

bubble and dew lines meet. There is a range of compositions for which the bubble temperature is lower than the boiling point of either pure compound, indicating that these solutions boil more easily than the pure components. In the Pxy graph the minimum boiling azeotrope is characterized by a maximum in the total pressure, that is, the solution is more volatile than the pure components. Maximum boiling azeotropic behavior is also encountered, though not as often. The Txy graph exhibits a maximum, which lies above the boiling point of either component. This solution is more difficult to boil compared to the pure components. The corresponding Pxy graph exhibits a minimum in the dew and bubble pressure.

The azeotropic point corresponds to the maximum or minimum on the phase diagram. At this point the bubble and dew lines meet and the composition of the vapor is identical to that of the liquid. A liquid solution that has exactly the azeotropic composition boils as a pure component: the composition of the vapor and the liquid phases are identical, while temperature remains constant throughout boiling. Similarly, a vapor with this concentration condenses as a pure component. The name *azeotrope* derives from the Greek and translates to “not altered by boiling.” Azeotropes are problematic in separations. Suppose we want to separate a solution of methanol in CCl_4 containing 10% methanol by mole. This composition lies to the left of the azeotrope. Subjecting this solution to distillation at 1 atm will produce a liquid that approaches pure carbon tetrachloride, and a liquid whose composition approaches the azeotropic point. This means that the liquid fraction cannot exceed the azeotropic concentration, preventing us from obtaining a stream of purified methanol. It is possible to alter the composition of the azeotrope and even remove the azeotrope altogether by changing the pressure and temperature. Alternatively, the addition of a suitable third component could have the same effect. In some cases, the formation of azeotropes is advantageous. Water and hydrochloric acid form an azeotrope; through boiling it is possible to collect a solution that has the azeotropic composition. Because its composition is precisely known (it depends only on the pressure during distillation), this solution may be used as a standard for acid/base titrations.

8.4 The xy Graph

Another graphical representation of binary vapor, liquid data, useful in material balances, is the xy graph, as shown in Figure 8-8. This graph gives the composition of the tie line by plotting the vapor mole fraction against the liquid mol fraction. In this graph, both axes run from 0 to 1 and the diagonal represents points where the vapor composition is equal to that of the liquid. By convention, the more volatile component is chosen as component 1; by this convention the xy graph generally lies

missing period

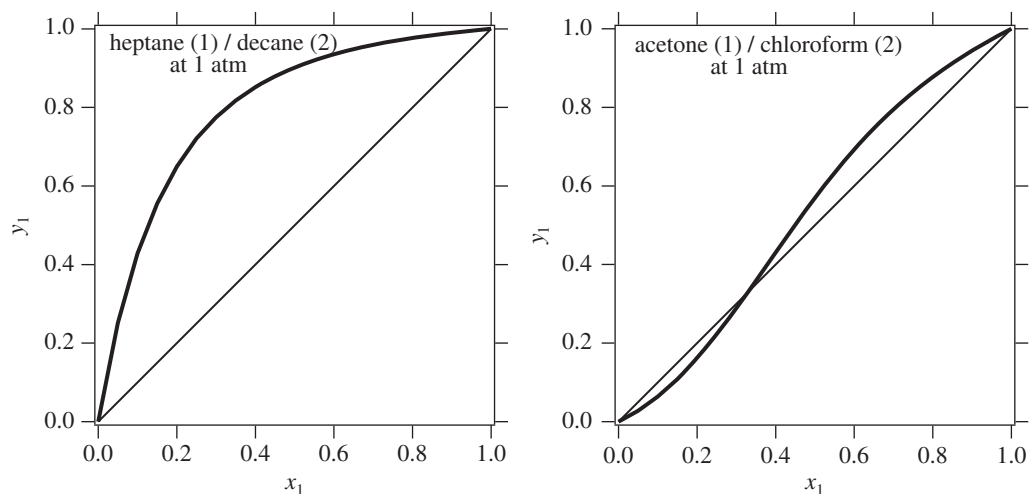


Figure 8-8: xy graphs for two binary systems.

above the diagonal. Azeotropes are easily identified on this graph because the xy line crosses the diagonal.

The distance of the xy line from the diagonal is a measure of the difference in the composition of the two phases, and thus a measure of the ease of separation. One way to quantify the difference between the compositions of the two phases is through the known as distribution coefficient, K_i , or K -factor for simplicity, which is defined as

$$K_i = \frac{y_i}{x_i}. \quad (8.4)$$

Good separation requires values substantially different from 1. A value larger than unity indicates that component i is preferentially found in the gas phase; a value less than 1 indicates preferential enrichment of the liquid phase. A related property is the relative volatility, α_{ij} , which is defined as

$$\alpha_{ij} = \frac{K_i}{K_j}.$$

In a binary mixture, this takes the form,

$$\alpha_{ij} = \frac{y_1(1-x_1)}{x_1(1-y_2)}.$$

The K_1 factor of binary mixture can be obtained graphically from the xy graph: if we connect a point of the xy graph to the origin, the slope of this line is K_1 . At $x_i = 1$ the value of K_i is unity for any component i ; at $x_i = 0$ it reaches a limiting value that

replace subscript ij with subscript 12

corresponds to the infinite dilution limit, namely, to the limit that the concentration of the component is reduced to zero by dilution in the other component.¹ That is, even though both y_i and x_i go to zero in this limit, the K_i factor is finite and equal to the slope of the xy line at $x_i = 0$.

If the K factors of a binary system are known as a function of pressure and temperature, the entire phase diagram can be constructed. As we will see in Chapter 10, thermodynamics provides methodologies for the estimation of these factors.

8.5 VLE at Elevated Pressures and Temperatures

The phase diagrams discussed so far extend over the entire range of the compositional axis, from $x_1 = 0$ (pure saturated component 2) to $x_1 = 1$ (pure saturated component 1). This behavior is observed when both components are below their respective critical points. If one of both components are above their critical point, the VLE region shrinks and does not cover the entire range of compositions. This situation is illustrated in Figure 8-9, which shows the Pxy graph of the system ethanol/water at several temperatures. At 200 °C the phase diagram has the usual form and extends over the entire compositional range. This system also exhibits a maximum boiling azeotrope. Upon increasing temperature, the phase diagram moves upwards but remains qualitatively the same, as long as the temperature remains below the critical of both components. At 275 °C ethanol is above its critical temperature (240.77 °C) but water is below its own (374 °C). The phase diagram now does not reach all the way to the ethanol axis. Instead, the dew and bubble lines meet at some intermediate point. The phase diagram is read in the usual way: We draw a tie line, identify the liquid phase on the right (above the dew line) and the vapor phase on the left (below the bubble line). Where the bubble and dew lines meet we have a critical point, which is characterized by its own temperature, pressure, and composition. It is identified as the point where the tie line is tangent to the VLE curve. If temperature is increased, the phase diagram moves up and shrinks further. This behavior continues until the critical temperature of water is reached (not shown on this graph). The dashed line in pane (a) of Figure 8-9 tracks the critical point of the mixture as temperature increases and connects the critical pressures of the pure components (the critical temperature of water is outside the range of this graph). This behavior can also be studied on the xy graph, shown in Figure 8-9(b). When both components are below the critical points, the xy graph extends from $x_1 = 0$ to $x_1 = 1$.² Once temperature exceeds the critical temperature

1. The limit of infinite dilution should be visualized as a single molecule of component i completely surrounded by molecules of component j .

2. This line intersects the diagonal at the azeotropic point, but this detail cannot be seen clearly at the magnification of this graph.

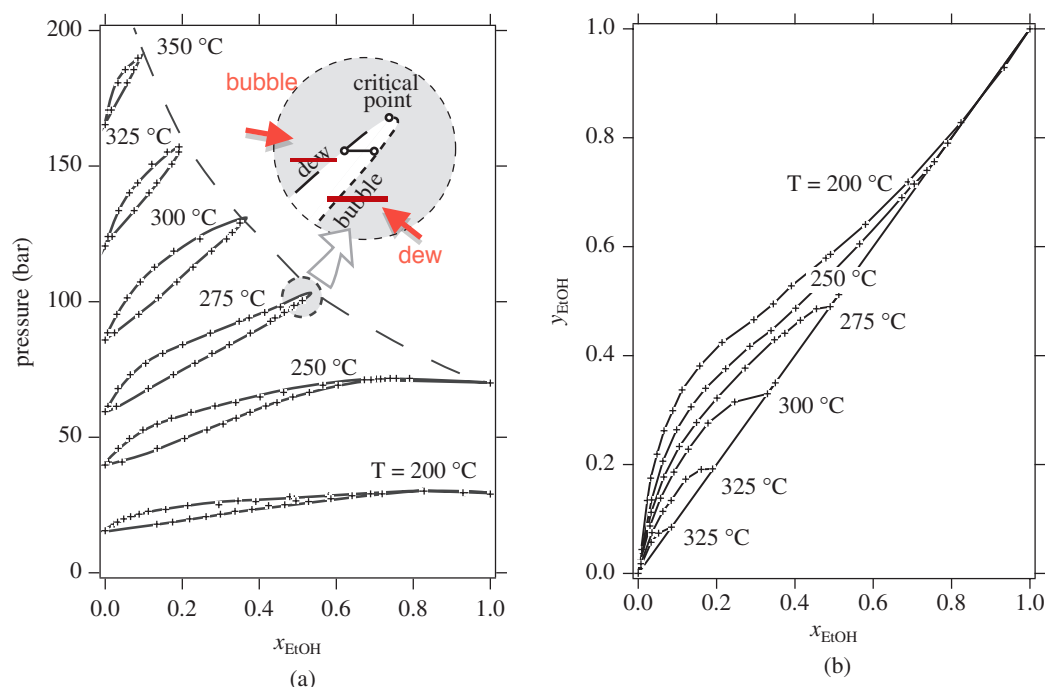


Figure 8-9: P_{xy} and T_{xy} graph of ethanol/water at elevated temperatures (data from Frank Barr-David and B. F. Dodge, *Journal of Chemical & Engineering Data*, 4 (2):107-121, 1959).

of compartment 1, the line intersects the diagonal and stops there. This marks the critical point of the mixture, where the composition of the two phases is identical.

Such incomplete phase diagrams occur commonly in systems involving typical gases (e.g., oxygen, nitrogen) in equilibrium with liquids (e.g., water) at room temperature. In this case the liquid is below its critical temperature but the gas above its own. Although such problems fall squarely in the scope of phase equilibrium they are often categorized as solubility problems. The thermodynamics of these systems are examined in Chapter 13.

8.6 Partially Miscible Liquids

Some liquids are only partially miscible in each other. This situation arises when the constituent molecules contain groups that have low affinity for each other. As an example we consider the system n-hexane/ethanol. Both molecules contain CH_2 and CH_3 groups which are very similar. Ethanol also contains a polar hydroxyl group, $-\text{OH}$, which has little affinity for the alkyl groups. A limited amount of hexane