An Empirical Equation for Thermodynamic Properties of Light Hydrocarbons and Their Mixtures II. Mixtures of Methane, Ethane, Propane, and nButane

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

II. Mixtures of Methane, Ethane, Propane, and n-Butane*

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(Received September 22, 1942)

An empirical equation is given for the isothermal variation with density of the work content of hydrocarbon mixtures in the gaseous or liquid state. From this fundamental equation are derived (a) an equation of state, (b) an equation for the fugacity, (c) an equation for the isothermal variation of the enthalpy, and (d) an equation for the isothermal variation of the entropy. These equations summarize P-V-T-x properties of the gaseous or liquid phase, liquid-vapor equilibria, critical properties, latent heats of evaporation, and heats of mixing. The equation is a generalization to mixtures of the equation for pure hydrocarbons given in the first paper of this series. Methods are proposed for determining the parameters in the equation for mixtures from the parameters in the equation for pure hydrocarbons. A comparison is made between observed properties of mixtures and those predicted by the equations. These comparisons show that the equations provide a satisfactory practical summary of the volumetric properties and liquid-vapor equilibria of mixtures of methane, ethane, propane, and n-butane.

A. INTRODUCTION

THE object of this paper is to describe an empirical equation which summarizes the following groups of thermodynamic properties of either gaseous or liquid mixtures of light hydrocarbons: (a) Pressure-volume-temperature-composition data, (b) Liquid-vapor equilibria, (c) Latent heats of evaporation and heats of mixing. The equation employed for this purpose is a generalization to mixtures of the equation for thermodynamic properties of pure hydrocarbons given in the first paper[1] of this series.

The use of a single equation to summarize these thermodynamic properties of mixtures has a number of practical advantages. It permits the condensation of experimental results obtained at a variety of temperatures, pressures, and compositions into a single compact expression. The formulation by a single equation of several types of experimental measurements, such as P-V-T data, heats of mixing and liquid-vapor equilibria, is necessarily thermodynamically consistent. Calculation of fugacities, partial volumes or partial enthalpies, by differentiation with respect to composition, can be carried out more readily by an equation than by graphical means. Use of the same equation for gaseous and liquid phases permits treatment of the critical region, in which satisfactory representation by conventional means is difficult. Finally, the most useful feature of an equation for mixtures is that it permits reliable prediction of thermodynamic properties of mixtures of any composition whatever, a feature of great practical value because of the impossibility of determining experimentally the properties of every mixture of interest.

Historical

Because of these useful aspects of a thermodynamic equation for mixtures, a number of rules or equations for predicting such thermodynamic properties have been proposed in the past. Although these former proposals are more limited in scope than the equation to be described in this paper, several of them have been useful in developing the present equation. These will be described briefly. For a more general discussion of methods for predicting thermodynamic properties of mixtures, reference may be made to review articles.†

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* Some of the material of this paper was presented at the Symposium on "Reactions and Equilibria in Chemical Systems under High Pressure" at the 100th meeting of the American Chemical Society at Detroit, Michigan, September 9-13, 1940.

[1] Benedict, Webb, and Rubin, J. Chem. Phys. **8**, 334 (1940).

† Wien and Harms, *Handbuch der Experimental Physik* (Akademische Verlagsanstalt, Leipzig, 1929), Vol. 8. Beattie and Stockmayer, *Reports on Progress in Physics* **7**, 195 (1940).

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The essential principle of van der Waals theory of the continuity of the gaseous and liquid states is the application to both states of the same equation for the variation of work content with density and composition. The same principle has been followed in developing the equation of this article. From such an equation for the work content the temperatures, pressures, and compositions of coexistent liquid and gaseous mixtures may be evaluated. Van der Waals[2] equation of state led to the correct qualitative aspects of phase equilibrium between liquid and vapor, but did not provide an accurate quantitative description, because of its failure to agree with P-V-T properties of actual mixtures.

A number of equations of state for gas mixtures more accurate than van der Waals have been developed, among which those of Keyes[3] and Beattie and Bridgeman[4] are perhaps the best known. These equations are suitable for gases up to their critical density, but they cannot be used for P-V-T properties of gases at higher density or for liquids, and cannot therefore be used to predict liquid-vapor equilibria. Beattie and Ikehara[5] have given a detailed account of equations of state for gas mixtures and have described various methods for expressing the dependence of parameters in these equations on composition.

General thermodynamic principles underlying the formulation of properties of mixtures have been discussed by Gillespie[6] and by Beattie[7] who showed that all thermodynamic properties of mixtures might be computed from certain limiting properties of the pure components at low pressures and experimental P-V-T data or an equation of state for the mixture.

A more fundamental approach to the prediction of the properties of mixtures is afforded by the statistico-mechanical treatment of J. E. Mayer.[8] In principle, this approach makes possible the calculation of an equation of state for gas mixtures from the interaction energies of aggregates of molecules making up the mixture. In practice,

too little is known of the molecular properties of complex substances, such as hydrocarbons, for this approach to be of quantitative value. Its principal applicability to the present problem is in the limitations it imposes on the functional form of equations of state for gas mixtures.

Each of the references cited above has been helpful in extending to mixtures the group of equations for pure hydrocarbons, given in the first paper of this series.[1] Our treatment resembles that of van der Waals,[2] in that a single equation is proposed for both the liquid and gaseous phases. It differs from it in that more exact correspondence with experimental data is obtained through use of a more complicated expression, which may be regarded as an extension of the equations of Beattie and Bridgeman[4] and Beattie and Ikehara.[5]

B. EQUATION FOR MIXTURES

Definition of Terms

The fundamental equation for thermodynamic properties of mixtures makes use of the same function as has been used[1] for pure hydrocarbons, namely, the residual work content $\tilde{A}$. For mixtures, the residual work content is defined as the difference between the actual work content A of one mole of mixture, and the work content of one mole of the mixture in the hypothetical ideal gas state at the same temperature, density, and composition. The work content is also known as the Helmholtz free energy or Gibbs ψ-function; it is related to the internal energy E, entropy S, and absolute temperature T, by the equation:

$$A = E - TS. \tag{B1}$$

A precise definition of the residual work content is afforded by the equation:

$$\tilde{A} = A - RT \ln d - \lim_{d \to 0} (A - RT \ln d), \tag{B2}$$

where R is the gas constant and d is the molal density. Symbols introduced in this section are listed in Table I.

The statistico-mechanical treatment of Mayer may be used to show that the limit of Eq. (B2) exists and has the following value:

$$\lim_{d \to 0} (A - RT \ln d) = \sum_i x_i [RT \ln x_i + \lim_{d \to 0} (A_i - RT \ln d)], \tag{B3}$$

[2] J. van der Waals, *Die Continuität des Gasförmigen und Flüssigen Zustandes* (Barth, Leipzig, 1899).
[3] F. G. Keyes, Proc. Nat. Acad. Sci., Wash. **3**, 323 (1917).
[4] J. A. Beattie and O. C. Bridgeman, Proc. Am. Acad. Sci. **63**, 229 (1928).
[5] J. A. Beattie and S. Ikehara, Proc. Am. Acad. Sci. **64**, 127 (1930).
[6] L. J. Gillespie, Phys. Rev. **34**, 352 (1929).
[7] J. A. Beattie, Phys. Rev. **31**, 680 (1928).
[8] J. E. Mayer, J. Phys. Chem. **43**, 71 (1939).

TABLE I. Nomenclature.

A	Work content of mixture, per mole
$\tilde{A}$	Residual work content, per mole
A_i	Work content of ith component, per mole
d	Molal density
E	Internal energy of mixture, per mole
F	Free energy of mixture, per mole
f_i	Fugacity of ith component
H	Enthalpy of mixture, per mole
n_i	Number of moles of ith component
N	Total number of moles ($\Sigma_i n_i$)
P	Pressure
R	Universal gas constant
S	Entropy, per mole
T	Absolute temperature
V	Volume
x_i	Mole fraction of ith component
μ_i	Chemical potential of ith component
$E_i{}^0$ $F_i{}^0$ $H_i{}^0$ $S_i{}^0$	Properties of pure ith component in hypothetical ideal gaseous state, at unit pressure.

where A_i is the work content of one mole of the pure ith component and x_i is its mole fraction. By combining Eqs. (B2) and (B3), an equation for the work content of a mixture is obtained:

$$A = \tilde{A} + \sum_i x_i [RT \ln dx_i$$
$$+ \lim_{d \to 0} (A_i - RT \ln d)]. \quad (B4)$$

The value of Eq. (B4) is that it segregates the work content into the part within the brackets, which may be evaluated from properties of the pure components at low pressure, and the residual work content $\tilde{A}$, which may be evaluated from P-V-T data for the mixture according to the equation:

$$\tilde{A} = \int_0^d \frac{P - RTd}{d^2} \delta d. \quad (B5)$$

Conversely, the pressure of a mixture is related to the residual work content by the equation:

$$P = RTd + d^2 (\partial \tilde{A} / \partial d)_{T, x}. \quad (B6)$$

The fugacity of the ith component in a mixture f_i is obtained from the residual work content as follows:

$$RT \ln f_i = (\partial N\tilde{A} / \partial n_i)_{T, V, n} + RT \ln dRTx_i, \quad (B7)$$

where n_i is the number of moles of the ith component and $N = \sum_i n_i$. Since the conditions for liquid-vapor equilibria may be expressed solely in terms of the pressure, temperature, and fugacity, it follows that the pressures, temperatures,

and compositions of coexistent liquid and vapor phases may be evaluated from the residual work content alone.

Other thermodynamic properties of mixtures may be evaluated from corresponding properties of the pure components in the ideal gas state at unit pressure and the residual work content according to the following equations:

Energy:

$$E = -T^2 \left(\frac{\partial \tilde{A}/T}{\partial T} \right)_{d, x} + \sum_i x_i E_i{}^0. \quad (B8)$$

Enthalpy:

$$H = -T^2 \left(\frac{\partial \tilde{A}/T}{\partial T} \right)_{d, x} + P/d - RT$$
$$+ \sum_i x_i H_i{}^0. \quad (B9)$$

Entropy:

$$S = -(\partial \tilde{A}/\partial T)_{d, x}$$
$$- \sum_i x_i [R \ln dRTx_i - S_i{}^0]. \quad (B10)$$

Free Energy:

$$F = \tilde{A} + P/d - RT$$
$$+ \sum_i x_i [RT \ln dRTx_i + F_i{}^0]. \quad (B11)$$

Chemical Potential:

$$\mu_i = (\partial N\tilde{A} / \partial n_i)_{V, T, n}$$
$$+ RT \ln dRTx_i + F_i{}^0. \quad (B12)$$

The properties of the pure components, $E_i{}^0$, $F_i{}^0$, $H_i{}^0$, and $S_i{}^0$, may be calculated either statistically, from molecular data, or with the third law, from calorimetric measurements down to low temperatures. This paper is not concerned further with these properties of pure components; its primary object is to develop an equation expressing the dependence of the residual work content of a mixture on density, temperature, and composition.

Development of Equation

In the first paper of this series,[1] it was shown that the residual work content of a pure hydrocarbon varied with temperature and density according to the equation:

$$\tilde{A} = (B_0 RT - A_0 - C_0/T^2)d$$
$$+ (bRT - a)d^2/2 + a\alpha d^5/5$$
$$+ \frac{cd^2}{T^2} \left[\frac{1 - \exp(-\gamma d^2)}{\gamma d^2} - \frac{\exp(-\gamma d^2)}{2} \right]. \quad (B13)$$

TABLE II. Empirical equations for thermodynamic properties of mixtures of hydrocarbons.

Pressure

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

Fugacity

$$RT \ln f_i = RT \ln dRTx_i$$
$$+ [(B_0 + B_{0i})^* RT - 2(A_0A_{0i})^{\frac{1}{2}} - 2(C_0C_{0i})^{\frac{1}{2}}/T^2]d$$
$$+ 3/2[RT(b^2b_i)^{\frac{1}{3}} - (a^2a_i)^{\frac{1}{3}}]d^2$$
$$+ 3/5[a(\alpha^2\alpha_i)^{\frac{1}{3}} + \alpha(a^2a_i)^{\frac{1}{3}}]d^5$$
$$+ \frac{3d^2(c^2c_i)^{\frac{1}{3}}}{T^2}\left[\frac{1 - \exp(-\gamma d^2)}{\gamma d^2} - \frac{\exp(-\gamma d^2)}{2}\right]$$
$$- \frac{2d^2c}{T^2}\left(\frac{\gamma_i}{\gamma}\right)^{\frac{1}{2}}\left[\frac{1 - \exp(-\gamma d^2)}{\gamma d^2}\right.$$
$$\left. - \exp(-\gamma d)^2 - \frac{\gamma d^2 \exp(-\gamma d^2)}{2}\right]. \quad \text{(b)}$$

Enthalpy

$$H = \Sigma_i x_iH_i^0 + (B_0RT - 2A_0 - 4C_0/T^2)d$$
$$+ (2bRT - 3a)d^2/2 + 6a\alpha d^5/5 + \frac{cd^2}{T^2}\left[3\frac{1 - \exp(-\gamma d^2)}{\gamma d^2}\right.$$
$$\left. - \frac{\exp(-\gamma d^2)}{2} + \gamma d^2 \exp(-\gamma d^2)\right]. \quad \text{(c)}$$

Entropy

$$S = \Sigma_i x_i(S_i^0 - R \ln dRTx_i) - (B_0R + 2C_0/T^3)d$$
$$- bRd^2/2 + \frac{2cd^2}{T^3}\left[\frac{1 - \exp(-\gamma d^2)}{\gamma d^2} - \frac{\exp(-\gamma d^2)}{2}\right]. \quad \text{(d)}$$

* This equation assumes linear combination of B_0 (Eq. B25). For Lorentz combination of B_0 (Eq. B26) the coefficient marked with an asterisk should be $\Sigma_j x_j[(B_0_j)^{\frac{1}{3}} + (B_0_i)^{\frac{1}{3}}]^3/4$.

It has been found experimentally that if an equation of state of a particular form applies to each of the components of a mixture, an equation of the same form usually applies to every mixture of the components, provided they do not react chemically. As a hypothesis, it is therefore assumed that Eq. (B13) expresses the variation with density and temperature of the residual work content of mixtures, as well as of pure hydrocarbons.

Development of an equation for the residual work content of mixtures is then reduced to formulating the dependence on composition of the eight parameters of Eq. (B13): B_0, A_0, C_0, b, a, c, α, and γ. In this formulation, use is made of the following result of the statistico-mechanical treatment of Mayer.[8] The residual work content of a mixture may be developed in the power series:

$$\tilde{A} = d \sum_{ij} x_ix_jQ'_{ij} + d^2 \sum_{ijk} x_ix_jx_kQ''_{ijk} + \cdots, \quad \text{(B14)}$$

where Q' and Q'' are functions of the temperature. From this result, it follows that six of the parameters of Eq. (B13) must depend on composition as follows:

$$B_0 = \sum_{ij} x_ix_jB_{0ij}, \quad \text{(B15)}$$

$$A_0 = \sum_{ij} x_ix_jA_{0ij}, \quad \text{(B16)}$$

$$C_0 = \sum_{ij} x_ix_jC_{0ij}, \quad \text{(B17)}$$

$$b = \sum_{ijk} x_ix_jx_kb_{ijk}, \quad \text{(B18)}$$

$$a = \sum_{ijk} x_ix_jx_ka_{ijk}, \quad \text{(B19)}$$

and

$$c = \sum_{ijk} x_ix_jx_kc_{ijk}, \quad \text{(B20)}$$

In these equations, constants with repeated suffixes, such as B_{011}, refer to pure components and their values are known. Those with dissimilar suffixes, such as B_{012}, are a property of the mixture, arising from interaction between unlike molecules; these may be termed interaction constants.

In this way, development of an equation for the residual work content of mixtures may be largely reduced to assignment of numerical values to the various interaction constants. When sufficient experimental data are available, they may be evaluated from the data; ordinarily, it will be preferable to calculate them from the properties of the pure components. The following types of equations have been assumed for this purpose:

for b, c, and a: $b_{ijk} = (b_ib_jb_k)^{\frac{1}{3}}$,   (B21)

for A_0 and C_0: $A_{0ij} = (A_{0i}A_{0j})^{\frac{1}{2}}$,   (B22)

and for B_0, either: $B_{0ij} = (B_{0i} + B_{0j})/2$,   (B23)

or:

$$B_{0ij} = [(B_{0i})^{\frac{1}{3}} + (B_{0j})^{\frac{1}{3}}]^3/8. \quad \text{(B24)}$$

Here, repeated suffixes, such as b_{iii}, have been contracted into a single suffix, such as b_i. Choice of these equations was made for the following reasons. Equations (B22), (B23), and (B24) have been used[5] for corresponding parameters in the Beattie-Bridgeman equation of state. Equation (B23) is termed "linear combination of B_0" and Eq. (B24) is termed "Lorentz combination of B_0." Equation (B21) was chosen so that a simple

equation for the fugacity in a mixture would result.

These hypotheses about the interaction constants, and two additional hypotheses about γ and α, result in the following equations for the dependence on composition of the parameters in Eq. (B13):

$$B_0 = \sum_i x_i B_{0i}. \quad \text{(Linear)} \quad \text{(B25)}$$

$$B_0 = \sum_{ij} x_i x_j [(B_{0i})^{\frac{1}{3}} + (B_{0j})^{\frac{1}{3}}]^3 / 8.$$
$$\text{(Lorentz)} \quad \text{(B26)}$$

$$A_0 = [\sum_i x_i (A_{0i})^{\frac{1}{2}}]^2. \quad \text{(B27)}$$

$$C_0 = [\sum_i x_i (C_{0i})^{\frac{1}{2}}]^2. \quad \text{(B28)}$$

$$b = [\sum_i x_i (b_i)^{\frac{1}{3}}]^3. \quad \text{(B29)}$$

$$a = [\sum_i x_i (a_i)^{\frac{1}{3}}]^3. \quad \text{(B30)}$$

$$c = [\sum_i x_i (c_i)^{\frac{1}{3}}]^3. \quad \text{(B31)}$$

$$\gamma = [\sum_i x_i (\gamma_i)^{\frac{1}{2}}]^2. \quad \text{(B32)}$$

$$\alpha = [\sum_i x_i (\alpha_i)^{\frac{1}{3}}]^3. \quad \text{(B33)}$$

From the foregoing hypotheses, consistent equations for all thermodynamic properties of gaseous or liquid mixtures of hydrocarbons may be derived. Equations for some of the more common functions are given in Table II. In these equations, parameters without the suffix (i), such as B_0, refer to the mixture and are evaluated from Eqs. (B25) through (B33). Those with the suffix i refer to pure components. Fractional powers of the constants required in the above equations for methane, ethane, propane, and n-butane are tabulated in Table III. These constants have been taken from Table II of the first paper of this series.[1]

TABLE III. Fractional powers of constants for pure hydrocarbons.

	Methane	Ethane	Propane	n-Butane
B_0	0.0426000	0.0627724	0.0973130	0.124361
$(B_0)^{\frac{1}{3}}$	0.349250	0.397426	0.459964	0.499147
$(A_0)^{\frac{1}{2}}$	1.36198	2.03852	2.62150	3.17564
$(C_0)^{\frac{1}{2}} \cdot 10^{-3}$	0.150233	0.423783	0.712921	0.996410
$(b)^{\frac{1}{3}}$	0.150075	0.223217	0.282310	0.341990
$(a)^{\frac{1}{3}}$	0.366924	0.701466	0.982254	1.23471
$(c)^{\frac{1}{3}} \cdot 10^{-2}$	0.136530	0.319997	0.505277	0.681415
$(\gamma)^{\frac{1}{2}}$	0.0774600	0.108628	0.148324	0.184391
$(\alpha)^{\frac{1}{3}}$	0.0499143	0.0624358	0.0846781	0.103269
Molecular Weight	16.031	30.047	44.062	58.078

$T_0 = 273.13°K.$
$R = 0.08207 \text{(liter)-(atmos.)}/(°K)-\text{(g mole)}.$

TABLE IV. Summarized comparison of equation with P-V-T data for methane-n-butane mixtures.

Mole % methane	0	25.06	50.44	74.90	25.06	50.44	74.90	100.00
Source of data	(a)	(b)	(b)	(b)	(b)	(b)	(b)	(c)
Density range, moles/liter	0.5-7	1.25-8	1.25-10	1.25-10	1.25-8	1.25-10	1.25-10	2-18
Temp., °C			Linear			Lorentz		
75	—	—	—	1.32	—	—	0.49	0.17
100	—	—	0.32	1.52	—	0.29	0.22	0.13
125	—	0.71	1.73	1.64	0.18	0.76	0.22	0.25
150	0.06	2.04	1.57	1.74	0.38	0.65	0.32	0.41
175	0.51	1.86	1.47	1.71	0.41	0.48	0.44	—
200	0.40	1.75	1.46	1.62	0.39	0.29	0.47	0.84
225	0.32	1.68	1.26	1.66	0.39	0.27	0.55	—
250	0.27	1.50	1.29	1.53	0.35	0.23	0.53	—
275	0.22	1.65	1.18	1.56	0.50	0.22	0.58	—
300	0.17	1.60	0.91	1.40	0.57	0.24	0.52	—
All	0.34	1.71	1.39	1.57	0.42	0.42	0.42	0.38

The row "Temp., °C" header spans "Average deviation (%)".

[a] Beattie, Simard, and Su, J. Am. Chem. Soc. 61, 24, 26 (1939).
[b] See reference 9.
[c] Kvalnes and Gaddy, J. Am. Chem. Soc. 53, 394 (1931); Michels and Nederbragt, Physica 3, 569 (1936).

C. COMPARISON OF EQUATION WITH P-V-T DATA FOR MIXTURES OF HYDROCARBONS

Introduction

To substantiate the assumptions employed in deriving the equations for mixtures, these equations will be compared with representative examples of the more precise measurements of thermodynamic properties of mixtures of methane, ethane, propane, and n-butane. This comparison will be made for both the Lorentz and the linear methods of calculating B_0 so that the more satisfactory of the two methods may be found. P-V-T data will be taken up first; then liquid-vapor equilibria will be considered.

Methane-n-Butane

Probably the most precise and extensive measurements of P-V-T properties of mixtures of light hydrocarbons are those of Beattie, Stockmayer, and Ingersoll[9] on the following mixtures of methane and n-butane:

Mole percent methane	25.06	50.44	74.90
Mole percent n-butane	74.94	49.56	25.10

These measurements extended from 75 to 300°C and from 30 to 300 atmos. A comparison of these data with pressures calculated by both the Lorentz and linear forms of the equation of state is summarized by Table IV. This table shows

[9] Beattie, Stockmayer, and Ingersoll, J. Chem. Phys. 9, 871 (1941).

TABLE V. Deviations of pressures calculated by the equation of state from observed pressures for gas containing 50.435 mole percent methane, 49.565 mole percent n-butane.

Density, moles/liter Temp., °C			1.251	1.501	2.001	2.502	3.002	3.502	4.003	4.503	5.004	6.004	7.005	8.006	9.006	10.007	Av. % Dev.
								Pressure, normal atmospheres									
100		Obs.	31.40	36.24													
	% Dev.,	Linear	−0.25	−0.39													0.32
		Lorentz	+0.29	+0.30													0.29
125		Obs.	34.61	40.25	50.54	59.83	68.37	76.42	84.30	92.18	100.29	118.58	140.30	170.37	214.98	284.73	
	% Dev.,	Linear	−0.26	−0.35	−0.49	−0.65	−0.78	−0.98	−1.20	−1.51	−1.89	−2.45	−3.50	−3.67	−3.35	−3.20	1.73
		Lorentz	+0.26	+0.30	+0.44	+0.57	+0.76	+0.89	+1.02	+1.06	+1.02	+1.10	+0.58	+0.72	+1.06	+0.91	0.76
150		Obs.	37.73	44.14	56.11	67.21	77.67	87.80	97.84	107.98	118.58	142.04	171.22	210.53	266.72	352.37	
	% Dev.,	Linear	−0.37	−0.41	−0.46	−0.58	−0.72	−0.88	−1.12	−1.46	−1.80	−2.62	−3.12	−3.08	−2.87	−2.53	1.57
		Lorentz	+0.13	+0.23	+0.43	+0.58	+0.72	+0.85	+0.91	+0.87	+0.82	+0.53	+0.44	+0.70	+0.91	+0.99	0.65
175		Obs.	40.84	47.99	61.57	74.42	86.76	98.90	111.08	123.55	136.62	165.90	202.23	250.71	319.09		
	% Dev.,	Linear	−0.37	−0.42	−0.49	−0.60	−0.76	−0.95	−1.22	−1.55	−1.90	−2.57	−2.95	−2.83	−2.45		1.47
		Lorentz	+0.15	+0.21	+0.37	+0.50	+0.60	+0.68	+0.68	+0.62	+0.51	· +0.29	+0.24	+0.53	+0.89		0.48
200		Obs.	43.92	51.82	66.99	81.49	95.68	109.77	124.14	138.86	154.51	189.50	232.85	291.10			
	% Dev.,	Linear	−0.36	−0.37	−0.45	−0.69	−0.88	−1.13	−1.38	−1.75	−2.04	−2.72	−3.10	−2.68			1.46
		Lorentz	+0.14	+0.23	+0.37	+0.38	+0.43	+0.42	+0.41	+0.27	+0.20	−0.08	−0.18	+0.37			0.29
225		Obs.	46.99	55.61	72.33	88.61	104.70	120.79	137.31	154.50	172.71	213.81	264.80				
	% Dev.,	Linear	−0.30	−0.34	−0.44	−0.62	−0.78	−1.07	−1.36	−1.66	−1.97	−2.53	−2.77				1.26
		Lorentz	+0.19	+0.25	+0.36	+0.41	+0.48	+0.41	+0.31	+0.25	+0.14	−0.07	−0.06				0.27
250		Obs.	50.02	59.36	77.62	95.57	113.48	131.60	150.29	169.85	190.66	237.81	296.17				
	% Dev.,	Linear	−0.30	−0.32	−0.45	−0.66	−0.86	−1.13	−1.44	−1.74	−2.04	−2.54	−2.76				1.29
		Lorentz	+0.18	+0.27	+0.33	+0.35	+0.35	+0.30	+0.20	+0.09	−0.03	−0.22					0.23
275		Obs.	53.02	63.08	82.87	102.50	122.23	142.36	163.24	185.18	208.55	261.77					
	% Dev.,	Linear	−0.30	−0.32	−0.45	−0.68	−0.91	−1.18	−1.49	−1.80	−2.11	−2.59					1.18
		Lorentz	+0.17	+0.25	+0.33	+0.30	+0.28	+0.20	+0.09	−0.04	−0.19	−0.37					0.22
300		Obs.	56.02	66.79	88.12	109.45	130.94	—	176.12	—	226.40						
	% Dev.,	Linear	−0.29	−0.30	−0.42	−0.64	−0.95	—	−1.55	—	−2.19						0.91
		Lorentz	+0.18	+0.27	+0.34	+0.32	+0.21	—	−0.02	—	−0.33						0.24
Av. % Dev.,		Linear	0.31	0.36	0.54	0.82	0.96	1.04	1.35	1.64	1.99	2.57	3.03	3.07	2.89	2.87	
		Lorentz	0.19	0.26	0.37	0.43	0.48	0.54	0.46	0.46	0.41	0.38	0.29	0.58	0.95	0.95	
Over-all Av. % Dev.,		Linear															1.39
		Lorentz															0.42

that the Lorentz form of the equation of state for mixtures fits the experimental data almost as well as the equation of state fits the data for pure methane and pure n-butane. The average deviation of 0.42 percent for the mixtures, over the temperature range 75–300°C, may be compared with 0.34 percent for pure n-butane, from 150 to 300°C, and 0.39 percent for pure methane, from 75 to 200°C. This agreement is very satisfactory. The linear form of the equation of state, with an average deviation of 1.56 percent, although less accurate than the Lorentz form, is in good enough agreement with the data for most practical purposes.

Space does not permit a complete comparison of all experimental points with the data. A partial comparison is afforded by Table V, for the equimolal mixture. Here the published molal composition and densities, which were based on 1941 molecular weights, have been converted to 1937 molecular weights, the latter having been used in obtaining the constants of Table III.

Except for a uniform tendency for pressures calculated by the Lorentz form to be slightly lower than observed pressures at this composition, there are no marked systematic deviations from the Lorentz form of the equation of state. At the other two compositions, pressures calculated by the Lorentz form are slightly high. Pressures calculated by the linear form are high at all points at every composition.

Methane-Ethane

Michels and Nederbragt[10] have made careful measurements of P-V-T properties of methane-ethane mixtures, over a rather narrow temperature range. In Table VI their observations are compared with those predicted by the Lorentz and linear forms of the equation of state. This comparison shows that for the gaseous phase, both the Lorentz and linear forms of the equation of state agree with the data within experimental

[10] A. Michels and G. W. Nederbragt, Physica 6, 656 (1939).

TABLE VI. Deviations of pressures calculated by equation of state from observed pressures for mixtures of methane and ethane.

Mole % CH₄	Temp., °C	Phase Density, moles/liter		1	2	Gas 3	4	5	9	Liquid or retrograde gas 10	11	13	Av. % deviation
							Pressure, normal atmospheres						
19.96	0		Obs.	18.59	30.36							57.76	
		% Dev.,	Linear	+0.27	+0.13							−3.39	1.25
			Lorentz	+0.27	+0.20							−2.03	0.83
	25.35		Obs.	21.04	36.03	46.22	52.90	57.31					
		% Dev.,	Linear	+0.19	+0.33	+0.35	+0.19	−0.05					0.22
			Lorentz	+0.24	+0.39	+0.48	+0.34	+0.17					0.33
	49.84		Obs.	23.38	41.28	54.93							
		% Dev.,	Linear	+0.17	+0.31	+0.51							0.33
			Lorentz	+0.21	+0.36	+0.60							0.39
40.06	0		Obs.	19.38	33.42	43.15			65.89	69.69	75.83		
		% Dev.,	Linear	±0.00	+0.06	−0.02			−0.49	−1.37	−2.10		0.67
			Lorentz	+0.05	+0.15	+0.12			+0.38	−0.37	−0.98		0.34
	25.35		Obs.	21.77	38.78	52.00							
		% Dev.,	Linear	±0.00	+0.10	+0.21							0.10
			Lorentz	+0.05	+0.18	+0.35							0.19
	49.84		Obs.	24.03	43.79	60.20							
		% Dev.,	Linear	−0.04	+0.07	+0.18							0.10
			Lorentz	±0.00	+0.14	+0.30							0.15
60.10	0		Obs.	20.10	36.13	48.83	58.98						
		%. Dev.,	Linear	−0.05	±0.00	+0.02	+0.05						0.03
			Lorentz	±0.00	+0.08	+0.14	+0.24						0.12
	25.35		Obs.	22.43	41.26	57.19							
		% Dev.,	Linear	−0.05	+0.05	+0.14							0.08
			Lorentz	±0.00	+0.12	+0.26							0.13
	49.84		Obs.	24.65	46.10	65.03							
		% Dev.,	Linear	−0.04	+0.04	+0.12							0.07
			Lorentz	±0.00	+0.11	+0.23							0.11
80.09	0		Obs.	20.74	38.50	53.81							
		% Dev.,	Linear	−0.05	−0.03	±0.00							0.03
			Lorentz	−0.05	+0.03	+0.07							0.05
	25.35		Obs.	23.01	43.42	61.75							
		% Dev.,	Linear	±0.00	+0.02	+0.08							0.03
			Lorentz	+0.04	+0.07	+0.16							0.09
	49.84		Obs.	25.20	48.14								
		% Dev.,	Linear	+0.04	+0.12								0.08
			Lorentz	+0.08	+0.17								0.13
Average % deviation,		Linear		0.08	0.11	0.16	0.12	0.05	0.49	1.37	2.10	3.39	
		Lorentz		0.08	0.17	0.27	0.29	0.17	0.38	0.37	0.98	2.03	
Over-all av. % deviation,		Linear											0.28
		Lorentz											0.25

error. At the few points given for the liquid phase, the Lorentz form is in better agreement with the data.

Methane-Propane

Figure 1 shows a graphical comparison of pressures observed by Sage, Lacey, and Schaafsma[11] for an equimolal mixture of methane and propane with those calculated by the linear form of the equation of state. These experimental points are more irregular than those considered above, so that the comparison with the equation is less conclusive. Nevertheless, practical agreement

[11] Sage, Lacey, and Schaafsma, Ind. Eng. Chem. **26**, 214 (1934).

with the data is found in both the gaseous and liquid regions.

Conclusion

The comparisons given above suggest that the Lorentz form of the equation of state for mixtures may be used to calculate pressures of gaseous or liquid mixtures of light hydrocarbons with an average error under 0.5 percent. The linear form of the equation of state is in less satisfactory agreement with the data, since it leads to pressures about 2 percent too high. In practical applications, where this error may not be serious, the linear form is recommended because it is easier to use.
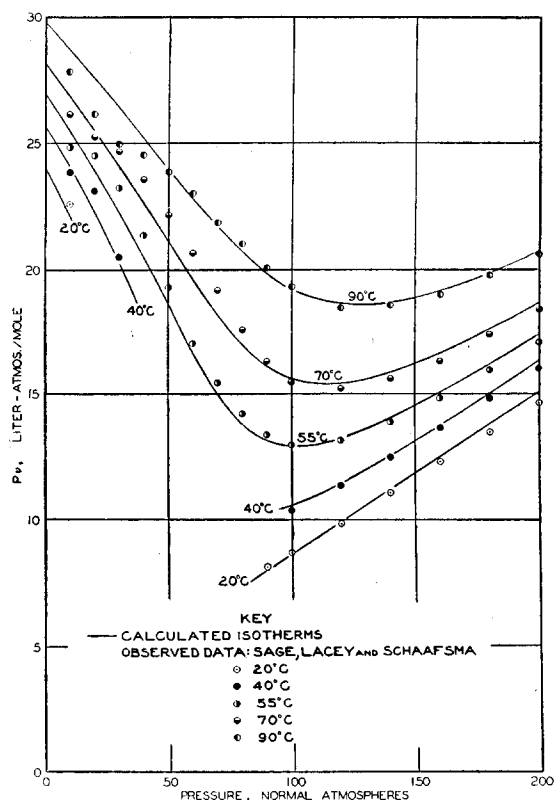
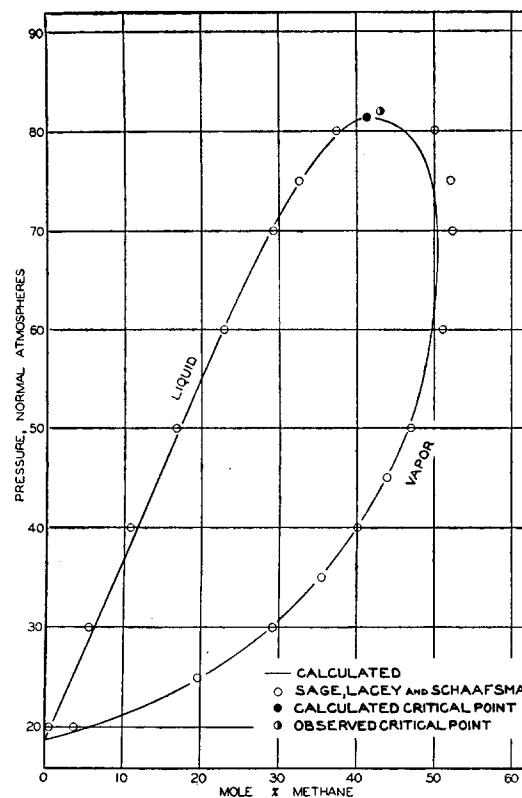FIG. 1. P-V-T data for equimolal mixture of methane and propane.

FIG. 2. Liquid-vapor equilibria for the system methane-propane at 55°C.

D. COMPARISON OF EQUATION WITH LIQUID-VAPOR EQUILIBRIA FOR MIXTURES OF HYDROCARBONS

Methane-Propane

Since the equation of state gives a satisfactory representation of P-V-T properties, it is to be anticipated that the basic equation for mixtures will be equally successful in predicting liquid-vapor equilibria.

In Fig. 2, the observed equilibrium points for the methane-propane system at 55°C [11] are compared with the border curve predicted by the equation, with linear combination of B_0. Except for the dew point curve at pressures above 60 atmospheres, observed and calculated data coincide within 1 mole percent methane; the agreement above 60 atmospheres is still quite satisfactory. The predicted border curve has the correct qualitative characteristics in the region of critical phenomena and retrograde condensation above 60 atmos. Furthermore, the agreement between the observed and calculated

critical points is noteworthy:

	Ob-served	Calcu-lated
Critical pressure—atmospheres	82.00	81.31
Critical composition—mole percent CH$_4$	43.2	41.4

The method used in calculating the coordinates of a pair of points on the border curve representing a liquid and a vapor phase in equilibrium makes use of the following principle: Assume a liquid composition x_1. Find by trial a liquid density d^L, a gaseous density d^G, and a gaseous composition y_1 such that the three conditions for liquid-vapor equilibrium,

$$P(d^L, x_1) = P(d^G, y_1), \qquad \text{(D1)}$$

$$RT \ln f_1(d^L, x_1) = RT \ln f_1(d^G, y_1), \quad \text{(D2)}$$

$$RT \ln f_3(d^L, x_1) = RT \ln f_3(d^G, y_1), \quad \text{(D3)}$$

are satisfied. Then P is the pressure at which liquid of composition x_1 is in equilibrium with vapor of composition y_1.

The critical point is calculated by finding by trial composition x_1 and pressure P at the tem-

TABLE VII. Distribution coefficients for the methane-n-butane system.

Temp. °F	Pressure lb./sq. in.	Mole fraction methane Liquid	Vapor	Methane Obs.	Calculated by equation Linear	Lorentz	% Deviation Linear	Lorentz	n-Butane Obs.	Calculated by equation Linear	Lorentz	% Deviation Linear	Lorent
70	400	0.1379	0.8831	6.402	6.203	5.523	+3.11	+13.7	0.1359	0.1291	0.1307	+5.00	+3.83
	800	0.2804	0.9174	3.269	3.230	2.956	+1.19	+9.58	0.1149	0.1117	0.1146	+2.78	+0.26
	1200	0.4161	0.9178	2.216	2.205	2.074	+0.50	+6.41	0.1403	0.1392	0.1441	+0.78	−2.71
	1600	0.5450	0.8942	1.641	1.647	1.589	−0.37	+3.17	0.2318	0.2279	0.2373	+1.68	−2.37
160	400	0.0885	0.6233	7.018	6.994	6.252	+0.34	+10.9	0.4142	0.4250	0.4279	−2.61	−3.31
	800	0.2119	0.7451	3.516	3.551	3.269	−1.00	+7.03	0.3236	0.3267	0.3326	−0.96	−2.78
	1200	0.3328	0.7593	2.283	2.309	2.182	−1.14	+4.42	0.3605	0.3588	0.3681	+0.47	−2.11
	1600	0.4696	0.7285	1.551	1.560	1.523	−0.58	+1.81	0.5118	0.5107	0.5226	+0.21	−0.16
250	800	0.1519	0.4147	2.731	2.706	2.570	+0.92	+5.90	0.6906	0.7045	0.7096	−2.01	−2.75
	1200	0.3020	0.4101	1.358	1.330	1.316	+1.84	+3.09	0.8453	0.8548	0.8597	−1.12	−1.70
Av. % Dev.							1.10	6.60				1.76	2.20

TABLE VIII. Distribution coefficients for the ethane-n-butane system.

Mole fraction ethane Liquid	Vapor	Temp. °F	Pressure lb./sq.in.	Ethane Obs.	Calculated by equation Linear	Lorentz	% Deviation Linear	Lorentz	n-Butane Obs.	Calculated by equation Linear	Lorentz	% Deviation Linear	Lorentz
0.1748	0.585	131.5	200	3.347	3.290	3.142	+1.70	+6.14	0.5029	0.5122	0.5122	−1.84	−1.84
	0.428	208.8	400	2.449	2.385	2.299	+2.61	+6.12	0.6932	0.7042	0.7046	−1.59	−1.60
	0.281	265.2	600	1.608	1.602	1.574	+0.37	+2.11	0.8713	0.8743	0.8748	−0.34	−0.40
0.4509	0.896	58.7	200	1.987	1.986	1.933	+0.05	+2.72	0.1894	0.1891	0.1873	+0.16	+1.11
	0.8075	128.8	400	1.791	1.774	1.744	+0.95	+2.62	0.3506	0.3579	0.3557	−2.08	−1.46
	0.703	181.8	600	1.559	1.562	1.531	−0.19	+1.80	0.5409	0.5438	0.5436	−0.54	−0.50
0.6577	0.962	26.0	200	1.436	1.450	1.432	+0.89	+2.12	0.1110	0.1087	0.1056	+2.07	+4.86
	0.9195	88.4	400	1.398	1.395	1.381	+0.21	+1.22	0.2352	0.2387	0.2332	−1.49	+0.85
	0.8635	133.4	600	1.313	1.313	1.305	±0.00	+0.61	0.3988	0.3964	0.3910	+0.60	+1.96
	0.7695	174.5	800	1.170	1.167	1.168	+0.26	+0.17	0.6734	0.6802	0.6724	−1.01	+0.15
0.8220	0.9665	63.8	400	1.176	1.171	1.168	+0.43	+0.68	0.1882	0.1894	0.1808	−0.64	+3.93
	0.9395	103.2	600	1.143	1.140	1.137	+0.26	+0.52	0.3399	0.3430	0.3306	−0.91	+2.74
	0.8765	138.5	800	1.066	1.064	1.066	+0.19	±0.00	0.6938	0.7038	0.6916	−1.44	+0.32
Av. % Dev.							0.62	2.06				1.13	1.67

perature T (in this case 55°C) such that the conditions,

$$\left[\frac{\partial(RT \ln f_1)}{\partial x_1}\right]_{P,T} = 0, \qquad (D4)$$

$$\left[\frac{\partial^2(RT \ln f_1)}{\partial x_1^2}\right]_{P,T} = 0, \qquad (D5)$$
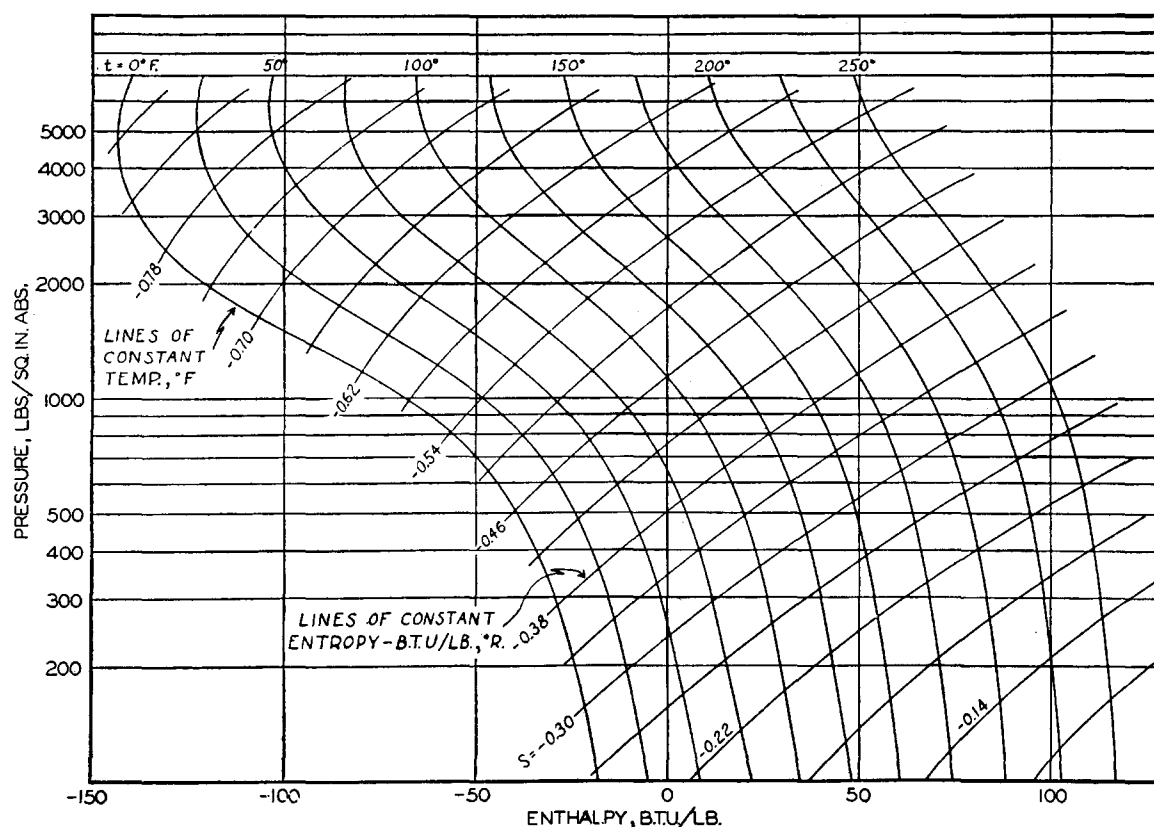
are satisfied.

The type of comparison between equation and data used for the methane-propane system requires laborious calculation. In the other mixtures of light hydrocarbons to be examined, a simpler, but less exact, method has been used. For these other mixtures, distribution coefficients (K_i) are calculated by the equation:

$$K_i = \frac{f_i^L}{x_i} \Big/ \frac{f_i^G}{y_i}, \qquad (D6)$$

where f_i^L/x_i and f_i^G/y_i are evaluated at the observed equilibrium compositions. In an exact treatment, f_i^L/x_i and f_i^G/y_i should be evaluated at the calculated equilibrium compositions, at which

$$f_i^L = f_i^G. \qquad (D7)$$

For ideal solutions and in cases where observed distribution coefficients equal those calculated by Eq. (B24), there will be no difference between results of approximate Eq. (D6) and the exact Eq. (D7). For the mixtures now to be considered, distribution coefficients evaluated from (D6) will not differ from the true calculated values by more than 2 or 3 percent. Use of Eq. (D6) has the practical advantage that it is unnecessary to solve by successive approximation for the calculated compositions. These distribution coef-

FIG. 3. Mollier chart for a natural gas of the following composition: methane—89.47 mole percent; ethane—7.91 mole percent; propane—1.92 mole percent; n-butane—0.70 mole percent.

ficients are also called K values, and are often used in practical calculations of liquid-vapor equilibria.

Methane-n-Butane

An investigation of liquid-vapor equilibria in the system methane-n-butane has been described by Sage, Hicks, and Lacey.[12] A comparison of their observed liquid-vapor equilibria with the predictions of the equation is presented in Table VII. The observed distribution coefficients quoted in this table are taken from Table I of the above authors. The points chosen for comparison were selected to include the extreme temperatures studied experimentally and to cover as wide a range of pressure as would permit accurate determination of distribution coefficients from the observed dew- and bubble-point data. Table VII shows that distribution coefficients calcu-

lated from the linear form of the equation are in very good agreement with the experimental data, since the average deviation, 1.10 percent for methane and 1.76 percent for n-butane, are of the order of the experimental error. Distribution coefficients calculated from the Lorentz form of the equation are in less satisfactory agreement with the observations, since the average deviations for this form are 6.60 percent for methane and 2.20 percent for n-butane.

Ethane-n-Butane

Liquid-vapor equilibria in the system ethane-n-butane have been reported by Kay.[13] To facilitate comparison with the equation, these data have been plotted on large-scale temperature-composition diagrams at pressures of 200, 400, 600, and 800 lb./sq. in. and have been interpolated to the liquid compositions studied

[12] Sage, Hicks, and Lacey, Ind. Eng. Chem. 32, 1085 (1940).

[13] W. B. Kay, Ind. Eng. Chem. 32, 353 (1940).

experimentally. These interpolated equilibrium conditions and the "observed" distribution coefficients calculated from them are listed in Table VIII. In this table a comparison is made between the "observed" distribution coefficients and those predicted by the linear and Lorentz forms of the equation; the results are similar to those found for the methane-n-butane system. The predictions of the linear form of the equation are in excellent agreement with the data, since the average deviations, 0.62 percent for ethane and 1.13 percent for n-butane, are of the order of the experimental error. The Lorentz form of the equation is less satisfactory.

Conclusion

The examples cited above show that the linear form of the equation is more satisfactory than the Lorentz form for predicting liquid-vapor equilibria. Since the linear form is simpler, and since it is fairly satisfactory for calculating P-V-T properties, the linear form is preferred in most applications of the equation for calculating thermodynamic properties of mixtures of hydrocarbons.

E. USE OF EQUATION

Three examples will be given of the use of the linear form of the equation to predict thermodynamic properties of mixtures of hydrocarbons for which no experimental data are available.

Mollier Chart

In compressing or expanding natural gas, calculations of pressure and temperature changes and input or withdrawal of work and heat are effected most conveniently with the aid of a Mollier chart, exhibiting the variables, pressure, temperature, enthalpy, and entropy. Figure 3 illustrates such a chart for a natural gas of the composition indicated. This chart has been calculated from the following equation:

Pressure: Eq. (a) of Table II;
Enthalpy: Eq. (c) of Table II;
Entropy: Eq. (d) of Table II.

The functions H^0 and S^0 occurring in these equations were evaluated from the limiting specific heat at zero pressure $C_p{}^0$ as follows:

$$H^0 = \int_{T_0}^T C_p{}^0 dT, \tag{E1}$$

$$S^0 = \int_{T_0}^T C_p{}^0 dT/T, \tag{E2}$$

where

$$T_0 = 273.13°K.$$

It has been assumed that $C_p{}^0$ for light hydrocarbons is given by the equation:

$$C_p{}^0 = A + BT, \tag{E3}$$

where A and B are:

	$A(L\text{-atmos.}/g \text{ mole-}°K)$	$B(L\text{-atmos.}/g \text{ mole-}°K^2)$
Methane	0.2231	0.0004681
Ethane	0.1764	0.001170
Propane	0.3718	0.001239
n-Butane	0.4255	0.001766

Enthalpy-Composition Diagram

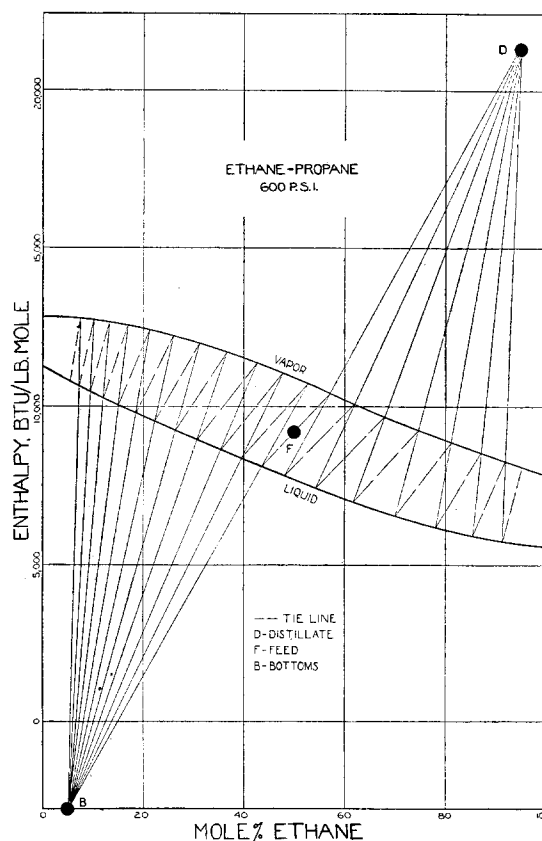Design of distilling columns operating at high pressures is complicated by the fact that dis-

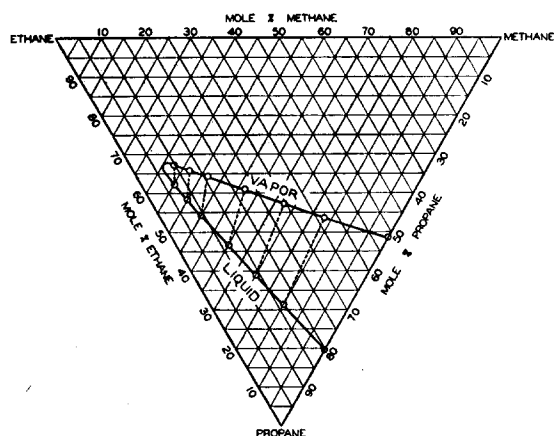FIG. 4. Enthalpy-composition diagram for the system ethane-propane at 600 lb./sq. in.

FIG. 5. Liquid-vapor equilibria for the system methane-ethane-propane at 800 lb./sq. in. and 131°F.

tribution coefficients and latent heats vary with composition. Despite these complications, columns separating two-component mixtures can be accurately designed with the aid of an enthalpy-composition diagram, by the method of Ponchon and Savarit.[14] Such a diagram for the system ethane-propane at 600 pounds per square inch absolute is illustrated in Fig. 4. Compositions of coexistent phases were calculated in the same manner as for Fig. 2, and enthalpies in the same manner as for the Mollier chart. The example worked out in Fig. 4 is for a column of the following characteristics:

	Feed	Overhead	Bottoms
Temperature, °F	141	82	196
Mole % Ethane	50	95	5

	Stripping	Enriching
Number theoretical trays	11	7
Heat input, B.t.u./lb. mole prod.	+13,200	−12,800

Three-Component System

Calculation of liquid-vapor equilibrium in multicomponent systems is difficult because of

the large number of simultaneous equations to be solved by trial. To illustrate this type of calculation, equilibrium compositions of liquid and vapor phases of the system methane-ethane-propane at 800 lb./sq. in. and 131°F are shown in Fig. 5.

Conditions for equilibrium in this problem are expressed by the following equations:

$$P(d^G, y_1, y_2) = 800 \text{ lb./sq.in.} \tag{E4}$$

$$P(d^L, x_1, x_2) = 800 \text{ lb./sq.in.} \tag{E5}$$

$$RT \ln f_1(d^G, y_1, y_2) = RT \ln f_1(d^L, x_1, x_2). \tag{E6}$$

$$RT \ln f_2(d^G, y_1, y_2) = RT \ln f_2(d^L, x_1, x_2). \tag{E7}$$

$$RT \ln f_3(d^G, y_1, y_2) = RT \ln f_3(d^L, x_1, x_2). \tag{E8}$$

The subscripts 1, 2, 3 refer to methane, ethane, and propane, respectively. To find the compositions of a pair of coexistent phases, one of the mole fractions, x_1 for example, is fixed. It is then necessary to find by trial the composition of the gas phase y_1, y_2, the density of the gas phase d^G, the density of the liquid phase d^L, and the mole fraction of ethane in the liquid x_2, such that the five equations of condition are satisfied.

The results of such a calculation are illustrated in Fig. 5. The full line of this figure represents the border curve computed for this system; the dotted lines represent tie lines connecting liquid and vapor phases. The occurrence of critical phenomena in this system at the specified temperature and pressure is demonstrated by the approach of the tie lines to tangency with the border curve as the mole fraction of ethane in the system is increased.

ACKNOWLEDGMENT

[14] C. S. Robinson and E. R. Gilliland, *Elements of Fractional Distillation* (McGraw-Hill Book Company, New York, 1939), p. 107.