mixtures containing other types of compounds such as aromatics and nonhydrocarbons. The correlation will fail completely if these other types of compounds are present in major amounts in the mixture.

It is impossible to estimate the accuracy of a correlation such as this because of the scarcity of good experimental data. The regions of greatest uncertainty in Figures 1 and 2 are those corresponding to high M.A.B.P.-low temperatures and the critical point of the region of high pressure-low temperature on Figure 1. The uncertainty in this latter region is due to uncertainty in PVT measurements on pure compounds in the vicinity of the critical point.

NOTATION

B = normal boiling point, °F.
C_p° = molal heat capacity for ideal gas state, B.t.u./(lb. mole)(°R.)
H = enthalpy of a real gas or liquid, B.t.u./lb. or B.t.u./lb. mole
H° = enthalpy of an ideal gas, B.t.u./lb. or B.t.u./lb. mole
M.A.B.P. = molal average boiling point, °F. ($\sum x_i B_i$)
P = pressure, lb./sq. in. abs.
T = temperature, °F.
x = mole fraction

Superscripts

L = liquid phase
V = vapor phase

Subscript

i = ith component in a mixture

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Vapor Pressures: The Saturated Aliphatic Hydrocarbons

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A rigorous analysis of the available data presented in the literature for all the saturated aliphatic hydrocarbons from methane through *n*-eicosane was conducted to establish the constants *A*, *B*, *C*, and *D* of the vapor-pressure equation developed by Frost and Kalkwarf (21). With all the constants determined, vapor pressures can be calculated accurately from the triple to the critical point. The actual constants *A*, *B*, *C*, and *D* have been calculated from the available reported vapor-pressure data of eighty-seven saturated aliphatic hydrocarbons and include all the normal paraffins through eicosane and all the isomeric paraffins through the nonanes.

In order to ascertain the validity of calculated-vapor-pressure constants, values of *A*, *B*, *C*, and *D* were produced from the molecular structure and normal boiling point for all the normal paraffins through eicosane and all the thirty-four isomeric nonanes. The normal paraffins were selected to cover the range of the saturated aliphatic hydrocarbons; whereas the nonanes were chosen because they represent the most complex structures for which reported vapor pressures are available.

With the calculated constants, vapor pressures were evaluated from the equation at several representative points and were compared with reported values to produce an overall absolute average percentage of deviation of 0.58 for the normal paraffins and 0.73 for the isomeric nonanes, or 0.68 for these fifty-four saturated aliphatic hydrocarbons.

In order to obtain information on the vapor-pressure behavior of substances for which experimental data are available in limited ranges, extrapolations and interpolations are necessary. The resulting degree of accuracy will depend upon the reliability of the methods used to extend the experimental data. To facilitate these extensions, several vapor-pressure expressions have been proposed. The familiar Clausius-Clapeyron vapor-pressure equation

$$\log P = A + \frac{B}{T} \qquad (1)$$

possesses considerable simplicity because of the assumptions used in its development from the rigorous thermodynamic relationship of Clapeyron and has been applied to define satisfactorily the vapor pressures of metals (*5, 41*). However, Equation (1) fails to represent properly the complete vapor-pressure behavior of many substances and must be applied over limited temperature ranges (*34*). Modifications of Equation (1) have been proposed by Antoine (*1*) and Cox (*16*).

Rankine (*44*), Kirchhoff (*31*), and Dupré (*18*) empirically proposed a refinement to Equation (1) with the introduction of a third constant to define the vapor-pressure equation as

$$\log P = A + \frac{B}{T} + C \log T \qquad (2)$$

Equation (2) can be developed from the Clapeyron equation by assuming the molar heat of vaporization to vary linearly with temperature. Although Equation (2) expresses the vapor-pressure behavior over wider ranges of temperature, still it fails generally to define satisfactorily the complete vapor-pressure function included between the triple and critical points. Modifications of Equation (2) have been proposed by van Laar (*56*), Riedel (*45*), and Gamson and Watson (*22*). Thodos (*53*) points out that a plot of precise experimental vapor pressures between the critical and triple points for normal paraffins produces an elongated *S*-shaped curve as presented in Figure 1. To retain the characteristics of the actual vapor-pressure function, Frost and Kalkwarf (*21*), beginning with the Clapeyron equation and assuming van der Waals' equation to apply, developed the semitheoretical expression

$$\log P = A + \frac{B}{T} + C \log T + D \frac{P}{T^2} \tag{3}$$

The shapes of curves resulting from Equations (1), (2), and (3) are presented in Figure 1.

VAPOR PRESSURES OF THE SATURATED ALIPHATIC HYDROCARBONS

In the past, considerable effort has been expended toward predicting the vapor pressures of organic substances. Owing to the industrial importance of the lighter hydrocarbons and the increasing importance of the heavier hydrocarbons, much of the recent work has dealt with the procurement of precise experimental vapor pressures in this field. Although considerable valuable experimental background has been established in the last 10 years for hydrocarbons, particularly by the exacting work of the Bureau of Standards group (*46*, *57*), the results produced are specific to the compounds studied for the pressure ranges investigated. The information provided should prove valuable in the development of a possible generalized pattern capable of handling hydrocarbons for which no experimental data are available and which can produce accurate calculated vapor-pressure values over extended pressure ranges.

The vapor-pressure function can be defined through Equation (3) over the pressure range included between the triple and critical points. To utilize this equation, the values of the four vapor-pressure constants, A, B, C, and D, which are specific to each substance, are required. The substitution of four reliable experimental vapor-pressure points in Equation (3) will produce four linear equations, the simultaneous solution of which yields the four vapor-pressure constants. Perry and Thodos (*42*) following this procedure established these constants for the normal paraffins through *n*-dodecane and were able to produce calculated vapor-pressure values of which the percentage of deviation was 0.27. Although this approach yields constants capable of producing precise vapor pressures, frequently the necessary experimental data to evaluate these constants may not be available.

In the general vapor-pressure equation the constant D is defined as equal to $a/2.303R^2$, where a represents the pressure van der Waals' constant. Therefore, knowledge of the value of a necessarily establishes the constant D. Both pressure and volume van der Waals' constants a and b, respectively, can be calculated from the critical point through the relationships

$$a = \frac{27R^2T_c^{\,2}}{64P_c} \tag{4}$$

$$b = \frac{RT_c}{8P_c} \tag{5}$$

and therefore the critical point can be utilized to establish the constant D.

Whenever experimental critical constants are not available, the methods proposed by Lydersen (*38*), Michaels and Thodos (*40*), and Thodos (*54*) may be applied. All these methods require the use of group contributions for the calculation of the critical temperature and pressure from the molecular structure of the compound. For the saturated aliphatic hydrocarbons presented in this investigation the values of constant D were established from the calculated van der Waals' constants a evaluated by Thodos (*54*). These calculated values of D are presented in Table 1.* This particular method was used because of the lack of experimental critical points for the majority of hydrocarbons studied and also because this approach produced more precise critical temperatures and pressures than were possible by the other two methods.

With constant D established, constants B and C can be evaluated from experimental vapor-pressure values by a reference-point procedure applied to the general vapor-pressure equation. This procedure consists of referring all the reported vapor-pressure points to a particular reliable reference value and rearranging the resultant expression to define constants B and C as the slope and intercept of a straight-line function.

Any point on the vapor-pressure function can be represented by Equation (3) as

$$\log P = A + \frac{B}{T} + C \log T + D \frac{P}{T^2} \tag{3}$$

For the reference point, this equation becomes

$$\log P_b = A + \frac{B}{T_b} + C \log T_b + D \frac{P_b}{T_b^{\,2}} \tag{6}$$

where P_b and T_b represent a selected vapor-pressure point. Subtracting Equation (6) from Equation (3) yields

$$\log \frac{P}{P_b} = B\left[\frac{1}{T} - \frac{1}{T_b}\right] + C \log \frac{T}{T_b} + D\left[\frac{P}{T^2} - \frac{P_b}{T_b^{\,2}}\right] \tag{7}$$

which when rearranged and divided through by $\log T/T_b$ produces

$$\frac{\log P/P_b - D[P/T^2 - P_b/T_b^{\,2}]}{\log T/T_b} = B\,\frac{[1/T - 1/T_b]}{\log T/T_b} + C \tag{8}$$

Equation (8) should be linear when

$$Y = \frac{\log P/P_b - D[P/T^2 - P_b/T_b^{\,2}]}{\log T/T_b}$$

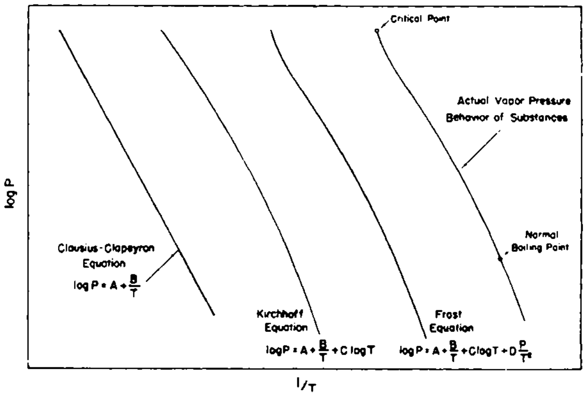
is plotted against

$$X = \frac{[1/T - 1/T_b]}{\log T/T_b}$$

if Equation (3) properly represents the vapor-pressure function and the constant D has been evaluated correctly. Figure 2 presents a plot of Y vs. X for *n*-heptane that is linear through the range included between the lowest experimental value of Willingham et al. (*57*), 47.66 mm. of mercury, and the experimental critical value of Beattie and Kay (*9*). The resulting linearity of Figure 2 strongly implies that Equation (3) properly represents the vapor-pressure function and that constant D has been correctly determined.

The constants B and C are discrete values for a particular substance, and therefore a plot of Y-vs.-X values resulting from any experimental investigation should produce a single straight line of slope B and intercept C, regardless of the choice of the reference point. This fact makes it possible to treat experimental points of various investigations whose range may be limited to certain pressure regions by the selection of a reliable value

Fig. 1. Graphical representation of some vapor-pressure equations.



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*Complete tables are available from the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., as document 4951, obtainable for $1.25 for microfilm or photoprints.

TABLE 1. CONSTANTS OF THE VAPOR-PRESSURE EQUATION LOG $P = A + B/T + C \log T + D(P/T^2)$ ESTABLISHED FROM A COMPREHENSIVE ANALYSIS OF VAPOR-PRESSURE DATA OF THE SATURATED ALIPHATIC HYDROCARBONS

	T_b, °K.	A	B	C	D	References
Methane	111.49	13.49190	−567.59	−2.70212	0.19212	*20, 29, 32, 54*
Ethane	184.466	16.85324	−1,070.59	−3.60963	0.46665	*8, 13, 25, 30, 32, 33, 36, 37, 43, 54*
Propane	231.105	19.07337	−1,427.41	−4.24329	0.78564	*11, 15, 17, 23, 28, 32, 47, 52, 54*
n-Butane	272.666	21.05182	−1,768.05	−4.80311	1.16463	*4, 12, 14, 26, 32, 48, 54*
n-Pentane	309.238	22.94265	−2,098.87	−5.33564	1.59674	*10, 32, 39, 54, 57, 61*
2,2-Dimethylpropane	282.665	21.68978	−1,838.01	−5.02604	1.43534	*3, 6, 32, 54*
n-Hexane	341.905	24.93410	−2,428.98	−5.90492	2.07790	*27, 32, 54, 55, 57*
2,3-Dimethylbutane	331.153	22.98513	−2,227.62	−5.31367	1.89817	*32,54, 57, 60*
n-Heptane	371.591	26.88236	−2,753.17	−6.46159	2.60489	*9, 25, 32, 49, 51, 54, 57, 58*
3-Methylhexane	365.015	25.94237	−2,642.58	−6.18037	2.47344	*32, 46, 54*
2,4-Dimethylpentane	353.665	25.47550	−2,515.62	−6.08036	2.40996	*19, 32, 54*
2,2,3-Trimethylbutane	354.037	22.86290	−2,360.79	−5.22840	2.23608	*19, 32, 50, 54*
n-Octane	398.830	29.23812	−3,099.36	−7.15220	3.17549	*32, 35, 54, 57, 59*
4-Methylheptane	390.874	27.64799	−2,936.97	−6.66209	3.03352	*32, 54, 57*
2,5-Dimethylhexane	382.268	26.82104	−2,812.77	−6.42726	2.96504	*32, 54, 57, 60*
3-Methyl-3-ethylpentane	391.424	24.13358	−2,702.61	−5.53952	2.78530	*32, 54, 57*
2,2,3,3-Tetramethylbutane	379.635	20.27060	−2,393.67	−4.30131	2.57544	*32, 46, 54*
n-Nonane	423.961	30.83077	−3,400.33	−7.59158	3.78666	*54, 57*
3-Methyloctane	417.345	30.60717	−3,312.44	−7.55782	3.63527	*46, 54*
4-Ethylheptane	414.365	30.29260	−3,258.78	−7.47429	3.57001	*46, 54*
2,5-Dimethylheptane	409.165	30.24904	−3,216.74	−7.47445	3.52393	*46, 54*
4,4-Dimethylheptane	408.365	26.81228	−2,994.56	−6.36295	3.41140	*46, 54*
2-Methyl-4-ethylhexane	406.965	28.49224	−3,072.73	−6.92721	3.45960	*46, 54*
2,2,4-Trimethylhexane	399.705	28.55469	−3,012.88	−6.97689	3.34912	*46, 54*
2,3,4-Trimethylhexane	412.165	26.79522	−3,017.34	−6.35117	3.35624	*46, 54*
3,3-Diethylpentane	419.333	25.24652	−2,961.91	−5.84034	3.31169	*46, 54*
2,3,3,4-Tetramethylpentane	414.716	25.15949	−2,920.50	−5.82578	3.15114	*46, 54*
n-Dodecane	489.443	38.36512	−4,465.27	−9.80767	5.85175	*54, 57*
n-Hexadecane	559.958	44.36486	−5,608.40	−11.45869	9.09708	*46, 54*
n-Eicosane	615.865	58.46119	−7,304.73	−15.68214	12.84792	*46, 54*

The dimensions of constants A, B, C and D presented in this table are consistent and produce, with absolute temperatures in degrees Kelvin, vapor pressures in millimeters of mercury.

within the particular set for a reference point. This analysis permits the examination of the consistency of a particular set of values within themselves to produce straight lines, which should coincide for all experimental investigations.

The results of this procedure are illustrated for n-heptane in Figure 2, in which the experimental data of Kay (*25*) are referred to his value of 521.055°K. and 15,510 mm.; those of Willingham et al. (*57*) are referred to their value of 345.095°K. and 324.97 mm. The results for n-heptane of six separate experimental investigations, each using its own reference point, produced straight lines which coincide and appear in Figure 2 as the single line of slope $B = -2{,}753.17$ and intercept $C = -6.46159$.

The use of an incorrect value of D with good experimental vapor-pressure values will yield curved lines of Y vs. X; whereas a correct value of D with inaccurate experimental vapor-pressure values will produce scattered points of correlation. In this investigation the values of B and C were determined by the selection of two points which fixed the best straight line that represented the reported data for a particular compound. With this procedure constants B and C were evaluated from the reported vapor-pressure

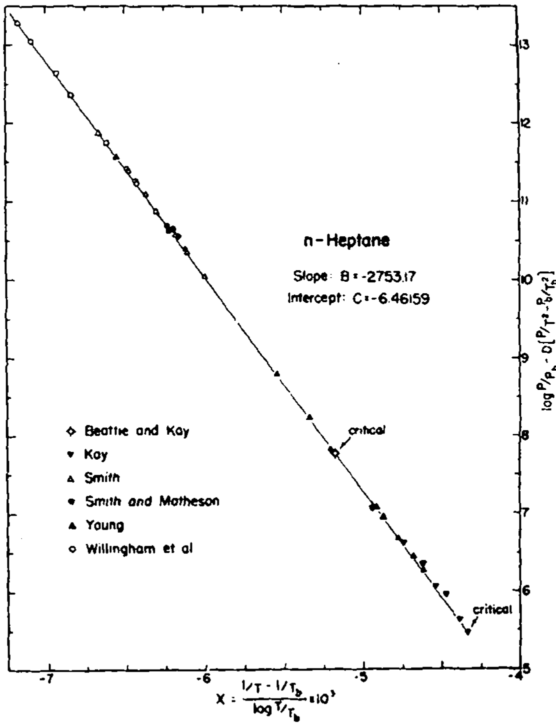


Fig. 2. Vapor-pressure–temperature reference moduli Y and X for n-heptane.

data of eighty-seven saturated aliphatic hydrocarbons, including all the normal paraffins through eicosane and all the isomeric paraffins through the nonanes. Both values *B* and *C* for these hydrocarbons appear in Table 1.

With the three constants *B*, *C*, and *D* established, the constant *A* can be evaluated by substituting a single reliable vapor-pressure value in Equation (3). By use of the normal boiling point as the reliable value, constant *A* was also calculated for these saturated aliphatic hydrocarbons and is included along with the other three constants in Table 1.

These constants calculated from reported vapor-pressure values are useful for producing exacting vapor pressures over the complete range, as illustrated in Table 5 for ethane and 2, 2, 4-trimethylhexane. However, their application is limited to the eighty-seven saturated aliphatic hydrocarbons appearing in Table 1. To facilitate the evaluation of these constants for the saturated aliphatic hydrocarbons, where no experimental vapor-pressure data are presently available, correlation procedures were undertaken to devise methods for their prediction.

RELATIONSHIP OF CONSTANT *B* AND MOLECULAR STRUCTURE

Attempts were made to correlate empirically the constants *B* and *C* with the normal boiling point and with each other, the normal boiling point being used as the property capable of differentiating between the isomeric paraffins. No reasonable correlation was found to exist between constants *B* and *C* and the normal boiling point or with each other and the normal boiling point. Therefore, a study for the prediction of either constant *B* or *C* from the molecular structure was undertaken. A procedure analogous to that proposed by Thodos (*54*) for the evaluation of the van der Waals' constants was adopted. This method produced *B* values, which were consistent with the slopes *B* resulting from the analysis of reported vapor-pressure data. On the other hand, no correlation was found for constant *C*.

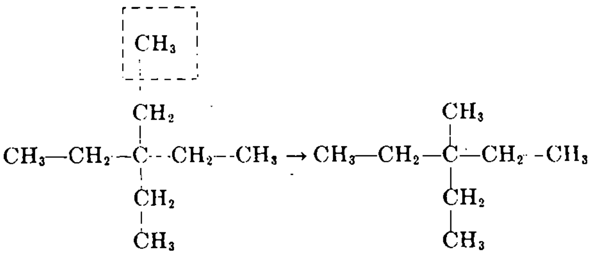
This analysis revealed that the constant *B* for the saturated aliphatic hydrocarbons varies linearly with the number of carbon atoms in the molecule and may be defined through the expression

$$B = -[B_0 + \Sigma\Delta(B)] \qquad (9)$$

where B_0 represents the constant *B* for the base group, methane, and $\Delta(B)$ the group contribution required in the successive substitution of hydrogen atoms by methyl groups. The numerical magnitude of the group contributions, $\Delta(B)$, depends primarily on the nature of the carbon atom on which the methyl substitution is made and second on the nature of the surrounding carbon atoms. The types of carbon atoms involved in this study were associated with the number of carbon-to-carbon linkages and may be defined as

Type	1	2	3	4
Structure	$-CH_3$	$-\overset{\vert}{C}H_2$	$-\overset{\vert}{\underset{\vert}{C}}H$	$-\overset{\vert}{\underset{\vert}{C}}-$

The numerical values of the different group contributions, $\Delta(B)$, presented in Table 2 are the results of average values obtained as differences between *B* values for hydrocarbons having similar structures but differing in molecular dimensions by a single methyl group. From Table 1, for example, the actual *B* values for 3,3-diethylpentane and 3-methyl-3-ethylpentane are −2,961.91 and −2,702.61, respectively. Thus the subtraction of a methyl group from 3,3-diethylpentane to produce 3-methyl-3-ethyl-pentane



$$CH_3-CH_2-\overset{\overset{\boxed{CH_3}}{|}}{\overset{CH_2}{\underset{\underset{CH_3}{CH_2}}{C}}}-CH_2-CH_3 \rightarrow CH_3-CH_2-\overset{CH_3}{\underset{\underset{CH_3}{CH_2}}{C}}-CH_2-CH_3$$

yields a group contribution value, $\Delta(B)$, of $-[-2{,}961.91-(-2{,}702.61)] = 259.30$. This contribution value, $\Delta(B)$, must be associated with the replacement of a hydrogen atom by a methyl group on a type-1 carbon atom adjoined to a type-4 carbon atom and designated as a 4← 1 group contribution value. The average value for this type of substitution was found to be 262.96 and appears in Table 2.

In Table 2 the type of carbon atom from which the arrows originate is the carbon atom involved in the replacement of a hydrogen atom by a methyl group; the adjacent carbon atoms are those to which the arrows are directed. Therefore the designation $1 \leftarrow \underset{\underset{1}{\downarrow}}{3} \rightarrow 2$ con-

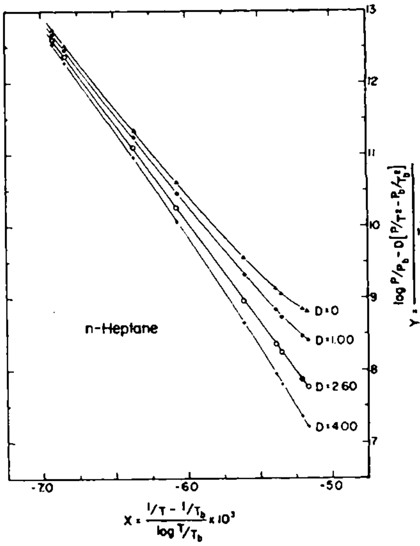


Fig. 3. Effect of variation of constant *D* on variables *Y* and *X* for *n*-heptane.

TABLE 2. METHYL GROUP CONTRIBUTIONS, $\Delta(B)$, IN THE REPLACEMENT OF HYDROGEN FOR THE SYNTHESIS OF MOLECULAR STRUCTURES OF SATURATED ALIPHATIC HYDROCARBONS

	$\Delta(B)$
A. Base group-methane $B_0 = 567.59$	
B. Primary methyl group contribution in the replacement of hydrogen of base group	503.00
C. Secondary methyl group contributions in the replacement of hydrogen of saturated aliphatic hydrocarbons	
$1 \leftarrow 1$	356.82
$2 \leftarrow 1$	334.39
$3 \leftarrow 1$	294.07
$4 \leftarrow 1$	262.96
$1 \leftarrow 2 \rightarrow 1$	227.60
$1 \leftarrow 2 \rightarrow 2$	200.39
$1 \leftarrow 2 \rightarrow 3$	191.86
$2 \leftarrow 2 \rightarrow 2$	187.91
$2 \leftarrow 2 \rightarrow 3$	194.36
$1 \leftarrow \underset{\underset{1}{\downarrow}}{3} \rightarrow 1$	183.00
$1 \leftarrow \underset{\underset{1}{\downarrow}}{3} \rightarrow 2$	149.28
$1 \leftarrow \underset{\underset{1}{\downarrow}}{3} \rightarrow 3$	133.76
$1 \leftarrow \underset{\underset{1}{\downarrow}}{3} \rightarrow 4$	125.00
$2 \leftarrow \underset{\underset{1}{\downarrow}}{3} \rightarrow 2$	89.89
$2 \leftarrow \underset{\underset{1}{\downarrow}}{3} \rightarrow 3$	83.01
$3 \leftarrow \underset{\underset{1}{\downarrow}}{3} \rightarrow 3$	228.58

The dimension of constant *B* resulting from the foregoing group contributions are in degrees Kelvin.

TABLE 3. CONSTANTS A, B, C, AND D CALCULATED FROM MOLECULAR STRUCTURE AND THE NORMAL BOILING POINT OF THE NORMAL PARAFFINS AND AVERAGE ABSOLUTE PERCENTAGE OF DEVIATION RESULTING FROM THEM

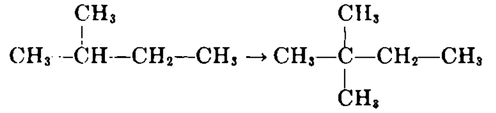
	Critical constants		Calculated constants				Average percentage of deviation*
	T_c, °K.	P_c, atm.	A	B	C	D	
Methane	191.065	45.8	13.47611	−567.59	−2.69441	0.19212	0.22
Ethane	305.465	48.2	16.82808	−1,070.59	−3.59870	0.46665	0.08
Propane	369.965	42.0	19.07662	−1,427.41	−4.24333	0.78564	0.51
n-Butane	425.165	37.5	20.87990	−1,761.80	−4.74193	1.16463	0.16
n-Hexane	507.865	29.9	25.01175	−2,430.58	−5.93372	2.07790	0.36
n-Octane	569.365	24.6	29.22028	−3,099.36	−7.14534	3.17549	0.21
n-Decane	619.4	20.84	33.56699	−3,768.14	−8.40515	4.43771	0.06
n-Pentadecane	716.2	15.02	44.73939	−5,440.09	−11,65290	8.23591	0.29
n-Eicosane	789.5	11.69	56.54187	−7,112.04	−15.10625	12.84792	2.24
							0.58

The critical temperatures and pressures through *n*-octane represent screened literature values; whereas those for *n*-nonane to *n*-eicosane, inclusive, are calculated values presented by Thodos (*54*).

*Percentage of deviation $= [(P_{calc} - P_{lit})/P_{lit}] \times 100$

The dimensions of constants A, B, C, and D presented in this table are consistent and produce, with absolute temperatures in degrees Kelvin, vapor pressures in millimeters of mercury.

notes the replacement of a hydrogen atom by a methyl group on a type-3 carbon atom (—$\overset{|}{\underset{|}{\mathrm{C}}}$H) surrounded by two type-1 carbon atoms (—$\mathrm{CH_3}$) and a single type-2 carbon atom (—$\overset{|}{\mathrm{C}}\mathrm{H_2}$). An illustration of this mode of methylation is the formation of 2,2-dimethylbutane from 2-methylbutane as follows:



$$\mathrm{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_3 \rightarrow CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-CH_3}$$

To avoid ambiguities in the order of construction of complex branched chain paraffins, the following procedures were adopted:

1. The longest normal carbon chain of the hydrocarbon is constructed initially.
2. Only single-methyl-group substitutions are made on the normal carbon chain, the substitutions beginning from the left end and proceeding always in a clockwise direction. Should side chains of greater lengths be required, this process is continued with the introduction of methyl groups on the side chains already established by continuing these substitutions in the same clockwise manner until the complete molecular structure is obtained.

The results of this study permit the evaluation of constant B from a knowledge of the molecular structure of a saturated aliphatic hydrocarbon. Furthermore, both van der Waals' constants a and b can be predicted from the molecular structure (*54*) and the critical temperature and pressure established through the relationships

$$T_c = \frac{8a}{27Rb} \tag{10}$$

$$P_c = \frac{a}{27b^2} \tag{11}$$

In addition, the pressure van der Waals' constant a permits the evaluation of the constant D through the relationship already developed (*21*),

$$D = \frac{a}{2.303R^2} \tag{12}$$

Therefore, for the saturated aliphatic hydrocarbons a knowledge of the molecular structure and a single experimental vapor-pressure point make possible the evaluation of all the constants of the general vapor-pressure equation, Equation (3). The accuracy of vapor pressures resulting with constants obtained from the molecular structure and a single vapor-pressure point was investigated for two comprehensive cases.

The constants A, B, C, and D of the normal paraffins through eicosane were calculated from the molecular structure and normal boiling point to cover the molecular dimension range of the saturated aliphatic hydrocarbons, for which reported vapor-pressure data are available. Vapor pressures at representative

TABLE 4. CONSTANTS A, B, C, AND D CALCULATED FROM MOLECULAR STRUCTURE AND THE NORMAL BOILING POINT OF THE ISOMERIC NONANES AND AVERAGE ABSOLUTE PERCENTAGE OF DEVIATION RESULTING FROM THEM

	Calculated critical values (*54*)		Calculated constants				Average percentage of deviation*
	T_c, °K.	P_c, atm.	A	B	C	D	
n-Nonane	595.4	22.57	31.37706	−3,433.75	−7.76950	3.78666	0.24
4-Methyloctane	593.9	23.38	30.57686	−3,287.27	−7.56217	3.63527	0.43
2,2-Dimethylheptane	582.5	23.39	29.24181	−3,114.64	−7.17033	3.49610	0.58
2,5-Dimethylheptane	584.7	23.39	29.30943	−3,153.27	−7.17410	3.52393	1.25
3,5-Dimethylheptane	592.4	24.27	29.33793	−3,140.79	−7.19662	3.48591	0.58
2-Methyl-4-ethylhexane	588.2	24.10	29.11430	−3,112.95	−7.12771	3.45960	0.24
2,2,4-Trimethylhexane	580.8	24.28	27.88253	−2,968.16	−6.76154	3.34912	0.18
2,3,4-Trimethylhexane	598.2	25.70	26.94831	−3,019.69	−6.40753	3.35624	0.62
3,3-Diethylpentane	621.8	28.01	24.68934	−2,899.91	−5.68426	3.31169	0.71
2,2-Dimethyl-3-ethylpentane	595.7	26.31	26.12492	−2,918.77	−6.16477	3.25076	0.15
2,2,3,3-Tetramethylpentane	593.9	27.84	21.18043	−2,698.95	−4.50432	3.05363	1.08
2,3,3,4-Tetramethylpentane	602.1	27.73	24.61675	−2,911.38	−5.62685	3.15114	2.40
							0.73

*Percentage of deviation $= [(P_{calc} - P_{lit})/P_{lit}] \times 100$

The dimension of constants A, B, C, and D presented in this table are consistent and produce, with absolute temperatures in degrees Kelvin, vapor pressures in millimeters of mercury.

points were evaluated by utilizing these calculated constants in Equation (3). Table 3* contains the calculated constants A, B, C, and D, along with the critical points evaluated by Thodos (*54*) and the average absolute percentage of deviation existing between calculated and *reported* vapor pressures for each normal paraffin. The over-all average absolute percentage of deviation obtained for all the normal paraffins investigated was 0.58 with a minimum for *n*-decane of 0.06 and a maximum for *n*-eicosane of 2.24.

The constants of all the isomeric nonanes were similarly determined to cover the case involving the highest molecular complexity for which reported vapor pressures are available. Again vapor pressures were calculated and compared with reported values to produce an average absolute percentage of deviation of 0.73 for all the thirty-four isomeric nonanes with a minimum of 0.15 for 2,2-dimethyl-3-ethylpentane and a maximum of 2.4 for 2,3,3,4-tetramethylpentane. The calculated constants for all the isomeric nonanes along with the calculated critical constants used and average absolute percentage of deviations obtained appear in Table 4.*

The vapor pressures produced by the use of calculated constants in Equation (3) for all the normal paraffins and all isomeric nonanes resulted in an over-all average percentage of deviation of 0.68 for the fifty-four hydrocarbons studied.

The vapor pressure of any substance can be calculated by the use of Equation (3), in which the constants A, B, C, and D may be established by treating experimental data according to the methods previously presented. If for this substance the van der Waals' constant a is not available, the constant D can be obtained by assuming various values of D until a linear plot of Y vs. X results from the experimental data as illustrated in Figure 3 for *n*-heptane when D is permitted to vary from zero to four.

If the substance for which vapor-pressure values are desired is a saturated aliphatic hydrocarbon presented in Table 1, the constants presented in this table can be used to calculate precise vapor-pressure values over the entire range from the triple to the critical point. However, if the saturated aliphatic hydrocarbon is an isomer of greater molecular weight than nonane, the constants of the vapor-pressure equation can be evaluated by the methods developed in this investigation.

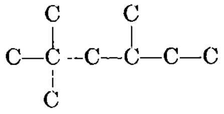
Example

To illustrate the application of the methods developed in this investigation, the calculation of constants A, B, C, and D of the general vapor-pressure equation is presented for 2, 2, 4-trimethylhexane, the normal boiling point of which is reported as 399.705°K. (*46*).

TABLE 5. COMPARISON OF VAPOR PRESSURES PRODUCED FROM THE EQUATION LOG $P = A + B/T + C \log T + D(P/T^2)$ EMPLOYING ACTUAL AND CALCULATED CONSTANTS

		Vapor pressures, mm. Hg				Percentage of deviation	
	T, °K.	Reported		Actual constants	Calculated constants	Actual constants	Calculated constants
				Ethane			
	135.736	18.62	(*36*)	18.54	18.46	−0.42	−0.30
	193.415	1,200.8	(*30*)	1,201.3	1,200.8	+0.04	0.00
	252.065	10,366	(*33*)	10,304	10,335	−0.60	−0.03
crit.	305.465	36,632	(*13*)	36,343	36,632	−0.79	0.00
						0.32	0.08
				2,2,4–Trimethylhexane			
	348.165	150.0	(*46*)	148.42	149.86	−1.06	−0.09
	417.665	1,200.0	(*46*)	1,199.1	1,197.1	−0.75	−0.24
						0.84	0.18

Calculation of Constant B. In order to establish constant B for this compound,



it is necessary to produce *n*-hexane from methane by the successive substitution of methyl groups for hydrogen atoms. Following the outlined procedure, successive methyl-group substitutions are made to form 2-methyl-hexane, 2, 4-dimethylhexane, and the desired compound, 2, 2, 4-trimethylhexane. From Table 2:

A. Base group–methane	567.59
B. Primary methyl substitution	503.00
C. Secondary methyl substitutions:	
$1 \leftarrow 1$	356.82
$2 \leftarrow 1$	334.39
$2 \leftarrow 1$	334.39
$2 \leftarrow 1$	334.39
$1 \leftarrow 2 \rightarrow 2$	200.39
$2 \leftarrow 2 \rightarrow 2$	187.91
$1 \leftarrow \underset{\substack{\downarrow \\ 1}}{3} \rightarrow 2$	149.28
	2,968.16

$$B_{calc} = -2{,}968.16$$
$$B_{act} = -3{,}012.88 \text{ (Table 1)}$$

Calculation of the Critical Point. Following a procedure similar to that used to calculate constant B, Thodos (*54*) evaluated the van der Waals' constants for this compound to be $a = 39.466 \times 10^6$ (cc./g. mole)^2 atm. and $b = 245.38$ cc./g. mole.
Therefore

$$T_c = \frac{8a}{27Rb}$$

$$= \frac{8(39.466 \times 10^6)}{27(82.055)(245.38)} = 580.8°\text{K.}$$

$$P_c = \frac{a}{27b^2} = \frac{39.466 \times 10^6}{27(245.38)^2}$$

$$= 24.28 \text{ atm. } (18{,}453 \text{ mm.})$$

For 2, 2, 4-trimethylhexane no critical constants are available.

Calculation of Constant D. With the pressure van der Waals' constant a established, by the method of Thodos (*54*), the constant D is calculated as

$$D = \frac{a}{2.303R^2} = \frac{29.466 \times 10^6}{2.303(62{,}360)^2}$$

$$= 3.34912 \ (°\text{K.})^2/\text{mm.}$$

where $R = 62{,}360$ (cc.)(mm.)/(g. mole) (°K.)

Calculation of Constants A *and* C. With constants B and D calculated and the critical point established from the molecular structure of this compound, a single vapor-pressure point permits the evaluation of constants A and C. Substitution of the normal boiling point and calculated critical point, in conjunction with the calculated constants B and C, produces two equations linear in A and C.
Thus

$$\log 760 = A - \frac{2{,}968.16}{399.705} + C \log 399.705 + 3.34912 \frac{760}{(399.705)^2}$$

$$\log 18{,}453 = A - \frac{2{,}968.16}{580.8} + C \log 580.8 + 3.34912 \frac{18{,}453}{(580.8)^2}$$

which can be solved simultaneously to yield

$$A = 27.88253$$

$$C = -6.76154$$

Therefore the general vapor-pressure equation for 2, 2, 4-trimethylhexane becomes

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*See footnote on page 348.

$$\log P = 27.88253 - \frac{2{,}968.16}{T} - 6.76154 \log T + 3.34912 \frac{P}{T^2} \quad (13)$$

Comparison of Calculated and Reported Vapor Pressures. Vapor pressures calculated by the use of Equation (13) were compared with the only available literature values and appear in Table 5* for 2, 2, 4-trimethylhexane. Since the reported values (*46*) for this compound are limited to pressures below 2 atm., the calculated vapor pressures above this pressure cannot be compared with any literature values. To illustrate the accuracy of vapor pressures obtained with the use of calculated constants, the vapor pressures of ethane were calculated from 18.62 mm. to the critical pressure, 36,632 mm., and appear with the reported literature values (*13, 25, 30, 33, 36, 43*) in Table 5. The actual constants presented in Table 1 have also been used to calculate vapor pressures for ethane and 2, 2, 4-trimethylhexane. The vapor-pressure values resulting from them are also presented in Table 5 and, when compared with reported values, show an average percentage of deviation of 0.32 for ethane and 0.84 for 2, 2, 4-trimethylhexane. Table 5 also illustrates, to some extent, the validity of the averaging process used to obtain ΔB values, as the calculated constants produce more accurate vapor-pressure values than those obtained from actual constants.

COMMENTS ON THE FROST-KALKWARF EQUATION

The Frost-Kalkwarf equation studied extensively in this investigation is transcendental in nature; solution of it for the vapor pressure P necessitates successive approximations, but, owing to the relatively small value of the term DP/T^2, only three to four repetitions are necessary to obtain essentially balanced values. Kalkwarf (*24*) claims an accuracy of less than ½% with not more than four repetitions for the most unfavorable case near the critical temperature. The term DP/T^2, because of its unusual nature, contributes significantly toward the reversal of curvature near the critical point. Equation (3) is continuous and requires four constants for the calculation of vapor pressures over the complete range between the triple and critical points.

NOTATION

a = pressure van der Waals' constant, (cc./g. mole)^{2}atm.

b = volume van der Waals' constant, cc./g. mole

A, B, C, D = constants for vapor-pressure equations

P = vapor pressure

R = gas constant

T = 273.165 + t °C., absolute temperature in degrees Kelvin

$$X = \frac{\frac{1}{T} - \frac{1}{T_b}}{\log \frac{T}{T_b}},$$

temperature modulus

$$Y = \frac{\log \frac{P}{P_b} - D\left(\frac{P}{T^2} - \frac{P_b}{T_b^{\,2}}\right)}{\log \frac{T}{T_b}},$$

vapor-pressure–temperature modulus

Subscripts

b = reference point or normal boiling point

c = critical

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*See footnote on page 348.

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