A DETAILED STUDY IN THE APPLICATION OF THE BENEDICT EQUATION TO ONE-COMPONENT SYSTEMS

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ABSTRACT

An investigation into the ability of the Benedict equation to describe volumetric and phase behavior in one-component systems of the light paraffin hydrocarbons has led to the following conclusions. In describing only the volumetric behavior of these compounds for both the gas and liquid phases, the Benedict equation performs remarkably well though the error in the predictions of this equation is considerably greater than that ascribable to random experimental errors, particularly in the region adjacent to the critical state. To make this equation predict accurate phase behavior simultaneously with accurate volumetric behavior for the liquid and gas has been found generally impractical in the absence of a modification of the equation itself. Such a modification is proposed. Accurate predictions of the critical state and of volumetric behavior for liquids and compressed gases have been found to be incompatible requirements for this equation.

Coefficients for the Benedict equation for the calculation of volumetric behavior to pressures of 10,000 p.s.i.a. for methane, ethane, propane, n-butane, and n-pentane are presented. Practical, general application of the Benedict equation necessitates the use of automatic digital computing equipment. This limitation implies that an equation with a sufficient number of parameters to permit the prediction of volumetric behavior within experimental uncertainty would be a more useful starting point for developing techniques for performing rapid thermodynamic calculations using high-speed automatic digital computing equipment.

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I. INTRODUCTION

An equation for interpolating volumetric properties of gases and liquids has several important advantages. It facilitates integration and differentiation of these properties when such operations are required in thermodynamic calculations as well as summarizing concisely large amounts of experimental information. In the analysis of thermodynamic problems involving multicomponent systems, it serves as a point of introduction for the effects of composition. Since high-speed digital computers require that the computation routine be stated in precise and non-intuitive terms, such an equation becomes almost indispensable for the application of these computers in the solution of thermodynamic problems.

In recognition of these advantages, Benedict, Webb, and Rubin(1) have proposed an empirical equation, 3, which meets many of the most pragmatic requirements for an analytical description of volumetric behavior. Among these requirements are simplicity sufficient to make its application feasible in many types of calculations without sacrificing accuracy in predicting the thermodynamic properties at states of greatest industrial interest, convergence to the perfect gas law, Equation 1, at infinite attenuation, and continuity in

$$P = RT\dot{V}^{-1} \qquad (1)$$

representing both the liquid and gas states at temperatures below the critical temperature. Because of the encouraging results obtained in several preliminary investigations(2,3,4,5,6,7) into the efficiency of the Benedict-Webb-Rubin equation in describing both volumetric and phase behavior in light hydrocarbon systems, a detailed investigation into the utility and limitations of this equation as an engineering tool has been undertaken in the Chemical Engineering Laboratory at the California Institute of Technology. The first part of this investigation was concerned with developing machine methods(6,7) for handling routine calculations of the coefficients* in this empirical equation of state and of the thermodynamic properties of materials for which such coefficients have been calculated. The second part, the subject of this thesis, has been concerned largely with the study of the efficacy of this equation in describing the volumetric and phase behavior in one-component systems. A third part of the investigation is concerned with the application of the Benedict** equation in the attempt to make calculations of thermodynamic behavior in multicomponent systems more tractable.

An equation of state expresses approximately the relationship which has been found to exist among the intensive state properties of temperature, pressure, and specific volume*** for systems composed of specified molecular species. This relationship is called the volumetric

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* The term coefficient denotes those parts of an expression which are independent of pressure, temperature, and specific volume. A coefficient may depend upon composition, molecular weight, or symmetry of the molecule.

** Throughout this thesis "Benedict" will refer to Benedict, Webb, and Rubin.

*** Specific volume is the volume of a unit weight of material.

behavior. Considerable effort has been devoted to the a priori deduction of the equation of state from microscopic considerations of statistical mechanics and the kinetic theory of gases and of liquids. From the engineering point of view, these efforts have been rewarded with but moderate success to date and are primarily of qualitative interest. An empirical equation of state, such as the Benedict equation, represents an effort to describe the volumetric behavior and therefore the thermodynamic behavior for each substance in terms of universal elementary functions of the state properties and of coefficients which characterize each molecular species. Values for these coefficients must be derived from experimental measurements of the volumetric behavior or from a combination of heat capacity and Joule-Thomson coefficient information. The empirical equation, then, represents an interpolation device and sheds little light on the behavior of thermodynamic systems from the microscopic point of view. This limitation is of practically no significance in engineering thermodynamic calculations however.

Thermodynamic calculations represent a significant portion of the effort which engineers apply to problems in petroleum reservoir mechanics, distillation, chemical processing, internal-combustion and jet-propulsion engine design, and in the study and application of the transport phenomena. Equations developed prior(6) to that of Beattie and Bridgeman(8) are restricted to rather low pressures for precise application in these calculations and even the Beattie-Bridgeman equation, 2, is of rather modest accuracy for states near the two-phase* region.

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[*] The two-phase region or the region of heterogeneous equilibrium refers to those states at which a liquid and a vapor phase coexist.

$$P = RT\rho + (B_oRT - A_o - C_oT^{-2})\rho^2 + (-B_obRT + A_oa - B_oRcT^{-2})\rho^3 + B_obRcT^{-2}\rho^4 \qquad (2)$$

Most thermodynamic calculations in the past and yet today are performed by graphical techniques if high accuracy is desired. Such techniques are, however, very tedious and are quite involved for multicomponent systems because of the inpossibility of representing functions of more than two variables on a single plane.

An equation of state with high precision would be a most useful engineering tool. The Benedict equation is certainly not the final equation to be proposed though the degree to which it describes volumetric behavior for both gases* and liquids is remarkable. Since the Benedict equation is typical of the more precise, non-linear, expressions which might be employed, a detailed study of its attributes has been needed. Probably a polynomial or a rational function of polynomials will eventually replace the Benedict equation for high-speed digital computer applications, but the present need is an extensive testing of the many hypotheses about the attributes which are desirable in an analytical description of volumetric behavior. While the following discussion does not exhaust the topic, it does describe several tests which have been

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* Liquid and vapor refer to the dense and to the attenuated phase respectively when they coexist. The distinction is unnecessary for temperatures greater than the critical temperature or for pressures greater than the critical pressure for one-component systems because the state of a fluid can be changed continuously without passing through two-phase states.

applied to the Benedict equation to determine its efficacy in describing the volumetric and phase behavior of one-component systems.

The discussion starts with a consideration of the mathematical nature of the Benedict equation and the consequences of using this empirical equation in developing thermodynamic relationships. Next the evaluation of the empirical coefficients is considered from a theoretical point of view. In many cases the criteria of the quality of these evaluations are intuitive so that their application in practice is largely through trial and error. Finally the results of the attempts to make the Benedict equation meet several of these criteria are presented and an interpretation is attempted.

II. DISCUSSION OF THE MATHEMATICAL NATURE OF THE BENEDICT EQUATION

The development of empirical equations of state has had a long and active history. Most of the proposed equations have provided but little improvement over the simple relationship expressed in the perfect gas law or the van der Waals equation. Most of the more useful equations of state have been written in closed form with pressure represented explicitly as a function of temperature and molal volume. In general the solution of these equations for molal volume has been possible only in power series representations. At this point a discussion of this unfortunate aspect of the Benedict equation will be useful in illustrating the mathematical nature of this equation of state. A discussion of the mathematical similarities and differences between the Benedict equation on the one hand and several simpler empirical expressions on the other will be useful as a basis for measuring the extent of progress which the Benedict equation represents. The greatest potential application of the Benedict equation is in the computation of thermodynamic properties of fluid systems. The relationship between the volumetric behavior represented by the Benedict equation and the other thermodynamic behavior is complicated as will be shown in the following analysis of the mathematical nature of the Benedict equation.

The Benedict Equation and Its Solution.

The term Benedict equation usually implies the pressure-explicit form as given in Equation 3 but the term might equally well apply to any

SEVERAL ALTERNATIVE FORMS OF THE BENEDICT EQUATION

$$P_e = RT\rho + (B_oRT - A_o - C_oT^{-2})\rho^2 + (bRT - a)\rho^3 + a\alpha\rho^6$$
$$+ cT^{-2}\rho^3(1 + \gamma\rho^2)\exp(-\gamma\rho^2) \qquad (3)$$

$$P_e = p_0 + \sum_{i=1}^{\infty} p_i(\rho - \rho_0)^i \qquad (4)$$

$$p_0 = RT\rho_0 + (B_oRT - A_o - C_oT^{-2})\rho_0^2 + (bRT - a)\rho_0^3 + a\alpha\rho_0^6$$
$$+ cT^{-2}\rho_0^3(1 + \gamma\rho_0^2)\exp(-\gamma\rho_0^2) \qquad (5)$$

$$p_1 = RT + 2(B_oRT - A_o - C_oT^{-2})\rho_0 + 3(bRT - a)\rho_0^2 + 6a\alpha\rho_0^5$$
$$+ cT^{-2}\rho_0^2(3(1 + \gamma\rho_0^2) - 2(\gamma\rho_0^2)^2)\exp(-\gamma\rho_0^2) \qquad (6)$$
$$= RT + 2(B_oRT - A_o - C_oT^{-2})\rho_0 + 3(bRT - a + cT^{-2})\rho_0^2$$
$$+ 6a\alpha\rho_0^5 - (7/2)cT^{-2}\rho_0^2(\gamma\rho_0^2)^2 + 3cT^{-2}\rho_0^2(\gamma\rho_0^2)^3 + \ldots$$

$$p_2 = (B_oRT - A_o - C_oT^{-2}) + 3(bRT - a)\rho_0 + 15a\alpha\rho_0^4$$
$$+ cT^{-2}\rho_0(3(1 + \gamma\rho_0^2) - 9(\gamma\rho_0^2)^2 + 2(\gamma\rho_0^2)^3)\exp(-\gamma\rho_0^2)$$
$$= (B_oRT - A_o - C_oT^{-2}) + 3(bRT - a + cT^{-2})\rho_0 \qquad (7)$$
$$+ 15a\alpha\rho_0^4 - (21/2)cT^{-2}\rho_0(\gamma\rho_0^2)^2 + 12cT^{-2}\rho_0(\gamma\rho_0^2)^3 + \ldots$$

$$p_3 = (bRT - a) + 20a\alpha\rho_0^3 + cT^{-2}(1 + \gamma\rho_0^2 - 17(\gamma\rho_0^2)^2$$
$$+ (32/3)(\gamma\rho_0^2)^3 - (4/3)(\gamma\rho_0^2)^4)\exp(-\gamma\rho_0^2) \qquad (8)$$
$$= (bRT - a + cT^{-2}) + 20a\alpha\rho_0^3 - (35/2)cT^{-2}(\gamma\rho_0^2)^2$$
$$+ 28cT^{-2}(\gamma\rho_0^2)^3 - (165/8)cT^{-2}(\gamma\rho_0^2)^4 + \ldots$$

$$\rho_e = \rho_0 + \sum_{j=1}^{\infty} s_j(P - p_0)^j \qquad (9)$$

$$s_1 = p_1^{-1} \qquad (10)$$

$$s_2 = -p_2p_1^{-3} \qquad (11)$$

$$s_3 = (2p_2^2 - p_1p_3)p_1^{-5} \qquad (12)$$

$$(R\rho + B_oR\rho^2 + bR\rho^3) + (-P_e - A_o\rho^2 - a\rho^3 + a\alpha\rho^6)T^{-1}$$
$$(-C_o\rho^2 + c\rho^3(1 + \gamma\rho^2)\exp(-\gamma\rho^2))T^{-3} = 0 \qquad (13)$$

of Equations* 4, 9, and 13 in as much as these equations are satisfied by the same sets of values for pressure, P, temperature, T, and reciprocal molal volume, σ .

An explicit form for the temperature might be obtained by solving the cubic equation, 13, analytically(9). However, the resulting formulae would be exceedingly complicated and their forms would depend upon the value of the discriminant of the equation in each case thereby restricting the utility of such forms. The preferred approach would involve the numerical solution of Equation 13 by iteration or by formula(9). Klein(10) describes a graphical method for solving cubic equations of the type of Equation 13 which has proven to be perhaps the most useful method of all. This procedure involves the use of a plot of a cubic parabola which applies universally to all cubic equations when they are reduced to the form in which the term of second degree is absent. This method is illustrated later when it is applied in the calculation of predicted critical state properties.

The situation with respect to Equation 9 which expresses the relationship of the reciprocal molal volume to the temperature and pressure is somewhat less tractable. The infinite series representation of σ is not summable into a closed analytic expression and for purposes of computing values for σ when P and T are given, an iterative solution

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* In these equations and in most of the remainder of this discussion the reciprocal molal volume, σ , replaces the specific volume as the volumetric state property. This substitution largely avoids negative exponents in the equations and places "infinite attenuation" at a convenient point on the graphs describing volumetric relationships.

of Equation 3 is much the simplest approach. The convergence of the infinite series representing σ is limited to an interval along an isotherm of no greater length than twice the interval between p_0 and the branch-point where $(\partial P/\partial \sigma)_T = 0$. Figure 1 shows the manner in which the partial sums of Equation 9 approach the isotherm (solid curve) described by Equation 3 for propane at 190 degrees Fahrenheit. Since all isotherms for temperatures below the critical temperature have two branch-points, one infinite series in P cannot represent both the liquid and gas phases. The interval of convergence, about p_0, of Equation 9 is indicated in Figure 1. At the right end of this interval the sum of the series oscillates infinitely and at the left end it becomes infinite monotonously. At least two such series would be required and in general the volumetric behavior can be described analytically only by the application of the principle of <u>analytic continuation</u>(11,12) if the equation of state is to be explicit in reciprocal molal volume or in specific volume. The crux of the difficulty in writing equations explicit in the volume functions lies not with the Benedict equation but with the multivaluedness of these functions with respect to two-phase pressures. Polynomials and integral functions are single-valued everywhere for finite values of the argument and thereby cannot represent the dependence of the volume functions upon pressure though they serve admirably in describing the dependence of pressure upon specific volume.

Equation 4 reduces to Equation 3 when σ_0 is chosen to be zero. The point $\sigma = \sigma_0$ is the center of the interval of convergence of the power series. Since Equation 3 is the closed form corresponding to the power series representation of the pressure as a function of reciprocal molal volume and temperature when the expansion is about the point at infinite attenuation, it describes a regular function for negative values of σ. Such a function is of no interest thermodynamically since negative values for σ are physically impossible. Thus, Equation 3 defines a function P_e which corresponds to the thermodynamic quantity pressure for a restricted interval of values of σ only. The further observation might be made that Equation 1 implies infinite compressibility. In actual gases and liquids a change in phase to a relatively incompressible type of state probably occurs for some large value of reciprocal molal volume. Bridgman(13), for example, has found water to exist as a solid at temperatures well above the triple-point temperature when the pressure becomes sufficiently high. If the equation of state is efficient for pressures in the interval $0 \leq P \leq 10{,}000$ p.s.i.a., it may be considered generally satisfactory for most present-day applications in hydrocarbon processing calculations.

To obtain the temperature dependent functions s_j for the reciprocal-molal-volume-explicit form of the Benedict equation, the reciprocals of the power series representations of the temperature dependent functions p_i are obtained by the methods outlined in Appendix A. Also the appropriate powers of these functions are obtained and the series of Equation 4 is reverted in the manner discussed in this same appendix. Equation 3 is a sufficient description of the volumetric behavior since it can be solved iteratively for temperature or reciprocal molal volume when the need arises.

The Power Series Equation.

The Benedict equation is, in essence, an extension of the Beattie-Bridgeman equation to permit more accuracy for predictions of volumetric properties at the higher values of reciprocal molal volume. The relationship of the Benedict equation to several of the simpler equations is illustrated by comparing the power series expansions of these expressions about the point at infinite attenuation.

Perfect gas law:

$$P = RT\underset{\circ}{\sigma} \tag{14}$$

van der Waals equation:

$$P = RT\underset{\circ}{\sigma}\,(1 - B_0\underset{\circ}{\sigma})^{-1} - A_0\underset{\circ}{\sigma}^2 \tag{15}$$

$$= RT\underset{\circ}{\sigma} + (B_0RT - A_0)\underset{\circ}{\sigma}^2 + B_0^{\,2}RT\underset{\circ}{\sigma}^3 + \cdots \tag{16}$$

Beattie-Bridgeman equation:

$$\begin{aligned} P = {} & RT\underset{\circ}{\sigma} + (B_0RT - A_0 - cRT^{-2})\underset{\circ}{\sigma}^2 \\ & + (-B_0bRT + A_0a - cB_0RT^{-2})\underset{\circ}{\sigma}^3 + B_0bcRT^{-2}\underset{\circ}{\sigma}^4 \end{aligned} \tag{17}$$

Benedict equation:

$$\begin{aligned} P = {} & RT\underset{\circ}{\sigma} + (B_0RT - A_0 - C_0T^{-2})\underset{\circ}{\sigma}^2 \\ & + (bRT - a + cT^{-2})\underset{\circ}{\sigma}^3 + a\alpha\underset{\circ}{\sigma}^6 - \tfrac{3}{2}cT^{-2}\gamma^2\underset{\circ}{\sigma}^7 + \cdots \end{aligned} \tag{18}$$

The general power series representation of the equation of state is called the "virial equation of state". This equation may be written symbolically as in Equation 19.

$$P = \sum_{i=0}^{\infty} B_i \rho^i \qquad (19)$$

The quantities B_i are called the virial coefficients (15) and depend upon temperature and composition but not upon pressure or the volume functions. The virial coefficients have proved to be extremely useful in making theoretical studies of the behavior of fluids since numerical values for the first three virial coefficients can usually be determined from very careful experimental measurements. If Equation 19 is differentiated and evaluated at infinite attentuation then

$$\left(\frac{\partial P}{\partial \rho}\right)_T \bigg|_{\rho=0} = B_1 \qquad (20)$$

But since all real gases approach perfect gas behavior as the pressure is reduced without limit, it follows that

$$B_1 = RT \qquad (21)$$

Further, at infinite attentuation

$$\left(\frac{\partial [P/B_1\rho]}{\partial \rho}\right)_T = \left(\frac{\partial Z}{\partial \rho}\right)_T = \left(\frac{\partial Z}{\partial P}\right)_T\left(\frac{\partial P}{\partial \rho}\right)_T = B_1\left(\frac{\partial Z}{\partial P}\right)_T = B_2/B_1 \qquad (22)$$

Consequently,

$$B_2 = B_1^2\left(\frac{\partial Z}{\partial P}\right)_T \qquad (23)$$

And

$$\left(\frac{\partial^2[P/B_1\sigma]}{\partial\sigma^2}\right)_T = \left(\frac{\partial^2 Z}{\partial\sigma^2}\right)_T\left(\frac{\partial P}{\partial\sigma}\right)_T^2 = B_1^2\left(\frac{\partial^2 Z}{\partial P^2}\right)_T = 2B_3/B_1 \qquad (24)$$

$$B_3 = \frac{B_1^3}{2}\left(\frac{\partial^2 Z}{\partial P^2}\right)_T \qquad (25)$$

The fact that $B_1^3/2$ is of the order 10^{11} when σ is in pound-moles per cubic foot, P is in pounds per square inch absolute, and T is in degrees Rankine makes the accurate calculation of the third virial coefficient a particularly delicate operation at best and practically precludes the experimental determination of the virial coefficients of higher order from extensions of this method. The second virial coefficient may also be obtained from measurements of the Joule-Thomson coefficients when they can be extrapolated to infinite attenuation along isothermal paths. From the familiar relationship

$$\underset{\cdot}{C}_p(\partial T/\partial P)_{H,m} = T(\partial \underset{\cdot}{V}/\partial T)_{P,m} - \underset{\cdot}{V} \qquad (26)$$

it follows that

$$\sigma\underset{\cdot}{C}_p(\partial T/\partial P)_{H,m} = \frac{T(\partial P/\partial T)_{\sigma,m} - \sigma(\partial P/\partial\sigma)_{T,m}}{\sigma(\partial P/\partial\sigma)_{T,m}} \qquad (27)$$

Substitution of Equation 19 into Equation 27 leads to

$$\underset{\cdot}{C}_p^*(\partial T/\partial P)_{H,m}^* = (T^2/R)(\partial[B_2T^{-2}]/\partial T)_m \qquad (28)$$

when evaluated at infinite attentuation. Equation 28 will give more accurate information with respect to the dependence of B_2 upon temperature than will Equation 23 primarily because the experimental measurement of the Joule-Thomson coefficient at low pressures is generally more precise than is the measurement of specific volume.

The arguments of statistical mechanics(15) have led to virial coefficients of the form

$$B_i = - RT\, \beta_{i-1}\, N^{i-1}(i-1)/i \qquad (29)$$

where the quantities β_i are the "irreducible cluster integrals".

$$\beta_1 = -\int_0^{\infty} 4\pi r^2 [1 - \exp(-U/kT)]\, dr \qquad (30)$$

where

$$U = 4\epsilon[(r_m/r)^{12} - (r_m/r)^6] \qquad (31)$$

Equation 31 represents the Lennard-Jones(16) hypothesis concerning the nature of intermolecular force fields for non-polar molecules. Stockmayer (16) has proposed a modification of the Lennard-Jones function for describing the intermolecular force field for polar molecules. Rice and

Hirschfelder(17) have recently calculated values for the reduced second virial coefficient.

At low densities Equation 19 implies that only the first and second virial coefficients are of importance. Since all reasonable equations of state will satisfy Equation 21, a comparison of several proposed forms to describe the dependence of the second virial coefficient on temperature will be of interest. Inasmuch as the power series representation of an analytic function is unique(18), the coefficients of σ^2 in Equations 14, 16, 17, and 18 are approximations of the same quantity if P is to be identified with the thermodynamic pressure.

Proposed Representations of the Second Virial Coefficient

Equation	B_2
Perfect gas	zero
van der Waals	$B_oRT - A_o$
Beattie-Bridgeman	$B_oRT - A_o - cRT^{-2}$
Benedict	$B_oRT - A_o - C_oT^{-2}$
Martin-Hou *(19)	$(B_2' + b'R)T + A_2' + C_2' \exp(-5.475T/T_c)$
Hirschfelder**	$(2\pi RT/3)\ (Nr_m^3)F(\epsilon/kT)$
	where: $F(\epsilon/kT) = -\int_0^\infty \frac{\exp(-U/kT)}{kT\ r_m^3} \frac{\partial U}{\partial r}\, dr$

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[*] Primes have been added to the notation of Martin and Hou in order to distinguish these coefficients from the virial coefficients where the symbol B is used with a different meaning.

[**] Hirschfelder, Bird, and Spotz(20) have evaluated $F(\epsilon/kT)$ numerically for the Lennard-Jones potential function.

The virial equation assumes that P is a regular function of $\underset{\cdot}{\sigma}$ when $\underset{\cdot}{\sigma} = 0$. The validity of this assumption is not subject to either experimental or thermodynamic proof. The virial equation cannot apply to the liquid phase as it is written in Equation 19, since the series must diverge for $\underset{\cdot}{\sigma} > \sigma_d$ for any temperature.

Figure 2 shows the second virial coefficient for propane as calculated from Equation 23. The values predicted by several of the proposed approximation functions are also included. The significant fact presented by this figure is the approximate linearity of the second virial coefficient with temperature for relatively low values of reduced temperature. This is also indicated by the calculations of Hirschfelder (6). Hirschfelder, Bird, and Spotz(20) show that the deviation from linearity is significant only at temperatures above the Boyle point temperature. Even for methane at 460 degrees Fahrenheit the deviation is not very great. The predictions of the approximation functions are not as good as might be desired.

Mayer and Mayer(21) show that the virial equation is the power series expansion about the origin of $\underset{\cdot}{\sigma}$ of

$$P = (\partial[kT \ln Q]/\partial \underset{\cdot}{V})_T \qquad (32)$$

where Q is the partition function. Consequently, the appropriate power series expansion for representing the pressure of condensed states would be the expansion of Equation 32 about some $\underset{\cdot}{\sigma} > \sigma_b$.

The virial equation can be considered to be the Laurent series expansion of P about the singularity at $\underset{\cdot}{V} = 0$. The difficulty of assigning a precise experimentally-confirmed value to the limiting specific volume of a substance as the pressure upon it becomes large without limit introduces some uncertainty into the validity of the virial expansion. The effect of the assignment of the location of the minimum molal volume upon the predictions in the gas phase is small, but at temperatures where the virial expansion converges for compressed gases it may be of greater importance.

The extension of the methods of statistical mechanics to the deduction of the equation of state for compressed gases and liquids has not been developed to as satisfactory a point as for dilute gases. Hirschfelder (16,22) has calculated values for the liquid compressibility factor from the reduced equation of state as deduced from the "free-volume theory" and the theory of Born, Green, and Yvon.

One objective of the statistical mechanical development of the equation of state is an understanding of condensation and critical state phenomena from the microscopic point of view. The need for such an understanding is not apparent for most thermodynamic applications of the equation of state. Thus considerable freedom is gained in the choice of approximating function if the convention(23) is adopted that the volumetric behavior in the two-phase region need not be predicted accurately or even approximately by the empirical equation. The retention of two restraints—continuity and

$$\int_{\underset{\cdot}{V}_b}^{\underset{\cdot}{V}_d} P \, d\underset{\cdot}{V} = P(\underset{\cdot}{V}_d - \underset{\cdot}{V}_b)$$

—is desirable. Under this convention, pressure is a continuous, differentiable, single-valued function of either specific volume or specific weight.

Empirical equations can, then, approximate the volumetric behavior precisely if only enough coefficients are allowed.

The statistical mechanical application of the virial equation to gaseous mixtures involves certain assumptions(24) concerning the nature of the intermolecular force field(20). The empirical approach should similarly allow for the deduction of the volumetric behavior of mixtures from the behavior of the components. The statistical argument(24) confirms the possibility of making such a deduction for dilute gases but for compressed gases and liquids the statistical argument is not appropriate because of the convention discussed above. Benedict, Webb, and Rubin(2,3,4) and Connolly(6) have shown that in many cases quite good predictions of phase behavior in mixtures are possible with the Benedict equation. This application of the empirical equations needs a much more extensive analysis than has yet been supplied.

Expressions for Thermodynamic Properties.

Many of the most useful thermodynamic properties of a multicomponent system can be expressed algebraically in terms of six canonical functions which depend upon the equation of state alone. Appropriate expressions for molal chemical potential, partial molal volume, partial molal enthalpy, partial molal entropy, partial molal internal energy, and the Joule-Thomson coefficient may be written in terms of these six functions. These functions may be expressed in terms of the Benedict equation. Appropriate expressions for mixtures are obtained from the partial molal properties by substitution into the familiar equation

$$\underset{\cdot}{G} \quad = \quad \sum_{k=1}^{N} \underset{\cdot}{n}_k \overline{\underset{\cdot}{G}}_k \tag{33}$$

where $\overline{\underset{\cdot}{G}}$ stands for a partial molal property. The six canonical functions are the following:

$$P \underset{\cdot}{V} \tag{34}$$

$$(\partial P/\partial \underset{\cdot}{\sigma})_{T,m} \tag{35}$$

$$T\underset{\cdot}{V}(\partial P/\partial T)_{\sigma,m} \tag{36}$$

$$RT \ln f_k \tag{37}$$

$$RT\underset{\cdot}{\sigma}(\partial \ln f_k/\partial \underset{\cdot}{\sigma})_{T,m} \tag{38}$$

$$RT^2(\partial \ln f_k/\partial T)_{\sigma,m} \tag{39}$$

In terms of these quantities

$$\underset{\cdot}{\mu}_k - \underset{\cdot}{\mu}_k^{o*} \quad = \quad [RT \ln f_k] \quad - \quad RT \ln P^* \tag{40}$$

$$\overline{\underset{\cdot}{V}}_k \quad = \quad \underset{\cdot}{V}[RT\underset{\cdot}{\sigma}(\partial \ln f \,/\partial \underset{\cdot}{\sigma})_{T,m}]/[(\partial P/\partial \sigma)_{T,m}] \tag{41}$$

$$\overline{\underset{\cdot}{H}}_k - \underset{\cdot}{H}_k^{o*} \quad = \quad - [RT^2(\partial \ln f_k/\partial T)_{\sigma,m}] + \frac{[RT\underset{\cdot}{\sigma}(\partial \ln f_k/\partial \underset{\cdot}{\sigma})_{T,m}][T\underset{\cdot}{V}(\partial P/\partial T)_{\sigma,m}]}{[(\partial P/\partial \underset{\cdot}{\sigma})_{T,m}]} \tag{42}$$

$$\overline{\underset{\cdot}{S}}_k - \underset{\cdot}{S}_k^{o*} \quad = \quad R \ln P^* - T^{-1}\Big\{[RT \ln f_k] + [RT^2(\partial \ln f_k/\partial T)_{\sigma,m}] + \frac{[RT\underset{\cdot}{\sigma}(\partial \ln f_k/\partial \underset{\cdot}{\sigma})_{T,m}][T\underset{\cdot}{V}(\partial P/\partial T)_{\sigma,m}]}{[(\partial P/\partial \underset{\cdot}{\sigma})_{T,m}]}\Big\} \tag{43}$$

$$\overline{\underset{\cdot}{E}}_k - \underset{\cdot}{E}_k^{o*} \quad = \quad RT - [RT^2(\partial \ln f_k/\partial T)_{\sigma,m}] + \frac{\{[TV(\partial P/\partial T)_{\sigma,m}] - P\underset{\cdot}{V}\}\,[RT\underset{\cdot}{\sigma}(\partial \ln f_k/\partial \underset{\cdot}{\sigma})_{T,m}]}{[(\partial P/\partial \underset{\cdot}{\sigma})_{T,m}]} \tag{44}$$

$$Z \quad = \quad [P\ \underset{\cdot}{V}]/RT \tag{45}$$

$$f_k \quad = \quad \exp([RT \ln f_k]/RT) \tag{46}$$

$$(\partial P\underline{V}/\partial \underset{\cdot}{m}_k)_{T,\underline{V},m_i} \quad = \quad RT\underset{\cdot}{\sigma}(\partial \ln f_k/\partial T)_{\sigma,m} \tag{47}$$

$$\underset{\cdot}{C}_p(\partial T/\partial P)_{H,m} = \frac{[T\underset{\cdot}{V}(\partial P/\partial T)_{\sigma,m}] - [(\partial P/\partial \underset{\cdot}{\sigma})_{T,m}]}{\sigma[(\partial P/\partial \sigma)_{T,m}]} \qquad (48)$$

Benedict(2) has postulated that the coefficients of the Benedict equation depend upon composition in the following way.

$$A_o = [\sum_{i=1}^{N} \underset{\cdot}{n}_i \sqrt[2]{A_{oi}}]^2 = \sum_{k=1}^{N} \underset{\cdot}{n}_k A'_{ok} \qquad (49)$$

$$B_o = [\sum_{i=1}^{N} \underset{\cdot}{n}_i \quad B_{oi}] = \sum_{k=1}^{N} \underset{\cdot}{n}_k B'_{ok} \qquad (50)$$

$$C_o = [\sum_{i=1}^{N} \underset{\cdot}{n}_i \sqrt[2]{C_{oi}}]^2 = \sum_{k=1}^{N} \underset{\cdot}{n}_k C'_{ok} \qquad (51)$$

$$a = [\sum_{i=1}^{N} \underset{\cdot}{n}_i \sqrt[3]{a_i}]^3 = \sum_{k=1}^{N} \underset{\cdot}{n}_k a'_k \qquad (52)$$

$$b = [\sum_{i=1}^{N} \underset{\cdot}{n}_i \sqrt[3]{b_i}]^3 = \sum_{k=1}^{N} \underset{\cdot}{n}_k b'_k \qquad (53)$$

$$c = [\sum_{i=1}^{N} \underset{\cdot}{n}_i \sqrt[3]{c_i}]^3 = \sum_{k=1}^{N} \underset{\cdot}{n}_k c'_k \qquad (54)$$

$$\alpha = [\sum_{i=1}^{N} \underset{\cdot}{n}_i \sqrt[3]{\alpha_i}]^3 = \sum_{k=1}^{N} \underset{\cdot}{n}_k \alpha'_k \qquad (55)$$

$$\gamma = [\sum_{i=1}^{N} \underset{\cdot}{n}_i \sqrt[2]{\gamma_i}]^2 = \sum_{k=1}^{N} \underset{\cdot}{n}_k \gamma'_k \qquad (56)$$

where

$$\begin{aligned} A'_{ok} &= \sqrt[2]{A_o A_{ok}} & a'_k &= \sqrt[3]{a^2 a_k} \\ B'_{ok} &= (B_o + B_{ok})/2 & b'_k &= \sqrt[3]{b^2 b_k} \\ C'_{ok} &= \sqrt[2]{C_o C_{ok}} & c'_k &= \sqrt[3]{c^2 c_k} \\ \alpha'_k &= \sqrt[3]{\alpha^2 \alpha_k} & \gamma'_k &= \sqrt[2]{\gamma\ \gamma_k} \end{aligned} \qquad (57)$$

The variables A'_{ok}, B'_{ok}, ..., γ'_k satisfy Equation 35, but they are not partial molal properties.

In terms of the Benedict equation the functions 34 through 39 are:

$$\begin{aligned} P\underset{\circ}{V} &= RT + (B_0RT - A_0 - C_0T^{-2})\underset{\circ}{\sigma} \\ &+ (bRT - a)\underset{\circ}{\sigma}^2 + a\alpha\underset{\circ}{\sigma}^5 \\ &+ cT^{-2}\underset{\circ}{\sigma}^2(1 + \gamma\underset{\circ}{\sigma}^2)\exp(-\gamma\underset{\circ}{\sigma}^2) \end{aligned} \tag{58}$$

$$\begin{aligned} (\partial P/\partial\underset{\circ}{\sigma})_{T,m} &= RT + 2(B_0RT - A_0 - C_0T^{-2})\underset{\circ}{\sigma} \\ &+ 3(bRT - a)\underset{\circ}{\sigma}^2 + 6a\alpha\underset{\circ}{\sigma}^5 \\ &+ 3T^{-2}\underset{\circ}{\sigma}^2(1 + \gamma\underset{\circ}{\sigma}^2) - \frac{2}{3}c(\gamma\underset{\circ}{\sigma}^2)^2)\exp(-\gamma\underset{\circ}{\sigma}^2) \end{aligned} \tag{59}$$

$$\begin{aligned} T\underset{\circ}{V}(\partial P/\partial T)_{\underset{\circ}{\sigma},m} &= RT + (B_0RT + 2C_0T^{-2})\underset{\circ}{\sigma} + bRT\underset{\circ}{\sigma}^2 \\ &- 2cT^{-2}\underset{\circ}{\sigma}^2(1 + \gamma\underset{\circ}{\sigma}^2)\exp(-\gamma\underset{\circ}{\sigma}^2) \end{aligned} \tag{60}$$

$$\begin{aligned} RT \ln f_k &= RT \ln RT\underset{\circ}{n}_k\underset{\circ}{\sigma} + 2(B'_{0k}RT \\ &- A'_{0k} - C'_{0k}T \quad)\underset{\circ}{\sigma} + \frac{3}{2}(b'_kRT - a'_k)\underset{\circ}{\sigma}^2 \\ &+ \frac{6}{10}(a\alpha'_k + \alpha a'_k)\underset{\circ}{\sigma}^5 + T^{-2}(3c'_k \\ &- 2c\gamma'/\gamma)\left\{\gamma^{-1} + \underset{\circ}{\sigma}^2\left(\frac{c(1 + \gamma\underset{\circ}{\sigma}^2)\gamma'_k}{(3c'-2c\gamma'_k/\gamma)\gamma}\right.\right. \\ &\left.\left. - (\gamma\underset{\circ}{\sigma}^2)^{-1} - (1/2)\right)\exp(-\gamma\underset{\circ}{\sigma}^2)\right\} \end{aligned} \tag{61}$$

$$\begin{aligned} RT\underset{\circ}{\sigma}(\partial \ln f_k/\partial\underset{\circ}{\sigma})_{T,m} &= RT + 2(B'_{0k}RT - A'_{0k} - C'_{0k}T^{-2})\underset{\circ}{\sigma} \\ &+ 3(b'_kRT - a'_k)\underset{\circ}{\sigma}^2 + \frac{6}{2}(a\alpha'_k + \alpha a'_k)\underset{\circ}{\sigma}^5 \\ &+ 3T^{-2}\underset{\circ}{\sigma}^2(c'_k(1 + \gamma\underset{\circ}{\sigma}^2) \\ &- \frac{2}{3}c(\gamma\underset{\circ}{\sigma}^2)^2\gamma'_k/\gamma)\exp(-\gamma\underset{\circ}{\sigma}^2) \end{aligned} \tag{62}$$

$$\begin{aligned} RT^2(\partial \ln f_k/\partial T)_{\underset{\circ}{\sigma},m} &= RT + 2(A'_{0k} + 3C'_{0k}T^{-2})\underset{\circ}{\sigma} \\ &+ \frac{3}{2}a'_k\underset{\circ}{\sigma}^2 - \frac{6}{10}(ac'_k + \alpha a'_k)\underset{\circ}{\sigma}^5 \\ &- 3T \quad (3c' - 2c\gamma'/\gamma)\left\{\gamma^{-1}\right. \\ &+ (c(1 + \gamma\underset{\circ}{\sigma}^2)\gamma'_k/\gamma(3c' - 2c\gamma'_k/\gamma) \\ &\left.- (\gamma\underset{\circ}{\sigma}^2)^{-1} - (1/2))\underset{\circ}{\sigma}^2\exp(-\gamma\underset{\circ}{\sigma}^2)\right\} \end{aligned} \tag{63}$$

For one-component systems all of the above equations apply if the primes are omitted. Under these circumstances Equation 41 reduces to an identity and the partial molal properties become the molal properties of the system.

III. FITTING THE BENEDICT EQUATION TO EXPERIMENTAL VOLUMETRIC AND PHASE BEHAVIOR DATA

Methods of fitting an empirical equation of state to experimental information are many. Probably the most familiar is the evaluation of the coefficients A_o and B_o for van der Waals' equation, 15, from knowledge of the critical temperature and pressure through the simultaneous solution of Equations 79 and 80. By no means does such an evaluation represent the only possible one or even the only useful one. For calculations involving gases at low pressure, A_o and B_o might better be evaluated from knowledge of the second virial coefficient. A similar state of affairs prevails with respect to the Benedict equation with the result that the appropriate methods to use in the evaluations of the coefficients depend to a large extent upon the intended application of the equation of state. For present purposes, the assumption is made that the Benedict equation is to be used to describe the volumetric behavior for the dense as well as the attentuated states of hydrocarbons, and similar fluids, for pressures up to 10,000 pounds per square inch and temperatures in the interval from 70 to 500 degrees Fahrenheit. That the Benedict equation is to be applied in phase behavior calculations involving multicomponent systems is also assumed.

Volumetric Fit.

The Benedict equation does not describe the volumetric behavior of fluids within the precision of the experimental knowledge. For this reason, statistical arguments in discussions of the fit of this equation are not appropriate inasmuch as the deviations of the experimental values from the values calculated from the Benedict equation are predictable. If the Benedict equation, with eight coefficients, is assumed to describe the volumetric behavior of a fluid, then more than eight observations of the volumetric properties over-specify the values for these coefficients. The equations which represent these observations in terms of the Benedict equation are inconsistent with respect to the assumption that each coefficient has one value uniformly for this set of equations. In Appendix C several criteria for the estimation of satisfactory values of the coefficients are discussed. The selection of the least squares criterion for the present analysis was on the basis of the usual pragmatic consideration of numerical convenience.

The method of least squares involves the minimization of the sum of the squares of the deviations of the experimental values from the predicted values for some function, or combination of functions, whose analytic expression contains all of the coefficients. The selection of a particular function is usually on the basis of obtaining normal* equations in which the parameters enter in as nearly a linear manner as is feasible. Such considerations indicate very strongly that the appropriate variable to fit the Benedict equation is the compressibility factor. The coefficients in the equation for fugacity of a one-component system, Equation 61, are as linear as they are for the compressibility factor but values for fugacity are not so conveniently obtained

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* Cf. Appendix C.

from experimental measurements. The compressibility factor is free of dimensions which provides considerable numerical convenience. From values for the reciprocal molal volume, obtained by iterative solution of Equation 3, and temperature, the compressibility factor may be obtained from the following form of the Benedict equation.

$$Z = 1 + (B_oRT - A_o - C_oT^{-2})\sigma/RT + (bRT - a)\sigma^2/RT$$

$$+ a\alpha\sigma^5/RT + c\sigma^2R^{-1}T^{-3}(1 + \gamma\sigma^2)\exp(-\gamma\sigma^2) \qquad (64)$$

Equation 3, however, presumes that the values of the coefficients are known. The use of pressure, then, as an independent variable in the least squares calculations is too tedious to be feasible. The desirability of using expressions more complicated than that expressing the dependence of the compressibility factor upon the reciprocal molal volume and the temperature is debatable. If the results of the application of this expression in the least squares evaluation of the coefficients of the Benedict equation are not as good as might be desired in a certain region, then a convenient method of improving the situation would be through the imposition of a rigid limitation on the deviation permitted in this region by application of the method of the Lagrange undetermined multipliers. The application of this method is discussed in Appendix C.

The quality of fit of Equation 64 with a particular set of values for its coefficients is reflected in the magnitude of the standard error of estimate(25) of the compressibility factor on temperature and reciprocal molal volume. The square of this term is called the variance* of

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* Variance of estimate $= \sum_{i=1}^{N} \frac{(Z_e - Z)_i^2}{N}$ where N is the number of experimental observations.

estimate of the compressibility factor on temperature and reciprocal molal volume. These terms will be shortened to simply "standard error of estimate" and "variance of estimate" in the ensuing discussion when temperature and reciprocal molal volume are considered to be the independent variables which define the state of the thermodynamic system. These measures of fit are the analogs of the statistical terms "standard deviation" and "variance".

The detailed character of the fit cannot be described by a single number since it must necessarily represent the result of an averaging process. If the fit is generally very good, it may still be quite poor in a small region without making the standard error of estimate very large. The standard error of estimate gives no indication as to which values of the independent variables lead to the poorest or to the finest predictions. If the experimental data which are used in the least squares evaluation of the coefficients are concentrated in a small region, the standard error of estimate may be very small and yet the fit of the equation may be inadequate for general application. The method of least squares is effectively an analytical device for minimizing the variance of estimate over all possible sets of values for the coefficients and it is from this characteristic that it derives its name. The details of the linear part of the least squares analysis of the Benedict equation are presented in Appendix D. The complete linearization of the Benedict equation has not been feasible for present purposes though the substitution of a rational-function(26) approximation for the exponential function in this equation would have much merit from the computational standpoint. The fact that the coefficient gamma enters the normal equations in a non-linear manner requires that the normal equations be solved iteratively. The iteration is straightforward and involves the computation of the standard error of estimate for several values of gamma and the selection of that value which corresponds to the minimum. A plot of the standard error of estimate for propane as a function of gamma is given in Figure 2 of Appendix F. Brough(27) has shown that the standard error of estimate must approach a limit as gamma becomes large without limit and that the standard error of estimate has a relative stationary point at gamma equal to zero.

For an equation to describe the volumetric behavior of low pressure gases, the coefficients should be evaluated in part at least from experimental measurements of the Joule-Thomson coefficients. From Equation 27

$$\underset{\cdot}{\sigma}^2\underset{\cdot}{C}_p(\partial T/\partial P)_{\underset{\cdot}{H},m}(\partial P/\partial \underset{\cdot}{\sigma})_{T,m} = T(\partial P/\partial T)_{\underset{\cdot}{\sigma},m} - \underset{\cdot}{\sigma}(\partial P/\partial \underset{\cdot}{\sigma})_{T,m} \quad (65)$$

The quantity $\underset{\cdot}{C}_p\ (\partial T/\partial P)_{\underset{\cdot}{H},m}$ can be determined from integration of

$$(\partial \underset{\cdot}{C}_p/\partial P)_{T,m} = -(\partial \underset{\cdot}{C}_p(\partial T/\partial P)_{\underset{\cdot}{H},m}/\partial T)_{P,m}$$

and knowledge of the heat capacity, $\underset{\cdot}{C}_p$, as a function of temperature at some pressure. Substitution of the expressions for the canonical functions from Equations 58 through 63 will yield an expression which is linear in all the coefficients except gamma and which may be used to obtain the coefficients by the method of least squares. To make a least squares fit of the Benedict equation which reflects the

Joule-Thomson coefficient measurements as well as the volumetric measurements requires a high degree of intuition. In general the elements of the normal matrices for the volumetric and for the Joule-Thomson data are of different orders of magnitude which means that linear combinations of these matrices, such as in the method of averages, would tend to emphasize the effect of the matrix with the large elements. The two matrices jointly correspond to a system of fourteen simultaneous, linear, inconsistent, equations. The method of least squares can be applied to this system of equations to reduce the number to seven and thereby permit values for the coefficients to be obtained. Such values have, however, no particular merits over values obtained from a system of seven equations selected at random from the fourteen except that the least squares evaluation uses an unambiguous procedure which leads to a unique solution to the problem. Such calculations have not been applied to the Benedict equation and will not be discussed further. The method-of-averages approach to an analogous situation which sought to make the Benedict equation predict phase behavior in the least squares sense, was singularly unproductive.

Fit Along the Two-Phase Boundary.

The equation of state must predict the phenomena associated with heterogeneous equilibrium with a reasonable degree of accuracy. In general, this requirement presents considerable difficulty from the mathematical point of view. A one-component system at heterogeneous equilibrium has one degree of freedom in the sense of the phase rule.

The familiar analysis leading to an equation for the vapor pressure curve from the Clausius-Clapeyron equation, Equation 66,

$$\frac{d \ln P''}{dT} = \frac{U_d - U_b}{RT^2} \tag{66}$$

implies that at least two parameters are required for the empirical description of phase behavior in one-component systems. If the Benedict equation with the criteria of heterogeneous equilibrium between phases g and ℓ, which are

$$T_g = T_\ell \tag{67}$$

$$P_g = P_\ell \tag{68}$$

$$f_{k,g} = f_{k,\ell} \tag{69}$$

is to describe phase behavior, the volumetric fit can be no better than the best six parameter equation.

The accurate description of the volumetric behavior of itself is not sufficient for an equation such as the Benedict equation to permit the accurate prediction of phase behavior or of the thermodynamic properties of the liquid phase. Assume that the Benedict equation can accurately describe pressure as the same function of temperature and molal volume as that observed experimentally in the regions of homogeneous equilibrium for one-component systems. Then, the temperature and molal volume derivatives and all combinations of pressure, temperature, and molal volume with these derivatives may be predicted accurately by the Benedict equation in this region. Thus the relationship expressed in Equation 70 determines the slope of the fugacity-molal volume isotherms accurately in this region of single-phase states.

$$\left(\frac{\partial \ln f}{\partial \underset{\cdot}{V}}\right)_{T,m} = \frac{\underset{\cdot}{V}}{R\,T}\left(\frac{\partial P}{\partial \underset{\cdot}{V}}\right)_{T,m} = \frac{1}{R\,T}\left(\frac{\partial P\underset{\cdot}{V}}{\partial \underset{\cdot}{V}}\right)_{T,m} - P \tag{70}$$

Equation 70 may be integrated to obtain an accurate expression for the ratio of the fugacities at two states lying at the extremes of an interval along a pressure-molal volume isotherm which lies entirely within the single-phase region. Thus, in the liquid region, the fugacity at any state, for which the temperature is below the critical temperature, is known accurately as a multiple of the bubble-point fugacity at the temperature of the state.

Equation 70 may be rewritten in the following manner.

$$\left(\frac{\partial \ln f}{\partial \underset{\cdot}{V}}\right)_{T,m} = \left(\frac{\underset{\cdot}{V}}{R\,T}\right)\left(\frac{\partial P}{\partial \underset{\cdot}{V}}\right)_{T,m} + \frac{1}{P}\left(\frac{\partial P}{\partial \underset{\cdot}{V}}\right)_{T,m} - \frac{1}{P}\left(\frac{\partial P}{\partial \underset{\cdot}{V}}\right)_{T,m} \tag{71}$$

This equation may be reduced to

$$\left(\frac{\partial \ln [f/P]}{\partial \underset{\cdot}{V}}\right)_{T,m} = -\frac{1}{R\,T}\left(\frac{RT}{P} - \underset{\cdot}{V}\right)\left(\frac{\partial P}{\partial \underset{\cdot}{V}}\right)_{T,m} \tag{72}$$

Since the quantity $(RT/P - \underset{\cdot}{V})$, called the residual molal volume, is defined and is known accurately all the way from dew-point to infinite attenuation for temperatures less than the critical temperature or for all molal volumes for temperatures greater than the critical temperature, Equation 72 may be integrated to give an accurate expression for the fugacity in these regions.

The presumption is made that the Benedict equation does not correctly portray the pressure as a function of temperature and of molal volume in the region of heterogeneous equilibrium. In such region Equations 70, 71, and 72 are not applicable if P is the pressure predicted by the Benedict equation. If an analytical expression for $(V/RT)dP$ from Equation 3 is integrated from a gaseous state along an isotherm through the region of heterogeneous equilibrium to a liquid state, that part of the integral contributed by the two-phase states must be subtracted from the total integral. In actual gases the contribution of these states is precisely zero since the dew-point fugacity equals the bubble-point fugacity. This contribution to the integration of the expression derived from the Benedict equation is a function of temperature alone. Call this function $F(T)$. $F(T)$ will be precisely zero in the gaseous region and

$$F(T) = \int_{P_d}^{P_b} \frac{\underset{\cdot}{V}}{RT} dP = \int_{\underset{\cdot}{V}_d}^{\underset{\cdot}{V}_b} \frac{(P'' - P)}{RT} d\underset{\cdot}{V} = \frac{1}{R\,T} \int_{\underset{\cdot}{\sigma}_d}^{\underset{\cdot}{\sigma}_b} \frac{(P - P'')}{\underset{\cdot}{\sigma}^2} d\underset{\cdot}{\sigma} \qquad (73)$$

for $\underset{\cdot}{V} < \underset{\cdot}{V}_b$. Thus $\ln f$, and consequently f, will be predicted accurately in the region of liquid states only if the function $F(T)$ is known accurately.

The preceding analysis can be reversed and the Benedict equation may be presumed to predict the fugacities of the states at homogeneous equilibrium accurately. Then Equations 70 and 72 may be integrated as before. In integrating across the region of heterogeneous equilibrium the Benedict equation will predict an increase in the pressure by an amount $F'(T)$ where

$$F'(T) = \int_{f_d}^{f_b} \frac{RT}{V}\, d \ln f = RT \int_{\sigma_d}^{\sigma_b} \ln (f/f'')\, d\sigma \qquad (74)$$

Unless the Benedict equation is of such a nature that it predicts pressure to be independent of specific volume along isothermal paths in the region of heterogeneous equilibrium, it will not in general predict correct liquid phase fugacities if fitted to P-V-T data or, conversely, predict correct liquid phase pressures if fitted to f-V-T data without special adjustments. It is, of course, conceivable that the Benedict equation would predict $F(T)$ and $F'(T)$ to be precisely zero for all temperatures but this can be coincidence only.

The direct experimental measurement of fugacity as a function of molal volume and temperature has not been possible to date. For this reason the Benedict equation will usually be fitted to P-V-T measurements and the correction $F(T)$ will be applied to the predicted fugacities. After such operations, on the Benedict equation it will necessarily permit the accurate prediction of values for the canonical functions and therefore also the thermodynamic properties of one-component systems.

The Clapeyron equation states that

$$\frac{dP''}{dT} = \frac{H_d - H_b}{T(V_d - V_b)} \qquad (75)$$

Thus the latent heat of vaporization is predicted accurately if the phase behavior is predicted accurately. The Clapeyron equation emphasizes the necessity for accurate volumetric predictions as well as accurate fugacity predictions if the enthalpy predictions are to be accurate in the liquid phase.

Equations 67, 68, and 69 represent three restraints which might be imposed upon the solution of the normal equations in order to make the prediction of the phase behavior agree with the experimental observations exactly. However, the possibility of imposing such restraints to obtain perfect predictions of phase behavior is only illusory. The difficulties involved arise first from the fact that Equation 9 which expresses the dependence of reciprocal molal volume upon temperature and pressure cannot be written in closed form in terms of elementary functions of pressure and temperature. Substitution of Equations 67 and 68 into the power series representation of reciprocal molal volume, one series each for the dew-point and bubble-point, yields a pair of functions each of which may be substituted into Equation 61 to obtain an expression for the logarithm of the fugacity as a function of temperature and pressure. Such a representation for the logarithm of the fugacity cannot be summed into a closed form comprising elementary functions of pressure and temperature. When such representations for the logarithm of the fugacity are combined with Equation 69 there results an infinite series in pressure, P, and temperature, T. But, the two-phase pressure is known experimentally as a function of temperature. If some simple, but accurate, expression for describing the vapor pressure curve is used to replace P in this infinite series, the final result will be an infinite series in T alone. Equation 69 expresses the fact that this series is invariant with respect to temperature. The fact that the coefficients of T in this series must be identically zero in order that the series be invariant forms a set of restraints upon the Benedict coefficients of which they are comprised. Such coefficients of T are independent of the thermodynamic variables; however, they are at the same time the sums of infinite numbers of terms which cannot be expressed in simple closed form. While such a method of making the Benedict equation predict phase behavior may appear optimum it is at the same time impossible.

Fitting the Benedict Equation at the Critical State.

Experimental measurements have abundantly confirmed that the following properties characterize the critical state for a one-component system.

$$(\partial f/\partial \underset{\cdot}{\sigma})_{T,m} = 0 \tag{76}$$

$$(\partial^2 f/\partial \underset{\cdot}{\sigma}^2)_{T,m} = 0 \tag{77}$$

$$(\partial P/\partial T)_{\underset{\cdot}{\sigma},m} = dP''/dT \tag{78}$$

In Appendix G Equations 76 and 77 are shown to be equivalent to Equations 79 and 80 for a one-component system.

$$(\partial P/\partial \rho)_{T,m} = 0 \tag{79}$$

$$(\partial^2 P/\partial \rho^2)_{T,m} = 0 \tag{80}$$

Since a one-component system has only two degrees of freedom, this set of equations is necessarily inconsistent or redundant. It is redundant for locating the critical state of a real gas and inconsistent for locating the critical state predicted by the Benedict equation. For convenience, Equations 79 and 80 will be assumed to define the critical state as predicted by the Benedict equation for a one-component system. This choice is also indicated by the isothermal integrations involved in the computation of fugacity using an empirical equation of state. For the Benedict equation then,

$$\begin{aligned}\frac{1}{RT}\left(\frac{\partial P}{\partial \rho}\right)_{T,m} &= 1 + 2K_1\rho + 2K_2\rho T^{-1} + 2K_3\rho T^{-3} \\ &+ 3K_4\rho^2 + 3K_5\rho^2 T^{-1} + 6K_6\rho^5 T^{-1} \\ &+ K_7\rho^2 T^{-3}(3(1+\gamma\rho^2) - 2(\gamma\rho^2)^2)\exp(-\gamma\rho^2) \\ &= 0\end{aligned} \tag{81}$$

and

$$\begin{aligned}\frac{1}{RT}\left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T,m} &= K_1 + K_2T^{-1} + K_3T^{-3} + 3K_4\rho + 3K_5\rho T^{-1} \\ &+ 15K_6\rho^4 T^{-1} + K_7\rho T^{-3}(3(1+\gamma\rho^2) \\ &- 9(\gamma\rho^2)^2 + 2(\gamma\rho^2)^3)\exp(-\gamma\rho^2) \\ &= 0\end{aligned} \tag{82}$$

The method of the Lagrange undetermined multipliers may be applied to make the Benedict equation predict the effects described in Equations 81 and 82 at the critical temperature and at the value of the reciprocal molal volume corresponding to the observed critical state. These restraints could be made to apply at the observed values of the critical temperature and pressure by an iterative process which would require successive estimates of the reciprocal molal volume predicted by the equation for the observed values of the critical temperature and pressure. Restraints in addition to those described in Equations 81 and 82 might be applied in the same manner. Such a procedure would give greater accuracy to the region adjacent to the critical state at a relatively great cost to the fit in regions removed from it. Martin and Hou(19), however, imposed seven restraints at the critical state in the evaluation of the coefficients of their equation and obtained an excellent fit for the low pressure gas phase. Clearly the use of so many critical state restraints on the Benedict equation coefficients would preclude the possibility of describing the volumetric behavior of liquids with this equation. Zimm(28,29) has supplied an argument in support of a postulate that all isothermal derivatives with respect to pressure are zero at the critical state for a one-component system. Thus there exist presumably an infinite number of possible restraints which one might impose at the critical state. Consequently the particular choice of restraints on the evaluation of the coefficients must be intuitive.

RESULTS OF THE INVESTIGATION OF THE UTILITY OF THE BENEDICT EQUATION FOR ONE-COMPONENT SYSTEMS

Experimental Program.

The present investigation of the application of the Benedict equation in precise thermodynamic calculations has considered three separate attributes which the equation should possess to a sufficient degree. First, the equation should describe the volumetric behavior of the fluid states in both the gas and liquid phases as well as at states well within the region of homogeneous equilibrium. This phase of the investigation involved the evaluation of coefficients for the first five light paraffin hydrocarbons from volumetric information alone. The effect of adjusting the data background of the calculations was investigated in detail for propane and the results of this investigation are discussed in the reprint included as Appendix F. The optimum values for these coefficients are presented in Table I. Table II presents the values of the coefficient which were proposed by Benedict and Table III supplements Tables II, IV, and V of Appendix F to present all of the sets of coefficients which have been evaluated in this investigation for purposes of predicting volumetric behavior. Those sets in Table III which have been included in Table I are indicated by an asterisk.

Second, the Benedict equation should be made to predict the phenomena associated with heterogeneous equilibrium with small error. Some of the difficulties associated with this phase of the investigation have been discussed in the preceding section. An unsuccessful attempt was made to formulate an analytic description of the phase behavior in terms of a set of coefficients differing from those describing the volumetric behavior. This course of action was suggested by the difficulty of making the Benedict equation predict correct liquid phase fugacity when high pressure volumetric data were included in the evaluation of the coefficients. The addition of another term to the Benedict equation to improve the vapor pressure predictions has been investigated for propane.

Third, the Benedict equation should be made to exhibit the characteristics of the critical state, Equations 79 and 80, for a temperature and a pressure reasonably close to the observed values. The effect on the volumetric predictions of making the equation satisfy Equations 78, 79, and 80 at the observed critical molal volume and temperature has been studied.

Experimental Information Used in Evaluating the Coefficients.

The volumetric and phase behavior of the light paraffin hydrocarbons has been carefully measured. These measurements were made at states which represent most of the regions of temperature and pressure which are of industrial interest, i.e., at states whose pressures are below 10,000 pounds per square inch absolute and whose temperatures are in the interval between 70 and 500 degrees Fahrenheit. With the aid of the concept called "the law of corresponding states" these measurements have permitted the general nature of the volumetric and phase behavior of these substances and their mixtures to be inferred for most of their fluid states. This experimental information is not of uniform density over the region of fluid states and in many regions it is absent altogether while in others the several investigators have duplicated each other. In these regions where the several investigations overlap, the agreement of the experimental measurements is excellent.

In Figures 3, 4, 5, and 6 and in Figures 1, 4, and 5 of Appendix F the states which were actually used in the evaluation of the coefficients of the Benedict equation are shown on pressure-temperature projections. In each case the source of the experimental information is noted. The region of the data used by Benedict(3) is enclosed within a hachured line in Figures 3, 4, 5, and 6. In Appendix F, the data points used by Benedict are shown. These figures show two interesting features. First, in general, the region of the data used by Benedict differed significantly from that used in the present investigation. Second, the data used by Benedict represent more nearly a uniform set of reduced states for the five light hydrocarbons considered here than do the data used in the evaluations reported in Tables I and III. The effects of these differences upon the values for the coefficients is shown in Tables I and II and Figures 7 and 8. The coefficients proposed by Benedict produce the smoother curves when plotted against molecular weight on a linear scale. The effect of intuitive, non-least-squares adjustments performed by Benedict(1) on his coefficients must also be considered when comparing Figures 7 and 8. The fact that the data used by Benedict do not include a significant number of states representing the liquid phase would be expected to produce a pronounced effect. The fact that the magnitudes of the corresponding entires in Tables I and II do not differ greatly implies that the accommodation of the coefficients to the liquid phase data occurs through a readjustment of their interrelationships.

Calculations for states representing the liquid phase involve the subtraction of relatively large numbers to obtain small differences with the result that very small percentage changes in the values of the coefficients result in large changes in the predictions of the volumetric properties for states at which the molal volume is small. Table IV presents several sample calculations of the pressure for three values of reciprocal molal volume to demonstrate the relative contribution of the several terms in the Benedict equation and to point out the great difficulty of obtaining precision in predictions for compressed states.

The data of the Chemical Engineering Laboratory at the California Institute of Technology were used unsmoothed while other data were taken from the literature and generally reflected smoothing operations. A logical difficulty arises with respect to the relative weighting to be assigned to the smooth and to the unsmootheddata in view of the fact that frequently the smoothed information was based upon a considerably greater or lesser number of observations than were reported thereby increasing, perhaps, its credibility per point. In the absence of a defensible reason for a different course of action, the decision was made to weight the information from each source equally. This decision was perhaps unfortunate for n-pentane because the available data from Beattie, Levine, and Douslin(30) represented a very small region adjacent to the computing the deviation for each state, squaring and summing these deviations, dividing this sum by the number of states and extracting the square root. Such a procedure will always lead to real positive values though the short method may not if the uncertainties in the coefficients are sufficiently great.

Figures 15 and 16 show a comparison of the fit of the coefficients of Table I and of Table II for n-pentane for two temperatures. The information in these figures indicates qualitatively the manner in which the predictions of compressibility factor deviate from the experimental values. Benedict(1) shows results for propane similar to those given for n-pentane in Figure 15 except that he shows density against pressure rather than compressibility factor against pressure. For both of these compounds predictions of pressure for compressed gases become very poor rapidly as the range of extrapolation is increased outside of the region in which Benedict fitted his equation of state. A comparison of average standard errors of estimate for the coefficients proposed by Benedict with those fitted to a broader range of pressures for the same value of gamma is instructive. Coefficient sets 1-B for both ethane and n-butane represent least squares fits to that portion of the volumetric information for which the compressibility factor is greater than that at the critical state and for which the value of gamma is nearly the same as that proposed by Benedict. The same situation applies to coefficient set 1-A for propane. Using this same portion of the volumetric information the least squares coefficients gave 0.0102, 0.0108, and 0.0068 for the average standard errors of estimate for ethane, propane, and n-butane respectively while the corresponding values for Benedict's coefficients were 0.0299, 0.2158, and 0.3203. This comparison represents a somewhat extreme case but it does illustrate the nature of extrapolations of the Benedict equation.

The coefficients recorded in Table III show quite clearly that the seven linear coefficients are related to the coefficient gamma in a very complicated way. The existence of a smooth functional dependence for these coefficients upon gamma may be inferred from the values for the larger gammas. The relationship appears to be oscillatory in the vicinity of gamma equal to zero. This oscillatory behavior could be of great importance in selecting a set of coefficients for use in making calculations on multicomponent systems. It seems to imply very strongly that the individual coefficients themselves are rather elusive when the optimum value for gamma is small.

Prediction of Phase Behavior.

The vapor pressure data for pure substances can be interpolated quite adequately from such a simple expression as the Antoine(32) equation

$$P'' = \exp(A'' + B''/(T + C'')) \qquad (83)$$

so the application of the Benedict equation in this field will be slight indeed. However, in order for the Benedict equation to be useful in predicting the phase behavior of multicomponent systems it must predict reasonably accurate phase behavior for one-component systems. From the description of heterogeneous equilibrium supplied by Equations 67, 68, and 69 the values for the vapor pressure and for the fugacity and molal volumes of the coexisting phases may be computed. Figure 17 depicts the form of the relationship between fugacity and pressure. This curve is parametric in reciprocal molal volume. The value of this parameter increases continuously along the curve from the point where both pressure and fugacity are zero. For a different temperature or a different compound, of course, the curve would change. The point of intersection of the curve with itself defines the predicted vapor pressure and the fugacity of the states in heterogeneous equilibrium because at this point two different values of reciprocal molal volume correspond to the same values of pressure, temperature, and fugacity. Clearly, the location of this point of intersection depends upon temperature. There exists a temperature at which the loop has become so small as to disappear altogether. This temperature corresponds to the predicted critical temperature.

The calculation of the vapor pressure from the Benedict equation is a straightforward iteration in which the values of the reciprocal molal volumes for the two phases are estimated and the subsequent predictions of the pressures and fugacities from Equations 3 and 46 are compared for equality. Figure 18 shows the deviation of the predictions of vapor pressure from the experimental values for propane and n-pentane using the coefficients of Table I and Figure 19 shows the same information for the coefficients proposed by Benedict and presented in Table II. Figure 20 shows the manner in which the vapor pressure predictions for n-pentane vary with the value of gamma.

An attempt was made to obtain coefficients which would describe the vapor pressure curve in the least squares sense and at the same time describe the volumetric behavior of the liquid and gas states. The method of the attempt involved the construction of the normal matrices for the minimization of the sum of the squares of the differences between the predicted dew-point and bubble-point pressures divided by the observed vapor pressure on the basis of the observed values for the orthobaric molal volumes; for the minimization of the logarithm of the ratio of the predicted dew-point and bubble-point fugacities again when these fugacities were calculated from the observed orthobaric molal volumes; and for the minimisation of the deviations of the predicted compressibility factor from the observed value when the molal volume is considered to be the independent state property, respectively. The differences in magnitude of the corresponding elements in these normal matrices were tremendous with the result that a linear combination of these matrices on the basis of equal weighting produced a set of coefficients which could predict the two-phase fugacities reasonably well, while the predictions of the volumetric behavior were wholly without merit. While these matrices might have been combined in accordance with the method of least squares as outlined in Appendix C such an approach will still not permit adequate volumetric predictions if the elements of the volumetric matrix are appreciably smaller than those of the fugacity matrix.

A second approach to the improvement of the phase behavior predictions problem considered the formulation of the problem in terms of two sets of coefficients—one to describe the volumetric behavior and the other to describe the fugacity as a function of state. Using the set of coefficients from Table III designated 5-A for propane and the experimental values of vapor pressure, values of fugacity and reciprocal molal volume for the dew point and the bubble-point states were computed from Equations 46 and 3 and may be found in Table VII. These data are presented for ten degree temperature intervals and represent the predicted properties along the boundary of the heterogeneous region.

Normal matrices were prepared, one for the minimization of the sum of the squares of the deviations in the compressibility factor at the values of reciprocal molal volume given in Table VII and one for the minimization of the sum of the squares of the deviations in the logarithm of the two-phase fugacity at the same values of reciprocal molal volume when the Table VII value of dew-point fugacity is assigned to the bubble-point. The normal matrix for the compressibility factor was reduced to three rows by adding the elements of adjacent rows and the normal matrix for fugacity was reduced to four rows by a similar process in the manner of the method of averages. The two resulting matrices jointly comprise a seven row matrix. In addition the restraints expressed in Equations 78, 79, and 80 were imposed by the method of Lagrange undetermined multipliers and the solution was then obtained. This set of coefficients is presented in Table VIII and is designated as set 5-C for purposes of future reference. A comparison of sets 5-A and 5-C indicates an appreciable difference in the values of the coefficients describing the volumetric and the phase behavior of propane.

Figure 21 shows the molal volume of propane at 160 degrees Fahrenheit as a function of pressure. There exists a small difference in the calculated volumetric behavior which is shown more clearly in Figure 22. This figure shows the compressibility factor as a function of pressure. The coefficients based upon the volumetric measurements in the region of homogeneous equilibrium yield calculated values in good agreement with experiment except in the low pressure gas region. The disagreement in this case results from the absence of direct experimental volumetric measurements in the gas phase at temperatures below 190 degrees Fahrenheit. The experimental points which are shown were based upon Joule-Thomson measurements(33) which were not used in establishing the coefficients of set 5-A. In the liquid region the good agreement shown in Figure 21 for set 5-A at pressures up to 2,000 pounds per square inch continues up to a pressure of 10,000 pounds per square inch. If the Joule-Thomson coefficient data had been included in the evaluation of the coefficients of set 5-A significantly better agreement in the low pressure gas region should have resulted.

In the case of set 5-C which was based upon only the molal volume at dew-point and bubble-point and the dew-point fugacity predictions together with the critical state restraints of Equations 78, 79, and 80, good agreement was obtained for the volumetric behavior in the gas region. Such a result is similar to that of Martin and Hou who fitted their equation to the critical state restraints and avoided the volumetric information in this region for the most part. The values for the compressibility factor of the liquid phase are in distinct disagreement with experiment at pressures above 1,000 pounds per square inch. Good agreement with experiment was obtained in predicting the molal volume along the dew-point and bubble-point curves up to a temperature of 180 degrees Fahrenheit. Above this temperature, in the vicinity of the critical state, the equation does not describe the bubble-point volumes satisfactorily.

Figure 23 shows the fugacity of propane as established experimentally and as calculated from the coefficients of sets 5-A and 5-C from Table VIII and Equation 46. The fugacity of propane at dew-point as calculated from the coefficients of set 5-A agrees reasonably well with the experimental values. However, the fugacity at bubble-point calculated from the coefficients of set 5-C differs widely from experiment. Near the critical state the fugacities established from the constants of set 5-A of Table VII do not correspond with the experimental values whereas the fugacities based upon the coefficients of set 5-C are in good agreement with experiment.

Figure 24 shows the behavior of the critical isotherm for propane as calculated from the coefficients of sets 5-A, 5-B, and 5-C. The predictions with set 5-A are not satisfactory but the predictions from set 5-C are in good agreement up to the critical pressure.

These comparisons indicate that the coefficients of set 5-A describe the behavior in the homogeneous regions with satisfacory accuracy. On the other hand, the coefficients of set 5-C describe the reciprocal molal volume of the coexisting phases and along the critical isotherm with reasonable accuracy but do not provide a useful description of the properties of propane in the homogeneous regions at pressures above 1,000 pounds per square inch. Moreover, set 5-C does not predict the vapor pressure with accuracy comparable to that of set 5-A obtained from volumetric data alone.

Thus no real improvement results from attempting to impose the restraints of the critical state upon the evaluation of the coefficients for the Benedict equation. Even when only the fugacity at dew-point and at bubble-point were employed as a basis for determining the coefficients as was done for set 5-C, the description of the vapor pressure and fugacity of the liquid phase was unsatisfactory as is shown in Figure 22. The accuracy with which an equation based upon volumetric data describes the vapor pressure leaves much to be desired but appears to be near the optimum that can be obtained with the Benedict equation if it is to be used at pressures in excess of those considered by Benedict (3).

The third approach to making the Benedict equation predict reasonable phase behavior considered the addition of a correction term which would apply primarily within the region of heterogeneous equilibrium. Before discussing the correction term itself several requirements which such a term should meet will be considered. If the Benedict equation predicts reasonable volumetric behavior then the correction term should not affect these predictions except that it might improve them.

The correction term must approximate the function -F(T) defined in Equation 73. The function -F(T) is not defined for temperatures greater than the critical temperature. In general the value for -F(T) is not zero at the critical state if the dew-point and bubble-point molal volumes are considered to be the roots of the critical isotherm at the critical pressure. Consequently, unless the Benedict equation predicts the critical state exactly, the function -F(T) must be different from zero at states outside the region of heterogeneous equilibrium for the opposite hypothesis would imply the existence of a discontinuity in fugacity, entropy, and enthalpy for paths crossing the critical isotherm into the liquid region. To the extent that the correction term approximates -F(T) the predictions in the region adjacent to the critical state will be improved. The effect of the correction in the region of homogeneous equilibrium can be confined to the critical region by suitable choice of approximating functions.

As shown in Figure 18 the vapor pressure predictions for n-pentane are adequate in the absence of a correction even though the prediction of the critical state leaves something to be desired. Such is not the case unfortunately for propane. Table IX presents the magnitude of the error in the liquid-phase fugacity predictions. The fact that the error becomes large at the low temperature is very important for the computation of liquid-phase fugacities, entropies, enthalpies, and chemical potentials, but of secondary importance with respect to vapor pressure predictions since the slope of the fugacity-pressure curve becomes so steep for the gas phase at low temperatures, that rather large errors in the bubble-point fugacity result in rather small errors in the vapor pressure prediction. Inasmuch as good vapor pressure predictions are of secondary importance with respect to good liquid-phase fugacity predictions, the precision of the correction term in approximating -F(T) should be rather great. Table IX shows a common but annoying characteristic of the error in the bubble-point fugacity prediction, namely, that it passes through a minimum and appears to be increasing as the critical state is approached. A precise approximation to -F(T) will have to be a rather complicated function of temperature, the form of which is not altogether apparent from the result of the present study. The utility of introducing a very complicated correction term of this character into the Benedict equation is open to considerable question and the conclusion that the Benedict equation is of limited use in describing the fugacity of the liquid phase has much merit. The fact that the vapor pressure predictions for n-pentane are satisfactory is explained in part in terms of the nature of the experimental background used in evaluating the coefficients which was discussed earlier and thereby does not contradict this conclusion. The cost of good vapor pressure fit in terms of the volumetric fit is reflected in the relative size of the average standard error of estimate for propane and n-pentane as shown in Table I. The nature of the error in the fugacity predictions in the close neighborhood of the observed values for critical temperature and pressure is not known because two of the pressure roots of the isotherms come into confluence and leave the real axis before the critical temperature is reached. Table IX shows that such confluence occurs below 200 degrees Fahrenheit for propane when gamma equals 4.24021.

Let the superscript o imply that the function is defined in terms of the Benedict equation which includes the correction term, and let the superscript $*$ imply the limit of the function as the molal volume becomes large. From Equation 70

$$RT(\partial \ln f/\partial P)_{T,m} = \underset{\bullet}{V} \quad \text{and} \quad \ln f^* = \ln RT\underset{\bullet}{\sigma}^* \tag{84}$$

Integration gives

$$-\ln f^o + \ln f^* = -\frac{1}{RT}\int_{P^*\underset{\bullet}{V}^*}^{P\underset{\bullet}{V}} d\,P^o\underset{\bullet}{V} + \frac{1}{RT}\int_{\underset{\bullet}{V}^*}^{\underset{\bullet}{V}} P^o d\underset{\bullet}{V} \tag{85}$$

Change of variable of integration and rearrangement give

$$\ln f^o = \ln RT + (Z^o - 1) + \left(\ln \underset{\bullet}{\sigma}^* + \frac{1}{RT}\int_{\underset{\bullet}{\sigma}^*}^{\underset{\bullet}{\sigma}} \frac{P^o d\underset{\bullet}{\sigma}}{\underset{\bullet}{\sigma}^2}\right) \tag{86}$$

Now define

$$P^o = P_e + \psi(T)\,\vartheta(\underset{\bullet}{\sigma}) \tag{87}$$

and so

$$\frac{1}{RT}\int_{\underset{\bullet}{\sigma}^*}^{\underset{\bullet}{\sigma}} \frac{P^o}{\underset{\bullet}{\sigma}^2}\,d\underset{\bullet}{\sigma} = \frac{1}{RT}\int_{\underset{\bullet}{\sigma}^*}^{\underset{\bullet}{\sigma}} \frac{P_e}{\underset{\bullet}{\sigma}^2}\,d\underset{\bullet}{\sigma} + \frac{\psi(T)}{RT}\int_{\underset{\bullet}{\sigma}^*}^{\underset{\bullet}{\sigma}} \frac{\vartheta(\underset{\bullet}{\sigma})}{\underset{\bullet}{\sigma}^2}\,d\underset{\bullet}{\sigma} \tag{88}$$

The function $\vartheta(\underset{\bullet}{\sigma})$ should meet the following requirements

$$\int_{\underset{\bullet}{\sigma}^*}^{\underset{\bullet}{\sigma}<\underset{\bullet}{\sigma}_d} \frac{\vartheta(\underset{\bullet}{\sigma})}{\underset{\bullet}{\sigma}^2}\,d\underset{\bullet}{\sigma} \approx 0 \;;\; \int_{\underset{\bullet}{\sigma}_b}^{\underset{\bullet}{\sigma}>\underset{\bullet}{\sigma}_b} \frac{\vartheta(\underset{\bullet}{\sigma})}{\underset{\bullet}{\sigma}^2}\,d\underset{\bullet}{\sigma} \approx 0 \;;\; \int_{\underset{\bullet}{\sigma}_d}^{\underset{\bullet}{\sigma}_b} \frac{\vartheta(\underset{\bullet}{\sigma})}{\underset{\bullet}{\sigma}^2}\,d\underset{\bullet}{\sigma} \approx 1 \tag{89}$$

and the function $\psi(T)$ must meet the following requirements:

continuity

$$\psi(T) \approx RT \ln (f_{d,e}/f_{b,e}) \qquad \text{for} \quad T < T_c \tag{90}$$

$$\psi(T) \to 0 \qquad \text{for} \quad T > T_c \tag{91}$$

Let $\xi = (\underset{\cdot}{\sigma} - \underset{\cdot}{\sigma}_c)$ then

$$\int_{\sigma^*}^{\sigma} \frac{\vartheta(\sigma)}{\sigma^2}\, d\sigma = \int_{-\sigma_c}^{\sigma-\sigma_c} \frac{\vartheta(\xi)\, d\xi}{(\xi + \sigma_c)^2} = \int_{0}^{\sigma-\sigma_c} \frac{\vartheta(\xi)\, d\xi}{(\xi + \sigma_c)^2} - \int_{0}^{-\sigma_c} \frac{\vartheta(\xi)\, d\xi}{(\xi + \sigma_c)^2} \tag{92}$$

From the standpoint of computation a convenient choice of integrand is

$$\begin{aligned} \vartheta(\xi)/(\xi + \underset{\cdot}{\sigma}_c)^2 &= \frac{C_1}{\sqrt{\pi}} \exp(- C_1^2(\underset{\cdot}{\sigma} - \underset{\cdot}{\sigma}_c)^2) \\ &= \frac{C_1}{\sqrt{\pi}} \exp(- C_1^2 \xi^2) \end{aligned} \tag{93}$$

The coefficient C_1 is so chosen that

$$\int_{0}^{-\sigma_c} \frac{\vartheta(\xi)\, d\xi}{(\xi + \underset{\cdot}{\sigma}_c)^2} = \int_{0}^{-\sigma_c} \frac{C_1}{\sqrt{\pi}} \exp(-C_1^2 \xi^2)\, d\xi = -\frac{1}{2} \operatorname{erf}(C_1 \underset{\cdot}{\sigma}_c) \approx \frac{-1}{2} \tag{94}$$

then

$$\begin{aligned} \int_{\sigma^*}^{\sigma} \frac{\vartheta(\sigma)}{\sigma^2}\, d\sigma &= \frac{1}{2} + \int_{0}^{\sigma-\sigma_c} \frac{C_1}{\sqrt{\pi}} \exp(-C_1^2(\sigma - \sigma_c)^2)\, d\sigma \\ &= \frac{1}{2} + \frac{1}{2} \operatorname{erf}(C_1(\underset{\cdot}{\sigma} - \sigma_c)) \end{aligned} \tag{95}$$

Thus

$$P^c = P_e + \frac{C_1}{\sqrt{\pi}} \psi(T)\, \underset{\cdot}{\sigma}^2 \exp(-C_1^2(\underset{\cdot}{\sigma} - \sigma_c)^2) \tag{96}$$

$$\ln f^c = \ln f_e + \frac{\psi(T)}{2RT} (1 + \operatorname{erf}(C_1(\underset{\cdot}{\sigma} - \sigma_c))) \tag{97}$$

$$\underset{\cdot}{S}^c = \underset{\cdot}{S}_e - \frac{1}{2}(\partial\psi/\partial T)(1 + \operatorname{erf}(C_1(\underset{\cdot}{\sigma} - \sigma_c))) \tag{98}$$

$$\underset{\cdot}{H}^c = \underset{\cdot}{H}_e - \frac{1}{2}(\psi + T\partial\psi/\partial T)(1 + \operatorname{erf}(C_1(\underset{\cdot}{\sigma} - \underset{\cdot}{\sigma}_c))) \tag{99}$$

If ψ (T) is assumed to be 0.0150RT and C_1 is assumed to be 6.18 (cu.ft.) per (lb.mole) then the correction term for pressure has the form shown in Figure 25. Figure 26 shows the effect of the correction term on the vapor pressure predictions for propane. Figure 27 shows the effect of the correction term on the predictions of volumetric behavior in the vicinity of the critical state. Other expressions for ψ (T) which damp out with increasing temperature might be preferable to the one used for the calculations leading to Figures 25, 26, and 27; however, such expressions would be appreciably more complicated and very likely would prohibit accurate predictions of the fugacity for the liquid phase altogether unless special effort was made to make them fit the error in bubble-point fugacity profile illustrated in Table IX. The present approach is thus more expedient than anything else.

Predicted Critical Properties.

Equations 81 and 82 are simultaneous cubic equations in reciprocal temperature and may be conveniently rewritten as

$$t^3 + u_1 t + v_1 = 0 \tag{100}$$

$$t^3 + u_2 t + v_2 = 0 \tag{101}$$

where

$$t = T^{-1} \tag{102}$$

$$u_1 = \frac{2K_2\sigma + 3K_5\sigma^2 + 6K_6\sigma^5}{2K_3\sigma + K_7\sigma^2(3(1 + \gamma\sigma^2) - 2(\gamma\sigma^2)^2)\exp(-\gamma\sigma^2)} \tag{103}$$

$$v_1 = \frac{1 + 2K_1\sigma + 3K_4\sigma^2}{2K_3\sigma + K_7\sigma^2(3(1 + \gamma\sigma^2) - 2(\sigma^2)^2)\exp(-\gamma\sigma^2)} \tag{104}$$

$$u_2 = \frac{K_2 + 3K_5\sigma + 15K_6\sigma^4}{K_3 + K_7\sigma\,(3(1 + \gamma\sigma^2) - 9(\gamma\sigma^2)^2 + 2(\gamma\sigma^2)^3)\exp(-\gamma\sigma^2)} \tag{105}$$

$$v_2 = \frac{K_1 + 3K_4\sigma}{K_3 + K_7\sigma\,(3(1 + \gamma\sigma^2) - 9(\gamma\sigma^2)^2 + 2(\gamma\sigma^2)^3)\exp(-\gamma\sigma^2)} \tag{106}$$

For any particular set of coefficients a plot of u_1, u_2, v_1, and v_2 against σ may be readily prepared. An example of such a plot is shown in Figure 28. This figure is based upon the coefficients for propane which are presented in Table I. Substitution of

$$x = t^3 \tag{107}$$

$$y = t \tag{108}$$

makes

$$t^3 + ut + v = 0 \tag{109}$$

equivalent to

$$x + uy + v = 0 \tag{110}$$

This equation represents a straight line with slope $-u$ and intercept $-v$. Further, the set of parametric Equations 107 and 108 defines a cubic parabola. The intersection of the straight lines which results from Equations 100 and 101 with the cubic parabola will locate those values of the parameter t which satisfy both Equations 100 and 101 and therefore also 81 and 82. These values of t are the roots of 81 and 82. The fact that the cubic parabola involves temperature alone, and therefore need be plotted only once, makes this geometric solution particularly useful. Figure 29 shows an example of this geometric solution for the predicted critical temperature and is based upon the information presented in Figure 28 for the values of u and of v. The values of the parameter T are shown along the cubic parabola and are expressed in degrees Rankine. The predicted critical temperature corresponds to the point on the cubic parabola where this curve and the two lines are concurrent for the same value of reciprocal molal volume. The point of intersection of the two straight lines is a function of reciprocal molal volume alone.

Benedict(1) describes the techniques which he applied to the adjustment of the coefficients which he obtained to fit the volumetric data in order to permit the equation to predict the phase behavior with somewhat greater accuracy. These techniques were intuitive and were beyond those associated with the method of least squares as applied to the volumetric information alone. The adjustment of the coefficients as performed by Benedict was at the sacrifice of fit in the liquid region. Table X shows that the predictions of the critical properties are not accurate unless special adjustments of the coefficients are made. Table XI illustrates the effect of the coefficient gamma upon the predicted critical properties.

The effect of imposing certain rigid restraints upon the evaluation of the coefficients to improve the predictions in the vicinity of the critical state has been partially investigated. The effect of making the critical isotherm satisfy both Equations 78 and 79 at the critical molal volume is illustrated in Figure 23. That the restraints are satisfied is apparent but the accuracy of the description of the pressure in the critical region has not been improved. To make the Benedict equation predict the experimental value of the critical pressure at the critical temperature and molal volume the restraints of the Equations 78, 79, and 80 and $P_{e,c} = P_c$ must be imposed at the critical temperature and critical molal volume. Since the Benedict equation cannot be reverted into a convenient expression for molal volume, these restraints are necessarily indirect. A calculation has shown that the restraint represented by Equation 78 is implied for the Benedict equation by Equations 79 and 80.

A practical limit to the number of restraints which one might desire to impose upon the evaluation of the coefficients is set by the number of coefficients in the equation. The more restraints are imposed at the critical state, the poorer the equation becomes as an extrapolation device.

The Benedict equation has too few coefficients to permit a very precise description of the critical state and at the same time give a reasonable representation of the volumetric behavior of the liquid phase.

CONCLUSIONS

The extension of the Benedict equation to the prediction of the volumetric properties of the liquid phase and the region of high pressure will be of considerable engineering utility. The fact that the predictions of this equation in the region of the critical state leave much to be desired does not preclude its wide application for thermodynamic calculations for regions removed from the critical state. If latent heats of vaporization are available then the difficulties associated with the correct prediction of fugacity, enthalpy, and entropy in the liquid phase may be of minor importance for calculations involving thermodynamic paths lying entirely within the liquid region since the correction needed for the predicted change of these properties with temperature can be obtained from the latent heat of vaporization information and the properties of the gas phase at dew-point. If such latent heat information is not available, the empirical correction term discussed in the preceding section may be useful.

The Benedict equation does not replace graphical procedures for very accurate thermodynamic calculation because the errors in its predictions are much greater than experimental uncertainty. Extensive application of the Benedict equation will necessitate the use of automatic digital computing equipment and for this reason the development of a more general expression which can be used more efficiently with the high-speed computers for interpolation within the accuracy of the experimental information appears to be worthwhile.

The methods discussed in the preceding sections for the evaluation of coefficients for the Benedict equation have produced coefficients which have a somewhat vague correlation with parameters which characterize the rather smooth transition of properties from one member of a homologous series to another. A revision of the method of evaluation to improve this correlation by evaluating coefficients for the Benedict equation to approximate the reduced equation of state appears to be desirable. The present hypotheses(2) concerning the relationship of the coefficients for mixture to those of the pure components imply regularity in the relationship of the coefficients to other physical properties of the system.

NOMENCLATURE

A	a matrix or an arbitrary function
A''	coefficient of the Antoine equation
A_o	coefficient of the equation of state, (p.s.i.a.)(cu.ft.)^2/(lb.mole)^2
a	coefficient of the equation of state, (p.s.i.a.)(cu.ft.)^3/(lb.mole)^3
a_{ij}	element of the matrix A
B	a matrix or an arbitrary function
B_i	ith virial coefficient
B''	coefficient of the Antoine equation
B_o	coefficient of the equation of state, (cu.ft.)/(lb.mole)
b	coefficient of the equation of state, (cu.ft.)^2/(lb.mole)^2
b_{ij}	element of the matrix B
C_1	coefficient of the heterogeneous correction term, (cu.ft.)/(lb.mole)
$\underset{\bullet}{C}_p$	molal isobaric heat capacity, (B.t.u.)/(lb.mole)(deg.R.)
$\underset{\bullet}{C}_v$	molal isochoric heat capacity, (B.t.u.)/(lb.mole)(deg.R.)
C_o	coefficient of the equation of state, (p.s.i.a.)(deg.R.)^2(cu.ft.)^2 per (lb.mole)^2
C''	coefficient of the Antoine equation
c	coefficient of the equation of state, (p.s.i.a.)(deg.R.)^2(cu.ft.)^3 per (lb.mole)^3
d	symbol of differentiation
E	specific internal energy, (B.t.u.)/(lb.)
$\underset{\bullet}{E}$	molal internal energy, (B.t.u.)/(lb.mole)
exp	exponential function
erf	error function

F	a function of temperature
f	fugacity, (p.s.i.a.)
G	general intensive thermodynamic state property
H	specific enthalpy, (B.t.u.)/(lb.)
$\underset{\bullet}{H}$	molal enthalpy, (B.t.u.)/(lb.mole)
K	a matrix
K_0	-1
K_1	B_o
K_2	$-A_o/R$
K_3	$-C_o/R$
K_4	b
K_5	$-a/R$
K_6	$a\alpha/R$
K_7	c/R
k	Boltzman constant, 7.268 (B.t.u.)/(deg.R.)(molecule)
M	molecular weight, (lb.)/(lb.mole)
N	total number of items in a set
N	Avogadro's number
n	position number in an ordered set
n	weight fraction
$\underset{\bullet}{n}$	mole fraction
P	absolute pressure, (p.s.i.a.)
p	coefficient in power series expansion for pressure
Q	partition function
R	universal gas constant, 10.73147 (p.s.i.a.)(cu.ft.)/(lb.mole)(deg.R.)
r	radial distance, (ft.)
r_m	distance parameter of intermolecular potential function
S	specific entropy, (B.t.u.)/(lb.)(deg.R.)
$\underset{\bullet}{S}$	molal entropy, (B.t.u.)/(lb.mole)(deg.R.)

s	coefficient in power series expansion for reciprocal molal volume
T	thermodynamic temperature, (deg.R.)
t	a parameter
U	intermolecular potential function
u	a parameter
V	specific volume, (cu.ft.)/(lb.)
$\underset{\bullet}{V}$	molal volume, (cu.ft.)/(lb.mole)
v	a parameter
x	a parameter
y	a parameter
Z	compressibility factor
α	coefficient of the equation of state, (cu.ft.)^3/(lb.mole)^3
β	a function of temperature alone
γ	coefficient of the equation of state, (cu.ft.)^2/(lb.mole)^2
∂	symbol of a partial derivative
ϵ	energy parameter of intermolecular potential function
ζ	a parameter
ϑ	a function of reciprocal molal volume alone
μ	chemical potential, (B.t.u.)/(lb.)
$\overset{\bullet}{\mu}$	molal chemical potential, (B.t.u.)/(lb.mole)
ξ	a parameter
π	the transcendental number
Σ	symbol of summation
σ	specific weight, (lb.)/(cu.ft.)

σ	reciprocal molal volume, (lb.mole)/(cu.ft.)
ϕ_0	$Z - 1$
ϕ_1	σ
ϕ_2	σ/T
ϕ_3	σ/T^3
ϕ_4	σ^2
ϕ_5	σ^2/T
ϕ_6	σ^5/T
ϕ_7	$\sigma^2 T^{-3}(1+\gamma\sigma^2)\exp(-\gamma\sigma^2)$
ψ	a function of temperature alone

Superscripts

——	partial or partial molal property
o	in the pure state
*	in a state at infinite attenuation
e	property has been computed using corrected form for Benedict equation
"	two-phase property

Subscripts

——	property is extensive
b	property pertains to the bubble-point state
c	property pertains to the critical state
d	property pertains to the dew-point state
e	property has been computed using the Benedict equation
g	property pertains to the vapor phase
i	ith element of a set or component i in a mixture
H	under isenthalpic conditions
j	jth element of a set or component j in a mixture
k	property pertains to component k

ℓ	property pertains to the condensed phase
m	under conditions of constant composition
P	under isobaric conditions
r	reduced property
T	under isothermal conditions
V, σ	under isochoric conditions
•	property is defined in terms of pound-molecular weights

REFERENCES

1. M. Benedict, G. B. Webb, and L. C. Rubin. J. Chem. Phys., 8, 334, (1940).

2. Ibid. 10, 747, (1942).

3. M. Benedict, G. B. Webb, L. C. Rubin, and L. Friend. Chem. Eng. Prog., 47, 419-422, 449-454, 571-578, 609-620, (1951)

4. H. H. Stotler and M. Benedict. Chem. Eng. Prog. Symposium Series, 49, 6, 25, (1953).

5. E. W. Hough and B. H. Sage. Chem. Reviews, 44, 193, (1949).

6. T. J. Connolly. Ph. D. Thesis, California Institute of Technology, (1950)

7. H. W. Brough. Chemical Engineer Thesis, California Institute of Technology, (1950)

8. J. A. Beattie and O. C. Bridgeman. Proc. Am. Acad. Arts Sci., 63, 229, (1928).

9. C. D. Hodgeman. Mathematical Tables from the Handbook of Chemistry and Physics, Ninth Edition, Chemical Rubber Publishing Co., Cleveland, (1949), p. 270.

10. F. Klein. Elementary Mathematics from an Advanced Standpoint, Vol. 1, Dover, New York, (1952), p. 88.

11. E. T. Copson. An Introduction to the Theory of Functions of a Complex Variable, Oxford University Press, London, (1935), p. 85.

12. C. N. Yang and T. D. Lee. Phys. Rev., 87, 404, (1952).

13. P. W. Bridgman. J. Chem. Phys., 3, 597. (1935).

14. J. E. Mayer and M. G. Mayer. Statistical Mechanics, John Wiley and Sons, New York, (1940), p. 269.

15. Ibid.

16. R. B. Bird, J. O. Hirschfelder, and C. F. Curtiss. Survey of the Equation of State and Transport of Gases and Liquids, Univ. of Wisconsin CM-758 NOrd-9938, (1952).

17. W. E. Rice and J. O. Hirschfelder. Second Virial Coefficients of Gases Obeying a Modified Buckingham Potential, Univ. of Wisconsin ONR-2, (1953).

18. K. Knopp. Theory of Functions, Part 1, Dover, New York, (1945), p. 79.

19. J. J. Martin and Y. C. Hou. "Development of a New Equation of State for Gases," Paper presented at Regional Meeting of the American Institute of Chemical Engineers at San Francisco, Calif., September 1953.

20. J. O. Hirschfelder, R. B. Bird and E. L. Spotz. Trans. ASME, 71, 921, (1949).

21. J. E. Mayer and M. G. Mayer. op. cit., p. 291.

22. R. J. Buehler, R. H. Wentorf, J. O. Hirschfelder, and C. F. Curtiss. Lennard-Jones and Devenshire Equation of State for Compressed Gases and Liquids, Univ. of Wisconsin CM-565 NOrd-9938, (1950).

23. J. E. Mayer and M. G. Mayer. op. cit., p. 274.

24. R. Fowler and E. A. Guggenheim. Statistical Thermodynamics, Cambridge, (1949), p. 264 ff.

25. S. S. Wilkes. Elementary Statistical Analysis, Princeton University Press, Princeton, N. J., (1949), p. 250.

26. C. Hastings, Jr.. The RAND Corporation Approximations in Numerical Analysis, (1952).

27. H. W. Brough, W. G. Schlinger, and B. H. Sage. Amer. Doc. Inst., Washington, D. C., Doc. No. 3235, (1951).

28. B. H. Zimm. J. Chem. Phys., 19, 1019, (1951).

29. J. E. Mayer. J. Chem. Phys., 19, 1024, (1951).

30. J. A. Beattie, S. W. Levine, and D. R. Douslin. J. Amer. Chem. Soc. 73, 4431, (1951).

31. D. R. Hartree. Numerical Analysis, Oxford University Press, London, (1952), p. 152.

32. F. D. Rossini and others. Selected Values of Properties of Hydrocarbons, N. B. S. Circ. C461. (1947), p. 121.

33. B. H. Sage and W. N. Lacey. Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen, American Petroleum Institute, (1950). p.34.

34. A. Michels and G. W. Nederbragt. *Physica*, 2, 1000, (1935), ibid., 3, 569, (1936).

35. R. H. Olds, H. H. Reamer, B. H. Sage, and W. N. Lacey. *Ind. Eng. Chem.*, 35, 922, (1943). Raw Data: CITCHE Data Book 116, Data Sheets 491-97.

36. H. M. Kvalnes and V. L. Gaddy. *J. Amer. Chem. Soc.*, 53, 394, (1931).

37. J. A. Beattie, G. L. Simard, and G.- J. Su., *J. Am. Chem. Soc.*, 61, 924-6, (1939).

38. H. H. Reamer, R. H. Olds, B. H. Sage, and W. N. Lacey. *Ind. Eng. Chem.*, 36, 956, (1944). Raw Data: CITCHE Data Book 284, Data Sheets 1204-8.

39. J. A. Beattie, C. Hadlock, and N. Poffenberger. *J. Am. Chem. Soc.*, 3, 93, (1935).

40. J. A. Beattie, G. L. Simard, and G.-J. Su. *J. Am. Chem. Soc.*, 61, 26, (1939).

41. R. H. Olds, H. H. Reamer, B. H. Sage, and W. N. Lacey. *Ind. Eng. Chem.*, 36, 282, (1944). Raw Data: CITCHE Data Book 112, Data Sheets 1023-30.

42. B. H. Sage and W. N. Lacey. *Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen*, American Petroleum Institute, New York, (1950). p. 71.

43. B. H. Sage and W. N. Lacey. *Ind. Eng. Chem.*, 34, 730, (1942). Raw Data: CITCHE Data Books 84 and 87.

44. H. B. Dwight. *Tables of Integrals and Other Mathematical Data*, Macmillan, New York, (1947), p. 11.

45. E. T. Copson. op. cit., p. 123.

46. E. T. Copson. op. cit., p. 72.

47. J. A. Beattie. *Chem. Reviews*, 44, 141, (1949).

48. I. E. Sokolnikoff and E. S. Sokolnikoff. *Higher Mathematics for Engineers and Physicists*, McGraw-Hill, (1941), p. 118.

49. Ibid., p. 534.

50. Ibid., p. 114

51. D. R. Hartree. op. cit., p. 70.

LIST OF TABLES

TABLE I

Optimum Coefficients for Volumetric Predictions for Liquids and Gases*

Coefficient**	Methane	Ethane	Propane	n-Butane	n-Pentane
R	10.73147	10.73147	10.73147	10.73147	10.73147
A_o	4910.53	7001.40	15913.1	22784.0	60215.5
B_o	0.455158	0.237507	0.550703	1.00517	3.69003
$C_o \times 10^{-6}$	448.753	3334.26	6315.35	15491.4	19628.9
a	4551.18	26547.9	67141.1	253507.0	203941.0
b	1.03508	3.43107	7.41650	19.7116	16.0875
$c \times 10^{-6}$	619.147	6476.86	19262.1	93708.5	116061.0
α	0.332260	0.742830	1.60300	2.39047	6.67703
γ	1.20000	2.50000	4.24021	6.40000	10.5000
M	16.042	30.068	44.094	58.120	72.146
Average Standard Error of Estimate	0.0156	0.0138	0.0094	0.0166	0.0258

---

* These coefficients are recommended only for prediction of volumetric behavior in the homogeneous regions.

** The values recorded are dimensionally consistent when used in the Benedict equation with pressure expressed in pounds per square inch, temperature in degrees Rankine, and molal volume in cubic feet per pound-mole.

TABLE II

Coefficients Proposed by Benedict for Describing Phase Behavior and Volumetric Behavior for Gases*

Coefficient**	Methane	Ethane	Propane	n-Butane	n-Pentane
R	10.73147	10.73147	10.73147	10.73147	10.73147
A_o	7000.05	15681.7	25934.2	38057.1	45961.9
B_o	0.682998	1.00643	1.56027	1.99393	2.51324
$C_o \times 10^{-6}$	275.952	2195.80	6214.44	12139.3	25935.9
a	2988.21	20879.3	57331.2	113870.0	246503.0
b	0.868679	2.85846	5.78303	10.2804	17.1721
$c \times 10^{-6}$	498.790	6422.11	25284.5	62015.2	161539.0
α	0.512225	1.00254	2.50121	4.53676	7.45603
γ	1.54172	3.03213	5.65344	8.73709	12.2062
M	16.042	30.068	44.094	58.120	72.146

---

* These coefficients were suggested by Benedict(1,3) and have been modified to be consistent with the values of the universal gas constant, R, and the molecular weights, M, indicated in the table.

** The values recorded are dimensionally consistent when used in the Benedict equation with pressure expressed in pounds per square inch, temperature in degrees Rankine, and molal volume in cubic feet per pound-mole.

TABLE III

Coefficients Computed in the Present Study for the Description of Volumetric Behavior in the Light Paraffin Hydrocarbons

<u>Methane</u>*

Coefficient	1-A**	1-B**	2-A	2-B***
A_o	7234.58	6383.54	8930.20	4910.53
B_o	0.695761	0.618857	0.838705	0.455158
$C_o \times 10^{-6}$	127.801	254.447	-52.1483	448.753
a	-195.741	1069.13	-1554.68	4551.18
b	0.579094	0.691890	0.480300	1.03508
c	-144.017	51.1136	-207.030	619.147
α	-5.88036	1.12510	-0.554049	0.332260
γ	0.00000	1.54169	0.00000	1.20000
Average Standard Error of Estimate	0.0147	0.0147	0.0166	0.0156

---

* R is 10.73147 (p.s.i.a.)(cu.ft.)/(lb.mole)(deg.R.) and molecular weight is 16.042.

** States at temperatures below 40 deg. Fahrenheit were not used in evaluating these coefficients.

*** Cf. Table I.

TABLE III (cont.)

Methane

Coefficient	2-C	2-D	2-E	2-F
A_o	7089.34	7316.35	7080.00	6472.56
B_o	0.653966	0.657546	0.629442	0.569888
$C_o \times 10^{-6}$	218.045	155.073	139.897	124.385
a	878.007	216.149	518.750	1358.77
b	0.715350	0.687169	0.725277	0.804517
$C \times 10^{-6}$	240.565	115.791	57.2446	-202.677
α	1.17173	3.81332	1.57440	0.650130
γ	2.00000	4.00000	6.00000	10.00000
Average Standard Error of Estimate	0.0162	0.0169	0.0172	0.0170

TABLE III (cont.)

Ethane*

Coefficient	1-A**	1-B**	2-A	2-B
A_o	22792.1	12768.7	28233.6	-596.485
B_o	1.41875	0.634985	1.87136	-0.360457
$C_o \times 10^{-6}$	-201.267	2006.29	-1165.62	4512.84
a	-8762.23	14103.2	17334.9	40964.0
b	0.936384	2.63063	0.208122	4.52568
$C \times 10^{-6}$	-2285.57	3804.50	-3732.38	8541.92
α	-1.11402	1.08104	-0.562675	0.539735
γ	0.00000	3.03239	0.00000	2.00000
Average Standard Error of Estimate	0.0154	0.0102	0.0209	0.0153

---

* R is 10.73147 (p.s.i.a.)(cu.ft.)/(lb.mole)(deg.R.) and molecular weight is 30.068.

** States for which the compressibility factor is less than that at the critical state were not used in evaluating these coefficients.

TABLE III (cont.)

Ethane

Coefficient	2-C*	2-D	2-E	2-F
A_o	7001.40	15068.8	17195.8	17175.7
B_o	0.237507	0.787454	0.894960	0.854064
C_o	3334.26	1832.58	1386.25	1184.59
a	26547.9	8906.28	3690.66	2063.53
b	3.43107	2.30275	2.05581	2.03067
c	6476.86	3344.57	2532.84	2113.91
α	0.742830	1.54844	2.94518	4.32996
γ	2.50000	4.00000	6.00000	10.00000
Average Standard Error of Estimate	0.0138	0.01515	0.0171	0.0206

---

* Cf. Table I.

TABLE III (cont.)

Propane*

Coefficient	5-A	5-D	5-E	5-F
A_o	12559.9	25451.1	26981.9	27052.4
B_o	0.375279	1.04838	1.02879	0.994030
$C_o \times 10^{-6}$	7294.90	3791.64	3181.87	3172.48
a	77386.0	33056.4	20966.2	16122.9
b	7.95782	5.56424	5.06201	4.82884
$c \times 10^{-6}$	22120.9	11034.8	8430.50	8003.38
α	1.48371	2.47482	3.28263	3.94183
γ	4.00000	6.00000	8.30000	10.00000
Average Standard Error of Estimate	0.0094	0.0119	0.0128	0.0161

---

* R is 10.73147 (p.s.i.a.)(cu.ft.)/(lb.mole)(deg.R.) and molecular weight is 44.094. These coefficients are supplementary to those in Appendix F. and represent evaluations based upon the experimental data presented in Figures 4 and 5 of Appendix F.

TABLE III (cont.)

n-Butane*

Coefficient	1-A**	1-B**	2-A	2-B
A_o	-8630.07	39213.1	-40296.8	-109327.0
B_o	-0.760315	1.31328	-4.24075	-8.59007
$C_o \times 10^{-6}$	3324.36	6282.73	22523.0	41082.1
a	23586.5	116194.0	160587.0	334011.0
b	2.25425	13.4004	17.0293	27.3220
$C \times 10^{-6}$	4266.38	3943.93	26741.6	74064.2
α	1.07422	3.26759	1.48772	1.08984
γ	0.00000	8.73741	0.00000	2.00000
Average Standard Error of Estimate	0.0273	0.0068	0.0294	0.0349

---

* R is 10.73147 (p.s.i.a.)(cu.ft.)/(lb.mole)(deg.R.) and molecular weight is 58.120.

** States for which the compressibility factor is less than that at the critical state were not used in evaluating these coefficients nor were the data from reference 33.

TABLE III (cont.)

n-Butane

Coefficient	2-C	2-D	2-E*	2-F
A_o	-3506.64	1543.38	22784.0	43021.6
B_o	-0.960795	0.120053	1.00517	1.46812
$C_o \times 10^{-6}$	16077.5	25517.7	15491.4	57340.1
a	172263.0	424606.0	253508.0	87982.2
b	15.6351	28.8433	19.7116	11.7515
$C \times 10^{-6}$	37570.0	160034.0	93708.5	35954.5
α	2.22473	2.03867	2.39047	3.88952
γ	4.00000	6.00000	6.40000	10.00000
Average Standard Error of Estimate	0.0344	0.0377	0.0166	0.0144

---

* Cf. Table I.

TABLE III (cont.)

n-Pentane*

Coefficient	1-A	1-B	1-C	1-D
A_o	-47185.8	-101024.0	55126.4	62714.2
B_o	-3.32146	-6.26527	6.46500	4.90966
$C_o \times 10^{-6}$	40987.7	59512.1	31260.1	23914.3
a	187930.0	323053.0	115555.0	220331.0
b	16.5332	23.4244	4.12847	14.4783
$c \times 10^{-6}$	48024.6	95344.1	76254.2	127847.0
α	3.99798	2.73668	9.94347	6.59891
γ	0.00000	2.00000	6.00000	9.40000
Average Standard Error of Estimate	0.0396	0.0402	0.0392	0.0279

---

* R is 10.73147 (p.s.i.a.)(cu.ft.)/(lb.mole)(deg.R.) and molecular weight is 72.146.

TABLE III (cont.)

n-Pentane

Coefficient	1-E	1-F	1-G	1-H
A_o	61331.8	60215.5	57121.7	57441.7
B_o	4.19623	3.69003	2.67363	2.11853
$C_o \times 10^{-6}$	21448.5	19628.9	15750.9	13217.5
a	214248.0	203941.0	162683.0	107423.0
b	15.6174	16.0875	15.8368	14.2458
$C \times 10^{-6}$	122649.0	116061.0	91659.1	71132.0
α	6.58641	6.67703	7.33645	9.36790
γ	10.00000	10.50000	12.0000	15.0000
Average Standard Error of Estimate	0.0266	0.0258	0.0261	0.0273

TABLE IV

Sample Calculation of Pressure Using the Benedict Equation and Coefficients 1-C for Propane at 190° F.

Term	ρ = 0.5	ρ = 0.3	ρ = 0.1
$RT\rho$	3486.07	2091.64	697.21
$B_oRT\rho^2$	698.49	251.46	27.94
$-A_o\rho^2$	-3195.04	-1150.21	-127.80
$-C_oT^{-2}\rho^2$	-4382.06	-1577.54	-175.28
$bRT\rho^3$	7136.26	1541.43	57.08
$-a\rho^3$	-10113.05	-2184.42	-80.90
$a\alpha\rho^6$	1328.67	85.32	0.12
$CT^{-2}\rho^3(1+\gamma\rho^2)\exp(-\gamma\rho^2)$	5118.92	1419.80	55.32
	578.26	477.48	453.70

ρ_c 0.3125 (lb.mole)/(cu.ft.)

P_c 617.4 (p.s.i.a.)

T_c 206.3 (deg. F.)

TABLE V

Coefficients for n-Butane Evaluated without Experimental Information for the Gas Phase[*]

Coefficient	3-A	3-B	3-C
A_o	-24638.5	-53649.1	19592.7
B_o	-3.42863	-5.12364	-1.23806
$C_o \times 10^{-6}$	15234.5	23696.9	9517.60
a	156.047	234205.0	151301.0
b	17.3059	21.6334	15.9336
$C \times 10^{-6}$	16912.3	39590.3	18315.5
α	1.66727	1.39585	2.21450
γ	0.00000	2.00000	4.00000

---

[*] The data of reference 33 were not used in the evaluation of these coefficients.

TABLE V (cont.)

Coefficient	3-D	3-E	3-F
A_o	6314.58	22635.2	37076.9
B_o	0.990863	0.990967	0.887654
$C_o \times 10^{-6}$	29566.4	15466.1	5143.54
a	447496.0	253382.0	102509.0
b	28.7840	19.7130	13.1431
$C \times 10^{-6}$	183695.0	93477.3	33097.2
α	2.10527	2.38920	3.34430
γ	6.00000	6.40000	10.0000

TABLE VI

Standard Error of Estimate for n-Butane Coefficients* with Respect to Each of the Sets of Experimental Data

Gamma	Source of Data		
	(33) 66 States	(40) 103 States	(41) 113 States
0.00000	0.0173	0.0287	0.0383
2.00000	0.0154	0.0359	0.0462
4.00000	0.0199	0.0326	0.0455
6.00000	0.0141	0.0259	0.0583
6.40000	0.0031	0.0116	0.0261
10.00000	0.0086	0.0157	0.0177

---

* Cf. Table III.

TABLE VII

Predicted Fugacities and Reciprocal Molal Volumes for Propane at Dew-Point and Bubble-Point

Coefficients of Set 5-A

Temperature	Experimental	Fugacity		Reciprocal Molal Volume	
	Vapor Pressure	Dew-Point	Bubble-Point	Dew-Point	Bubble-Point
(deg. F.)	(p.s.i.a.)	(p.s.i.a.)	(p.s.i.a.)	(lb.mole)/(cu.ft.)	(lb.mole)/(cu.ft.)
100	188.7	155.8	151.9	0.03988	0.6657
110	214.5	174.6	171.0	0.04562	0.6508
120	242.6	194.5	191.3	0.05204	0.6351
130	273.5	215.9	212.9	0.05936	0.6197
140	307.1	238.5	235.7	0.06766	0.6013
150	343.8	262.5	259.7	0.07725	0.5828
160	683.8	287.9	284.9	0.08844	0.5629
170	427.3	314.6	311.3	0.10175	0.5414
180	474.9	342.8	338.9	0.11830	0.5181
190	524.8	371.5	367.6	0.13846	0.4920
200	580.1	401.7	397.5	0.16951	0.4635

TABLE VII (cont.)

Coefficients of Set 5-B

Temperature (deg. F.)	Experimental Vapor Pressure (p.s.i.a.)	Fugacity Dew-Point (p.s.i.a.)	Fugacity Bubble-Point (p.s.i.a.)	Reciprocal Molal Volume Dew-Point (lb.mole)/(cu.ft.)	Reciprocal Molal Volume Bubble-Point (lb.mole)/(cu.ft.)
100	188.7	155.4	173.0	0.03999	0.6582
110	214.5	174.1	191.4	0.04574	0.6420
120	242.6	193.9	210.9	0.05218	0.6248
130	273.5	215.2	231.4	0.05951	0.6061
140	307.1	237.7	253.1	0.06782	0.5856
150	343.8	261.6	275.7	0.07738	0.5626
160	383.8	286.9	299.4	0.08851	0.5363
170	427.3	313.5	324.1	0.10166	0.5048
180	474.9	341.5	350.0	0.11778	0.4654
190	524.8	370.1	376.3	0.13689	0.4040
200	580.1	400.2	-	0.16312	-

TABLE VIII

Coefficients for Propane Obtained Using Critical State Restraints and Phase Behavior Data

Coefficient	5-A[*]	5-B[**]	5-C
A_o	12559.9	10553.9	-144500.0
B_o	0.375279	0.148506	-14.3549
$C_o \times 10^{-6}$	7294.90	7684.24	30854.6
a	77386.0	108172.0	514882.0
b	7.95782	10.2395	45.3994
c	22120.9	30260.8	99747.1
α	1.48371	1.25633	0.917335
γ	4.00000	4.00000	4.00000

---

[*] Cf. Table III.

[**] Set 5-B differs from 5-A only in the respect that the method of Lagrange undetermined multipliers was applied to make the coefficients with the Benedict equation satisfy Equations 78, 79, and 80.

TABLE IX

Ratio of Predicted Dew-Point and Bubble-Point Fugacities for Propane Using Coefficients of Table I

Temperature (deg. F)	f_d/f_b	$\ln(f_d/f_b)$
100	1.01095	0.0108905
110	1.00793	0.0078987
120	1.00540	0.0053855
130	1.00420	0.0041912
140	1.00353	0.0035238
150	1.00371	0.0037031
160	1.00451	0.0044998
170	1.00571	0.0056938
180	1.00743	0.0074025
190	1.00755	0.0075216

TABLE X

Predicted Critical Properties

Compound		Pressure (p.s.i.a.)	Temperature (deg. F.)	Molal Volume (cu.ft.)/(lb.mole)
Ethane	Experimental	716.0	90.1	2.27
	Table I	1166	100	2.55
	Benedict	718	91	2.29
Propane	Experimental	614.7	206.3	3.20
	Table I	703	224	3.48
	Benedict	621	207	3.20
n-Butane	Experimental	550.7	305.6	4.13
	Table I	595	315	4.56
	Benedict	551	306	4.27
n-Pentane	Experimental	494.2	387.4	5.05
	Table I	535	397	5.57
	Benedict	484	384	5.67

TABLE XI

Variation of Critical Properties Predictions with the Magnitude of Gamma

Compound	Gamma	Pressure (p.s.i.a.)	Temperature (deg.F.)	Molal Volume (cu.ft.)/(lb.mole)
Propane	4.00000	705	225	3.50
	4.24021	703	224	3.48
	10.00000	728	222	3.04
n-Pentane	9.40000	572	402	5.35
	10.50000	535	397	5.57
	12.00000	525	395	5.56

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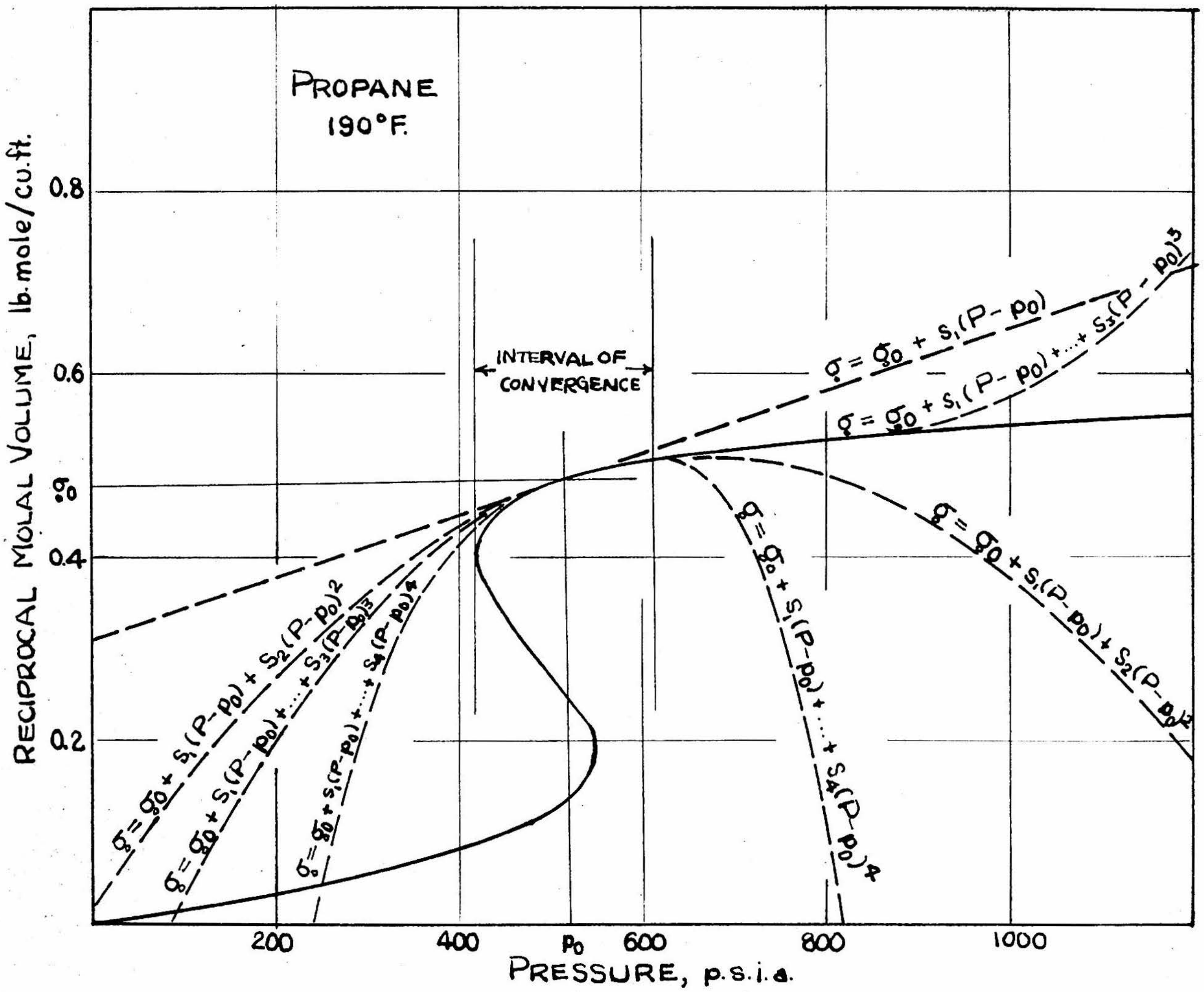
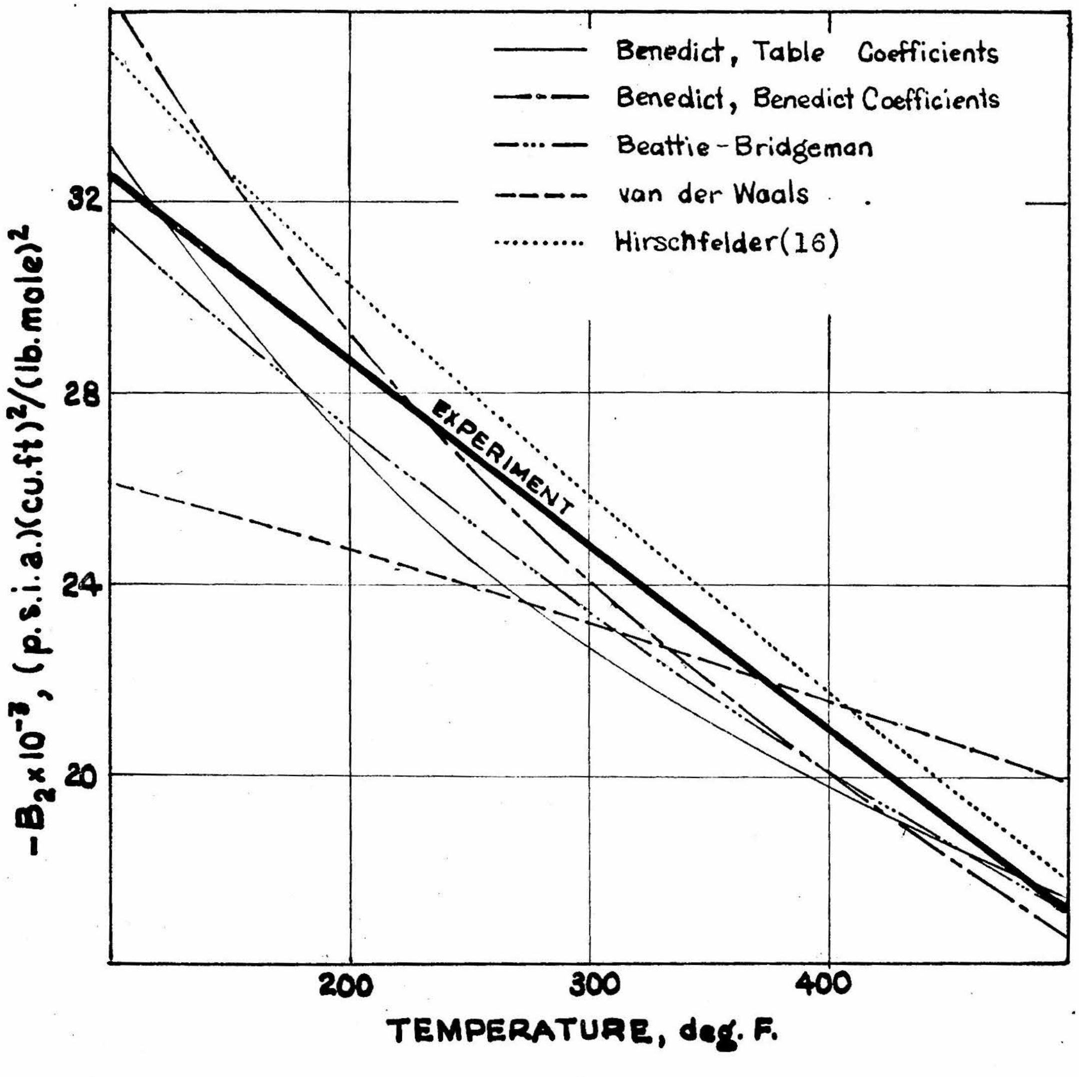


Fig. 1. Partial Sums of the Power Series Representation of Reciprocal Molal Volume as a Function of Temperature and Pressure.



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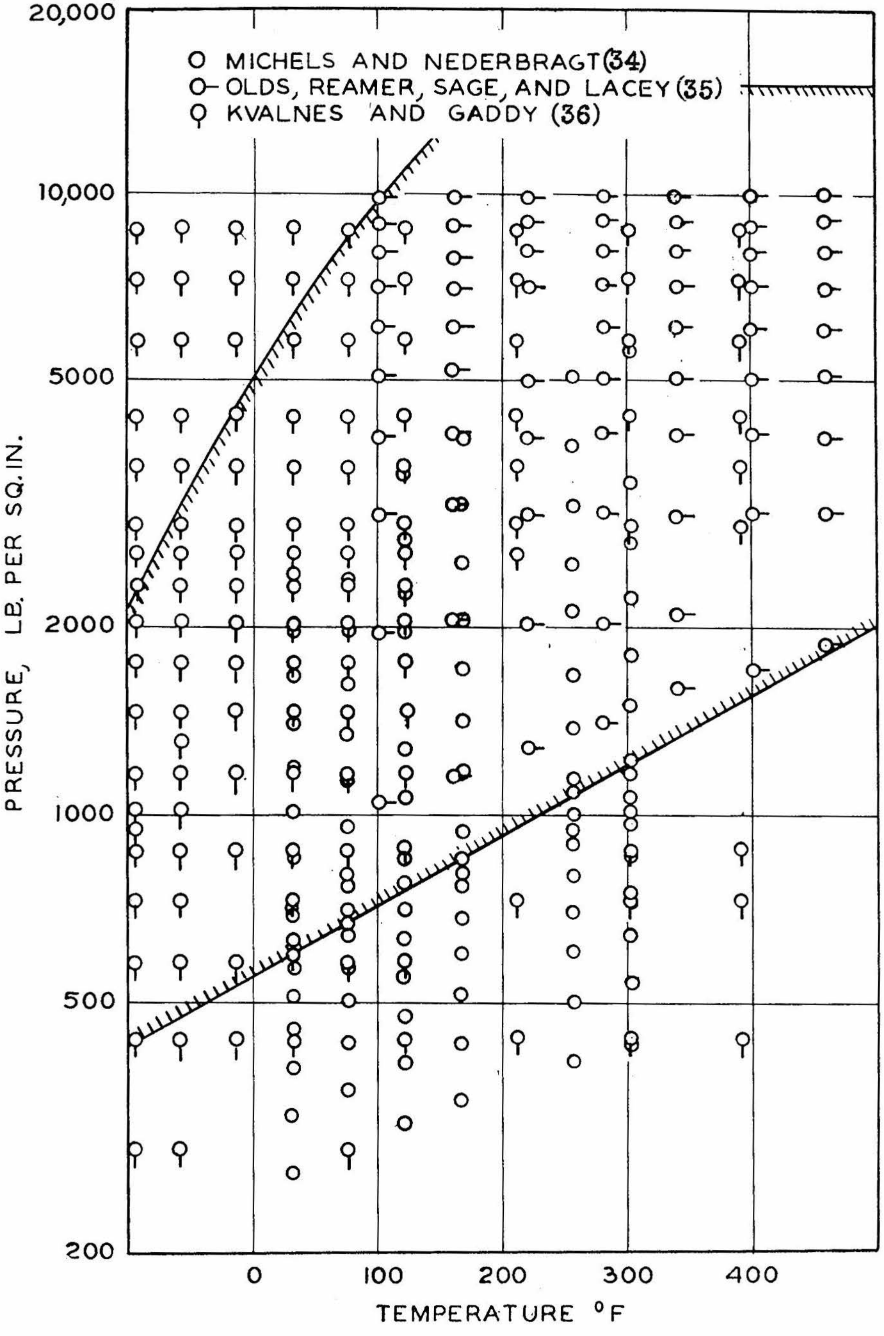


Fig. 3 . Experimental Data Used in Evaluating Coefficients for Methane

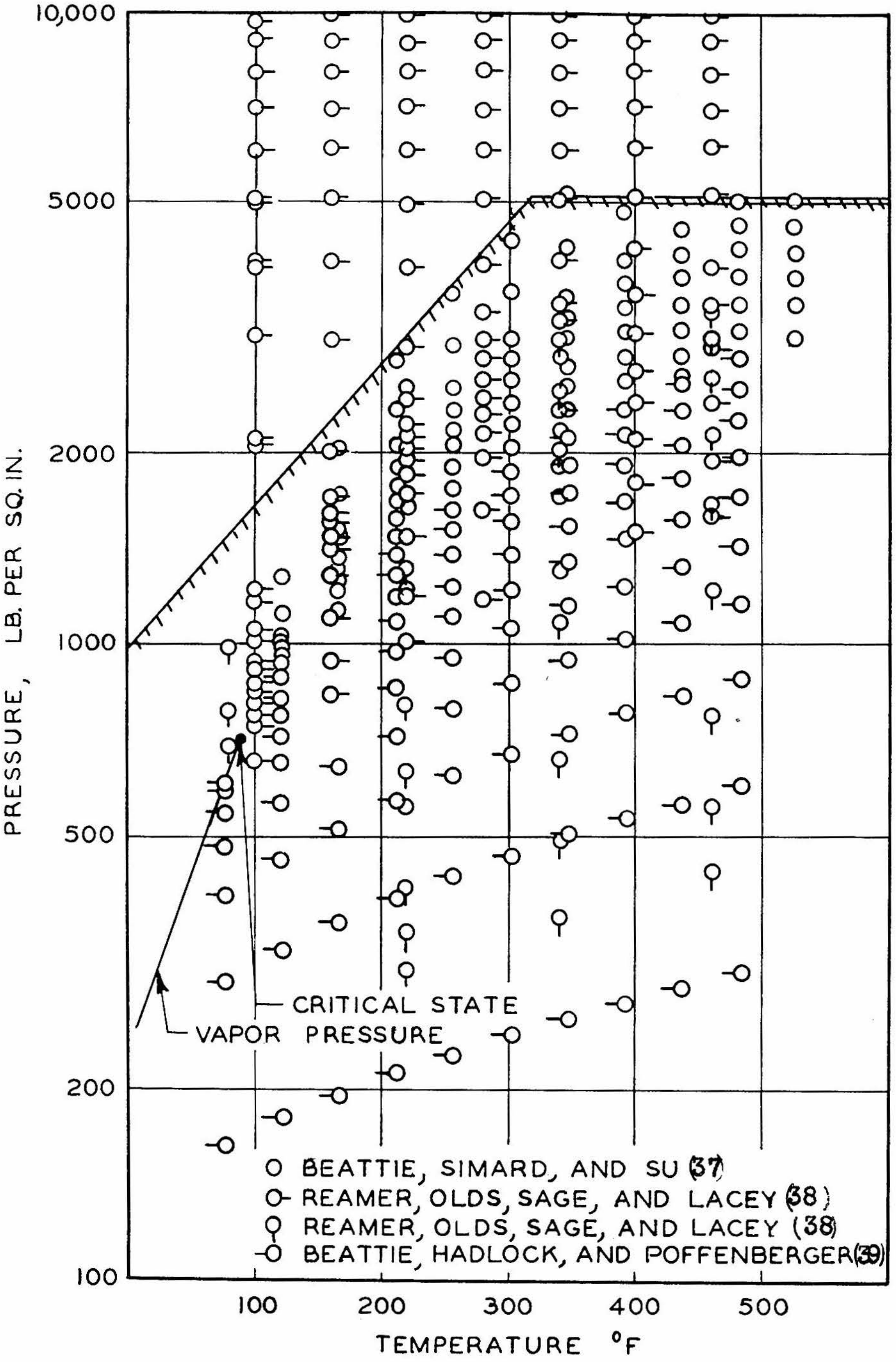


Fig. 4. Experimental Data Used in Evaluating Coefficients for Ethane

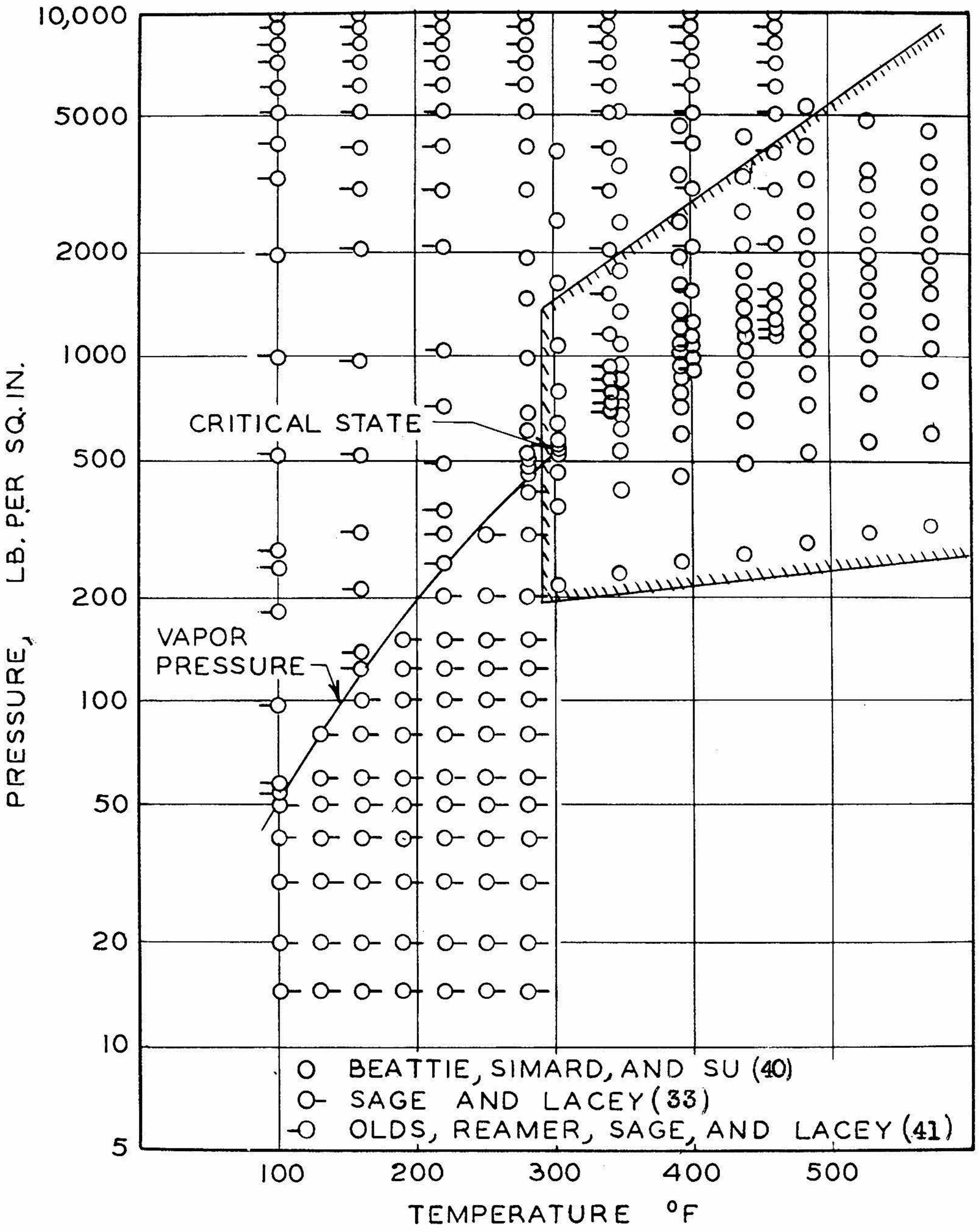
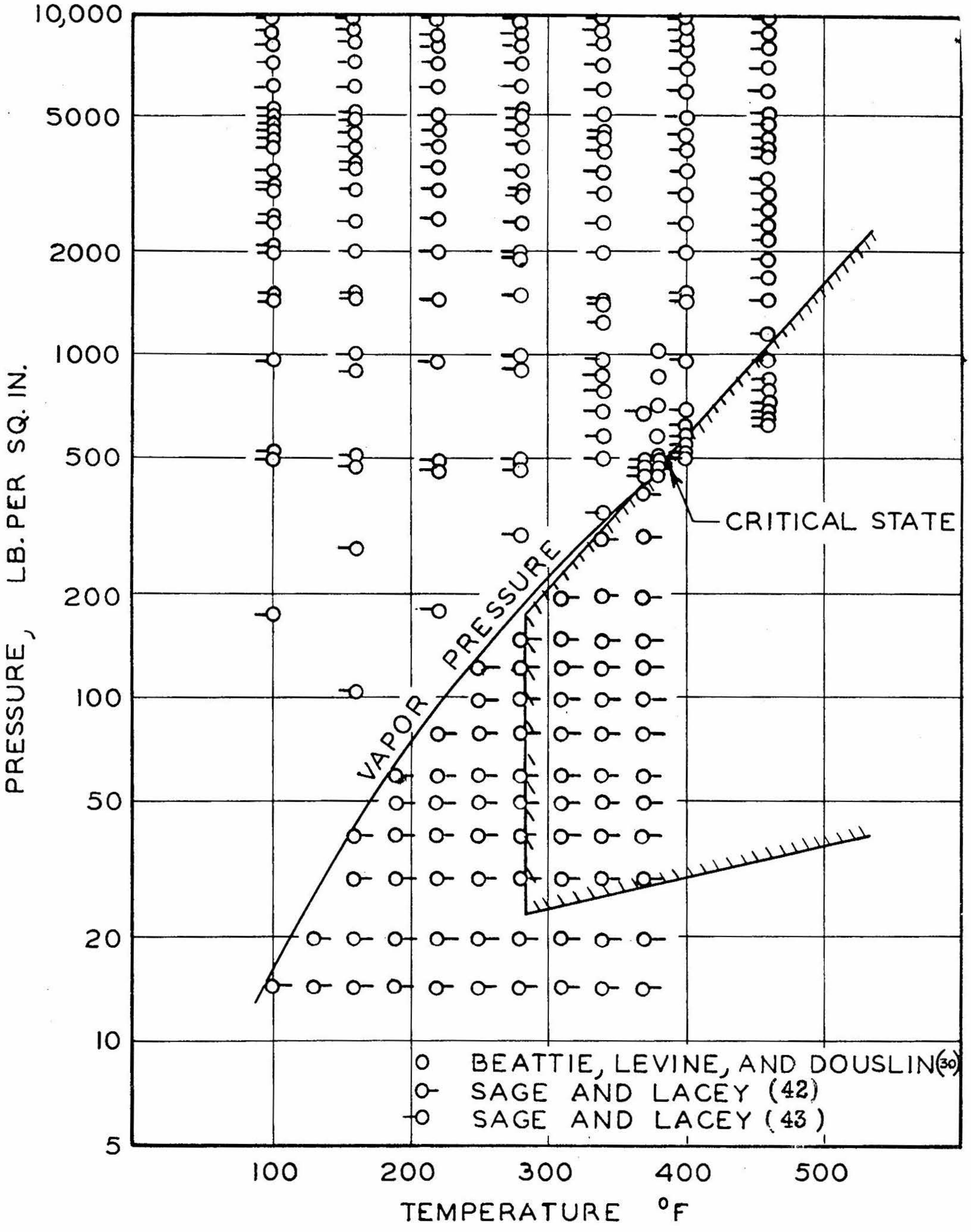


Fig. 5. Experimental Data Used in Evaluating Coefficients for n-Butane



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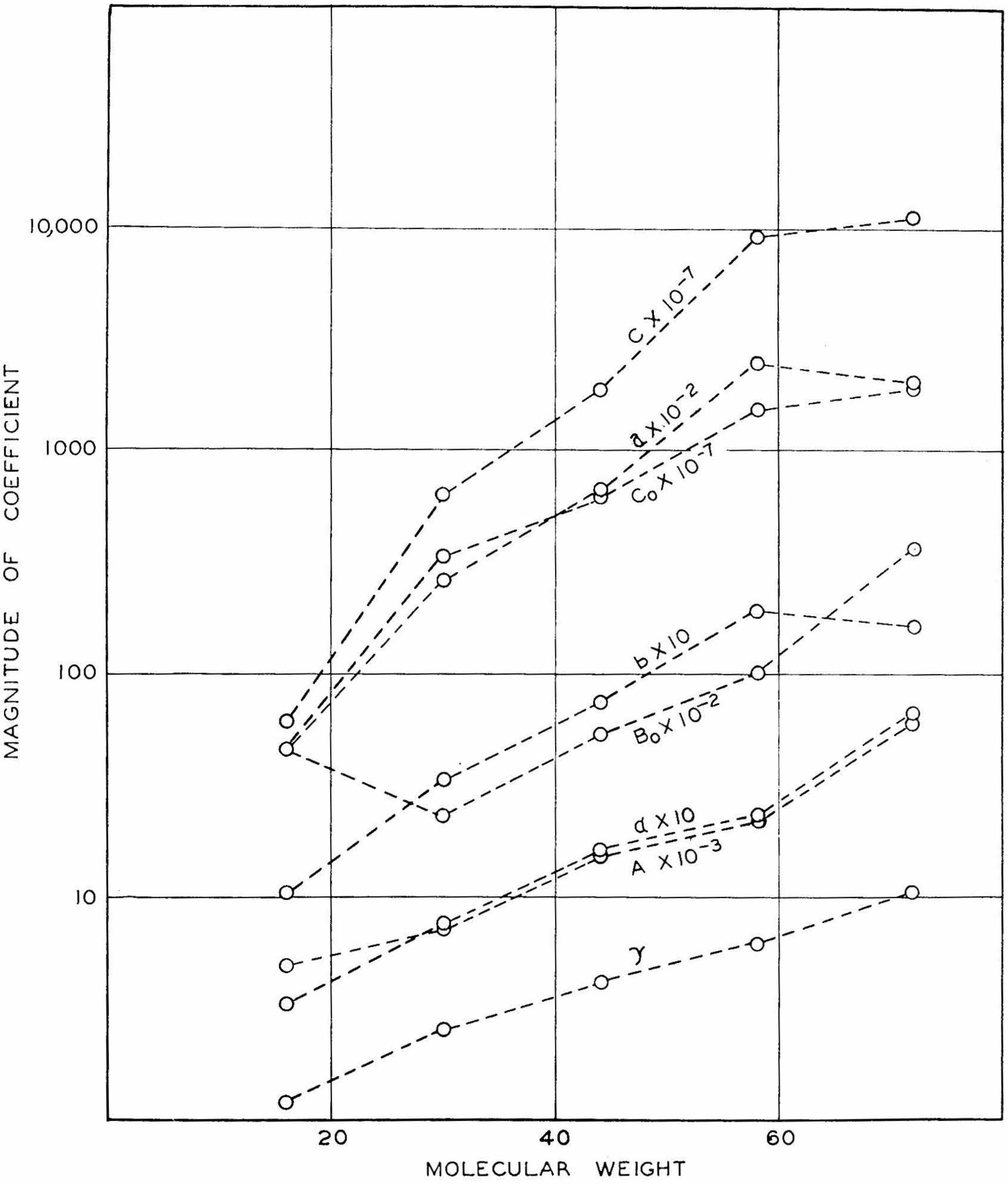
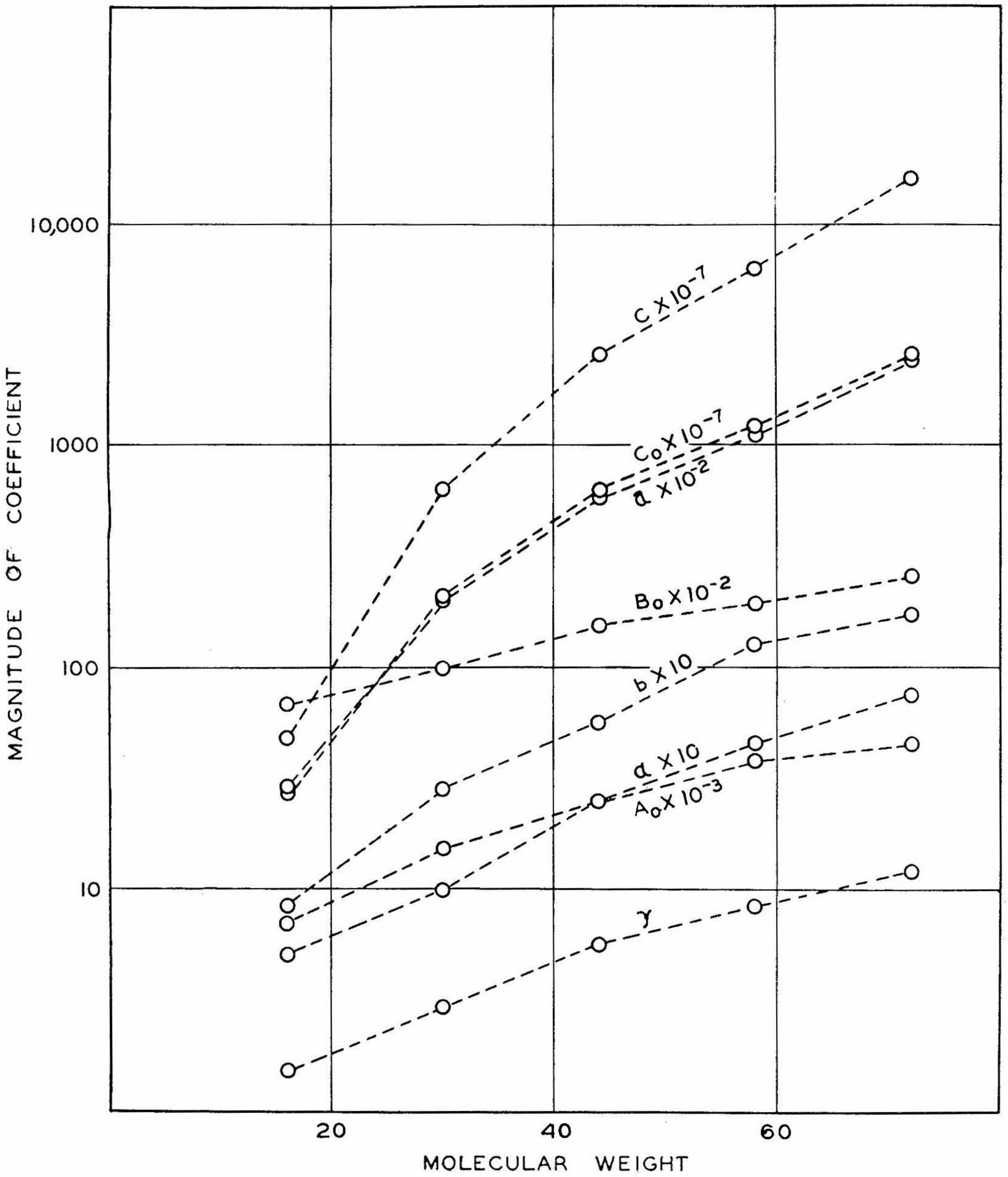


Fig. 7. Effect of Molecular Weight upon Magnitude of Coefficients of Table I.



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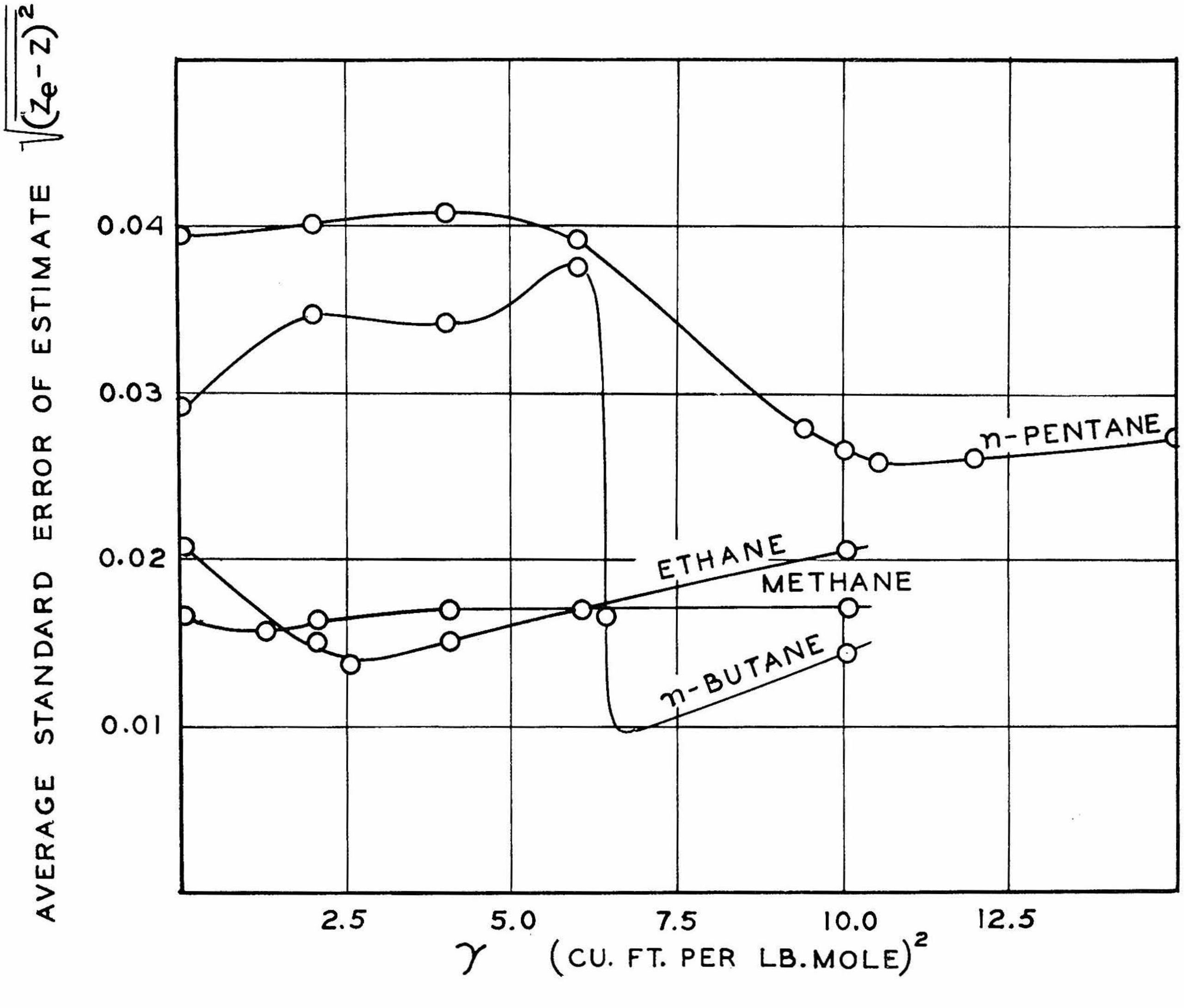

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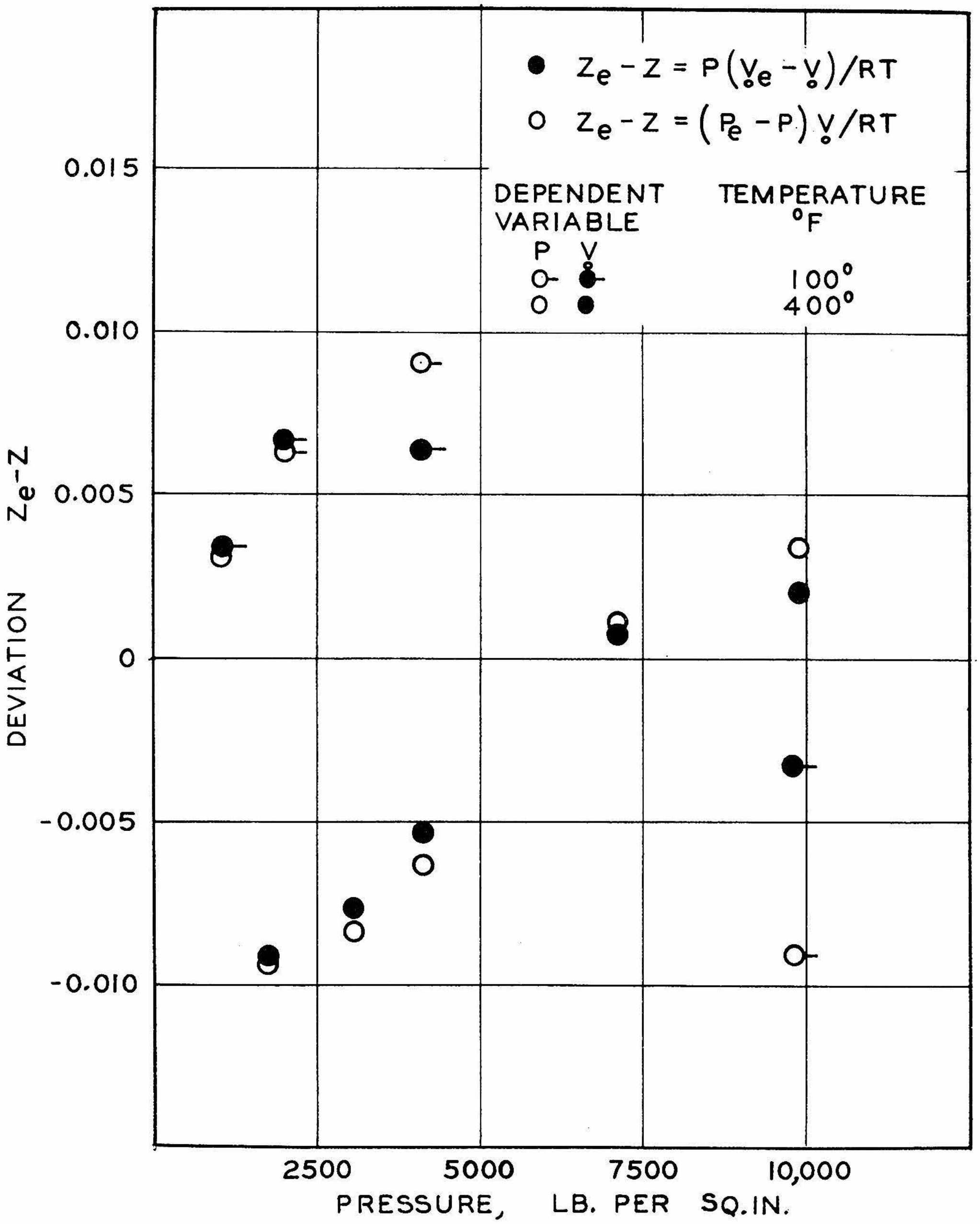

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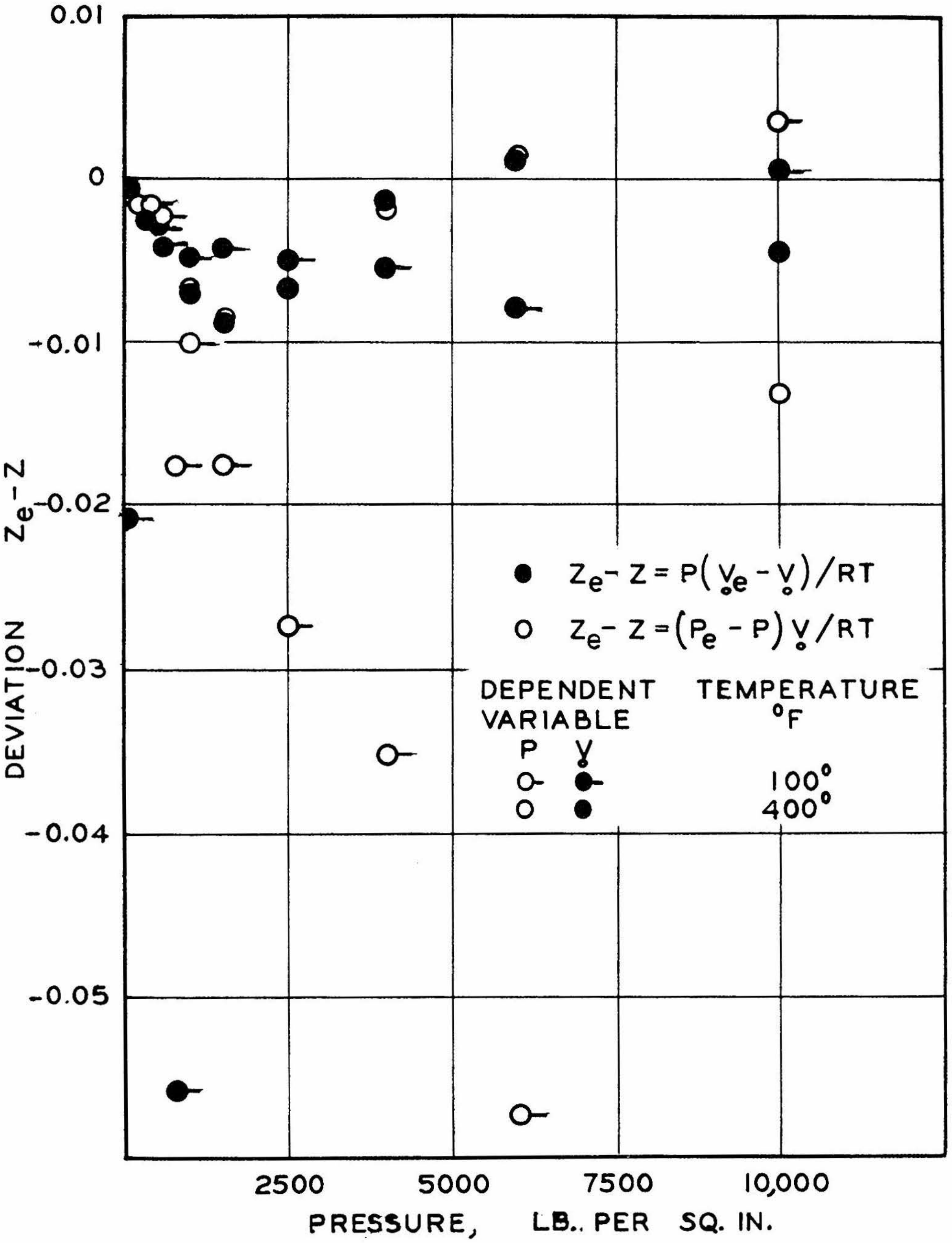

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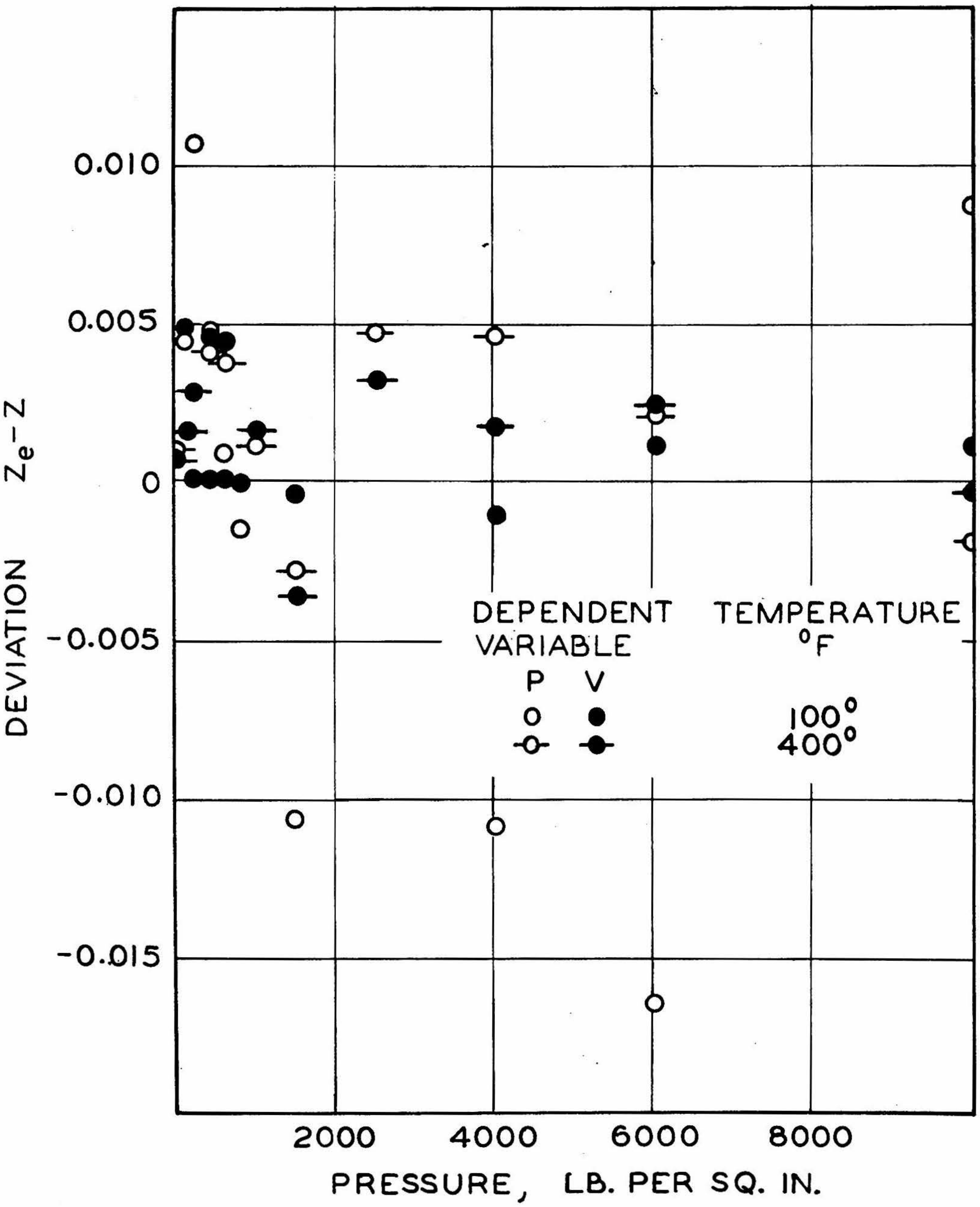

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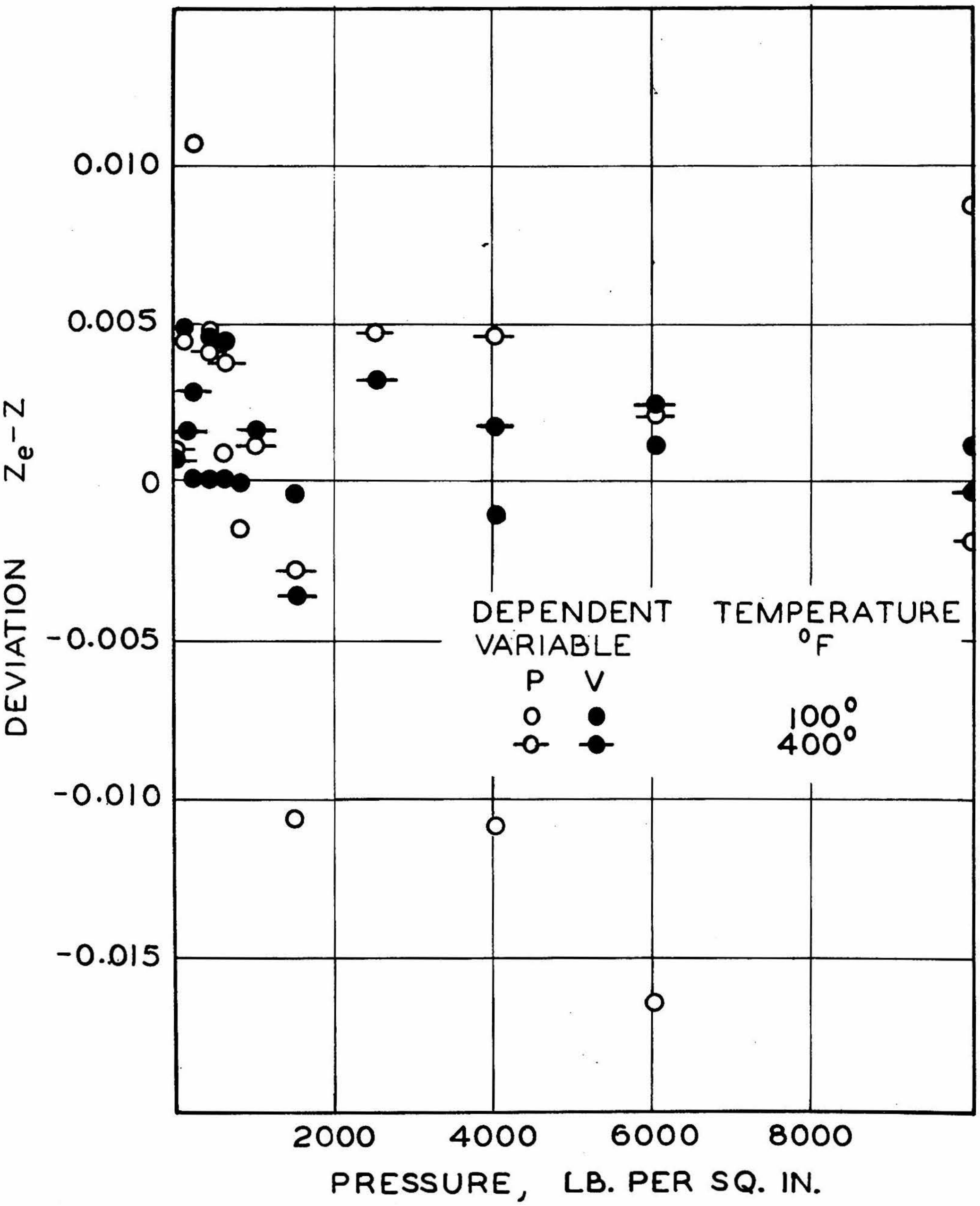
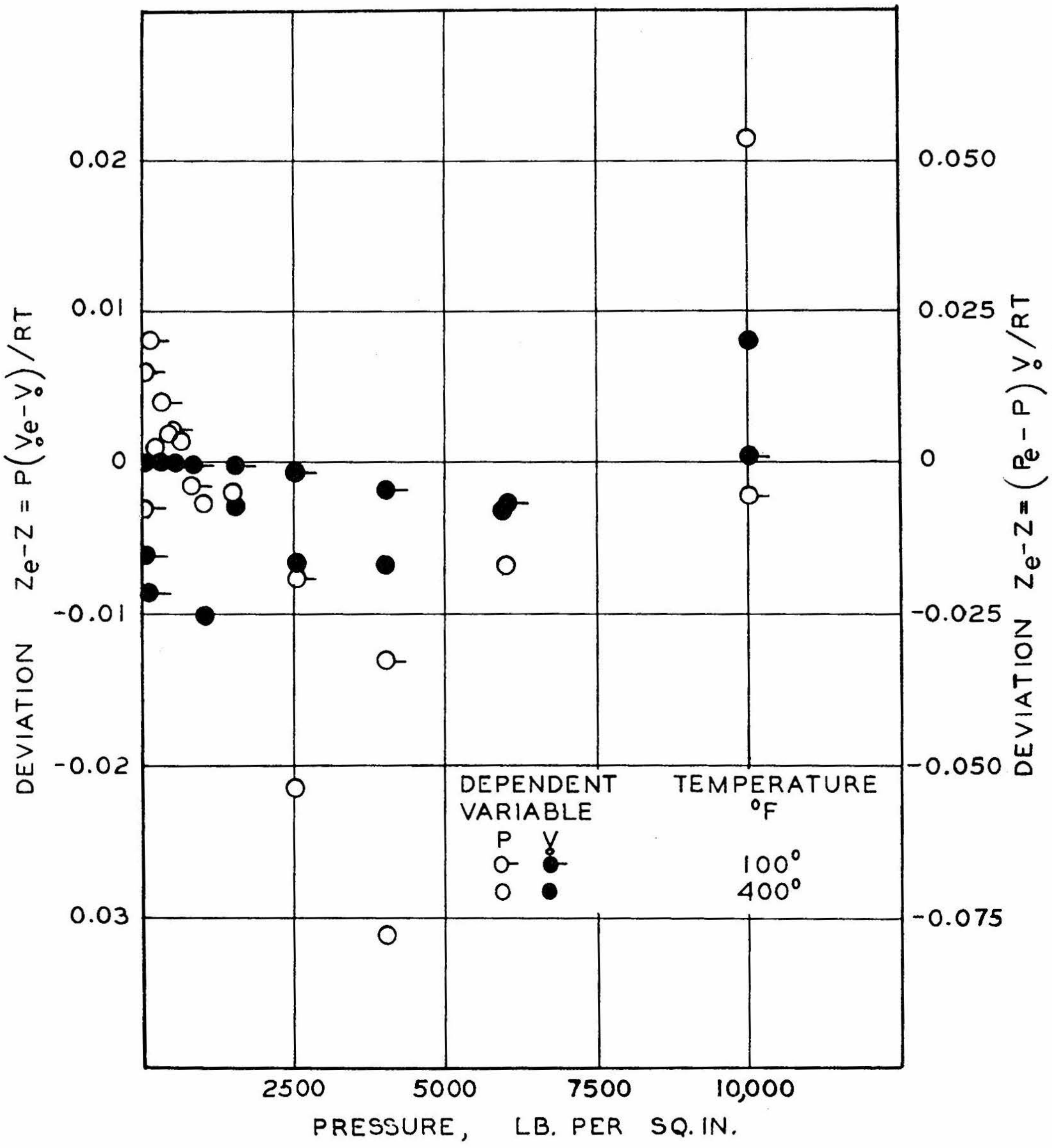


Fig.12. Deviations of Compressibility Factor for Propane with Author's Coefficients



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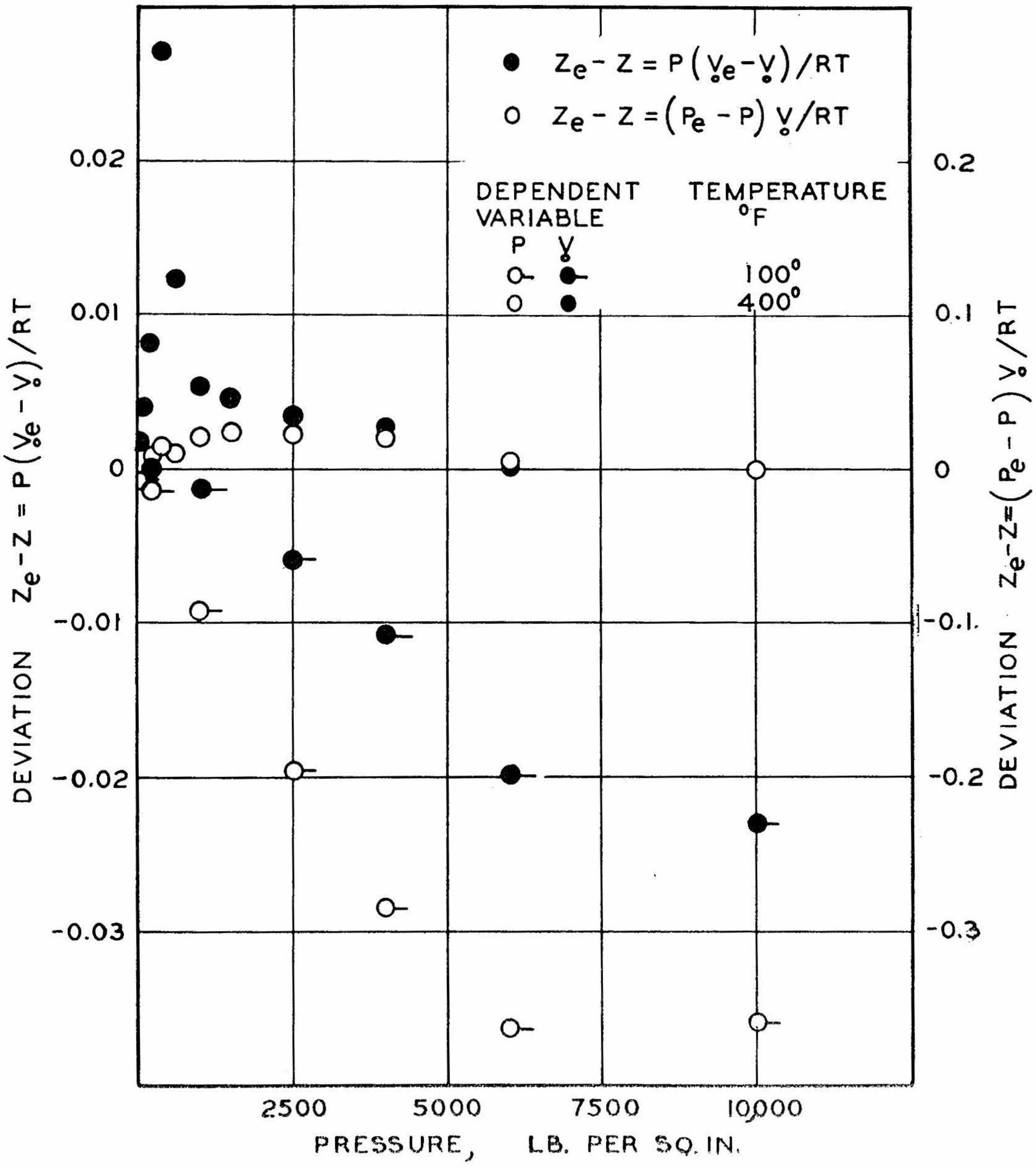

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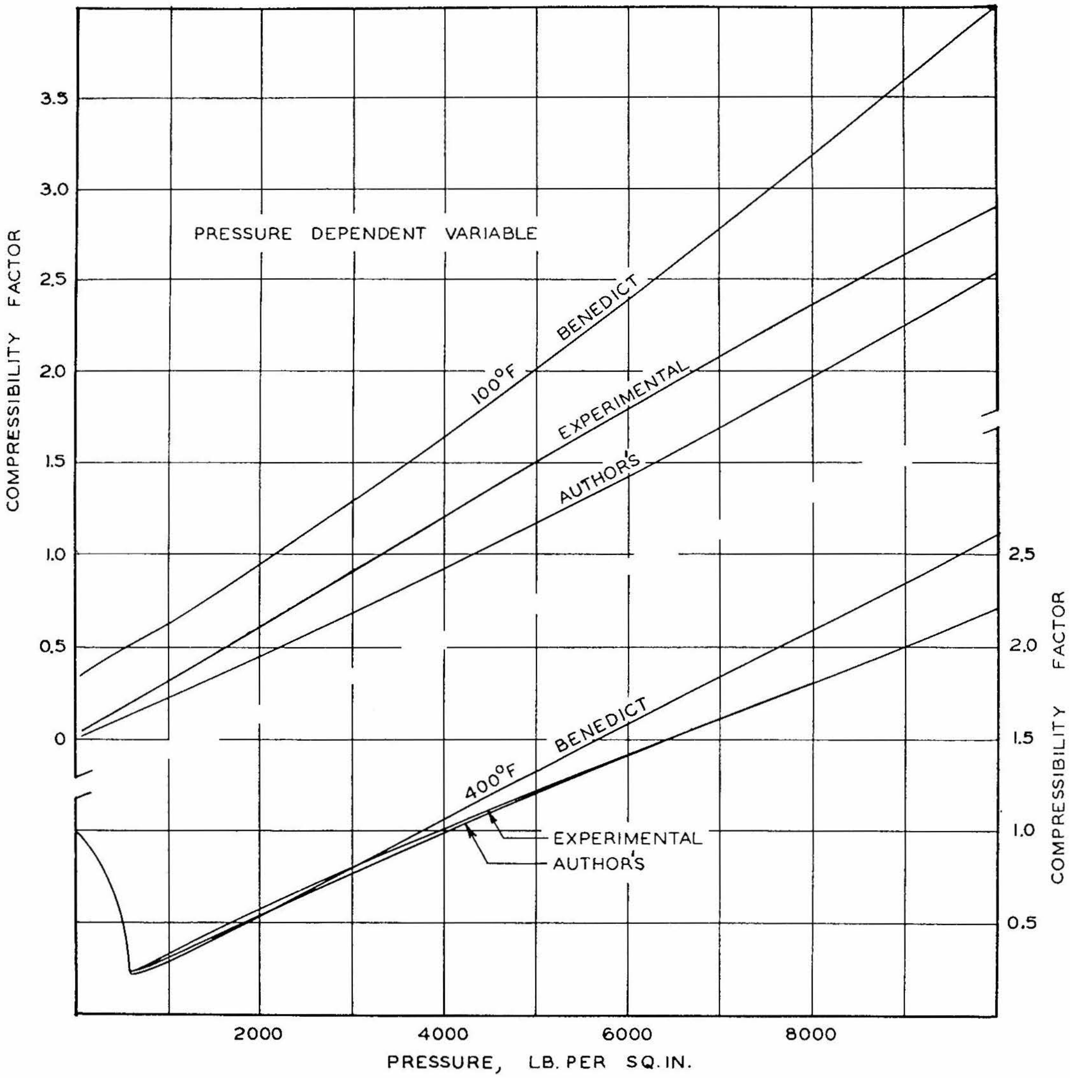

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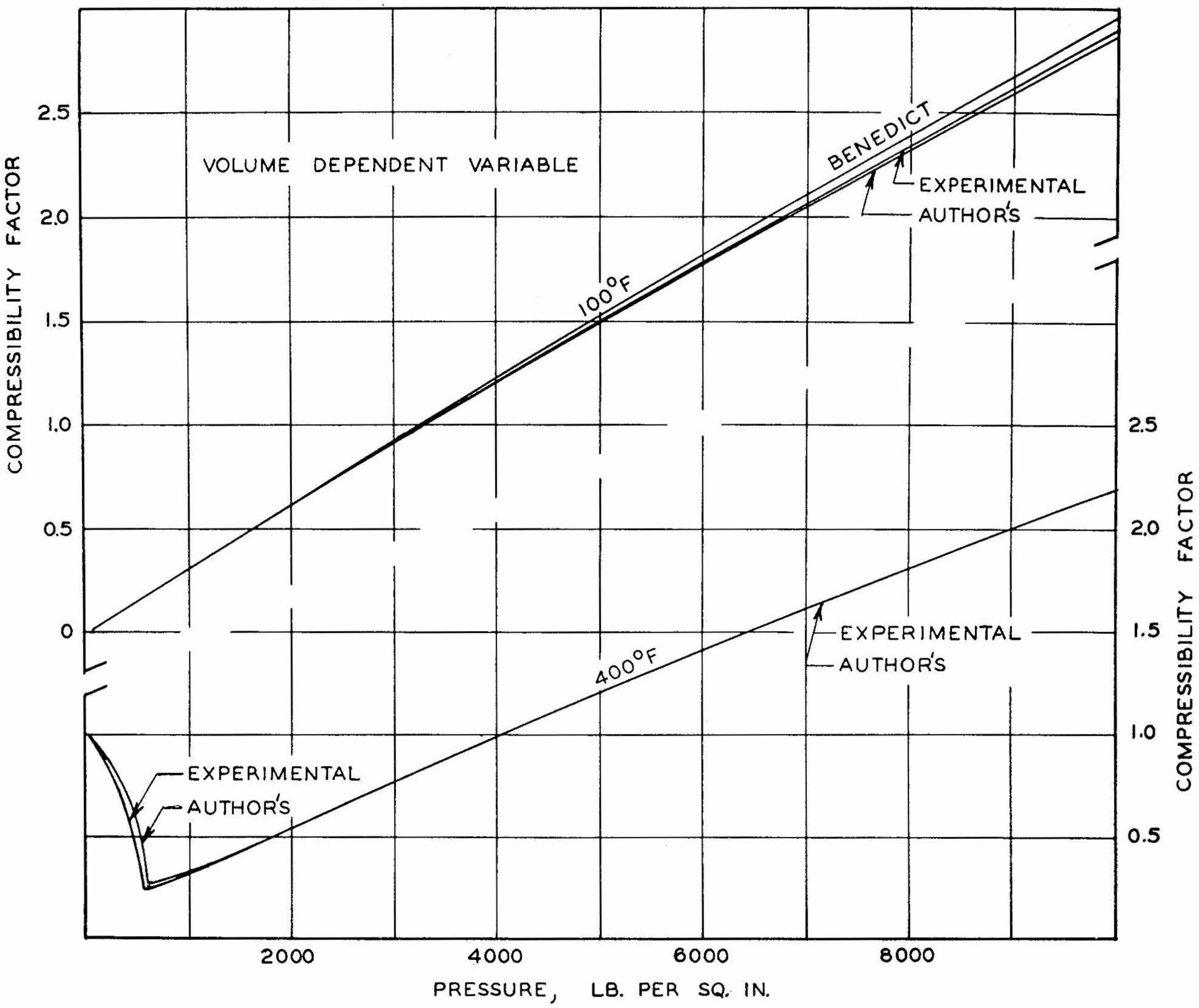

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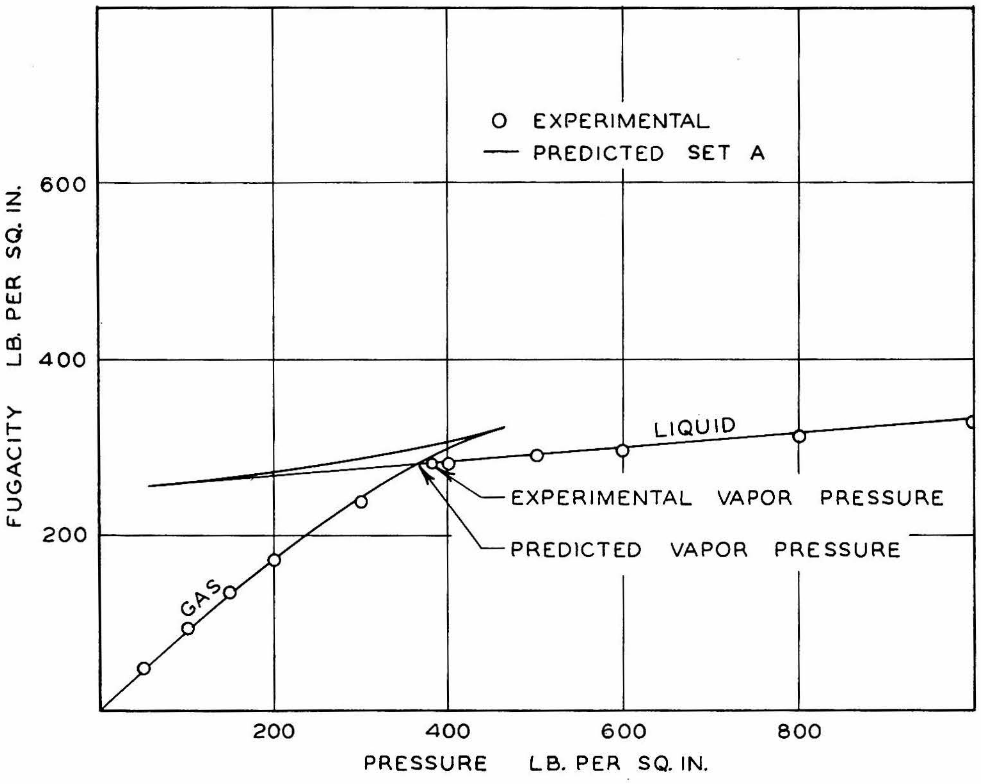

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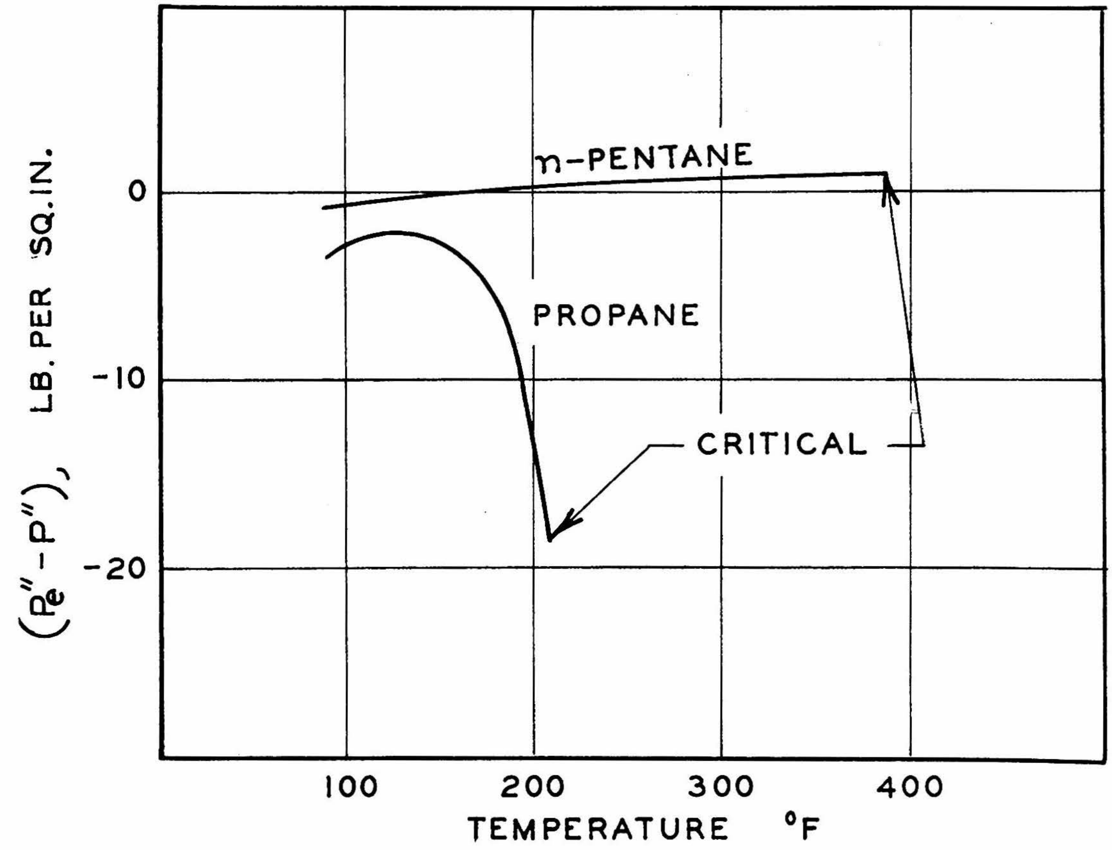

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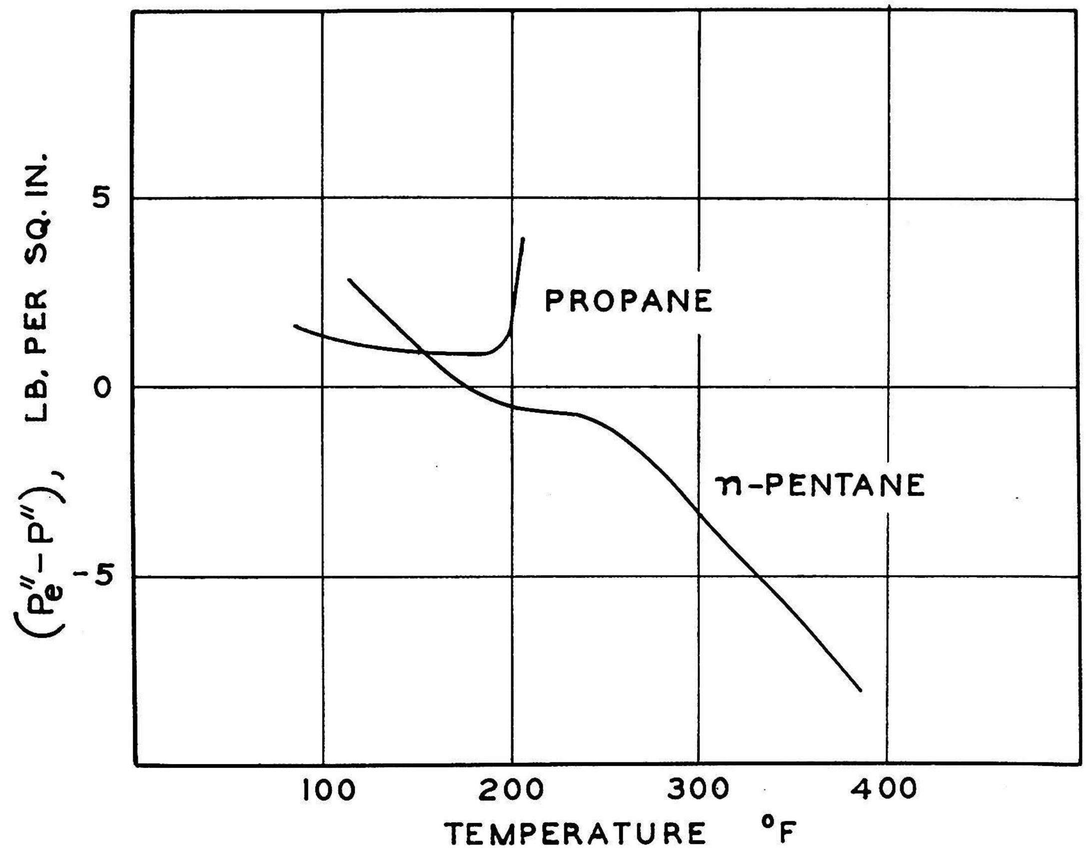

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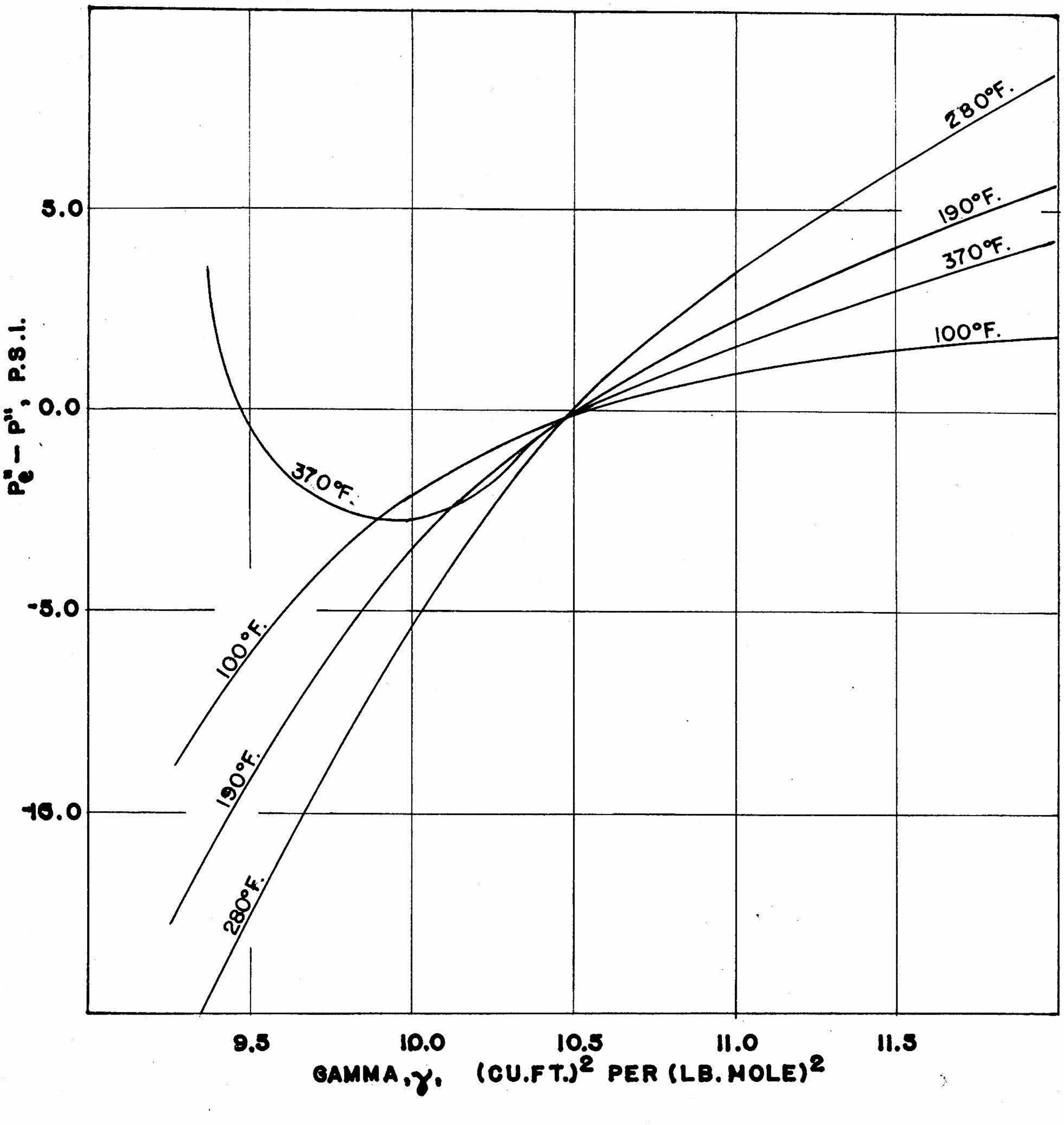

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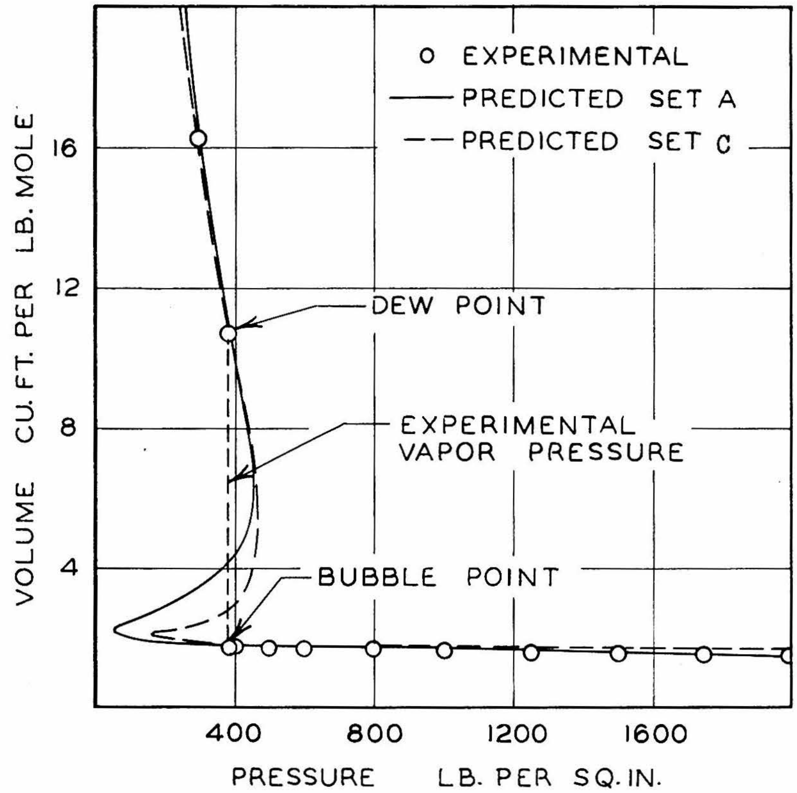

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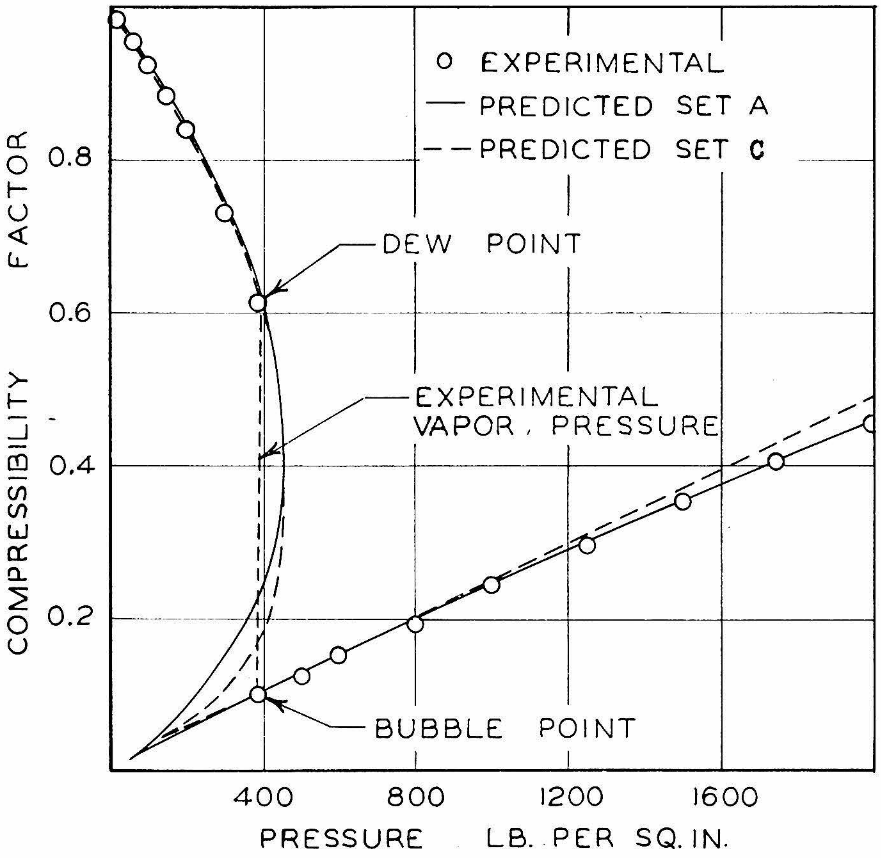

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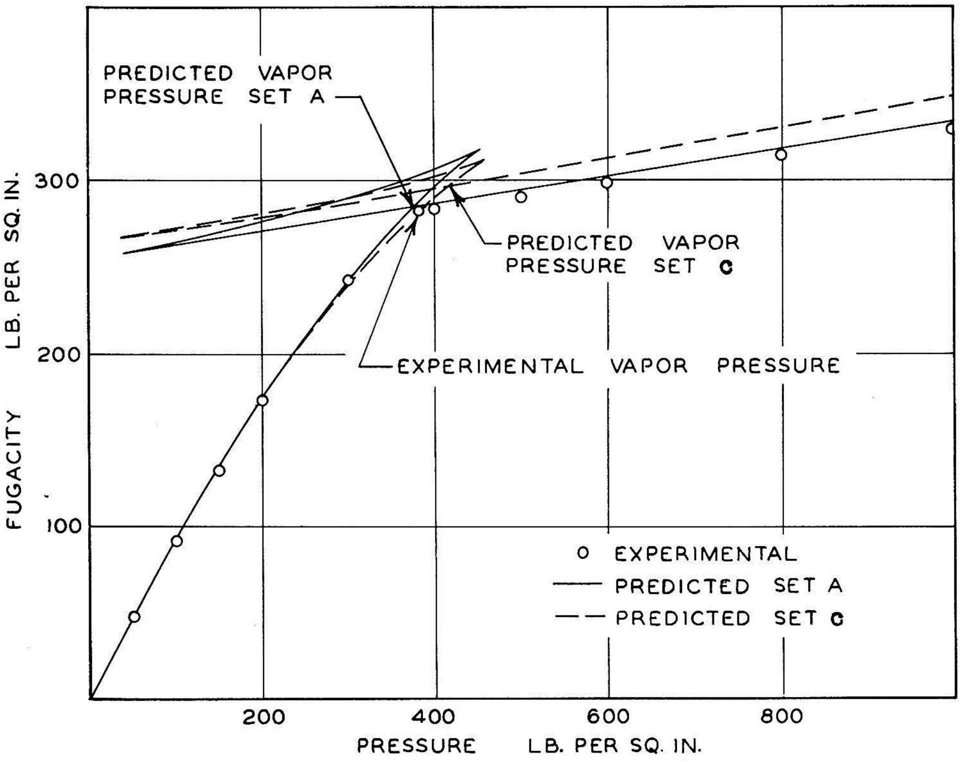

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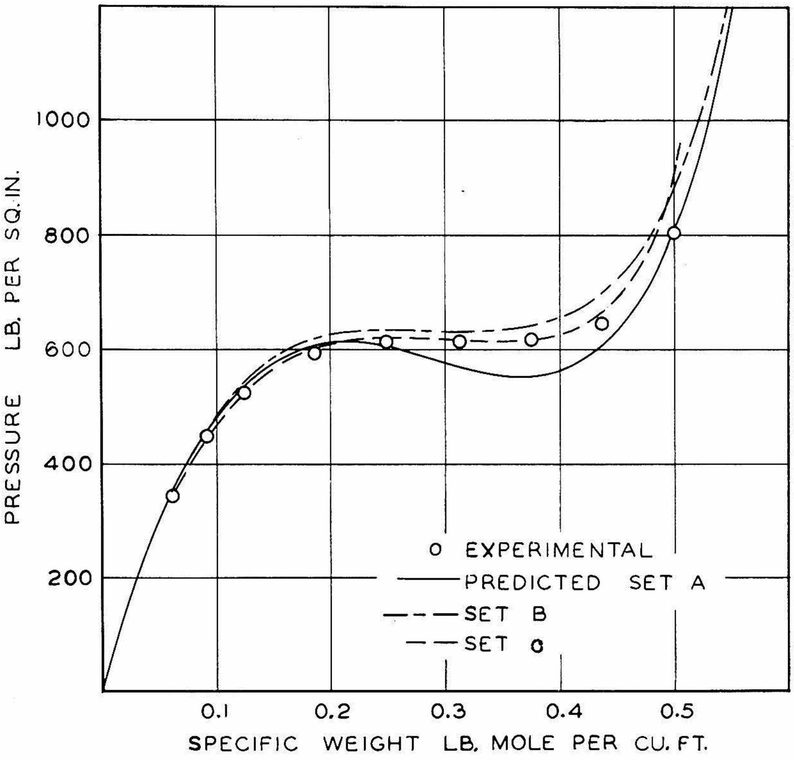

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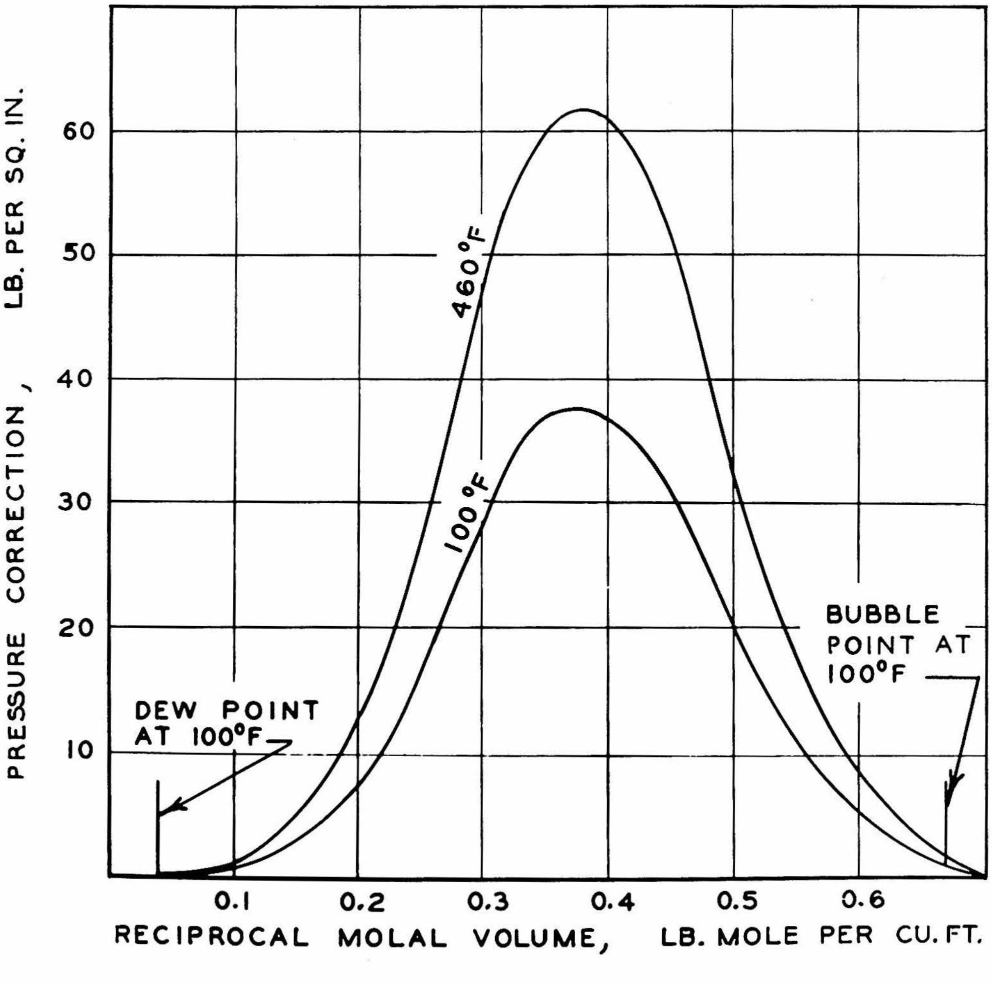

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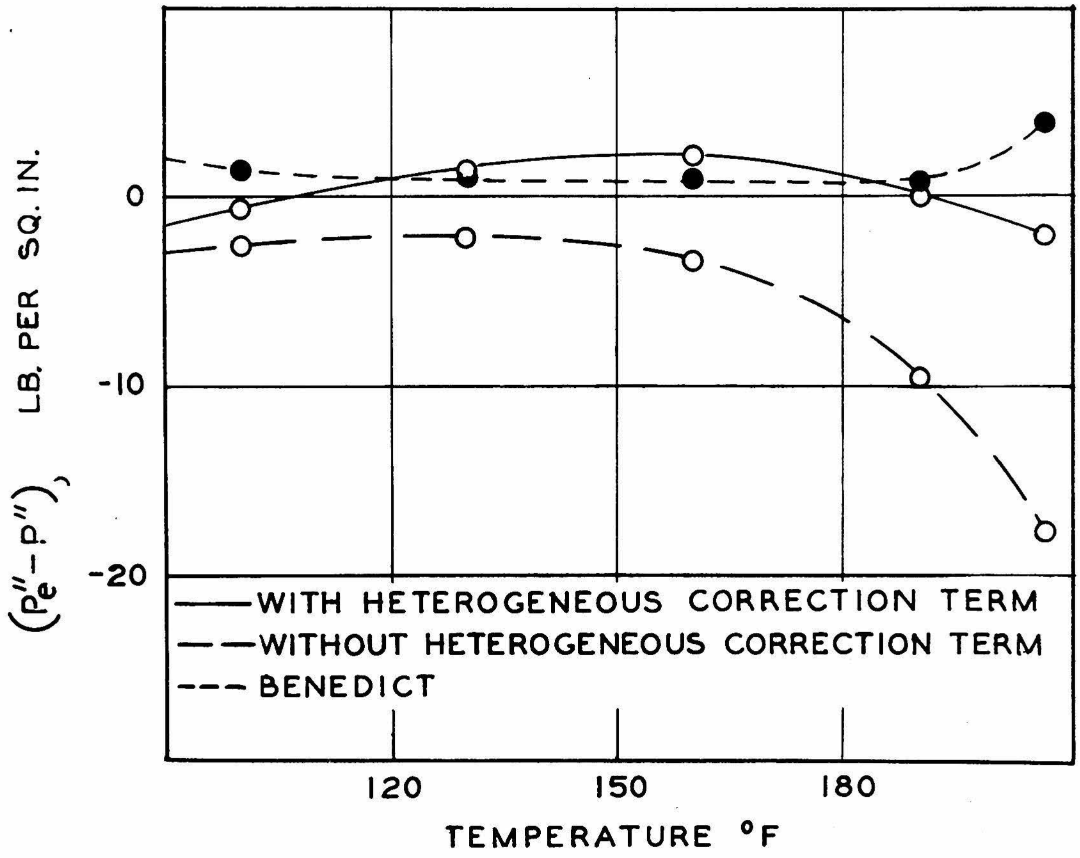

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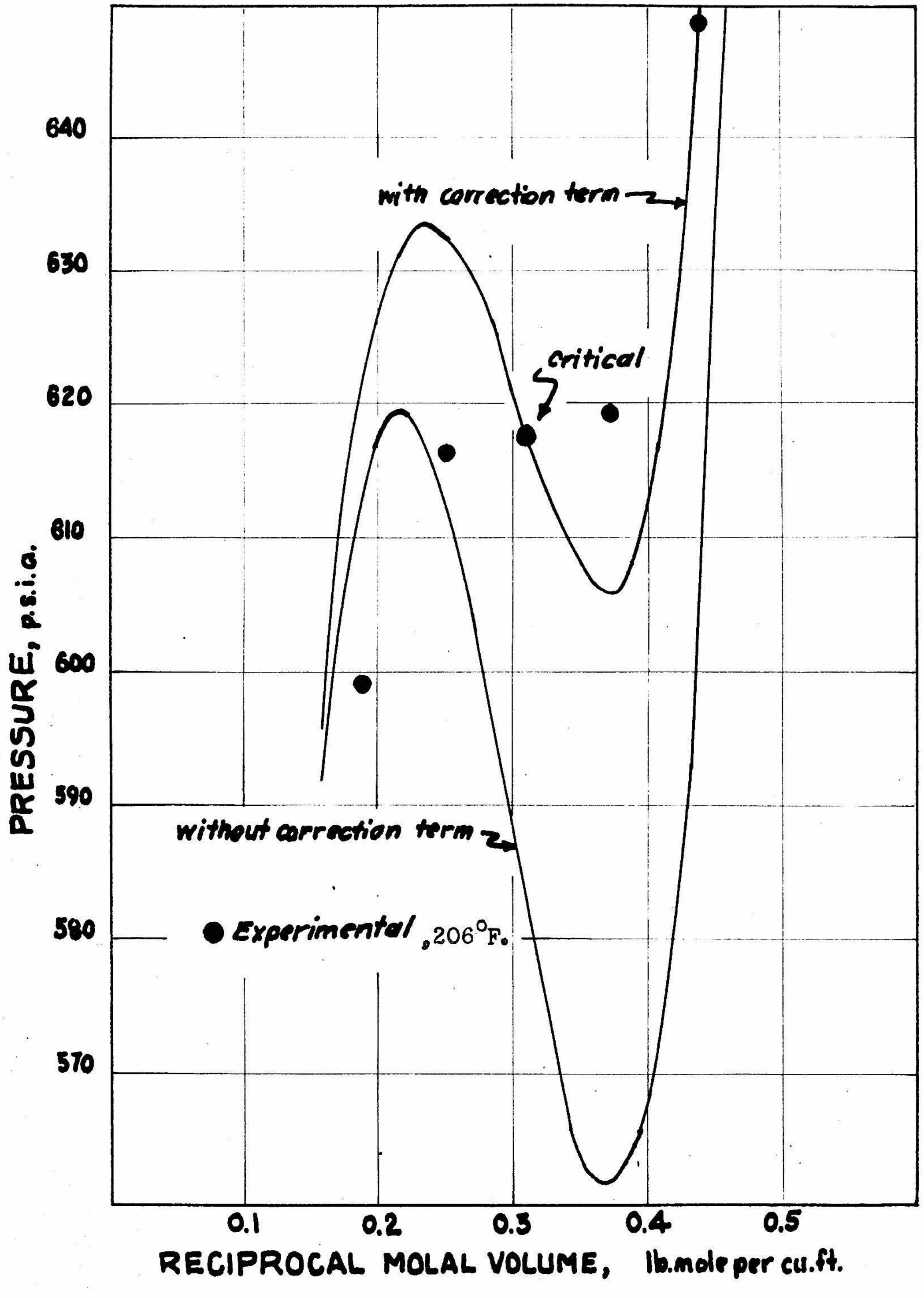

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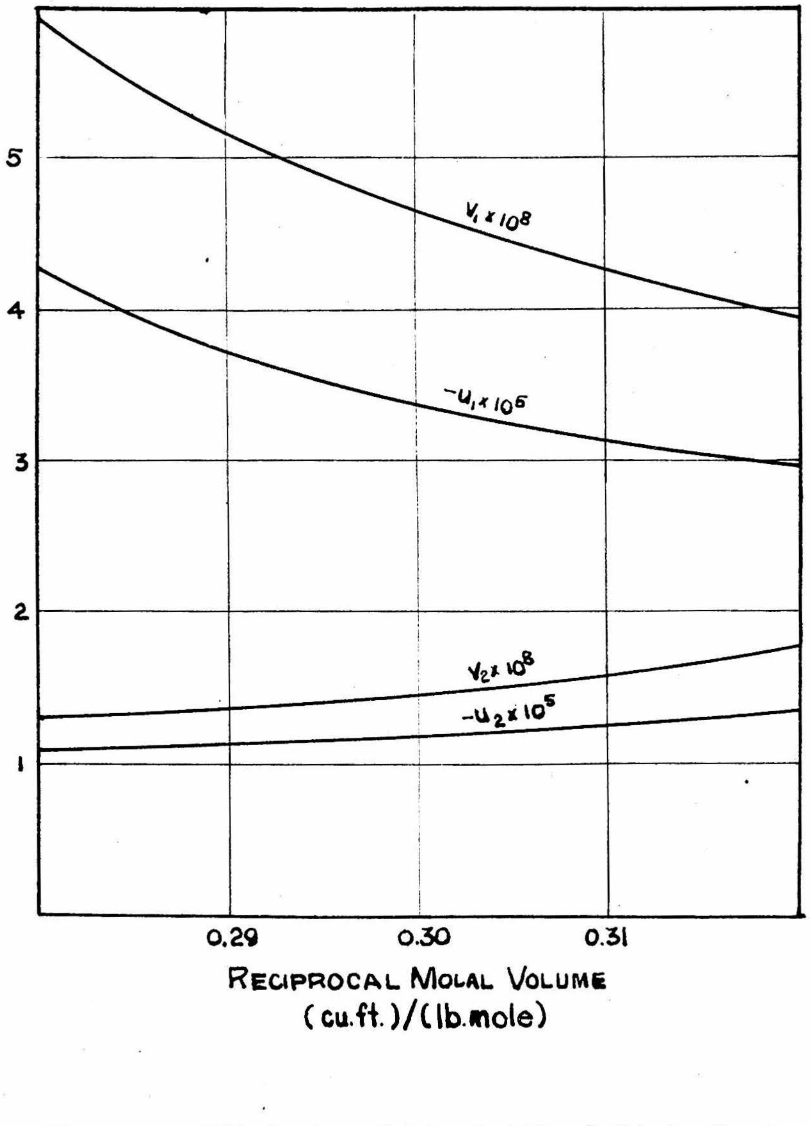

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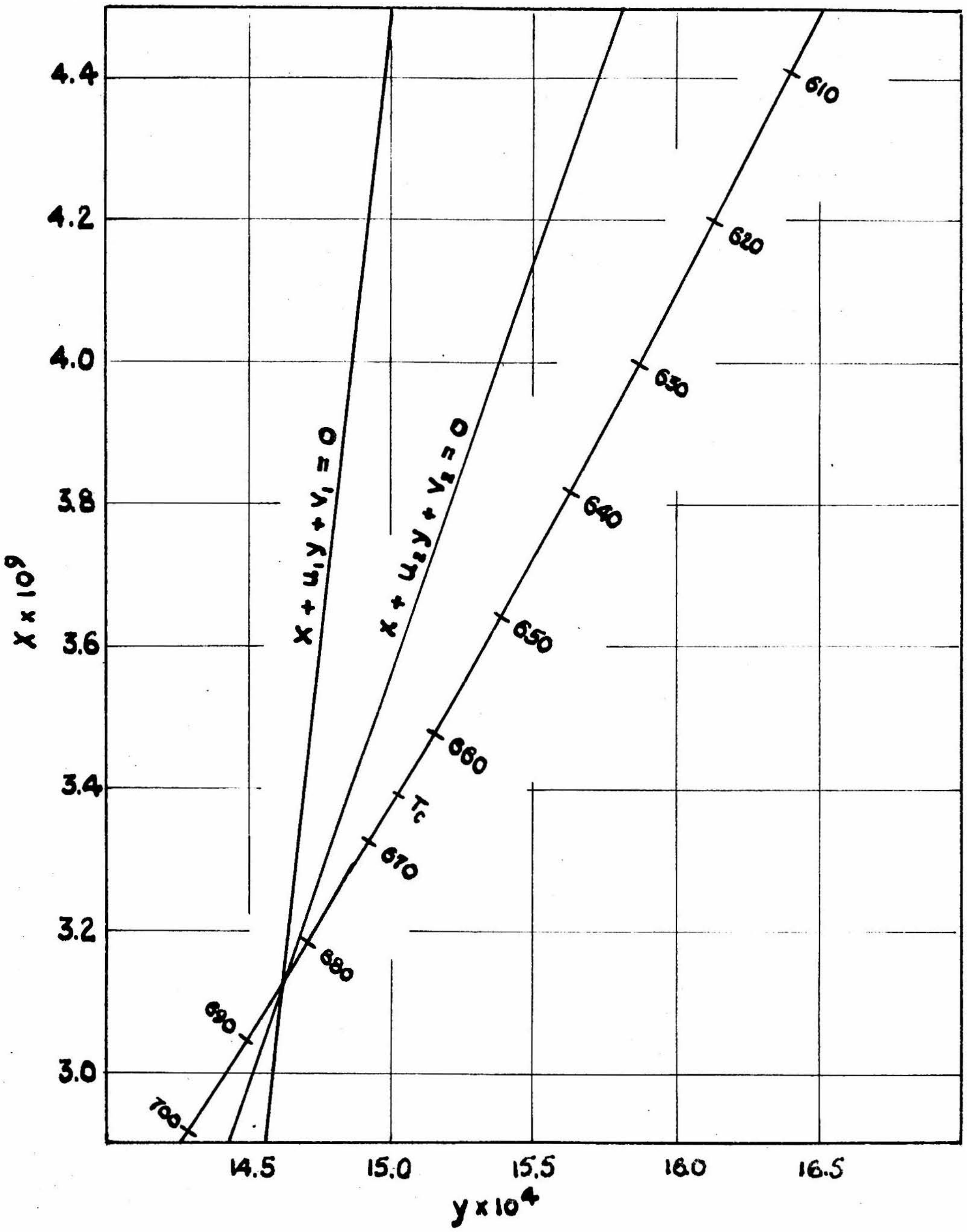

Fig. 29. Geometrical Solution of the Critical State Restraint Equations.

APPENDIX

APPENDIX A

ALGEBRA OF POWER SERIES

Reciprocal of Convergent Power Series.

Let

$$(\xi_0 + \xi_1 x + \xi_2 x^2 + \dots)^{-1} = \zeta_0 + \zeta_1 x + \zeta_2 x^2 + \dots \quad (111)$$

then

$$\left(\sum_{n=0}^{\infty} \xi_n x^n\right)\left(\sum_{m=0}^{\infty} \zeta_m x^m\right) = 1 \quad (112)$$

But

$$\begin{aligned}\left(\sum_{n=0}^{\infty} \xi_n x^n\right)\left(\sum_{m=0}^{\infty} \zeta_m x^m\right) = \; & \xi_0\zeta_0 + \xi_0\zeta_1 x + \xi_0\zeta_2 x^2 + \dots \\ & \xi_1\zeta_0 x + \xi_1\zeta_1 x^2 + \xi_1\zeta_2 x^3 + \dots \\ & \xi_2\zeta_0 x^2 + \xi_2\zeta_1 x^3 + \xi_2\zeta_2 x^4 + \dots \\ & + \dots\end{aligned} \quad (113)$$

The following formulae are obtained by equating coefficients of like powers of x, i. e., summing along the diagonal and then writing

$$\begin{aligned} \xi_0\zeta_0 &= 1 & \zeta_0 &= \xi_0^{-1} \\ \xi_0\zeta_1 + \xi_1\zeta_0 &= 0 & \zeta_1 &= -\xi_1\xi_0^{-2} \\ \xi_0\zeta_2 + \xi_1\zeta_1 + \xi_2\zeta_0 &= 0 & \zeta_2 &= \xi_1^2\xi_0^{-3} - \xi_2\xi_0^{-2} \\ \dots & & \dots & \end{aligned} \quad (114)$$

Positive Integral Powers of Convergent Power Series.

Since $$\sum_{i=0}^{\infty} \xi_i x^i = \lim_{m \to \infty} \sum_{i=0}^{m} \xi_i x^i \quad (115)$$

then

$$\left(\sum_{i=0}^{\infty} \xi_i x^i\right)^n = \lim_{m\to\infty} \left(\sum_{i=0}^{m} \xi_i x^i\right)^n \tag{116}$$

$$= \lim_{m\to\infty} \sum_{\nu_0=0}^{n} \sum_{\nu_1=0}^{n-\nu_0} \cdots \sum_{\nu_{m-1}=0}^{n-\nu_0-\cdots-\nu_{m-2}} \binom{n}{\nu_0\nu_1\cdots\nu_m} (\xi_0)^{\nu_0}(\xi_1 x)^{\nu_1}\cdots(\xi_m x^m)^{\nu_m} \tag{117}$$

$$\left(\sum_{i=0}^{\infty} \xi_i x^i\right) = \xi_0 + \xi_1 x + \xi_2 x^2 + \xi_3 x^3 + \dots \tag{118}$$

$$\begin{aligned} \left(\sum_{i=0}^{\infty} \xi_i x^i\right)^2 = \; & \xi_0^2 + \xi_0\xi_1 x + \xi_0\xi_2 x^2 + \xi_0\xi_3 x^3 + \dots \\ & + \xi_1\xi_0 x + \xi_1^2 x^2 + \xi_1\xi_2 x^3 + \xi_1\xi_3 x^4 + \dots \\ & + \xi_2\xi_0 x^2 + \xi_2\xi_1 x^3 + \xi_2^2 x^4 + \xi_2\xi_3 x^5 + \dots \\ & + \dots \end{aligned} \tag{119}$$

$$\begin{aligned} \left(\sum_{i=0}^{\infty} \xi_i x^i\right)^3 = \; & \xi_0^3 + 3\xi_0^2\xi_1 x + 3(\xi_0^2\xi_2 + \xi_1^2\xi_0)x^2 \\ & + (\xi_1^3 + 3\xi_0^2\xi_3 + 6\xi_0\xi_1\xi_2)x^3 + \dots \end{aligned} \tag{120}$$

In every case

$$\sum_{j=0}^{m} \nu_j = n \tag{121}$$

Reversion of Power Series(44,45).

Let

$$y = f(x) = y_0 + \sum_{n=1}^{\infty} \xi_n (x - x_0)^n \tag{122}$$

be convergent for $|x - x_0| < r$ and if $x = x_0$ then

$$\left.\frac{\partial y}{\partial x}\right|_{x=x_0} = \xi_1 \neq 0 \tag{123}$$

Clearly, the power series defines x as a function of y as well as y as a function of x. Consider a small neighborhood of the point y_0 throughout which x is defined and single-valued and differentiable. In such a neighborhood x may be expanded uniquely in Taylor's series about y_o

$$x = x_o + \sum_{m=1}^{\infty} \zeta_m (y - y_o)^m \tag{124}$$

Taylor's theorem assures that the radius of convergence of this power series is greater than zero. Substitution of Equation 124 into Equation 122 gives

$$y - y_o = \sum_{n=1}^{\infty} \xi_n \left(\sum_{m=1}^{\infty} \zeta_m (y - y_o)^m \right)^n \tag{125}$$

The radius of convergence is equal to the distance from y_o to the nearest singularity in the complex plane of y. At a singularity, one of the following situations occurs; 1) x becomes multivalued, 2) x becomes infinite, 3) the derivative of x with respect to y does not exist.

Since power series may be multiplied within their circles of convergence to give convergent power series, Equation 125 may be expanded and terms collected to give

$$\begin{aligned} \xi_1 \zeta_1 &= 1 & \zeta_1 &= \xi_1^{-1} \\ \xi_2 \zeta_1^2 + \xi_1 \zeta_2 &= 0 & \zeta_2 &= -\xi_2 \xi_1^{-3} \\ \xi_3 \zeta_1^3 + 2\xi_2 \zeta_1 \zeta_2 + \xi_1 \zeta_3 &= 0 & \zeta_3 &= (2\xi_2^2 - \xi_1 \xi_3)\xi_1^{-5} \end{aligned} \tag{126}$$

APPENDIX B

DERIVATION OF THERMODYNAMIC EXPRESSIONS

Beattie(47) has described the "general limit method" for deriving expressions for thermodynamic properties in terms of heat capacities and volumetric properties. This method may be applied to the Benedict equation directly as Beattie has done with the Beattie-Bridgeman equation, but a more convenient approach uses the six canonical functions defined in Section II. The distinctive feature of the "general limit method" is the application of a limiting process which permits all changes of temperature on the system of interest to be considered to act on a perfect gas at infinite attenuation. The fact that real gases at infinite attenuation are not perfect gases with respect to residual volume and Joule-Thomson coefficient must be observed in applications of this method. This difference is of significance in relatively few applications of this method. Infinite attenuation, literally speaking, does not exist, but certain thermodynamic properties do approach finite limits as the pressure on the system is decreased without limit or the volume containing unit weight of matter is increased without limit. A system is said to be at "infinite attenuation" when the specific volume is so large that the properties of the system differ imperceptibly from these limiting values.

Equations 58 through 63 may be derived in terms of the Benedict equation simply by partial differentiation. The derivation of Equations 40 through 43 is not so obvious however. In a multicomponent system, the fugacity, f_k, may be defined in terms of the chemical potential, μ_k, by the differential equation

$$\frac{RT}{f_k}\left(\frac{\partial f_k}{\partial P}\right)_{T,m} = \left(\frac{\partial \mu_k}{\partial P}\right)_{T,m} \qquad (127)$$

and the boundary conditions: $f_k \rightarrow P$ as $V \rightarrow \infty$ along an isothermal path and $f_k^* = n_k P^*$. This differential equation may be rewritten as an integral equation where the path of integration is an isothermal one.

$$\mu_k - \mu_k^* = \int_{P^*}^{P}\left(\frac{\partial \mu_k}{\partial P}\right)_{T,m} dP = RT\int_{P^*}^{P}\frac{1}{f_k}\left(\frac{\partial f_k}{\partial P}\right)_{T,m} dP \qquad (128)$$

or

$$\mu_k - \mu_k^{o*} = RT \ln f_k - RT \ln P^* \qquad (129)$$

since

$$\mu_k^* = H_k^{o*} - TS_k^{o*} + RT \ln n_k \qquad (130)$$

This definition of the relationship between f_k and μ_k avoided the introduction of a temperature dependent constant of integration since all integrations have been isothermal. Equation 129 may be written in the form

$$\beta_k = \mu_k - RT \ln f_k = \beta_k^* = \mu_k^* - RT \ln P^* - RT \ln n_k \qquad (131)$$

since by Equation 128 $\beta_k (= \beta_k^*)$ depends upon temperature alone

$$\mu_k^* - RT \ln n_k = \mu_k^{o*} = \beta_k^* + RT \ln P^* \qquad (132)$$

therefore

$$\beta_k = \mu_k^{o*} - RT \ln P^* \qquad (133)$$

and

$$\frac{d\,\beta_k}{dT} = -S_k^{o*} - R \ln P^* \qquad (134)$$

or

$$\beta_k(T) - \beta_k(0) = -RT \ln P^* - \int_{T=0}^{T} S_k^{o*} dT \qquad (135)$$

An expression for the partial molal volume can be deduced from the equation defining the chemical potential.

$$\mu_k = \bar{\bar{E}}_k + P\bar{\bar{V}}_k - T\bar{\bar{S}}_k \qquad (136)$$

Differentiation with respect to pressure at constant temperature and composition gives

$$\left(\frac{\partial \mu_k}{\partial P}\right)_{T,m} = \left(\frac{\partial \bar{\bar{E}}_k}{\partial P}\right)_{T,m} + P \left(\frac{\partial \bar{\bar{V}}_k}{\partial P}\right)_{T,m} - T \left(\frac{\partial \bar{\bar{S}}_k}{\partial P}\right)_{T,m} + \bar{\bar{V}}_k = \bar{\bar{V}}_k \qquad (137)$$

Substitution of Equation 129 into Equation 137 produces

$$\bar{V}_k = \frac{RT}{f_k}\left(\frac{\partial f_k}{\partial P}\right)_{T,m} = RT \left(\frac{\partial \ln f_k}{\partial \sigma}\right)_{T,m} \Big/ \left(\frac{\partial P}{\partial \sigma}\right)_{T,m} \qquad (138)$$

From Equation 129

$$\left(\frac{\partial \mu_k}{\partial T}\right)_{P,m} - \left(\frac{\partial \mu^*_k}{\partial T}\right)_{P,m} = R \ln f_k - R \ln f^*_k + RT \left(\frac{\partial \ln f_k}{\partial T}\right)_{P,m} \qquad (139)$$

But

$$\left(\frac{\partial \mu_k}{\partial T}\right)_{P,m} = -\bar{S}_k \qquad (140)$$

Hence,

$$\bar{S}^*_k - \bar{S}_k = -R \ln f^*_k + \frac{1}{T}\left\{ RT \ln f_k + RT^2 \left(\frac{\partial \ln f_k}{\partial T}\right)_{P,m} \right\} \qquad (141)$$

Since

$$\bar{S}^*_k = S^{o*}_k - R \ln n_k \qquad (142)$$

and

$$\ln f^*_k = \ln P^* + \ln n_k \qquad (143)$$

$$\bar{S}_k - S^{o*}_k = R \ln P^* - \frac{1}{T}\left\{ RT \ln f_k + RT^2 \left(\frac{\partial \ln f_k}{\partial T}\right)_{P,m} \right\} \qquad (144)$$

The partial molal enthalpy is readily obtained from Equations 129 and 144.

$$\bar{H}_k - H^{o*}_k = (\mu_k - \mu^{o*}_k) + T(\bar{S}_k - S^{o*}_k) = -RT^2 \left(\frac{\partial \ln f_k}{\partial T}\right)_{P,m} \qquad (145)$$

At constant composition and in the absence of external force fields, a single phase multicomponent system has two degrees of freedom; hence,

$$d \ln f_k = \left(\frac{\partial \ln f_k}{\partial T}\right)_{\underset{\cdot}{\sigma},m} dT + \left(\frac{\partial \ln f_k}{\partial \underset{\cdot}{\sigma}}\right)_{T,m} d\underset{\cdot}{\sigma} \quad (146)$$

but at constant pressure

$$d\underset{\cdot}{\sigma} = \left(\frac{\partial \underset{\cdot}{\sigma}}{\partial T}\right)_{P,m} dT = - \frac{(\partial P/\partial T)_{\underset{\cdot}{\sigma},m}}{(\partial P/\partial \underset{\cdot}{\sigma})_{T,m}} \quad (147)$$

so that

$$\left(\frac{\partial \ln f_k}{\partial T}\right)_{P,m} = \left(\frac{\partial \ln f_k}{\partial T}\right)_{\underset{\cdot}{\sigma},m} - \left(\frac{\partial \ln f_k}{\partial \underset{\cdot}{\sigma}}\right)_{T,m} \frac{(\partial P/\partial T)_{\underset{\cdot}{\sigma},m}}{(\partial P/\partial \underset{\cdot}{\sigma})_{T,m}} \quad (148)$$

Equations 58 through 63 follow from these relationships.

APPENDIX C

SOLUTION OF SYSTEMS OF INCONSISTENT, LINEAR ALGEBRAIC EQUATIONS

A system of m linear equations in n variables is said to be consistent(48) if these m equations have at least one common solution. A set for which no common solution exists is called inconsistent. Let K represent the m x n matrix of the coefficients of the m equations, x represent the vector (ordered set of numbers) of the variables, and k represent the vector which the product Kx is presumed to approximate, for example, experimental observations.

$$K x = k \tag{149}$$

This system of equations will have at least one non-zero solution for x if the rank of both K and its augmented matrix are the same and less than or equal to n.

In the problem of fitting empirical expressions to experimental information, systems of linear equations when obtained are generally such that the rank of the augmented matrix is greater than n. Since no non-zero exact solution is then possible, a criterion must be chosen to measure the degree to which various sets of values for the variables approach a solution in the respect of satisfying the equations precisely. The least squares criterion is most generally used for this purpose. It selects that set of values for the variables (represented by the vector x) which yields the minimum value for the sum $\sum_{i=1}^{m} (K_i x - k_i)^2$. A little algebra will show readily that application of the least squares criterion is equivalent to substituting the following matrix equation for Equation 149.

$$K^T K x = K^T k \qquad (150)$$

Equation 150 has a unique solution, by Cramer's rule, if the rank of $K^T K$ and its augmented matrix are precisely n, which is generally the case. Equation 150 represents, in matrix notation, the normal equations of the least squares method.

Other criteria can be used equally well for establishing the best fit for an empirical equation to experimental observations. One might be the minimization of $\sum_{i=1}^{m} |K_i x - k_i|$. This criterion has the advantage of applying less weight to the effect of the least typical equation than does the method of least squares. However, this criterion does not imply as direct a method for obtaining values for the components of x as does the method of least squares. The general method, using this criterion, would select from the total number of ways in which m equations can form n combinations that way which supplies, by such combinations, n equations yielding a solution giving the minimum value of $\sum_{i=1}^{m} |K_i x - k_i|$. This is substantially the method of averages(49,50).

Either of these methods yields a unique solution for the inconsistent equations problem. The method of least squares has the advantage of directness in obtaining that solution most appropriate to its criterion. The method of averages has the advantage of ease of calculation if one is satisfied with a fit which is only near the fit most appropriate to its criterion. The latter method becomes exceedingly tedious for obtaining the best fit if the number of variables involved is at all large.

The preceding discussion indicates the nature of the aid which statistical methods provide for solving systems of inconsistent linear equations, once a particular system has been chosen. Essentially the same considerations apply for systems of non-linear equations except that values of those variables which occur as the non-linear elements are established by iterative methods. In general, the normal equations will be satisfied by more than one set of values for the variables if any of the variables occur in a non-linear manner since the variance of estimate may have several relative stationary points. The selection of the system of equations to be solved in empirical curve fitting must be intuitive for it depends upon non-mathematical considerations of the reliability of the k terms and the elements K_{ij} of the matrix K.

Lagrange Undetermined Multipliers.

The method of Lagrange undetermined multipliers is a device for determining constrained minima. The principle can be conveniently described by an example. Let the sum of the squares of the deviations of the experimental compressibility factors from those predicted by an empirical equation of state be denoted by the symbol A. The conventional least squares method seeks to determine that set of values for the coefficients in the empirical equation which minimize A. A necessary condition that A take its minimum value is that all partial derivatives of A with respect to these coefficients be zero.

Sometimes, the minimization is to be constrained in such a manner that the parameters also satisfy another condition in addition to those which equate the partial derivatives to zero. Let this condition be that a function B is identically zero. The left-hand side of Equation 80 might be such a function B. If m is a constant, independent of the values of the coefficients, then (A - mB) is equal to A for any particular set of values for the parameters. The equations which equate the partial derivatives to zero have solutions which depend upon the undetermined multiplier m. But m can be determined from the fact that B is identically zero and the parameters which correspond to the constrained minimum can be determined. The method can be extended to several restraints provided only that the number of restraints does not exceed the number of parameters.

Most textbooks of mathematical physics or of statistical mechanics discuss this method in detail.

APPENDIX D

LEAST SQUARES ANALYSIS(7) OF THE LINEAR PART OF THE BENEDICT EQUATION

Let K be a column vector with components K_i, $(i = 0,1,\ldots,7)$ and let ϕ_j be a row vector with components $\phi_{ji}(\sigma,T)$, $(j = 1,2,\ldots,N)$. The difference between the experimentally observed value of the quantity Z and the value, Z_e, predicted by the equation which has been proposed to describe Z in terms of the experimental quantities σ and T is given by the following expression.

$$(Z_e - Z)_j = (\phi_j, K) = \sum_{i=0}^{7} \phi_{ji} K_i \quad ; \quad (j=1,2,\ldots,N) \tag{151}$$

If Φ represents the matrix(10) whose rows are the vectors ϕ_j then Equation 151 may be written:

$$(Z_e - Z) = \Phi K \tag{152}$$

and the sum of the squares of the $(Z_e - Z)_j$'s is:

$$\sum_{j=1}^{N} (zZ_e - Z)_j^2 = (\Phi K)^T \Phi K = K^T A K \tag{153}$$

where: $A = \Phi^T \Phi$, i. e., $a_{ij} = (\phi_i, \phi_j) = \sum_{k=1}^{N} \phi_{ik} \phi_{kj}$ (154)

Thus $K^T A K$ is a positive-definite quadratic form and A is a symmetric positive-definite square matrix of order eight. The variance of estimate is $K^T A K/N$.

To satisfy the least squares criterion $K^T A\, K$ must be at its minimum value, therefore:

$$(\partial/\partial K_i)\; K^T A\; K \;=\; (\partial K^T/\partial K_i)\; A\; K \;+\; K^T(\partial A/\partial K_i)\; K \;+\; K^T A\; (\partial K/\partial K_i) \qquad (155)$$

$$=\; 2\; B_i\; K \;=\; 0 \quad ; \quad (i = 1,2,\ldots,7) \qquad (155)$$

The matrix B is the matrix A less the row corresponding to i = 0. A vector which satisfies the <u>normal equation</u>

$$B\; K \;=\; 0 \qquad (156)$$

will also satisfy

$$K^T A\; K \;=\; -\,(a_0,K) \;=\; -\sum_{i=0}^{7} a_{i0} K_i \qquad (157)$$

Equation 155 is not a sufficient condition for defining a relative minimum.

To solve Equation 156 for the vector K, the elements of B = $B^{(0)}$ are arranged in the scheme:

$$\left\|\begin{array}{ccccc} b_{11}^{0*} & b_{12}^{0} & \cdot\cdot & b_{17}^{0} & b_{10}^{0} \\ b_{21}^{0} & b_{22}^{0} & \cdot\cdot & b_{27}^{0} & b_{20}^{0} \\ \cdot\cdot & \cdot\cdot & B^{0} & \cdot\cdot & \cdot\cdot \\ b_{71}^{0} & b_{72}^{0} & \cdot\cdot & b_{77}^{0} & b_{70}^{0} \\ \hline b_{01}^{0} & b_{02}^{0} & \cdot\cdot & b_{07}^{0} & b_{00}^{0} \end{array}\right\| \qquad \left\|\begin{array}{lll} b_{11}^{1} = 1 & b_{12}^{1} = \dfrac{b_{12}^{0}}{b_{11}^{0}} & \cdots \\ b_{21}^{1} = 0 & b_{22}^{1*} = b_{22}^{0} - \dfrac{b_{21}^{0} b_{12}^{0}}{b_{11}^{0}} & \cdot\cdot \\ \cdot\cdot & \cdot\cdot\;\; B^{1} = M^{1}B^{0} & \cdots \\ b_{71}^{1} = 0 & \cdot\cdot & \cdots \\ \hline b_{01}^{1} = 0 & \cdot\cdot & \cdots \end{array}\right\|$$

$$\left\|\begin{array}{llllll} m_{11}^{1} = & 1/b_{11}^{0}* & 0 & . & 0 & 0 \\ m_{21}^{1} = & \frac{-b_{21}^{0}}{b_{11}^{0}*} & 1 & . & 0 & 0 \\ .. & & .. & M^{1} & .. & .. \\ m_{71}^{1} = & \frac{-b_{71}^{0}}{b_{11}^{0}*} & 0 & . & 0 & 0 \\ \hdashline m_{01}^{1} = & \frac{-b_{01}^{0}}{b_{11}^{0}*} & 0 & . & 0 & 1 \end{array}\right\| \quad \left\|\begin{array}{lllll} 1 & m_{12}^{2} & = & -b_{12}^{1}/b_{22}^{1}* & \cdots \\ 0 & m_{22}^{2} & = & 1\ /b_{22}^{1}* & \cdots \\ .. & .. & M^{2} & & \cdots \\ 0 & m_{72}^{2} & = & -b_{72}^{1}/b_{22}^{1}* & \cdots \\ \hdashline 0 & m_{02}^{2} & = & -b_{02}^{1}/b_{22}^{1}* & \cdots \end{array}\right\|$$

Note that $b_{oj}^{o} = a_{oj}$ but is not an element of the matrix B. The pivot element of reduction r is indicated by * . The result of the foregoing process is the matrix $B^7 = M^7 B^6$ which may be written

$$\left\|\begin{array}{lllll} 1 & 0 & .. & 0 & K_1 \\ 0 & 1 & .. & 0 & K_2 \\ .. & .. & B^7 & .. & .. \\ 0 & 0 & .. & 1 & K_7 \\ \hdashline 0 & 0 & .. & 0 & b_{oo}^{7} \end{array}\right\|$$

The general formulae for the reduction may be written

$$b_{ij}^{(r+1)} = b_{ij}^{(r)} - \frac{b_{ik}^{(r)}}{b_{kk}^{(r)}} b_{kj}^{(r)} \quad ; \quad (i \neq k) \tag{158}$$

$$b_{kj}^{(r+1)} = b_{kj}^{(r)} / b_{kk}^{(r)} \quad ; \quad (i = k) \tag{159}$$

Furthermore

$$A = b_{11}^{0} b_{22}^{1} b_{33}^{2} \ldots b_{77}^{6} b_{00}^{7} \tag{160}$$

The largest minor in each $B^{(r)}$ in which no rows or columns contain reduced pivot elements, is symmetric. Thus, the elements of the matrices $B^{(r)}$ will be exactly the same if the reduction is done by the following operations on the IBM 604 computer which is described in Appendix E.

1) calculate $1/b_{kk}^{(r)*}$
2) calculate $b_{kj}^{(r)} / b_{kk}^{(r)*}$ and punch it into every card of column j. $(j = 0,1,\ldots,7)$
3) multiply $b_{kj}^{(r)} / b_{kk}^{(r)*}$ by $b_{ik}^{(r)}$ (excepting $i = k$) subtract the product from $b_{ij}^{(r)}$ to obtain $b_{ij}^{(r\ 1)}$ Discard all cards of column k. The multiplier $b_{ik}^{(r)}$ is carried in the computer storage unit during this operation. For $i = k$, $b_{ij} = b_{ij}^{(r)} / b_{kk}^{(r)*}$.

Each of these three operations requires a different set of wired panels for the computer.

During the reduction arbitrary rows of $B^{(r)}$ may be multiplied by ten if such rows do not contain reduced pivot elements and if the determinant is divided by ten for each such operation after the calculation is complete.

The average variance of estimate times the number of data sources may be computed by a short method. Using the panels of 3) let the computer carry K_i as it carried $b_{ik}^{(r)}$ and let the card carry a_{10} as it carried $b_{kj}^{(r)}/b_{kk}^{(r)*}$. The card field which bore $b_{ij}^{(r)}$ is left blank. The computer punches $-a_{10}K_i$ where it punched $b_{ij}^{(r+1)}$ in step 3) above. These quantities are summed on the tabulating machine.

APPENDIX E

DESCRIPTION OF THE DIGITAL COMPUTING EQUIPMENT

The semi-automatic digital computing equipment used in performing calculations described in this thesis consists of the following pieces of machinery; an International Business Machines Corporation (IBM) Type 604 Electronic Calculating Punch (computer), an IBM Type 402 Accounting Machine (tabulator), and an IBM Type 521 Reproducing Punch (reproducer). The computer consists of two electrically connected components the first of which is called the punching unit and the second the calculating section. The punching unit reads information from Hollerith-type punched cards at the rate of about one hundred cards per minute and transmits this information by way of the electrical connection to the calculating unit. The punching unit also punches information which it receives from the calculating unit into the 3.25" by 7.375" manila cards. Other functions of this unit include checking for blank fields* which should contain punching, indicating when the calculation is too long for the calculating section to complete during the allotted "calculate time" (unfinished program), and indicating when insufficient space has been allotted on the card to receive the information from the calculating section (product overflow). The calculating section performs the arithmetic operations of addition and subtraction. Multiplication is performed by the high-speed addition of the multiplicand or some power

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* The term field is used here to denote a set of card columns which, when punched, represents a particular number.

of ten times the multiplicand to itself a total number of times equal to the sum of the digits in the multiplier. Division is performed by subtractions from the dividend in the manner of long division. The computer can obtain four separate five digit quotients during calculate time. The operations which the computer performs during one card cycle are controlled by two panels, one for each section, which are specially wired to complete the necessary circuits in the machine. For many standard types of problems these panels are wired permanently and are stored between uses, but for small problems it is frequently desirable to have the panels wired only when needed in order to reduce storage space requirements.

The reproducer will reproduce numbers from one card into another card in the same or in a different field and will at the same time originate punches which are to be uniform throughout a given deck of cards (gang punching). When coupled electrically with the tabulator this machine will punch information received from the tabulator. Usually such information represents sums which the tabulator has computed and the operation of punching such sums with the reproducer is called summary punching. Multiplication by ten is performed on this machine by the obvious method of shifting the number one column to the left in its field.

The tabulator prints information which it receives from cards, adds cumulatively either positively or negatively, and prints totals with or without transmitting this information to the reproducer for summary punching. The arithmetical and printing operations are controlled by wiring a panel similar to those used in the computer. The panel for the tabulator may be wired to fit several different problems and the appropriate circuit for a given problem selected by means of a "set-up switch".

Auxiliary equipment includes a sorter, a keypunch, and a collator. The sorter is able to separate the cards in a deck into thirteen different classes which correspond to holes in the twelve card rows and to no hole at all in a given card column. The keypunch is the primary device by which experimental data is translated into punched holes in cards. The collator merges two decks of cards in the sequences required for those calculations which require information from two different cards or for situations in which the computer result is to be punched in a card different from the one supplying input information. A typical example is the computation of the exponential function of the variable y. Cards bearing the values of y are merged with part of the exponential function master deck in such a manner that the argument x in the exponential function master card is less than 0.001 greater than y. The exponential function cards carry, in addition to the argument, exp (x), exp (-x), and the first four central differences of these functions for intervals of 0.001 in x. From such a merged deck the exponential functions of x can be computed by Bessel's formula(41) translated into wiring in the computer control panels.

Application of Benedict Equation of State to Propane

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THE equation of state developed by Benedict, Webb, and Rubin (*6,7*) is a satisfactory framework within which the volumetric and phase behavior of the lighter hydrocarbons and their mixtures may be described. This equation of state, utilized with the "general limit method" discussed by Beattie (*1*), affords a ready means of evaluating the thermodynamic properties of such compounds and their mixtures with an accuracy sufficient for most industrial needs. The coefficients of this equation of state were originally established by graphical and conventional numerical methods which were somewhat intuitive. Such calculations, although tedious, can be accomplished with a minimum of effort by the use of available commercial digital computing equipment (*10*). Statistical methods of estimating coefficients for an equation of state for nitrogen were considered by Benedict (*3*). Recently Brough and coworkers (*9*) extended the application of these methods to the determination, by matrix techniques (*17*), of the coefficients of the Benedict equation of state for methane and propane. In this instance sets of coefficients were obtained for several values of the exponential term of the equation of state. The purpose of the present discussion is to establish the effects of different sets of experimental data and ranges of pressure upon the agreement of the Benedict equation of state with experiment and to determine the feasibility of applying it to the liquid phase as well as to gaseous states.

For present purposes the Benedict equation of state may be expressed as

$$Z_e = 1 + \left(B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3}\right) d + \left(b - \frac{a}{RT}\right) d^2 + a\alpha \frac{d^5}{RT} + \frac{cd^2}{RT^3}(1 + \gamma d^2)e^{-\gamma d^2} \quad (1)$$

It is convenient to establish by least squares techniques (*9*) the set of coefficients which corresponds to a minimum root-mean square deviation of predicted from observed pressures for a series of assumed values of the exponent γ of Equation 1. Several possible effects of γ upon the average standard error of estimate of Equation 1 from a chosen group of experimental data have been indicated (*9*). Such effects were not investigated quantitatively.

At present there are available several sets of coefficients of the Benedict equation of state for many of the lighter hydrocarbons. The original values of Benedict (*6,7*) appear to be satisfactory for

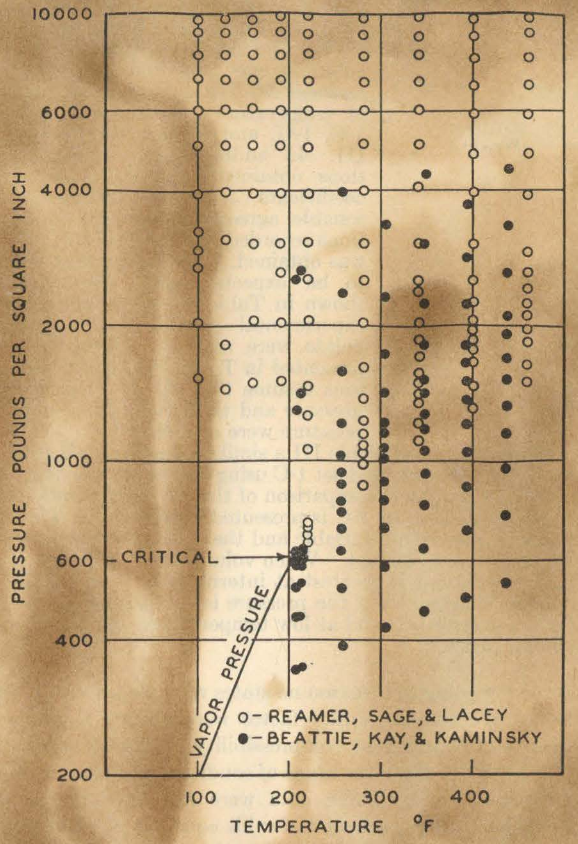

Figure 1. Experimental Data for Propane Used to Establish Coefficients

the description of the volumetric and phase behavior of these compounds and their mixtures at pressures up to about 3000 pounds per square inch. At higher pressures large variations from experiment are realized and these coefficients do not describe the behavior in the liquid region satisfactorily. Marchman and coworkers (*12*, *14*) computed coefficients for propene and mixtures of propene and ethane. More recently Benedict, Webb, and Rubin (*4*) reported values of the coefficients for 12 hydrocarbons including propane. In addition, a detailed description of the techniques to be followed in applying this equation of state to the prediction of the thermodynamic properties is available (*5*, *8*). Although these new coefficients extend the applicability of the Benedict equation to a variety of the lighter hydrocarbons and their mixtures, the coefficients are limited to application at pressures below 3000 pounds per square inch. In addition, the available coefficients do not necessarily yield the minimum standard error of estimate from existing experimental data that may be obtained with the exceedingly flexible relationship presented in Equation 1.

METHOD OF APPROACH

The least squares procedure to establish a set of coefficients for the Benedict equation of state which yields a minimum deviation from a particular set of experimental volumetric data has been described (*9*). The present approach follows the same technique except that several matrix equations have been solved simultaneously to decrease the computing time required. Some of the details of such calculations are available (*13*). Modifications of the methods which have been described result in a decrease in the extent and complexity of the numerical calculations when several values of γ are to be utilized.

When utilizing the revised method (*13*) with a commercial electronic calculator without extended sequential control, the calculation of the elements of the original matrix required about 30 hours. The use of 316 cards and a period of approximately 2 hours was then required for the evaluation of a set of coefficients for an assumed value of γ. The calculations reported here are based on approximately 200 experimental points. After the first set of coefficients has been obtained other sets of coefficients based upon the same experimental data but for different values of γ may be calculated in not more than 45 minutes of computing time. The method involves the use of a set of experimental volumetric measurements covering the range of conditions within which it is desired to apply the equation. Figure 1 shows upon a pressure-temperature diagram the experimental data used in studying the application of the Benedict equation of state to propane. Two sets of data were employed, the first being the measurements of Beattie, Kay, and Kaminsky (*2*) and the second the unpublished experimental background for the volumetric behavior of propane at pressures up to 10,000 pounds per square inch (*15*). A rather large range of pressures and temperatures is covered by both sets of data and thus it is possible to compare directly the agreement of the measurements from the two sources in the region of overlap. Data at values of the compressibility factor less than that at the critical state were excluded. A total of 83 smoothed points from the measurements of Beattie *et al.* (*2*) and 131 experimental points from the more recent study at higher pressures were included. It should be emphasized that the methods outlined here apply primarily to the estimation of the optimum coefficients for the prediction of thermodynamic data in the homogeneous regions and do not necessarily yield the optimum predictions of vapor pressure for pure substances or of the heterogeneous equilibrium of mixtures. Benedict utilized the data of Kemp and Egan (*11*) to adjust the coefficients to improve the prediction of heterogeneous equilibrium.

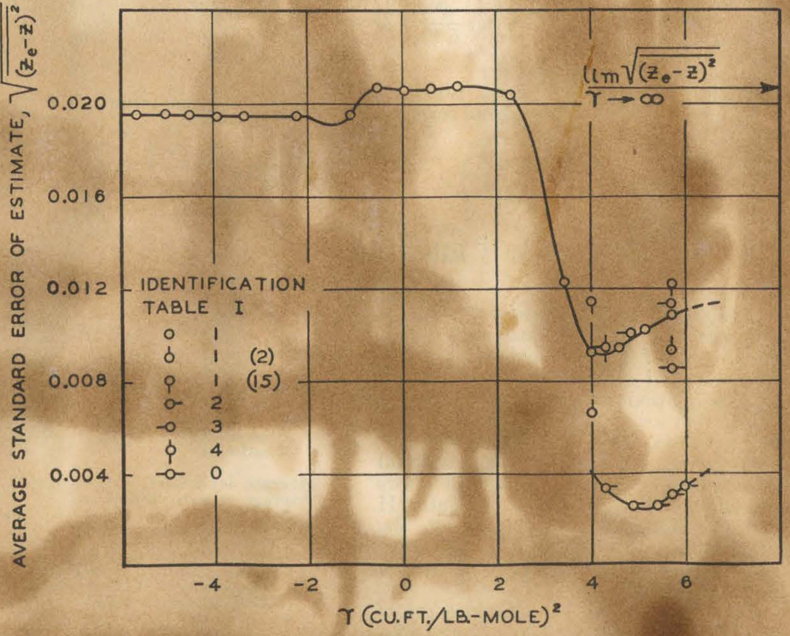

Figure 2. Average Standard Error of Estimate of Compressibility Factor for Propane as a Function of Exponent γ

Table I. Experimental Background for Evaluating Coefficients for Benedict Equation of State

Identification No.[a]	References		Range of Data					
			Pressure, lb./sq. inch		Temperature, ° F.			
	Data	Coefficients	Min.	Max.	Min.	Max.	No. states	Relative Weight
Benedict (0)	(*2*)[b]	(*4, 6*)	343	4494	206	527	108[c]	..
1	(*2, 15*)	Authors	343	4494	206	437	83[d]	0.5
			659	9946	100	460	131[d]	0.5
2	(*2*)	Authors (*9*)	343	4494	206	527	111	..
3	(*15*)	Authors	202	9946	100	460	153	..
4	(*2, 15*)	Authors	343	4494	206	527	111	0.42
			202	9946	100	460	153	0.58

[a] Corresponding values of γ for each coefficient set given in Tables II, IV, and V.
[b] Data of Kemp and Egan (*11*) employed for adjustment of coefficients to predict vapor pressures.
[c] Three states with specific volume less than 1.6 cu. ft./lb. mole excluded by Benedict *et al.*
[d] States excluded for which Z was less than Z_c and for which the temperature was greater than 460° F.

From the experimental data indicated in Figure 1 the coefficients of the Benedict equation (*6*) were predicted by use of conventional least squares procedures (*9, 13, 17*). An appropriate solution of the normal equations was obtained for several values of γ. A listing of the several sets of experimental data and the corresponding values of γ that have been used is shown in Table I. Identification numbers and letters have been used to designate independently the set of data employed in a particular calculation and the several values of γ chosen for investigation. It should be realized that the letter designations are not interchangeable between different sets of data.

Table II presents 10 sets of coefficients for propane evaluated by the described method, with several measures of the agreement with the experimental data shown in Figure 1. For comparison the coefficients of Benedict are included. In Figure 2 the average standard error of estimate of the compressibility factor is shown as a function of γ. In this instance all the error was assumed to be in pressure, and thus rather large uncertainties would be expected at low temperatures and pressures in the liquid phase. It is apparent that the behavior of the standard errors for positive and negative values of γ is similar to that which was predicted qualitatively (*9*). Assuming that c is always finite, for an infinite value of γ, Equation 1 reduces to

$$Z_e = 1 + \left(B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3}\right) d + \left(b - \frac{a}{RT}\right) d^2 + a\alpha \frac{d^5}{RT} \quad (2)$$

and for a value of γ of zero, Equation 1 assumes the following special form:

$$Z_e = 1 + \left(B_0 - \frac{A_0}{RT} - \frac{C_0}{RT^3}\right) d + \left(b - \frac{a}{RT}\right) d^2 + a\alpha \frac{d^5}{RT} + \frac{cd^2}{RT^3} \quad (3)$$

An interpolated minimum value of the standard error of estimate is obtained for a value of γ of approximately 4.135. The standard error of estimate for this case is approximately 80% of that obtained by using Benedict's coefficients (*6*) for data limited to pressures below 4500 pounds per square inch. It should be emphasized that the standard errors of estimate shown in a part of Table II and in Figure 2 are based upon the premise that all the error is in the pressure and none in either the temperature or specific volume.

In order to check the standard errors of estimate shown in Table II and Figure 2, a number of values of the compressibility factor were computed from each of five different sets of coefficients corresponding to widely different values of γ. The detailed results of these calculations are available (*13, 16*). The average relative deviations as functions of temperature for coefficient sets 1-A, 1-C, 1-G, and 1-J are shown in Table III. In addition, the average deviations obtained when using Benedict's coefficients (*4, 6*) were included. Reasonable agreement between the deviations recorded in Table II and Table III was obtained. Precise agreement is not to be expected since the deviations shown in Table II were based upon 214 experimental points whereas only 42 points were used to develop the data presented in Table III. These comparisons assume that all the error is in the pressure and that the volume and temperature were established.

In a second part of Table III a similar comparison is made for Benedict's coefficients and set 1-C using volume as the dependent variable. A graphical comparison of the deviations from experiment for coefficient set 1-C is presented in Figure 3. The effect of choice of dependent variable and the trends with temperature and pressure are indicated. When volume is the dependent variable, the deviation is greatest at intermediate pressures for the gas phase, whereas when the pressure is the dependent variable the greatest error is found at low temperatures and pressures for the liquid phase.

In the foregoing comparison no states were employed for which values of the compressibility factor were smaller than the experimentally determined compressibility factor at the critical state. Figure 4 shows the range of conditions covered by Beattie and coworkers (*2*). These data were employed by Benedict (*4, 6*) in predicting coefficients for his equation of state. Three experimental points at low specific volume shown in this figure with a separate designation were not used by Benedict in his calculations. Table IV records several sets of coefficients for the Benedict equation of state which were computed from the data of

Table II. Coefficients for Benedict Equation of State for Propane

Coefficient	Identification					
	1-A	1-B	1-C	1-D	1-E	1-F
γ	5.65361	4.52289	3.95753	3.39217	2.26144	0.565361
B_0	0.911510	0.765331	0.400735	−0.414751	−0.616434	−0.511265
$A_0 \times 10^{-3}$	23.4245	19.3891	12.7802	0.520830	2.56235	5.96872
$C_0 \times 10^{-9}$	4.10427	5.56129	7.39862	10.02100	7.04527	5.72859
b	5.77322	6.89394	8.18833	9.91381	7.63062	6.65541
$a \times 10^{-3}$	36.4646	58.0494	80.9044	108.2314	61.2673	42.1686
α	2.30632	1.75505	1.44658	1.18657	1.30370	1.51553
$c \times 10^{-9}$	10.9890	17.3119	23.3692	28.7030	9.18664	3.35711
Average standard error of estimate	0.0108[a] 0.0093[b] 0.0121[c]	0.0094	0.0092[a] 0.0066[b] 0.0114[c]	0.0122	0.0203	0.0206 .. ..
Average deviation[d]	..	..	0.0057[b]	..	..	..
Average relative deviation[d]	..	..	0.0108[b]	..	..	..
Average deviation	..	..	−0.0025[b]	..	..	..

Coefficient	Identification				
	1-G	1-H	1-I	1-J	Benedict[e]
γ	0.0000	−0.565361	−5.65361	+ ∞	+5.65170
B_0	−0.824791	1.57611	0.156299	0.411348	1.55997
$A_0 \times 10^{-3}$	2.25654	32.3300	15.2859	17.5190	25.9451
$C_0 \times 10^{-9}$	6.41943	0.513578	3.81056	3.45547	6.21704
b	7.04485	3.57008	5.45457	5.31753	5.78016
$a \times 10^{-3}$	46.4507	2.79954	24.7386	25.3555	57.3552
α	1.35142	22.0732	2.39531	2.50348	2.50044
$c \times 10^{-9}$	4.13518	−4.50779	−0.048834	..	25.2951
Average standard error of estimate	0.0205	0.0206	0.0195	0.0207	0.2158[a] 0.0085[b] 0.305[c]
Average deviation[d]	..	..	..	..	0.00370[f]
Average relative deviation[d]	..	..	..	..	0.0062[f]
Average deviation	..	..	..	..	−0.00043[f]

[a] Average value based on equal weighting of data sets shown in Figure 1.
[b] Based on data of Beattie *et al.* shown in Figure 1 (*2*).
[c] Based on data of Reamer *et al.* shown in Figure 1 (*15*).
[d] Without regard to sign.
[e] Coefficients proposed by Benedict *et al.* on the basis of the following atomic weights: $C = 12.010$, $H = 1.0080$.
[f] Based on data of Beattie *et al.* shown in Figure 4 (*2*) as presented by Brough (*9*).

TABLE III. COMPARISON OF DEVIATIONS OF OBSERVED AND PREDICTED COMPRESSIBILITY FACTORS FOR PROPANE

Identification of Coefficients	100° F.	190° F.	220° F.	340° F.	460° F.
			Pressure as Dependent Variable		
Benedict	0.5469[a]	..	0.1029	0.0262	0.0078
1-C	0.0216	0.0137	0.0135	0.0047	0.0044
1-A	0.0220	..	0.0094	0.00101	0.0076
1-G	0.0240	..	0.0458	0.0126	0.0084
1-J	0.0246	..	0.0454	0.0122	0.0053
4-A	0.0460	0.0141	..	..	..
			Volume as Dependent Variable		
Benedict	0.0289	..	0.0145	0.0110	0.0036
1-C	0.0037	..	0.0089	0.0032	0.0024
Benedict[b]	..	..	0.0051	0.0022	0.0016
2-C[b]	..	..	0.000	0.000	0.000
		206.3°	347.0° F.	482.0° F.	
			Pressure as Dependent Variable		
Benedict[b]		0.0242	0.0055	0.0015	
2-C[b]		0.0066	0.0031	0.0014	

[a] Figures in body of table are average relative deviation without regard to sign.

[b] These comparisons apply only to the experimental data (*2*) used by Benedict (*4, 6*).

Beattie, Kay, and Kaminsky (*2*) shown in Figure 4, extending only to pressures of 4500 pounds per square inch. For the sake of completeness the coefficients recommended by Benedict (*4, 6*) and Brough (*9*) and shown in Table I have been included in Table IV with coefficients evaluated from recent experimental data (*15*).

A comparison of the volumetric behavior observed and predicted from coefficient set 2-C and from the Benedict set is shown in the lower part of Table III for temperatures of 206.3°, 347.0°, and 482.0° F. Similar comparisons with volume as the dependent variable are also shown in another part of Table III. In this instance a much smaller deviation was obtained with values predicted from coefficient set 2-C.

In the gaseous region the agreement with experiment is satisfactory. Comparisons of observed and predicted data (*13*) for high specific weights confirm the need for the use of experimental data throughout the range of conditions for which the Benedict equation is to be employed. The marked variation of coefficients shown in Tables II and IV is an indication of the potentialities of the Benedict equation in interpolating the experimental behavior of hydrocarbon fluids with nearly the same accuracy for widely different sets of coefficients.

In order to ascertain the potentialities of the equation, one set of coefficients was evaluated with all the data from Beattie shown in Figure 4 and the recent data for high pressures depicted in Figure 5 which included a substantial amount of information for the liquid phase (*15*) as well as the data (*2, 15*) for the gas phase which were used in deriving the coefficients of Table II. The coefficients based upon both the liquid and gas phases are recorded in Table V and yield a standard error of estimate which is but little different (*13*) from the minimum value found in Table II. Comparison of predicted and observed behavior with this set of coefficients identified as 4-A is shown in a part of Table III for 100° and 190° F.

TABLE V. COEFFICIENTS[a] FOR BENEDICT EQUATION OF STATE FOR PROPANE APPLICABLE TO LIQUID AND GAS PHASES

γ	4.24021
B_0	0.550703
$A_0 \times 10^{-3}$	15.9131
$C_0 \times 10^{-9}$	6.31535
b	7.41650
$a \times 10^{-3}$	67.1411
α	1.60300
$c \times 10^{-9}$	19.2621
Average standard error of estimate	0.0094

[a] Based upon data group 4 as identified in Table I. Coefficients are identified as set 4-A.

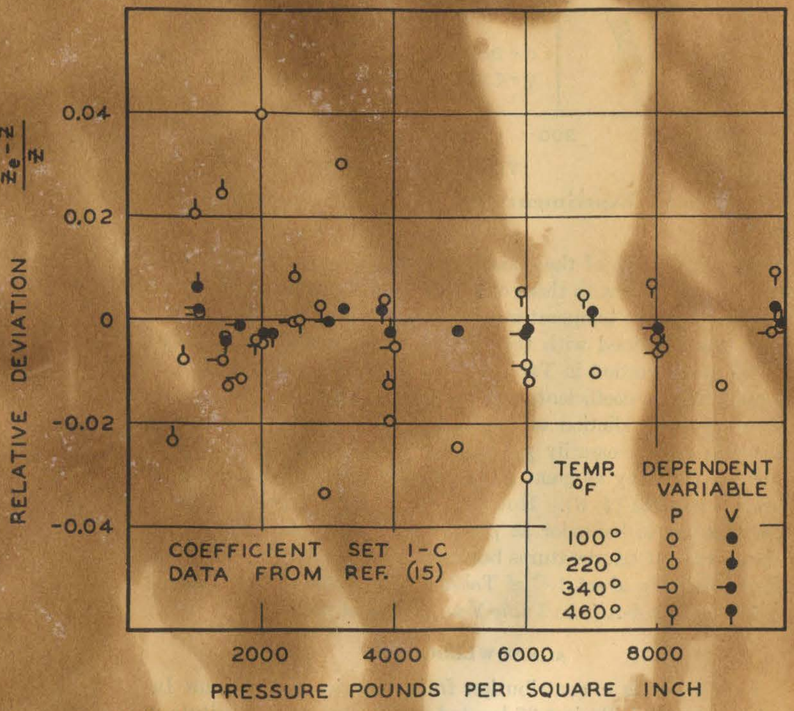

Figure 3. Relative Deviation in Compressibility Factor for One Set of Coefficients

TABLE IV. COEFFICIENTS FOR BENEDICT EQUATION OF STATE FOR PROPANE

Coefficient	Identification								
	Benedict	2-A	2-B	2-C	2-D	2-E	3-A	3-B	3-C
γ	5.65170	5.94629	5.65361	5.37093	4.80557	4.24021	5.65361	4.80557	4.24021
B_0	1.55997	1.59131	1.44801	1.27567	0.770058	0.072770	0.540336	0.484874	0.283876
$A_0 \times 10^{-3}$	25.9451	28.2230	26.0603	23.5130	16.3759	6.77038	20.7841	18.2494	14.1205
$C_0 \times 10^{-9}$	6.21704	5.02389	5.53625	6.12290	7.67489	9.66786	3.58093	4.48459	5.56119
b	5.78016	4.65564	5.15750	5.74018	7.28261	9.40853	6.66571	7.05149	7.63840
$a \times 10^{-3}$	57.3552	35.0889	42.9274	51.8469	74.7481	104.7969	44.0121	53.9029	65.7719
α	2.50044	3.02732	2.63661	2.32171	1.81981	1.43752	1.9012	1.72068	1.53829
$c \times 10^{-9}$	25.2951	17.8654	19.7139	21.7594	26.7975	32.8976	10.379	13.0718	15.8667
Average standard error of estimate	0.0085	0.00340	0.0030	0.0025	0.0025	0.0033	0.0113	0.0100	0.0094
Average deviation[a]	0.00370	0.00273	0.00229	0.00191	..	..	..	..	..
Average relative deviation[a]	0.0062	0.00483	0.00401	0.00332	..	..	..	..	..
Average deviation	−0.0043	−0.00018	−0.00011	−0.00004	..	..	..	..	..

[a] Without regard to sign

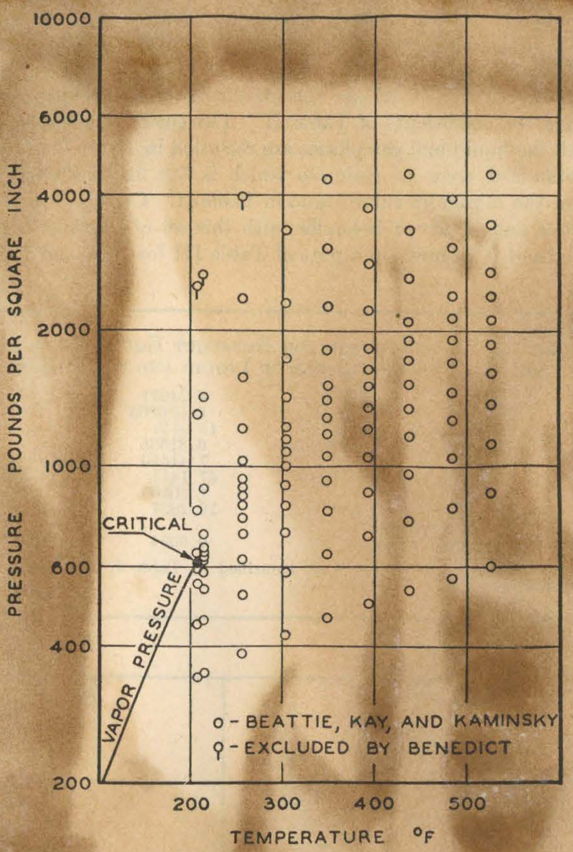

Figure 4. Experimental Data of Beattie for Propane

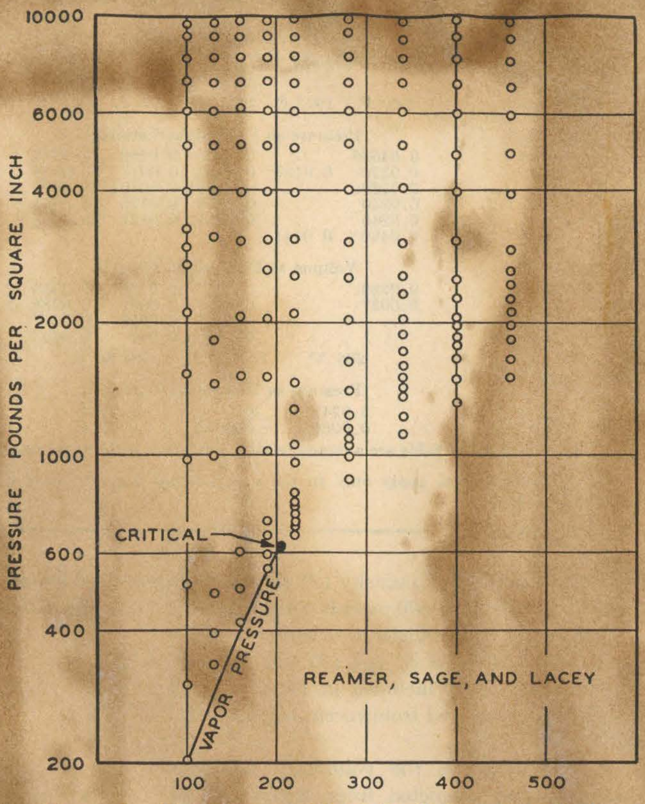

Figure 5. Experimental Data for Propane at High Pressures and Small Specific Volumes

The agreement of the compressibility factors calculated from these coefficients with those obtained by experiment at high pressures and at low temperatures in the liquid phase is much better than was obtained with the coefficients suggested by Benedict (*4, 6*) and recorded in Table II. It should be realized that although the new coefficients recorded in Tables II and V give greater accuracy of prediction of the volumetric behavior of propane, they do not necessarily predict the heterogeneous equilibrium with an accuracy as great as that obtained from coefficients already available (*4, 6*). However, if accurate representation of the volumetric behavior at pressures up to 10,000 pounds per square inch at temperatures between 100° and 460° F. is desired, the coefficients of set 1-C of Table I for a value of γ of 3.95753 or those of set 4-A from Table V appear to be satisfactory.

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NOMENCLATURE

$A_0, a, B_0, b,$
C_0, c, α, γ = coefficients of Benedict equation of state
d = molal weight, lb. mole/cu. ft.
M = molecular weight, lb./lb. mole = 44.094
P = absolute pressure, lb./sq. inch absolute
R = universal gas constant, (lb./sq. inch) (cu. ft.)/(lb. mole)(°R.) = 10.73147
T = absolute temperature, °R.
Z = compressibility factor PV/RT
$\hat{\sigma}$ = average standard error of estimate

Subscripts

c = critical state
e = value of property calculated by using Benedict equation of state

LITERATURE CITED

(1) Beattie, J. A., *Chem. Revs.*, **44**, 141–92 (1949).
(2) Beattie, J. A., Kay, W. C., and Kaminsky, J., *J. Am. Chem. Soc.*, **59**, 1589–90 (1937).
(3) Benedict, M., *Ibid.*, **59**, 2224–33 (1937).
(4) Benedict, M., Webb, G. B., and Rubin, L. C., *Chem. Eng. Progr.*, **47**, 419–22 (1951).
(5) *Ibid.*, pp. 449–54.
(6) Benedict, M., Webb, G. B., and Rubin, L. C., *J. Chem. Phys.*, **8**, 334–45 (1940).
(7) *Ibid.*, **10**, 747–58 (1942).
(8) Benedict, M., Webb, G. B., Rubin, L. C., and Friend, L., *Chem. Eng. Progr.*, **47**, 609–20 (1951).
(9) Brough, H. W., Schlinger, W. G., and Sage, B. H., IND. ENG. CHEM., **43**, 2442–6 (1951).
(10) Connolly, T. J., Frankel, S. P., and Sage, B. H., *Elec. Eng.*, **70**, 47 (1950); Am. Doc. Inst., Washington, D.C., Doc. No. 3036 (1951).
(11) Kemp, J. D., and Egan, C. J., *J. Am. Chem. Soc.*, **60**, 1521–5 (1938).
(12) Marchman, H., Prengle, H. W., Jr., and Motard, R. L., IND. ENG. CHEM., **41**, 2658–60 (1949).
(13) Opfell, J. B., and Sage, B. H., Washington, D. C., Am. Doc. Inst., Doc. No. 3849 (1952).
(14) Prengle, H. W., Jr., and Marchman, H., IND. ENG. CHEM., **42**, 2371–4 (1950).
(15) Reamer, H. H., Sage, B. H., and Lacey, W. N., IND. ENG. CHEM., **41**, 482–4 (1949).
(16) Selleck, F. T., and Sage, B. H., Washington, D. C., Am. Doc. Inst., Doc. No. 3914 (1953).
(17) Whittaker, E. T., and Robinson, G., "The Calculus of Observations," London, Blackie and Sons Ltd., 1940.

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APPENDIX G

CHARACTERISTICS OF THE CRITICAL STATE

For a one-component system, two of the principal characteristics of the critical state are the following

$$(\partial f/\partial \underset{\cdot}{\sigma})_{T,m} = 0 \qquad (76)$$

$$(\partial^2 f/\partial \underset{\cdot}{\sigma}^2)_{T,m} = 0 \qquad (77)$$

Consequently

$$(\partial \ln f/\partial \underset{\cdot}{\sigma})_{T,m} = 0 \qquad (161)$$

$$(\partial^2 \ln f/\partial \underset{\cdot}{\sigma}^2)_{T,m} = 0 \qquad (162)$$

But

$$(\partial \ln f/\partial \underset{\cdot}{\sigma})_{T,m} = (\underset{\cdot}{V}/RT)(\partial P/\partial \underset{\cdot}{\sigma})_{T,m} \qquad (163)$$

and so

$$\left(\frac{\partial^2 \ln f}{\partial \underset{\cdot}{\sigma}^2}\right)_{T,m} = \frac{\underset{\cdot}{V}}{R\ T}\left(\frac{\partial^2 P}{\partial \underset{\cdot}{\sigma}^2}\right)_{T,m} - \frac{\underset{\cdot}{V}^2}{R\ T}\left(\frac{\partial P}{\partial \underset{\cdot}{\sigma}}\right)_{T,m} \qquad (164)$$

Hence

$$(\partial P/\partial \underset{\cdot}{\sigma})_{T,m} = 0 \qquad (79)$$

$$(\partial^2 P/\partial \underset{\cdot}{\sigma}^2)_{T,m} = 0 \qquad (80)$$

at the critical state.

Propositions submitted by John Burton Opfell

Ph.D. Oral Examination, December 4, 1953 at 9:00 A.M., Crellin Conference Room.
Committee: Professors Sage (Chairman), Corcoran, Niemann, Schomaker and Ward.

Mathematics.

1. Newton's method for the extraction of square root is but a special case of the more general iterative method which is described by the formula

$$(b)^{1/n} = \lim_{i \to \infty} x_i$$

$$x_i = \frac{1}{n}\left((n-1)x_{i-1} + b/x_{i-1}^{n-1} \right)$$

This iteration is second order[1] and consequently converges rapidly even for crude starting values. In many applications of automatic digital computers, the use of such efficient iterative processes as this are more convenient than the use of tables for transcendental functions.

2. The hydrodynamic and heat transfer equations associated with a rotating infinite flat plate have been solved exactly[2]. This solution should be extended, through numerical methods, if necessary, to the case in which a rigid wall is located at a finite distance from the axis of rotation. Such a solution would be helpful in the design of mixing vessels and in the design of cyclone dryers for heat sensitive materials such as milk.

3. Hartree[3] proposes that ill-conditioning of simultaneous linear equations can be given quantitative significance in terms of the ratio of the largest to the smallest latent root of the matrix of the coefficients. Since this matrix may be changed by multiplication of any row by a constant, without changing the solution of the system of equations, the value of this ratio may change also.

Chemistry.

4. The theory of steady-state thermodynamics implies a coupling effect[4] between the rate of momentum transport and the progress of chemical change in fluid systems. The effect has not yet been observed experimentally. Since such an effect would be useful in controlling reactions rates, an investigation into the magnitude of this effect would be most worthwhile.

5. Kuhn and Silberberg[5] have reported that in a field of shear, they observed a shift in the mutual solubility of two liquid phases. This phenomenon should be interpreted on the basis of steady-state

thermodynamics rather than on the basis of equilibrium thermodynamics. The fact that steady and non zero temperature gradients exist in a field of shear in viscous fluids makes the direct observation of temperature very difficult. It seems likely that in part the reported phenomenon can be explained by the existence of a steady non-uniform temperature distribution in the system investigated.

Chemical Engineering.

6. Coefficients for the Benedict equation for the reduced volumetric properties would be most useful for extrapolating the volumetric properties of compounds and mixtures for which little volumetric information is available. The success of the pseudo-critical concept suggests the possibility of describing the volumetric properties of a broad class of compounds in terms of the reduced coefficients for the Benedict equation and of three numbers which correspond to the effective critical properties.

7. Gemant[6] has proposed a correlation between the viscosity coefficient and the compressibility for liquids and plastics. Since, the viscosity and diffusivity are correlated in fluid systems, a similar correlation between diffusivity and the compressibility should be possible for fluid systems. Such a correlation would be most useful in practice since the elastic properties can be obtained easily from velocity of sound measurements.

8. Pohlhausen[7] has integrated the hydrodynamic equations describing the temperature distribution in the boundary layer arising from the flowing of a viscous in compressible fluid along a flat plate. A study of the results showed that the recovery factor was very nearly equal to the square root of the Prandtl number Pr for Prandtl numbers near unity. The same equations may be integrated for the case of a fluid flowing between parallel plates to give a recovery factor of 54/35 Pr. The indiscrimant use of the relation

$$\text{recovery factor} = (\text{Prandtl number})^{\frac{1}{2}}$$

is to be discouraged.

9. Bernoulli's theorem is a special case of the more general theorem

$$dh + \frac{du^2}{2g} + V \frac{\partial p}{\partial x} dx + j' + \zeta' = 0$$

which applies at every point in a moving fluid. The function represents the infinitesimal amount of work which an infinitesimal element of the fluid, considered as a closed system, does upon its surroundings as a result of its velocity relative to its surroundings and the forces acting at the boundary. $j'/d\theta$ is the Reynolds dissipation function and x is distance along the streamline. This more general theorem is a consequence only of the conservation of momentum and the definition of work.

h	elevation (feet)
u	speed, ft/sec
p	pressure, p.s.i.a.
g	gravitational constant

10. When stripping a volatile component A , from a relatively nonvolatile absorbent low pressure operation is usually desirable. Since the equilibrium distribution of the component being stripped is described by the equation

$$Y = \frac{KX}{1-(K-1)X}$$

it is apparent that the stripping gas carries away the highest concentration of A when $1 - (K-1)X$ is zero. For a given feed stock, i.e., fixed value of X, K should be as nearly unity as possible. In hydrocarbon systems[8], at a given temperature K is unity at the critical state as well as at a pressure which is approximately the vapor pressure of pure A at that temperature. Consequently, there should exist situations in which stripping operations might be performed at pressures nearer to the critical pressure of the system than at nearly vapor pressure. The advantages to arise from use of such pressures would result from the small specific volume of the gas phase.

11. When at rest many types of powders and finely divided solids are unable to support a shear stress in the bulk. This property is a characteristic feature of fluids. The analysis of the flow of powders through orifices and short tubes might profitably be made on the basis of the equations of motion for fluid and the use of an effective viscosity coefficient for the powder.

Nomenclature

K	equilibrium vaporization ratio
Pr	Prandtl number
X	lb. moles of A per lb. mole of solute-free absorbent
Y	lb. moles of A per lb. mole of solute-free stripping gas

References

1. D. R. Hartree. Numerical Analysis, Oxford, London, (1952), p. 192.

2. K. Millsaps, and K. Pohlhausen. "Heat Transfer by Laminar Flow from a Rotating Plate." Wright Air Development Center, Navy Research Section, U20674, (1951).

3. D. R. Hartree, op. cit. p. 153.

4. J. O. Hirschfelder, C. F. Curtiss, R. B. Bird, and E. L. Spotz. "The Properties of Gases," Univ. of Wisc. CFs 1501A and 1510A. 31 July 1952, NOrd 9938, p. 25.

5. W. Kuhn and A. Silberberg. Nature, 170, 450, (1952).

6. A. Gemant. Frictional Phenomena, Chemical Publishing Co., Brooklyn, (1950), Chapt. XIV.

7. E. Pohlhausen. Zeit. angw. Math. Mech., Bd. 1, 115, (1921).

8. M. J. Rzasa, E. D. Glass, and J. B. Opfell. Chem. Eng. Prog. Symposium Series, 48, 2, 28, (1952).