

different concentrations. The ethanol-rich phase (the phase which originated as pure ethanol) has the composition of point  $C_1$  and the hexane-rich phase the composition of point  $C_2$ . The two-phase system is represented by a single point,  $C$ , which lies inside the two-phase region at the overall composition of the two-phase system. This composition is calculated by the lever rule:

$$z_i = L_1 x_i^{(1)} + L_2 x_i^{(2)},$$

where  $L_1$  is the fraction of mass (or moles) in the hexane-rich phase,  $L_2$  is the fraction of the ethanol-rich phase, and  $x_i^{(1)}$ ,  $x_i^{(2)}$ , are the compositions (mass or mol fractions) of component  $i$  in the two phases. These compositions correspond to points  $C_1$  and  $C_2$  and are read off the horizontal axis of the graph. If we continue to add hexane, more and more of the ethanol in the ethanol-rich phase is incorporated into the hexane-rich phase. During this part of the process the system consists of two liquid phase. The compositions of these phases remain fixed at those of points  $C_1$  and  $C_2$ , but the relative amounts of each liquid change, with the hexane-rich phase increasing at the expense of the ethanol-rich phase. When the overall composition reaches point  $C_1$ , enough hexane exists to solubilize all of the available ethanol so that the ethanol-rich phase disappears. Adding more hexane at this point produces a homogeneous solution whose concentration approaches that of pure hexane. The liquid branches of the phase boundary are determined experimentally by measuring the composition of the coexisting liquids at various temperatures. Mutual solubility generally increases with temperature and this is reflected in the (slight) convergence of the liquid branches as temperature increases. Some partially miscible systems become fully miscible at higher temperatures. In the case of hexane/ethanol, however, partial miscibility persists until the liquid reaches the boiling point.

To demonstrate the phase behavior of a two-liquid system in the boiling region, suppose we start with state  $C$  in the two-phase region (see Figure 8-10). The overall composition is  $z_1 = 0.2$  at 60 °C, 1.96 bar and the system consists of two liquids whose compositions are given by points  $C_1$  and  $C_2$ . The onset of boiling (bubble point) is shown by point  $D$ . At this point, the liquid boils and produces a vapor whose composition corresponds to point  $V$ , while the two liquids are represented by points  $A$  and  $B$ . Thus at the bubble point there are three phases present, two liquids and the vapor. As long as two liquids are present in boiling, the state of the system remains pegged at point  $D$ : the boiling temperature is constant, and the composition of all phases is also constant, and are given by points  $A$ ,  $V$ , and  $B$ . In other words, the system forms an azeotrope. The only change observed during this stage of the process is the continuous decrease of the amounts of the liquids, and the increase in the amount of the vapor. Once any of the liquid phases is completely depleted, the state moves up. Which phase is depleted first depends on the overall composition