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INTERNAL REPORT

THE THERMODYNAMIC PROPERTIES OF A VAN DER WAALS FLUID IN THE TWO-PHASE REGION

BY

Robert E. Barieau

BRANCH Fundamental Research

PROJECT NO. 4335

DATE May 1966

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by

Robert E. Barieau[1]

ABSTRACT

General expressions for evaluating various thermodynamic properties applicable to the van der Waals equation of state have been derived. These formulas were subsequently used to evaluate various thermodynamic functions in the two-phase region.

The results indicate that, for a van der Waals fluid, there is a finite discontinuity in the second derivative of the vapor pressure curve, in the second derivative of the chemical potential or Gibbs free energy at the critical point, and in the heat capacity at constant volume measured at the critical density.

Numerical values are tabulated and graphs are presented for all functions calculated.

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INTRODUCTION

The Helium Research Center has, as one of its long-range objectives, the development of an equation of state for helium that will allow all of the thermodynamic properties to be calculated within the accuracy with which they are known. This includes the calculation of the vapor pressure-temperature relationship in the two-phase region.

In a previous report (1)[2/], we have derived the formulas for calculating practically all of the thermodynamic properties of interest from an empirical equation of state.

As a means of becoming proficient in our ability to carry out calculations in the two-phase region, it was decided to carry out such calculations using the van der Waals equation of state. As far as we know, these calculations have not previously been published. The results of these calculations indicate that there has been some misunderstanding in the literature about the continuity of thermodynamic properties at the critical point. It will be shown that for a van der Waals fluid there is a discontinuity in the second derivative of the vapor pressure, in the second derivative of the chemical potential or Gibbs free energy, and in the heat capacity at constant volume measured at the critical density.

Numerical results are presented for practically all of the thermodynamic properties of interest. The numerical results are

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

presented in E format, which means that the number appearing to the left of E in the tables must be multiplied by a power of ten, which is given to the right of E. The tabulated values have been truncated and not rounded to the number of figures given.

ACKNOWLEDGMENT

The Automatic Data Processing Branch of the Helium Activity carried out all of the computer calculations and in addition prepared all of the graphs with an automatic plotter. The author thanks Anthony J. Carroll, Chief of the ADP Branch, for this invaluable aid.

VAN DER WAALS EQUATION OF STATE

Van der Waals equation of state (8) is

$$(P + a\rho^2)(1 - b\rho) = \rho RT \qquad (1)$$

where P is the pressure, ρ is the molal density, R is the gas constant, and T is the absolute thermodynamic temperature and a and b are constants.

In terms of the compressibility factor, equation (1) may be written

$$\frac{P}{\rho RT} = Z = \frac{1}{1-b\rho} - \frac{a\rho}{RT} \qquad (2)$$

where Z is the compressibility factor and is defined by equation (2).

We now define the reduced variables

$$\alpha = \rho/\rho_c \tag{3}$$

$$\gamma = T/T_c \tag{4}$$

$$\beta = P/P_c \tag{5}$$

where ρ_c, T_c, and P_c are the molal density, temperature, and pressure at the critical point. Substituting equations (3) and (4) into equation (2), we have

$$Z = \frac{1}{1-b\rho_c\alpha} - \frac{a\rho_c\alpha}{RT_c\gamma} \tag{6}$$

Van der Waals postulated that at the critical point,

$$\left(\frac{\partial P}{\partial \rho}\right)_{T_{c.p.}} = 0 \tag{7}$$

$$\left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T_{c.p.}} = 0 \tag{8}$$

We have shown in our previous report (1) that in terms of the compressibility factor and in terms of reduced variables, equations (7) and (8) are equivalent to

$$\left(\frac{\partial Z}{\partial \alpha}\right)_{\gamma} (\alpha=1;\ \gamma=1) = -Z_c \tag{9}$$

and

$$\left(\frac{\partial^2 Z}{\partial \alpha^2}\right)_{\gamma} (\alpha=1;\ \gamma=1) = 2Z_c \tag{10}$$

Differentiating equation (6), we have

$$\left(\frac{\partial Z}{\partial \alpha}\right)_{\gamma} = \frac{b\rho_c}{(1-b\rho_c\alpha)^2} - \frac{a\rho_c}{RT_c\gamma} \tag{11}$$

$$\left(\frac{\partial^2 Z}{\partial \alpha^2}\right)_{\gamma} = \frac{2b^2\rho_c^2}{(1-b\rho_c\alpha)^3} \tag{12}$$

We then have at the critical point, where $\alpha=1$, $\gamma=1$

$$\frac{1}{1-b\rho_c} - \frac{a\rho_c}{RT_c} = Z_c \tag{13}$$

$$\left(\frac{\partial Z}{\partial \alpha}\right)_{\gamma} \begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = \frac{b\rho_c}{(1-b\rho_c)^2} - \frac{a\rho_c}{RT_c} = -Z_c \tag{14}$$

$$\left(\frac{\partial^2 Z}{\partial \alpha^2}\right)_{\gamma} \begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = \frac{2b^2\rho_c^2}{(1-b\rho_c)^3} = 2Z_c \tag{15}$$

Adding equations (13) and (14), we have

$$\frac{1}{(1-b\rho_c)^2} - \frac{2a\rho_c}{RT_c} = 0 \qquad (16)$$

Adding equation (14) twice to equation (15), we have

$$\frac{2b\rho_c}{(1-b\rho_c)^2} + \frac{2b^2\rho_c^2}{(1-b\rho_c)^3} - \frac{2a\rho_c}{RT_c} = 0 \qquad (17)$$

or

$$\frac{2b\rho_c}{(1-b\rho_c)^3} - \frac{2a\rho_c}{RT_c} = 0 \qquad (18)$$

Subtracting equations (16) and (18), we have

$$\frac{1}{(1-b\rho_c)^2} - \frac{2b\rho_c}{(1-b\rho_c)^3} = 0 \qquad (19)$$

or

$$1 - b\rho_c - 2b\rho_c = 0 \qquad (20)$$

and it follows

$$b\rho_c = \frac{1}{3} \qquad (21)$$

Substituting equation (21) into equation (16), we have

$$\frac{9}{4} - \frac{2a\rho_c}{RT_c} = 0 \qquad (22)$$

and it follows

$$\frac{a\rho_c}{RT_c} = \frac{9}{8} \qquad (23)$$

Substituting equations (21) and (23) into equation (13), we have

$$Z_c = \frac{3}{2} - \frac{9}{8} = \frac{3}{8} \qquad (24)$$

Substituting equations (21) and (23) into equation (6), we find

$$Z = \frac{3}{3-\alpha} - \frac{9\alpha}{8\gamma} \qquad (25)$$

Equation (25) is the equation of the compressibility factor for a van der Waals fluid, expressed in terms of reduced variables.

In our previous report (1) we show that the reduced pressure is given by

$$\beta = \frac{\alpha\gamma Z}{Z_c} \qquad (26)$$

Substituting equations (24) and (25) into equation (26), we have

$$\beta = \frac{8\alpha\gamma}{3-\alpha} - 3\alpha^2 \qquad (27)$$

Equation (27) is the expression for the reduced pressure of a van der Waals fluid, expressed in terms of reduced variables.

THE PRESSURE-TEMPERATURE COEFFICIENT AT CONSTANT DENSITY

Differentiating equation (27), we have

$$\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha} = \frac{8\alpha}{3-\alpha} \qquad (28)$$

At the critical point, we have

$$\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha}\begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = 4 \qquad (29)$$

THE PRESSURE-DENSITY COEFFICIENT AT CONSTANT TEMPERATURE

Differentiating equation (27), we have

$$\left(\frac{\partial\beta}{\partial\alpha}\right)_{\gamma} = \frac{8\gamma}{3-\alpha} + \frac{8\alpha\gamma}{(3-\alpha)^2} - 6\alpha \qquad (30)$$

or

$$\left(\frac{\partial\beta}{\partial\alpha}\right)_{\gamma} = \frac{24\gamma}{(3-\alpha)^2} - 6\alpha \qquad (31)$$

At the critical point, we have

$$\left(\frac{\partial\beta}{\partial\alpha}\right)_{\gamma}\begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = 0 \qquad (32)$$

THE DENSITY-TEMPERATURE COEFFICIENT AT CONSTANT PRESSURE

From mathematics, we have

$$\left(\frac{\partial\alpha}{\partial\gamma}\right)_{\beta} = -\frac{\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha}}{\left(\frac{\partial\beta}{\partial\alpha}\right)_{\gamma}} \qquad (33)$$

and substituting equations (28) and (31) into equation (33), we have

$$\left(\frac{\partial\alpha}{\partial\gamma}\right)_{\beta} = -\frac{8\alpha(3-\alpha)^2}{(3-\alpha)[24\gamma - 6\alpha(3-\alpha)^2]} \qquad (34)$$

or

$$\left(\frac{\partial\alpha}{\partial\gamma}\right)_\beta = -\frac{4\alpha(3-\alpha)}{3[4\gamma - \alpha(3-\alpha)^2]} \tag{35}$$

At the critical point, we have

$$\left(\frac{\partial\alpha}{\partial\gamma}\right)_\beta \binom{\alpha=1}{\gamma=1} = \pm\infty \tag{36}$$

THE COEFFICIENT OF COMPRESSIBILITY AT CONSTANT TEMPERATURE

$$-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial\rho}{\partial P}\right)_T = \frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial\beta}\right)_\gamma \frac{1}{P_c} \tag{37}$$

where V is the molal volume or

$$-\frac{P_c}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\alpha\left(\frac{\partial\beta}{\partial\alpha}\right)_\gamma} \tag{38}$$

Substituting equation (31) into equation (38), we have

$$-\frac{P_c}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{(3-\alpha)^2}{6\alpha[4\gamma - \alpha(3-\alpha)^2]} \tag{39}$$

At the critical point, we have

$$-\frac{P_c}{V}\left(\frac{\partial V}{\partial P}\right)_T \binom{\alpha=1}{\gamma=1} = \pm\infty \tag{40}$$

THE COEFFICIENT OF THERMAL EXPANSION AT CONSTANT PRESSURE

$$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\alpha}\left(\frac{\partial\alpha}{\partial\gamma}\right)_\beta \frac{1}{T_c} \tag{41}$$

or

$$\frac{T_c}{V}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{1}{\alpha}\left(\frac{\partial \alpha}{\partial \gamma}\right)_\beta \tag{42}$$

Substituting equation (35) into equation (42), we have

$$\frac{T_c}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{4(3-\alpha)}{3[4\gamma - \alpha(3-\alpha)^2]} \tag{43}$$

At the critical point, we have

$$\frac{T_c}{V}\left(\frac{\partial V}{\partial T}\right)_P \begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = \pm\infty \tag{44}$$

THE SECOND DERIVATIVE OF THE PRESSURE WITH REGARD TO THE TEMPERATURE AT CONSTANT DENSITY

Differentiating equation (28) with regard to the reduced temperature, we have

$$\left(\frac{\partial^2 \beta}{\partial \gamma^2}\right)_\alpha = 0 \text{ everywhere} \tag{45}$$

THE FUGACITY FUNCTION

In our previous report (1) we show that

$$\ln \frac{f}{P} = (Z-1) - \ln Z + \int_0^\alpha (Z-1)\,\frac{d\alpha}{\alpha} \tag{46}$$

From equation (25) we then have

$$Z-1 = \frac{\alpha}{3-\alpha} - \frac{9\alpha}{8\gamma} \tag{47}$$

Then

$$\int_0^{\alpha} (Z-1)\,\frac{d\alpha}{\alpha} = \int_0^{\alpha} \frac{d\alpha}{3-\alpha} - \frac{9}{8\gamma}\int_0^{\alpha} d\alpha \qquad (48)$$

$$\int_0^{\alpha} (Z-1)\,\frac{d\alpha}{\alpha} = -\ln\frac{3-\alpha}{3} - \frac{9\alpha}{8\gamma} \qquad (49)$$

Substituting equations (25), (47), and (49) into equation (46), we have

$$\ln\frac{f}{P} = \frac{\alpha}{3-\alpha} - \frac{9\alpha}{4\gamma} - \ln\left[1 - \frac{3\alpha(3-\alpha)}{8\gamma}\right] \qquad (50)$$

At the critical point, we have

$$\ln\frac{f_c}{P_c}\begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = \frac{1}{2} - \frac{9}{4} - \ln\left[1 - \frac{3}{4}\right] \qquad (51)$$

$$\ln\frac{f_c}{P_c}\begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = -\frac{7}{4} + \ln 4 = -0.363706 \qquad (52)$$

Taking the antilogarithm, we have

$$\frac{f_c}{P_c}\begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = 0.695096 \qquad (53)$$

THE RELATIVE INTERNAL ENERGY

In our previous report (1) we show that

$$\frac{E-E^{o}}{RT_c} = -\gamma^2 \int_0^{\alpha} \left(\frac{\partial Z}{\partial \gamma}\right)_{\alpha} \frac{d\alpha}{\alpha} \qquad (54)$$

where E is the internal energy at α and γ and E^o is the internal energy at zero density at the same temperature, γ.

From equation (25), we have

$$\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha = \frac{9\alpha}{8\gamma^2} \qquad (55)$$

Then

$$\int_0^\alpha \left(\frac{\partial Z}{\partial \gamma}\right)_\alpha \frac{d\alpha}{\alpha} = \frac{9\alpha}{8\gamma^2} \qquad (56)$$

and it follows

$$\frac{E-E^o}{RT_c} = -\frac{9\alpha}{8} \qquad (57)$$

At the critical point we have

$$\frac{E_c-E^o}{RT_c} = -\frac{9}{8} \qquad (58)$$

THE RELATIVE HEAT CAPACITY AT CONSTANT VOLUME

Differentiating equation (57), we have

$$\frac{1}{RT_c}\left[\left(\frac{\partial E}{\partial T}\right)_\alpha - \left(\frac{\partial E^o}{\partial T}\right)_\alpha\right] = \frac{C_V-C_V^o}{RT_c} = 0 \qquad (59)$$

so that

$$C_V - C_V^o = 0 \text{ everywhere} \qquad (60)$$

THE RELATIVE HEAT CONTENT OR ENTHALPY

As

$$H = E + PV \tag{61}$$

and

$$H^o = E^o + (PV)^o = E^o + RT \tag{62}$$

where H is the enthalpy at α and γ, and H^o is the enthalpy at zero density but at the same temperature γ.

Subtracting equation (62) from equation (61), we have

$$L = H-H^o = E-E^o + PV - RT \tag{63}$$

where L is the relative heat content or enthalpy. Then

$$\frac{L}{RT_c} = \frac{E-E^o}{RT_c} + \gamma(Z-1) \tag{64}$$

Substituting equation (47) and equation (57) into equation (64), we have

$$\frac{L}{RT_c} = -\frac{9\alpha}{8} + \frac{\alpha\gamma}{3-\alpha} - \frac{9\alpha}{8} \tag{65}$$

and then

$$\frac{L}{RT_c} = \frac{\alpha\gamma}{3-\alpha} - \frac{9\alpha}{4} \tag{66}$$

At the critical point we have

$$\frac{L_c}{RT_c} = \frac{1}{2} - \frac{9}{4} = -\frac{7}{4} \tag{67}$$

THE RELATIVE HEAT CAPACITY AT CONSTANT PRESSURE

In our previous report (1) we show that

$$\frac{C_p - C_p^o}{R} = \left(\frac{\partial \frac{L}{RT_c}}{\partial \gamma}\right)_\alpha + \left(\frac{\partial \frac{L}{RT_c}}{\partial \alpha}\right)_\gamma \left(\frac{\partial \alpha}{\partial \gamma}\right)_\beta \qquad (68)$$

where C_p is the heat capacity at constant pressure at α and γ and C_p^o is the heat capacity at constant pressure at zero density and at the same temperature, γ.

We have from equation (66)

$$\left(\frac{\partial \frac{L}{RT_c}}{\partial \gamma}\right)_\alpha = \frac{\alpha}{3-\alpha} \qquad (69)$$

Also

$$\left(\frac{\partial \frac{L}{RT_c}}{\partial \alpha}\right)_\gamma = \frac{\gamma}{3-\alpha} + \frac{\alpha\gamma}{(3-\alpha)^2} - \frac{9}{4} \qquad (70)$$

$$\left(\frac{\partial \frac{L}{RT_c}}{\partial \alpha}\right)_\gamma = \frac{3\gamma}{(3-\alpha)^2} - \frac{9}{4} \qquad (71)$$

or

$$\left(\frac{\partial \frac{L}{RT_c}}{\partial \alpha}\right)_\gamma = \frac{3[4\gamma - 3(3-\alpha)^2]}{4(3-\alpha)^2} \qquad (72)$$

Multiplying equations (35) and (72), we have

$$\left(\frac{\partial \frac{L}{RT_c}}{\partial\alpha}\right)_{\gamma} \left(\frac{\partial\alpha}{\partial\gamma}\right)_{\beta} = -\frac{[4\gamma - 3(3-\alpha)^2]\;\alpha(3-\alpha)}{(3-\alpha)^2 \cdot [4\gamma - \alpha(3-\alpha)^2]} \tag{73}$$

or

$$\left(\frac{\partial \frac{L}{RT_c}}{\partial\alpha}\right)_{\gamma} \left(\frac{\partial\alpha}{\partial\gamma}\right)_{\beta} = -\frac{\alpha[4\gamma - 3(3-\alpha)^2]}{(3-\alpha)[4\gamma - \alpha(3-\alpha)^2]} \tag{74}$$

Adding equations (69) and (74) and substituting in equation (68), we have

$$\frac{C_p - C_p^o}{R} = \frac{\alpha}{3-\alpha} - \frac{\alpha}{3-\alpha}\,\frac{[4\gamma - 3(3-\alpha)^2]}{[4\gamma - \alpha(3-\alpha)^2]} \tag{75}$$

or

$$\frac{C_p - C_p^o}{R} = \frac{\alpha}{(3-\alpha)}\,\frac{[4\gamma - \alpha(3-\alpha)^2 - 4\gamma + 3(3-\alpha)^2]}{[4\gamma - \alpha(3-\alpha)^2]} \tag{76}$$

Then finally,

$$\frac{C_p - C_p^o}{R} = \frac{\alpha(3-\alpha)^2}{4\gamma - \alpha(3-\alpha)^2} \tag{77}$$

At the critical point we have

$$\frac{C_p - C_p^o}{R}\begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = \pm\,\infty \tag{78}$$

THE RELATIVE ENTROPY

In our previous report (1) we show that

$$S-S^{o} = \frac{L}{T} - R \ln f \tag{79}$$

where S is the entropy at α and γ, and S^{o} is the entropy of the hypothetical gas in the ideal state at a pressure of one atmosphere. We call the quantity $S-S^{o}$ the relative entropy. Then from equation (79), we have

$$\frac{S-S^{o}}{R} = \frac{L}{RT} - \ln \frac{f}{P} - \ln P \tag{80}$$

or

$$\frac{S-S^{o} + R \ln P_c}{R} = \frac{L}{RT_c\gamma} - \ln \frac{f}{P} - \ln \beta \tag{81}$$

Substituting equation (27), equation (50), and equation (66) into equation (81), we have

$$\frac{S-S^{o} + R \ln P_c}{R} = \ln\left[1 - \frac{3\alpha(3-\alpha)}{8\gamma}\right] - \ln \frac{\alpha}{3-\alpha}\left[8\gamma - 3\alpha(3-\alpha)\right] \tag{82}$$

Then

$$\frac{S-S^{o} + R \ln P_c}{R} = \ln \frac{(3-\alpha)}{8\alpha\gamma} \tag{83}$$

At the critical point, we have

$$\frac{S-S^{o} + R \ln P_c}{R}\begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = -\ln 4 = -1.38629 \tag{84}$$

THE REDUCED SECOND VIRIAL COEFFICIENT

In our previous report (1) we defined the reduced second virial coefficient as

$$B_r = \left(\frac{\partial Z}{\partial \alpha}\right)_\gamma (\alpha=0) \tag{85}$$

From equation (25), we have

$$\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma = \frac{3}{(3-\alpha)^2} - \frac{9}{8\gamma} \tag{86}$$

Then

$$\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma (\alpha=0) = B_r = \frac{1}{3} - \frac{9}{8\gamma} \tag{87}$$

For the critical isotherm, we have

$$B_r(\gamma=1) = \frac{1}{3} - \frac{9}{8} = -\frac{19}{24} = -0.79167 \tag{88}$$

THE BOYLE TEMPERATURE

If we define the reduced Boyle temperature, γ_{Boyle}, as the temperature where the second virial coefficient is zero, we have

$$\frac{1}{3} - \frac{9}{8\gamma_{Boyle}} = 0 \tag{89}$$

or

$$\gamma_{Boyle} = \frac{27}{8} = 3\,\frac{3}{8} = 3.375 \tag{90}$$

THE REDUCED THIRD VIRIAL COEFFICIENT

In our previous report(1) we defined the reduced third virial coefficient as

$$C_r = \left(\frac{\partial^2 Z}{\partial \alpha^2}\right)_\gamma (\alpha=0) \tag{91}$$

From equation (86), we have

$$\left(\frac{\partial^2 Z}{\partial \alpha^2}\right)_\gamma = \frac{6}{(3-\alpha)^3} \tag{92}$$

and thus

$$C_r = \frac{2}{9} \tag{93}$$

For a van der Waals fluid all virial coefficients higher than the second are independent of temperature.

THE SECOND DERIVATIVE OF THE CHEMICAL POTENTIAL OR GIBBS FREE ENERGY WITH REGARD TO THE TEMPERATURE AT CONSTANT DENSITY

In our previous report (1) we show that

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_\rho = -\frac{C_V}{T} + \frac{1}{\rho}\left(\frac{\partial^2 P}{\partial T^2}\right)_\rho \tag{94}$$

which in reduced variables can be expressed as

$$\frac{-T\left(\frac{\partial^2 G}{\partial T^2}\right)_\rho - C_V}{R} = -Z_c \frac{\gamma}{\alpha}\left(\frac{\partial^2 \beta}{\partial \gamma^2}\right)_\alpha \tag{95}$$

From equation (45) we have $\left(\frac{\partial^2 \beta}{\partial \gamma^2}\right)_\alpha = 0$ and from equation (60), we have $C_V = C_V^o$. Therefore

$$\frac{-T\left(\frac{\partial^2 G}{\partial T^2}\right)_\rho - C_V^o}{R} = 0 \text{ everywhere} \tag{96}$$

THE DIFFERENCE BETWEEN THE HEAT CAPACITIES AT CONSTANT PRESSURE AND AT CONSTANT VOLUME

In our previous report (1) we show that

$$\frac{C_p - C_V}{R} = \frac{\left[Z + \gamma\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha\right]^2}{\left[Z + \alpha\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma\right]} \tag{97}$$

which may be written

$$\frac{C_p - C_V}{R} = \frac{\left[\frac{\partial(\gamma Z)}{\partial \gamma}\right]_\alpha^2}{\left(\frac{\partial \alpha Z}{\partial \alpha}\right)_\gamma} \tag{98}$$

From equation (25) we have

$$\gamma Z = \frac{3\gamma}{3-\alpha} - \frac{9\alpha}{8} \tag{99}$$

Then

$$\left[\frac{\partial(\gamma Z)}{\partial \gamma}\right]_\alpha = \frac{3}{3-\alpha} \tag{100}$$

and

$$\left[\frac{\partial(\gamma Z)}{\partial \gamma}\right]_\alpha^2 = \frac{9}{(3-\alpha)^2} \tag{101}$$

Also from equation (25) we have

$$\alpha Z = \frac{3\alpha}{3-\alpha} - \frac{9\alpha^2}{8\gamma} \tag{102}$$

So that

$$\left[\frac{\partial(\alpha Z)}{\partial\alpha}\right]_\gamma = \frac{9}{(3-\alpha)^2} - \frac{9\alpha}{4\gamma} \tag{103}$$

and it follows

$$\left[\frac{\partial(\alpha Z)}{\partial\alpha}\right]_\gamma = \frac{9[4\gamma - \alpha(3-\alpha)^2]}{4\gamma(3-\alpha)^2} \tag{104}$$

Substituting equations (101) and (104) into equation (98), we have

$$\frac{C_p - C_V}{R} = \frac{4\gamma}{4\gamma - \alpha(3-\alpha)^2} \tag{105}$$

At the critical point we have

$$\frac{C_p - C_V}{R}\begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = \pm\,\infty \tag{106}$$

THE RATIO OF THE HEAT CAPACITIES AT CONSTANT PRESSURE TO THAT AT CONSTANT VOLUME

Multiplying equation (105) by $\frac{R}{C_V}$, we have

$$\frac{C_p}{C_V} - 1 = \frac{4R\gamma}{C_V[4\gamma - \alpha(3-\alpha)^2]} \tag{107}$$

and thus

$$\frac{C_p}{C_V} = 1 + \frac{4R\gamma}{C_V[4\gamma - \alpha(3-\alpha)^2]} \tag{108}$$

and since $C_V = C_V^o$, we have

$$\frac{C_p}{C_V} = 1 + \frac{R}{C_V^o} \frac{4\gamma}{[4\gamma - \alpha(3-\alpha)^2]} \tag{109}$$

At the critical point we have

$$\frac{C_p}{C_V}\begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = \pm \infty \tag{110}$$

THE VELOCITY OF SOUND

In our previous report (1) we show that

$$Ma^2 = \frac{C_p}{C_V}\left(\frac{\partial P}{\partial \rho}\right)_T \tag{111}$$

where M is the molecular weight of the gas and a is the velocity of sound. In reduced variables equation (111) can be written

$$\frac{Ma^2}{RT_c} = \frac{C_p}{C_V} Z_c\left(\frac{\partial \beta}{\partial \alpha}\right)_\gamma \tag{112}$$

Substituting equation (24), equation (31), and equation (109) into equation (112), we have

$$\frac{Ma^2}{RT_c} = \frac{9[4\gamma - \alpha(3-\alpha)^2]}{4(3-\alpha)^2} + \frac{R}{C_V^o} \frac{9\gamma}{(3-\alpha)^2} \tag{113}$$

From equation (105), we have at $\alpha = 0$

$$\frac{C_p^o - C_V^o}{R} = 1 \tag{114}$$

or

$$R = C_p^o - C_V^o \tag{115}$$

Substituting equation (115) into equation (113), we have

$$\frac{Ma^2}{RT_c} = \frac{C_p^o}{C_V^o}\,\frac{9\gamma}{(3-\alpha)^2} - \frac{9\alpha}{4} \tag{116}$$

At the critical point we have

$$\frac{Ma^2}{RT_c}\begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = \frac{9}{4}\left(\frac{C_p^o}{C_V^o} - 1\right) \tag{117}$$

$$\frac{Ma^2}{RT_c}\begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = \frac{9}{4}\,\frac{R}{C_V^o} \tag{118}$$

THE TEMPERATURE-PRESSURE COEFFICIENT AT CONSTANT ENTHALPY OR THE JOULE-THOMSON COEFFICIENT

In our previous report (1) we show that the Joule-Thomson coefficient

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H \tag{119}$$

can be written

$$\frac{\mu P_c}{T_c} = \left(\frac{\partial \gamma}{\partial \beta}\right)_H = \frac{\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma - \frac{\gamma}{\alpha}\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha}{\left[\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma - \frac{\gamma}{\alpha}\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha\right]\left(\frac{\partial \beta}{\partial \gamma}\right)_\alpha - \frac{1}{\gamma}\left[\frac{C_V}{R} + Z + \gamma\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha\right]\left(\frac{\partial \beta}{\partial \alpha}\right)_\gamma} \tag{120}$$

From equation (25) we have

$$\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha = \frac{9\alpha}{8\gamma^2} \tag{121}$$

so that

$$-\frac{\gamma}{\alpha}\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha = -\frac{9}{8\gamma} \tag{122}$$

Adding equations (86) and (122), we have

$$\left(\frac{\partial Z}{\partial \alpha}\right)_{\gamma} - \frac{\gamma}{\alpha}\left(\frac{\partial Z}{\partial \gamma}\right)_{\alpha} = \frac{3}{(3-\alpha)^2} - \frac{9}{4\gamma} \tag{123}$$

or

$$\left(\frac{\partial Z}{\partial \alpha}\right)_{\gamma} - \frac{\gamma}{\alpha}\left(\frac{\partial Z}{\partial \gamma}\right)_{\alpha} = \frac{3[4\gamma - 3(3-\alpha)^2]}{4\gamma(3-\alpha)^2} \tag{124}$$

From equation (100) we have

$$\left[\frac{\partial(\gamma Z)}{\partial \gamma}\right]_{\alpha} = Z + \gamma\left(\frac{\partial Z}{\partial \gamma}\right)_{\alpha} = \frac{3}{3-\alpha} \tag{125}$$

So that

$$\frac{C_V}{R} + Z + \gamma\left(\frac{\partial Z}{\partial \gamma}\right)_{\alpha} = \frac{C_V^o}{R} + \frac{3}{3-\alpha} \tag{126}$$

From equation (28) we have

$$\left(\frac{\partial \beta}{\partial \gamma}\right)_{\alpha} = \frac{8\alpha}{3-\alpha} \tag{28}$$

and from equation (31) we have

$$\left(\frac{\partial \beta}{\partial \alpha}\right)_{\gamma} = \frac{6[4\gamma - \alpha(3-\alpha)^2]}{(3-\alpha)^2} \tag{127}$$

Substituting equations (28), (124), (126), and (127) into equation (120), we have

$$\frac{\mu P_c}{T_c} = \frac{3[4\gamma - 3(3-\alpha)^2]}{4\gamma(3-\alpha)^2\left[\frac{3[4\gamma - 3(3-\alpha)^2]}{4\gamma(3-\alpha)^2}\,\frac{8\alpha}{(3-\alpha)} - \frac{1}{\gamma}\left[\frac{C_V^o}{R} + \frac{3}{3-\alpha}\right]\frac{6[4\gamma - \alpha(3-\alpha)^2]}{(3-\alpha)^2}\right]} \tag{128}$$

or

$$\frac{\mu P_c}{T_c} = \frac{[4\gamma - 3(3-\alpha)^2](3-\alpha)}{8\alpha[4\gamma - 3(3-\alpha)^2] - 8\left[\frac{C_V^o(3-\alpha)}{R} + 3\right][4\gamma - \alpha(3-\alpha)^2]} \qquad (129)$$

At the critical point we have

$$\frac{\mu P_c}{T_c}\begin{pmatrix}\alpha=1\\ \gamma=1\end{pmatrix} = \frac{1}{4} = 0.25 \qquad (130)$$

THE JOULE-THOMSON INVERSION CURVE

From equation (129) we see that $\mu = 0$ when

$$4\gamma = 3(3-\alpha)^2 \qquad (131)$$

or

$$\gamma = \frac{3}{4}(3-\alpha)^2 \qquad (132)$$

Substituting equation (132) into equation (27), we have

$$\beta = \frac{8\alpha \cdot 3}{(3-\alpha) \cdot 4}(3-\alpha)^2 - 3\alpha^2 \qquad (133)$$

$$\beta = 6\alpha(3-\alpha) - 3\alpha^2 \qquad (134)$$

$$\beta = 3\alpha(6 - 2\alpha - \alpha) = 3\alpha(6-3\alpha) \qquad (135)$$

$$\beta = 9\alpha(2-\alpha) \qquad (136)$$

Equations (132) and (136) determine the β-γ Joule-Thomson inversion curve. From equation (136) we have

$$\left(\frac{\partial \beta}{\partial \alpha}\right)_{\mu=0} = 9(2-\alpha) - 9\alpha = 18-18\alpha \qquad (137)$$

$$\left(\frac{\partial \beta}{\partial \alpha}\right)_{\mu=0} = 18(1-\alpha) \qquad (138)$$

From equation (132) we have

$$\left(\frac{\partial \gamma}{\partial \alpha}\right)_{\mu=0} = \frac{3}{2}(3-\alpha) \qquad (139)$$

Dividing equation (138) by (139) we have

$$\left(\frac{\partial \beta}{\partial \gamma}\right)_{\mu=0} = \frac{12(1-\alpha)}{3-\alpha} \qquad (140)$$

$$\text{and } \left(\frac{\partial \beta}{\partial \gamma}\right)_{\mu=0} = 0, \text{ when } \alpha = 1 \qquad (141)$$

The β-γ inversion curve therefore has a maximum when $\alpha = 1$, where

$$\gamma = 3 \quad \text{and} \quad \beta = 9 \qquad (142)$$

THE PRESSURE-TEMPERATURE COEFFICIENT AT CONSTANT ENTROPY

In our previous report (1) we show that

$$\frac{T_c}{P_c}\left(\frac{\partial P}{\partial T}\right)_S = \left(\frac{\partial \beta}{\partial \gamma}\right)_S = -\frac{\alpha^2}{Z_c}\left[\left(\frac{\partial Z}{\partial \alpha}\right)_\gamma - \frac{\gamma}{\alpha}\left(\frac{\partial Z}{\partial \gamma}\right)_\alpha\right] + \frac{\alpha^2\left[\frac{C_V}{R} + \frac{Z_c}{\alpha}\left(\frac{\partial \beta}{\partial \gamma}\right)_\alpha\right]\left(\frac{\partial \beta}{\partial \alpha}\right)_\gamma}{Z_c\gamma\left(\frac{\partial \beta}{\partial \gamma}\right)_\alpha} \qquad (143)$$

Substituting equations (24), (28), (124), and (127) into equation (143), we have

$$\left(\frac{\partial \beta}{\partial \gamma}\right)_S = -2\alpha^2 \cdot \frac{[4\gamma - 3(3-\alpha)^2]}{\gamma(3-\alpha)^2} + \frac{\alpha\left[\frac{C_V}{R} + \frac{3}{(3-\alpha)}\right]2[4\gamma - \alpha(3-\alpha)^2]}{\frac{\gamma(3-\alpha)^2}{(3-\alpha)}} \qquad (144)$$

$$\left(\frac{\partial\beta}{\partial\gamma}\right)_S = \frac{-2\alpha}{\gamma(3-\alpha)^2}\left[\alpha[4\gamma - 3(3-\alpha)^2] - \left[\frac{C_V}{R}(3-\alpha) + 3\right][4\gamma - \alpha(3-\alpha)^2]\right] \tag{145}$$

At the critical point we have

$$\left(\frac{\partial\beta}{\partial\gamma}\right)_S = -\frac{2}{4}[-8] = 4 \tag{146}$$

EQUATIONS FOR TWO-PHASE EQUILIBRIUM

All of the equations derived so far apply to any single phase. We now derive formulas that are applicable only when a liquid phase and a vapor phase are present in thermodynamic equilibrium.

We let α_1 be the reduced density of the saturated vapor and α_3 be the reduced density of saturated liquid.

From equation (27) we have

$$\beta_1 = \frac{8\alpha_1\gamma_1}{3-\alpha_1} - 3\alpha_1^2 \tag{147}$$

and

$$\beta_3 = \frac{8\alpha_3\gamma_3}{3-\alpha_3} - 3\alpha_3^2 \tag{148}$$

Chemical equilibrium requires

$$\beta_1 = \beta_3 = \beta \tag{149}$$

and

$$\gamma_1 = \gamma_3 = \gamma \tag{150}$$

Equating equations (147) and (148) and substituting equations (149) and (150), we have

$$\frac{8\alpha_1\gamma}{3-\alpha_1} - 3\alpha_1^2 = \frac{8\alpha_3\gamma}{3-\alpha_3} - 3\alpha_3^2 \tag{151}$$

or

$$8\gamma\left[\frac{\alpha_1}{3-\alpha_1} - \frac{\alpha_3}{3-\alpha_3}\right] = 3(\alpha_1^2 - \alpha_3^2) \tag{152}$$

$$\frac{8\gamma(3\alpha_1 - 3\alpha_3)}{(3-\alpha_1)(3-\alpha_3)} = 3(\alpha_1 + \alpha_3)(\alpha_1 - \alpha_3) \tag{153}$$

or

$$8\gamma = (3-\alpha_1)(3-\alpha_3)(\alpha_1 + \alpha_3) \tag{154}$$

Then

$$\gamma = \frac{(3-\alpha_1)(3-\alpha_3)(\alpha_1 + \alpha_3)}{8} \tag{155}$$

Substituting equations (149), (150), and (154) into equation (147), we have

$$\beta = \alpha_1(3-\alpha_3)(\alpha_1 + \alpha_3) - 3\alpha_1^2 \tag{156}$$

$$\beta = \alpha_1(3\alpha_3 - \alpha_1\alpha_3 - \alpha_3^2) \tag{157}$$

$$\beta = \alpha_1\alpha_3(3-\alpha_1-\alpha_3) \tag{158}$$

Equations (155) and (158) enable the temperature and pressure to be calculated, once the densities of the coexisting phases are known.

EQUALITY OF THE CHEMICAL POTENTIAL OR GIBBS FREE ENERGY

In our previous report (1) we show that the equality of the chemical potential or Gibbs free energy in the coexisting phases requires

$$Z_1 - Z_3 = \int_{\alpha_1}^{\alpha_3} Z \frac{d\alpha}{\alpha} \tag{159}$$

where the integral on the right is to be evaluated at constant temperature.

From equation (25) we have

$$\int_{\alpha_1}^{\alpha_3} Z \frac{d\alpha}{\alpha} = 3\int_{\alpha_1}^{\alpha_3} \frac{d\alpha}{\alpha(3-\alpha)} - \frac{9}{8\gamma}\int_{\alpha_1}^{\alpha_3} d\alpha \tag{160}$$

Then

$$\int_{\alpha_1}^{\alpha_3} Z \frac{d\alpha}{\alpha} = \ln \frac{\alpha_3(3-\alpha_1)}{\alpha_1(3-\alpha_3)} - \frac{9(\alpha_3 - \alpha_1)}{8\gamma} \tag{161}$$

Also from equation (25) we have

$$Z_1 = \frac{3}{3-\alpha_1} - \frac{9\alpha_1}{8\gamma} \tag{162}$$

and

$$Z_3 = \frac{3}{3-\alpha_3} - \frac{9\alpha_3}{8\gamma} \tag{163}$$

So that

$$Z_1 - Z_3 = \frac{3(\alpha_1 - \alpha_3)}{(3-\alpha_1)(3-\alpha_3)} + \frac{9(\alpha_3 - \alpha_1)}{8\gamma} \tag{164}$$

$$z_1 - z_3 = \frac{-3(\alpha_3 - \alpha_1)}{(3-\alpha_1)(3-\alpha_3)} + \frac{9(\alpha_3 - \alpha_1)}{8\gamma} \tag{165}$$

Equating equations (161) and (165) we have

$$\frac{-3(\alpha_3 - \alpha_1)}{(3-\alpha_1)(3-\alpha_3)} + \frac{9(\alpha_3 - \alpha_1)}{8\gamma} = \ln \frac{\alpha_3(3-\alpha_1)}{\alpha_1(3-\alpha_3)} - \frac{9(\alpha_3 - \alpha_1)}{8\gamma} \tag{166}$$

or

$$\frac{-3(\alpha_3 - \alpha_1)}{(3-\alpha_1)(3-\alpha_3)} + \frac{18(\alpha_3 - \alpha_1)}{8\gamma} = \ln \frac{\alpha_3(3-\alpha_1)}{\alpha_1(3-\alpha_3)} \tag{167}$$

Substituting for 8γ from equation (154), we have

$$\frac{-3(\alpha_3 - \alpha_1)}{(3-\alpha_1)(3-\alpha_3)} + \frac{18(\alpha_3 - \alpha_1)}{(3-\alpha_1)(3-\alpha_3)(\alpha_1 + \alpha_3)} = \ln \frac{\alpha_3(3-\alpha_1)}{\alpha_1(3-\alpha_3)} \tag{168}$$

Then

$$\frac{3(\alpha_3 - \alpha_1)}{(3-\alpha_1)(3-\alpha_3)} \left[-1 + \frac{6}{\alpha_1 + \alpha_3}\right] = \ln \frac{\alpha_3(3-\alpha_1)}{\alpha_1(3-\alpha_3)} \tag{169}$$

and finally

$$\frac{3(\alpha_3 - \alpha_1)(6-\alpha_1-\alpha_3)}{(3-\alpha_1)(3-\alpha_3)(\alpha_1 + \alpha_3)} = \ln \frac{\alpha_3(3-\alpha_1)}{\alpha_1(3-\alpha_3)} \tag{170}$$

Equation (170) is the functional relationship between α_1 and α_3 when liquid and vapor coexist in equilibrium for a van der Waals gas. These equations are to be used as follows. A value of α_1 is assumed and then equation (170) is solved for α_3. These values of α_1 and α_3 are then substituted in equations (155) and (158) and values of γ and β calculated.

THE METHOD OF NUMERICAL CALCULATION OF THE REDUCED DENSITIES OF THE COEXISTING PHASES

In this section we give the details of the method used to solve equation (170). We used the Newton-Raphson method (6) in the following way. We form the function

$$Y = \ln \frac{\alpha_3(3-\alpha_1)}{\alpha_1(3-\alpha_3)} - \frac{3(\alpha_3 - \alpha_1)(6-\alpha_1-\alpha_3)}{(3-\alpha_1)(3-\alpha_3)(\alpha_1 + \alpha_3)} \tag{171}$$

We pick a value of α_1 and the problem then is to find the value of α_3 that reduces Y to zero. We assume a value of α_3 and then we calculate the value of Y. We then calculate $\left(\frac{\partial Y}{\partial \alpha_3}\right)_{\alpha_1}$ for the assumed values of α_1 and α_3. The correction, $\Delta\alpha_3$, to be added to our α_3 is then given by

$$\Delta\alpha_3 = - \frac{Y}{\left(\frac{\partial Y}{\partial \alpha_3}\right)_{\alpha_1}} \tag{172}$$

Then starting with $(\alpha_3 + \Delta\alpha_3)$, the iteration is repeated until Y = 0 to within some predescribed small quantity.

Differentiating Y, we have

$$\left(\frac{\partial Y}{\partial \alpha_3}\right)_{\alpha_1} = \left[\begin{array}{l} \frac{1}{\alpha_3} + \frac{1}{3-\alpha_3} - \frac{3(6-2\alpha_3)}{(3-\alpha_1)(3-\alpha_3)(\alpha_1 + \alpha_3)} \\ \\ + \frac{3(\alpha_3 - \alpha_1)(6-\alpha_1-\alpha_3)(3-\alpha_3-\alpha_1-\alpha_3)}{(3-\alpha_1)(3-\alpha_3)^2(\alpha_1 + \alpha_3)^2} \end{array}\right]$$

$$\left(\frac{\partial Y}{\partial \alpha_3}\right)_{\alpha_1} = \left[\frac{3}{\alpha_3(3-\alpha_3)} - \frac{6(3-\alpha_3)}{(3-\alpha_1)(3-\alpha_3)(\alpha_1 + \alpha_3)} + \frac{3(\alpha_3 - \alpha_1)(6-\alpha_1-\alpha_3)(3-\alpha_1-2\alpha_3)}{(3-\alpha_1)(3-\alpha_3)^2(\alpha_1 + \alpha_3)^2}\right]$$

$$= \left[\frac{3}{\alpha_3(3-\alpha_3)(3-\alpha_1)(\alpha_1 + \alpha_3)}\begin{bmatrix}(3-\alpha_1)(\alpha_1 + \alpha_3) \\ - 2\alpha_3(3-\alpha_3)\end{bmatrix} + \frac{3(\alpha_3 - \alpha_1)(6-\alpha_1-\alpha_3)(3-\alpha_1-2\alpha_3)}{(3-\alpha_1)(3-\alpha_3)^2(\alpha_1 + \alpha_3)^2}\right]$$

$$= \left[\frac{3}{\alpha_3(3-\alpha_1)(3-\alpha_3)(\alpha_1 + \alpha_3)}\begin{bmatrix}3\alpha_1 + 3\alpha_3 \\ - \alpha_1^2 - \alpha_1\alpha_3 \\ - 6\alpha_3 + 2\alpha_3^2\end{bmatrix} + \frac{3(\alpha_3 - \alpha_1)(6-\alpha_1-\alpha_3)(3-\alpha_1-2\alpha_3)}{(3-\alpha_1)(3-\alpha_3)^2(\alpha_1 + \alpha_3)^2}\right]$$

$$\left(\frac{\partial Y}{\partial \alpha_3}\right)_{\alpha_1} = \left[\frac{3\left[-3(\alpha_3 - \alpha_1) + (\alpha_3 - \alpha_1)(2\alpha_3 + \alpha_1)\right]}{\alpha_3(3-\alpha_1)(3-\alpha_3)(\alpha_1 + \alpha_3)} + \frac{3(\alpha_3 - \alpha_1)(6-\alpha_1-\alpha_3)(3-\alpha_1-2\alpha_3)}{(3-\alpha_1)(3-\alpha_3)^2(\alpha_1+\alpha_3)^2}\right]$$

$$= \left[\frac{-3(\alpha_3 - \alpha_1)(3-\alpha_1-2\alpha_3)}{\alpha_3(3-\alpha_1)(3-\alpha_3)(\alpha_1 + \alpha_3)} + \frac{3(\alpha_3 - \alpha_1)(3-\alpha_1-2\alpha_3)(6-\alpha_1-\alpha_3)}{(3-\alpha_1)(3-\alpha_3)^2(\alpha_1+\alpha_3)^2}\right]$$

$$= \frac{3(\alpha_3 - \alpha_1)(3-\alpha_1-2\alpha_3)}{(3-\alpha_1)(3-\alpha_3)(\alpha_1 + \alpha_3)}\left[\frac{6-\alpha_1-\alpha_3}{(3-\alpha_3)(\alpha_1 + \alpha_3)} - \frac{1}{\alpha_3}\right]$$

$$= \frac{3(\alpha_3 - \alpha_1)(3-\alpha_1-2\alpha_3)(6\alpha_3 - 3\alpha_1 - 3\alpha_3)}{\alpha_3(3-\alpha_1)(3-\alpha_3)^2(\alpha_1 + \alpha_3)^2}$$

$$= \frac{3(\alpha_3 - \alpha_1)(3-\alpha_1-2\alpha_3)\left[3(\alpha_3 - \alpha_1)\right]}{\alpha_3(3-\alpha_1)(3-\alpha_3)^2(\alpha_1 + \alpha_3)^2}$$

$$\left(\frac{\partial Y}{\partial \alpha_3}\right)_{\alpha_1} = \frac{9(\alpha_3 - \alpha_1)^2(3-\alpha_1-2\alpha_3)}{\alpha_3(3-\alpha_1)(3-\alpha_3)^2(\alpha_1 + \alpha_3)^2} \qquad (173)$$

Equations (171), (172), and (173) were used in an iteration procedure to calculate α_3 for values of α_1 from $\alpha_1 = 0.00005$ to $\alpha_1 = 0.999$.

Above $\alpha_1 = 0.05$, it was assumed as a first approximation that $\alpha_3 = 2-\alpha_1$, while below $\alpha_1 = 0.05$, it was assumed as a first approximation that $\alpha_3 = 2.99 - \alpha_1$.

THE METHOD OF NUMERICAL CALCULATION NEAR THE CRITICAL POINT AND THE FUNCTIONAL RELATIONSHIP OF COEXISTING PHASES NEAR THE CRITICAL POINT

When the method of the previous section was applied to $\alpha_1 = 0.9999$, the method failed because of the limit of the number of significant figures that could be carried in the computer. As a result of this, the method of this section was derived. The method of this section is applicable for values of α_1 near the critical value of 1.

We start by making the following substitution in equation (170).

$$\alpha_3 - \alpha_1 = t \tag{174}$$

and

$$1-\alpha_1 = \delta \tag{175}$$

Substituting equations (174) and (175) into equation (170), we find

$$\frac{3t(4 - t + 2\delta)}{(2 + \delta)(2 - t + \delta)(2 + t - 2\delta)} = \ln \frac{(2 + \delta)(1 + t - \delta)}{(1 - \delta)(2 - t + \delta)} \tag{176}$$

Now

$$\ln \frac{(2 + \delta)(1 + t - \delta)}{(1 - \delta)(2 - t + \delta)} = \ln \left[1 + \frac{3t}{(1 - \delta)(2 - t + \delta)}\right] \tag{177}$$

We now make the substitution

$$v = \frac{3t}{(1 - \delta)(2 - t + \delta)} \tag{178}$$

so that

$$\ln \frac{(2 + \delta)(1 + t - \delta)}{(1 - \delta)(2 - t + \delta)} = \ln(1 + v) \qquad (179)$$

Now as the critical point is approached, t and therefore v approach zero. Therefore, for values of v less than 1, we may expand the logarithm into the power series

$$\ln(1 + v) = v - \frac{1}{2} v^2 + \frac{1}{3} v^3 - \frac{1}{4} v^4 + \ldots \qquad (180)$$

Substituting into equation (176) we have

$$\frac{3t(4 - t + 2\delta)}{(2 + \delta)(2 - t + \delta)(2 + t - 2\delta)} = v - \frac{1}{2} v^2 + \frac{1}{3} v^3 - \frac{1}{4} v^4 + \ldots \qquad (181)$$

From the definition of v, equation (178), we have

$$3t = (1 - \delta)(2 - t + \delta)v \qquad (182)$$

and substituting this value in equation (181), we have

$$\frac{(1 - \delta)(4 - t + 2\delta)v}{(2 + \delta)(2 + t - 2\delta)} = v - \frac{1}{2} v^2 + \frac{1}{3} v^3 - \frac{1}{4} v^4 + \ldots \qquad (183)$$

Cancelling v we have

$$\frac{(1 - \delta)(4 - t + 2\delta)}{(2 + \delta)(2 + t - 2\delta)} = 1 - \frac{1}{2} v + \frac{1}{3} v^2 - \frac{1}{4} v^3 + \frac{1}{5} v^4 - \ldots \qquad (184)$$

or

$$\frac{(1 - \delta)(4 - t + 2\delta) - (2 + \delta)(2 + t - 2\delta)}{(2 + \delta)(2 + t - 2\delta)} = - \frac{1}{2} v + \frac{1}{3} v^2 - \frac{1}{4} v^3 + \frac{1}{5} v^4 - \ldots \qquad (185)$$

Then

$$\frac{-t - 2t}{(2 + \delta)(2 + t - 2\delta)} = -\frac{1}{2}v + \frac{1}{3}v^2 - \frac{1}{4}v^3 + \ldots \qquad (186)$$

Thus

$$\frac{-3t}{(2 + \delta)(2 + t - 2\delta)} = -\frac{1}{2}v + \frac{1}{3}v^2 - \frac{1}{4}v^3 + \ldots \qquad (187)$$

Substituting from equation (182) for 3t, we have

$$\frac{-(1 - \delta)(2 - t + \delta)v}{(2 + \delta)(2 + t - 2\delta)} = -\frac{1}{2}v + \frac{1}{3}v^2 - \frac{1}{4}v^3 + \ldots \qquad (188)$$

and cancelling v, we have

$$\frac{-(1 - \delta)(2 - t + \delta)}{(2 + \delta)(2 + t - 2\delta)} = -\frac{1}{2} + \frac{1}{3}v - \frac{1}{4}v^2 + \ldots \qquad (189)$$

or

$$\frac{-(1 - \delta)(2 - t + \delta)2 + (2 + \delta)(2 + t - 2\delta)}{2(2 + \delta)(2 + t - 2\delta)} = \frac{1}{3}v - \frac{1}{4}v^2 + \frac{1}{5}v^3 - \ldots \qquad (190)$$

and

$$\frac{4t - \delta t}{2(2 + \delta)(2 + t - 2\delta)} = \frac{1}{3}v - \frac{1}{4}v^2 + \frac{1}{5}v^3 - \ldots \qquad (191)$$

So that

$$\frac{t(4 - \delta)}{2(2 + \delta)(2 + t - 2\delta)} = \frac{1}{3}v - \frac{1}{4}v^2 + \frac{1}{5}v^3 - \ldots \qquad (192)$$

Substituting for t, from equation (182), we have

$$\frac{(1 - \delta)(2 - t + \delta)\,v\,(4 - \delta)}{6(2 + \delta)(2 + t - 2\delta)} = \frac{1}{3}v - \frac{1}{4}v^2 + \frac{1}{5}v^3 - \ldots \qquad (193)$$

Cancelling v we have

$$\frac{(1 - \delta)(2 - t + \delta)(4 - \delta)}{6(2 + \delta)(2 + t - 2\delta)} = \frac{1}{3} - \frac{1}{4} v + \frac{1}{5} v^2 - \frac{1}{6} v^3 + \ldots \qquad (194)$$

or

$$\frac{(4 - \delta)(1 - \delta)(2 - t + \delta) - 2(2 + \delta)(2 + t - 2\delta)}{6(2 + \delta)(2 + t - 2\delta)} = - \frac{1}{4} v + \frac{1}{5} v^2 - \frac{1}{6} v^3 + \ldots \qquad (195)$$

This last equation reduces to

$$\frac{-\delta(2 + \delta)(1 - \delta) - t(8 - 3\delta + \delta^2)}{6(2 + \delta)(2 + t - 2\delta)} = - \frac{1}{4} v + \frac{1}{5} v^2 - \frac{1}{6} v^3 + \ldots \qquad (196)$$

We may now solve this equation by the Newton-Raphson method in the following way. We form the function

$$W = \frac{\delta(2 + \delta)(1 - \delta) + t(8 - 3\delta + \delta^2)}{6(2 + \delta)(2 + t - 2\delta)} - \frac{1}{4} v + \frac{1}{5} v^2 - \frac{1}{6} v^3 + \ldots \qquad (197)$$

Then

$$\left(\frac{\partial W}{\partial t}\right)_\delta = \left[\begin{array}{l} \dfrac{8 - 3\delta + \delta^2}{6(2 + \delta)(2 + t - 2\delta)} - \dfrac{[\delta(2 + \delta)(1 - \delta) + t(8 - 3\delta + \delta^2)]}{6(2 + \delta)(2 + t - 2\delta)^2} \\ + \left[- \dfrac{1}{4} + \dfrac{2}{5} v - \dfrac{3}{6} v^2 + \ldots \right] \left(\dfrac{\partial v}{\partial t}\right)_\delta \end{array} \right] \qquad (198)$$

From equation (178)

$$\left(\frac{\partial v}{\partial t}\right)_\delta = \frac{3}{(1 - \delta)(2 - t + \delta)} + \frac{3t}{(1 - \delta)(2 - t + \delta)^2}$$

$$\left(\frac{\partial v}{\partial t}\right)_\delta = \frac{3(2 + \delta)}{(1 - \delta)(2 - t + \delta)^2} \qquad (199)$$

We now take as a first approximation

$$t_1 = 2\delta \tag{200}$$

Substituting this value of t in equation (197), we have

$$W_1 = \frac{\delta(2 + \delta)(1 - \delta) + 2\delta(8 - 3\delta + \delta^2)}{6(2 + \delta)(2 + 2\delta - 2\delta)} - \frac{1}{4} v_1 + \frac{1}{5} v_1^2 - \frac{1}{6} v_1^3 + \dots$$

$$W_1 = \frac{\delta(2 - \delta - \delta^2 + 16 - 6\delta + 2\delta^2)}{6(2 + \delta) \cdot 2} - \frac{1}{4} v_1 + \frac{1}{5} v_1^2 - \frac{1}{6} v_1^3 + \dots$$

$$W_1 = \frac{\delta(18 - 7\delta + \delta^2)}{12(2 + \delta)} - \frac{1}{4} v_1 + \frac{1}{5} v_1^2 - \frac{1}{6} v_1^3 + \dots \tag{201}$$

Substituting equation (200) into equation (178), we have

$$v_1 = \frac{6\delta}{(1 - \delta)(2 - 2\delta + \delta)}$$

$$v_1 = \frac{6\delta}{(1 - \delta)(2 - \delta)} \tag{202}$$

Substituting this value of v_1 in equation (201), we have

$$W_1 = \frac{\delta(18 - 7\delta + \delta^2)}{12(2 + \delta)} - \frac{6\delta}{4(1 - \delta)(2 - \delta)} + \frac{1}{5} v_1^2 - \frac{1}{6} v_1^3 + \dots$$

$$W_1 = \frac{\delta[(18 - 7\delta + \delta^2)(1 - \delta)(2 - \delta) - 18(2 + \delta)]}{12(2 + \delta)(1 - \delta)(2 - \delta)} + \frac{1}{5} v_1^2 - \frac{1}{6} v_1^3 + \dots$$

$$W_1 = \frac{\delta[\delta(-18 - 36 - 18 - 14) + \delta^2(2 + 18 + 14 + 7) + \delta^3(-2 - 1 - 7) + \delta^4]}{12(2 + \delta)(1 - \delta)(2 - \delta)}$$

$$+ \frac{1}{5} v_1^2 - \frac{1}{6} v_1^3 + \dots$$

$$W_1 = \frac{\delta^2(-86 + 41\delta - 10\delta^2 + \delta^3)}{12(2 + \delta)(1 - \delta)(2 - \delta)} + \frac{1}{5} v_1^2 - \frac{1}{6} v_1^3 + \dots \qquad (203)$$

Substituting for v_1 from equation (202), we have

$$W_1 = \frac{\delta^2(-86 + 41\delta - 10\delta^2 + \delta^3)}{12(2 + \delta)(1 - \delta)(2 - \delta)} + \frac{1}{5} \frac{36\delta^2}{(1 - \delta)^2(2 - \delta)^2} - \frac{1}{6} v_1^3 + \frac{1}{7} v_1^4 - \dots$$

$$W_1 = \frac{\delta^2[5(-86 + 41\delta - 10\delta^2 + \delta^3)(1 - \delta)(2 - \delta) + 36 \cdot 12(2 + \delta)]}{60(2 + \delta)(1 - \delta)^2(2 - \delta)^2}$$

$$- \frac{1}{6} v_1^3 + \frac{1}{7} v_1^4 - \dots \qquad (204)$$

Now for sufficiently small δ, we may neglect δ^3 with respect to δ^2, and we have

$$W_1 = \frac{\delta^2(-860 + 864)}{60 \times 2 \times 4} = \frac{\delta^2}{120} \qquad (205)$$

We now calculate $\left(\frac{\partial W}{\partial t}\right)_\delta$ for $t_1 = 2\delta$.

We substitute in equation (198) and find

$$\left(\frac{\partial W_1}{\partial t_1}\right)_\delta = \begin{aligned} &\frac{8 - 3\delta + \delta^2}{6(2 + \delta) \cdot 2} - \frac{[\delta(2 + \delta)(1 - \delta) + 2\delta(8 - 3\delta + \delta^2)]}{6(2 + \delta) \cdot 4} \\ &+ \left[- \frac{1}{4} + \frac{2}{5} v_1 - \frac{3}{6} v_1^2 + \dots\right]\left(\frac{\partial v_1}{\partial t_1}\right)_\delta \end{aligned} \qquad (206)$$

From equation (199) with $t_1 = 2\delta$, we have

$$\left(\frac{\partial v_1}{\partial t_1}\right)_\delta = \frac{3(2 + \delta)}{(1 - \delta)(2 - \delta)^2} \qquad (207)$$

Substituting equation (207) into (206), we have

$$\left(\frac{\partial W_1}{\partial t_1}\right)_\delta = \frac{8 - 3\delta + \delta^2}{12(2 + \delta)} - \frac{\delta[2 - \delta - \delta^2 + 16 - 6\delta + 2\delta^2]}{24(2 + \delta)} - \frac{3(2 + \delta)}{4(1 - \delta)(2 - \delta)^2} + \left(\frac{2}{5} v_1 - \frac{3}{6} v_1^2\right)\left(\frac{\partial v_1}{\partial t_1}\right)_\delta \qquad (208)$$

Then for sufficiently small δ, we may write

$$\left(\frac{\partial W_1}{\partial t_1}\right)_\delta = \frac{8}{24} - \frac{6}{16} = \frac{1}{3} - \frac{3}{8} = \frac{8 - 9}{24} = -\frac{1}{24} \qquad (209)$$

We then have as the correction Δt_1 to our first approximation

$$\Delta t_1 = -\frac{W_1}{\left(\frac{\partial W_1}{\partial t_1}\right)_\delta} = \frac{\delta^2 \times 24}{120} \qquad (210)$$

$$\Delta t_1 = \frac{1}{5} \delta^2 \qquad (211)$$

We may then take as our second approximation

$$t_2 = t_1 + \Delta t_1 = 2\delta + \frac{1}{5} \delta^2 \qquad (212)$$

Substituting this value of t in equation (197), we have

$$W_2 = \frac{\delta(2 + \delta)(1 - \delta) + 2\delta(1 + \frac{1}{10} \delta)(8 - 3\delta + \delta^2)}{6(2 + \delta)(2 + \frac{1}{5} \delta^2)} - \frac{1}{4} v_2 + \frac{1}{5} v_2^2 - \frac{1}{6} v_2^3 + \ldots$$

$$W_2 = \left[\begin{array}{l} \dfrac{\delta\left[2 - \delta - \delta^2 + 16 - 6\delta + 2\delta^2 + \frac{8}{5} \delta - \frac{3}{5} \delta^2 + \frac{1}{5} \delta^3\right]}{12(2 + \delta)(1 + \frac{1}{10} \delta^2)} \\ \\ - \frac{1}{4} v_2 + \frac{1}{5} v_2^2 - \frac{1}{6} v_2^3 + \ldots \end{array}\right]$$

$$W_2 = \frac{\delta(18 - 7\delta + \delta^2 + \frac{8}{5}\delta - \frac{3}{5}\delta^2 + \frac{1}{5}\delta^3)}{12(2 + \delta)(1 + \frac{1}{10}\delta^2)} - \frac{1}{4}v_2 + \frac{1}{5}v_2^2 - \frac{1}{6}v_2^3 + \dots \qquad (213)$$

We have from equation (178) with $t_2 = 2\delta + \frac{1}{5}\delta^2$

$$v_2 = \frac{6\delta + \frac{3}{5}\delta^2}{(1 - \delta)(2 - 2\delta - \frac{1}{5}\delta^2 + \delta)}$$

$$v_2 = \frac{6\delta(1 + \frac{1}{10}\delta)}{(1 - \delta)(2 - \delta - \frac{1}{5}\delta^2)} \qquad (214)$$

Substituting this value of v_2 into equation (213), we have

$$W_2 = \left[\frac{\delta(18 - 7\delta + \delta^2 + \frac{8}{5}\delta - \frac{3}{5}\delta^2 + \frac{1}{5}\delta^3)}{12(2 + \delta)(1 + \frac{1}{10}\delta^2)} - \frac{6\delta(1 + \frac{1}{10}\delta)}{4(1 - \delta)(2 - \delta - \frac{1}{5}\delta^2)} + \frac{1}{5}v_2^2 - \frac{1}{6}v_2^3 + \dots\right]$$

$$W_2 = \left[\frac{\delta\left[(18 - 7\delta + \delta^2 + \frac{8}{5}\delta - \frac{3}{5}\delta^2 + \frac{1}{5}\delta^3)(1 - \delta)(2 - \delta - \frac{1}{5}\delta^2) - 18(1 + \frac{1}{10}\delta)(2 + \delta)(1 + \frac{1}{10}\delta^2)\right]}{12(2 + \delta)(1 - \delta)(1 + \frac{1}{10}\delta^2)(2 - \delta - \frac{1}{5}\delta^2)} + \frac{1}{5}v_2^2 - \frac{1}{6}v_2^3 + \dots\right]$$

$$W_2 = \left[\frac{\delta^2\left(-86\frac{2}{5} + \frac{130}{5}\delta - \frac{92}{25}\delta^2 - \frac{77}{50}\delta^3 + \frac{6}{25}\delta^4 + \frac{1}{25}\delta^5\right)}{12(2 + \delta)(1 - \delta)(1 + \frac{1}{10}\delta^2)(2 - \delta - \frac{1}{5}\delta^2)} + \frac{1}{5}v_2^2 - \frac{1}{6}v_2^3 + \ldots \right] \qquad (215)$$

Substituting

$$v_2^2 = \frac{36\delta^2(1 + \frac{1}{10}\delta)^2}{(1 - \delta)^2(2 - \delta - \frac{1}{5}\delta^2)^2} \qquad (216)$$

we have

$$W_2 = \left[\frac{\delta^2\left(-86\frac{2}{5} + \frac{130}{5}\delta - \frac{92}{25}\delta^2 - \frac{77}{50}\delta^3 + \frac{6}{25}\delta^4 + \frac{1}{25}\delta^5\right)}{12(2 + \delta)(1 - \delta)(1 + \frac{1}{10}\delta^2)(2 - \delta - \frac{1}{5}\delta^2)} + \frac{36\delta^2(1 + \frac{1}{10}\delta)^2}{5(1 - \delta)^2(2 - \delta - \frac{1}{5}\delta^2)^2} - \frac{1}{6}v_2^3 + \frac{1}{7}v_2^4 - \ldots \right]$$

It then follows

$$W_2 = \frac{\delta^2\left[5\left(-86\frac{2}{5} + \frac{130}{5}\delta - \frac{92}{25}\delta^2 - \frac{77}{50}\delta^3 + \frac{6}{25}\delta^4 + \frac{1}{25}\delta^5\right)(1 - \delta)(2 - \delta - \frac{1}{5}\delta^2) + 36 \cdot 12(1 + \frac{1}{10}\delta)^2(2 + \delta)(1 + \frac{1}{10}\delta^2)\right]}{60(2 + \delta)(1 + \frac{1}{10}\delta^2)(1 - \delta)^2(2 - \delta - \frac{1}{5}\delta^2)^2} \qquad (217)$$

$$- \frac{1}{6}v_2^3 + \frac{1}{7}v_2^4 - \ldots$$

Retaining only the first two terms, we may write, for sufficiently small δ

$$W_2 = \frac{\delta^2(1556\delta + \frac{3024}{5}\delta)}{60 \cdot 2 \cdot 4} - \frac{1}{6} v_2^3$$

or

$$W_2 = \frac{10,804\delta^3}{2400} - \frac{1}{6} v_2^3 \tag{218}$$

Substituting

$$v_2^3 = \frac{6^3\delta^3}{2^3} = 27\delta^3 \tag{219}$$

We have

$$W_2 = \delta^3\left(\frac{10,804}{2400} - \frac{9}{2}\right)$$

$$= \delta^3\left(\frac{10,804 - 10,800}{2400}\right)$$

$$W_2 = \frac{4}{2400}\delta^3 = \frac{1}{600}\delta^3 \tag{220}$$

On substituting

$$t_2 = 2\delta + \frac{1}{5}\delta^2 \tag{212}$$

into (198), we find for sufficiently small δ,

$$\left(\frac{\partial W_2}{\partial t_2}\right)_\delta = -\frac{1}{24} \tag{221}$$

We then have as the correction, Δt_2, to our second approximation

$$\Delta t_2 = -\frac{W_2}{\left(\frac{\partial W_2}{\partial t_2}\right)_\delta} = \frac{1}{25}\,\delta^3 \qquad (222)$$

We then have as a third approximation, for the relationship between t and δ

$$t = 2\delta + \frac{1}{5}\,\delta^2 + \frac{1}{25}\,\delta^3 \qquad (223)$$

Since

$$t = \alpha_3 - \alpha_1 \qquad (174)$$

and

$$\delta = 1 - \alpha_1 \qquad (175)$$

we have

$$\alpha_3 = \alpha_1 + 2(1-\alpha_1) + \frac{1}{5}\,(1-\alpha_1)^2 + \frac{1}{25}\,(1-\alpha_1)^3$$

$$\alpha_3 = 2 - \alpha_1 + \frac{1}{5}\,(1-\alpha_1)^2 + \frac{1}{25}\,(1-\alpha_1)^3 \qquad (224)$$

or

$$\alpha_3 - 1 = 1 - \alpha_1 + \frac{1}{5}\,(1-\alpha_1)^2 + \frac{1}{25}\,(1-\alpha_1)^3 \qquad (225)$$

and equation (225) is the relationship between α_1 and α_3 near the critical point.

Table 1 gives values of α_1 and α_3 and of the rectilinear diameter, $\frac{\alpha_1 + \alpha_3}{2}$, as a function of the reduced temperature, γ. These data are illustrated in figure 1.

TABLE 1. - VAN DER WAALS FLUID, SATURATED DENSITIES AS A FUNCTION OF TEMPERATURE

$\alpha = \rho/\rho_c$ $\gamma = T/T_c$

γ	α_1	α_3	$\frac{\alpha_1 + \alpha_3}{2}$
2.50000E-01	5.12589E-05	2.75830E-00	1.37917E-00
3.00000E-01	3.99065E-04	2.70416E-00	1.35228E-00
3.50000E-01	1.68745E-03	2.64749E-00	1.32458E-00
4.00000E-01	4.91088E-03	2.58793E-00	1.29642E-00
4.50000E-01	1.12174E-02	2.52509E-00	1.26815E-00
5.00000E-01	2.17468E-02	2.45849E-00	1.24011E-00
5.50000E-01	3.75800E-02	2.38754E-00	1.21256E-00
6.00000E-01	5.97781E-02	2.31155E-00	1.18566E-00
6.50000E-01	8.94753E-02	2.22959E-00	1.15953E-00
7.00000E-01	1.28022E-01	2.14044E-00	1.13423E-00
7.50000E-01	1.77209E-01	2.04235E-00	1.10978E-00
8.00000E-01	2.39666E-01	1.93270E-00	1.08618E-00
8.50000E-01	3.19729E-01	1.80714E-00	1.06343E-00
9.00000E-01	4.25741E-01	1.65727E-00	1.04150E-00
9.50000E-01	5.79014E-01	1.46172E-00	1.02037E-00
9.52000E-01	5.86871E-01	1.45221E-00	1.01954E-00
9.54000E-01	5.94927E-01	1.44250E-00	1.01871E-00
9.56000E-01	6.03194E-01	1.43257E-00	1.01788E-00
9.58000E-01	6.11687E-01	1.42243E-00	1.01706E-00
9.60000E-01	6.20421E-01	1.41205E-00	1.01623E-00
9.62000E-01	6.29415E-01	1.40141E-00	1.01541E-00
9.64000E-01	6.38689E-01	1.39049E-00	1.01459E-00
9.66000E-01	6.48265E-01	1.37927E-00	1.01377E-00
9.68000E-01	6.58171E-01	1.36773E-00	1.01295E-00
9.70000E-01	6.68436E-01	1.35582E-00	1.01213E-00
9.72000E-01	6.79098E-01	1.34353E-00	1.01131E-00
9.74000E-01	6.90197E-01	1.33080E-00	1.01049E-00
9.76000E-01	7.01786E-01	1.31758E-00	1.00968E-00
9.78000E-01	7.13925E-01	1.30381E-00	1.00887E-00
9.80000E-01	7.26691E-01	1.28942E-00	1.00805E-00
9.82000E-01	7.40178E-01	1.27431E-00	1.00724E-00
9.84000E-01	7.54510E-01	1.25836E-00	1.00643E-00
9.86000E-01	7.69848E-01	1.24140E-00	1.00562E-00
9.88000E-01	7.86416E-01	1.22322E-00	1.00482E-00
9.90000E-01	8.04535E-01	1.20349E-00	1.00401E-00
9.92000E-01	8.24696E-01	1.18172E-00	1.00320E-00
9.94000E-01	8.47727E-01	1.15708E-00	1.00240E-00
9.96000E-01	8.75242E-01	1.12796E-00	1.00160E-00
9.98000E-01	9.11404E-01	1.09019E-00	1.00080E-00
9.99000E-01	9.37171E-01	1.06362E-00	1.00040E-00
1.00000E-00	1.00000E-00	1.00000E-00	1.00000E-00

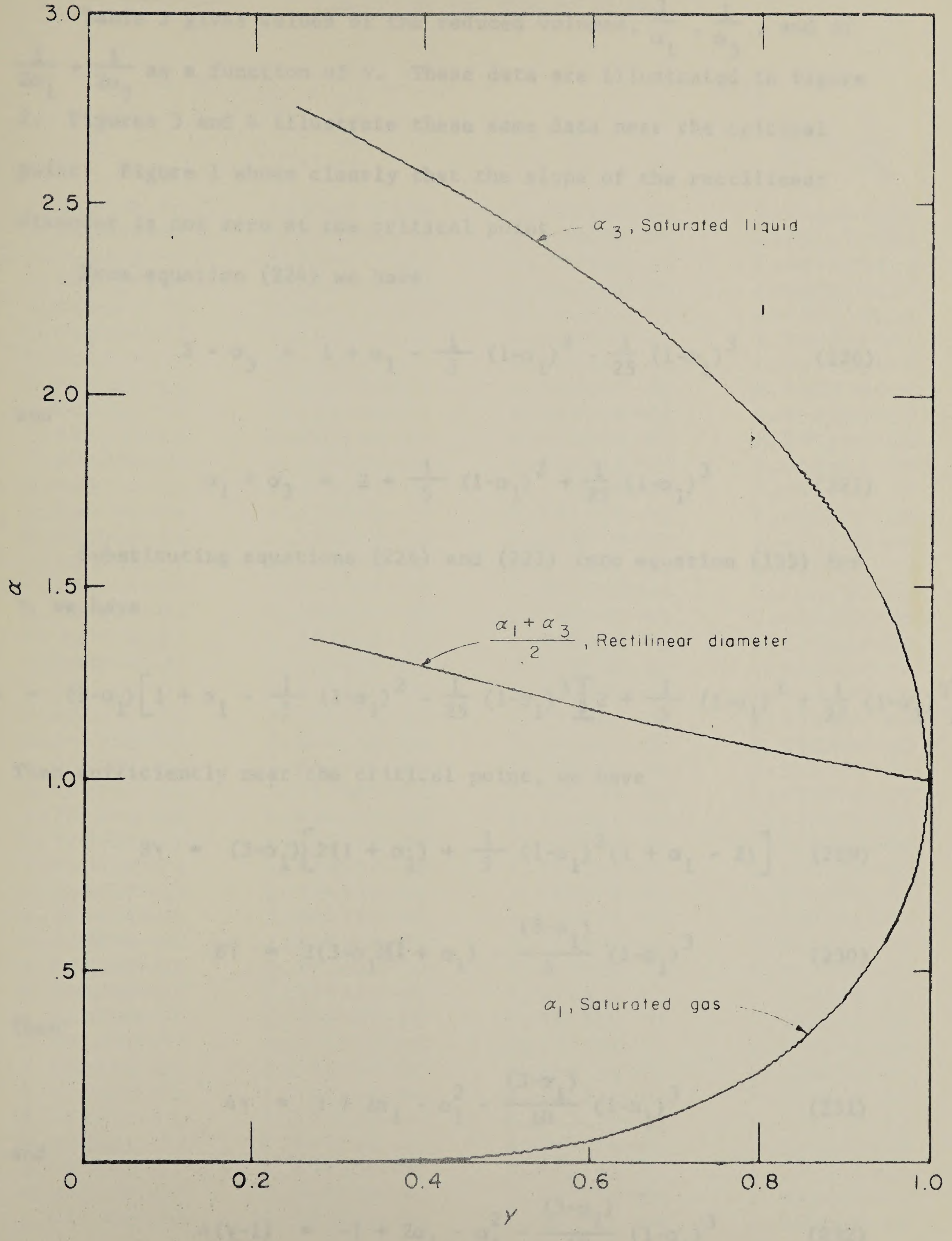

FIGURE 1.- Van der Waals Fluid,
Saturated Densities vs γ
$\alpha = \rho/\rho_c$; $\gamma = T/T_c$

Table 2 gives values of the reduced volumes, $\frac{1}{\alpha_1}$, $\frac{1}{\alpha_3}$, and of $\frac{1}{2\alpha_1} + \frac{1}{2\alpha_3}$ as a function of γ. These data are illustrated in figure 2. Figures 3 and 4 illustrate these same data near the critical point. Figure 1 shows clearly that the slope of the rectilinear diameter is not zero at the critical point.

From equation (224) we have

$$3 - \alpha_3 = 1 + \alpha_1 - \frac{1}{5}(1-\alpha_1)^2 - \frac{1}{25}(1-\alpha_1)^3 \tag{226}$$

and

$$\alpha_1 + \alpha_3 = 2 + \frac{1}{5}(1-\alpha_1)^2 + \frac{1}{25}(1-\alpha_1)^3 \tag{227}$$

Substituting equations (226) and (227) into equation (155) for γ, we have

$$8\gamma = (3-\alpha_1)\left[1 + \alpha_1 - \frac{1}{5}(1-\alpha_1)^2 - \frac{1}{25}(1-\alpha_1)^3\right]\left[2 + \frac{1}{5}(1-\alpha_1)^2 + \frac{1}{25}(1-\alpha_1)^3\right] \tag{228}$$

Then sufficiently near the critical point, we have

$$8\gamma = (3-\alpha_1)\left[2(1 + \alpha_1) + \frac{1}{5}(1-\alpha_1)^2(1 + \alpha_1 - 2)\right] \tag{229}$$

$$8\gamma = 2(3-\alpha_1)(1 + \alpha_1) - \frac{(3-\alpha_1)}{5}(1-\alpha_1)^3 \tag{230}$$

Then

$$4\gamma = 3 + 2\alpha_1 - \alpha_1^2 - \frac{(3-\alpha_1)}{10}(1-\alpha_1)^3 \tag{231}$$

and

$$4(\gamma-1) = -1 + 2\alpha_1 - \alpha_1^2 - \frac{(3-\alpha_1)}{10}(1-\alpha_1)^3 \tag{232}$$

TABLE 2. - VAN DER WAALS FLUID, SATURATED VOLUMES AS A FUNCTION OF TEMPERATURE

$\alpha = \rho/\rho_c$ $\gamma = T/T_c$

γ	$\frac{1}{\alpha_1}$	$\frac{1}{\alpha_3}$	$\frac{1}{2\alpha_1} + \frac{1}{2\alpha_3}$
2.50000E-01	1.95087E&04	3.62541E-01	9.75456E&03
3.00000E-01	2.50585E&03	3.69800E-01	1.25311E&03
3.50000E-01	5.92607E&02	3.77716E-01	2.96492E&02
4.00000E-01	2.03629E&02	3.86408E-01	1.02007E&02
4.50000E-01	8.91467E&01	3.96024E-01	4.47713E&01
5.00000E-01	4.59837E&01	4.06753E-01	2.31952E&01
5.50000E-01	2.66098E&01	4.18839E-01	1.35143E&01
6.00000E-01	1.67285E&01	4.32608E-01	8.58057E-00
6.50000E-01	1.11762E&01	4.48511E-01	5.81238E-00
7.00000E-01	7.81113E-00	4.67193E-01	4.13916E-00
7.50000E-01	5.64305E-00	4.89631E-01	3.06634E-00
8.00000E-01	4.17245E-00	5.17409E-01	2.34493E-00
8.50000E-01	3.12763E-00	5.53360E-01	1.84049E-00
9.00000E-01	2.34884E-00	6.03401E-01	1.47612E-00
9.50000E-01	1.72707E-00	6.84122E-01	1.20559E-00
9.52000E-01	1.70395E-00	6.88604E-01	1.19627E-00
9.54000E-01	1.68087E-00	6.93240E-01	1.18705E-00
9.56000E-01	1.65784E-00	6.98041E-01	1.17794E-00
9.58000E-01	1.63482E-00	7.03019E-01	1.16892E-00
9.60000E-01	1.61180E-00	7.08189E-01	1.15999E-00
9.62000E-01	1.58877E-00	7.13566E-01	1.15117E-00
9.64000E-01	1.56570E-00	7.19168E-01	1.14243E-00
9.66000E-01	1.54257E-00	7.25018E-01	1.13379E-00
9.68000E-01	1.51936E-00	7.31137E-01	1.12524E-00
9.70000E-01	1.49602E-00	7.37556E-01	1.11679E-00
9.72000E-01	1.47254E-00	7.44306E-01	1.10842E-00
9.74000E-01	1.44885E-00	7.51426E-01	1.10014E-00
9.76000E-01	1.42493E-00	7.58965E-01	1.09195E-00
9.78000E-01	1.40070E-00	7.66978E-01	1.08384E-00
9.80000E-01	1.37610E-00	7.75538E-01	1.07581E-00
9.82000E-01	1.35102E-00	7.84734E-01	1.06787E-00
9.84000E-01	1.32536E-00	7.94682E-01	1.06002E-00
9.86000E-01	1.29895E-00	8.05536E-01	1.05224E-00
9.88000E-01	1.27159E-00	8.17510E-01	1.04455E-00
9.90000E-01	1.24295E-00	8.30914E-01	1.03693E-00
9.92000E-01	1.21256E-00	8.46222E-01	1.02939E-00
9.94000E-01	1.17962E-00	8.64242E-01	1.02193E-00
9.96000E-01	1.14254E-00	8.86554E-01	1.01454E-00
9.98000E-01	1.09720E-00	9.17265E-01	1.00723E-00
9.99000E-01	1.06704E-00	9.40177E-01	1.00360E-00
1.00000E-00	1.00000E-00	1.00000E-00	1.00000E-00

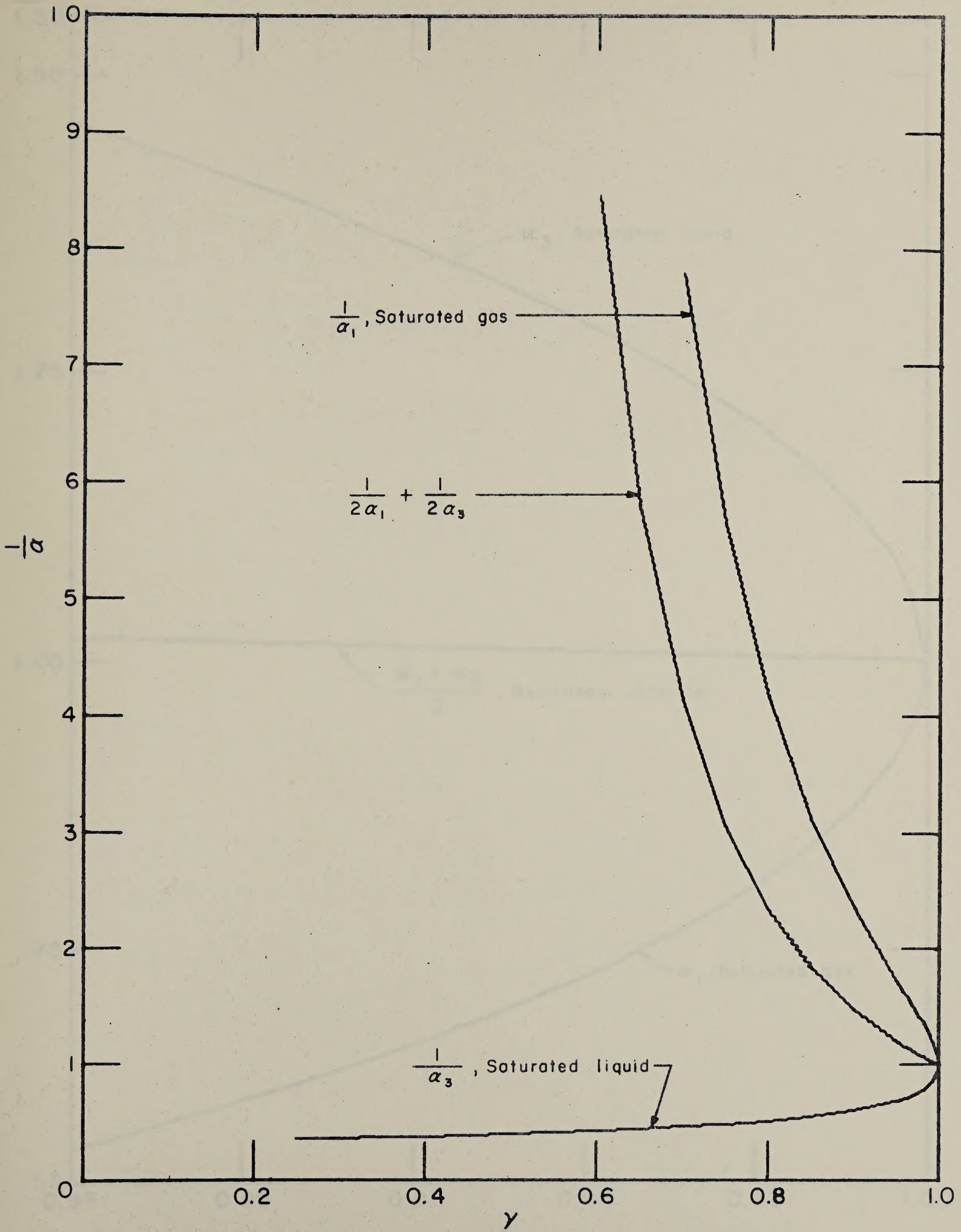

FIGURE 2.-Van der Waals Fluid, Volume Coexistence Curves vs γ;
$\gamma = T/T_c$; $\alpha = \rho/\rho_c$

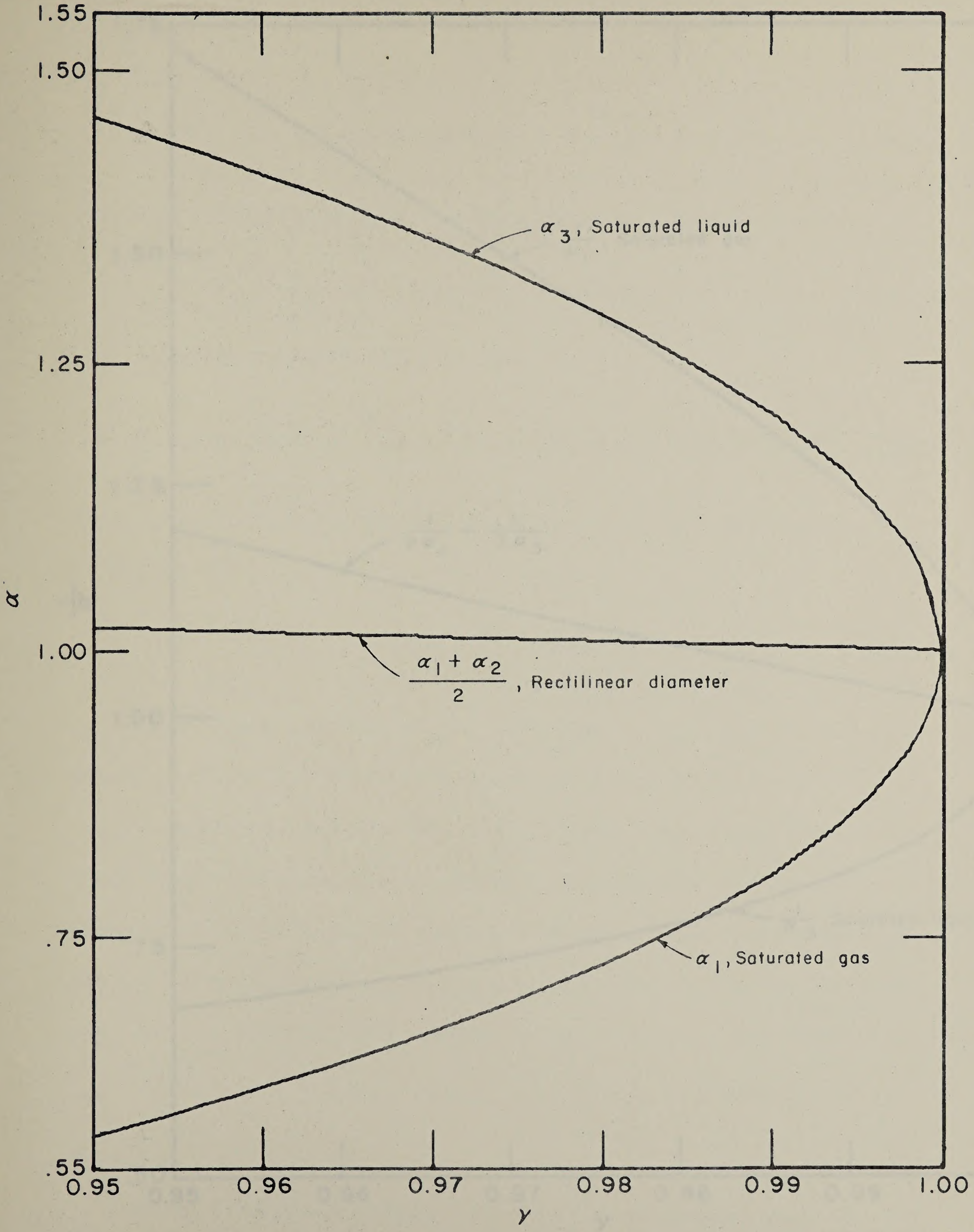

FIGURE 3.- Van der Waals Fluid, Saturated Densities vs γ; $\alpha = \rho/\rho_c$; $\gamma = T/T_c$

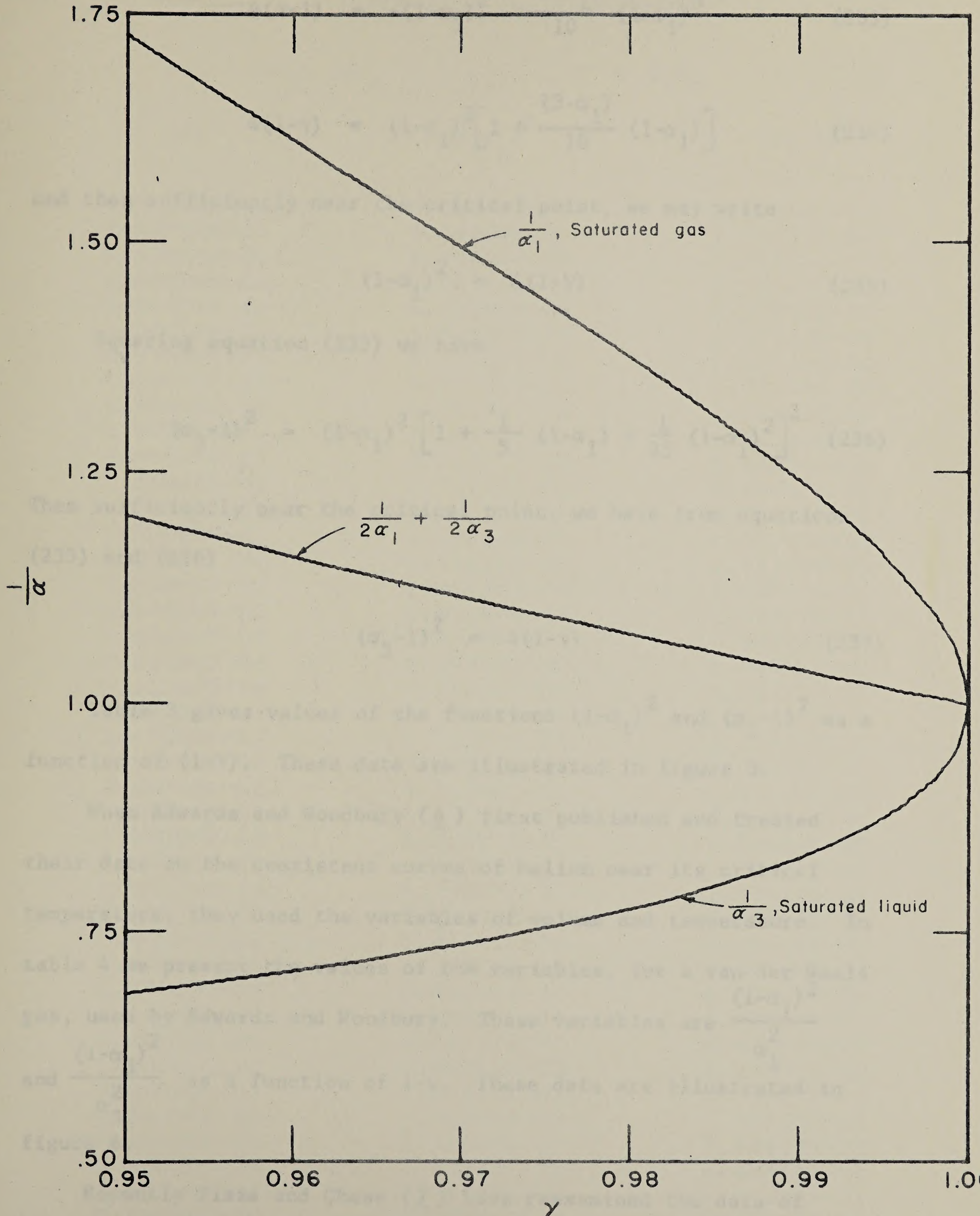

FIGURE 4.- Van der Waals Fluid,
Saturated Volumes vs γ
$\frac{1}{\alpha} = {}^{v}/_{v_c}$; $\gamma = {}^{T}/_{T_c}$

$$4(\gamma-1) = -(1-\alpha_1)^2 - \frac{(3-\alpha_1)}{10}(1-\alpha_1)^3 \qquad (233)$$

$$4(1-\gamma) = (1-\alpha_1)^2\left[1 + \frac{(3-\alpha_1)}{10}(1-\alpha_1)\right] \qquad (234)$$

and then sufficiently near the critical point, we may write

$$(1-\alpha_1)^2 = 4(1-\gamma) \qquad (235)$$

Squaring equation (225) we have

$$(\alpha_3-1)^2 = (1-\alpha_1)^2\left[1 + \frac{1}{5}(1-\alpha_1) + \frac{1}{25}(1-\alpha_1)^2\right]^2 \qquad (236)$$

Then sufficiently near the critical point, we have from equations (235) and (236)

$$(\alpha_3-1)^2 = 4(1-\gamma) \qquad (237)$$

Table 3 gives values of the functions $(1-\alpha_1)^2$ and $(\alpha_3-1)^2$ as a function of $(1-\gamma)$. These data are illustrated in figure 5.

When Edwards and Woodbury (4) first published and treated their data on the coexistent curves of helium near its critical temperature, they used the variables of volume and temperature. In table 4 we present the values of the variables, for a van der Waals gas, used by Edwards and Woodbury. These variables are $\frac{(1-\alpha_1)^2}{\alpha_1^2}$ and $\frac{(1-\alpha_3)^2}{\alpha_3^2}$ as a function of $1-\gamma$. These data are illustrated in figure 6.

Recently Tisza and Chase (7) have reexamined the data of Edwards and Woodbury, using the variables of density and temperature.

TABLE 3. - VAN DER WAALS FLUID, DENSITY-COEXISTENCE DATA AS A FUNCTION OF TEMPERATURE

$\alpha = \rho/\rho_c$　　　$\gamma = T/T_c$

$1-\gamma$	$(1-\alpha_1)^2$	$(\alpha_3-1)^2$
7.50000E-01	9.99897E-01	3.09164E-00
7.00000E-01	9.99202E-01	2.90417E-00
6.50000E-01	9.96627E-01	2.71422E-00
6.00000E-01	9.90202E-01	2.52154E-00
5.50000E-01	9.77690E-01	2.32592E-00
5.00000E-01	9.56979E-01	2.12719E-00
4.50000E-01	9.26252E-01	1.92529E-00
4.00000E-01	8.84017E-01	1.72018E-00
3.50000E-01	8.29055E-01	1.51191E-00
3.00000E-01	7.60345E-01	1.30060E-00
2.50000E-01	6.76985E-01	1.08650E-00
2.00000E-01	5.78106E-01	8.69940E-01
1.50000E-01	4.62767E-01	6.51475E-01
1.00000E-01	3.29772E-01	4.32004E-01
5.00000E-02	1.77228E-01	2.13192E-01
4.80000E-02	1.70675E-01	2.04495E-01
4.60000E-02	1.64083E-01	1.95806E-01
4.40000E-02	1.57454E-01	1.87124E-01
4.20000E-02	1.50786E-01	1.78451E-01
4.00000E-02	1.44079E-01	1.69786E-01
3.80000E-02	1.37332E-01	1.61131E-01
3.60000E-02	1.30545E-01	1.52485E-01
3.40000E-02	1.23717E-01	1.43850E-01
3.20000E-02	1.16846E-01	1.35226E-01
3.00000E-02	1.09934E-01	1.26614E-01
2.80000E-02	1.02977E-01	1.18014E-01
2.60000E-02	9.59773E-02	1.09429E-01
2.40000E-02	8.89312E-02	1.00859E-01
2.20000E-02	8.18384E-02	9.23046E-02
2.00000E-02	7.46976E-02	8.37676E-02
1.80000E-02	6.75071E-02	7.52496E-02
1.60000E-02	6.02651E-02	6.67524E-02
1.40000E-02	5.29695E-02	5.82782E-02
1.20000E-02	4.56177E-02	4.98295E-02
1.00000E-02	3.82063E-02	4.14097E-02
8.00000E-03	3.07313E-02	3.30229E-02
6.00000E-03	2.31868E-02	2.46749E-02
4.00000E-03	1.55643E-02	1.63742E-02
2.00000E-03	7.84918E-03	8.13545E-03
1.00000E-03	3.94747E-03	4.04868E-03
0.00000E-99	0.00000E-99	0.00000E-99

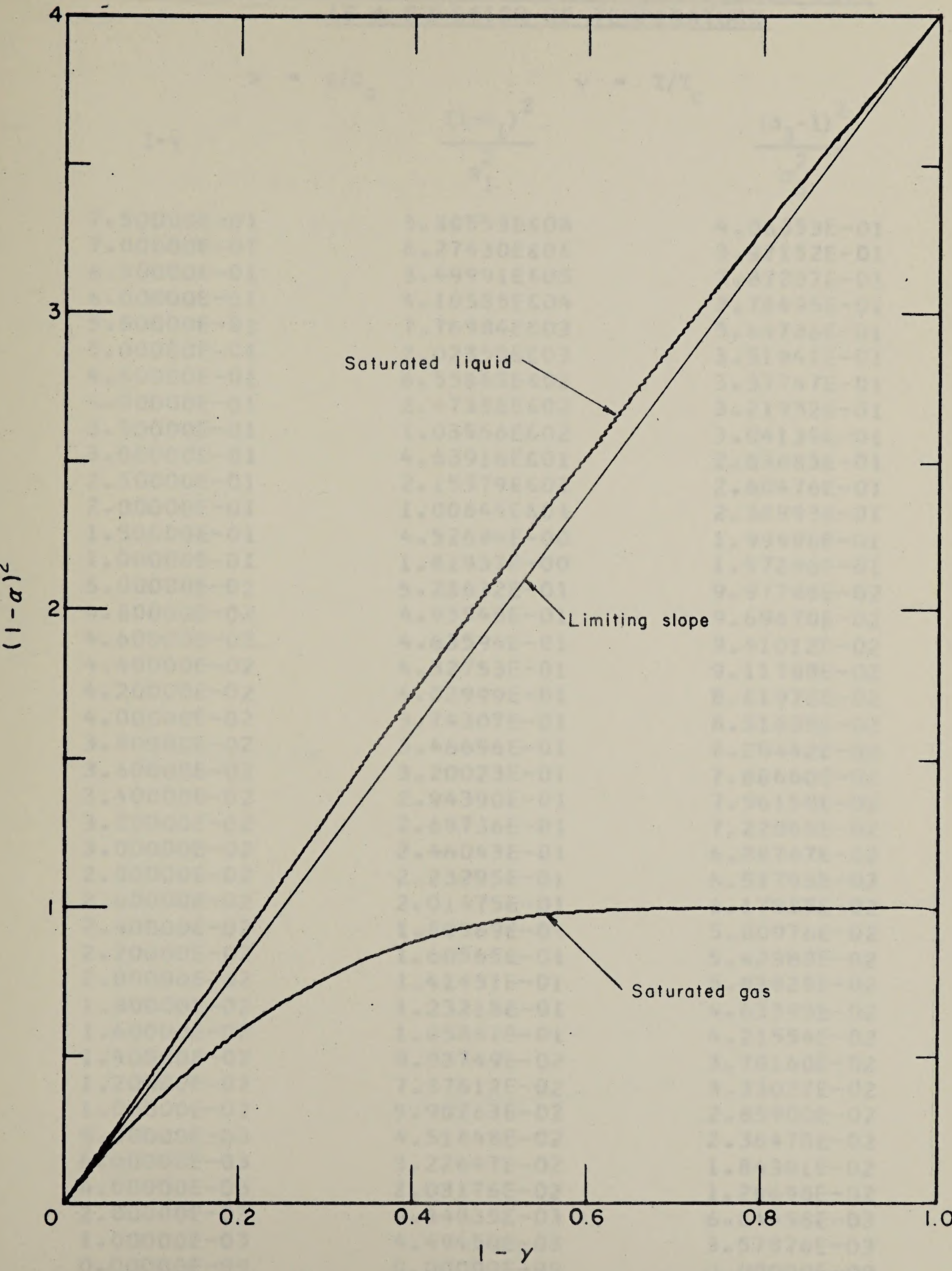

FIGURE 5.- Van der Waals Fluid, Density - Coexistence Curves vs $(1-y)$; $y = T/T_c$; $\alpha_1 = \rho_g/\rho_c$; $\alpha_3 = \rho_l/\rho_c$

TABLE 4. - VAN DER WAALS FLUID, VOLUME-COEXISTENCE DATA AS A FUNCTION OF TEMPERATURE

$\alpha = \rho/\rho_c \qquad \gamma = T/T_c$

$1-\gamma$	$\frac{(1-\alpha_1)^2}{\alpha_1^2}$	$\frac{(\alpha_3-1)^2}{\alpha_3^2}$
7.50000E-01	3.80553E&08	4.06353E-01
7.00000E-01	6.27430E&06	3.97152E-01
6.50000E-01	3.49991E&05	3.87237E-01
6.00000E-01	4.10585E&04	3.76495E-01
5.50000E-01	7.76984E&03	3.64786E-01
5.00000E-01	2.02353E&03	3.51941E-01
4.50000E-01	6.55865E&02	3.37747E-01
4.00000E-01	2.47386E&02	3.21932E-01
3.50000E-01	1.03556E&02	3.04139E-01
3.00000E-01	4.63916E&01	2.83883E-01
2.50000E-01	2.15579E&01	2.60476E-01
2.00000E-01	1.00644E&01	2.32893E-01
1.50000E-01	4.52684E-00	1.99486E-01
1.00000E-01	1.81937E-00	1.57290E-01
5.00000E-02	5.28632E-01	9.97788E-02
4.80000E-02	4.95545E-01	9.69670E-02
4.60000E-02	4.63594E-01	9.41012E-02
4.40000E-02	4.32753E-01	9.11788E-02
4.20000E-02	4.02999E-01	8.81972E-02
4.00000E-02	3.74307E-01	8.51535E-02
3.80000E-02	3.46656E-01	8.20442E-02
3.60000E-02	3.20023E-01	7.88660E-02
3.40000E-02	2.94390E-01	7.56150E-02
3.20000E-02	2.69736E-01	7.22868E-02
3.00000E-02	2.46043E-01	6.88767E-02
2.80000E-02	2.23295E-01	6.53793E-02
2.60000E-02	2.01475E-01	6.17885E-02
2.40000E-02	1.80569E-01	5.80976E-02
2.20000E-02	1.60565E-01	5.42988E-02
2.00000E-02	1.41451E-01	5.03828E-02
1.80000E-02	1.23218E-01	4.63393E-02
1.60000E-02	1.05861E-01	4.21554E-02
1.40000E-02	8.93749E-02	3.78160E-02
1.20000E-02	7.37612E-02	3.33022E-02
1.00000E-02	5.90263E-02	2.85900E-02
8.00000E-03	4.51848E-02	2.36475E-02
6.00000E-03	3.22647E-02	1.84301E-02
4.00000E-03	2.03176E-02	1.28698E-02
2.00000E-03	9.44935E-03	6.84498E-03
1.00000E-03	4.49450E-03	3.57876E-03
0.00000E-99	0.00000E-99	0.00000E-99

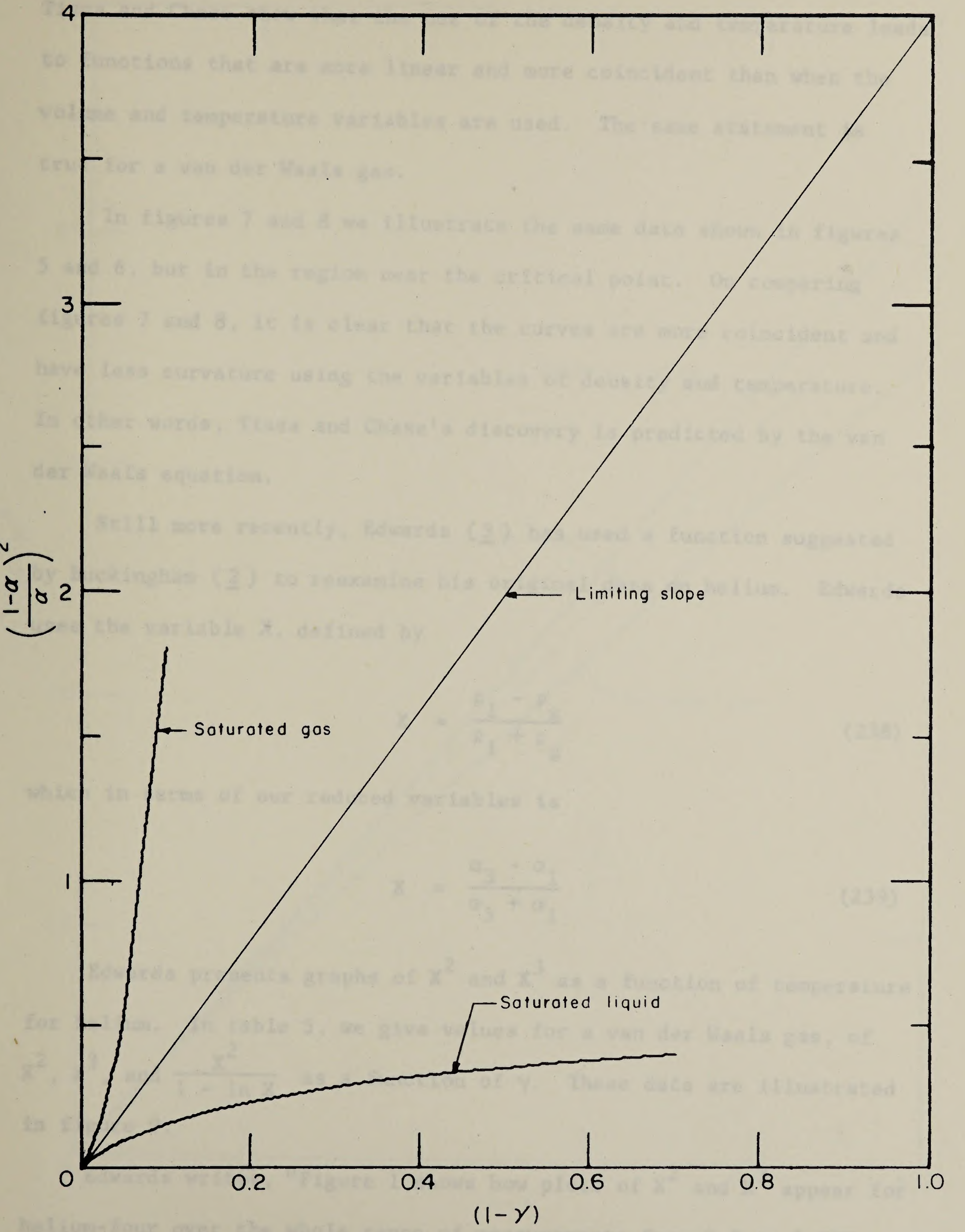

FIGURE 6.-Van der Waals Fluid, Volume-Coexistence Curves vs $(1-\gamma)$; $\gamma = T/T_c$; $\alpha = \rho/\rho_c$

Tisza and Chase show that the use of the density and temperature leads to functions that are more linear and more coincident than when the volume and temperature variables are used. The same statement is true for a van der Waals gas.

In figures 7 and 8 we illustrate the same data shown in figures 5 and 6, but in the region near the critical point. On comparing figures 7 and 8, it is clear that the curves are more coincident and have less curvature using the variables of density and temperature. In other words, Tisza and Chase's discovery is predicted by the van der Waals equation.

Still more recently, Edwards (3) has used a function suggested by Buckingham (2) to reexamine his original data on helium. Edwards uses the variable X, defined by

$$X = \frac{\rho_l - \rho_g}{\rho_l + \rho_g} \tag{238}$$

which in terms of our reduced variables is

$$X = \frac{\alpha_3 - \alpha_1}{\alpha_3 + \alpha_1} \tag{239}$$

Edwards presents graphs of X^2 and X^3 as a function of temperature for helium. In table 5, we give values for a van der Waals gas, of X^2, X^3, and $\frac{X^2}{1 - \ln X}$ as a function of γ. These data are illustrated in figure 9.

Edwards writes, "Figure 1 shows how plots of X^2 and X^3 appear for helium-four over the whole range of measurements from 0.3 to $0.99T_c$. Clearly, X^3 is nearly linear above about $0.8T_c$ (but not too near T_c;

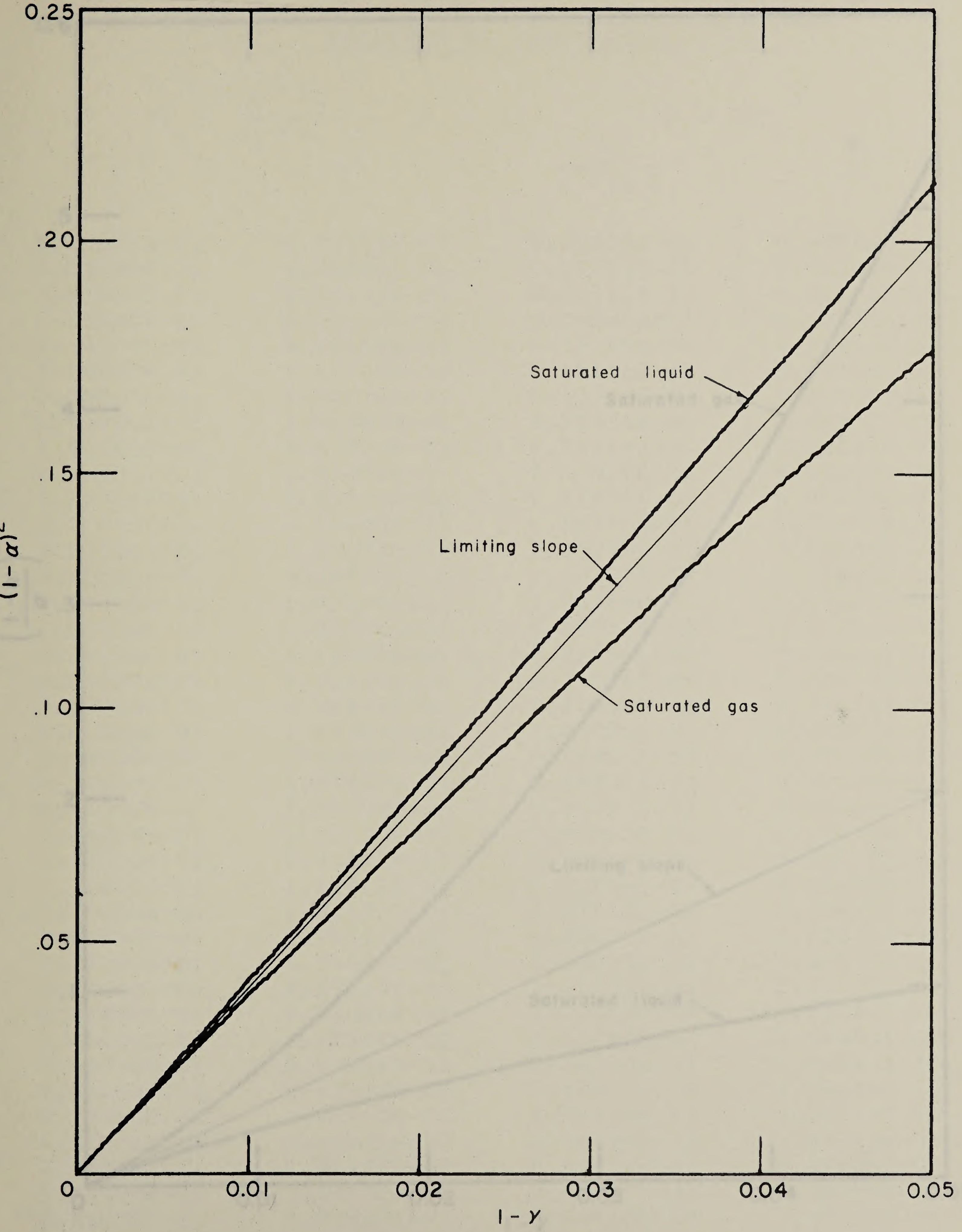

FIGURE 7.- Van der Waals Fluid, Density - Coexistence Curves vs $(1-\gamma)$; $\gamma = T/T_c$; $\alpha = \rho/\rho_c$

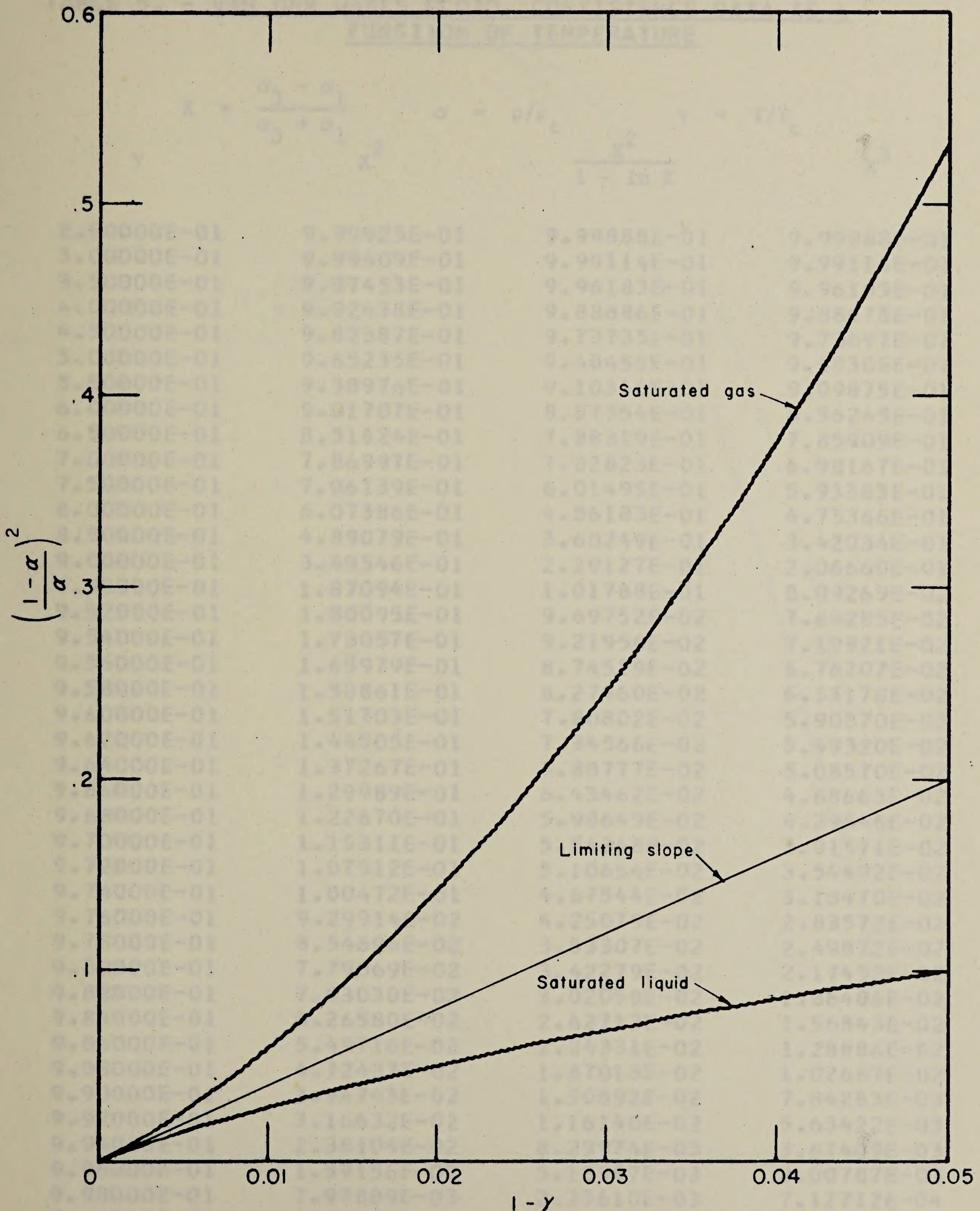

FIGURE 8.–Van der Waals Fluid, Volume-Coexistence Curves vs $(1-\gamma)$; $\gamma = T/T_c$; $\alpha = \rho/\rho_c$

TABLE 5. - VAN DER WAALS FLUID, COEXISTENCE DATA AS A FUNCTION OF TEMPERATURE

$X = \frac{\alpha_3 - \alpha_1}{\alpha_3 + \alpha_1}$ $\alpha = \rho/\rho_c$ $\gamma = T/T_c$

γ	X^2	$\frac{X^2}{1 - \ln X}$	X^3
2.50000E-01	9.99925E-01	9.99888E-01	9.99888E-01
3.00000E-01	9.99409E-01	9.99114E-01	9.99114E-01
3.50000E-01	9.97453E-01	9.96183E-01	9.96183E-01
4.00000E-01	9.92438E-01	9.88686E-01	9.88678E-01
4.50000E-01	9.82387E-01	9.73735E-01	9.73697E-01
5.00000E-01	9.65235E-01	9.48455E-01	9.48308E-01
5.50000E-01	9.38976E-01	9.10316E-01	9.09875E-01
6.00000E-01	9.01707E-01	8.57354E-01	8.56245E-01
6.50000E-01	8.51624E-01	7.88319E-01	7.85909E-01
7.00000E-01	7.86997E-01	7.02823E-01	6.98167E-01
7.50000E-01	7.06139E-01	6.01495E-01	5.93383E-01
8.00000E-01	6.07386E-01	4.86183E-01	4.73366E-01
8.50000E-01	4.89079E-01	3.60249E-01	3.42034E-01
9.00000E-01	3.49546E-01	2.29127E-01	2.06660E-01
9.50000E-01	1.87094E-01	1.01788E-01	8.09269E-02
9.52000E-01	1.80095E-01	9.69752E-02	7.64285E-02
9.54000E-01	1.73057E-01	9.21956E-02	7.19921E-02
9.56000E-01	1.65979E-01	8.74519E-02	6.76207E-02
9.58000E-01	1.58861E-01	8.27460E-02	6.33178E-02
9.60000E-01	1.51703E-01	7.80802E-02	5.90870E-02
9.62000E-01	1.44505E-01	7.34566E-02	5.49320E-02
9.64000E-01	1.37267E-01	6.88777E-02	5.08570E-02
9.66000E-01	1.29989E-01	6.43462E-02	4.68663E-02
9.68000E-01	1.22670E-01	5.98649E-02	4.29646E-02
9.70000E-01	1.15311E-01	5.54368E-02	3.91571E-02
9.72000E-01	1.07912E-01	5.10654E-02	3.54492E-02
9.74000E-01	1.00472E-01	4.67544E-02	3.18470E-02
9.76000E-01	9.29914E-02	4.25079E-02	2.83572E-02
9.78000E-01	8.54696E-02	3.83307E-02	2.49872E-02
9.80000E-01	7.79069E-02	3.42279E-02	2.17452E-02
9.82000E-01	7.03030E-02	3.02058E-02	1.86406E-02
9.84000E-01	6.26580E-02	2.62713E-02	1.56843E-02
9.86000E-01	5.49716E-02	2.24331E-02	1.28886E-02
9.88000E-01	4.72437E-02	1.87013E-02	1.02687E-02
9.90000E-01	3.94743E-02	1.50892E-02	7.84283E-03
9.92000E-01	3.16632E-02	1.16140E-02	5.63422E-03
9.94000E-01	2.38104E-02	8.29974E-03	3.67409E-03
9.96000E-01	1.59156E-02	5.18387E-03	2.00787E-03
9.98000E-01	7.97889E-03	2.33610E-03	7.12712E-04
9.99000E-01	3.99472E-03	1.06203E-03	2.52481E-04
1.00000E-00	0.00000E-99	0.00000E-99	0.00000E-99

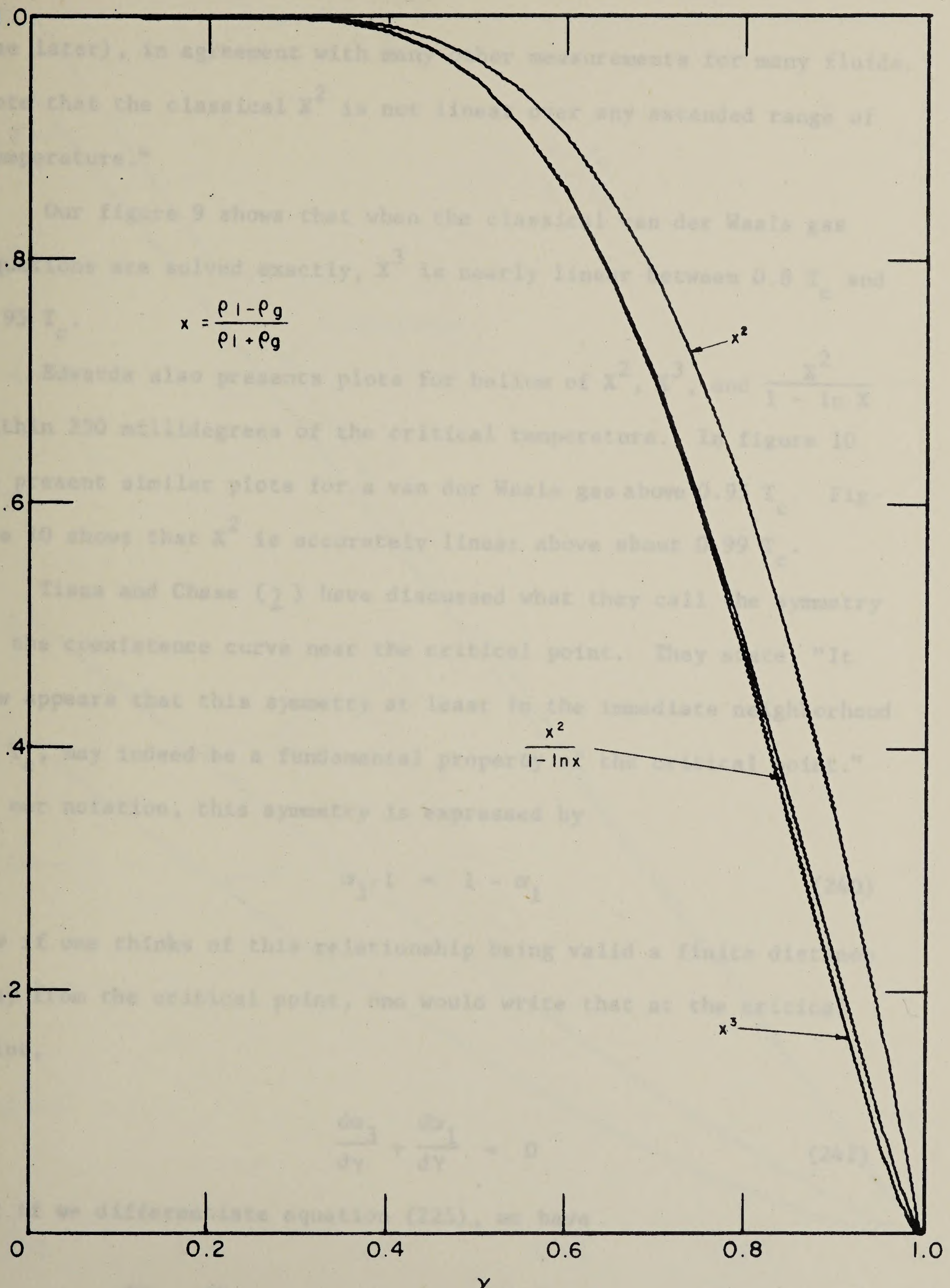

FIGURE 9.-Van der Waals Fluid, Coexistence Curves vs Y; $Y = T/T_c$

see later), in agreement with many other measurements for many fluids. Note that the classical X^2 is not linear over any extended range of temperature."

Our figure 9 shows that when the classical van der Waals gas equations are solved exactly, X^3 is nearly linear between 0.8 T_c and 0.95 T_c.

Edwards also presents plots for helium of X^2, X^3, and $\frac{X^2}{1 - \ln X}$ within 250 millidegrees of the critical temperature. In figure 10 we present similar plots for a van der Waals gas above 0.95 T_c. Figure 10 shows that X^2 is accurately linear above about 0.99 T_c.

Tisza and Chase (7) have discussed what they call the symmetry of the coexistence curve near the critical point. They state, "It now appears that this symmetry at least in the immediate neighborhood of T_c, may indeed be a fundamental property of the critical point." In our notation, this symmetry is expressed by

$$\alpha_3 - 1 = 1 - \alpha_1 \qquad (240)$$

Now if one thinks of this relationship being valid a finite distance away from the critical point, one would write that at the critical point,

$$\frac{d\alpha_3}{dY} + \frac{d\alpha_1}{dY} = 0 \qquad (241)$$

But if we differentiate equation (225), we have

$$\frac{d\alpha_3}{dY} + \frac{d\alpha_1}{dY} = -\frac{2}{5}(1-\alpha_1)\frac{d\alpha_1}{dY} - \frac{3}{25}(1-\alpha_1)^2\frac{d\alpha_1}{dY} \qquad (242)$$

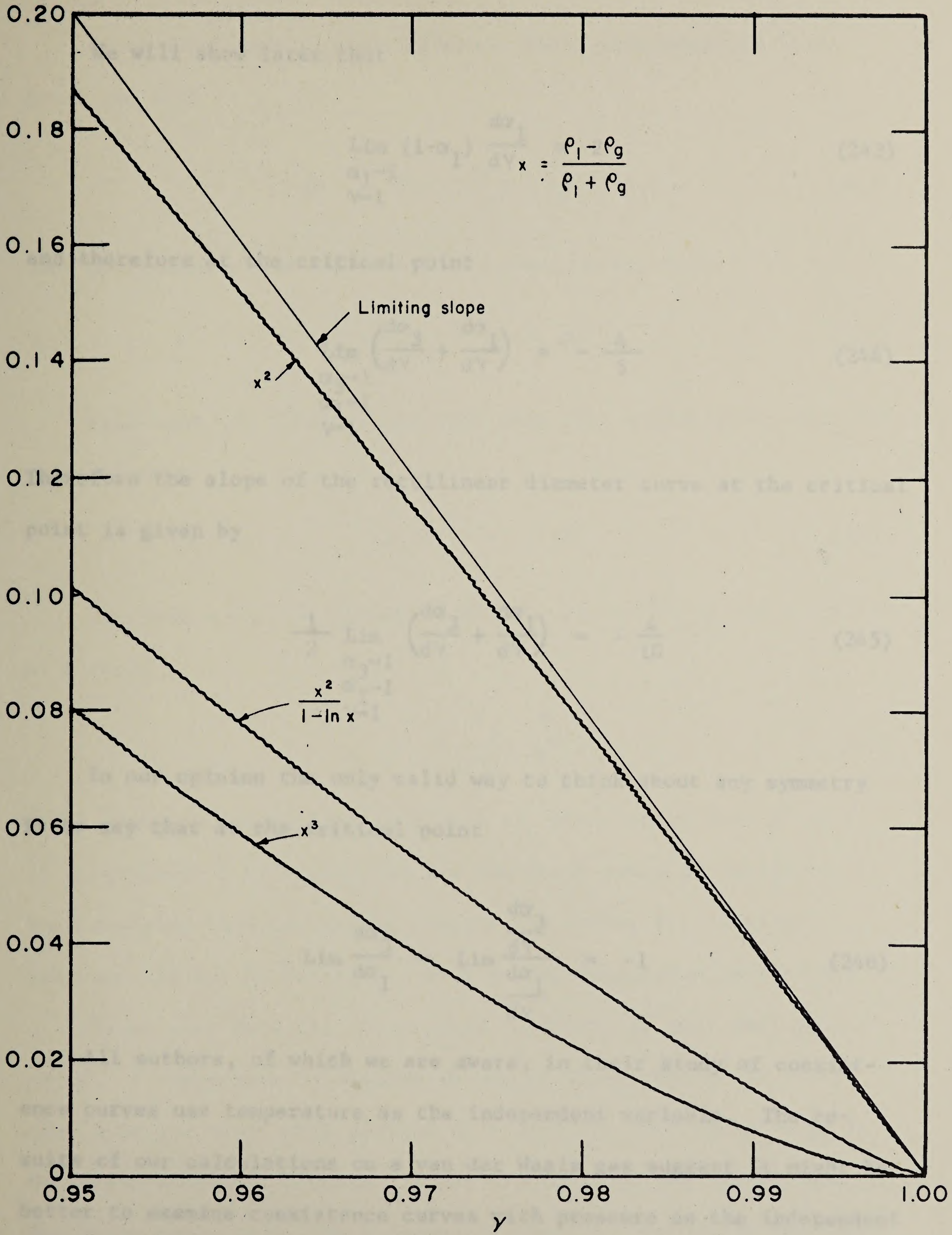

FIGURE 10.- Van der Waals Fluid, Coexistence Curves vs γ; $\gamma = T/T_c$

We will show later that

$$\lim_{\substack{\alpha_1 \to 1 \\ \gamma \to 1}} (1-\alpha_1) \frac{d\alpha_1}{d\gamma} = 2 \tag{243}$$

and therefore at the critical point

$$\lim_{\substack{\alpha_3 \to 1 \\ \alpha_1 \to 1 \\ \gamma \to 1}} \left(\frac{d\alpha_3}{d\gamma} + \frac{d\alpha_1}{d\gamma}\right) = -\frac{4}{5} \tag{244}$$

Therefore the slope of the rectilinear diameter curve at the critical point is given by

$$\frac{1}{2} \lim_{\substack{\alpha_3 \to 1 \\ \alpha_1 \to 1 \\ \gamma \to 1}} \left(\frac{d\alpha_3}{d\gamma} + \frac{d\alpha_1}{d\gamma}\right) = -\frac{4}{10} \tag{245}$$

In our opinion the only valid way to think about any symmetry is to say that at the critical point

$$\lim \frac{d\alpha_3}{d\alpha_1} = \lim \frac{\frac{d\alpha_3}{d\gamma}}{\frac{d\alpha_1}{d\gamma}} = -1 \tag{246}$$

All authors, of which we are aware, in their study of coexistence curves use temperature as the independent variable. The results of our calculations on a van der Waals gas suggest it might be better to examine coexistence curves with pressure as the independent variable.

If we substitute α_3 from equation (224) into equation (158) for β, we find

$$(1-\beta) = (1-\alpha_1)^2\left[1 + \frac{\alpha_1}{5}(1-\alpha_1)\right] \tag{247}$$

Then sufficiently near the critical point, we may write

$$(1-\alpha_1)^2 = (1-\beta) \tag{248}$$

From equation (236) we can also show that sufficiently near the critical point

$$(\alpha_3-1)^2 = (1-\beta) \tag{249}$$

In table 6 we list values of X^2, X^3, and $\frac{X^2}{1 - \ln X}$ as a function of β where

$$X = \frac{\alpha_3 - \alpha_1}{\alpha_3 + \alpha_1} \tag{239}$$

These data are illustrated in figure 11, which shows that X^2 vs β is essentially a straight line for the whole range of variables. This suggests that in testing coexistence curves for classical behavior, it may be better to use β as the independent variable.

These same data are illustrated in figure 12 near the critical point. A comparison of figures 10 and 12 shows that X^2 is linear over a larger range when plotted as a function of β rather than γ. We intend to repeat Edwards' latest treatment of his helium data, but using pressure as the independent variable instead of the temperature.

TABLE 6. - VAN DER WAALS FLUID, COEXISTENCE DATA AS A FUNCTION OF PRESSURE

$$X = \frac{\alpha_3 - \alpha_1}{\alpha_3 + \alpha_1} \qquad \alpha = \rho/\rho_c \qquad \beta = P/P_c$$

β	X^2	$\frac{X^2}{1 - \ln X}$	X^3
3.41653E-05	9.99925E-01	9.99888E-01	9.99888E-01
3.18816E-04	9.99409E-01	9.99114E-01	9.99114E-01
1.56730E-03	9.97453E-01	9.96183E-01	9.96183E-01
5.17452E-03	9.92438E-01	9.88686E-01	9.88678E-01
1.31339E-02	9.82387E-01	9.73735E-01	9.73697E-01
2.77886E-02	9.65235E-01	9.48455E-01	9.48308E-01
5.15798E-02	9.38976E-01	9.10316E-01	9.09875E-01
8.68692E-02	9.01707E-01	8.57354E-01	8.56245E-01
1.35840E-01	8.51624E-01	7.88319E-01	7.85909E-01
2.00458E-01	7.86997E-01	7.02823E-01	6.98167E-01
2.82458E-01	7.06139E-01	6.01495E-01	5.93383E-01
3.83361E-01	6.07386E-01	4.86183E-01	4.73366E-01
5.04491E-01	4.89079E-01	3.60249E-01	3.42034E-01
6.46998E-01	3.49546E-01	2.29127E-01	2.06660E-01
8.11879E-01	1.87094E-01	1.01788E-01	8.09269E-02
8.18952E-01	1.80095E-01	9.69752E-02	7.64285E-02
8.26063E-01	1.73057E-01	9.21956E-02	7.19921E-02
8.33210E-01	1.65979E-01	8.74519E-02	6.76207E-02
8.40396E-01	1.58861E-01	8.27460E-02	6.33178E-02
8.47618E-01	1.51703E-01	7.80802E-02	5.90870E-02
8.54878E-01	1.44505E-01	7.34566E-02	5.49320E-02
8.62176E-01	1.37267E-01	6.88777E-02	5.08570E-02
8.69511E-01	1.29989E-01	6.43462E-02	4.68663E-02
8.76883E-01	1.22670E-01	5.98649E-02	4.29646E-02
8.84294E-01	1.15311E-01	5.54368E-02	3.91571E-02
8.91742E-01	1.07912E-01	5.10654E-02	3.54492E-02
8.99228E-01	1.00472E-01	4.67544E-02	3.18470E-02
9.06751E-01	9.29914E-02	4.25079E-02	2.83572E-02
9.14313E-01	8.54696E-02	3.83307E-02	2.49872E-02
9.21912E-01	7.79069E-02	3.42279E-02	2.17452E-02
9.29549E-01	7.03030E-02	3.02058E-02	1.86406E-02
9.37224E-01	6.26580E-02	2.62713E-02	1.56843E-02
9.44938E-01	5.49716E-02	2.24331E-02	1.28886E-02
9.52689E-01	4.72437E-02	1.87013E-02	1.02687E-02
9.60479E-01	3.94743E-02	1.50892E-02	7.84283E-03
9.68306E-01	3.16632E-02	1.16140E-02	5.63422E-03
9.76172E-01	2.38104E-02	8.29974E-03	3.67409E-03
9.84076E-01	1.59156E-02	5.18387E-03	2.00787E-03
9.92019E-01	7.97889E-03	2.33610E-03	7.12712E-04
9.96004E-01	3.99472E-03	1.06203E-03	2.52481E-04
1.00000E-00	0.00000E-99	0.00000E-99	0.00000E-99

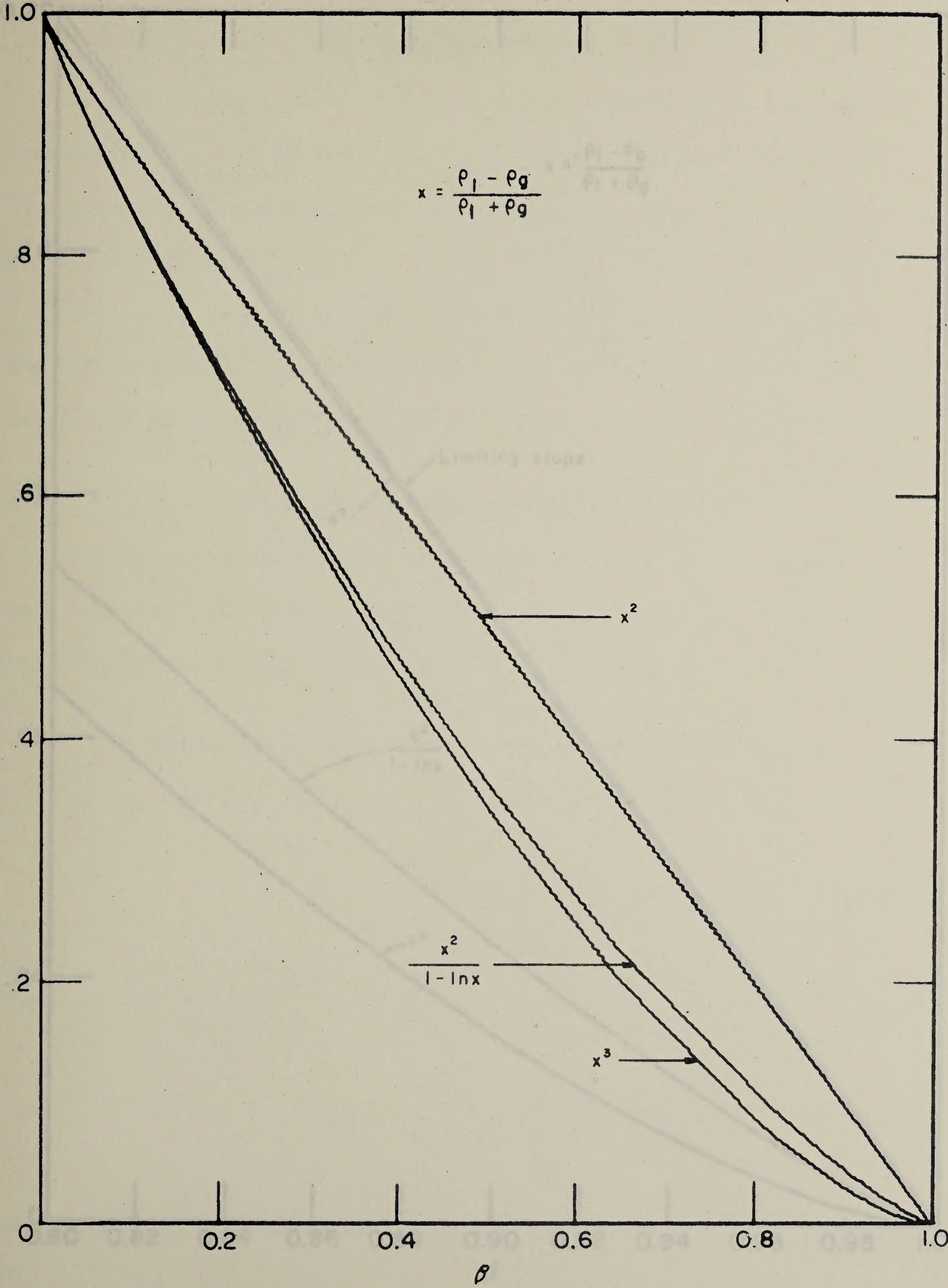

FIGURE 11.– Van der Waals Fluid, Coexistence Curves vs β; $\beta = P/P_c$

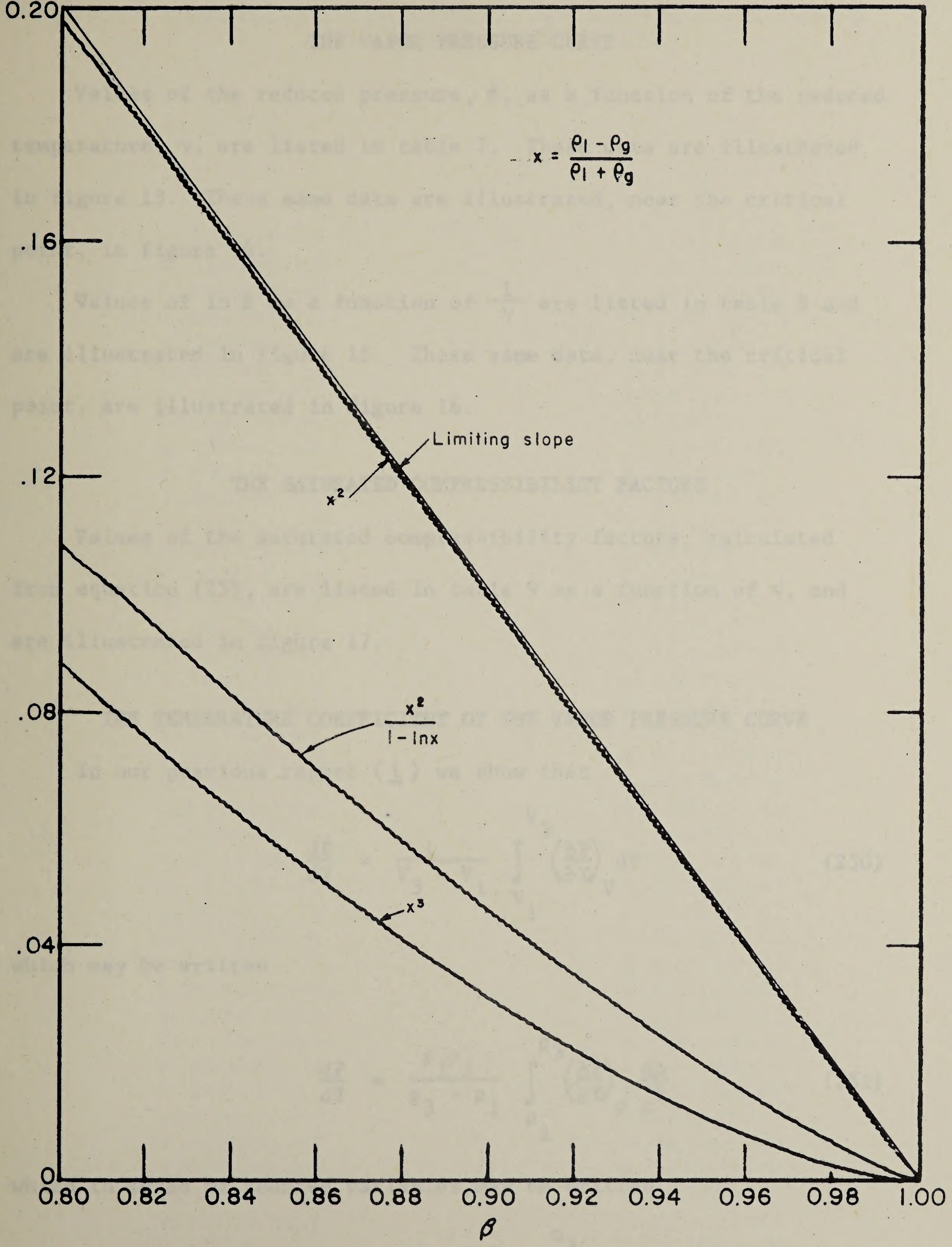

FIGURE 12.- Van der Waals Fluid, Coexistence Curves vs β; $\beta = P/P_c$

THE VAPOR PRESSURE CURVE

Values of the reduced pressure, β, as a function of the reduced temperature, γ, are listed in table 7. These data are illustrated in figure 13. These same data are illustrated, near the critical point, in figure 14.

Values of $\ln \beta$ as a function of $\frac{1}{\gamma}$ are listed in table 8 and are illustrated in figure 15. These same data, near the critical point, are illustrated in figure 16.

THE SATURATED COMPRESSIBILITY FACTORS

Values of the saturated compressibility factors, calculated from equation (25), are listed in table 9 as a function of γ, and are illustrated in figure 17.

THE TEMPERATURE COEFFICIENT OF THE VAPOR PRESSURE CURVE

In our previous report (1) we show that

$$\frac{dP}{dT} = \frac{1}{V_3 - V_1} \int_{V_1}^{V_3} \left(\frac{\partial P}{\partial T}\right)_V dV \qquad (250)$$

which may be written

$$\frac{dP}{dT} = \frac{\rho_1 \rho_3}{\rho_3 - \rho_1} \int_{\rho_1}^{\rho_3} \left(\frac{\partial P}{\partial T}\right)_\rho \frac{d\rho}{\rho^2} \qquad (251)$$

which in terms of reduced variables may be written

$$\frac{d\beta}{d\gamma} = \beta' = \frac{\alpha_1 \alpha_3}{\alpha_3 - \alpha_1} \int_{\alpha_1}^{\alpha_3} \left(\frac{\partial \beta}{\partial \gamma}\right)_\alpha \frac{d\alpha}{\alpha^2} \qquad (252)$$

TABLE 7. - VAN DER WAALS FLUID, VAPOR PRESSURE DATA AS A FUNCTION OF TEMPERATURE

$\beta = P/P_c$ $\gamma = T/T_c$

γ	β
2.50000E-01	3.41653E-05
3.00000E-01	3.18816E-04
3.50000E-01	1.56730E-03
4.00000E-01	5.17452E-03
4.50000E-01	1.31339E-02
5.00000E-01	2.77886E-02
5.50000E-01	5.15798E-02
6.00000E-01	8.68692E-02
6.50000E-01	1.35840E-01
7.00000E-01	2.00458E-01
7.50000E-01	2.82458E-01
8.00000E-01	3.83361E-01
8.50000E-01	5.04491E-01
9.00000E-01	6.46998E-01
9.50000E-01	8.11879E-01
9.52000E-01	8.18952E-01
9.54000E-01	8.26063E-01
9.56000E-01	8.33210E-01
9.58000E-01	8.40396E-01
9.60000E-01	8.47618E-01
9.62000E-01	8.54878E-01
9.64000E-01	8.62176E-01
9.66000E-01	8.69511E-01
9.68000E-01	8.76883E-01
9.70000E-01	8.84294E-01
9.72000E-01	8.91742E-01
9.74000E-01	8.99228E-01
9.76000E-01	9.06751E-01
9.78000E-01	9.14313E-01
9.80000E-01	9.21912E-01
9.82000E-01	9.29549E-01
9.84000E-01	9.37224E-01
9.86000E-01	9.44938E-01
9.88000E-01	9.52689E-01
9.90000E-01	9.60479E-01
9.92000E-01	9.68306E-01
9.94000E-01	9.76172E-01
9.96000E-01	9.84076E-01
9.98000E-01	9.92019E-01
9.99000E-01	9.96004E-01
1.00000E-00	1.00000E-00

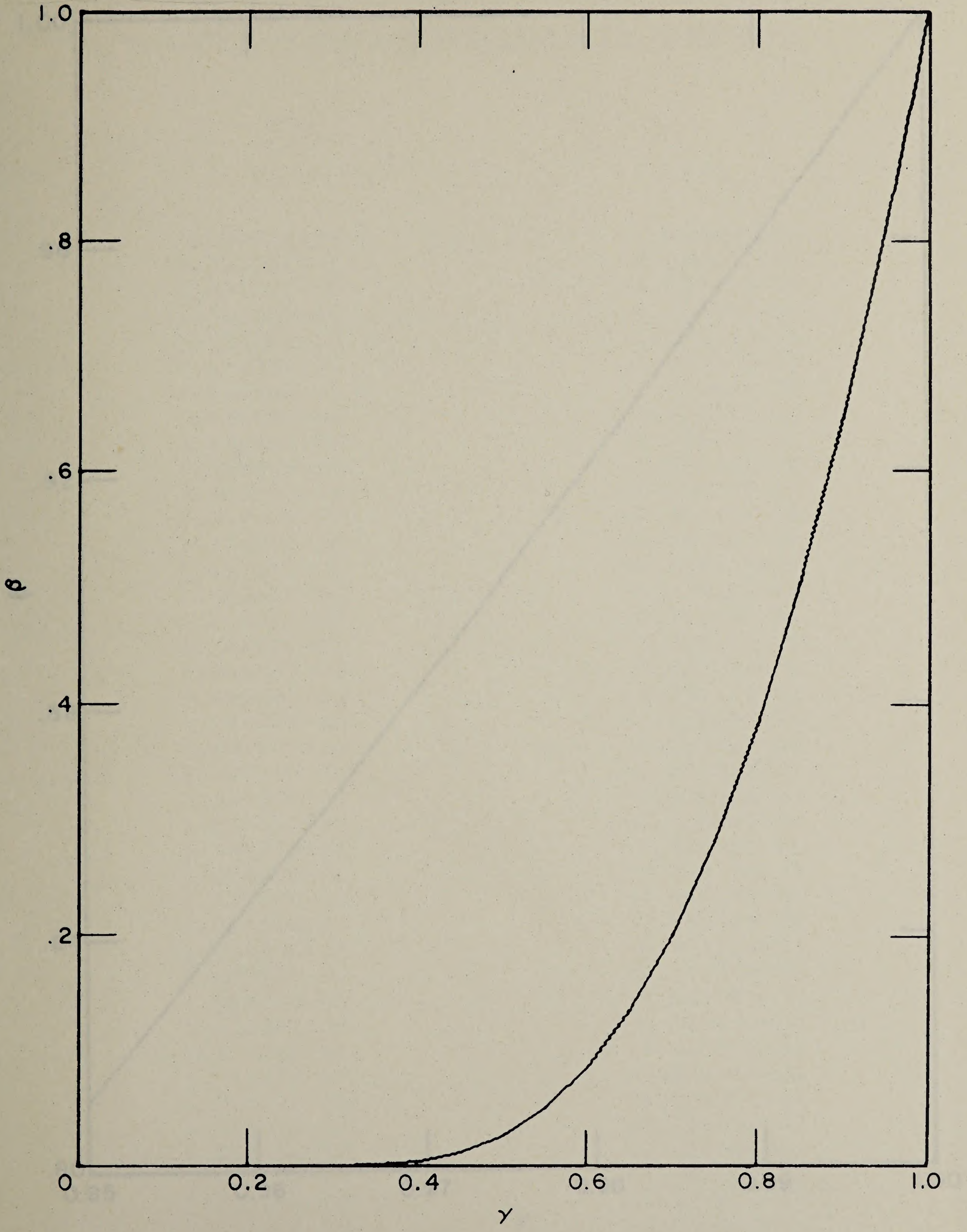

FIGURE 13.- Van der Waals Fluid,
Vapor Pressure Curve
$\beta = P/P_c$; $\gamma = T/T_c$

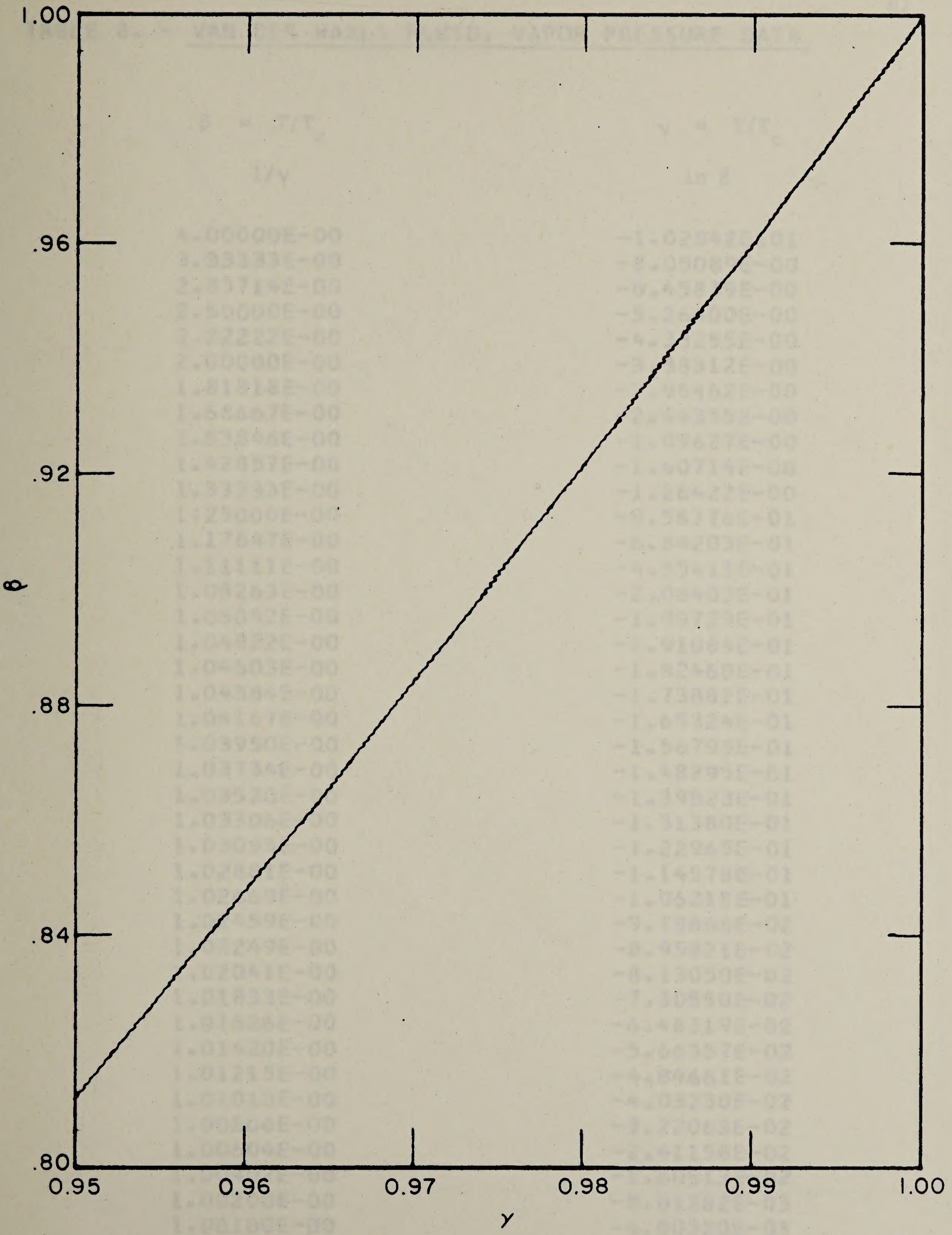

FIGURE 14.- Van der Waals Fluid,
Vapor Pressure Curve;
$\beta = P/P_c$; $\gamma = T/T_c$

TABLE 8. - VAN DER WAALS FLUID, VAPOR PRESSURE DATA

$\beta = T/T_c$ $1/\gamma$	$\gamma = T/T_c$ $\ln \beta$
4.00000E-00	-1.02842E&01
3.33333E-00	-8.05089E-00
2.85714E-00	-6.45839E-00
2.50000E-00	-5.26400E-00
2.22222E-00	-4.33255E-00
2.00000E-00	-3.58312E-00
1.81818E-00	-2.96462E-00
1.66667E-00	-2.44335E-00
1.53846E-00	-1.99627E-00
1.42857E-00	-1.60714E-00
1.33333E-00	-1.26422E-00
1.25000E-00	-9.58776E-01
1.17647E-00	-6.84203E-01
1.11111E-00	-4.35411E-01
1.05263E-00	-2.08403E-01
1.05042E-00	-1.99729E-01
1.04822E-00	-1.91084E-01
1.04603E-00	-1.82468E-01
1.04384E-00	-1.73882E-01
1.04167E-00	-1.65324E-01
1.03950E-00	-1.56795E-01
1.03734E-00	-1.48295E-01
1.03520E-00	-1.39823E-01
1.03306E-00	-1.31380E-01
1.03093E-00	-1.22965E-01
1.02881E-00	-1.14578E-01
1.02669E-00	-1.06218E-01
1.02459E-00	-9.78866E-02
1.02249E-00	-8.95821E-02
1.02041E-00	-8.13050E-02
1.01833E-00	-7.30550E-02
1.01626E-00	-6.48319E-02
1.01420E-00	-5.66357E-02
1.01215E-00	-4.84661E-02
1.01010E-00	-4.03230E-02
1.00806E-00	-3.22063E-02
1.00604E-00	-2.41158E-02
1.00402E-00	-1.60513E-02
1.00200E-00	-8.01282E-03
1.00100E-00	-4.00320E-03
1.00000E-00	0.00000E-99

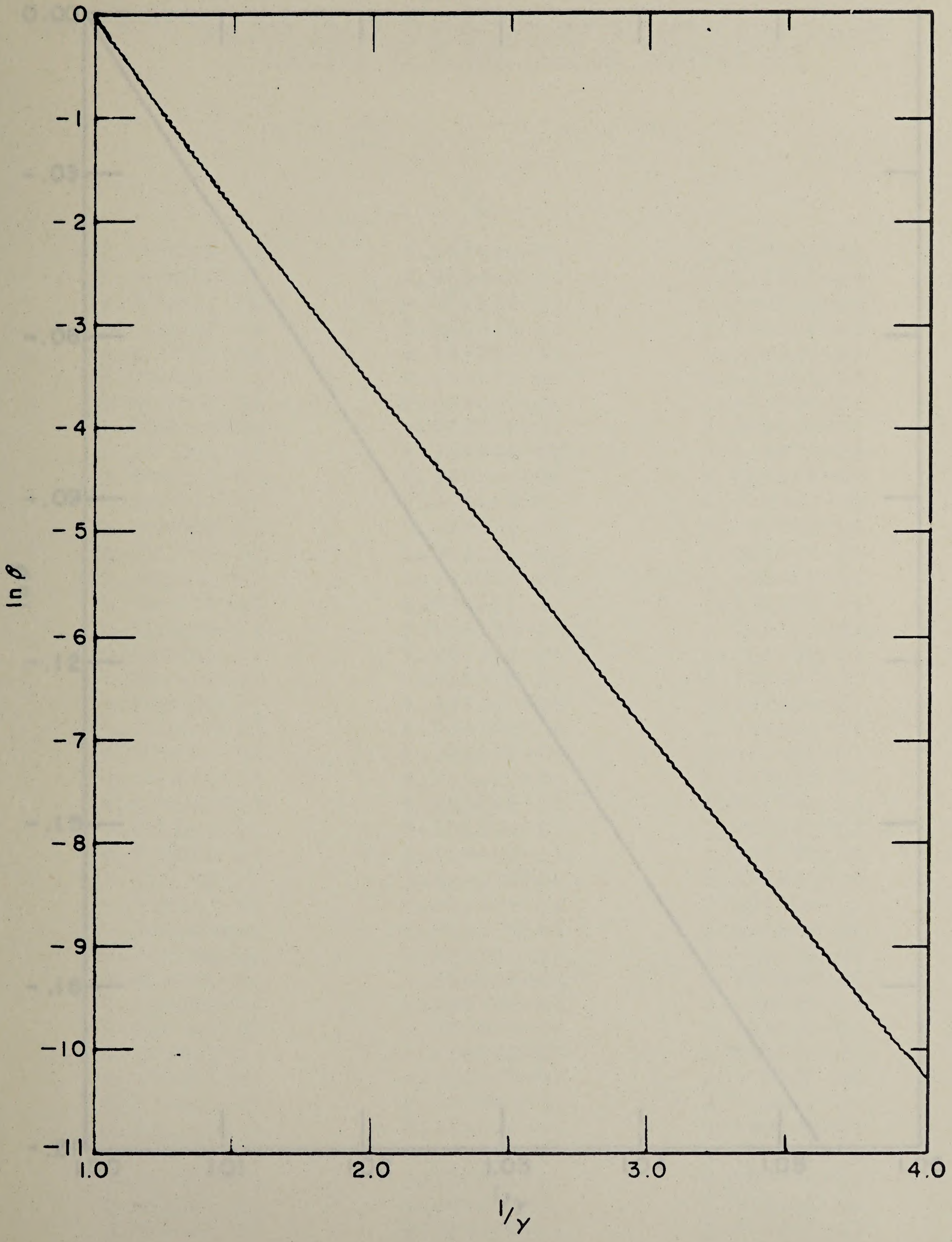

FIGURE 15.- Van der Waals Fluid,
$\ln \beta$ vs $^1/_\gamma$; $\beta = {}^P/_{P_c}$; $\gamma = {}^T/_{T_c}$

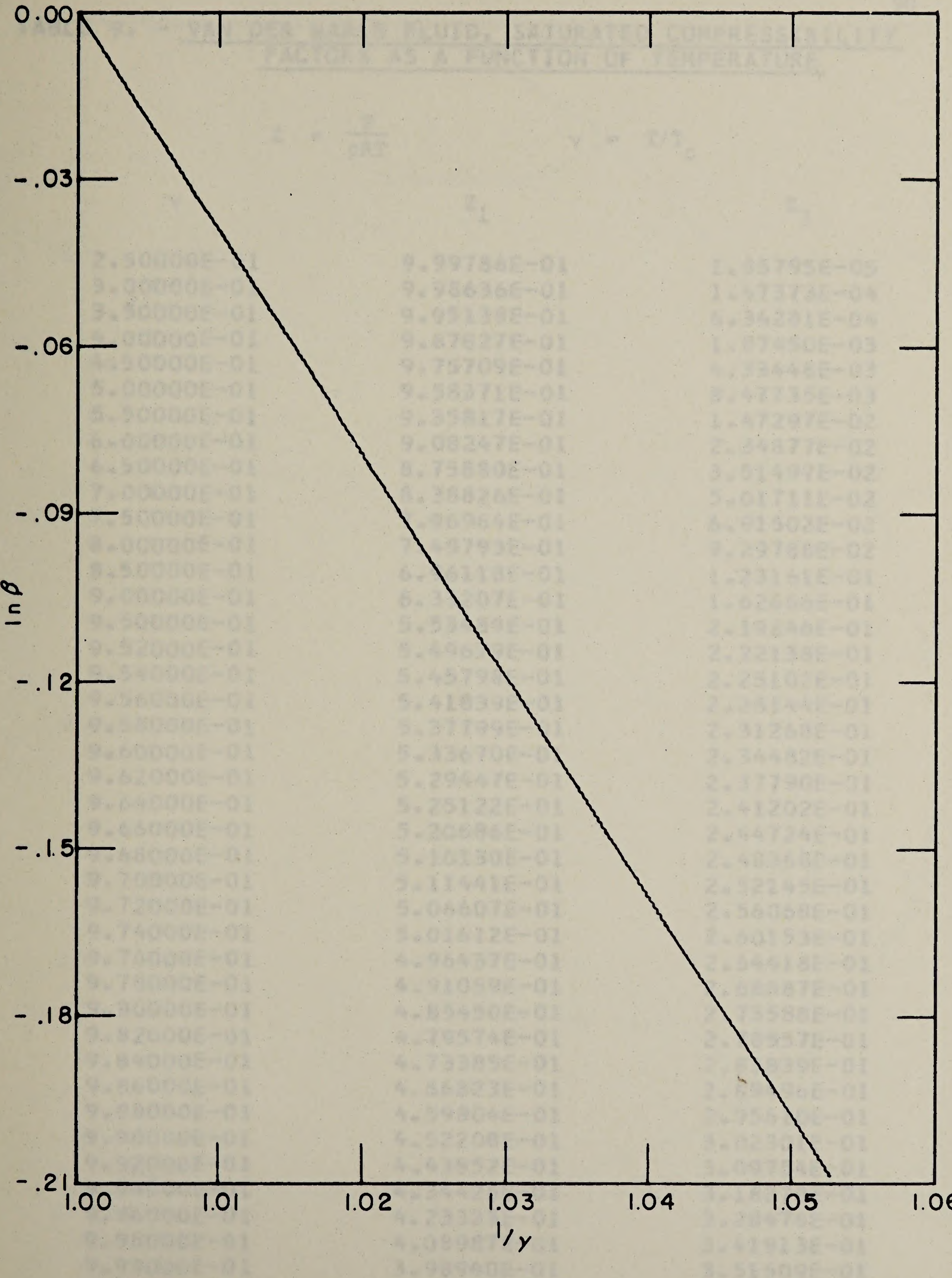

FIGURE 16.- Van der Waals Fluid, ln β vs $1/\gamma$; $\beta = P/P_c$; $\gamma = T/T_c$

TABLE 9. - VAN DER WAALS FLUID, SATURATED COMPRESSIBILITY FACTORS AS A FUNCTION OF TEMPERATURE

$Z = \frac{P}{\rho RT}$ $\gamma = T/T_c$

γ	Z_1	Z_3
2.50000E-01	9.99786E-01	1.85795E-05
3.00000E-01	9.98636E-01	1.47373E-04
3.50000E-01	9.95138E-01	6.34281E-04
4.00000E-01	9.87827E-01	1.87450E-03
4.50000E-01	9.75709E-01	4.33448E-03
5.00000E-01	9.58371E-01	8.47735E-03
5.50000E-01	9.35817E-01	1.47297E-02
6.00000E-01	9.08247E-01	2.34877E-02
6.50000E-01	8.75880E-01	3.51497E-02
7.00000E-01	8.38826E-01	5.01711E-02
7.50000E-01	7.96964E-01	6.91502E-02
8.00000E-01	7.49793E-01	9.29788E-02
8.50000E-01	6.96118E-01	1.23161E-01
9.00000E-01	6.33207E-01	1.62666E-01
9.50000E-01	5.53489E-01	2.19246E-01
9.52000E-01	5.49679E-01	2.22138E-01
9.54000E-01	5.45798E-01	2.25102E-01
9.56000E-01	5.41839E-01	2.28144E-01
9.58000E-01	5.37799E-01	2.31268E-01
9.60000E-01	5.33670E-01	2.34482E-01
9.62000E-01	5.29447E-01	2.37790E-01
9.64000E-01	5.25122E-01	2.41202E-01
9.66000E-01	5.20686E-01	2.44724E-01
9.68000E-01	5.16130E-01	2.48368E-01
9.70000E-01	5.11441E-01	2.52145E-01
9.72000E-01	5.06607E-01	2.56068E-01
9.74000E-01	5.01612E-01	2.60153E-01
9.76000E-01	4.96437E-01	2.64418E-01
9.78000E-01	4.91059E-01	2.68887E-01
9.80000E-01	4.85450E-01	2.73588E-01
9.82000E-01	4.79574E-01	2.78557E-01
9.84000E-01	4.73385E-01	2.83839E-01
9.86000E-01	4.66823E-01	2.89496E-01
9.88000E-01	4.59804E-01	2.95610E-01
9.90000E-01	4.52208E-01	3.02301E-01
9.92000E-01	4.43852E-01	3.09754E-01
9.94000E-01	4.34425E-01	3.18278E-01
9.96000E-01	4.23323E-01	3.28478E-01
9.98000E-01	4.08987E-01	3.41913E-01
9.99000E-01	3.98940E-01	3.51509E-01
1.00000E-00	3.75000E-01	3.75000E-01

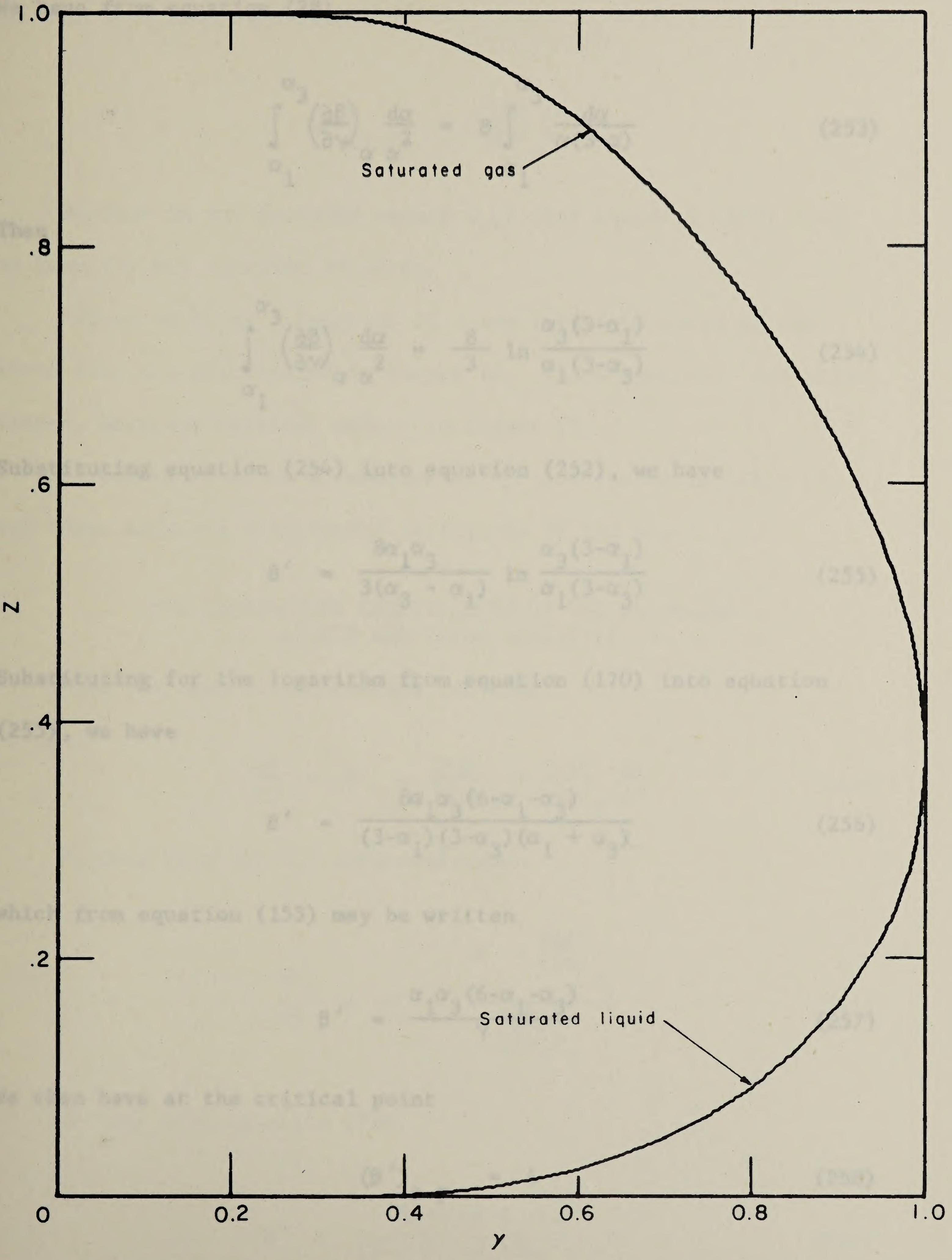

FIGURE 17.- Van der Waals Fluid, Saturated Compressibility Factors vs y; $Z = \frac{P}{\rho RT}$; $y = T/T_c$

We have from equation (28)

$$\int_{\alpha_1}^{\alpha_3} \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha} \frac{d\alpha}{\alpha^2} = 8\int_{\alpha_1}^{\alpha_3} \frac{d\alpha}{\alpha(3-\alpha)} \tag{253}$$

Then

$$\int_{\alpha_1}^{\alpha_3} \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha} \frac{d\alpha}{\alpha^2} = \frac{8}{3} \ln \frac{\alpha_3(3-\alpha_1)}{\alpha_1(3-\alpha_3)} \tag{254}$$

Substituting equation (254) into equation (252), we have

$$\beta' = \frac{8\alpha_1\alpha_3}{3(\alpha_3 - \alpha_1)} \ln \frac{\alpha_3(3-\alpha_1)}{\alpha_1(3-\alpha_3)} \tag{255}$$

Substituting for the logarithm from equation (170) into equation (255), we have

$$\beta' = \frac{8\alpha_1\alpha_3(6-\alpha_1-\alpha_3)}{(3-\alpha_1)(3-\alpha_3)(\alpha_1 + \alpha_3)} \tag{256}$$

which from equation (155) may be written

$$\beta' = \frac{\alpha_1\alpha_3(6-\alpha_1-\alpha_3)}{\gamma} \tag{257}$$

We then have at the critical point

$$(\beta')_{c.p.} = 4 \tag{258}$$

We then have from equation (29)

$$(\beta')_{c.p.} = \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha} \left(\begin{matrix}\alpha=1\\ \gamma=1\end{matrix}\right) \tag{259}$$

We show in our previous report (1) that equation (259) will be true for any equation of state.

Values of β' as a function of γ are listed in table 10 and these data are illustrated in figure 18. These same data are illustrated, near the critical point, in figure 19.

Values of $\ln \beta'$ as a function of $\frac{1}{\gamma}$ are listed in table 11, and these data are illustrated in figures 20 and 21.

THE TEMPERATURE COEFFICIENTS OF THE SATURATED LIQUID AND VAPOR DENSITIES

From the laws of mathematics, we have

$$\frac{d\beta}{d\gamma} = \beta' = \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha} + \left(\frac{\partial\beta}{\partial\alpha}\right)_{\gamma} \frac{d\alpha}{d\gamma} \tag{260}$$

We then have for the saturated vapor

$$\frac{d\alpha_1}{d\gamma} = \alpha_1' = \frac{\beta' - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1}}{\left(\frac{\partial\beta}{\partial\alpha_1}\right)_{\gamma}} \tag{261}$$

We have from equation (256)

$$\beta' = \frac{8\alpha_1\alpha_3(6-\alpha_1-\alpha_3)}{(3-\alpha_1)(3-\alpha_3)(\alpha_1 + \alpha_3)} \tag{256}$$

TABLE 10. - VAN DER WAALS FLUID, TEMPERATURE COEFFICIENT OF THE VAPOR PRESSURE CURVE AS A FUNCTION OF TEMPERATURE

$\beta' = \frac{d\beta}{d\gamma}$ $\beta = P/P_c$ $\gamma = T/T_c$

γ	β'
2.50000E-01	1.83331E-03
3.00000E-01	1.18541E-02
3.50000E-01	4.27711E-02
4.00000E-01	1.08254E-01
4.50000E-01	2.18021E-01
5.00000E-01	3.76363E-01
5.50000E-01	5.83186E-01
6.00000E-01	8.35684E-01
6.50000E-01	1.12972E-00
7.00000E-01	1.46075E-00
7.50000E-01	1.82430E-00
8.00000E-01	2.21622E-00
8.50000E-01	2.63280E-00
9.00000E-01	3.07078E-00
9.50000E-01	3.52733E-00
9.52000E-01	3.54594E-00
9.54000E-01	3.56458E-00
9.56000E-01	3.58324E-00
9.58000E-01	3.60193E-00
9.60000E-01	3.62064E-00
9.62000E-01	3.63938E-00
9.64000E-01	3.65815E-00
9.66000E-01	3.67693E-00
9.68000E-01	3.69575E-00
9.70000E-01	3.71458E-00
9.72000E-01	3.73345E-00
9.74000E-01	3.75233E-00
9.76000E-01	3.77124E-00
9.78000E-01	3.79018E-00
9.80000E-01	3.80914E-00
9.82000E-01	3.82812E-00
9.84000E-01	3.84712E-00
9.86000E-01	3.86615E-00
9.88000E-01	3.88520E-00
9.90000E-01	3.90428E-00
9.92000E-01	3.92338E-00
9.94000E-01	3.94250E-00
9.96000E-01	3.96164E-00
9.98000E-01	3.98081E-00
9.99000E-01	3.99040E-00
1.00000E-00	4.00000E-00

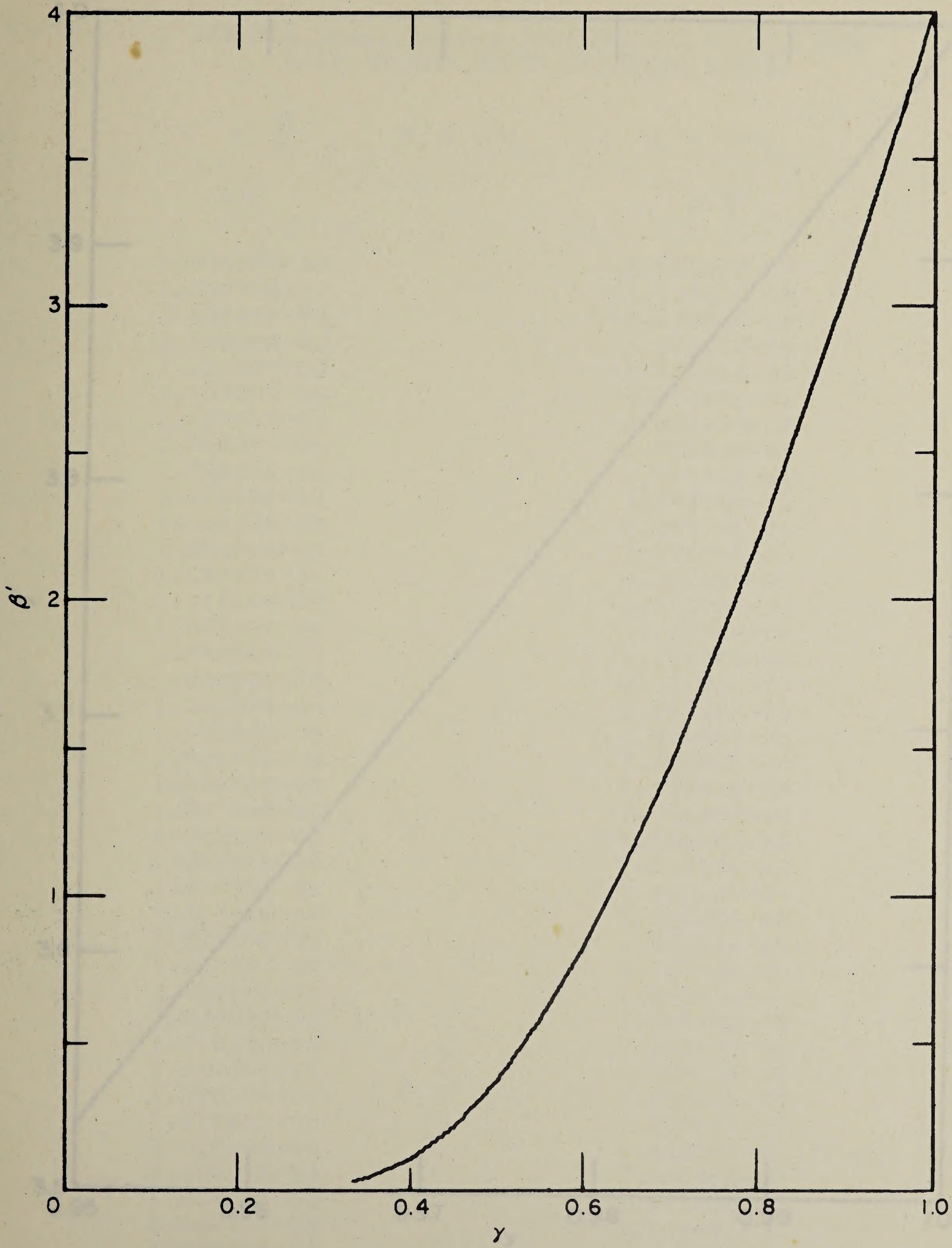

FIGURE 18.- Van der Waals Fluid, β' vs γ;
$\beta' = \frac{d\beta}{d\gamma}$; $\beta = P/P_c$; $\gamma = T/T_c$

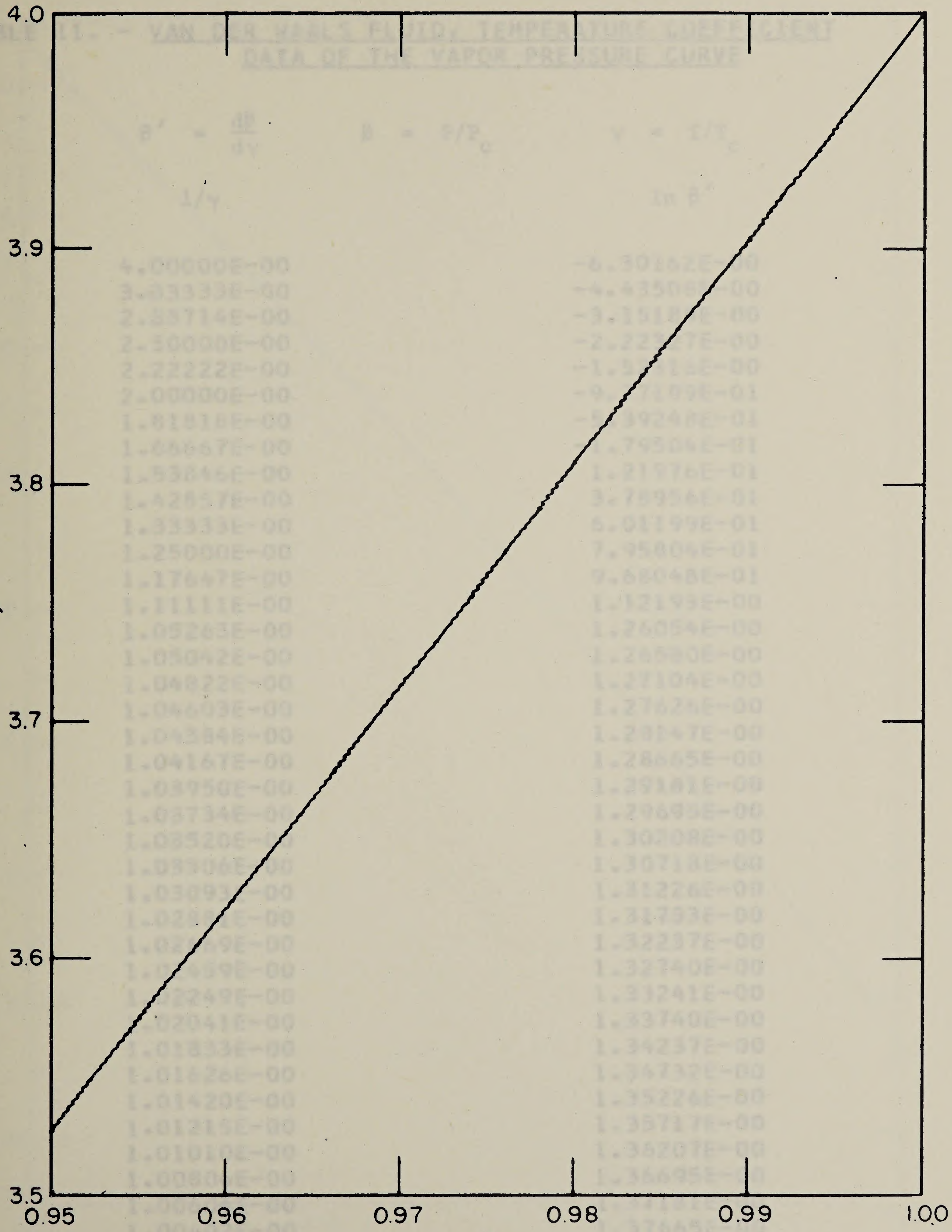

FIGURE 19.- Van der Waals Fluid β' vs γ; $\beta' = \frac{d\beta}{d\gamma}$; $\beta = P/P_c$; $\gamma = T/T_c$

TABLE 11. - VAN DER WAALS FLUID, TEMPERATURE COEFFICIENT DATA OF THE VAPOR PRESSURE CURVE

$\beta' = \frac{d\beta}{d\gamma}$ $\beta = P/P_c$ $\gamma = T/T_c$

$1/\gamma$	$\ln \beta'$
4.00000E-00	-6.30162E-00
3.33333E-00	-4.43508E-00
2.85714E-00	-3.15189E-00
2.50000E-00	-2.22327E-00
2.22222E-00	-1.52316E-00
2.00000E-00	-9.77199E-01
1.81818E-00	-5.39248E-01
1.66667E-00	-1.79504E-01
1.53846E-00	1.21976E-01
1.42857E-00	3.78956E-01
1.33333E-00	6.01199E-01
1.25000E-00	7.95804E-01
1.17647E-00	9.68048E-01
1.11111E-00	1.12193E-00
1.05263E-00	1.26054E-00
1.05042E-00	1.26580E-00
1.04822E-00	1.27104E-00
1.04603E-00	1.27626E-00
1.04384E-00	1.28147E-00
1.04167E-00	1.28665E-00
1.03950E-00	1.29181E-00
1.03734E-00	1.29695E-00
1.03520E-00	1.30208E-00
1.03306E-00	1.30718E-00
1.03093E-00	1.31226E-00
1.02881E-00	1.31733E-00
1.02669E-00	1.32237E-00
1.02459E-00	1.32740E-00
1.02249E-00	1.33241E-00
1.02041E-00	1.33740E-00
1.01833E-00	1.34237E-00
1.01626E-00	1.34732E-00
1.01420E-00	1.35226E-00
1.01215E-00	1.35717E-00
1.01010E-00	1.36207E-00
1.00806E-00	1.36695E-00
1.00604E-00	1.37181E-00
1.00402E-00	1.37665E-00
1.00200E-00	1.38148E-00
1.00100E-00	1.38389E-00
1.00000E-00	1.38629E-00

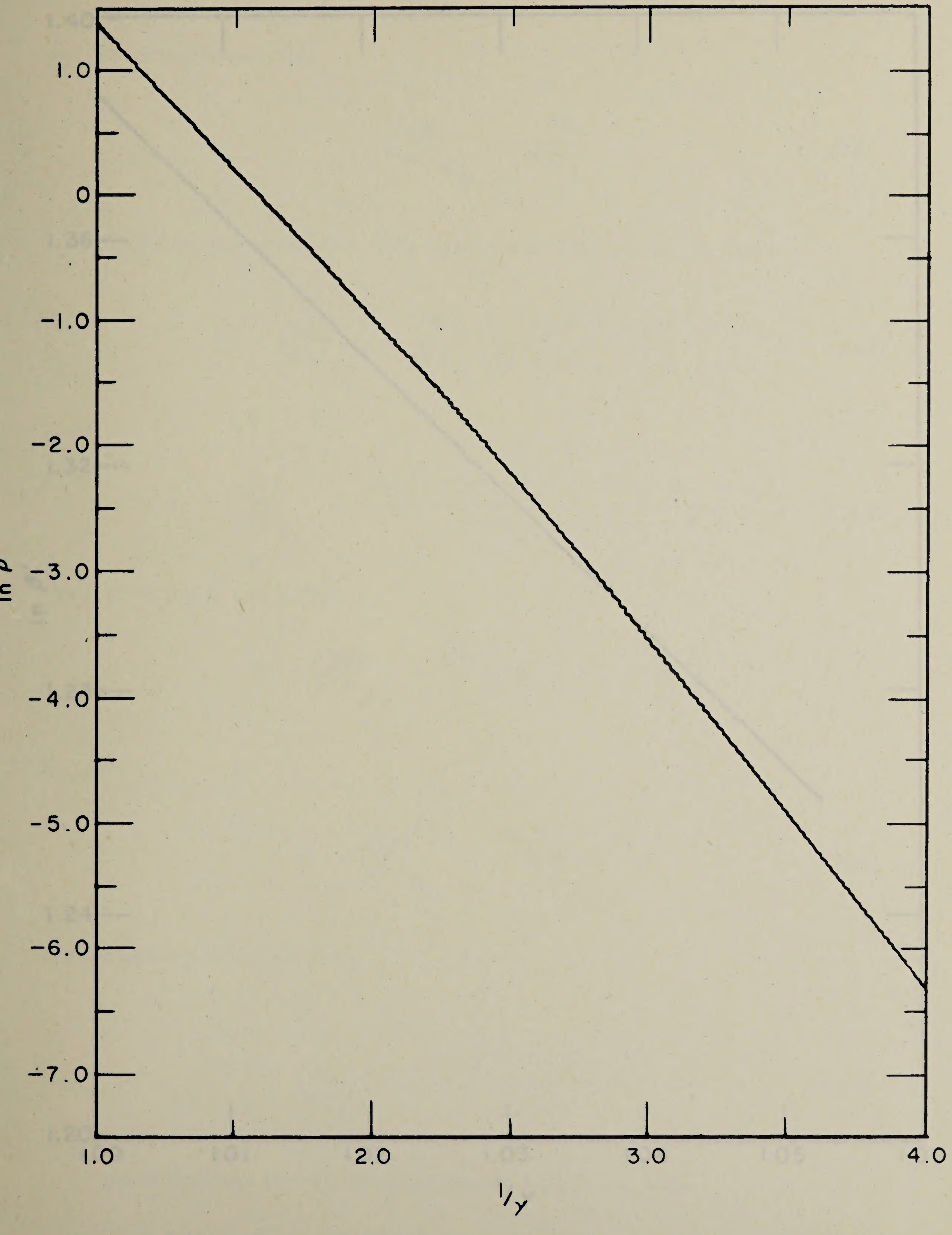

FIGURE 20.- Van der Waals Fluid,
$\ln \beta'$ vs $1/\gamma$; $\beta' = \frac{d\beta}{d\gamma}$
$\beta = P/P_c$; $\gamma = T/T_c$

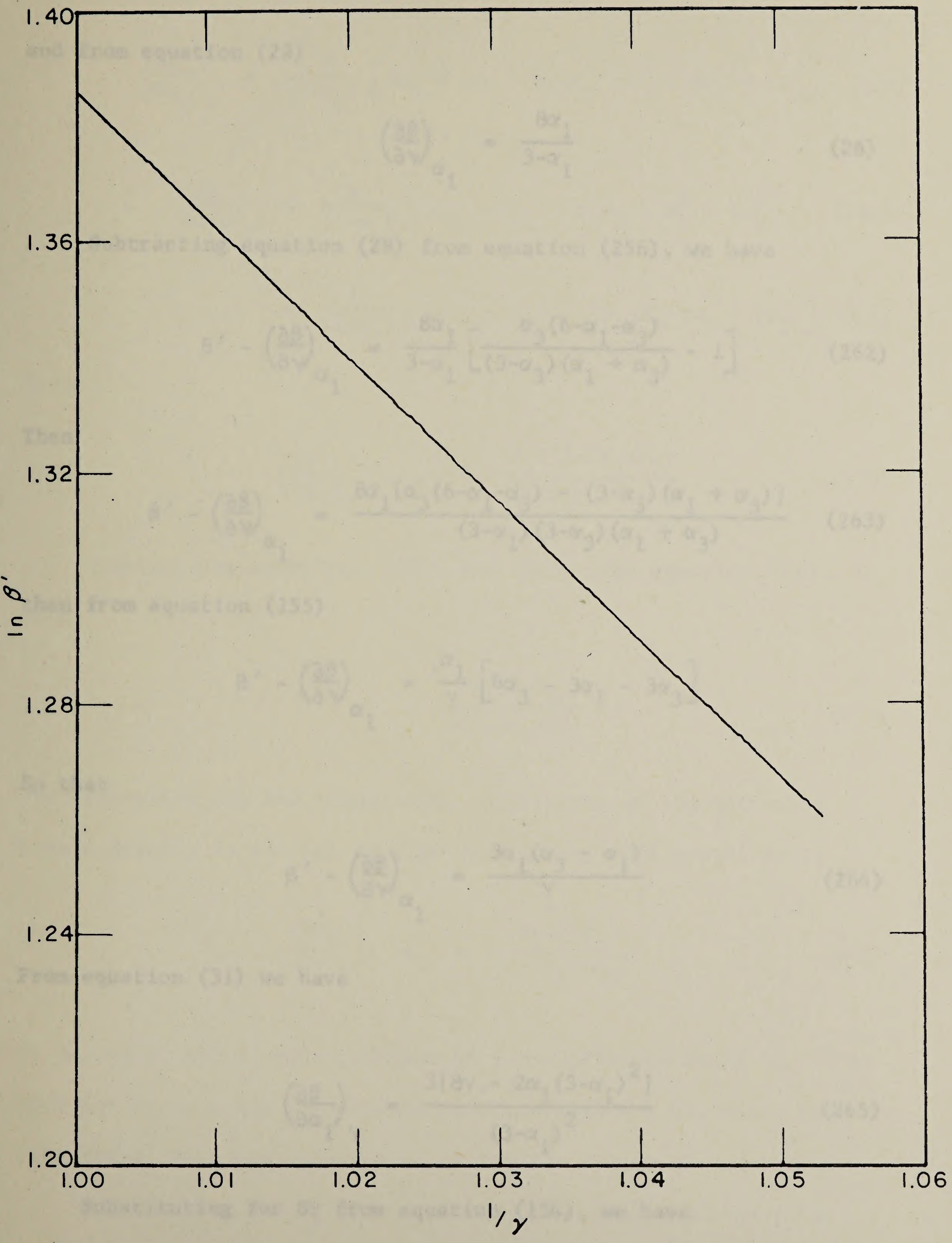

FIGURE 21.- Van der Waals Fluid, ln β' vs $1/\gamma$; $\beta = P/P_c$; $\gamma = T/T_c$

and from equation (28)

$$\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1} = \frac{8\alpha_1}{3-\alpha_1} \tag{28}$$

Subtracting equation (28) from equation (256), we have

$$\beta' - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1} = \frac{8\alpha_1}{3-\alpha_1}\left[\frac{\alpha_3(6-\alpha_1-\alpha_3)}{(3-\alpha_3)(\alpha_1+\alpha_3)} - 1\right] \tag{262}$$

Then

$$\beta' - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1} = \frac{8\alpha_1[\alpha_3(6-\alpha_1-\alpha_3) - (3-\alpha_3)(\alpha_1+\alpha_3)]}{(3-\alpha_1)(3-\alpha_3)(\alpha_1+\alpha_3)} \tag{263}$$

then from equation (155)

$$\beta' - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1} = \frac{\alpha_1}{\gamma}\left[6\alpha_3 - 3\alpha_1 - 3\alpha_3\right]$$

So that

$$\beta' - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1} = \frac{3\alpha_1(\alpha_3-\alpha_1)}{\gamma} \tag{264}$$

From equation (31) we have

$$\left(\frac{\partial\beta}{\partial\alpha_1}\right)_{\gamma} = \frac{3[8\gamma - 2\alpha_1(3-\alpha_1)^2]}{(3-\alpha_1)^2} \tag{265}$$

Substituting for 8γ from equation (154), we have

$$\left(\frac{\partial\beta}{\partial\alpha_1}\right)_{\gamma} = \frac{3(3-\alpha_1)}{(3-\alpha_1)^2}\left[(3-\alpha_3)(\alpha_1+\alpha_3) - 2\alpha_1(3-\alpha_1)\right] \tag{266}$$

$$\left(\frac{\partial \beta}{\partial \alpha_1}\right)_\gamma = \frac{3}{(3-\alpha_1)}\left[3\alpha_1 + 3\alpha_3 - \alpha_1\alpha_3 - \alpha_3^2 - 6\alpha_1 + 2\alpha_1^2\right] \quad (267)$$

$$\left(\frac{\partial \beta}{\partial \alpha_1}\right)_\gamma = \frac{3}{(3-\alpha_1)}\left[3\alpha_3 - 3\alpha_1 - \alpha_1\alpha_3 - \alpha_3^2 + 2\alpha_1^2\right] \quad (268)$$

$$= \frac{3}{(3-\alpha_1)}\left[3(\alpha_3 - \alpha_1) + (\alpha_1-\alpha_3)(\alpha_3 + 2\alpha_1)\right] \quad (269)$$

Then

$$\left(\frac{\partial \beta}{\partial \alpha_1}\right)_\gamma = \frac{3(\alpha_3 - \alpha_1)(3-2\alpha_1-\alpha_3)}{(3-\alpha_1)} \quad (270)$$

Substituting equations (264) and (270) into equation (261), we have

$$\alpha_1' = \frac{\alpha_1(3-\alpha_1)}{\gamma(3-2\alpha_1-\alpha_3)} \quad (271)$$

The derivation for the temperature coefficient of the saturated liquid density is similar to that just given. The result is

$$\frac{d\alpha_3}{d\gamma} = \alpha_3' = \frac{\alpha_3(3-\alpha_3)}{\gamma(3-\alpha_1-2\alpha_3)} \quad (272)$$

Values of α_1' and α_3' as a function of γ are given in table 12. The data for α_1' vs γ are illustrated in figures 22 and 23, while the data for α_3' vs γ are illustrated in figures 24 and 25.

Substituting for α_3 from equation (224) into equation (271), we find near the critical point

TABLE 12. - VAN DER WAALS FLUID, TEMPERATURE COEFFICIENTS OF SATURATED LIQUID AND VAPOR DENSITIES AS A FUNCTION OF TEMPERATURE

$\alpha' = \frac{d\alpha}{d\gamma}$ $\alpha = \rho/\rho_c$ $\gamma = T/T_c$

γ	α'_1	α'_3
2.50000E-01	2.54602E-03	-1.05960E-00
3.00000E-01	1.35241E-02	-1.10706E-00
3.50000E-01	4.14047E-02	-1.16101E-00
4.00000E-01	9.14163E-02	-1.22248E-00
4.50000E-01	1.64660E-01	-1.29272E-00
5.00000E-01	2.60102E-01	-1.37336E-00
5.50000E-01	3.76731E-01	-1.46669E-00
6.00000E-01	5.14926E-01	-1.57603E-00
6.50000E-01	6.77395E-01	-1.70636E-00
7.00000E-01	8.70326E-01	-1.86551E-00
7.50000E-01	1.10566E-00	-2.06654E-00
8.00000E-01	1.40647E-00	-2.33327E-00
8.50000E-01	1.82181E-00	-2.71525E-00
9.00000E-01	2.47888E-00	-3.33996E-00
9.50000E-01	3.88058E-00	-4.71049E-00
9.52000E-01	3.97706E-00	-4.80575E-00
9.54000E-01	4.07957E-00	-4.90703E-00
9.56000E-01	4.18877E-00	-5.01502E-00
9.58000E-01	4.30545E-00	-5.13048E-00
9.60000E-01	4.43052E-00	-5.25434E-00
9.62000E-01	4.56509E-00	-5.38770E-00
9.64000E-01	4.71043E-00	-5.53183E-00
9.66000E-01	4.86811E-00	-5.68831E-00
9.68000E-01	5.04002E-00	-5.85901E-00
9.70000E-01	5.22849E-00	-6.04628E-00
9.72000E-01	5.43641E-00	-6.25300E-00
9.74000E-01	5.66745E-00	-6.48284E-00
9.76000E-01	5.92631E-00	-6.74050E-00
9.78000E-01	6.21917E-00	-7.03217E-00
9.80000E-01	6.55430E-00	-7.36611E-00
9.82000E-01	6.94313E-00	-7.75375E-00
9.84000E-01	7.40192E-00	-8.21135E-00
9.86000E-01	7.95480E-00	-8.76305E-00
9.88000E-01	8.63947E-00	-9.44653E-00
9.90000E-01	9.51886E-00	-1.03247E&01
9.92000E-01	1.07080E&01	-1.15127E&01
9.94000E-01	1.24476E&01	-1.32511E&01
9.96000E-01	1.53608E&01	-1.61631E&01
9.98000E-01	2.19251E&01	-2.27263E&01
9.99000E-01	3.11978E&01	-3.19983E&01
1.00000E-00	$+\infty$	$-\infty$

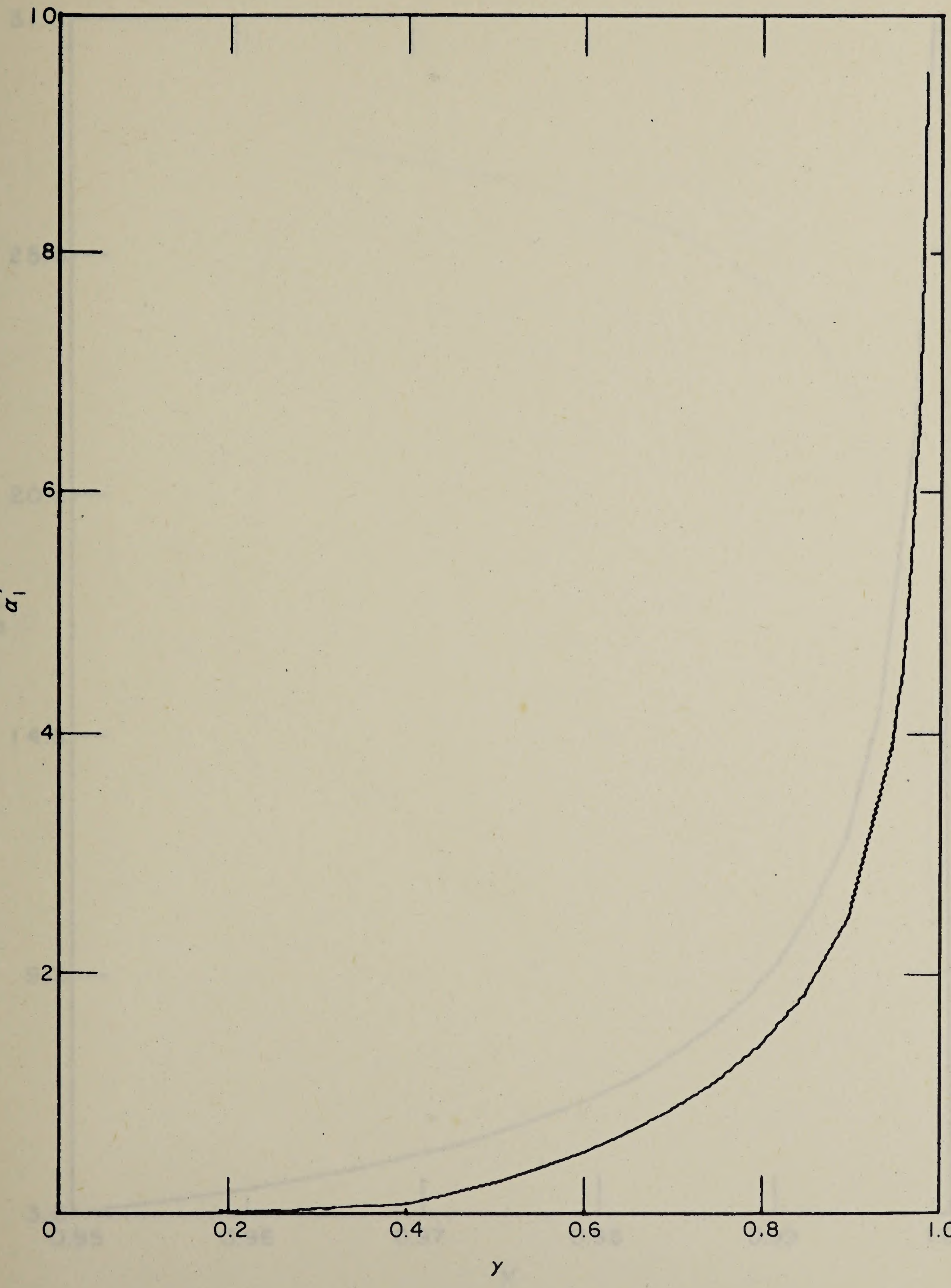

FIGURE 22.-Van der Waals Fluid, α_1' vs γ;

$\alpha_1' = \frac{d\alpha_1}{d\gamma}$; $\alpha_1 = \rho_g/\rho_c$; $\gamma = T/T_c$

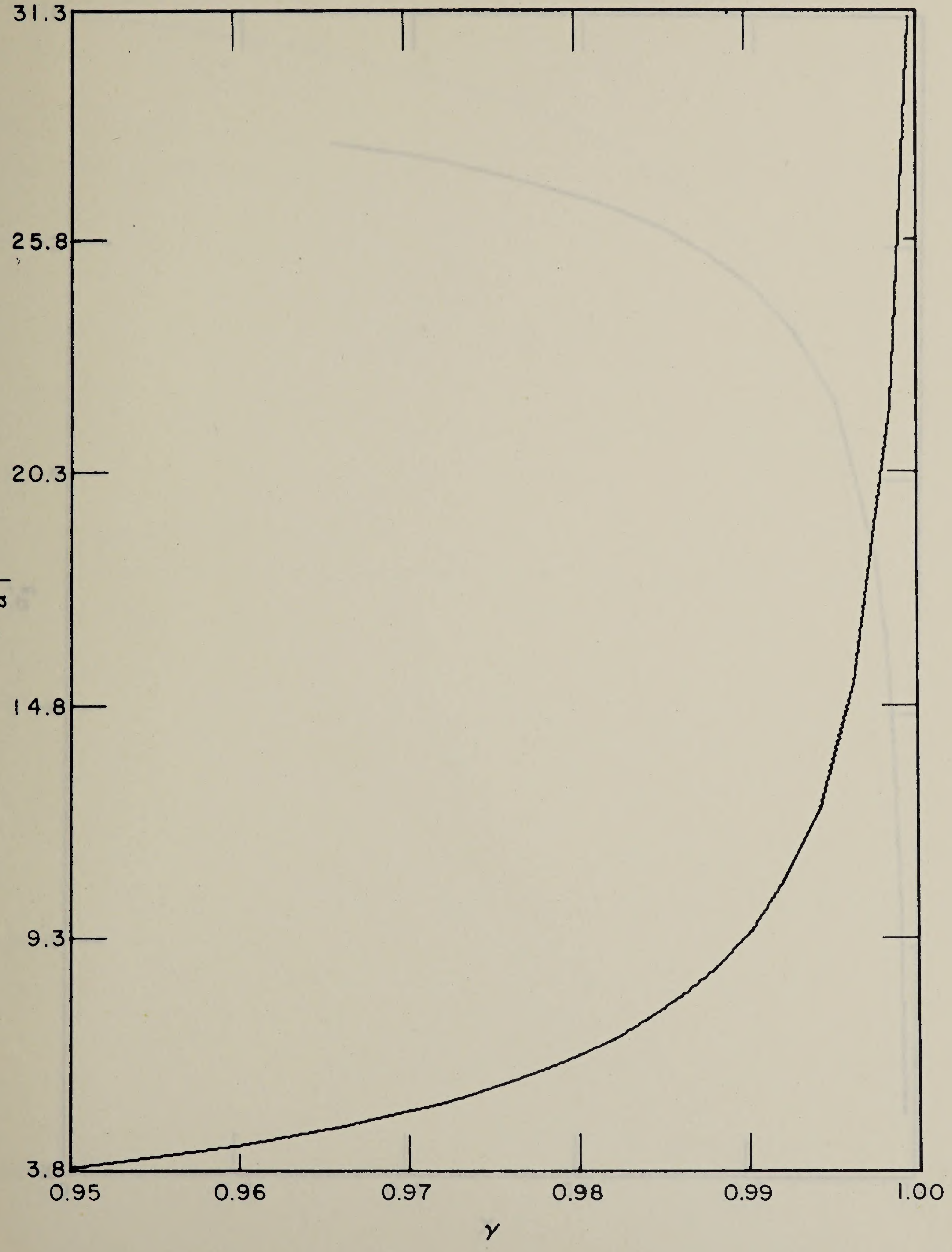

FIGURE 23.- Van der Waals Fluid, α_1' vs γ; $\alpha_1' = d\alpha_1/d\gamma$; $\alpha_1 = \rho_g/\rho_c$; $\gamma = T/T_c$

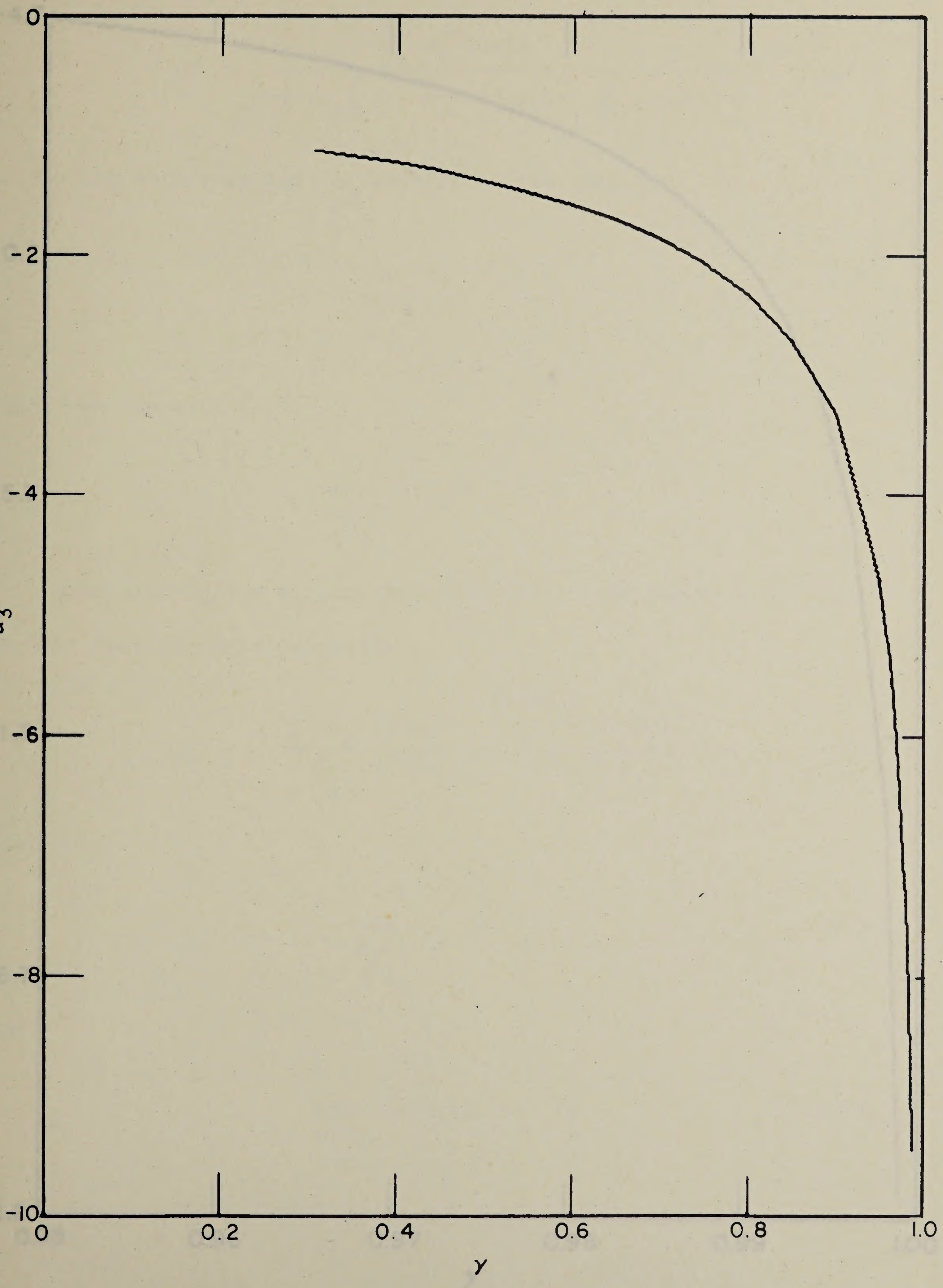

FIGURE 24.- Van der Waals Fluid, α_3' vs γ;
$\alpha_3' = \frac{d\alpha_3}{d\gamma}$; $\alpha_3 = \rho_l/\rho_c$; $\gamma = T/T_c$

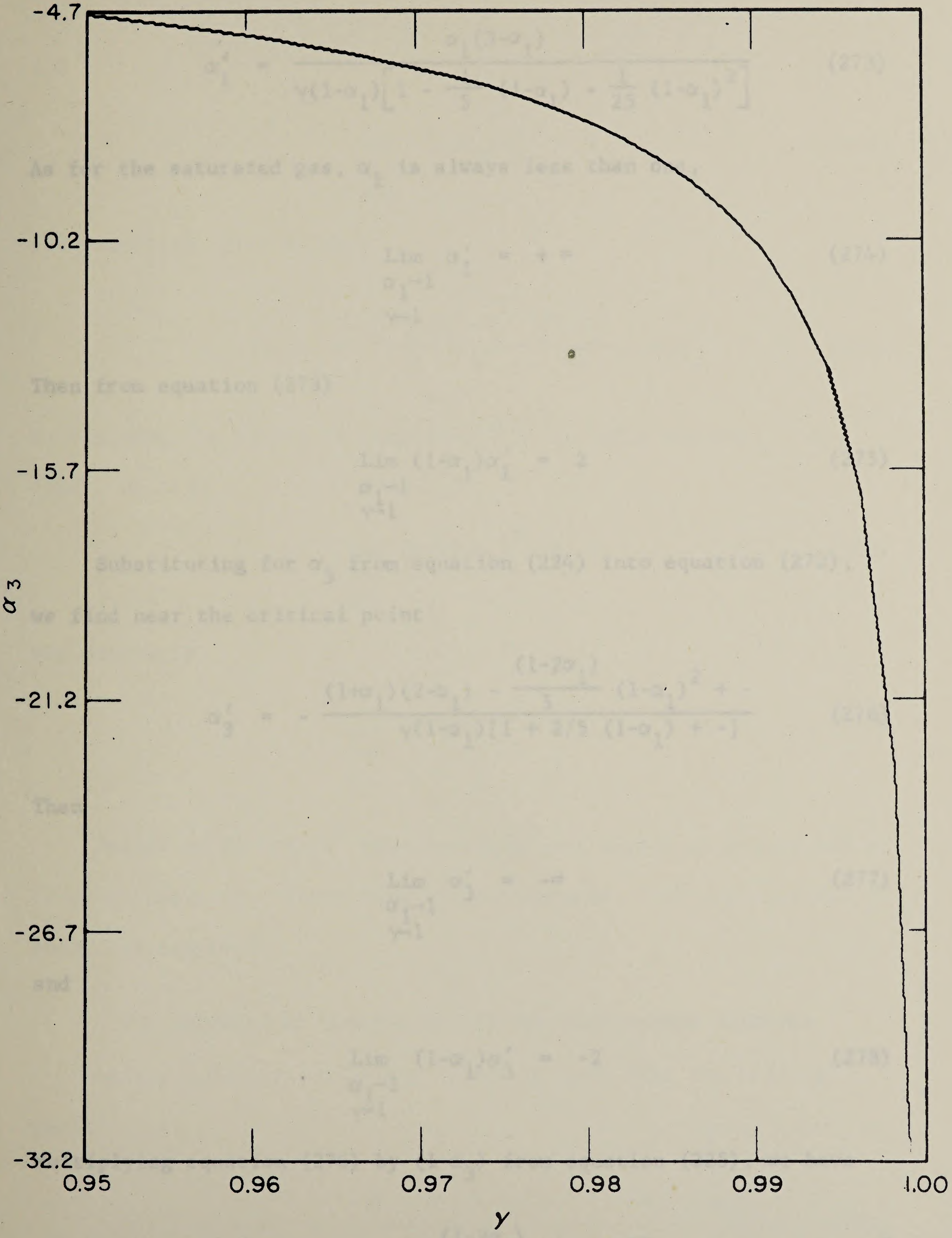

FIGURE 25.- Van der Waals Fluid, α_3' vs γ; $\alpha_3' = d\alpha_3/d\gamma$; $\alpha_3 = \rho_l/\rho_c$; $\gamma = T/T_c$

$$\alpha_1' = \frac{\alpha_1(3-\alpha_1)}{\gamma(1-\alpha_1)\left[1 - \frac{1}{5}(1-\alpha_1) - \frac{1}{25}(1-\alpha_1)^2\right]} \qquad (273)$$

As for the saturated gas, α_1 is always less than one,

$$\lim_{\substack{\alpha_1 \to 1 \\ \gamma \to 1}} \alpha_1' = +\infty \qquad (274)$$

Then from equation (273)

$$\lim_{\substack{\alpha_1 \to 1 \\ \gamma \to 1}} (1-\alpha_1)\alpha_1' = 2 \qquad (275)$$

Substituting for α_3 from equation (224) into equation (272), we find near the critical point

$$\alpha_3' = -\frac{(1+\alpha_1)(2-\alpha_1) - \frac{(1-2\alpha_1)}{5}(1-\alpha_1)^2 + -}{\gamma(1-\alpha_1)[1 + 2/5\,(1-\alpha_1) + -]} \qquad (276)$$

Then

$$\lim_{\substack{\alpha_1 \to 1 \\ \gamma \to 1}} \alpha_3' = -\infty \qquad (277)$$

and

$$\lim_{\substack{\alpha_1 \to 1 \\ \gamma \to 1}} (1-\alpha_1)\alpha_3' = -2 \qquad (278)$$

Multiplying equation (276) by $(1-\alpha_3)$ from equation (225), we have

$$(1-\alpha_3)\alpha_3' = \frac{\left[(1+\alpha_1)(2-\alpha_1) - \frac{(1-2\alpha_1)}{5}(1-\alpha_1)^2\right]\left[1 + \frac{1}{5}(1-\alpha_1) + -\right]}{\gamma[1 + 2/5\,(1-\alpha_1) + --]} \qquad (279)$$

and

$$\lim_{\substack{\alpha_3\to 1\\ \gamma\to 1}} (1-\alpha_3)\alpha_3' = 2 \tag{280}$$

From equation (234) we have

$$(1-\gamma) = \frac{(1-\alpha_1)^2}{4}\left[1 + \frac{(3-\alpha_1)}{10}(1-\alpha_1)\right] \tag{281}$$

Multiplying the square of equation (273) by (281) and taking the limit, we find

$$\lim_{\substack{\gamma\to 1\\ \alpha\to 1}} (1-\gamma)(\alpha_1')^2 = 1 \tag{282}$$

and similarly

$$\lim_{\substack{\gamma\to 1\\ \alpha\to 1}} (1-\gamma)(\alpha_3')^2 = 1 \tag{283}$$

Values of $(1-\gamma)(\alpha_1')^2$ and $(1-\gamma)(\alpha_3')^2$ are listed as a function of $(1-\gamma)$ in table 13. These data are illustrated, near the critical point, in figure 26.

THE TEMPERATURE COEFFICIENT OF THE RECTILINEAR DIAMETER

Adding equations (273) and (276), we have near the critical point

$$\alpha_1' + \alpha_3' = \frac{-(8 - 7\alpha_1 + 3\alpha_1^2) + (1-2\alpha_1)(1-\alpha_1)}{5\left[1 - \frac{1}{5}(1-\alpha_1)\right]\left[1 + \frac{2}{5}(1-\alpha_1)\right]} \tag{284}$$

TABLE 13. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE TEMPERATURE COEFFICIENTS OF THE SATURATED LIQUID AND VAPOR DENSITIES

$\alpha' = \frac{d\alpha}{d\gamma}$ $\alpha = \rho/\rho_c$ $\gamma = T/T_c$

$1-\gamma$	$(1-\gamma)(\alpha_1')^2$	$(1-\gamma)(\alpha_3')^2$
7.50000E-01	4.86167E-06	8.42067E-01
7.00000E-01	1.28031E-04	8.57921E-01
6.50000E-01	1.11432E-03	8.76171E-01
6.00000E-01	5.01416E-03	8.96683E-01
5.50000E-01	1.49121E-02	9.19125E-01
5.00000E-01	3.38267E-02	9.43066E-01
4.50000E-01	6.38669E-02	9.68038E-01
4.00000E-01	1.06059E-01	9.93552E-01
3.50000E-01	1.60602E-01	1.01908E-00
3.00000E-01	2.27240E-01	1.04404E-00
2.50000E-01	3.05621E-01	1.06764E-00
2.00000E-01	3.95633E-01	1.08883E-00
1.50000E-01	4.97850E-01	1.10589E-00
1.00000E-01	6.14486E-01	1.11553E-00
5.00000E-02	7.52947E-01	1.10943E-00
4.80000E-02	7.59219E-01	1.10857E-00
4.60000E-02	7.65574E-01	1.10763E-00
4.40000E-02	7.72015E-01	1.10661E-00
4.20000E-02	7.78550E-01	1.10551E-00
4.00000E-02	7.85183E-01	1.10432E-00
3.80000E-02	7.91922E-01	1.10303E-00
3.60000E-02	7.98775E-01	1.10164E-00
3.40000E-02	8.05750E-01	1.10013E-00
3.20000E-02	8.12860E-01	1.09849E-00
3.00000E-02	8.20114E-01	1.09672E-00
2.80000E-02	8.27529E-01	1.09480E-00
2.60000E-02	8.35120E-01	1.09270E-00
2.40000E-02	8.42908E-01	1.09042E-00
2.20000E-02	8.50917E-01	1.08793E-00
2.00000E-02	8.59178E-01	1.08519E-00
1.80000E-02	8.67727E-01	1.08217E-00
1.60000E-02	8.76615E-01	1.07882E-00
1.40000E-02	8.85905E-01	1.07507E-00
1.20000E-02	8.95687E-01	1.07084E-00
1.00000E-02	9.06088E-01	1.06600E-00
8.00000E-03	9.17304E-01	1.06035E-00
6.00000E-03	9.29667E-01	1.05356E-00
4.00000E-03	9.43821E-01	1.04499E-00
2.00000E-03	9.61428E-01	1.03297E-00
1.00000E-03	9.73303E-01	1.02389E-00
0.00000E-99	1.00000E-00	1.00000E-00

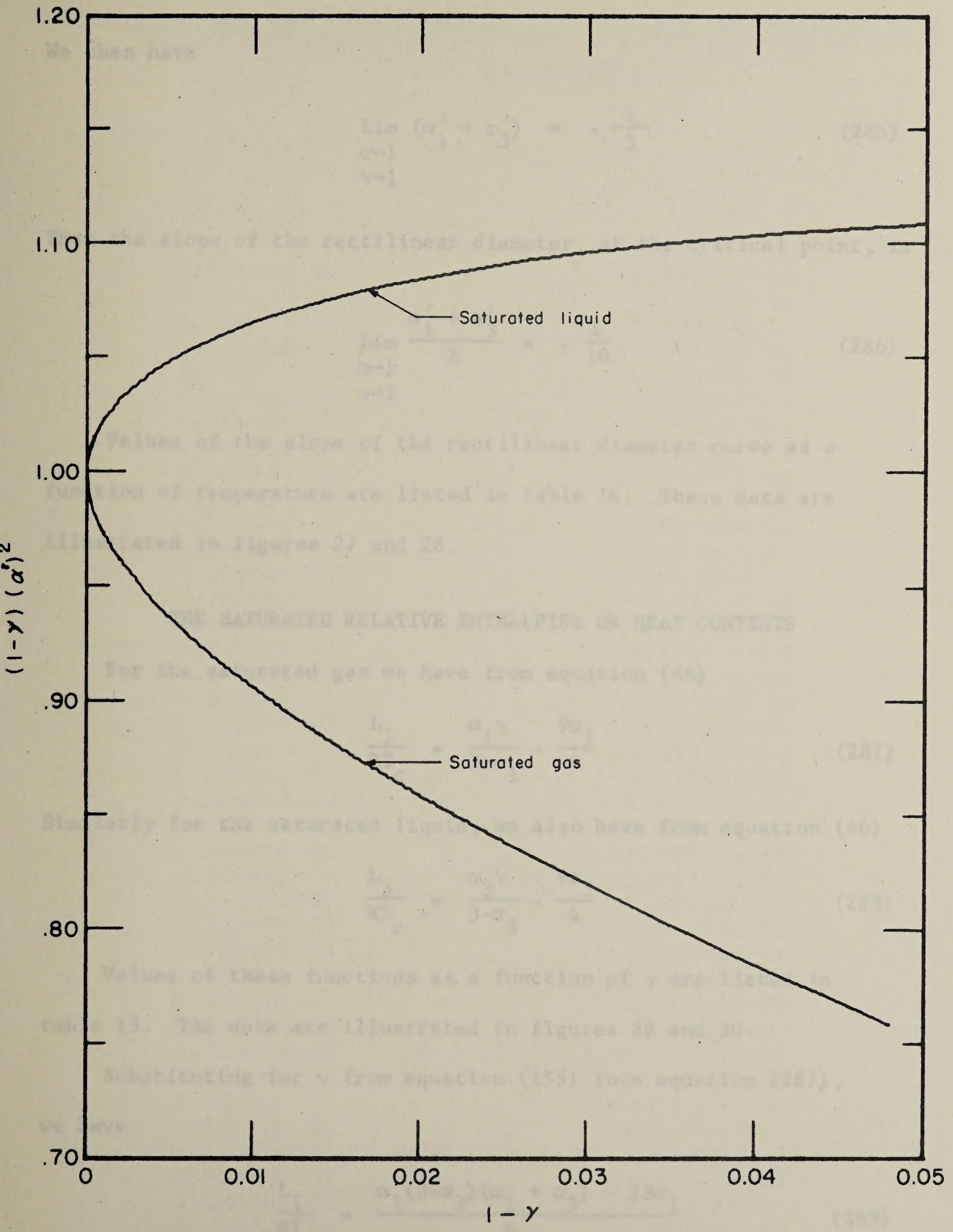

FIGURE 26.- Van der Waals Fluid , Asymptotic Function of the Temperature Coefficient of the Saturated Liquid and Vapor Densities; $\alpha' = \frac{d\alpha}{d\gamma}$; $\alpha = \rho/\rho_c$; $\gamma = T/T_c$

We then have

$$\lim_{\substack{\alpha\to 1\\ \gamma\to 1}} (\alpha_1' + \alpha_3') = -\frac{4}{5} \tag{285}$$

Then the slope of the rectilinear diameter, at the critical point, is

$$\lim_{\substack{\alpha\to 1\\ \gamma\to 1}} \frac{\alpha_1' + \alpha_3'}{2} = -\frac{4}{10} \tag{286}$$

Values of the slope of the rectilinear diameter curve as a function of temperature are listed in table 14. These data are illustrated in figures 27 and 28.

THE SATURATED RELATIVE ENTHALPIES OR HEAT CONTENTS

For the saturated gas we have from equation (66)

$$\frac{L_1}{RT_c} = \frac{\alpha_1\gamma}{3-\alpha_1} - \frac{9\alpha_1}{4} \tag{287}$$

Similarly for the saturated liquid, we also have from equation (66)

$$\frac{L_3}{RT_c} = \frac{\alpha_3\gamma}{3-\alpha_3} - \frac{9\alpha_3}{4} \tag{288}$$

Values of these functions as a function of γ are listed in table 15. The data are illustrated in figures 29 and 30.

Substituting for γ from equation (155) into equation (287), we have

$$\frac{L_1}{RT_c} = \frac{\alpha_1(3-\alpha_3)(\alpha_1 + \alpha_3) - 18\alpha_1}{8} \tag{289}$$

TABLE 14. - VAN DER WAALS FLUID, TEMPERATURE COEFFICIENT OF THE RECTILINEAR DIAMETER AS A FUNCTION OF TEMPERATURE

$\alpha' = \frac{d\alpha}{d\gamma}$ $\alpha = \rho/\rho_c$ $\gamma = T/T_c$

γ	$\frac{\alpha_1' + \alpha_3'}{2}$
2.50000E-01	-5.28528E-01
3.00000E-01	-5.46772E-01
3.50000E-01	-5.59805E-01
4.00000E-01	-5.65534E-01
4.50000E-01	-5.64032E-01
5.00000E-01	-5.56631E-01
5.50000E-01	-5.44982E-01
6.00000E-01	-5.30553E-01
6.50000E-01	-5.14484E-01
7.00000E-01	-4.97592E-01
7.50000E-01	-4.80440E-01
8.00000E-01	-4.63402E-01
8.50000E-01	-4.46720E-01
9.00000E-01	-4.30541E-01
9.50000E-01	-4.14953E-01
9.52000E-01	-4.14342E-01
9.54000E-01	-4.13733E-01
9.56000E-01	-4.13124E-01
9.58000E-01	-4.12517E-01
9.60000E-01	-4.11910E-01
9.62000E-01	-4.11305E-01
9.64000E-01	-4.10701E-01
9.66000E-01	-4.10097E-01
9.68000E-01	-4.09495E-01
9.70000E-01	-4.08894E-01
9.72000E-01	-4.08294E-01
9.74000E-01	-4.07694E-01
9.76000E-01	-4.07096E-01
9.78000E-01	-4.06499E-01
9.80000E-01	-4.05903E-01
9.82000E-01	-4.05308E-01
9.84000E-01	-4.04714E-01
9.86000E-01	-4.04121E-01
9.88000E-01	-4.03529E-01
9.90000E-01	-4.02938E-01
9.92000E-01	-4.02348E-01
9.94000E-01	-4.01760E-01
9.96000E-01	-4.01172E-01
9.98000E-01	-4.00585E-01
9.99000E-01	-4.00292E-01
1.00000E-00	-4.00000E-01

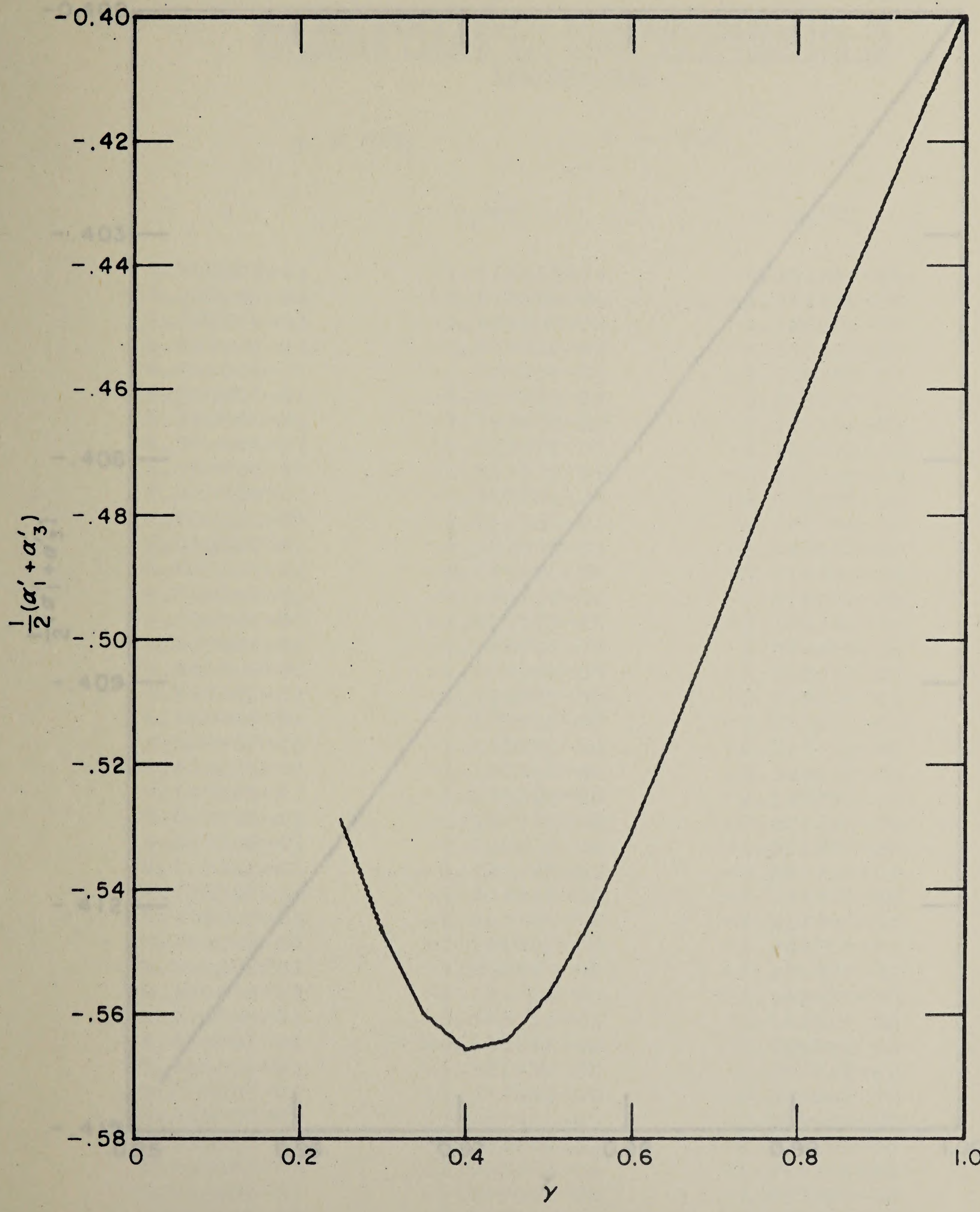

FIGURE 27.- Van der Waals Fluid, Temperature Coefficient of the Rectilinear Diameter as a Function of Temperature; $\alpha' = \frac{d\alpha}{d\gamma}$; $\alpha = \rho/\rho_c$; $\gamma = T/T_c$

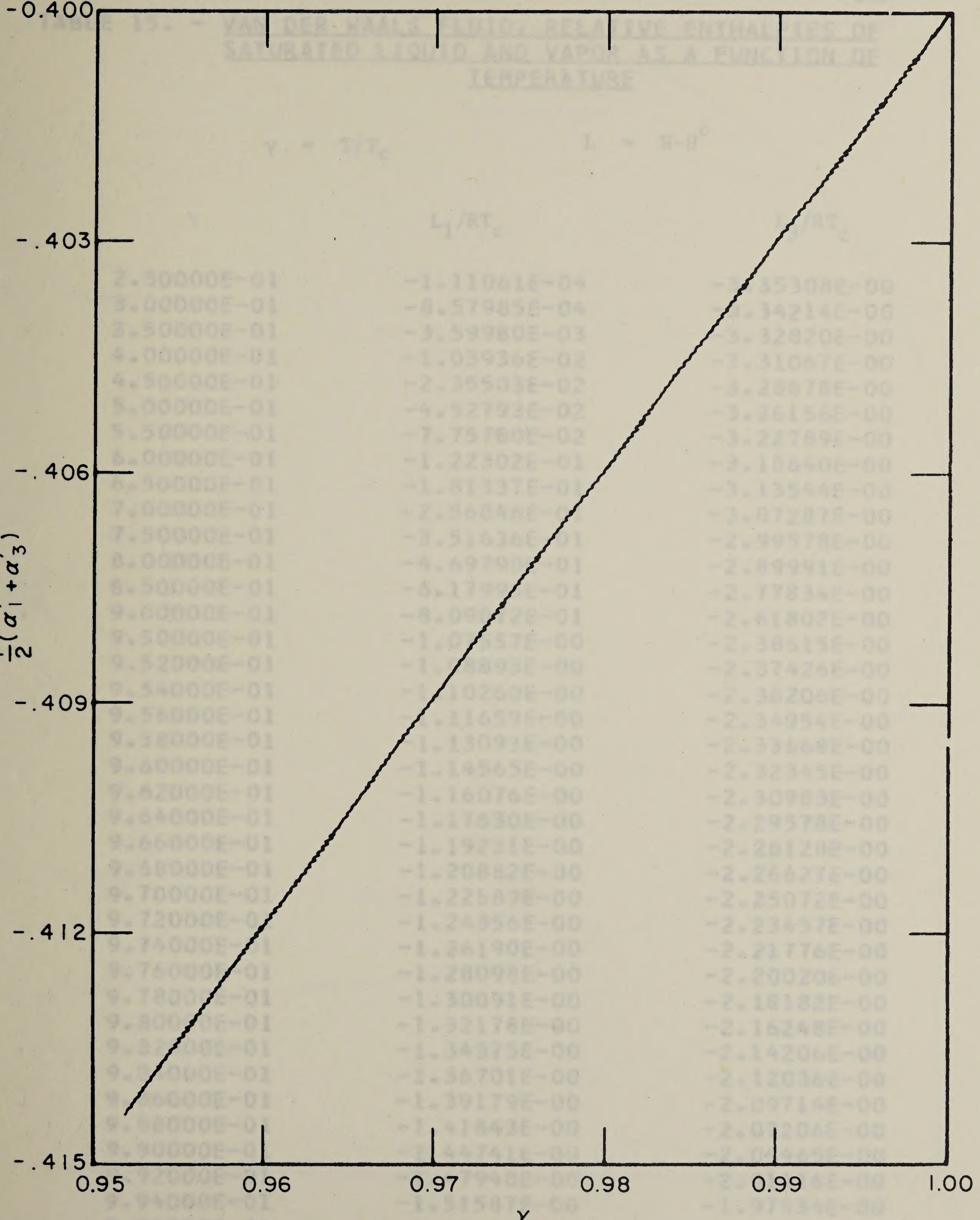

FIGURE 28.- Van der Waals Fluid, Temperature Coefficient of the Rectilinear Diameter as Function of Temperature; $\alpha' = \frac{d\alpha}{d\gamma}$; $\alpha = \rho/\rho_c$; $\gamma = T/T_c$

TABLE 15. - VAN DER WAALS FLUID, RELATIVE ENTHALPIES OF SATURATED LIQUID AND VAPOR AS A FUNCTION OF TEMPERATURE

$Y = T/T_c$ $L = H-H^o$

Y	L_1/RT_c	L_3/RT_c
2.50000E-01	-1.11061E-04	-3.35308E-00
3.00000E-01	-8.57985E-04	-3.34214E-00
3.50000E-01	-3.59980E-03	-3.32820E-00
4.00000E-01	-1.03936E-02	-3.31067E-00
4.50000E-01	-2.35503E-02	-3.28878E-00
5.00000E-01	-4.52793E-02	-3.26156E-00
5.50000E-01	-7.75780E-02	-3.22789E-00
6.00000E-01	-1.22302E-01	-3.18640E-00
6.50000E-01	-1.81337E-01	-3.13544E-00
7.00000E-01	-2.56846E-01	-3.07287E-00
7.50000E-01	-3.51636E-01	-2.99578E-00
8.00000E-01	-4.69790E-01	-2.89991E-00
8.50000E-01	-6.17995E-01	-2.77834E-00
9.00000E-01	-8.09072E-01	-2.61802E-00
9.50000E-01	-1.07557E-00	-2.38615E-00
9.52000E-01	-1.08893E-00	-2.37426E-00
9.54000E-01	-1.10260E-00	-2.36206E-00
9.56000E-01	-1.11659E-00	-2.34954E-00
9.58000E-01	-1.13093E-00	-2.33668E-00
9.60000E-01	-1.14565E-00	-2.32345E-00
9.62000E-01	-1.16076E-00	-2.30983E-00
9.64000E-01	-1.17630E-00	-2.29578E-00
9.66000E-01	-1.19231E-00	-2.28128E-00
9.68000E-01	-1.20882E-00	-2.26627E-00
9.70000E-01	-1.22589E-00	-2.25072E-00
9.72000E-01	-1.24356E-00	-2.23457E-00
9.74000E-01	-1.26190E-00	-2.21776E-00
9.76000E-01	-1.28098E-00	-2.20020E-00
9.78000E-01	-1.30091E-00	-2.18182E-00
9.80000E-01	-1.32178E-00	-2.16248E-00
9.82000E-01	-1.34375E-00	-2.14206E-00
9.84000E-01	-1.36701E-00	-2.12036E-00
9.86000E-01	-1.39179E-00	-2.09714E-00
9.88000E-01	-1.41843E-00	-2.07206E-00
9.90000E-01	-1.44741E-00	-2.04465E-00
9.92000E-01	-1.47948E-00	-2.01416E-00
9.94000E-01	-1.51587E-00	-1.97934E-00
9.96000E-01	-1.55901E-00	-1.93779E-00
9.98000E-01	-1.61516E-00	-1.88324E-00
9.99000E-01	-1.65477E-00	-1.84442E-00
1.00000E-00	-1.75000E-00	-1.75000E-00

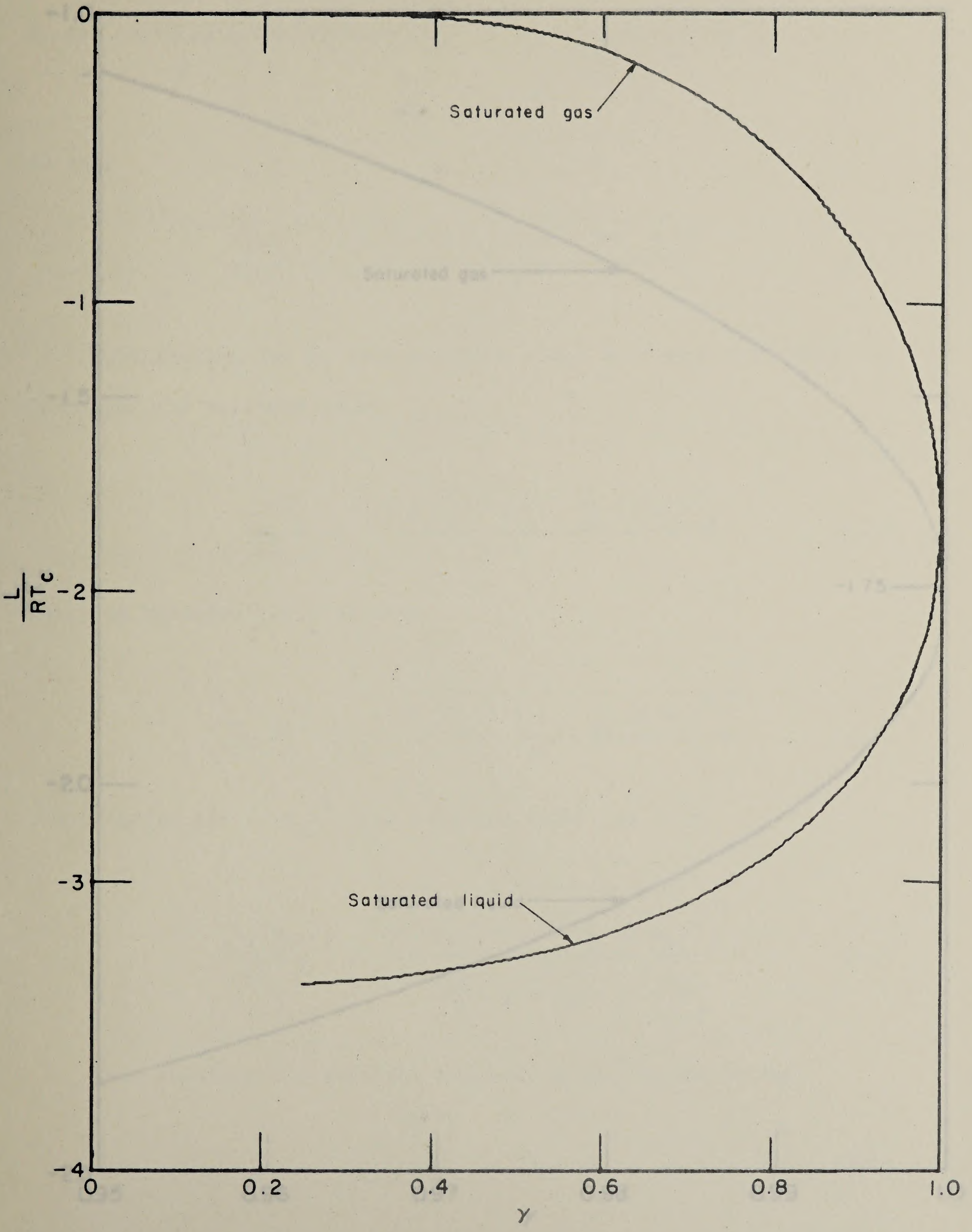

FIGURE 29.- Van der Waals Fluid, Saturated Relative Enthalpies vs γ; $\gamma = T/T_c$; $L = H - H°$

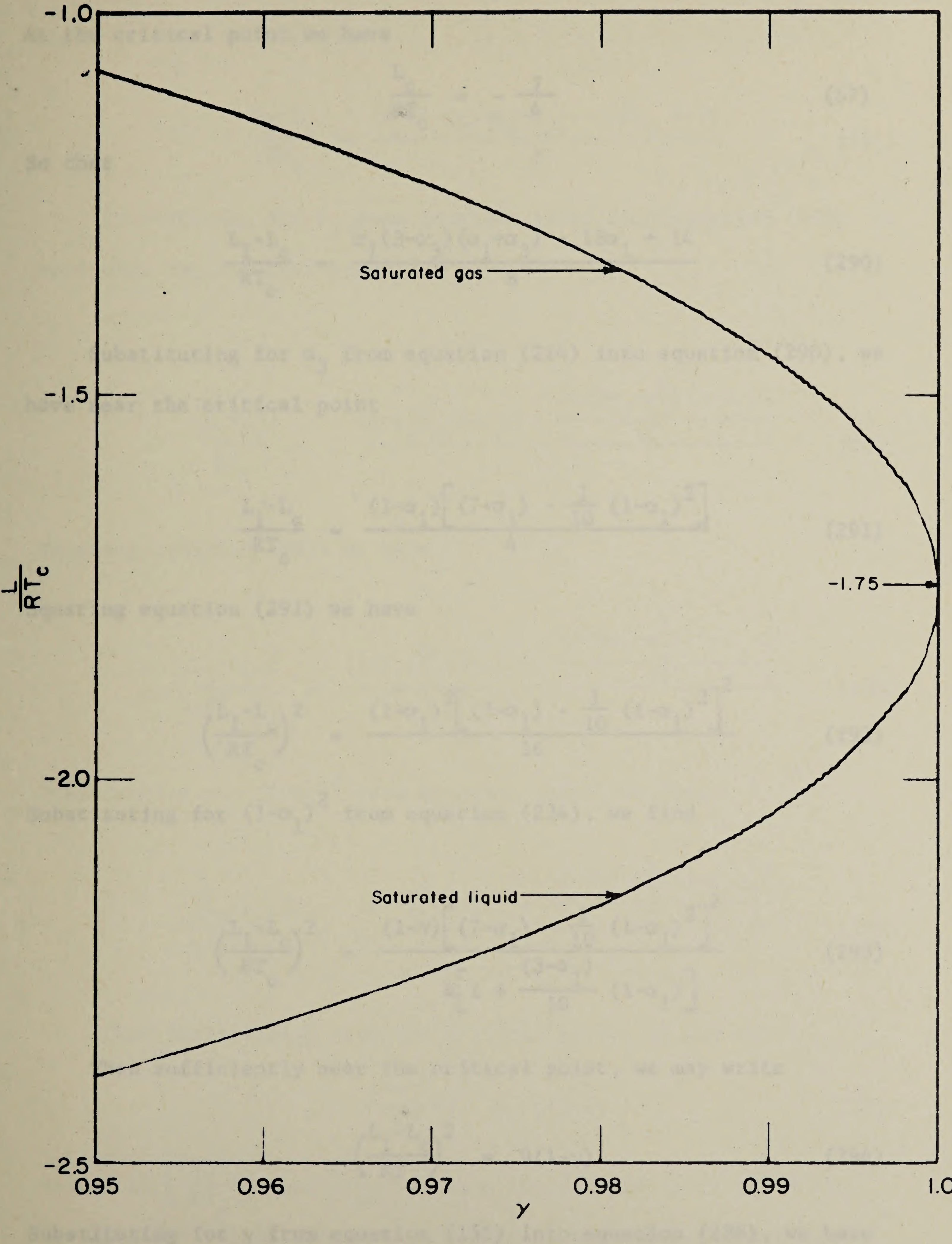

FIGURE 30.- Van der Waals Fluid, Saturated Relative Enthalpies vs γ ; $\gamma = T/T_c$; L = H-H°

At the critical point we have

$$\frac{L_c}{RT_c} = -\frac{7}{4} \tag{67}$$

So that

$$\frac{L_1-L_c}{RT_c} = \frac{\alpha_1(3-\alpha_3)(\alpha_1+\alpha_3) - 18\alpha_1 + 14}{8} \tag{290}$$

Substituting for α_3 from equation (224) into equation (290), we have near the critical point

$$\frac{L_1-L_c}{RT_c} = \frac{(1-\alpha_1)\left[(7-\alpha_1) - \frac{1}{10}(1-\alpha_1)^2\right]}{4} \tag{291}$$

Squaring equation (291) we have

$$\left(\frac{L_1-L_c}{RT_c}\right)^2 = \frac{(1-\alpha_1)^2\left[(7-\alpha_1) - \frac{1}{10}(1-\alpha_1)^2\right]^2}{16} \tag{292}$$

Substituting for $(1-\alpha_1)^2$ from equation (234), we find

$$\left(\frac{L_1-L_c}{RT_c}\right)^2 = \frac{(1-\gamma)\left[(7-\alpha_1) - \frac{1}{10}(1-\alpha_1)^2\right]^2}{4\left[1 + \frac{(3-\alpha_1)}{10}(1-\alpha_1)\right]} \tag{293}$$

Then sufficiently near the critical point, we may write

$$\left(\frac{L_1-L_c}{RT_c}\right)^2 = 9(1-\gamma) \tag{294}$$

Substituting for γ from equation (155) into equation (288), we have

$$\frac{L_3}{RT_c} = \frac{\alpha_3(3-\alpha_1)(\alpha_1+\alpha_3) - 18\alpha_3}{8} \tag{295}$$

Then

$$\frac{L_3-L_c}{RT_c} = \frac{\alpha_3(3-\alpha_1)(\alpha_1+\alpha_3) - 18\alpha_3 + 14}{8} \tag{296}$$

Substituting for α_3 from equation (224) into equation (296), we have near the critical point

$$\frac{L_3-L_c}{RT_c} = -\frac{(1-\alpha_1)\left[(5+\alpha_1) + \frac{(6+7\alpha_1-\alpha_1^2)(1-\alpha_1)}{10}\right]}{4} \tag{297}$$

Squaring equation (297) we have

$$\left(\frac{L_3-L_c}{RT_c}\right)^2 = \frac{(1-\alpha_1)^2\left[(5+\alpha_1) + \frac{(6+7\alpha_1-\alpha_1^2)(1-\alpha_1)}{10}\right]^2}{16} \tag{298}$$

Substituting for $(1-\alpha_1)^2$ from equation (234), we find

$$\left(\frac{L_3-L_c}{RT_c}\right)^2 = \frac{(1-\gamma)\left[(5+\alpha_1) + \frac{(6+7\alpha_1-\alpha_1^2)(1-\alpha_1)}{10}\right]^2}{4\left[1 + \frac{(3-\alpha_1)}{10}(1-\alpha_1)\right]} \tag{299}$$

Then sufficiently near the critical point, we may write

$$\left(\frac{L_3-L_c}{RT_c}\right)^2 = 9(1-\gamma) \tag{300}$$

Values of $\left(\frac{L_1-L_c}{RT_c}\right)^2$ and $\left(\frac{L_3-L_c}{RT_c}\right)^2$ as a function of $(1-\gamma)$ are listed in table 16. These data are illustrated, near the critical point, in figure 31.

TABLE 16. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE RELATIVE ENTHALPIES OF SATURATED LIQUID AND VAPOR

$\gamma = T/T_c$

$1-\gamma$	$\left(\frac{L_1-L_c}{RT_c}\right)^2$	$\left(\frac{L_3-L_c}{RT_c}\right)^2$
7.50000E-01	3.06211E-00	2.56989E-00
7.00000E-01	3.05949E-00	2.53491E-00
6.50000E-01	3.04991E-00	2.49073E-00
6.00000E-01	3.02623E-00	2.43572E-00
5.50000E-01	2.98062E-00	2.36785E-00
5.00000E-01	2.90607E-00	2.28482E-00
4.50000E-01	2.79699E-00	2.18416E-00
4.00000E-01	2.64940E-00	2.06326E-00
3.50000E-01	2.46070E-00	1.91947E-00
3.00000E-01	2.22950E-00	1.75000E-00
2.50000E-01	1.95541E-00	1.55198E-00
2.00000E-01	1.63893E-00	1.32229E-00
1.50000E-01	1.28143E-00	1.05749E-00
1.00000E-01	8.85343E-01	7.53474E-01
5.00000E-02	4.54846E-01	4.04698E-01
4.80000E-02	4.37006E-01	3.89704E-01
4.60000E-02	4.19124E-01	3.74623E-01
4.40000E-02	4.01202E-01	3.59455E-01
4.20000E-02	3.83239E-01	3.44198E-01
4.00000E-02	3.65238E-01	3.28851E-01
3.80000E-02	3.47199E-01	3.13413E-01
3.60000E-02	3.29123E-01	2.97883E-01
3.40000E-02	3.11011E-01	2.82259E-01
3.20000E-02	2.92866E-01	2.66541E-01
3.00000E-02	2.74688E-01	2.50726E-01
2.80000E-02	2.56478E-01	2.34814E-01
2.60000E-02	2.38239E-01	2.18801E-01
2.40000E-02	2.19973E-01	2.02687E-01
2.20000E-02	2.01681E-01	1.86470E-01
2.00000E-02	1.83366E-01	1.70146E-01
1.80000E-02	1.65031E-01	1.53713E-01
1.60000E-02	1.46679E-01	1.37168E-01
1.40000E-02	1.28312E-01	1.20507E-01
1.20000E-02	1.09937E-01	1.03726E-01
1.00000E-02	9.15571E-02	8.68199E-02
8.00000E-03	7.31799E-02	6.97812E-02
6.00000E-03	5.48144E-02	5.26011E-02
4.00000E-03	3.64740E-02	3.52661E-02
2.00000E-03	1.81816E-02	1.77534E-02
1.00000E-03	9.06767E-03	8.91608E-03
0.00000E-99	0.00000E-99	0.00000E-99

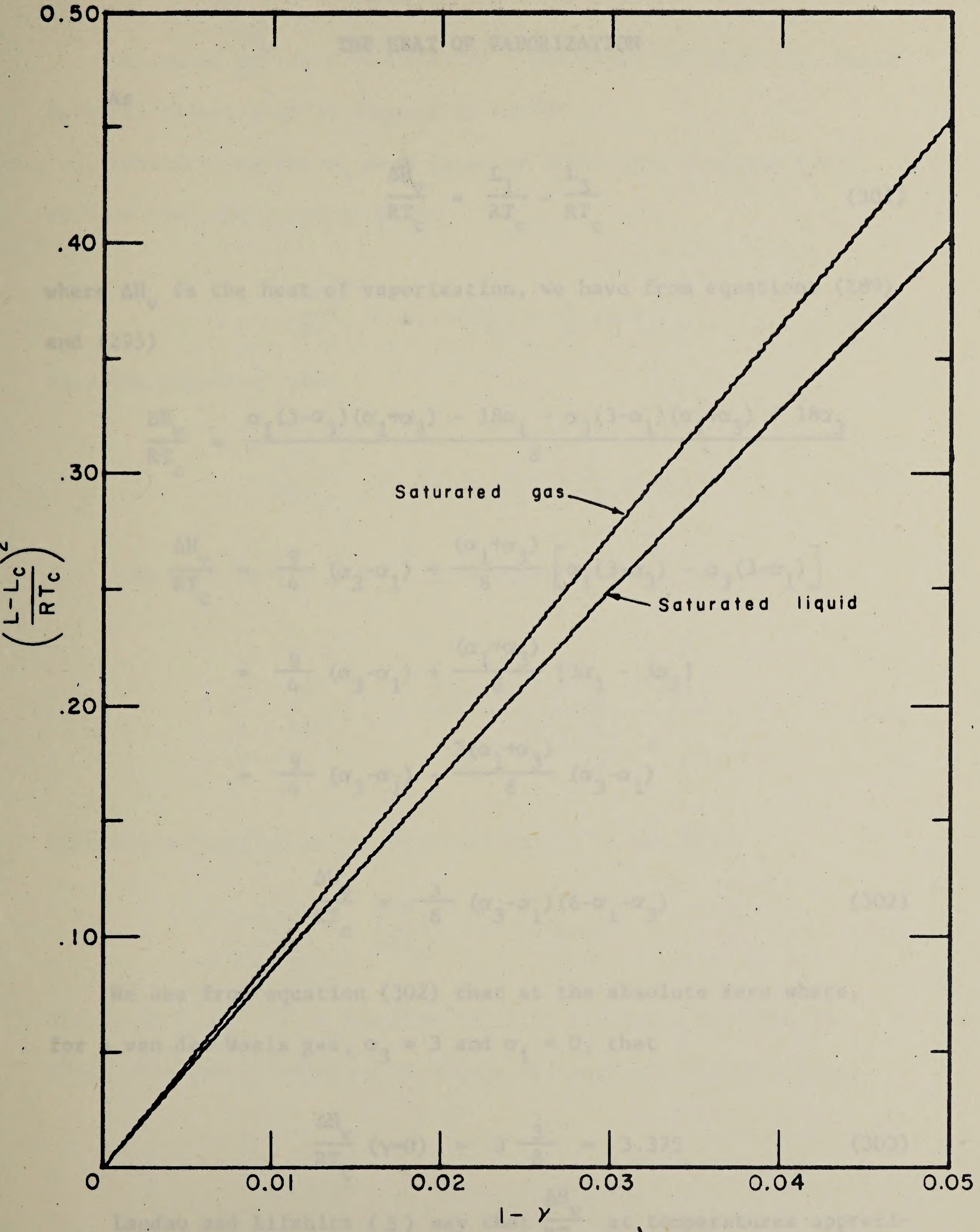

FIGURE 31. - Van der Waals Fluid, Asymptotic Function of the Relative Enthalpies of Saturated Liquid and Vapor; $\gamma = T/T_c$; L = H-H°

THE HEAT OF VAPORIZATION

As

$$\frac{\Delta H_v}{RT_c} = \frac{L_1}{RT_c} - \frac{L_3}{RT_c} \tag{301}$$

where ΔH_v is the heat of vaporization, we have from equations (289) and (295)

$$\frac{\Delta H_v}{RT_c} = \frac{\alpha_1(3-\alpha_3)(\alpha_1+\alpha_3) - 18\alpha_1 - \alpha_3(3-\alpha_1)(\alpha_1+\alpha_3) + 18\alpha_3}{8}$$

$$\frac{\Delta H_v}{RT_c} = \frac{9}{4}(\alpha_3-\alpha_1) + \frac{(\alpha_1+\alpha_3)}{8}\left[\alpha_1(3-\alpha_3) - \alpha_3(3-\alpha_1)\right]$$

$$= \frac{9}{4}(\alpha_3-\alpha_1) + \frac{(\alpha_1+\alpha_3)}{8}[3\alpha_1 - 3\alpha_3]$$

$$= \frac{9}{4}(\alpha_3-\alpha_1) - \frac{3(\alpha_1+\alpha_3)}{8}(\alpha_3-\alpha_1)$$

$$\frac{\Delta H_v}{RT_c} = \frac{3}{8}(\alpha_3-\alpha_1)(6-\alpha_1-\alpha_3) \tag{302}$$

We see from equation (302) that at the absolute zero where, for a van der Waals gas, $\alpha_3 = 3$ and $\alpha_1 = 0$, that

$$\frac{\Delta H_v}{RT_c}(\gamma=0) = 3\frac{3}{8} = 3.375 \tag{303}$$

Landau and Lifshitz (5) say that $\frac{\Delta H_v}{RT_c}$ at temperatures appreciably below the critical is approximately equal to ten. This is certainly not true for a van der Waals fluid.

Values of $\frac{\Delta H_v}{RT_c}$ as a function of γ are given in table 17. These data are illustrated in figures 32 and 33.

Substituting for α_3 from equation (224) into equation (302), we have near the critical point

$$\frac{\Delta H_v}{RT_c} = 3(1-\alpha_1)\left[1 + \frac{1}{10}(1-\alpha_1)\right] \tag{304}$$

Squaring equation (304)

$$\left(\frac{\Delta H_v}{RT_c}\right)^2 = 9(1-\alpha_1)^2\left[1 + \frac{1}{10}(1-\alpha_1)\right]^2 \tag{305}$$

Substituting for $(1-\alpha_1)^2$ from equation (234), we find

$$\left(\frac{\Delta H_v}{RT_c}\right)^2 = \frac{36(1-\gamma)\left[1 + \frac{1}{10}(1-\alpha_1)\right]^2}{1 + \frac{(3-\alpha_1)(1-\alpha_1)}{10}} \tag{306}$$

Then sufficiently near the critical point, we may write

$$\left(\frac{\Delta H_v}{RT_c}\right)^2 = 36(1-\gamma) \tag{307}$$

Values of $\left(\frac{\Delta H_v}{RT_c}\right)^2$ as a function of $(1-\gamma)$ are given in table 18. These data are illustrated in figure 34, near the critical point.

TABLE 17. - VAN DER WAALS FLUID, HEAT OF VAPORIZATION AS A FUNCTION OF THE TEMPERATURE

$\gamma = T/T_c$

γ	$\frac{\Delta H_v}{RT_c}$
2.50000E-01	3.35297E-00
3.00000E-01	3.34128E-00
3.50000E-01	3.32460E-00
4.00000E-01	3.30028E-00
4.50000E-01	3.26523E-00
5.00000E-01	3.21628E-00
5.50000E-01	3.15031E-00
6.00000E-01	3.06410E-00
6.50000E-01	2.95411E-00
7.00000E-01	2.81603E-00
7.50000E-01	2.64414E-00
8.00000E-01	2.43012E-00
8.50000E-01	2.16034E-00
9.00000E-01	1.80895E-00
9.50000E-01	1.31058E-00
9.52000E-01	1.28532E-00
9.54000E-01	1.25946E-00
9.56000E-01	1.23295E-00
9.58000E-01	1.20574E-00
9.60000E-01	1.17780E-00
9.62000E-01	1.14906E-00
9.64000E-01	1.11947E-00
9.66000E-01	1.08896E-00
9.68000E-01	1.05744E-00
9.70000E-01	1.02483E-00
9.72000E-01	9.91013E-01
9.74000E-01	9.55860E-01
9.76000E-01	9.19222E-01
9.78000E-01	8.80911E-01
9.80000E-01	8.40701E-01
9.82000E-01	7.98303E-01
9.84000E-01	7.53349E-01
9.86000E-01	7.05349E-01
9.88000E-01	6.53633E-01
9.90000E-01	5.97236E-01
9.92000E-01	5.34679E-01
9.94000E-01	4.63474E-01
9.96000E-01	3.78774E-01
9.98000E-01	2.68081E-01
9.99000E-01	1.89649E-01
1.00000E-00	0.00000E-99

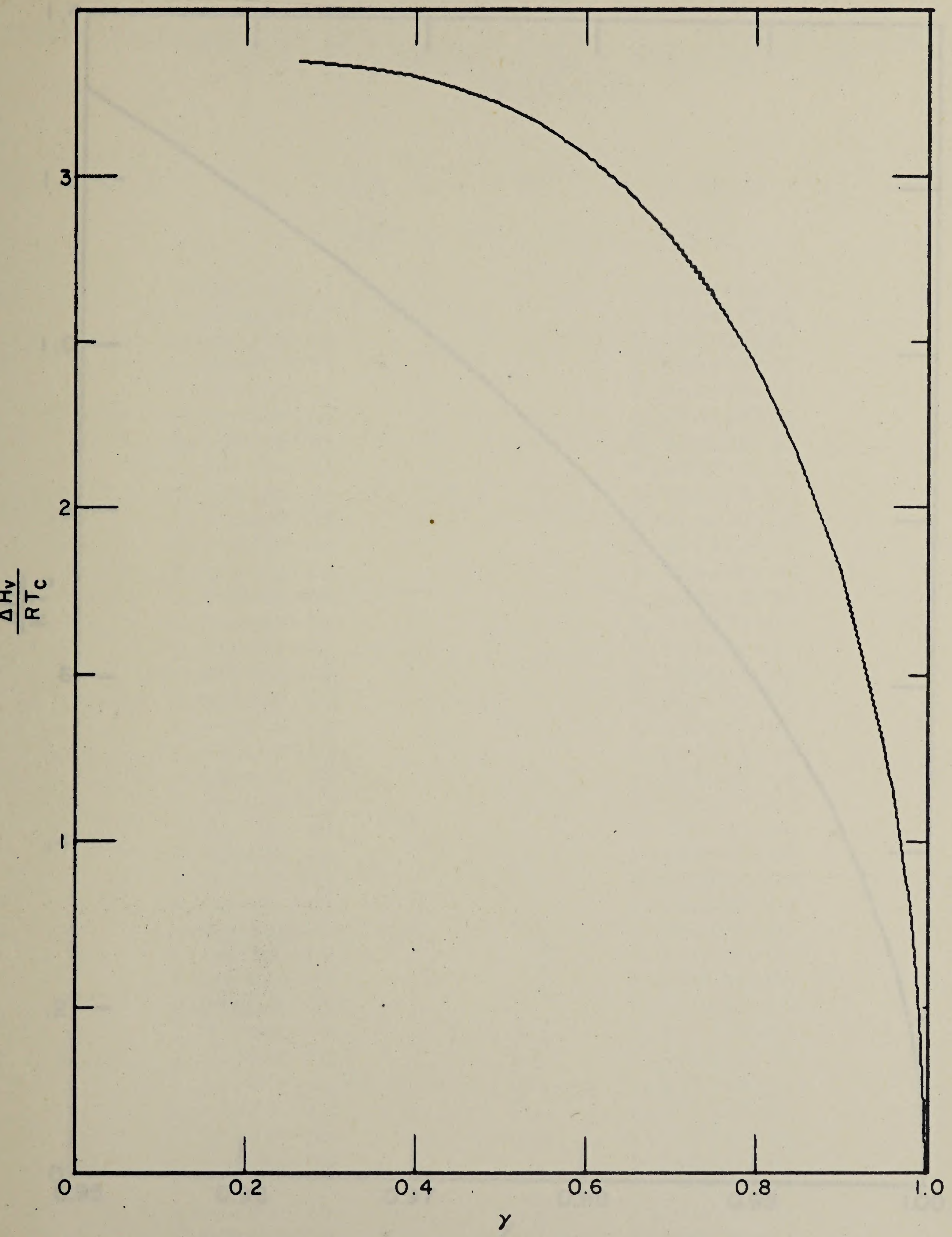

FIGURE 32.- Van der Waals Fluid, $\frac{\Delta H_v}{RT_c}$ vs γ; $\gamma = T/T_c$

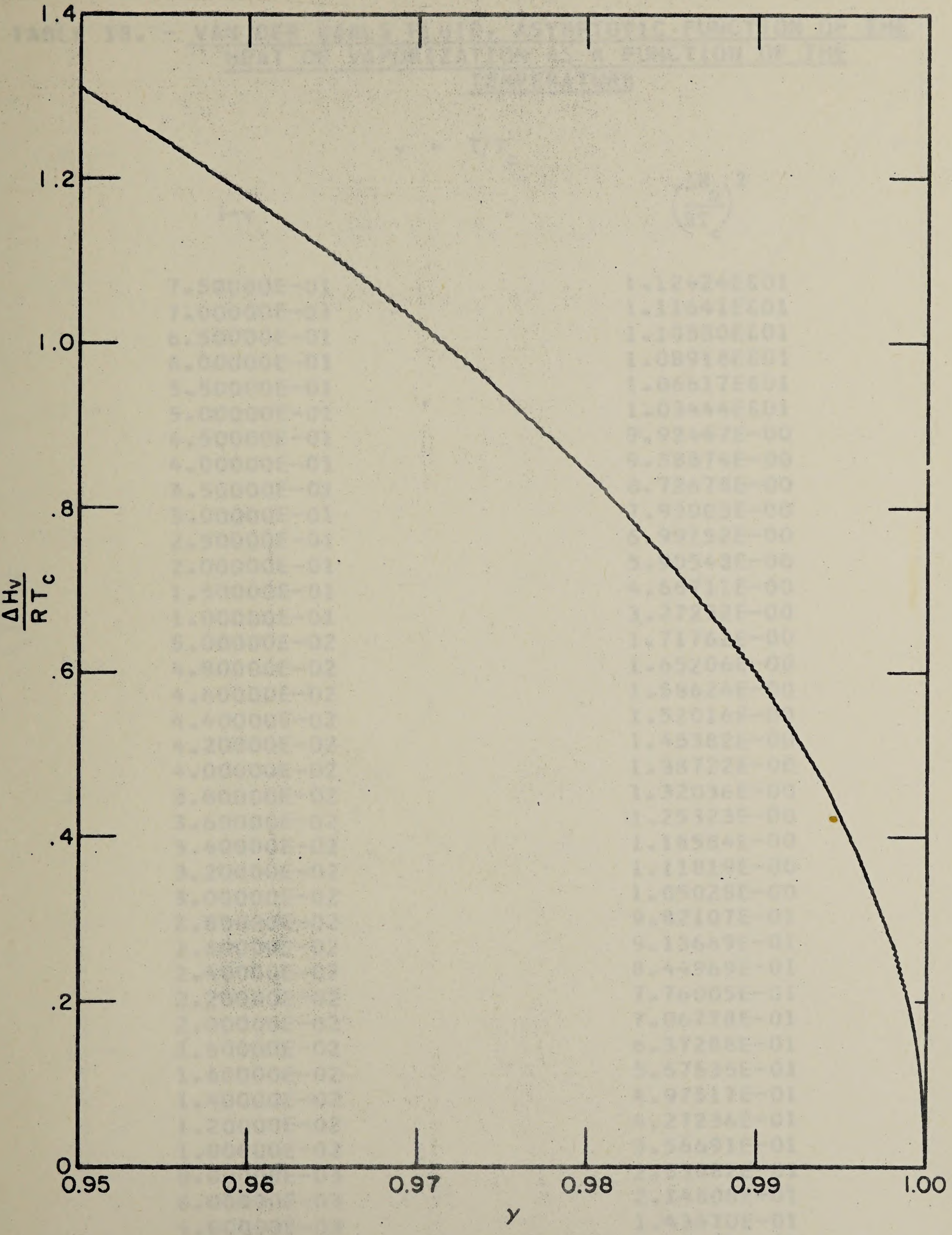

FIGURE 33.- Van der Waals Fluid, $\frac{\Delta H_v}{RT_c}$ vs y; $y = T/T_c$

TABLE 18. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE HEAT OF VAPORIZATION AS A FUNCTION OF THE TEMPERATURE

$\gamma = T/T_c$

$1-\gamma$	$\left(\frac{\Delta H_v}{RT_c}\right)^2$
7.50000E-01	1.12424E&01
7.00000E-01	1.11641E&01
6.50000E-01	1.10530E&01
6.00000E-01	1.08918E&01
5.50000E-01	1.06617E&01
5.00000E-01	1.03444E&01
4.50000E-01	9.92447E-00
4.00000E-01	9.38874E-00
3.50000E-01	8.72678E-00
3.00000E-01	7.93003E-00
2.50000E-01	6.99152E-00
2.00000E-01	5.90548E-00
1.50000E-01	4.66711E-00
1.00000E-01	3.27232E-00
5.00000E-02	1.71762E-00
4.80000E-02	1.65206E-00
4.60000E-02	1.58624E-00
4.40000E-02	1.52016E-00
4.20000E-02	1.45382E-00
4.00000E-02	1.38722E-00
3.80000E-02	1.32036E-00
3.60000E-02	1.25323E-00
3.40000E-02	1.18584E-00
3.20000E-02	1.11819E-00
3.00000E-02	1.05028E-00
2.80000E-02	9.82107E-01
2.60000E-02	9.13669E-01
2.40000E-02	8.44969E-01
2.20000E-02	7.76005E-01
2.00000E-02	7.06778E-01
1.80000E-02	6.37288E-01
1.60000E-02	5.67535E-01
1.40000E-02	4.97517E-01
1.20000E-02	4.27236E-01
1.00000E-02	3.56691E-01
8.00000E-03	2.85882E-01
6.00000E-03	2.14808E-01
4.00000E-03	1.43470E-01
2.00000E-03	7.18675E-02
1.00000E-03	3.59668E-02
0.00000E-99	0.00000E-99

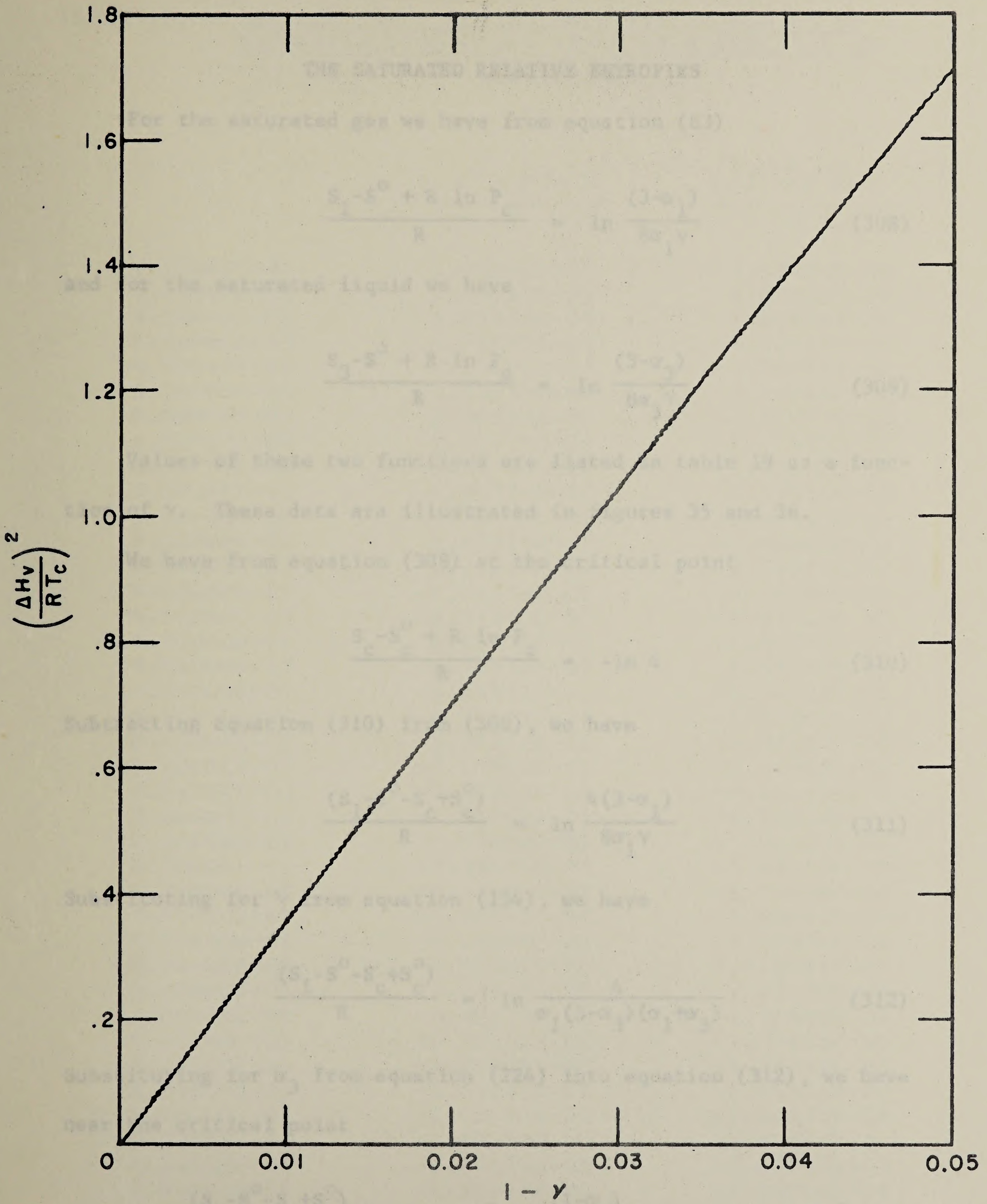

FIGURE 34.- Van der Waals Fluid, Asymptotic Function of the Heat of Vaporization as a Function of Temperature; $y = T/T_c$

THE SATURATED RELATIVE ENTROPIES

For the saturated gas we have from equation (83)

$$\frac{S_1 - S^o + R \ln P_c}{R} = \ln \frac{(3-\alpha_1)}{8\alpha_1\gamma} \qquad (308)$$

and for the saturated liquid we have

$$\frac{S_3 - S^o + R \ln P_c}{R} = \ln \frac{(3-\alpha_3)}{8\alpha_3\gamma} \qquad (309)$$

Values of these two functions are listed in table 19 as a function of γ. These data are illustrated in figures 35 and 36.

We have from equation (308) at the critical point

$$\frac{S_c - S_c^o + R \ln P_c}{R} = -\ln 4 \qquad (310)$$

Subtracting equation (310) from (308), we have

$$\frac{(S_1 - S^o - S_c + S_c^o)}{R} = \ln \frac{4(3-\alpha_1)}{8\alpha_1\gamma} \qquad (311)$$

Substituting for γ from equation (154), we have

$$\frac{(S_1 - S^o - S_c + S_c^o)}{R} = \ln \frac{4}{\alpha_1(3-\alpha_3)(\alpha_1+\alpha_3)} \qquad (312)$$

Substituting for α_3 from equation (224) into equation (312), we have near the critical point

$$\frac{(S_1 - S^o - S_c + S_c^o)}{R} = -\ln \alpha_1\left[1 - \frac{(1-\alpha_1)}{2}\left[1 + \frac{1}{10}(1-\alpha_1)^2\right]\right] \qquad (313)$$

TABLE 19. - VAN DER WAALS FLUID, RELATIVE ENTROPIES OF SATURATED LIQUID AND VAPOR AS A FUNCTION OF TEMPERATURE

$\gamma = T/T_c$

γ	$\frac{S_1 - S^o + R \ln P_c}{R}$	$\frac{S_3 - S^o + R \ln P_c}{R}$
2.50000E-01	1.02840E&01	-3.12784E-00
3.00000E-01	8.04939E-00	-3.08821E-00
3.50000E-01	6.45296E-00	-3.04591E-00
4.00000E-01	5.25012E-00	-3.00059E-00
4.50000E-01	4.30421E-00	-2.95185E-00
5.00000E-01	3.53333E-00	-2.89923E-00
5.50000E-01	2.88568E-00	-2.84215E-00
6.00000E-01	2.32698E-00	-2.77985E-00
6.50000E-01	1.83346E-00	-2.71132E-00
7.00000E-01	1.38778E-00	-2.63511E-00
7.50000E-01	9.76392E-01	-2.54913E-00
8.00000E-01	5.87558E-01	-2.45009E-00
8.50000E-01	2.09273E-01	-2.33231E-00
9.00000E-01	-1.74596E-01	-2.18454E-00
9.50000E-01	-5.97546E-01	-1.97710E-00
9.52000E-01	-6.16378E-01	-1.96651E-00
9.54000E-01	-6.35453E-01	-1.95564E-00
9.56000E-01	-6.54791E-01	-1.94448E-00
9.58000E-01	-6.74412E-01	-1.93302E-00
9.60000E-01	-6.94340E-01	-1.92122E-00
9.62000E-01	-7.14600E-01	-1.90905E-00
9.64000E-01	-7.35223E-01	-1.89650E-00
9.66000E-01	-7.56242E-01	-1.88353E-00
9.68000E-01	-7.77696E-01	-1.87010E-00
9.70000E-01	-7.99629E-01	-1.85615E-00
9.72000E-01	-8.22096E-01	-1.84165E-00
9.74000E-01	-8.45158E-01	-1.82653E-00
9.76000E-01	-8.68890E-01	-1.81071E-00
9.78000E-01	-8.93383E-01	-1.79411E-00
9.80000E-01	-9.18749E-01	-1.77660E-00
9.82000E-01	-9.45128E-01	-1.75806E-00
9.84000E-01	-9.72702E-01	-1.73830E-00
9.86000E-01	-1.00171E-00	-1.71707E-00
9.88000E-01	-1.03248E-00	-1.69406E-00
9.90000E-01	-1.06550E-00	-1.66877E-00
9.92000E-01	-1.10150E-00	-1.64049E-00
9.94000E-01	-1.14170E-00	-1.60797E-00
9.96000E-01	-1.18852E-00	-1.56881E-00
9.98000E-01	-1.24817E-00	-1.51679E-00
9.99000E-01	-1.28947E-00	-1.47931E-00
1.00000E-00	-1.38629E-00	-1.38629E-00

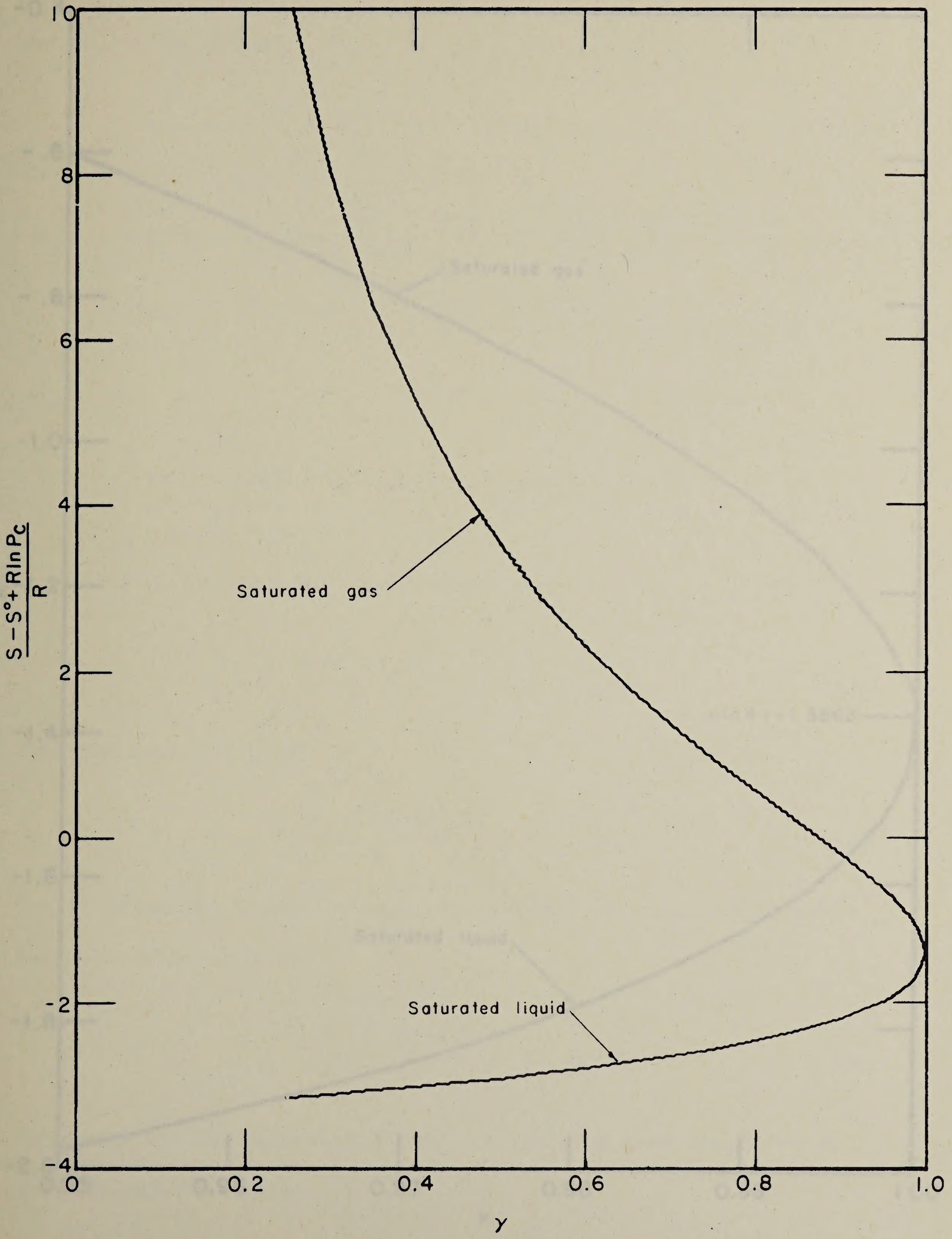

FIGURE 35.- Van der Waals Fluid, Saturated Relative Entropies vs γ; $\gamma = T/T_c$

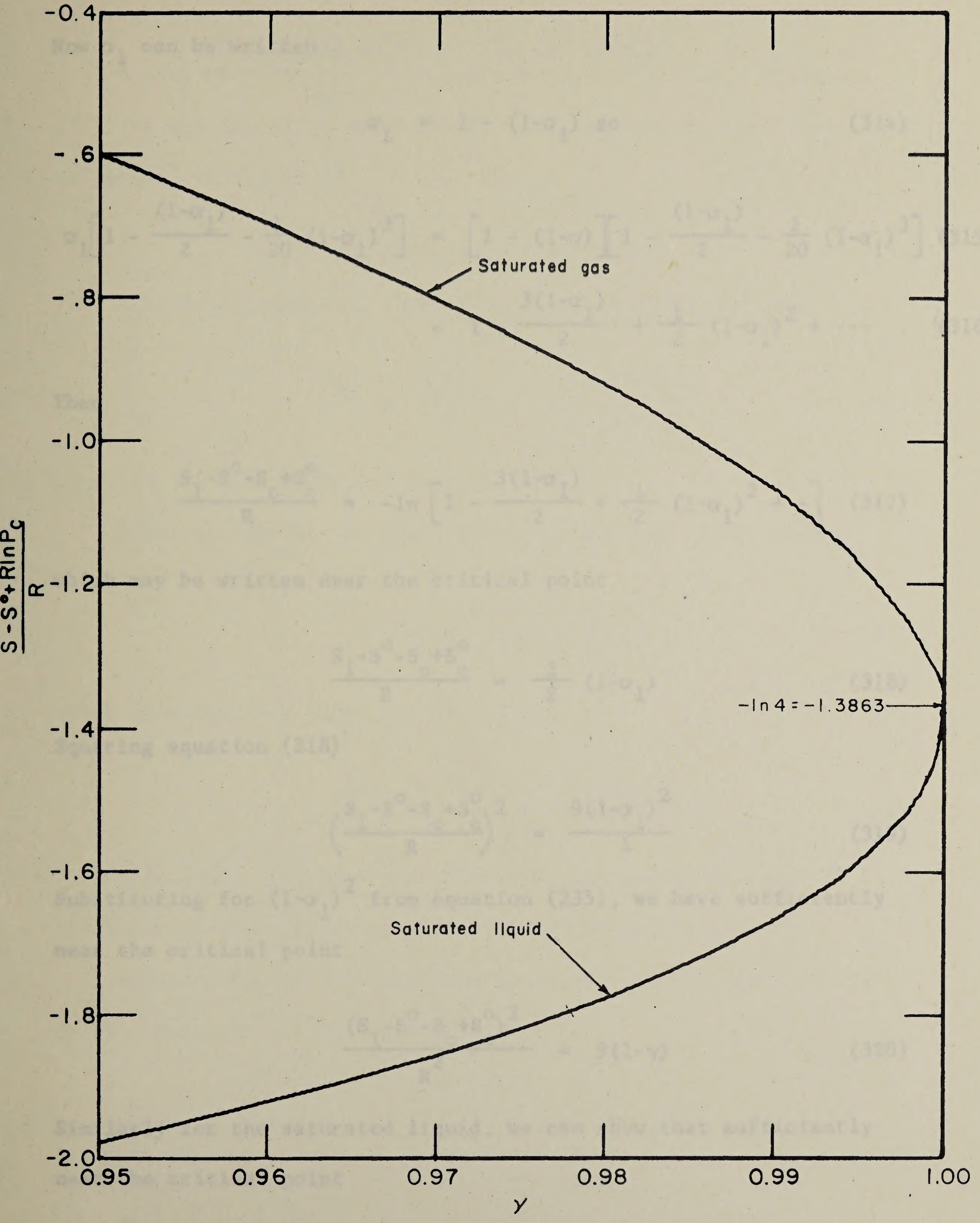

FIGURE 36.- Van der Waals Fluid, Saturated Relative Entropies vs γ; $\gamma = T/T_c$

Now α_1 can be written

$$\alpha_1 = 1 - (1-\alpha_1) \text{ so} \tag{314}$$

$$\alpha_1\left[1 - \frac{(1-\alpha_1)}{2} - \frac{1}{20}(1-\alpha_1)^3\right] = \left[1 - (1-\alpha)\right]\left[1 - \frac{(1-\alpha_1)}{2} - \frac{1}{20}(1-\alpha_1)^3\right] \tag{315}$$

$$= 1 - \frac{3(1-\alpha_1)}{2} + \frac{1}{2}(1-\alpha_1)^2 + --- \tag{316}$$

Then

$$\frac{S_1-S^o-S_c+S_c^o}{R} = -\ln\left[1 - \frac{3(1-\alpha_1)}{2} + \frac{1}{2}(1-\alpha_1)^2 + -\right] \tag{317}$$

which may be written near the critical point

$$\frac{S_1-S^o-S_c+S_c^o}{R} = \frac{3}{2}(1-\alpha_1) \tag{318}$$

Squaring equation (318)

$$\left(\frac{S_1-S^o-S_c+S_c^o}{R}\right)^2 = \frac{9(1-\alpha_1)^2}{4} \tag{319}$$

Substituting for $(1-\alpha_1)^2$ from equation (235), we have sufficiently near the critical point

$$\frac{(S_1-S^o-S_c+S_c^o)^2}{R^2} = 9(1-\gamma) \tag{320}$$

Similarly for the saturated liquid, we can show that sufficiently near the critical point

$$\frac{(S_3-S^o-S_c+S_c^o)^2}{R^2} = 9(1-\gamma) \tag{321}$$

Values of $\frac{(S_1 - S^o - S_c + S^o_c)^2}{R^2}$ and $\frac{(S_3 - S^o - S_c + S^o_c)^2}{R^2}$ as a function of $(1-\gamma)$ are listed in table 20 and are illustrated, near the critical point, in figure 37.

THE ENTROPY OF VAPORIZATION

Subtracting equation (309) from equation (308), we have

$$\frac{\Delta S_v}{R} = \frac{S_1 - S_3}{R} = \ln \frac{\alpha_3 (3-\alpha_1)}{\alpha_1 (3-\alpha_3)} \qquad (322)$$

where ΔS_v is the entropy of vaporization.

Substituting for the logarithm from equation (170), we have

$$\frac{\Delta S_v}{R} = \frac{3(\alpha_3 - \alpha_1)(6-\alpha_1-\alpha_3)}{(3-\alpha_1)(3-\alpha_3)(\alpha_1+\alpha_3)} \qquad (323)$$

which from equation (154) may be written

$$\frac{\Delta S_v}{R} = \frac{3(\alpha_3-\alpha_1)(6-\alpha_1-\alpha_3)}{8\gamma} \qquad (324)$$

Values of $\frac{\Delta S_v}{R}$, as a function of γ, are listed in table 21, and these data are illustrated in figures 38 and 39.

Substituting for α_3 from equation (224) into equation (323), we find near the critical point

$$\frac{\Delta S_v}{R} = \frac{3(1-\alpha_1)\left[1 + \frac{1}{10}(1-\alpha_1)\right]}{1 - \frac{1}{4}(1-\alpha_1)^2} \qquad (325)$$

Squaring equation (325) and substituting for $(1-\alpha_1)^2$ from equation (235), we find sufficiently near the critical point

TABLE 20. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE SATURATED RELATIVE ENTROPIES AS A FUNCTION OF THE TEMPERATURE

$\gamma = T/T_c$

$1-\gamma$	$\left(\frac{S_1-S^o-S_c+S^o_c}{R}\right)^2$	$\left(\frac{S_3-S^o-S_c+S^o_c}{R}\right)^2$
7.50000E-01	1.36197E&02	3.03300E-00
7.00000E-01	8.90322E&01	2.89652E-00
6.50000E-01	6.14539E&01	2.75433E-00
6.00000E-01	4.40420E&01	2.60595E-00
5.50000E-01	3.23819E&01	2.45098E-00
5.00000E-01	2.42027E&01	2.28900E-00
4.50000E-01	1.82497E&01	2.11954E-00
4.00000E-01	1.37884E&01	1.94202E-00
3.50000E-01	1.03668E&01	1.75569E-00
3.00000E-01	7.69551E-00	1.55955E-00
2.50000E-01	5.58228E-00	1.35220E-00
2.00000E-01	3.89609E-00	1.13166E-00
1.50000E-01	2.54583E-00	8.94954E-01
1.00000E-01	1.46821E-00	6.37209E-01
5.00000E-02	6.22122E-01	3.49059E-01
4.80000E-02	5.92770E-01	3.36653E-01
4.60000E-02	5.63761E-01	3.24161E-01
4.40000E-02	5.35096E-01	3.11581E-01
4.20000E-02	5.06775E-01	2.98911E-01
4.00000E-02	4.78800E-01	2.86146E-01
3.80000E-02	4.51172E-01	2.73283E-01
3.60000E-02	4.23893E-01	2.60319E-01
3.40000E-02	3.96965E-01	2.47249E-01
3.20000E-02	3.70391E-01	2.34068E-01
3.00000E-02	3.44175E-01	2.20772E-01
2.80000E-02	3.18318E-01	2.07355E-01
2.60000E-02	2.92827E-01	1.93812E-01
2.40000E-02	2.67706E-01	1.80134E-01
2.20000E-02	2.42961E-01	1.66314E-01
2.00000E-02	2.18598E-01	1.52344E-01
1.80000E-02	1.94627E-01	1.38213E-01
1.60000E-02	1.71058E-01	1.23908E-01
1.40000E-02	1.47903E-01	1.09416E-01
1.20000E-02	1.25178E-01	9.47199E-02
1.00000E-02	1.02904E-01	7.97960E-02
8.00000E-03	8.11070E-02	6.46167E-02
6.00000E-03	5.98245E-02	4.91425E-02
4.00000E-03	3.91138E-02	3.33148E-02
2.00000E-03	1.90758E-02	1.70310E-02
1.00000E-03	9.37432E-03	8.65236E-03
0.00000E-99	0.00000E-99	0.00000E-99

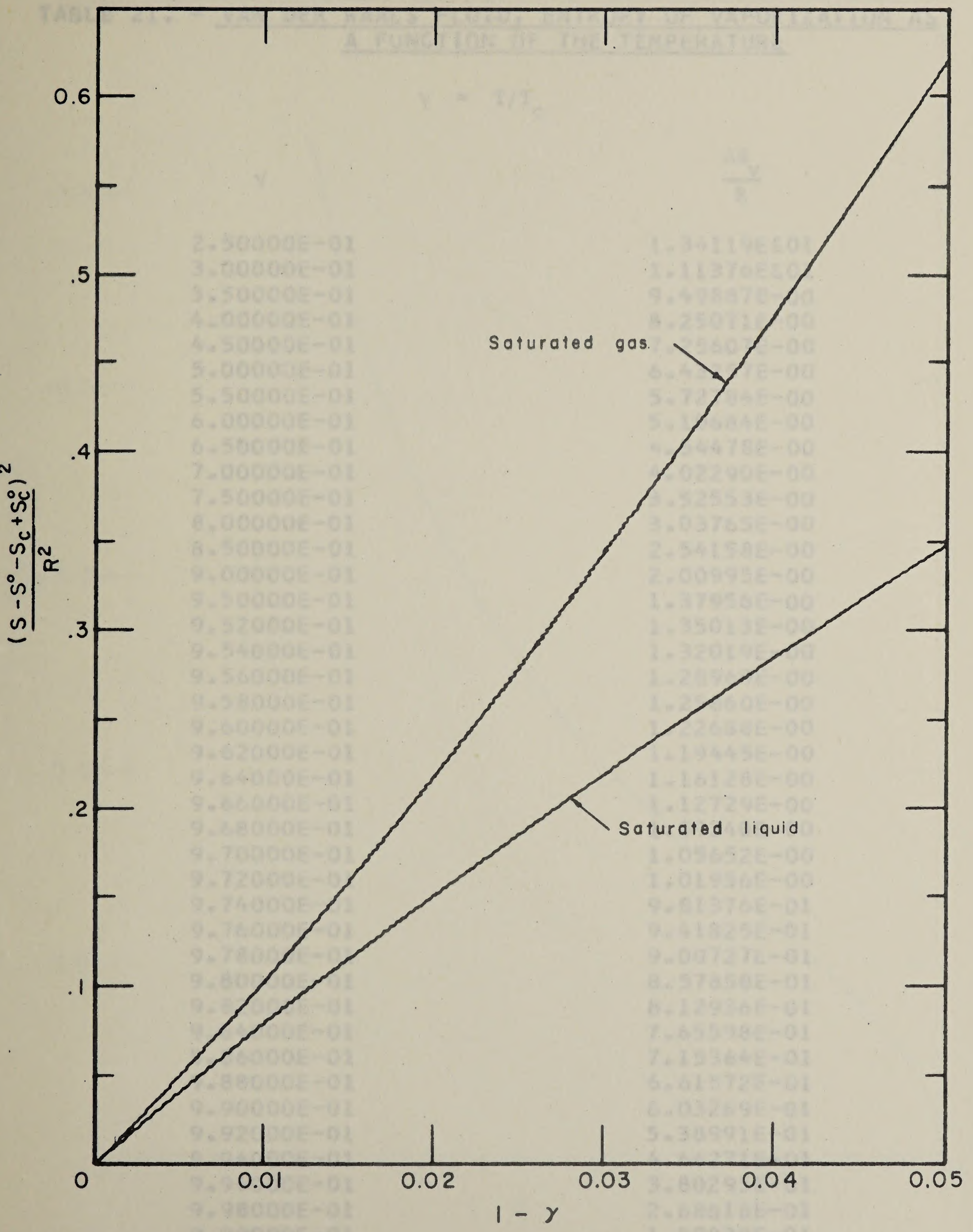

FIGURE 37.- Van der Waals Fluid, Asymptotic Function of the Saturated Relative Entropies as a Function of $(1-\gamma)$; $\gamma = T/T_c$

TABLE 21. - VAN DER WAALS FLUID, ENTROPY OF VAPORIZATION AS A FUNCTION OF THE TEMPERATURE

$\gamma = T/T_c$

γ	$\frac{\Delta S_v}{R}$
2.50000E-01	1.34119E&01
3.00000E-01	1.11376E&01
3.50000E-01	9.49887E-00
4.00000E-01	8.25071E-00
4.50000E-01	7.25607E-00
5.00000E-01	6.43257E-00
5.50000E-01	5.72784E-00
6.00000E-01	5.10684E-00
6.50000E-01	4.54478E-00
7.00000E-01	4.02290E-00
7.50000E-01	3.52553E-00
8.00000E-01	3.03765E-00
8.50000E-01	2.54158E-00
9.00000E-01	2.00995E-00
9.50000E-01	1.37956E-00
9.52000E-01	1.35013E-00
9.54000E-01	1.32019E-00
9.56000E-01	1.28969E-00
9.58000E-01	1.25860E-00
9.60000E-01	1.22688E-00
9.62000E-01	1.19445E-00
9.64000E-01	1.16128E-00
9.66000E-01	1.12729E-00
9.68000E-01	1.09240E-00
9.70000E-01	1.05652E-00
9.72000E-01	1.01956E-00
9.74000E-01	9.81376E-01
9.76000E-01	9.41825E-01
9.78000E-01	9.00727E-01
9.80000E-01	8.57858E-01
9.82000E-01	8.12936E-01
9.84000E-01	7.65598E-01
9.86000E-01	7.15364E-01
9.88000E-01	6.61572E-01
9.90000E-01	6.03269E-01
9.92000E-01	5.38991E-01
9.94000E-01	4.66271E-01
9.96000E-01	3.80295E-01
9.98000E-01	2.68618E-01
9.99000E-01	1.89839E-01
1.00000E-00	0.00000E-99

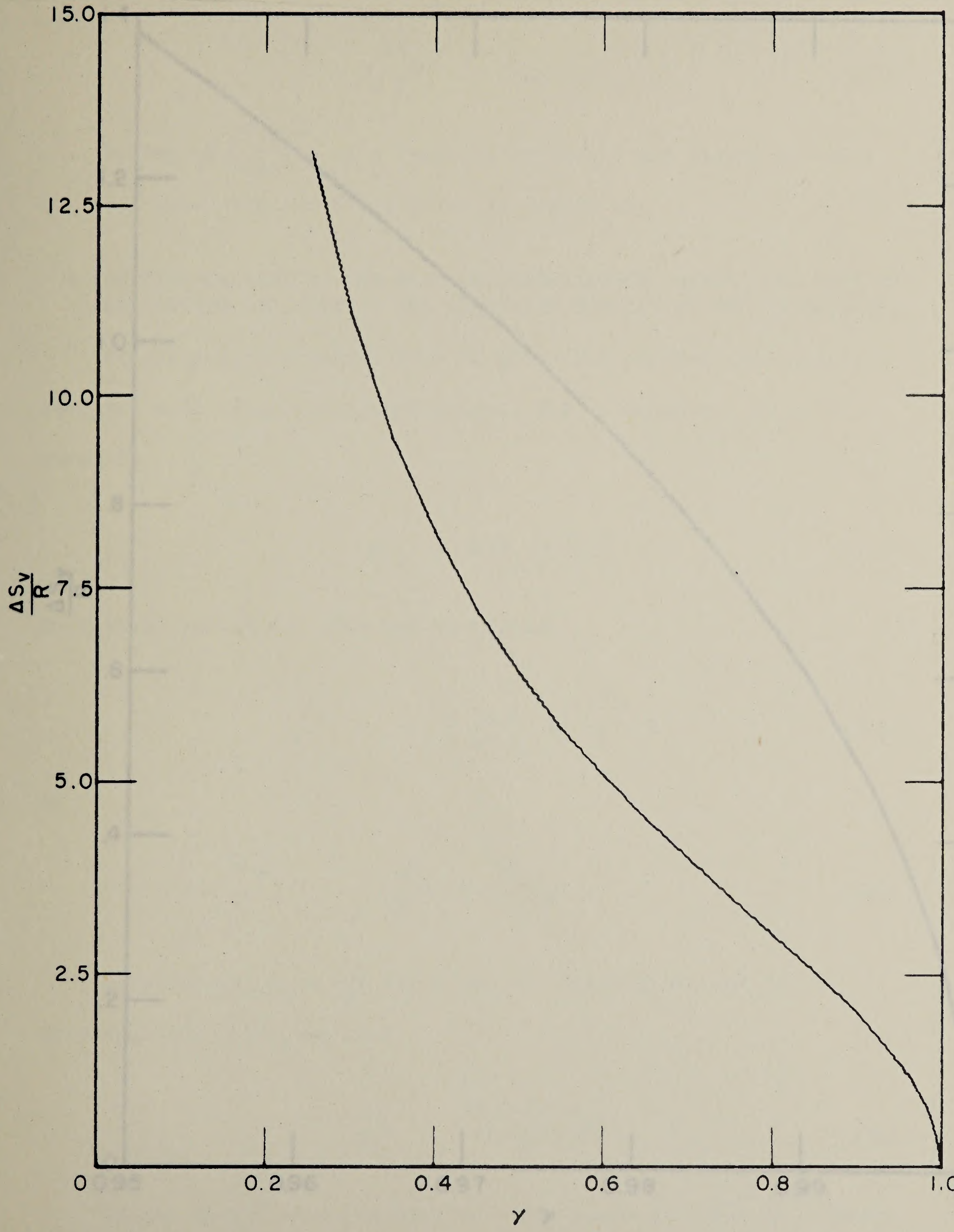

FIGURE 38.-Van der Waals Fluid, Entropy of Vaporization vs γ; $\gamma = {}^{T}/_{T_c}$

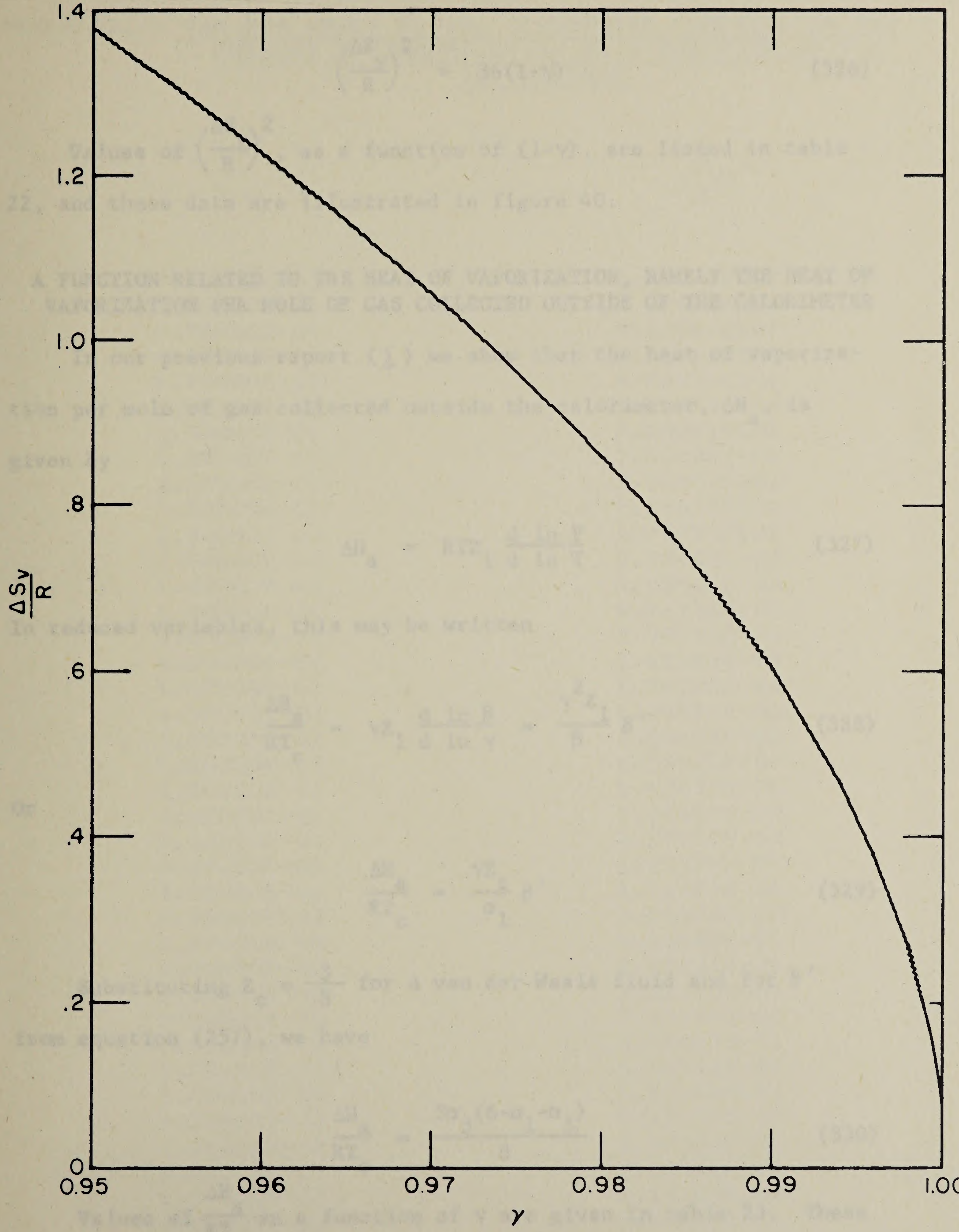

FIGURE 39. - Van der Waals Fluid, Entropy of Vaporization vs γ; $\gamma = T/T_c$

$$\left(\frac{\Delta S_v}{R}\right)^2 = 36(1-\gamma) \tag{326}$$

Values of $\left(\frac{\Delta S_v}{R}\right)^2$, as a function of $(1-\gamma)$, are listed in table 22, and these data are illustrated in figure 40.

A FUNCTION RELATED TO THE HEAT OF VAPORIZATION, NAMELY THE HEAT OF VAPORIZATION PER MOLE OF GAS COLLECTED OUTSIDE OF THE CALORIMETER

In our previous report (1) we show that the heat of vaporization per mole of gas collected outside the calorimeter, ΔH_a, is given by

$$\Delta H_a = RTZ_1 \frac{d \ln P}{d \ln T} \tag{327}$$

In reduced variables, this may be written

$$\frac{\Delta H_a}{RT_c} = \gamma Z_1 \frac{d \ln \beta}{d \ln \gamma} = \frac{\gamma^2 Z_1}{\beta} \beta' \tag{328}$$

Or

$$\frac{\Delta H_a}{RT_c} = \frac{\gamma Z_c}{\alpha_1} \beta' \tag{329}$$

Substituting $Z_c = \frac{3}{8}$ for a van der Waals fluid and for β' from equation (257), we have

$$\frac{\Delta H_a}{RT_c} = \frac{3\alpha_3(6-\alpha_1-\alpha_3)}{8} \tag{330}$$

Values of $\frac{\Delta H_a}{RT_c}$ as a function of γ are given in table 23. These data are illustrated in figures 41 and 42.

TABLE 22. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE ENTROPY OF VAPORIZATION AS A FUNCTION OF THE TEMPERATURE

$\gamma = T/T_c$

$1-\gamma$	$\left(\frac{\Delta S_v}{R}\right)^2$
7.50000E-01	1.79879E&02
7.00000E-01	1.24046E&02
6.50000E-01	9.02286E&01
6.00000E-01	6.80743E&01
5.50000E-01	5.26505E&01
5.00000E-01	4.13779E&01
4.50000E-01	3.28081E&01
4.00000E-01	2.60798E&01
3.50000E-01	2.06551E&01
3.00000E-01	1.61837E&01
2.50000E-01	1.24293E&01
2.00000E-01	9.22732E-00
1.50000E-01	6.45967E-00
1.00000E-01	4.03990E-00
5.00000E-02	1.90318E-00
4.80000E-02	1.82286E-00
4.60000E-02	1.74290E-00
4.40000E-02	1.66332E-00
4.20000E-02	1.58409E-00
4.00000E-02	1.50523E-00
3.80000E-02	1.42673E-00
3.60000E-02	1.34858E-00
3.40000E-02	1.27079E-00
3.20000E-02	1.19334E-00
3.00000E-02	1.11625E-00
2.80000E-02	1.03950E-00
2.60000E-02	9.63099E-01
2.40000E-02	8.87035E-01
2.20000E-02	8.11310E-01
2.00000E-02	7.35921E-01
1.80000E-02	6.60865E-01
1.60000E-02	5.86141E-01
1.40000E-02	5.11746E-01
1.20000E-02	4.37677E-01
1.00000E-02	3.63933E-01
8.00000E-03	2.90511E-01
6.00000E-03	2.17409E-01
4.00000E-03	1.44624E-01
2.00000E-03	7.21558E-02
1.00000E-03	3.60389E-02
0.00000E-99	0.00000E-99

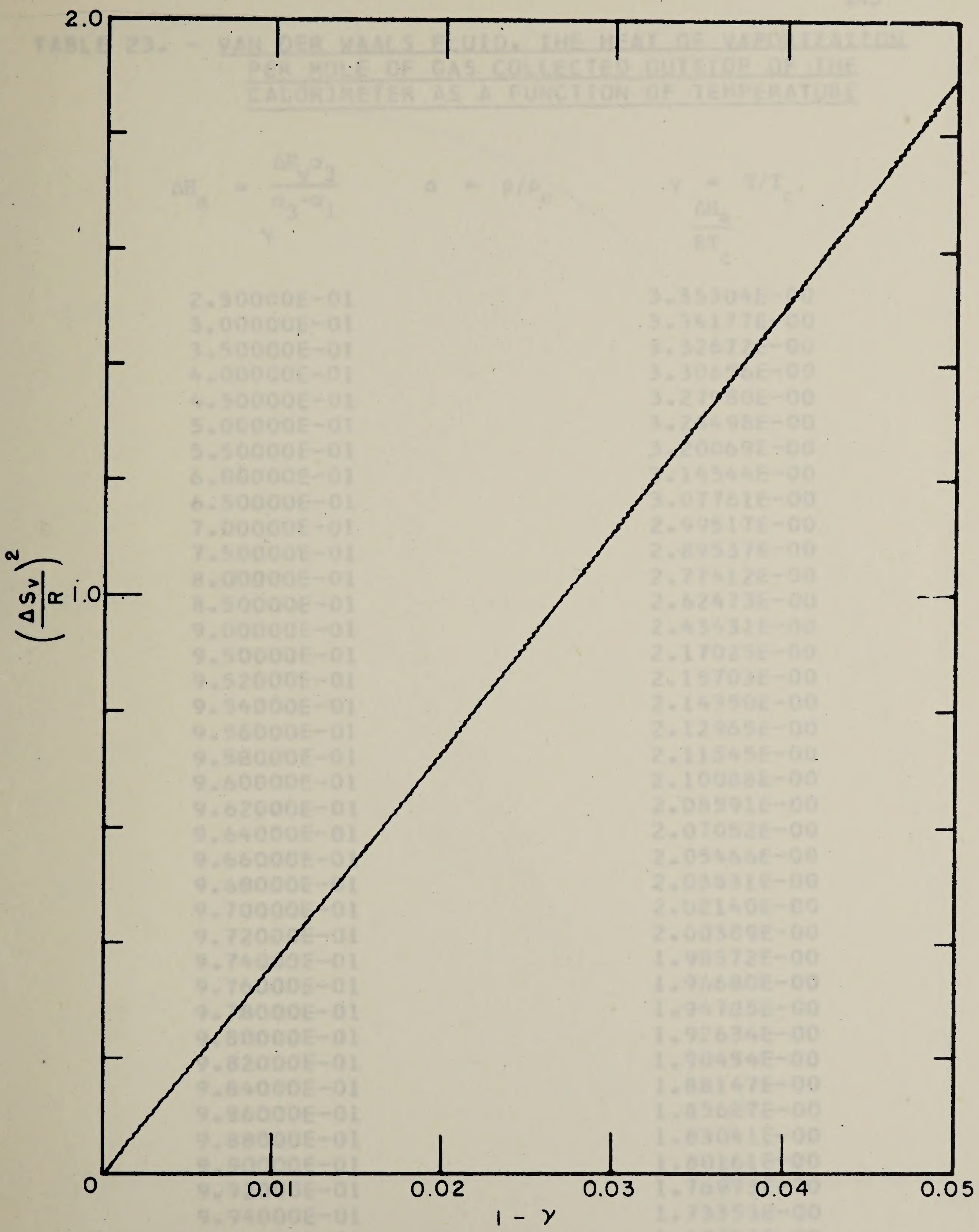

FIGURE 40.- Van der Waals Fluid, Asymptotic Function of the Entropy of Vaporization as a Function of $(1-\gamma)$; $\gamma = T/T_c$

TABLE 23. - VAN DER WAALS FLUID, THE HEAT OF VAPORIZATION PER MOLE OF GAS COLLECTED OUTSIDE OF THE CALORIMETER AS A FUNCTION OF TEMPERATURE

$\Delta H_a = \dfrac{\Delta H_v \alpha_3}{\alpha_3 - \alpha_1}$ $\alpha = \rho/\rho_c$ $\gamma = T/T_c$

γ	$\dfrac{\Delta H_a}{RT_c}$
2.50000E-01	3.35304E-00
3.00000E-01	3.34177E-00
3.50000E-01	3.32672E-00
4.00000E-01	3.30656E-00
4.50000E-01	3.27980E-00
5.00000E-01	3.24498E-00
5.50000E-01	3.20069E-00
6.00000E-01	3.14544E-00
6.50000E-01	3.07761E-00
7.00000E-01	2.99517E-00
7.50000E-01	2.89537E-00
8.00000E-01	2.77412E-00
8.50000E-01	2.62473E-00
9.00000E-01	2.43431E-00
9.50000E-01	2.17025E-00
9.52000E-01	2.15703E-00
9.54000E-01	2.14350E-00
9.56000E-01	2.12965E-00
9.58000E-01	2.11545E-00
9.60000E-01	2.10088E-00
9.62000E-01	2.08591E-00
9.64000E-01	2.07052E-00
9.66000E-01	2.05466E-00
9.68000E-01	2.03831E-00
9.70000E-01	2.02140E-00
9.72000E-01	2.00389E-00
9.74000E-01	1.98572E-00
9.76000E-01	1.96680E-00
9.78000E-01	1.94705E-00
9.80000E-01	1.92634E-00
9.82000E-01	1.90454E-00
9.84000E-01	1.88147E-00
9.86000E-01	1.85687E-00
9.88000E-01	1.83041E-00
9.90000E-01	1.80161E-00
9.92000E-01	1.76973E-00
9.94000E-01	1.73353E-00
9.96000E-01	1.69058E-00
9.98000E-01	1.63464E-00
9.99000E-01	1.59512E-00
1.00000E-00	1.50000E-00

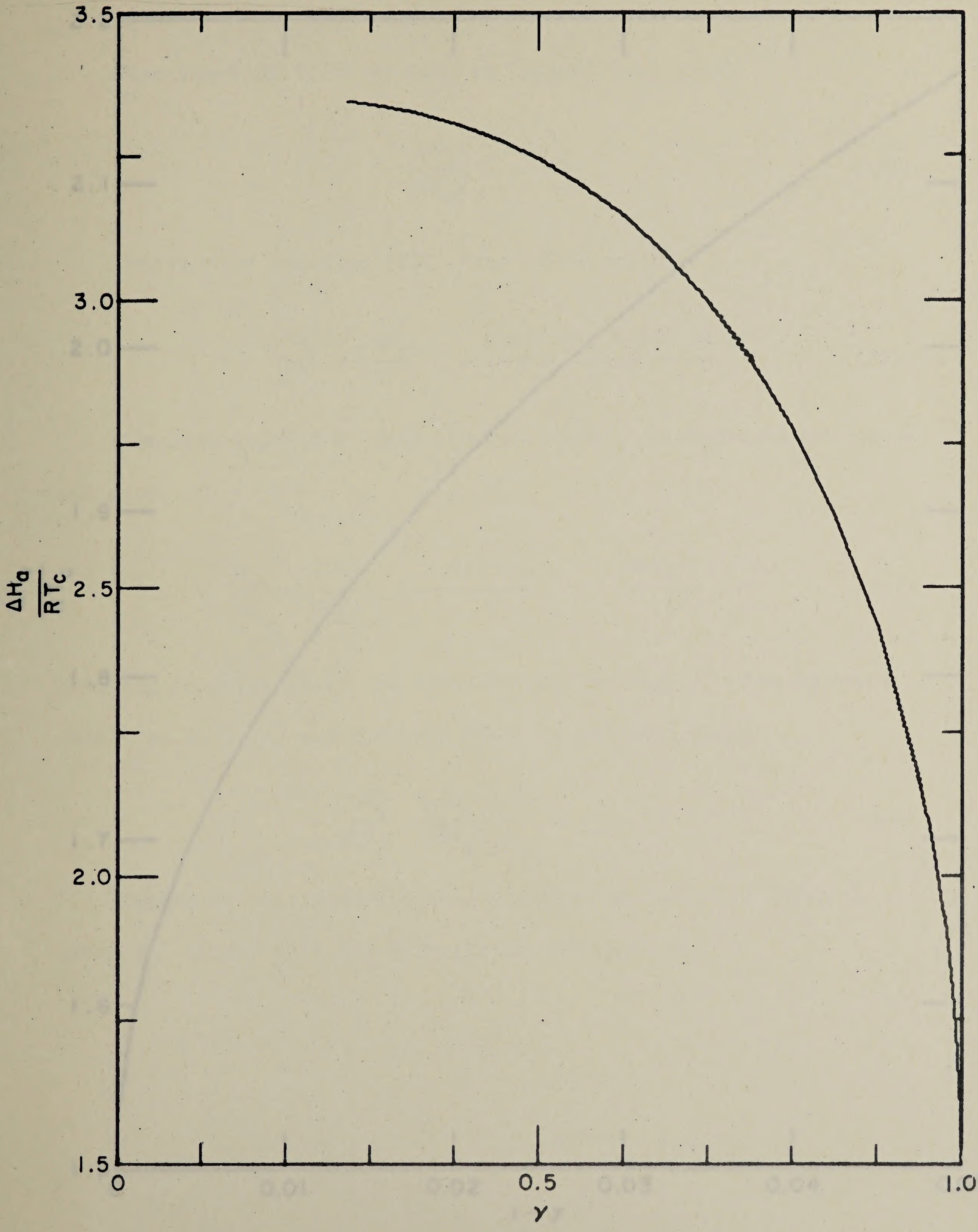

FIGURE 41. - Van der Waals Fluid, The Heat of Vaporization per Mole of Gas Collected Outside of the Calorimeter as a Function of Temperature; $\gamma = T/T_c$

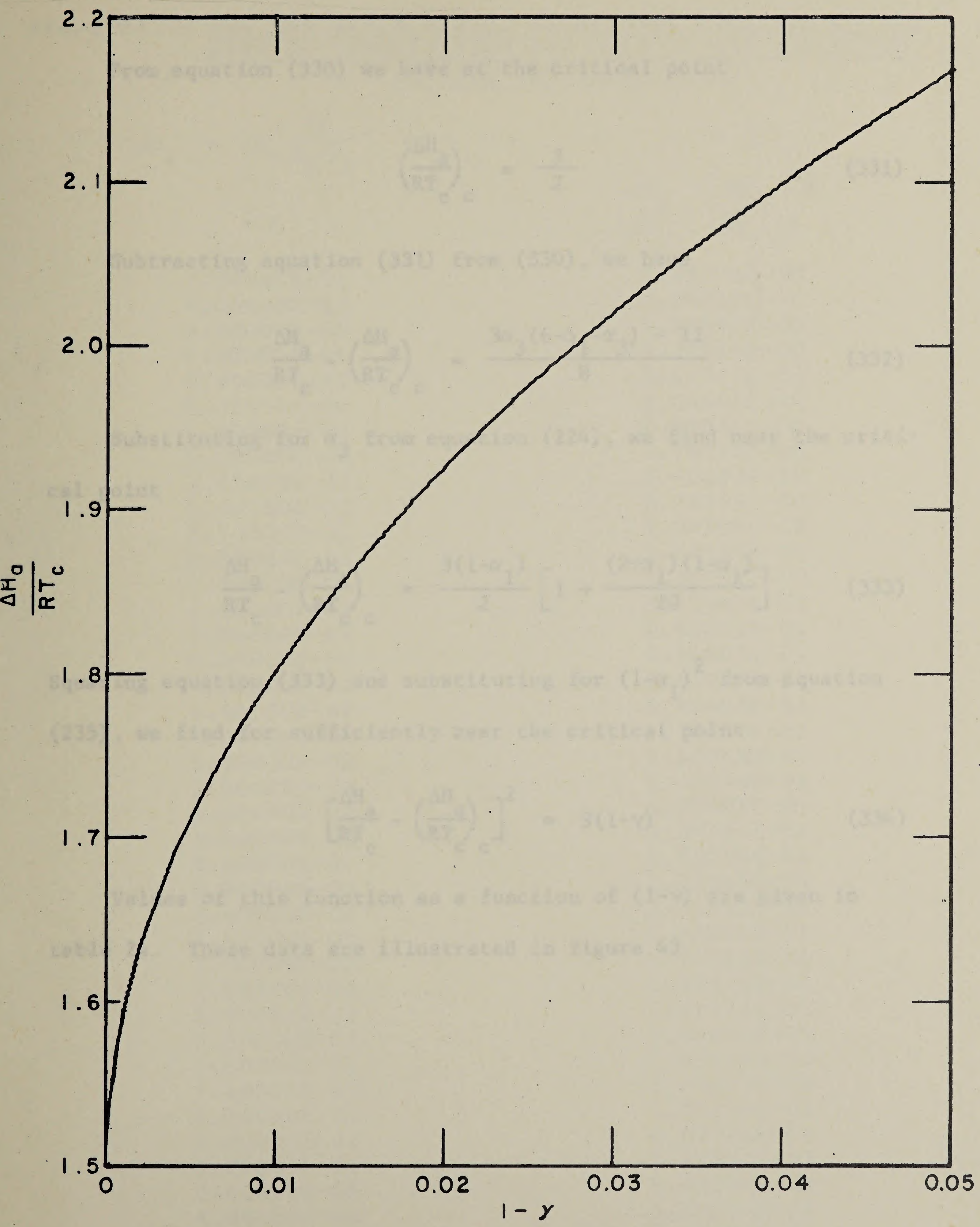

FIGURE 42.- Van der Waals Fluid, The Heat of Vaporization per Mole of Gas Collected Outside of the Calorimeter as a Function of Temperature; $\gamma = T/T_c$

From equation (330) we have at the critical point

$$\left(\frac{\Delta H_a}{RT_c}\right)_c = \frac{3}{2} \tag{331}$$

Subtracting equation (331) from (330), we have

$$\frac{\Delta H_a}{RT_c} - \left(\frac{\Delta H_a}{RT_c}\right)_c = \frac{3\alpha_3(6-\alpha_1-\alpha_3) - 12}{8} \tag{332}$$

Substituting for α_3 from equation (224), we find near the critical point

$$\frac{\Delta H_a}{RT_c} - \left(\frac{\Delta H_a}{RT_c}\right)_c = \frac{3(1-\alpha_1)}{2}\left[1 + \frac{(2+\alpha_1)(1-\alpha_1)}{20}\right] \tag{333}$$

Squaring equation (333) and substituting for $(1-\alpha_1)^2$ from equation (235), we find for sufficiently near the critical point

$$\left[\frac{\Delta H_a}{RT_c} - \left(\frac{\Delta H_a}{RT_c}\right)_c\right]^2 = 9(1-\gamma) \tag{334}$$

Values of this function as a function of $(1-\gamma)$ are given in table 24. These data are illustrated in figure 43.

TABLE 24. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE HEAT OF VAPORIZATION PER MOLE OF GAS COLLECTED OUTSIDE THE CALORIMETER

$$\Delta H_a = \Delta H_v \frac{\alpha_3}{\alpha_3 - \alpha_1} \qquad \alpha = \rho/\rho_c \qquad \gamma = T/T_c$$

$1-\gamma$	$\left[\frac{\Delta H_a}{RT_c} - \left(\frac{\Delta H_a}{RT_c}\right)_c\right]^2$
7.50000E-01	3.43376E-00
7.00000E-01	3.39213E-00
6.50000E-01	3.33692E-00
6.00000E-01	3.26366E-00
5.50000E-01	3.16769E-00
5.00000E-01	3.04498E-00
4.50000E-01	2.89235E-00
4.00000E-01	2.70750E-00
3.50000E-01	2.48888E-00
3.00000E-01	2.23555E-00
2.50000E-01	1.94706E-00
2.00000E-01	1.62340E-00
1.50000E-01	1.26502E-00
1.00000E-01	8.72945E-01
5.00000E-02	4.49246E-01
4.80000E-02	4.31693E-01
4.60000E-02	4.14098E-01
4.40000E-02	3.96460E-01
4.20000E-02	3.78780E-01
4.00000E-02	3.61059E-01
3.80000E-02	3.43298E-01
3.60000E-02	3.25497E-01
3.40000E-02	3.07657E-01
3.20000E-02	2.89779E-01
3.00000E-02	2.71863E-01
2.80000E-02	2.53912E-01
2.60000E-02	2.35926E-01
2.40000E-02	2.17906E-01
2.20000E-02	1.99853E-01
2.00000E-02	1.81771E-01
1.80000E-02	1.63659E-01
1.60000E-02	1.45520E-01
1.40000E-02	1.27357E-01
1.20000E-02	1.09174E-01
1.00000E-02	9.09728E-02
8.00000E-03	7.27591E-02
6.00000E-03	5.45394E-02
4.00000E-03	3.63234E-02
2.00000E-03	1.81280E-02
1.00000E-03	9.04870E-03
0.00000E-99	0.00000E-99

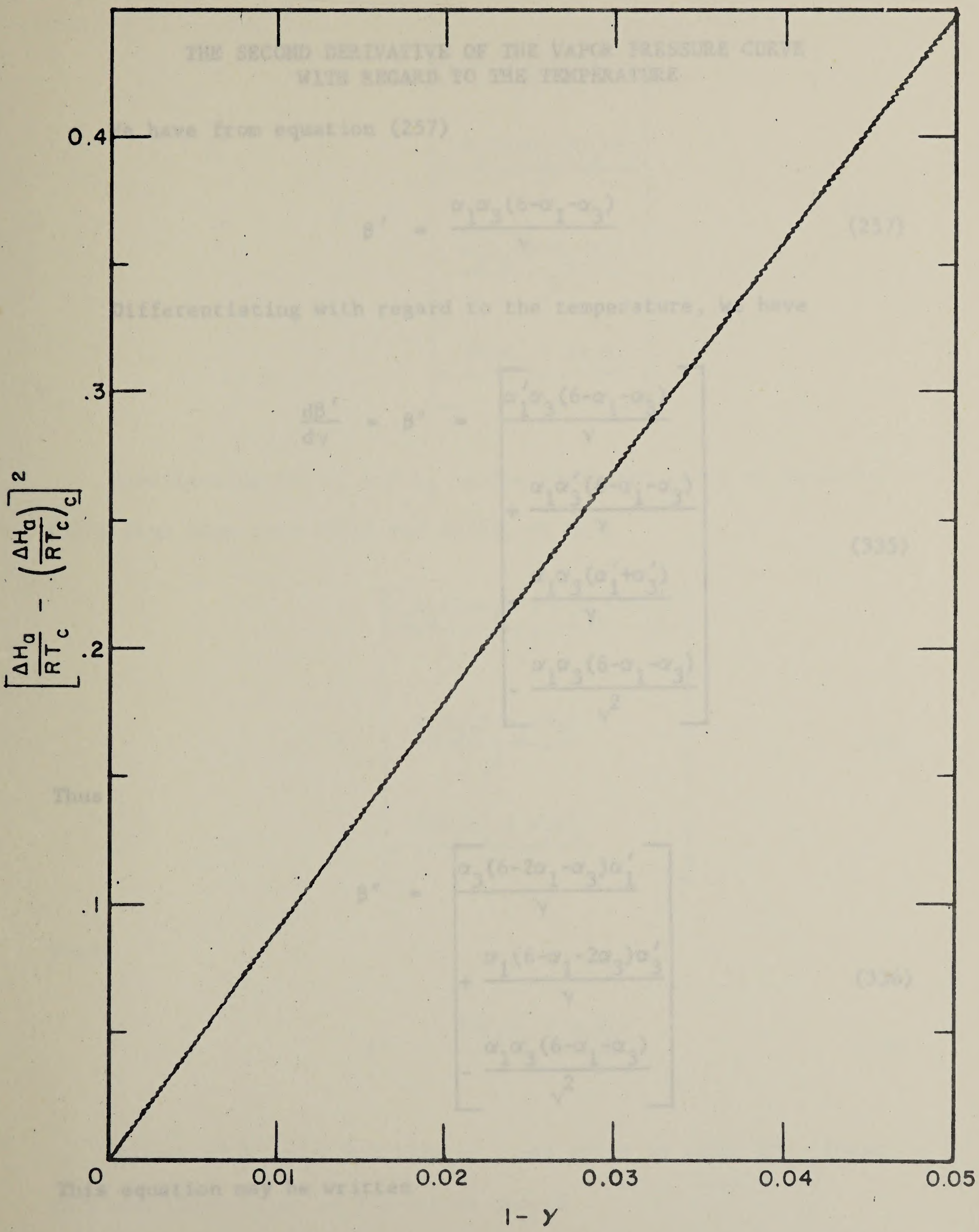

FIGURE 43.- Van der Waals Fluid, Asymptotic Function of the Heat of Vaporization per Mole of Gas Collected Outside of the Calorimeter vs $(1-\gamma)$; $\gamma = T/T_c$

THE SECOND DERIVATIVE OF THE VAPOR PRESSURE CURVE WITH REGARD TO THE TEMPERATURE

We have from equation (257)

$$\beta' = \frac{\alpha_1\alpha_3(6-\alpha_1-\alpha_3)}{\gamma} \qquad (257)$$

Differentiating with regard to the temperature, we have

$$\frac{d\beta'}{d\gamma} = \beta'' = \left[\begin{array}{l} \dfrac{\alpha_1'\alpha_3(6-\alpha_1-\alpha_3)}{\gamma} \\ + \dfrac{\alpha_1\alpha_3'(6-\alpha_1-\alpha_3)}{\gamma} \\ - \dfrac{\alpha_1\alpha_3(\alpha_1'+\alpha_3')}{\gamma} \\ - \dfrac{\alpha_1\alpha_3(6-\alpha_1-\alpha_3)}{\gamma^2} \end{array}\right] \qquad (335)$$

Thus

$$\beta'' = \left[\begin{array}{l} \dfrac{\alpha_3(6-2\alpha_1-\alpha_3)\alpha_1'}{\gamma} \\ + \dfrac{\alpha_1(6-\alpha_1-2\alpha_3)\alpha_3'}{\gamma} \\ - \dfrac{\alpha_1\alpha_3(6-\alpha_1-\alpha_3)}{\gamma^2} \end{array}\right] \qquad (336)$$

This equation may be written

$$\beta'' = \left[\begin{array}{l} \dfrac{\alpha_3(3-2\alpha_1-\alpha_3)\alpha_1'}{\gamma} \\[2ex] + \dfrac{\alpha_1(3-\alpha_1-2\alpha_3)\alpha_3'}{\gamma} \\[2ex] - \dfrac{\alpha_1\alpha_3(6-\alpha_1-\alpha_3)}{\gamma^2} \\[2ex] + \dfrac{3\alpha_3\alpha_1' + 3\alpha_1\alpha_3'}{\gamma} \end{array}\right] \qquad (337)$$

Substituting for α_1' and α_3' in the first two terms of equation (337) from equations (271) and (272), we have

$$\beta'' = \left[\begin{array}{l} \dfrac{\alpha_1\alpha_3(3-\alpha_1) + \alpha_1\alpha_3(3-\alpha_3)}{\gamma^2} \\[2ex] - \dfrac{\alpha_1\alpha_3(6-\alpha_1-\alpha_3)}{\gamma^2} \\[2ex] + \dfrac{3(\alpha_3\alpha_1' + \alpha_1\alpha_3')}{\gamma} \end{array}\right] \qquad (338)$$

Then

$$\beta'' = \frac{3(\alpha_3\alpha_1' + \alpha_1\alpha_3')}{\gamma} \qquad (339)$$

Values of β'' as a function of γ are given in table 25. These data are illustrated in figures 44 and 45.

TABLE 25. – VAN DER WAALS FLUID, THE SECOND TEMPERATURE DERIVATIVE OF THE VAPOR PRESSURE AS A FUNCTION OF TEMPERATURE

$\beta'' = \dfrac{d^2\beta}{d\gamma^2}$ $\beta = P/P_c$ $\gamma = T/T_c$

γ	β''
2.50000E-01	8.36208E-02
3.00000E-01	3.61296E-01
3.50000E-01	9.22795E-01
4.00000E-01	1.72932E-00
4.50000E-01	2.67520E-00
5.00000E-01	3.65756E-00
5.50000E-01	4.60552E-00
6.00000E-01	5.48034E-00
6.50000E-01	6.26603E-00
7.00000E-01	6.96024E-00
7.50000E-01	7.56775E-00
8.00000E-01	8.09658E-00
8.50000E-01	8.55573E-00
9.00000E-01	8.95406E-00
9.50000E-01	9.29972E-00
9.52000E-01	9.31256E-00
9.54000E-01	9.32532E-00
9.56000E-01	9.33802E-00
9.58000E-01	9.35064E-00
9.60000E-01	9.36319E-00
9.62000E-01	9.37567E-00
9.64000E-01	9.38808E-00
9.66000E-01	9.40042E-00
9.68000E-01	9.41270E-00
9.70000E-01	9.42490E-00
9.72000E-01	9.43704E-00
9.74000E-01	9.44910E-00
9.76000E-01	9.46110E-00
9.78000E-01	9.47304E-00
9.80000E-01	9.48491E-00
9.82000E-01	9.49671E-00
9.84000E-01	9.50844E-00
9.86000E-01	9.52011E-00
9.88000E-01	9.53171E-00
9.90000E-01	9.54325E-00
9.92000E-01	9.55473E-00
9.94000E-01	9.56614E-00
9.96000E-01	9.57749E-00
9.98000E-01	9.58877E-00
9.99000E-01	9.59439E-00
1.00000E-00	9.60000E-00

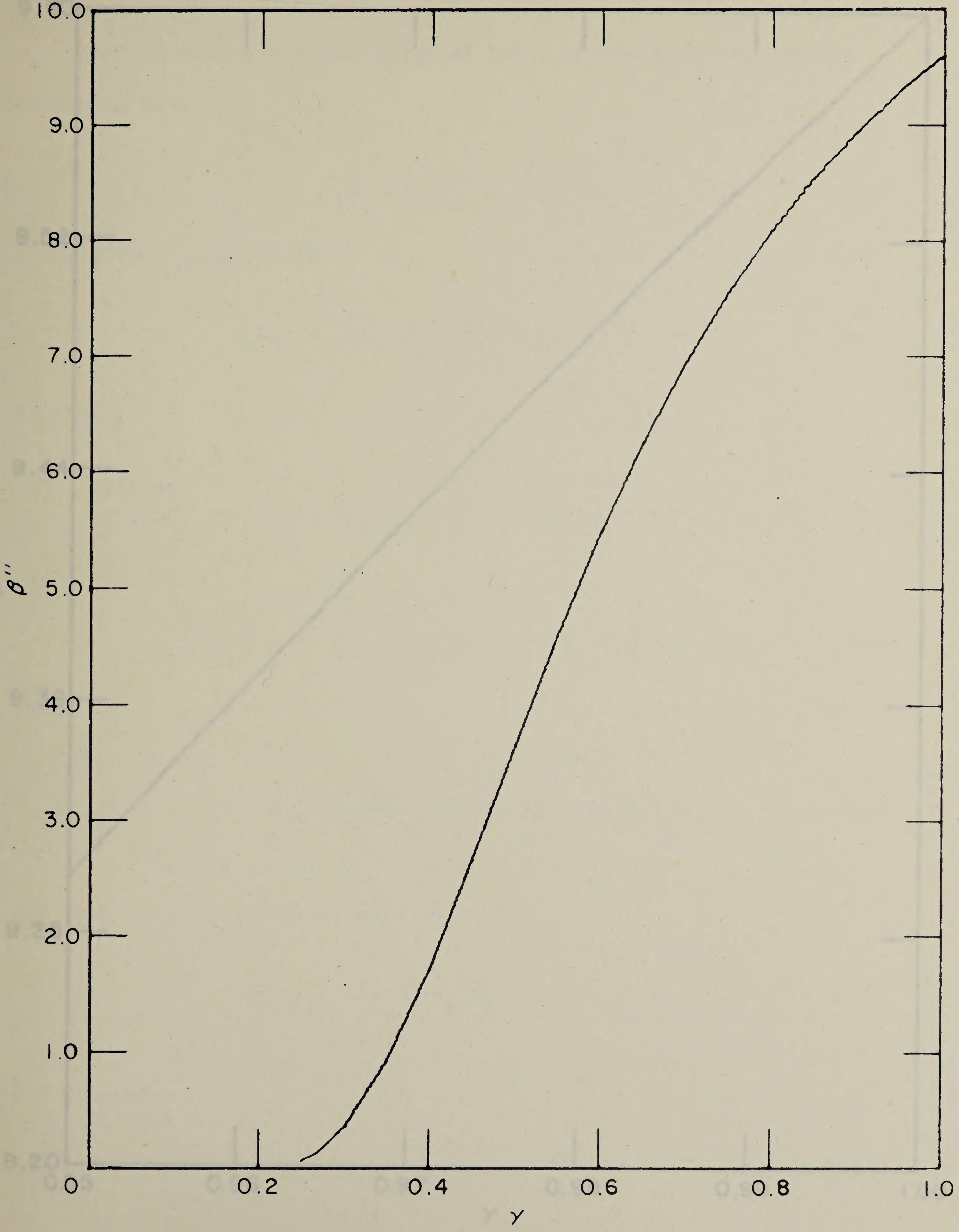

FIGURE 44.- Van der Waals Fluid,
β'' vs γ ; $\beta'' = \frac{d^2\beta}{d\gamma^2}$
$\beta = P/P_c$; $\gamma = T/T_c$

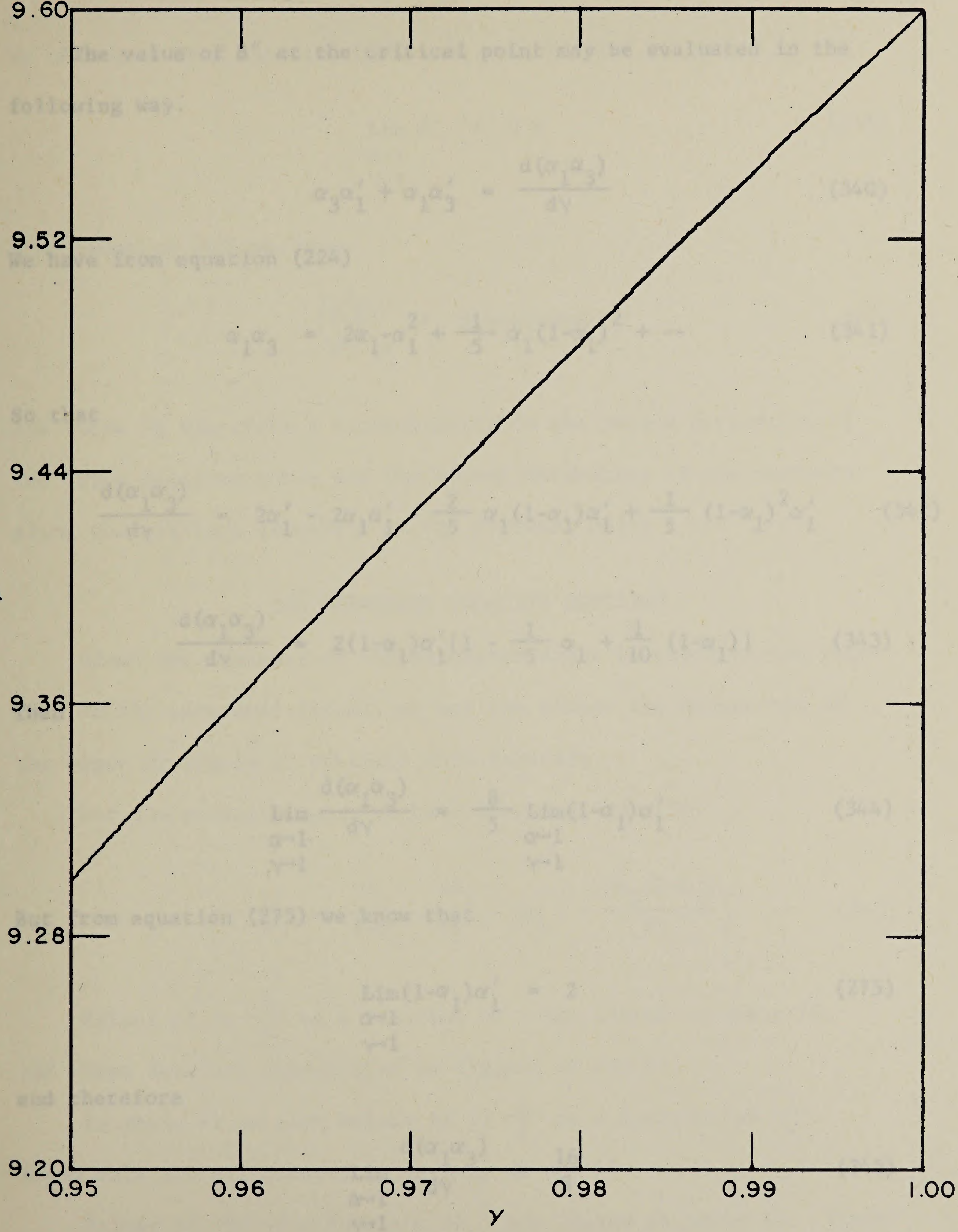

FIGURE 45.- Van der Waals Fluid,
β'' vs γ; $\beta'' = d^2\beta/d\gamma^2$;
$\beta = P/P_c$; $\gamma = T/T_c$

The value of β'' at the critical point may be evaluated in the following way.

$$\alpha_3\alpha_1' + \alpha_1\alpha_3' = \frac{d(\alpha_1\alpha_3)}{d\gamma} \qquad (340)$$

We have from equation (224)

$$\alpha_1\alpha_3 = 2\alpha_1 - \alpha_1^2 + \frac{1}{5}\alpha_1(1-\alpha_1)^2 + -- \qquad (341)$$

So that

$$\frac{d(\alpha_1\alpha_3)}{d\gamma} = 2\alpha_1' - 2\alpha_1\alpha_1' - \frac{2}{5}\alpha_1(1-\alpha_1)\alpha_1' + \frac{1}{5}(1-\alpha_1)^2\alpha_1' \qquad (342)$$

$$\frac{d(\alpha_1\alpha_3)}{d\gamma} = 2(1-\alpha_1)\alpha_1'[1 - \frac{1}{5}\alpha_1 + \frac{1}{10}(1-\alpha_1)] \qquad (343)$$

Then

$$\lim_{\substack{\alpha\to 1\\ \gamma\to 1}} \frac{d(\alpha_1\alpha_3)}{d\gamma} = \frac{8}{5}\lim_{\substack{\alpha\to 1\\ \gamma\to 1}}(1-\alpha_1)\alpha_1' \qquad (344)$$

But from equation (275) we know that

$$\lim_{\substack{\alpha\to 1\\ \gamma\to 1}}(1-\alpha_1)\alpha_1' = 2 \qquad (275)$$

and therefore

$$\lim_{\substack{\alpha\to 1\\ \gamma\to 1}} \frac{d(\alpha_1\alpha_3)}{d\gamma} = \frac{16}{5} \qquad (345)$$

We then have from equation (339), at the critical point

$$\lim_{\substack{\alpha \to 1 \\ \gamma \to 1}} \beta'' = 9.6 \tag{346}$$

From equation (45) we have

$$\left(\frac{\partial^2 \beta}{\partial \gamma^2}\right)_\alpha = 0 \text{ everywhere} \tag{45}$$

and there is therefore a discontinuity in the second derivative of the vapor pressure curve and the second derivative of the pressure along the critical isometric at the critical point.

THE SATURATED FUGACITY FUNCTION

Since the fugacity of the saturated vapor is equal to the fugacity of the saturated liquid, we may use either the properties of the vapor or liquid to evaluate this function.

For the saturated gas, we have from equation (50)

$$\ln \frac{f}{P} = \frac{\alpha_1}{3-\alpha_1} - \frac{9\alpha_1}{4\gamma} - \ln\left[1 - \frac{3\alpha_1(3-\alpha_1)}{8\gamma}\right] \tag{347}$$

Values of $\ln \frac{f}{P}$ as a function of γ are listed in table 26, and these data are illustrated in figures 46 and 47.

In table 27 we give values of $\ln \frac{f}{P}$ as a function of $\frac{1}{\gamma}$. These data are illustrated in figures 48 and 49.

Values of $\frac{f}{P}$ as a function of γ are listed in table 28. These data are illustrated in figures 50 and 51.

TABLE 26. - VAN DER WAALS FLUID, THE LOG FUGACITY FUNCTION AT SATURATION AS A FUNCTION OF TEMPERATURE

$\gamma = T/T_c$

γ	$\ln \frac{f}{P}$
2.50000E-01	-2.13556E-04
3.00000E-01	-1.36253E-03
3.50000E-01	-4.84947E-03
4.00000E-01	-1.20988E-02
4.50000E-01	-2.39976E-02
5.00000E-01	-4.07636E-02
5.50000E-01	-6.21101E-02
6.00000E-01	-8.74708E-02
6.50000E-01	-1.16176E-01
7.00000E-01	-1.47560E-01
7.50000E-01	-1.81017E-01
8.00000E-01	-2.16019E-01
8.50000E-01	-2.52123E-01
9.00000E-01	-2.88961E-01
9.50000E-01	-3.26235E-01
9.52000E-01	-3.27732E-01
9.54000E-01	-3.29228E-01
9.56000E-01	-3.30726E-01
9.58000E-01	-3.32223E-01
9.60000E-01	-3.33720E-01
9.62000E-01	-3.35218E-01
9.64000E-01	-3.36716E-01
9.66000E-01	-3.38214E-01
9.68000E-01	-3.39713E-01
9.70000E-01	-3.41211E-01
9.72000E-01	-3.42710E-01
9.74000E-01	-3.44209E-01
9.76000E-01	-3.45708E-01
9.78000E-01	-3.47208E-01
9.80000E-01	-3.48707E-01
9.82000E-01	-3.50206E-01
9.84000E-01	-3.51706E-01
9.86000E-01	-3.53206E-01
9.88000E-01	-3.54706E-01
9.90000E-01	-3.56205E-01
9.92000E-01	-3.57705E-01
9.94000E-01	-3.59205E-01
9.96000E-01	-3.60705E-01
9.98000E-01	-3.62205E-01
9.99000E-01	-3.62955E-01
1.00000E-00	-3.63705E-01

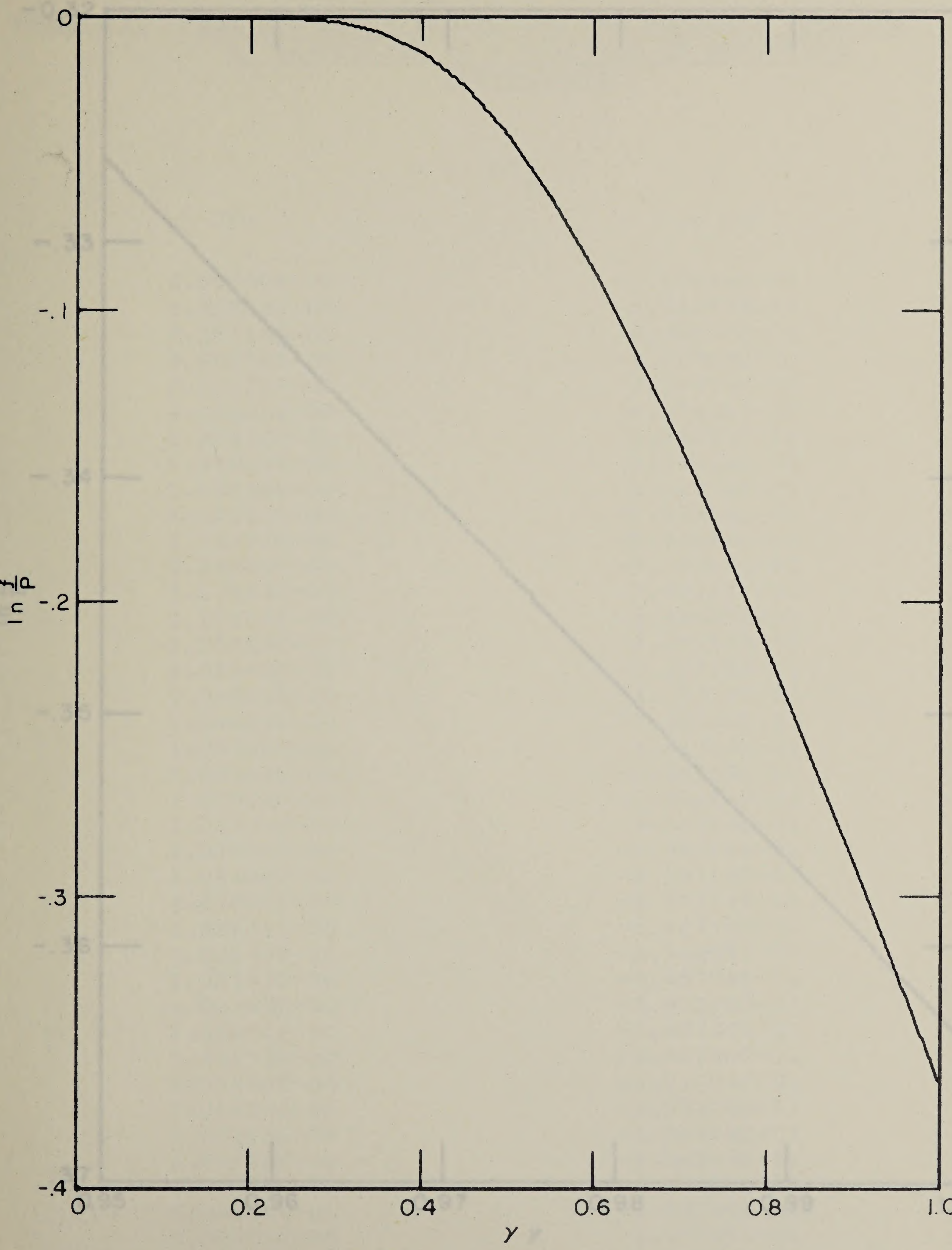

FIGURE 46.- Van der Waals Fluid, $\ln \frac{f}{P}$ at Saturation vs γ; $\gamma = T/T_c$; f = Fugacity

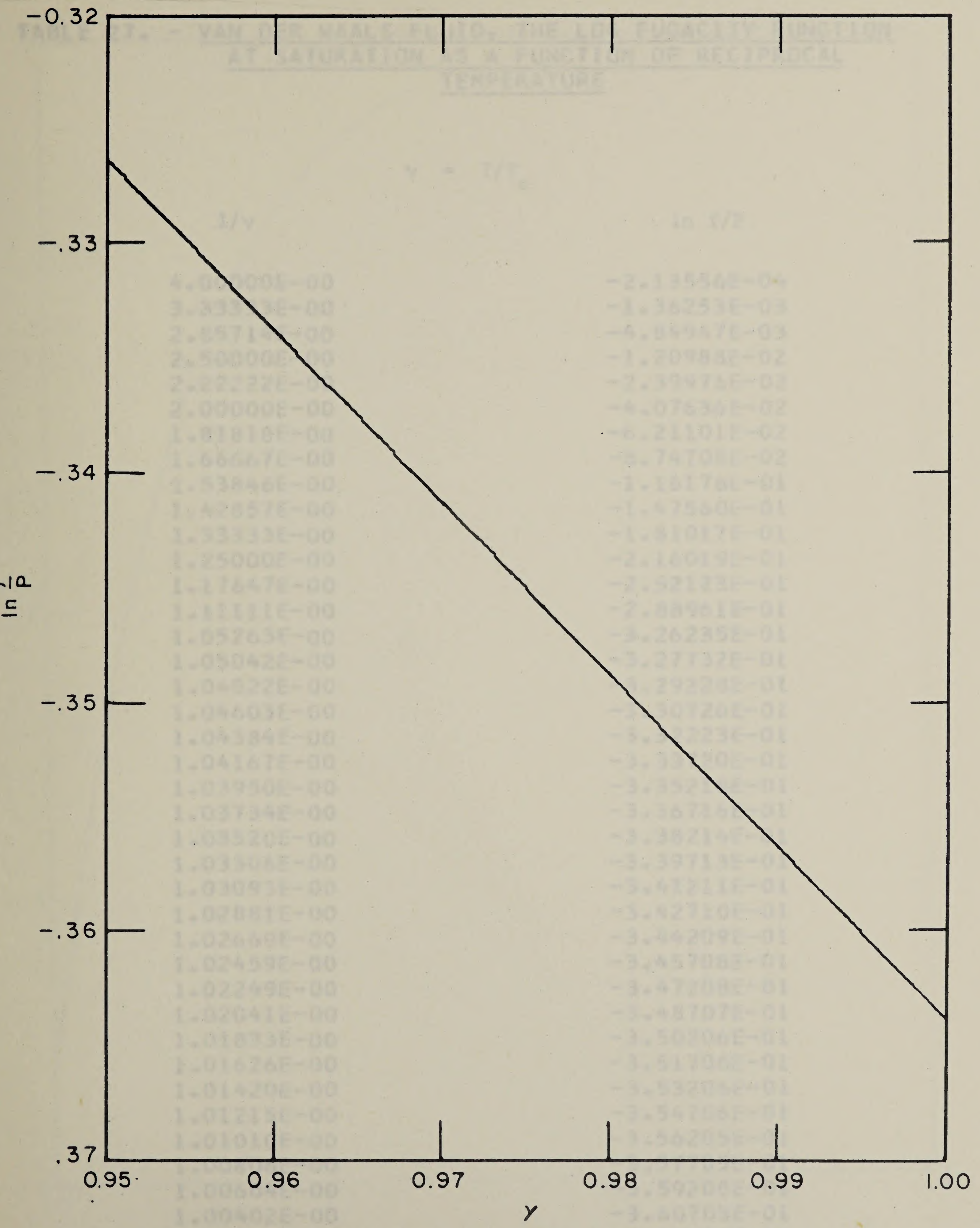

FIGURE 47.- Van der Waals Fluid, $\ln\frac{f}{P}$ at Saturation vs γ; $\gamma = T/T_c$; f = Fugacity

TABLE 27. - VAN DER WAALS FLUID, THE LOG FUGACITY FUNCTION AT SATURATION AS A FUNCTION OF RECIPROCAL TEMPERATURE

$\gamma = T/T_c$

$1/\gamma$	$\ln f/P$
4.00000E-00	-2.13556E-04
3.33333E-00	-1.36253E-03
2.85714E-00	-4.84947E-03
2.50000E-00	-1.20988E-02
2.22222E-00	-2.39976E-02
2.00000E-00	-4.07636E-02
1.81818E-00	-6.21101E-02
1.66667E-00	-8.74708E-02
1.53846E-00	-1.16176E-01
1.42857E-00	-1.47560E-01
1.33333E-00	-1.81017E-01
1.25000E-00	-2.16019E-01
1.17647E-00	-2.52123E-01
1.11111E-00	-2.88961E-01
1.05263E-00	-3.26235E-01
1.05042E-00	-3.27732E-01
1.04822E-00	-3.29228E-01
1.04603E-00	-3.30726E-01
1.04384E-00	-3.32223E-01
1.04167E-00	-3.33720E-01
1.03950E-00	-3.35218E-01
1.03734E-00	-3.36716E-01
1.03520E-00	-3.38214E-01
1.03306E-00	-3.39713E-01
1.03093E-00	-3.41211E-01
1.02881E-00	-3.42710E-01
1.02669E-00	-3.44209E-01
1.02459E-00	-3.45708E-01
1.02249E-00	-3.47208E-01
1.02041E-00	-3.48707E-01
1.01833E-00	-3.50206E-01
1.01626E-00	-3.51706E-01
1.01420E-00	-3.53206E-01
1.01215E-00	-3.54706E-01
1.01010E-00	-3.56205E-01
1.00806E-00	-3.57705E-01
1.00604E-00	-3.59205E-01
1.00402E-00	-3.60705E-01
1.00200E-00	-3.62205E-01
1.00100E-00	-3.62955E-01
1.00000E-00	-3.63705E-01

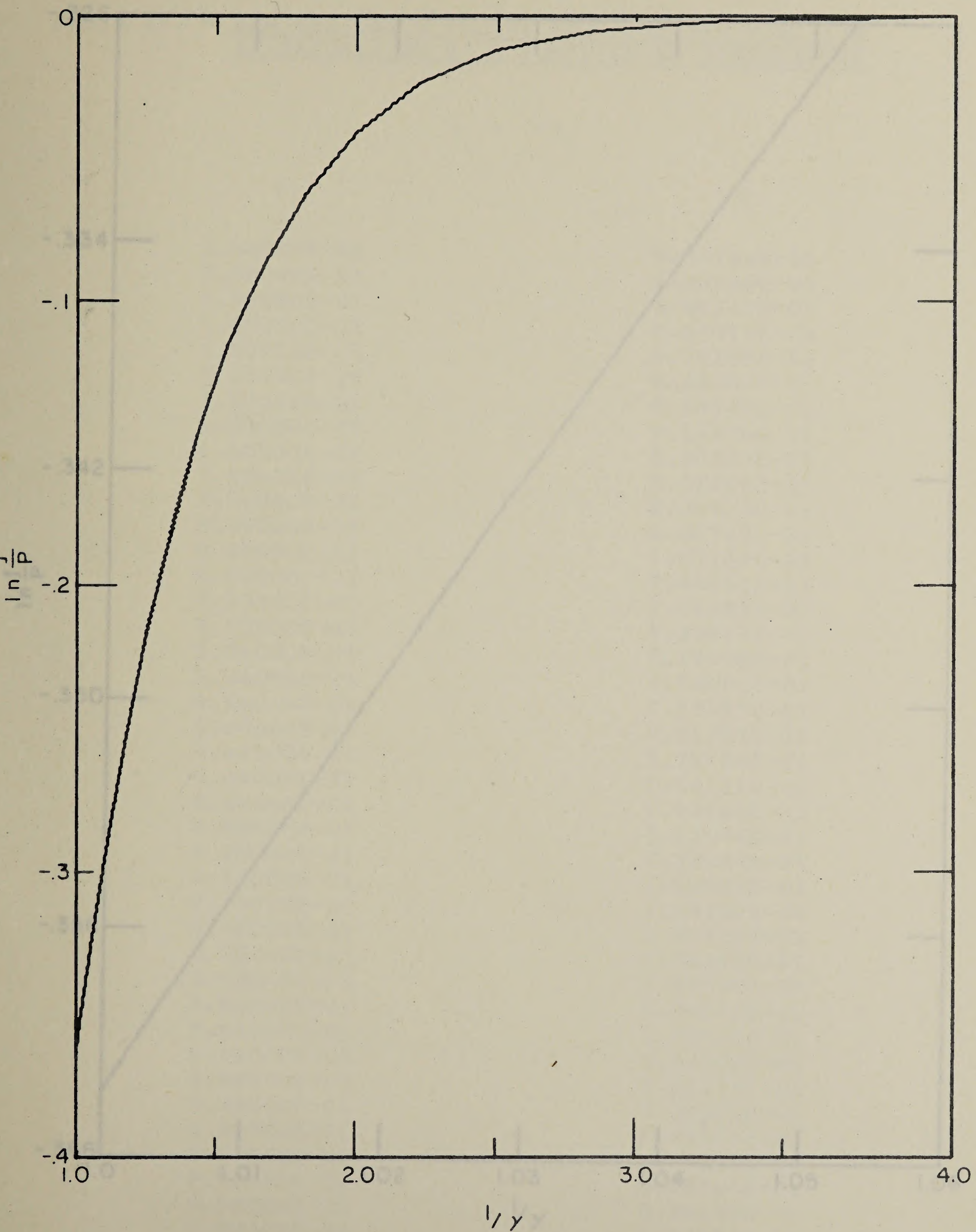

FIGURE 48.- Van der Waals Fluid, $\ln \frac{f}{P}$ at Saturation vs $^1/\gamma$; $\gamma = {}^T/_{T_c}$; f = Fugacity

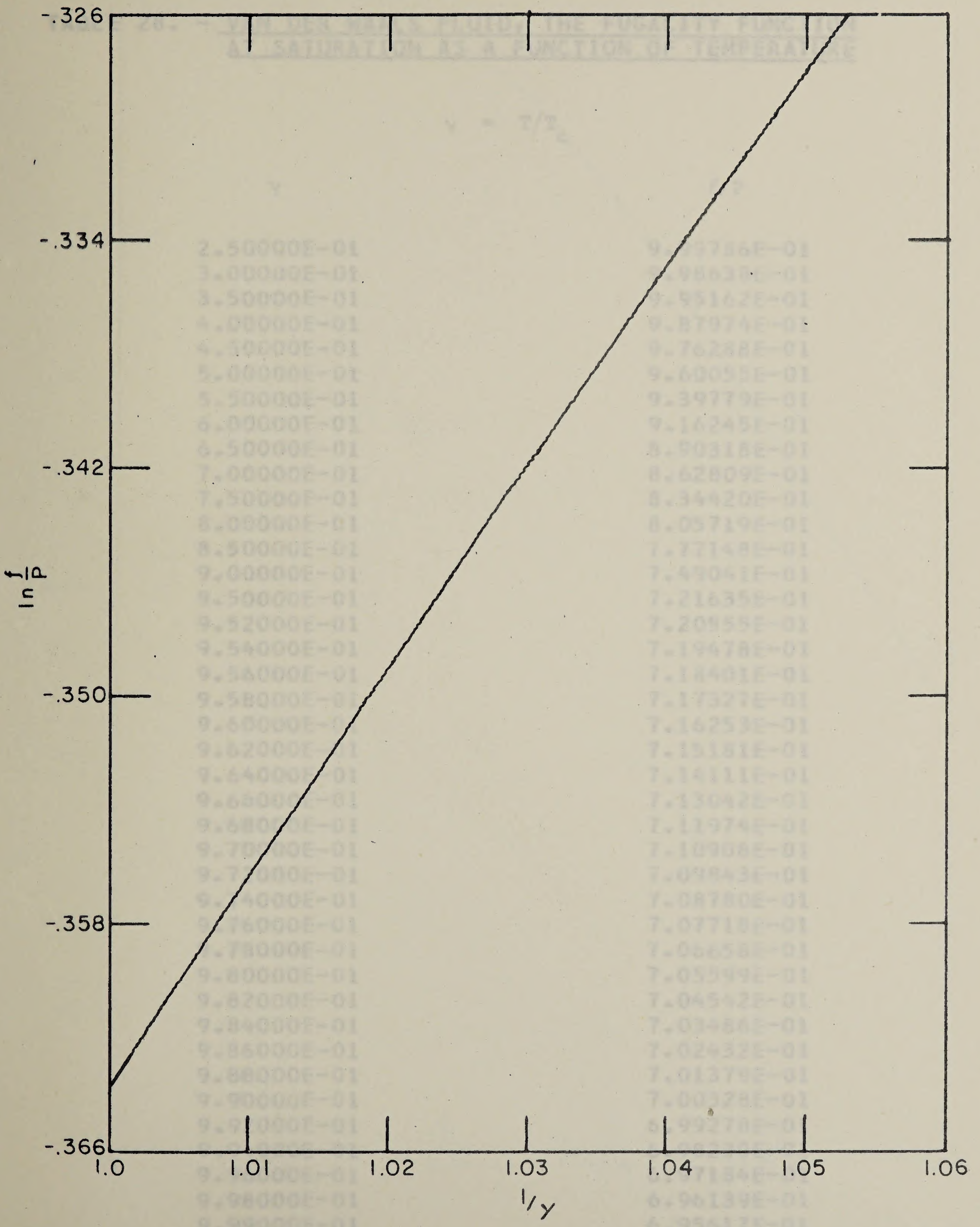

FIGURE 49.- Van der Waals Fluid, $\ln \frac{f}{P}$ at Saturation vs $^1/_y$; $y = {}^T/_{T_c}$; f = Fugacity

TABLE 28. - VAN DER WAALS FLUID, THE FUGACITY FUNCTION AT SATURATION AS A FUNCTION OF TEMPERATURE

$\gamma = T/T_c$

γ	f/P
2.50000E-01	9.99786E-01
3.00000E-01	9.98638E-01
3.50000E-01	9.95162E-01
4.00000E-01	9.87974E-01
4.50000E-01	9.76288E-01
5.00000E-01	9.60055E-01
5.50000E-01	9.39779E-01
6.00000E-01	9.16245E-01
6.50000E-01	8.90318E-01
7.00000E-01	8.62809E-01
7.50000E-01	8.34420E-01
8.00000E-01	8.05719E-01
8.50000E-01	7.77148E-01
9.00000E-01	7.49041E-01
9.50000E-01	7.21635E-01
9.52000E-01	7.20555E-01
9.54000E-01	7.19478E-01
9.56000E-01	7.18401E-01
9.58000E-01	7.17327E-01
9.60000E-01	7.16253E-01
9.62000E-01	7.15181E-01
9.64000E-01	7.14111E-01
9.66000E-01	7.13042E-01
9.68000E-01	7.11974E-01
9.70000E-01	7.10908E-01
9.72000E-01	7.09843E-01
9.74000E-01	7.08780E-01
9.76000E-01	7.07718E-01
9.78000E-01	7.06658E-01
9.80000E-01	7.05599E-01
9.82000E-01	7.04542E-01
9.84000E-01	7.03486E-01
9.86000E-01	7.02432E-01
9.88000E-01	7.01379E-01
9.90000E-01	7.00328E-01
9.92000E-01	6.99278E-01
9.94000E-01	6.98230E-01
9.96000E-01	6.97184E-01
9.98000E-01	6.96139E-01
9.99000E-01	6.95617E-01
1.00000E-00	6.95095E-01

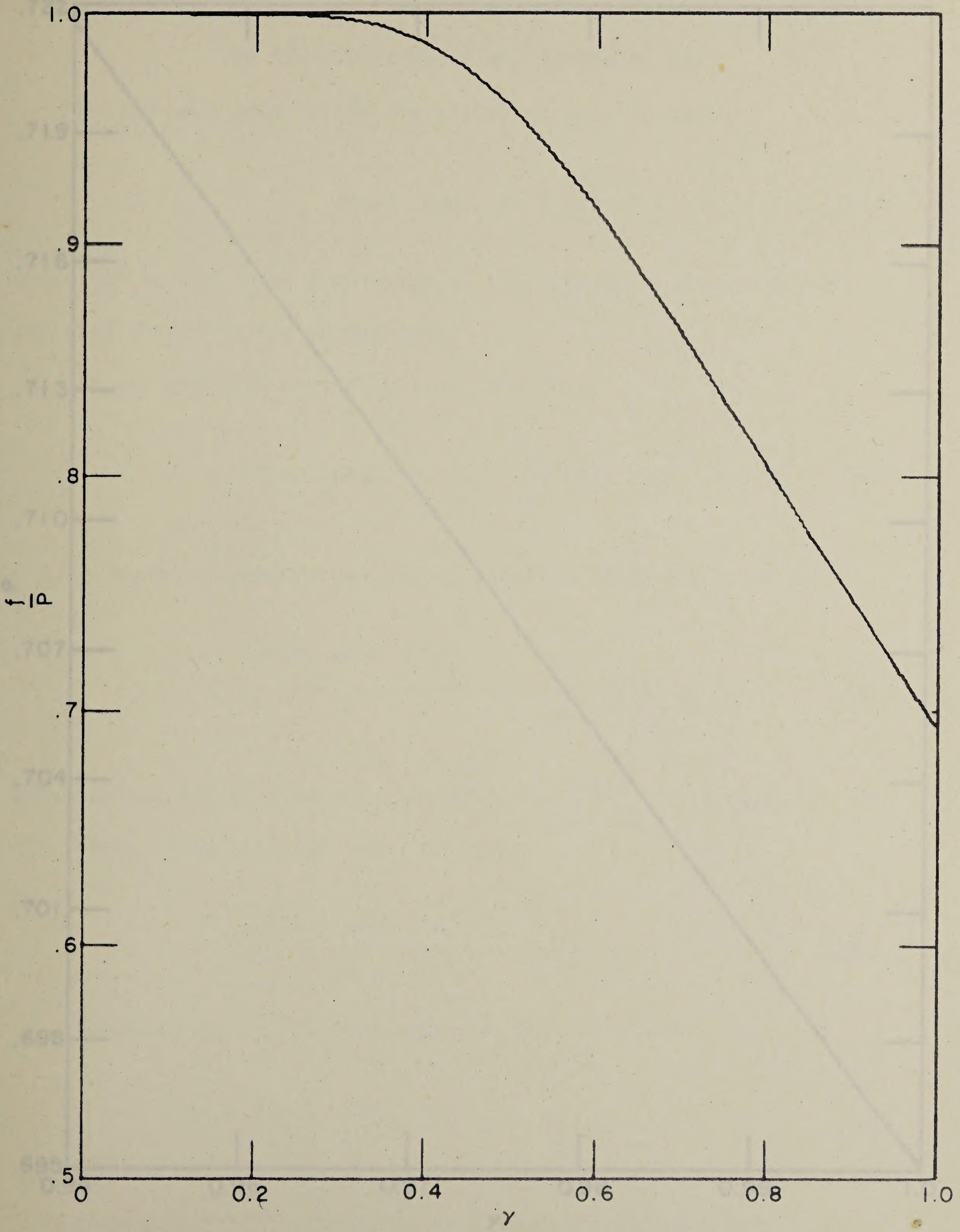

FIGURE 50.-Van der Waals Fluid, $\frac{f}{P}$ at Saturation vs γ; γ = $^T/_{T_c}$; f = Fugacity

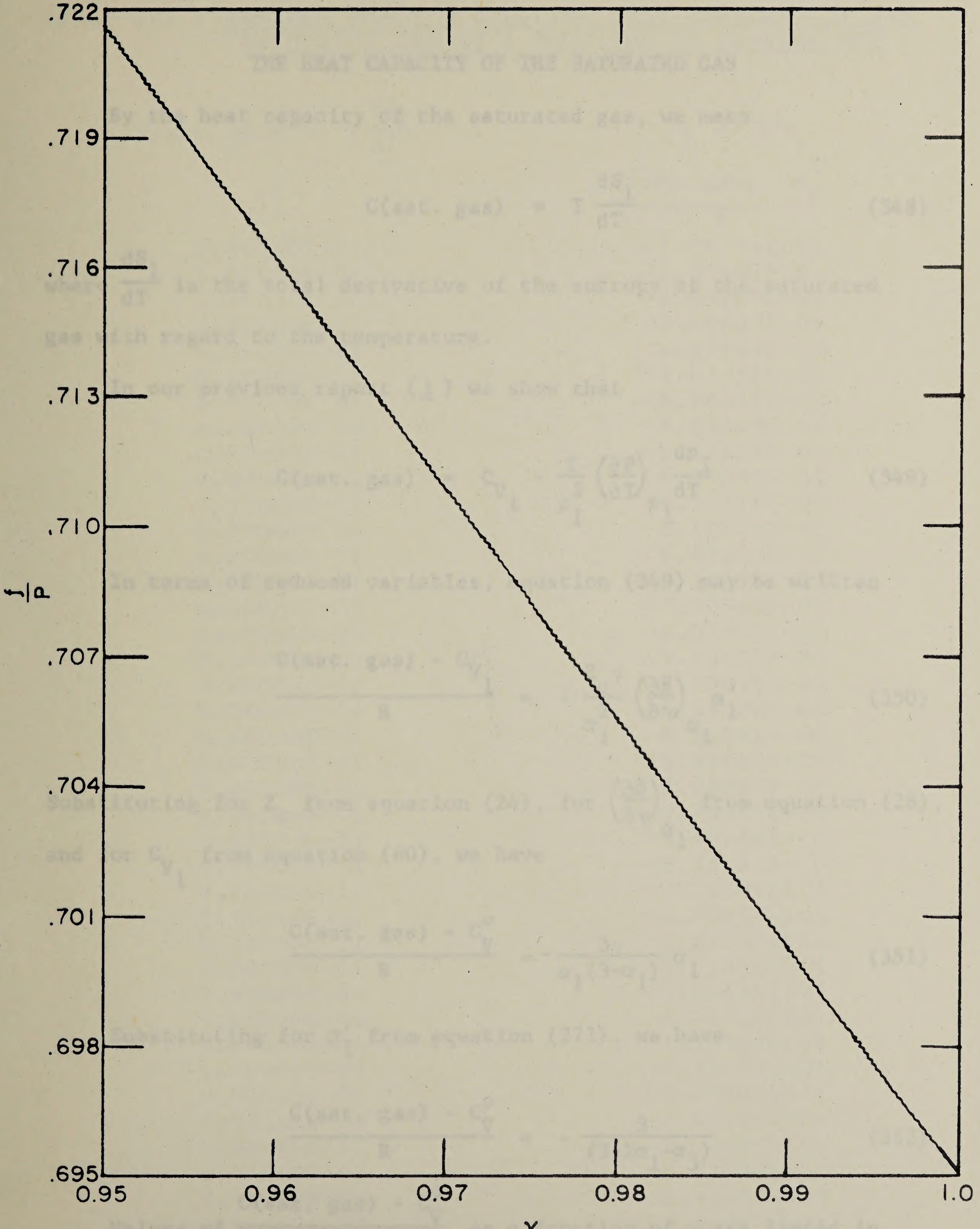

FIGURE 51.- Van der Waals Fluid, $\frac{f}{P}$ at Saturation vs y; $y = T/T_c$; f = Fugacity

THE HEAT CAPACITY OF THE SATURATED GAS

By the heat capacity of the saturated gas, we mean

$$C(\text{sat. gas}) = T \frac{dS_1}{dT} \tag{348}$$

where $\frac{dS_1}{dT}$ is the total derivative of the entropy of the saturated gas with regard to the temperature.

In our previous report (1) we show that

$$C(\text{sat. gas}) = C_{V_1} - \frac{T}{\rho_1^2} \left(\frac{\partial P}{\partial T}\right)_{\rho_1} \frac{d\rho_1}{dT} \tag{349}$$

In terms of reduced variables, equation (349) may be written

$$\frac{C(\text{sat. gas}) - C_{V_1}}{R} = - \frac{Z_c \gamma}{\alpha_1^2} \left(\frac{\partial \beta}{\partial \gamma}\right)_{\alpha_1} \alpha_1' \tag{350}$$

Substituting for Z_c from equation (24), for $\left(\frac{\partial \beta}{\partial \gamma}\right)_{\alpha_1}$ from equation (28), and for C_{V_1} from equation (60), we have

$$\frac{C(\text{sat. gas}) - C_V^o}{R} = - \frac{3\gamma}{\alpha_1 (3-\alpha_1)} \alpha_1' \tag{351}$$

Substituting for α_1' from equation (271), we have

$$\frac{C(\text{sat. gas}) - C_V^o}{R} = - \frac{3}{(3-2\alpha_1-\alpha_3)} \tag{352}$$

Values of $\frac{C(\text{sat. gas}) - C_V^o}{R}$ as a function of γ are listed in table 29. These data are illustrated in figures 52 and 53.

TABLE 29. - VAN DER WAALS FLUID, THE HEAT CAPACITY OF THE SATURATED GAS AS A FUNCTION OF TEMPERATURE

$C(\text{sat. gas}) = T \frac{dS_1}{dT}$ $\gamma = T/T_c$

γ	$\frac{C(\text{sat. gas}) - C_V^o}{R}$
2.50000E-01	-1.24176E&01
3.00000E-01	-1.01681E&01
3.50000E-01	-8.59269E-00
4.00000E-01	-7.45822E-00
4.50000E-01	-6.63029E-00
5.00000E-01	-6.02392E-00
5.50000E-01	-5.58357E-00
6.00000E-01	-5.27345E-00
6.50000E-01	-5.07226E-00
7.00000E-01	-4.97089E-00
7.50000E-01	-4.97324E-00
8.00000E-01	-5.10238E-00
8.50000E-01	-5.42103E-00
9.00000E-01	-6.10691E-00
9.50000E-01	-7.88969E-00
9.52000E-01	-8.02043E-00
9.54000E-01	-8.16003E-00
9.56000E-01	-8.30951E-00
9.58000E-01	-8.47002E-00
9.60000E-01	-8.64292E-00
9.62000E-01	-8.82983E-00
9.64000E-01	-9.03267E-00
9.66000E-01	-9.25375E-00
9.68000E-01	-9.49588E-00
9.70000E-01	-9.76252E-00
9.72000E-01	-1.00579E&01
9.74000E-01	-1.03877E&01
9.76000E-01	-1.07587E&01
9.78000E-01	-1.11801E&01
9.80000E-01	-1.16644E&01
9.82000E-01	-1.22286E&01
9.84000E-01	-1.28968E&01
9.86000E-01	-1.37052E&01
9.88000E-01	-1.47101E&01
9.90000E-01	-1.60055E&01
9.92000E-01	-1.77635E&01
9.94000E-01	-2.03442E&01
9.96000E-01	-2.46807E&01
9.98000E-01	-3.44849E&01
9.99000E-01	-4.83647E&01
1.00000E-00	$-\infty$

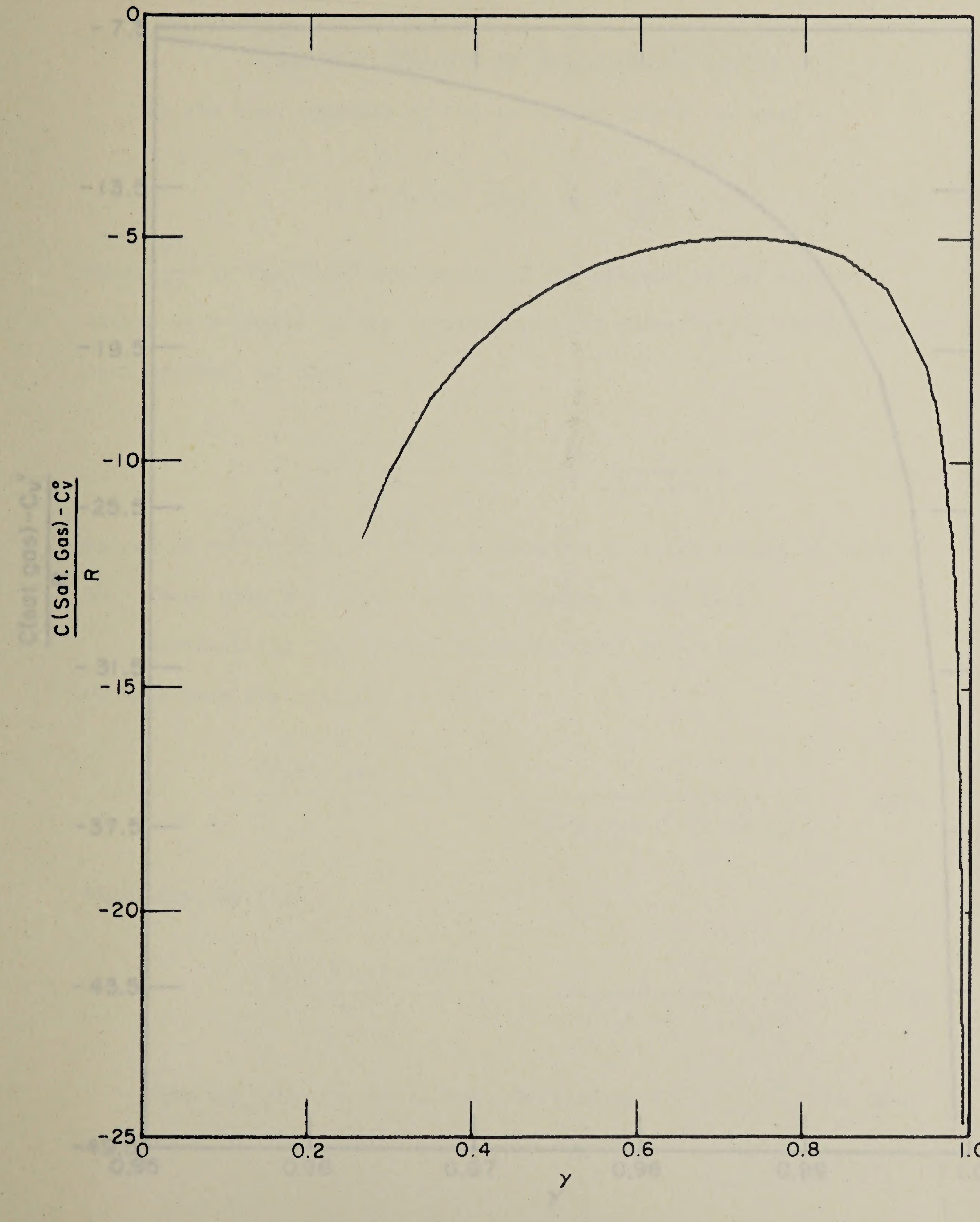

FIGURE 52.– Van der Waals Fluid, Heat Capacity of Saturated Gas vs γ; $\gamma = T/T_c$

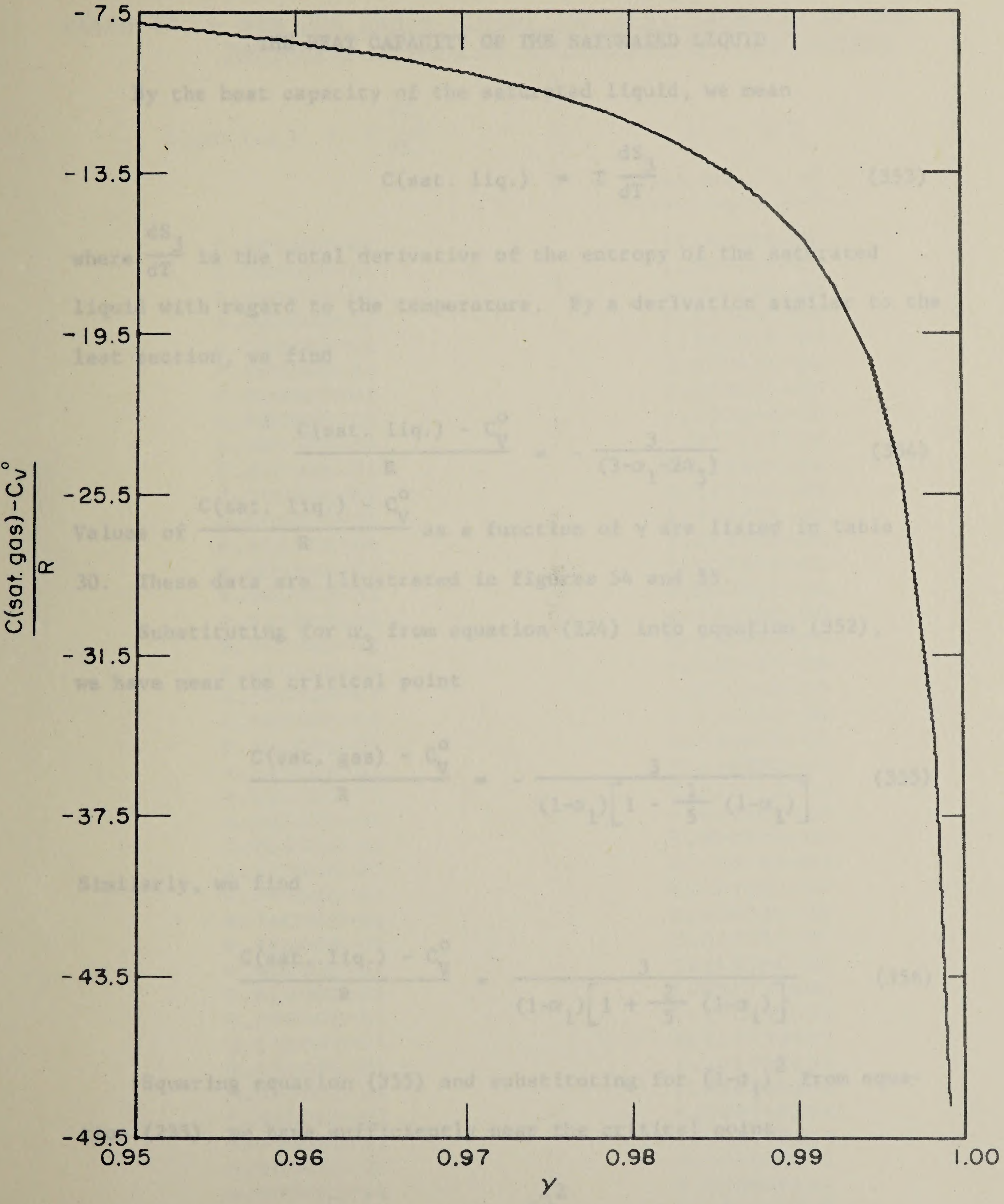

FIGURE 53.- Van der Waals Fluid, Heat Capacity of Saturated gas vs γ ; $\gamma = T/T_c$

THE HEAT CAPACITY OF THE SATURATED LIQUID

By the heat capacity of the saturated liquid, we mean

$$C(\text{sat. liq.}) = T \frac{dS_3}{dT} \tag{353}$$

where $\frac{dS_3}{dT}$ is the total derivative of the entropy of the saturated liquid with regard to the temperature. By a derivation similar to the last section, we find

$$\frac{C(\text{sat. liq.}) - C_V^o}{R} = - \frac{3}{(3-\alpha_1-2\alpha_3)} \tag{354}$$

Values of $\frac{C(\text{sat. liq.}) - C_V^o}{R}$ as a function of γ are listed in table 30. These data are illustrated in figures 54 and 55.

Substituting for α_3 from equation (224) into equation (352), we have near the critical point

$$\frac{C(\text{sat. gas}) - C_V^o}{R} = - \frac{3}{(1-\alpha_1)\left[1 - \frac{1}{5}(1-\alpha_1)\right]} \tag{355}$$

Similarly, we find

$$\frac{C(\text{sat. liq.}) - C_V^o}{R} = \frac{3}{(1-\alpha_1)\left[1 + \frac{2}{5}(1-\alpha_1)\right]} \tag{356}$$

Squaring equation (355) and substituting for $(1-\alpha_1)^2$ from equation (235), we have sufficiently near the critical point

$$\frac{\left[C(\text{sat. gas}) - C_V^o\right]^2}{R^2} = \frac{9}{4(1-\gamma)} \tag{357}$$

TABLE 30. - VAN DER WAALS FLUID, THE HEAT CAPACITY OF THE SATURATED LIQUID AS A FUNCTION OF TEMPERATURE

$C(\text{sat.liq.}) = T \dfrac{dS_3}{dT}$ $\qquad$ $\gamma = T/T_c$

γ	$\dfrac{C(\text{sat.liq.}) - C_V^o}{R}$
2.50000E-01	1.19205E-00
3.00000E-01	1.24547E-00
3.50000E-01	1.30623E-00
4.00000E-01	1.37565E-00
4.50000E-01	1.45531E-00
5.00000E-01	1.54740E-00
5.50000E-01	1.65500E-00
6.00000E-01	1.78264E-00
6.50000E-01	1.93714E-00
7.00000E-01	2.12930E-00
7.50000E-01	2.37733E-00
8.00000E-01	2.71473E-00
8.50000E-01	3.21195E-00
9.00000E-01	4.05250E-00
9.50000E-01	5.97051E-00
9.52000E-01	6.10630E-00
9.54000E-01	6.25093E-00
9.56000E-01	6.40542E-00
9.58000E-01	6.57090E-00
9.60000E-01	6.74876E-00
9.62000E-01	6.94060E-00
9.64000E-01	7.14835E-00
9.66000E-01	7.37431E-00
9.68000E-01	7.62130E-00
9.70000E-01	7.89277E-00
9.72000E-01	8.19304E-00
9.74000E-01	8.52755E-00
9.76000E-01	8.90332E-00
9.78000E-01	9.32953E-00
9.80000E-01	9.81854E-00
9.82000E-01	1.03873E&01
9.84000E-01	1.10603E&01
9.86000E-01	1.18733E&01
9.88000E-01	1.28828E&01
9.90000E-01	1.41828E&01
9.92000E-01	1.59454E&01
9.94000E-01	1.85307E&01
9.96000E-01	2.28716E&01
9.98000E-01	3.26804E&01
9.99000E-01	4.65624E&01
1.00000E-00	+ ∞

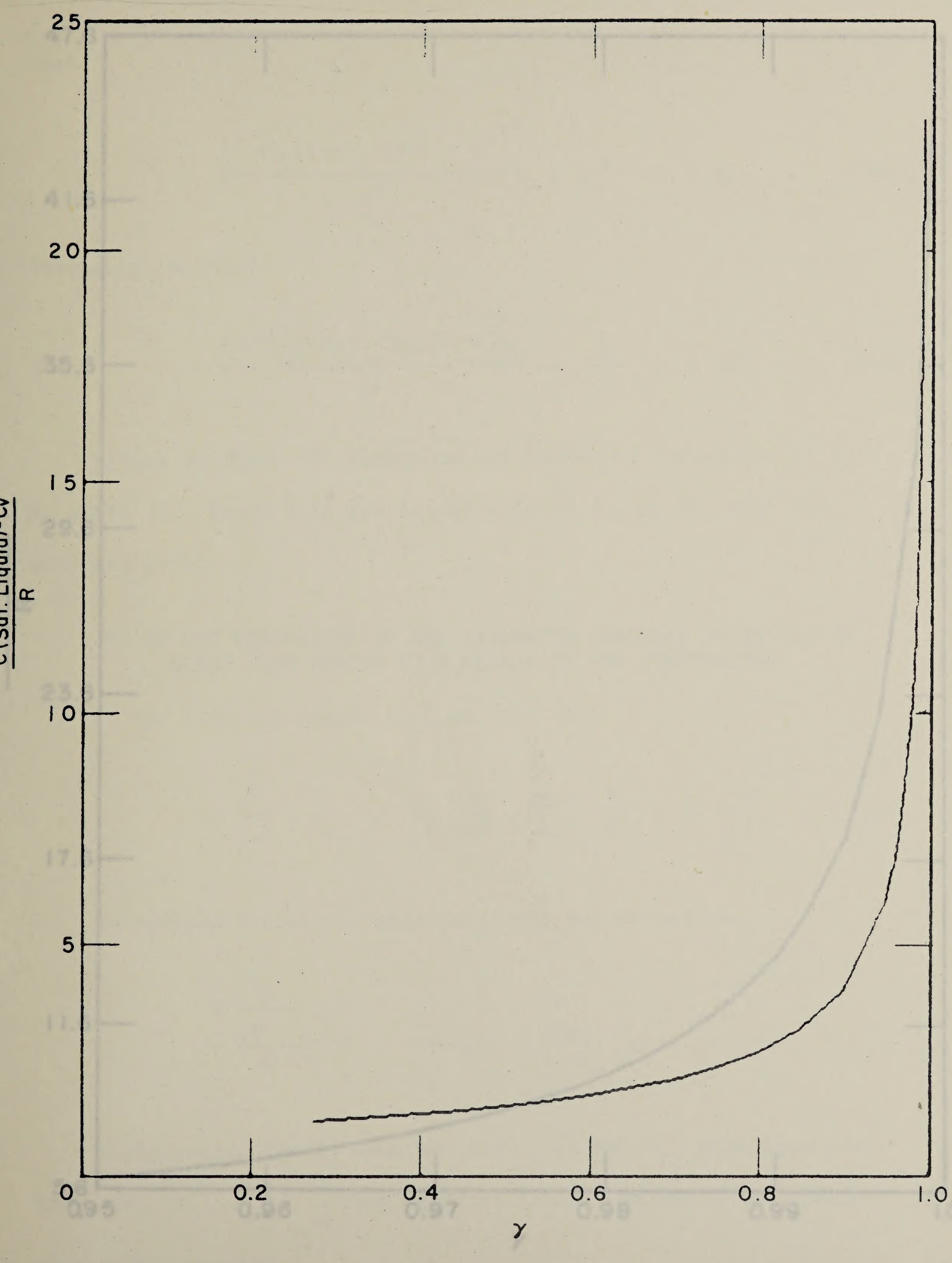

FIGURE 54.- Van der Waals Fluid, Heat Capacity of Saturated Liquid vs γ; $\gamma = T/T_c$

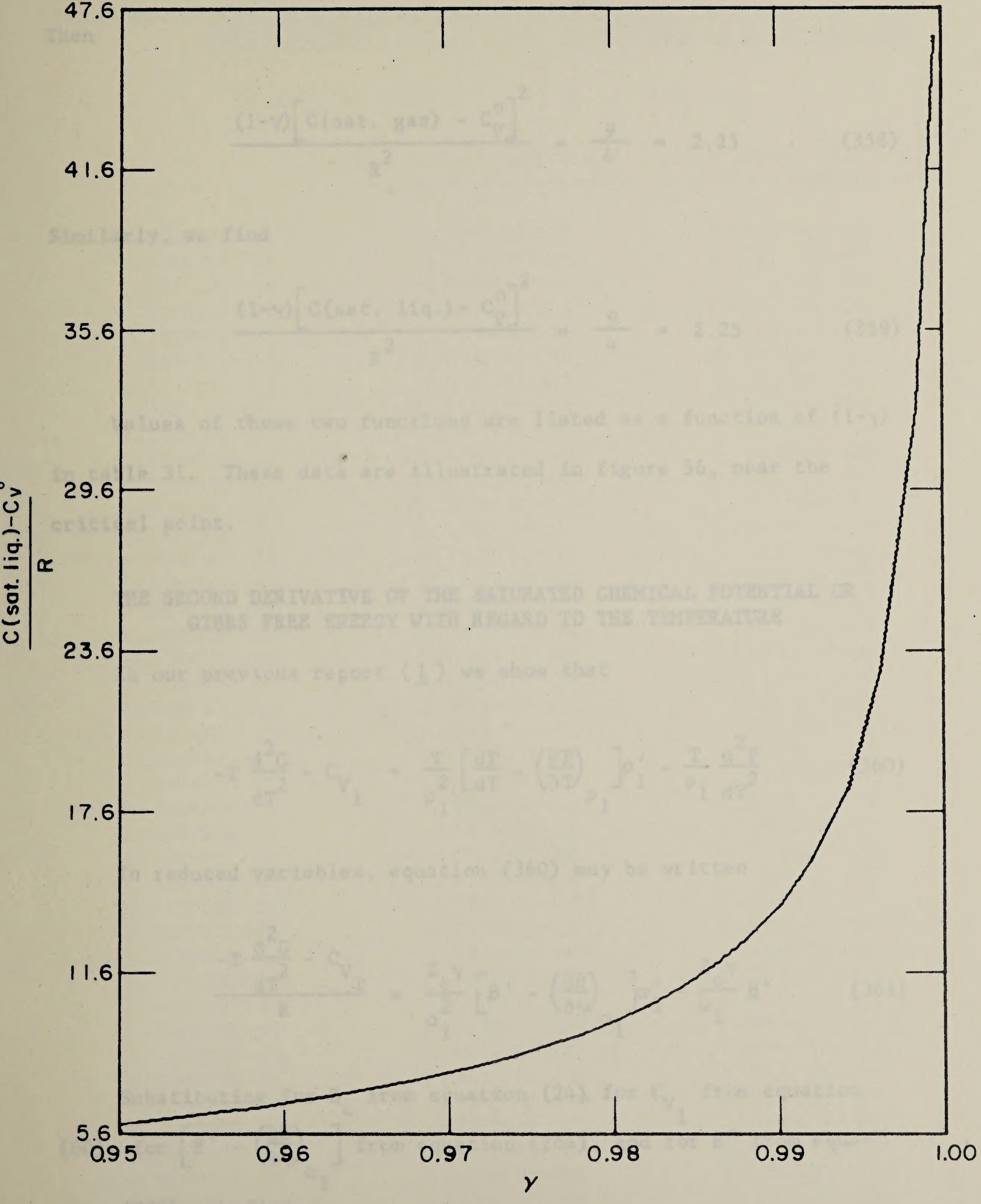

FIGURE 55– Van der Waals Fluid, Heat Capacity of Saturated Liquid vs γ ; $\gamma = T/T_c$

Then

$$\frac{(1-\gamma)\left[C(\text{sat. gas}) - C_V^o\right]^2}{R^2} = \frac{9}{4} = 2.25 \qquad (358)$$

Similarly, we find

$$\frac{(1-\gamma)\left[C(\text{sat. liq.}) - C_V^o\right]^2}{R^2} = \frac{9}{4} = 2.25 \qquad (359)$$

Values of these two functions are listed as a function of (1-γ) in table 31. These data are illustrated in figure 56, near the critical point.

THE SECOND DERIVATIVE OF THE SATURATED CHEMICAL POTENTIAL OR GIBBS FREE ENERGY WITH REGARD TO THE TEMPERATURE

In our previous report (1) we show that

$$-T\frac{d^2G}{dT^2} - C_{V_1} = \frac{T}{\rho_1^2}\left[\frac{dP}{dT} - \left(\frac{\partial P}{\partial T}\right)_{\rho_1}\right]\rho_1' - \frac{T}{\rho_1}\frac{d^2P}{dT^2} \qquad (360)$$

In reduced variables, equation (360) may be written

$$\frac{-T\dfrac{d^2G}{dT^2} - C_{V_1}}{R} = \frac{Z_c\gamma}{\alpha_1^2}\left[\beta' - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1}\right]\alpha_1' - \frac{Z_c\gamma}{\alpha_1}\beta'' \qquad (361)$$

Substituting for Z_c from equation (24), for C_{V_1} from equation (60), for $\left[\beta' - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1}\right]$ from equation (264), and for β'' from equation (339), we find

$$\frac{-T\dfrac{d^2G}{dT^2} - C_V^o}{R} = -\frac{9}{8}(\alpha_1' + \alpha_3') \qquad (362)$$

TABLE 31. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE HEAT CAPACITIES OF THE SATURATED LIQUID AND GAS

$C(\text{sat.}) = T\frac{dS}{dT}$ $\qquad \gamma = T/T_c$

$1-\gamma$	$\frac{(1-\gamma)\left[C(\text{sat. gas}) - C_V^o\right]^2}{R^2}$	$\frac{(1-\gamma)\left[C(\text{sat. liq.} - C_V^o\right]^2}{R^2}$
7.50000E-01	1.15648E&02	1.06574E-00
7.00000E-01	7.23745E&01	1.08583E-00
6.50000E-01	4.79923E&01	1.10906E-00
6.00000E-01	3.33750E&01	1.13544E-00
5.50000E-01	2.41784E&01	1.16486E-00
5.00000E-01	1.81438E&01	1.19722E-00
4.50000E-01	1.40293E&01	1.23257E-00
4.00000E-01	1.11237E&01	1.27113E-00
3.50000E-01	9.00475E-00	1.31338E-00
3.00000E-01	7.41294E-00	1.36018E-00
2.50000E-01	6.18328E-00	1.41293E-00
2.00000E-01	5.20686E-00	1.47396E-00
1.50000E-01	4.40814E-00	1.54749E-00
1.00000E-01	3.72943E-00	1.64228E-00
5.00000E-02	3.11236E-00	1.78234E-00
4.80000E-02	3.08771E-00	1.78977E-00
4.60000E-02	3.06296E-00	1.79741E-00
4.40000E-02	3.03811E-00	1.80529E-00
4.20000E-02	3.01313E-00	1.81342E-00
4.00000E-02	2.98800E-00	1.82183E-00
3.80000E-02	2.96271E-00	1.83053E-00
3.60000E-02	2.93721E-00	1.83956E-00
3.40000E-02	2.91148E-00	1.84893E-00
3.20000E-02	2.88549E-00	1.85869E-00
3.00000E-02	2.85920E-00	1.86887E-00
2.80000E-02	2.83256E-00	1.87952E-00
2.60000E-02	2.80551E-00	1.89069E-00
2.40000E-02	2.77799E-00	1.90245E-00
2.20000E-02	2.74992E-00	1.91488E-00
2.00000E-02	2.72120E-00	1.92807E-00
1.80000E-02	2.69170E-00	1.94215E-00
1.60000E-02	2.66127E-00	1.95728E-00
1.40000E-02	2.62968E-00	1.97367E-00
1.20000E-02	2.59666E-00	1.99161E-00
1.00000E-02	2.56177E-00	2.01152E-00
8.00000E-03	2.52436E-00	2.03406E-00
6.00000E-03	2.48333E-00	2.06032E-00
4.00000E-03	2.43654E-00	2.09245E-00
2.00000E-03	2.37842E-00	2.13602E-00
1.00000E-03	2.33914E-00	2.16806E-00
0.00000E-99	2.25000E-00	2.25000E-00

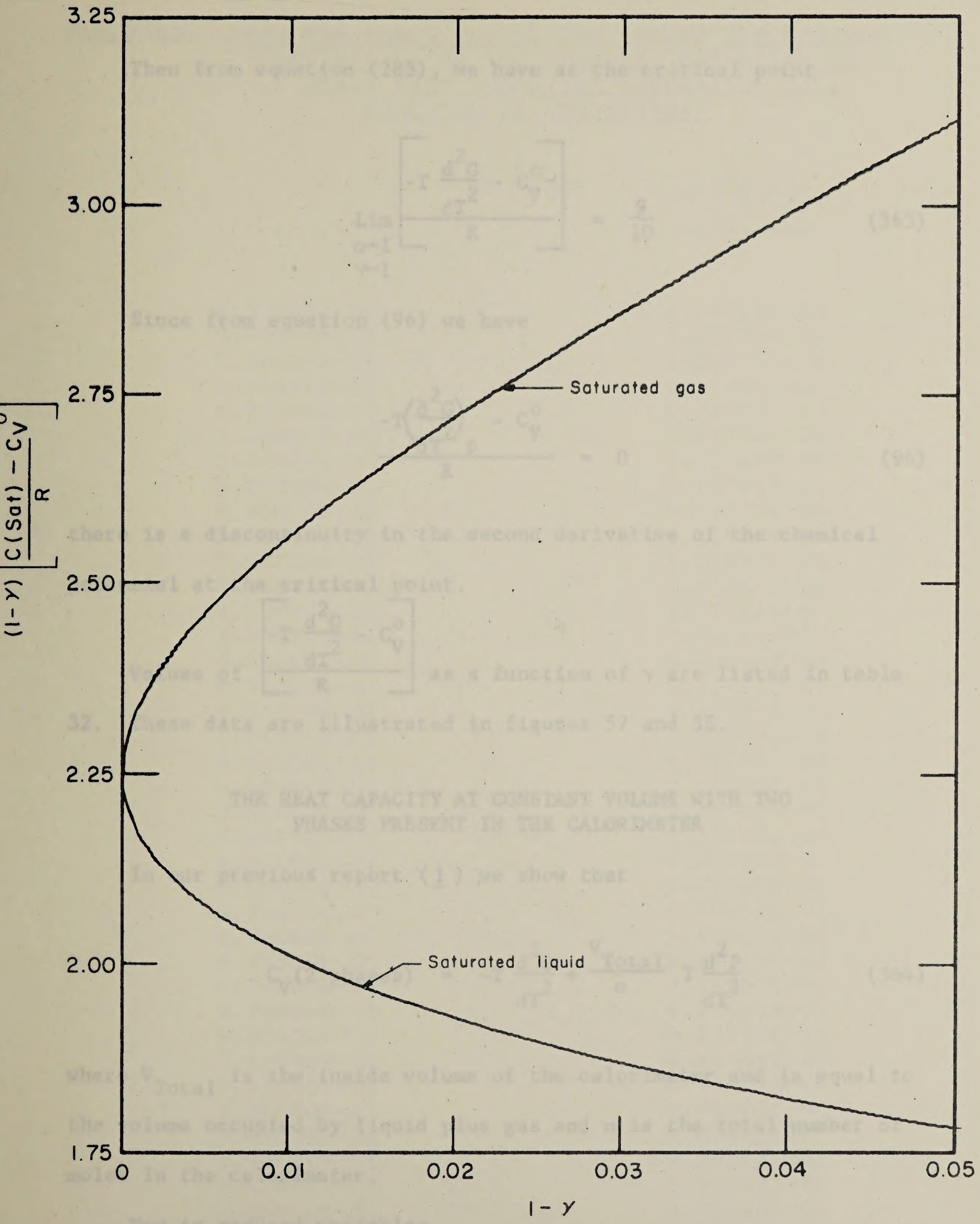

FIGURE 56.- Van der Waals Fluid, Asymptotic Function of the Heat Capacities of the Saturated Liquid and Gas vs $(1-\gamma)$; $\gamma = T/T_c$

Then from equation (285), we have at the critical point

$$\lim_{\substack{\alpha \to 1 \\ \gamma \to 1}} \left[\frac{-T \frac{d^2G}{dT^2} - C_V^o}{R} \right] = \frac{9}{10} \tag{363}$$

Since from equation (96) we have

$$\frac{-T\left(\frac{\partial^2 G}{\partial T^2}\right)_\rho - C_V^o}{R} = 0 \tag{96}$$

there is a discontinuity in the second derivative of the chemical potential at the critical point.

Values of $\left[\frac{-T \frac{d^2G}{dT^2} - C_V^o}{R} \right]$ as a function of γ are listed in table 32. These data are illustrated in figures 57 and 58.

THE HEAT CAPACITY AT CONSTANT VOLUME WITH TWO PHASES PRESENT IN THE CALORIMETER

In our previous report (1) we show that

$$C_V(2 \text{ phases}) = -T \frac{d^2G}{dT^2} + \frac{V_{Total}}{n} T \frac{d^2P}{dT^2} \tag{364}$$

where V_{Total} is the inside volume of the calorimeter and is equal to the volume occupied by liquid plus gas and n is the total number of moles in the calorimeter.

Now in reduced variables

$$T \frac{d^2P}{dT^2} = \frac{P_c\gamma}{T_c} \frac{d^2\beta}{d\gamma^2} = R\rho_c Z_c \gamma\beta'' \tag{365}$$

TABLE 32. - VAN DER WAALS FLUID, THE SECOND TEMPERATURE DERIVATIVE OF THE CHEMICAL POTENTIAL OR GIBBS FREE ENERGY AT SATURATION AS A FUNCTION OF TEMPERATURE

$\gamma = T/T_c$

γ	$\dfrac{-T \dfrac{d^2G}{dT^2} - C_V^o}{R}$
2.50000E-01	1.18918E-00
3.00000E-01	1.23023E-00
3.50000E-01	1.25956E-00
4.00000E-01	1.27245E-00
4.50000E-01	1.26907E-00
5.00000E-01	1.25242E-00
5.50000E-01	1.22620E-00
6.00000E-01	1.19374E-00
6.50000E-01	1.15759E-00
7.00000E-01	1.11958E-00
7.50000E-01	1.08099E-00
8.00000E-01	1.04265E-00
8.50000E-01	1.00512E-00
9.00000E-01	9.68718E-01
9.50000E-01	9.33644E-01
9.52000E-01	9.32271E-01
9.54000E-01	9.30899E-01
9.56000E-01	9.29530E-01
9.58000E-01	9.28164E-01
9.60000E-01	9.26799E-01
9.62000E-01	9.25437E-01
9.64000E-01	9.24077E-01
9.66000E-01	9.22720E-01
9.68000E-01	9.21365E-01
9.70000E-01	9.20012E-01
9.72000E-01	9.18661E-01
9.74000E-01	9.17313E-01
9.76000E-01	9.15967E-01
9.78000E-01	9.14624E-01
9.80000E-01	9.13283E-01
9.82000E-01	9.11944E-01
9.84000E-01	9.10607E-01
9.86000E-01	9.09273E-01
9.88000E-01	9.07941E-01
9.90000E-01	9.06612E-01
9.92000E-01	9.05285E-01
9.94000E-01	9.03960E-01
9.96000E-01	9.02637E-01
9.98000E-01	9.01317E-01
9.99000E-01	9.00658E-01
1.00000E-00	9.00000E-01

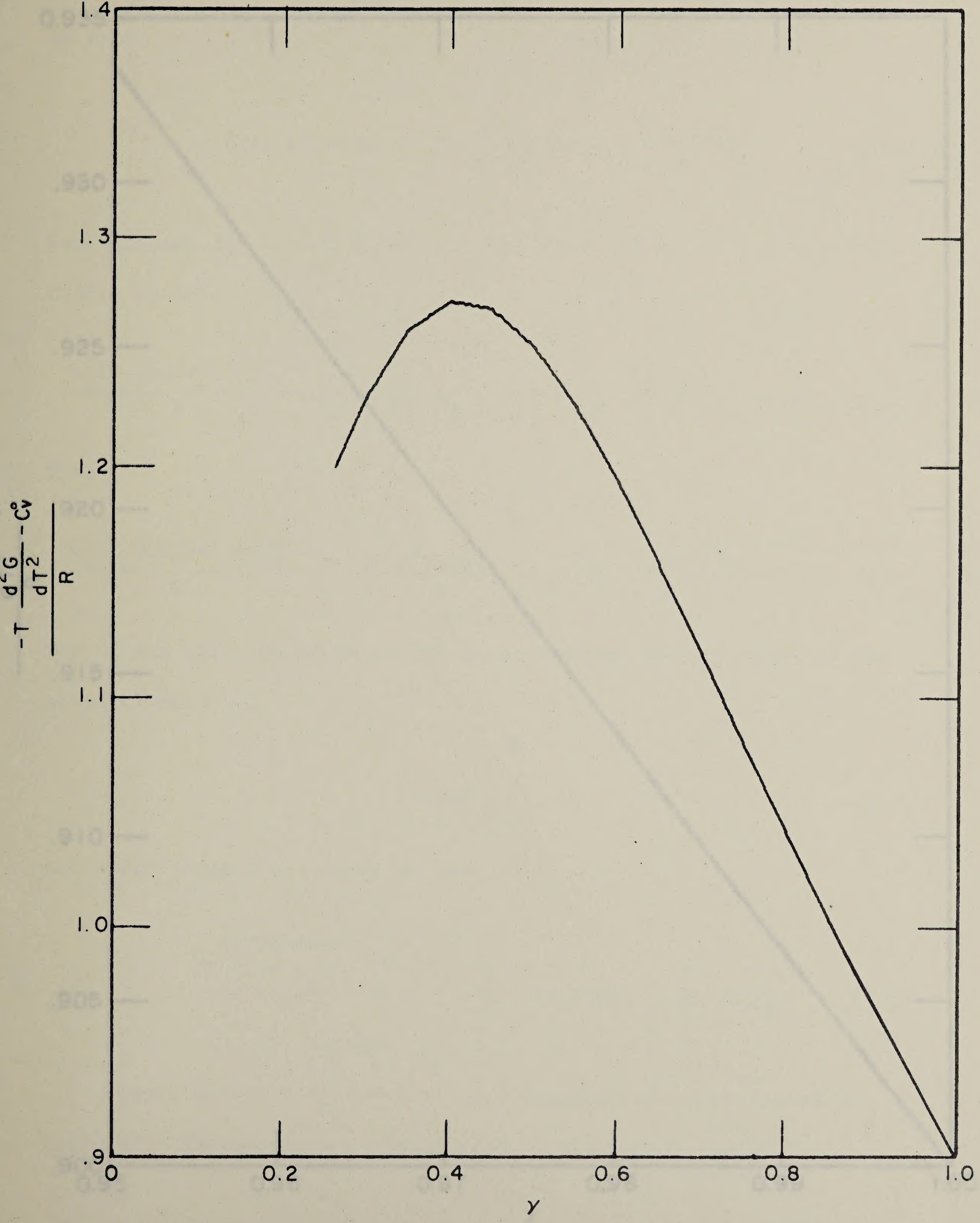

FIGURE 57.- Van der Waals Fluid, Second Derivative of Gibbs Free Energy vs γ; $\gamma = T/T_c$

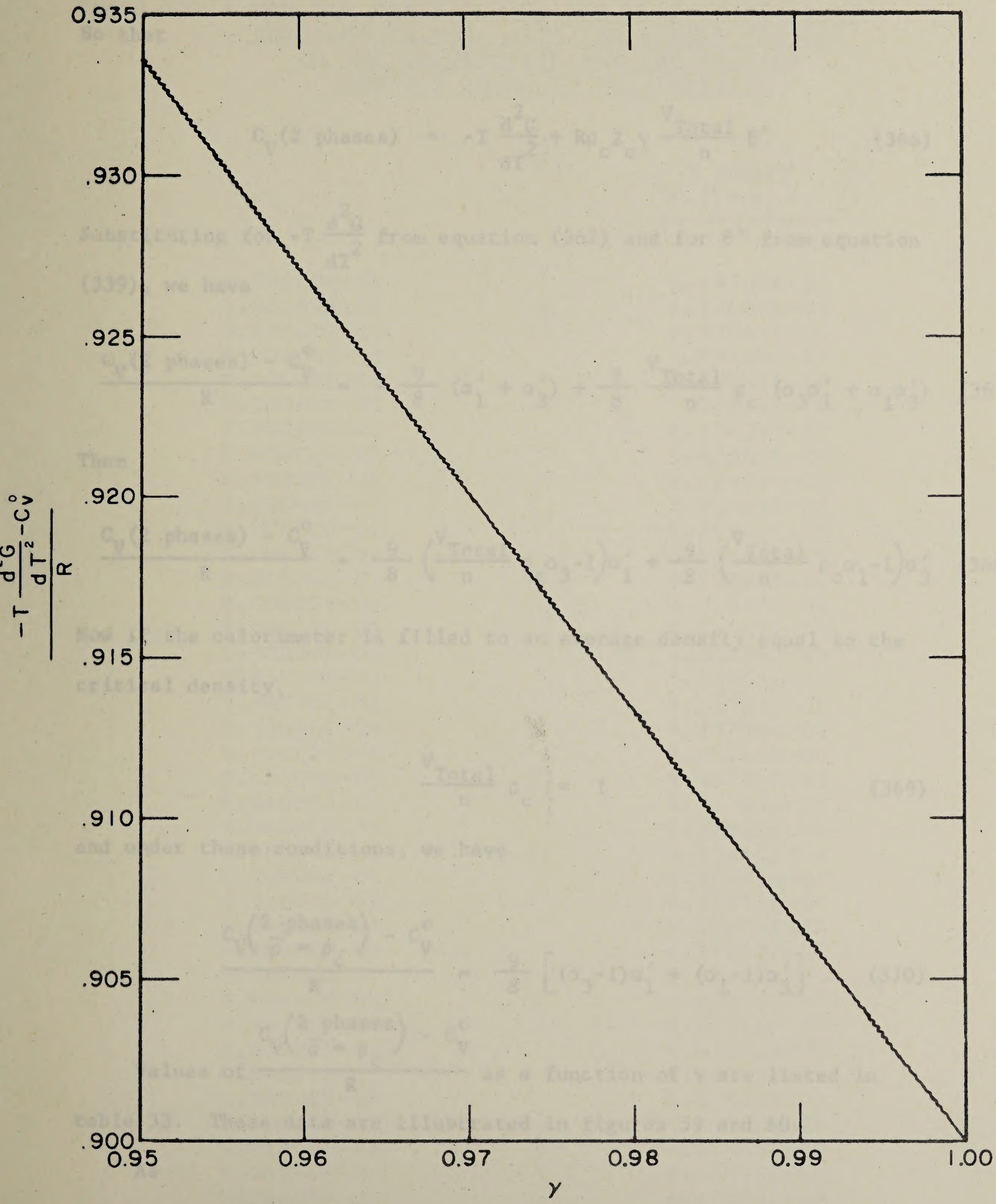

FIGURE 58. - Van der Waals Fluid, Second Derivative of Gibbs Free Energy vs γ ; $\gamma = T/T_c$

So that

$$C_V(2\text{ phases}) = -T\frac{d^2G}{dT^2} + R\rho_c Z_c \gamma \frac{V_{\text{Total}}}{n}\beta'' \qquad (366)$$

Substituting for $-T\frac{d^2G}{dT^2}$ from equation (362) and for β'' from equation (339), we have

$$\frac{C_V(2\text{ phases}) - C_V^o}{R} = -\frac{9}{8}(\alpha_1' + \alpha_3') + \frac{9}{8}\frac{V_{\text{Total}}}{n}\rho_c(\alpha_3\alpha_1' + \alpha_1\alpha_3') \qquad (367)$$

Then

$$\frac{C_V(2\text{ phases}) - C_V^o}{R} = \frac{9}{8}\left(\frac{V_{\text{Total}}}{n}\rho_c\alpha_3 - 1\right)\alpha_1' + \frac{9}{8}\left(\frac{V_{\text{Total}}}{n}\rho_c\alpha_1 - 1\right)\alpha_3' \qquad (368)$$

Now if the calorimeter is filled to an average density equal to the critical density,

$$\frac{V_{\text{Total}}}{n}\rho_c = 1 \qquad (369)$$

and under these conditions, we have

$$\frac{C_V\left(\begin{matrix}2\text{ phases}\\ \bar{\rho} = \rho_c\end{matrix}\right) - C_V^o}{R} = \frac{9}{8}\left[(\alpha_3 - 1)\alpha_1' + (\alpha_1 - 1)\alpha_3'\right] \qquad (370)$$

Values of $\frac{C_V\left(\begin{matrix}2\text{ phases}\\ \bar{\rho} = \rho_c\end{matrix}\right) - C_V^o}{R}$ as a function of γ are listed in table 33. These data are illustrated in figures 59 and 60.

As

$$\frac{d(\alpha_3\alpha_1 - \alpha_3 - \alpha_1)}{d\gamma} = (\alpha_3 - 1)\alpha_1' + (\alpha_1 - 1)\alpha_3' \qquad (371)$$

TABLE 33. - VAN DER WAALS FLUID, THE HEAT CAPACITY AT CONSTANT VOLUME, WITH TWO PHASES PRESENT IN THE CALORIMETER AND THE FILLING DENSITY EQUAL TO THE CRITICAL

$Y = T/T_c$

Y	$\dfrac{C_V\left(\begin{smallmatrix}2\ \text{phases}\\ \bar{\rho}\,=\,\rho_c\end{smallmatrix}\right) - C_V^o}{R}$
2.50000E-01	1.19702E-00
3.00000E-01	1.27088E-00
3.50000E-01	1.38067E-00
4.00000E-01	1.53185E-00
4.50000E-01	1.72051E-00
5.00000E-01	1.93821E-00
5.50000E-01	2.17609E-00
6.00000E-01	2.42682E-00
6.50000E-01	2.68493E-00
7.00000E-01	2.94664E-00
7.50000E-01	3.20942E-00
8.00000E-01	3.47163E-00
8.50000E-01	3.73226E-00
9.00000E-01	3.99071E-00
9.50000E-01	4.24667E-00
9.52000E-01	4.25685E-00
9.54000E-01	4.26703E-00
9.56000E-01	4.27721E-00
9.58000E-01	4.28738E-00
9.60000E-01	4.29754E-00
9.62000E-01	4.30771E-00
9.64000E-01	4.31787E-00
9.66000E-01	4.32802E-00
9.68000E-01	4.33817E-00
9.70000E-01	4.34832E-00
9.72000E-01	4.35846E-00
9.74000E-01	4.36860E-00
9.76000E-01	4.37873E-00
9.78000E-01	4.38886E-00
9.80000E-01	4.39898E-00
9.82000E-01	4.40910E-00
9.84000E-01	4.41922E-00
9.86000E-01	4.42933E-00
9.88000E-01	4.43944E-00
9.90000E-01	4.44954E-00
9.92000E-01	4.45964E-00
9.94000E-01	4.46974E-00
9.96000E-01	4.47983E-00
9.98000E-01	4.48991E-00
9.99000E-01	4.49495E-00
1.00000E-00	4.50000E-00

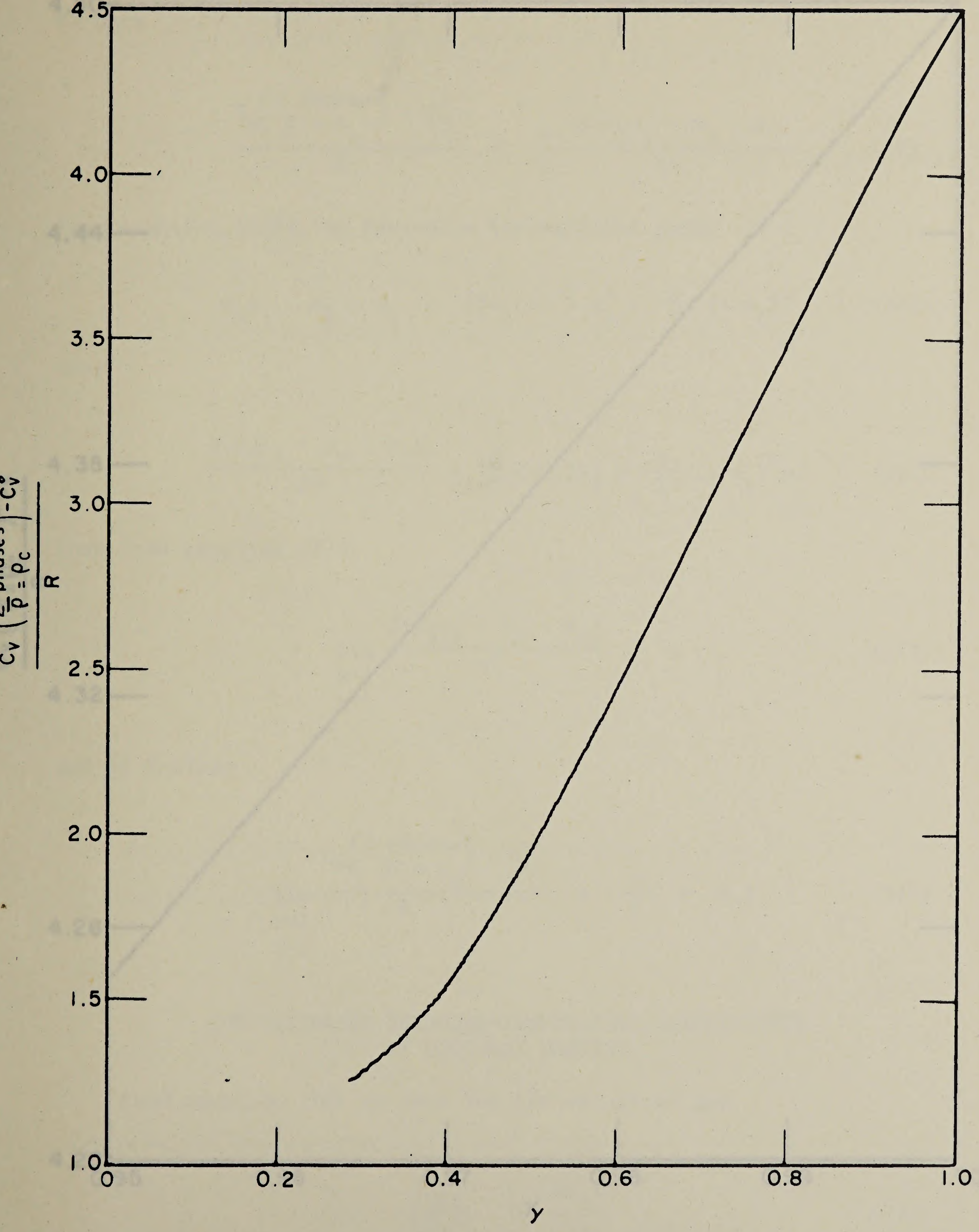

FIGURE 59.- Van der Waals Fluid, Two Phase Heat Capacity vs Y; $Y = T/T_c$

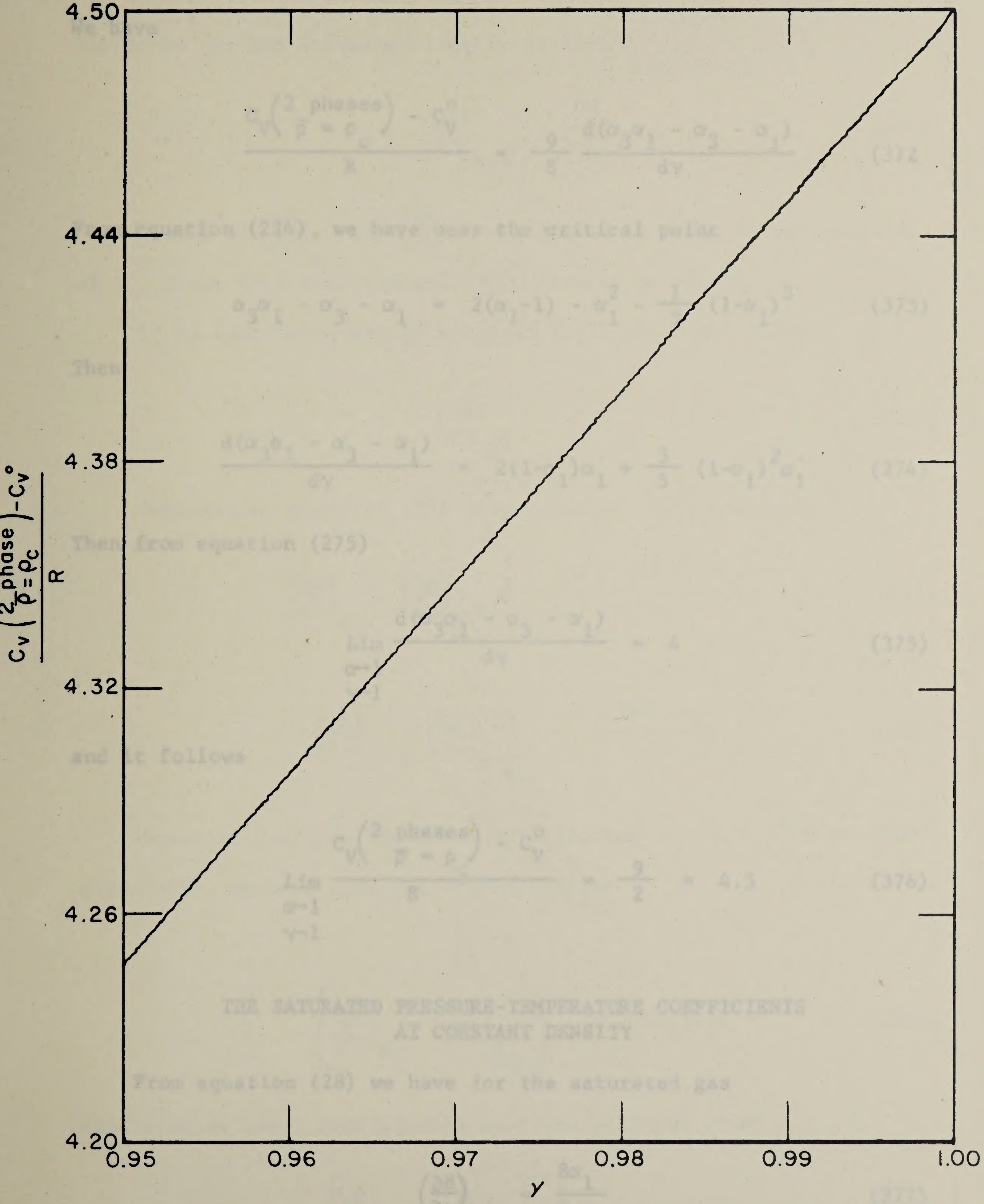

FIGURE 60.-Van der Waals Fluid, Two Phase Heat Capacity vs γ; $\gamma = T/T_c$

We have

$$\frac{C_V\left(\begin{matrix}2\text{ phases}\\ \bar{\rho} = \rho_c\end{matrix}\right) - C_V^o}{R} = \frac{9}{8}\,\frac{d(\alpha_3\alpha_1 - \alpha_3 - \alpha_1)}{d\gamma} \qquad (372$$

From equation (224), we have near the critical point

$$\alpha_3\alpha_1 - \alpha_3 - \alpha_1 = 2(\alpha_1 - 1) - \alpha_1^2 - \frac{1}{5}(1-\alpha_1)^3 \qquad (373)$$

Then

$$\frac{d(\alpha_3\alpha_1 - \alpha_3 - \alpha_1)}{d\gamma} = 2(1-\alpha_1)\alpha_1' + \frac{3}{5}(1-\alpha_1)^2\alpha_1' \qquad (374)$$

Then from equation (275)

$$\lim_{\substack{\alpha\to 1\\ \gamma\to 1}} \frac{d(\alpha_3\alpha_1 - \alpha_3 - \alpha_1)}{d\gamma} = 4 \qquad (375)$$

and it follows

$$\lim_{\substack{\alpha\to 1\\ \gamma\to 1}} \frac{C_V\left(\begin{matrix}2\text{ phases}\\ \bar{\rho} = \rho_c\end{matrix}\right) - C_V^o}{R} = \frac{9}{2} = 4.5 \qquad (376)$$

THE SATURATED PRESSURE-TEMPERATURE COEFFICIENTS AT CONSTANT DENSITY

From equation (28) we have for the saturated gas

$$\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1} = \frac{8\alpha_1}{3-\alpha_1} \qquad (377)$$

Similarly for the saturated liquid, we have

$$\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_3} = \frac{8\alpha_3}{3-\alpha_3} \tag{378}$$

Values of $\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1}$ and $\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_3}$ are listed in table 34 as functions of γ. These data are illustrated in figures 61 and 62.

If we substitute $\alpha=1$ in equation (377) or (378), we have

$$\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_{c.p.}} = 4 \tag{29}$$

Subtracting equation (29) from equation (377), we have

$$\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1} - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_{c.p.}} = \frac{8\alpha_1 - 12 + 4\alpha_1}{3-\alpha_1} \tag{379}$$

$$\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1} - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_{c.p.}} = -\frac{12(1-\alpha_1)}{3-\alpha_1} \tag{380}$$

Squaring equation (380) and substituting for $(1-\alpha_1)^2$ from equation (235), we have near the critical point

$$\left[\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1} - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_{c.p.}}\right]^2 = 144(1-\gamma) \tag{381}$$

Similarly we have, sufficiently near the critical point

$$\left[\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_3} - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_{c.p.}}\right]^2 = 144(1-\gamma) \tag{382}$$

TABLE 34. - VAN DER WAALS FLUID, THE PRESSURE-TEMPERATURE COEFFICIENTS AT CONSTANT DENSITY, AT SATURATION, AS A FUNCTION OF TEMPERATURE

$\alpha = \rho/\rho_c$ $\beta = P/P_c$ $\gamma = T/T_c$

γ	$\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1}$	$\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_3}$
2.50000E-01	1.36692E-04	9.12991E&01
3.00000E-01	1.06431E-03	7.31261E&01
3.50000E-01	4.50242E-03	6.00834E&01
4.00000E-01	1.31171E-02	5.02435E&01
4.50000E-01	3.00255E-02	4.25366E&01
5.00000E-01	5.84149E-02	3.63206E&01
5.50000E-01	1.01484E-01	3.11868E&01
6.00000E-01	1.62649E-01	2.68612E&01
6.50000E-01	2.45936E-01	2.31525E&01
7.00000E-01	3.56610E-01	1.99213E&01
7.50000E-01	5.02223E-01	1.70614E&01
8.00000E-01	6.94602E-01	1.44867E&01
8.50000E-01	9.54321E-01	1.21197E&01
9.00000E-01	1.32307E-00	9.87403E-00
9.50000E-01	1.91332E-00	7.60191E-00
9.52000E-01	1.94559E-00	7.50600E-00
9.54000E-01	1.97890E-00	7.40931E-00
9.56000E-01	2.01332E-00	7.31178E-00
9.58000E-01	2.04893E-00	7.21332E-00
9.60000E-01	2.08582E-00	7.11384E-00
9.62000E-01	2.12408E-00	7.01324E-00
9.64000E-01	2.16384E-00	6.91140E-00
9.66000E-01	2.20523E-00	6.80819E-00
9.68000E-01	2.24840E-00	6.70346E-00
9.70000E-01	2.29352E-00	6.59702E-00
9.72000E-01	2.34080E-00	6.48866E-00
9.74000E-01	2.39050E-00	6.37815E-00
9.76000E-01	2.44289E-00	6.26519E-00
9.78000E-01	2.49834E-00	6.14941E-00
9.80000E-01	2.55729E-00	6.03038E-00
9.82000E-01	2.62030E-00	5.90753E-00
9.84000E-01	2.68809E-00	5.78015E-00
9.86000E-01	2.76160E-00	5.64728E-00
9.88000E-01	2.84215E-00	5.50762E-00
9.90000E-01	2.93162E-00	5.35926E-00
9.92000E-01	3.03294E-00	5.19930E-00
9.94000E-01	3.15100E-00	5.02283E-00
9.96000E-01	3.29540E-00	4.82025E-00
9.98000E-01	3.49097E-00	4.56673E-00
9.99000E-01	3.63450E-00	4.39432E-00
1.00000E-00	4.00000E-00	4.00000E-00

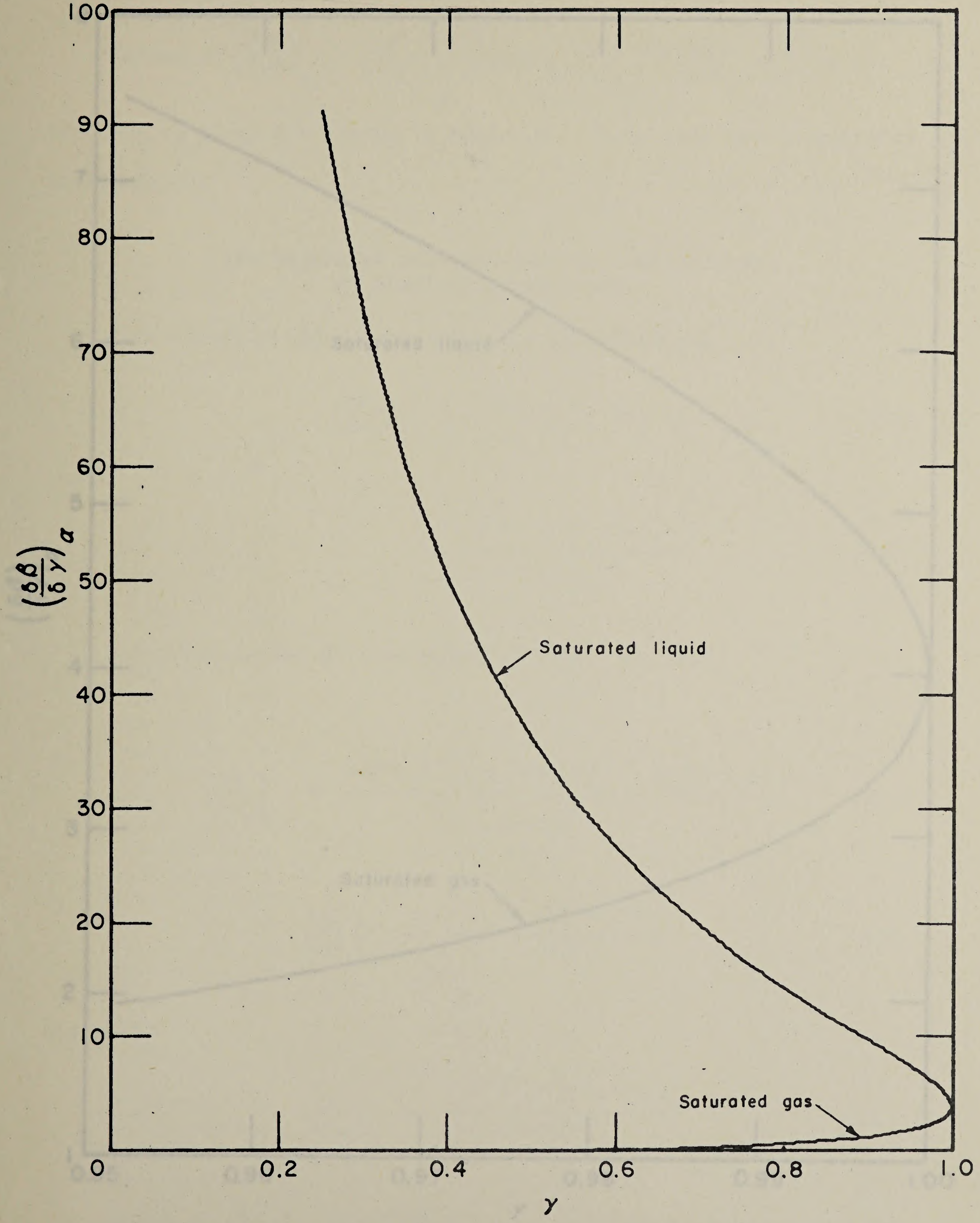

FIGURE 61.- Van der Waals Fluid, The Pressure-Temperature Coefficients at Constant Density, at Saturation, as a Function of Temperature; $\alpha = \rho/\rho_c$; $\beta = P/P_c$; $\gamma = T/T_c$

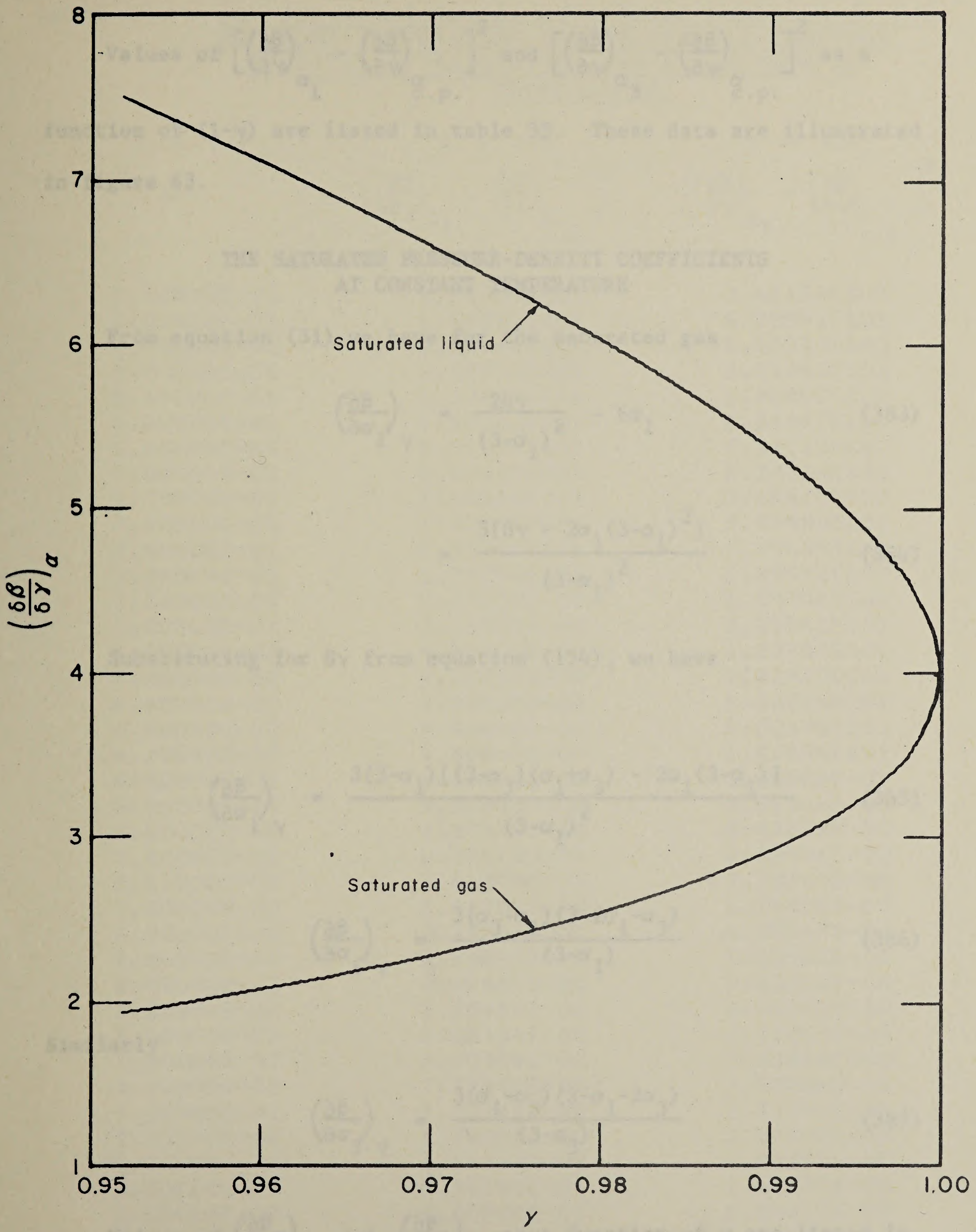

FIGURE 62.- Van der Waals Fluid, The Pressure-Temperature Coefficients at Constant Density, at Saturation, as a Function of Temperature; $\alpha = \rho/\rho_c$; $\beta = P/P_c$; $\gamma = T/T_c$

Values of $\left[\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1} - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_{c.p.}}\right]^2$ and $\left[\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_3} - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_{c.p.}}\right]^2$ as a function of $(1-\gamma)$ are listed in table 35. These data are illustrated in figure 63.

THE SATURATED PRESSURE-DENSITY COEFFICIENTS AT CONSTANT TEMPERATURE

From equation (31) we have for the saturated gas

$$\left(\frac{\partial\beta}{\partial\alpha_1}\right)_\gamma = \frac{24\gamma}{(3-\alpha_1)^2} - 6\alpha_1 \qquad (383)$$

$$= \frac{3[8\gamma - 2\alpha_1(3-\alpha_1)^2]}{(3-\alpha_1)^2} \qquad (384)$$

Substituting for 8γ from equation (154), we have

$$\left(\frac{\partial\beta}{\partial\alpha_1}\right)_\gamma = \frac{3(3-\alpha_1)[(3-\alpha_3)(\alpha_1+\alpha_3) - 2\alpha_1(3-\alpha_1)]}{(3-\alpha_1)^2} \qquad (385)$$

$$\left(\frac{\partial\beta}{\partial\alpha_1}\right)_\gamma = \frac{3(\alpha_3-\alpha_1)(3-2\alpha_1-\alpha_3)}{(3-\alpha_1)} \qquad (386)$$

Similarly

$$\left(\frac{\partial\beta}{\partial\alpha_3}\right)_\gamma = \frac{3(\alpha_1-\alpha_3)(3-\alpha_1-2\alpha_3)}{(3-\alpha_3)} \qquad (387)$$

Values of $\left(\frac{\partial\beta}{\partial\alpha_1}\right)_\gamma$ and $\left(\frac{\partial\beta}{\partial\alpha_3}\right)_\gamma$ as a function of γ are listed in table 36. These data are illustrated in figures 64 and 65.

TABLE 35. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE PRESSURE-TEMPERATURE COEFFICIENT AT CONSTANT DENSITY, AT SATURATION, AS A FUNCTION OF TEMPERATURE

$\alpha = \rho/\rho_c$ $\beta = P/P_c$ $\gamma = T/T_c$

$1-\gamma$	$\left[\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_1} - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_{c.p.}}\right]^2$	$\left[\left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_3} - \left(\frac{\partial\beta}{\partial\gamma}\right)_{\alpha_{c.p.}}\right]^2$
7.50000E-01	1.59989E&01	7.62114E&03
7.00000E-01	1.59914E&01	4.77841E&03
6.50000E-01	1.59640E&01	3.14535E&03
6.00000E-01	1.58952E&01	2.13846E&03
5.50000E-01	1.57606E&01	1.48507E&03
5.00000E-01	1.55360E&01	1.04462E&03
4.50000E-01	1.51984E&01	7.39123E&02
4.00000E-01	1.47252E&01	5.22636E&02
3.50000E-01	1.40929E&01	3.66820E&02
3.00000E-01	1.32742E&01	2.53489E&02
2.50000E-01	1.22344E&01	1.70601E&02
2.00000E-01	1.09256E&01	1.09972E&02
1.50000E-01	9.27615E-00	6.59298E&01
1.00000E-01	7.16593E-00	3.45042E&01
5.00000E-02	4.35423E-00	1.29737E&01
4.80000E-02	4.22057E-00	1.22920E&01
4.60000E-02	4.08481E-00	1.16234E&01
4.40000E-02	3.94686E-00	1.09678E&01
4.20000E-02	3.80665E-00	1.03254E&01
4.00000E-02	3.66408E-00	9.69602E-00
3.80000E-02	3.51905E-00	9.07964E-00
3.60000E-02	3.37145E-00	8.47628E-00
3.40000E-02	3.22118E-00	7.88596E-00
3.20000E-02	3.06809E-00	7.30869E-00
3.00000E-02	2.91206E-00	6.74451E-00
2.80000E-02	2.75291E-00	6.19347E-00
2.60000E-02	2.59048E-00	5.65563E-00
2.40000E-02	2.42457E-00	5.13109E-00
2.20000E-02	2.25496E-00	4.61998E-00
2.00000E-02	2.08138E-00	4.12244E-00
1.80000E-02	1.90354E-00	3.63868E-00
1.60000E-02	1.72110E-00	3.16894E-00
1.40000E-02	1.53362E-00	2.71355E-00
1.20000E-02	1.34061E-00	2.27292E-00
1.00000E-02	1.14142E-00	1.84759E-00
8.00000E-03	9.35199E-01	1.43832E-00
6.00000E-03	7.20790E-01	1.04618E-00
4.00000E-03	4.96449E-01	6.72812E-01
2.00000E-03	2.59106E-01	3.21193E-01
1.00000E-03	1.33584E-01	1.55488E-01
0.00000E-99	0.00000E-99	0.00000E-99

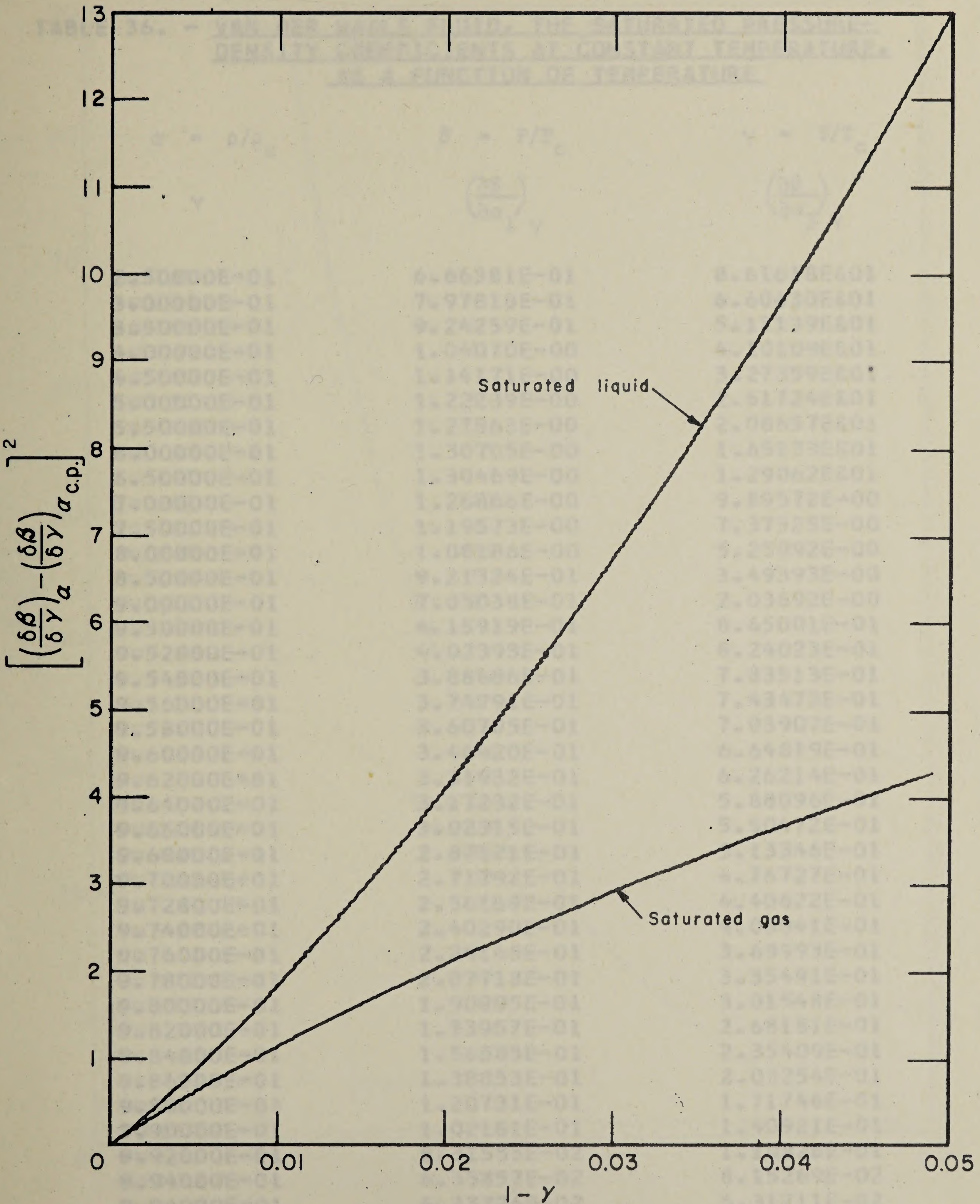

FIGURE 63. - Van der Waals Fluid, Asymptotic Function of the Pressure - Temperature Coefficients at Constant Density, at Saturation, as a Function of Temperature; $\alpha = \rho/\rho_c$; $\beta = P/P_c$; $\gamma = T/T_c$

TABLE 36. - VAN DER WAALS FLUID, THE SATURATED PRESSURE-DENSITY COEFFICIENTS AT CONSTANT TEMPERATURE, AS A FUNCTION OF TEMPERATURE

$\alpha = \rho/\rho_c$	$\beta = P/P_c$	$\gamma = T/T_c$
γ	$\left(\frac{\partial\beta}{\partial\alpha_1}\right)_\gamma$	$\left(\frac{\partial\beta}{\partial\alpha_3}\right)_\gamma$
2.50000E-01	6.66381E-01	8.61618E&01
3.00000E-01	7.97818E-01	6.60430E&01
3.50000E-01	9.24259E-01	5.17139E&01
4.00000E-01	1.04070E-00	4.10109E&01
4.50000E-01	1.14171E-00	3.27359E&01
5.00000E-01	1.22239E-00	2.61724E&01
5.50000E-01	1.27863E-00	2.08657E&01
6.00000E-01	1.30705E-00	1.65133E&01
6.50000E-01	1.30469E-00	1.29062E&01
7.00000E-01	1.26866E-00	9.89572E-00
7.50000E-01	1.19573E-00	7.37325E-00
8.00000E-01	1.08186E-00	5.25892E-00
8.50000E-01	9.21324E-01	3.49393E-00
9.00000E-01	7.05038E-01	2.03692E-00
9.50000E-01	4.15919E-01	8.65001E-01
9.52000E-01	4.02393E-01	8.24023E-01
9.54000E-01	3.88686E-01	7.83513E-01
9.56000E-01	3.74791E-01	7.43473E-01
9.58000E-01	3.60705E-01	7.03907E-01
9.60000E-01	3.46420E-01	6.64819E-01
9.62000E-01	3.31932E-01	6.26214E-01
9.64000E-01	3.17232E-01	5.88096E-01
9.66000E-01	3.02315E-01	5.50472E-01
9.68000E-01	2.87171E-01	5.13346E-01
9.70000E-01	2.71792E-01	4.76727E-01
9.72000E-01	2.56169E-01	4.40622E-01
9.74000E-01	2.40290E-01	4.05041E-01
9.76000E-01	2.24145E-01	3.69993E-01
9.78000E-01	2.07718E-01	3.35491E-01
9.80000E-01	1.90995E-01	3.01548E-01
9.82000E-01	1.73957E-01	2.68181E-01
9.84000E-01	1.56585E-01	2.35409E-01
9.86000E-01	1.38853E-01	2.03254E-01
9.88000E-01	1.20731E-01	1.71746E-01
9.90000E-01	1.02181E-01	1.40921E-01
9.92000E-01	8.31555E-02	1.10826E-01
9.94000E-01	6.35857E-02	8.15269E-02
9.96000E-01	4.33724E-02	5.31211E-02
9.98000E-01	2.23412E-02	2.57818E-02
9.99000E-01	1.14076E-02	1.26230E-02
1.00000E-00	0.00000E-99	0.00000E-99

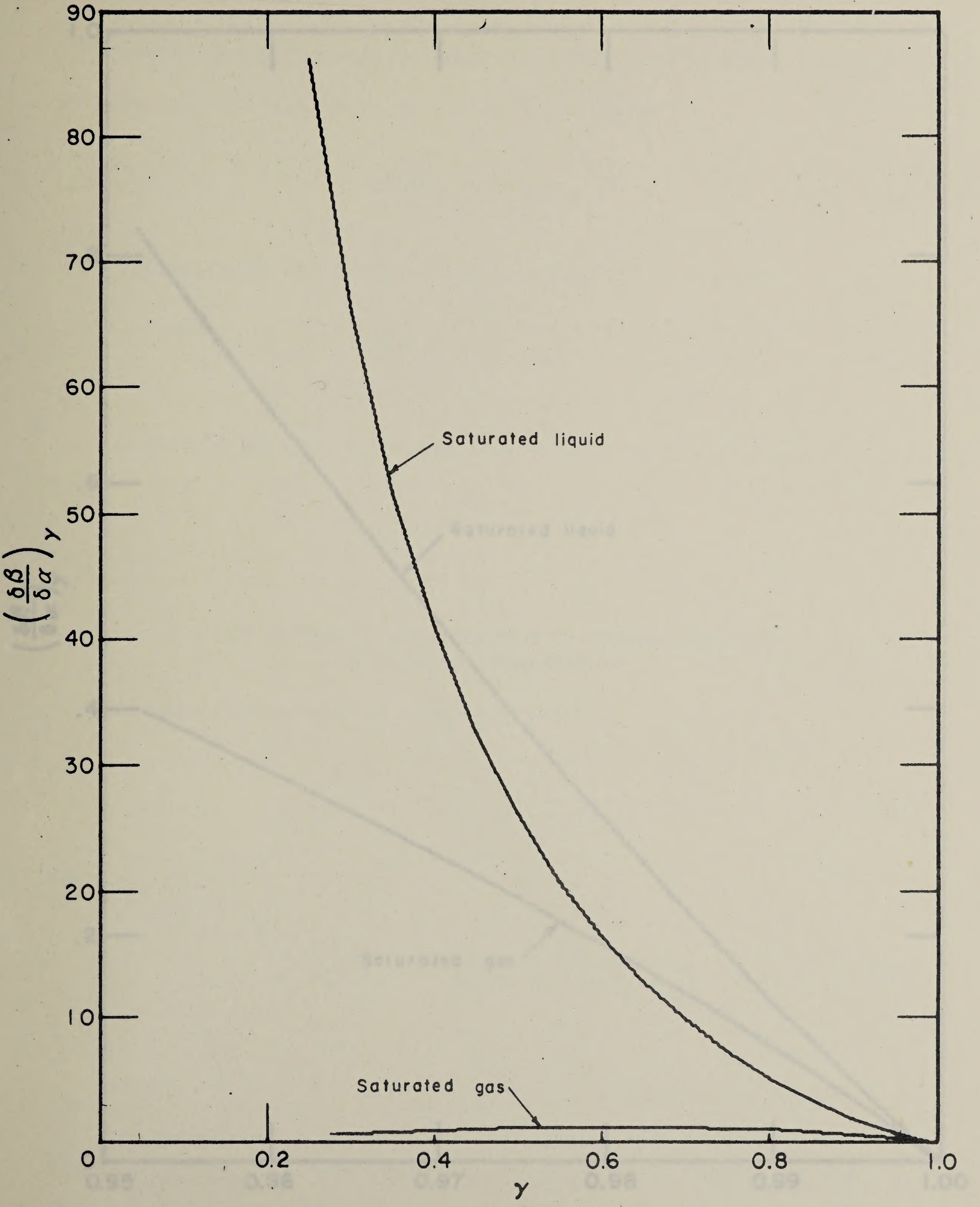

FIGURE 64.- Van der Waals Fluid, The Pressure-Density Coefficients at Constant Temperature, at Saturation, as a Function of Temperature; $\alpha = \rho/\rho_c$; $\beta = P/P_c$; $\gamma = T/T_c$

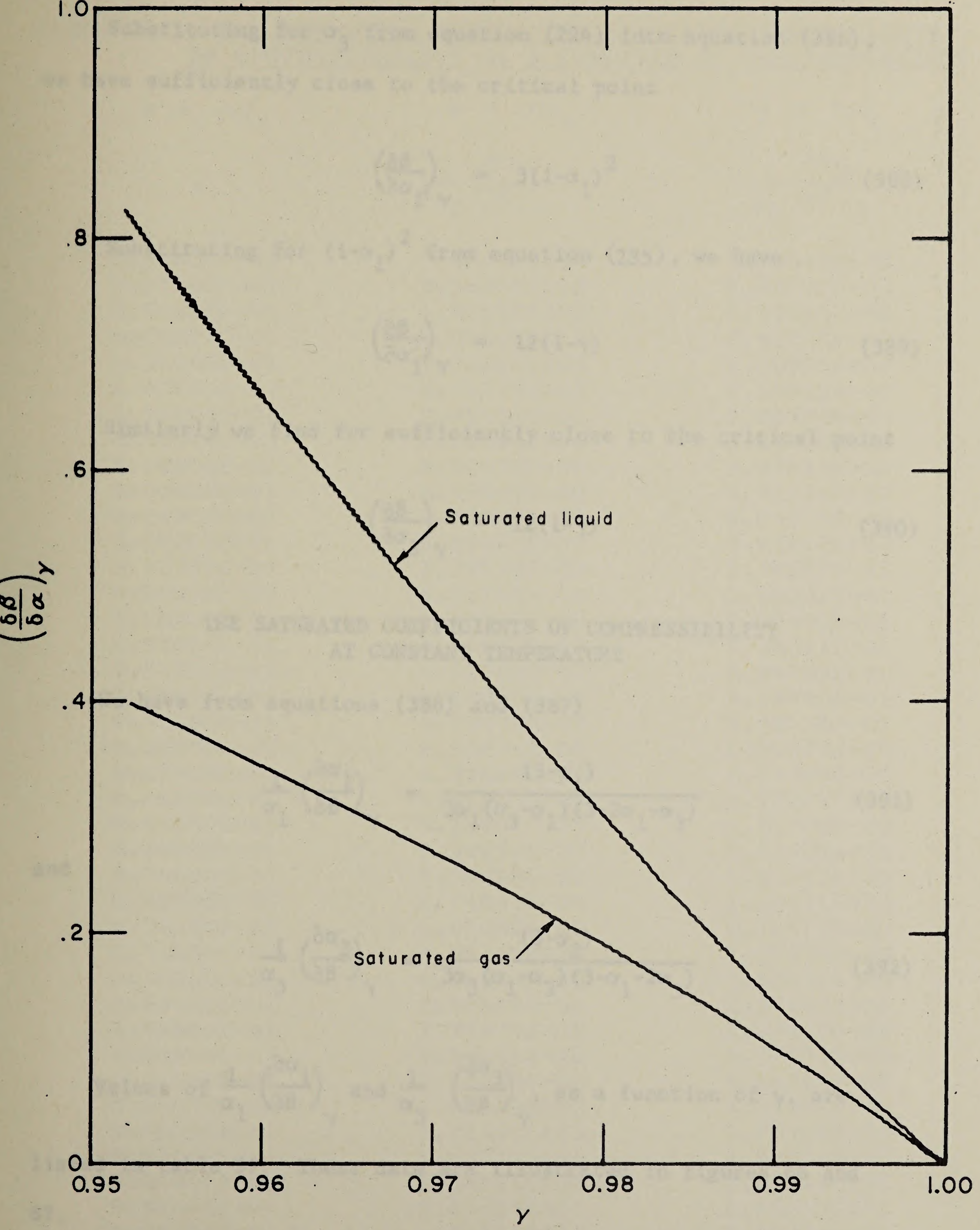

FIGURE 65. - Van der Waals Fluid, The Pressure - Density Coefficients at Constant Temperature, at Saturation, as a Function of Temperature; $\alpha = \rho/\rho_c$; $\beta = P/P_c$; $\gamma = T/T_c$

Substituting for α_3 from equation (224) into equation (386), we have sufficiently close to the critical point

$$\left(\frac{\partial \beta}{\partial \alpha_1}\right)_\gamma = 3(1-\alpha_1)^2 \tag{388}$$

Substituting for $(1-\alpha_1)^2$ from equation (235), we have

$$\left(\frac{\partial \beta}{\partial \alpha_1}\right)_\gamma = 12(1-\gamma) \tag{389}$$

Similarly we find for sufficiently close to the critical point

$$\left(\frac{\partial \beta}{\partial \alpha_3}\right)_\gamma = 12(1-\gamma) \tag{390}$$

THE SATURATED COEFFICIENTS OF COMPRESSIBILITY AT CONSTANT TEMPERATURE

We have from equations (386) and (387)

$$\frac{1}{\alpha_1}\left(\frac{\partial \alpha_1}{\partial \beta}\right)_\gamma = \frac{(3-\alpha_1)}{3\alpha_1(\alpha_3-\alpha_1)(3-2\alpha_1-\alpha_3)} \tag{391}$$

and

$$\frac{1}{\alpha_3}\left(\frac{\partial \alpha_3}{\partial \beta}\right)_\gamma = \frac{(3-\alpha_3)}{3\alpha_3(\alpha_1-\alpha_3)(3-\alpha_1-2\alpha_3)} \tag{392}$$

Values of $\frac{1}{\alpha_1}\left(\frac{\partial \alpha_1}{\partial \beta}\right)_\gamma$ and $\frac{1}{\alpha_3}\left(\frac{\partial \alpha_3}{\partial \beta}\right)_\gamma$, as a function of γ, are listed in table 37. These data are illustrated in figures 66 and 67.

TABLE 37. - VAN DER WAALS FLUID, THE SATURATED COEFFICIENTS OF COMPRESSIBILITY AS A FUNCTION OF THE TEMPERATURE

$\alpha = \rho/\rho_c$	$\beta = P/P_c$	$\gamma = T/T_c$
γ	$\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\beta}\right)_\gamma$	$\frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\beta}\right)_\gamma$
2.50000E-01	2.92756E&04	4.20767E-03
3.00000E-01	3.14088E&03	5.59937E-03
3.50000E-01	6.41169E&02	7.30395E-03
4.00000E-01	1.95665E&02	9.42206E-03
4.50000E-01	7.80810E&01	1.20975E-02
5.00000E-01	3.76177E&01	1.55412E-02
5.50000E-01	2.08111E&01	2.00731E-02
6.00000E-01	1.27986E&01	2.61975E-02
6.50000E-01	8.56620E-00	3.47514E-02
7.00000E-01	6.15699E-00	4.72116E-02
7.50000E-01	4.71929E-00	6.64063E-02
8.00000E-01	3.85671E-00	9.83868E-02
8.50000E-01	3.39472E-00	1.58377E-01
9.00000E-01	3.33150E-00	2.96232E-01
9.50000E-01	4.15241E-00	7.90891E-01
9.52000E-01	4.23453E-00	8.35661E-01
9.54000E-01	4.32451E-00	8.84784E-01
9.56000E-01	4.42336E-00	9.38892E-01
9.58000E-01	4.53229E-00	9.98738E-01
9.60000E-01	4.65274E-00	1.06523E-00
9.62000E-01	4.78644E-00	1.13949E-00
9.64000E-01	4.93551E-00	1.22287E-00
9.66000E-01	5.10254E-00	1.31708E-00
9.68000E-01	5.29078E-00	1.42425E-00
9.70000E-01	5.50429E-00	1.54712E-00
9.72000E-01	5.74831E-00	1.68921E-00
9.74000E-01	6.02960E-00	1.85518E-00
9.76000E-01	6.35719E-00	2.05129E-00
9.78000E-01	6.74329E-00	2.28613E-00
9.80000E-01	7.20489E-00	2.57185E-00
9.82000E-01	7.76638E-00	2.92613E-00
9.84000E-01	8.46413E-00	3.37574E-00
9.86000E-01	9.35486E-00	3.96318E-00
9.88000E-01	1.05323E&01	4.75997E-00
9.90000E-01	1.21641E&01	5.89627E-00
9.92000E-01	1.45819E&01	7.63554E-00
9.94000E-01	1.85516E&01	1.06006E&01
9.96000E-01	2.63425E&01	1.66893E&01
9.98000E-01	4.91113E&01	3.55779E&01
9.99000E-01	9.35370E&01	7.44808E&01
1.00000E-00	$+\infty$	$+\infty$

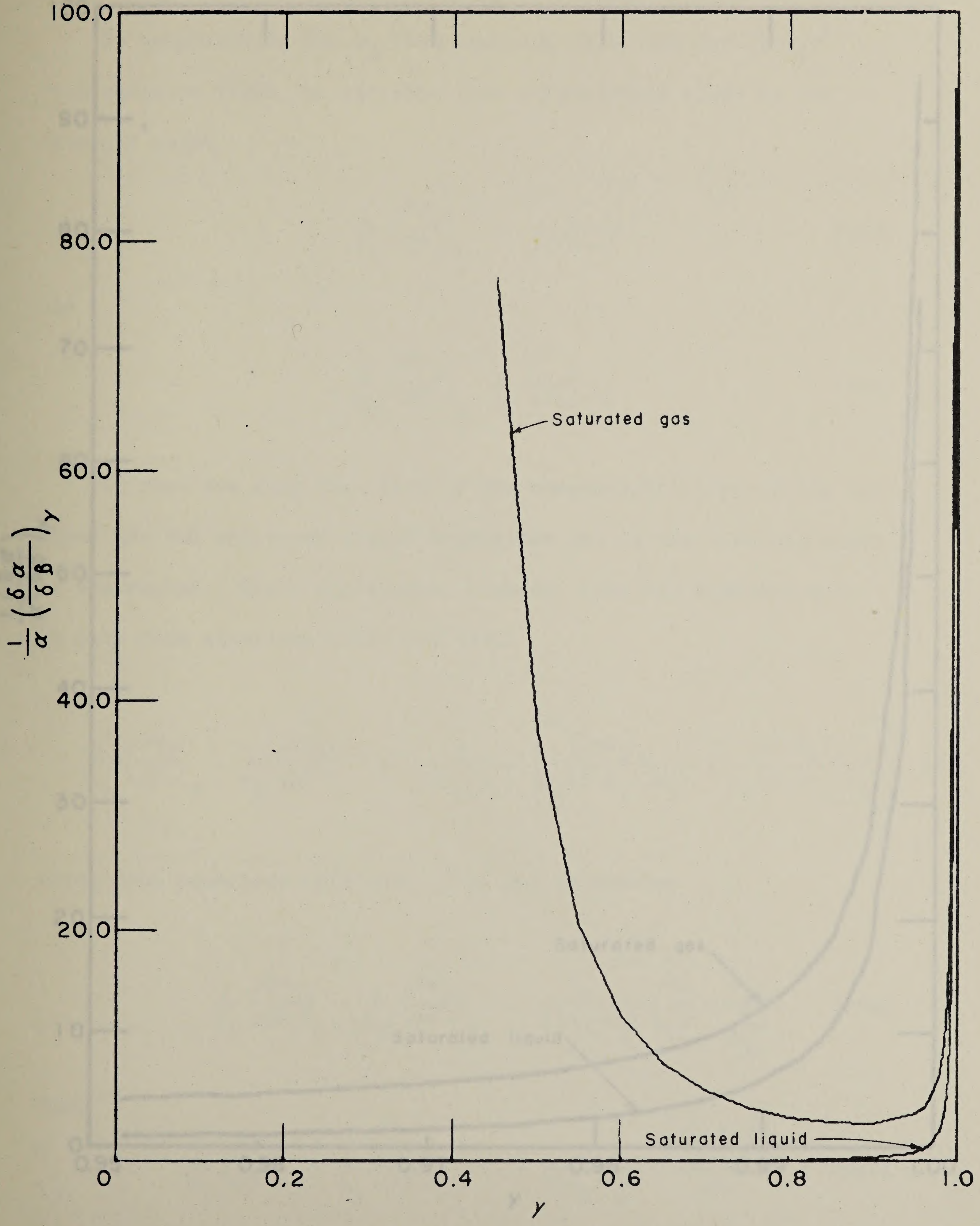

FIGURE 66.- Van der Waals Fluid, Saturated Coefficients of Compressibility vs γ; $\gamma = T/T_c$; $\alpha = \rho/\rho_c$; $\beta = P/P_c$

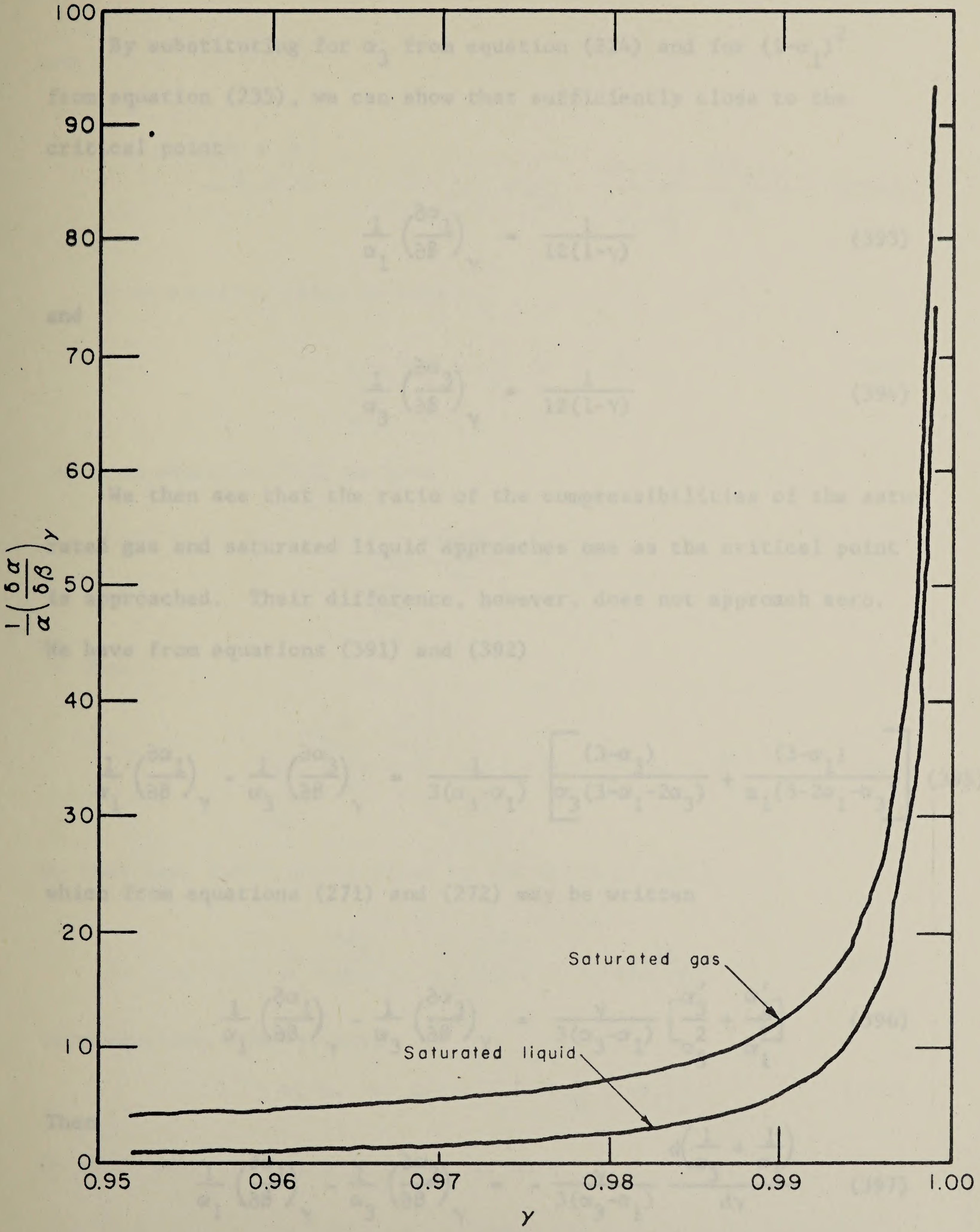

FIGURE 67. - Van der Waals Fluid, Saturated Coefficients of Compressibility vs γ; $\alpha = \rho/\rho_c$; $\beta = P/P_c$; $\gamma = T/T_c$

By substituting for α_3 from equation (224) and for $(1-\alpha_1)^2$ from equation (235), we can show that sufficiently close to the critical point

$$\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\beta}\right)_\gamma = \frac{1}{12(1-\gamma)} \tag{393}$$

and

$$\frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\beta}\right)_\gamma = \frac{1}{12(1-\gamma)} \tag{394}$$

We then see that the ratio of the compressibilities of the saturated gas and saturated liquid approaches one as the critical point is approached. Their difference, however, does not approach zero. We have from equations (391) and (392)

$$\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\beta}\right)_\gamma - \frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\beta}\right)_\gamma = \frac{1}{3(\alpha_3-\alpha_1)}\left[\frac{(3-\alpha_3)}{\alpha_3(3-\alpha_1-2\alpha_3)} + \frac{(3-\alpha_1)}{\alpha_1(3-2\alpha_1-\alpha_3)}\right] \tag{395}$$

which from equations (271) and (272) may be written

$$\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\beta}\right)_\gamma - \frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\beta}\right)_\gamma = \frac{\gamma}{3(\alpha_3-\alpha_1)}\left[-\frac{\alpha_3'}{\alpha_3^2} + \frac{\alpha_1'}{\alpha_1^2}\right] \tag{396}$$

Then

$$\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\beta}\right)_\gamma - \frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\beta}\right)_\gamma = -\frac{\gamma}{3(\alpha_3-\alpha_1)}\,\frac{d\left(\frac{1}{\alpha_3} + \frac{1}{\alpha_1}\right)}{d\gamma} \tag{397}$$

Now

$$\frac{1}{\alpha_3} + \frac{1}{\alpha_1} = \frac{\alpha_1+\alpha_3}{\alpha_1\alpha_3} \tag{398}$$

and

$$\frac{d\left(\frac{1}{\alpha_3}+\frac{1}{\alpha_1}\right)}{d\gamma} = \frac{1}{\alpha_1\alpha_3}(\alpha_1' + \alpha_3') - \frac{(\alpha_1+\alpha_3)}{\alpha_1^2\alpha_3^2}\frac{d(\alpha_1\alpha_3)}{d\gamma} \qquad (399)$$

From equation (285) we have

$$\lim_{\substack{\alpha\to 1\\ \gamma\to 1}} (\alpha_1' + \alpha_3') = -\frac{4}{5} \qquad (285)$$

and from equation (345) we have

$$\lim_{\substack{\alpha\to 1\\ \gamma\to 1}} \frac{d(\alpha_1\alpha_3)}{d\gamma} = \frac{16}{5} \qquad (345)$$

So that

$$\lim_{\substack{\alpha\to 1\\ \gamma\to 1}} \frac{d\left(\frac{1}{\alpha_3}+\frac{1}{\alpha_1}\right)}{d\gamma} = -\frac{4}{5} - \frac{32}{5} = -\frac{36}{5} \qquad (400)$$

We then have sufficiently close to the critical point

$$\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\beta}\right)_\gamma - \frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\beta}\right)_\gamma = \frac{12}{5(\alpha_3-\alpha_1)} \qquad (401)$$

From equation (224) we have

$$\alpha_3-\alpha_1 = 2(1-\alpha_1)\left[1 + \frac{1}{10}(1-\alpha_1)\right] \qquad (402)$$

So that, near the critical point, we have

$$\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\beta}\right)_\gamma - \frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\beta}\right)_\gamma = \frac{6}{5(1-\alpha_1)} \qquad (403)$$

and we see from equation (403) that the compressibility of the saturated gas exceeds that of the saturated liquid, and their difference becomes infinite at the critical point.

Substituting for $(1-\alpha_1)$ from equation (235), we have

$$\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\beta}\right)_\gamma - \frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\beta}\right)_\gamma = \frac{3}{5(1-\gamma)^{1/2}} \tag{404}$$

Values of the functions $\frac{(1-\gamma)}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\beta}\right)_\gamma$ and $\frac{(1-\gamma)}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\beta}\right)_\gamma$ as a function of $(1-\gamma)$ are listed in table 38. These data are illustrated in figure 68.

Values of the difference of the compressibilities squared, multiplied by $(1-\gamma)$ are listed as a function of $(1-\gamma)$ in table 39. These data are illustrated in figure 69.

As the way in which the coefficients of compressibility approach infinity at the critical point is of interest, in table 40 we list values of $\ln \frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\beta}\right)_\gamma$ and $\ln \frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\beta}\right)_\gamma$ as a function of $\ln(1-\gamma)$. These data are illustrated in figure 70.

THE CRITICAL ISOTHERM

From equation (27) we have for the critical isotherm

$$\beta(\gamma=1) = \frac{8\alpha}{3-\alpha} - 3\alpha^2 \tag{405}$$

Values of β, for the critical isotherm as a function of α, are listed in table 41. These data are illustrated in figure 71.

From equation (25) we have for the critical isotherm

$$Z(\gamma=1) = \frac{3}{3-\alpha} - \frac{9\alpha}{8} \tag{406}$$

TABLE 38. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE SATURATED COEFFICIENTS OF COMPRESSIBILITY AS A FUNCTION OF TEMPERATURE

$\alpha = \rho/\rho_c$ $\beta = P/P_c$ $\gamma = T/T_c$

$1-\gamma$	$\frac{(1-\gamma)}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\beta}\right)_\gamma$	$\frac{(1-\gamma)}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\beta}\right)_\gamma$
7.50000E-01	2.19567E&04	3.15575E-03
7.00000E-01	2.19861E&03	3.91956E-03
6.50000E-01	4.16760E&02	4.74756E-03
6.00000E-01	1.17399E&02	5.65324E-03
5.50000E-01	4.29445E&01	6.65364E-03
5.00000E-01	1.88088E&01	7.77064E-03
4.50000E-01	9.36502E-00	9.03289E-03
4.00000E-01	5.11946E-00	1.04790E-02
3.50000E-01	2.99817E-00	1.21629E-02
3.00000E-01	1.84709E-00	1.41634E-02
2.50000E-01	1.17982E-00	1.66015E-02
2.00000E-01	7.71342E-01	1.96773E-02
1.50000E-01	5.09208E-01	2.37566E-02
1.00000E-01	3.33150E-01	2.96232E-02
5.00000E-02	2.07620E-01	3.95445E-02
4.80000E-02	2.03257E-01	4.01117E-02
4.60000E-02	1.98927E-01	4.07001E-02
4.40000E-02	1.94627E-01	4.13112E-02
4.20000E-02	1.90356E-01	4.19470E-02
4.00000E-02	1.86109E-01	4.26093E-02
3.80000E-02	1.81884E-01	4.33006E-02
3.60000E-02	1.77678E-01	4.40234E-02
3.40000E-02	1.73486E-01	4.47808E-02
3.20000E-02	1.69305E-01	4.55762E-02
3.00000E-02	1.65128E-01	4.64136E-02
2.80000E-02	1.60952E-01	4.72979E-02
2.60000E-02	1.56769E-01	4.82348E-02
2.40000E-02	1.52572E-01	4.92310E-02
2.20000E-02	1.48352E-01	5.02949E-02
2.00000E-02	1.44097E-01	5.14370E-02
1.80000E-02	1.39795E-01	5.26703E-02
1.60000E-02	1.35426E-01	5.40119E-02
1.40000E-02	1.30968E-01	5.54845E-02
1.20000E-02	1.26388E-01	5.71196E-02
1.00000E-02	1.21641E-01	5.89627E-02
8.00000E-03	1.16655E-01	6.10843E-02
6.00000E-03	1.11310E-01	6.36041E-02
4.00000E-03	1.05370E-01	6.67572E-02
2.00000E-03	9.82226E-02	7.11558E-02
1.00000E-03	9.35370E-02	7.44808E-02
0.00000E-99	8.33333E-02	8.33333E-02

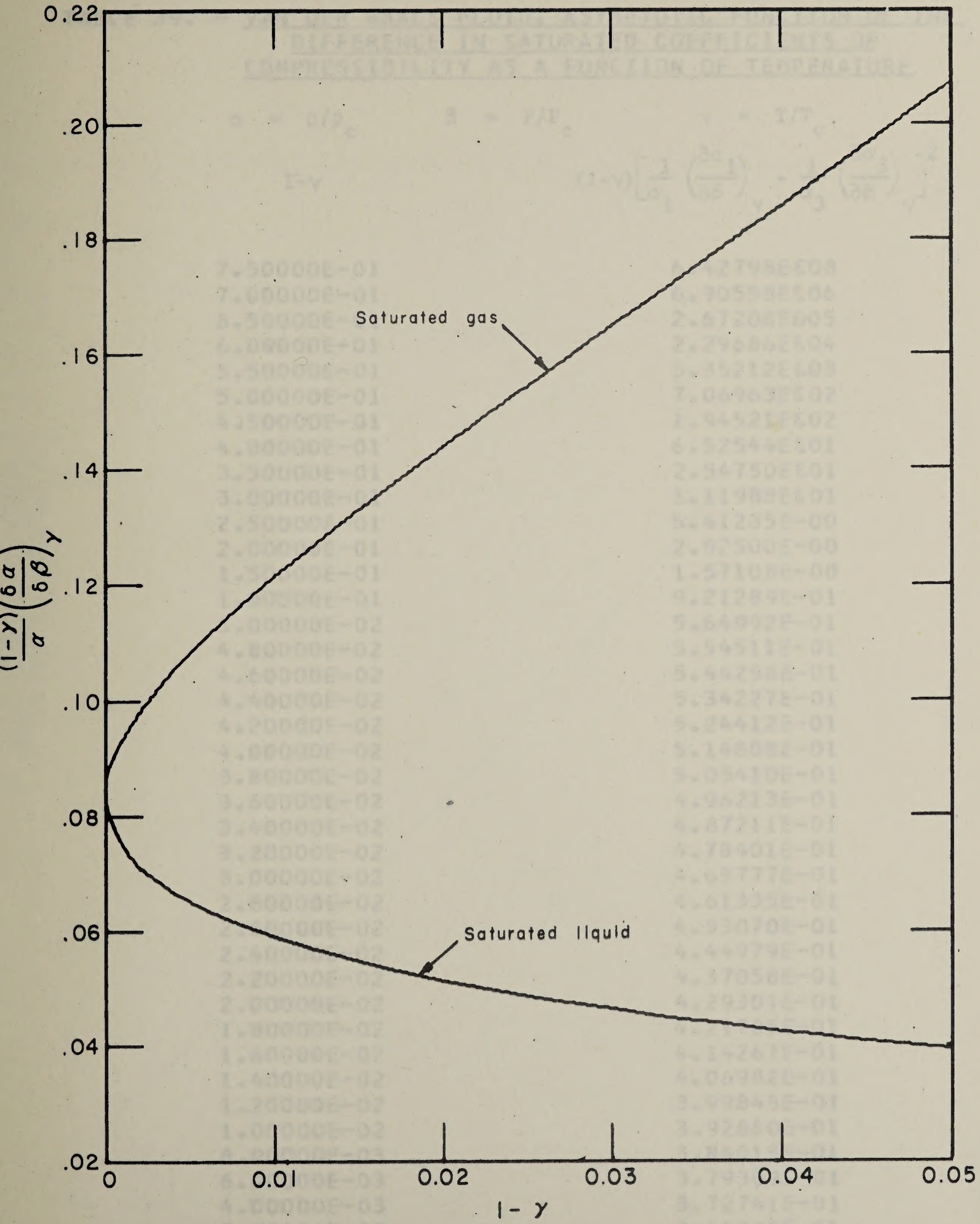

FIGURE 68.- Van der Waals Fluid, Asymptotic Function of the Saturated Coefficients of Compressibility as a Function of $(1-\gamma)$; $\alpha = \rho/\rho_c$; $\beta = P/P_c$; $\gamma = T/T_c$

TABLE 39. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE DIFFERENCE IN SATURATED COEFFICIENTS OF COMPRESSIBILITY AS A FUNCTION OF TEMPERATURE

$\alpha = \rho/\rho_c$ $\beta = P/P_c$ $\gamma = T/T_c$

$1-\gamma$	$(1-\gamma)\left[\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\beta}\right)_\gamma - \frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\beta}\right)_\gamma\right]^2$
7.50000E-01	6.42798E&08
7.00000E-01	6.90558E&06
6.50000E-01	2.67208E&05
6.00000E-01	2.29686E&04
5.50000E-01	3.35212E&03
5.00000E-01	7.06963E&02
4.50000E-01	1.94521E&02
4.00000E-01	6.52544E&01
3.50000E-01	2.54750E&01
3.00000E-01	1.11988E&01
2.50000E-01	5.41235E-00
2.00000E-01	2.82500E-00
1.50000E-01	1.57108E-00
1.00000E-01	9.21289E-01
5.00000E-02	5.64992E-01
4.80000E-02	5.54511E-01
4.60000E-02	5.44258E-01
4.40000E-02	5.34227E-01
4.20000E-02	5.24412E-01
4.00000E-02	5.14808E-01
3.80000E-02	5.05410E-01
3.60000E-02	4.96213E-01
3.40000E-02	4.87211E-01
3.20000E-02	4.78401E-01
3.00000E-02	4.69777E-01
2.80000E-02	4.61335E-01
2.60000E-02	4.53070E-01
2.40000E-02	4.44979E-01
2.20000E-02	4.37058E-01
2.00000E-02	4.29301E-01
1.80000E-02	4.21705E-01
1.60000E-02	4.14267E-01
1.40000E-02	4.06982E-01
1.20000E-02	3.99848E-01
1.00000E-02	3.92860E-01
8.00000E-03	3.86015E-01
6.00000E-03	3.79309E-01
4.00000E-03	3.72741E-01
2.00000E-03	3.66305E-01
1.00000E-03	3.63136E-01
0.00000E-99	3.60000E-01

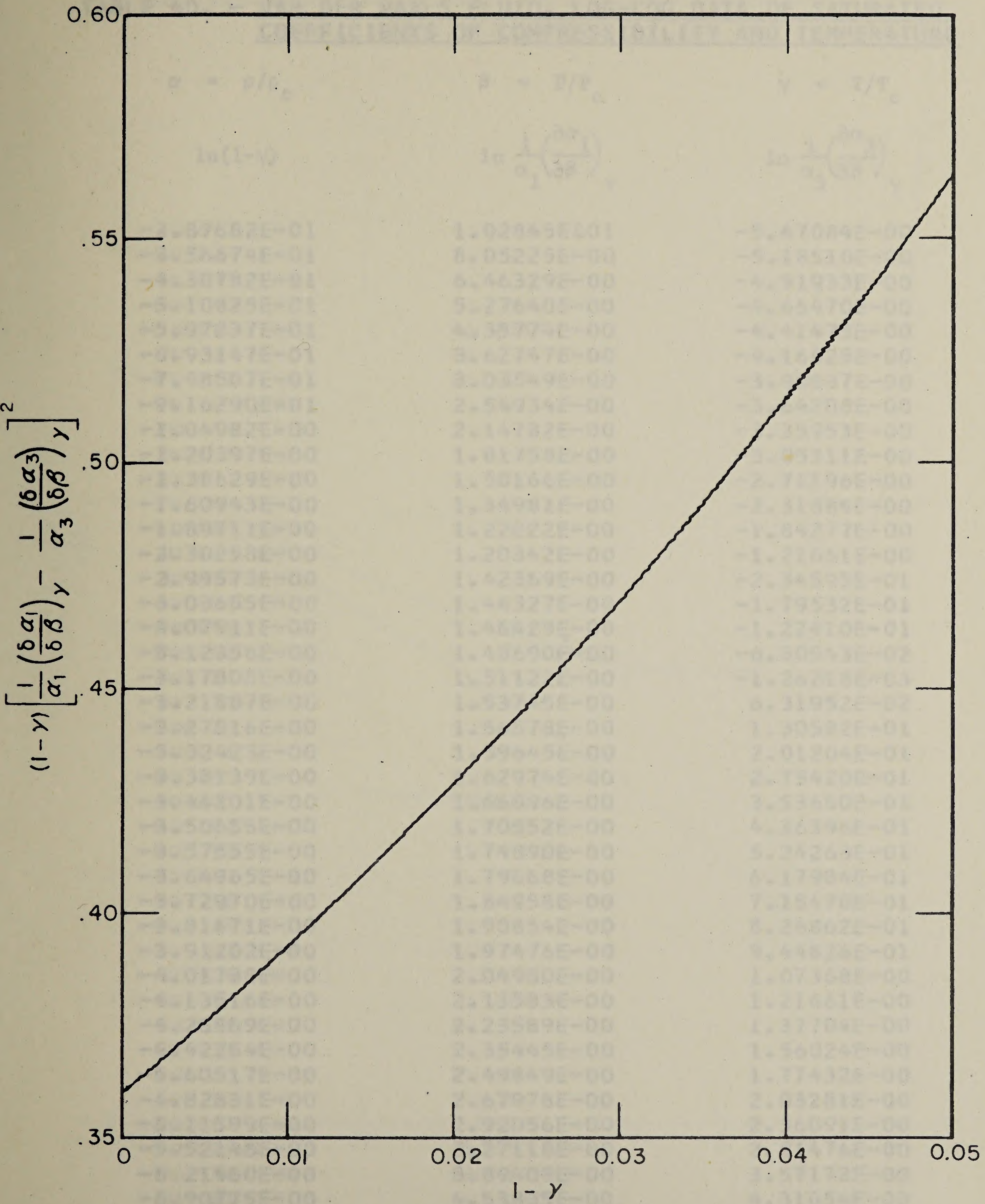

FIGURE 69.—Van der Waals Fluid, Asymptotic Function of the Difference in Saturated Coefficients of Compressibility as a Function of $(1-\gamma)$; $\alpha = \rho/\rho_c$; $\beta = P/P_c$; $\gamma = T/T_c$

TABLE 40. - VAN DER WAALS FLUID, LOG-LOG DATA OF SATURATED COEFFICIENTS OF COMPRESSIBILITY AND TEMPERATURE

$\alpha = \rho/\rho_c$	$\beta = P/P_c$	$\gamma = T/T_c$
$\ln(1-\gamma)$	$\ln \frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\beta}\right)_\gamma$	$\ln \frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\beta}\right)_\gamma$
-2.87682E-01	1.02845E&01	-5.47084E-00
-3.56674E-01	8.05225E-00	-5.18510E-00
-4.30782E-01	6.46329E-00	-4.91933E-00
-5.10825E-01	5.27640E-00	-4.66470E-00
-5.97837E-01	4.35774E-00	-4.41475E-00
-6.93147E-01	3.62747E-00	-4.16425E-00
-7.98507E-01	3.03549E-00	-3.90837E-00
-9.16290E-01	2.54934E-00	-3.64208E-00
-1.04982E-00	2.14782E-00	-3.35953E-00
-1.20397E-00	1.81758E-00	-3.05311E-00
-1.38629E-00	1.55166E-00	-2.71196E-00
-1.60943E-00	1.34981E-00	-2.31884E-00
-1.89711E-00	1.22222E-00	-1.84277E-00
-2.30258E-00	1.20342E-00	-1.21661E-00
-2.99573E-00	1.42369E-00	-2.34595E-01
-3.03655E-00	1.44327E-00	-1.79532E-01
-3.07911E-00	1.46429E-00	-1.22410E-01
-3.12356E-00	1.48690E-00	-6.30543E-02
-3.17008E-00	1.51122E-00	-1.26218E-03
-3.21887E-00	1.53745E-00	6.31952E-02
-3.27016E-00	1.56578E-00	1.30582E-01
-3.32423E-00	1.59645E-00	2.01204E-01
-3.38139E-00	1.62974E-00	2.75420E-01
-3.44201E-00	1.66596E-00	3.53650E-01
-3.50655E-00	1.70552E-00	4.36396E-01
-3.57555E-00	1.74890E-00	5.24263E-01
-3.64965E-00	1.79668E-00	6.17984E-01
-3.72970E-00	1.84958E-00	7.18470E-01
-3.81671E-00	1.90854E-00	8.26862E-01
-3.91202E-00	1.97476E-00	9.44626E-01
-4.01738E-00	2.04980E-00	1.07368E-00
-4.13516E-00	2.13583E-00	1.21661E-00
-4.26869E-00	2.23589E-00	1.37704E-00
-4.42284E-00	2.35445E-00	1.56024E-00
-4.60517E-00	2.49849E-00	1.77432E-00
-4.82831E-00	2.67978E-00	2.03281E-00
-5.11599E-00	2.92056E-00	2.36091E-00
-5.52146E-00	3.27118E-00	2.81476E-00
-6.21460E-00	3.89408E-00	3.57172E-00
-6.90775E-00	4.53835E-00	4.31054E-00

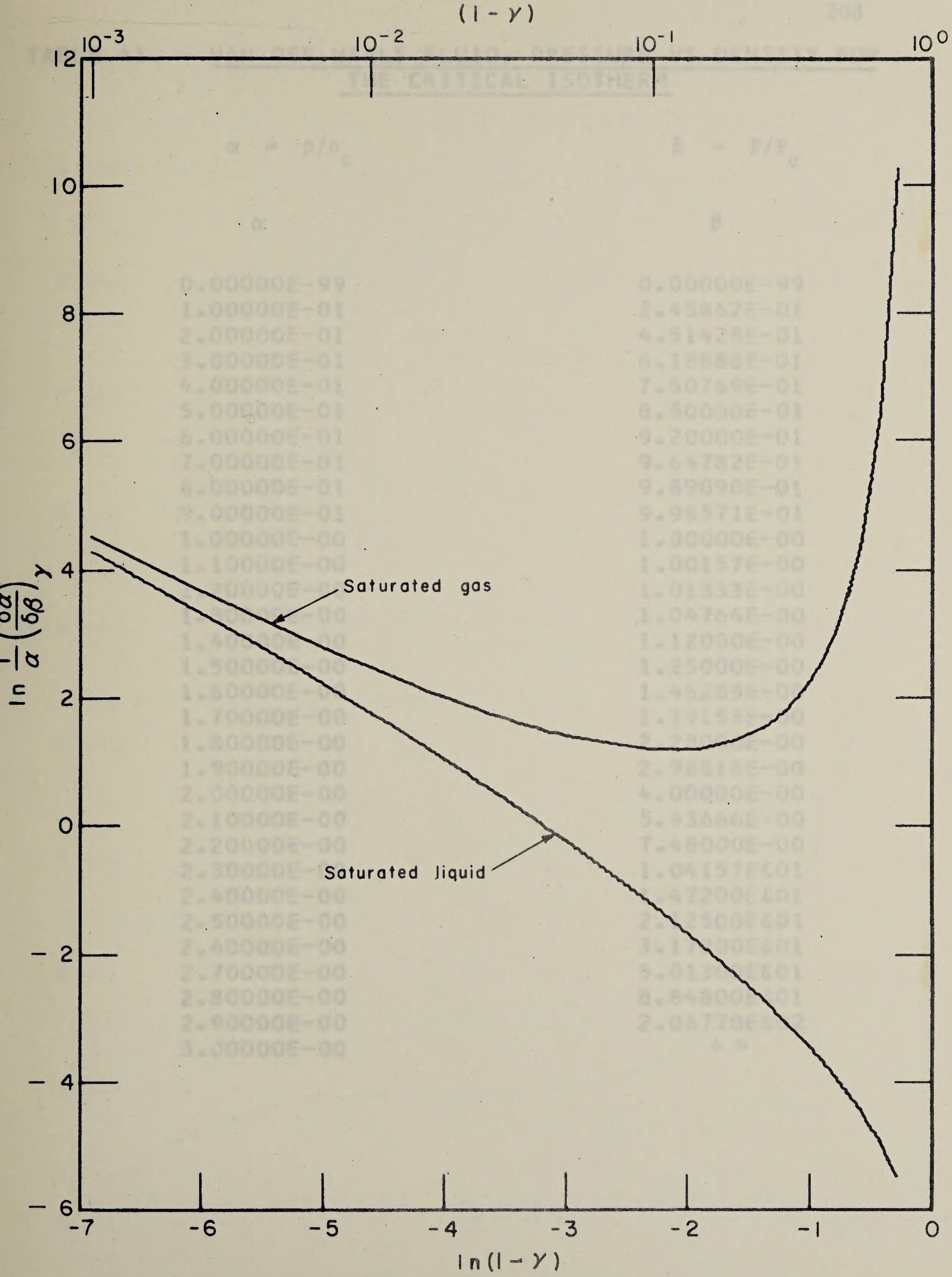

FIGURE 70.- Van der Waals Fluid, Log-Log Curves of Saturated Coefficients of Compressibility and $(1-\gamma)$; $\alpha = \rho/\rho_c$; $\beta = P/P_c$; $\gamma = T/T_c$

TABLE 41. - VAN DER WAALS FLUID, PRESSURE VS DENSITY FOR THE CRITICAL ISOTHERM

$\alpha = \rho/\rho_c$ $\beta = P/P_c$

α	β
0.00000E-99	0.00000E-99
1.00000E-01	2.45862E-01
2.00000E-01	4.51428E-01
3.00000E-01	6.18888E-01
4.00000E-01	7.50769E-01
5.00000E-01	8.50000E-01
6.00000E-01	9.20000E-01
7.00000E-01	9.64782E-01
8.00000E-01	9.89090E-01
9.00000E-01	9.98571E-01
1.00000E-00	1.00000E-00
1.10000E-00	1.00157E-00
1.20000E-00	1.01333E-00
1.30000E-00	1.04764E-00
1.40000E-00	1.12000E-00
1.50000E-00	1.25000E-00
1.60000E-00	1.46285E-00
1.70000E-00	1.79153E-00
1.80000E-00	2.28000E-00
1.90000E-00	2.98818E-00
2.00000E-00	4.00000E-00
2.10000E-00	5.43666E-00
2.20000E-00	7.48000E-00
2.30000E-00	1.04157E&01
2.40000E-00	1.47200E&01
2.50000E-00	2.12500E&01
2.60000E-00	3.17200E&01
2.70000E-00	5.01300E&01
2.80000E-00	8.84800E&01
2.90000E-00	2.06770E&02
3.00000E-00	+ ∞

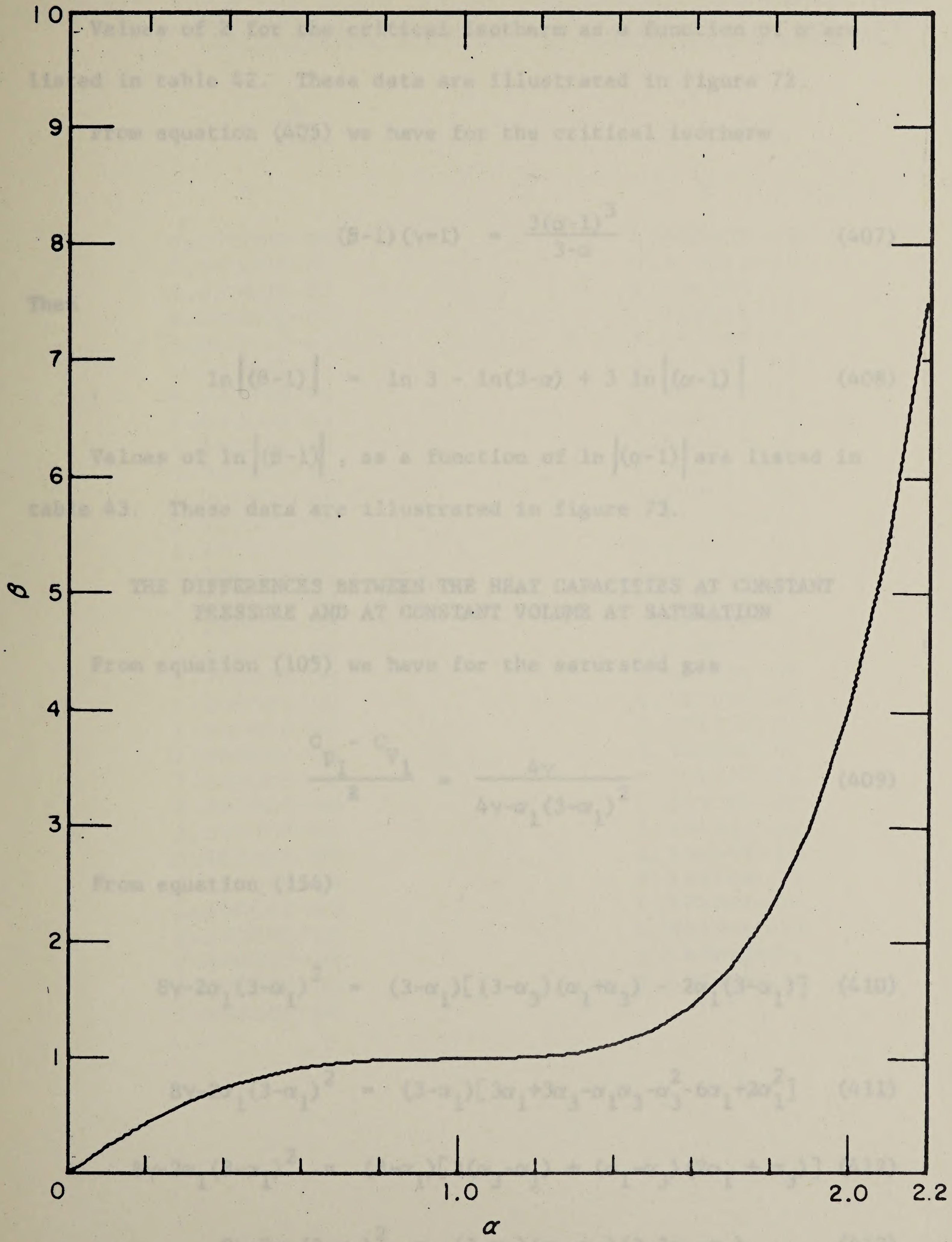

FIGURE 71.- Van der Waals Fluid, Pressure of the Critical Isotherm as a Function of Density; $\alpha = \rho/\rho_c$; $\beta = P/P_c$

Values of Z for the critical isotherm as a function of α are listed in table 42. These data are illustrated in figure 72.

From equation (405) we have for the critical isotherm

$$(\beta-1)(\gamma=1) = \frac{3(\alpha-1)^3}{3-\alpha} \qquad (407)$$

Then

$$\ln\left|(\beta-1)\right| = \ln 3 - \ln(3-\alpha) + 3\ln\left|(\alpha-1)\right| \qquad (408)$$

Values of $\ln\left|(\beta-1)\right|$, as a function of $\ln\left|(\alpha-1)\right|$ are listed in table 43. These data are illustrated in figure 73.

THE DIFFERENCES BETWEEN THE HEAT CAPACITIES AT CONSTANT PRESSURE AND AT CONSTANT VOLUME AT SATURATION

From equation (105) we have for the saturated gas

$$\frac{C_{p_1} - C_{V_1}}{R} = \frac{4\gamma}{4\gamma-\alpha_1(3-\alpha_1)^2} \qquad (409)$$

From equation (154)

$$8\gamma-2\alpha_1(3-\alpha_1)^2 = (3-\alpha_1)[(3-\alpha_3)(\alpha_1+\alpha_3) - 2\alpha_1(3-\alpha_1)] \qquad (410)$$

$$8\gamma-2\alpha_1(3-\alpha_1)^2 = (3-\alpha_1)[3\alpha_1+3\alpha_3-\alpha_1\alpha_3-\alpha_3^2-6\alpha_1+2\alpha_1^2] \qquad (411)$$

$$8\gamma-2\alpha_1(3-\alpha_1)^2 = (3-\alpha_1)[3(\alpha_3-\alpha_1) + (\alpha_1-\alpha_3)(2\alpha_1 + \alpha_3)] \qquad (412)$$

$$8\gamma-2\alpha_1(3-\alpha_1)^2 = (3-\alpha_1)(\alpha_3-\alpha_1)(3-2\alpha_1-\alpha_3) \qquad (413)$$

TABLE 42. - VAN DER WAALS FLUID, COMPRESSIBILITY FACTOR FOR THE CRITICAL ISOTHERM AS A FUNCTION OF DENSITY

$Z = \frac{P}{\rho RT}$ $\alpha = \rho/\rho_c$

α	Z
0.00000E-99	1.00000E-00
1.00000E-01	9.21982E-01
2.00000E-01	8.46428E-01
3.00000E-01	7.73611E-01
4.00000E-01	7.03846E-01
5.00000E-01	6.37500E-01
6.00000E-01	5.75000E-01
7.00000E-01	5.16847E-01
8.00000E-01	4.63636E-01
9.00000E-01	4.16071E-01
1.00000E-00	3.75000E-01
1.10000E-00	3.41447E-01
1.20000E-00	3.16666E-01
1.30000E-00	3.02205E-01
1.40000E-00	3.00000E-01
1.50000E-00	3.12500E-01
1.60000E-00	3.42857E-01
1.70000E-00	3.95192E-01
1.80000E-00	4.75000E-01
1.90000E-00	5.89772E-01
2.00000E-00	7.50000E-01
2.10000E-00	9.70833E-01
2.20000E-00	1.27500E-00
2.30000E-00	1.69821E-00
2.40000E-00	2.30000E-00
2.50000E-00	3.18750E-00
2.60000E-00	4.57500E-00
2.70000E-00	6.96250E-00
2.80000E-00	1.18500E&01
2.90000E-00	2.67375E&01
3.00000E-00	+ ∞

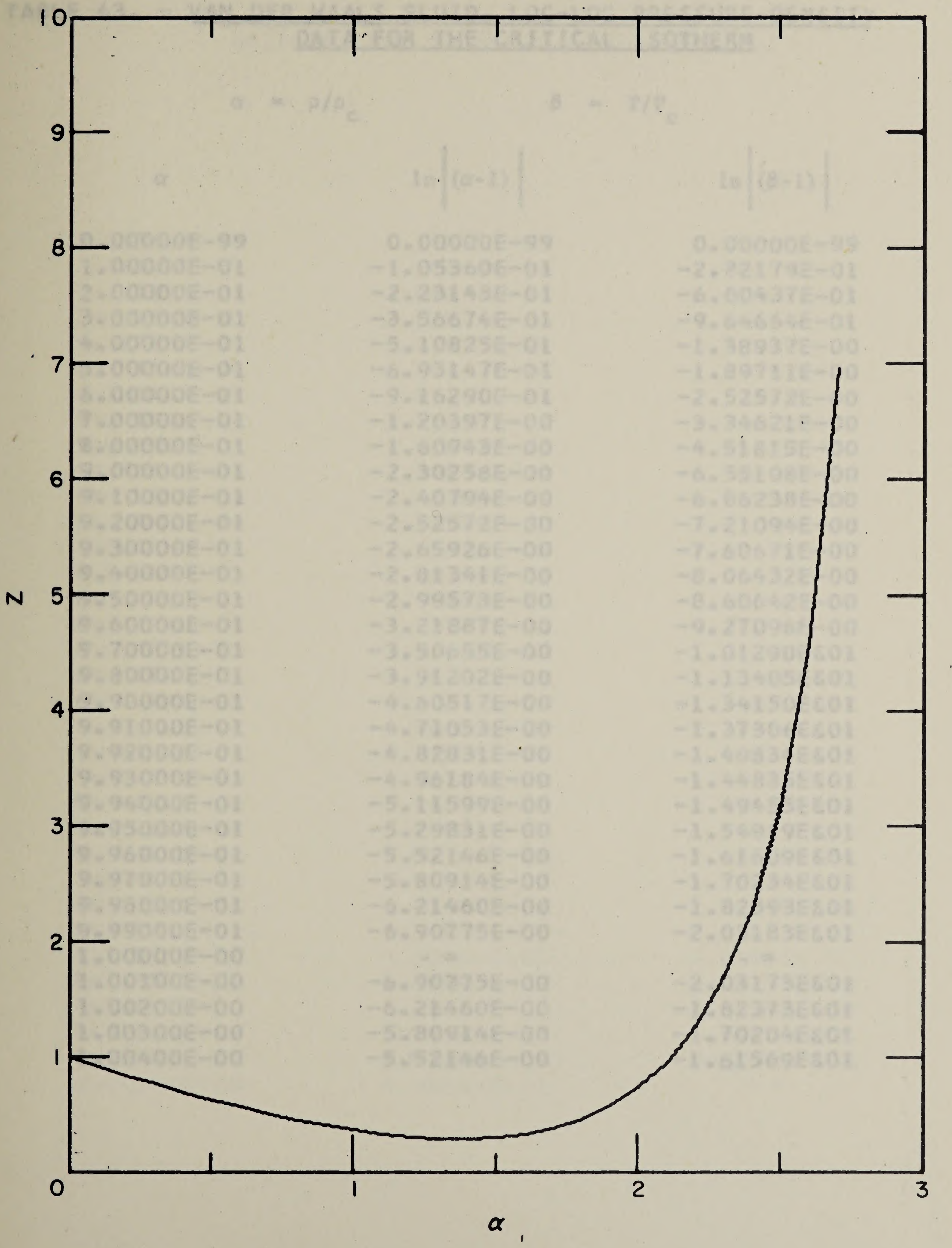

FIGURE 72.- Van der Waals Fluid, Compressibity Factor for the Critical Isotherm as a Function of Density; $Z = \frac{P}{\rho RT}$; $\alpha = \rho/\rho_c$

TABLE 43. - VAN DER WAALS FLUID, LOG-LOG PRESSURE-DENSITY DATA FOR THE CRITICAL ISOTHERM

$\alpha = \rho/\rho_c$ $\beta = P/P_c$

α	$\ln\left\|(\alpha-1)\right\|$	$\ln\left\|(\beta-1)\right\|$
0.00000E-99	0.00000E-99	0.00000E-99
1.00000E-01	-1.05360E-01	-2.82179E-01
2.00000E-01	-2.23143E-01	-6.00437E-01
3.00000E-01	-3.56674E-01	-9.64664E-01
4.00000E-01	-5.10825E-01	-1.38937E-00
5.00000E-01	-6.93147E-01	-1.89711E-00
6.00000E-01	-9.16290E-01	-2.52572E-00
7.00000E-01	-1.20397E-00	-3.34621E-00
8.00000E-01	-1.60943E-00	-4.51815E-00
9.00000E-01	-2.30258E-00	-6.55108E-00
9.10000E-01	-2.40794E-00	-6.86238E-00
9.20000E-01	-2.52572E-00	-7.21094E-00
9.30000E-01	-2.65926E-00	-7.60671E-00
9.40000E-01	-2.81341E-00	-8.06432E-00
9.50000E-01	-2.99573E-00	-8.60642E-00
9.60000E-01	-3.21887E-00	-9.27096E-00
9.70000E-01	-3.50655E-00	-1.01290E&01
9.80000E-01	-3.91202E-00	-1.13405E&01
9.90000E-01	-4.60517E-00	-1.34150E&01
9.91000E-01	-4.71053E-00	-1.37306E&01
9.92000E-01	-4.82831E-00	-1.40834E&01
9.93000E-01	-4.96184E-00	-1.44835E&01
9.94000E-01	-5.11599E-00	-1.49455E&01
9.95000E-01	-5.29831E-00	-1.54919E&01
9.96000E-01	-5.52146E-00	-1.61609E&01
9.97000E-01	-5.80914E-00	-1.70234E&01
9.98000E-01	-6.21460E-00	-1.82393E&01
9.99000E-01	-6.90775E-00	-2.03183E&01
1.00000E-00	$-\infty$	$-\infty$
1.00100E-00	-6.90775E-00	-2.03173E&01
1.00200E-00	-6.21460E-00	-1.82373E&01
1.00300E-00	-5.80914E-00	-1.70204E&01
1.00400E-00	-5.52146E-00	-1.61569E&01

TABLE 43. - VAN DER WAALS FLUID, LOG-LOG PRESSURE-DENSITY DATA FOR THE CRITICAL ISOTHERM (CON.)

$\alpha = \rho/\rho_c$ $\beta = P/P_c$

α	$\ln\left\|(\alpha-1)\right\|$	$\ln\left\|(\beta-1)\right\|$
1.00500E-00	-5.29831E-00	-1.54869E&01
1.00600E-00	-5.11599E-00	-1.49395E&01
1.00700E-00	-4.96184E-00	-1.44765E&01
1.00800E-00	-4.82831E-00	-1.40754E&01
1.00900E-00	-4.71053E-00	-1.37216E&01
1.01000E-00	-4.60517E-00	-1.34050E&01
1.02000E-00	-3.91202E-00	-1.13205E&01
1.03000E-00	-3.50655E-00	-1.00990E&01
1.04000E-00	-3.21887E-00	-9.23095E-00
1.05000E-00	-2.99573E-00	-8.55641E-00
1.06000E-00	-2.81341E-00	-8.00430E-00
1.07000E-00	-2.65926E-00	-7.53668E-00
1.08000E-00	-2.52572E-00	-7.13089E-00
1.09000E-00	-2.40794E-00	-6.77232E-00
1.10000E-00	-2.30258E-00	-6.45099E-00
1.20000E-00	-1.60943E-00	-4.31748E-00
1.30000E-00	-1.20397E-00	-3.04393E-00
1.40000E-00	-9.16290E-01	-2.12026E-00
1.50000E-00	-6.93147E-01	-1.38629E-00
1.60000E-00	-5.10825E-01	-7.70336E-01
1.70000E-00	-3.56674E-01	-2.33776E-01
1.80000E-00	-2.23143E-01	2.46860E-01
1.90000E-00	-1.05360E-01	6.87220E-01
2.00000E-00	0.00000E-99	1.09861E-00
2.10000E-00	9.53101E-02	1.48990E-00
2.20000E-00	1.82321E-01	1.86872E-00
2.30000E-00	2.62364E-01	2.24238E-00
2.40000E-00	3.36472E-01	2.61885E-00
2.50000E-00	4.05465E-01	3.00815E-00
2.60000E-00	4.70003E-01	3.42491E-00
2.70000E-00	5.30628E-01	3.89446E-00
2.80000E-00	5.87786E-01	4.47141E-00
2.90000E-00	6.41853E-01	5.32675E-00
3.00000E-00	6.93147E-01	$+\infty$

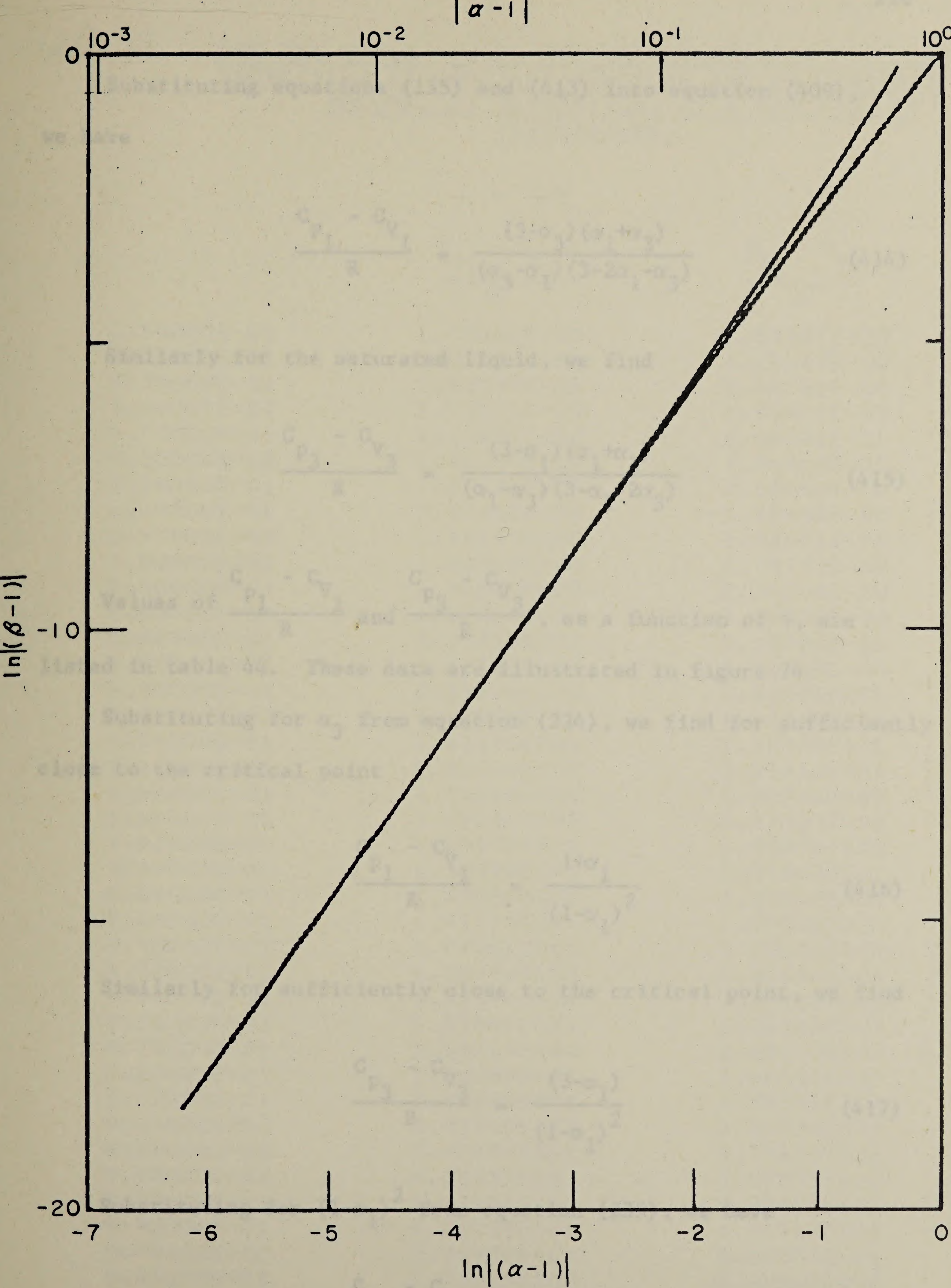

FIGURE 73.- Van der Waals Fluid, Log-Log Pressure-Density Data for the Critical Isotherm; $\alpha = \rho/\rho_c$; $\beta = P/P_c$

Substituting equations (155) and (413) into equation (409), we have

$$\frac{C_{p_1} - C_{V_1}}{R} = \frac{(3-\alpha_3)(\alpha_1+\alpha_3)}{(\alpha_3-\alpha_1)(3-2\alpha_1-\alpha_3)} \tag{414}$$

Similarly for the saturated liquid, we find

$$\frac{C_{p_3} - C_{V_3}}{R} = \frac{(3-\alpha_1)(\alpha_1+\alpha_3)}{(\alpha_1-\alpha_3)(3-\alpha_1-2\alpha_3)} \tag{415}$$

Values of $\frac{C_{p_1} - C_{V_1}}{R}$ and $\frac{C_{p_3} - C_{V_3}}{R}$, as a function of γ, are listed in table 44. These data are illustrated in figure 74.

Substituting for α_3 from equation (224), we find for sufficiently close to the critical point

$$\frac{C_{p_1} - C_{V_1}}{R} = \frac{1+\alpha_1}{(1-\alpha_1)^2} \tag{416}$$

Similarly for sufficiently close to the critical point, we find

$$\frac{C_{p_3} - C_{V_3}}{R} = \frac{(3-\alpha_1)}{(1-\alpha_1)^2} \tag{417}$$

Substituting for $(1-\alpha_1)^2$ from equation (235), we have

$$\frac{C_{p_1} - C_{V_1}}{R} = \frac{1+\alpha_1}{4(1-\gamma)} \tag{418}$$

TABLE 44. - VAN DER WAALS FLUID, DIFFERENCE BETWEEN THE HEAT CAPACITIES AT CONSTANT PRESSURE AND AT CONSTANT VOLUME, AT SATURATION, AS A FUNCTION OF TEMPERATURE

$\gamma = T/T_c$

γ	$\frac{C_{p_1} - C_{V_1}}{R}$	$\frac{C_{p_3} - C_{V_3}}{R}$
2.50000E-01	1.00046E-00	1.19207E-00
3.00000E-01	1.00300E-00	1.24567E-00
3.50000E-01	1.01095E-00	1.30716E-00
4.00000E-01	1.02831E-00	1.37862E-00
4.50000E-01	1.05895E-00	1.46281E-00
5.00000E-01	1.10674E-00	1.56360E-00
5.50000E-01	1.17634E-00	1.68654E-00
6.00000E-01	1.27441E-00	1.83988E-00
6.50000E-01	1.41147E-00	2.03651E-00
7.00000E-01	1.60546E-00	2.29779E-00
7.50000E-01	1.88920E-00	2.66196E-00
8.00000E-01	2.32918E-00	3.20505E-00
8.50000E-01	3.08219E-00	4.10333E-00
9.00000E-01	4.62313E-00	5.88169E-00
9.50000E-01	9.35279E-00	1.11391E&01
9.52000E-01	9.75070E-00	1.15740E&01
9.54000E-01	1.01836E&01	1.20464E&01
9.56000E-01	1.06564E&01	1.25612E&01
9.58000E-01	1.11748E&01	1.31246E&01
9.60000E-01	1.17456E&01	1.37437E&01
9.62000E-01	1.23773E&01	1.44274E&01
9.64000E-01	1.30798E&01	1.51863E&01
9.66000E-01	1.38660E&01	1.60337E&01
9.68000E-01	1.47514E&01	1.69860E&01
9.70000E-01	1.57561E&01	1.80641E&01
9.72000E-01	1.69058E&01	1.92950E&01
9.74000E-01	1.82340E&01	2.07135E&01
9.76000E-01	1.97856E&01	2.23665E&01
9.78000E-01	2.16219E&01	2.43177E&01
9.80000E-01	2.38285E&01	2.66560E&01
9.82000E-01	2.65295E&01	2.95101E&01
9.84000E-01	2.99110E&01	3.30726E&01
9.86000E-01	3.42659E&01	3.76458E&01
9.88000E-01	4.00826E&01	4.37335E&01
9.90000E-01	4.82414E&01	5.22409E&01
9.92000E-01	6.05050E&01	6.49767E&01
9.94000E-01	8.09922E&01	8.61558E&01
9.96000E-01	1.22078E&02	1.28402E&02
9.98000E-01	2.45768E&02	2.54712E&02
9.99000E-01	4.93915E&02	5.06564E&02
1.00000E-00	$+\infty$	$+\infty$

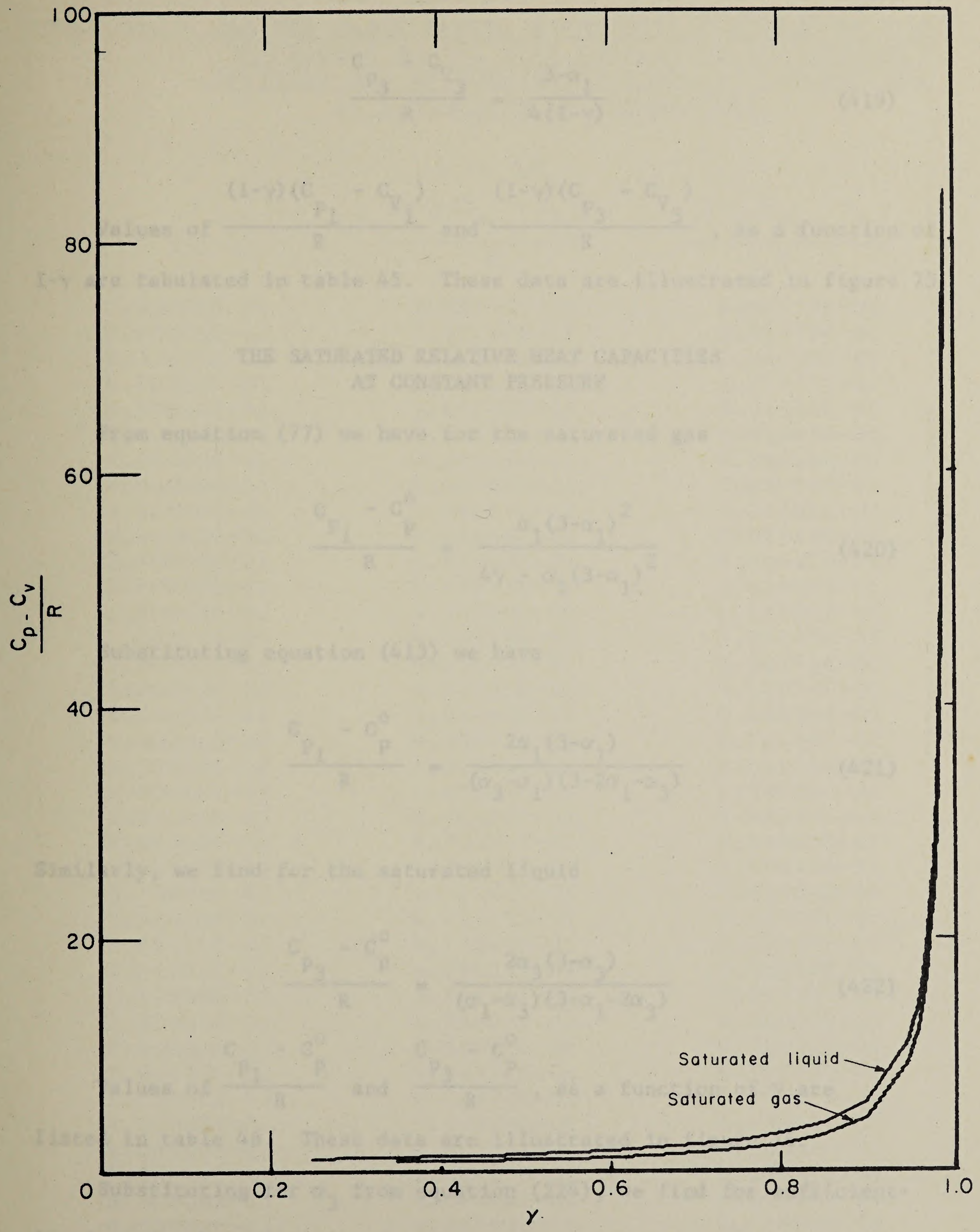

FIGURE 74.- Van der Waals Fluid, Difference Between the Heat Capacities at Constant Pressure and Constant Volume, at Saturation, vs γ; $\gamma = T/T_c$

$$\frac{C_{p_3} - C_{V_3}}{R} = \frac{3-\alpha_1}{4(1-\gamma)} \tag{419}$$

Values of $\frac{(1-\gamma)(C_{p_1} - C_{V_1})}{R}$ and $\frac{(1-\gamma)(C_{p_3} - C_{V_3})}{R}$, as a function of $1-\gamma$ are tabulated in table 45. These data are illustrated in figure 75.

THE SATURATED RELATIVE HEAT CAPACITIES AT CONSTANT PRESSURE

From equation (77) we have for the saturated gas

$$\frac{C_{p_1} - C_p^o}{R} = \frac{\alpha_1(3-\alpha_1)^2}{4\gamma - \alpha_1(3-\alpha_1)^2} \tag{420}$$

Substituting equation (413) we have

$$\frac{C_{p_1} - C_p^o}{R} = \frac{2\alpha_1(3-\alpha_1)}{(\alpha_3-\alpha_1)(3-2\alpha_1-\alpha_3)} \tag{421}$$

Similarly, we find for the saturated liquid

$$\frac{C_{p_3} - C_p^o}{R} = \frac{2\alpha_3(3-\alpha_3)}{(\alpha_1-\alpha_3)(3-\alpha_1-2\alpha_3)} \tag{422}$$

Values of $\frac{C_{p_1} - C_p^o}{R}$ and $\frac{C_{p_3} - C_p^o}{R}$, as a function of γ are listed in table 46. These data are illustrated in figure 76.

Substituting for α_3 from equation (224), we find for sufficiently close to the critical point

$$\frac{C_{p_1} - C_p^o}{R} = \frac{\alpha_1(3-\alpha_1)}{(1-\alpha_1)^2} \tag{423}$$

TABLE 45. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE DIFFERENCE IN THE HEAT CAPACITIES AT CONSTANT PRESSURE AND AT CONSTANT VOLUME, AT SATURATION, AS A FUNCTION OF TEMPERATURE

$\gamma = T/T_c$

$1-\gamma$	$\frac{(1-\gamma)(C_{p_1} - C_{V_1})}{R}$	$\frac{(1-\gamma)(C_{p_3} - C_{V_3})}{R}$
7.50000E-01	7.50346E-01	8.94058E-01
7.00000E-01	7.02100E-01	8.71970E-01
6.50000E-01	6.57120E-01	8.49660E-01
6.00000E-01	6.16987E-01	8.27172E-01
5.50000E-01	5.82422E-01	8.04546E-01
5.00000E-01	5.53370E-01	7.81803E-01
4.50000E-01	5.29355E-01	7.58946E-01
4.00000E-01	5.09764E-01	7.35954E-01
3.50000E-01	4.94017E-01	7.12781E-01
3.00000E-01	4.81640E-01	6.89339E-01
2.50000E-01	4.72300E-01	6.65492E-01
2.00000E-01	4.65836E-01	6.41011E-01
1.50000E-01	4.62329E-01	6.15500E-01
1.00000E-01	4.62313E-01	5.88169E-01
5.00000E-02	4.67639E-01	5.56956E-01
4.80000E-02	4.68033E-01	5.55554E-01
4.60000E-02	4.68448E-01	5.54134E-01
4.40000E-02	4.68884E-01	5.52694E-01
4.20000E-02	4.69343E-01	5.51233E-01
4.00000E-02	4.69827E-01	5.49750E-01
3.80000E-02	4.70337E-01	5.48243E-01
3.60000E-02	4.70876E-01	5.46709E-01
3.40000E-02	4.71445E-01	5.45147E-01
3.20000E-02	4.72047E-01	5.43553E-01
3.00000E-02	4.72685E-01	5.41925E-01
2.80000E-02	4.73363E-01	5.40260E-01
2.60000E-02	4.74085E-01	5.38552E-01
2.40000E-02	4.74856E-01	5.36798E-01
2.20000E-02	4.75682E-01	5.34990E-01
2.00000E-02	4.76571E-01	5.33121E-01
1.80000E-02	4.77532E-01	5.31183E-01
1.60000E-02	4.78577E-01	5.29162E-01
1.40000E-02	4.79722E-01	5.27042E-01
1.20000E-02	4.80991E-01	5.24802E-01
1.00000E-02	4.82414E-01	5.22409E-01
8.00000E-03	4.84040E-01	5.19814E-01
6.00000E-03	4.85953E-01	5.16935E-01
4.00000E-03	4.88313E-01	5.13610E-01
2.00000E-03	4.91536E-01	5.09424E-01
1.00000E-03	4.93915E-01	5.06564E-01
0.00000E-99	5.00000E-01	5.00000E-01

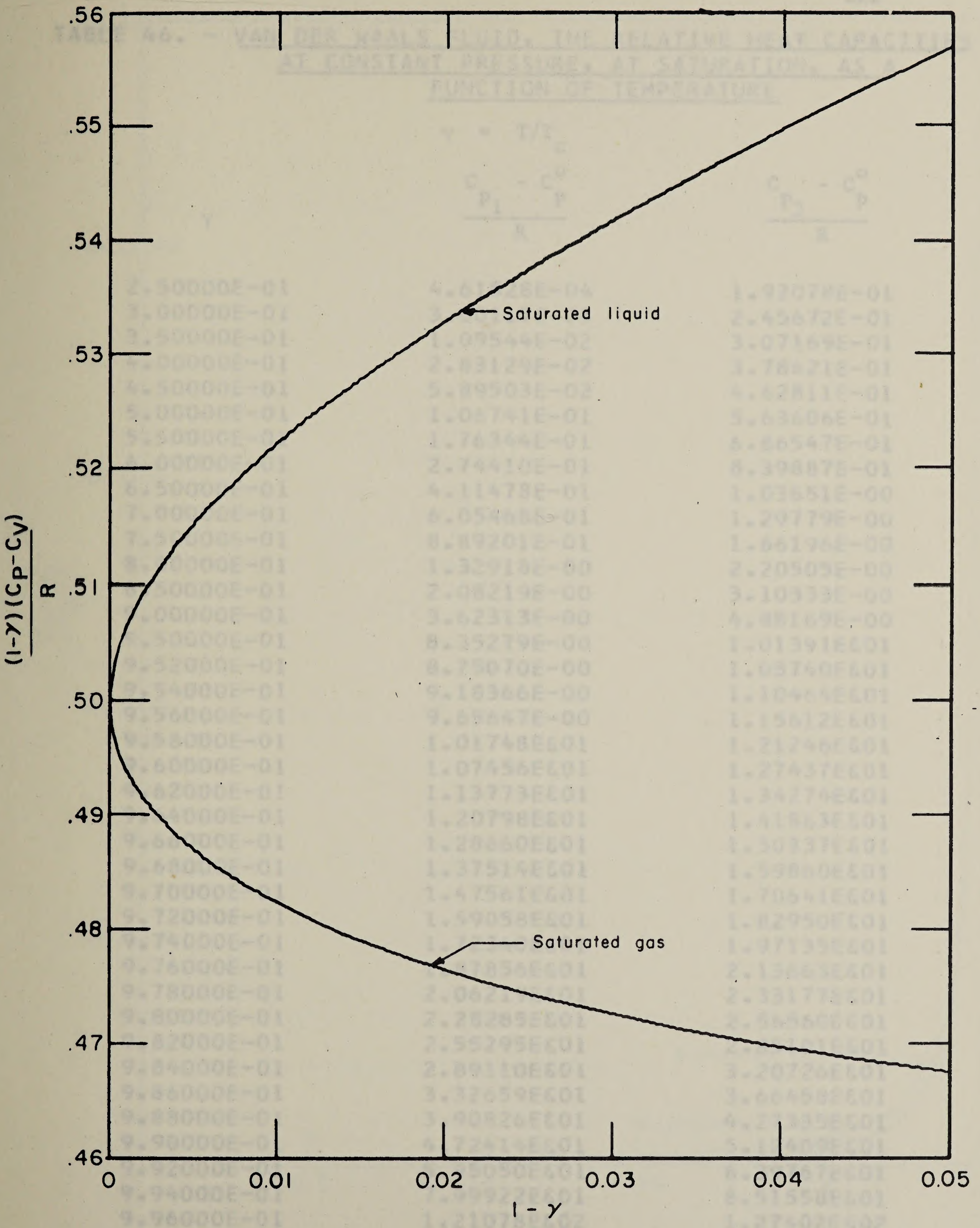

FIGURE 75. - Van der Waals Fluid, Asymptotic Function of the Difference in the Heat Capacities at Constant Pressure and at Constant Volume, at Saturation, as a Function of Temperature; $\gamma = T/T_c$

TABLE 46. - VAN DER WAALS FLUID, THE RELATIVE HEAT CAPACITIES AT CONSTANT PRESSURE, AT SATURATION, AS A FUNCTION OF TEMPERATURE

$\gamma = T/T_c$

γ	$\frac{C_{p_1} - C_p^o}{R}$	$\frac{C_{p_3} - C_p^o}{R}$
2.50000E-01	4.61528E-04	1.92078E-01
3.00000E-01	3.00117E-03	2.45672E-01
3.50000E-01	1.09544E-02	3.07169E-01
4.00000E-01	2.83129E-02	3.78621E-01
4.50000E-01	5.89503E-02	4.62811E-01
5.00000E-01	1.06741E-01	5.63606E-01
5.50000E-01	1.76344E-01	6.86547E-01
6.00000E-01	2.74410E-01	8.39887E-01
6.50000E-01	4.11478E-01	1.03651E-00
7.00000E-01	6.05468E-01	1.29779E-00
7.50000E-01	8.89201E-01	1.66196E-00
8.00000E-01	1.32918E-00	2.20505E-00
8.50000E-01	2.08219E-00	3.10333E-00
9.00000E-01	3.62313E-00	4.88169E-00
9.50000E-01	8.35279E-00	1.01391E&01
9.52000E-01	8.75070E-00	1.05740E&01
9.54000E-01	9.18366E-00	1.10464E&01
9.56000E-01	9.65647E-00	1.15612E&01
9.58000E-01	1.01748E&01	1.21246E&01
9.60000E-01	1.07456E&01	1.27437E&01
9.62000E-01	1.13773E&01	1.34274E&01
9.64000E-01	1.20798E&01	1.41863E&01
9.66000E-01	1.28660E&01	1.50337E&01
9.68000E-01	1.37514E&01	1.59860E&01
9.70000E-01	1.47561E&01	1.70641E&01
9.72000E-01	1.59058E&01	1.82950E&01
9.74000E-01	1.72340E&01	1.97135E&01
9.76000E-01	1.87856E&01	2.13665E&01
9.78000E-01	2.06219E&01	2.33177E&01
9.80000E-01	2.28285E&01	2.56560E&01
9.82000E-01	2.55295E&01	2.85101E&01
9.84000E-01	2.89110E&01	3.20726E&01
9.86000E-01	3.32659E&01	3.66458E&01
9.88000E-01	3.90826E&01	4.27335E&01
9.90000E-01	4.72414E&01	5.12409E&01
9.92000E-01	5.95050E&01	6.39767E&01
9.94000E-01	7.99922E&01	8.51558E&01
9.96000E-01	1.21078E&02	1.27402E&02
9.98000E-01	2.44768E&02	2.53712E&02
9.99000E-01	4.92915E&02	5.05564E&02
1.00000E-00	+ ∞	+ ∞

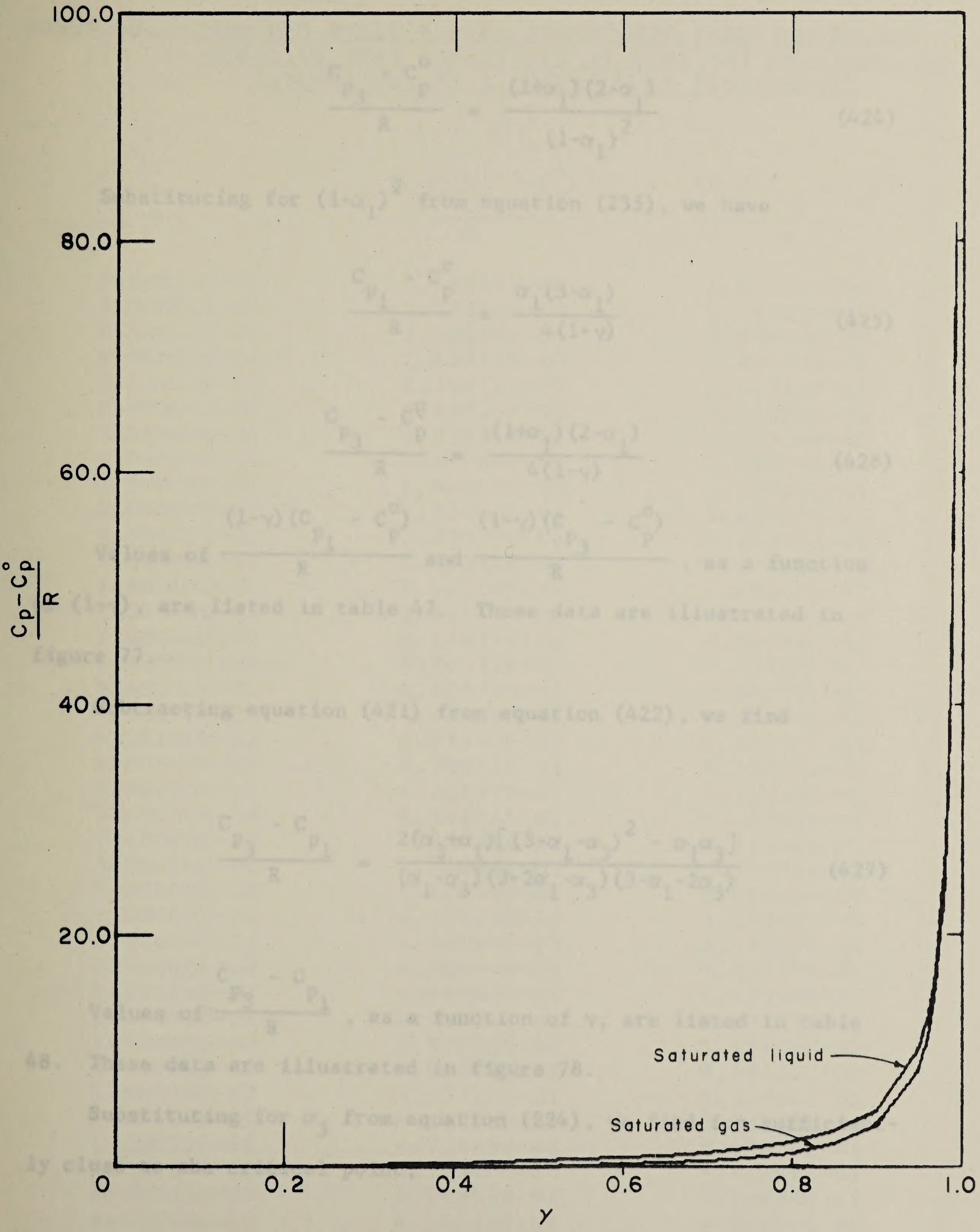

FIGURE 76.- Van der Waals Fluid, Saturated Relative Heat Capacities at Constant Pressure vs γ; $\gamma = T/T_c$

$$\frac{C_{p_3} - C_p^o}{R} = \frac{(1+\alpha_1)(2-\alpha_1)}{(1-\alpha_1)^2} \tag{424}$$

Substituting for $(1-\alpha_1)^2$ from equation (235), we have

$$\frac{C_{p_1} - C_p^o}{R} = \frac{\alpha_1(3-\alpha_1)}{4(1-\gamma)} \tag{425}$$

$$\frac{C_{p_3} - C_p^o}{R} = \frac{(1+\alpha_1)(2-\alpha_1)}{4(1-\gamma)} \tag{426}$$

Values of $\frac{(1-\gamma)(C_{p_1} - C_p^o)}{R}$ and $\frac{(1-\gamma)(C_{p_3} - C_p^o)}{R}$, as a function of $(1-\gamma)$, are listed in table 47. These data are illustrated in figure 77.

Subtracting equation (421) from equation (422), we find

$$\frac{C_{p_3} - C_{p_1}}{R} = \frac{2(\alpha_3+\alpha_1)[(3-\alpha_1-\alpha_3)^2 - \alpha_1\alpha_3]}{(\alpha_1-\alpha_3)(3-2\alpha_1-\alpha_3)(3-\alpha_1-2\alpha_3)} \tag{427}$$

Values of $\frac{C_{p_3} - C_{p_1}}{R}$, as a function of γ, are listed in table 48. These data are illustrated in figure 78.

Substituting for α_3 from equation (224), we find for sufficiently close to the critical point,

$$\frac{C_{p_3} - C_{p_1}}{R} = \frac{2(3-\alpha_1)}{5(1-\alpha_1)} \tag{428}$$

TABLE 47. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE RELATIVE HEAT CAPACITIES AT CONSTANT PRESSURE, AT SATURATION, AS A FUNCTION OF TEMPERATURE

$\gamma = T/T_c$

$1-\gamma$	$\frac{(1-\gamma)(C_{p_1} - C_p^o)}{R}$	$\frac{(1-\gamma)(C_{p_3} - C_p^o)}{R}$
7.50000E-01	3.46146E-04	1.44058E-01
7.00000E-01	2.10082E-03	1.71970E-01
6.50000E-01	7.12038E-03	1.99660E-01
6.00000E-01	1.69877E-02	2.27172E-01
5.50000E-01	3.24226E-02	2.54546E-01
5.00000E-01	5.33709E-02	2.81803E-01
4.50000E-01	7.93551E-02	3.08946E-01
4.00000E-01	1.09764E-01	3.35954E-01
3.50000E-01	1.44017E-01	3.62781E-01
3.00000E-01	1.81640E-01	3.89339E-01
2.50000E-01	2.22300E-01	4.15492E-01
2.00000E-01	2.65836E-01	4.41011E-01
1.50000E-01	3.12329E-01	4.65500E-01
1.00000E-01	3.62313E-01	4.88169E-01
5.00000E-02	4.17639E-01	5.06956E-01
4.80000E-02	4.20033E-01	5.07554E-01
4.60000E-02	4.22448E-01	5.08134E-01
4.40000E-02	4.24884E-01	5.08694E-01
4.20000E-02	4.27343E-01	5.09233E-01
4.00000E-02	4.29827E-01	5.09750E-01
3.80000E-02	4.32337E-01	5.10243E-01
3.60000E-02	4.34876E-01	5.10709E-01
3.40000E-02	4.37445E-01	5.11147E-01
3.20000E-02	4.40047E-01	5.11553E-01
3.00000E-02	4.42685E-01	5.11925E-01
2.80000E-02	4.45363E-01	5.12260E-01
2.60000E-02	4.48085E-01	5.12552E-01
2.40000E-02	4.50856E-01	5.12798E-01
2.20000E-02	4.53682E-01	5.12990E-01
2.00000E-02	4.56571E-01	5.13121E-01
1.80000E-02	4.59532E-01	5.13183E-01
1.60000E-02	4.62577E-01	5.13162E-01
1.40000E-02	4.65722E-01	5.13042E-01
1.20000E-02	4.68991E-01	5.12802E-01
1.00000E-02	4.72414E-01	5.12409E-01
8.00000E-03	4.76040E-01	5.11814E-01
6.00000E-03	4.79953E-01	5.10935E-01
4.00000E-03	4.84313E-01	5.09610E-01
2.00000E-03	4.89536E-01	5.07424E-01
1.00000E-03	4.92915E-01	5.05564E-01
0.00000E-99	5.00000E-01	5.00000E-01

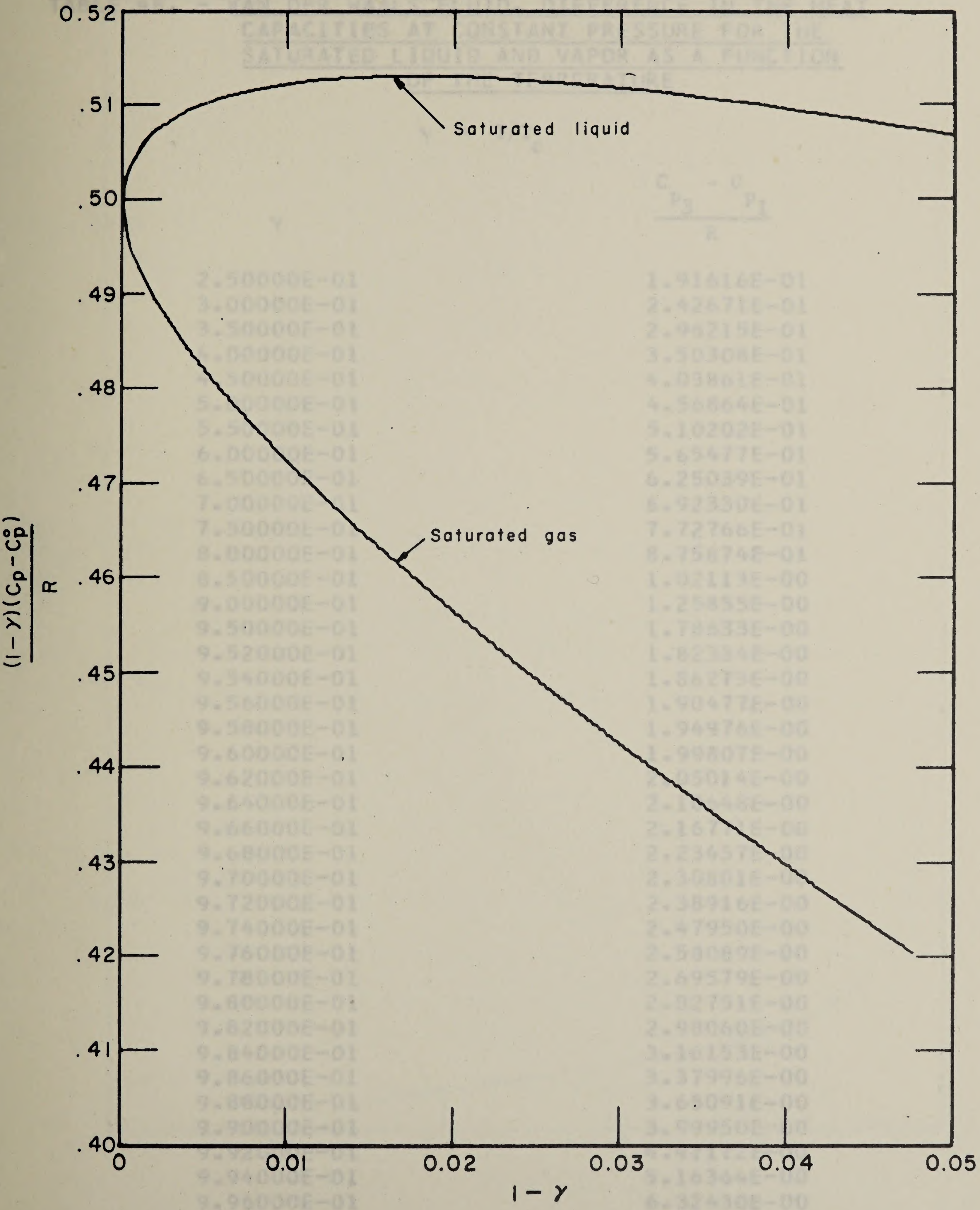

FIGURE 77.- Van der Waals Fluid, Asymptotic Function of the Relative Heat Capacities at Constant Pressure, at Saturation, as a Function of Temperature; $\gamma = T/T_c$

TABLE 48. - VAN DER WAALS FLUID, DIFFERENCE IN THE HEAT CAPACITIES AT CONSTANT PRESSURE FOR THE SATURATED LIQUID AND VAPOR AS A FUNCTION OF THE TEMPERATURE

$Y = T/T_c$

Y	$\frac{C_{P_3} - C_{P_1}}{R}$
2.50000E-01	1.91616E-01
3.00000E-01	2.42671E-01
3.50000E-01	2.96215E-01
4.00000E-01	3.50308E-01
4.50000E-01	4.03861E-01
5.00000E-01	4.56864E-01
5.50000E-01	5.10202E-01
6.00000E-01	5.65477E-01
6.50000E-01	6.25039E-01
7.00000E-01	6.92330E-01
7.50000E-01	7.72766E-01
8.00000E-01	8.75874E-01
8.50000E-01	1.02113E-00
9.00000E-01	1.25855E-00
9.50000E-01	1.78633E-00
9.52000E-01	1.82334E-00
9.54000E-01	1.86273E-00
9.56000E-01	1.90477E-00
9.58000E-01	1.94976E-00
9.60000E-01	1.99807E-00
9.62000E-01	2.05014E-00
9.64000E-01	2.10648E-00
9.66000E-01	2.16771E-00
9.68000E-01	2.23457E-00
9.70000E-01	2.30801E-00
9.72000E-01	2.38916E-00
9.74000E-01	2.47950E-00
9.76000E-01	2.58089E-00
9.78000E-01	2.69579E-00
9.80000E-01	2.82751E-00
9.82000E-01	2.98060E-00
9.84000E-01	3.16153E-00
9.86000E-01	3.37996E-00
9.88000E-01	3.65091E-00
9.90000E-01	3.99950E-00
9.92000E-01	4.47172E-00
9.94000E-01	5.16364E-00
9.96000E-01	6.32430E-00
9.98000E-01	8.94410E-00
9.99000E-01	1.26489E&01
1.00000E-00	+ ∞

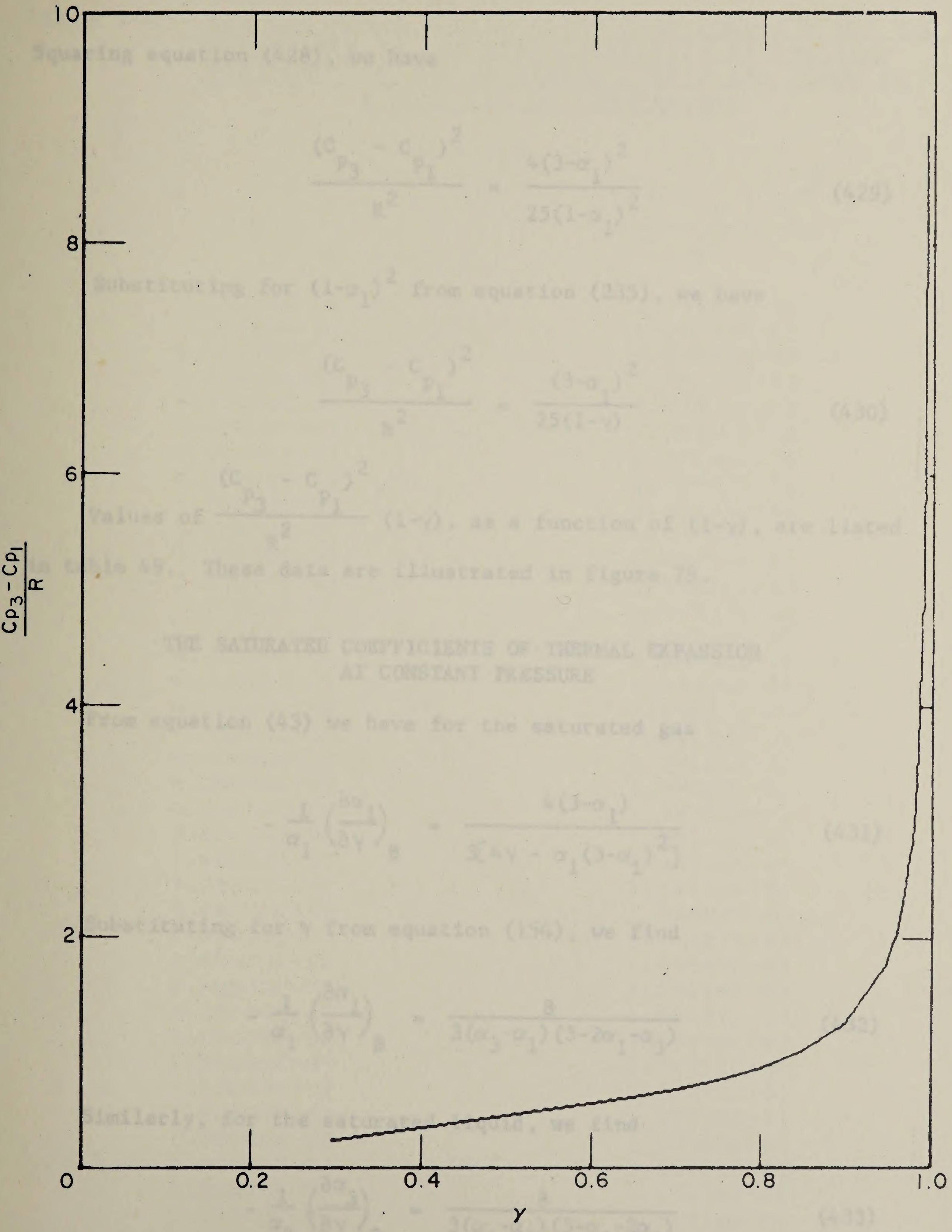

FIGURE 78.- Van der Walls Fluid; Difference Between Saturated Heat Capacities at Constant Pressures vs γ; $\gamma = T/T_c$

Squaring equation (428), we have

$$\frac{(C_{p_3} - C_{p_1})^2}{R^2} = \frac{4(3-\alpha_1)^2}{25(1-\alpha_1)^2} \tag{429}$$

Substituting for $(1-\alpha_1)^2$ from equation (235), we have

$$\frac{(C_{p_3} - C_{p_1})^2}{R^2} = \frac{(3-\alpha_1)^2}{25(1-\gamma)} \tag{430}$$

Values of $\frac{(C_{p_3} - C_{p_1})^2}{R^2}(1-\gamma)$, as a function of $(1-\gamma)$, are listed in table 49. These data are illustrated in figure 79.

THE SATURATED COEFFICIENTS OF THERMAL EXPANSION AT CONSTANT PRESSURE

From equation (43) we have for the saturated gas

$$-\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\gamma}\right)_\beta = \frac{4(3-\alpha_1)}{3[4\gamma - \alpha_1(3-\alpha_1)^2]} \tag{431}$$

Substituting for γ from equation (154), we find

$$-\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\gamma}\right)_\beta = \frac{8}{3(\alpha_3-\alpha_1)(3-2\alpha_1-\alpha_3)} \tag{432}$$

Similarly, for the saturated liquid, we find

$$-\frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\gamma}\right)_\beta = \frac{8}{3(\alpha_1-\alpha_3)(3-\alpha_1-2\alpha_3)} \tag{433}$$

TABLE 49. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION FOR THE DIFFERENCE IN THE HEAT CAPACITIES AT CONSTANT PRESSURE FOR THE SATURATED LIQUID AND VAPOR AS A FUNCTION OF TEMPERATURE

$\gamma = T/T_c$

$1-\gamma$	$\frac{(1-\gamma)(C_{P_3} - C_{P_1})^2}{R^2}$
7.50000E-01	2.75377E-02
7.00000E-01	4.12226E-02
6.50000E-01	5.70332E-02
6.00000E-01	7.36295E-02
5.50000E-01	8.97071E-02
5.00000E-01	1.04362E-01
4.50000E-01	1.17138E-01
4.00000E-01	1.27905E-01
3.50000E-01	1.36735E-01
3.00000E-01	1.43796E-01
2.50000E-01	1.49292E-01
2.00000E-01	1.53431E-01
1.50000E-01	1.56407E-01
1.00000E-01	1.58396E-01
5.00000E-02	1.59550E-01
4.80000E-02	1.59580E-01
4.60000E-02	1.59610E-01
4.40000E-02	1.59638E-01
4.20000E-02	1.59666E-01
4.00000E-02	1.59692E-01
3.80000E-02	1.59717E-01
3.60000E-02	1.59741E-01
3.40000E-02	1.59764E-01
3.20000E-02	1.59786E-01
3.00000E-02	1.59807E-01
2.80000E-02	1.59827E-01
2.60000E-02	1.59846E-01
2.40000E-02	1.59864E-01
2.20000E-02	1.59881E-01
2.00000E-02	1.59896E-01
1.80000E-02	1.59911E-01
1.60000E-02	1.59925E-01
1.40000E-02	1.59938E-01
1.20000E-02	1.59949E-01
1.00000E-02	1.59960E-01
8.00000E-03	1.59970E-01
6.00000E-03	1.59979E-01
4.00000E-03	1.59987E-01
2.00000E-03	1.59994E-01
1.00000E-03	1.59997E-01
0.00000E-99	1.60000E-01

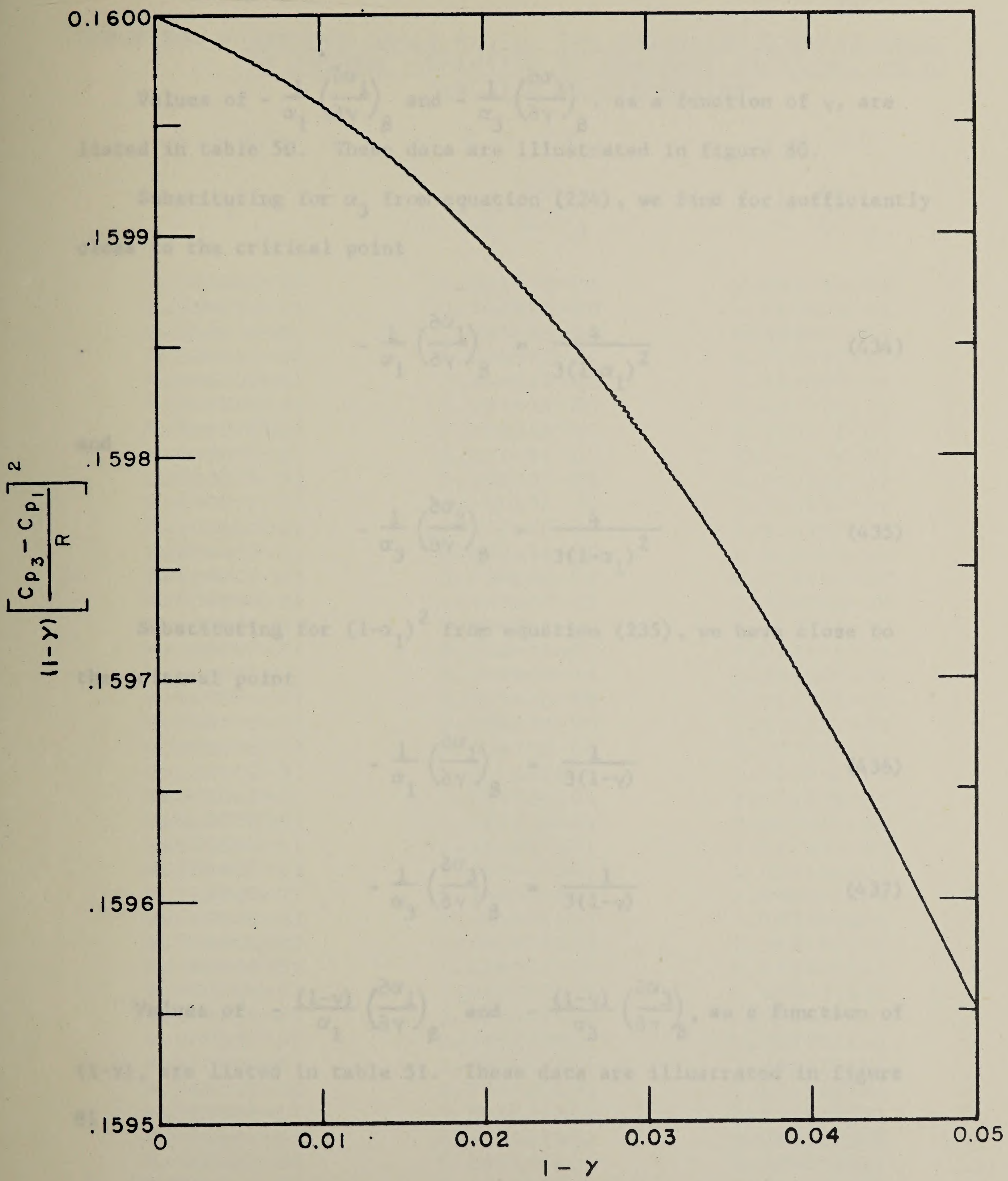

FIGURE 79.- Van der Waals Fluid, Asymptotic Function for the Difference in the Heat Capacities at Constant Pressure for the Saturated Liquid and Vapor as a Function of Temperature; $\gamma = T/T_c$

Values of $-\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\gamma}\right)_\beta$ and $-\frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\gamma}\right)_\beta$, as a function of γ, are listed in table 50. These data are illustrated in figure 80.

Substituting for α_3 from equation (224), we find for sufficiently close to the critical point

$$-\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\gamma}\right)_\beta = \frac{4}{3(1-\alpha_1)^2} \tag{434}$$

and

$$-\frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\gamma}\right)_\beta = \frac{4}{3(1-\alpha_1)^2} \tag{435}$$

Substituting for $(1-\alpha_1)^2$ from equation (235), we have close to the critical point

$$-\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\gamma}\right)_\beta = \frac{1}{3(1-\gamma)} \tag{436}$$

$$-\frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\gamma}\right)_\beta = \frac{1}{3(1-\gamma)} \tag{437}$$

Values of $-\frac{(1-\gamma)}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\gamma}\right)_\beta$ and $-\frac{(1-\gamma)}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\gamma}\right)_\beta$, as a function of $(1-\gamma)$, are listed in table 51. These data are illustrated in figure 81.

TABLE 50. - VAN DER WAALS FLUID, THE SATURATED COEFFICIENTS OF THERMAL EXPANSION AT CONSTANT PRESSURE, AS A FUNCTION OF TEMPERATURE

$\alpha = \rho/\rho_c$ $\beta = P/P_c$ $\gamma = T/T_c$

γ	$-\frac{1}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\gamma}\right)_\beta$	$-\frac{1}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\gamma}\right)_\beta$
2.50000E-01	4.00177E-00	3.84157E-01
3.00000E-01	3.34289E-00	4.09460E-01
3.50000E-01	2.88681E-00	4.38846E-01
4.00000E-01	2.56657E-00	4.73398E-01
4.50000E-01	2.34442E-00	5.14588E-01
5.00000E-01	2.19743E-00	5.64470E-01
5.50000E-01	2.11201E-00	6.26016E-01
6.00000E-01	2.08169E-00	7.03699E-01
6.50000E-01	2.10673E-00	8.04583E-01
7.00000E-01	2.19565E-00	9.40519E-01
7.50000E-01	2.37014E-00	1.13298E-00
8.00000E-01	2.67888E-00	1.42530E-00
8.50000E-01	3.23965E-00	1.91949E-00
9.00000E-01	4.40782E-00	2.92500E-00
9.50000E-01	7.94490E-00	6.01228E-00
9.52000E-01	8.23869E-00	6.27247E-00
9.54000E-01	8.55780E-00	6.55564E-00
9.56000E-01	8.90567E-00	6.86497E-00
9.58000E-01	9.28637E-00	7.20422E-00
9.60000E-01	9.70478E-00	7.57791E-00
9.62000E-01	1.01668E&01	7.99153E-00
9.64000E-01	1.06796E&01	8.45178E-00
9.66000E-01	1.12523E&01	8.96696E-00
9.68000E-01	1.18958E&01	9.54745E-00
9.70000E-01	1.26242E&01	1.02064E&01
9.72000E-01	1.34556E&01	1.09607E&01
9.74000E-01	1.44137E&01	1.18326E&01
9.76000E-01	1.55299E&01	1.28517E&01
9.78000E-01	1.68470E&01	1.40583E&01
9.80000E-01	1.84250E&01	1.55092E&01
9.82000E-01	2.03503E&01	1.72862E&01
9.84000E-01	2.27523E&01	1.95123E&01
9.86000E-01	2.58344E&01	2.23812E&01
9.88000E-01	2.99346E&01	2.62161E&01
9.90000E-01	3.56607E&01	3.15997E&01
9.92000E-01	4.42261E&01	3.96995E&01
9.94000E-01	5.84564E&01	5.32455E&01
9.96000E-01	8.68094E&01	8.04466E&01
9.98000E-01	1.71446E&02	1.62475E&02
9.99000E-01	3.39961E&02	3.27292E&02
1.00000E-00	$+\infty$	$+\infty$

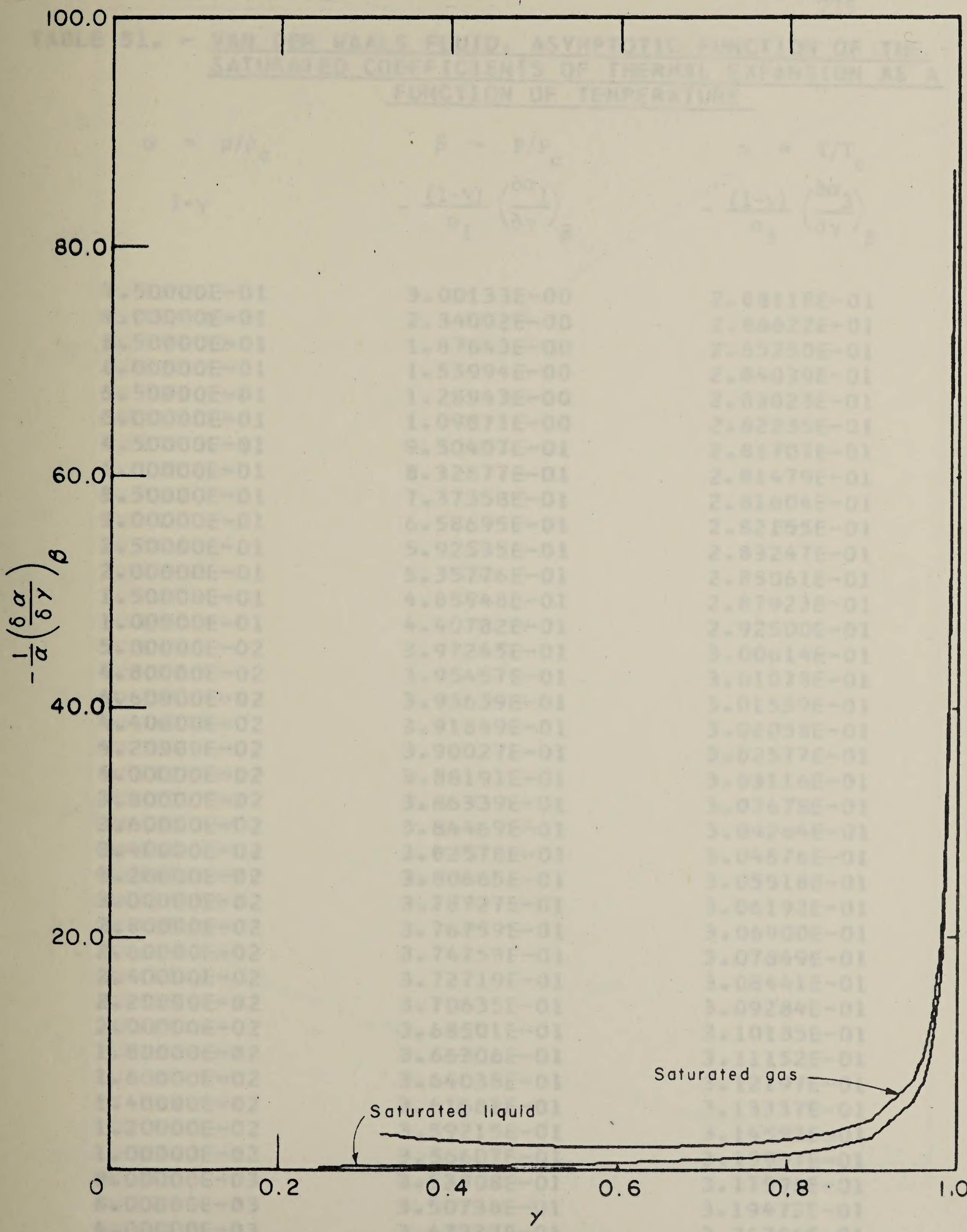

FIGURE 80.- Van der Waals Fluid, Saturated Coefficients of Thermal Expansion vs γ; $\alpha = \rho/\rho_c$; $\gamma = T/T_c$

TABLE 51. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE SATURATED COEFFICIENTS OF THERMAL EXPANSION AS A FUNCTION OF TEMPERATURE

$\alpha = \rho/\rho_c$	$\beta = P/P_c$	$\gamma = T/T_c$
$1-\gamma$	$-\frac{(1-\gamma)}{\alpha_1}\left(\frac{\partial\alpha_1}{\partial\gamma}\right)_\beta$	$-\frac{(1-\gamma)}{\alpha_3}\left(\frac{\partial\alpha_3}{\partial\gamma}\right)_\beta$
7.50000E-01	3.00133E-00	2.88118E-01
7.00000E-01	2.34002E-00	2.86622E-01
6.50000E-01	1.87643E-00	2.85250E-01
6.00000E-01	1.53994E-00	2.84039E-01
5.50000E-01	1.28943E-00	2.83023E-01
5.00000E-01	1.09871E-00	2.82235E-01
4.50000E-01	9.50407E-01	2.81707E-01
4.00000E-01	8.32677E-01	2.81479E-01
3.50000E-01	7.37358E-01	2.81604E-01
3.00000E-01	6.58695E-01	2.82155E-01
2.50000E-01	5.92535E-01	2.83247E-01
2.00000E-01	5.35776E-01	2.85061E-01
1.50000E-01	4.85948E-01	2.87923E-01
1.00000E-01	4.40782E-01	2.92500E-01
5.00000E-02	3.97245E-01	3.00614E-01
4.80000E-02	3.95457E-01	3.01078E-01
4.60000E-02	3.93659E-01	3.01559E-01
4.40000E-02	3.91849E-01	3.02058E-01
4.20000E-02	3.90027E-01	3.02577E-01
4.00000E-02	3.88191E-01	3.03116E-01
3.80000E-02	3.86339E-01	3.03678E-01
3.60000E-02	3.84469E-01	3.04264E-01
3.40000E-02	3.82578E-01	3.04876E-01
3.20000E-02	3.80665E-01	3.05518E-01
3.00000E-02	3.78727E-01	3.06192E-01
2.80000E-02	3.76759E-01	3.06900E-01
2.60000E-02	3.74758E-01	3.07649E-01
2.40000E-02	3.72719E-01	3.08441E-01
2.20000E-02	3.70635E-01	3.09284E-01
2.00000E-02	3.68501E-01	3.10185E-01
1.80000E-02	3.66306E-01	3.11152E-01
1.60000E-02	3.64038E-01	3.12197E-01
1.40000E-02	3.61681E-01	3.13337E-01
1.20000E-02	3.59215E-01	3.14593E-01
1.00000E-02	3.56607E-01	3.15997E-01
8.00000E-03	3.53808E-01	3.17596E-01
6.00000E-03	3.50738E-01	3.19473E-01
4.00000E-03	3.47237E-01	3.21786E-01
2.00000E-03	3.42892E-01	3.24950E-01
1.00000E-03	3.39961E-01	3.27292E-01
0.00000E-99	3.33333E-01	3.33333E-01

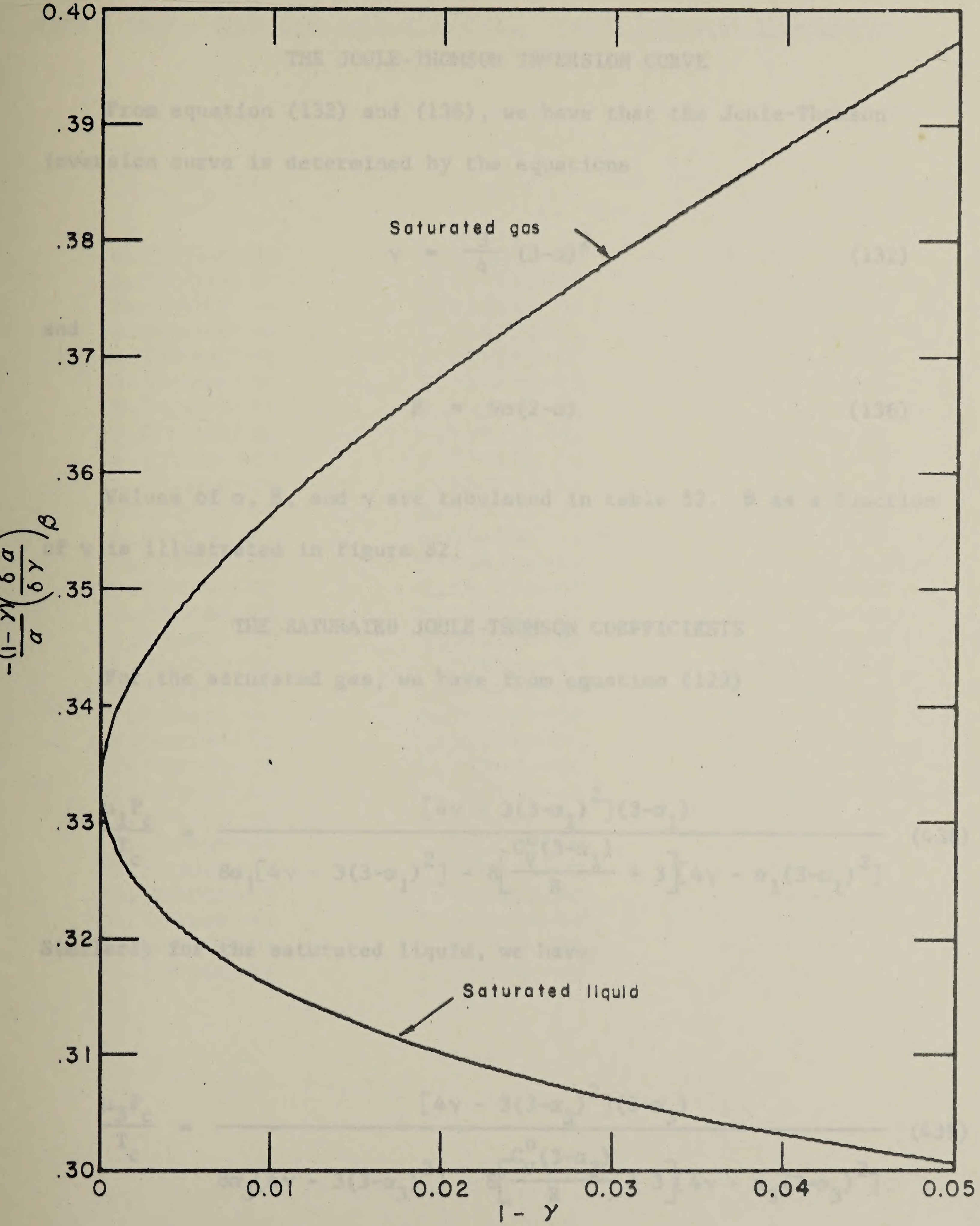

FIGURE 81.- Van der Waals Fluid, Asymptotic Function of the Saturated Coefficients of Thermal Expansion as a Function of $(1-\gamma)$; $\alpha = \rho/\rho_c$; $\beta = P/P_c$; $\gamma = T/T_c$

THE JOULE-THOMSON INVERSION CURVE

From equation (132) and (136), we have that the Joule-Thomson inversion curve is determined by the equations

$$\gamma = \frac{3}{4}(3-\alpha)^2 \tag{132}$$

and

$$\beta = 9\alpha(2-\alpha) \tag{136}$$

Values of α, β, and γ are tabulated in table 52. β as a function of γ is illustrated in figure 82.

THE SATURATED JOULE-THOMSON COEFFICIENTS

For the saturated gas, we have from equation (129)

$$\frac{\mu_1 P_c}{T_c} = \frac{[4\gamma - 3(3-\alpha_1)^2](3-\alpha_1)}{8\alpha_1[4\gamma - 3(3-\alpha_1)^2] - 8\left[\frac{C_V^o(3-\alpha_1)}{R} + 3\right][4\gamma - \alpha_1(3-\alpha_1)^2]} \tag{438}$$

Similarly for the saturated liquid, we have

$$\frac{\mu_3 P_c}{T_c} = \frac{[4\gamma - 3(3-\alpha_3)^2](3-\alpha_3)}{8\alpha_3[4\gamma - 3(3-\alpha_3)^2] - 8\left[\frac{C_V^o(3-\alpha_3)}{R} + 3\right][4\gamma - \alpha_3(3-\alpha_3)^2]} \tag{439}$$

TABLE 52. - VAN DER WAALS FLUID, JOULE-THOMSON INVERSION CURVE

$\alpha = \rho/\rho_c$ $\beta = P/P_c$ $\gamma = T/T_c$

γ	α	β
6.75000E-00	0.00000E-99	0.00000E-99
6.50000E-00	5.60797E-02	9.81130E-01
6.25000E-00	1.13248E-01	1.92304E-00
6.00000E-00	1.71572E-01	2.82337E-00
5.75000E-00	2.31125E-01	3.67948E-00
5.50000E-00	2.91987E-01	4.48846E-00
5.25000E-00	3.54248E-01	5.24704E-00
5.00000E-00	4.18011E-01	5.95160E-00
4.75000E-00	4.83388E-01	6.59801E-00
4.50000E-00	5.50510E-01	7.18163E-00
4.25000E-00	6.19523E-01	7.69714E-00
4.00000E-00	6.90598E-01	8.13843E-00
3.75000E-00	7.63932E-01	8.49844E-00
3.50000E-00	8.39753E-01	8.76888E-00
3.25000E-00	9.18334E-01	8.93997E-00
3.00000E-00	1.00000E-00	9.00000E-00
2.75000E-00	1.08514E-00	8.93475E-00
2.50000E-00	1.17425E-00	8.72670E-00
2.25000E-00	1.26794E-00	8.35382E-00
2.00000E-00	1.36700E-00	7.78775E-00
1.75000E-00	1.47247E-00	6.99090E-00
1.50000E-00	1.58578E-00	5.91168E-00
1.25000E-00	1.70900E-00	4.47580E-00
1.00000E-00	1.84529E-00	2.56921E-00
9.50000E-01	1.87453E-00	2.11666E-00
9.00000E-01	1.90455E-00	1.63602E-00
8.50000E-01	1.93541E-00	1.12492E-00
8.00000E-01	1.96720E-00	5.80640E-01
7.79000E-01	1.98085E-00	3.41399E-01

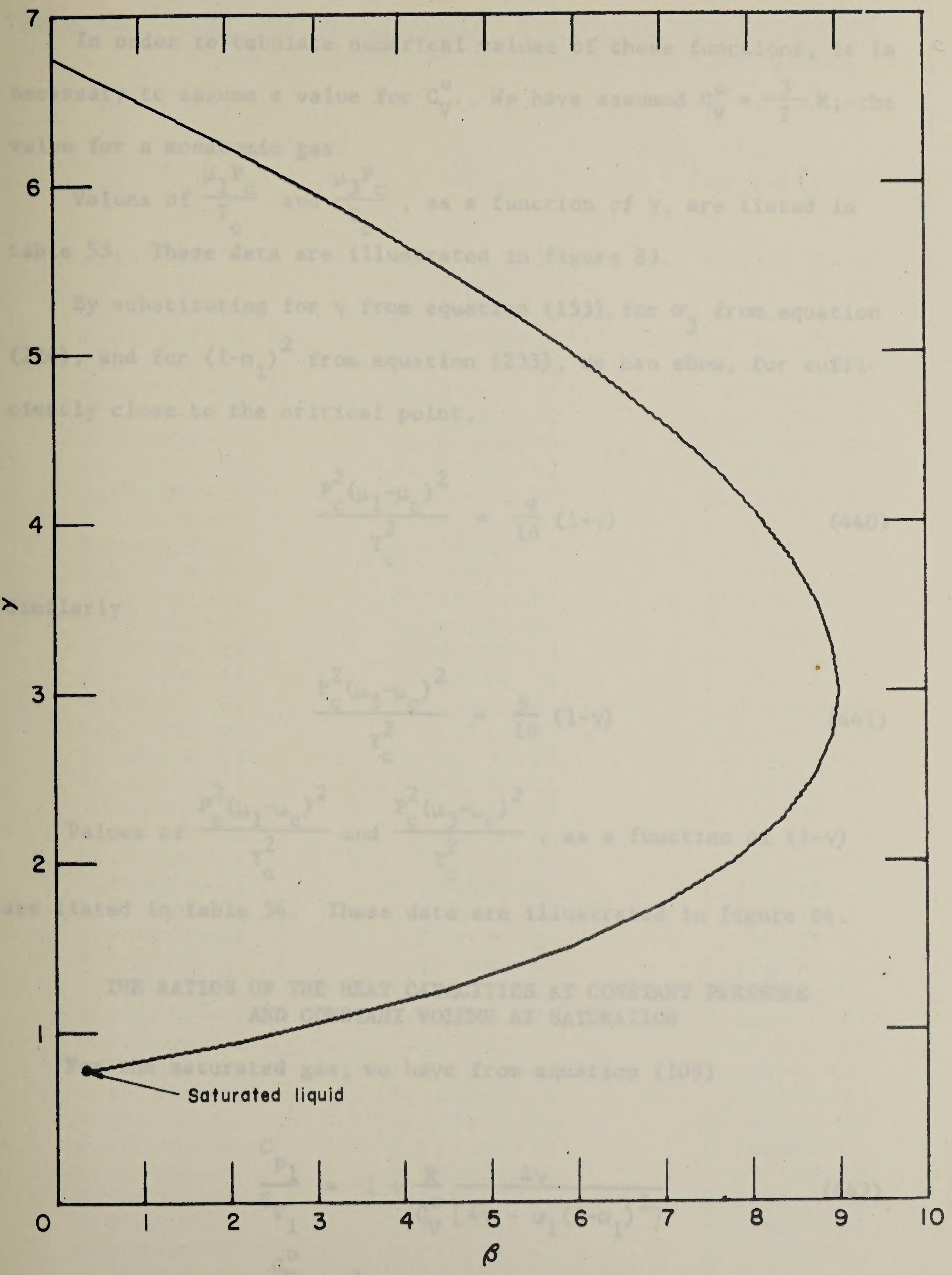

FIGURE 82.- Van der Waals Fluid, Joule-Thomson Inversion Curve. γ vs β ; $\gamma = T/T_c$; $\beta = P/P_c$; $\left(\frac{\delta T}{\delta P}\right)_H = 0$

In order to tabulate numerical values of these functions, it is necessary to assume a value for C_V^o. We have assumed $C_V^o = \frac{3}{2} R$; the value for a monatomic gas.

Values of $\frac{\mu_1 P_c}{T_c}$ and $\frac{\mu_3 P_c}{T_c}$, as a function of γ, are listed in table 53. These data are illustrated in figure 83.

By substituting for γ from equation (155), for α_3 from equation (224), and for $(1-\alpha_1)^2$ from equation (235), we can show, for sufficiently close to the critical point,

$$\frac{P_c^2(\mu_1-\mu_c)^2}{T_c^2} = \frac{9}{16}(1-\gamma) \tag{440}$$

Similarly

$$\frac{P_c^2(\mu_3-\mu_c)^2}{T_c^2} = \frac{9}{16}(1-\gamma) \tag{441}$$

Values of $\frac{P_c^2(\mu_1-\mu_c)^2}{T_c^2}$ and $\frac{P_c^2(\mu_3-\mu_c)^2}{T_c^2}$, as a function of $(1-\gamma)$ are listed in table 54. These data are illustrated in figure 84.

THE RATIOS OF THE HEAT CAPACITIES AT CONSTANT PRESSURE AND CONSTANT VOLUME AT SATURATION

For the saturated gas, we have from equation (109)

$$\frac{C_{P_1}}{C_{V_1}} = 1 + \frac{R}{C_V^o} \frac{4\gamma}{[4\gamma - \alpha_1(3-\alpha_1)^2]} \tag{442}$$

We again assume $\frac{C_V^o}{R} = \frac{3}{2}$, the value for a monatomic gas. Then

TABLE 53. - VAN DER WAALS FLUID, SATURATED JOULE-THOMSON COEFFICIENTS AS A FUNCTION OF TEMPERATURE

$\beta = P/P_c$ $\gamma = T/T_c$ $C_V^o = \frac{3}{2} R$

γ	$\left(\frac{\partial\gamma}{\partial\beta}\right)_{H_1}$	$\left(\frac{\partial\gamma}{\partial\beta}\right)_{H_3}$
2.50000E-01	1.30031E-00	-4.56510E-02
3.00000E-01	1.07663E-00	-4.43025E-02
3.50000E-01	9.19177E-01	-4.27076E-02
4.00000E-01	8.04276E-01	-4.08057E-02
4.50000E-01	7.18397E-01	-3.85173E-02
5.00000E-01	6.53039E-01	-3.57364E-02
5.50000E-01	6.02556E-01	-3.23189E-02
6.00000E-01	5.63049E-01	-2.80645E-02
6.50000E-01	5.31726E-01	-2.26864E-02
7.00000E-01	5.06474E-01	-1.57601E-02
7.50000E-01	4.85521E-01	-6.62888E-03
8.00000E-01	4.67093E-01	5.78351E-03
8.50000E-01	4.48881E-01	2.33890E-02
9.00000E-01	4.26811E-01	5.00422E-02
9.50000E-01	3.90738E-01	9.56363E-02
9.52000E-01	3.88659E-01	9.81904E-02
9.54000E-01	3.86503E-01	1.00829E-01
9.56000E-01	3.84262E-01	1.03559E-01
9.58000E-01	3.81931E-01	1.06386E-01
9.60000E-01	3.79503E-01	1.09317E-01
9.62000E-01	3.76970E-01	1.12358E-01
9.64000E-01	3.74323E-01	1.15519E-01
9.66000E-01	3.71554E-01	1.18809E-01
9.68000E-01	3.68650E-01	1.22240E-01
9.70000E-01	3.65599E-01	1.25824E-01
9.72000E-01	3.62386E-01	1.29575E-01
9.74000E-01	3.58993E-01	1.33512E-01
9.76000E-01	3.55399E-01	1.37655E-01
9.78000E-01	3.51581E-01	1.42028E-01
9.80000E-01	3.47505E-01	1.46663E-01
9.82000E-01	3.43136E-01	1.51597E-01
9.84000E-01	3.38423E-01	1.56879E-01
9.86000E-01	3.33302E-01	1.62574E-01
9.88000E-01	3.27686E-01	1.68768E-01
9.90000E-01	3.21450E-01	1.75586E-01
9.92000E-01	3.14403E-01	1.83219E-01
9.94000E-01	3.06225E-01	1.91986E-01
9.96000E-01	2.96302E-01	2.02503E-01
9.98000E-01	2.83051E-01	2.16350E-01
9.99000E-01	2.73499E-01	2.26200E-01
1.00000E-00	2.50000E-01	2.50000E-01

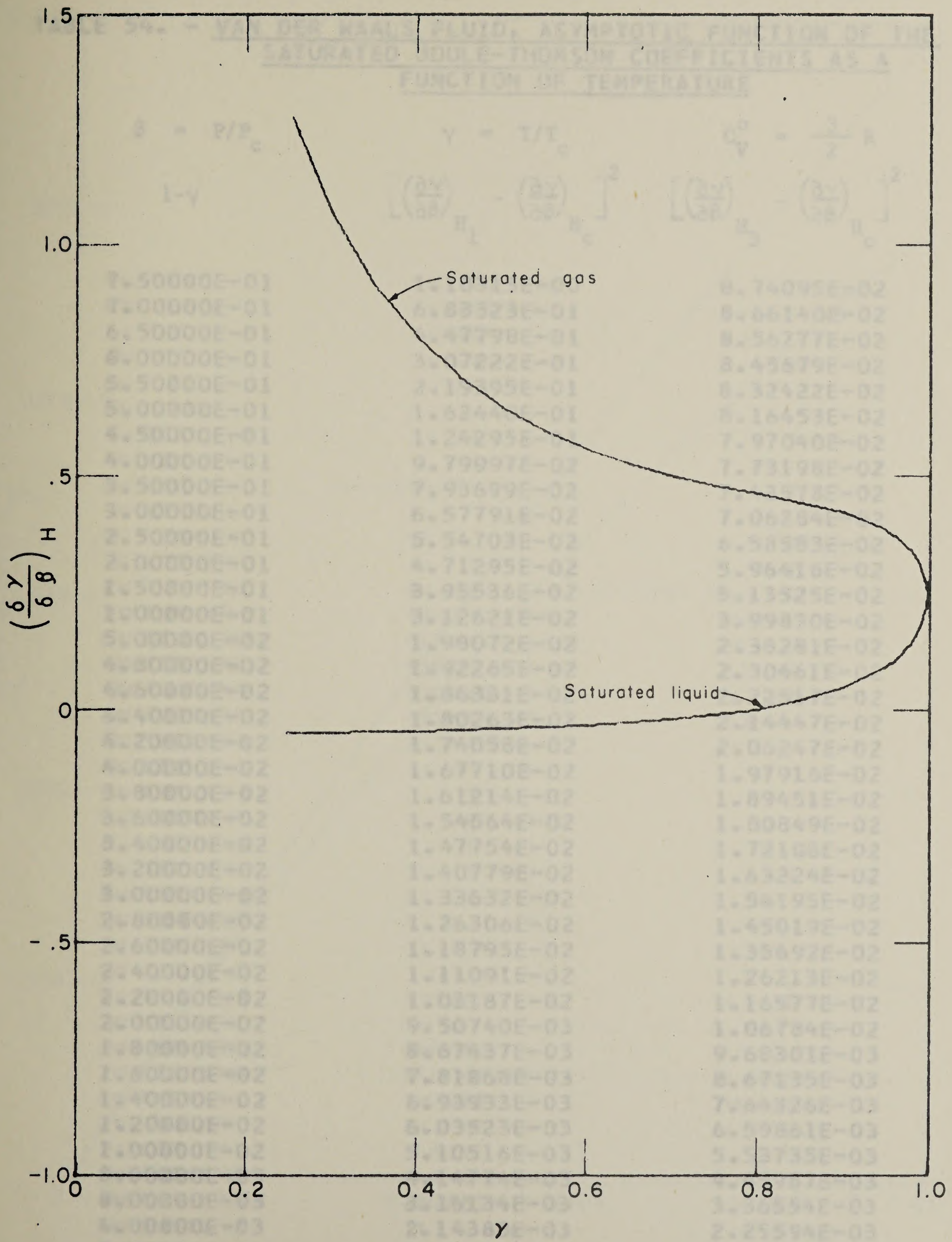

FIGURE 83.- Van der Waals Fluid, Saturated Joule-Thomson Coefficients vs γ; $\gamma = T/T_c$; Monatomic Gas; $C_p^o/C_v^o = 5/3$

TABLE 54. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE SATURATED JOULE-THOMSON COEFFICIENTS AS A FUNCTION OF TEMPERATURE

$\beta = P/P_c$ $\gamma = T/T_c$ $C_V^o = \frac{3}{2} R$

$1-\gamma$	$\left[\left(\frac{\partial\gamma}{\partial\beta}\right)_{H_1} - \left(\frac{\partial\gamma}{\partial\beta}\right)_{H_c}\right]^2$	$\left[\left(\frac{\partial\gamma}{\partial\beta}\right)_{H_3} - \left(\frac{\partial\gamma}{\partial\beta}\right)_{H_c}\right]^2$
7.50000E-01	1.10315E-00	8.74095E-02
7.00000E-01	6.83323E-01	8.66140E-02
6.50000E-01	4.47798E-01	8.56777E-02
6.00000E-01	3.07222E-01	8.45679E-02
5.50000E-01	2.19395E-01	8.32422E-02
5.00000E-01	1.62440E-01	8.16453E-02
4.50000E-01	1.24295E-01	7.97040E-02
4.00000E-01	9.79997E-02	7.73198E-02
3.50000E-01	7.93699E-02	7.43578E-02
3.00000E-01	6.57791E-02	7.06284E-02
2.50000E-01	5.54703E-02	6.58583E-02
2.00000E-01	4.71295E-02	5.96416E-02
1.50000E-01	3.95536E-02	5.13525E-02
1.00000E-01	3.12621E-02	3.99830E-02
5.00000E-02	1.98072E-02	2.38281E-02
4.80000E-02	1.92265E-02	2.30461E-02
4.60000E-02	1.86331E-02	2.22517E-02
4.40000E-02	1.80263E-02	2.14447E-02
4.20000E-02	1.74058E-02	2.06247E-02
4.00000E-02	1.67710E-02	1.97916E-02
3.80000E-02	1.61214E-02	1.89451E-02
3.60000E-02	1.54564E-02	1.80849E-02
3.40000E-02	1.47754E-02	1.72108E-02
3.20000E-02	1.40779E-02	1.63224E-02
3.00000E-02	1.33632E-02	1.54195E-02
2.80000E-02	1.26306E-02	1.45019E-02
2.60000E-02	1.18795E-02	1.35692E-02
2.40000E-02	1.11091E-02	1.26213E-02
2.20000E-02	1.03187E-02	1.16577E-02
2.00000E-02	9.50740E-03	1.06784E-02
1.80000E-02	8.67437E-03	9.68301E-03
1.60000E-02	7.81868E-03	8.67135E-03
1.40000E-02	6.93933E-03	7.64326E-03
1.20000E-02	6.03523E-03	6.59861E-03
1.00000E-02	5.10516E-03	5.53735E-03
8.00000E-03	4.14774E-03	4.45957E-03
6.00000E-03	3.16134E-03	3.36554E-03
4.00000E-03	2.14388E-03	2.25594E-03
2.00000E-03	1.09238E-03	1.13231E-03
1.00000E-03	5.52234E-04	5.66408E-04
0.00000E-99	0.00000E-99	0.00000E-99

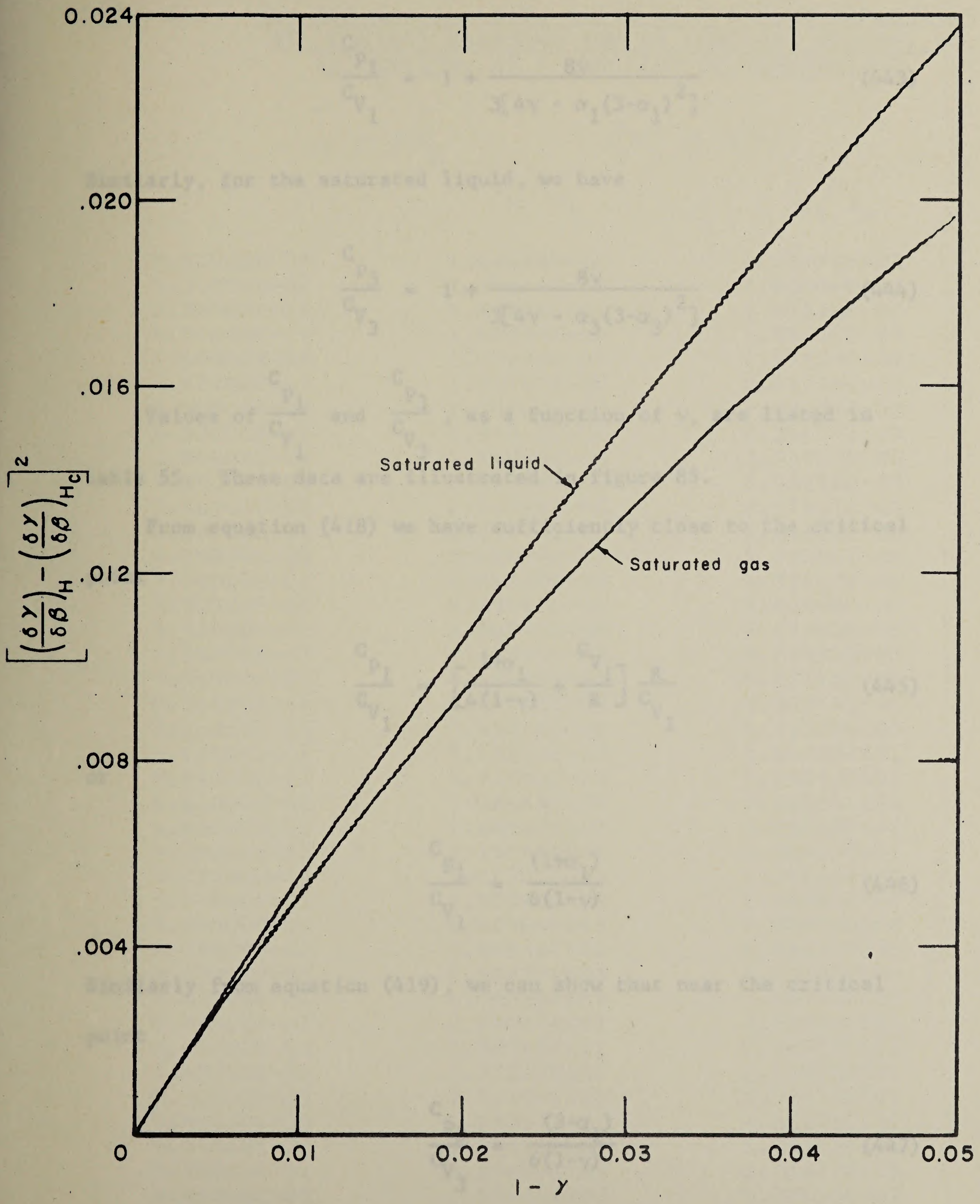

FIGURE 84.- Van der Waals Fluid, Asymptotic Saturated Joule-Thomson Coefficients as a Function of $(1-\gamma)$; $\beta = P/P_c$; $\gamma = T/T_c$; $C_V^o = 3/2R$

$$\frac{C_{p_1}}{C_{V_1}} = 1 + \frac{8\gamma}{3[4\gamma - \alpha_1(3-\alpha_1)^2]} \tag{443}$$

Similarly, for the saturated liquid, we have

$$\frac{C_{p_3}}{C_{V_3}} = 1 + \frac{8\gamma}{3[4\gamma - \alpha_3(3-\alpha_3)^2]} \tag{444}$$

Values of $\frac{C_{p_1}}{C_{V_1}}$ and $\frac{C_{p_3}}{C_{V_3}}$, as a function of γ, are listed in table 55. These data are illustrated in figure 85.

From equation (418) we have sufficiently close to the critical point

$$\frac{C_{p_1}}{C_{V_1}} = \left[\frac{1+\alpha_1}{4(1-\gamma)} + \frac{C_{V_1}}{R}\right] \frac{R}{C_{V_1}} \tag{445}$$

or

$$\frac{C_{p_1}}{C_{V_1}} = \frac{(1+\alpha_1)}{6(1-\gamma)} \tag{446}$$

Similarly from equation (419), we can show that near the critical point

$$\frac{C_{p_3}}{C_{V_3}} = \frac{(3-\alpha_1)}{6(1-\gamma)} \tag{447}$$

TABLE 55. - VAN DER WAALS FLUID, RATIO OF THE HEAT CAPACITIES AT CONSTANT PRESSURE AND AT CONSTANT VOLUME, AT SATURATION, AS A FUNCTION OF TEMPERATURE

$\gamma = T/T_c$ $\qquad$ $C_p^o/C_V^o = 5/3$

γ	C_{p_1}/C_{V_1}	C_{p_3}/C_{V_3}
2.50000E-01	1.66697E-00	1.79471E-00
3.00000E-01	1.66866E-00	1.83044E-00
3.50000E-01	1.67396E-00	1.87144E-00
4.00000E-01	1.68554E-00	1.91908E-00
4.50000E-01	1.70596E-00	1.97520E-00
5.00000E-01	1.73782E-00	2.04240E-00
5.50000E-01	1.78422E-00	2.12436E-00
6.00000E-01	1.84960E-00	2.22659E-00
6.50000E-01	1.94098E-00	2.35767E-00
7.00000E-01	2.07031E-00	2.53186E-00
7.50000E-01	2.25946E-00	2.77464E-00
8.00000E-01	2.55278E-00	3.13670E-00
8.50000E-01	3.05479E-00	3.73555E-00
9.00000E-01	4.08208E-00	4.92112E-00
9.50000E-01	7.23519E-00	8.42608E-00
9.52000E-01	7.50047E-00	8.71603E-00
9.54000E-01	7.78910E-00	9.03093E-00
9.56000E-01	8.10431E-00	9.37416E-00
9.58000E-01	8.44990E-00	9.74974E-00
9.60000E-01	8.83046E-00	1.01625E&01
9.62000E-01	9.25153E-00	1.06183E&01
9.64000E-01	9.71992E-00	1.11242E&01
9.66000E-01	1.02440E&01	1.16891E&01
9.68000E-01	1.08343E&01	1.23240E&01
9.70000E-01	1.15041E&01	1.30427E&01
9.72000E-01	1.22705E&01	1.38633E&01
9.74000E-01	1.31560E&01	1.48090E&01
9.76000E-01	1.41904E&01	1.59110E&01
9.78000E-01	1.54146E&01	1.72118E&01
9.80000E-01	1.68857E&01	1.87707E&01
9.82000E-01	1.86863E&01	2.06734E&01
9.84000E-01	2.09407E&01	2.30484E&01
9.86000E-01	2.38439E&01	2.60972E&01
9.88000E-01	2.77217E&01	3.01556E&01
9.90000E-01	3.31609E&01	3.58272E&01
9.92000E-01	4.13367E&01	4.43178E&01
9.94000E-01	5.49948E&01	5.84372E&01
9.96000E-01	8.23855E&01	8.66017E&01
9.98000E-01	1.64845E&02	1.70801E&02
9.99000E-01	3.30277E&02	3.38709E&02
1.00000E-00	$+\infty$	$+\infty$

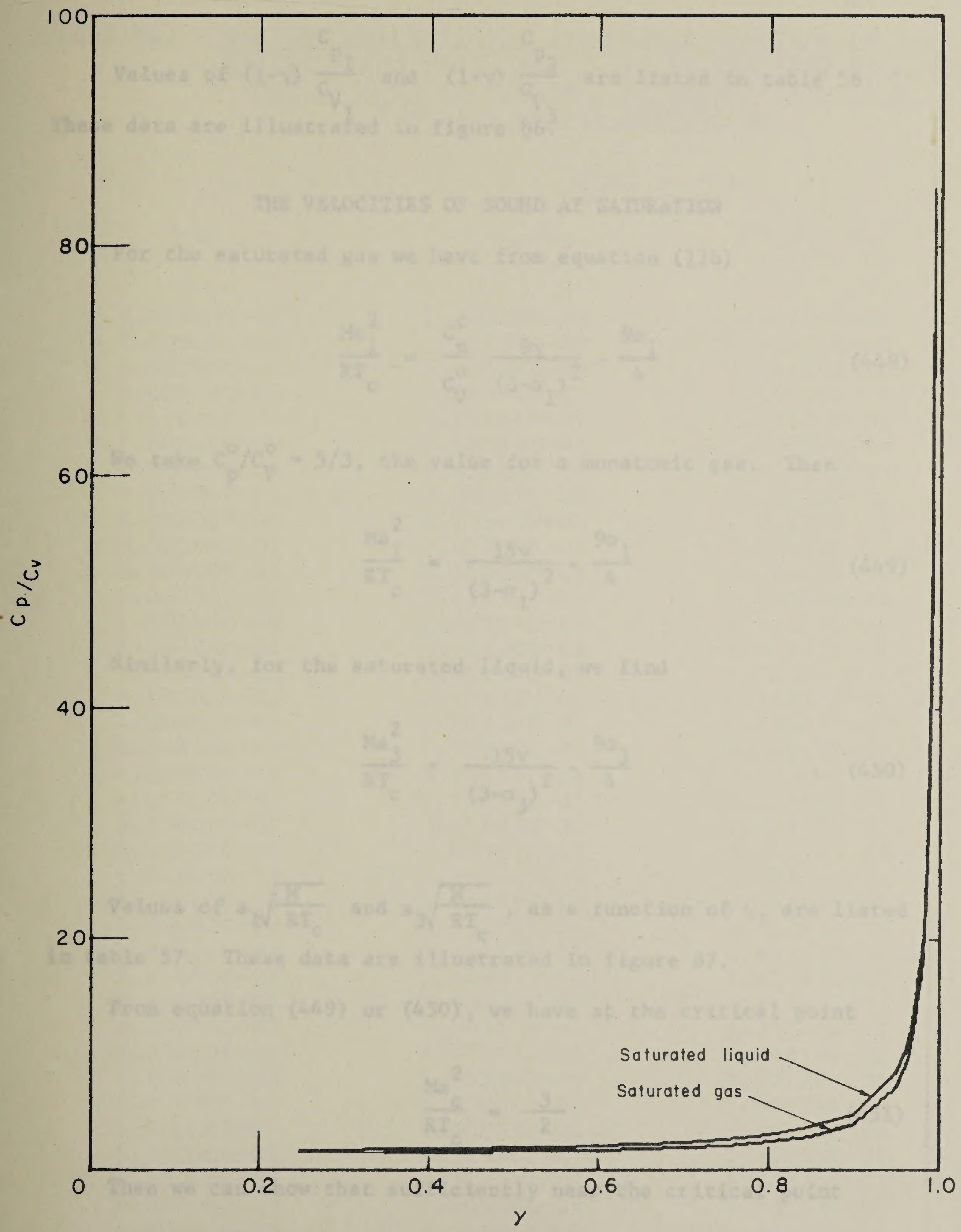

FIGURE 85.- Van der Waals Fluid, Saturated Ratio of Heat Capacities at Constant Pressure to that at Constant Volume vs y; $y = T/T_c$; Monatomic Gas; $C_p^o/C_v^o = 5/3$

Values of $(1-\gamma)\frac{C_{p_1}}{C_{V_1}}$ and $(1-\gamma)\frac{C_{p_3}}{C_{V_3}}$ are listed in table 56. These data are illustrated in figure 86.

THE VELOCITIES OF SOUND AT SATURATION

For the saturated gas we have from equation (116)

$$\frac{Ma_1^2}{RT_c} = \frac{C_p^o}{C_V^o}\frac{9\gamma}{(3-\alpha_1)^2} - \frac{9\alpha_1}{4} \tag{448}$$

We take $C_p^o/C_V^o = 5/3$, the value for a monatomic gas. Then

$$\frac{Ma_1^2}{RT_c} = \frac{15\gamma}{(3-\alpha_1)^2} - \frac{9\alpha_1}{4} \tag{449}$$

Similarly, for the saturated liquid, we find

$$\frac{Ma_3^2}{RT_c} = \frac{15\gamma}{(3-\alpha_3)^2} - \frac{9\alpha_3}{4} \tag{450}$$

Values of $a_1\sqrt{\frac{M}{RT_c}}$ and $a_3\sqrt{\frac{M}{RT_c}}$, as a function of γ, are listed in table 57. These data are illustrated in figure 87.

From equation (449) or (450), we have at the critical point

$$\frac{Ma_c^2}{RT_c} = \frac{3}{2} \tag{451}$$

Then we can show that sufficiently near the critical point

$$M^2\left(\frac{a_1^2 - a_c^2}{RT_c}\right)^2 = 9(1-\gamma) \tag{452}$$

TABLE 56. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF THE RATIO OF THE HEAT CAPACITIES AT CONSTANT PRESSURE AND AT CONSTANT VOLUME, AT SATURATION, AS A FUNCTION OF THE TEMPERATURE

$\gamma = T/T_c$ $\qquad C_p^o/C_V^o = 5/3$

$1-\gamma$	$(1-\gamma)C_{p_1}/C_{V_1}$	$(1-\gamma)C_{p_3}/C_{V_3}$
7.50000E-01	1.25023E-00	1.34603E-00
7.00000E-01	1.16806E-00	1.28131E-00
6.50000E-01	1.08808E-00	1.21644E-00
6.00000E-01	1.01132E-00	1.15144E-00
5.50000E-01	9.38281E-01	1.08636E-00
5.00000E-01	8.68913E-01	1.02120E-00
4.50000E-01	8.02903E-01	9.55964E-01
4.00000E-01	7.39842E-01	8.90636E-01
3.50000E-01	6.79344E-01	8.25187E-01
3.00000E-01	6.21093E-01	7.59559E-01
2.50000E-01	5.64866E-01	6.93661E-01
2.00000E-01	5.10557E-01	6.27340E-01
1.50000E-01	4.58219E-01	5.60333E-01
1.00000E-01	4.08208E-01	4.92112E-01
5.00000E-02	3.61759E-01	4.21304E-01
4.80000E-02	3.60022E-01	4.18369E-01
4.60000E-02	3.58298E-01	4.15422E-01
4.40000E-02	3.56589E-01	4.12463E-01
4.20000E-02	3.54895E-01	4.09489E-01
4.00000E-02	3.53218E-01	4.06500E-01
3.80000E-02	3.51558E-01	4.03495E-01
3.60000E-02	3.49917E-01	4.00473E-01
3.40000E-02	3.48296E-01	3.97431E-01
3.20000E-02	3.46698E-01	3.94369E-01
3.00000E-02	3.45123E-01	3.91283E-01
2.80000E-02	3.43575E-01	3.88173E-01
2.60000E-02	3.42057E-01	3.85035E-01
2.40000E-02	3.40571E-01	3.81865E-01
2.20000E-02	3.39121E-01	3.78660E-01
2.00000E-02	3.37714E-01	3.75414E-01
1.80000E-02	3.36354E-01	3.72122E-01
1.60000E-02	3.35051E-01	3.68774E-01
1.40000E-02	3.33815E-01	3.65361E-01
1.20000E-02	3.32660E-01	3.61868E-01
1.00000E-02	3.31609E-01	3.58272E-01
8.00000E-03	3.30693E-01	3.54542E-01
6.00000E-03	3.29968E-01	3.50623E-01
4.00000E-03	3.29542E-01	3.46406E-01
2.00000E-03	3.29690E-01	3.41616E-01
1.00000E-03	3.30277E-01	3.38709E-01
0.00000E-99	3.33333E-01	3.33333E-01

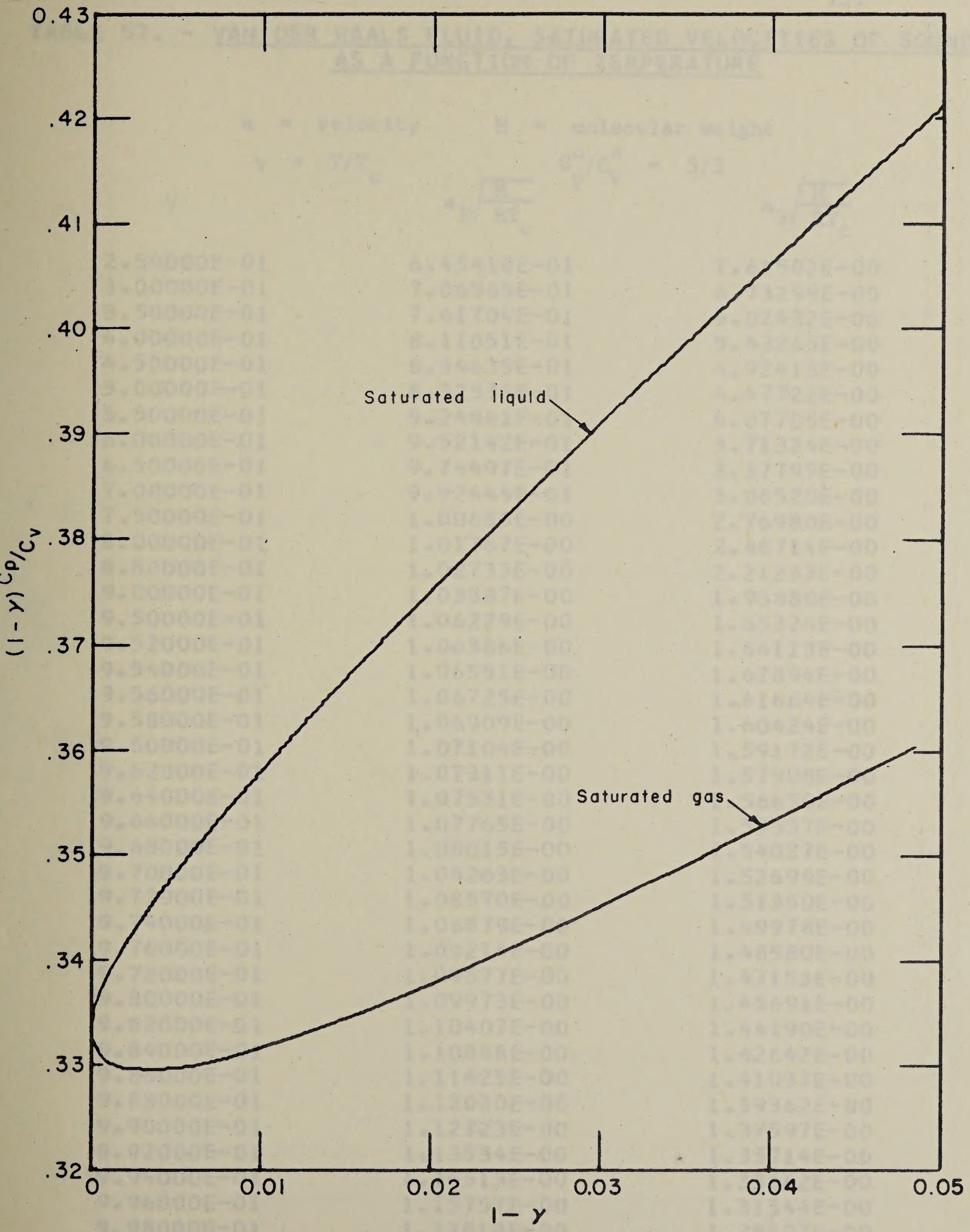

FIGURE 86.- Van der Waals Fluid, Asymptotic Function of the Ratio of the Heat Capacities at Constant Pressure and at Constant Volume, at Saturation, as a Function of Temperature; $y = T/T_c$; $C_p^\circ / C_v^\circ = 5/3$

TABLE 57. - VAN DER WAALS FLUID, SATURATED VELOCITIES OF SOUND AS A FUNCTION OF TEMPERATURE

a = velocity   M = molecular weight

γ = T/T_c C_p^o/C_V^o = 5/3

γ	$a_1\sqrt{\frac{M}{RT_c}}$	$a_3\sqrt{\frac{M}{RT_c}}$
2.50000E-01	6.45418E-01	7.61502E-00
3.00000E-01	7.06565E-01	6.73299E-00
3.50000E-01	7.61704E-01	6.02432E-00
4.00000E-01	8.11051E-01	5.43265E-00
4.50000E-01	8.54635E-01	4.92418E-00
5.00000E-01	8.92534E-01	4.47722E-00
5.50000E-01	9.24941E-01	4.07705E-00
6.00000E-01	9.52142E-01	3.71324E-00
6.50000E-01	9.74497E-01	3.37799E-00
7.00000E-01	9.92444E-01	3.06520E-00
7.50000E-01	1.00655E-00	2.76980E-00
8.00000E-01	1.01767E-00	2.48714E-00
8.50000E-01	1.02733E-00	2.21233E-00
9.00000E-01	1.03887E-00	1.93880E-00
9.50000E-01	1.06229E-00	1.65324E-00
9.52000E-01	1.06386E-00	1.64113E-00
9.54000E-01	1.06551E-00	1.62894E-00
9.56000E-01	1.06725E-00	1.61664E-00
9.58000E-01	1.06909E-00	1.60424E-00
9.60000E-01	1.07104E-00	1.59172E-00
9.62000E-01	1.07311E-00	1.57908E-00
9.64000E-01	1.07531E-00	1.56630E-00
9.66000E-01	1.07765E-00	1.55337E-00
9.68000E-01	1.08015E-00	1.54027E-00
9.70000E-01	1.08283E-00	1.52698E-00
9.72000E-01	1.08570E-00	1.51350E-00
9.74000E-01	1.08879E-00	1.49978E-00
9.76000E-01	1.09214E-00	1.48580E-00
9.78000E-01	1.09577E-00	1.47153E-00
9.80000E-01	1.09973E-00	1.45691E-00
9.82000E-01	1.10407E-00	1.44190E-00
9.84000E-01	1.10888E-00	1.42642E-00
9.86000E-01	1.11425E-00	1.41037E-00
9.88000E-01	1.12030E-00	1.39362E-00
9.90000E-01	1.12723E-00	1.37597E-00
9.92000E-01	1.13534E-00	1.35714E-00
9.94000E-01	1.14513E-00	1.33662E-00
9.96000E-01	1.15757E-00	1.31344E-00
9.98000E-01	1.17518E-00	1.28507E-00
9.99000E-01	1.18864E-00	1.26622E-00
1.00000E-00	1.22474E-00	1.22474E-00

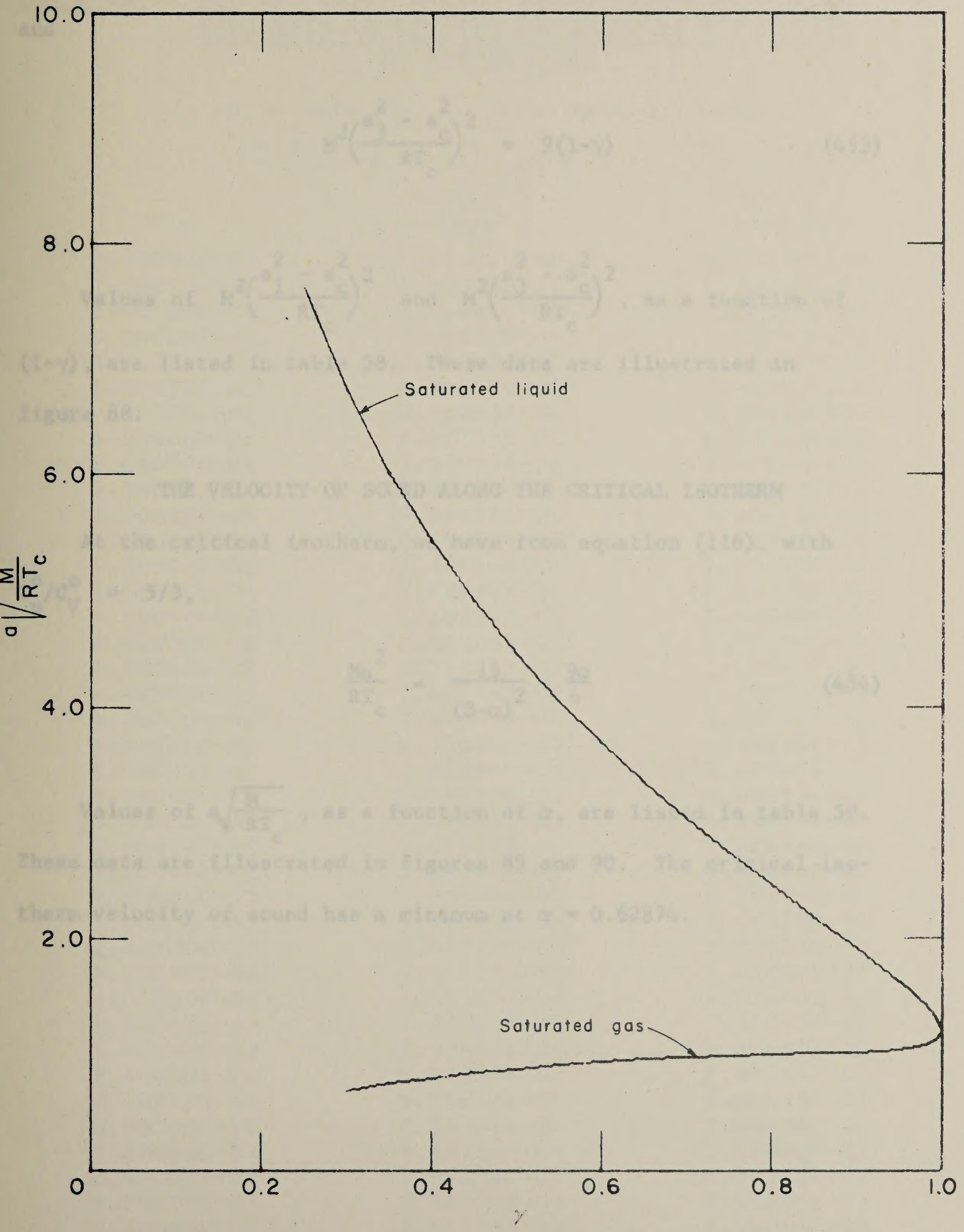

FIGURE 87.- Van der Waals Fluid, Saturated Velocity of Sound vs γ; $\gamma = T/T_c$; Monatomic gas $C_p^o/C_v^o = 5/3$; a = Velocity of Sound; M = Molecular Weight

and

$$M^2\left(\frac{a_3^2 - a_c^2}{RT_c}\right)^2 = 9(1-\gamma) \tag{453}$$

Values of $M^2\left(\frac{a_1^2 - a_c^2}{RT_c}\right)^2$ and $M^2\left(\frac{a_3^2 - a_c^2}{RT_c}\right)^2$, as a function of $(1-\gamma)$, are listed in table 58. These data are illustrated in figure 88.

THE VELOCITY OF SOUND ALONG THE CRITICAL ISOTHERM

At the critical isotherm, we have from equation (116), with $C_p^o/C_V^o = 5/3$,

$$\frac{Ma^2}{RT_c} = \frac{15}{(3-\alpha)^2} - \frac{9\alpha}{4} \tag{454}$$

Values of $a\sqrt{\frac{M}{RT_c}}$, as a function of α, are listed in table 59. These data are illustrated in figures 89 and 90. The critical isotherm velocity of sound has a minimum at $\alpha = 0.62874$.

TABLE 58. - VAN DER WAALS FLUID, ASYMPTOTIC FUNCTION OF SATURATED VELOCITIES OF SOUND AS A FUNCTION OF TEMPERATURE

a = velocity M = molecular weight

$\gamma = T/T_c$ $C_p^o/C_V^o = 5/3$

$1-\gamma$	$\left[\frac{M(a_1^2-a_c^2)}{RT_c}\right]^2$	$\left[\frac{M(a_3^2-a_c^2}{RT_c}\right]^2$
7.50000E-01	1.17383E-00	3.19096E&03
7.00000E-01	1.00153E-00	1.92134E&03
6.50000E-01	8.46044E-01	1.21051E&03
6.00000E-01	7.09292E-01	7.84770E&02
5.50000E-01	5.92282E-01	5.17454E&02
5.00000E-01	4.94747E-01	3.43935E&02
4.50000E-01	4.15359E-01	2.28686E&02
4.00000E-01	3.52153E-01	1.50999E&02
3.50000E-01	3.02890E-01	9.82244E&01
3.00000E-01	2.65280E-01	6.23387E&01
2.50000E-01	2.37022E-01	3.80913E&01
2.00000E-01	2.15603E-01	2.19575E&01
1.50000E-01	1.97649E-01	1.15220E&01
1.00000E-01	1.77020E-01	5.10299E-00
5.00000E-02	1.38032E-01	1.52082E-00
4.80000E-02	1.35568E-01	1.42404E-00
4.60000E-02	1.32991E-01	1.33043E-00
4.40000E-02	1.30294E-01	1.23997E-00
4.20000E-02	1.27469E-01	1.15260E-00
4.00000E-02	1.24506E-01	1.06830E-00
3.80000E-02	1.21395E-01	9.87045E-01
3.60000E-02	1.18126E-01	9.08783E-01
3.40000E-02	1.14686E-01	8.33494E-01
3.20000E-02	1.11062E-01	7.61148E-01
3.00000E-02	1.07239E-01	6.91721E-01
2.80000E-02	1.03199E-01	6.25188E-01
2.60000E-02	9.89237E-02	5.61529E-01
2.40000E-02	9.43899E-02	5.00727E-01
2.20000E-02	8.95729E-02	4.42766E-01
2.00000E-02	8.44431E-02	3.87640E-01
1.80000E-02	7.89656E-02	3.35343E-01
1.60000E-02	7.30991E-02	2.85880E-01
1.40000E-02	6.67929E-02	2.39265E-01
1.20000E-02	5.99845E-02	1.95523E-01
1.00000E-02	5.25937E-02	1.54698E-01
8.00000E-03	4.45138E-02	1.16861E-01
6.00000E-03	3.55952E-02	8.21271E-02
4.00000E-03	2.56089E-02	5.06895E-02
2.00000E-03	1.41443E-02	2.29246E-02
1.00000E-03	7.58878E-03	1.06777E-02
0.00000E-99	0.00000E-99	0.00000E-99

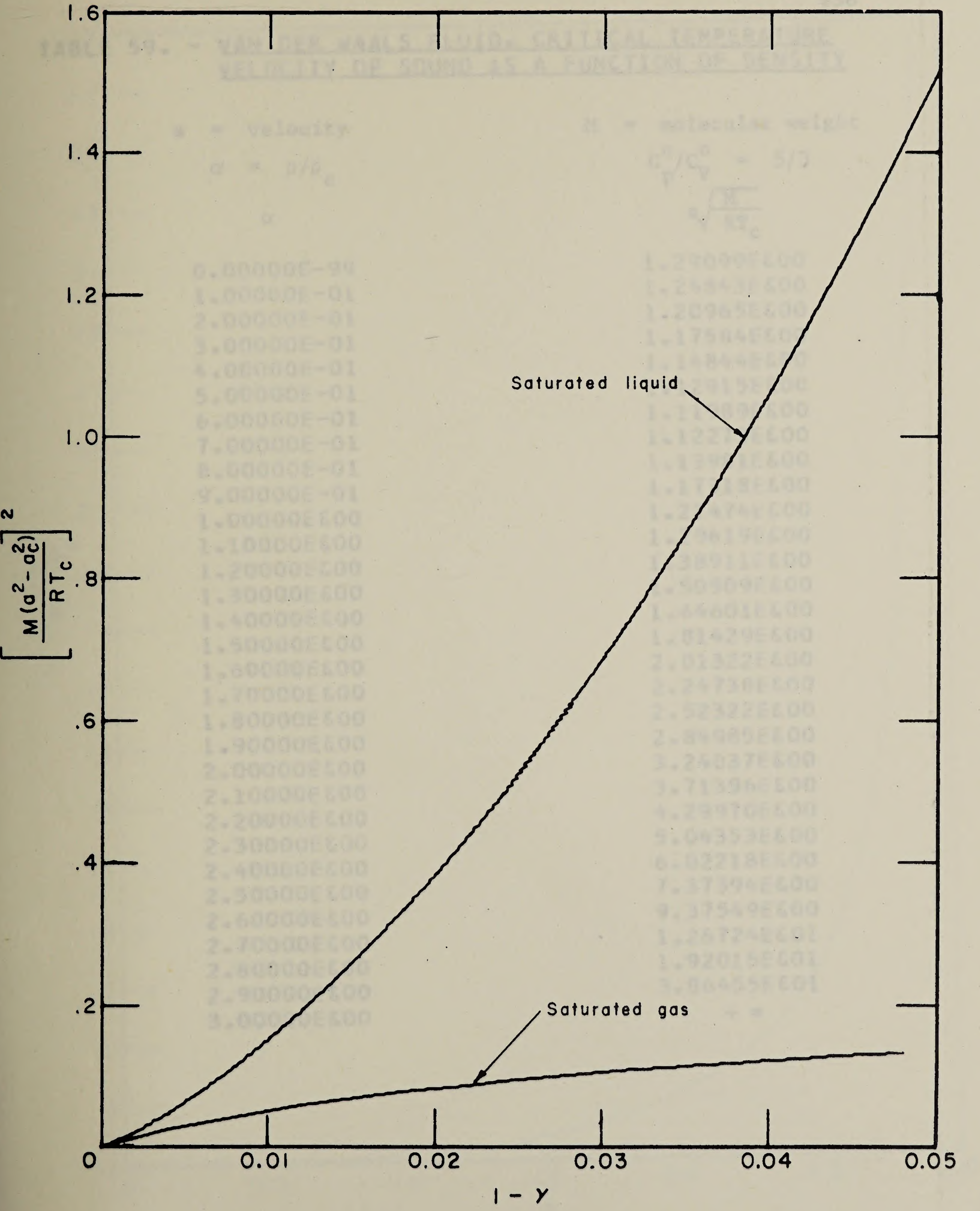

FIGURE 88.- Van der Waals Fluid, Asymptotic Function of Saturated Velocities of Sound as a Function of Temperature; a = Velocity; M = Molecular Weight; $\gamma = T/T_c$; $C_p^o/C_v^o = 5/3$

TABLE 59. - VAN DER WAALS FLUID, CRITICAL TEMPERATURE VELOCITY OF SOUND AS A FUNCTION OF DENSITY

a = velocity

$\alpha = \rho/\rho_c$

M = molecular weight

$C_p^o/C_V^o = 5/3$

α	$a\sqrt{\frac{M}{RT_c}}$
0.00000E-99	1.29099E&00
1.00000E-01	1.24843E&00
2.00000E-01	1.20965E&00
3.00000E-01	1.17584E&00
4.00000E-01	1.14844E&00
5.00000E-01	1.12915E&00
6.00000E-01	1.11989E&00
7.00000E-01	1.12273E&00
8.00000E-01	1.13981E&00
9.00000E-01	1.17318E&00
1.00000E&00	1.22474E&00
1.10000E&00	1.29619E&00
1.20000E&00	1.38911E&00
1.30000E&00	1.50509E&00
1.40000E&00	1.64601E&00
1.50000E&00	1.81429E&00
1.60000E&00	2.01322E&00
1.70000E&00	2.24738E&00
1.80000E&00	2.52322E&00
1.90000E&00	2.84985E&00
2.00000E&00	3.24037E&00
2.10000E&00	3.71396E&00
2.20000E&00	4.29970E&00
2.30000E&00	5.04353E&00
2.40000E&00	6.02218E&00
2.50000E&00	7.37394E&00
2.60000E&00	9.37549E&00
2.70000E&00	1.26724E&01
2.80000E&00	1.92015E&01
2.90000E&00	3.86455E&01
3.00000E&00	+ ∞

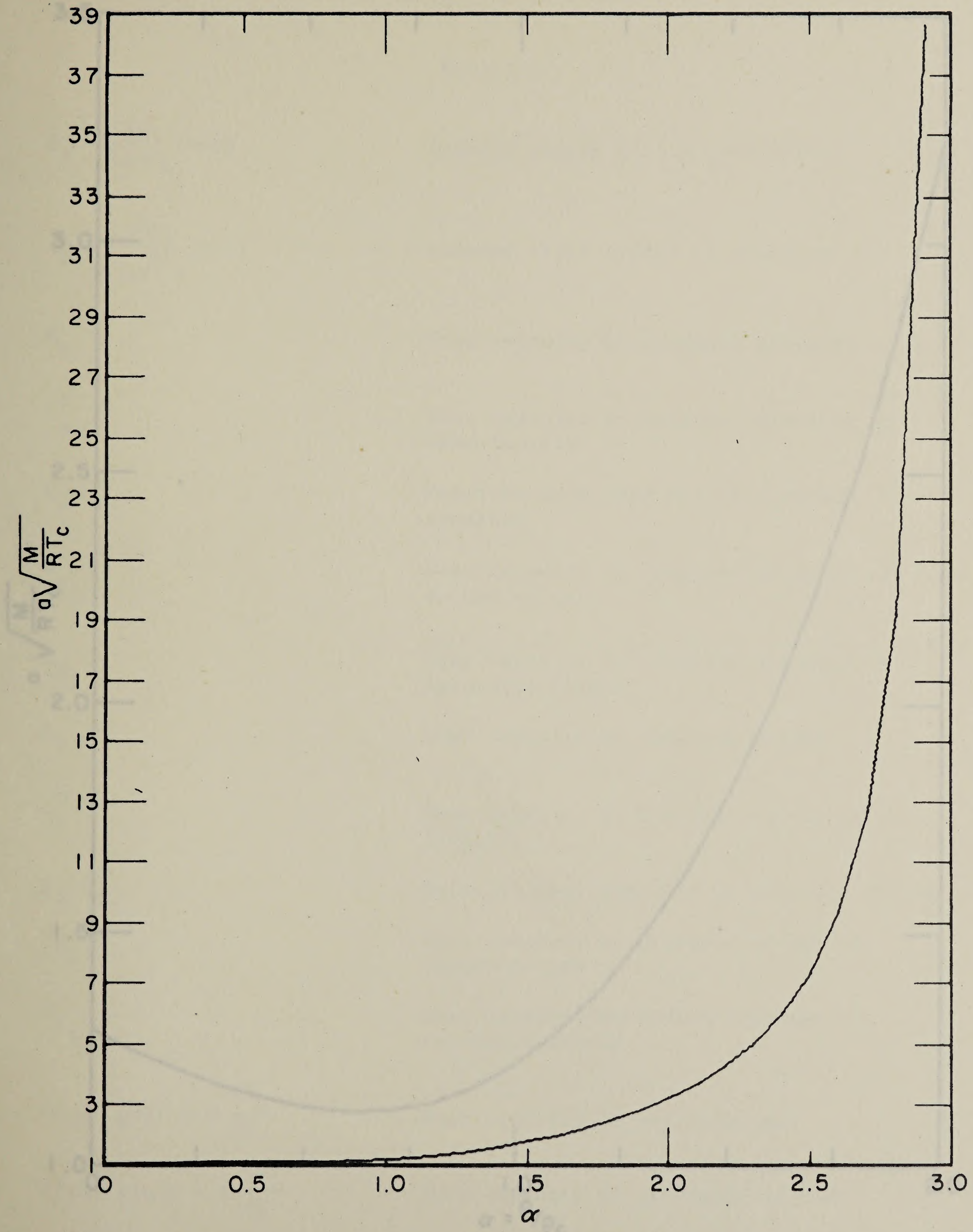

FIGURE 89.- Van der Waals Fluid, Critical Temperature Velocity of Sound vs $\alpha = \rho/\rho_c$ a= Velocity of Sound.

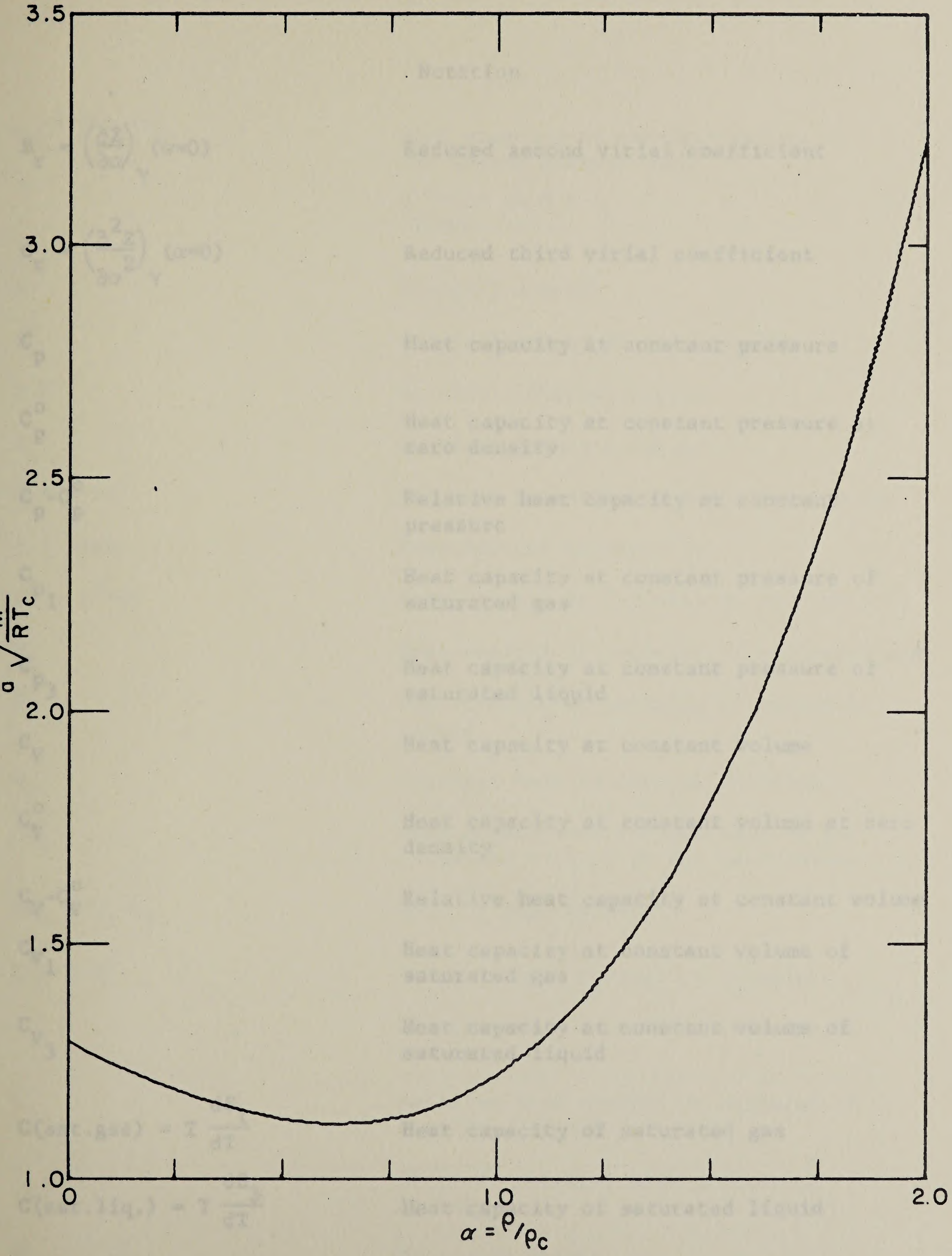

FIGURE 90.- Van der Waals Fluid, Velocity of Sound for the Critical Isotherm

Notation

$B_r = \left(\frac{\partial Z}{\partial \alpha}\right)_\gamma (\alpha=0)$	Reduced second virial coefficient
$C_r = \left(\frac{\partial^2 Z}{\partial \alpha^2}\right)_\gamma (\alpha=0)$	Reduced third virial coefficient
C_p	Heat capacity at constant pressure
C_p^o	Heat capacity at constant pressure at zero density
$C_p - C_p^o$	Relative heat capacity at constant pressure
C_{p_1}	Heat capacity at constant pressure of saturated gas
C_{p_3}	Heat capacity at constant pressure of saturated liquid
C_V	Heat capacity at constant volume
C_V^o	Heat capacity at constant volume at zero density
$C_V - C_V^o$	Relative heat capacity at constant volume
C_{V_1}	Heat capacity at constant volume of saturated gas
C_{V_3}	Heat capacity at constant volume of saturated liquid
$C(\text{sat.gas}) = T \frac{dS_1}{dT}$	Heat capacity of saturated gas
$C(\text{sat.liq.}) = T \frac{dS_3}{dT}$	Heat capacity of saturated liquid
$C_V(\text{2 phases})$	Heat capacity at constant volume with two phases present

$C_V\left(\begin{matrix}2\ \text{phases}\\ \bar{\rho}=\rho_c\end{matrix}\right)$	Heat capacity at constant volume with two phases present with $\frac{n}{V_{\text{Total}}} = \bar{\rho} = \rho_c$
E	Internal energy
E^o	Internal energy at zero density
$E-E^o$	Relative internal energy
E_c	Critical internal energy
$G = H-TS$	Chemical potential or Gibbs free energy
$H = E+PV$	Heat content or enthalpy
$H^o = E^o+RT$	Heat content or enthalpy at zero density
H_1	Heat content or enthalpy of saturated gas
H_3	Heat content or enthalpy of saturated liquid
H_c	Critical heat content or enthalpy
ΔH_a	Heat of vaporization per mole of gas collected outside of the calorimeter
$\Delta H_v = L_1-L_3$	Heat of vaporization
$L = H-H^o$	Relative heat content or enthalpy
L_1	Relative heat content or enthalpy of saturated gas
L_3	Relative heat content or enthalpy of saturated liquid
L_c	Critical relative heat content or enthalpy
M	Molecular weight
P	Pressure
P_c	Critical pressure

R	Universal gas constant in the equation $PV = RT$
S	Entropy
S^o	Entropy of the ideal gas in the hypothetical standard state at unit fugacity
S_c	Critical entropy
S^o_c	Critical temperature entropy of the ideal gas in the hypothetical standard state at unit fugacity
S_1	Entropy of the saturated gas
S_3	Entropy of the saturated liquid
$S-S^o$	Relative entropy
ΔS_v	Entropy of vaporization
T	Temperature
T_c	Critical temperature
V	Molal volume
V_{Total}	Total volume of saturated gas and saturated liquid
$W = W(t,\delta) = 0$	Functional relationship between t and δ
$X = \frac{\rho_3-\rho_1}{\rho_3+\rho_1} = \frac{\alpha_3-\alpha_1}{\alpha_3+\alpha_1}$	A functional relation between the densities of coexisting phases
$Y = Y(\alpha_1,\alpha_3) = 0$	The functional relationship between the reduced densities of coexisting phases
$Z = \frac{P}{\rho RT}$	Compressibility factor
Z_c	Critical compressibility factor
Z_1	Compressibility factor of saturated gas
Z_3	Compressibility factor of saturated liquid

a	A constant in the van der Waals equation
a	Velocity of sound
a_c	Critical velocity of sound
a_1	Velocity of sound of saturated gas
a_3	Velocity of sound of saturated liquid
b	A constant in the van der Waals equation
f	Fugacity
f_c	Critical fugacity
n	Total number of moles of gas and liquid
$t = \alpha_3 - \alpha_1$	A functional relation between reduced densities of coexisting phases
$\alpha = \rho/\rho_c$	Reduced density
α_1	Reduced density of saturated gas
α_3	Reduced density of saturated liquid
$\alpha_1' = \frac{d\alpha_1}{d\gamma}$	Reduced temperature coefficient of the reduced density of saturated gas
$\alpha_3' = \frac{d\alpha_3}{d\gamma}$	Reduced temperature coefficient of the reduced density of saturated liquid
$\beta = P/P_c$	Reduced pressure
$\beta' = \frac{d\beta}{d\gamma}$	Reduced temperature coefficient of the reduced vapor pressure
$\beta'' = \frac{d^2\beta}{d\gamma^2}$	Second reduced temperature coefficient of the reduced vapor pressure
$\gamma = T/T_c$	Reduced temperature

γ_{Boyle}	Reduced temperature where the second virial coefficient is zero.
Δ	An incremental quantity
δ	$1-\alpha_1$
ρ	Molal density
ρ_c	Critical molal density
ρ_1	Molal density of saturated gas
ρ_3	Molal density of saturated liquid
$\mu = \left(\frac{\partial T}{\partial P}\right)_H$	Joule-Thomson coefficient
μ_1	Joule-Thomson coefficient of saturated gas
μ_3	Joule-Thomson coefficient of saturated liquid

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