DEVELOPMENT OF AN EQUATION OF STATE FOR GASES

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I. Pressure-Volume-Temperature Behavior of Pure Gases and Liquids

More than a hundred equations of state relating the pressure, volume, and temperature of gases have been proposed according to Dodge(7), but only a very few of them have attained any practical importance as the majority do not represent the data with sufficient accuracy. In this work the significant pressure-volume-temperature (hereafter referred to as *PVT*) characteristics of pure gases have been examined in detail, and an equation has been developed to fit precisely the characteristics common to different gases.

PVT data may be plotted on different types of graphs, of which probably the oldest is that of pressure vs. volume with temperature as a parameter, as shown in Figure 1. From this graph van der Waals deduced two properties of the critical isotherm namely, that at the critical point the slope is zero and an inflection occurs.* Van der Waals expressed these two properties algebraically in the following well-known manner:

$$(dP/dV)_T = 0 \text{ at the critical point} \tag{1}$$

$$(d^2P/dV^2)_T = 0 \text{ at the critical point} \tag{2}$$

where P is pressure, V is volume, and T is temperature, as indicated above. Van der Waals employed these two conditions to evaluate the two arbitrary constants in the equation of state he proposed.

A number of other two-constant (exclusive of the gas constant) equations of state have been proposed, the best known being those of Berthelot and Dieterici. None of them, however, actually represent the *PVT* data over a wide range with any great degree of precision and not one of them is considered suitable for the calculation of accurate thermodynamic diagrams. This does not imply, however, that these two-constant equations have not been extremely useful. Van der Waals' equation was of the greatest value in leading to the principle of corresponding states.

In one form the corresponding-state principle suggests that the compressibility factor, $z = PV/RT$, depends only on the reduced temperature and pressure, which are defined respectively as $T_r = T/T_c$ and $P_r = P/P_c$. On a generalized compressibility chart for many different compounds single average lines are drawn for each isotherm; however, to demonstrate that the principle is approximate, Figure 2 has been constructed to emphasize the differences which actually exist among compounds.

From the compressibility chart it is noted that all gases follow the ideal-gas law as the pressure approaches zero, regardless of the temperature. This may be expressed as

$$Z = PV/RT = 1 \text{ at } P = 0 \text{ for all temperatures} \tag{3}$$

A curious corollary of this is the seemingly contradictory fact that in general V does not equal RT/P at $P = 0$. By definition of a derivative at any point (P_o, Z_o) on the compressibility chart,

$$(dZ/dP_r)_{Tr} = \lim (Z - Z_o)/(P_r - P_o) \text{ as } P_r \to P_o \tag{4}$$

With any isotherm taken at

$$P_o = 0,\ Z_o = 1.0,$$

$$(dZ/dP_r)_{Tr} = \lim (Z-1)/(P_r - 0) \text{ as } P_r \to 0$$

$$= \lim RT(Z-1)/RTP_r \text{ as } P_r \to 0$$

$$= (P_c/RT) \lim (ZRT/P - RT/P) \tag{5}$$

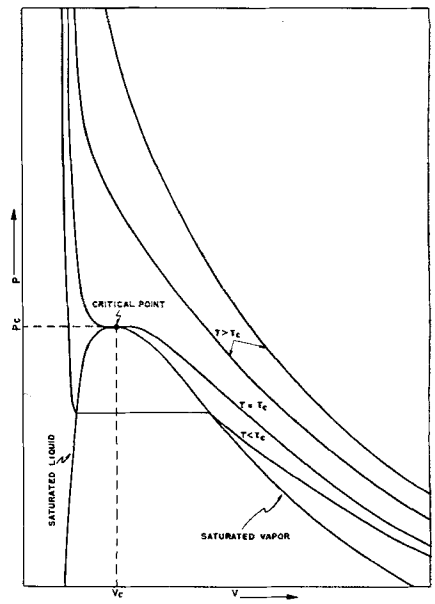

FIG. 1. PRESSURE-VOLUME DIAGRAM.

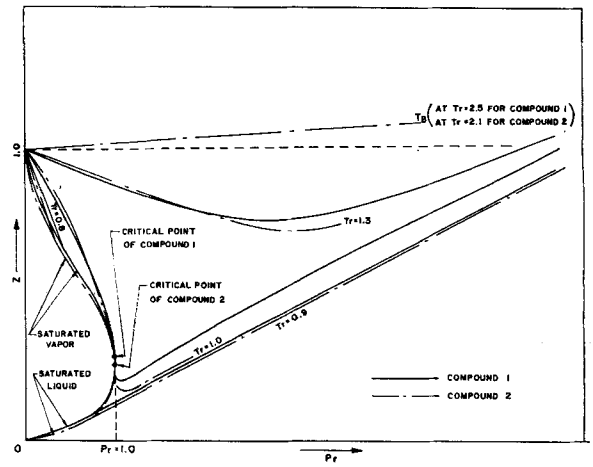

FIG. 2. COMPRESSIBILITY CHART.

*Some investigations (13) indicate that the critical isotherm is not the smoothly inflected curve shown in Figure 1. This result seems to be attributed to the indefiniteness of the critical state and possibly to the lack of attainment of true equilibrium.

Since by definition $Z = PV/RT$, or

$$ZRT/P = V, (dZ/dP_r)_{T_r} =$$

$$(P_c/RT) \lim (V - RT/P) \text{ as } P_r \to 0$$

$$= -(P_c/RT)(\alpha)_{P_r \to 0} \quad (6)$$

where α is defined as the residual volume, $(RT/P\text{-}V)$.
If Equation (6) is rewritten,

at 0 pressure α

$$= -(RT/P_c)(dZ/\alpha P_r)_{T_r} \quad (7)$$

which relates α to the slope of an isotherm on the compressibility chart. Since in general this slope is not zero at zero pressure, α is a finite quantity. The one isotherm for which the slope is zero is known as the Boyle point.

Most generalized compressibilty charts show the Boyle point occurring at a T_r of about 2.5. This is probably true only for such compounds as nitrogen, carbon monoxide, and methane, which were considered in making the plots. These compounds all have critical temperatures of approximately the same magnitude. For hydrogen with a much lower critical temperature the data indicate that the Boyle point is around a T_r of 3.3. For compounds with higher critical temperatures there are no experimental data at the required high temperatures. However, by extrapolation of the experimental data on isometric plots (*see* Figure 6), it appears that the Boyle-point reduced temperature goes down as the critical temperature goes up and that many compounds have Boyle points much lower than a T_r of 2.5. Figure 3 is a plot of the Boyle point vs. critical temperature, prepared by consideration of the measured points wherever possible and utilization of extrapolations to higher temperatures where necessary, as just mentioned.

A characteristic of gas behavior noted on both the compressibility chart and the pressure-volume plot is the straightness of the critical isotherm for a considerable range on either side of the critical point. The length of the straight portion indicates the possibility that derivatives of pressure with respect to volume higher than the two of van der Waals may be zero or at least very small. Examination of experimental data to prove whether any derivatives higher than the second are zero is difficult, since the data are often not too accurate. The higher derivatives cannot be assumed indiscriminately either, or the essential inflection at the critical point may not be preserved.

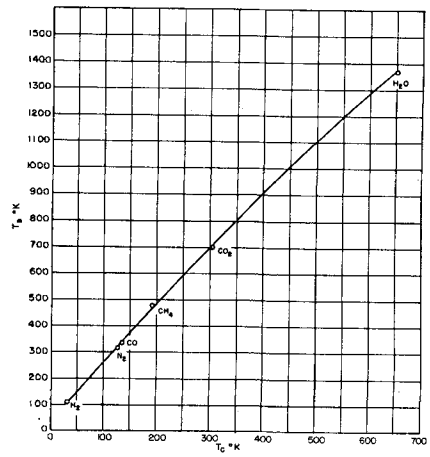

FIG. 3. T_B AS FUNCTION OF T_C.

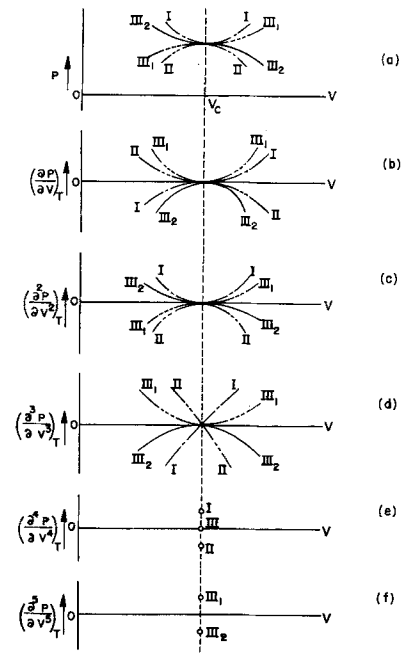

FIG. 4. PRESSURE-VOLUME DERIVATIVES WHEN $\left(\frac{\partial^3 P}{\partial V^3}\right)_T = 0$ AT CRITICAL POINT. [IT IS TAKEN FOR GRANTED THAT $\left(\frac{\partial P}{\partial V}\right)_T = 0$, AND $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$ AT CRITICAL POINT.]

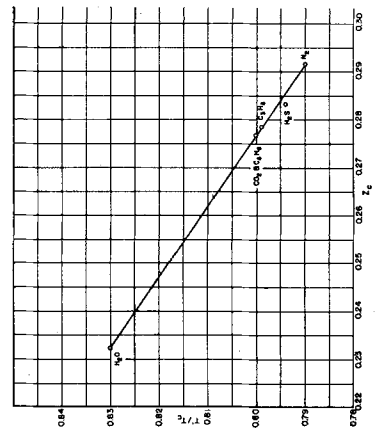

FIG. 5. T'/T_c AS FUNCTION OF Z_c.

In Figure 4 the necessary implications of the assumption that the third derivative is zero are considered. In Figure 4*d* four possible curves have been drawn, all of which go through zero according to the assumption. If the true situation is similar to curve I, the fourth derivative must be positive, as shown in Figure 4*e;* the second derivative will pass through a minimum, as shown in Figure 4*c;* the first derivative will have an inflection, as shown in Figure 4*b;* and the primary pressure vs. volume curve will exhibit a minimum, as shown in Figure 4*a*. As the primary curve must show an inflection, it is obvious that curve I cannot be correct. A similar analysis of curves II and III_1 shows that they cannot be used; however, curve III_2 does give the required character of the pressure vs. volume curve and therefore one concludes that if the third derivative is assumed to vanish, then the fourth must also vanish, as shown in Figure 4*e*, and the fifth must be negative or zero, as shown in Figure 4*f*.

Another assumption which can be made is that the fourth derivative vanishes while the third remains. An analysis similar to that above shows that for this case the third derivative must be negative in order to preserve the correct inflection at the critical point. The hypothesis which is advanced here is that in addition to the vanishing of the first two derivatives, as suggested by van der Waals, the third derivative is either zero or a small negative number and the fourth derivative is zero. Assumptions regarding the derivatives higher than the fourth might be made, but these derivatives would have much smaller effects. In current studies the fifth and sixth derivatives are being given some attention.

Another characteristic of gas behavior noted on the compressibility chart is that for compounds with different values of $Z_c (PV/RT$ at the critical point) lines which connect the critical point to the point $Z = 1.0$, $P_r = 0$ are tangent to isotherms whose reduced temperature is about 0.8. Algebraically this condition is

$$(dZ/dP_r)_{T_r} = -(1 - Z_c)$$

$$\text{at } T' \cong 0.8 T_c \quad (8)$$

The meager data available indicate that T' varies slightly from

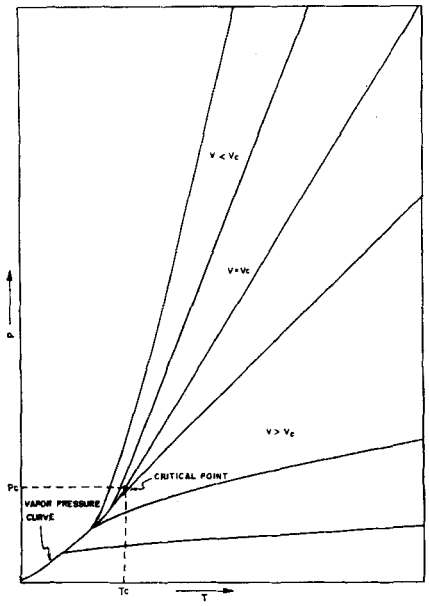

FIG. 6. PRESSURE-TEMPERATURE DIAGRAM.

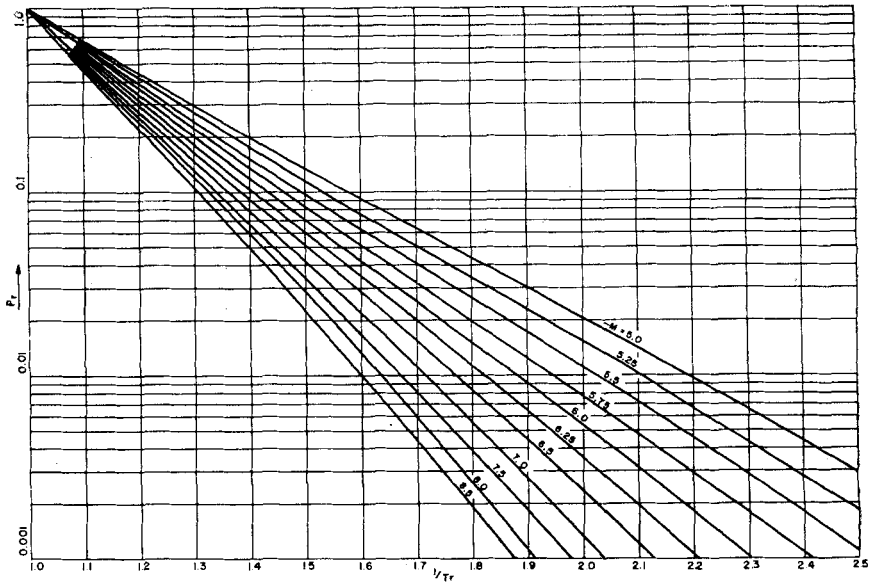

FIG. 7. REDUCED VAPOR-PRESSURE PLOT.

0.8 according to the value of Z_c. Figure 5 is a plot of the relation between T' and Z_c, and it is seen that were it not for the low Z_c of water, it would be difficult to draw any curve. Of course, there are other compounds with low Z_c's, but their data at a T_r of 0.8 are insufficient to warrant their use.

There are other characteristics of gas behavior indicated on the compressibility chart that seem to be of lesser importance than those previously mentioned. Some isotherms not only go through a minimum point but also exhibit inflections, notably those between a T_r of 1.0 and about 1.3. Isotherms above the Boyle point are almost straight. The compressibility factor is approximately 1.1 to 1.2 for all isotherms at a reduced pressure of about 10. Although these conditions are not utilized in this paper for the obtaining of an equation of state, they have been given some consideration.

Another important diagram of PVT data is the pressure-temperature (isometric) plot shown in Figure 6. The most important fact noted here is that the isometrics are almost straight. In fact there are three places where the lines can be considered straight: one is for large volumes at low pressures, another is for the critical volume, and the third is for all volumes at high temperatures. The three conditions can be expressed as

$$(d^2P/dT^2)_V = 0 \text{ as } P \longrightarrow 0 \quad (9)$$

$$(d^2P/dT^2)_V = 0 \text{ at } V = V_c \quad (10)$$

$$(d^2P/dT^2)_V = 0 \text{ for high } T \quad (11)$$

Also the isometrics below the critical density curve down, and those above the critical density curve up.* These conditions are given by the equations

$$(d^2P/dT^2)_V < 0 \text{ at } V > V_c \quad (12)$$

and

$$(d^2P/dT^2)_V > 0 \text{ at } V < V_c \quad (13)$$

A final observation on the isometric chart is that the slope of the vapor-pressure curve at the critical point is identical with the slope of the critical-density isometric. The experimental verification of this fact is difficult because the slope of the vapor-pressure curve is changing very rapidly. Usually the slope obtained by differentiating a vapor-pressure equation at the critical point is slightly less than the slope of the critical isometric. This may be attributed to the fact that in many cases the vapor-pressure equation may not reflect the slight upward curvature of the vapor-pressure curve on a log P vs. $1/T$ plot in the region near the critical, as emphasized by Thodos(*23*). Also the critical volume is difficult to determine accurately, and any error in its value would result in an error in its slope. From a thermodynamic point of view, the equality of the slope of the vapor-pressure curve and the critical isometric has been justified by the following analysis. From the Clapeyron equation the slope of the vapor-pressure curve is $dP/dT = \Delta S/\Delta V$ at any temperature. At the critical point $\Delta S/\Delta V$ becomes $(dS/dV)_T$, but from the Maxwell relation this is $(dP/dT)_{V_c}$. Therefore, the vapor pressure slope $dP/dT = (dP/dT)_{V_c}$, which is the desired equality.

Another important graph is the reduced-vapor-pressure plot of log P_r vs. $1/T_r$, as shown in Figure 7. The different curves are for a number of different compounds. Implication of the plot is that if two compounds fall on the same curve at any point, they tend to lie together over the whole range of temperature. The plot is extremely useful in filling in unexplored ranges of vapor pressure, provided that the critical temperature and pressure and one other point on the vapor-pressure curve are known. The plot is also useful for predicting the slope of the vapor-pressure curve at the critical point. Each curve approaches the critical point $(T_r = 1, P_r = 1)$ with a unique slope, $d \log P_r/d(1/T_r)$. This is called M and is designated on each curve. If a compound is known to follow one of the curves, then M is known. From this $(dP/dT)_{V_c}$ may be obtained as follows:

$$dP_r/P_r = -M dT_r/T_r^2 \quad (14)$$

from the definition of M. Since P_r and T_r are both 1,

$$dP_r/dT_r = -M \quad (15)$$

*Data on hydrogen indicate that the isometrics above the critical density may curve up for a while, but at the highest reduced temperatures they start to curve down. Since these high reduced temperatures are not encountered with other compounds, the negative curvature of all isometrics at such high temperatures is not important. Also at very high densities indications are that all isometrics curve down for all reduced temperatures. This means that at some very high density the isometrics for moderate temperatures are straight.

or from the definitions of P_r and T_r,

$$dP/dT = -MP_c/T_c =$$

$$(dP/dT)_{V_c} = m \qquad (16)$$

This fact is of great value because it means that vapor pressure determines the *PVT* behavior along the critical isometric.

A study of the interdependency of the characteristic properties of gases, as here presented, has led to a consideration of the minimum number of conditions or facts necessary to characterize the *PVT* behavior of any given compound. A new hypothesis is advanced that four properties are necessary to give the complete characterization for any compound. These are the critical temperature, critical pressure, critical volume, and one point on the vapor-pressure curve. The one point on the vapor-pressure curve determines the slope m of the critical isometric, as given above. Mathematically this hypothesis is written as

$$f(P, V, T, P_c, T_c, V_c, m) = 0 \quad (17)$$

or in terms of Z_c,

$$f(P, V, T, P_c, T_c, Z_c, m) = 0 \quad (18)$$

If this hypothesis is compared with previous work, it is seen that it is not so simple as van der Waals', which states that the compressibility is dependent only upon the critical temperature and pressure, or as that which says that the critical temperature, pressure, and volume determine the compressibility; however, accurate data show that neither of these latter hypotheses is correct.

It is the primary objective of this work to develop an equation which will represent the function implied by Equations (17) and (18). One might also develop graphical representations of those equations, which could be in the form of compressibility plots (Z vs. P_r with T_r as a parameter) for various values of Z_c, T_c, and M. Probably a number of plots would be required to cover the widest ranges, but such plots might prove sufficiently useful to justify their preparation. Part II considers only the equation and not the graphs.

II. Derivation of the Equation

Although there have been a number of attempts to develop an equation of state from kinetic theory and statistical mechanics, only token results have been obtained to date. The important practical equations which are in use today, such as the Benedict, Webb, and Rubin(*5*) and the Beattie and Bridgeman(*1*), are empirical. The equation about to be developed is also empirical; however, it is believed that this equation fits more of the known behavior characteristics of gases than does any previous equation.

The form of equation representing empirically the *PVT* behavior is chosen so that the data are represented as nearly as possible within the precision of the experiment. The equation should also be reasonably simple in order to be useful in thermodynamic calculations. Obviously, more terms may be put into an equation to get better agreement with the data, but complexity is the penalty. In this study various polynomial and exponential equations were considered. In view of the fact that it is the derivatives of pressure which are given by the van der Waals analysis and that pressure is almost a linear function of temperature at constant volume, equations explicit in pressure were preferred.

Because of its symmetry and the ease of differentiation and integration, the following equation was chosen over the others:

$$P = f_1/(V-b) + f_2/(V-b)^2 + f_3/(V-b)^3 + f_4/(V-b)^4 + f_5/(V-b)^5 \qquad (19)$$

where f's are functions of temperature and b is a constant.

In choosing the temperature functions for Equation (19), one first considers the character of the isometrics of Figure 6. Since these are straight at the high-temperature ends and curve only at the low ends near the saturation curve, any equation to represent the isometrics must become linear at high temperatures. Beattie and Bridgeman(*1*) suggested the form

$$P = A + BT + C/T^2 \qquad (20)$$

where A, B, and C are functions of volume. Benedict, Webb, and Rubin employed the same form. The last term, which is the curvature term, was considered carefully in the more general form C/T^n. It was found that to represent the experimental data for many different compounds n varied from about 2 to 5, depending largely upon the critical temperature of the substance in question. For most compounds with critical temperatures near room temperature n was about 3, and for compounds with high critical temperatures, such as water, n was about 5. In view of this variation, a different form of equation was selected:

$$P = A + BT + Ce^{-kT/T_c} \qquad (21)$$

Equation (21) was found to represent the curvature of isometrics of many different compounds with only one value of k, this value being 5.475. (This could be rounded off, but as with other constants will be carried to preserve internal consistency.) If Equation (21) is compared with Equation (19), it is seen that the temperature functions, f_1 to f_5, must be of the form

$$f_1 = A_1 + B_1T + C_1e^{-5.475T/T_c}$$

$$f_2 = A_2 + B_2T + C_2e^{-5.475T/T_c}$$

etc. (22)

where A_1, B_1, C_1, A_2, etc., are constants which may be finite or zero. Thus, with the selection of the complete form of the equation of state through Equations (19) and (22), the problem now is to find a method of evaluating the constants.

By virtue of the hypothesis given in Part I that the *PVT* behavior of a given compound depends only upon P_c, T_c, V_c, and m, one must have recourse to the general properties of gas behavior to see just how many arbitrary constants can be determined. The general properties to be used are restated in the following summary:

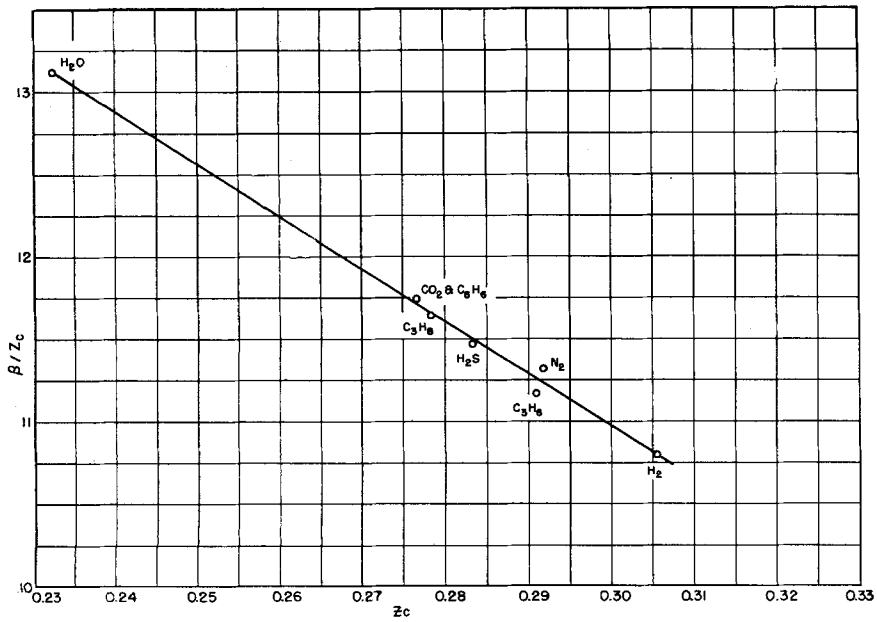

FIG. 8. β/Z_c AS FUNCTION OF Z_c.

$$PV = RT \text{ as } P \rightarrow 0 \quad (23)$$

$$(dP/dV)_T = 0 \text{ at critical} \quad (24)$$

$$(d^2P/dV^2)_T = 0 \text{ at critical} \quad (25)$$

$$(d^3P/dV^3)_T = 0 \text{ at critical} \quad (26)$$

$$(d^4P/dV^4)_T = 0 \text{ at critical} \quad (27)$$

$$[(dZ/dP_r)_{T_r}]_{P_r=0} = -(1-Z_c) \text{ at } T' \cong 0.8T_c \quad (28)$$

$$(dZ/dP_r)_{T_r}]_{P_r=0} = 0 \text{ at Boyle-point temperature } T_B \quad (29)$$

$$(d^2P/dT^2)_V = 0 \text{ at } V = V_c \quad (30)$$

$$(dP/dT)_V = m = -MP_c/T_c \text{ at } V = V_c \quad (31)$$

By use of the foregoing nine conditions plus the PVT relation at the critical point (since P_c, T_c, and V_c are to be given) determination of an equation of state with ten arbitrary constants might be expected. Equation (26) however is not determinate as it stands, and so a total of only nine constants can be obtained from the conditions listed.

Equation (23) is utilized by multiplying through Equation (19) by V-b and letting P approach zero while V, and therefore V-b, approaches infinity:

$$PV = f_1 \text{ as } P \rightarrow 0 \quad (32)$$

and in the light of Equation (23),

$$f_1 = RT \quad (33)$$

The equation of state now becomes

$$P = RT/(V-b) + f_2/(V-b)^2 + f_3/(V-b)^3 + f_4/(V-b)^4 + f_5/(V-b)^5 \quad (34)$$

Next are employed the four derivative conditions, (24) to (27), and the condition that the equation of state must be satisfied at the critical point. There are five equations containing five unknowns, $f_2(T_c)$ through $f_5(T_c)$, and b, where $f(T_c)$ means the temperature function evaluated at the critical temperature. However, Equation (26) cannot be used directly until the inequality is removed. The solution of the remaining four equations in terms of b is

$$f_2(T_c) = 9P_c(V_c-b)^2 - 3.8RT_c(V_c-b) \quad (35)$$

$$f_3(T_c) = 5.4RT_c(V_c-b)^2 - 17P_c(V_c-b)^3 \quad (36)$$

$$f_4(T_c) = 12P_c(V_c-b)^4 - 3.4RT_c(V_c-b)^3 \quad (37)$$

$$f_5(T_c) = 0.8RT_c(V_c-b)^4 - 3P_c(V_c-b)^5 \quad (38)$$

If $(d^3P/dV^3)_T$ in Equation (26) is assumed to be zero, Equations (35) through (38) may be substituted into Equation (26) to determine b as*

$$b = V_c - 3RT_c/15P_c \quad (39)$$

or in terms of Z_c,

$$b = V_c - 3V_c/15Z_c \quad (40)$$

The equation of state is now determined along the critical isotherm; however, a comparison of the equation with the data for a number of different gases showed that the equation predicted pressures too high for volumes greater than the critical volume. Previous comparisons using only the two van der Waals derivatives and a correspondingly shorter equation of state (i.e., one terminating at f_4 and with $b = 0$) showed that pressures in this region were predicted too low. In another trial the third derivative condition was completely neglected when an equation terminating with f_4, but otherwise the same as Equation (19), was utilized. This implies that f_5 is arbitrarily set equal to zero; therefore, from Equation (38),

$$b = V_c - 4RT_c/15P_c = V_c - 4V_c/15Z_c \quad (41)$$

This assumption predicted pressures too low; therefore, some in-

*Sometime after working out the analysis of the derivatives at the critical point, it was found that Plank and Joffe (*20, 11*) had studied equations similar to Equation (19). They assumed five equal roots at the critical point, which is the same as assuming the first four derivatives to be zero. This equality may be shown by considering the meaning of five equal roots at the critical point. Let P be a function of V, with five equal roots at the critical point. Then $P = f(V)$ at $T = T_c$ and $P-P_c = f(V)-P_c$. At $P = P_c$ the $f(V)-P_c$ must be zero, and because of the equality of five roots this must be equivalent to another function $F(V)(V-V_c)^5$ set equal to zero or $P-P_c = F(V)(V-V_c)^5$, where $F(V_c) \neq 0$. Differentiating with respect to V gives

$$dP/dV = 5(V-V_c)^4 F(V) + (V-V_c)^5 F'(V)$$

Since $V = V_c$, this is zero. Carrying on three more differentiations will continue to give factors of $V-V_c$, which will cause the derivatives to vanish, until one comes to the fifth derivative, where at least one term will not have $V-V_c$, i.e., $120F(V)$. Then the derivative is not zero.

termediate value between Equations (40) and (41) is required. For this purpose let

$$b = V_c - \beta V_c/15Z_c \qquad (42)$$

where β is a constant for a given compound. It can be shown that β cannot be less than 3.0 or more than 4.0.

By trial with the data of a number of different compounds along the critical temperature line, it was found that β depended upon Z_c. Use of the varying values of β permitted very accurate representation of the data up to densities about 1.5 times the critical density.

Figure 8 is a plot which gives β as a function of Z_c*.

Since one of the original ten conditions was used to evaluate f_1 as RT and since one condition was indeterminate but can be satisfied by setting the magnitude of the third pressure-volume derivative through the term β, there are eight conditions left to evaluate the temperature functions f_2 to f_5. Each temperature function may contain a maximum of three constants, A, B, and C, and so a total of twelve constants must be fixed. In view of the eight conditions, four constants must be set equal to zero. As mentioned earlier, more conditions might be utilized, in which case all twelve constants might be finite. However, it has been found that some constants are much less important than others and that dropping four of them still leaves an equation which represents the data with a high order of accuracy.

When the eight constants to remain in the temperature functions were chosen, it was felt that the slope constants, B, and the intercept constants, A, were most important, the curvature constants, C, being of less significance. In order to apply Equation (30), however, it is necessary that there be at least two C terms in the equation. The six constants left were divided equally between A's and B's. The following was decided upon as being at least as good as any other arrangement:

$$f_1 = RT \qquad (43)$$

$$f_2 = A_2 + B_2T + C_2e^{-5.475T_r} \qquad (44)$$

$$f_3 = A_3 + B_3T + C_3e^{-5.475T_r} \qquad (45)$$

$$f_4 = A_4 \qquad (46)$$

$$f_5 = B_5T \qquad (47)$$

The problem of evaluating these eight constants is now mathematical manipulation of the eight conditions. From Equation (46) f_4 is a constant independent of temperature and directly equal to A_4. Therefore, from Equation (37),

$$A_4 = f_4(T_c) = 12P_c(V_c-b)^4 - 3.4RT_c(V_c-b)^3 \qquad (48)$$

Since Equation (47) sets $f_5 = B_5T$, $f_5(T_c) = B_5T_c$ and from Equation (38),

$$B_5 = f_5(T_c)/T_c = 0.8R(V_c-b)_4 - 3P_c(V_c-b)^5/T_c \qquad (49)$$

The derivation of the remaining six constants is a little more involved. Starting with Equation (19), one multiplies through by $V-b$, substitutes $PV = ZRT$ to eliminate variable V, and then differentiates partially with respect to pressure at constant temperature, to obtain

$$(dZ/dP)_TRT-b = \left\{(ZRT-bP)f_2 - f_2P[(dZ/dP)_TRT-b]\right\}/(ZRT-bP)^2 + \left\{(ZRT-bP)f_3P(2) - 2f_3P^2[(dZ/dP)_TRT-b]\right\}/(ZRT-bP)^3 + \left\{(ZRT-bP)f_4P^2(3) - 3f_4P^3[(dZ/dP)_TRT-b]\right\}/(ZRT-bP)^4 + \left\{(ZRT-bP)f_5P^3(4) - 4f_5P^4[(dZ/dP)_TRT-b]\right\}/ZRT-bP)^5 \qquad (50)$$

Since at $P_r = 0$, $Z = 1.0$, Equation (50) simplifies to

$$f_2 = \left\{\left[(dZ/dP_r)_{P_r=0}\right](RT)^2/P_c\right\} - bRT \qquad (51)$$

Combining Equations (28) and (51) at $T_r = T/T_c$ gives

$$f_2(T') = A_2 + B_2T' + C_2e^{-5.475T'/T_c} = [(RT')^2(Z_c-1)/P_c] - bRT' \qquad (52)$$

From Equation (29) $[(dZ/dP_r)_T]_{T=T_B,\ P_r=0} = 0$, and inserting this into Equation (51) gives

$$f_2(T_B) = A_2 + B_2T_B + C_2e^{-5.475T_B/T_c} = -bRT_B \qquad (53)$$

Equations (52) and (53) with

$$f_2(T_c) = A_2 + B_2T_c + C_2e^{-5.475} \qquad (54)$$

which is known by Equation (35) in terms of P_c, T_c, V_c, and b, form a set of simultaneous equations with three unknowns, A_2, B_2, and C_2. The solution of this set of simultaneous equations is

$$C_2 = \frac{[f_2(T_c)+bRT'+(RT')^2(1-Z_c)/P_c](T_B-T_c)+[f_2(T_c)+bRT_B](T_c-T')}{(T_B-T_c)\left\{e^{-5.475}-e^{-5.475T'/T_c}\right\}-(T_c-T')\left\{e^{-5.475T_B/T_c}-e^{-5.475}\right\}} \qquad (55)$$

$$B_2 = [-f_2(T_c) - bRT_B - C_2(e^{-5.475T_B/T_c}-e^{-5.475})]/(T_B-T_C) \qquad (56)$$

$$A_2 = f_2(T_c) - B_2T_c - C_2e^{-5.475} \qquad (57)$$

Substituting Equations (43) to (47) into Equation (19), rearranging in the form of Equation (21), and differentiating twice with respect to volume give, by use of Equation (30),

$$C_3 = -C_2(V_c-b) \qquad (58)$$

Applying Equations (31) and (58) gives

$$B_3 = m(V_c-b)^3 - R(V_c-b)^2 - B_2(V_c-b) - B_5/(V_c-b)^2 \qquad (59)$$

From Equation (45), with $T = T_c$, one obtains

$$A_3 = f_3(T_c) - B_3T_c - C_3e^{-5.475} \qquad (60)$$

This now completes the solution for all the constants in the equation of state. If the critical temperature, critical pressure, critical volume, and one point on the vapor-pressure curve are known for a given compound, appropriate graphs will give slope m of the critical isometric; the Boyle point, T_B; the T' point (about $0.8T_c$); and β, the determinant of the value of the third derivative of pressure

*It will be noted on Figure 8 that β never exceeds a value of 3.35 for the gases which have been studied so far. One might wonder about the nature of the five roots of the equation at the critical point for β lying between 3.0 and 3.35, since for β = 3.0, it has been shown that the five roots are equal. Further analysis shows that there are three real equal roots and two complex roots for β greater than 3.0 and less than 3.5.

with respect to volume at the critical point.

When gases were chosen to test the new equation, two considerations were paramount: first, the *PVT* data for any gas had to be fairly complete and accurate, and, second, the gases had to be as different as possible. Seven gases have been studied so far, and it is felt that the selection of CO_2, H_2O, C_6H_6, N_2, C_3H_6, H_2S, and C_3H_8 is sufficiently broad to test the versatility of the equation. The application of this new equation of state will be discussed and the calculated results for the seven gases studied will be presented in Part III.

III. Application and Discussion of the Equation

In the two foregoing parts of this paper *PVT* behavior of gases is considered in some detail and appropriate algebraic equations are given to represent that behavior. A new hypothesis is stated concerning the minimum amount of information necessary to characterize any given gas and an equation of state with nine constants is developed which requires only the minimum information according to the hypothesis for evaluation of the constants. This equation has been applied to seven different gases within a maximum error of 1%, and usually much less, for densities up to about 1.5 times the critical density.* Table 1 gives the constants that were calculated from the required P_r, T_c V_c, and m information for each of the gases. Tables have been made of comparisons of the pressures predicted from the equation of state with the experimentally measured pressures reported in the literature.

The points which are compared in these tables have been selected at places where the equation would represent the data least well. It is probable that the average deviation for the equation if compared at regularly spaced intervals over all ranges of temperature and pressure would be less than the average of the deviations listed in the tables. which is about 0.4%.

The precision of experimental data was important in the equation of state at almost every turn in its development. It was necessary in many cases to decide which data points of different investigators and which data points in different ranges were the most reliable, an especially necessary decision because of the desire to hold the maximum deviation under 1%. Data taken in the region of the critical point are more inconsistent than those from anywhere else. This reflects the inherent experimental difficulties in this region. The critical volume is the most unreliable measurement, and it is not uncommon to find differences of 5% in this value. Naturally slope m inherits any error in the determination of critical volume when fitting the equation to specific data is attempted.

The procedures used in developing the equation of state might well be of value in helping to determine a better value of critical volume. Usually this value is not measured experimentally but is determined by a rectilinear diameter plot, wherein the mean saturated liquid and vapor density is extrapolated to the critical temperature, which has been determined by disappearance of the meniscus. Another procedure which has been used is to determine the critical temperature as the lowest temperature at which a measured pressure-volume line undergoes a smooth inflection, the point of the inflection being the critical volume. These

TABLE 1.—CONSTANTS EVALUATED FOR THE EQUATION

	CO_2	H_2O	C_6H_6	N_2	C_3H_6	H_2S	C_3H_8
T_c	547.5°R.	1165.1°R.	562.66°K.	126.1°K.	364.92°K.	672.4°R.	666°R.
P_c	1069.4 lb./sq. in.	32062 lb./sq. in.	48.7 atm.	33.5 atm.	45.61 atm.	1,306.0 lb./sq. in.	618 lb./sq. in.
V_c	0.03454 cu. ft./lb.	0.0503 cu. ft./lb.	3.36 cc./g.	90.1 cc./g. mole	0.191 liter/g. mole	1.565 cu. ft./lb. mole	3.220 cu. ft./lb. mole
Z_c	0.27671	0.23246	0.27683	0.29171	0.290932	0.28329	0.278465
m	14.0	22.6	0.625	1.647	0.81	12.8	6.47
β	3.25	3.05	3.25	3.30*	3.25	3.25	3.25
T_B/T_c	2.3	2.1	2.15	2.5	2.3	2.3	2.3
T'/T_c	0.80	0.83	0.80	0.79	0.791	0.794	0.799
b	0.007495	0.0063101	0.730231	22.1466*	0.0487575	0.368095	0.714598
R	0.24381	0.59545	1.05052	82.055	0.082055	10.73	10.73
A_2	−8.9273631	−85.7394396	−4104.138	−1592238.2	−10.2233898	−21206.0776	−44105.1544
B_2	0.005262476	0.0312961744	2.62510	3,221.616	0.0081804454	9.7631723	21.127023
C_2	−150.97587	−2590.5815	−59333.234	−22,350,930	−153.061055	−318,608.803	−736,929.321
A_3	0.18907819	3.09248249	8553.304	89,845,367	1.219453756	21133.013	88,025.6002
B_3	−0.0000704617	−0.00082418321	−3.89165685	−134,024.05	0.00074168283	−7.41557245	−28.1649342
C_3	+0.0831424	113.95968	156032.7	1,518,821,653	21.7717909	381,344.629	1,846,304.2
A_4	−0.002112459	−0.0567185967	−8599.2791	−2,467,297,480	−0.068940713	−9897.9772	−89,907.6635
B_5	1.9565593×10^{-8}	4.2388378×10^{-7}	7.53651	244,915,183	5.0385878×10^{-6}	3.3036675	63.416365

All the constants for the equation of state are given in units of T_c, P_c, and V_c for that compound.

*β for N_2 could be 3.25 depending upon the manner by which the checked points on the critical isotherm are interpolated from experimental data reported.

*Calculations performed after the writing of this paper indicate that at about one and one half times the critical density the equation predicts too much curvature of the isometrics. It has been found that this may be improved by adding a C_5 term to the equation and utilizing the condition stated in the first paper, that at some very high density (approximately twice the critical density) the isometric is straight. With this condition the only changes in the equations for the constants are

$$C_3 = \frac{C_2\left[(V_c-b)^3 - \left(\frac{V_c}{n}-b\right)^3\right]}{\left[\left(\frac{V_c}{n}-b\right)^2 - (V_c-b)^2\right]}$$

$$C_5 = -C_2(V_c-b)^3 - C_3(V_c-b)^2$$

$$B_5 = \frac{f_5(T_c) - C_5 e^{-5.475}}{T_c}$$

Here n is approximately 2.

procedures do not agree too well in many cases, and two alternatives are suggested here. First, one can plot the vapor-pressure data on Figure 7 to determine slope m. Then referring to the experimental data, he can establish the critical volume as that volume whose slope agrees with the m so selected. This, of course, means that he is relying on the inherent accuracy of the slopes of the generalized vapor-pressure curves. An alternative to this is to differentiate the vapor-pressure curve directly for the compound and use that slope m as the determining factor in picking the critical volume. However, as mentioned in the first paper, this must be done with care for often the slight increase in the slope of the vapor-pressure curve near the critical is overlooked. Second, one may fix the critical volume by fitting the data points on the critical isotherm as in step 5 in the procedure, which will be described later, for obtaining an equation of state to fit data. When the best possible fit of the critical isotherm has been obtained by adjusting the critical volume and β, one may say that the critical volume has been determined by analytical means. This is equivalent to fixing the critical volume by a study of graphs of the isotherms and noting the lowest temperature and point at which a pressure-volume line undergoes a smooth inflection.

The Boyle-point temperature is worthy of further discussion in this work. In the estimation of Boyle points for most compounds, the procedure was simply to extrapolate a large volume isometric to the point where $Z = PV/RT = 1$. This has two drawbacks: first, the extrapolated isometric instead of being straight may have a slight negative curvature, which will be important when the extrapolation is carried over a wide range of temperature; second, the Boyle point should be determined at zero pressure. It is seen on the compressibility chart, however, that the Boyle-point isotherm follows $Z = 1$ up to fairly appreciable pressures, so that the procedure seems justified. Furthermore, as the equation is not very sensitive to the Boyle point except at high temperatures, it seems that Figure 3, which correlates these extrapolated Boyle points with the critical temperature, is sufficiently accurate for most purposes.

As better critical data become available, it is expected that some of the correlations will change. Possibly new ones will be developed; for example, even now there is a tendency for the reduced slope M of the critical isometric to be a function of Z_c. Several compounds seem to fall out of line, but if future experimental work were to change some of the critical values for these compounds the correlation might be good.

In general it is claimed that the equation reproduces the experimental data within 1% up to densities of about 1.5 times the critical density and up to temperatures of about 1.5 times the critical temperature. At about 1.5 times the critical density the isotherms become so steep that a 1% error in volume may cause 5% or more error in pressure. Therefore, it is not to be expected that the equation will predict closely above 1.5 times the critical density. This region, which is really the compressed-liquid region, has been given some consideration, and it is believed that to represent it properly either the term b in the equation will have to become a function of volume or more terms will have to be added to the equation. That b might change with volume seems reasonable when one recalls that the b in van der Waals' equation accounts for the effective volume of the molecules themselves, and the effective volume of the molecules might become smaller as the gas is compressed. This is, in fact, the direction of the necessary change in b to get agreement at very high densities, for the equation at present tends to predict pressures too high. Decreasing b will increase the denominators of the higher power positive terms and thus decrease the pressure.

An interesting application of the question is contemplated for mixtures. Ordinarily when one wishes to get an equation of state for mixtures, he averages the constants in the equation of state for the pure gases involved according to some method of averaging such as arithmetical mean or geometrical mean. This process may be applied to the proposed equation; however, an alternate process is permitted here. The fundamental constants that determine the equation, P_c, T_c, V_c, and m, may be averaged at the start and the equation of state for the mixture determined by the same process as would be used for a pure component. It is expected to try this out in the near future.

Comparison of this equation with other equations has been deliberately avoided, largely because of the misinterpretation of the term *average deviation.* Although it may be generally accepted that the average deviation of the Beattie-Bridgeman and Benedict-Webb-Rubin equations is 0.18 and 0.34% respectively (*7, 10*), experience in applying the equations within the density limits claimed showed these values to be misleading, because deviations over 1% were found in certain places. Therefore, this work did not try to compare different equations but tried to determine maximum errors between the equation proposed and the data.

This new equation is valuable when applied to a compound whose experimental data are limited to only the critical temperature, pressure, and volume and one point on the vapor-pressure curve. Table 2 gives a summary of the formulas for evaluation of the constants in the equation of state, together with the procedure for application to any gas for which the P_c, T_c, V_c, and m can be obtained.

Another situation often arises when it is desired to fit an equation of state to a rather complete set of PVT data for a specific compound. The procedure of application can be modified. Of course, to start, one may obtain the equation by using only the P_c, T_c, V_c, and m; however, it is possible that a better fit may be obtained by utilizing all the data in the following procedure:

1. Select the best values of P_c, T_c, V_c, as would be done when the generalized equation, is developed.
2. Calculate Z_c and read off from Figure 8 a value of β/Z_c *or* $\beta = -31.883Z^2_c + 20.533Z_c$.
3. Calculate the temperature functions along the critical isotherm, i.e., $f_2(T_c)$, $f_3(T_c)$, etc.
4. With the equation established from 3, at the critical temperature calculate a series of pressures for different densities along this isotherm. The maximum density to which this calculation should be carried should not exceed about 1.5 times the critical density, as above this density it is known that the error becomes large.
5. If the agreement of the calculated and experimentally measured pressures is not considered satisfactory in step 4 (it ought to be within 1% if the data are reliable), it is likely that an improvement can be made by adjusting V_c and β. This may not seem quite right to adjust a data point such as V_c to get an equation of state; however, usually V_c cannot be determined experimentally with a very high degree of accuracy and it is quite possible that the value first chosen is somewhat in error. As usually the critical temperature and pressure are known with greater precision than the critical volume, it

TABLE 2.—SUMMARY OF THE FORMULAS AND PROCEDURES FOR EVALUATING THE ARBITRARY CONSTANTS IN THE EQUATION OF STATE

Equation of state

$$P=\frac{RT}{V-b}+\frac{A_2+B_2T+C_2e^{-5.475T/T_c}}{(V-b)^2}+\frac{A_3+B_3T+C_3e^{-5.475T/T_c}}{(V-b)^3}+\frac{A_4}{(V-b)^4}+\frac{B_5T}{(V-b)^5}$$

Formulas (in order of evaluation)

$$b = V_c - \frac{\beta V_c}{15Z_c} \text{ where } Z_c = \frac{P_cV_c}{RT_c} \quad (42)$$

$$f_2(T_c)=9P_c(V_c-b)^2-3.8RT_c(V_c-b) \quad (35)$$

$$f_3(T_c) = 5.4RT_c(V_c-b)^2 - 17P_c(V_c-b)^3 \quad (36)$$

$$f_4(T_c) = 12P_c(V_c-b)^4 - 3.4RT_c(V_c-b)^3 \quad (37)$$

$$f_5(T_c) = 0.8RT_c(V_c-b)^4 - 3P_c(V_c-b)^5 \quad (38)$$

$$C_3 = -(V_c-b)C_2 \quad (58)$$

$$A_2 = f_2(T_c) - B_2T_c - C_2e^{-5.475} \quad (57)$$

$$A_4 = f_4(T_c) \quad (48)$$

$$B_5 = \frac{f_5(T_c)}{T_c} \quad (49)$$

$$B_3 = m(V_c-b)^3 - R(V_c-b)^2 - B_2(V_c-b) - \frac{B_5}{(V_c-b)_2} \quad (59)$$

$$A_3 = f_3(T_c) - B_3T_c - C_3e^{-5.475} \quad (60)$$

$$= \frac{[f_2(T_c)+bRT'+\frac{(RT')^2}{P_c}(1-Z_c)](T_B-T_c)+[f_2(T_c)+bRT_B](T_c-T')}{(T_B-T_c)(e^{-5.475}-e^{-5.475\,T'/T_c})-(T_c-T')(e^{-5.475\,T_B/T_c}-e^{-5.475})} \quad (55)$$

$$B_2 = \frac{-f_2(T_c) - bRT_B - C_2(e^{-5.475\,T_B/T_c}-e^{-5.475})}{T_B-T_c} \quad (56)$$

Procedure for application of the foregoing formulas to obtain the equation of state for a given compound

1. Select the best values of T_c, P_c and V_c. In case any of these are not known or are in doubt, refer to Hougen and Watson(*10*) for procedures for estimating.
2. Calculate $Z_c = P_cV_c/RT_c$.
3. Read off the Boyle temperature T_B from Figure 3.
4. Read off the T' temperature from Figure 5, or $\frac{T_c}{T'} = -0.6751Z_c + 0.9869$.
5. Read off the third derivative characteristic β from Figure 8, or $\beta = -31.883Z_c^2 + 20.533Z_c$.
6. Calculate the reduced temperature and pressure of a vapor-pressure point and place on Figure 7. By interpolation estimate the value of M. and from this calculate $dp/dT = m = -MP_c/T_c$.
7. With P_c, T_c, V_c, m, T_B, T', and β now fixed, substitute in the foregoing formulas.

is not recommended that these be changed unless the experimental values have been determined or presented with a considerable lack of precision. Also as V_c is changed, the value of Z_c will change and a different β will be predicted from Figure 8. One need not limit the values of β to this graph, however, for if the selection of another β value which does not fit the graph will give a better fit of the data, that is the one to use. From the nature of the equation β must lie between 3 and 4 to retain the correct inflection at the critical point. As a guide in predicting the effects of adjusting β and V_c, it has been found by trial that increasing β tends to decrease all pressures on the critical isotherm except at the critical point itself; whereas, increasing V_c tends to increase all pressures on the critical isotherm.

6. When the critical isotherm is represented accurately by the equation, read off a value of T_B and T'/T_c from Figures 3 and 5, or
$T'/T_c = -0.6751Z_c + 0.9869$
7. Obtain slope m by reference to the data for the critical isometric. Usually this can be done easily by reading off one high temperature point on the critical isometric and calculating $m = (P-P_c)/(T-T_c)$.
8. Evaluate all the constants in the temperature functions so that the equation is completely determined.
9. Calculate a few points at high temperatures and low temperatures (near the saturation curve) for several isometrics, the latter being taken for example at densities about 25% greater than the critical density, about two thirds the critical density, about one quarter the critical density, and about one tenth or one twentieth the critical density. Of course, the exact densities will be those available from the data.
10. If the calculated points do not agree with the data with the desired degree of precision, the values of m, T_B, and T' may be adjusted. The effect of changing these values is approximately as follows. Increasing m increases the pressure at higher temperatures for densities near the critical. Increasing the Boyle temperature T_B decreases the pressure at higher temperatures for low densities. Increasing T' increases the pressure at higher temperature for medium densities at about half the critical density while it decreases the pressure for temperatures near the saturation curve. There is one other parameter which may be changed in the equation, the constant in the exponential term, which is given as 5.475, but it might be shifted a little in a particular case. In general increasing this constant has about the same effect as increasing T'.
11. It is good practice to check on the calculation of the constants by substituting V_c into the equation obtained at the end of step 3 to see whether it produces the critical pressure. The procedure should be re-

peated at the end of step 8. These are not considered complete checks on the work, but they reveal most of the errors which might be introduced into the calculations.

In conclusion the new equation should have some value where one wishes accurate PVT representation from a minimum of data or where one wishes to represent some data with an empirical equation. Even at this time the equation is being employed to calculate the thermodynamic properties of a compound for which the PVT data are meager. The equation permits all the usual differentiations and integrations required for such thermodynamic treatment. For example, the changes in enthalpy and entropy may be given in terms of the ideal-gas heat capacities and the equation of state.

$$\Delta H = \int_{T_1}^{T_2} C_v^o\, dT + \Bigg| PV + \frac{A_2 + \left(1 + \frac{5.475T}{T_c}\right) C_2\, e^{-5.475T/T_c}}{(V-b)} + \frac{A_3 + \left(1+\frac{5.475T}{T_c}\right) C_3\, e^{-5.475T/T_c}}{2\,(V-b)^2} + \frac{A_4}{3\,(V-b)^3} \Bigg|_{V_1,\,T_1}^{V_2,\,T_2} \qquad (61)$$

and

$$\Delta S = \int_{T_1}^{T_2} C_v^o\, dT + \Bigg| R \ln (V-b) - \frac{B_2}{V-b} - \frac{B_3}{2\,(V-b)^2} + \left(\frac{C_2}{V-b} + \frac{C_3}{2\,(V-b)^2}\right) \left(\frac{5.475}{T_c}\right) e^{-5.475\,T/T_c} \Bigg|_{V_1,\,T_1}^{V_2,\,T_2} \qquad (62)$$

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NOTATION

A, B, and C = functions of specific volume

A_2, B_2, C_2, A_3, B_3, C_3, A_4, and B_5 = characteristic constants

C_p = heat capacity at constant pressure

H = enthalpy

M = slope of reduced vapor pressure curve at critical point = $\frac{dP_r}{dT_r} = -m\frac{P_c}{T_c}$

P = pressure

R = universal gas constant

S = entropy

T = temperature in absolute scale

T_B = absolute temperature at Boyle point

T' = absolute temperature for which the slope at $P_r = 0$ of the isotherm on the compressibility chart equals the slope of the line joining the critical point and ($Z = 1$, $P_r = 0$)

V = specific volume or mole volume

Z = compressibility factor = $\frac{PV}{RT}$

b = a characteristic constant for a given substance

e = base of natural logarithm, 2.71828

f_1, f_2, f_3, f_4, f_5 = temperature functions

$f_1(T_c)$, $f_2(T_c)$, $f_3(T_c)$, $f_4(T_c)$, and $f_5(T_c)$ = temperature functions evaluated at $T = T_c$

m = slope of the critical isometric on pressure-temperature diagram

$$\left(\frac{dP}{dT}\right)_{V=V_c} = -M\frac{P_c}{T_c}$$

Greek Letters

α = residual volume = $\frac{RT}{P} - V$

β = a characteristic constant in $V_c - b = \frac{\beta V_c}{10\omega_2}$

μ = Joule-Thompson coefficient = $\left(\frac{dT}{dP}\right)_H$

Subscripts

c = the value at critical point, e.g., T_c, P_c, V_c, and Z_c

r = reduced property, $T_r = \frac{T}{T_c}$, $P_r = \frac{P}{P_c}$, etc.

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