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An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures

I. Methane, Ethane, Propane and *n*-Butane

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An empirical equation is given for the isothermal variation with density of the work content of pure hydrocarbons in the gaseous or liquid state. From this fundamental equation are derived (a) an equation of state, (b) an equation for the fugacity, and (c) an equation for the isothermal variation of the enthalpy. These equations summarize P-V-T properties of the gaseous or liquid phase, critical properties, vapor pressures, and latent heats of evaporation. A procedure is suggested for determining numerical values of the parameters in the equation. Such values are given for methane, ethane, propane, and *n*-butane. A comparison is made between observed properties of these hydrocarbons and those predicted by the equations.

A. Introduction

Recent experimental studies of pure light hydrocarbons by Sage and Lacey and co-workers and by Beattie and co-workers are useful in developing an equation to represent the thermodynamic properties of these substances. An equation for this purpose has several advantages: it permits interpolation of experimental data; it facilitates thermodynamic calculations involving integration and differentiation; it provides a concise summary of a large mass of data; and it provides a point of departure for the treatment of the thermodynamic properties of mixtures.

Concurrent with this advance in experimental knowledge there has taken place development of statistico-mechanical methods for deducing the thermodynamic properties of fluids in bulk from the interaction energies of aggregates of the constituent molecules. A method for the rigorous treatment of this problem, as applied to gases, was first given by Ursell[1] and has recently been extended and clarified by Mayer and coworkers.[2] A less rigorous treatment, leading to a single equation describing the thermodynamic properties of both the liquid and gaseous phases, has been given by Lennard-Jones and coworkers.[3] These theoretical treatments are particularly valuable for suggesting the correct qualitative features of suitable equations. They do not lead to simple expressions in terms of familiar functions, and in the present state of our knowledge of molecular fields, they do not lead to correct numerical values for the properties of matter in bulk. It has, therefore, seemed worth while to attack the problem of representing the thermodynamic properties of hydrocarbons from a more empirical standpoint, and to use the theoretical results only to suggest the proper general characteristics of the formulation.

These theoretical analyses demonstrate that the phase integral summarizing all thermodynamic properties of a fluid may be expressed as the product of two factors, one arising from the internal degrees of freedom of each molecule and the other arising from the interaction energies between aggregates of two or more molecules. From the first factor may be derived equations for the specific heats, entropy, work content, and free energy of the fluid in the hypothetical ideal gas state. From the second factor may be derived equations for the difference between the thermodynamic properties of a real gas or liquid and the corresponding properties of the fluid in the hypothetical ideal gas state. The object of the present paper is to present an empirical equation for this second class of properties.

Definition of terms

Our equation expresses the isothermal variation with density of the work content A of a mole of gaseous or liquid hydrocarbons. The work content is also known as the Helmholtz free energy or the Gibbs ψ-function; it is related to the internal energy E, absolute temperature T, and entropy S by the equation

$$A=E-TS.$$

We are concerned with the residual work content $\tilde{A}$, here defined as the difference between the work content of a mole of hydrocarbons at molal density d and absolute temperature T and its work content in the hypothetical ideal gas state at the same density and temperature. The residual work content $\tilde{A}$ may be defined more rigorously by the equation:

$$\tilde{A}=A-RT\ln d-\lim_{d\to 0}(A-RT\ln d). \qquad \text{(A1)}$$

The method of Ursell and Mayer may be used to prove that the limit occurring in Eq. (A1) exists and is finite.

An equation of the form (A1) is a fundamental equation in the sense that from it a number of thermodynamic properties of the fluid may be computed, no one of which alone would permit the computation of all the others. The thermodynamic properties of a fluid which may be computed from the fundamental equation of this paper include: (1) P-V-T properties of the gas or liquid phase. (2) Critical properties. (3) The effect of pressure on the enthalpy. (4) The effect of pressure on the free energy; i.e., the fugacity. (5) Vapor pressures. For instance, an equation of state in which the pressure P is expressed as a function of the density and temperature may be obtained by the relation:

$$P=RTd+d^2(\partial\tilde{A}/\partial d)_T. \qquad \text{(A2)}$$

The fugacity f is given by:

$$RT\ln f=\tilde{A}+RT\ln dRT+P/d-RT, \qquad \text{(A3)}$$

and the isothermal variation of the enthalpy H by:

$$H(T,d)-H(T,0)=-T^2\left(\frac{\partial\tilde{A}/T}{\partial T}\right)_d+P/d-RT. \qquad \text{(A4)}$$

Conversely, the residual work content of the gas phase may be obtained by integration of an equation of state:

$$\tilde{A}=\int_0^d\frac{P-RTd}{d^2}\delta d. \qquad \text{(A5)}$$

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[1] Ursell, Proc. Camb. Phil. Soc. **23**, 685 (1927).

[2] Mayer, J. Chem. Phys. **5**, 67 (1937); Mayer and Ackermann, *Ibid.* 74; Mayer and Harrison, *Ibid.* **6**, 87, 101 (1938).

[3] Lennard-Jones and Devonshire, Proc. Roy. Soc. London **A163**, 53 (1937).

Relationship to other equations of state

Of the many equations of state that have been proposed perhaps the best known are the van der Waals and the Beattie-Bridgeman equations. The van der Waals[4] equation,

$$P=\frac{RTd}{1-bd}-ad^2, \qquad \text{(A6)}$$

has the advantage of simplicity, and for this reason is often used in discussing the thermodynamic relationships of the gaseous and liquid states and the critical region between them. By substituting the van der Waals equation of state (A6) in (A5), Eq. (A7) for the residual work content of the gas phase is obtained:

$$\tilde{A}=-RT\ln(1-bd)-ad. \qquad \text{(A7)}$$

When derived in this way, Eq. (A7) applies rigorously only to the gas phase. In the van der Waals theory of the continuity of the liquid and gaseous states the assumption is made that this equation is valid for the liquid phase, as well. From this standpoint, Eq. (A7) is the fundamental equation of the van der Waals theory for both the gaseous and liquid phases. It may be used to calculate the equation of state and fugacity of either phase, and from them, the vapor pressure. Vapor pressures calculated in this way from the van der Waals equation are in only qualitative agreement with observed vapor pressures. This need not invalidate the significant assumption of the van der Waals theory, that a single fundamental equation can be found for both the liquid and gaseous phases, as the discrepancy may be due to the recognized failure of the van der Waals equation to correspond accurately to observed P-V-T data.

Among the many equations of state which have been proposed as improvements on the van der Waals equation, the Beattie-Bridgeman[5] equation,

$$\begin{aligned}P=RTd&+(B_0RT-A_0-Rc/T^2)d^2\\&+(-B_0bRT+A_0a-RB_0c/T^2)d^3\\&+RB_0bcd^4/T^2, \qquad \text{(A8)}\end{aligned}$$

has, perhaps, most satisfactorily combined mathematical simplicity with accurate representation of P-V-T data over a wide temperature range. In its present form the Beattie-Bridgeman equation does not correspond accurately with the P-V-T properties of liquids or gases above their critical density, so that it cannot be used to calculate the residual work content above this density or the vapor pressure.

The present equation

The equation of state proposed in this article may be regarded as a modification of the Beattie-Bridgeman equation to enable it to represent more accurately the properties of fluids at high densities. The van der Waals assumption of the continuity of the liquid and gaseous states is retained, in that a common fundamental equation and a common equation of state are used for both gaseous and liquid phases. The fundamental equation proposed for expressing the dependence of the residual work content $\tilde{A}$ of a mole of gaseous or liquid hydrocarbon on the molal density d and absolute temperature T is:

$$\begin{aligned}\tilde{A}=&(B_0RT-A_0-C_0/T^2)d\\&+(bRT-a)d^2/2+a\alpha d^5/5\\&+\frac{cd^2}{T^2}\left[\frac{1-\exp(-\gamma d^2)}{\gamma d^2}-\frac{\exp(-\gamma d^2)}{2}\right]. \qquad \text{(A9)}\end{aligned}$$

The equation of state corresponding to (A9) is:

$$\begin{aligned}P=RTd&+(B_0RT-A_0-C_0/T^2)d^2\\&+(bRT-a)d^3+a\alpha d^6\\&+\frac{cd^3(1+\gamma d^2)\exp(-\gamma d^2)}{T^2}. \qquad \text{(A10)}\end{aligned}$$

The isometrics of this equation of state have the same form as the isometrics of the Beattie-Bridgeman equation:

$$P=T\psi(d)-\phi(d)-\Gamma(d)/T^2. \qquad \text{(A11)}$$

The parameters B_0, A_0, and C_0 of Eq. (A10) play the same role and have about the same numerical values as corresponding parameters in the Beattie-Bridgeman equation. The parameters b, a, c, γ, and α are not directly related to any occurring in the Beattie-Bridgeman equation.

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[4] Van der Waals, *Die Continuität des Gasförmigen und Flüssigen Zustandes* (Barth, Leipzig, 1899).

[5] Beattie and Bridgeman, Proc. Am. Acad. Arts Sci. **63**, 229 (1928).

B. Considerations Influencing Adoption of Present Equation

The work of Ursell and Mayer may be used to prove that the residual work content $\tilde{A}$ of a gas can be expressed by the series

$$\tilde{A}=Q_1(T)d+Q_2(T)d^2+\cdots, \qquad \text{(B1)}$$

convergent in the region of stable existence of the gas phase. An equation for both the gaseous and liquid phases was sought which would reduce to (B1) at low densities, which would constitute a suitable compromise between simplicity of application and accurate correspondence with observed thermodynamic properties of gases and liquids, which would contain a minimum number of independent parameters to be fitted numerically, and which would summarize as well as possible the following classes of properties: (1) P-V-T properties of the gas phase. (2) Critical properties. (3) Vapor pressures. It is believed that emphasis on these properties results in the most generally satisfactory equations for pure light hydrocarbons on which to base the prediction of liquid-vapor equilibria of their mixtures. This is the ultimate object of the project described in part in this article.

The functional form of the equation finally adopted as most satisfactorily filling these three requirements was determined primarily from an examination of the P-V-T properties of the gas phase; then, for each hydrocarbon, the best numerical values of the parameters in the equation were estimated from a consideration of all three classes of properties.

Equation of state

In developing the equation of state, attention was first directed to the isometrics of $(P-Rtd)/d^2$ *versus* temperature; these are very nearly straight. For each hydrocarbon it was found that these isometrics could be represented by an equation of the form:

$$(P-RTd)/d^2=RTB(d)-A(d)-C(d)/T^2. \qquad \text{(B2)}$$

These isometrics are illustrated with the example of propane in Fig. 1. The plotted points are derived from the observed pressures of Beattie, Kay and Kaminsky;[6] the lines represent the equation of state for propane given in Section D.

Equations, consistent with expression (B1), were then sought to express the dependence of

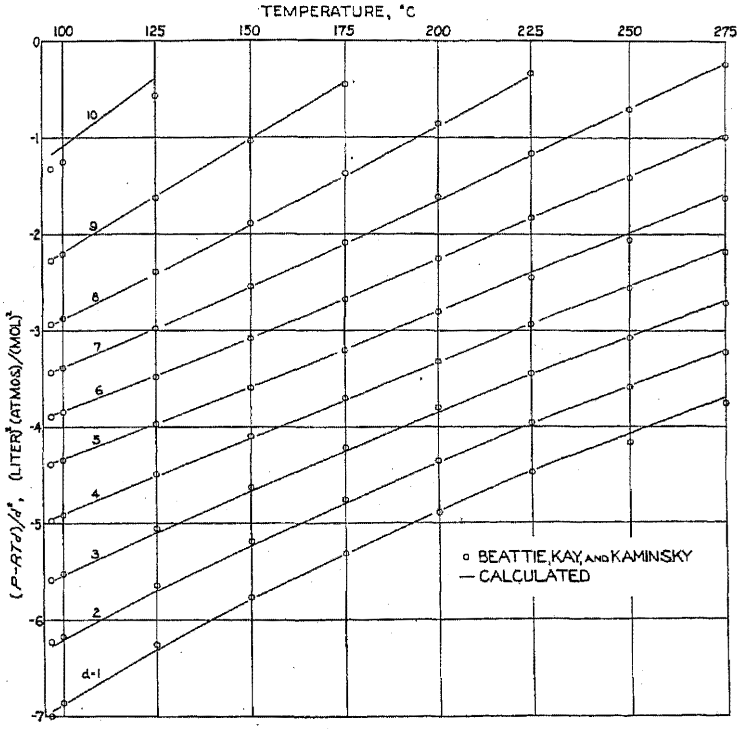

FIG. 1. Isometrics of gaseous propane.

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[6] Beattie, Kay and Kaminsky, J. Am. Chem. Soc. **59**, 1589 (1937).

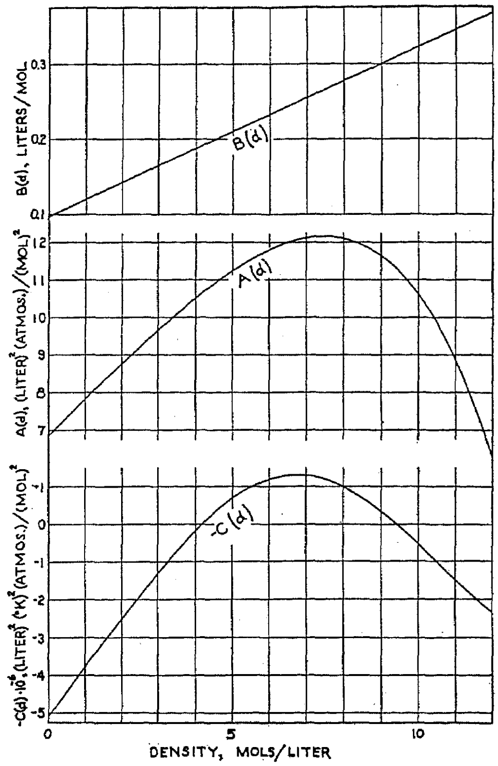

FIG. 2. Functions of density in equation of state.

$B(d)$, $A(d)$, and $C(d)$ on density. It was found that $B(d)$ could be represented by the simple linear equation

$$B(d)=B_0+bd, \tag{B3}$$

but that plots of $A(d)$ and $C(d)$ against density showed marked curvature. $A(d)$ was finally represented by an equation of the form:

$$A(d)=A_0+ad(1-\alpha d^3), \tag{B4}$$

and $C(d)$ by an equation of the form:

$$C(d)=C_0-cd(1+\gamma d^2)\exp(-\gamma d^2). \tag{B5}$$

A simple polynomial would have sufficed to express $C(d)$ for the gas phase, but in order to represent the fugacities of the liquid phase at high densities and low temperatures, the more complicated expression (B5) was required.

The functions $B(d)$, $A(d)$, and $C(d)$ for propane are illustrated in Fig. 2. The same qualitative features of these functions were found for each hydrocarbon studied. The properties of $C(d)$ are of especial interest. Since

$$(\partial^2P/\partial T^2)_d=-6d^2C(d)/T^4, \tag{B6}$$

$-C(d)$ has the sign of the curvature of the isometrics. It appears to be a general rule that the isometrics of the gas phase at densities less than the critical have negative curvature.[5] Near the critical density the curvature of the isometrics becomes positive, as first noted by Sydney Young.[7] The isometrics of the compressed liquid phase at still higher density have negative curvature, as shown by Bridgman.[8] These properties of the isometrics of real gases and liquids are paralleled by Eq. (B5) for $C(d)$. As shown in Fig. 2, $-C(d)$ is negative up to approximately the critical density. Between this density and about twice the critical density, it is positive. Above twice the critical density, in the region corresponding to the compressed liquid, $C(d)$ is again negative.

When expressions (B2), (B3), (B4), and (B5)

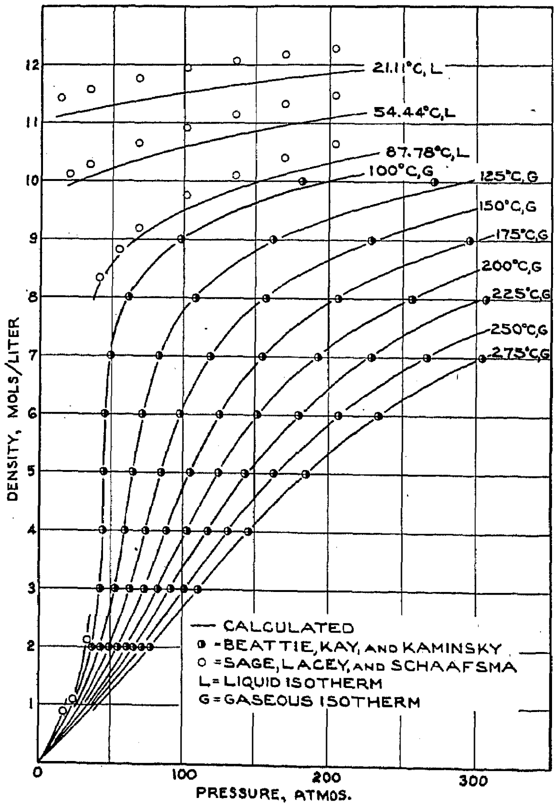

FIG. 3. Isotherms of propane.

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[7] Young, Proc. Phys. Soc. London **13**, 602 (1895).
[8] Bridgman, Proc. Am. Acad. Arts Sci. *66*, 185 (1931).

are combined, the equation of state (B7) is obtained. This is the isometric form of

$$P = RTd + d^2\left\{RT[B_0 + bd] - [A_0 + ad - a\alpha d^4] - \frac{1}{T^2}[C_0 - cd(1 + \gamma d^2)\exp(-\gamma d^2)]\right\}, \quad \text{(B7)}$$

Eq. (A10), useful in computing pressures at constant density. This equation is integrable and differentiable with respect to density, volume, and temperature. Its eight parameters is the smallest number with which the P-V-T properties of the gas phase could be represented up to about twice the critical density. In Section E it is shown that the average error in calculated pressures up to this density is only 0.34 percent. Owing primarily to limitations in Eq. (B4) for $A(d)$, the error at higher densities becomes much larger; better agreement at higher densities could not have been obtained without the use of several more parameters.

To illustrate in terms of familiar properties the agreement of equation of state (B7) with observed data, isotherms of density versus pressure for propane are plotted in Fig. 3. This figure is typical of all hydrocarbons studied. The complex dependence of density on pressure, especially near the critical temperature, 96.8°C, is clearly shown. Up to 9 moles per liter, about twice the critical density, the equation of state accurately reproduces this dependence. Above this density, the equation predicts densities too low by from 2 to 3 percent, because of the limitations of the equation noted in the preceding paragraph.

Critical properties

Since the equation of state (B7) reproduces observed P-V-T properties of the gas phase in the critical region, it necessarily satisfies our second requirement, that it summarize observed critical properties. Except for methane, calculated and observed critical temperatures and pressures agree within 0.25°C and 0.4 atmos., respectively. However, it should be noted that our equation describes what may be termed the "classical" picture of the critical region between liquid and vapor; at each temperature below the critical point it leads to only one pair of phases of different densities which can be in equilibrium. This picture differs from the recent observations of Maass[9] and the predictions of the theory of Mayer,[2] which indicate that for several degrees below the critical temperature it is possible for an infinite number of phases of different density to coexist.

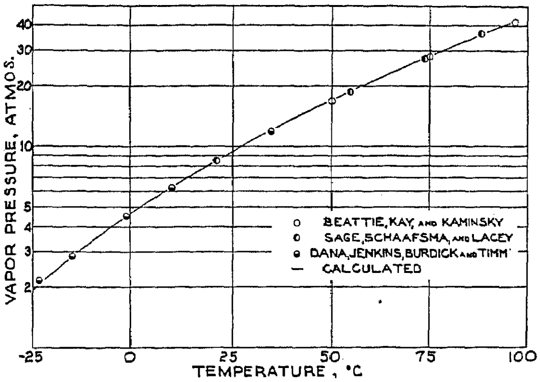

FIG. 4. Vapor pressure of propane.

Vapor pressures

The fundamental equation (A9), summarizing P-V-T properties of both phases, critical properties, and vapor pressures, was developed from the equation of state as follows.

(1) An equation for the residual work content of the gas phase was obtained by substitution of equation of state (B7) in the thermodynamic relation (A5).

(2) It was then assumed that the resulting Eq. (A9) was valid for the liquid phase also, as in the van der Waals treatment of the continuity between the gaseous and liquid states.

This assumption may be tested by seeing how well vapor pressures computed from an equation of the form (A9) agree with observed data. Detailed comparison between observed and calculated vapor pressures is deferred to Section E. Here it may be stated that the average error in calculated vapor pressures above one atmosphere is only 1.1 percent. This justifies the use of Eq. (A9) as a fundamental equation for both the gaseous and liquid phases.

Figure 4 illustrates vapor pressures of propane predicted by the equation and those observed by various authorities. Approximately the same

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[9] Maass, Chem. Rev. 23, 17 (1938).

agreement is found for vapor pressures of methane, ethane, and n-butane.

To calculate vapor pressures from the fundamental equation (A9), Eq. (B8) for the fugacity f is first obtained from it by the thermodynamic relation (A3).

$$\begin{aligned} RT\ln f = {} & RT\ln dRT+2d(B_0RT-A_0-C_0/T^2) \\ & +3d^2(bRT-a)/2+6a\alpha d^5/5 \\ & +\frac{cd^2}{T^2}\left[\frac{1-\exp(-\gamma d^2)}{\gamma d^2}\right. \\ & \left.+\frac{\exp(-\gamma d^2)}{2}+\gamma d^2\exp(-\gamma d^2)\right]. \qquad \text{(B8)} \end{aligned}$$

A gaseous density d^G and a liquid density d^L are found by trial such that

$$P(d^G,T)=P(d^L,T) \qquad \text{(B9)}$$

and

$$RT\ln f(d^G,T)=RT\ln f(d^L,T). \qquad \text{(B10)}$$

P is the calculated vapor pressure at absolute temperature T.

Isothermal variation of enthalpy

From fundamental equation (A9) and thermodynamic relation (A4) it is possible to derive an equation for the change in enthalpy H with density at constant temperature. We obtain:

$$\begin{aligned} H(T,d)-H(T,0) = {} & (B_0RT-2A_0-4C_0/T^2)d \\ & +(2bRT-3a)d^2/2+6a\alpha d^5/5 \\ & +\frac{cd^2}{T^2}\left[3\frac{1-\exp(-\gamma d^2)}{\gamma d^2}\right. \\ & \left.-\frac{\exp(-\gamma d^2)}{2}+\gamma d^2\exp(-\gamma d^2)\right]. \qquad \text{(B11)} \end{aligned}$$

Eq. (B11) may be used to compute the change in enthalpy of the gas upon isothermal expansion or to compute the latent heat of evaporation of the liquid. In the latter application, the densities of the saturated liquid and vapor which satisfy Eqs. (B9) and (B10) above should be used, rather than the observed saturation densities.

Simplified equations for the gas phase

It is an advantage of the present formulation that simpler equations can be used when the density does not exceed one-half the critical density. When fundamental equation (A9) is expanded in ascending powers of the density, we obtain:

$$\begin{aligned} \tilde{A} = {} & (B_0RT-A_0-C_0/T^2)d \\ & +(bRT-a+c/T^2)d^2/2 \\ & +a\alpha d^5/5-c\gamma^2d^6/12T^2+\cdots. \qquad \text{(B12)} \end{aligned}$$

At low densities the terms in the fifth and higher powers of d may be neglected in comparison with the others. We then have for the fundamental equation:

$$\tilde{A}=Q_1d+Q_2d^2,$$

where

$$\begin{aligned} Q_1 &= B_0RT-A_0-C_0/T^2, \\ Q_2 &= (bRT-a+c/T^2)/2; \end{aligned} \qquad \text{(B13)}$$

for the equation of state:

$$P=RTd+Q_1d^2+2Q_2d^3; \qquad \text{B(14)}$$

for the fugacity:

$$RT\ln f=RT\ln dRT+2Q_1d+3Q_2d^2; \qquad \text{(B15)}$$

and for the isothermal variation of the enthalpy:

$$\begin{aligned} H(T,d)-H(T,0) = {} & (B_0RT-2A_0-4C_0/T^2)d \\ & +(2bRT-3a+5c/T^2)d^2/2. \qquad \text{(B16)} \end{aligned}$$

The fundamental equation (B13) for the gas phase at low densities is in the form (B1) required by general statistico-mechanical considerations, except that a definite temperature dependence is here proposed for the coefficients Q_1 and Q_2. It may be noted that Q_1 and Q_2 are related to the coefficients in the "virial" equation of state,

$$P/RTd=1+\beta_1d+\beta_2d^2+\cdots, \qquad \text{(B17)}$$

as follows:

$$\beta_1=Q_1/RT \qquad \text{(B18)}$$

and

$$\beta_2=2Q_2/RT. \qquad \text{(B19)}$$

Table I indicates the order of magnitude of the errors made by using the simplified equations.

TABLE I. *Comparison of simplified and complete equations for propane. Density = 2.565 moles/l. Temp. = 96.81°C.*

EQUATION	SIMPLIFIED	COMPLETE
Pressure, atmos.	39.108	39.121
Fugacity, atmos.	26.737	26.743
Enthalpy, l-atmos./mole	−55.134	−55.147

Here, the pressure, fugacity, and isothermal change in enthalpy of propane at its critical temperature and one-half its critical density have been calculated with the simplied Eqs. (B14), (B15) and (B16) and with the complete Eqs. (B7), (B8) and (B11). At lower densities the errors resulting from using the simplified equations are still smaller, so that for most purposes it is permissible to use them when the density is less than one-half the critical. On the other hand, the simplified equations may not be used for the gas phase at higher density or for the liquid phase, since the errors rapidly become larger as the density increases.

C. Determination of the Numerical Values of the Parameters from Experimental Data

The foregoing general remarks on the considerations which led to the form of the present equation may be made more concrete by an outline of the procedure followed in determining from experimental data the most suitable numerical values of the parameters for a particular hydrocarbon. This procedure will be found convenient in fitting the present equation to substances other than those treated in this article.

(1) Interpolate experimental P-V-T data for the gas phase to even temperatures and densities. Pressures at these even temperatures and densities will be referred to as the observed pressures, P_{obs}.

(2) At each density fit an equation of the form:

$$P=RTd+d^2[RTB(d)-A(d)-C(d)/T^2] \quad \text{(C1)}$$

to the observed pressures by the method of least squares; give equal weight to each pressure.

(3) Plot $B(d)$, determined in step (2), against density. Pass a straight line through the points; give greater weight to the points at the higher densities. The equation of this line is:

$$B=B_0+bd. \quad \text{(C2)}$$

(4) Let the "cohesive pressure," π_{obs}, be defined by the equation:

$$\pi_{\text{obs}}=RT(d+B_0d^2+bd^3)-P_{\text{obs}}. \quad \text{(C3)}$$

At each density fit an equation of the form:

$$\pi=d^2[A'(d)+C'(d)/T^2] \quad \text{(C4)}$$

to the cohesive pressures by the method of least squares; give equal weight to each pressure.

(5) Find by trial a value of γ such that when $C'(d)$ is plotted against $d(1+\gamma d^2)\exp(-\gamma d^2)$ the points fall on an approximately straight line. Pass a straight line through these points; give greater weight to the points at the higher densities. The equation of this line is:

$$C'(d)=C_0-cd(1+\gamma d^2)\exp(-\gamma d^2). \quad \text{(C5)}$$

(6) Let A_{obs} be defined by the equation:

$$d^2A_{\text{obs}}=\pi_{\text{obs}} -\frac{d^2}{T^2}[C_0-cd(1+\gamma d^2)\exp(-\gamma d^2)]. \quad \text{(C6)}$$

If $B(d)$ and $C'(d)$ have been properly determined, A_{obs} will be practically independent of temperature. "Best" values of $A(d)$, denoted by $A''(d)$, are selected as follows: At densities near the critical take the value of A_{obs} at the critical temperature; in this way the equation being fitted will be more nearly consistent with observed critical properties. At other densities use an average value of A_{obs}.

(7) Find by trial a value of α such that when $A''(d)$ is plotted against $d(1-\alpha d^3)$ the points fall on an approximately straight line. Pass a straight line through these points; give greatest weight to the points in the neighborhood of the critical density. The equation of this line is:

$$A''(d)=A_0+ad(1-\alpha d^3). \quad \text{(C7)}$$

(8) The values of A_0, a and α, given in Eq. (C7); C_0, c and γ, given in Eq. (C5); and B_0 and b, given in Eq. (C2) constitute provisional values of these eight parameters. If these provisional values give a satisfactory representation of the observed pressures and critical properties, the values of b, a, c, γ, and α may be accepted as final.

(9) There remains the adjustment of B_0, A_0, and C_0, to give the best representation of observed vapor pressures. At each temperature, with provisional values of B_0, A_0, and C_0 and final values of the other parameters, compute $RT\ln f$ at the observed vapor pressure for the gaseous and

TABLE II. *Numerical values of parameters. Units: atmospheres, liters, g-mole, °K. Atomic weights: $C=12.000$, $H=1.0078$. Universal gas constant: $R=0.08207$. $T\ (°K)=t\ (°C)+273.13$.*

	METHANE	ETHANE	PROPANE	n-BUTANE
B_0	0.0426000	0.0627724	0.0973130	0.124361
A_0	1.85500	4.15556	6.87225	10.0847
$C_0\cdot 10^{-6}$	0.0225700	0.179592	0.508256	0.992830
b	0.00338004	0.0111220	0.0225000	0.0399983
a	0.0494000	0.345160	0.947700	1.88231
$c\cdot 10^{-6}$	0.00254500	0.0327670	0.129000	0.316400
γ	0.0060000	0.0118000	0.0220000	0.0340000
α	0.000124359	0.000243389	0.000607175	0.00110132

liquid phases, as follows: Find by trial a liquid density d^L and a vapor density d^G such that when these densities are substituted in equation of state (B7), the computed pressures equal the observed vapor pressure. Compute the vapor fugacity f^G and the liquid fugacity f^L at d^G and d^L, respectively, by means of Eq. (B8).

B_0, A_0, and C_0 have now to be adjusted so that f^G and f^L at the observed vapor pressure are made as nearly equal as possible. The effect on the calculated fugacities of adjusting B_0, A_0, and C_0 may be estimated through its effect on Q_1, defined as:

$$Q_1=B_0RT-A_0-C_0/T^2. \tag{C8}$$

It may be proved that

$$RT(\partial \ln f/\partial Q_1)_P=d, \tag{C9}$$

so that the effect on f of changing B_0, A_0, and C_0 by ΔB_0, ΔA_0, and ΔC_0 is given to the first order by:

$$\begin{aligned} RT\Delta \ln f&=d\Delta Q_1\\ &=d(RT\Delta B_0-\Delta A_0-\Delta C_0/T^2). \end{aligned} \tag{C10}$$

To make f^G and f^L equal at the observed vapor pressure, Q_1 must therefore be changed by an amount ΔQ_1, given by:

$$\Delta Q_1=\frac{RT\ln f^G/f^L}{d^L-d^G}. \tag{C11}$$

TABLE III. *Summarized comparison of observed properties of light hydrocarbons with those predicted by present equation.*

	METHANE	ETHANE	PROPANE	n-BUTANE	AVE. FOR 4 HYDROCARBONS
1. *Pressures of Gaseous Phase*					
Source of Data	10, 11, 13	13, 14, 15	6, 21	22, 24	
Range of Density, moles/liter	2 to 18	0.5 to 10	1 to 9	0.5 to 7	
Range of Temperature, °C	−70 to 200	25 to 275	96.81 to 275	150 to 300	
Ave. % Dev. of Pressures	0.34	0.31	0.40	0.31	0.34
Observed Normal Density, g/l.	0.7168	1.3566	1.8325 (25°C)	2.70324	
% Deviation	−0.01	+0.15	−0.005	−0.10	0.07
2. *Critical Properties*					
Source of Data	12	15, 16	18	22	
Deviation of Pressure, atmos.	−1.5	−0.17	−0.42	−0.05	−0.54
Deviation of Temperature, °C	−0.3	−0.25	−0.16	−0.06	−0.19
Deviation of Density, moles/liter	+0.06	+0.06	0.00	+0.13	+0.06
3. *Properties of Saturated Liquid*					
Source of Data	12	14, 17	18, 19, 20	20, 22, 23	
Range of Temperature, °C	−139.50 to −85.13	−50 to 25	−25 to 75	4.44 to 121.11	
Range of Vapor Pressure, atmos.	4.51 to 41.81	5.45 to 41.37	2.01 to 28.0	1.20 to 22.48	
Ave. % Dev. of Densities	2.7	2.7	2.3	1.2	2.2
Ave. % Dev. of Vapor Pressures	2.4	0.4	1.0	0.7	1.1

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TABLE IV. *Deviations of pressures calculated by equation of state from observed pressures for gaseous n-butane.*[22]

DENSITY, MOLES/LITER		0.5	1	2	3	4	5	6	7	8	
TEMP. °C		PRESSURE, NORMAL ATMOSPHERES									AVERAGE % DEV.
150	Obs.	14.68	24.68	34.39							
	% Dev.	−0.07	−0.04	−0.06							0.06
152.01	Obs.					37.46	37.76	43.40	73.27	168.11	
	% Dev.					−0.11	−0.82	−0.51	+0.33	(−5.39)	0.44
175	Obs.	15.91	27.50	41.31	47.89	52.20	58.30	74.32	120.59	239.49	
	% Dev.	−0.06	+0.04	+0.56	+0.69	−0.33	−1.60	−0.57	+0.24	(−3.87)	0.51
200	Obs.	17.11	30.24	47.88	58.99	68.61	81.96	109.23	172.87	315.71	
	% Dev.	−0.12	+0.07	+0.56	+0.66	−0.20	−1.05	−0.13	+0.38	(−3.31)	0.40
225	Obs.	18.30	32.92	54.29	69.93	85.20	106.23	145.02	225.65		
	% Dev.	−0.11	+0.03	+0.48	+0.50	−0.13	−0.63	+0.23	+0.47		0.32
250	Obs.	19.48	35.55	60.62	80.74	101.84	130.80	181.11	278.51		
	% Dev.	−0.10	0.00	+0.43	+0.27	−0.16	−0.44	+0.31	+0.42		0.27
275	Obs.	20.65	38.18	66.82	91.58	118.57	155.59	217.50	331.20		
	% Dev.	−0.10	+0.05	+0.31	+0.17	−0.19	−0.37	+0.30	+0.25		0.22
300	Obs.	21.81	40.76	72.97	102.28	135.27	180.56	253.96			
	% Dev.	−0.05	+0.05	+0.22	−0.01	−0.32	−0.36	+0.17			0.17
Average % Deviation		0.09	0.04	0.37	0.38	0.21	0.75	0.32	0.35	(4.19)	
Over-all Ave. % Dev.											0.31

These values of ΔQ_1 are to be fitted by an equation of the form:

$$\Delta Q_1 = RT\Delta B_0 - \Delta A_0 - \Delta C_0/T^2. \qquad \text{(C12)}$$

Find by trial values of ΔB_0, ΔA_0, and ΔC_0 such that ΔQ_1 computed by (C11) is represented as well as possible, subject to the restrictions: (a) ΔQ_1 vanishes at the critical temperature. (b) ΔQ_1 is made as small as possible between the critical temperature and the highest temperature at which gaseous pressures are to be computed. Requirement (a) ensures that the calculated critical properties will not be affected by adjusting B_0, A_0, and C_0: requirement (b) ensures that gaseous pressures will be changed as little as possible while fitting the vapor pressure data.

To obtain the final value of B_0, A_0 or C_0, add ΔB_0, ΔA_0 or ΔC_0 to the provisional value of the corresponding parameter.

(10) As a check on the process described in the preceding paragraphs, observed vapor pressures and observed P-V-T properties of the gas phase should be compared with those computed with final values of the eight parameters.

D. NUMERICAL VALUES OF THE PARAMETERS

In Table II are listed numerical values of the eight parameters B_0, A_0, C_0, b, a, c, γ, and α for the hydrocarbons methane, ethane, propane, and *n*-butane. These values were determined by the procedure outlined in Section C from the data listed in Table III of Section E, following. These data comprise: (1) P-V-T properties of the gas and liquid phases up to 1.8 times the critical density. (2) Critical properties. (3) Vapor pressures above one atmos.

Atomic weights, the value of the universal gas constant R and the centigrade temperature of the ice point listed in Table II should be used in conjunction with the parameters given there, because they were employed in fitting the equation to the experimental data.

It is, of course, impossible to assign unique values accurate to six significant figures to each of these parameters. Nevertheless the full six figures given in Table II should be used in calculating the properties of liquids, and four or five should be used for gases. A change of one in the sixth place of one constant by itself will alter the calculated pressure of a liquid by about 0.01

TABLE V. *Miscellaneous properties of n-butane.*

1. *Properties of Gas at Low Pressure*

	Obs.[24]	% Dev.
Normal density, g/liter	2.70324	−0.10

2. *Critical Properties*

	Obs.[22]	Obs.-Calc.
Pressure, atmos.	37.48	−0.05
Temperature, °K	425.14	−0.06
Density, moles/liter	3.88	+0.13

3. *Properties of Saturated Liquid*

	Density, moles/l.		Vapor Press., atmos.	
Temp., °C.	Obs.	% Dev.	Obs.	% Dev.
4.44	10.26[20]	+0.6	1.20[20]	+1.2
37.78	9.66[23]	+2.2	3.51[23]	−1.0
71.11	8.93[23]	+1.8	8.23[23]	−0.4
100.00	8.07[23]	+0.6	15.19[23] 15.09[22]	−0.5 −1.1
121.11	7.26[23]	−0.8	22.48[23]	+0.1

atmos. However, it is possible to change all the constants simultaneously by about 5 percent without seriously prejudicing the calculated results. This point should be borne in mind in any attempted correlation of the constants with other properties of the hydrocarbons.

E. COMPARISON OF OBSERVED AND CALCULATED PROPERTIES OF LIGHT HYDROCARBONS

There is not space here for a detailed comparison of observed properties of methane, ethane, propane, and *n*-butane with those predicted by the present equation. Table III summarizes the results of such a comparison and indicates the source of the data used. Since the predictions of the equation correspond about equally well with experimental data for each hydrocarbon, the detailed comparison for *n*-butane, given in Tables IV and V, may be considered as typical of the results for methane, ethane, and propane as well. In these tables, "% Dev." is defined by

$$100\frac{\text{Obs. Property}-\text{Calc. Property}}{\text{Obs. Property}},$$

and "Ave. % Dev." is the average of the absolute values of the individual deviations.

Tables IV and V illustrate the agreement between observed data for *n*-butane and values calculated by the equation of state. Similar tables for methane, ethane, and propane give about as good agreement between observed and calculated properties as here illustrated for *n*-butane. A comparison between the columns in Table III helps to show this point.

It was impossible to fit the points for *n*-butane (Table IV) at 8 moles/liter, about twice the critical density, and these were not used in determining the parameters. Excluding these three points, the average deviation of the calculated pressures is 0.31 percent. Up to 4 moles/liter the average deviation is only 0.22 percent, whereas over approximately the same density range the average deviation from the Beattie-Bridgeman equation[22] is 0.36 percent. It may be said that the equation fits the data well for all four hydrocarbons up to about 1.8 times the critical density, but above this density calculated pressures are high.

In Part 2 calculated critical properties are shown to be in good agreement with those observed by Beattie, Simard and Su.[22] Table III, Part 2, shows fair agreement for the other three hydrocarbons. Calculated critical pressures are somewhat high, though with the exception of methane the deviations are less than 0.5 atmos.

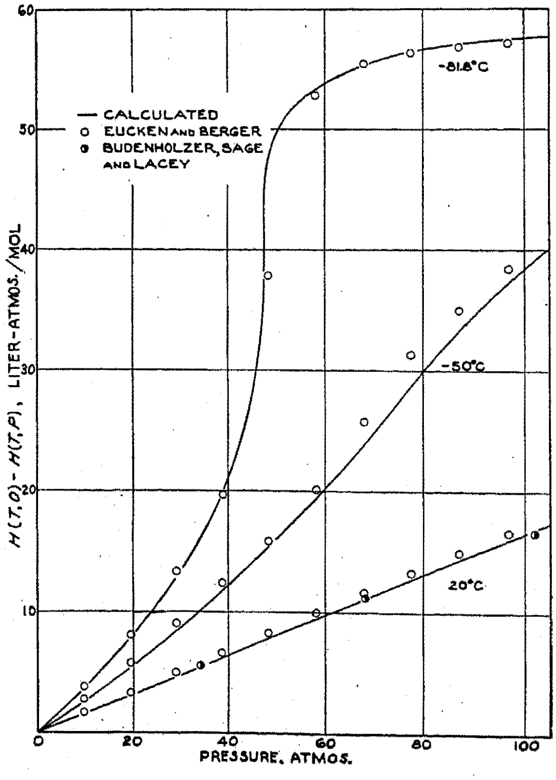

FIG. 5. Effect of pressure on enthalpy of methane.

Calculated critical temperatures are from 0.06 to 0.3°C high.

In Part 3 of Table V calculated vapor pressures of *n*-butane are shown to agree with observed vapor pressures practically within experimental error. Calculated liquid densities differ from observed liquid densities with an average deviation of 1.2 percent. For the other hydrocarbons as well as for *n*-butane calculated liquid densities are from 0 to 3 percent low. Vapor pressures agree well down to pressures of the order of 2 atmos.; at lower pressures calculated vapor pressures are low.

The average deviations summarized in Table III indicate the error resulting when the present equations are used to compute thermodynamic properties of these hydrocarbons within the regions of density, pressure, and temperature in which the equations have been fitted. Caution should be exercised in using the present equations at higher densities or lower temperatures. Extrapolation to higher temperatures or lower densities is less hazardous.

The use of the equation for calculating thermodynamic properties other than those considered in evaluating the parameters is illustrated by the following examples: (1) the effect of pressure on the enthalpy of methane, and (2) the latent heat of evaporation of *n*-butane.

Eucken and Berger[25] have determined the effect of pressure on the enthalpy of methane calorimetrically below 20°C, and Budenholzer, Sage and Lacey[26] have computed it from Joule-Thomson coefficients measured above 21.11°C. In Fig. 5 experimental values of $H(0, T) - H(P, T)$ at -81.8, -50, and 20°C are compared with those calculated by Eqs. (B7) and (B11). The agreement at -81.8°C, the computed critical temperature, and at 20°C, is probably within the error of the measurements. At -50°C the agreement is less satisfactory.

The calculated latent heat of evaporation of *n*-butane at 37.78°C is compared below with that measured calorimetrically by Sage, Webster and Lacey:[23]

Calculated	202.6	liter-atmos./mole
Observed	201.1	liter-atmos./mole

The calculated latent heat is the difference in enthalpy between the liquid and vapor, each evaluated by Eq. (B11) at the calculated saturation density.

The minor discrepancies between observed properties of pure hydrocarbons and those calculated by the present equation, although real, do not seriously impair the value of the present equation. It provides in a single expression a concise and reasonably accurate summary of several classes of thermodynamic data pertaining to hydrocarbons and covers a wider range of data than any equation proposed up to the present time. It may be applied both to the gas phase and to the saturated liquid. Perhaps the greatest value of the equation is that it provides a point of departure for the prediction of thermodynamic properties of mixtures.

The next paper of this series will show how the present equation may be generalized to describe the thermodynamic properties of mixtures. Work is also planned on extending the equation to substances other than those treated in this first paper.

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