straight line between two points lies above the curve, producing a two-phase system with higher Gibbs energy (and thus less favorable) than the single-phase liquid. Therefore, the presence of a concave portion is necessary and sufficient condition for phase splitting. The compositions of the coexisting liquids are then identified by drawing a double-tangent line, that is, one that is tangent to the Gibbs free energy at both contact points.

change superscript to "I"

Equilibrium and Stability Having identified points B'' and C'' as the miscibility limits, the Gibbs graph must be corrected by removing the portion of the curve that represents nonequilibrium states. To do that, we erase the portion of the curve between points B'' and C'' and connect the two points with a straight tie line. The resulting Gibbs free energy is shown in Figure 13-3 by the solid line with points B'' and C'' now relabeled as II and I, respectively. The system consists of a single liquid in the regions $0 \le x_1 \le x_i^{\mathrm{II}}$ and $x_1^{\mathrm{II}} \le x_1 \le 1$; between x_1^{II} and x_1^{I} the system forms two liquid phases and the Gibbs free energy of this two-phase mixture lies on the straight tie-line that connects points I and II. The portion of the Gibbs energy between points I and II contains one concave region near the center (shown by large dashes in Figure 13-3) with two convex portions to each side. The convex parts represent metastable states and may be observed under special

change subscript to "1" (not "i")

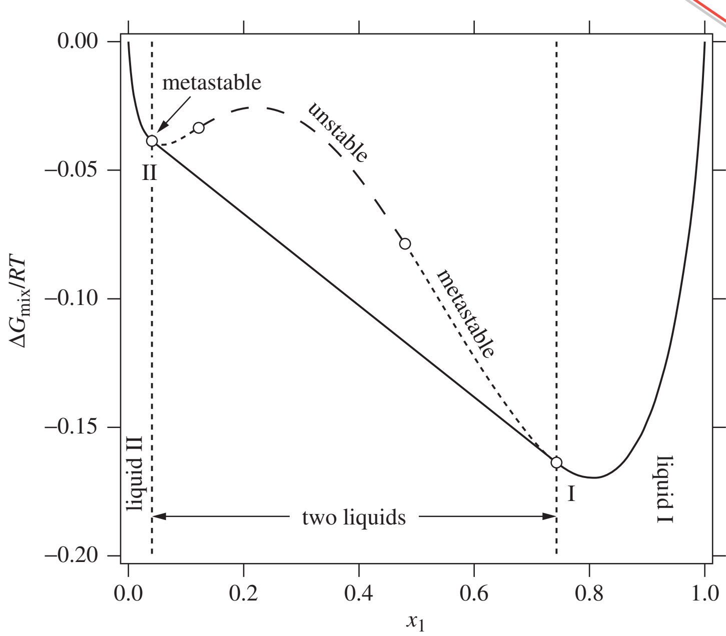

Figure 13-3: Stable (solid lines), metastable (dotted line), and unstable (large dashes) portions of the Gibbs free energy of solution. Concave parts on the Gibbs curve are unstable; convex parts are stable or metastable.