



Figure 14.3 Three types of temperature behavior during a simple distillation. (A) A single pure component. (B) Two components of similar boiling points. (C) Two components with widely differing boiling points. Good separations are achieved in A and C.

For any horizontal line (constant temperature), such as that shown at t , the intersections of the line with the curves give the compositions of the liquid and the vapor that are in equilibrium with each other at that temperature. In the diagram, at temperature t , the intersection of the curve at x indicates that liquid of composition w will be in equilibrium with vapor of composition z , which corresponds to the intersection at y . Composition is given as a mole percentage of A and B in the mixture. Pure A, which boils at temperature t_A , is represented at the left. Pure B, which boils at temperature t_B , is represented at the right. For either pure A or pure B, the vapor and liquid curves meet at the boiling point. Thus, either pure A or pure B will distill at a constant temperature (t_A or t_B). Both the vapor and the liquid must have the same composition in either of these cases. This is not the case for mixtures of A and B.

A mixture of A and B of composition w will have the following behavior when heated. The temperature of the liquid mixture will increase until the boiling point of the mixture is reached. This corresponds to following line wx from w to x , the boiling point of the mixture t . At temperature t the liquid begins to vaporize, which corresponds to line xy . The vapor has the composition corresponding to z . In other words, the first vapor obtained in distilling a mixture of A and B does not consist of pure A. It is richer in A than the original mixture but still contains a significant amount of the higher-boiling component B, even from the very beginning of the distillation. The result is that it is never possible to separate a mixture completely by a simple distillation. However, in two cases it is possible to get an acceptable separation into relatively pure components. In the first case, if the boiling points of A and B differ by a large amount ($>100^\circ\text{C}$) and if the distillation is carried out carefully, it will be possible to get a fair separation of A and B. In the second case, if A contains a fairly small amount of B ($<10\%$), a reasonable separation of A from B can be achieved. When the boiling-point differences are not large and when highly pure components are desired, it is necessary to perform a **fractional distillation**. Fractional distillation is described in Technique 15, where the behavior during a simple distillation is also considered in detail. Note only that as vapor distills from the mixture of composition w (see Figure 14.4) it is richer in A than is the solution. Thus, the composition of the material left behind in the distillation becomes richer in B (moves to the right from w toward pure B in the graph). A mixture of 90% B (dotted line on the right side in Figure 14.4) has a higher boiling point than at w . Hence, the temperature of the liquid in the distillation flask will increase during the distillation, and the composition of the distillate will change (as is shown in Figure 14.3B).