Equation of State for Phase Equilibrium:

I. Pure Component

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An equation of state for the two-phase region whose constants depend only on the critical pressure, the critical temperature, the normal boiling temperature, and the latent heat at the normal boiling point is shown to describe vapor pressure, latent heat, and saturation volumes of methane well.

It is often necessary to estimate the cost of a process from a minimum of data. When distillation is a dominant element in a process, the liquid-vapor equilibrium data selected influence the estimated cost markedly. For this reason methods of predicting liquid-vapor equilibria are being developed continually. In 1963 Wilson published (*1*) a modification of the Redlich-Kwong equation which improved its ability to predict two-phase equilibrium values. The present paper starts with a different equation, and modifies it in a different manner, but the thermodynamic principles and the ultimate goal are the same. Recently Flory and co-workers of Stanford University (*2* to *5*) have contributed a series of papers on an equation of state for chain molecules in the liquid phase. They have shown that this equation gives a good interpretation of the thermal expansion, compressibility, and the thermal pressure coefficient of liquids. In the present paper this Flory equation has been modified to permit the calculation of vapor pressures and latent heats. The constants for the modified equation are derived from the critical temperature, the critical pressure, the normal boiling point temperature, and the latent heat at the normal boiling point. Thus this equation is a step more complicated than the simple two-parameter equations which can be determined completely when one knows the critical temperature and pressure. A considerable gain is made in predicting the two-phase properties of pure substances with this additional fitting at the normal boiling point level. The simple two-parameter equations often lead to reasonably good liquid-vapor equilibrium compositions. It is probable that a four-parameter equation will yield correspondingly better mixture properties.

THE FLORY EQUATION

The Flory equation is expressed in dimensionless groups as

$$\tilde{P} = \frac{\tilde{T}}{\tilde{V} - \tilde{V}^{2/3}} - \frac{1}{\tilde{V}^{2}} \qquad (1)$$

where

$$\tilde{P} = \frac{P}{P^*}$$

$$\tilde{V} = \frac{V}{NV^*}$$

$$\tilde{T} = \frac{T}{T^*}$$

The characteristic pressure P^*, volume V^*, and temperature T^* (not the critical Pc, Vc, Tc used in the usual reduced equation) are determined from the physical properties of the fluid, such as the coefficient of thermal expansion, the coefficient of compressibility, and the thermal pressure coefficient. Table 1 lists the constants for methane and nitrogen.

It is to be remembered here that these characteristic constants are derived from the properties of liquid phase.

To be of interest in liquid-vapor equilibrium study, an equation of state must exhibit a critical point and a liquid-vapor dome. The critical point of the Flory equation was computed by combining (1) with the conditions:

$$\frac{\partial \tilde{P}}{\partial \tilde{V}} = 0 \quad \text{and} \quad \frac{\partial^2 \tilde{P}}{\partial \tilde{V}^2} = 0 \qquad (2)$$

The simultaneous solution of these three equations resulted in the dimensionless values at the critical point shown in the first column of Table 2. The second column shows the Flory values of P^*, V^*, and T^* in the units shown at the right. From these values the critical point may be computed. It will be noted that Flory's values which were not meant to fit the critical are reasonably close to the experimental values for the critical. A slight adjustment of the reducing parameters permits correct fitting at the critical point.

However, a liquid-vapor equation will have to fit the vapor at low pressures. This requires that the perfect gas law should hold among the reducing parameters

$$V^* = RT^*/P^* = 51.2 \text{ cc./g.-mole} \qquad (3)$$

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This will give a critical volume nearly double the experimental.

In addition to fitting at the critical, a two-phase equation of state, in the sense that the term is used here, refers to a group of algebraic expressions connecting the saturated liquid and vapor values. These expressions are all obtained by differentiating a single characteristic equation of state. One of the interesting features of the Flory equation is that these expressions are readily developed. At the vapor pressure of the pure component, the Maxwell equal area rule requires that the integral $\int PdV$ should equal the product of pressure and volume change on condensation.

$$P^0\,(V_g - V_1)$$

$$= P^*V^*\left[3\,\tilde{T}\,\ln\left(\frac{\tilde{V}_g^{1/3} - 1}{\tilde{V}_1^{1/3} - 1}\right) + \frac{1}{\tilde{V}_g} - \frac{1}{\tilde{V}_1}\right] \qquad (4)$$

Matching chemical potentials results in formula (4) also. The latent heat L may be derived from the expression for enthalpy.

$$H = \int_v^\infty \left[P - T\left(\frac{\partial P}{\partial T}\right)_v\right] dV + PV + Ne^0$$

$$L = H_g - H_1$$

$$= P^*V^*\left[\left(\frac{1}{\tilde{V}_1} - \frac{1}{\tilde{V}_g}\right) + \tilde{P}\,(\tilde{V}_g - \tilde{V}_1)\right]$$

Combining with the expression for Maxwell rule, it becomes

$$L = P^*V^*\;3\,\tilde{T}\,\ln\left(\frac{\tilde{V}_g^{1/3} - 1}{\tilde{V}_1^{1/3} - 1}\right) \qquad (5)$$

Figures 1, 2, and 3 show the result of combining Equations (1), (4), and (5) and computing the vapor pressure, latent heat, and implied saturation volumes in the dome. In making these plots the adjusted values of $P^* = 2580$, $T^* = 1609$ and $V^* = 51.2$ were used. Figure 1 shows the computed vapor pressure as against the literature value. Although P^* and T^* were chosen to make the pressure correct at the critical point, the vapor pressure at lower temperatures is reasonably close to the literature values and its locus shows very little curvature with respect to the inverted temperature scale and is fairly straight. At this point the equation gives promise of computing vapor pressure after further adjustments.

Table 1. Characteristic Constants of the Flory Equation

	P^*, atm.	V^*, cc./g.-mole	T^*, °K.
Methane	2,820	28.88	1,693
Nitrogen	2,490	26.0	1,126

Table 2. Critical Point of Methane by Flory Equation

	$\tilde{P}c, \tilde{V}c, \tilde{T}c$	P^*, V^*, T^*	Computed Pc, Vc, Tc	Experimental Pc, Vc, Tc	Adjusted P^*, V^*, T^*
P	0.017758	2820	50.04	45.8	2,580 atm.
V	3.5831	28.88	103.5	98.72	27.6 cc./g.-mole
T	0.11875	1693	201	191.06	1,609 °K.

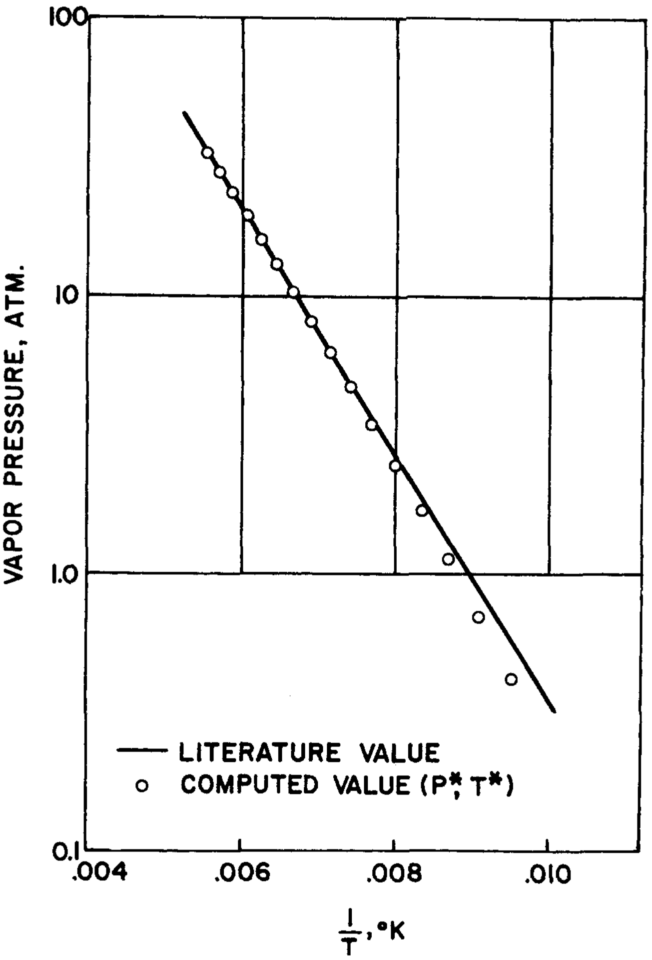

Fig. 1. Vapor pressure of methane.

The latent heats on Figure 2 for the adjusted P^*, T^* values show that the latent heat disappears at the critical and has approximately the right shape, but is entirely too large.

The saturation volumes shown on Figure 3 are too large to be acceptable by any standards. As all the thermodynamic functions are related to the volume or the derivatives of it, a good fit on the volumetric behavior is a prime requisite. So some modification of the equation is required. Of course, here the equation is being applied to the low-pressure gas region so far away from the liquid region originally intended. This equation has successfully correlated the properties of liquids and their solutions. Our interest is in the area of phase equilibrium correlation, for which an equation good for both phases is essential. It is usually more difficult to develop a satisfactory equation for the liquid phase than the vapor phase, so we thought perhaps it might be easier to use this equation as a starting point and try to extend it to the vapor phase.

THE MODIFIED FLORY EQUATION

It is clear that with restrictive condition (3) among the parameters for the perfect gas law, the original equation with three independent parameters will be reduced to a two-parameter equation. As we know, a two-parameter equation is not quite adequate enough as a basis for a generalized correlation. So the Flory equation is general-

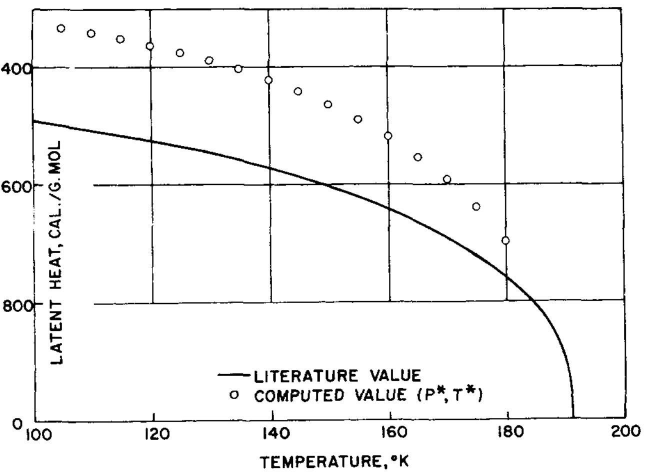

Fig. 2. Latent heat of methane.

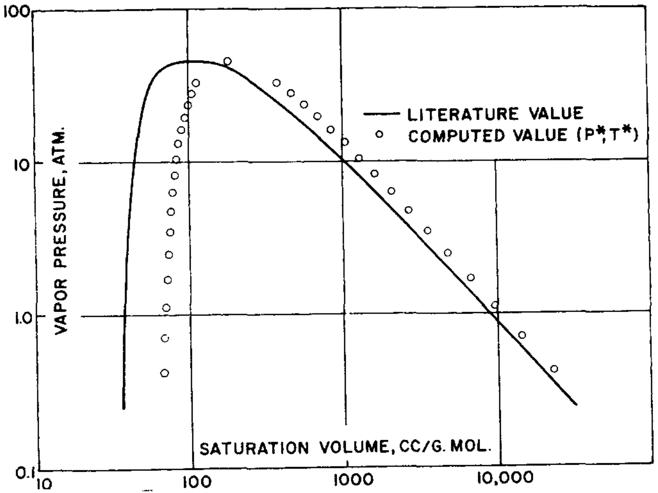

Fig. 3. Saturation PVT relation of methane.

ized with its exponential indices changed into adjustable parameters (*m*, *n*) and the relationship between the parameters for fulfilling certain basic requirements studied. The modified Flory equation now appears as follows:

$$\tilde{P} = \frac{\tilde{T}}{\tilde{V} - \tilde{V}^m} - \frac{1}{\tilde{V}^n} \qquad (6)$$

This form is convenient because the new expressions involving *V*'s are easily integrable and amenable to analysis.

$$\int \frac{dV}{V - V^m} = \frac{1}{(1-m)} \ln \left(V^{1-m} - 1\right)$$

$$-\int \frac{dV}{V^n} = \frac{1}{(n-1)} \frac{1}{V^{n-1}}$$

The immediate effect of making *m* and *n* adjustable was the ability to improve almost any property while sacrificing the computed values for some other property. After a rather lengthy trial and error period, it was noticed that adjusting *m*, *n*, P^*, and T^* permitted one to obtain correct values for the critical pressure, the critical temperature, the normal boiling point temperature, and the latent heat at the normal boiling point. Furthermore it was noticed that this choice sacrificed some volume accuracy in the neighborhood of the critical and very little else.

Figure 4 shows that the vapor pressure of methane is predicted as closely as can be plotted by the modified equation. It is not surprising that the pressure at the critical point is exact, because P^* and T^* were chosen to make it so, nor that the normal boiling point temperature is exact because *n* and *m* were chosen to make it so. But the agreement along the length of the curve seems to be at least a fortuitous consequence of the form of the Flory equation. A correct vapor pressure at every point implies that the slope of the vapor pressure curve is also moderately good. The Clausius-Clapeyron equation states that the slope of vapor pressure equation is proportional to the ratio of latent heat to change in volume on condensation. Since no volumes and only one latent heat are used in establishing this equation, it is indeed fortuitous that the proper ratio of these two quantities exists at all temperature levels.

Note also the dotted extension of the vapor pressure curve above the critical point in Figure 4. This is the slope of the critical isochore as computed from the equation:

$$\left(\frac{\partial P}{\partial T}\right)_{V_c} = \frac{R}{V_c\left[1 - \left(\frac{V^*}{V_c}\right)^{1-m}\right]}$$

The slope of the critical isochore should match the slope of the vapor pressure curve at the critical point in order to conform with the behavior of real gases. This slope has been proposed by some investigators as a possible choice for the third parameter according to the corresponding state principle.

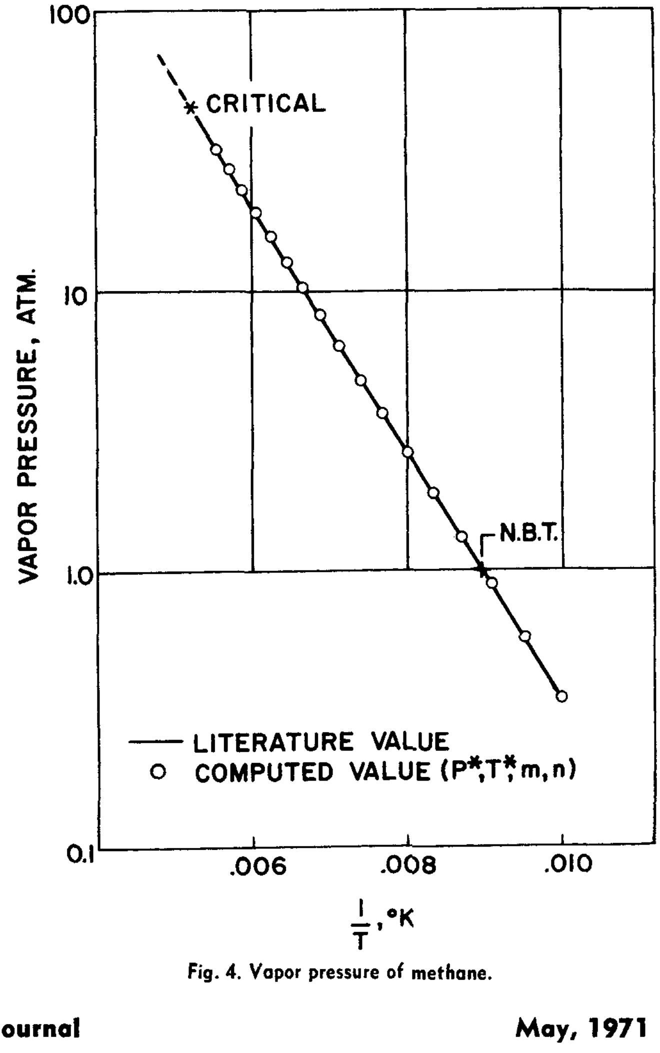

Fig. 4. Vapor pressure of methane.

The latent heat for methane as computed from the modified equation is shown in Figure 5. The constants n and m have been chosen so that the proper latent heat is computed at the normal boiling point. An excellent description of the latent heat is obtained over about half the temperature range. Again this demonstrates that the Flory form of equation is well-suited to two-phase work.

The saturation dome for methane is shown in Figure 6. The good fit in volume along the saturated vapor line is most gratifying. Since no volumetric data were used in the fitting, it shows that the modified Flory equation really describes the *PVT* relationship of the vapor phase quite well. The agreement in liquid volumes in the neighborhood of the critical point is qualitative rather than quantitative but improves as the pressure falls. Because of the logarithmic scale, the error in the liquid volume is exaggerated on this plot. At 10 atm. the very visible deviation in liquid volume corresponds to only 0.4 of 1% of the difference in volume between phases.

This demonstration that the Flory equation leads to a good, simple description of the two-phase region can be regarded as a triumph of statistical thermodynamics. Thirty years ago Eyring and Hirschfelder developed this form of equation as a consequence of the free volume theory of liquids (*6* to *8*). In recent years Flory has modified the equation for special molecular shapes. The Flory name has been used here because his recent articles led to this investigation.

THERMODYNAMIC FUNCTIONS OF THE MODIFIED FLORY EQUATION

The thermodynamic functions of the modified Flory equation are obtained by integrating with respect to volume at constant temperature, and adding reference pressure properties as constants of integration as detailed by Beattie (*9*).

$$P = \frac{NRT}{V\left[1 - \frac{1}{\tilde{V}^{1-m}}\right]} - \frac{NRT^*}{V\tilde{V}^{n-1}} \qquad (7)$$

$$A = \frac{NRT}{(1-m)} \ln \frac{\tilde{V}^{1-m}}{\tilde{V}^{1-m} - 1} - \frac{NRT^*}{(n-1)\tilde{V}^{n-1}} - NRT \ln \frac{V}{NRT} + N(e^0 - Ts^0) \qquad (8)$$

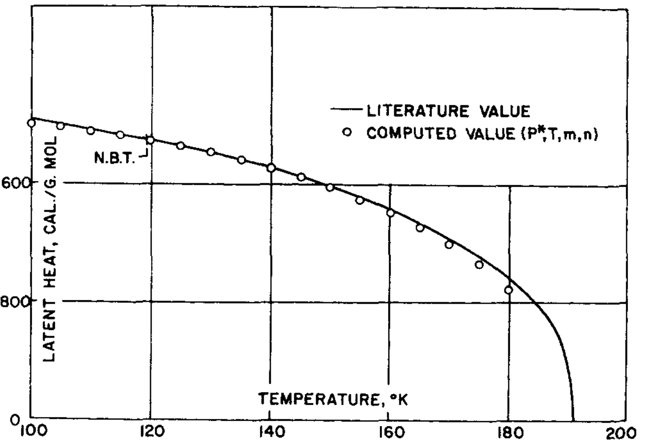

Fig. 5. Latent heat of methane.

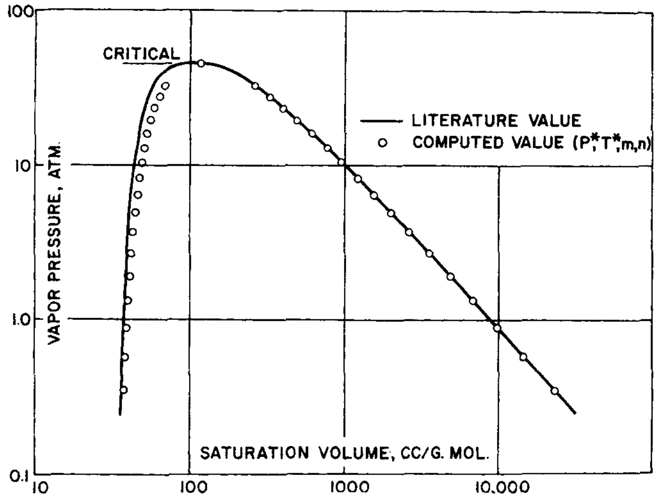

Fig. 6. Saturation PVT relation of methane.

$$H = \frac{NRT\,\tilde{V}^{1-m}}{(\tilde{V}^{1-m} - 1)} - \frac{n}{(n-1)} \frac{NRT^*}{\tilde{V}^{n-1}} + Ne^0 \qquad (9)$$

$$S = \frac{NR}{(1-m)} \ln \left[1 - \frac{1}{V^{1-m}}\right] + NR \ln \frac{V}{NRT} + Ns^0 \qquad (10)$$

The first equation is the pressure equation (7) in its dimensional form. The second equation gives the Helmholtz free energy at constant volume. When the free energy at constant volume is expressed in terms of V and T as it is here, it is the characteristic equation for these dimensions, and all other properties may be obtained from it by differentiation and algebraic rearrangement. This equation permits a check on the listed equations since $A = H - TS - PV$.

Enthalpy values are needed for process heat balances and form a part of any table of properties. Entropy values serve two purposes—they are necessary in processes which contain compressors and expanders, and they are part of the equation of state system which is used for vapor pressure evaluation. The $\Delta H - T\Delta S = 0$ condition is another way of expressing equal chemical potentials, or the Maxwell equal area rule $\int PdV = P^0 \Delta V$ across the dome. The important thing to notice now is that these equations P, A, H, and S are assembled from simple functions whose values are readily evaluated by slide rule or by computer.

If it were also possible to express the vapor pressure directly in terms of V, T by rearrangement of the characteristic equation, the whole course of liquid vapor equilibrium calculations would have been standardized on a thermodynamically consistent basis many years ago. But unfortunately the vapor pressure of pure substances and the partial pressures of mixtures can be calculated from an equation of state only with the help of an electronic computer.

To use the equation for computing thermodynamic properties at a given temperature and pressure, first we compute the volume. This is solved iteratively because the equation of state is implicit in volume. For temperature below that of the critical, there are three possible solutions of volume for a given pressure; and we have to choose one for the vapor phase and one for the liquid phase. The isotherm of the equation bears a close resemblance to the van der Waals equation and is very well behaved. The other thermodynamic functions, such as the Helmholtz function and the enthalpy and the entropy values, can then be evaluated from the computed volume. The calculation of vapor pressure is a little bit more complex as the pressure is also unknown here and it involves a double iteration procedure with the Maxwell equal area rule as the additional criteria for closure.

CONSTANT FINDING PROCEDURE

The basic requirements for a two-phase equation of state are

1. Perfect gas law at low pressure
2. Critical criteria—that the first and the second derivatives of P with respect to V should be zero at the critical isotherm
3. The vapor pressure and the Maxwell equal area rule
4. The relationship of temperature and saturation densities to the latent heat of vaporization

These requirements may be expressed mathematically by eight simultaneous equations.

The first step in constant finding is to rearrange the conditions at the critical point which are written:

$$\tilde{P}_c = \frac{\tilde{T}_c}{\tilde{V}_c - \tilde{V}_c^m} - \frac{1}{\tilde{V}_c^n} \qquad (11)$$

$$\left.\frac{\partial \tilde{P}}{\partial \tilde{V}}\right|_c = \frac{-\tilde{T}_c\,(1 - m\,\tilde{V}_c^{m-1})}{(\tilde{V}_c - \tilde{V}_c^m)^2} + \frac{n}{\tilde{V}_c^{n+1}} = 0 \qquad (12)$$

$$\left.\frac{\partial^2 \tilde{P}}{\partial \tilde{V}^2}\right|_c = \frac{\tilde{T}_c(\tilde{V}_c - \tilde{V}_c^m)\,m(m-1)\,\tilde{V}_c^{m-2} + 2\tilde{T}_c(1 - m\tilde{V}_c^{m-1})^2}{(\tilde{V}_c - \tilde{V}_c^m)^3} - \frac{n(n+1)}{\tilde{V}_c^{n+2}} = 0 \qquad (13)$$

These three equations involve $\tilde{P}_c$, $\tilde{T}_c$, $\tilde{V}_c$, and m and n. Whenever trial values of m and n are chosen, values of the other three can be found. In particular $\tilde{P}_c$ occurs only in Equation (11), and that equation may be set aside as the definition of $\tilde{P}$. Equation (12) may be rearranged to be explicit in $\tilde{T}_c$:

$$\tilde{T}_c = \frac{n}{\tilde{V}_c^{n+1}} \; \frac{(\tilde{V}_c - \tilde{V}_c^m)^2}{\left(1 - \dfrac{m}{\tilde{V}_c^{1-m}}\right)}$$

For convenience we now write

$$x = \tilde{V}_c^{1-m}$$

so that

$$\tilde{T}_c = \frac{\tilde{V}_c^2\,(1 - 1/x)^2}{(1 - m/x)} \cdot \frac{n}{\tilde{V}_c^{n+1}} \qquad (14)$$

Substitution of this value of $\tilde{T}_c$ in Equation (13) leads to a quadratic for x in terms of m and n.

$$(n-1)x^2 - [n + 1 - (4-n)m + m^2]\,x + m(n-m) = 0 \qquad (15)$$

Trial values of m and n are selected; the quadratic yields two values of x. The larger value has been found useful; it is back substituted in (14) and (11) to develop values $\tilde{V}_c$, $\tilde{T}_c$, and $\tilde{P}_c$.

Since P_c and T_c are known

$$P^* = P_c/\tilde{P}_c$$

$$T^* = T_c/\tilde{T}_c$$

$$V^* = RT^*/P^*$$

At this point the trial set of values m and n has been expanded to a trial set P^*, V^*, T^*, m, and n. This set of five trial values is taken to the equations to compute the vapor pressure and latent heat at normal boiling point (or other reference temperature).

$$P^0(V_g - V_l) = P^*V^*\left[\frac{\tilde{T}}{(1-m)}\ln\left(\frac{\tilde{V}_g^{1-m} - 1}{\tilde{V}_l^{1-m} - 1}\right) + \frac{1}{n-1}\left(\frac{1}{\tilde{V}_g^{n-1}} - \frac{1}{\tilde{V}_l^{n-1}}\right)\right]$$

$$L = \frac{RT}{(1-m)}\ln\left(\frac{\tilde{V}_g^{1-m} - 1}{\tilde{V}_l^{1-m} - 1}\right)$$

Generally the computed vapor pressure and latent heat values derived from a pair of assumed m and n values will not match the experimental values on the first try. So the problem of the constant finding reduces to that of a double iterative procedure to find a unique pair of m and n values such that both the vapor pressure and the latent heat values are matched at a chosen temperature. This is a four-parameter equation, namely, m, n, P^*, and T^*. V^* is not an independent parameter through the perfect gas law condition that $V^* = RT^*/P^*$. The conditions for the fitting are the critical temperature, the critical pressure, the

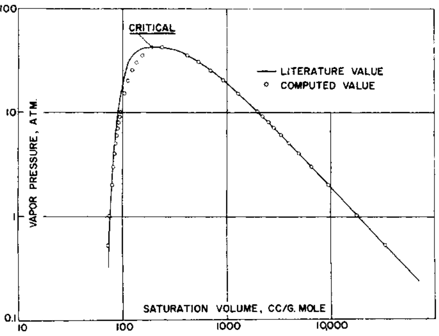

Fig. 7. Saturation PVT relation of propane.

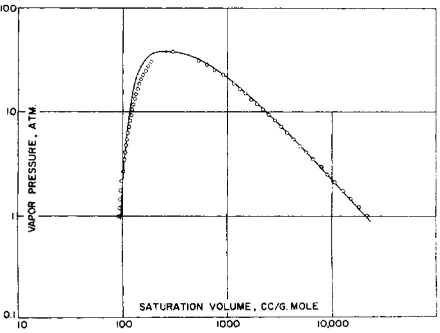

Fig. 8. Saturation PVT relation of n-butane.

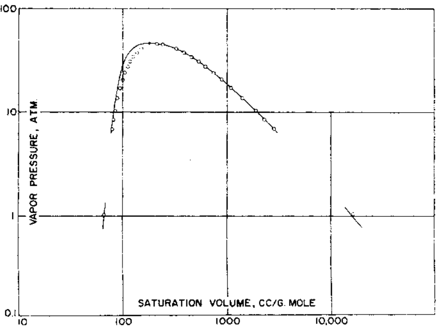

Fig. 9. Saturation PVT relation of propylene.

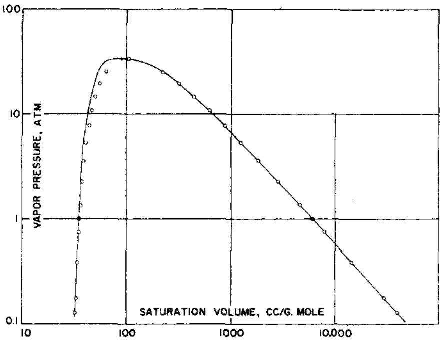

Fig. 10. Saturation PVT relation of nitrogen.

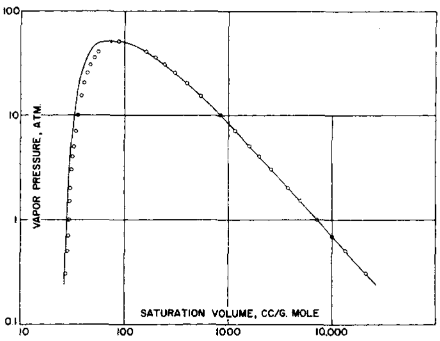

Fig. 11. Saturation PVT relation of oxygen.

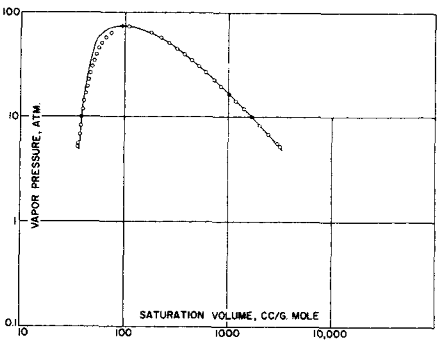

Fig. 12. Saturation PVT relation of carbon dioxide.

vapor pressure at a reference temperature, and its latent heat at the same temperature. Just enough parameters for the number of the conditions and a unique set of the constants exist for a substance characterized by these four physical properties. The vapor pressures at the other intermediate temperatures are expected to fit well since the fit on latent heat fixes the slope of the vapor pressure curve through the Clausius-Clapeyron equation. The real test of the fitting, and of the adequacy of the form of the equation as well, lies in the fitting of the volume, since no volumetric data was used at all during the fitting. Table 3 lists the constants for nitrogen, oxygen, argon, carbon monoxide, carbon dioxide, methane, ethane, propane, *n*-butane, ethylene, and propylene. The physical properties from which the constants were derived are also listed together with the computed value of critical volume and critical compressibility. Any tie line data can be used in place of the normal boiling temperature, pressure and latent heat. The easy-to-find values have been emphasized here. Figures 6 to 12 present the volumetric fitting along the saturated vapor and liquid lines of methane, propane, *n*-butane, propylene, nitrogen, oxygen, and carbon dioxide. The plots are quite typical.

DISCUSSION

The authors use four readily measurable properties for constant finding. Traditionally, simple reduced equations

TABLE 3. THE CONSTANTS FOR THE MODIFIED FLORY EQUATION

	Nitrogen	Oxygen	Argon	CO	CO_2
P^* [‡]	49.99228	72.28351	65.91794	52.78804	154.2602
V^*	25.14978	21.24442	22.59613	26.14825	22.10907
T^*	632.7004	772.7607	749.5464	694.6069	1716.268
m	0.5008157	0.4920340	0.4775940	0.5235088	0.6095532
n	1.789820	1.801860	1.822936	1.794644	1.702716
Based on					
Tc	126.26	154.780	150.860	132.88	304.20
Pc	33.54	50.150	48.340	34.53	72.85
Tb	80.00	90.198	87.285	81.62	223.16
P°	1.349	1.000	1.000	1.000	6.747
L	1310.9	1635.1	1552.85	1443.6	3547.7
Computed Vc	105.89	87.836	90.64	110.53	110.89
Computed Zc	0.3428	0.3468	0.3539	0.3500	0.3236

	Methane	Ethane	Propane[†]	*n*-Butane	Ethylene	Propylene[†]
P^* [‡]	63.69156	82.26552	77.7785	76.98645	83.2957	82.44835
V^*	28.85141	38.76326	51.08209	61.31161	35.68593	45.47427
T^*	924.7192	1604.719	1999.351	2375.298	1495.824	1886.725
m	0.4705245	0.5457211	0.5727378	0.6014671	0.5427728	0.5528042
n	1.804861	1.756898	1.733821	1.709659	1.769146	1.726180
Based on						
Tc	191.06	305.50	(370.0)	425.17	283.06	(365.1)
Pc	45.80	48.50	(41.898)	37.47	50.5	(45.2)
Tb	115.00	184.52	275.24	272.66	169.45	293.72
P^o	1.319	1.00	5.00	1.00	1.00	10.166
L	1933.4	3517.00	3929.0	5351.34	3238.53	3400.0
T_2			317.42			343.49
P_2			15.00			30.62
Computed Vc	117.82	173.75	239.63	302.81	157.17	213.45
Computed Zc	0.3442	0.3362	0.3307	0.3252	0.3417	0.3220

[†] A variation of the fitting method was used where the constant sets were determined by the vapor pressures at two boiling temperatures and one latent heat value. The numbers in the parenthesis are the computed Tc and Pc values at the point of inflection on the critical isotherm. The experimental Tc, Pc values are 370.0°K. and 42.1 atm. for propane (F. Din, Vol. 2) and 365°K. and 45.4 atm. for propylene (API Project 44).

[‡] P^*, cal./cc. To convert: (P^*, cal./cc.) 82.0567/1.98719 = (P^*, atm.).

of state have been presented in terms of critical temperature and critical pressure. Later investigations indicate that a third parameter is required. The early attempts use the critical compressibility as the third parameter. The more recent attempts use properties associated with the vapor pressure curve as third parameter; among these may be mentioned Riedel's modulus α, Martin and Hou's slope M, and Pitzer's acentric factor ω. The authors have extended the reduced parameter from critical temperature and critical pressure to include vapor pressure and latent heat. It has been shown through the analysis that the vapor pressure and latent heat are readily related to the various terms of the equation.

Normally the constants for the equation are fitted from PVT data. This equation is fitted on PTH data. Enthalpy is of course related to the slope of the PVT surface through the enthalpy expression. If one is fortunate enough to start with a reduced equation of reasonably good form, then the process of determining the constants can be vastly simplified. The data on vapor pressure and latent heat are generally available. In contrast, accurate PVT data with the necessary range are scarce and great effort and skill are needed for its determination. This study tries to present an equation of simple form fitted only with the most important parameters in terms of corresponding state principle, and to see if this is adequate for general engineering applications.

NOTATION

A = Helmholtz free energy
e^0 = molal internal energy for pure gas at temperature T and reference pressure
H = enthalpy
L = latent heat
m = constant, dimensionless
n = constant, dimensionless
N = number of moles
P = pressure, atm.
P^0 = vapor pressure, atm.
P^* = characteristic pressure, cal./cc. or atm. (P^*, cal./cc.) 82.0567/1.98719 = (P^*, atm.)
$\tilde{P}$ = reduced pressure, dimensionless = P/P^*
R = universal gas constant, 1.98719 cal./g.-mole, or (82.0567 cc.) (atm.)/g.-mole
S = entropy
s^0 = molal entropy for pure gas at temperature T and reference pressure
T = temperature, °K.
T^* = characteristic temperature, °K.
$\tilde{T}$ = reduced temperature, dimensionless = T/T^*
V = volume, cc.
V^* = characteristic volume, cc./g.-mole
$\tilde{V}$ = reduced volume, dimensionless = V/NV^*
x = $\tilde{V}^{1-m}$
Z = compressibility factor = PV/RT

Subscripts

b = boiling point
c = critical point
g = saturated vapor phase
l = saturated liquid phase
2 = second reference temperature

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II. Mixtures

A four-parameter reduced equation of state was extended to interpret multicomponent phase equilibrium behavior. The equation with the exponential combination rule succeeded in correlating the nitrogen-methane system but failed in propylene-propane system. The combination rule seems to be a function of the nature of the system. It is felt that binary interacting constants are needed to interpret the mixture behavior.

The following equation of state for the phase equilibrium was described in an earlier paper (*1*) as it applied to pure methane.

$$\tilde{P} = \frac{\tilde{T}}{\tilde{V} - \tilde{V}^m} - \frac{1}{\tilde{V}^n} \qquad (1)$$

where

$$\tilde{P} = \frac{P}{P^*}$$

$$\tilde{V} = \frac{V}{NV^*}$$