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ABSTRACT

PART ONE

An equation of state has been developed which is a series expansion in orthogonal polynomials. The evaluation of coefficients by least squares methods is significantly simpler than for the case of a power series expansion. The values of the expansion coefficients are independent of the point of truncation of the series. Additional terms may be added to the equation without necessitating recomputation of existing coefficients. The Tchebichef and Gram polynomials were used.

The equation of state has been applied to propane for pressures up to 10,000 psia in the temperature interval 100° to 460° F. Terms involving eighth and higher powers of reciprocal molal volume were found not to contribute significantly to the description. The equation predicts volumetric behavior, phase behavior, thermodynamic properties, the critical state, and the second virial coefficient with an accuracy that is promising. Limited experience in application indicates that the equation is easier to handle with automatic digital computing equipment than is the Benedict equation of state.

PART TWO

Values of the coefficients for the Benedict equation of state were determined by least squares methods from experimental data for each of a series of mixtures of the methane-n-pentane system. In addition, values were obtained for the interaction constants for groupings of the Benedict coefficients corresponding to the second and third virial coefficients. Corresponding values of the interaction constants predicted by the methods suggested by Benedict are included for comparison. Measures of the accuracy of description for the interaction constants determined by the several different methods are reported.

Interaction constants were evaluated by least squares methods for the methane-n-pentane system in the liquid and gas phases at pressures up to 5,000 pounds per square inch in the temperature interval between 100° and 460° F. The accuracy of description of the volumetric behavior was improved severalfold over that obtained with the constants calculated from the behavior of the components by the method suggested by Benedict. Such methods may prove useful in evaluating interaction constants for mixtures as a function of the characteristics of the system involved.

PART THREE

The isobaric heat capacity at bubble point of n-decane was determined in the temperature interval 80° to 200° F. Measurements were made in the two-phase region utilizing a constant-volume calorimeter. The energy required to change the temperature of the calorimeter and contents was determined for each of two quantities of n-decane. The effect of the gross heat capacity of the bomb was eliminated by considering the difference of these two sets of measurements. The two-phase isochoric measurements were transformed to values of the isobaric heat capacity at bubble point by applying a thermodynamic correction involving the volumetric properties of the gas and liquid phases and the heat capacity of the gas phase.

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PART ONE

PART ONE. AN ORTHOGONAL POLYNOMIAL EQUATION OF STATE

I. INTRODUCTION

J. D. van der Waals proposed his now famous equation of state in 1899 (1). His was apparently the first recorded attempt to present an analytical expression which would account for the departure from perfect gas behavior of the pressure-volume-temperature behavior of fluid systems. Since van der Waals' contribution, over one hundred investigators have reported equations of state of varying degrees of complexity and utility (2).

These continuing attempts reflect both the need for an acceptable equation, and, unfortunately, the fact that none of these proposals has been entirely successful. Some were intended only for use in localized regions of the PVT surface. Others purported to describe the surface over extended ranges of pressure and temperature but failed to give quantitative description of the volumetric and phase behavior over the extended range. Particular difficulties have been encountered in attempts to develop expressions that would successfully cope with the two phase region and describe the continuous transition from liquids to gases in the vicinity of the critical state.

No attempt will be made in the present writing to review the extensive previous work in this field. The reader who is interested in detailed discussions of the origin and application of a variety of equations of state is referred to the thorough review article by Beattie and Stockmayer (3) or to the books of Hirschfelder (4) and Taylor and Glasstone (5).

The type of mathematical surface with which the present investigation is concerned is shown in Figure 1, which has been constructed from data for propane near the critical state. Projection of this surface onto the pressure-volume plane is given in Figure 2. The boundary of the two phase region and the critical state have been indicated. In addition to the actual isotherms, this figure also shows in the two-phase region continuous curves of the type given by equations of state such as the van der Waals, Beattie-Bridgeman, and Benedict-Webb-Rubin. These two figures show a part of the PVT surface which usually affords a major portion of the difficulties in attempting to find an acceptable equation of state. At temperatures and pressures progressively higher than those of the critical state, the curves are usually well behaved.

The present investigation was primarily concerned with pressures up to 10,000 psia and temperatures from 100° F. to 460° F. We shall tacitly assume in subsequent discussions that temperatures are neither so low that quantum effects are significant, nor so high that a problem in chemical dissociation is involved. For present purposes solid phases will also be excluded. Primary emphasis will be on one component systems, for which a thermodynamically acceptable equation of state must specify the interdependence of three intensive (or derived intensive) variables. The three chosen are pressure, temperature, and molal volume (or its reciprocal).

At temperatures sufficiently high and pressures sufficiently low, the perfect gas law expresses volume as a function of temperature and pressure with an accuracy adequate for many engineering computations. It has no quantitative value except for reference purposes for liquids and for gases at moderate pressures below the critical temperature. Even at infinite attenuation, the perfect gas law does not predict the correct interrelation of several thermodynamic quantities which are dependent on volumetric derivatives.

The van der Waals equation (1,3), involving two parameters in addition to the universal gas constant, can be used to give a fairly satisfactory representation of the volumetric behavior of gases at low pressures over a short temperature range, provided that the values of the parameters are determined from the data in the region of interest. Below a certain temperature, the isotherms of the van der Waals equation go through local minimum-maximum reversal of which the dotted line of Figure 2 would be typical. At one certain temperature, there exists a volume at which the first and second derivatives of pressure with respect to volume at constant temperature are both zero. Hence this equation of state at least qualitatively predicts a two phase region and a critical state. Unfortunately for real substances the description is not quantitative.

The Beattie-Bridgeman equation of state (6,7) involves five parameters in addition to the universal gas constant. It gives a satisfactory representation of the compressibility of non-polar gases and a fair representation for most polar gases from low densities up to about the critical density. Like the van der Waals equation, it predicts qualitatively a liquid phase and a critical state but fails to yield a quantitative description of these phenomena.

Benedict, Webb, and Rubin (8,9,10,11,12) proposed an extension of the Beattie-Bridgeman equation involving eight parameters in addition to the universal gas constant. Unlike the Beattie-Bridgeman equation, the Benedict equation is not linear in the parameters but involves an exponential term, which considerably increases the complexity of application. However this equation is noteworthy in that it has been successful in quantitatively describing phase behavior and a critical state. These phase behavior predictions have included satisfactory description of the composition and partial thermodynamic properties of coexisting phases in multicomponent systems. The coefficients that Benedict has reported for this equation for a variety of substances (9,10,11) have been largely evaluated from data in the low and moderate pressure regions. Brough, Selleck, Opfell, Pings, and Sage (13,14,15,16,17) have reported coefficients based on data extending to pressures of 10,000 psia. With these latter coefficients this equation of state does not quantitatively describe the phase behavior and the critical region. A conclusion derived from these latter investigations is that the Benedict equation can be used either for volumetric description over an extended range or for both volumetric and phase behavior descriptions up to moderate pressures. The Benedict equation of state apparently is not the answer to the quest for an equation which describes both volumetric and phase behavior over extended ranges of temperature and pressure. Furthermore, it appears fair to state that at the time of writing none of the equations of state of closed form has been successful in obtaining this objective.

II. THE VIRIAL EQUATION OF STATE

Developments of new equations of state, of which those mentioned in the preceding paragraphs are typical, have usually involved the expression of compressibility factor as a polynomial in successively higher terms in reciprocal molal volume. The van der Waals equation is approximately linear in reciprocal volume; the Beattie-Bridgeman, cubic; and the Benedict, fifth power plus an exponential term. The increasing success of these equations suggests that a useful relationship might be obtained if pressure were expressed as a formal power series in reciprocal molal volume with temperature-dependent coefficients. As a matter of fact as early as 1901, Kamerlingh Onnes and his co-workers (18) were using expressions of the following form to represent the compressibility of gaseous systems.

$$\frac{PV}{RT} = Z = 1 + B(T)\frac{1}{V} + C(T)\frac{1}{V^2} + ----- \tag{1}$$

This infinite series in 1/V is commonly known as the virial equation of state, and B(T), C(T) ---- are the second, third ---- virial coefficients, which as indicated are functions of temperature. The series converges uniformly to Z within the circle about the origin of 1/V which is free of singularities of Z (19,20).

The virial equation of state has attracted much interest for two reasons. The first was mentioned previously: many successful empirical equations have had the form of the partial sums of a power series. The second is that statistical mechanical analysis of molecular models has resulted in successful prediction of values of the first several virial coefficients.

The designation "virial" equation of state for this series is not particularly appropriate. The association apparently arose from the natural use of the virial theorem of classical mechanics in one possible derivation (4). The same power series may be obtained without employing the virial theorem as such. Also, the analysis based on the virial theorem might culminate in some other type of infinite series expansion. Although the designation "power series equation of state" might be more satisfactory, the present writing will generally adhere to the entrenched convention, except in those cases where a definite distinction is necessary.

As mentioned, a number of the existing equations of state may be regarded as truncated forms of the virial equation. To take a specific example, the Beattie-Bridgeman equation may be written in the following form (3):

$$\frac{PV}{RT} = 1 + \left(B_0 - \frac{A_0}{RT} - \frac{c}{T^3}\right)\frac{1}{V} + \left(-B_0 b + \frac{A_0 a}{RT} - \frac{B_0 c}{T^3}\right)\frac{1}{V^2} + \frac{B_0 b c}{T^3}\frac{1}{V^3} \tag{2}$$

In this case the following identifications may be made:

$$B(T) = \left(B_0 - \frac{A_0}{RT} - \frac{c}{T^3} \right) \tag{3}$$

$$C(T) = \left(-B_0 b + \frac{A_0 a}{RT} - \frac{B_0 c}{T^3} \right) \tag{4}$$

$$D(T) = \frac{B_0 b c}{T^3} \tag{5}$$

$$E(T) = F(T) = \cdots = 0 \tag{6}$$

When equations of closed form are grouped so that they may be directly compared with the virial expansion, it is possible to deduce from the theoretical model some definite limitations of any given equation. To be precise, it is worth noting in the case above that the temperature dependence of the second virial coefficient has been definitely specified in terms of three parameters. Although the theory of intermolecular attractions is not precise, it does indicate that the temperature dependence of the virial coefficients should be of a different nature for different types of molecular species. In a given temperature range, a relation of the type given in equation 3 may be quite adequate for describing the temperature dependence of non-polar, nearly spherical molecules. In the same temperature interval, however, several more parameters may be necessary to describe the temperature dependence of the second virial coefficient of a polar or oblate molecule. As a matter of fact, the Beattie-Bridgeman equation is less successful in describing polar gases than it is for non-polar substances (3). In addition there is no a priori reason why the parameters of the successive virial coefficients should be interrelated as they are in the above example.

For temperatures below the critical, the power series expansion of equation 1 will represent the compressibility factor only up to the value of 1/V corresponding to the dew point. In terms of Figure 2, a power series representation may be found for the portion LD of the HBGDL isotherm. The same power series about the origin of 1/V will not converge to the horizontal portion BGD of this isotherm. If it should happen that the gas and liquid isotherms both have the same analytic continuation into the two-phase region, then it would be possible to represent the gas phase, liquid phase, and their mutual continuations by one power series about the origin. Such a continuation might have the appearance of the dotted line of Figure 2. If this continuation into the two-phase region satisfies certain thermodynamic differentiation and integration restraints, then a power series could be found which describes correctly both the volumetric and phase behavior of fluid systems.

These restrictions on the two-phase continuation are stringent. The author is not aware of any study which would insure that these requirements may be satisfied. However even if power series representation is not possible, the Weierstrass theorem (Appendix A) indicates that the non-analytic isotherms can be uniformly approximated by polynomials.

The success that has been attained with empirical equations of state which resemble the partial sums of the virial series might suggest that the answer to the search for an acceptable equation of state is to use open-ended polynomials in temperature and reciprocal molal volume with the truncation being made when sufficient terms have been included to reduce the approximation error to an acceptable level. This procedure is in principle a sound one. However real difficulties are encountered in attempts to evaluate the parameters from experimental data. The problem is sufficiently fundamental that it merits some discussion.

Consider any smooth pressure-volume isotherm of the type HBCFDL shown in Figure 2. There exists a power series representation of pressure as a function of the volume of the type of equation 1. Suppose now that the series is truncated after n terms and that it is desired to evaluate the parameters in the resulting n'th degree polynomial from experimental PV data. In principle the virial coefficients could be obtained by evaluating the successive derivatives of the experimental data at the origin, $(V)^{-1} = 0$. However the limitations of graphical and numerical differentiation are such that this procedure would be virtually worthless for third and higher derivatives. Consequently the method usually employed in such circumstances for evaluating the coefficients is either to fix the intercepts at n selected points or to use a procedure such as the method of least squares. Unfortunately the numerical coefficients obtained by the latter means are not in general the power series values. For example if, instead of an n term polynomial, an n + 1 term polynomial were employed, value obtained for the coefficient of any of the lower powers would be different, and furthermore neither would in general be equal to the value obtained in the limiting case of an infinite number of terms. As a matter of fact there has recently been some question raised as to the validity of the second and third virial coefficients reported by several investigators because of the arbitrary polymomial forms employed in the analysis of experimental data (21,22).

One might question whether it is really of great concern that the coefficients obtained in any given case are not the actual power series values. In order to answer this fully some consideration must be given to the methods and problems of evaluation of these coefficients. Suppose the experimental data were being fitted with an n'th order polynomial in temperature and reciprocal volume. Whether the intercepts of the equation are fixed at n points or whether the method of least squares is employed, it is necessary to solve n equations in n unknowns. Anticipating that seven terms in reciprocal molal volume would be required and that each of the seven virial coefficients would require four constants to describe temperature dependence, it would be necessary to solve for twenty-eight unknowns. This would involve inverting an 841 element matrix. If the analysis is by least squares, it would be necessary to compute 435 unique inner products to obtain the matrix. The matrix could supposedly be solved numerically to yield explicit values for the constants. However the practical problems would likely be significant. 16 x 16 matrices are still themselves subjects for recent mathematical research (23). Experience obtained in computing the Benedict coefficients for butane (15) indicates that ill-conditioned matrices may be encountered; the misery associated with attempts to invert an ill-conditioned 28 x 28 matrix would not be insignificant.

A further obstacle is apparent: the constants once obtained are decidedly interdependent. Another arbitrary truncation, say one involving one additional term in reciprocal molal volume, would have resulted in an entirely different set of coefficients. In any given case the most efficient truncation is unknown and would presumably have to be sought empirically, with each new assumed form of the equation necessitating the inversion of a complete matrix. Furthermore it would be necessary to worry not only about the truncation of the reciprocal volume power series but also the truncation of each of the series approximating the temperature dependence of the virial coefficients. The time required for this type of investigation would be appreciable even with high speed computing equipment.

It might be pointed out further that once the coefficients had been obtained for a given polynomial approximation to the virial equation of state, the interdependence would require that the entire set of coefficients be employed for all prediction purposes. Arbitrary deletion of terms that had been included in the evaluation procedure would in general lead to significant error. Also the finite polynomial would in general be useless for extrapolation procedures.

The preceding paragraphs have explored a number of the merits of the virial equation of state. Comparison with equations of closed form seems to indicate that there is promise of success in an equation of state expressing the compressibility factor as an open-ended series of increasing powers of temperature and reciprocal molal volume. There is a complex but workable theory developed from statistical mechanics for such a series. Values for the virial coefficients are much sought after, both for their immediate application to the equation of state and for their application to studies of intermolecular attractions. Counterbalancing these advantages and incentives are the formidable computational difficulties discussed above.

It will be the objective of the present investigation to develop an equation of state that is an open-ended series in temperature and reciprocal molal volume, but which eliminates the bulk of the computational difficulties encountered with the orthodox power series expansion. Fortuitously the results will be such that the resulting equation may be regrouped into the virial form, thus maintaining the advantages of association with developed theory and at the same time presenting a powerful method for evaluating the virial coefficients.

III. THERMODYNAMICS

Independent Variables

In many of the applications of equations of state, situations frequently present temperature and pressure as independent variables, a solution being required for volume. Consequently from the viewpoint of application, it would be efficient to have an equation of state expressing volume as an explicit function of pressure and temperature. This would be quite practicable if only a gas phase were being described. However if the equation of state is to represent liquid as well as gaseous regions, the problem of crossing the two-phase region requires that the pressure be expressed as a function of the volume and temperature. This may be seen by a consideration of isotherm HBGDL of Figure 2. The coexisting phases are characterized by the existence of two values of specific volume at a specified pressure and temperature. In order to approximate the volumetric surface adequately with a reasonably small number of terms in the independent variables, it is desirable to replace the discontinuities of the two-phase region by a smooth path. In terms of Figure 2, the horizontal portion of the BGD isotherm may be replaced with the smooth curve BCFD. This process results in a surface giving pressure as a single valued function of volume and temperature. For temperatures below the critical there are two (as a matter of fact three) values of volume which correspond to the same pressure, a necessary requirement for the coexistence of phases. An equation of state consisting of a polynomial of degree greater than three may possess this necessary property of three roots in volume for a given value of pressure.

By appropriate integration restraints, the substituted smooth surface may be chosen so that it predicts correct changes in thermodynamic properties across the two-phase region. Also it might be noted that the substituted path is not entirely devoid of physical association; the portions BC and DF of the isotherm HBCFDL of Figure 2 may be regarded as representing the volumetric behavior in the unstable region. It thus appears that substitution of a smoothed surface in the two-phase domain may result in significant simplification of an equation of state expressing pressure as a function of volume and temperature.

However if one attempts to regard volume as a function of pressure (for example turn Figure 2 on its side) the substituted path results in three values of the dependent variable for certain values of pressure and temperature. Functions, if indeed the designation function is appropriate, that demonstrate this type of behavior are not simple analytically and would likely be impractical for an equation of state. In the present work, volume and temperature are regarded as the independent variables.

It is convenient to use the reciprocal of the molal volume in place of the molal volume as one of the independent variables. The symbol $\underline{\sigma}$ will be employed for reciprocal molal volume.

$$\underline{\sigma} = \underline{V}^{-1} \tag{7}$$

The Function L($\underline{\sigma}$, T)

The following expressions may be educed for several thermodynamic variables as a function of temperature and reciprocal molal volume. f is fugacity, $\underline{H}$ molal enthalpy, $\underline{S}$ molal entropy, and Z the compressibility factor.

$$\ln \frac{f}{RT\underline{\sigma}} = Z - 1 + \int_0^{\underline{\sigma}} \left(\frac{Z(\zeta, T) - 1}{\zeta} \right) d\zeta \qquad [T] \tag{8}$$

$$\frac{\underset{\cdot}{H} - \underset{\cdot}{H}^{\circ}}{RT} = Z - 1 - \int_{0}^{\underset{\cdot}{\sigma}} T \left(\frac{\partial \, \frac{Z(\xi, T) - 1}{\xi}}{\partial \, T} \right)_{\xi} d\xi \qquad [T] \qquad (9)$$

$$\frac{\underset{\cdot}{S} - \underset{\cdot}{S}_{1}}{R} = \ln \frac{\underset{\cdot}{\sigma}_{1}}{\underset{\cdot}{\sigma}} + \int_{\underset{\cdot}{\sigma}_{1}}^{\underset{\cdot}{\sigma}} \left\{ T \left(\frac{\partial \, \frac{Z(\xi, T) - 1}{\xi}}{\partial \, T} \right)_{\xi} - \frac{Z(\xi, T) - 1}{\xi} \right\} d\xi \qquad (10) \quad [T]$$

The derivation of these expressions is given in Appendix D. Discussions of similar derivations are also available (5,24).

Inspection of the above expressions for fugacity, enthalpy, and entropy will reveal that a certain grouping of variables appears repetitively, namely $(Z - 1)/\underset{\cdot}{\sigma}$. This function possesses such basic utility for the present investigation that it will be denoted by a special symbol $L(\underset{\cdot}{\sigma}, T)$.

$$L = L(\underset{\cdot}{\sigma}, T) = \frac{Z - 1}{\underset{\cdot}{\sigma}} = \frac{1}{\underset{\cdot}{\sigma}} \left(\frac{P}{RT\underset{\cdot}{\sigma}} - 1 \right) \qquad (11)$$

By simple rearrangement of equation 11 the following expression for pressure as a function of L, $\underset{\cdot}{\sigma}$, and T may be obtained:

$$P = RT\left[L(\sigma,T)+1\right]\sigma = RTL\sigma^2 + RT\sigma \qquad (12)$$

Hence instead of using an equation of state which expresses P directly as a function of σ and T, equation 12 indicates that it would be equally acceptable to express L as a function of σ and T. As a matter of fact, for reasons that will be discussed in the following section, this is precisely the procedure adopted in the present investigation.

In terms of L, equations 8 - 10 may be rewritten.

$$\ln\frac{f}{RT\sigma} = Z - 1 + \int_0^{\sigma} L(\xi,T)\,d\xi \qquad [T] \qquad (13)$$

$$\frac{H - H^{\circ}}{RT} = Z - 1 - \int_0^{\sigma} T\left(\frac{\partial L(\xi,T)}{\partial T}\right)_{\xi} d\xi \qquad [T] \qquad (14)$$

$$\frac{S - S_1}{R} = \ln\frac{\sigma_1}{\sigma} + \int_{\sigma_1}^{\sigma}\left\{T\left(\frac{\partial L(\xi,T)}{\partial T}\right)_{\xi} - L(\xi,T)\right\} d\xi \qquad (15)$$

$$[T]$$

At first appearance L($\underset{\cdot}{\sigma}$, T) appears to be indeterminate as $\underset{\cdot}{\sigma}$ approaches zero for a fixed value of T. Actually the limiting value is finite, as may be deduced by use of L'Hospital's rule.

$$\lim_{\underset{\cdot}{\sigma}\to 0} L = \lim_{\underset{\cdot}{\sigma}\to 0} \frac{Z-1}{\underset{\cdot}{\sigma}} = \lim_{\underset{\cdot}{\sigma}\to 0} \frac{\left(\frac{\partial\, Z-1}{\partial\, \underset{\cdot}{\sigma}}\right)_T}{\left(\frac{\partial\, \underset{\cdot}{\sigma}}{\partial\, \underset{\cdot}{\sigma}}\right)_T} = \lim_{\underset{\cdot}{\sigma}\to 0} \left(\frac{\partial\, Z}{\partial\, \underset{\cdot}{\sigma}}\right)_T \tag{16}$$

$$= \text{finite}$$

An analogy to the residual molal volume might be noted (25).

$$\lim_{P\to 0} \underset{\cdot}{\tilde{V}} = (-RT) \lim_{P\to 0} \frac{Z-1}{P} = \lim_{P\to 0} (-RT)\left(\frac{\partial\, Z}{\partial\, P}\right)_T = \text{finite} \tag{17}$$

In the two-phase region L has the following form in terms of the vapor pressure P'':

$$L''(\underset{\cdot}{\sigma}, T) = \frac{P''}{RT\underset{\cdot}{\sigma}^2} - \frac{1}{\underset{\cdot}{\sigma}} \tag{18}$$

It should be noted that, at a fixed temperature, L may exhibit a relative minimum at

$$\underset{\cdot}{\sigma} = \frac{2\, P''}{RT} \qquad \left[\text{min}\right] \tag{19}$$

IV. THE EQUATION OF STATE

Range of Independent Variables

In the analysis that follows it will be necessary that the range of reciprocal molal volume be the same for each temperature involved. In other words it is desirable to deal with a rectangular domain in the plane of the independent variables. It might happen that the experimental data available satisfy this requirement; in general they will not. Consequently either a process of deletion or extrapolation is necessary. If the extrapolation is regarded only as an aid to analysis and computation, it should be an acceptable procedure. Assuming then that the data have been selected so as to cover a uniform range in both temperature and volume, it is convenient to utilize normalized variables that have a range convenient for purposes of analysis. For example the dependence on σ will be expressed in the equation of state by a series of Tchebichef polynomials, $T_n(x)$, which are usually defined for $-1 \leqq x \leqq 1$. For a given PVT surface, σ will range from $\sigma = 0$ up to some maximum value which will be denoted by σ_m . Therefore define x by

$$x = 2\frac{\sigma}{\sigma_m} - 1 \tag{20}$$

It may be immediately verified that $-1 \leqq x \leqq 1$ for $0 \leqq \sigma \leqq \sigma_m$.

The temperature dependence will be expressed in two separate ways.

In one, the Tchebichef polynomials will also be used. Letting T_{max} and T_{min} denote the maximum and minimum values of temperature, a variable y may be selected such that $-1 \leq y \leq 1$.

$$y = 2 \frac{T - T_{min}}{T_{max} - T_{min}} - 1 \tag{21}$$

In the second case the Gram polynomials will be employed for the temperature dependence. Suppose there are h evenly spaced isotherms. Define a variable ε as follows:

$$\varepsilon = \frac{T - T_{min}}{T_{max} - T_{min}} (h-1) - \frac{h-1}{2} \tag{22}$$

$$\varepsilon = \frac{h-1}{2} \left[2 \frac{T - T_{min}}{T_{max} - T_{min}} - 1 \right] \tag{23}$$

Reference to equation 149 of Appendix C will show that this is an acceptable variable for these polynomials.

Dependent Variable

Prior discussion indicated the necessity of taking temperature and reciprocal molal volume as independent variables and pressure as the fundamental dependent variable. Actually there are more efficient procedures than expanding pressure directly as a function of σ and T. It might be expected that fewer terms would be necessary to describe the deviation from some idealized behavior than the actual absolute value of the pressure directly. In many graphical and numerical evaluations of thermodynamic properties (25,26) use is made of the compressibility factor and residual volume, both of which account for deviation from the perfect gas law. As a matter of fact, for the present work the compressibility factor Z might be expanded as a function of σ and T. However regardless of the point of truncation of the expansion, it is necessary that Z should go to precisely unity at infinite attenuation. This is desirable in order to maintain contact with the kinetic theory of rarefied systems and in order to ensure that the integral describing the fugacity, equation 8, will remain bounded at zero values of σ. The requirement that Z go to precisely unity as goes to zero may be simply met if $(Z-1)/\sigma$ is expressed as a function of σ and T which remains finite at zero values of σ. This is the procedure adopted.

$$L(\sigma, T) = \frac{Z-1}{\sigma} = \text{Polynomial in } \sigma \text{ and } T \qquad (24)$$

The exact form of the polynomial will be developed in succeeding paragraphs.

If the equation of state is to bridge successfully the two-phase region thermodynamically, the path of the equation must satisfy certain requirements. The conditions for phase equilibrium in a one-component system are the following (27):

$$f_g = f_l \tag{25}$$

$$P_g = P_l \tag{26}$$

$$T_g = T_l \tag{27}$$

Combining these expressions with equation 13 for the fugacity, the following may be derived:

$$\ln \frac{f_b}{f_d} = 0 = Z_b - Z_d + \int_{\sigma_d}^{\sigma_b} L(\sigma, T)\, d\sigma + \ln \frac{\sigma_b}{\sigma_d} \qquad [T] \tag{28}$$

$$\int_{\sigma_d}^{\sigma_b} L(\sigma, T)\, d\sigma = \frac{r}{RT} \left\{ \frac{1}{\sigma_d} - \frac{1}{\sigma_b} \right\} + \ln \frac{\sigma_d}{\sigma_b} \tag{29}$$

A further requirement is necessary. From equation 14,

$$-\int_{\underset{\cdot}{\sigma}_d}^{\underset{\cdot}{\sigma}_b} T \left(\frac{\partial L(\underset{\cdot}{\sigma},T)}{\partial T}\right)_{\underset{\cdot}{\sigma}} d\underset{\cdot}{\sigma} = \frac{\underset{\cdot}{H}_d - H_b}{RT} - \frac{P''}{RT}\left\{\frac{1}{\underset{\cdot}{\sigma}_d} - \frac{1}{\underset{\cdot}{\sigma}_b}\right\} \qquad [T] \tag{30}$$

Equation 29, which is essentially an integration restraint on the variable L($\underset{\cdot}{\sigma}$, T), may be satisfied in a straight-forward and rather precise manner. Since a differentiation is involved in equation 30, the second restraint is not easy to satisfy directly for substituted paths which are defined graphically. However if the equation of state gives a good representation of the data in the homogeneous regions including the phase boundary, and if the restraint of equation 29 is met, then the restraint of equation 30 will also be met. This conclusion follows from the fact that satisfaction of the restraint of equation 29 will result in correct prediction of the vapor pressure as a function of temperature. If this prediction is sufficiently good so that the derivatives of the vapor pressure curve are accurate, then the correct enthalpies of vaporization will be predicted according to the Clapeyron-Clausius equation (27).

$$\underset{\cdot}{H}_d - \underset{\cdot}{H}_b = (\underset{\cdot}{V}_d - \underset{\cdot}{V}_b)\, T \,\frac{dP''}{dT} \qquad [T] \tag{31}$$

Since isothermal changes in enthalpy, whether in the two-phase or homogeneous regions, involve a differentiation, it should be realistically anticipated that any finite truncation of the equation of state will yield poorer predictions of enthalpy than of fugacity or pressure.

Unless definitely stated to the contrary the dependent variable under consideration in the present work will be the function L(σ, T). In replacing the actual two-phase data with a smooth path, it will be assumed that the integration restraint of equation 29 is satisfied.

Tchebichef-Gram Form of the Equation of State

The discussions of the preceding sections and the mathematical definitions and theorems of Appendices A, B, and C present sufficient background to permit the direct expansion of L(σ, T) in series of polynomials in σ and T. Characteristics of this type of expansion are indicated in Appendix A. Properties of the Tchebichef and Gram polynomials are discussed in Appendices B and C. The Gram polynomials for h = 13 are listed in Table I. Several each of the Gram polynomials and the Tchebichef polynomials are shown as a function of their arguments in Figures 3 and 4.

Assume that the ranges of the independent variables have been normalized and that L(σ, T) has been adjusted so that the volumetric surface is everywhere smooth. Express the reciprocal molal volume dependence in Tchebichef polynomials of ascending order and the temperature dependence in Gram polynomials of ascending order.

$$\begin{aligned} L(\sigma, T) = \frac{Z - 1}{\sigma} = \; & a_{00} V_0^{(h)}(\varepsilon) T_0(x) + a_{10} V_1^{(h)}(\varepsilon) T_0(x) + --- \\ & + a_{01} V_0^{(h)}(\varepsilon) T_1(x) + a_{11} V_1^{(h)}(\varepsilon) T_1(x) + -- \\ & + a_{02} V_0^{(h)}(\varepsilon) T_2(x) + --- \\ & + \; - - - \qquad\qquad\qquad\qquad (32) \\ & \quad - - - - \end{aligned}$$

The equation is an open-ended series in both the ϵ and x directions. Furthermore Theorems I and II of Appendix A make it possible to approximate L(σ, T) uniformly to any pre-assigned accuracy with a finite number of terms of equation 32. It is pointed out in Appendix C that for the Gram polynomials, h must be greater than the index of the highest order polynomial. Birge and Weinberg (40) demonstrate that in the limit as $h \rightarrow \infty$ the Gram polynomials are closely associated with the classical Legendre polynomials.

Tchebichef-Tchebichef Form of the Equation of State

Assume that the ranges of the variables σ and T have been normalized to convenient standard ranges by equation 20 and 21. Express the reciprocal molal volume dependence of L(σ, T) in a series of Tchebichef polynomials $T_j(x)$ and the temperature dependence in a series of Tchebichef polynomials $T_i(y)$.

$$\begin{aligned} L(\sigma, T) = \frac{Z-1}{\sigma} = \quad & c_{00} T_0(y) T_0(x) + c_{10} T_1(y) T_0(x) + \cdots \\ & + c_{01} T_0(y) T_1(x) + c_{11} T_1(y) T_1(x) + \cdots \\ & + c_{02} T_0(y) T_2(x) + \cdots \\ & + \cdots \\ & \cdots \end{aligned} \qquad (33)$$

The equation is an infinite series in both the x and y directions which may be truncated at a point yielding any desired degree of approximation. Whether these truncations can be accomplished in a number of terms that is practical for application will be the subject of the study of the application to propane.

Different letter designations have been purposely used for coefficients of the two forms of the expansion, namely a_{ij} for the Tchebichef-Gram form and c_{ij} for the Tchebichef-Tchebichef form.

Notation

For the sake of convenience in using the equation of state, abbreviations will be used for equations 32 and 33.

$$L(\sigma, T) = a_{ij} V_i^{(h)}(\varepsilon) T_j(x) \tag{34}$$

$$L(\sigma, T) = c_{ij} T_i(y) T_j(x) \tag{35}$$

In this notation a repeated subscript is to indicate summation over the range of the index. In these two cases the range is $0 \leq i \leq \infty$ and $0 \leq j \leq \infty$. This notation is called the Einstein or summation convention. Equations 34 and 35 are merely abbreviations for equations 32 and 33 or for the following:

$$L(\sigma, T) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} a_{ij} V_i^{(h)}(\varepsilon)\, T_j(x) \tag{36}$$

$$L(\sigma, T) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} c_{ij}\, T_i(y)\, T_j(x) \tag{37}$$

The actual equation of state will be finite truncations of either equation 34 or 35. In order to quite definitely distinguish between the approximation equations and the infinite series, an asterisk superscript will be used on the coefficient operator, and the equality sign will be replaced by an approximation indication.

$$L(\sigma, T) \cong a^*_{ij} V_i^{(h)}(\varepsilon)\, T_j(x) \tag{38}$$

or

$$L(\sigma, T) \cong c^*_{ij}\, T_i(y)\, T_j(x) \tag{39}$$

This notation is to be regarded as a warning that the range of the summation is finite. The following identities are used:

$$a_{ij}^{*}\, V_i^{(h)}(\varepsilon)\, T_j(x) \equiv \sum_{i=0}^{m} \sum_{j=0}^{n} a_{ij} V_i^{(h)}(\varepsilon)\, T_j(x) \qquad h > m \tag{40}$$

$$c_{ij}^{*}\, T_i(y)\, T_j(x) \equiv \sum_{i=0}^{m} \sum_{j=0}^{n} c_{ij}\, T_i(y)\, T_j(x) \tag{41}$$

V. THERMODYNAMIC FUNCTIONS IN TERMS OF THE ORTHOGONAL POLYNOMIAL EQUATION OF STATE

Pressure, Fugacity, Enthalpy, and Entropy

Equations 8, 9, and 10 may be combined with either equation 34 or 35 to give exact expressions for pressure, fugacity, enthalpy, and entropy as functions of σ and T. Approximations to these quantities may be similarily obtained by using the truncated forms, equations 38 and 39. Since the latter are the actual equations that would be used in practice, they will be used below for the explicit equations for these thermodynamic quantities. The equations for the Tchebichef-Tchebichef form of the equation of state follow.

Pressure:

$$P \cong RT\sigma + RT\sigma^2 c_{ij}^{*}\, T_i(y)\, T_j(x) \tag{42}$$

Fugacity:

$$\ln \frac{f}{RT\underset{\cdot}{\sigma}} \cong \underset{\cdot}{\sigma}\, c^{*}_{ij}\, T_i(y)\, T_j(x) + \frac{\underset{\cdot}{\sigma}_m}{2}\, c^{*}_{ij}\, T_i(y) \left\{ \int_{-1}^{x} T_j(\xi)\, d\xi \right\} \tag{43}$$

Enthalpy:

$$\frac{H - H^{\circ}}{RT} \cong \underset{\cdot}{\sigma}\, c^{*}_{ij}\, T_i(y)\, T_j(x) \qquad \frac{\underset{\cdot}{\sigma}_m\, T}{(T_{max} - T_{min})}\, c^{*}_{ij} \left\{ \frac{d\, T_i(y)}{d\, y} \right\} \left\{ \int_{-1}^{x} T_j(\xi)\, d\xi \right\} \tag{44}$$

Entropy:

$$\frac{\underset{\cdot}{S} - \underset{\cdot}{S}_1}{R} \cong \ln \frac{\underset{\cdot}{\sigma}_1}{\underset{\cdot}{\sigma}} + \frac{\underset{\cdot}{\sigma}_m}{}\, c^{*}_{ij} \left\{ \frac{T}{T_{max} - T_{min}}\, \frac{d\, T_i(y)}{d\, y} + T_i(y) \right\} \left\{ \int_{x_1}^{x} T_j(\xi)\, d\xi \right\} \tag{45}$$

Equations 42 and 45 are to be used with the following definitions of x and y:

$$x = 2\, \frac{\underset{\cdot}{\sigma}}{\underset{\cdot}{\sigma}_m} - 1 \tag{20}$$

$$y = 2\, \frac{T - T_{min}}{T_{max} - T_{min}} - 1 \tag{21}$$

The values of $\underset{\cdot}{\sigma}_m$, T_{max}, and T_{min} must be precisely those used in the determination of the coefficients c^{*}_{ij}.

For the Tchebichef-Gram form, the following equations pertain:

Pressure:

$$P \cong RT\underset{\cdot}{\sigma} + RT\underset{\cdot}{\sigma}^2 a^*_{ij} V^{(h)}_i(\varepsilon)\, T_j(x) \qquad (46)$$

Fugacity:

$$\ln \frac{f}{RT\underset{\cdot}{\sigma}} \cong \underset{\cdot}{\sigma}\, a^*_{ij} V^{(h)}_i(\varepsilon)\, T_j(x) + \frac{\underset{\cdot}{\sigma}_m}{2} a^*_{ij} V^{(h)}_i(\varepsilon) \left\{ \int_{-1}^{x} T_j(\xi)\, d\xi \right\} \qquad (47)$$

Enthalpy:

$$\frac{\underset{\cdot}{H} - \underset{\cdot}{H}^\circ}{RT} \cong \underset{\cdot}{\sigma}\, a^*_{ij} V^{(h)}_i(\varepsilon)\, T_j(x) + \frac{\underset{\cdot}{\sigma}_m (h-1)\, T}{2(T_{max} - T_{min})} a^*_{ij} \left\{ \frac{d V^{(h)}_i(\varepsilon)}{d\varepsilon} \right\} \left\{ \int_{-1}^{x} T_j(\xi)\, d\xi \right\} \qquad (48)$$

Entropy:

$$\frac{\underset{\cdot}{S} - \underset{\cdot}{S}_1}{R} \cong \ln \frac{\underset{\cdot}{\sigma}_1}{\underset{\cdot}{\sigma}} + \frac{\underset{\cdot}{\sigma}_m}{2} a^*_{ij} \left\{ \frac{T(h-1)}{T_{max} - T_{min}} \frac{d V^{(h)}_i(\varepsilon)}{d\varepsilon} + V^{(h)}_i(\varepsilon) \right\} \left\{ \int_{x_1}^{x} T_j(\xi)\, d\xi \right\} \qquad (49)$$

Equations 46 through 49 are to be used with the following definitions of x and ε :

$$x = 2\,\frac{\sigma}{\sigma_m} - 1 \tag{20}$$

$$\varepsilon = \frac{h-1}{2}\left[2\,\frac{T - T_{min}}{T_{max} - T_{min}} - 1\right] \tag{23}$$

The values of σ_m, T_{max}, T_{min}, and h must be precisely those used in the determination of the coefficients a^*_{ij}.

The factors of $\sigma_m/2$, $2/(T_{max} - T_{min})$, etc. which appear in the above expressions are a result of the normalization employed in equations 20, 21, and 23. To take a specific example, the expression for enthalpy involves the following integral.

$$\begin{aligned}
I &= \int_0^{\sigma} \left(\frac{\partial L(\xi, T)}{\partial T}\right)_{\xi} d\xi \\
&\cong \int_0^{\sigma} \left(\frac{\partial\, a^*_{ij}\, V_i^{(h)}(\varepsilon)\, T_j(\xi)}{\partial T}\right)_{\xi} d\xi \\
&\cong \frac{d\varepsilon}{dT}\,\frac{d\sigma}{dx} \int_{-1}^{x} a^*_{ij} \left(\frac{dV_i^{(h)}(\varepsilon)}{d\varepsilon}\right) T_j(\xi)\, d\xi \\
&\cong \frac{(h-1)}{T_{max} - T_{min}}\,\frac{\sigma_m}{2} \int_{-1}^{x} a^*_{ij} \left(\frac{dV_i^{(h)}(\varepsilon)}{d\varepsilon}\right) T_j(\xi)\, d\xi
\end{aligned}$$

$$\cong \frac{(h-1)\,\sigma_m}{2(T_{max} - T_{min})}\; a^*_{ij}\; \frac{dV_i^{(h)}(\varepsilon)}{d\varepsilon} \int_{-1}^{x} T_j(\xi)\, d\xi \tag{50}$$

Some care should be taken whenever the equation of state utilizing these normalized variables is either integrated or differentiated. A formal reduction as in the above example is a wise precaution.

Several of the above expressions involve integrals and derivatives of the Gram and Tchebichef polynomials. One method of evaluating these would be to operate directly upon the polynomials as given by equations 120 - 130 and 150 - 153 (Appendices B and C). For the Gram polynomials this is the only convenient method known and was used in the present investigation. However in the case of the Tchebichef polynomials, the integration and differentiation formulas of equations 141 and 142 may be conveniently exploited. Application of these relations may be systematized into simple matrix operations. For the present work the following matrices were employed. Omitted terms in the coefficient matrices are identically zero.

Integration:

$$\begin{bmatrix} 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{1}{4} & 0 & \frac{1}{4} & 0 & 0 & 0 & 0 & 0 & 0 \\ -\frac{1}{3} & -\frac{1}{2} & 0 & \frac{1}{6} & 0 & 0 & 0 & 0 & 0 \\ \frac{1}{8} & & -\frac{1}{4} & 0 & \frac{1}{8} & 0 & 0 & 0 & 0 \\ -\frac{1}{15} & & & -\frac{1}{6} & 0 & \frac{1}{10} & 0 & 0 & 0 \\ \frac{1}{24} & & & & -\frac{1}{8} & 0 & \frac{1}{12} & 0 & 0 \\ -\frac{1}{35} & & & & & -\frac{1}{10} & 0 & \frac{1}{14} & 0 \\ \frac{1}{48} & & & & & & -\frac{1}{12} & 0 & \frac{1}{16} \end{bmatrix} \begin{bmatrix} T_0(z) \\ T_1(z) \\ T_2(z) \\ T_3(z) \\ T_4(z) \\ T_5(z) \\ T_6(z) \\ T_7(z) \\ T_8(z) \end{bmatrix} = \begin{bmatrix} \int_{-1}^{z} T_0(\xi)\,d\xi \\ \int_{-1}^{z} T_1(\xi)\,d\xi \\ \\ \\ \\ \\ \\ \int_{-1}^{z} T_7(\xi)\,d\xi \end{bmatrix} \qquad (51)$$

Differentiation:

$$\begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{1}{2} & 0 & -\frac{1}{2} & 0 & 0 & 0 & 0 & 0 & 0 \\ & 1 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ & & \frac{3}{2} & 0 & -\frac{3}{2} & 0 & 0 & 0 & 0 \\ & & & 2 & 0 & -2 & 0 & 0 & 0 \\ & & & & \frac{5}{2} & 0 & -\frac{5}{2} & 0 & 0 \\ & & & & & 3 & 0 & -3 & 0 \\ & & & & & & \frac{7}{2} & 0 & -\frac{7}{2} \end{bmatrix} \begin{bmatrix} T_0(z) \\ T_1(z) \\ \vdots \\ T_7(z) \\ T_8(z) \end{bmatrix} = \begin{bmatrix} (1-z^2)\,T_0'(z) \\ (1-z^2)\,T_1'(z) \\ \vdots \\ (1-z^2)\,T_7'(z) \end{bmatrix} \qquad (52)$$

In the process of predicting thermodynamic properties at a given value of σ and T the values of $T_j(x)$ and $T_i(y)$ were first computed. These values were then used directly in equation 42 for pressure. These values could also be used with the matrices 51 and 52 to obtain the indicated integration and differentiation vectors, which could in turn be employed in equations 43 and 44 for the fugacity and enthalpy. In punched card operations these matrices can be kept on file as standard operational decks.

Virial Coefficients

An equation of state has been developed in a form involving orthogonal polynomials. For purposes of application it may be employed in this form or it may be regrouped into an orthodox polynomial. In view of the extremely useful integration and differentiation formulas available for the Tchebichef polynomials, the orthogonal expansion form is essentially as convenient to use as would be the orthodox polynomial. In addition, the orthogonal expansion possesses the distinct advantage of being susceptible to arbitrary truncation if only an approximate representation is desired.

Nevertheless it is desirable to be able conveniently to revert the orthogonal polynomial form to the conventional polynomial of the virial equation of state. This is particularly important if one desires to obtain explicit expressions for the virial coefficients, as would be the case in a study of intermolecular forces. Consequently a scheme of regrouping is given below. The method is general but will be specialized here to a truncation of the σ dependent series at $T_6(x)$. Consider first the Tchebichef-Gram form of the equation of state.

$$L(\sigma, T) = \frac{Z-1}{\sigma} \cong a^{*}_{ij} V^{(h)}_{i}(\varepsilon)\, T_j(x) \tag{53}$$

Regroup this as follows:

$$L(\sigma, T) = K_0(T)\, T_0(x) + K_1(T)\, T_1(x) + \cdots + K_6(T)\, T_6(x) \tag{54}$$

where

$$\begin{aligned} K_0(T) &= a_{00}V_0^{(h)}(\varepsilon) + a_{10}V_1^{(h)}(\varepsilon) + \cdots \\ K_1(T) &= a_{01}V_0^{(h)}(\varepsilon) + a_{11}V_1^{(h)}(\varepsilon) + \cdots \\ &\vdots \\ K_6(T) &= a_{06}V_0^{(h)}(\varepsilon) + \cdots \end{aligned} \tag{55}$$

Now it is desired to obtain the virial coefficients B(T), C(T), - - - of equation 1 in terms of $K_0(T)$, $K_1(T)$, ----- $K_6(T)$. The actual algebra is simple but tedious and has been placed in Appendix E. The final result follows. Terms below the diagonal in the matrix are identically zero.

$$\beta = -\frac{2}{\sigma_m} \tag{56}$$

$$\begin{bmatrix} 1 & -1 & 1 & -1 & 1 & -1 & 1 \\ & -\beta & 4\beta & -9\beta & 16\beta & -25\beta & 36\beta \\ & & 2\beta^2 & -12\beta^2 & 40\beta^2 & -100\beta^2 & 210\beta^2 \\ & & & -4\beta^3 & 32\beta^3 & -140\beta^3 & 448\beta^3 \\ & & & & 8\beta^4 & -80\beta^4 & 432\beta^4 \\ & & & & & 16\beta^5 & 192\beta^5 \\ & & & & & & 32\beta^6 \end{bmatrix} \begin{bmatrix} K_0(T) \\ K_1(T) \\ \vdots \\ \\ \\ \\ K_6(T) \end{bmatrix} = \begin{bmatrix} B(T) \\ C(T) \\ \vdots \\ \\ \\ \\ H(T) \end{bmatrix} \tag{57}$$

A similar result may be obtained for the Tchebichef-Tchebichef form. Let

$$
\begin{aligned}
J_0(T) &= c_{00}T_0(y) + c_{10}T_1(y) + \cdots \\
&\vdots \\
J_0(T) &= c_{06}T_0(y) + c_{16}T_1(y) + \cdots
\end{aligned}
\tag{58}
$$

If in equation 57 the $K_i(T)$ vector is replaced by the $J_i(T)$ vector, the results are valid for the case in which the expansion coefficients have been obtained for the Tchebichef-Tchebichef form. Note that the second virial coefficient involves a particularly simple combination of the $K_i(\epsilon)$ and does not directly depend on β or σ_m. The matrix equation 57 gives the virial coefficients in terms of the $K_i(\epsilon)$ or $J_i(y)$, which are linear combinations of orthogonal polynomials. These combinations could also be regrouped to yield conventional polynomials in powers of T. Such a procedure was not employed in the present investigation.

VI. LEAST SQUARES EVALUATION OF EXPANSION COEFFICIENTS

The discussion that follows will consider the evaluation of the expansion coefficients of the equation of state by approximation in the mean or the method of least squares. In Appendix A certain characteristics of this method are presented. In Appendices B and C the properties of the Tchebichef and Gram polynomials are discussed, particularly with reference to their summation orthogonality. The nature of the present problem virtually assures that the data to be approximated will be available in graphical or tabular form rather than as analytical expressions. Therefore it will be convenient to adopt the summation method of evaluating the coefficients.

It will be necessary to consider separately the two forms of the equation. Both, however, involve expression of the dependence on reciprocal molal volume in terms of the Tchebichef polynomials, $T_n(x)$. Considering first the Tchebichef-Gram form, assume that the data are available on h equally spaced isotherms $\mathcal{E}_\nu$, $\nu = 0, 1, 2, 3$ ----, h-1. Assume now that the data points along each isotherm are taken at the very definite points $x_\alpha, \alpha = 0, 1, 2, ---- t-1$. x_α will be given by

$$T_t(x_\alpha) = 0 \tag{59}$$

$$x_\alpha = \cos \frac{2\alpha + 1}{2t} \pi \qquad \alpha = 0, 1, 2, \cdots t - 1 \tag{60}$$

As h-1 and t are taken very large, the values obtained for the expansion coefficients will approach those obtained by integration procedures. Although for computation it will be necessary to take a practical number of grid points, it will be assumed that the number of divisions in both the x and $\mathcal{E}$ directions are significantly in excess of the highest order terms of the approximation.

The values of the coefficients a_{ij} are desired for which the following sum is a minimum:

$$\mathcal{S} = \sum_{\mathcal{E}_\nu, x_\alpha} \left[L(x_\alpha, \mathcal{E}_\nu) - a_{ij} V_i^{(h)}(\mathcal{E}_\nu) T_j(x_\alpha) \right] \tag{61}$$

The conventional least squares analysis leads to the following expression for the coefficients $a_{k\ell}$:

$$a_{k\ell} = \frac{\sum_{\mathcal{E}_\nu, x_\alpha} L(x_\alpha, \mathcal{E}_\nu) V_k^{(h)}(\mathcal{E}_\nu) T_\ell(x_\alpha)}{\sum_{\mathcal{E}_\nu} \left\{ V_k^{(h)}(\mathcal{E}_\nu) \right\}^2 \cdot \sum_{x_\alpha} \left\{ T_k(x_\alpha) \right\}^2} \tag{62}$$

This is the general expression; a formally identical equation for each of the a_{ij} of equation 32 may be obtained by permuting the $k\ell$ indices of equation 62. For the terms $\sum \left\{ V_k^{(h)}(\varepsilon) \right\}^2$ and $\sum T_\ell^2(x)$, the indicated summation does not have to be performed for each computation. These values are obtained from the orthogonality properties of the polynomials. For the Tchebichef system, the values are given by equation 136. For the Gram system, values are equal to $N_t^{(h)}$ and may be obtained from the tabulations (40,41).

The sum in the numerator is simply a three-factor inner product over the points of the ε_ν, x_α grid. To every point of this grid on the σ-T plane (or the x-ε plane), there corresponds a value of $L(x_\alpha, \varepsilon_\nu)$, $V_k^{(h)}(\varepsilon_\nu)$ and $T_\ell(x_\alpha)$. These three factors are multiplied together and then the resulting products are summed over all points of the grid. The resulting sum when divided by the product of $\sum V_k^2$ by $\sum T_\ell^2$ gives the value of the coefficient $a_{k\ell}$.

Note that each of the a_{ij} are obtained independently. There is no matrix inversion. For n coefficients there are (n + 1) inner products as compared to $\frac{1}{2}(n^2 + 3n + 1)$ that are necessary in fitting an orthodox polynomial.

If there are N points on the data grid and if s^2 represents the mean square error of the approximation, then an expansion of equation 61 yields the following expression:

$$s^2 = \frac{1}{N} \sum_{\varepsilon_\nu, x_\alpha} \left[L^2(x_\alpha, \varepsilon_\nu) - a_{k\ell} L(x_\alpha, \varepsilon_\nu) V_k^{(h)}(\varepsilon_\nu) T_\ell(x_\alpha) \right] \qquad (63)$$

Because of the independence of the coefficients this may be combined with equation 62 to yield the following useful expression for the mean square error of the approximation:

$$s^2 = \frac{1}{N}\sum_{\varepsilon_\nu, x_\alpha} L^2(x_\alpha, \varepsilon_\nu) - \frac{1}{N}\sum_{k}\sum_{\ell} \frac{\left\{\sum\limits_{\varepsilon_\nu, x_\alpha} L(x_\alpha, \varepsilon_\nu)\, V_k^{(h)}(\varepsilon_\nu)\, T_\ell(x_\alpha)\right\}^2}{\sum\limits_{\varepsilon_\nu}\left\{V_k^{(h)}(\varepsilon_\nu)\right\}^2 \cdot \sum\limits_{x_\alpha} T_\ell^2(x_\alpha)} \qquad (64)$$

Contemplation of equation 64 will reveal that each additional term, $V_m^{(h)}(\varepsilon)\,T_n(x)$ which is added (or included) to the equation of state makes a contribution to reducing the mean square error which is independent of the contribution of the other terms. This affords a powerful means for quickly evaluating the adequacy of the approximation as additional coefficients are computed one by one.

It will be useful to define a quantity s_{ij} as follows:

$$s_{ij} = \frac{\left\{\sum\limits_{\varepsilon_\nu, x_\alpha} L(x_\alpha, \varepsilon_\nu)\, V_i^{(h)}(\varepsilon_\nu)\, T_j(x_\alpha)\right\}^2}{\sum\limits_{\varepsilon_\nu}\left\{V_i^{(h)}(\varepsilon_\nu)\right\}^2 \cdot \sum\limits_{x_\alpha} T_j^2(x_\alpha)} \cdot \frac{1}{\sum\limits_{\varepsilon_\nu, x_\alpha} L^2(x_\alpha, \varepsilon_\nu)} \qquad (65)$$

Combining with equation 64 the following is obtained:

$$s^2 = \left[1 - \sum_{ij} s_{ij} \right] \cdot \frac{1}{N} \sum L^2(x_\alpha, \varepsilon_\nu) \tag{66}$$

Values of s_{ij} may be rapidly computed once a value has been obtained for a_{ij}. If zero terms are included in the equation of state (equivalent to assuming that perfect gas law applies) then the error of the approximation is given by

$$s^2 = \frac{1}{N} \sum L^2(x_\alpha, \varepsilon_\nu) \qquad \left[\frac{Z-1}{\sigma} = 0 \right] \tag{67}$$

As each additional term is included in the equation of state, this value diminishes, approaching zero for the limiting case of an infinite number of terms. By the nature of the expansion leading to equation 64, s_{ij} is between 0 and 1. As a matter of fact the following relation holds:

$$0 \leq \sum_{ij} s_{ij} \leq 1 \tag{68}$$

The properties of this expansion are therefore such that additional terms may be computed until equation 64 indicates that an average square error acceptably small has been attained, whereupon the computations may be stopped. It is apparent that there is no need for recomputation of all pre-existing coefficients if it is desired to include an additional term in the equation.

The procedure utilized for the Tchebichef-Tchebichef form is very similar. Instead of the data grid being prepared with equally spaced isotherms, the points are selected at points y_η , $\eta = 0,1,2,$ --- r given by

$$T_r(y_\eta) = 0 \tag{69}$$

$$y_\eta = \cos \frac{2\eta + 1}{2r} \qquad \eta = 0, 1, 2, \cdots r-1 \tag{70}$$

Since the reciprocal molal volume dependence still employs the Tchebichef polynomials $T_j(x)$, the nature of the division in the x direction remains the same. The equations in the preceding paragraphs will pertain with $T_k(y_\eta)$ substituted for $V_k^{(h)}(\varepsilon_\nu)$ and with the appropriate change of the index of summation from ε_ν to y_η . The necessary values of $\sum_{y_\eta} T_k^2(y_\eta)$ can be obtained from equation 136.

VII. APPLICATION OF THE EQUATION OF STATE TO PROPANE

Data

Propane was chosen for the initial test of the practicability of the orthogonal polynomial equation of state. There were several reasons for this selection. Reliable experimental data are available over an extensive range of pressure and temperature including the critical region. Thermodynamic properties have also been computed. Furthermore propane was used as a model for many of the investigations of the applicability of the Benedict equation of state made by Brough, Opfell and co-workers (13,14, 15,16). Propane is not an overly complex molecule, yet it is not trivially simple. It is non-polar.

The data employed were primarily those of Sage and Lacey (26) involving temperatures from 100° F to 460° F and pressures from zero to 10,000 psia. The only additional data used were those describing the experimental critical isotherm reported by Beattie, Poffenberger, and Hadlock (28). This latter information was used only in the second application, namely in obtaining the coefficients for the Tchebichef-Tchebichef form.

Other experimental data for propane are available in the range of temperature and pressure considered. They were not employed in the present work because the objective of this initial investigation was to explore the feasibility of approximating a smooth internally consistent system.

Tchebichef-Gram Form. Expansion Coefficients

The data are reported in reference 26 for thirteen isotherms spaced at 30° F intervals ranging from 100° F to 460° F. It was the occurrence of the data in this convenient form that recommended the use of the Gram polynomials to express the temperature dependence.

The tabulated values of pressure, molal volume, and temperature were key punched into IBM cards. The range and density of points available are indicated in Figure 5. As mentioned previously, the critical isotherm of Beattie was not used in this first computation. From the tabulated data, values of $L(\sigma, T)$ and σ were computed. $L(\sigma, T)$ was then plotted versus σ for the thirteen isotherms on a good quality graph paper approximately 20 by 36 inches. Several of these isotherms are reproduced in Figure 6. The 100° F isotherm in the two-phase region exhibits a relative minimum of the type discussed in section III, equation 19. The 100° F isotherm extended to a value of reciprocal molal volume of approximately 0.82 lb mole per ft^3, which was chosen as the value of σ_m. All the remaining isotherms terminated at smaller values. Rather than delete data, the short isotherms were all extrapolated to values of $\sigma = \sigma_m = 0.82$ in order to provide a uniform boundary. The necessity of this procedure was discussed in section IV. These extrapolations were required to be smooth both on the basic plot and on an L versus T cross-plot. Several of the extrapolations are reproduced in Figure 6.

Four of the isotherms, 100° F, 130° F, 160° F, and 190° F, passed through the two-phase region. In this region the actual data were replaced by alternate paths which were smooth at the phase boundaries. These paths were made to satisfy the integration restraint of equation 29 and in addition were required to cross-plot smoothly on a L versus T graph. The integrations between dew point and bubble point were performed numerically. The path finally accepted is shown by the dotted curves for the 100° F isotherm in Figure 6. The final values of the integrations are compared in Table II with the values computed from the experimental data using equation 29. No attempt was made to satisfy directly the restraint of equation 30 for the enthalpy of vaporization. The difficulties associated with this latter requirement were indicated in section IV. Needless to say the two-phase paths that were used are not unique.

For the points of summation along the σ axis the values of x_α given by the following were used:

$$T_{46}(x_\alpha) = 0 \tag{71}$$

$$x_\alpha = \cos \frac{2\alpha + 1}{90}\pi \qquad \alpha = 0, 1, 2, --- 44 \tag{72}$$

$$x_\alpha = \cos(2 + 4\alpha)^\circ \qquad \alpha = 0, 1, 2 --- 44 \tag{73}$$

Values of x_α were read directly from a table of cosines. In order to facilitate the reading of values of $L(\sigma, T)$ from the working graph, guide lines were drawn parallel to the L axis at values of σ_α corresponding to equations 20 and 73.

$$\sigma_\alpha = (x_\alpha + 1)\frac{\sigma_m}{2} \tag{74}$$

Values of $L(\sigma, T)$ were read from the working graph at the intersection of the isotherms with the σ_α guide lines. Each value with identifying coding was punched into an IBM card. These cards were then ordered by the α index and the first differences were computed for each isotherm. Subsequently the first differences in temperature at constant values of σ were calculated. This differencing proved a remarkably effective means of detecting errors in reading the graph and in key punching. The final data set consisted of 585 points (13 isotherms, 45 points each). 120 of these were in the high reciprocal molal volume extrapolated region and 79 were in the two-phase region. For computational purposes, the graph was thus supplanted with a deck of 585 punched cards, each card corresponding to one grid point. Each card contained a value of $L(\sigma, T)$ and coding identifying location of the grid point.

Values of the Gram polynomials for $h = 13$ were obtained from DeLury (41) and Birge and Weinberg (40). The actual numerical values are given in Table I and several of the polynomials are plotted in Figure 4. These data were checked to verify that the orthogonality requirements of equation 144 were satisfied.

Values of the Tchebichef polynomials, $T_j(x_\alpha)$ for the grid points x_α

were obtained from a table of cosines.

$$T_j(x_\alpha) = \cos j \cos^{-1} x_\alpha \qquad (75)$$

$$T_j(x_\alpha) = \cos j \frac{2\alpha+1}{90}\pi \qquad \begin{matrix}\alpha = 0,1,2,\cdots 44 \\ j < 45\end{matrix} \qquad (76)$$

The cosine data used in these preparations were obtained from reliable tables (29). For the grid chosen, all the values of $T_j(x_\alpha)$ were necessarily the cosines of integer multiples of 2 degrees. The entire cosine table (29) was key punched at 2 degree intervals, and the first and second differences were computed. When the consistency of these data had been verified, the set $T_j(x_\alpha)$ was obtained by selection of the appropriate cards as indicated by equation 76. Several members of the resulting set were checked to verify that the orthogonality relationship of equation 136 was satisfied.

Utilizing the data and polynomials discussed in the previous paragraphs, the expansion coefficients for propane were computed according to equation 62. Each successive coefficient required that the 585 card data set with attendant polynomial cards be passed once through an IBM 604 digital computer. The computer multiplied $L(x_\alpha, \mathcal{E}_\nu) \times V_k^{(h)}(\mathcal{E}_\nu) \times T_\ell(x_\alpha)$ for each grid point and provided the sum of this product over all the grid points on the last card of the deck. These products are listed in Table III. For each value of k and ℓ the product of $\sum \{V_k^{(h)}\}^2 \cdot \sum T_\ell^2$ is also shown.

The quotient is the coefficient $a_{k\ell}$. For each successive coefficient a new set of polynomials cards had to be merged with the data set deck.

The value of $\sum_{\varepsilon_\nu, x_\alpha} L^2(x_\alpha, \varepsilon_\nu)$ is given at the top of Table III. Values of

$$\frac{\left\{\sum_{\varepsilon_\nu, x_\alpha} L(x_\alpha, \varepsilon_\nu)\, V_k^{(h)}(\varepsilon_\nu)\, T_\ell(x_\alpha)\right\}^2}{\sum_{\varepsilon_\nu}\left\{V_k^{(h)}(\varepsilon_\nu)\right\}^2 \cdot \sum_{x_\alpha} T_\ell^2(x_\alpha)}$$

are also reported. For each coefficient, s_{ij} is given.

A total of thirty-four coefficients were evaluated. It is interesting to note the rapid decrease in the effectiveness of the coefficients. 65% of the square error that would arise from using the perfect gas law is absorbed by one term of the equation, namely $a_{01} V_0^{(13)}(\varepsilon)\, T_1(x) = a_{01} x$ Four terms, those corresponding to a_{00} , a_{10} , a_{01} , and a_{02} , absorb 98.1% of this error. All 34 coefficients listed absorb 99.9506%. The perfect gas law would give a root-mean-square error of approximately 2.42 ft^3 per lb mole in $L(\sigma, T)$. The four terms corresponding to a_{00}, a_{10} , a_{01} and a_{02} would result in a value of 0.34. For all the 34 coefficients listed the root-mean-square error would be 0.022 ft^3 per lb mole.

The relative effectiveness of the coefficients, or more precisely the terms which they represent, is portrayed in Figure 7.

Tchebichef-Gram Form. Prediction

For the present case the series was truncated after twenty-seven terms. Seven of the computed coefficients in Table III, indicated by asterisks, were not included in the equation of state. This truncation is arbitrary. All of the coefficients listed could have been used; more might have been computed; more might have been deleted. However with the method employed of reporting with each coefficient its associated effect on the error, a definite guide to an efficient point of truncation is available. These computed approximation errors include the deviations in the non-realistic extrapolated and two-phase regions. Nevertheless the values obtained should be a reliable indication of the error in the region of real data. For the twenty-seven coefficients selected, the computed root-mean-square error was 0.023 ft^3 per lb mole.

Predictions of $L(\underset{\bullet}{\sigma}, T)$ were made with the equation of state for each of the 585 points of the original data grid. For a number of the isotherms the error of the equation is shown in Figure 8. The most significant deviations were in the two-phase region and near the bubble point boundary in the liquid phase. The poorest prediction was obtained on the 100° F isotherm which is included in Figure 8. It might be reported that the equation faithfully reproduced a rather peculiar reversion at low values of $\underset{\bullet}{\sigma}$ for the 100° F, 130° F, and 160° F isotherms, an example of which may be seen in Figure 6. It might also be noted that the error curve for the 100° F isotherm bears a similarity in form to a Tchebichef polynomial of seventh or eighth order. Appendix A contains a discussion of this property.

The equation of state was used to predict pressure for 377 of the data grid points corresponding to the region of the original data. The deviations for several of the isotherms are shown in Figure 9. The worst relative error in pressure revealed by this computation was on the 130° isotherm near the bubble point boundary, amounting to 18.4%. The P versus σ curves are steep in this region resulting in significant errors for small displacements of an isotherm. Away from the bubble point boundaries the prediction was much better. The arithmetic average of the absolute values of these 377 relative errors was 0.505%.

Although the equation of state is explicit in pressure, actual problems in application will usually present pressure and temperature as independent variables, requiring a solution for molal volume. Although **comparitively** time consuming, the equation of state can be solved for volume by an iterative process. Since the majority of applications of the equation will probably be of this type, evaluation of the utility of the equation should include an estimate of error in volume with pressure and temperature as independent variables.

For the present purposes, the errors in volume were estimated from the computed errors in pressure by the following relations:

$$\Delta \underset{\cdot}{V} \cong \frac{\Delta P}{\left(\frac{\partial P}{\partial \underset{\cdot}{V}}\right)_T} \tag{77}$$

For this computation the necessary derivatives were approximated by finite differencing of the experimental data. A sample of computed relative errors in molal volume is shown in Figure 10. An abnormally large error is associated with the isotherms immediately above the critical state. This is a consequence of the virtually horizontal nature of a P versus σ curve in this region; very small displacements of the curve result in large errors in volume although the curves may be "close" in the sense of normal deviation. The actual behavior for the 220° F, 250° F, and 280° F isotherms is shown in Figure 11 (critical temperature is 206.3° F).

The maximum relative error in volume was 8.3% occurring on the 220° F isotherm. The arithmetic average of the absolute value of all these computed relative errors in volume was 0.27%. This average includes the 7 and 8% deviations near the critical state! On the high temperature isotherm 460° F, the maximum relative error in volume was 0.27%.

For each of five temperatures the vapor pressure, two-phase fugacity, and the reciprocal molal volume of the coexisting phases were obtained by iterative solution of the system of equations 25, 26, and 27. Equations 46 and 47 for the pressure and fugacity were used. The computed values of the vapor pressure are compared with the experimental data in Table IV. The maximum deviation is 3.7 psi occurring at the critical temperature. The maximum relative error is 0.79%, at 100° F. The relative errors are shown in Figure 12. Also included in this figure are errors in the vapor pressure predicted by the Benedict equation of state using two different sets of coefficients (30). The present system results in considerably better vapor pressure predictions than the Benedict equation using Opfell's coefficients, which pertain to the same range of pressure and temperature as the present work. As a matter of fact, the phase equilibrium prediction is somewhat better than obtained with the Benedict equation using coefficients based on low pressure data.

The equation of state was also used to compute the thermodynamic properties as a function of $\dot{\sigma}$ and T for a small number of states corresponding to tabulated entries in the source reference (26). The states chosen, 37 in all, are indicated by the values of $\dot{\sigma}$ and T listed in Table V. States were selected from the lowest and highest temperatures, 100° F and 460° F, encountered in the evaluation of the coefficients. The other isotherms included either cut the two-phase region or were near the critical state, the difficult domains to describe. Representative values of $\dot{\sigma}$ were selected up to the maximum for which the coefficients were valid. For each state pressure, fugacity, and enthalpy were computed. Equations 46, 47, and 48 were used. The enthalpy computations involve the temperature-dependent reference H^o.

The results of the calculations are shown in Table V. Several of the phase behavior predictions discussed previously have also been included. The table includes the relative approximation error of each quantity. The pressure predictions at 100° F again reveal the difficulties encountered very close to the bubble point boundary. Aside from the striking 70% error at this point, the pressure predictions appear to be acceptable. The predictions of fugacity are in good agreement with the values reported in the source reference (26). The enthalpy predictions are somewhat poorer; relatively large errors at low values of reciprocal molal volume are particularly perplexing. It must be borne in mind however that the enthalpy prediction depends on a differentiation of the approximation surface, which would be expected to increase the errors. The arithmetic averages of the absolute values of relative errors recorded in Table V are 0.86% for fugacity and 1.26% for enthalpy. A word of caution is necessary about these averages; namely, that no attempt was made to select the points by a statistical sampling procedure. The resulting averages consequently may not be representative.

The computations given in Table V were also used to estimate the errors of prediction with pressure and temperature as independent variables. The results are shown in Table VI. The experimental values for this case were graphically or numerically interpolated from the tabulated data of the source reference. The arithmetic averages of the absolute values of the recorded relative errors are 0.21% for reciprocal molal volume, 0.51% for fugacity and 1.22% for enthalpy. The average error in fugacity is apparently significantly less with pressure (rather than molal volume) as an independent variable. The description of the enthalpy does not improve markedly.

The critical state predicted by the Tchebichef-Gram form of the equation of state was located by solving interatively for the values σ_c and T_c which resulted in simultaneous vanishing of the first and second partial derivatives of pressure with respect to volume at constant temperature. The predicted critical state is as follows:

$$\sigma_c = 0.325 \ \frac{\text{lb mole}}{\text{ft}^3} \tag{78}$$

$$t_c = 216.1 \ {}^\circ\text{F} \tag{79}$$

$$P_c = 683.48 \ \text{psia} \tag{80}$$

The experimental values are the following (28):

$$\sigma_c = 0.3125 \ \frac{\text{lb mole}}{\text{ft}^3} \tag{81}$$

$$t_c = 206.3^\circ \ \text{F} \tag{82}$$

$$P_c = 617.4 \ \text{psia} \tag{83}$$

The agreement is not as precise as might be desired. However it is probably as good as could be expected in the present case considering the fact that the experimental data employed in evaluating the coefficients did not precisely identify the critical state. The data used contained a smooth isotherm at 220° F and an isotherm at 190° F possessing a relative minimum and a relative maximum. There was consequently a 30° F range of temperature in which the equation could demonstrate the behavior characteristic of a critical state.

Tchebichef-Tchebichef Form. Expansion Coefficients

In preparing the data for the determination of the coefficients for the Tchebichef-Tchebichef form of the equation, the same fundamental information was used as discussed above in connection with the Tchebichef-Gram form. In addition the data of Beattie (28) for a portion of the critical isotherm were included.

The variable T was transformed to y by equation 21. The smoothed data used in the first investigation were then plotted on a large working graph of $L(\sigma, y)$ versus y. The y axis was then subdivided at the zeros of $T_{45}(y)$.

$$T_{45}(y_\eta) = 0$$

$$y_\eta = \cos \frac{2\eta + 1}{45} \frac{\pi}{2}$$

$$\eta = 0, 1, 2, \cdots 44 \qquad (85)$$

Guide lines were drawn on the graph at the values of y given by equation 85. The arbitrary selection of 45 points along the y axis appeared to give a fairly detailed decomposition of the region adjacent to the critical state. The same subdivision along the σ axis was used as in the preceding determination; namely, the 45 points of equation 126. The grid thus consisted of 45 x 45 $=$ 2025 points. Values of $L(\sigma, T)$ were read from the smoothed graph and key punched into IBM cards. Again the data were checked by differencing in both the σ and T directions.

The procedure used for computation of the coefficients c_{ij} of the Tchebichef-Tchebichef expansion was essentially the same as described for the calculations associated with the Tchebichef-Gram form. The coefficients and their associated error parameters s_{ij} are reported in Table VII. The trends of decreasing magnitude and alternating sign of the coefficients are very similar to those observed in the Tchebichef-Gram investigation. A total of 33 coefficients were computed. For these 33, the resulting root-mean-square error in $L(\sigma, T)$ was 0.01932 ft^3 per lb mole.

An interesting phenomenon is observable by inspection of coefficients c_{21}, c_{31}, c_{41}, and c_{51}. Instead of following an anticipated trend of a regular decrease in magnitude, c_{31}, c_{41}, and c_{51} remain approximately equal in magnitude, alternating in sign. This behavior may well be a reflection of statistical fluctuations in $L(\sigma, T)$ arising from rounding errors in reading data from graphs (38).

Tchebichef-Tchebichef Form. Prediction

For the purpose of making actual computations, 29 of the coefficients of Table VII were selected. (The coefficients not used are designated with an asterisk). Again this selection was largely arbitrary. The equation might have been used with more or fewer terms. For the set of coefficients selected, the corresponding root-mean-square error of the approximation was 0.01952 ft^3 per lb mole in $L(\sigma, T)$.

The computed vapor pressures are compared with the experimental data in Table VIII and Figure 12. The agreement with experiment is even better than obtained with the Tchebichef-Gram form of the equation and is as good or better at all points of comparison than the results obtained with the Benedict equation using phase behavior coefficients.

Pressure, fugacity, and enthalpy were computed for a number of selected states with σ and T as independent variables. The results are compared with experiment in Table IX. For the states in this table the arithmetic average of the absolute values of the relative errors is 5.7% for pressure, 1.1% for fugacity, and 2.7% for enthalpy. This value for the average error in pressure is again dominated by the very poor prediction near the bubble point boundary at 100° F. It would be anticipated that a more detailed averaging over the entire surface would yield a value close to the 0.5% computed for the Tchebichef-Gram case.

For the Tchebichef-Tchebichef form of the equation of state the following critical state was predicted:

$$\sigma_c = 0.325 \frac{\text{lb mole}}{\text{ft}^3} \tag{86}$$

$$t_c = 214.2\ ^\circ F \tag{87}$$

$$P_c = 666.3 \ \text{psia} \tag{88}$$

The corresponding experimental values are given in equations 81 - 83. The description of the critical state is somewhat better than obtained with the Tchebichef-Gram coefficients. However the present prediction still leaves room for improvement. Apparently more terms would have to be included in the equation of state in order to provide the requisite precision of approximation in the critical region.

Computation of Virial Coefficients

The coefficients obtained for the Tchebichef-Gram form of the equation of state were regrouped to the conventional virial form. Let the virial coefficients be expressed in terms of the Gram polynomials and a set of coefficients d_{ij},

$$\begin{aligned} B(T) &= d_{00} V_0^{(h)}(\varepsilon) + d_{10} V_1^{(h)}(\varepsilon) + d_{20} V_2^{(h)}(\varepsilon) + - - - \\ C(T) &= d_{01} V_0^{(h)}(\varepsilon) + d_{11} V_1^{(h)}(\varepsilon) + - - - \\ &- \quad - - - \quad - - - \end{aligned} \tag{89}$$

ε is of course the normalized temperature variable, equation 23. Equation 1 may now be expressed as follows:

$$\frac{Z-1}{\sigma} = B(T) + C(T)\sigma + D(T)\sigma^2 + - - \tag{90}$$

$$\begin{aligned}\frac{Z-1}{\sigma} = \; & d_{00}V_0^{(h)}(\varepsilon) + d_{01}V_0^{(h)}(\varepsilon)\sigma + d_{02}V_0^{(h)}(\varepsilon)\sigma^2 + - - \\ & + d_{10}V_1^{(h)}(\varepsilon) + d_{11}V_1^{(h)}(\varepsilon)\sigma + - - - \\ & + - - - - \\ & + - - - -\end{aligned} \tag{91}$$

or

$$\begin{aligned} L(\sigma,T) = \frac{Z-1}{\sigma} & = \sum_i \sum_j d_{ij}V_i^{(h)}(\varepsilon)\sigma^j \\ & = d_{ij}V_i^{(h)}(\varepsilon)\sigma^j \end{aligned} \tag{92}$$

By a transformation of the type given by equation 57, the coefficients d_{ij} are expressible as linear combinations of the coefficients $a_{k\ell}$ of the Tchebichef-Gram expansion. The values obtained by regrouping of the 27 coefficients $a_{k\ell}$ of Table III are given in Table X. Using these coefficients and the equation of state in the form of equation 92, precisely the same results would be obtained as with the equation of state in the form of equation 33. However a word of warning should be injected, namely, that the coefficients of Table X are decidedly interdependent. All the terms represented by the coefficients of this table must be used to obtain satisfactory prediction. The arbitrary deletion of terms which was possible with the equation in the Tchebichef-Gram form is not permissible in this case.

By referring to equation 57 it may be seen that the virial coefficients are linear combinations of the coefficients $K_o(T)$, $K_1(T)$, ---$K_n(T)$ ---. The second virial coefficient is particularly simple, involving constants of only plus and minus unity. In general, the values obtained for any of the virial coefficients will change as more and more terms are included in the equation of state. It might be anticipated that as the number of terms included become larger and larger the values obtained for $B(T)$ would change less and less with each additional term and finally remain essentially constant. If this is the case, this method provides a simple but powerful procedure for determining the adequacy of the approximation polynomial.

In order to explore the application of this method, the data of the present study were employed to compute the successive approximations to the second virial coefficient. The resulting approximation curves are shown as a function of temperature in Figure 13. The experimental points included on this figure were obtained from the data of the source reference (26) by graphical evaluation of the following intercepts:

$$B(T) = \lim_{\sigma \to 0} L(\sigma, T) = \lim_{\sigma \to 0} \frac{Z-1}{\sigma}(\sigma, T) \qquad (93)$$

The validity of equation 93 is apparent from the fundamental virial equation of state, equation 1. The final approximation curve and the experimental values are compared in Table XI. The successive curves of Figure 13 correspond to the results obtained as each additional term $K_i(T)\ T_i(x)$ is added to equation 54. It appears that beyond $K_4(T)\ T_4(x)$ the additional terms do not significantly affect the results obtained for the second virial coefficient. The final approximation curve is compared with several sets of experimental investigations in Figure 14. For reference purposes the second virial coefficients have been included for the van der Waals equation (30) and the Benedict equation (30). The present investigation predicts values which compare favorably with experiment.

These approximations for the second virial coefficient are those that would have been obtained by least squares fitting of conventional polynomials with successively more terms. However in this latter case each new approximation would have necessitated the solving of progressively larger sets of simultaneous equations. Even if the sole objective of an investigation is to solve for the virial coefficients, much time can be saved by utilizing the orthogonal polynomials followed by a regrouping of the type indicated by equation 92.

In a similar manner, the successive approximations to the third virial coefficient were computed and are shown in Figure 15. Approximations 7 and 8 agree quite well throughout the temperature range. As might have been anticipated, the oscillations were more persistent than in the case of the second virial coefficient.

The Lennard-Jones $\{6 - 12\}$ potential

$$\phi(r) = 4e\left[\left(\frac{r_o}{r}\right)^{12} - \left(\frac{r_o}{r}\right)^{6}\right] \tag{94}$$

has been widely used for the calculation of properties of matter from a kinetic model (31). In this expression $\phi(r)$ is the potential energy of a pair of molecules with centers separated the distance r. e and r_o are parameters characteristic of a particular molecular species. Hirschfelder (4) and Fowler and Guggenheim (32) discuss the computation of the virial coefficients for a kinetic model possessing such a potential function. Hirschfelder includes tabulations of the second and third virial coefficients as a function of T, e, and r_o. If one assumes that this theory applies to a given system, then the intermolecular potential parameters e and r_o may be evaluated by comparing the experimental (or equation of state) and the theoretical second virial coefficients at two temperatures. In the present case the theoretical values were compared with those predicted by the equation of state at 100° F and 460° F. The resulting values of e and r_o are the following:

$$\frac{e}{k} = 444.6\ ^\circ R \tag{95}$$

$$r_o = 5.448\ \mathring{A} \tag{96}$$

These compare with the following values reported by Hirschfelder for determinations from experimental PVT data and, separately, from experimental viscosity data:

PVT data:

$$\frac{e}{k} = 435.6 \ {}^{\circ}R \tag{97}$$

$$r_o = 5.637 \ \text{Å} \tag{98}$$

Viscosity data:

$$\frac{e}{k} = 457.2 \ {}^{\circ}R \tag{99}$$

$$r_o = 5.061 \ \text{Å} \tag{100}$$

k is Boltzmann's constant. The Lennard-Jones second virial coefficient with the parameters assigned the values of equations 95 and 96 has been included in Table XI. The agreement with the equation of state is good over this comparatively short temperature interval.

The Lennard-Jones third virial coefficient based on these same parameters is compared with the final approximation of the equation of state in Figure 16. The data of this figure are reported on a conventional reduced basis using the variables

$$C^{\dagger}(T) = \frac{C(T)}{b_o^2} \tag{101}$$

and

$$T^{\dagger} = \frac{T}{\left(\frac{e}{k}\right)} \tag{102}$$

$b_o = \frac{2}{3} \pi \tilde{N} r_o^3$, and $\tilde{N}$ is Avogadro's number. For the r_o of equation 96, the corresponding value of b_o, the so-called co-volume, is 3.270 ft^3 per lb mole.

Computations for the virial coefficients beyond the third were not carried out, although the calculations could be performed using the data of Tables III or VII and equation 57. Limitations on the accuracy of the higher virial coefficients may be imposed by statistical fluctuations introduced into the data by the graphical methods employed. Also it is not clear whether or not the substituted two-phase path will introduce physically unreal behavior in these higher coefficients.

Comparative Computing Time

The equation of state presented in this work may appear somewhat formidable. An expression involving on the order of 30 parameters would perhaps be regarded as impractical for any application. However the experience gained in the course of the present work definitely indicates that, if digital computing equipment is available, this new equation of state is at least as simple to use as is that of Benedict. For example the following comparisons might be made for the time required to obtain the parameters. The actual machine time in the digital computer to obtain the Tchebichef-Gram expansion coefficients of Table III was 6 hours. We might estimate the following machine time for fitting the Benedict equation to propane.

Inner products	6 hours
Matrix inversion	1-2 hours
	7-8 hours

This would give a solution for only one assumed value of the parameter in the exponential term of the Benedict equation. If the process were repeated a number of times to obtain the optimum set of coefficients (13), the time required could easily be increased by a factor of four or five. An orthodox polynomial of 32 terms might require

Inner products	100	hours
Matrix inversion	20-25	hours
	120-125	hours

These latter figures assume no difficulties such as ill-conditioned matrices (15).

The linear nature of the new equation of state greatly facilitates the use of formal systematic matrix operations. This linearity is particularly advantageous in the expressions for the thermodynamic properties involving derivatives and integrals. With a digital computing installation, the computing time involved in applications is estimated to be less than for the Benedict equation of state, which involves only 1/3 as many parameters.

VIII. SUMMARY AND RECOMMENDATIONS

New Concepts

1. The present work used a particular grouping of PVT variables so extensively that it was found convenient to introduce the symbol $L(\sigma, T)$ and regard it as a fundamental thermodynamic variable.

2. As in previous work on equations of state, in the two-phase region the actual data were replaced by a smooth surface. However in this case this surface was made to satisfy very definite thermodynamic integration restraints.

3. The equation of state was presented as an open-ended series, with the truncation being made at whatever point yielded an acceptable approximation.

4. The series expansion utilizes orthogonal polynomials.

Conclusions

1. The orthogonal polynomial expansion results in acceptable approximations with a workable number of terms in the equation of state.

2. With a truncation of the expansion at about 30 terms, the average relative error in pressure as a function of volume and temperature is about 0.51%. The corresponding error in volume as a function of pressure and temperature is about 0.27%. The description of the vapor pressure curve is excellent.

3. The orthogonal polynomial offers a powerful method of obtaining the virial coefficients.

4. The equation of state is practical. With digital computing equipment, both the evaluation of the expansion coefficients and the application of the equation are less time consuming than use of the Benedict equation of state.

Limitations

1. The particular truncations examined in the present work involved significant errors in pressure as a function of volume and temperature very close to the bubble point boundary in the liquid phase.

2. For these truncations the descriptions of the critical state and the enthalpy of the system were only moderately successful.

3. The reported expansion coefficients were obtained from data which included sizeable regions of substitution or extrapolation. Although these

auxiliary data do not impair the utility of the equation in the region of actual data, they may impose some definite limitations on correlation of expansion coefficients from substance to substance and on the association of the virial coefficients with intermolecular potential functions.

4. THE EQUATION OF STATE CANNOT BE EXTRAPOLATED BEYOND THE RANGE OF THE EXPERIMENTAL DATA UPON WHICH IT IS BASED.

Suggestions for Further Research

1. Some consideration should be given to the selection of the value of σ_m used in the normalization of the reciprocal molal volume. A consistent and physically realistic system should be employed, particularly if it is hoped to correlate the expansion coefficients from substance to substance.

2. There may be more elegant methods of specifying the smooth two-phase surface than employed here.

3. Some investigation should be given to the limitations imposed on the significance of the virial coefficients owing to the smoothed two-phase surface. The author suspects that, if this path is thermodynamically consistent, it may not vitiate the computed values for intermolecular force parameters.

4. Other truncations of the equation for propane involving more terms might be inspected to see if the description of the critical state and the enthalpy of the system improve markedly.

5. In principle the equation of state should be immediately adaptable to the study of mixtures. For a binary system each of the coefficients

a_{ij} of the Tchebichef-Gram expansion may be assumed to have an expansion in a series of orthogonal polynomials which are functions of the mole fraction of one of the constituents. For example the following might be used:

$$L(\underset{\cdot}{\sigma}, T, \underset{\cdot}{n}) = b_{ijk} V_i^{(h)}(T)\, T_j(\underset{\cdot}{\sigma})\, T_k(\underset{\cdot}{n}) \tag{103}$$

The computational advantages of the orthogonal systems may render feasible the study of multicomponent molecular interaction over an extended range of pressure and temperature. It would be particularly interesting to determine whether or not the quadratic forms in mole fraction predicted by kinetic theory are adequate for the description of the second virial coefficients of mixtures (4,5,17,31,39,40).

6. The methods presented here have been sufficiently general so that it should be possible to describe a system exhibiting two phase transitions with an orthogonal polynomial equation of state. Apparently nobody has reported an equation of state which embraces the gas, liquid, and solid regions. The work of Yang and Lee (19,20) indicates qualitatively that one intermolecular force function is sufficient to describe a system in all three phases. (The volume change anomaly associated with the liquid-solid transition in water would make this substance a difficult one to cope with).

7. The usefulness of the Gram polynomials would be greatly increased if simple integration and differentiation formulas were available.

APPENDIX A

MATHEMATICAL PRINCIPLES

In this appendix several of the basic principles of orthogonal expansions will be indicated. More detailed discussions of the methods have been described by Churchill (35), Szego (36), and Courant and Hilbert (37).

Orthogonality

It will be convenient for present purposes to use the definitions of orthogonality given by Szego.

Definition 1. Let $\alpha(x)$ be a non-decreasing function in the interval $a \leq x \leq b$. If $a = -\infty$ (or $b = +\infty$) we require that $\alpha(-\infty) = \lim_{x \to -\infty} \alpha(x)$ and $\alpha(+\infty) = \lim_{x \to +\infty} \alpha(x)$ should be finite. The scalar product of two real functions f(x) and g(x) where x ranges over the real interval $a \leq x \leq b$ is defined by

$$(f, g) = \int_a^b f(x)\, g(x)\, d\,\alpha(x) \tag{104}$$

The assumption is made that f(x) g(x) is Stieltjes - Lebesgue integrable with respect to $\alpha(x)$ over $a \leq x \leq b$. For a fixed function $\alpha(x)$ the orthogonality with respect to the distribution $d\alpha(x)$ may be defined by the requirement that the scalar product be zero.

$$(f, g) = 0 \tag{105}$$

Definition 2. An orthogonal set of functions $\phi_0(x)$, $\phi_1(x)$ ——— $\phi_\ell(x)$, ℓ finite or infinite is defined by the relations

$$(\phi_n, \phi_m) = \int_a^b \phi_n(x)\, \phi_m(x)\, d\alpha(x) = \begin{cases} 0, & n \neq m \\ \varphi_n, & n = m \end{cases}$$

$$n, m = 0, 1, 2, ---- \ell \tag{106}$$

$\alpha(x)$ is a fixed non-decreasing function which is not constant in the interval $a \leq x \leq b$. $\phi_n^2(x)$ is Stieltjes - Lebesgue integrable. φ_n is a non-zero constant, depending on $\alpha(x)$ and the index n; it is not a function of x.

For the present discussion we have adopted these rather general definitions because they embrace a class of orthogonal polynomials for which, by choosing $\alpha(x)$ as an appropriate step function, the scalar integration may be replaced by summation over discrete values of the independent variable x. Thus the concept of the Stieltjes integral will be useful. No use will be made of the Lebesgue integral as such in this work.

As an illustration of these definitions, we might select the interval $0 \leq x \leq L$, $\alpha(x) = x$, and

$$\phi_n(x) = \sqrt{\frac{2}{L}} \sin\frac{n\pi x}{L} \qquad n=1,2 --- \tag{107}$$

In this case

$$(\phi_n, \phi_m) = \frac{2}{L}\int_0^L \sin\frac{n\pi x}{L} \sin\frac{m\pi x}{L}\, dx = \delta_{mn} = \begin{cases} 0 & m \neq n \\ 1 & m = n \end{cases} \tag{108}$$

This example is, of course, a well known orthogonal set employed in conventional Fourier expansions. It will be shown shortly that certain classes of polynomials satisfy Definitions 1 and 2.

Function Expansion

Given a complete set of orthogonal functions $\{\phi_n(x)\}$, $n = 1,2,$ —— , it may be possible to represent an arbitrary function in a fundamental interval $a \leq x \leq b$ as a linear combination of the functions $\phi_n(x)$.

$$f(x) = c_1 \phi_1(x) + c_2 \phi_2(x) + - - - - + c_n \phi_n(x) + - - -$$

$$a \leq x \leq b \tag{109}$$

If the series converges and if after being multiplied by $\phi_n(x)$, it can be Stieltjes integrated term by term with respect to the distribution $d\alpha(x)$ over the fundamental interval $a \leq x \leq b$, the coefficients c_n can be directly obtained.

$$(f, \phi_n) = c_1(\phi_1, \phi_n) + c_2(\phi_2, \phi_n) + - - + c_n(\phi_n, \phi_n) + - - \tag{110}$$

$$(f, \phi_n) = c_n(\phi_n, \phi_n) \tag{111}$$

All the scalar products except (ϕ_n, ϕ_n) vanish.

$$c_n = \frac{(f, \phi_n)}{(\phi_n, \phi_n)} = \frac{\int_a^b f(x)\, \phi_n(x)\, d\alpha(x)}{\int_a^b \phi_n^2(x)\, d\alpha(x)} \tag{112}$$

$$c_n = \frac{1}{Q_n} \int_a^b f(x)\, \phi_n(x)\, d\alpha(x) \tag{113}$$

The numbers c_n are frequently referred to as the Fourier constants or expansion coefficients of f(x) corresponding to the orthogonal system $\{\phi_n(x)\}$ and the distribution $d\alpha(x)$.

Approximation in the Mean

Let $F_m(x)$ represent a finite linear combination of m functions of an orthogonal set $\{\phi_n(x)\}$, n = 1,2, ——, $a \leq x \leq b$.

$$F_m(x) = \gamma_1 \phi_1(x) + \gamma_2 \phi_2(x) + ---- + \gamma_m \phi_m(x) \tag{114}$$

The values of the constants γ_i can be easily found for which $F_m(x)$ is the best approximation in the mean to any given function f(x); this means the best approximation in the sense that the value of the integral

$$J = \int_a^b \left[f(x) - F_m(x) \right]^2 d\alpha(x) \tag{115}$$

is to be minimized. It is also the approximation in the sense of least squares. The resulting expression is the following:

$$\gamma_i = c_i = \frac{1}{\varphi_i}\int_a^b f(x)\,\phi_i(x)\,d\alpha(x)$$

$$i = 1, 2, --- m \tag{116}$$

If the integrations can be performed, the coefficients are obtained directly without the necessity of solving m equations in m unknowns. Furthermore the value for γ_i, the coefficient of $\phi_i(x)$ in the approximation function $F_m(x)$, is precisely the value c_i, the coefficient of $\phi_i(x)$ in the infinite series expansion. Finally the coefficients γ_i are independent one of the other.

Expansion Theorems

The results of the previous paragraphs are dependent on a) the convergence of the series of equation 109, and b) the validity of the term by term integration. But the integration is justified if the convergence of the series is uniform. Hence requirements a and b are met if the series on the right side of equation 109 converges uniformly to the function f(x) in the interval $a \leq x \leq b$. This may be proved true for those complete orthogonal sets which are the eigenfunctions of a large class of second order differential equations with specified boundary conditions. The interested reader is referred to chapters II, V, and VI of

Courant and Hilbert, from which the following theorem is quoted:

> Theorem I. "Every piecewise continuous function in the fundamental domain with a square-integrable first derivative may be expanded in an eigenfunction series which converges absolutely and uniformly in all subdomains free of points of discontinuity; at the points of discontinuity it represents (like the Fourier series) the arithmetic mean of the right and left hand limits."

We might note in passing that the eigenfunction expansions may be used to approximate certain discontinuous functions; this is not possible with the power series expansion.

In the course of the present work it was found convenient to employ the Gram polynomials, which are orthogonal but which in general constitute a finite set. Theorem I therefore does not apply directly to expansions in a series of these polynomials. However if the functions which are to be approximated are restricted to continuous functions, the following approximation theorem of Weierstrass pertains (37):

> Theorem II. "Any function which is continuous in the interval $a \leq x \leq b$ may be approximated uniformly by polynomials in this interval."

APPENDIX B

TCHEBICHEF POLYNOMIALS (38,39)

Definition

The Tchebichef polynomials are defined by the following equation:

$$T_n(x) = \cos n \cos^{-1} x \qquad -1 \leq x \leq 1$$

$$n = 0, 1, 2, \cdots \tag{117}$$

Orthogonality

For this case an appropriate distribution function is

$$\alpha(x) = -\cos^{-1} x \tag{118}$$

Substituting into equation 106, the following result is obtained:

$$(T_n, T_m) = -\int_{-1}^{1} T_n(x)\, T_m(x)\, d(\cos^{-1} x) = \int_{-1}^{1} T_n(x)\, T_m(x) \frac{dx}{\sqrt{1-x^2}}$$

$$= \int_0^{\pi} \cos n\theta \cos m\theta \, d\theta = \begin{cases} 0 & , \quad m \neq n \\ \pi & , \quad m = n = 0 \\ \frac{\pi}{2} & , \quad m = n \neq 0 \end{cases} \tag{119}$$

Thus the Tchebichef polynomials are orthogonal with respect to $\alpha(x) = -\cos^{-1}x$ in the interval $-1 \leq x \leq 1$. $T_n(x)$ is a polynomial of degree n in x. It contains only even or odd powers of x according as n is even or odd. Consequently $T_n(-x) = (-1)^n T_n(x)$. The first ten Tchebichef polynomials are listed below.

$$T_0(x) = 1 \tag{120}$$

$$T_1(x) = x \tag{121}$$

$$T_2(x) = 2x^2 - 1 \tag{122}$$

$$T_3(x) = 4x^3 - 3x \tag{123}$$

$$T_4(x) = 8x^4 - 8x^2 + 1 \tag{124}$$

$$T_5(x) = 16x^5 - 20x^3 + 5x \tag{125}$$

$$T_6(x) = 32x^6 - 48x^4 + 18x^2 - 1 \tag{126}$$

$$T_7(x) = 64x^7 - 112x^5 + 56x^3 - 7x \tag{127}$$

$$T_8(x) = 128x^8 - 256x^6 + 160x^4 - 32x^2 + 1 \tag{128}$$

$$T_9(x) = 256x^9 - 576x^7 + 432x^5 - 120x^3 + 9x \tag{129}$$

$$T_{10}(x) = 512x^{10} - 1280x^{8} + 1120x^{6} - 400x^{4} + 50x^{2} - 1 \tag{130}$$

T_1, T_2, T_3, and T_6 are plotted as a function of x in Figure 3. $T_n(x)$ has exactly n zeros in the interval $-1 \leq x \leq 1$. The maxima are equal to unity in magnitude and alternate in sign.

The Tchebichef polynomials, $y = T_n(x)$ are the eigenfunctions of the following second order differential equation, with the boundary conditions that the solution be regular at $x = \pm 1$, the singularities of the equation

$$\left(\sqrt{1-x^2}\, y'\right)' + \frac{\lambda}{\sqrt{1-x^2}} = 0 \tag{131}$$

Tchebichef Polynomial Expansions

In order to examine the expansion of an arbitrary function, let us assume that the range of the variable is normalized to the fundamental interval $-1 \leq x \leq 1$. Now expand f(x) as a series in the $T_n(x)$.

$$f(x) = c_0 + c_1 T_1(x) + c_2 T_2(x) + \cdots + c_n T_n(x) + \cdots \tag{132}$$

Suppose that the series is truncated after n terms, and that this partial sum is employed as an approximation to the function f(x).

$$f(x) \cong \sum_{k=0}^{n-1} c_k T_k(x) \tag{133}$$

The error of the approximation is given by

$$\mathcal{E}(x) = \sum_{k=n}^{\infty} c_k T_k(x) \tag{134}$$

If the convergence is sufficiently rapid, we obtain an acceptable estimate of $\mathcal{E}(x)$ with one term.

$$\mathcal{E}(x) \cong c_n T_n(x) \tag{135}$$

The error of the approximation is then approximately of an oscillatory nature; the maxima are approximately equal in magnitude and oscillate between bounds of $\pm\ c_n$. Hence we have a fit in the "Tchebichef sense", i.e. in the sense of minimizing the maximum error. Clement (39) discusses the use of these polynomials to approximate functions by this criterion.

If the series in the $T_n(x)$ is cut off at the m^{th} term, it will represent the function f(x) more closely than the power series if cut off after the same number of terms.

If the data being fitted contain statistical fluctuations, the coefficients up to a certain c_m will decrease with a certain regularity. Then from this c_m on the coefficients remain small but irregular in sign and magnitude.

Summation Orthogonality

A previous paragraph noted the orthogonality of the $T_n(x)$ when integrated with respect to the weighting function $(1 - x^2)^{-\frac{1}{2}}$. It also happens that if data are being fitted with a series in $T_i(x)$, then the expansion coefficients may be obtained by summing inner products over the zeros of $T_k(x)$, where k is any integer greater than the index of highest order term of the approximation polynomial. Use is made of the following relationship:

$$\sum_{\alpha=0}^{k-1} T_i(x_\alpha)\, T_j(x_\alpha) = \begin{cases} k & , \; i = j = 0 \\ \frac{k}{2} & , \; i = j \neq 0 \\ 0 & , \; i \neq j \end{cases}$$

$$i, j < k \tag{136}$$

The x_α are given by the roots of the following equation:

$$T_k(x_\alpha) = 0 \tag{137}$$

Thus the expansion coefficients of an arbitrary function f(x) may be approximated by the following:

$$c_0 = \frac{1}{k} \sum_{\alpha=0}^{k-1} f(x_\alpha)\, T_0(x_\alpha) \tag{138}$$

$$c_j = \frac{2}{k} \sum_{\alpha=0}^{k-1} f(x_\alpha)\, T_j(x_\alpha) \qquad 1 \leq j \leq k-1 \tag{139}$$

Recalling that there are precisely k zeros of $T_k(x)$ in the fundamental interval, the number of points x_α of the summation grid increases directly with the index k. The actual numerical value obtained for the expansion coefficients from equations 138 and 139 will change somewhat as the grid is varied. However if there are a large number of grid points compared to the degree of the approximating polynomial, then it would be expected that the values obtained for the expansion coefficients would vary but little with increasing grid density.

Recalling the definition of equation 117, the zeros x_α are given by

$$x_\alpha = \cos \frac{2\alpha + 1}{2k} \pi \qquad \alpha = 0, 1, 2 \cdots k-1 \qquad (140)$$

The points x_α are thus not evenly spaced along the x axis but are bunched more closely together in the vicinity of ± 1, than at the middle of the range.

If the function f(x) to be approximated is given graphically, there are two possible methods of obtaining the coefficients for the approximation polynomial. One involves the use of equation 119, which requires evaluation $(1-x^2)^{-\frac{1}{2}}$ at each point of the interval. If the function is only known graphically or tabularly, it would presumably be necessary to employ some approximation technique to evaluate the integrals involved. The well-known graphical and numerical integration methods approximate the integrals by a finite sum. In this case it is probably somewhat simpler to employ directly the summation procedure which is made available by the summation orthogonality over a special grid. The latter procedure also eliminates the necessity for introducing the factor $(1 - x^2)^{-\frac{1}{2}}$. As in the case of the numerical approximation of integrals, this approximation may be refined to any pre-assigned accuracy by taking finer and finer grids. This summation technique was the one employed in the present work.

Analytical and Algebraic Properties

Below are listed several of the properties of the Tchebichef polynomials which greatly facilitate the application of approximation curves involving $T_n(x)$.

Integration

$$\int T_n(x)\,dx = \frac{1}{2}\left[\frac{T_{n+1}(x)}{n+1} - \frac{T_{n-1}(x)}{n-1}\right] + \text{constant}$$

$$n = 2, 3, \cdots \qquad (141)$$

Differentiation

$$T_n'(x) = \frac{n}{2(1-x^2)}\left[T_{n-1}(x) - T_{n+1}(x)\right] \qquad (142)$$

Recursion formula

$$T_{n+1}(x) = 2x\,T_n(x) - T_{n-1}(x) \qquad (143)$$

The latter equation is a very useful formula for generating numerical values. For a given value of x, one may start with $T_0 = 1$ and $T_1(x) = x$, and work up to successively higher indexes. In the process of the present investigation a comparatively simple procedure was devised for an IBM digital computer which permitted this recursion to be performed automatically at electronic speeds, giving values of $T_n(x)$ up to n = 999 starting from the value of x.

Equations 141 and 142 were used in section V to reduce differentiation and integration of the partial sums of f(x) to comparatively simple matrix operations.

APPENDIX C

GRAM POLYNOMIALS

Class I Gram Polynomials

In many operations involving the approximation of functions or experimental data by polynomials, the data are available at evenly spaced values of the independent variable. In such cases the computations associated with fitting the polynomials can be greatly simplified if one employs a class of polynomials which have the characteristic that they are orthogonal with respect to summation over integer values of the independent variable. Although these polynomials are much employed in applied mathematics and statistics, there is considerable confusion over the name associated with them. We wish therefore to point out that we are here referring to the class of polynomials which Birge and Weinberg (40) call "Tchebichef Polynomials" and which De Lury (41) calls "The Orthogonal Polynomials". Neither of these designations is particularly apt. We shall adopt the suggestion of Lanczos (38) and use the name Gram polynomials.

The polynomials are perhaps best defined by the orthogonality requirements. Pick an integer h. Require that $P_t^{(h)}(x)$ be a polynomial of degree t in x for $0 \leq x \leq h - 1$. Then the equations

$$\sum_{\substack{x=0,1\\2,3\cdots\\\cdots h-1}} P_i^{(h)}(x)\, P_j^{(h)}(x) = \begin{cases} 0 & , i \neq j \\ M_j^{(h)} & , i = j \end{cases}$$

$$i, j < h \qquad (144)$$

define the polynomials $P_k^{(h)}(x)$ and the values of $M_k^{(h)}$ within multiplicative factors. If it is further required that the coefficient of x^t in the polynomial $P_t^{(h)}(x)$ be unity, then the set of polynomials $P_k^{(h)}(x)$ and their summed squares $M_k^{(h)}$ are uniquely specified. These polynomials with lead coefficient unity will be called Class I Gram polynomials.

Equation 40 is consistent with the general definition of orthogonality since

$$\int_{-\infty}^{\infty} P_i^{(h)}(x)\, P_j^{(h)}(x)\, d\alpha(x) = \sum_{\substack{x=0,\\1,2\cdots\\\cdots h-1}} P_i^{(h)}(x)\, P_j^{(h)}(x) = \begin{cases} 0 & , i \neq j \\ M_j^{(h)} & , i = j \end{cases} \qquad (145)$$

if α (x) is taken as a step function with unit jumps at the points $x = 0, 1, 2, \text{----} h - 1$.

The reader's attention is called to the use of a superscript integer in parenthesis to indicate the order of the summation grid. Care should be taken to avoid confusion with powers or derivatives.

Birge and Weinberg (40) in a recent work have derived many of the pertinent properties of this class of polynomials and have given extensive examples of applications.

$P_t^{(h)}(x)$ is a polynomial of degree t in x. For example

$$P_0^{(h)}(x) = 1 \tag{146}$$

$$P_1^{(h)}(x) = x - \frac{h-1}{2} \tag{147}$$

$$P_2^{(h)}(x) = \left(x - \frac{h-1}{2}\right)^2 - \frac{h-1}{2} \tag{148}$$

It is convenient to introduce a shifted variable ε .

$$\varepsilon = x - \frac{h-1}{2} \tag{149}$$

As x runs from 0,1,2, —— h - 1, corresponding to h observations, ε will range symmetrically about zero in unit steps from $-\frac{1}{2}(h-1)$ to $\frac{1}{2}(h-1)$. Equations 146 - 148 assume the following form.

$$P_0^{(h)}(\varepsilon) = 1 \tag{150}$$

$$P_1^{(h)}(\varepsilon) = \varepsilon \tag{151}$$

$$P_2^{(h)}(\varepsilon) = \varepsilon^2 - \frac{h^2-1}{12} \tag{152}$$

$$P_3^{(h)}(\varepsilon) = \varepsilon^3 - \frac{3h^2-7}{20}\varepsilon \tag{153}$$

Note that $P_t^{(h)}(\varepsilon)$ contains only odd or even powers of ε according as t is even or odd. Also $P_t^{(h)}(-\varepsilon) = (-)^t P_t^{(h)}(\varepsilon)$. If $t > h$, $P_t^{(h)}(\varepsilon)$ may be regarded as undefined or taken equal to zero for all values of ε. As in the case of the Tchebichef polynomials, there exists a recursion formula for the Class I Gram polynomials.

$$P_{t+1}^{(h)}(\varepsilon) = \varepsilon P_t^{(h)}(\varepsilon) - \frac{t^2(h^2-t^2)}{4(4t^2-1)} P_{t-1}^{(h)}(\varepsilon) \tag{154}$$

This bears a formal similarity to equation 143 but is lacking in the simplicity of the latter. There also exists an explicit expression for the symmetric inner product.

$$\sum_{\varepsilon=-\frac{1}{2}(h-1)}^{\varepsilon=\frac{1}{2}(h-1)} \left\{ P_t^{(h)}(\varepsilon) \right\}^2 = M_t^{(h)} = \frac{(t!)^2 \binom{h+t}{2t+1}}{\binom{2t}{t}} \tag{155}$$

The terms in parentheses in this expression are conventional binomial coefficients.

Gram Polynomials

For particular values of h and t there is usually a particular integer factor that can be removed from the Class I Gram polynomial, $P_t^{(h)}(\varepsilon)$. Values obtained by factoring the set $P_k^{(h)}(\varepsilon)$ will be called simply the Gram polynomials and will be denoted by $V_k^{(h)}(\varepsilon)$. $V_t^{(h)}(\varepsilon)$ is related to $P_t^{(h)}(\varepsilon)$ by the symbol $S_{tt}^{(h)}$ as follows:

$$V_t^{(h)}(\varepsilon) = S_{tt} P_t^{(h)}(\varepsilon) \tag{156}$$

The polynomials $V_t^{(h)}(\varepsilon)$ have the advantage that their values at the integer coordinates are all integers of the lowest possible order.

In the $P_t^{(h)}(\varepsilon)$ system the lead coefficient (i.e. the coefficient of ε^t) was unity. However in the $V_t^{(h)}(\varepsilon)$ system, the coefficient of ε^t will be $S_{tt}^{(h)}$ and will not in general be unity.

$S_{tt}^{(h)}$ is obtained by empirical factorization. In most applications the $V_t^{(h)}(\varepsilon)$ system is preferred because of the numerical simplicity; most available tables for Gram polynomials report values in this system.

For $h = 13$ several of the polynomials are listed below and are plotted in Figure 4.

$$V_0^{(13)}(\varepsilon) = 1 \tag{157}$$

$$V_1^{(13)}(\varepsilon) = \varepsilon \tag{158}$$

$$V_2^{(13)}(\varepsilon) = \varepsilon^2 - 14 \tag{159}$$

$$V_3^{(13)}(\varepsilon) = \frac{1}{6}\varepsilon^3 - 4\frac{1}{6}\varepsilon \tag{160}$$

$$V_4^{(13)}(\varepsilon) = \frac{7}{12}\varepsilon^4 - 20\frac{7}{12}\varepsilon^2 + 84 \tag{161}$$

In this system the symmetric inner product is denoted by $N_t^{(h)}$

and is related to $M_t^{(h)}$ by the following equation:

$$N_t^{(h)} = \left\{S_{tt}^{(h)}\right\}^2 M_t^{(h)} = \left\{S_{tt}^{(h)}\right\}^2 \frac{(t!)^2 \binom{h+t}{2t+1}}{\binom{2t}{t}} \tag{162}$$

Tabulations of the polynomials are available (40,41). However to illustrate the numerical simplicity, a brief tabulation of $V_t^{(h)}(\varepsilon)$ and $S_{tt}^{(h)}$ for $h = 13$ is given in Table I.

Relative Merits of Tchebichef and Gram Polynomials

The primary advantage offered by the Tchebichef polynomials is their analytical simplicity. They possess convenient integration, differentiation and recursion formulas. In addition to the recursion relations, they may be quickly generated with the aid of cosine tables. Numerically their values are always between plus and minus unity, a convenience in planning computations on digital computers. For function approximation they result in ideal error curves. A possible disadvantage is that their summation orthogonality is with respect to an unevenly spaced grid.

The Gram polynomials are unwieldy analytically. Their derivatives and integrals are apparently not expressible in terms of simple combinations of Gram polynomials. The recursion formula 154 contains a variable factor, and even this formula does not apply to the factored $V_t^{(h)}(\varepsilon)$ set.

The primary advantages are the summation orthogonality with respect to an evenly spaced grid and, for the factored $V_t^{(h)}(\varepsilon)$ set, comparative numerical simplicity.

APPENDIX D

THERMODYNAMIC DERIVATIONS

Fugacity:

$$RT\left(\frac{\partial \ln f}{\partial P}\right)_T = \underset{\cdot}{V} \tag{163}$$

$$\underset{\cdot}{V} = \frac{1}{\underset{\cdot}{\sigma}} \tag{164}$$

$$d\underset{\cdot}{V} = -\frac{1}{\underset{\cdot}{\sigma}^2}\, d\underset{\cdot}{\sigma} \tag{165}$$

$$\frac{d\underset{\cdot}{V}}{\underset{\cdot}{V}} = -\frac{d\underset{\cdot}{\sigma}}{\underset{\cdot}{\sigma}} \tag{166}$$

$$Z = \frac{P\underset{\cdot}{V}}{RT} = \frac{P}{RT\underset{\cdot}{\sigma}} \tag{167}$$

Integrating 163 at constant T.

$$RT\int d\ln f = \int \underset{\cdot}{V}\, dP \qquad [T] \tag{168}$$

$$d(P\underset{\cdot}{V}) = P\,d\underset{\cdot}{V} + \underset{\cdot}{V}\,dP \tag{169}$$

$$\begin{aligned}
RT\int d\ln f &= \int d(P\underset{\cdot}{V}) - \int P\,d\underset{\cdot}{V} \\
&= \Delta(P\underset{\cdot}{V}) - \int P\underset{\cdot}{V}\,\frac{d\underset{\cdot}{V}}{\underset{\cdot}{V}} \\
&= \Delta(P\underset{\cdot}{V}) + RT\int Z/\underset{\cdot}{\sigma}\,d\underset{\cdot}{\sigma} \\
&= \Delta(P\underset{\cdot}{V}) + RT\int\frac{Z-1}{\underset{\cdot}{\sigma}}\,d\underset{\cdot}{\sigma} + RT\int\frac{d\underset{\cdot}{\sigma}}{\underset{\cdot}{\sigma}}
\end{aligned} \tag{170}$$

$$\begin{aligned}
RT\ln f = RT\ln f^{*} + P\underset{\cdot}{V} - (P\underset{\cdot}{V})^{*} &+ \int_{\underset{\cdot}{\sigma}^{*}}^{\underset{\cdot}{\sigma}}\frac{Z(\xi,T)-1}{\xi}\,d\xi \\
&+ RT\ln\underset{\cdot}{\sigma} - RT\ln\underset{\cdot}{\sigma}^{*}
\end{aligned} \tag{171}$$

$$\begin{aligned}
-RT\ln\underset{\cdot}{\sigma} &= RT\ln\frac{1}{\underset{\cdot}{\sigma}} = RT\ln\frac{RTZ}{P} \\
&= RT\ln RT + RT\ln Z + RT\ln\frac{1}{P}
\end{aligned} \tag{172}$$

$$RT\ln f = RT\ln f^{*} + P\underset{\cdot}{V} - (P\underset{\cdot}{V})^{*} + RT\int_{\underset{\cdot}{\sigma}^{*}}^{\underset{\cdot}{\sigma}} \frac{Z(\xi,T)-1}{\xi}\,d\xi$$

$$+ RT\ln\underset{\cdot}{\sigma} + RT\ln RT + RT\ln Z^{*}$$

$$+ RT\ln\frac{1}{P} \qquad (173)$$

$$RT\ln f = RT\ln\left(\frac{f}{P}\right)^{*} + RT(Z - Z^{*}) + RT\ln Z^{*}$$

$$+ RT\ln RT\underset{\cdot}{\sigma} + RT\int_{\underset{\cdot}{\sigma}^{*}}^{\underset{\cdot}{\sigma}} \frac{Z(\xi,T)-1}{\xi}\,d\xi \qquad (174)$$

Now let the starred state approach infinite attenuation.

$$\sigma^{*} \longrightarrow 0$$
$$\left(\frac{f}{P}\right)^{*} \longrightarrow 1$$
$$\ln\left(\frac{f}{P}\right)^{*} \longrightarrow 0$$
$$Z^{*} \longrightarrow 1$$
$$\ln Z^{*} \longrightarrow 0$$

$$\ln\frac{f}{RT\underset{\cdot}{\sigma}} = Z - 1 + \int_{0}^{\underset{\cdot}{\sigma}} \frac{Z(\xi,T)-1}{\xi}\,d\xi \qquad (175)$$

Enthalpy:

$$d\underset{\cdot}{E} = T\,d\underset{\cdot}{S} - P\,d\underset{\cdot}{V} \tag{176}$$

$$\left(\frac{\partial \underset{\cdot}{E}}{\partial \underset{\cdot}{V}}\right)_T = T\left(\frac{\partial \underset{\cdot}{S}}{\partial \underset{\cdot}{V}}\right)_T - P = T\left(\frac{\partial P}{\partial T}\right)_{\underset{\cdot}{V}} - P \tag{177}$$

$$\int d\underset{\cdot}{E} = \int \left\{ T\left(\frac{\partial P}{\partial T}\right)_{\underset{\cdot}{V}} - P \right\} d\underset{\cdot}{V} \tag{178}$$

$$\frac{Z-1}{\underset{\cdot}{\sigma}} = (Z-1)\underset{\cdot}{V} = \left(\frac{P\underset{\cdot}{V}}{RT} - 1\right)\underset{\cdot}{V} \tag{179}$$

$$\left(\frac{\partial \frac{Z-1}{\underset{\cdot}{\sigma}}}{\partial T}\right)_{\underset{\cdot}{\sigma}} = \frac{\underset{\cdot}{V}^2}{RT}\left(\frac{\partial P}{\partial T}\right)_{\underset{\cdot}{V}} - \frac{P\underset{\cdot}{V}^2}{RT^2} \tag{180}$$

$$\left(\frac{\partial P}{\partial T}\right)_{\underset{\cdot}{V}} = \frac{RT}{\underset{\cdot}{V}^2}\left(\frac{\partial \frac{Z-1}{\underset{\cdot}{\sigma}}}{\partial T}\right)_{\underset{\cdot}{\sigma}} + \frac{P}{T} \tag{181}$$

$$T\left(\frac{\partial P}{\partial T}\right)_{\underset{\cdot}{V}} d\underset{\cdot}{V} = -RT^2\left(\frac{\partial \frac{Z-1}{\underset{\cdot}{\sigma}}}{\partial T}\right)_{\underset{\cdot}{\sigma}} d\underset{\cdot}{\sigma} + P\,d\underset{\cdot}{V} \tag{182}$$

Substituting into equation 178:

$$\underset{\cdot}{E} - \underset{\cdot}{E}^{*} = -RT^{2} \int_{\underset{\cdot}{\sigma}^{*}}^{\underset{\cdot}{\sigma}} \left(\frac{\partial \frac{Z(\xi,T)-1}{\xi}}{\partial T} \right)_{\xi} d\xi \tag{183}$$

$$\underset{\cdot}{H} = \underset{\cdot}{E} + P\underset{\cdot}{V} \tag{184}$$

$$\frac{\underset{\cdot}{H} - \underset{\cdot}{H}^{\circ}}{RT} = Z - 1 + \int_{0}^{\underset{\cdot}{\sigma}} \left(\frac{\partial \frac{Z(\xi,T)-1}{\xi}}{\partial T} \right)_{\xi} d\xi \tag{185}$$

Entropy:

$$T\underset{\cdot}{S} = \underset{\cdot}{H} - RT\ln f + \omega(T) \tag{185a}$$

Using equations 175 and 185 the following is obtained:

$$\frac{\underset{\cdot}{S} - \underset{\cdot}{S}_{1}}{R} = \ln \frac{\underset{\cdot}{\sigma}_{1}}{\underset{\cdot}{\sigma}} + \int_{\underset{\cdot}{\sigma}_{1}}^{\underset{\cdot}{\sigma}} \left\{ \left(\frac{\partial \frac{Z(\xi,T)-1}{\xi}}{\partial T} \right)_{\xi} - \frac{Z(\xi,T)-1}{\xi} \right\} d\xi \tag{186}$$

APPENDIX E

VIRIAL REGROUPING

From equation 54,

$$\frac{Z-1}{\underset{\cdot}{\sigma}} = K_0(T)\,T_0(x) + K_1(T)\,T_1(x) + ---- + K_6(T)\,T_6(x) \tag{54}$$

Now decompose the $T_n(x)$ according to equations 120 - 130 of Appendix B. Substitute into 54 and collect terms.

$$\begin{aligned}\frac{Z-1}{\underset{\cdot}{\sigma}} = \; & \{K_0 - K_2 + K_4 - K_6\} \\ & + \{K_1 - 3K_3 + 5K_5\}\,x \\ & + \{2K_2 - 8K_4 + 18K_6\}\,x^2 \\ & + \{4K_3 - 20K_5\}\,x^3 \\ & + \{8K_4 - 48K_6\}\,x^4 \\ & + \{16K_5\}\,x^5 \\ & + \{32K_6\}\,x^6\end{aligned} \tag{187}$$

$$x^n = \left(\frac{2\underset{\cdot}{\sigma}}{\underset{\cdot}{\sigma}_m} - 1\right)^n = \sum_{i=0}^{n} \binom{n}{i} (-)^i \left(\frac{2}{\underset{\cdot}{\sigma}_m}\right)^i \underset{\cdot}{\sigma}^i \tag{188}$$

$$\text{Let } \beta = -\frac{2}{\underset{\cdot}{\sigma}_m} \tag{56}$$

$$\text{Then} \quad x = -(1 + \beta \underset{\cdot}{\sigma}) \tag{189}$$

$$\begin{bmatrix} -1 & -1 & 0 & 0 & 0 & 0 & 0 \\ 1 & 2 & 1 & 0 & 0 & 0 & 0 \\ -1 & -3 & -3 & -1 & 0 & 0 & 0 \\ 1 & 4 & 6 & 4 & 1 & 0 & 0 \\ -1 & -5 & -10 & -10 & -5 & -1 & 0 \\ 1 & 6 & 15 & 20 & 15 & 6 & 1 \end{bmatrix} \begin{bmatrix} 1 \\ \beta \underset{\cdot}{\sigma} \\ \beta^2 \underset{\cdot}{\sigma}^2 \\ \beta^3 \underset{\cdot}{\sigma}^3 \\ \vdots \\ \vdots \\ \beta^6 \underset{\cdot}{\sigma}^6 \end{bmatrix} = \begin{bmatrix} x \\ x^2 \\ x^3 \\ x^4 \\ x^5 \\ x^6 \end{bmatrix} \tag{190}$$

If equations 190 are substituted into equation 187 and the terms collected the following is obtained:

$$\begin{bmatrix} 1 & -1 & 1 & -1 & 1 & -1 & 1 \\ & -1 & 4 & -9 & 16 & -25 & 36 \\ & & 2 & -12 & 40 & -100 & 210 \\ & & & -4 & 32 & -140 & 448 \\ & & & & 8 & -80 & 432 \\ & & & & & -16 & 192 \\ & & & & & & 32 \end{bmatrix} \begin{bmatrix} K_0(T) \\ K_1(T) \\ | \\ | \\ | \\ | \\ K_6(T) \end{bmatrix}^{\gamma} \begin{bmatrix} \underset{\cdot}{\sigma} \\ \beta\ \underset{\cdot}{\sigma}^{2} \\ \beta^{2}\ \underset{\cdot}{\sigma}^{3} \\ | \\ | \\ | \\ \beta^{6}\ \underset{\cdot}{\sigma}^{7} \end{bmatrix} = Z - 1 \tag{191}$$

NOMENCLATURE

Special Notation

$[G]$	Restrictions on equations are occasionally indicated by a bracket following the equation. Appearance of a variable within the bracket is to indicate that the variable is held constant during the process indicated by the equation. Absence of a bracket does not necessarily imply that an equation is free of restriction.
(f,g)	This symbol is used for the scalar or inner product of the two functions f and g. See Definition 1 and equation 104.
$\overset{*}{a}_{ij}$	An asterisk on a coefficient tensor indicates that the range of summation is finite. See equations 40 and 41.
$[\quad]^{T}$	T appearing as an upper right superscript on a matrix is to be regarded as a transpose operator.

Abbreviations

Btu	British thermal unit
ft^3	cubic feet
lb	pound
psi	pounds per square inch
psia	pounds per square inch, absolute
PVT	pressure-volume-temperature

Symbols

a_{ij}	coefficient tensor of Tchebichef-Gram expansion; the coefficient of $V_i^{(h)}(\varepsilon)\ T_j(x)$; ft^3 per lb mole.
$B(T)$, $C(T)$ ---	second, third ---- virial coefficients
B_o, A_o, a, b, c	parameters of Beattie-Bridgeman equation of state.
b_o	$\frac{2}{3}\ \pi\ \tilde{N}\ r_o^3$; the co-volume, ft^3 per lb mole.
c_{ij}	coefficient tensor of Tchebichef-Tchebichef expansion; the coefficient of $T_i(y)\ T_j(x)$; ft^3 per lb mole.
c_i	expansion coefficients.
d_{ij}	coefficient tensor of virial-Gram expansion; the coefficient of $V_i^{(h)}(\varepsilon)\ \sigma^j$.
$\underset{\cdot}{E}$	molal internal energy, Btu per lb mole.
$\xi(x)$	truncation error
e	parameter of Lennard-Jones potential, Btu. See equation 94.
$F_m(x)$	approximation function comprised of a linear combination of m members of an orthogonal set.
^oF	degrees Fahrenheit.
$f(x) = f$	Function of x.
f	fugacity, psia.
$g(x) = g$	function of x.
$\underset{\cdot}{H}$	molal enthalpy, Btu per lb mole.
h	an integer; order of summation grid for Gram polynomials.

i,j,k,l	dummy indices; integers.
$K_i(T)$	temperature dependent coefficients. See equation 55.
k	Boltzmann's constant.
$J_i(T)$	temperature dependent coefficients. See equation 58.
L	$\frac{Z-1}{\sigma}$, ft^3 per lb mole.
$M_t^{(h)}$	symmetric inner product for Class I Gram polynomial of degree t and grid order h.
N	total number of points on a data point grid.
$\tilde{N}$	Avogadro's number.
$N_t^{(h)}$	symmetric inner product for Gram polynomial of degree t and grid order h.
n	mole fraction.
P	pressure, psia.
$P_t^{(h)}(\varepsilon)$	Class I Gram polynomial of argument ε , degree t and grid order h.
Q_n	symmetric inner product of orthogonal function of index n. See equation 106.
R	universal gas constant, (psia)(ft^3) per (lb mole) (°R).
r	order of data grid for Tchebichef polynomials $T_n(y)$.
r	distance variable in Lennard-Jones potential
r_o	parameter in Lennard-Jones potential.
S	molal entropy, Btu per (lb mole)(°R).
$S_{tt}^{(h)}$	empirical integer factor converting Class I Gram polynomial of degree t to Gram polynomial of degree t; both for an h order grid.

s^2	mean square error of approximation.
s_{ij}	error parameter corresponding to the coefficient a_{ij} or c_{ij}. See equation 65.
T	thermodynamic temperature, ^{o}R.
$T_n(x)$	Tchebichef polynomial of argument x and degree n.
t	temperature, ^{o}F.
t	order of data grid for Tchebichef polynomials $T_n(x)$.
V	specific volume, ft^3 per lb.
$\underset{\cdot}{V}$	molal volume, ft^3 per lb mole.
$\tilde{\underset{\cdot}{V}}$	residual molal volume, ft^3 per lb mole
$V_t^{(h)}(\varepsilon)$	Gram polynomial of argument ε , degree t and grid order h.
x	a variable; normalized σ variable. See equation 20.
y	a variable; normalized T variable. See equation 21.
Z	compressibility factor.
z	a variable

$\alpha(x)$	a function of x. See equation 104.
α, η, ν	indices; integers.
β	$-2/\sigma_m$.
γ_i	coefficients in approximation function.
δ_{ij}	Kronecker's delta operator.
ε	normalized T variable. See equation 23.
ξ	variable of integration.

σ	reciprocal molal volume, lb mole per ft^3.
σ_m	maximum value of σ .
$\phi_n(x)$	set of orthogonal functions; nth member of set of orthogonal functions.
$\phi(r)$	Lennard-Jones potential function, Btu.
$\omega(T)$	a function of temperature.

Subscripts

b	refers to bubble point.
c	refers to critical state.
d	refers to dew point.
e	refers to value of property predicted by equation.
g	refers to gas phase.
ℓ	refers to liquid phase.
max	refers to maximum value of a variable.
min	refers to minimum value of a variable.

Superscripts

$''$	refers to two-phase state.
$\ddagger$	indicates reduced variable.
o	refers to value of a variable at infinite attenuation

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LIST OF TABLES

TABLE I

GRAM POLYNOMIALS FOR h = 13

$\lvert\varepsilon\rvert^*$	$V_0^{(13)}(\varepsilon)$	$V_1^{(13)}(\varepsilon)$	$V_2^{(13)}(\varepsilon)$	$V_3^{(13)}(\varepsilon)$	$V_4^{(13)}(\varepsilon)$	$V_5^{(13)}(\varepsilon)$
6	1	6	22	11	99	22
5	1	5	11	0	-66	-33
4	1	4	2	-6	-96	-18
3	1	3	-5	-8	-54	11
2	1	2	-10	-7	11	26
1	1	1	-13	-4	64	20
0	1	0	-14	0	84	0

* Note that $V_t^{(h)}(-\varepsilon) = (-1)^t\, V_t^{(h)}(\varepsilon)$

TABLE II

TWO PHASE INTEGRATION

$$I = \int_{\sigma_d}^{\sigma_b} \frac{Z-1}{\sigma}\, d\sigma = \frac{P''}{RT}\left\{\frac{1}{\sigma_d} - \frac{1}{\sigma_b}\right\} - \ln\frac{\sigma_b}{\sigma_d} \qquad (30)$$

Temp. °F	I Eqn. 30	I Substituted Path Graphical Integration
100	-2.0745	-2.0736
130	-1.6825	-1.6820
160	-1.2884	-1.2878
190	-.8225	-.8232

TABLE III

EXPANSION COEFFICIENTS. TCHEBICHEF-GRAM FORM

$$\sum L^2(x_\alpha, t_v) = 3438.313261$$

Index i	 j	$\sum L V_i^{(h)} T_j$	$\sum\{V_i^{(h)}\}^2 \cdot \sum T_j^2$	a_{ij} ft³/lb mole	$\frac{\{\sum L V_i^{(h)} T_j\}^2}{\sum\{V_i^{(h)}\}^2 \cdot \sum T_j^2}$	s_{ij}
0	0	-577.46890	585	-0.987126	570.035	0.165789
1	0	1,912.59115	8,190	0.233528	446.644	.129902
2	0	-1,094.13732	90,090	-0.012145	13.288	.003865
3	0	116.23603	25,740	0.004516	.525	.000153
4	0	-174.87602	3,063,060	-0.000057	.010	.000003
5	0	-2.59905	278,468	-0.000009*	.000	.000000
0	1	810.49380	292.5	2.770918	2,245.812	.653173
1	1	-191.95504	4,095	-0.046875	8.998	.002617
2	1	97.29029	45,045	0.002160	.210	.000061
3	1	-13.16190	12,870	-0.001023	.013	.000004
0	2	178.04847	292.5	0.608712	108.380	.031521
1	2	85.31456	4,095	0.020834	1.777	.000517
2	2	-198.73986	45,045	-0.004412	.876	.000255
3	2	52.29347	12,870	0.004063	.212	.000062
4	2	-141.49890	1,531,530	-0.000092	.013	.000004
0	3	100.42343	292.5	0.343328	34.478	.010028
1	3	-83.23777	4,095	-0.020327	1.692	.000492
2	3	5.42023	45,045	0.000120*	.000	.000000
3	3	5.78696	12,870	0.000450*	.002	.000001
0	4	24.40526	292.5	0.083437	2.036	.000592
1	4	-86.10122	4,095	-0.021026	1.810	.000526
2	4	87.48971	45,045	0.001942	.170	.000049
3	4	-4.90093	12,870	-0.000381*	.002	.000001
0	5	-10.33068	292.5	-0.035319	.365	.000106
1	5	29.60233	4,095	0.007229	.214	.000062
2	5	-82.38807	45,045	-0.001829	.151	.000044
3	5	14.76260	12,870	0.001147	.017	.000005
0	6	1.80149	292.5	0.006159	.011	.000003
1	6	-26.55438	4,095	-0.006485	.172	.000050
2	6	60.81777	45,045	0.001350	.082	.000024
3	6	-14.76508	12,870	-0.001147	.017	.000005
0	7	-0.53050	292.5	-0.001814*	.001	.000000
1	7	5.03045	4,095	0.001228*	.006	.000002
2	7	-12.35343	45,045	-0.000274*	.003	.000001

* Coefficient not used for prediction purposes

TABLE IV

ERROR IN PREDICTED VAPOR PRESSURE. TCHEBICHEF-GRAM FORM

Temp. °F	P'' Experimental psia	P'' Equation psia	$P'' - P'''_e$ psia	$\frac{\Delta P''}{P''}$
100	188.7	190.2	-1.5	-0.0079
130	273.5	274.4	-0.9	-0.0033
160	383.8	384.3	-0.5	-.0013
190	524.8	524.5	+0.3	+.0006
206.3	617.4	621.1	-3.7	-.0060

TABLE V

PREDICTION OF THERMODYNAMIC PROPERTIES. TCHEBICHEF-GRAM FORM

Temp. °F.	σ lb.mole/ft.^{3}	P psia Experimental	P psia Equation	$P_e - P$ psia	$\frac{P_e - P}{P}$
100	0.66934	200	340.8	140.8	0.704000
	0.69396	1,000	1,055.9	55.9	0.055900
	0.76511	5,000	4,774.5	-225.5	-0.045100
	0.81500	10,000	9,909.10	-90.9	-0.009900
	DP	188.7	190.1	1.4	0.007459
	BP	188.7	189.8	1.1	0.005829
130	0.03926	200	199.9	-0.1	-0.000500
	0.65790	1,000	1,089.8	89.8	0.089800
	0.74349	5,000	4,989.9	-10.1	-0.000202
	0.79936	10,000	10,175.7	175.7	0.017570
	DP	273.5	274.3	00.8	0.002925
	BP	273.5	273.2	-00.3	-0.001097
160	0.03571	200	199.9	-00.1	-0.000500
	0.61463	1,000	1,007.1	7.1	0.007100
	0.72098	5,000	5,027.7	27.7	0.005540
	0.78125	10,000	10,080.3	80.3	0.008030
	DP	383.8	384.2	0.6	0.001563
	BP	383.8	384.1	0.5	0.001303
190	0.03311	200	200.3	0.3	0.001500
	0.56593	1,000	1,001.9	1.9	0.001900
	0.69881	5,000	5,029.8	29.8	0.005960
	0.76453	10,000	10,076.8	76.8	0.007680
	DP	524.8	524.6	-0.2	-0.000381
	BP	524.8	524.6	-0.2	-0.000381
220	0.03086	200	199.9	-0.1	-0.000500
	0.49628	1,000	988.6	-11.4	-0.011400
	0.67613	5,000	4,991.3	-28.9	-0.005780
	0.74738	10,000	9,981.7	-18.3	-0.001830
460	0.02053	200	200.0	0.0	0.000000
	0.12315	1,000	999.4	-0.6	-0.000600
	0.50429	5,000	5,011.1	11.1	0.002220
	0.62775	10,000	10,075.0	75.0	0.007500

TABLE V (continued)

Temp. °F.	ρ lb.mole/ft.^{3}	f psia Experimental	f psia Equation	$f_e - f$	$\frac{f_e - f}{f}$
100	0.66934	155.82	161.82	6.00	0.037078
	0.69396	189.41	192.69	3.28	0.017022
	0.76511	469.56	448.03	-21.53	-0.045851
	0.81500	1,344.1	1,318.30	-25.80	-0.019195
	DP	155.39	155.80	0.41	0.002638
	BP	155.39	155.83	0.44	0.002832
130	0.03926	168.32	167.97	-0.35	-0.002079
	0.65790	255.19	261.02	5.83	0.022846
	0.74349	624.32	624.56	0.24	0.000384
	0.79936	1,736.3	1,801.22	64.92	0.037390
	DP	213.42	213.42	0.00	0.000000
	BP	213.42	213.42	0.00	0.000000
160	0.03571	172.89	172.71	-0.18	-0.001041
	0.61463	329.52	330.56	1.04	0.003156
	0.72098	800.62	807.65	7.03	0.008781
	0.78125	2,172.0	2,213.71	41.71	0.013149
	DP	281.96	282.03	0.07	0.000248
	BP	281.96	282.03	0.07	0.000248
190	0.03311	176.55	176.83	0.28	0.001586
	0.56593	409.42	411.06	1.64	0.004001
	0.69881	994.16	1,004.79	10.63	0.010692
	0.76453	2,641.4	2,692.79	51.39	0.019455
	DP	360.46	361.25	0.79	0.002192
	BP	360.46	361.25	0.79	0.002192
220	0.03086	179.57	179.61	0.04	0.000223
	0.49628	492.51	492.50	-0.01	-0.000020
	0.67613	1,205.7	1,207.49	1.79	0.001485
	0.74738	3,145.9	3,144.96	-0.94	-0.000299
460	0.02053	192.49	192.54	0.05	0.000260
	0.12315	830.50	830.75	0.25	0.000301
	0.50429	3,004.0	3,017.72	13.72	0.004567
	0.62775	7,275.6	7,388.93	113.33	0.015577

TABLE V (continued

Temp. °F.	σ lb.mole/ft.^{3}	H-H° Btu/lb.mole Experimental	H-H° Btu/lb.mole Equation	H_e-H Btu/lb.mole	$\frac{H_e - H}{(H - H^o)}$
100	0.66934	-6,721.4	-6,561.4	160.0	-0.023805
	0.69396	-6,733.2	-6,579.7	153.5	-0.022797
	0.76511	-6,384.7	-6,366.4	18.4	-0.002882
	0.81500	-5,744.7	-5,769.4	-24.7	0.004300
	DP	-833.4	-830.8	2.6	-0.003120
	BP	-6,720.5	-6,551.2	169.3	-0.025192
130	0.03926	-713.5	-735.7	-22.2	0.031114
	0.65790	-6,418.3	-6,331.6	86.7	-0.013508
	0.74349	-6,180.4	-6,130.6	49.8	-0.008058
	0.79936	-5,569.7	-5,531.5	38.2	-0.006859
	DP	-1,157.5	-1,177.4	-19.9	0.017192
	BP	-6,337.4	-6,256.4	81.0	-0.012781
160	0.03571	-593.5	-620.8	-27.3	0.045998
	0.61463	-6,056.0	-6,035.5	20.5	-0.003385
	0.72098	-5,953.7	-5,919.0	34.1	-0.005728
	0.78125	-5,359.7	-5,341.6	18.1	-0.003377
	DP	-1,602.4	-1,644.1	-46.7	0.026023
	BP	-5,860.2	-5,871.9	-11.7	0.001997
190	0.03311	-519.9	-536.4	-16.5	0.031737
	0.56593	-5,642.4	-5,648.5	-6.1	0.001081
	0.69881	-5,728.9	-5,709.2	19.7	-0.003439
	0.76453	-5,174.6	-5,144.2	30.4	-0.005875
	DP	-2,274.4	-2,295.9	-21.5	0.009453
	BP	-5,261.0	-5,285.1	-24.1	0.004581
220	0.03086	-466.1	-469.6	-3.5	0.007509
	0.49628	-5,107.5	-5,077.3	30.2	-0.005913
	0.67613	-5,505.7	-5,493.1	12.6	-0.002289
	0.74738	-4,988.5	-4,962.5	26.0	-0.005212
460	0.02053	-283.6	-285.6	-2.0	0.007052
	0.12315	-1,441.1	-1,469.7	-28.6	0.019846
	0.50429	-3,963.7	-4,018.7	-55.0	0.013876
	0.62775	-3,748.1	-3,846.7	-98.6	0.026307

TABLE VI

PREDICTION OF THERMODYNAMIC PROPERTIES. VOLUME AS DEPENDENT VARIABLE.

TCHEBICHEF-GRAM FORM

Temp °F	P psia	σ lb.mole/ft.^{3} Experimental	σ lb.mole/ft.^{3} Equation	$\sigma_e - \sigma$	$\frac{\sigma_e - \sigma}{\sigma}$
100	340.8	0.67476	0.66934	-0.00542	0.008098
	1,055.9	.69541	.69396	-0.00145	0.002089
	4,774.5	.76278	.76511	0.00233	0.003045
	9,909.10	.81300	.81500	0.00200	0.002454
130	199.9	.03924	.03926	0.00002	0.000509
	1,089.8	.66138	.65790	-0.00348	0.005290
	4,989.9	.74794	.74349	-0.00445	0.005985
	10,175.7	.80128	.79936	-0.00192	0.002402
160	199.9	.03569	.03571	0.00020	0.000560
	1,007.1	.61652	.61463	-0.00189	-0.003066
	5,027.7	.72307	.72098	-0.00209	-0.002890
	10,080.3	.78186	.78125	-0.00061	-0.000780
190	200.3	.03316	.03311	-0.00005	-0.001508
	1,001.9	.56721	.56593	-0.00128	-0.002257
	5,009.8	.70028	.69881	-0.00147	-0.002099
	10,076.8	.76511	.76453	-0.00058	-0.000758
220	199.9	.03084	.03086	0.00002	0.000648
	988.6	.49480	.49628	0.00148	0.002991
	4,991.3	.67568	.67613	0.00067	0.000992
	9,981.7	.74683	.74738	0.00055	0.000736
460	200.0	.02053	.02053	0.00000	0.000000
	999.4	.12315	.12315	0.00000	0.000000
	5,011.1	.50479	.50429	-0.00050	-0.000990
	10,075.0	.62854	.62775	-0.00079	-0.001257

TABLE VI (continued)

Temp °F.	P psia	f psia Experimental	f psia Equation	f_e-f psia	$\frac{f_e-f}{f}$
100	340.8	157.4	161.82	4.4	0.0280
	1,055.9	192.2	192.69	0.5	0.0026
	4,774.5	439.3	448.03	8.7	0.0198
	9,909.10	1,298.1	1,318.30	20.2	0.0156
130	199.9	168.3	167.97	-0.3	-0.0018
	1,089.8	259.4	261.02	0.6	0.0023
	4,989.9	623.1	624.56	1.5	0.0024
	10,175.7	1,811.3	1,801.22	-10.1	-0.0056
160	199.9	172.9	172.71	-0.2	-0.0012
	1,007.1	331.9	330.56	-1.3	-0.0059
	5,027.7	805.1	807.65	2.5	0.0031
	10,080.3	2,197.5	2,213.71	16.2	0.0074
190	200.3	176.6	176.83	0.2	0.0011
	1,001.9	410.2	411.06	0.9	0.0022
	5,009.8	1,000.1	1,004.79	4.7	0.0047
	10,076.8	2,700.6	2,692.79	-7.8	-0.0029
220	199.9	179.6	179.61	0.0	0.0000
	988.6	492.3	492.50	0.2	0.0004
	4,991.3	1,203.6	1,207.49	3.9	0.0032
	9,981.7	3,140.1	3,144.96	4.9	0.0016
460	200.0	192.5	192.54	0.0	0.0000
	999.4	830.0	830.75	0.8	0.0010
	5,011.1	3,010.7	3,017.72	10.0	0.0033
	10,075.0	7,330.2	7,388.93	58.7	0.0080

TABLE VI (continued)

Temp. °F.	P psia	$\underset{\cdot}{H}-H_o$ Btu/lb.mole Experimental	$\underset{\cdot}{H}-H_o$ Btu/lb.mole Equation	$\underset{\cdot}{H}_e-\underset{\cdot}{H}$ Btu/lb.mole	$\frac{\underset{\cdot}{H}_e-\underset{\cdot}{H}}{(\underset{\cdot}{H}-H_o)}$
100	340.8	-6,721.4	-6,561.4	160.0	-0.0238
	1,055.9	-6,733.2	-6,579.7	153.5	-0.0228
	4,774.5	-6,409.9	-6,366.4	43.5	-0.0068
	9,909.10	-5,765.6	-5,769.4	-3.8	0.0007
130	199.9	-713.5	-735.7	-22.2	0.0311
	1,089.8	-6,418.3	-6,331.6	86.7	-0.0135
	4,989.9	6,180.0	-6,130.6	49.4	-0.0080
	10,175.7	5,547.0	-5,531.5	15.5	-0.0028
160	199.9	-593.5	-620.8	-27.3	0.0460
	1,007.1	-6,056.0	-6,035.5	20.5	-0.0034
	5,027.7	-5,952.5	-5,919.0	33.5	-0.0056
	10,080.3	-5,349.1	-5,341.6	7.5	-0.0014
190	200.3	-519.9	-536.4	-16.5	0.0317
	1,001.9	-5,642.4	-5,648.5	-6.1	0.0011
	5,009.8	-5,727.3	-5,709.2	18.1	-0.0032
	10,076.8	-5,164.0	-5,144.2	19.8	-0.0038
220	199.9	-466.1	-469.6	-3.5	0.0075
	988.6	-5,066.6	-5,077.3	-10.7	0.0021
	4,991.3	-5,505.0	-5,493.1	11.9	-0.0021
	9,981.7	-4,990.6	-4,962.5	28.1	-0.0056
460	200.0	-283.6	-285.6	-2.0	0.0071
	999.4	-1,441.1	-1,469.7	-28.6	0.0198
	5,011.1	-3,963.3	-4,018.7	-55.4	0.0140
	10,075.0	-3,740.8	-3,846.7	-105.9	0.0283

TABLE VII

EXPANSION COEFFICIENTS. TCHEBICHEF-TCHEBICHEF FORM

$\sum L^2(x_\alpha, y_\eta)$ = 12,625.412097

Index i	j	$\sum L\, T_i(y)\, T_j(x)$	$\sum T_i^2 \cdot \sum T_j^2$	c_{ij} ft³/lb mole	$\dfrac{\{\sum L\, T_i\, T_j\}^2}{\sum T_i^2(y) \cdot \sum T_j^2(x)}$	S_{ij}
0	0	-2,098.073000	2,025	-1.03608543	2,173.782866	0.172175
1	0	1,430.206540	1,012.5	1.41254967	2,020.237785	0.160014
2	0	-222.408704	1,012.5	-0.21966292	48.854945	0.003870
3	0	39.779805	1,012.5	0.03928870	1.562897	0.000124
4	0	-3.664356	1,012.5	-0.00361912	0.013262	0.000001
5	0	-0.253901	1,012.5	-0.00025077*	0.000064	0.000000
0	1	2,814.223513	1,012.5	2.77948001	7,822.077995	0.619550
1	1	-143.556373	506.25	-0.28356814	40.708014	0.003224
2	1	19.930367	506.25	0.03936863	0.78463	0.000062
3	1	-4.193405	506.25	-1.00828327	0.034735	0.000003
4	1	5.176313	506.25	0.01022482	0.052927	0.000004
5	1	-3.833536	506.25	-0.00757242	0.029029	0.000002
0	2	599.305008	1,012.5	0.59190618	354.732338	0.028097
1	2	67.892090	506.25	0.13410783	9.104861	0.000721
2	2	-41.432895	506.25	-0.08184276	3.390982	0.000269
3	2	19.500120	506.25	0.03851876	0.751120	0.000059
4	2	-4.988904	506.25	-0.00985463	0.049164	0.000004
0	3	347.115278	1,012.5	0.34282990	119.001496	0.009426
1	3	-60.160559	506.25	-0.11883567	7.149220	0.000566
2	3	1.721439	506.25	0.00340037*	0.005853	0.000000
0	4	93.638614	1,012.5	0.09248258	8.659942	0.000686
1	4	-64.888864	506.25	-0.12817554	8.317165	0.000659
2	4	17.494953	506.25	0.03455793	0.604589	0.000048
3	4	-1.277598	506.25	-0.00252365*	0.003224	0.000000
0	5	-42.819115	1,012.5	-0.04229048	1.810841	0.000143
1	5	22.476748	506.25	0.04439851	0.997934	0.000079
2	5	-16.660693	506.25	-0.03291001	0.548304	0.000043
3	5	5.257033	506.25	0.01038426	0.054590	0.000004
0	6	11.050566	1,012.5	0.01091414	0.120607	0.000010
1	6	-20.369060	506.25	-0.04023518	0.819553	0.000065
2	6	12.760142	506.25	0.02520522	0.321622	0.000025
3	6	-5.854205	506.25	-0.01156386	0.067697	0.000005
0	7	-2.496626	1,012.5	-0.00246580*	0.006156	0.000000

* Coefficient not used for prediction

TABLE VIII

ERROR IN PREDICTED VAPOR PRESSURE. TCHEBICHEF-TCHEBICHEF FORM

Temp °F	P'' Experimental psia	P'' Equation psia	$P''-P''_e$ psia	$\frac{\Delta P''}{P}$
100	188.7	190.2	-1.5	-0.0079
130	273.5	273.9	-0.4	-0.0015
160	383.8	383.3	+0.5	+0.0013
190	524.8	524.4	+0.4	+0.0008
206.3	617.4	617.4	0.0	0.0000

TABLE IX

PREDICTION OF THERMODYNAMIC PROPERTIES. TCHEBICHEF-TCHEBICHEF FORM.

Temp. °F	σ lb.mole/ft.^{3}	P psia Experimental	P psia Equation	P_e-P psia	$\frac{P_e-P}{P}$
100	0.66934	200	373.5	173.5	0.867500
	.69396	1,000	1,087.3	87.3	0.087300
	.76511	5,000	4,805.6	-194.4	-0.038880
	.81500	10,000	9,958.9	-41.1	-0.004110
130	.03926	200	200.0	0.0	0.000000
	.65790	1,000	1,053.0	53.0	0.053000
	.74349	5,000	4,929.7	-70.3	-0.014060
	.79936	10,000	10,103.2	103.2	0.010320
160	.08571	200	199.9	-0.1	-0.000500
	.61463	1,000	974.7	-25.3	-0.025300
	.72098	5,000	4,974.3	-26.0	-0.005200
	.78125	10,000	10,021.2	21.2	0.002120
220	.03086	200	199.9	-0.1	-0.000500
	.49628	1,000	991.6	-8.4	-0.008400
	.67613	5,000	4,998.1	-1.7	-0.000380
	.74738	10,000	10,014.3	14.3	0.001430
460	.02053	200	200.0	0.0	0.000000
	.12315	1,000	998.7	-0.3	-0.003000
	.50429	5,000	5,007.8	7.8	-0.001560
	.10775	10,000	10,079.2	79.2	0.007920

TABLE IX (continued)

Temp. °F.	ρ lb.mole/ft.^{3}	f psia Experimental	f psia Equation	f_e-f	$\frac{f_e-f}{f}$
100	0.66934	155.82	163.05	7.23	0.046400
	.69396	189.41	194.07	4.66	0.024603
	.76511	469.56	451.20	-18.36	-0.039100
	.81500	1,344.1	1,332.73	-11.37	-0.008459
130	.03926	168.32	168.10	-0.22	-0.001307
	.65790	255.19	258.13	3.24	0.012696
	.74349	624.32	615.19	-9.13	-0.014624
	.79936	1,736.3	1,769.78	33.48	0.019282
160	.08571	172.89	172.85	-0.04	-0.000231
	.61463	329.52	327.25	-2.27	-0.006889
	.72098	800.62	795.92	-4.70	-0.005870
	.78125	2,172.0	2,179.30	7.30	0.003361
220	.03086	179.57	179.52	-0.05	-0.000278
	.49628	492.51	491.23	-1.28	-0.002599
	.67613	1,205.7	1,204.92	-0.78	-0.000647
	.74738	3,145.9	3,154.79	8.89	0.002826
460	.02053	192.49	192.58	0.09	0.000468
	.12315	830.50	830.81	0.31	0.000373
	.50429	3,004.0	3,016.44	12.44	0.004141
	.10775	7,275.6	7,395.99	120.39	0.016547

TABLE IX (continued)

Temp. °F.	ρ lb.mole/ft.^{3}	$H-H_o$ Btu/lb.mole Experimental	$H-H_o$ Btu/lb.mole Equation	H_e-H Btu/lb.mole	$\frac{H_e-H}{(H-H_o)}$
100	0.66934	-6,721.4	-6,566.1	155.3	-0.023652
	.69396	-6,733.2	-6,562.7	170.5	-0.025322
	.76511	-6,384.7	-6,384.3	0.4	-0.000063
	.81500	-5,744.7	-5,628.5	116.2	-0.020227
130	.03926	-713.5	-838.7	-125.2	0.175473
	.65790	-6,418.3	-6,314.0	104.3	-0.016250
	.74349	-6,180.4	-6,100.2	80.2	-0.012976
	.79936	-5,569.7	-5,494.2	75.5	-0.013555
160	.08571	-593.5	-612.8	-19.3	0.031495
	.61463	-6,056.0	-6,005.5	50.5	-0.008339
	.72098	-5,953.7	-5,907.6	46.1	-0.007743
	.78125	-5,359.7	-5,345.9	13.8	-0.002575
220	.03086	-466.1	-464.7	1.4	-0.003004
	.49628	-5,107.5	-5,072.7	34.8	-0.006814
	.67613	-5,505.7	-5,515.9	-10.2	0.001853
	.74738	-4,988.5	-4,994.5	-6.0	0.001203
460	.02053	-283.6	-291.4	-7.8	0.027504
	.12315	-1,441.1	-1,519.3	-78.2	0.054264
	.50429	-3,963.7	-4,157.8	-194.1	0.048969
	.10775	-3,748.1	-3,981.6	-233.5	0.062298

TABLE X

COEFFICIENTS FOR VIRIAL EQUATION OF STATE

See equation 92

i	j	d_{ij}
0	0	-3.36774500
1	0	.28682400
2	0	-.01359600
3	0	.00730800
4	0	-.00014900
0	1	2.40568497
1	1	1.06694373
2	1	-.25753410
3	1	.12851705
4	1	.00089756
0	2	.31292421
1	2	-.15706108
2	2	.03184151
3	2	-.02066889
4	2	-.00001095
0	3	-1.30592428
1	3	.65420727
2	3	-.13392197
3	3	.09785634
4	3	.00000000
0	4	.21777141
1	4	-.12556071
2	4	.02636655
3	4	-.02078249
4	4	.00000000
0	5	-.15084480
1	5	.11745447
2	5	-.02489843
3	5	.02059241
4	5	.00000000
0	6	.04149126
1	6	-.04368742
2	6	.00909453
3	6	-.00772698
4	6	.00000000

TABLE XI

SECOND VIRIAL COEFFICIENT

Temp °F	Experimental Data See Eqn. 93	Equation of State Tchebichef-Gram Form See Sect. VII	Lennard-Jones Potential See Sect. VII
100	-5.549*	-5.483	-5.46
130	-4.928	-4.942	-4.99
160	-4.487	-4.484	-4.54
190	-4.097	-4.091	-4.14
220	-3.783	-3.756	-3.77
250	-3.466	-3.458	-3.46
280	-3.191	-3.190	-3.19
310	-2.933	-2.943	-2.94
340	-2.687	-2.711	-2.71
370	-2.483	-2.490	-2.49
400	-2.264	-2.277	-2.28
430	-2.070	-2.073	-2.07
460	-1.893	-1.880	-1.88

* Second virial coefficient, B(T), ft^3 per lb. mole

LIST OF FIGURES

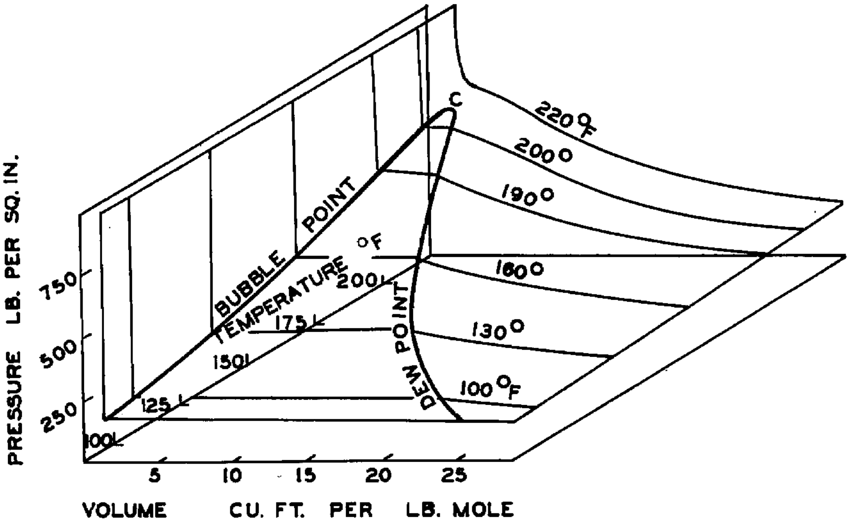

Fig. 1. PVT Surface. Propane

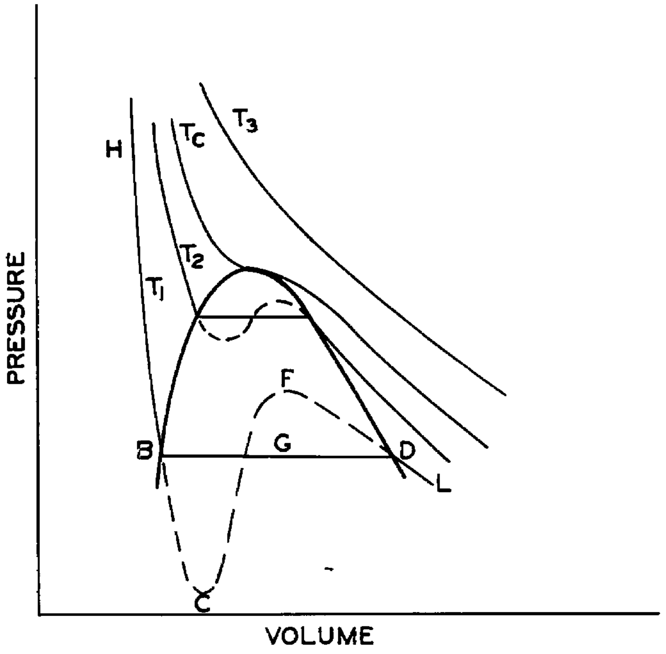

Fig. 2. Isothermal Projections of PVT Surface

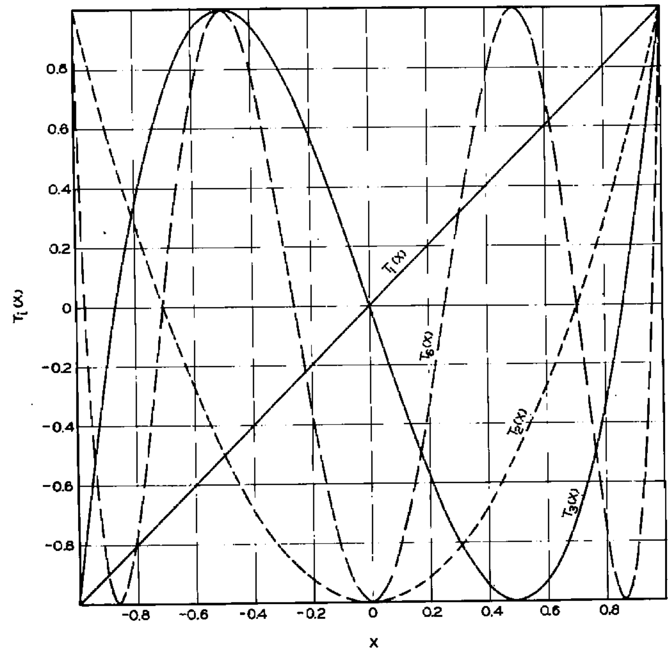

Fig. 3. Tchebichef Polynomials

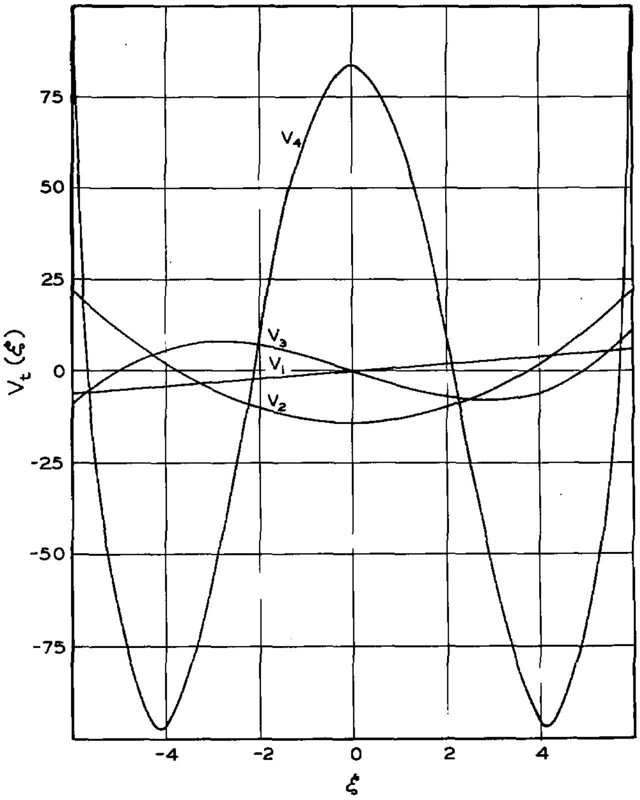

Fig. 4. Gram Polynomials

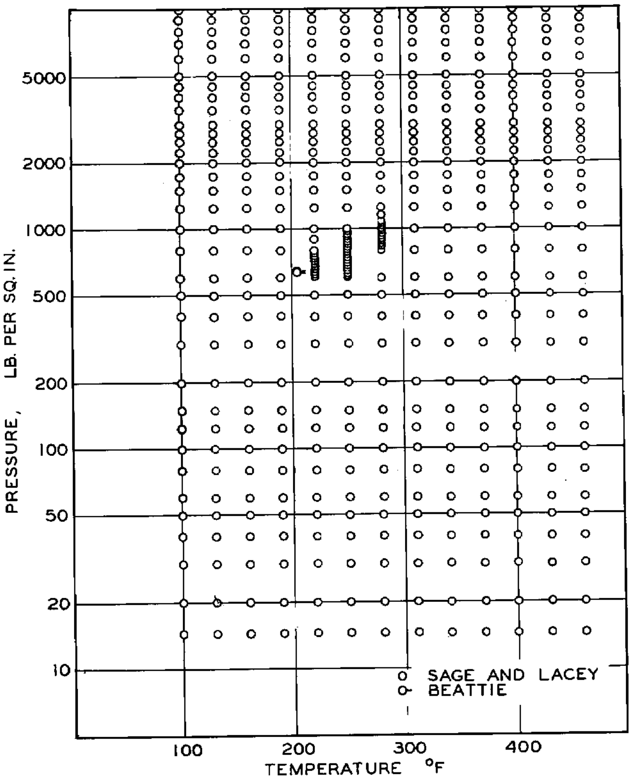

Fig. 5. Experimental Data Used to Establish Coefficients for Propane

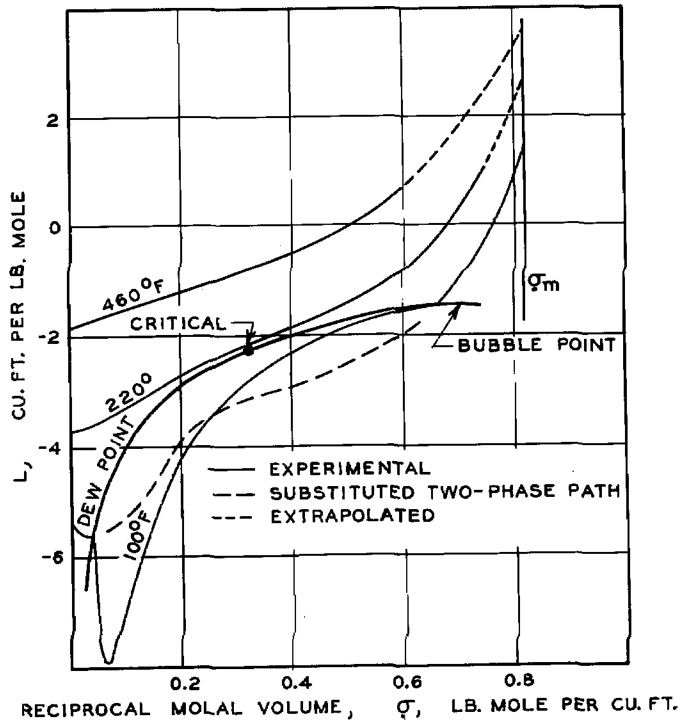

Fig. 6. L(σ ,T) for Propane

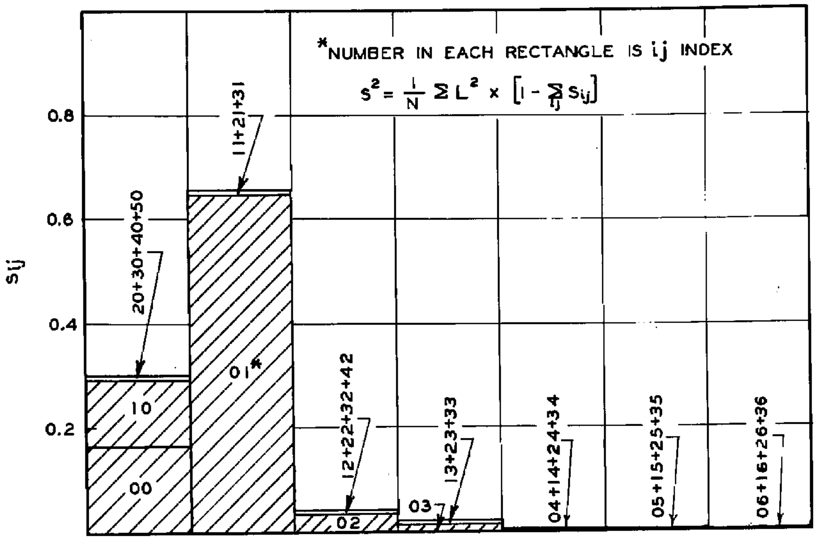

Fig. 7. Error Parameter. Tchebichef-Gram Form. The Height of Each Rectangle, S_{ij}, is Proportional to the Increase in the Mean Square Error in L(σ , T) Resulting from the Deletion of the Coefficient a_{ij} from the Equation of State

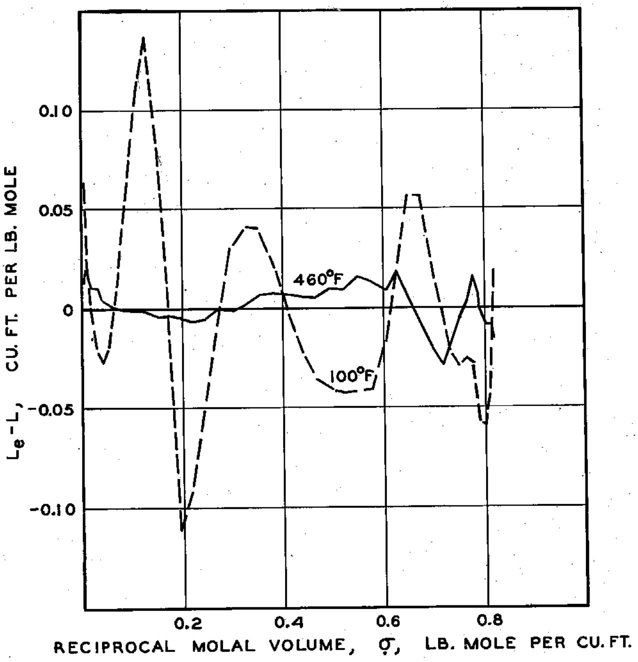

Fig. 8. Deviations of L(σ ,T) for Propane

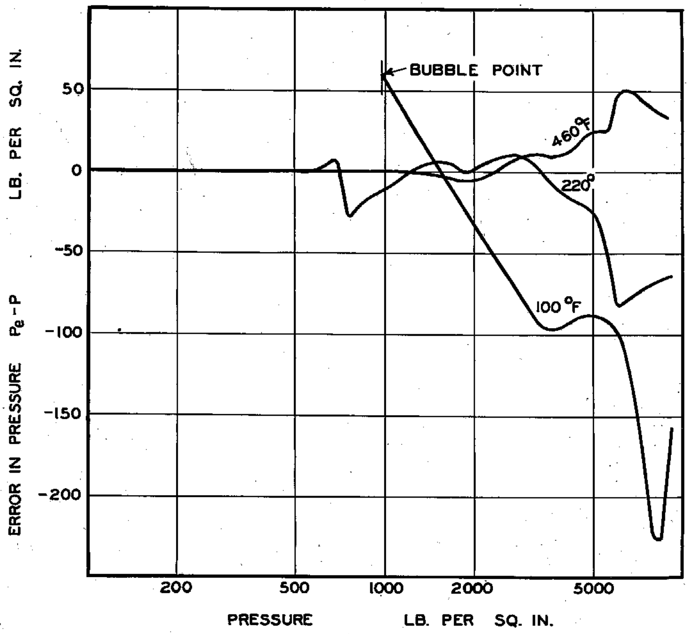

Fig. 9. Deviations of Pressure for Propane

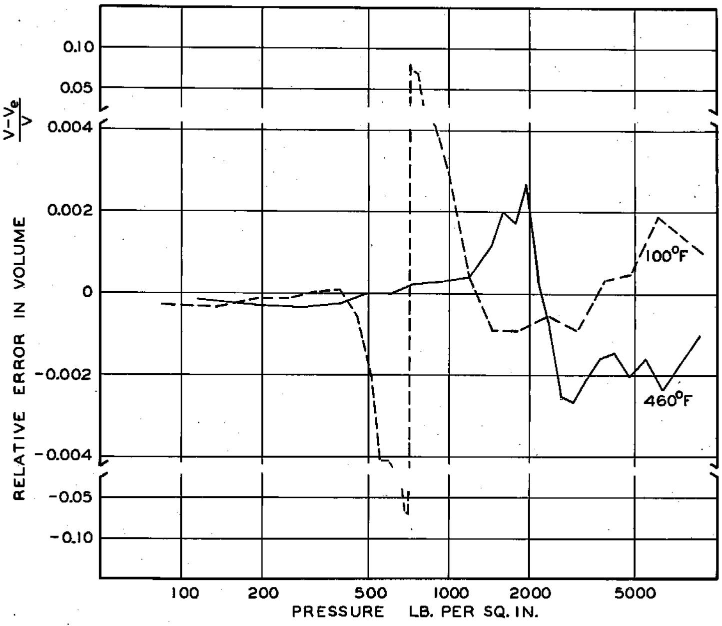

Fig. 10. **Relative Deviations in Volume for Propane**

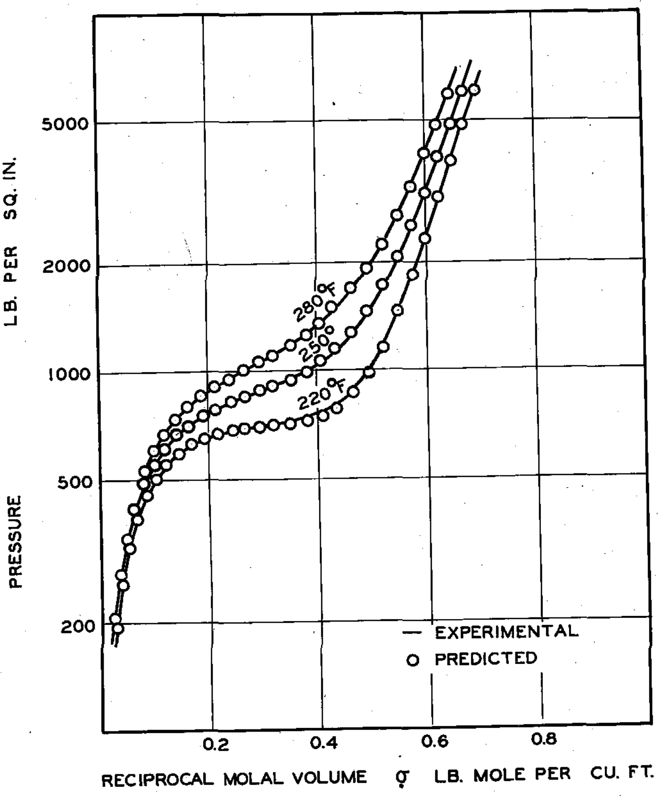

Fig. 11. Predicted and Experimental Values of Pressure for Propane. Critical Region

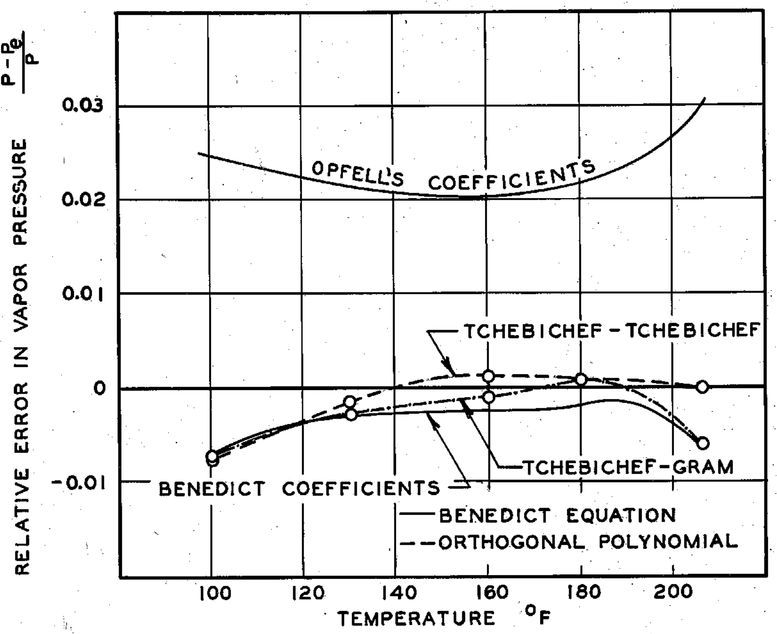

Fig. 12. Relative Deviations in Vapor Pressure for Propane

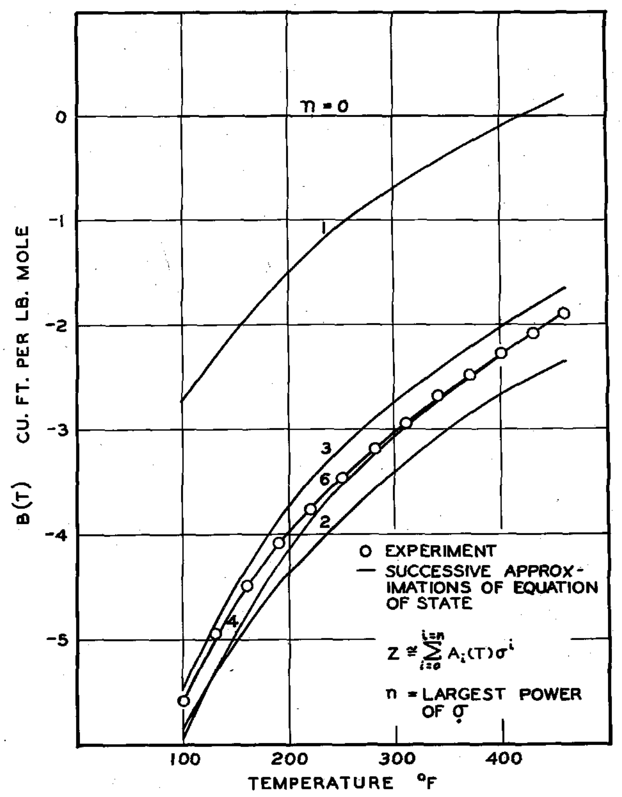

Fig. 13. Successive Approximation to Second Virial Coefficient for Propane

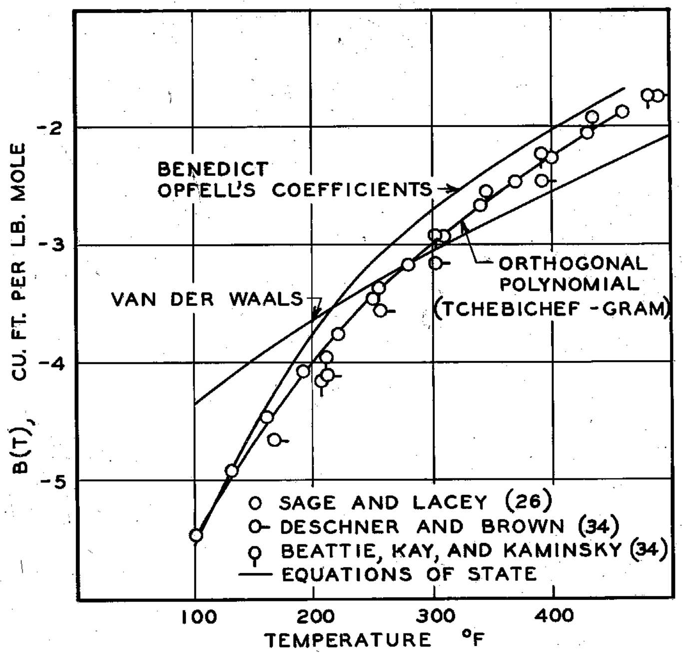

Fig. 14. Second Virial Coefficient for Propane

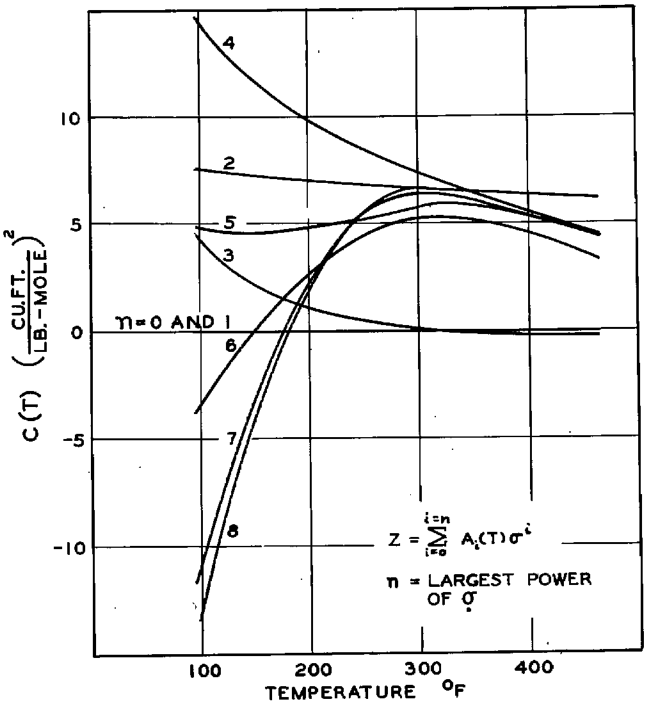

Fig. 15. Successive Approximations to Third Virial Coefficient for Propane

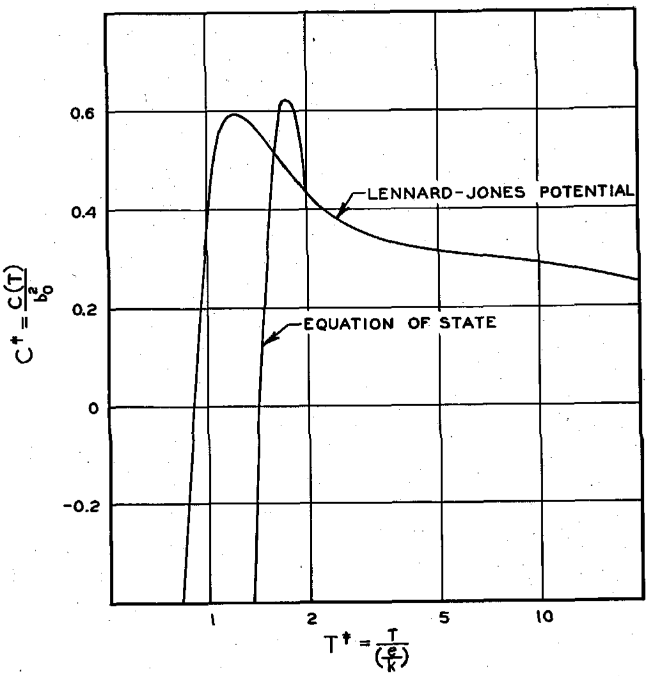

Fig. 16. Third Virial Coefficient for Propane

PART TWO

PART TWO. APPLICATION OF THE BENEDICT EQUATION OF STATE TO THE METHANE-n-PENTANE SYSTEM

I. INTRODUCTION

Benedict, Webb, and Rubin (3,4,5,6,7) developed an empirical equation of state which describes the volumetric behavior of gaseous hydrocarbons with satisfactory accuracy at pressures up to 4,000 pounds per square inch and gives a good prediction of the phase behavior of many hydrocarbon mixtures. Brough (8) proposed an analytical method based on least squares techniques for evaluating the coefficients, which extended earlier proposals of Benedict (2). Selleck and coworkers (15) extended the application of this equation for propane to pressures up to 10,000 pounds per square inch in the temperature interval between 40° and 460° F. and included a description of the behavior of the liquid phase. Similarly Opfell (12, 13) evaluated coefficients of the Benedict equation for nine of the lighter hydrocarbons from methane through n-decane for describing the volumetric behavior in both the liquid and gas phases for the same range of pressures and temperatures as was covered by Selleck (15). It should be emphasized that the coefficients suggested by Selleck (15) and Opfell (12,13) are suitable only for the prediction of the volumetric behavior whereas the coefficients suggested by Benedict, while they are of primary utility in describing the volumetric behavior of the gas phase at lower pressures, are suitable for estimation of phase behavior as well.

For present purposes the Benedict equation may be written with pressure or compressibility factor as an explicit function of temperature and volume. The latter form of the equation may be written in the following way:

$$Z = \frac{PV}{RT} = 1 + \left[B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3}\right]\frac{1}{V} + \left[b - \frac{a}{RT}\right]\frac{1}{V^3} + \frac{a\alpha}{RT}\frac{1}{V^5} + \frac{c}{RT^3}\left[\frac{1}{V^2} + \frac{\gamma}{V^4}\right]\exp\left(-\frac{\gamma}{V^2}\right) \qquad (1)$$

In applying the equation to a one-component system, the values of the coefficients A_0, B_0, C_0, a, b, c, α, and γ are found to be characteristic of the substance. The values of the coefficients for a multicomponent system would vary in a regular fashion with composition and they would approach the values of the coefficients for the individual components as the respective mole fraction approached unity. Little has been reported concerning computation of coefficients from experimental data for mixtures. The applications of the equation to multicomponent systems has for the most part (3) depended on coefficients obtained by averaging the coefficients of the constituents of the mixture.

Benedict's extension (3,4,6) of the equation to mixtures was based on two primary assumptions. The coefficients for the mixture were described as specific continuous functions of composition involving the coefficients for the components and a set of interaction constants.

$$A_o = n_i^2 A_{o_i} + 2 n_i n_j A_{o_{ij}} + n_j^2 A_{o_j} \qquad (2)$$

$$b = n_i^3 b_i + 3 n_i^2 n_j b_{iij} + 3 n_i n_i^2 b_{ijj} + n_j^3 b_j \qquad (3)$$

In equations 2 and 3, the single subscript symbols A_{oi}, A_{oj}, b_i, b_j, are the coefficients for the components. The double and triple subscript symbols, $A_{o_{ij}}$, b_{iij}, b_{ijj}, are the interaction constants. These mixture coefficients become equal to the coefficient for a given molecular species when its mole fraction equals unity.

Benedict's second assumption was that the interaction constants could be satisfactorily approximated by averaging the coefficients of the components. Two general types of expressions were suggested.

$$A_{o_{ij}} = \left[A_{o_i} A_{o_j}\right]^{\frac{1}{2}} \qquad (4)$$

$$b_{iij} = \left[b_i b_i b_j\right]^{\frac{1}{3}} \qquad (5)$$

In later work (7) Benedict apparently preferred a linear average for $B_{o_{ij}}$.

Benedict's first assumption is suggested by comparison of his equation with the virial equation of state predicted by statistical mechanical analysis of a system of particles with intermolecular potential functions. The single subscript constants in this analysis represent interaction of molecules of the same type whereas double and triple subscript constants correspond to interactions between unlike molecules (10). The second assumption, which suggests an approximation for the interaction constants, has no apparent foundation in theory or from experimental data, although it has yielded results which have proven useful (3,4,7).

Guggenheim (9) computed the interaction constants for six binary gaseous systems at low pressures and showed that for these systems the constants may be predicted with fair accuracy from a universal reduced second virial coefficient determined by data from pure substances. Hirschfelder and coworkers (10) suggested semi-empirical methods of predicting the equivalent of interaction constants which should be suitable for application at low pressures. Beattie and Stockmayer (1) investigated a variety of methods of predicting the interaction constants of the second virial coefficients for the gaseous methane-butane system. Recently Stotler and Benedict (17) indicated that an empirical adjustment of the interaction constant A_{o12} for the nitrogen-methane system materially increased the accuracy of the description by the Benedict equation.

The present discussion describes the application of least squares methods to the evaluation of mixture coefficients and selected interaction constants in the Benedict equation of state for the methane-n-pentane system. The mathematical procedures employed were similar to those described by Brough (8) and extended by Selleck (15,16), and no details of the extended calculations associated with this work will be presented. The program was divided into three steps. First, independent sets of coefficients were obtained for each of six mixtures. Secondly, the data for all six mixtures were used in the computation of the interaction constants associated with the coefficients A_o, B_o, and C_o. Finally, the interaction constants associated with A_o, B_o, C_o, a, b, and c were computed simultaneously.

II. EXPERIMENTAL DATA

The experimental data for the methane-n-pentane system were based on an experimental investigation (14) which extended to a pressure of 5,000 pounds per square inch in the temperature interval between 100° and 460° F. The study included six mixtures varying from 0.03 to 0.92 weight fraction methane. All the experimental data involving states in the heterogeneous regions were excluded, leaving a total of 733 states in the homogeneous regions. Of this total, 132 states were in the liquid phase. For simplicity of description the term "liquid" will indicate a state with a temperature below the critical temperature and with a pressure in excess of the bubble point pressure. Representative samples of the experimental points employed in this investigation is presented upon the temperature-pressure diagram of Figures 1 and 2.

The coefficients used for methane and n-pentane were those recently obtained by Opfell (13). They were based upon values of γ giving the best volumetric description of the experimental data. The coefficients for methane were based upon experimental data extending up to 10,000 pounds per square inch in the temperature interval between -100° and 500° F. The data used to establish the coefficients for n-pentane were limited to temperatures between 100° and 460° F. and to pressures up to 10,000 pounds per square inch. The values of the coefficients employed are recorded in Table I for the convenience of the reader.

III. COEFFICIENTS FOR INDIVIDUAL MIXTURES

The coefficients of the Benedict equation of state with the exception of γ were computed for each of the six individual mixtures. The values of γ were determined in accordance with Benedict's suggestion (4,6) as indicated in the following expression:

$$\gamma = n_1^2\gamma_1 + 2n_1n_5\left[\gamma_1\gamma_5\right]^{\frac{1}{2}} + n_5^2\gamma_5 \qquad (6)$$

Values for each of the other coefficients of equation 1 were established by minimizing the sum of the squares of the residuals in compressibility factor, with temperature and volume as the independent variables. The unsmoothed, unweighted experimental data (14) were employed for this evaluation. The results are shown in Table II.

The root-mean-square error for the combined six data sets was 0.00705. The average relative error in pressure, which is defined by the following expression, was 0.00461:

$$\mathcal{E}_p = \frac{1}{N}\sum_{1}^{N}\frac{|P_e - P|}{P} \qquad (7)$$

For many applications the error in volume with pressure and temperature as the independent variables is more indicative of the utility of the equation of state. The relative error in volume at each state was estimated from

$$\frac{\underset{\cdot}{V}_e - \underset{\cdot}{V}}{\underset{\cdot}{V}} \cong \frac{P_e - P}{P} \; \frac{P}{\underset{\cdot}{V}} \left(\frac{\partial \underset{\cdot}{V}}{\partial P}\right)_{T,n_i} \tag{8}$$

The values of the derivative of volume with respect to pressure at constant temperature and composition were computed from the Benedict equation. The average relative error in volume, which is defined by the following expression, was estimated to be 0.00298:

$$\mathcal{E}_{\underset{\cdot}{v}} = \frac{1}{N} \sum \frac{\underset{\cdot}{V}_e - \underset{\cdot}{V}}{\underset{\cdot}{V}} \tag{9}$$

A more detailed review of the accuracy of agreement of the Benedict equation with the coefficients evaluated for each mixture is set forth in a part of Table II. The deviations indicated for each individual mixture represent the minimum deviations to be expected with the continuous variation in γ employed. Mixture coefficients which are the continuous functions of composition will yield deviations from the experimental data which are at best equal to those recorded in Table II.

The variations in several of the coefficients with composition are shown in Figure 3. The experimental data yield rather smooth variations in the coefficients with composition except for the mixture near 0.12 mole fraction methane. This mixture appears to deviate markedly from the behavior found for the other mixtures. Since these coefficients are not continuous functions of composition, they do not permit the equation to be used to obtain partial thermodynamic properties (11), to obtain derivatives with respect to composition, or to interpolate with respect to composition.

IV. EVALUATION OF INTERACTION CONSTANTS

As a guide to the study of the interaction constants, the Benedict equation was compared with the virial equation of state by expanding the exponential term of equation 1 in a power series.

$$Z = 1 + \left[B_o - \frac{A_o}{RT} - \frac{C_o}{RT^3}\right]\frac{1}{V} + \left[b - \frac{a}{RT} + \frac{c}{RT^3}\right]\frac{1}{V^2} + \frac{a\alpha}{RT}\frac{1}{V^5}$$

$$+ \frac{c\gamma^2}{RT^3}\left[\frac{1}{2!} - \frac{1}{1}\right]\frac{1}{V^6} + \frac{c\gamma^3}{RT^3}\left[\frac{1}{2!} - \frac{1}{3!}\right]\frac{1}{V^8} + - - - \qquad (10)$$

Expressed in this form, the term involving the coefficients A_0, B_0, and C_0 is seen to be similar to the second virial coefficient. The term involving b, a, and c is similar to the third virial coefficient. In keeping with this analogy we shall refer to these groupings as the second and third virial coefficients of the equation, bearing in mind that the pre-assigned form of the equation may result in poor approximation to the virial coefficients of a substance predicted by other means.

Benedict's expressions similar to equations 2 and 3 for the mixture coefficients may be substituted in equation 1 resulting in an equation of state with twelve interaction constants. Interaction constants involved in the coefficients ($a\alpha$) and γ appear only in the higher order terms of the virial analogy given in equation 10. For these, the approximations of Benedict (2) similar to equations 4 and 5 were assumed to be adequate.

In order to study the remaining nine interaction constants, two separate approaches were employed. In the first the suggestions of Benedict (6) typified by equation 5 were assumed to be adequate for the terms appearing in the third virial coefficient. A least squares solution was then found for $A_{o_{15}}$, $B_{o_{15}}$, and $C_{o_{15}}$, which appear in the second virial coefficient. In the second evaluation, the least squares solution was found for all nine of the interaction constants in the second and third virial coefficients. Since the constants of the equation are interdependent, the values obtained for $A_{o_{15}}$, $B_{o_{15}}$, and $C_{o_{15}}$ would not be expected to be the same in the two methods of evaluation. In both cases the entire data set comprised of mixtures of six different compositions and a total of 733 points was employed. Interaction constants were determined by minimizing the sum of the squares of the residuals in compressibility factor with temperature, molal volume, and mole fraction as the independent variables.

The results of the calculations for the interaction constants

A_{o15}, B_{o15}, and C_{o15} are shown in Table III. A second virial coefficient based on these least squares values is plotted as a function of temperature in Figure 4. For comparison the values of the interaction constants predicted by Benedict's averages have been included in Table III. Using the least squares interaction constants, an average relative error in volume of 0.66% was computed for the 733 point data set. Predictions employing Benedict's interaction constants yielded average relative errors in volume of 1.2% and 3.2%, depending on whether a square root or linear average was used for B_{o15}.

Figure 5 depicts the average relative error in volume with pressure and temperature as the independent variables. This diagram indicates that Benedict's interaction constants for the second virial coefficient yield relatively large errors near the center of the composition interval. Least squares interaction constants for the second virial coefficient yield relatively uniform average relative error in volume throughout the composition interval.

In the second study of interaction constants, it was necessary to solve for a total of nine constants: B_{o15}, A_{o15}, C_{o15}, b_{115}, b_{155}, a_{115}, a_{155}, c_{115}, and c_{155}. The results are shown in Table III. The average relative error in volume was 0.54% as compared to 0.66% with only A_{o15}, B_{o15}, and C_{o15} established by least squares methods. In the case of the evaluation of the coefficients for the individual mixtures, the average relative error in volume was 0.29%. Using the continuous combining functions typified by equations 2 and 3, it thus appears possible to describe the volumetric behavior of mixtures with an uncertainty only about twice as large as that found with the use of the Benedict equation to describe the volumetric behavior of each individual mixture.

Figure 5 shows the average relative error as a function of composition when the interaction constants of both the second and third virial coefficients are evaluated by least squares techniques. In this instance the average error is relatively uniform throughout the composition interval and is only slightly greater than that obtained with the evaluation of the coefficients for each individual mixture. Figure 6 depicts the average error in pressure, with volume and temperature as the independent variables, for each of the several methods of predicting the interaction constants. The root-mean-square error in the compressibility factor with volume and temperature as the independent variables is shown in Figure 7. The general nature of the deviations is similar to that shown in Figures 5 and 6.

Figure 8 presents a bar chart showing graphically the variation in the average relative error in volume for the different interaction constants. In the first column, the interaction constants were determined by the methods suggested by Benedict utilizing a linear average for $B_{o_{15}}$. The second column used the same interaction constants except that a square root average for $B_{o_{15}}$ was substituted. In the third column is reported the behavior with the interaction constants $A_{o_{15}}$, $B_{o_{15}}$, and $C_{o_{15}}$ established by least squares techniques. In column 4, Benedict's suggestions for interaction constants for only γ and $a\alpha$ were utilized; least squares techniques were employed in establishing the remaining interaction constants. In column 5 no interaction constants as such were employed except those for γ ; the coefficients for each individual mixture were determined by least squares techniques. The effect of composition upon the accuracy of description of the experimental data is summarized in Table IV. Both this table and Figure 8 indicate separately the behavior of the gas and liquid phases. The improvement effected by the least squares interaction constants is particularly apparent for the liquid phase.

It appears that the use of interaction constants established by least squares techniques affords an improved method of describing the volumetric behavior of mixtures for which experimental data are available. Much additional work upon other binary mixtures will be required before it will be possible to predict interaction constants from the nature of the components of the mixtures. In any event it appears that the interaction constants suggested by Benedict for all the coefficients except those of the second virial coefficient are adequate for describing the volumetric behavior of mixtures. No information has been presented in this discussion as to the improvements to be realized by use of empirically evaluated values of γ. However, experience (13,15) with variations in this exponential coefficient indicates that the improvement would be small.

NOMENCLATURE

A_o, B_o, C_o, a, b, c, α, γ	coefficients for the Benedict equation of state
exp( )	exponential function
N	number of states represented
$\underset{\cdot}{n}$	mole fraction
P	pressure, lb. per sq. inch, absolute
R	universal gas constant, (lb./sq.inch)(cu.ft.) per (lb.mole)(°R.)
T	absolute temperature, °R.
$\underset{\bullet}{V}$	molal volume, cu. feet per lb. mole
Z	compressibility factor
∂	partial differential operator
$\mathcal{E}$	average relative error
Σ	summation operator

Subscripts

e	value of property predicted using the Benedict equation of state
i	refers to component i
j	refers to component j
$\underset{\cdot}{n}_i$	differentiation at constant $\underset{\cdot}{n}_i$
P	pressure as dependent variable
T	differentiation at constant T
$\underset{\bullet}{V}$	volume as dependent variable

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LIST OF TABLES

TABLE I

CONSTANTS OF BENEDICT EQUATION FOR METHANE AND n-PENTANE[a]

Constant	Methane	Pentane
R	10.73147	10.73147
$A_o \times 10^{-3}$	4.91053	60.2155
B_o	0.455158	3.69003
$C_o \times 10^{-9}$	0.448753	19.6289
$a \times 10^{-3}$	4.55118	203.9410
b	1.03508	16.0875
$c \times 10^{-9}$	0.619147	116.0610
α	0.332260	6.67703
γ	1.200000	10.50000
M	16.042	72.146

[a] Reference 14

[b] The values recorded are dimensionally consistent when used in the equation of state with pressure expressed in pounds per square inch, temperature in degrees Rankine, and volume in cubic feet per pound mole.

TABLE II

CONSTANTS OF BENEDICT EQUATION FOR SIX MIXTURES

Mole Fraction Methane	0.9822	0.9404	0.7385	0.4636	0.2933	0.1263
Constant						
$A_o \times 10^{-3}$	9.681615	5.714402	11.284436	21.086886	30.299301	37.106893
B_o	0.976771	0.589944	0.883116	1.141549	1.400853	1.081886
$C_o \times 10^{-9}$	0.133002	1.096448	3.204144	7.193561	9.773934	9.612066
$a \times 10^{-3}$	-6.771065	6.653650	17.384449	77.513929	133.381453	192.036492
b	-0.092306	1.138778	2.453100	7.753380	12.571227	18.809025
$c \times 10^{-9}$	-0.629810	1.656143	6.855081	30.225136	52.155148	59.837555
α	0.006639	0.538037	1.224530	1.965381	2.838144	3.694810
γ	1.284958[a]	1.496238	2.743651	5.044583	6.818292	8.817651
Root-Mean-Square Error	0.0073	0.0039	0.0056	0.0043	0.0113	0.0098

[a] Values for γ were obtained from equation 6

TABLE III

INTERACTION CONSTANTS OF BENEDICT EQUATION

	Benedict Linear	Benedict Square Root	Least Squares 2nd Virial Coefficient	Least Squares 2nd and 3rd Virial Coefficients
γ_{15}	3.549648[a]	3.549648	3.549648	3.549648
α_{115}	0.903330	0.903330	0.903330	0.903330
α_{155}	2.455923	2.455923	2.455923	2.455923
B_{o15}	2.072593	1.295973	$\underline{0.745524}$[b]	$\underline{0.615646}$
$A_{o15} \times 10^{-3}$	17.195641	17.195641	$\underline{10.277994}$	$\underline{12.462433}$
$C_{o15} \times 10^{-9}$	2.967918	2.967918	$\underline{3.169343}$	$\underline{1.659504}$
b_{115}	2.583128	2.583128	2.583128	$\underline{3.474415}$
b_{155}	6.446390	6.446390	6.446390	$\underline{7.900746}$
$a_{115} \times 10^{-3}$	16.165302	16.165302	16.165302	$\underline{18.427891}$
$a_{155} \times 10^{-3}$	57.417496	57.417496	57.417496	$\underline{69.183760}$
$c_{115} \times 10^{-9}$	3.543440	3.543440	3.543440	$\underline{1.017588}$
$c_{155} \times 10^{-9}$	20.279449	20.279449	20.279449	$\underline{20.031450}$
Root-Mean-Square Error	0.0575	0.0408	0.0122	0.0106
$Av \frac{1}{P}\lvert\Delta P\rvert$	0.0563	0.0294	0.0108	0.0092
$Av \frac{1}{V}\lvert\Delta V\rvert$	0.0325	0.0124	0.00664	0.00541

[a] See footnote b of Table I concerning units.

[b] In the two least squares cases, the underlined values are the results of the computations. The values for the other constants in these two columns are based on Benedict's approximations.

TABLE IV

INFLUENCE OF INTERACTION CONSTANTS ON ERROR OF PREDICTION

	Least Squares Coefficients for Individual Mixtures	Benedict Interaction Constants		Least Squares Interaction Constants	
		$B_{o_{15}}$ Linear	$B_{o_{15}}$ Square Root	2nd Virial Coefficient	2nd & 3rd Virial Coefficients
Root-Mean-Square Error in Z					
Gas	0.0060	0.0472	0.0171	0.0093	0.0081
Liquid	0.1055	0.0908	0.0889	0.0207	0.0185
Total	0.0070	0.0575	0.0407	0.0122	0.0107
Average $\frac{1}{P}\lvert\Delta P\rvert$					
Gas	0.0033	0.0377	0.0125	0.0076	0.0062
Liquid	0.0104	0.1411	0.1060	0.0254	0.0227
Total	0.0046	0.0563	0.0294	0.0108	0.0092
Average $\frac{1}{Y}\lvert\Delta Y\rvert$					
Gas	0.0033	0.0324	0.0104	0.0072	0.0059
Liquid	0.0017	0.0325	0.0215	0.0040	0.0034
Total	0.0030	0.0325	0.0124	0.0066	0.0054

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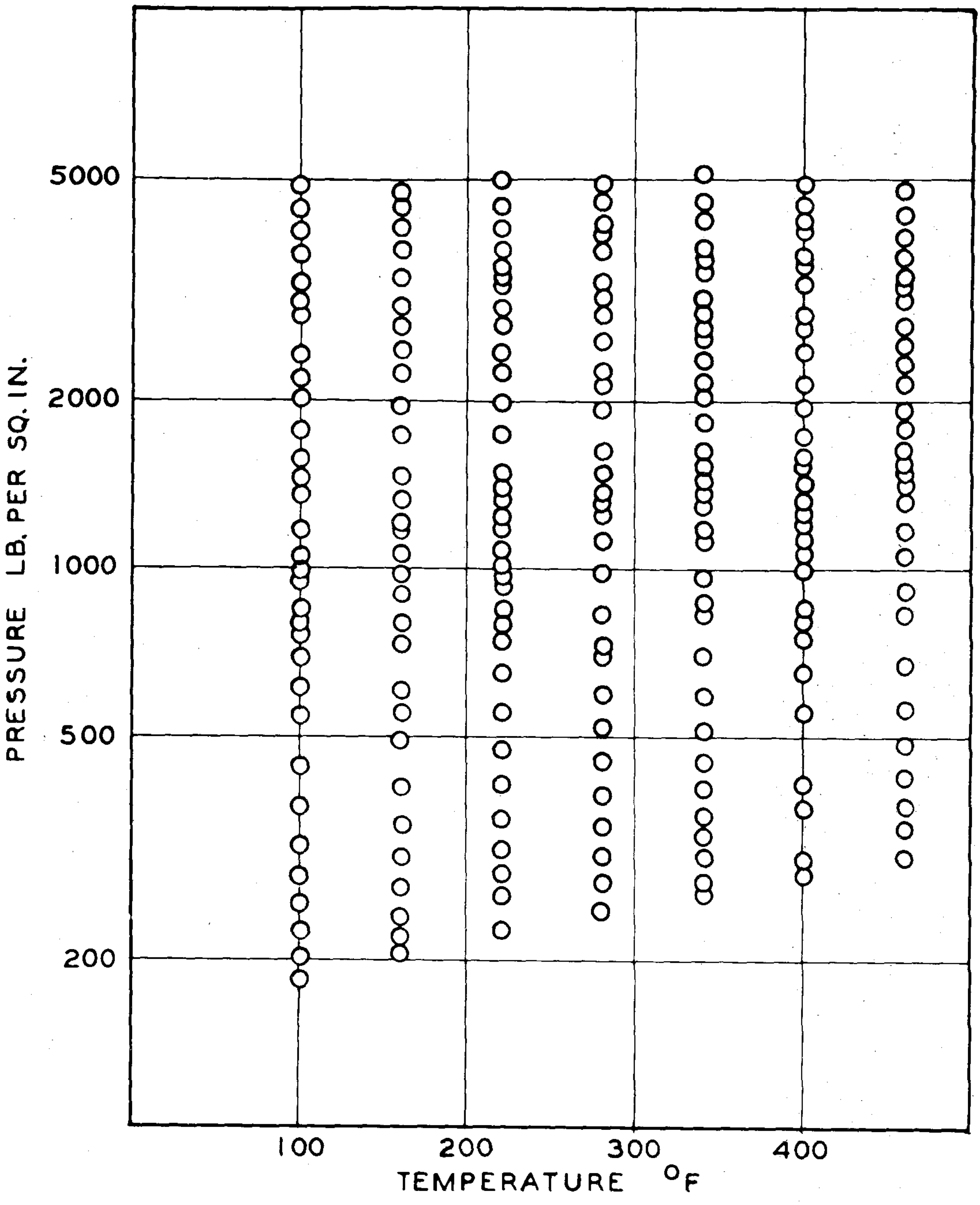

Fig. 1 Experimental Data Used to Establish Coefficients for a Mixture Containing 0.9822 Mole Fraction Methane

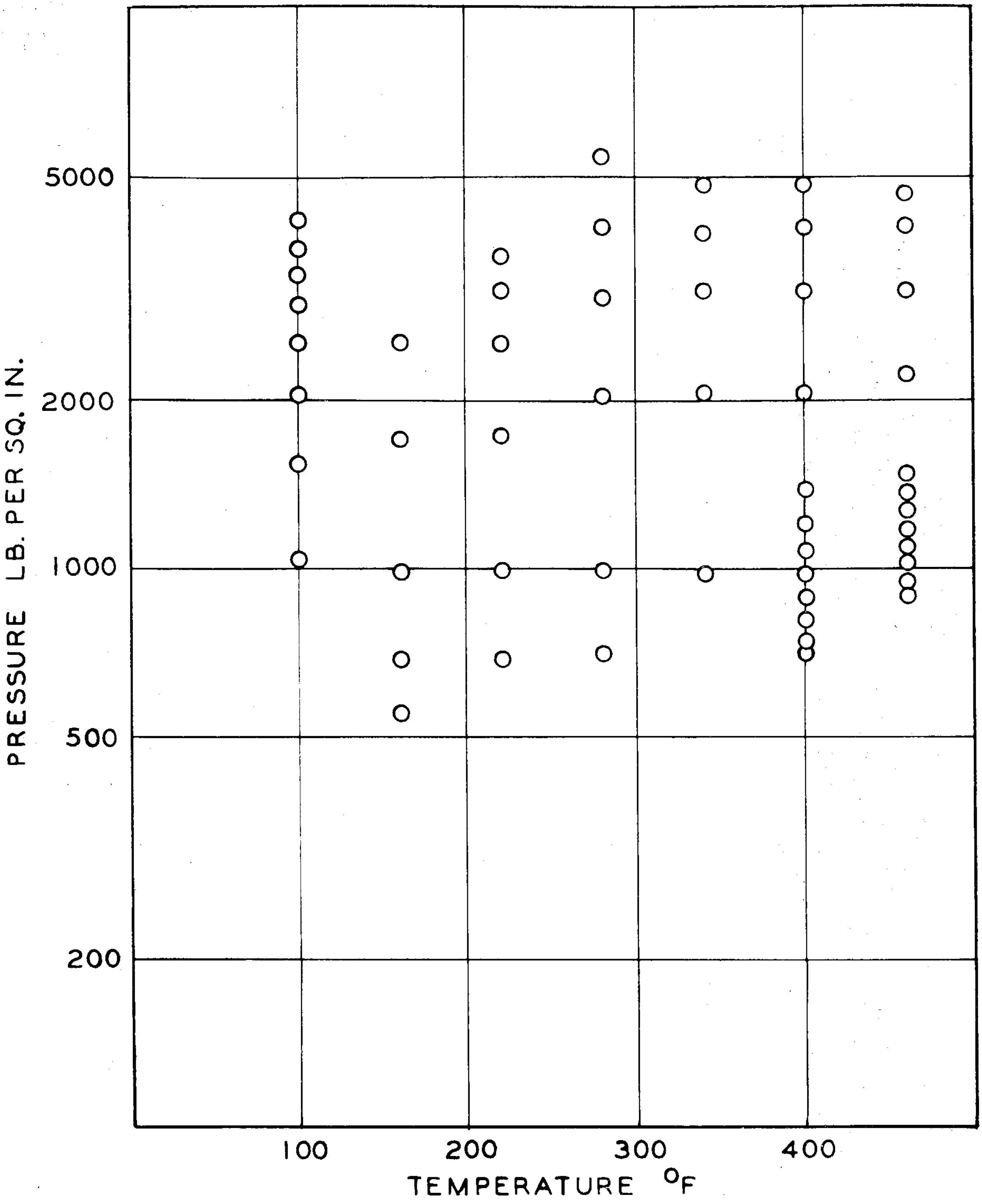

Fig. 2 Experimental Data Used to Establish Coefficients for a Mixture Containing 0.1263 Mole Fraction Methane

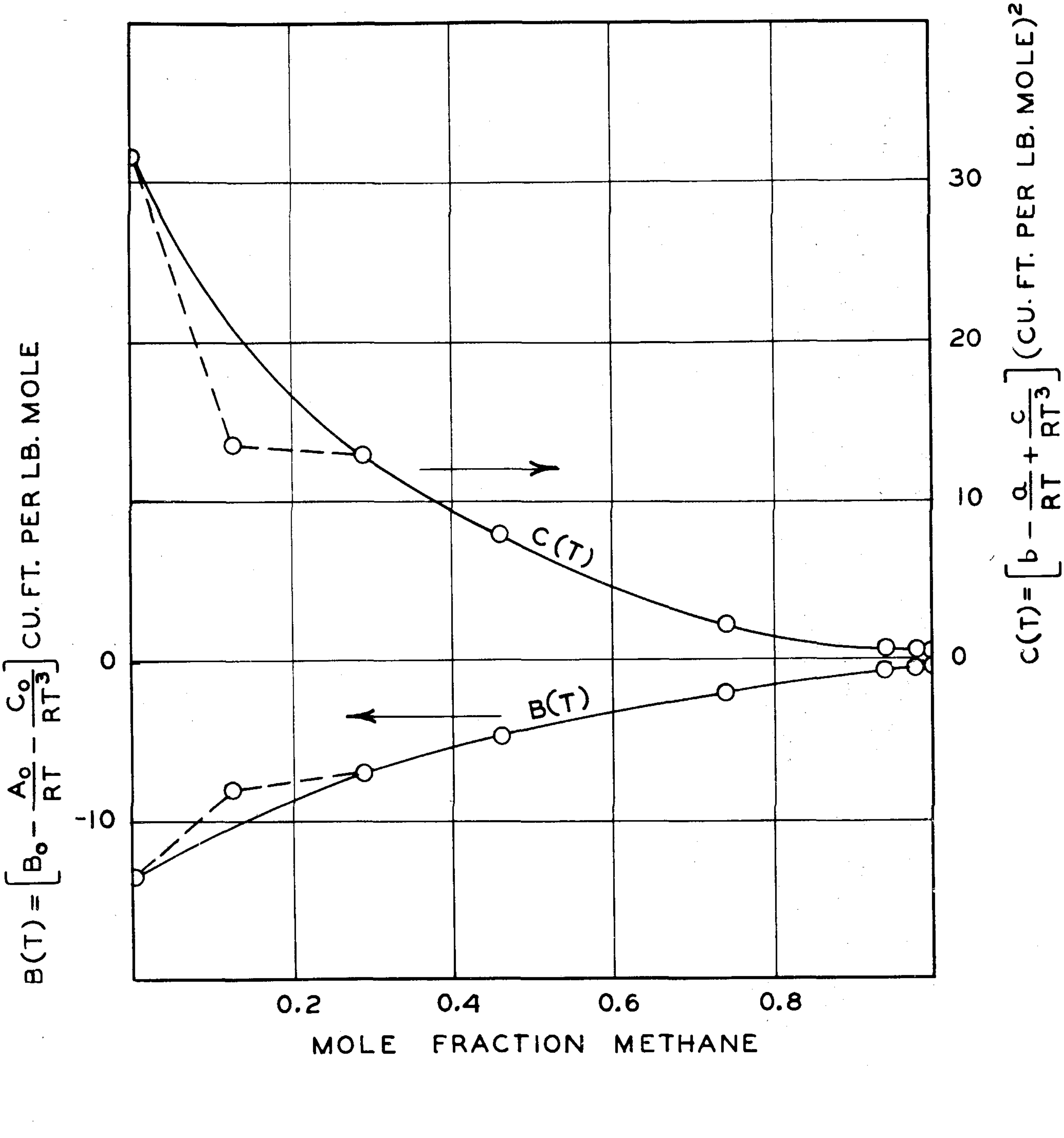

Fig. 3 Effect of Composition upon Coefficients of Benedict Equation at 160° F.

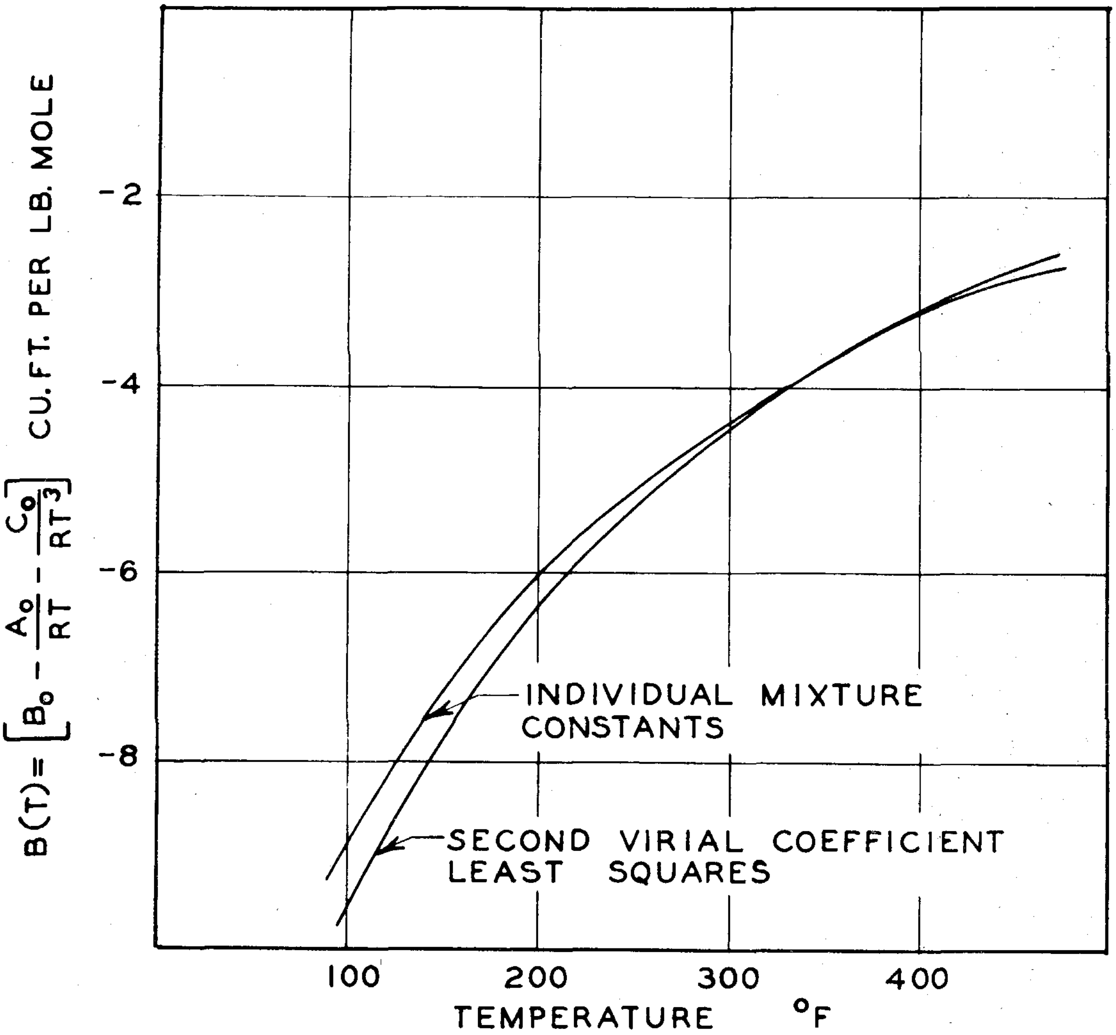

Fig. 4 Second Virial Coefficient for a Mixture of Methane and n-Pentane Containing 0. 2933 Mole Fraction Methane

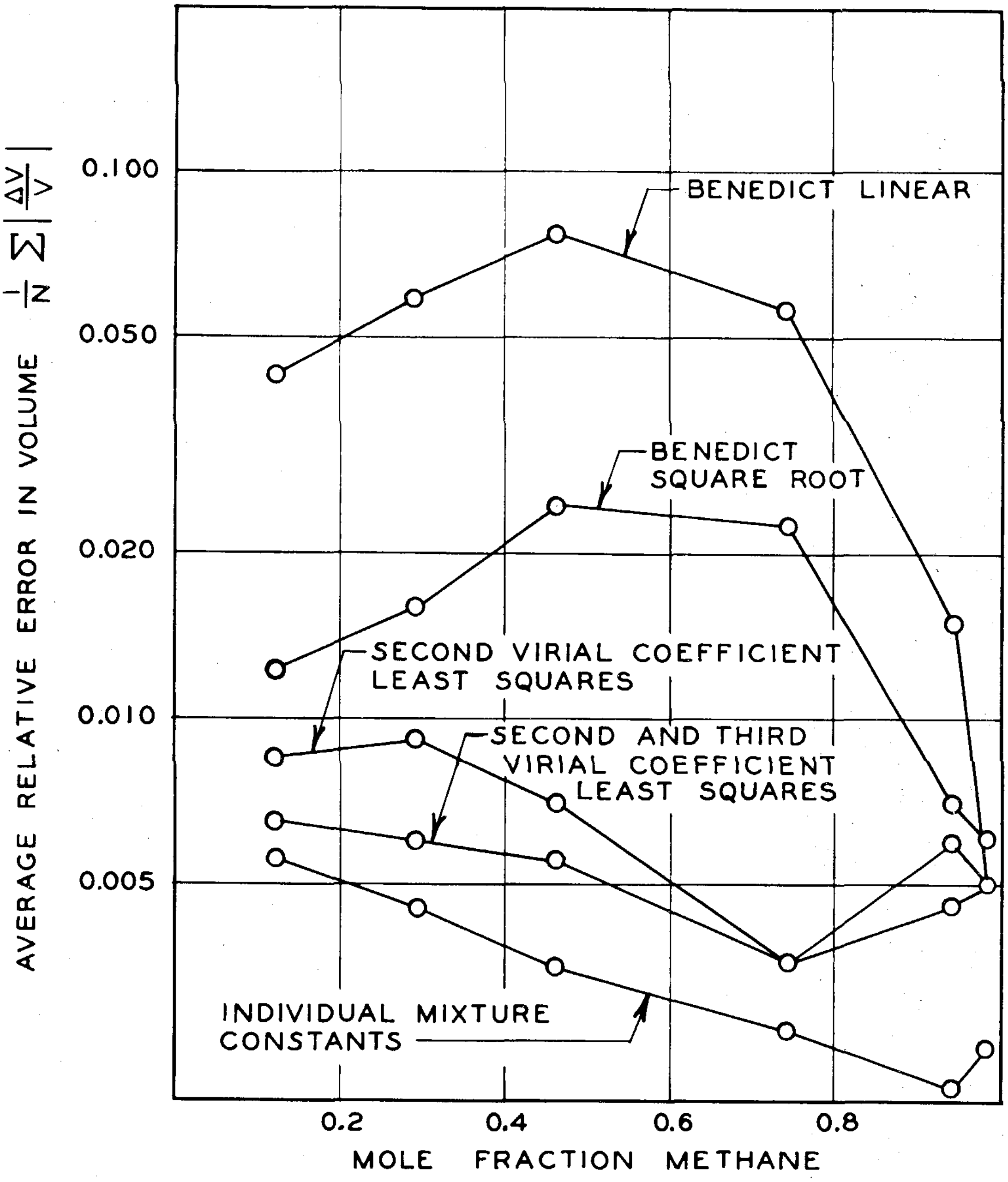

Fig. 5 Average Relative Error in Volume as a Function of Composition

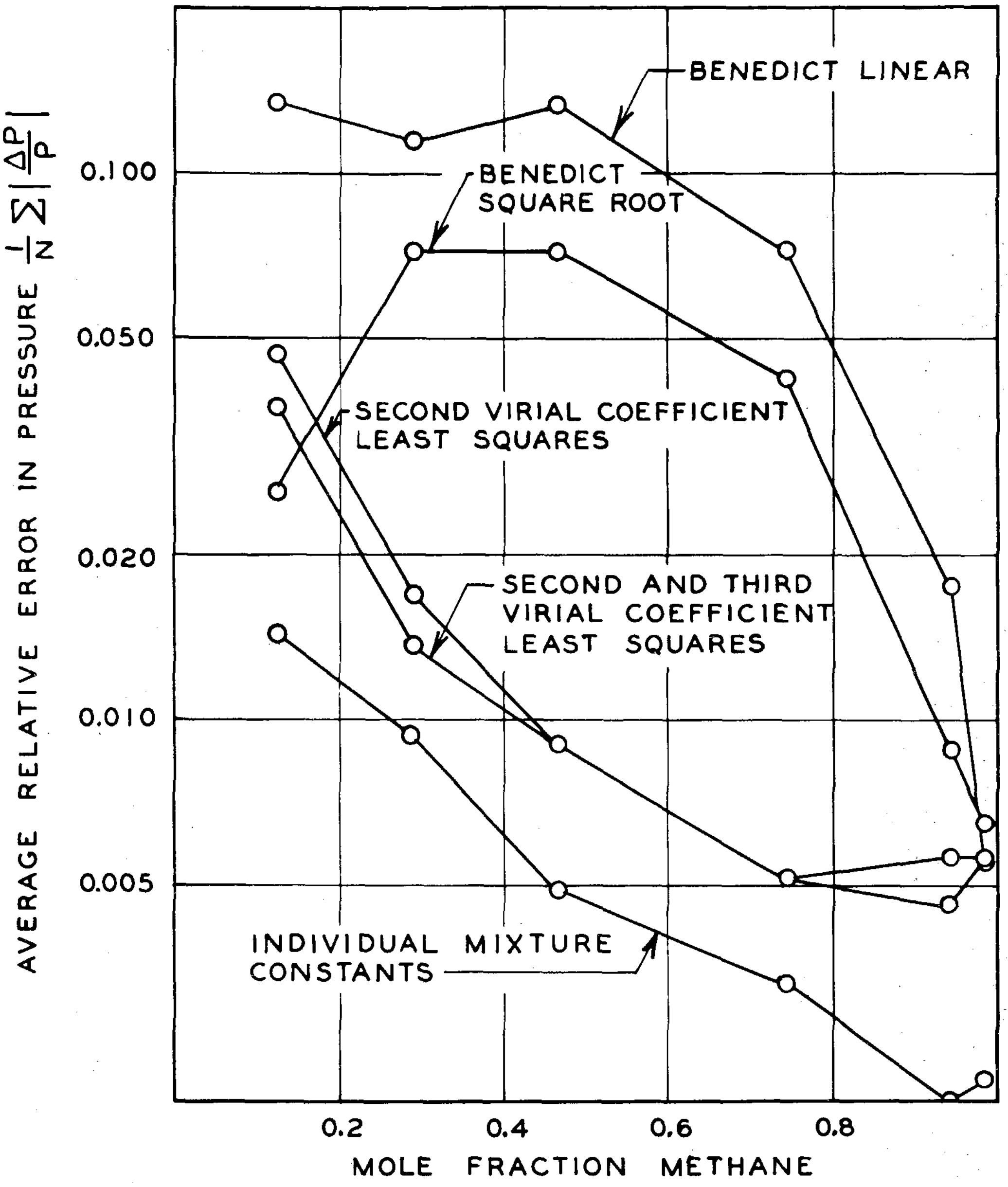

Fig. 6 Average Relative Error in Pressure as a Function of Composition

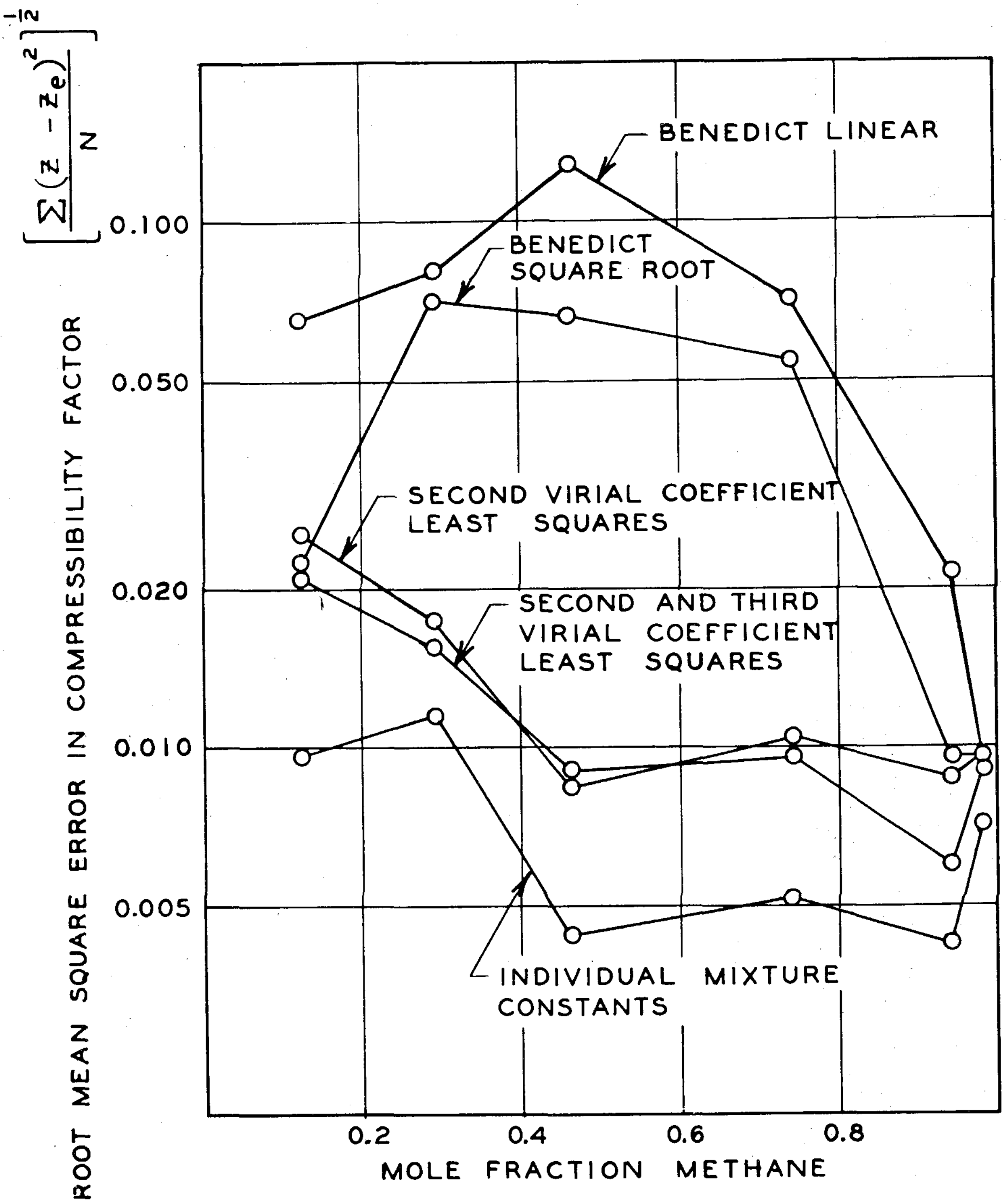

Fig. 7 Root-Mean-Square Error in Compressibility Factor as a Function of Composition

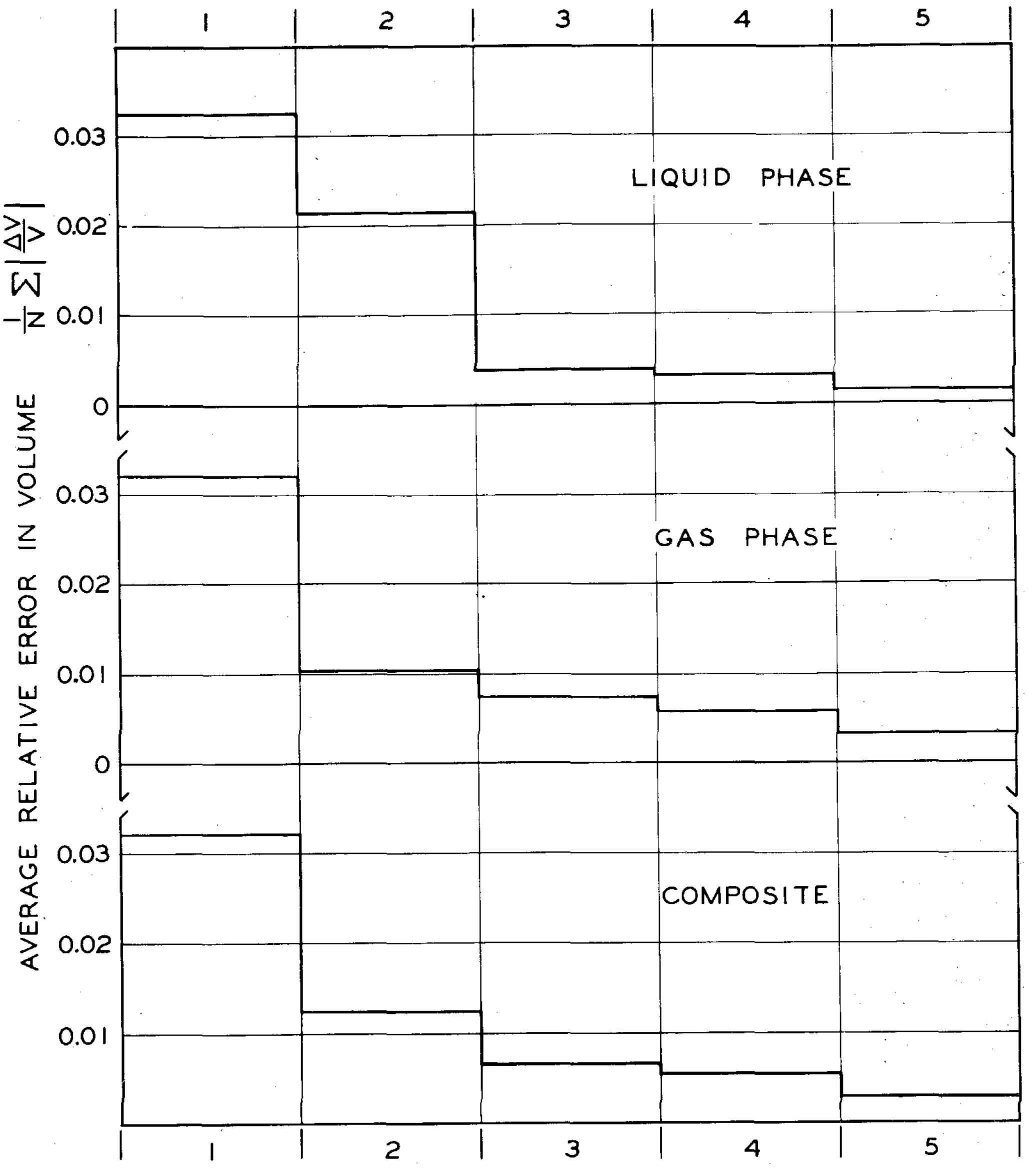

Fig. 8 Average Relative Error in Volume for Several Sets of Coefficients

Column (1) Benedict's interaction constants. Linear combination for B_{o15}

Column (2) Benedict's interaction constants. Square root combination for B_{o15}.

Column (3) Least squares interaction constants. A_{o15}, B_{o15}, C_{o15}, by least squares; $a_{115}, a_{155}, b_{115}, b_{155}, c_{115}, c_{155}, \alpha_{115}, \alpha_{155}$, γ_{15} by Benedict functions.

Column (4) Least squares interaction constants. A_{o15}, B_{o15}, C_{o15}, $a_{115}, a_{155}, b_{115}, b_{155}, c_{115}, c_{155}$ by least squares; α_{115}, α_{155}, γ_{15}, by Benedict functions.

Column (5) Individual mixture constants.

PART THREE

PART THREE. ISOBARIC HEAT CAPACITY AT BUBBLE POINT OF n-DECANE

I. INTRODUCTION

Available experimental information concerning the isobaric heat capacity of n-decane in the liquid phase is limited to temperatures between 0° F. and 110° F. Huffman, Parks, Barmore, and Thomas (1,2) determined the heat capacities of the solid and liquid phases at temperatures up to 75° F. Osborne and Ginnings (3) reported values of the heat capacity at bubble point at temperatures up to 110° F. Schultz (4) and Pitzer (5) proposed a generalization of the heat capacity of hydrocarbon gases at low pressures. The thermodynamic properties of the lighter hydrocarbons were critically reviewed by Rossini (6).

The present investigation was carried out in order to extend the knowledge of the isobaric heat capacity of liquid n-decane to 200° F. The measurements were made in the two-phase region utilizing a constant volume calorimeter. The energy required to change the temperature of the calorimeter and contents was determined for each of two quantities of n-decane. The effect of the gross heat capacity of the sample bomb was eliminated by considering the difference of these two sets of measurements. The two-phase isochoric determinations were transformed to values of the isobaric heat capacity at bubble point by applying a thermodynamic correction involving the volumetric properties of the gas and liquid phases and the heat capacity of the gas phase.

II. THERMODYNAMICS

From the first and second laws of thermodynamics and a material balance, the following equation may be derived relating the isobaric heat capacity at bubble point to measurable heat exchanges, temperature changes, and the differences in weights of the two samples.

$$C_{P,b} = \frac{\frac{q_1}{dT} - \frac{q_2}{dT}}{m_1 - m_2}\left(\frac{V_d - V_b}{V_d}\right) + T\left(\frac{\partial V}{\partial T}\right)_{P,b}\frac{dP''}{dT}$$

$$+ T\frac{dP''}{dT}\left(\frac{V_d\frac{dV_b}{dT} - V_b\frac{dV_d}{dT}}{V_d}\right)$$

$$+ \frac{V_b}{V_d}\left(C_{P,d} - T\left(\frac{\partial V}{\partial T}\right)_{P,d}\frac{dP''}{dT}\right) \qquad (1)$$

Detailed derivations of this relationship have been presented by Schlinger and Sage (7) and Auerbach (8). The quantity q/dT represents the net heat transferred to the system per unit temperature change of the calorimeter and its contents. It can be reliably measured over a range of temperatures with two different weights, m_1 and m_2, of material in the bomb.

These weights or their difference can also be obtained experimentally. The remaining terms in equation 1 demand a knowledge of the volumetric behavior of the liquid and gas phases and the isobaric heat capacity of the dew point gas.

Fortuitously in the case of n-decane the total contribution of these terms does not at any temperature in the range of interest exceed 0.2% of $C_{\beta b}$. Consequently approximate values of the required properties may be employed satisfactorily if necessary. The volumetric behavior of the liquid phase of n-decane has been investigated in some detail; for the present purposes the measurements of Reamer, Olds, Sage, Lacey, and Lavender (9,10) were employed. Volumetric derivatives of the gas phase were estimated from the perfect gas law. Schultz's generalization was adopted for the heat capacity of the dew point gas. The magnitude of these corrections to the two-phase isochoric data may be advantageously studied by rewriting equation 1 as follows.

$$C_{\beta,b} = \frac{\frac{q_1}{dT} - \frac{q_2}{dT}}{m_1 - m_2} \; \frac{1}{(1 - c)} \tag{2}$$

The correction parameter c appearing in equation 2 is shown as a function of temperature in Figure 1. The maximum value of c, at 200° F. is < 0.002.

III. APPARATUS

The calorimeter used for these measurements has been described in some detail by previous investigators (7,8). The equipment consisted of a cylindrical steel container with hemispherical closures within which the hydrocarbon liquid was confined. Energy was added electrically to the interior of the calorimeter by means of a short length of glass-insulated constantan wire encased within a stainless steel tube approximately 0.05 inches in diameter. A potentiometer and standard resistor unit were used to measure the electromotive force applied and the current flowing through this heater. The rate of electrical energy addition to the calorimeter was known with an uncertainty of less than 0.05%. Energy was added to the calorimeter in periods of approximately 1000 seconds; the exact length of these intervals was determined with an electrical timer. The uncertainty of the total energy thus added to the equipment was less than 0.1%.

In order to decrease the thermal losses, the calorimeter was surrounded by an adiabatic jacket and the space between the jacket and the calorimeter was evacuated. It was possible by calibration to establish the magnitude of the thermal losses as a function of the measured temperature difference between the calorimeter and wall of the jacket. For the measurements on n-decane the energy losses to the wall of the jacket were in all cases less than 1% of the energy added electrically. Uncertainties resulting from thermal losses are believed not to exceed 0.15% of the corrected values of energy added to the calorimeter.

Temperatures of the contents of the calorimeter and the walls of the adiabatic jacket were determined with ± 0.005° F. from the electromotive force of calibrated copper-constatan thermocouples.

The n-decane was introduced into the calorimeter by high vacuum and liquid air trap techniques (11). The difference in weight of the two samples was known within 0.02%

IV. SAMPLE

The n-decane was obtained from Research Project 44 of the American Petroleum Institute and was reported to be substantially pure. The sample as received was subjected to a single fractionation at reduced pressures to eliminate the air dissolved. The fractionated sample had a refractive index of 1.4119 for the D-lines of sodium at 68° F. as compared with a value of 1.41203 reported by Shepherd (12) and a value of 1.41189 reported by Forziati (13). On the basis of the measured value of the refractive index it is probable that the impurities were not greater in amount than in the sample used by Forziati (13), which was reported as 0.003 mole fraction. On the basis of ideal solutions, Schlinger and Sage (14) have estimated that the presence of 0.003 mole fraction impurity would result in only 0.03% error in the heat capacity, which is less than 1/25 of the standard deviation of the heat capacity measurements and about 2% of the estimated total uncertainty of measurement.

V. EXPERIMENTAL MEASUREMENTS

With a fixed amount of sample in the calorimeter the temperature of the system was raised in steps of approximately 6° F. from room temperature to 210° F. by the addition of electrical energy. Each six degree rise took approximately 1000 seconds and was followed by a 1000 second calming period to allow the system to come to thermal equilibrium. The rate of energy addition was measured at short intervals by standard resistor and potentiometer as discussed previously. The total energy for each period was obtained by numerical integration of these rates. The thermal losses to the surrounding jacket were determined from periodic measurements of temperature differences. The net thermal transfer to the calorimeter and contents, $\underline{Q}$, during an energy addition period was taken as the sum of the electrical energy, $\underline{Q}_E$, and transfer from the surroundings, $\underline{Q}_S$. ($\underline{Q}_S$ was always positive).

$$\underline{Q} = \underline{Q}_E + \underline{Q}_s \tag{3}$$

If T_A and T_B denote respectively the temperatures at the beginning and end of an addition period, the following estimate was used for the net thermal energy per unit temperature change of the calorimeter bomb and its contents.

$$\frac{\text{đ}q}{dT} \cong \frac{\underline{Q}}{T_B - T_A} = \frac{\underline{Q}_E + \underline{Q}_s}{T_B - T_A} \tag{4}$$

The left hand side of equation 4 was assumed to apply at the mean of T_A and T_B. As indicated previously $\underline{Q}_S$ was never larger than 1% of $\underline{Q}_E$.

The experimental values of Q/ T are recorded in Table I and plotted as a function of temperature in Figure 2 for two different sample weights of n-decane. The curves shown were fitted by eye. The standard deviation of the differences of these two sets of measurements was 0.0020 Btu per °F. or approximately 0.0090 of the difference between the two curves. The 95% confidence limits for the difference was approximately 0.0008 Btu per °F. or 0.0036 of the difference.

VI. COMPUTATION OF $C_{p,b}$

Values of $C_{p,b}$ were computed from equations 1 and 2 using the thermodynamic correction term of Figure 1 and the smoothed values of Q/ T shown in Figure 2. The results are presented in Table II and Figure 3. These values probably do not involve combined uncertainties greater than 1%. The work of Osborne and Ginnings and that of Huffman, Parks, and Barmore have been included in Figure 3 for comparison. Agreement with Huffman is satisfactory. The values from these two investigations are approximately 1% lower than those reported by Osborne and Ginnings.

The results of the present investigation have been presented in the literature in conjunction with the results of two similar projects carried on in this laboratory (14).

NOMENCLATURE

C_p	isobaric heat capacity, Btu per lb./°F.
m	weight of material in calorimeter, lb.
P	pressure, lb./sq. in., absolute
Q	heat associated with process, Btu
q	heat associated with infinitesimal change in state, Btu
T	thermodynamic temperature, °R
V	specific volume cu. ft./lb.

Subscripts

A,B	state A and state B
b	bubble point
d	dew point
E	energy added electrically
S	energy added from surroundings
1,2	conditions with different quantities of sample in calorimeter

Superscript

$''$	two-phase state

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TABLE I

HEAT CAPACITY OF CALORIMETER AND CONTENTS

n-DECANE

m_1

Temp. °F.	$Q/\Delta T$ Btu/°R
78.03	0.3286
82.94	0.3299
85.20	0.3320
94.20	0.3347
101.56	0.3360
109.27	0.3402
116.87	0.3440
124.38	0.3443
131.83	0.3479
139.27	0.3461
146.72	0.3473
154.11	0.3498
161.47	0.3503
168.83	0.3504
176.17	0.3494
183.46	0.3517
190.69	0.3538
197.89	0.3540
205.01	0.3585
83.39	0.3312
98.07	0.3391
112.83	0.3412
119.99	0.3445
127.11	0.3449
134.21	0.3460
141.31	0.3493
148.40	0.3479
155.47	0.3480
162.46	0.3516
169.42	0.3475
176.39	0.3515
183.36	0.3503
190.28	0.3543
197.12	0.3563

m_1 + 0.40188 lb.

Temp. °F.	$Q/\Delta T$ Btu/°R
107.25	0.5493
114.37	0.5601
121.41	0.5574
128.37	0.5702
135.25	0.5671
142.15	0.5705
149.05	0.5715
155.94	0.5741
162.76	0.5772
169.52	0.5797
176.20	0.5881
189.30	0.5890
83.96	0.5455
99.57	0.5503
107.15	0.5519
114.65	0.5584
122.06	0.5629
129.41	0.5667
136.70	0.5683
144.06	0.5670
158.78	0.5771
165.96	0.5775
173.09	0.5843
180.18	0.5823
187.24	0.5846
194.24	0.5898

TABLE II

ISOBARIC HEAT CAPACITY AT BUBBLE POINT OF n-DECANE

Temp. °F.	$C_{p,b}$ Btu per(lb)(°R)
80	0.5242
90	.5279
100	.5318
110	.5359
120	.5405
130	.5454
140	.5510
150	.5568
160	.5630
170	.5696
180	.5762
190	.5831
200	.5901

LIST OF FIGURES

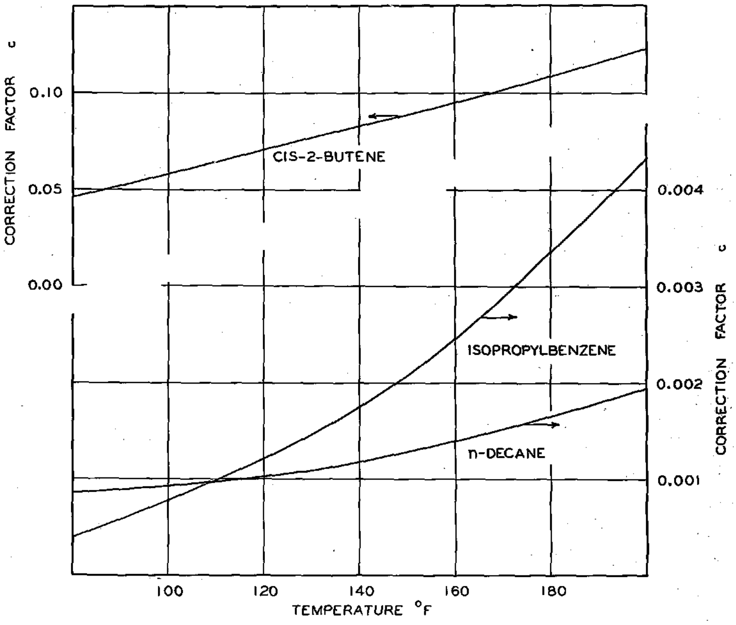

Fig. 1. Thermodynamic Correction Factor

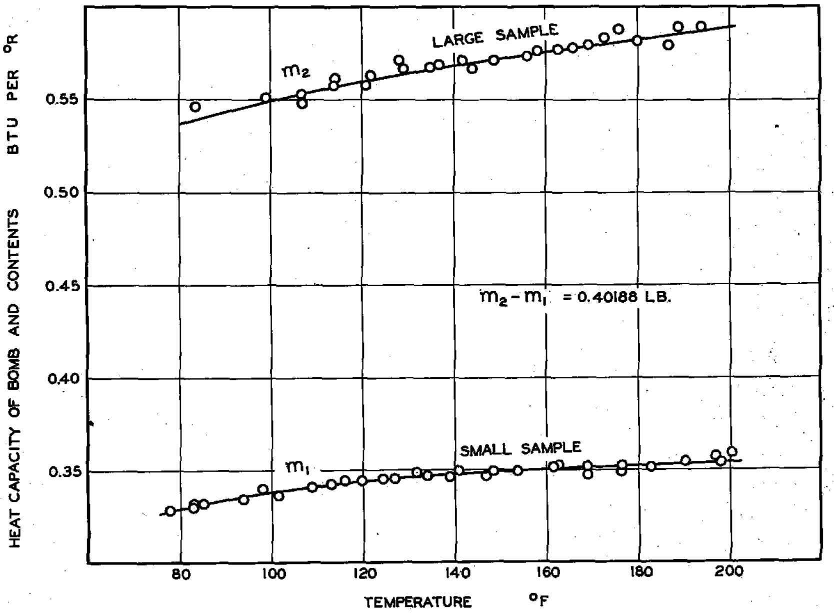

Fig. 2. Experimental Measurements

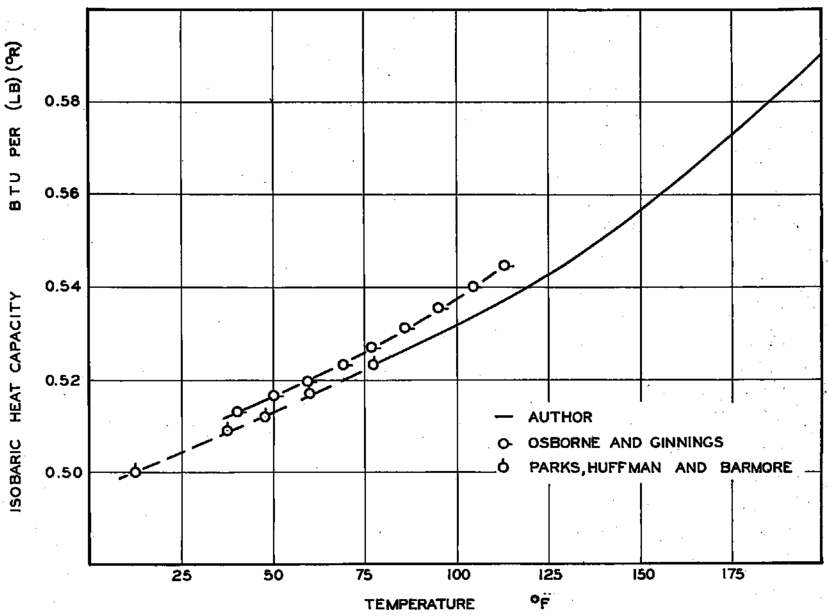

Fig. 3. Isobaric Heat Capacity at Bubble Point

Ph.D. Final Examination — Cornelius J. Pings, Jr.
Monday, May 9, 1955 at 1:30 P. M. in Crellin Confefence Room
Committee: Professors Lacey, Corcoran, Schomaker, Yost and Ward

PROPOSITIONS

1. a. The pressure-volume isotherms of both the gas phase and liquid phase have analytic continuations into the two phase region. Effort should be devoted to establishing whether or not these continuations are the same and whether or not they possess thermodynamic significance.

b. In fitting an equation of state to a PVT surface, only one analytic restraint is necessary in order to assure precise vapor pressure prediction at a given temperature.

c. Lacey and Sage (1) have presented explicit expressions for the paths of a number of thermodynamic processes for substances conforming to the van der Waals equation of state. It would be worthwhile to develop similar expressions in terms of the virial equation of state.

d. Pitzer (2) has proposed an extension of the law of corresponding states which utilizes two fundamental reduced PVT surfaces. In order to facilitate interpolation and estimation of thermodynamic properties, these surfaces might be advantageously represented by an orthogonal polynomial equation of state.

e. Metropolis, Rosenbluth, and co-workers (3,4) have presented a Monte-Carlo equation of state. For the statistical model which they employ, occasional regions of low density, or holes, are evident in the fluid. This behavior might provide useful information regarding the phenomena of nucleation and bubble formation.

2. Lewis, Gilliland, and Bauer (5) have suggested a correlation function for describing the behavior of fluidized beds. Their proposal was based on experimental data obtained for fluidization of glass beads in air and water. Unpublished experimental data (6,7) indicate that this correlation can be used with moderate success to describe the fluidization of lead and steel spheres in oil.

3. Preliminary computations indicate that a system of predicting the critical state of mixtures might be based on the use of quadratic forms involving the properties of the pure substances, the composition, and a set of interaction parameters. For example,

$$P_c = n_i^2 P_{c_i} + 2n_i n_j P_{c_{ij}} + n_j^2 P_{c_j}$$

4. Jenkins (8) has suggested a modification of the momentum and vorticity transport hypotheses for turbulent flow. A further modification is proposed.

5. In certain areas, precipitation of asphaltic residues from crude oils results in troublesome and expensive clogging of sand bodies, separators, and pipe lines. A survey of available literature (9,10,11,12,13,14,15) indicates that decreasing the pressure on a crude oil system causes a decrease in solubility of the bituminous precipitate; decreasing the solution gas oil ratio causes an increase in solubility. Consequently there may exist optimum operating pressures which minimize the precipitation.

6. The molecular theory of transport phenomena in dilute gases indicates that for a water-air mixture the viscosity decreases with increasing moisture content between 100 and 500°K (16). Above 800°K, viscosity increases with increasing moisture. This reversion should be investigated experimentally.

7. Widom (7) has proposed that the ideal Bose-Einstein gas would be a useful prototype for classical fluid systems exhibiting condensation phenomena. He conjectures that the virial series of the Bose-Einstein gas has a radius of convergence which is infinite. The radius of convergence may well be infinite; however, this power series will cease to represent the physical behavior of the system for densities greater than the condensation density.

8. In one step in the commercial production of titanium metal, gaseous $TiCl_4$ is reduced with molten magnesium in a batch process (18). This reaction might be adaptable to a flow process utilizing impinging fluid streams.

9. a. Conventional least squares methods used in curve fitting are based on a minimization of the sum (or integral) of the squares of deviations (19,20). In many instances a more useful approximation would be obtained if the fitting were based on minimization of the sum of the squares of the relative deviations. Such an evaluation is formally no more difficult than widely used methods.

b. Consider the expansion of an arbitrary function $f(x)$, $a \leq x \leq b$, in an infinite series of a set of orthogonal functions, $\phi_n(x)$.

$$f(x) = \sum_{k=o}^{\infty} a_k \phi_k(x) \qquad a \leq x \leq b$$

The n^{th} partial sum, $S_n(x)$, of this series affords an approximation to $f(x)$ with an associated mean-square error, $E^2\{S_n(x)\}$. $f(x)$ may also be approximated by

$$f(x) \cong S_n(x) + A_{n+1} \phi_{n+1}(x)$$

where A_{n+1} is an arbitrary constant. The increase in error caused by the addition of this arbitrary multiple of $\phi_{n+1}(x)$ is a quadratic in the coefficient A_{n+1}

$$E^2\{S_n(x) + A_{n+1} \phi_{n+1}(x)\} - E^2\{S_n(x)\} = c_o + c_1 A_{n+1} + c_2 A_{n+1}^2$$

The increase in error has a minimum at the Fourier value, a_{n+1}, and has zeros at $A_{n+1} = 0$ and $A_{n+1} = 2a_{n+1}$. This may serve as a guide to imposing restraints on approximation curves in a simpler manner than possible with the method of undetermined multipliers.

c. The expansion of a simple step function in a series of Tchebichef polynomials has been investigated for Gibbs phenomenom. The nature and magnitude of the "overshoot" at the point of discontinuity is the same as for the Fourier expansion (21).

10. Given a five card draw poker game with a deck containing a joker good in aces, straights, and flushes. Suppose a player is dealt a non-ace pair and one ace (or the joker). Let H denote the play of holding the ace and taking two cards in the draw. Let D denote the play of discarding the ace and drawing three cards. The probability of making two pair or better is 0.2899 for play H and 0.2854 for play D. The chances of making a full hand are 23.4% greater for play H than for play D.

Nomenclature

A_{n+1}	arbitrary constant
a_k	a constant
c_i	a constant
E^2	mean square error of approximation
$f(x)$	an arbitrary function of x
n_i	mole fraction of component 1
P_c	critical pressure
$P_{c_{ij}}$	interaction parameter
$S_n(x)$	n^th partial sum of an infinite series
$\phi_n(x)$	a set of orthogonal functions; n^th member of set of orthogonal functions

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