A Technique of Measuring the Critical Temperatures and Pressures of Thermally Unstable Substances. The Results of Measurements and Correlations

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A method of measuring the critical temperatures and pressures of thermally unstable substances has been developed. The method is based on measuring the temperature of the attainable superheat of liquids with the help of a wire probe 0.002 cm in diameter heated with electric-current pulses with a duration from 0.01 to 1 ms. With increasing pressure the temperature of the attainable superheat tends to the critical temperature. The critical temperature and pressure of a thermally unstable substance measured by this technique depend on the time of heating due to its decomposition. The authors have obtained formulae by which the dependences of the apparent critical temperature or pressure on the heating time are extrapolated to the critical constants of an undecomposed substance.

The critical properties of the aquatic solutions of hydrogen peroxide with a mole fraction from 0 to 0.83 have been measured. Then by extrapolation the critical constants of pure hydrogen peroxide have been determined. The measurements of the critical temperatures and pressures have been carried out for n-alkanes with from 17 to 36 carbon atoms, some low-molecular-weight methylphenylsiloxanes, polyethylene glycols (PEG) (mono-, di-, tri-, tetra-ethylene glycols, PEG(300), PEG(400), PEG(600)). The results are compared with the values predicted by various methods.

In an approximation of a self-consistent field for a polymeric fluid, equations of state of the van der Waals and Redlich-Kwong type have been used. The scaling dependences of the critical constants of chain molecules on the number of mers has been obtained. The critical temperatures and pressures of n-alkanes and polyethylene glycols have been correlated using these dependences.

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