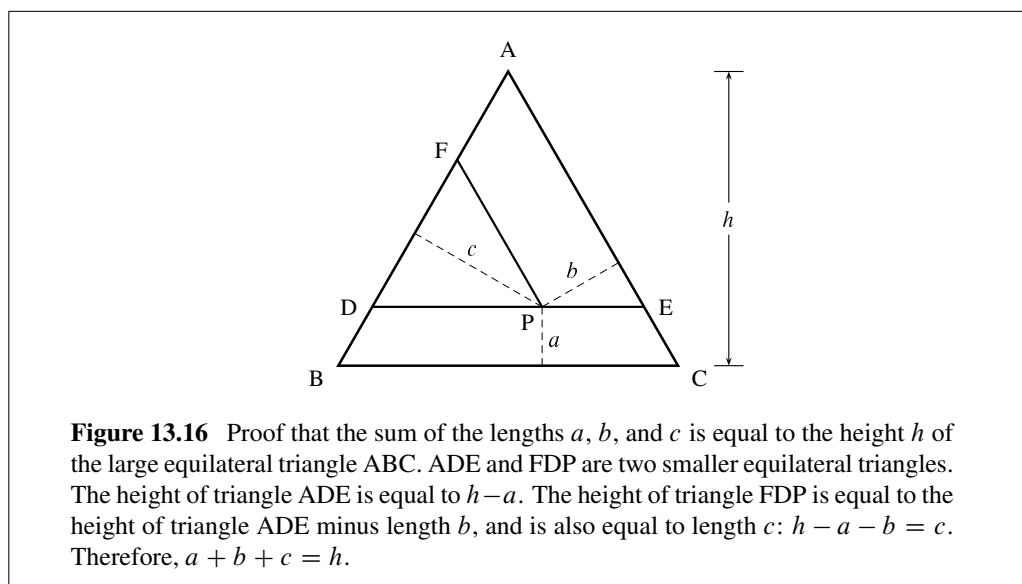
13.3 PHASE DIAGRAMS: TERNARY SYSTEMS

A ternary system is one with three components. We can independently vary the temperature, the pressure, and two independent composition variables for the system as a whole. A two-dimensional phase diagram for a ternary system is usually drawn for conditions of constant T and p .

Although we could draw a two-dimensional phase diagram with Cartesian coordinates to express the mole fractions of two of the components, there are advantages in using instead the triangular coordinates shown in Fig. 13.15. Each vertex of the equilateral triangle represents one of the pure components A, B, or C. A point on the side of the triangle opposite a vertex represents a binary system of the other two components, and a point within the triangle represents a ternary system with all three components.

To determine the mole fraction z_A of component A in the system as a whole represented by a point within the triangle, we measure the distance to the point from the side of the triangle that is opposite the vertex for pure A, then express this distance as a fraction of the height of the triangle. We follow the same procedure to determine z_B and z_C . The concept is shown in Fig. 13.15(a).

As an aid for the conversion between the position of a point and the overall composition, we can draw equally-spaced lines within the triangle parallel to the sides as shown in Fig. 13.15(b). One of these lines, being at a constant distance from one side of the triangle, represents a constant mole fraction of one component. In the figure, the lines divide the distance from each side to the opposite vertex into ten equal parts; thus, adjacent parallel lines represent a difference of 0.1 in the mole fraction of a component, starting with 0 at the side of the triangle and ending with 1 at the vertex. Using the lines, we see that the filled circle in the figure represents the overall composition $z_A = 0.20$, $z_B = 0.30$, and



$$z_C = 0.50.$$

The sum of z_A , z_B , and z_C must be 1. The method of representing composition with a point in an equilateral triangle works because the sum of the lines drawn from the point to the three sides, perpendicular to the sides, equals the height of the triangle. The proof is shown in Fig. 13.16.

Two useful properties of this way of representing a ternary composition are as follows:

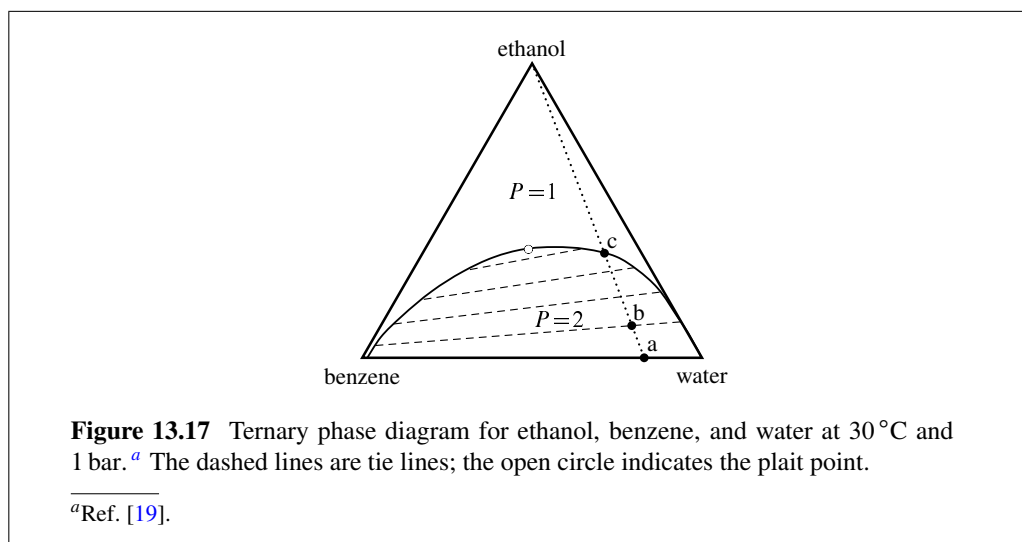
1. Points on a line parallel to a side of the triangle represent systems in which one of the mole fractions remains constant.
2. Points on a line passing through a vertex represent systems in which the ratio of two of the mole fractions remains constant.

13.3.1 Three liquids

Figure 13.17 on the next page is the ternary phase diagram of a system of ethanol, benzene, and water at a temperature and pressure at which the phases are liquids. When the system point is in the area labeled $P=1$, there is a single liquid phase whose composition is described by the position of the point. The one-phase area extends to the side of the triangle representing binary mixtures of ethanol and benzene, and to the side representing binary mixtures of ethanol and water. In other words, ethanol and benzene mix in all proportions, and so also do ethanol and water.

When the overall composition is such that the system point falls in the area labeled $P=2$, two liquid phases are present. The compositions of these phases are given by the positions of the ends of a tie line through the system point. Four representative tie lines are included in the diagram, and these must be determined experimentally. The relative amounts of the two phases can be determined from the lever rule.⁷ In the limit of zero mole

⁷The lever rule works, according to the general derivation in Sec. 8.2.4, because the ratio n_A/n , which is equal to z_A , varies linearly with the position of the system point along a tie line on the triangular phase diagram.



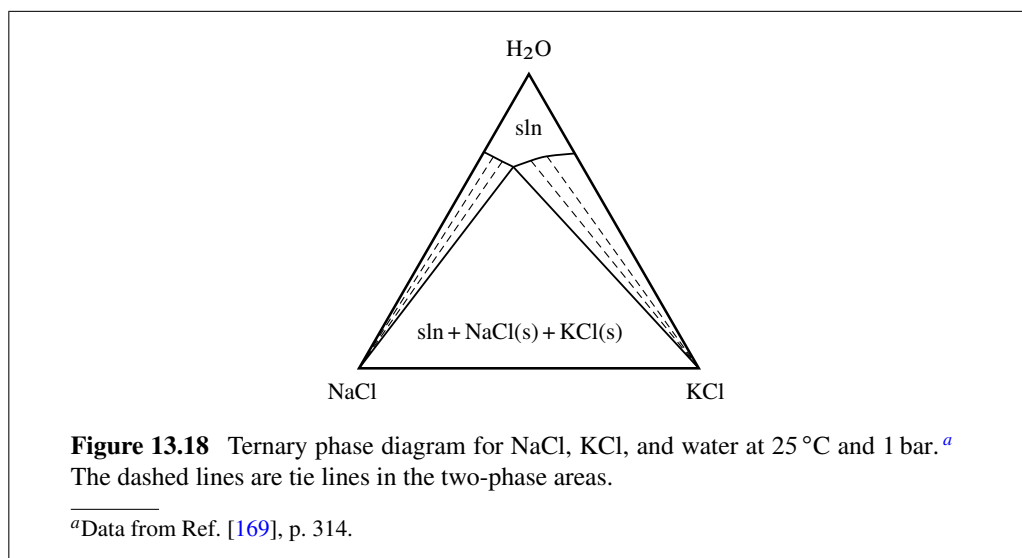
fraction of ethanol, the tie line falls along the horizontal base of the triangle and displays a miscibility gap for the binary system of benzene and water. (The conjugate phases are very nearly pure benzene and pure water).

The *plait point* shown as an open circle in the figure is also called a *critical solution point*. As the system point approaches the plait point from within the two-phase area, the length of the tie line through the system point approaches zero, the miscibility gap disappears, and the compositions of the two conjugate liquid phases become identical.

Suppose we have the binary system of benzene and water represented by point a. Two liquid phases are present: one is wet benzene and the other is water containing a very small mole fraction of benzene. If we gradually stir ethanol into this system, the system point moves along the dotted line from point a toward the vertex for pure ethanol, but can never quite reach the vertex. At point b, there are still two phases, and we can consider the ethanol to have distributed itself between two partially-miscible solvents, benzene and water (Sec. 12.6.3). From the position of point b relative to the ends of the tie line passing through point b, we see that the mole fraction of ethanol is greater in the water-rich phase. As we continue to add ethanol, the amount of the water-rich phase increases and the amount of the benzene-rich phase decreases, until at point c the benzene-rich phase completely disappears. The added ethanol has increased the mutual solubilities of benzene and water and resulted in a single liquid phase.

13.3.2 Two solids and a solvent

The phase diagram in Fig. 13.18 on the next page is for a ternary system of water and two salts with an ion in common. There is a one-phase area for solution, labeled sln; a pair of two-phase areas in which the phases are a single solid salt and the saturated solution; and a triangular three-phase area. The upper vertex of the three-phase area, the *eutonic point*, represents the composition of solution saturated with respect to both salts. Some representative tie lines are drawn in the two-phase areas.



A system of three components and three phases has two degrees of freedom; at fixed values of T and p , each phase must have a fixed composition. The fixed compositions of the phases that are present when the system point falls in the three-phase area are the compositions at the three vertices of the inner triangle: solid NaCl, solid KCl, and solution of the eutonic composition $x_{\text{NaCl}} = 0.20$ and $x_{\text{KCl}} = 0.11$.

From the position of the curved boundary that separates the one-phase solution area from the two-phase area for solution and solid KCl, we can see that adding NaCl to the saturated solution of KCl decreases the mole fraction of KCl in the saturated solution. Although it is not obvious in the phase diagram, adding KCl to a saturated solution of NaCl decreases the mole fraction of NaCl. These decreases in solubility when a common ion is added are examples of the *common ion effect* mentioned in Sec. 12.5.5.