LETTERS TO THE EDITOR

To the Editor:

In a recent paper [*AIChE J.*, **25**, 653 (1979)] Hankinson and Thomson point out that for my saturated-liquid-volume equation (Rackett, 1970),

$$\log V_f = [1 + (1 - T_r)^{2/7}]\log Z_c - \log(P_c/RT_c) \quad (1)$$

$$\frac{\partial \log V_f}{\partial \log Z_c} = [1 + (1 - T_r)^{2/7}] > 1$$

at all T_r, and $\rightarrow 2$ as $T_r \rightarrow 0$; and that for the equation of Gunn and Yamada (1971),

$$\frac{\partial \log V_f}{\partial \log V_f'} = 1$$

at all T_r and all T_r', where V_f' is an experimental standard volume measured at $T_r = T_r'$. Nevertheless, if Z_c in Eq. 1 or in the derived equation,

$$V_f = \{V_f'/Z_c^{[(1-T_r')^{2/7}]}\}Z_c^{[(1-T_r)^{2/7}]} \quad (2)$$

is given by Eq. 3 (*q.v.* next paragraph) when in Eq. 3, $V_f = V_f'$ and $T_r = T_r'$, the sensitivity of my equation to variation of a standard volume,

$$\frac{\partial \log V_f}{\partial \log V_f'} = \frac{1 + (1 - T_r)^{2/7}}{1 + (1 - T_r')^{2/7}} > 1$$

when $T_r < T_r'$, but <1 when $T_r > T_r'$.

The Z_c (critical compressibility factor) given by a rearrangement of Eq. 1,

$$\log Z_c = \frac{\log V_f + \log(P_c/RT_c)}{1 + (1 - T_r)^{2/7}} \quad (3)$$

or by the linear-regression equation (Rackett, 1970),

$$\log Z_c = \{\Sigma[1 + (1 - T_r)^{2/7}]\log V_f + \log(P_c/RT_c)\Sigma[1 + (1 - T_r)^{2/7}]\} / \Sigma[1 + (1 - T_r)^{2/7}]^2 \quad (4)$$

(wherein V_f is or are measured liquid volumes) and the V_c (critical volume) given by the corresponding equation,

$$\log V_c = \frac{\log V_f - (1 - T_r)^{2/7}\log(P_c/RT_c)}{1 + (1 - T_r)^{2/7}} \quad (5)$$

or

$$\log V_c = \{\Sigma[1 + (1 - T_r)^{2/7}]\log V_f - \log(P_c/RT_c)\Sigma[(1 - T_r)^{2/7} + (1 - T_r)^{4/7}]\}/\Sigma[1 + (1 - T_r)^{2/7}]^2 \quad (6)$$

are the Z_c and V_c for each component that should be used in my method for estimating the volumes of liquid mixtures (Rackett, 1971). Hankinson and Thomson, however, inferred from a paper by Spencer and Danner (1973) that published V_c are to be used in my mixture method. The use of such V_c would bring about larger mean errors for almost all mixtures.

Hankinson and Thomson presume that Spencer and Danner (1972) have "significantly improved" my liquid-volume equation, Eq. 1, and consequently refer to the "modified" equation as the SDR equation (standing for *Spencer, Danner, Rackett*). Spencer and Danner, however, have merely designated the Z_c to be used in my equation Z_{RA} (to distinguish these Z_c from the only approximately equal Z_c given by the formula $Z_c = V_cP_c/RT_c$, wherein V_c, P_c, and T_c are A.P.I. critical values, taken as standards by Spencer and Danner). They have made no change other than this change of subscript; their Z_{RA} and my "best" Z_c are calculated using the same equation, Eq. 4, and thus are identical quantities when the same measured liquid volumes and the same T_c and P_c are used.

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Reply:

H. G. Rackett makes three points in the above letter:

(1) We are wrong in our claim that a given error in Z_c in Rackett's equation causes a larger error in the calculated saturated liquid volume than does the same error in V_{sc} in the Gunn-Yamada equation, (2) We did not use the correct V_c and Z_c in the mixing rules for his equation, and (3) Spencer and Danner did not "significantly improve" and "modify" his equation and that it should not be called the "SDR equation." I will reply to his comments in this order. Note that Rackett's V_f and our V_s are the same.

(1) Sensitivities of the Gunn-Yamada and the Rackett equations to errors in their adjustable parameters. When the Gunn-Yamada equation is written

$$V_s = V_{sc}V_R^{(0)}(1 - \omega_{SRK}\delta)$$

it is apparent that V_s is directly proportional to V_{sc}, and that an error in V_{sc} will produce the same error in V_s. On the other hand when the Rackett equation is written

$$V_s = (RT_c/P_c)Z_{RA}^{[1+(1-T_R)^{2/7}]}$$

it is apparent that V_s is proportional to $Z_{RA}^{[1+(1-T_R)^{2/7}]}$. For values of T_R between 0 and 0.99, the term $(1 - T_R)^{2/7}$ will be positive, and $1 + (1 - T_R)^{2/7}$ will be greater than one. Thus an error in Z_{RA} will produce a larger error in V_s. This will be true regardless of how the equations are written.

(2) Mixing rules used. In Rackett's 1970 paper the symbols "V_c" and "Z_c" are defined as "critical volume" and "critical compressibility factor", V_c is substituted for Z_cRT_c/P_c, and Z_c is defined as V_cP_c/RT_c. In the 1971 paper there is no indication that the V_c and Z_c used in the mixing rules were anything other than the usual critical constants from the literature. Rackett now says they were regressed from experimental data as Spencer and Danner's (1973) and our Z_{RA}'s were. The only indication that regression might be used is in a section on the precision of the equations tested (Rackett, 1970): "The precision of any of the equations, however, can be determined by making Z_c a free parameter . . . ." There are no conclusions or recommendations relating to the source or type of V_c's or Z_c's to be used. We inferred that Rackett intended the discussion of precision to be a secondary point and that his intention was to use critical constants from the literature in his equation and in his mixing rules. Spencer and Danner also thought Rackett meant pure component critical constants because they wrote about the Rackett equation, "This equation is the simplest in form of all the equations considered and requires no arbitrary constants for its evaluation. One simply needs the critical constants T_c, P_c, and Z_c." (Spencer and Danner, 1972), and ". . . where V_{cm} and Z_{cm} are molar averages of the pure component critical volumes and critical compressibility factors." (Spencer and Danner, 1973).

(3) Spencer and Danner's improvement and modification of Rackett's equation. Again the question is whether Rackett stated or clearly implied that the V_c and Z_c to be used in his equation should be adjustable parameters regressed or calculated from experimental density data. We feel that he did not and that Spencer and Danner should be given credit for "significantly improving" Rackett's equation since they clearly pointed out that the accuracy of the equation could be improved if Z_{RA} were treated as an adjustable parameter and since they published Z_{RA}'s calculated from carefully evaluated data.

I apologize for the phrase ". . . the SDR equation as modified by Spencer and Danner." in the abstract of our paper. It should certainly have read, ". . . the Rackett equation as modified by Spencer and Danner."

We realize this reply will not satisfy Rackett, but we hope it will clarify our thoughts and intentions.

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