Closed-Form Equations for the van der Waals Gas-Liquid Critical Point

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Knowledge of the gas-liquid critical states of mixtures is of great practical importance for classifying reservoir fluids as gases or volatile oils. This is because many hydrocarbon processing operations take place at high pressures and involve retrograde phenomena which are characteristic of the behavior of mixtures in the critical region. It is therefore often necessary to locate the critical point of a multicomponent system prior to carrying out other calculations in the critical region. Attempts to predict critical properties have relied mainly on two approaches: empirical methods and the rigorous methods involving the solution of Gibbs criteria for the critical point in a mixture. Although the Gibbs approach is preferable to the first, because of its basis in thermodynamics, the method, however, does not always lead to a solution, and sometimes requires a large amount of computing time in reservoir simulations. Moreover, methods that are based on two and three parameter equations of state are inadequate to resolve the critical properties of fluids, and the predicted critical volumes show the greatest deviations from the experimental measurements.

The cubic equation of state, being a third-order polynomial equation, requires four parameters for unifying the van der Waals gas-liquid critical point with fluid critical properties. Therefore, four critical constraint derivatives are developed to resolve the four-parameter equation of state with a mixture critical point. Binary interaction parameters that relate the binaries in the mixture composition with the critical parameters derived from the four-parameter equation of state are utilized to predict the critical point of multicomponent systems with varying size ratios. The predicted critical points are internally consistent with other thermodynamic properties derived from the four-parameter equation of state. This development provides a means of theoretically correcting the pseudocritical properties established by the van der Waals theory of cubic equations of state, and the development also provides a basis in the theory of the equation of state to correct the one-fluid theory for large molecules and asymmetric systems. The analytical equations developed in this paper are simple to use and require significantly less computational effort than the rigorous methods that solve the equations for the Gibbs criteria at the critical point. The paper is very attractive for compositional simulation studies involving retrograde phenomena.