

Abstract Submitted
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Chemical Kinetics at the Critical Point of Solution JAMES BAIRD, YEONG KIM, University of Alabama in Huntsville — We have measured the rate of decomposition of acetone dicarboxylic acid in a mixture of isobutyric acid + water near its consolute point. At temperatures close to the critical solution temperature, the rate constant oscillated in magnitude by about 10 percent as it passed through two complete cycles of slowing down followed by speeding up. This is to be compared with our observations of the rates the SN1 hydrolysis reactions of 2-chloro-2-methylbutane in isobutyric acid + water and 2-bromo-2-methylpropane in triethylamine + water near their respective consolute points. In both mixtures, we observed a single cycle of slowing down above the critical temperature followed by speeding up above it [J. Phys. Chem. A 107, 8435 (2003)]. Whereas we can find no ready explanation for the speeding up, we suggest that because none of these mixtures contains any inert components, the observed slowing down should belong to the Griffiths-Wheeler class of strong critical effects [Phys. Rev. A 2, 1047 (1970)]. To check this hypothesis, we measured the rate of decomposition of ethyl diazoacetate in isobutyric acid + water near the critical solution temperature. In this mixture, isobutyric acid is inert, and no critical effect was observed.

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