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UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
HELIUM ACTIVITY
HELIUM RESEARCH CENTER

INTERNAL REPORT

SHAPE OF THE COEXISTENCE CURVE OF AN ANALYTICAL FLUID IN THE CRITICAL REGION. MATHEMATICAL EXPRESSIONS CARRIED OUT TO THE THIRD ORDER

BY

Donald R. Smith

BRANCH Laboratory Services

ROJECT NO. 820.4

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by

Donald R. Smith[1/]

ABSTRACT

The purpose of this report is to arrive at a better expression for the relationships between coexisting phases of an analytical fluid. This expression is

$$a_3 = -a_1 \left\{ 1 + \left(\frac{3D}{5B} - \frac{C}{3A}\right) a_1 + \left(\frac{3D}{5B} - \frac{C}{3A}\right)^2 a_1^2 + \left[\frac{C^2}{54A^3B}(9AD-5BC) + \frac{27D^2}{50AB^3}(AD-BC) - \frac{BCE}{9A^3} + \frac{DF}{5AB} - \frac{G}{25AB^2}(18AD-5BC) \right] a_1^3 \right\},$$

where

$$a_1 = \frac{\rho_{gas}}{\rho_c} - 1 ;$$

$$a_3 = \frac{\rho_{liq}}{\rho_c} - 1 ;$$

[1/] Mathematician, Helium Research Center, Bureau of Mines, Amarillo, Tex.

$$A = p_{at} \;;$$

$$B = \frac{1}{2} p_{aaa} \;;$$

$$C = - p_{at} + p_{aat} \;;$$

$$D = \frac{1}{6} \left(-3p_{aaa} + p_{aaaa} \right) \;;$$

$$E = \frac{1}{2} p_{att} \;;$$

$$F = \frac{1}{2} \left(2p_{at} - 2p_{aat} + p_{aaat} \right) \;;$$

$$G = \frac{1}{24} \left(12p_{aaa} - 4p_{aaaa} + p_{aaaaa} \right) \;;$$

$$a = \frac{\rho}{\rho_c} - 1 \;;$$

$$p = \frac{P}{P_c} - 1 \;;$$

$$t = \frac{T}{T_c} - 1 \;;$$

and p with subscripts represents the partial derivatives of p at $a = 0$, $t = 0$.

INTRODUCTION

As a result of a journal article by Barieau (1)[2/], I became

[2/] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

interested in the treatment of the expansion of the chemical potential of an analytical fluid to the third and fourth order.

An analytical fluid is one in which the chemical potential can be expanded in a Taylor series about the critical point.

Landau and Lifshitz (6) expanded to the first order,

$$-\left(\frac{\partial P}{\partial V}\right)_T$$

in a power series in the variables of v and t, where $v = V-V_c$ and $t = T-T_c$.

Edwards and Woodbury (3) tried to extend Landau and Lifshitz' (6) expansion to the second order. They included a t^2 term, which should have been omitted, and did not include a v^3 term. Giterman (4) pointed out this error, and he correctly expanded the pressure in a series in v and t to the second order.

Tisza and Chase (8) expanded the chemical potential to the first order in the variables of t and ρ', where $t = T-T_c$ and $\rho' = \rho-\rho_c$.

Mistura and Sette (7) attempted to extend Tisza and Chase's (8) expansion to the second order. They included a t^2 term, which clearly should have been omitted, and did not include a $(\rho')^3$ term.

Griffiths (5) observed that if Mistura and Sette's (7) expansion exists, this precludes the possibility of any infinite singularity in the specific heat at constant volume.

Barieau (1) correctly treated the problem to the second order by expanding the chemical potential in a power series in the variables of reduced density and reduced temperature. He pointed out that to

arrive at the correct expression for the slope of

$$\frac{\left(a_3 - a_1\right)^2}{-t} \text{ vs } t,$$

it is necessary to include additional terms in the expansion.

THIRD-ORDER EXPANSION

Let

$$a = \frac{\rho}{\rho_c} - 1 \quad , \tag{1}$$

$$t = \frac{T}{T_c} - 1 \quad , \tag{2}$$

and

$$p = \frac{P}{P_c} - 1 \quad , \tag{3}$$

where ρ is the density, T is the temperature, P is the pressure, ρ_c is the critical density, T_c is the critical temperature, and P_c is the critical pressure.

The third order expansion of the chemical potential in the variables of density and temperature leads to

$$\frac{\rho_c^2}{P_c}\left(\frac{\partial \mu}{\partial \rho}\right)_T = \frac{1}{1+a}\left(\frac{\partial p}{\partial a}\right)_t = At + Ba^2 + Cat + Da^3 + Et^2 + Fa^2t + Ga^4 \quad , \tag{4}$$

where μ is the chemical potential.[3/]

[3/] Barieau (1) had previously arrived at this relationship.

The third order expansion contains terms of the order of a^4. With t being of the order of a^2, it is not necessary to include at^2 or at^3 terms as these would be of the order of a^5 and a^7, respectively. The constants A, B, C, D, E, F, and G, in terms of the equation of state, are given by

$$A = p_{at} \quad ; \tag{5}$$

$$B = \frac{1}{2} p_{aaa} \quad ; \tag{6}$$

$$C = -p_{at} + p_{aat} \quad ; \tag{7}$$

$$D = \frac{1}{6}\left(-3p_{aaa} + p_{aaaa}\right) \quad ; \tag{8}$$

$$E = \frac{1}{2} p_{att} \quad ; \tag{9}$$

$$F = \frac{1}{2}\left(2p_{at} - 2p_{aat} + p_{aaat}\right) \quad ; \tag{10}$$

$$G = \frac{1}{24}\left(12p_{aaa} - 4p_{aaaa} + p_{aaaaa}\right) \quad ; \tag{11}$$

where

$$p_{at} = \left(\frac{\partial^2 p}{\partial t \partial a}\right)_{a=0,\ t=0} \quad ; \tag{12}$$

$$p_{aaa} = \left(\frac{\partial^3 p}{\partial a^3}\right)_{a=0,\ t=0} \quad ; \tag{13}$$

$$p_{aat} = \left(\frac{\partial^3 p}{\partial t \partial a^2}\right)_{a=0,\ t=0} \quad ; \tag{14}$$

$$p_{aaaa} = \left(\frac{\partial^4 p}{\partial a^4}\right)_{a=0,\ t=0} \quad ; \tag{15}$$

$$p_{att} = \left(\frac{\partial^3 p}{\partial t^2 \partial a}\right)_{a=0,\ t=0} ; \tag{16}$$

$$p_{aaat} = \left(\frac{\partial^4 p}{\partial t \partial a^3}\right)_{a=0,\ t=0} ; \tag{17}$$

and

$$p_{aaaaa} = \left(\frac{\partial^5 p}{\partial a^5}\right)_{a=0,\ t=0} . \tag{18}$$

Equality of the chemical potential for coexisting phases requires

$$\int_{\rho_1}^{\rho_3} \left(\frac{\partial \mu}{\partial \rho}\right)_T d\rho = 0 = At\left(a_3 - a_1\right) + \frac{1}{3} B\left(a_3^3 - a_1^3\right) + \frac{1}{2} Ct\left(a_3^2 - a_1^2\right)$$

$$+ \frac{1}{4} D\left(a_3^4 - a_1^4\right) + Et^2\left(a_3 - a_1\right) + \frac{1}{3} Ft\left(a_3^3 - a_1^3\right)$$

$$+ \frac{1}{5} G\left(a_3^5 - a_1^5\right) . \tag{19}$$

Equality of the pressure for coexisting phases requires

$$\int_{\rho_1}^{\rho_3} \left(\frac{\partial P}{\partial \rho}\right)_T d\rho = \int_{\rho_1}^{\rho_3} \rho\left(\frac{\partial \mu}{\partial \rho}\right) d\rho = 0 , \tag{20}$$

where the subscript 1 refers to saturated gas and the subscript 3 refers to saturated liquid.

Equation 20 becomes

$$\frac{1}{2} At\left(a_3^2 - a_1^2\right) + \frac{1}{4} B\left(a_3^4 - a_1^4\right) + \frac{1}{3} Ct\left(a_3^3 - a_1^3\right) + \frac{1}{5} D\left(a_3^5 - a_1^5\right) + \frac{1}{2} Et^2\left(a_3^2 - a_1^2\right)$$

$$+ \frac{1}{4} Ft\left(a_3^4 - a_1^4\right) + \frac{1}{6} G\left(a_3^6 - a_1^6\right) = 0 . \tag{21}$$

Dividing equations 19 and 21 by $\left(a_3 - a_1\right)$, we have

$$At + \frac{1}{3} B\Sigma aa + \frac{1}{2} Ct\Sigma a + \frac{1}{4} D\Sigma aaa + Et^2$$

$$+ \frac{1}{3} Ft\Sigma aa + \frac{1}{5} G\Sigma aaaa = 0 \quad , \tag{22}$$

and

$$\frac{1}{2} At\Sigma a + \frac{1}{4} B\Sigma aaa + \frac{1}{3} Ct\Sigma aa + \frac{1}{5} D\Sigma aaaa + \frac{1}{2} Et^2\Sigma a$$

$$+ \frac{1}{4} Ft\Sigma aaa + \frac{1}{6} G\Sigma aaaaa = 0 \quad , \tag{23}$$

where

$$\Sigma a = a_3 + a_1 \quad ; \tag{24}$$

$$\Sigma aa = a_3^2 + a_3 a_1 + a_1^2 \quad ; \tag{25}$$

$$\Sigma aaa = a_3^3 + a_3^2 a_1 + a_3 a_1^2 + a_1^3 \quad ; \tag{26}$$

$$\Sigma aaaa = a_3^4 + a_3^3 a_1 + a_3^2 a_1^2 + a_3 a_1^3 + a_1^4 \quad ; \tag{27}$$

and

$$\Sigma aaaaa = a_3^5 + a_3^4 a_1 + a_3^3 a_1^2 + a_3^2 a_1^3 + a_3 a_1^4 + a_1^5 \quad . \tag{28}$$

Multiplying equation 22 by 60 and equation 23 by 120, we have

$$60At + 20B\Sigma aa + 30Ct\Sigma a + 15D\Sigma aaa + 60Et^2$$

$$+ 20Ft\Sigma aa + 12G\Sigma aaaa = 0 \tag{29}$$

and

$$60At\Sigma a + 30B\Sigma aaa + 40Ct\Sigma aa + 24D\Sigma aaaa + 60Et^2\Sigma a$$

$$+ 30Ft\Sigma aaa + 20G\Sigma aaaaa = 0 \quad . \tag{30}$$

Solving equation 29 for $60Et^2$, we find

$$60Et^2 = - 60At - 20B\Sigma aa - 30Ct\Sigma a - 15D\Sigma aaa$$

$$- 20Ft\Sigma aa - 12G\Sigma aaaa \quad . \tag{31}$$

Multiplying equation 31 by Σa, we obtain

$$60Et^2\Sigma a = -60At\Sigma a - 20B\Sigma a\Sigma aa - 30Ct(\Sigma a)^2 - 15D\Sigma a\Sigma aaa$$
$$- 20Ft\Sigma a\Sigma aa - 12G\Sigma a\Sigma aaaa \quad . \tag{32}$$

Substituting equation 32 into equation 30 yields

$$60At\Sigma a + 30B\Sigma aaa + 40Ct\Sigma aa + 24D\Sigma aaaa - 60At\Sigma a - 20B\Sigma a\Sigma aa$$
$$-30Ct(\Sigma a)^2 - 15D\Sigma a\Sigma aaa - 20Ft\Sigma a\Sigma aa - 12G\Sigma a\Sigma aaaa$$
$$+ 30Ft\Sigma aaa + 20G\Sigma aaaaa = 0 \quad . \tag{33}$$

Simplifying,

$$t[10C(4\Sigma aa - 3\Sigma a\Sigma a) + 10F(3\Sigma aaa - 2\Sigma a\Sigma aa)] + 10B(3\Sigma aaa - 2\Sigma a\Sigma aa)$$
$$+ 3D(8\Sigma aaaa - 5\Sigma a\Sigma aaa) + 4G(5\Sigma aaaaa - 3\Sigma a\Sigma aaaa) = 0 \quad . \tag{34}$$

From equations 24, 25, 26, 27, and 28, we find

$$4\Sigma aa = 4a_3^2 + 4a_3a_1 + 4a_1^2 \; ; \tag{35}$$

$$3\Sigma a\Sigma a = 3a_3^2 + 6a_3a_1 + 3a_1^2 \; ; \tag{36}$$

$$3\Sigma aaa = 3a_3^3 + 3a_3^2a_1 + 3a_3a_1^2 + 3a_1^3 \; ; \tag{37}$$

$$2\Sigma a\Sigma aa = 2a_3^3 + 4a_3^2a_1 + 4a_3a_1^2 + 2a_1^3 \; ; \tag{38}$$

$$8\Sigma aaaa = 8a_3^4 + 8a_3^3a_1 + 8a_3^2a_1^2 + 8a_3a_1^3 + 8a_1^4 \; ; \tag{39}$$

$$5\Sigma a\Sigma aaa = 5a_3^4 + 10a_3^3a_1 + 10a_3^2a_1^2 + 10a_3a_1^3 + 5a_1^4 \; ; \tag{40}$$

$$5\Sigma aaaaa = 5a_3^5 + 5a_3^4a_1 + 5a_3^3a_1^2 + 5a_3^2a_1^3 + 5a_3a_1^4 + 5a_1^5 \; ; \tag{41}$$

and $$3\Sigma a\Sigma aaaa = 3a_3^5 + 6a_3^4a_1 + 6a_3^3a_1^2 + 6a_3^2a_1^3 + 6a_3a_1^4 + 3a_1^5 \quad . \tag{42}$$

From equations 35 and 36, we obtain

$$4\Sigma aa - 3\Sigma a\Sigma a = \left(a_3 - a_1\right)^2 \quad . \tag{43}$$

From equations 37 and 38, we find

$$3\Sigma aaa - 2\Sigma a\Sigma aa = \left(a_3 - a_1\right)^2 \Sigma a \quad . \tag{44}$$

From equations 39 and 40, we have

$$8\Sigma aaaa - 5\Sigma a\Sigma aaa = \left(a_3 - a_1\right)^2 \left(3a_3^2 + 4a_3a_1 + 3a_1^2\right) \quad . \tag{45}$$

From equations 41 and 42, we obtain

$$5\Sigma aaaaa = 3\Sigma a\Sigma aaaa = \left(a_3 - a_1\right)^2 \left(2a_3^3 + 3a_3^2a_1 + 3a_3a_1^2 + 2a_1^3\right) \quad . \tag{46}$$

Substituting equations 43, 44, 45, and 46 into equation 34, we have

$$\begin{aligned} t &\left[10C\left(a_3 - a_1\right)^2 + 10F\left(a_3 - a_1\right)^2 \Sigma a\right] + 10B\left(a_3 - a_1\right)^2 \Sigma a \\ &+ 3D\left(a_3 - a_1\right)^2 \left(3a_3^2 + 4a_3a_1 + 3a_1^2\right) \\ &+ 4G\left(a_3 - a_1\right)^2 \left(2a_3^3 + 3a_3^2a_1 + 3a_3a_1^2 + 2a_1^3\right) = 0 \quad . \end{aligned} \tag{47}$$

Solving equation 47 for t yields

$$t = -\frac{10B\Sigma a + 3D\left(3a_3^2 + 4a_3a_1 + 3a_1^2\right) + 4G\left(2a_3^3 + 3a_3^2a_1 + 3a_3a_1^2 + 2a_1^3\right)}{10(C + F\Sigma a)} \quad . \tag{48}$$

Squaring equation 48, we have

$$t^2 = \frac{\left[10B\Sigma a + 3D\left(3a_3^2 + 4a_3a_1 + 3a_1^2\right) + 4G\left(2a_3^3 + 3a_3^2a_1 + 3a_3a_1^2 + 2a_1^3\right)\right]^2}{100(C + F\Sigma a)^2} \quad . \tag{49}$$

Equation 29 may be written as

$$10t(6A + 3C\Sigma a + 2F\Sigma aa) + 60Et^2 + 20B\Sigma aa + 15D\Sigma aaa + 12G\Sigma aaaa = 0 \ . \qquad (50)$$

Substituting for t and t^2 in equation 50, we find for the equation relating a_3 and a_1,

$$- \frac{10B\Sigma a + 3D\left(3a_3^2+4a_3a_1+3a_1^2\right) + 4G\left(2a_3^3+3a_3^2a_1+3a_3a_1^2+2a_1^3\right)}{C + F\Sigma a}\left[6A+3C\Sigma a+2F\Sigma aa\right]$$

$$+ (60E)\frac{\left[10B\Sigma a + 3D\left(3a_3^2+4a_3a_1+3a_1^2\right) + 4G\left(2a_3^3+3a_3^2a_1+3a_3a_1^2+2a_1^3\right)\right]^2}{100(C + F\Sigma a)^2}$$

$$+ 20B\Sigma aa + 15D\Sigma aaa + 12G\Sigma aaaa = 0 \ . \qquad (51)$$

Multiplying equation 51 by $5(C + F\Sigma a)^2$ yields

$$- 5(C + F\Sigma a)(6A + 3C\Sigma a + 2F\Sigma aa)\left[10B\Sigma a + 3D\left(3a_3^2 + 4a_3a_1 + 3a_1^2\right)\right.$$

$$\left. + 4G\left(2a_3^3 + 3a_3^2a_1 + 3a_3a_1^2 + 2a_1^3\right)\right] + 3E\left[10B\Sigma a + 3D\left(3a_3^2 + 4a_3a_1 + 3a_1^2\right)\right.$$

$$\left. + 4G\left(2a_3^3 + 3a_3^2a_1 + 3a_3a_1^2 + 2a_1^3\right)\right]^2 + 5(C + F\Sigma a)^2\left[20B\Sigma aa\right.$$

$$\left. + 15D\Sigma aaa + 12G\Sigma aaaa\right] = 0 \ . \qquad (52)$$

Now, developing a_3 as a power series in a_1, expanded to the fourth order, we have[4/]

[4/] The details of this development are given in Appendix A.

$$a_3 = -a_1\left\{1 + \left(\frac{3D}{5B} - \frac{C}{3A}\right)a_1 + \left(\frac{3D}{5B} - \frac{C}{3A}\right)^2 a_1^2 + \left[\frac{C^2}{54A^3B}(9AD-BC) + \frac{27D^2}{50AB^3}(AD-BC) - \frac{BCE}{9A^3} + \frac{DF}{5AB} - \frac{G}{25AB^2}(18AD-5BC)\right]a_1^3\right\} . \qquad (53)$$

Now, developing t as a power series in a_1, we find[5/]

[5/] The details of this development are given in Appendix B.

$$t = -\frac{B}{3A}a_1^2 - \frac{(9AD-5BC)}{45A^2}a_1^3 - \frac{1}{1350A^3B}\left[\begin{array}{l}150B^3E - (9AD-5BC)(9AD+5BC) \\ + 30AB(9AG-5BF)\end{array}\right]a_1^4 . \qquad (54)$$

Similarly, we find

$$t = -\frac{B}{3A}a_3^2 - \frac{(9AD-5BC)}{45A^2}a_3^3 - \frac{1}{1350A^3B}\left[\begin{array}{l}150B^3E - (9AD-5BC)(9AD+5BC) \\ + 30AB(9AG-5BF)\end{array}\right]a_3^4 . \qquad (55)$$

Therefore,

$$t = -\frac{B}{3A}a_i^2 - \frac{(9AD-5BC)}{45A^2}a_i^3 - \frac{1}{1350A^3B}\left[\begin{array}{l}150B^3E - (9AD-5BC)(9AD+5BC) \\ + 30AB(9AG-5BF)\end{array}\right]a_i^4 , \qquad (56)$$

where i = 1 or 3.

Now, developing a_3 and a_1 as a power series in y, where $y = \sqrt{-t}$, we obtain[6/]

6/ The details of this development are given in Appendix C.

$$a_1 = -\sqrt{\frac{-3At}{B}}\left\{1 + \frac{(9AD-5BC)}{30AB}\sqrt{\frac{-3At}{B}} + \frac{1}{600A^2B^2}\begin{bmatrix}(9AD-5BC)(21AD-5BC) - 100B^3E\\ -20AB(9AG-5BF)\end{bmatrix}\left(-\frac{3At}{B}\right)\right\}, \tag{57}$$

and

$$a_3 = \sqrt{\frac{-3At}{B}}\left\{1 - \frac{(9AD-5BC)}{30AB}\sqrt{\frac{-3At}{B}} + \frac{1}{600A^2B^2}\begin{bmatrix}(9AD-5BC)(21AD-5BC) - 100B^3E\\ - 20AB(9AG-5BF)\end{bmatrix}\left(-\frac{3At}{B}\right)\right\}. \tag{58}$$

Now

$$a_3+a_1 = \sqrt{\frac{-3At}{B}}\left[-\frac{2(9AD-5BC)}{30AB}\sqrt{\frac{-3At}{B}}\right] \tag{59}$$

or

$$a_3+a_1 = \left(\frac{9AD-5BC}{5B^2}\right)t \quad . \tag{60}$$

Thus, the reduced rectilinear diameter is given by

$$\frac{1}{2}\left(a_3+a_1\right) + 1 = \left(\frac{9AD-5BC}{10B^2}\right)t + 1 \quad . \tag{61}$$

Then the slope of the reduced rectilinear diameter at the critical point is given by

$$\frac{1}{2}\left[\frac{d\left(a_3+a_1\right)}{dt}\right] = \frac{9AD-5BC}{10B^2} \ . \tag{62}$$

Substituting equations 5, 6, 7, and 8 into equation 62, we have

$$\frac{1}{2}\left[\frac{d\left(a_3+a_1\right)}{dt}\right] = \frac{9p_{at}\left[\frac{1}{6}\left(-3p_{aaa}+p_{aaaa}\right)\right] - 5\left(\frac{1}{2}\,p_{aaa}\right)\left(-p_{at}+p_{aat}\right)}{10\left(\frac{1}{2}\,p_{aaa}\right)^2} \tag{63}$$

or

$$\frac{1}{2}\left[\frac{d\left(a_3+a_1\right)}{dt}\right] = \frac{1}{5\left(p_{aaa}\right)^2}\left[3p_{at}p_{aaaa} - 4p_{at}p_{aaa} - 5p_{aat}p_{aaa}\right].^{7/} \tag{64}$$

7/ Barieau (1) had previously arrived at this relationship.

From equations 57 and 58, we find

$$a_3-a_1 = \sqrt{\frac{-3At}{B}}\left\{2 + \frac{1}{300A^2B^2}\left[\begin{matrix}(9AD-5BC)(21AD-5BC) - 100B^3E \\ - 20AB(9AG-5BF)\end{matrix}\right]\left(-\frac{3At}{B}\right)\right\} \tag{65}$$

or

$$a_3-a_1 = \sqrt{\frac{-3At}{B}}\left\{2 - \frac{1}{100AB^3}\left[\begin{matrix}(9AD-5BC)(21AD-5BC) - 100B^3E \\ - 20AB(9AG-5BF)\end{matrix}\right]t\right\} . \tag{66}$$

Squaring equation 66, we obtain

$$\left(a_3-a_1\right)^2 = -\frac{3At}{B}\left\{4 - \frac{1}{25AB^3}\left[\begin{matrix}(9AD-5BC)(21AD-5BC) - 100B^3E \\ - 20AB(9AG-5BF)\end{matrix}\right]t\right\} . \tag{67}$$

The t^2 term is not included because the coefficient of t^2 obtained from the fourth-order expansion is different from the coefficient in the third-order expansion.

Dividing equation 67 by (-t), we have

$$\frac{\left(a_3-a_1\right)^2}{-t} = \frac{3A}{B}\left\{4 - \frac{1}{25AB^3}\begin{bmatrix}(9AD-5BC)(21AD-5BC) - 100B^3E \\ - 20AB(9AG-5BF)\end{bmatrix}t\right\} . \qquad (68)$$

Thus, the slope of

$$\frac{\left(a_3-a_1\right)^2}{-t}$$

at the critical point is given by

$$\frac{d}{dt}\left[\frac{\left(a_3-a_1\right)^2}{-t}\right] = -\frac{3}{25B^4}\begin{bmatrix}(9AD-5BC)(21AD-5BC) - 100B^3E \\ - 20AB(9AG-5BF)\end{bmatrix} . \qquad (69)$$

The second order treatment shows that this slope is zero for all fluids. Mistura and Sette (7) show that this slope is constant.

I have carried out the treatment of the expansion of the chemical potential to the fourth order. That is,

$$\frac{\rho_c^2}{P_c}\left(\frac{\partial\mu}{\partial\rho}\right)_T = \frac{1}{1+a}\left(\frac{\partial p}{\partial a}\right)_t = \begin{bmatrix}At+Ba^2+Cat+Da^3+Et^2+Fa^2t \\ +Ga^4+Hat^2+Ja^3t+Ka^5\end{bmatrix} . \qquad (70)$$

The coefficient of t in equation 68 is the same as the coefficient of t obtained from the fourth-order expansion.

For a van der Waals fluid, we have (2)

$$p_{at} = 6, \quad p_{aaa} = 9, \quad p_{aat} = 6 ,$$

$$p_{aaaa} = 18, \quad p_{att} = 0, \quad p_{aaat} = 9 ,$$

$$\text{and } p_{aaaaa} = 45 ,$$

so that

$$A = 6, \quad B = \frac{9}{2}, \quad C = 0 ,$$

$$D = -\frac{3}{2}, \quad E = 0, \quad F = \frac{9}{2} ,$$

$$\text{and } G = \frac{27}{8} .$$

Substituting the above values into equation (69), we find

$$\frac{d}{dt}\left[\frac{\left(a_3 - a_1\right)^2}{-t}\right] = 8.32 ,$$

which agrees with the results previously obtained by Barieau (2).

REFERENCES

1. Barieau, Robert E. Shape of the Coexistence Curve of an Analytical Fluid in the Critical Region. J. Chem. Phys., v. 45, No. 9, 1966, pp. 3175-3177.

2. Barieau, Robert E. Thermodynamic Properties of the van der Waals Fluid in the Two-Phase Region. BuMines Rept. of Inv. 6950, 1967, 184 pp.

3. Edwards, M. H. and W. C. Woodbury. Saturated He^4 Near its Critical Temperature. Phys. Rev., v. 129, No. 5, 1963, pp. 1911-1918.

4. Giterman, M. S. The Shape of the Liquid-Gas Coexistence Curve Near the Critical Point. Russian J. Phys. Chem., v. 39, 1965, pp. 522-524.

5. Griffiths, R. B. Power-Series Expansions and Specific-Heat Singularities Near the He^4 Critical Point. Phys. Rev. Letters, v. 16, No. 18, 1966, pp. 787-788.

6. Landau, L. D. and E. M. Lifshitz. Statistical Physics. Addison-Wesley Publ. Co., Inc., Reading, Mass., 1958, pp. 264-268.

7. Mistura, L. and D. Sette. Shape of the Coexistence Curve in the Critical Region. Phys. Rev. Letters, v. 16, No. 7, 1966, pp. 268-270.

8. Tisza, L. and C. E. Chase. Equation of State of ^4He in the Critical Region. Phys. Rev. Letters, v. 15, No. 1, 1965, pp. 4-6.

APPENDIX A.

Let

$$X = C + F\Sigma a \quad ; \tag{A-1}$$

$$Y = 6A + 3C\Sigma a + 2F\Sigma aa \quad ; \tag{A-2}$$

$$Z = 10B\Sigma a + 3D\left(3a_3^2 + 4a_3a_1 + 3a_1^2\right) + 4G\left(2a_3^3 + 3a_3^2a_1 + 3a_3a_1^2 + 2a_1^3\right) \; ; \tag{A-3}$$

$$W = 20B\Sigma aa + 15D\Sigma aaa + 12G\Sigma aaaa \quad ; \tag{A-4}$$

or,

$$X = C + F\left(a_3+a_1\right) \; ; \tag{A-5}$$

$$Y = 6A + 3C\left(a_3+a_1\right) + 2F\left(a_3^2 + a_3a_1 + a_1^2\right) \; ; \tag{A-6}$$

$$Z = 10B\left(a_3+a_1\right) + 3D\left(3a_3^2+4a_3a_1+3a_1^2\right) + 4G\left(2a_3^3+3a_3^2a_1+3a_3a_1^2+2a_1^3\right) \; ; \tag{A-7}$$

and

$$W = 20B\left(a_3^2+a_3a_1+a_1^2\right) + 15D\left(a_3^3+a_3^2a_1+a_3a_1^2+a_1^3\right) + 12G\left(a_3^4+a_3^3a_1+a_3^2a_1^2+a_3a_1^3+a_1^4\right). \tag{A-8}$$

Let

$$\frac{dX}{da_1} = X' \, , \quad \frac{d^2X}{da_1^2} = X'' \, , \ldots$$

and

$$\frac{dY}{da_1} = Y' \, , \quad \frac{d^2Y}{da_1^2} = Y'' \, , \ldots, \text{ etc.}$$

Now

$$(X)_{a_3=0,\ a_1=0} = C \quad ; \tag{A-9}$$

$$(X')_{a_3=0,\ a_1=0} = F\left(a_3'+1\right) \ ; \qquad \text{(A-10)}$$

$$(X'')_{a_3=0,\ a_1=0} = Fa_3'' \ ; \qquad \text{(A-11)}$$

$$(X''')_{a_3=0,\ a_1=0} = Fa_3''' \ ; \qquad \text{(A-12)}$$

$$(X'''')_{a_3=0,\ a_1=0} = Fa_3'''' \ ; \qquad \text{(A-13)}$$

$$(Y)_{a_3=0,\ a_1=0} = 6A \ ; \qquad \text{(A-14)}$$

$$(Y')_{a_3=0,\ a_1=0} = 3C\left(a_3' + 1\right) \ ; \qquad \text{(A-15)}$$

$$(Y'')_{a_3=0,\ a_1=0} = 3Ca_3'' + 2F\left(2a_3'a_3' + 2a_3' + 2\right) \ ; \qquad \text{(A-16)}$$

$$(Y''')_{a_3=0,\ a_1=0} = 3Ca_3''' + 2F\left(6a_3'a_3'' + 3a_3''\right) \ ; \qquad \text{(A-17)}$$

$$(Y'''')_{a_3=0,\ a_1=0} = 3Ca_3'''' + 2F\left(8a_3'a_3''' + 6a_3''a_3'' + 4a_3'''\right) \ ; \qquad \text{(A-18)}$$

$$(Z)_{a_3=0,\ a_1=0} = 0 \ ; \qquad \text{(A-19)}$$

$$(Z')_{a_3=0,\ a_1=0} = 10B\left(a_3' + 1\right) \ ; \qquad \text{(A-20)}$$

$$(Z'')_{a_3=0,\ a_1=0} = 10Ba_3'' + 3D\left(6a_3'a_3' + 8a_3' + 6\right) \ ; \qquad \text{(A-21)}$$

$$(Z''')_{a_3=0,\ a_1=0} = 10Ba_3''' + 3D\left(18a_3'a_3'' + 12a_3''\right)$$

$$+ 4G\left[12\left(a_3'\right)^3 + 18\left(a_3'\right)^2 + 18a_3' + 12\right]; \qquad \text{(A-22)}$$

$$(Z'''')_{a_3=0,\ a_1=0} = 10Ba_3'''' + 3D\left(24a_3'a_3''' + 18a_3''a_3'' + 16a_3'''\right)$$

$$+ 4G\left(72a_3'a_3'a_3'' + 72a_3'a_3'' + 36a_3''\right) \quad ; \qquad \text{(A-23)}$$

$$(W)_{a_3=0,\ a_1=0} = 0 \quad ; \qquad \text{(A-24)}$$

$$(W')_{a_3=0,\ a_1=0} = 0 \quad ; \qquad \text{(A-25)}$$

$$(W'')_{a_3=0,\ a_1=0} = 20B\left(2a_3'a_3' + 2a_3' + 2\right) \quad ; \qquad \text{(A-26)}$$

$$(W''')_{a_3=0,\ a_1=0} = 20B\left(6a_3'a_3'' + 3a_3''\right) + 15D\left[6\left(a_3'\right)^3 + 6\left(a_3'\right)^2 + 6a_3' + 6\right] \; ; \qquad \text{(A-27)}$$

and $$(W'''')_{a_3=0,\ a_1=0} = 20B\left[8a_3'a_3''' + 4a_3''' + 6\left(a_3''\right)^2\right]$$

$$+ 15D\left[36\left(a_3'\right)^2 a_3'' + 24a_3'a_3'' + 12a_3''\right]$$

$$+ 12G\left[24\left(a_3'\right)^4 + 24\left(a_3'\right)^3 + 24\left(a_3'\right)^2\right.$$

$$\left.+ 24a_3' + 24\right] . \qquad \text{(A-28)}$$

Substituting equations A-1, A-2, A-3, and A-4 into equation 52, we have

$$-5XYZ + 3EZ^2 + 5X^2W = 0 \quad . \qquad \text{(A-29)}$$

Thus,

$$-5(XYZ'+XZY'+YZX') + 6EZZ' + 5(X^2W'+2XWX') = 0 \quad ; \qquad \text{(A-30)}$$

$$-5(XYZ''+XZY''+YZX''+2XY'Z'+2YX'Z'+2ZX'Y') + 6E\left[ZZ''+(Z')^2\right]$$

$$+5\left[X^2W''+4XX'W'+2XWX''+2W(X')^2\right] = 0 \quad ; \qquad \text{(A-31)}$$

$$-5(XYZ'''+XZY'''+YZX'''+3XY'Z''+3YX'Z''+3XZ'Y''+6X'Y'Z'+3YZ'X''+3ZX'Y''+3ZY'X'')$$

$$+6E(ZZ'''+3Z'Z'') + 5\left[X^2W'''+2XWX'''+6XX'W''+6XW'X''+6W'(X')^2+6WX'X''\right] = 0 \; ; \qquad \text{(A-32)}$$

and

$$-5(XYZ''''+XZY''''+YZX''''+4XY'Z'''+4YX'Z'''+4XZ'Y'''+4YZ'X'''+4ZX'Y'''+4ZY'X'''$$

$$+12X'Y'Z''+12X'Z'Y''+12Y'Z'X''+6XY''Z''+6YX''Z''+6ZX''Y'')$$

$$+ 6E\left[ZZ''''+4Z'Z'''+3(Z'')^2\right] + 5\left[X^2W''''+ 8XX'W'''+2XWX''''+8XW'X'''+8WX'X'''+12XX''W''\right.$$

$$\left.+12(X')^2W''+24X'W'X''+6W(X'')^2\right] = 0 \quad . \qquad \text{(A-33)}$$

Substituting equations A-9, A-14, A-19, A-20, A-24, and A-25 into equation A-30, we obtain

$$-5C(6A)(10B)\left(a_3'+1\right) = 0 \qquad \text{(A-34)}$$

or

$$a_3' = -1 \quad . \qquad \text{(A-35)}$$

Substituting equation A-35 into equations A-10, A-15, A-16, A-17, A-18, A-20, A-21, A-22, A-23, A-26, A-27, and A-28, we have

$$(X')_{a_3=0,\ a_1=0} = 0 \quad ; \qquad \text{(A-36)}$$

$$(Y')_{a_3=0,\ a_1=0} = 0 \quad ; \tag{A-37}$$

$$(Y'')_{a_3=0,\ a_1=0} = 3Ca_3'' + 4F \quad ; \tag{A-38}$$

$$(Y''')_{a_3=0,\ a_1=0} = 3Ca_3''' - 6Fa_3'' \ ; \tag{A-39}$$

$$(Y'''')_{a_3=0,\ a_1=0} = 3Ca_3'''' + 4F\left[3\left(a_3''\right)^2 - 2_3'''\right] \quad ; \tag{A-40}$$

$$(Z')_{a_3=0,\ a_1=0} = 0 \quad ; \tag{A-41}$$

$$(Z'')_{a_3=0,\ a_1=0} = 10Ba_3'' + 12D \quad ; \tag{A-42}$$

$$(Z''')_{a_3=0,\ a_1=0} = 10Ba_3''' - 18Da_3'' \ ; \tag{A-43}$$

$$(Z'''')_{a_3=0,\ a_1=0} = 10Ba_3'''' + 6D\left[9\left(a_3''\right)^2 - 4a_3'''\right] + 144Ga_3'' \quad ; \tag{A-44}$$

$$(W'')_{a_3=0,\ a_1=0} = 40B \quad ; \tag{A-45}$$

$$(W''')_{a_3=0,\ a_1=0} = -\ 60Ba_3'' \quad ; \tag{A-46}$$

and $$(W'''')_{a_3=0,\ a_1=0} = 40B\left[3\left(a_3''\right)^2 - 2a_3'''\right] + 360Da_3'' + 288G \ . \tag{A-47}$$

Substituting equations A-9, A-14, A-19, A-20, A-24, A-36, A-42, A-45, and A-31, we obtain

$$-5C(6A)\left(10Ba_3'' + 12D\right) + 5C^2(40B) = 0 \qquad \text{(A-48)}$$

or

$$a_3'' = -2\left(\frac{3D}{5B} - \frac{C}{3A}\right) \quad . \qquad \text{(A-49)}$$

Similarly, equation A-32 becomes

$$-5C(6A)\left(10Ba_3''' - 18Da_3''\right) + 5C^2\left(-60Ba_3''\right) = 0 \quad ; \qquad \text{(A-50)}$$

thus

$$a_3''' = \left(\frac{9D}{5B} - \frac{C}{A}\right) a_3'' \qquad \text{(A-51)}$$

or

$$a_3''' = -\, 6\left(\frac{3D}{5B} - \frac{C}{3A}\right)^2 \quad . \qquad \text{(A-52)}$$

Similarly, equation A-33 becomes

$$-5C(6A)\left\{10Ba_3'''' + 6D\left[9\left(a_3''\right)^2 - 4a_3'''\right] + 144Ga_3''\right\} - 30C\left(3Ca_3''+4F\right)\left(10Ba_3''+12D\right)$$

$$-30(6A)\left(Fa_3''\right)\left(10Ba_3''+12D\right) + 18E\left(10Ba_3''+12D\right)^2 + 5C^2\left\{40B\left[3\left(a_3''\right)^2 - 2a_3'''\right]\right.$$

$$\left. + 360Da_3'' + 288G\right\} + 60C\left(Fa_3''\right)(40B) = 0 \quad . \qquad \text{(A-53)}$$

Equation A-53 may be written as

$$75ABCa_3'''' - 20\left(9ACD-5BC^2\right)a_3''' + 15\left(30ABF+27ACD-30B^2E+5BC^2\right)\left(a_3''\right)^2$$

$$+ 60\left(18ACG+9ADF-5BCF-18BDE-3C^2D\right)a_3'' + 72\left(5CDF-5C^2G-9D^2E\right) = 0 \quad . \qquad \text{(A-54)}$$

Substituting equations A-49 and A-52 into equation A-54 yields

$$25ABCa_3'''' + \frac{8C(9AD-5BC)^3}{45A^2B^2} + \frac{4(9AD-5BC)^2}{45A^2B^2}(30ABF+27ACD-30B^2E+5BC^2)$$

$$- \frac{8(9AD-5BC)}{3AB}(18ACG+9ADF-5BCF-18BDE-3C^2D) + 24(5CDF-5C^2G-9D^2E) = 0. \quad \text{(A-55)}$$

Simplifying,

$$25ABCa_3'''' + \frac{100C^3}{9A^2}(9AD-BC) + \frac{324CD^2}{B^2}(AD-BC) - \frac{200B^2C^2E}{3A^2}$$

$$+ 120CDF - \frac{24CG}{B}(18AD-5BC) = 0 \quad . \qquad \text{(A-56)}$$

Solving for a_3'''', we have

$$a_3'''' = - \frac{4C^2}{9A^3B}(9AD-BC) - \frac{324D^2}{25AB^3}(AD-BC) + \frac{8BCE}{3A^3}$$

$$- \frac{24DF}{5AB} + \frac{24G}{25AB^2}(18AD-5BC) \quad . \qquad \text{(A-57)}$$

We now have the equation for a_3 as a function of a_1 expanded to the fourth order,

$$a_3 = - a_1 \left\{ 1 + \left(\frac{3D}{5B} - \frac{C}{3A}\right)a_1 + \left(\frac{3D}{5B} - \frac{C}{3A}\right)^2 a_1^2 \right.$$

$$+ \left[\frac{C^2}{54A^3B}(9AD-BC) + \frac{27D^2}{50AB^3}(AD-BC) - \frac{BCE}{9A^3} + \frac{DF}{5AB} \right.$$

$$\left. \left. - \frac{G}{25AB^2}(18AD-5BC) \right] a_1^3 \right\} . \qquad \text{(A-58)}$$

APPENDIX B

Let

$$\delta = 3a_3^2 + 4a_3a_1 + 3a_1^2 \tag{B-1}$$

and

$$\epsilon = 2a_3^3 + 3a_3^2a_1 + 3a_3a_1^2 + 2a_1^3 \ . \tag{B-2}$$

Substituting equations 24, B-1, and B-2 into equation 48, we have

$$t = -\frac{10B\left(a_3+a_1\right) + 3D\delta + 4G\epsilon}{10\left[C + F\left(a_3+a_1\right)\right]} \ . \tag{B-3}$$

Let

$$\frac{da_3}{da_1} = a_3' \ , \quad \frac{d^2a_3}{da_1^2} = a_3'' \ , \ldots$$

$$\frac{d\delta}{da_1} = \delta' \ , \quad \frac{d^2\delta}{da_1^2} = \delta'', \ldots, \text{ etc.}$$

Now

$$\left(a_3'\right)_{a_1=0} = -1 \ ; \tag{B-4}$$

$$\left(a_3''\right)_{a_1=0} = -\frac{2(9AD-5BC)}{15AB} \ ; \tag{B-5}$$

$$\left(a_3'''\right)_{a_1=0} = -\frac{2(9AD-5BC)^2}{75A^2B^2} \ ; \tag{B-6}$$

$$\left(a_3''''\right)_{a_1=0} = -24\left[\frac{C^2}{54A^3B}(9AD-BC) + \frac{27D^2}{50AB^3}(AD-BC) - \frac{BCE}{9A^3} + \frac{DF}{5AB}\right.$$

$$\left. - \frac{G}{25AB^2}(18AD-5BC)\right] \; ; \qquad \text{(B-7)}$$

$$(\delta)_{a_3=0,\ a_1=0} = 0 \; ; \qquad \text{(B-8)}$$

$$(\delta')_{a_3=0,\ a_1=0} = 0 \; ; \qquad \text{(B-9)}$$

$$(\delta'')_{a_3=0,\ a_1=0} = 6\left(a_3'\right)^2 + 8a_3' + 6 \; ; \qquad \text{(B-10)}$$

$$(\delta''')_{a_3=0,\ a_1=0} = 18a_3'a_3'' + 12a_3'' \; ; \qquad \text{(B-11)}$$

$$(\delta'''')_{a_3=0,\ a_1=0} = 24a_3'a_3''' + 18\left(a_3''\right)^2 + 16a_3''' \; ; \qquad \text{(B-12)}$$

$$(\epsilon)_{a_3=0,\ a_1=0} = 0 \; ; \qquad \text{(B-13)}$$

$$(\epsilon')_{a_3=0,\ a_1=0} = 0 \; ; \qquad \text{(B-14)}$$

$$(\epsilon'')_{a_3=0,\ a_1=0} = 0 \; ; \qquad \text{(B-15)}$$

$$(\epsilon''')_{a_3=0,\ a_1=0} = 12\left(a_3'\right)^3 + 18\left(a_3'\right)^2 + 18a_3' + 12 \; ; \qquad \text{(B-16)}$$

and $$(\epsilon'''')_{a_3=0,\ a_1=0} = 72\left(a_3'\right)^2 a_3'' + 72a_3'a_3'' + 36a_3'' . \qquad \text{(B-17)}$$

Substituting equations B-4, B-5, and B-6 into equations B-10, B-11, B-12, B-16, and B-17, we have

$$(\delta'')_{a_3=0,\ a_1=0} = 4 \ ; \qquad \text{(B-18)}$$

$$(\delta''')_{a_3=0,\ a_1=0} = \frac{4(9AD-5BC)}{5AB} \ ; \qquad \text{(B-19)}$$

$$(\delta'''')_{a_3=0,\ a_1=0} = \frac{8(9AD-5BC)^2}{15A^2B^2} \ ; \qquad \text{(B-20)}$$

$$(\epsilon''')_{a_3=0,\ a_1=0} = 0 \ ; \qquad \text{(B-21)}$$

and $$(\epsilon'''')_{a_3=0,\ a_1=0} = -\frac{24(9AD-5BC)}{5AB} . \qquad \text{(B-22)}$$

From equation B-3, we have

$$t' = -\frac{10B\left(a_3'+1\right) + 3D\delta' + 4G\epsilon'}{10\left[C + F\left(a_3+a_1\right)\right]} + \frac{\left[10B\left(a_3+a_1\right) + 3D\delta + 4G\epsilon\right]\left[F\left(a_3'+1\right)\right]}{10\left[C + F\left(a_3+a_1\right)\right]^2} \ ; \qquad \text{(B-23)}$$

$$t'' = -\frac{10Ba_3'' + 3D\delta'' + 4G\epsilon''}{10\left[C + F\left(a_3+a_1\right)\right]} + \frac{2\left[10B\left(a_3'+1\right) + 3D\delta' + 4G\epsilon'\right]\left[F\left(a_3'+1\right)\right]}{10\left[C + F\left(a_3+a_1\right)\right]^2}$$

$$+ \frac{\left[10B\left(a_3+a_1\right) + 3D\delta + 4G\epsilon\right]\left(Fa_3''\right)}{10\left[C + F\left(a_3+a_1\right)\right]^2} - \frac{2\left[10B\left(a_3+a_1\right) + 3D\delta + 4G\epsilon\right]\left[F\left(a_3'+1\right)\right]^2}{10\left[C + F\left(a_3+a_1\right)\right]^3} ; \qquad \text{(B-24)}$$

$$t''' = -\frac{10Ba_3''' + 3D\delta''' + 4G\epsilon'''}{10\left[C + F\left(a_3+a_1\right)\right]} + \frac{3\left(10Ba_3'' + 3D\delta'' + 4G\epsilon''\right)\left[F\left(a_3'+1\right)\right]}{10\left[C + F\left(a_3+a_1\right)\right]^2}$$

$$+ \frac{3\left[10B\left(a_3'+1\right) + 3D\delta' + 4G\epsilon'\right]\left(Fa_3''\right)}{10\left[C + F\left(a_3+a_1\right)\right]^2} - \frac{6\left[10B\left(a_3'+1\right) + 3D\delta' + 4G\epsilon'\right]\left[F\left(a_3'+1\right)\right]^2}{10\left[C + F\left(a_3+a_1\right)\right]^3}$$

$$+ \frac{\left[10B\left(a_3+a_1\right) + 3D\delta + 4G\epsilon\right]\left(Fa_3'''\right)}{10\left[C + F\left(a_3+a_1\right)\right]^2} - \frac{6\left[10B\left(a_3+a_1\right) + 3D\delta + 4G\epsilon\right]\left[F\left(a_3'+1\right)\right]\left(Fa_3''\right)}{10\left[C + F\left(a_3+a_1\right)\right]^3}$$

$$+ \frac{6\left[10B\left(a_3+a_1\right) + 3D\delta + 4G\epsilon\right]\left[F\left(a_3'+1\right)\right]^3}{10\left[C + F\left(a_3+a_1\right)\right]^4} ; \qquad \text{(B-25)}$$

and

$$t'''' = -\frac{10Ba_3'''' + 3D\delta'''' + 4G\epsilon''''}{10\left[C + F\left(a_3+a_1\right)\right]} + \frac{4\left(10Ba_3''' + 3D\delta''' + 4G\epsilon'''\right)\left[F\left(a_3'+1\right)\right]}{10\left[C + F\left(a_3+a_1\right)\right]^2}$$

$$+ \frac{6\left(10Ba_3'' + 3D\delta'' + 4G\epsilon''\right)\left(Fa_3''\right)}{10\left[C + F\left(a_3+a_1\right)\right]^2} - \frac{12\left(10Ba_3'' + 3D\delta'' + 4G\epsilon''\right)\left[F\left(a_3'+1\right)\right]^2}{10\left[C + F\left(a_3+a_1\right)\right]^3}$$

$$+ \frac{24\left[10B\left(a_3'+1\right) + 3D\delta' + 4G\epsilon'\right]\left[F\left(a_3'+1\right)\right]^3}{10\left[C + F\left(a_3+a_1\right)\right]^4} + \frac{\left[10B\left(a_3+a_1\right) + 3D\delta + 4G\epsilon\right]\left(Fa_3''''\right)}{10\left[C + F\left(a_3+a_1\right)\right]^2}$$

$$- \frac{8\left[10B\left(a_3+a_1\right) + 3D\delta + 4G\epsilon\right]\left[F\left(a_3'+1\right)\right]\left(Fa_3'''\right)}{10\left[C + F\left(a_3+a_1\right)\right]^3} - \frac{6\left[10B\left(a_3+a_1\right) + 3D\delta + 4G\epsilon\right]\left(Fa_3''\right)^2}{10\left[C + F\left(a_3+a_1\right)\right]^3}$$

$$+ \frac{36\left[10B\left(a_3+a_1\right) + 3D\delta + 4G\epsilon\right]\left[F\left(a_3'+1\right)\right]^2\left(Fa_3''\right)}{10\left[C + F\left(a_3+a_1\right)\right]^4} - \frac{24\left[10B\left(a_3+a_1\right) + 3D\delta + 4G\epsilon\right]\left[F\left(a_3'+1\right)\right]^4}{10\left[C + F\left(a_3+a_1\right)\right]^5}$$

$$+ \frac{4\left[10B\left(a_3'+1\right) + 3D\delta' + 4G\epsilon'\right]\left(Fa_3'''\right)}{10\left[C + F\left(a_3+a_1\right)\right]^2} - \frac{24\left[10B\left(a_3'+1\right) + 3D\delta' + 4G\epsilon'\right]\left[F\left(a_3'+1\right)\right]\left(Fa_3''\right)}{10\left[C + F\left(a_3+a_1\right)\right]^3} . \qquad \text{(B-26)}$$

Substituting equations B-8 and B-13 into equation B-3, we obtain

$$(t)_{a_3=0,\ a_1=0} = 0 \ . \qquad \text{(B-27)}$$

Substituting equations B-4, B-9, and B-14 into B-23, we have

$$(t')_{a_3=0,\ a_1=0} = 0 \ . \qquad \text{(B-28)}$$

Similarly, equation B-24 becomes

$$(t'')_{a_3=0,\ a_1=0} = \frac{10B\left[\frac{-2(9AD-5BC)}{15AB}\right] + 3D(4)}{-10C} \qquad \text{(B-29)}$$

or

$$(t'')_{a_3=0,\ a_1=0} = -\frac{2B}{3A} \ . \qquad \text{(B-30)}$$

Similarly, equation B-25 becomes

$$(t''')_{a_3=0,\ a_1=0} = \frac{10B\left[-\frac{2(9AD-5BC)^2}{75A^2B^2}\right] + 3D\left[\frac{4(9AD-5BC)}{5AB}\right]}{-10C} \qquad \text{(B-31)}$$

or

$$(t''')_{a_3=0,\ a_1=0} = -\frac{2(9AD-5BC)}{15A^2} \ . \qquad \text{(B-32)}$$

Similarly, equation B-26 becomes

$$(t'''')_{a_3=0,\ a_1=0} = \frac{10B(-24)}{-10C}\left[\frac{C^2}{54A^3B}(9AD-BC) + \frac{27D^2}{50AB^3}(AD-BC) - \frac{BCE}{9A^3} + \frac{DF}{5AB} - \frac{G}{25AB^2}(18AD-5BC)\right]$$

$$+ \frac{3D\left[\frac{8(9AD-5BC)^2}{15A^2B^2}\right] + 4G\left[\frac{-24(9AD-5BC)}{5AB}\right]}{-10C}$$

$$+ \frac{6F\left[\frac{-2(9AD-5BC)}{15AB}\right]\left[10B\left(\frac{-2(9AD-5BC)}{15AB}\right) + 3D(4)\right]}{10C^2}, \quad \text{(B-33)}$$

or

$$(t'''')_{a_3=0,\ a_1=0} = \frac{4}{225A^3B}\left[\begin{matrix}(9AD-5BC)(9AD+5BC) \\ -150B^3E - 30AB(9AG-5BF)\end{matrix}\right]. \quad \text{(B-34)}$$

We now have the equation for t as a function of a_1,

$$t = \frac{-B}{3A}a_1^2 - \frac{(9AD-5BC)}{45A^2}a_1^3$$

$$- \frac{1}{1350A^3B}\left[\begin{matrix}150B^3E - (9AD-5BC)(9AD+5BC) \\ + 30AB(9AG-5BF)\end{matrix}\right]a_1^4. \quad \text{(B-35)}$$

APPENDIX C

Let

$$\alpha = \frac{B}{3A} , \qquad \text{(C-1)}$$

$$\beta = \frac{9AD-5BC}{45A^2} , \qquad \text{(C-2)}$$

and

$$\gamma = \frac{1}{1350A^3B}\left[\begin{array}{l}150B^3E - (9AD-5BC)(9AD+5BC)\\ + 30AB(9AG-5BF)\end{array}\right] . \qquad \text{(C-3)}$$

Thus,

$$-t = \alpha a_i^2 + \beta a_i^3 + \gamma a_i^4 . \qquad \text{(C-4)}$$

Let

$$-t = y^2 \qquad \text{(C-5)}$$

or

$$y = \pm\sqrt{-t} , \ (t < 0)^{1/} , \qquad \text{(C-6)}$$

1/ t is below the critical point and is, therefore, negative.

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where the minus sign in front of the square root applies to the saturated gas (a_1) and the positive sign in front of the square root applies to the saturated liquid (a_3).

Differentiating equation C-4, we find

$$-\frac{da_i}{dt} = \frac{1}{2\alpha a_i + 3\beta a_i^2 + 4\gamma a_i^3} . \qquad \text{(C-7)}$$

Differentiating equation C-5, we find

$$-\frac{dt}{dy} = 2y = 2\left(\alpha a_i^2 + \beta a_i^3 + \gamma a_i^4\right)^{1/2} \quad . \tag{C-8}$$

Thus,

$$\left(\frac{da_i}{dy}\right) = \frac{2\left(\alpha + \beta a_i + \gamma a_i^2\right)^{1/2}}{2\alpha + 3\beta a_i + 4\gamma a_i^2} \quad ; \tag{C-9}$$

$$\left(\frac{d^2 a_i}{dy^2}\right) = \frac{2\left(\beta+2\gamma a_i\right)}{\left(2\alpha+3\beta a_i+4\gamma a_i^2\right)^2} - \frac{4\left(\alpha+\beta a_i+\gamma a_i^2\right)\left(3\beta+8\gamma a_i\right)}{\left(2\alpha+3\beta a_i+4\gamma a_i^2\right)^3} \quad ; \tag{C-10}$$

and

$$\left(\frac{d^3 a_i}{dy^3}\right) = \frac{8\gamma\left(\alpha+\beta a_i+\gamma a_i^2\right)^{1/2}}{\left(2\alpha+3\beta a_i+4\gamma a_i^2\right)^3} - \frac{16\left(\beta+2\gamma a_i\right)\left(3\beta+8\gamma a_i\right)\left(\alpha+\beta a_i+\gamma a_i^2\right)^{1/2}}{\left(2\alpha+3\beta a_i+4\gamma a_i^2\right)^4}$$

$$- \frac{64\gamma\left(\alpha+\beta a_i+\gamma a_i^2\right)^{3/2}}{\left(2\alpha+3\beta a_i+4\gamma a_i^2\right)^4} + \frac{24\left(\alpha+\beta a_i+\gamma a_i^2\right)^{3/2}\left(3\beta+8\gamma a_i\right)^2}{\left(2\alpha+3\beta a_i+4\gamma a_i^2\right)^5} \quad . \tag{C-11}$$

Now

$$\left(\frac{da_i}{dy}\right)_{a_i=0} = \frac{1}{\sqrt{\alpha}} \quad ; \tag{C-12}$$

$$\left(\frac{d^2 a_i}{dy^2}\right)_{a_i=0} = -\frac{\beta}{\alpha^2} \quad ; \tag{C-13}$$

and

$$\left(\frac{d^3 a_i}{dy^3}\right)_{a_i=0} = -\frac{3\gamma}{\alpha^{5/2}} + \frac{15\beta^2}{4\alpha^{7/2}} \quad . \tag{C-14}$$

We now have the equation for a_i as a function of y,

$$a_i = \frac{1}{\sqrt{\alpha}} y - \frac{\beta}{2\alpha^2} y^2 + \frac{1}{2}\left(\frac{-\gamma}{\alpha^{5/2}} + \frac{5\beta^2}{4\alpha^{7/2}}\right) y^3 \quad ; \qquad \text{(C-15)}$$

or

$$a_i = \frac{y}{\sqrt{\alpha}} \left[1 - \frac{\beta}{2\alpha}\left(\frac{y}{\alpha^{1/2}}\right) - \frac{1}{2\alpha}\left(\gamma - \frac{5\beta^2}{4\alpha}\right)\frac{y^2}{\alpha}\right]. \qquad \text{(C-16)}$$

For i = 1, $y = -\sqrt{-t}$, so that

$$a_1 = -\sqrt{\frac{-t}{\alpha}}\left[1 + \frac{\beta}{2\alpha}\sqrt{\frac{-t}{\alpha}} - \frac{1}{2\alpha}\left(\gamma - \frac{5\beta^2}{4\alpha}\right)\left(\frac{-t}{\alpha}\right)\right]. \qquad \text{(C-17)}$$

Substituting equations C-1, C-2, C-3 into equation C-17, we obtain

$$a_1 = -\sqrt{\frac{-3At}{B}}\left\{1 + \frac{(9AD-5BC)}{30AB}\sqrt{\frac{-3At}{B}} + \frac{1}{600A^2B^2}\left[\begin{matrix}(9AD-5BC)(21AD-5BC) - 100B^3E \\ -20AB(9AG-5BF)\end{matrix}\right]\left(\frac{-3At}{B}\right)\right\}. \qquad \text{(C-18)}$$

For i = 3, $y = +\sqrt{-t}$, so that

$$a_3 = \sqrt{\frac{-t}{\alpha}}\left[1 - \frac{\beta}{2\alpha}\sqrt{\frac{-t}{\alpha}} - \frac{1}{2\alpha}\left(\gamma - \frac{5\beta^2}{4\alpha}\right)\left(\frac{-t}{\alpha}\right)\right]. \qquad \text{(C-19)}$$

Substituting equations C-1, C-2, and C-3 into equation C-19, we have

$$a_3 = \sqrt{\frac{-3At}{B}}\left\{1 - \frac{(9AD-5BC)}{30AB}\sqrt{\frac{-3At}{B}} + \frac{1}{600A^2B^2}\left[\begin{matrix}(9AD-5BC)(21AD-5BC) - 100B^3E \\ - 20AB(9AG-5BF)\end{matrix}\right]\left(\frac{-3At}{B}\right)\right\}. \qquad \text{(C-20)}$$