LETTER TO THE EDITOR

Reply to the Letter of Salim:

This reply to the letter of Salim (Vol. 39, April 1993, p. 724) was received by the Editorial Office on June 8, 1992. It, however, was omitted inadvertently from the April issue. AIChE Journal regrets this error.

Salim and Trebble (1991) have proposed a criterion that the first temperature derivative of the molecular parameter, b, in equations of state should be greater than or equal to zero so that $(\partial P/\partial T)_v > 0$ in the very high-pressure region. This and other related criteria were developed initially for van der Waals-type equations of state and, in his letter, Salim has extended these to include other perturbation-theory-based equations.

In our opinion, this criterion is unnecessary. Thermodynamic perturbation theories are now well established for nonpolar fluids (Henderson, 1979). The perturbation theory of Barker and Henderson clearly shows:

$$b = (2\pi\, N_A/3)\int(1 - e^{-\beta\phi_o})\, dr$$

where $\beta = 1/kT$, ϕ_o is the reference fluid pair potential, and r is the pair separation. Here, $(db/dT) < 0$ for all ϕ_o modeled using either soft-repulsive or hard-sphere potentials. Clearly, this is at odds with Salim's criterion. $(db/dT) < 0$ implies that as the temperature is increased, at constant volume, the repulsive iteractions are weakened. This is physically realistic. Salim's criterion on the first temperature derivative of b is inconsistent both physically and with statistical thermodynamics.

The simple equations of the type utilized in our study, which were used to model low-and medium-pressure data, may not work well at very high pressures. This, however, does not imply the need for the criterion proposed by Salim, but rather for more accurate attraction and repulsion terms. It is hoped that an ongoing effort in this direction, which we and others are currently pursuing, will lead to positive results at higher pressures in the near future.

Literature cited

Henderson, D., "Practical Calculations of the Equation of State of Fluids and Fluid Mixtures Using Perturbation Theory and Related Theories," *Equations of State in Engineering and Research*, K. C. Chao and R. L. Robinson, eds., *Adv. in Chemistry Ser.*, No. 182, ACS, Washington, DC (1979).

Salim, P. H., and Trebble, M. A., "A Modified Trebble-Bishnoi Equation of State: Thermodynamic Consistency Revisited," *Fluid Phase Equil.*, **65**, 59 (1991).

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