

The Spinodal Temperature of Binary Liquid Hydrocarbon Mixtures

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The boiling point of a liquid or a liquid mixture is often thought of as the upper temperature limit of the liquid state. However, droplets of a liquid immersed in a properly selected second liquid can be raised to temperatures far beyond their boiling point into metastable, superheated states. When these liquid droplets reach their limit of superheating or spinodal temperature they vaporize with a physical explosion. For saturated hydrocarbons this temperature is some 110 degrees beyond the boiling point at atmospheric pressure. Using an apparatus that is a modification of one devised by Wakeshima and Takata, the spinodal temperature has been determined for the two liquid hydrocarbon mixtures *n*-pentane + *n*-hexane and *n*-pentane + *n*-heptane. The spinodal temperature was found to be a linear function of mole fraction for both of these mixtures.

Theoretical predictions of the spinodal temperature for these systems have been performed using the second-law-based, two-by-two stability determinant that contains the mechanical and diffusional stability conditions. Thus, the density and composition fluctuations in a metastable, superheated liquid will damp out below the spinodal temperature, but not in the unstable region above that temperature. An equation of state (EoS) for a two-component fluid is required for these calculations and the two-parameter van der Waals and Redlich-Kwong models have been explored. In both cases a linear mixing rule was employed for the molecular size parameter and a quadratic rule for the intermolecular attraction parameter. If the attractive mixing rule incorporates a binary interaction parameter in the cross term, that parameter can be adjusted so as to produce a linear spinodal curve for either mixture. Although both equations of state can thus provide a linear spinodal curve, the Redlich-Kwong model yields predictions that are in much closer accord with experiment for each component of the mixture.