

Critical Properties of Carbon Dioxide-Sulphur Hexafluoride-Trifluoromethane Systems

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The use of binary and multicomponent fluid mixtures as solvents in supercritical fluid processes offers a variety of challenges but experimental critical data of potential solvent mixtures are not always available for all binary mixtures of interest and the available data for some systems are often limited to narrow range of compositions to be encountered in the supercritical fluid extractions. This paper establishes a procedure based on the van der Waals theory of cubic equations-of-state for computing accurate critical point of fluid mixtures from a previously established generic cubic equation-of-state developed by the corresponding author during a doctoral degree. Four criticality criteria are imposed on the generic equation-of-state to yield analytical expression for the van der Waals vapor-liquid critical point. The input to the analytical expression is the critical characteristic constants, molecular weight and acentric factor of the pure constituents of the mixtures. By relating the pure substance parameters to the composition of the mixture, critical temperature, critical pressure and critical volume of binary, ternary and multicomponent systems are accurately predicted from the analytical expression for the van der Waals critical point with binary interaction terms expressed in molecular and critical constants of the species involved in the mixtures. Several critical data reported within the last ten years in the Journal of Chemical Thermodynamics by various authors, particularly, Diefenbacher-Turk, are used to validate the analytical expression for the van der Waals critical point. The paper provides a unique way of computing mixture critical properties from the pure constituents without resorting to the rigorous Gibbs criticality criteria or scaling laws corrections for the critical point. This paper provides possible answer to the question of how the thermodynamic properties of fluids cross over from a singular non-classical critical behavior to a classical van der Waals - like behavior outside the critical region by predicting the location of the critical point for actual fluids or fluid mixtures.