del(*4, 5*) and extends his work to include the critical volume. Critical values for the unsaturated aliphatic hydrocarbons, for which literature data are available and appear in Table 2, have been calculated by these methods and compared to produce the following average percentage deviations:

Critical value	(*4,5*)	(*2*)	This work
Temperature	1.53	1.71	1.30
Pressure	3.58	3.70	2.99
Volume	....	1.97	1.50

The comparisons in the present investigation appearing in Table 2 point to significant deviations of critical temperature for propadiene and 2-butyne, of critical pressure for the pentenes and 2-methyl-2-butene, and of critical volume for ethene. If the deviations for these compounds are not included in the over-all average values, the deviations become 0.78% for the critical temperature, 0.63% for the critical pressure, and 0.90% for the critical volume.

NOTATION

a = pressure van der Waals' constant, (cc./g. mole)^2 atm.
b = volume van der Waals' constant, cc./g. mole
p_c = critical pressure, atm.
R = gas constant, 82.055 (atm.) (cc.) / (g. mole) (°K.)
T_c = critical temperature, °K.
v_c = critical volume, cm./g. mole
β_s = volume factor for saturated aliphatic hydrocarbons
β_u = volume factor for unsaturated aliphatic hydrocarbons

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CRITICAL CONSTANTS OF SATURATED ALIPHATIC HYDROCARBONS

Through the use of group contributions the van der Waals' constants, *a* and *b*, were estimated for a number of saturated aliphatic hydrocarbons from a knowledge of the chemical structure of these compounds and were used to define the critical temperature and pressure of these substances.

By the use of methane as the base group, both van der Waals' constants were estimated for a number of saturated aliphatic hydrocarbons of considerable size and complexity through the additive contribution of methyl groups in the seccessive substitution of hydrogen until the desired structure of the substance was obtained. For the normal saturated hydrocarbons these contributions were found to be additive for the evaluation of $a^{0.626}$ and $b^{0.76}$ up through *n*-octane, and these exponents have been assumed to apply in the scaling up of larger normal and isomeric hydrocarbon molecules for which experimental data are lacking.

The volume van der Waals' constant *b* alone serves to define the critical volume of these compounds through the expression $v_c = 3\ \beta\ b$, where β represents a factor which has been found to depend on the size and arrangement of the molecule.

By following this procedure the critical temperatures, pressures and volumes of the normal saturated hydrocarbons through eicosane ($C_{20}H_{42}$), inclusive, and all the isomeric hydrocarbons up to and through the nonanes were calculated and compared, whenever possible, with values already available in the literature with an agreement of 0.43% for the estimation of the critical temperature, 0.69% for the critical pressure, and 0.86% for the critical volume. A combined consideration of these average deviations points to the estimation of the critical constants of the aliphatic saturated hydrocarbons with an average error of 0.7%.

George Thodos
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The ever-present problem of the prediction of the critical constants of substances has received considerable attention from a number of investigators. For the estimation of the critical values some of the common physical properties of a substance such as density, normal boiling point, molecular weight, and surface tension have been used as correlating variables. When information is available, these properties prove satisfactory for estimating the critical constants for a

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number of compounds, but frequently the required information on the physical properties of substances is not readily available.

For the estimation of the critical temperature of a compound, Watson(*13*) proposed a method which uses the normal boiling point, liquid density at this temperature, and the molecular weight of the substance. For some normal saturated paraffins, Wan(*12*) was able to predict critical temperatures from molar refraction. Gamson and Watson(*4*) defined the critical pressure of hydrocarbons through a vapor-presure equation of the reduced state, Meissner and Redding (*8*) introduced the use of the parachor and normal boiling point, and Herzog(*5*) followed a similar procedure to present the critical constants for a number of hydrocarbons. Boas(*2*) used the Albertosi equation in reduced form to estimate the critical temperatures of organic compounds from liquid density data which when associated with viscosity data in the Souders equation also make possible the estimation of critical densities. Riedel(*10, 11*) through the use of group contributions, the normal boiling point, and molecular weight of a substance was able to predict the critical temperature and pressure of substances. The work of Riedel was refined and extended to include the critical volume by Lydersen(*6*). These methods, although valuable in themselves, are frequently inconvenient to apply because of the lack of some one needed physical property. Michael and Thodos(*9*) estimated the parachor from a knowledge of the chemical structure of hydrocarbons and used it for the estimation of van der Waals' constants, which in turn define the critical temperature and pressure of these compounds. Although this method is capable of predicting critical constants with an absolute average error of 1.8%, its use for various types of hydrocarbons demands the determination of the parachor from which the van der Waals' constants can be calculated.

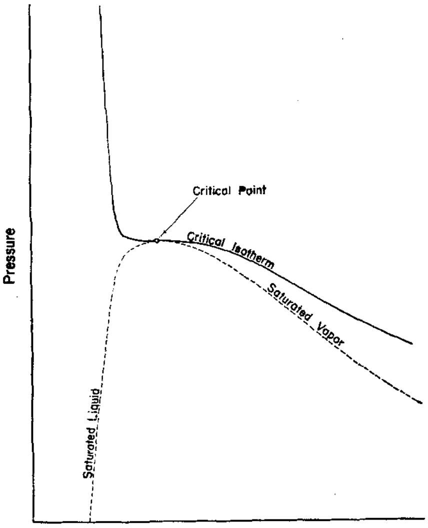


FIG. 1. TYPICAL PRESSURE-VOLUME RELATIONSHIP OF A SUBSTANCE AT ITS CRITICAL ISOTHERM.

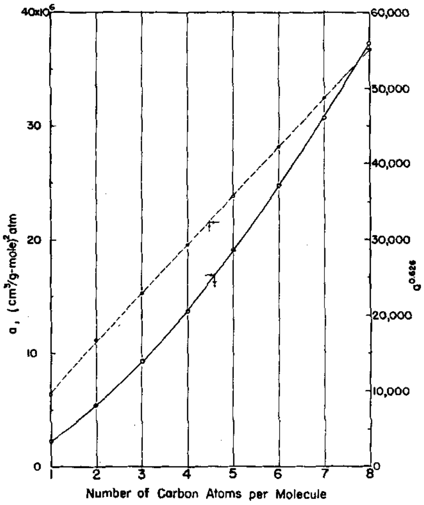


FIG. 2. RELATIONSHIPS OF PRESSURE VAN DER WAALS' CONSTANT *a* VS. NUMBER OF CARBON ATOMS PER MOLECULE FOR THE LIGHT NORMAL PARAFFINS.

The present investigation was undertaken objectively to establish the van der Waals' constants directly from a knowledge of the chemical structure of the compound without any recourse to parachor evaluation.

RELATIONSHIPS OF CRITICAL CONSTANTS AND VAN DER WAALS' CONSTANTS

The pressure-volume relationship of real gases at isothermal conditions as expressed by the van der Waals' equation of state:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT \quad (1)$$

makes possible the development of fundamental expressions relating the critical temperature, pressure, and volume of pure substances with their van der Waals' constants. In this connection, use is made of the pressure-volume relationship at the critical isotherm which is continuous and exhibits an inflection point of zero slope at the critical pressure and volume of the substance. This behavior is illustrated for a typical case in Figure 1, from which it is apparent for this restricted case of isothermal conditions at the critical temperature that $[\partial p/\partial v]_{T_c} = 0$ and $[\partial^2 p/\partial v^2]_{T_c} = 0$. By application of these restrictions to the critical isotherm, it is possible to define the critical volume, temperature, and pressure of a substance in terms of the van der Waals' constants *a* and *b*. These developments have been presented by Dodge(*3*), the final results being summarized as follows:

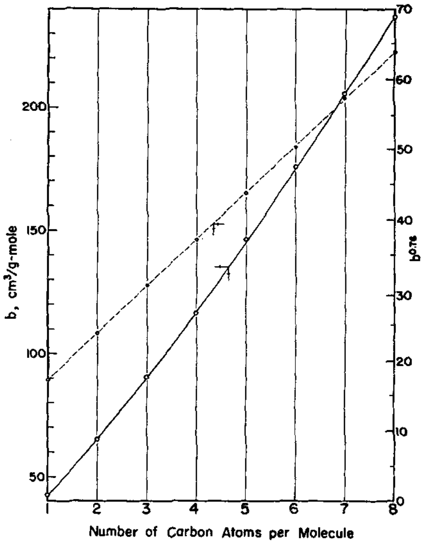


FIG. 3. RELATIONSHIPS OF VOLUME VAN DER WAALS' CONSTANT *b* VS. NUMBER OF CARBON ATOMS PER MOLECULE FOR THE LIGHT NORMAL PARAFFINS.

$$v_c = 3b \quad (2)$$

$$T_c = \frac{8a}{27Rb} \quad (3)$$

and

$$p_c = \frac{a}{27b^2} \quad (4)$$

Table 1.—Critical Temperatures and Pressures and Calculated van der Waals' Constants for the Light Normal Saturated Hydrocarbons

			Van der Waals' Constants	
	T_c, °K.	p_c, atm.	a (cc./g.-mole)^2 atm.	b cc./g.-mole
Methane	191.065	45.8	2.264×10^6	42.79
Ethane	305.465	48.2	5.499	65.00
Propane	369.965	42.0	9.257	90.35
n-Butane	425.165	37.5	13.692	116.29
n-Pentane	469.765	33.3	18.824	144.70
n-Hexane	507.865	29.9	24.503	174.22
n-Heptane	540.165	27.0	30.696	205.20
n-Octane	569.365	24.6	37.432	237.40

By use of Equations (2), (3), and (4), it is possible to define both van der Waals' constants in terms of the critical temperature and pressure of a substance:

$$a = \frac{27R^2T_c^{\,2}}{64p_c} \tag{5}$$

and

$$b = \frac{RT_c}{8p_c} \tag{6}$$

Equations (5) and (6) permit the evaluation of the van der Waals' constants from the critical temperature and pressure of the substance and conversely the critical temperature and pressure of a substance becomes possible of definition through a knowledge of the van der Waals' constants with the aid of Equations (3) and (4).

FUNDAMENTAL CONSIDERATIONS

The recent exhaustive literature survey of Kobe and Lynn (*7*) dealing with the critical constants of substances was used as the source of critical data from which van der Waals' constants were calculated with the aid of Equations (5) and (6). The critical values recommended by these authors represent the best constants available to date and consequently have been accepted as sufficiently reliable to evaluate from them the van der Waals' constants a and b, which were studied further in detail. For purpose of presentation, the critical constants of the normal saturated hydrocarbons from methane through *n*-octane have been presented in Table 1 along with the corresponding van der Waals' constants calculated from them. A study of these constants reveals that their variation with the number of carbon atoms is not linear but instead curved, as shown in Figures 2 and 3.

Table 2.—Methyl Group Contributions $\Delta a^{0.626}$ and $\Delta b^{0.76}$ in the Replacement of Hydrogen from Saturated Aliphatic Hydrocarbons

Base group values

	$a^{0.626}$	$b^{0.76}$
Methane	9509	17.371

Methyl Group Contributions in the Replacement of Hydrogen from Methane

$\Delta a^{0.626}$	$\Delta b^{0.76}$
7065	6.497

Methyl Group Contributions in the Replacement of Hydrogen from Saturated Aliphatic Hydrocarbons

	$\Delta a^{0.626}$	$\Delta b^{0.76}$
$1 \leftarrow 1$	6388	6.583
$2 \leftarrow 1$	6417	6.686
$3 \leftarrow 1$	5742	5.450
$4 \leftarrow 1$	5968	4.870
$1 \leftarrow 2 \rightarrow 1$	5629	6.475
$1 \leftarrow 2 \rightarrow 2$	5261	5.879
$1 \leftarrow 2 \rightarrow 3$	5250	5.065
$1 \leftarrow 2 \rightarrow 4$	5189	4.351
$2 \leftarrow 2 \rightarrow 2$	4865	4.663
$2 \leftarrow 2 \rightarrow 3$	4758	3.882
$2 \leftarrow 2 \rightarrow 4$	4750	3.354
$3 \leftarrow 2 \rightarrow 3$	5137	3.481
$1 \leftarrow 3 \rightarrow 1$ $\downarrow$ 1	4895	5.817
$1 \leftarrow 3 \rightarrow 2$ $\downarrow$ 1	4575	4.455
$3 \leftarrow 3 \rightarrow 1$ $\downarrow$ 1	4307	3.781
$1 \leftarrow 3 \rightarrow 4$ $\downarrow$ 1	4087	3.471
$2 \leftarrow 3 \rightarrow 2$ $\downarrow$ 1	4082	3.658
$3 \leftarrow 3 \rightarrow 2$ $\downarrow$ 1	3814	2.984
$3 \leftarrow 3 \rightarrow 3$ $\downarrow$ 1	3719	2.200
$2 \leftarrow 3 \rightarrow 2$ $\downarrow$ 2	3770	2.401

In order to obtain linear variations, both constants a and b were arbitrarily raised to different exponents, m and n respectively, until linear distributions of a^m and b^n were realized with the number of carbon atoms present in the chain length. A trial-and-error procedure revealed that values of $m = 0.626$ and $n = 0.76$ produced good linear relationships for all the normal saturated hydrocarbons from propane through *n*-octane. Since the critical values for the normal hydrocarbons used in this analysis are well established and represent considerable accuracy and since establishing a method applicable to hydrocarbons in general is desired, these exponents have been assumed to apply in the same manner to the isomeric hydrocarbons as well.

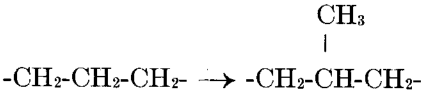
An exhaustive analysis of the calculated van der Waals' constants a and b raised to the 0.626 and 0.76 powers, respectively, indicated that there exists an additive contribution in the substitution of hydrogen by a methyl group. Changes in the values $a^{0.626}$ and $b^{0.76}$, designated as $\Delta a^{0.626}$ and $\Delta b^{0.76}$, appeared to be consistent as postulated by Andersen, Beyer, and Watson (*1*) for comparable substitutions in the evaluation of the thermodynamic properties of compounds. The classification of the types of carbon atoms involved in these studies has been arbitrarily selected to be that proposed by Andersen, Beyer, and Watson (*1*), summarized as follows:

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

In the present study it was found that the values $\Delta a^{0.626}$ and $\Delta b^{0.76}$ were dependent not only on the type of carbon atom on which the methyl group substitution was made, but were also influenced by the nature of the carbon atoms adjacent to the carbon atom. Therefore, it became necessary to associate both the type of carbon atom directly involved in the substitution and also the nature of the carbon atoms immediately surrounding it. The results of a detailed analysis of the available data for all the saturated aliphatic hydrocarbons through the octanes produced the average group contributions for both $\Delta a^{0.626}$ and $\Delta b^{0.76}$ appearing in Table 2. In this table the designation given to the type of carbon atom involved in the substitution has been arbitrarily tagged as the one from which the arrows point away and toward the types of carbon atoms adjoining it. For instance, the designation 3-←1 indicates the substitution of a hydrogen atom by a methyl group on a carbon atom of type 1 (— CH_3) adjoined to a carbon atom of type 3 ($-\overset{|}{\underset{|}{C}}H$). Thus, the following structures are representative of this kind of substitution:

$$\begin{array}{ccc} & & CH_3 \\ & & | \\ CH_3 & & CH_2 \\ | & & | \\ -CH_2\text{-}CH\text{-}CH_2\text{-} & \longrightarrow & -CH_2\text{-}CH\text{-}CH_2\text{-} \end{array}$$

The designation 2-←2→-2 indicates the substitution of a methyl group for hydrogen on a type 2 carbon atom ($-\overset{|}{C}H_2$) adjoined on both sides by carbon atoms of similar type. For this case this type of substitution suggests the following structural transformation:

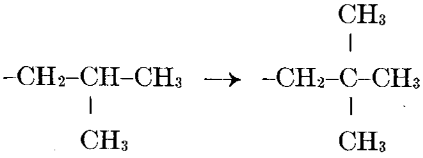


$$\begin{array}{ccc} & & CH_3 \\ & & | \\ -CH_2\text{-}CH_2\text{-}CH_2\text{-} & \longrightarrow & -CH_2\text{-}CH\text{-}CH_2\text{-} \end{array}$$

Furthermore, the designation

$$\begin{tikzcd} 2 & 3 \arrow[l] \arrow[r] \arrow[d] & 1 \\ & 1 & \end{tikzcd}$$

considers the methyl group substitution on the type 3 carbon atom ($-\overset{|}{\underset{|}{C}}H$) for its hydrogen atom to produce the resulting structure:



$$\begin{array}{ccc} & & CH_3 \\ & & | \\ -CH_2\text{-}CH\text{-}CH_3 & \longrightarrow & -CH_2\text{-}C\text{-}CH_3 \\ | & & | \\ CH_3 & & CH_3 \end{array}$$

Through this proposed method the evaluation of both $a^{0.626}$ and $b^{0.76}$ for the normal saturated hydrocarbons is direct and no ambiguity can arise, because the constructive process for building up molecules consists of successive methyl group substitutions for the hydrogen atoms present at the end of the hydrocarbon chain. However, considerable ambiguity can arise in the introduction of methyl groups to produce branched chain hydrocarbons because the order of these substitutions can be varied. For this reason the following sequence pattern has been adopted in the construction of molecular structures for branched hydrocarbons:

1. Construct the longest normal chain present in the hydrocarbon.
2. Produce only single methyl group substitutions directly on the normal chain beginning from the left end of the normal chain and moving always in a clockwise direction.
3. If necessary, continue methyl group substitutions on already substituted methyl groups by maintaining the previously established clockwise direction until the desired structure is realized.

In accordance with this approach van der Waals' constants for all the saturated aliphatic hydrocarbons were calculated and were found to agree closely with those obtained directly from the critical values of Kobe and Lynn(*7*).

Since Equations (5) and (6) utilize the critical temperature and pressure to define both van der Waals' constants, compatibility necessarily must exist between the critical temperature and pressure with both van der Waals' constants *a* and *b*. An extension of this background to consider the critical volume in this study produced results that were not consistent with the theoretical development presented in Equation (2). Van der Waals' constant *b* when divided into the critical volumes reported in the literature(*7*) produced ratios inconsistent with the value of 3 dictated by Equation (2) and varied from 2.314 for methane to 2.065 for *n*-octane. In view of this behavior Equation (2) has been modified in order to produce with the volume van der Waals' constant *b*, critical volumes that are consistent with those reported in the literature. With the introduction of the empirical volume factor, β, Equation (2) becomes

$$v_c = 3\beta b \qquad (7)$$

where β has been found to be a function of the number of carbon atoms in the hydrocarbon and to depend on the arrangement of the molecule. The volume factor, β_n, for the normal paraffins can be defined as

$$\beta_n = 0.7849 - 0.01337\, n_c \qquad (8)$$

where n_c represents the number of carbon atoms present in the normal paraffin. A review of volume factors, β, revealed that this factor remained essentially constant for isomeric paraffins having the same number of carbon atoms and decreased with increasing molecular weight of the hydrocarbon. The resulting average values of β_i for the isomers when divided by the volume factor of the corresponding normal paraffin produced essentially constant ratios as indicated:

	$\frac{\beta_i}{\beta_n}$
butanes	1.032
pentanes	1.000
hexanes	1.026
heptanes	1.032
octanes	1.039

By elimination of the value for the pentanes, the average value of the ratios β_i/β_n resulting from the value for butanes, hexanes, heptanes, and octanes becomes

$$\frac{\beta_i}{\beta_n} = 1.032 \qquad (9)$$

where β_i represents the volume factor for any isomeric paraffin and β_n is the volume factor of the corresponding normal paraffin as calculated by Equation (8). Combining Equations (8) and (9) results in an expression defining the volume factor of isomeric paraffins, β_i

$$\beta_i = 0.8100 - 0.0138\, n_c \qquad (10)$$

For the normal paraffins pentane through dodecane, critical volumes have been calculated by the present method and that of Boas(*2*), who utilized liquid density and viscosity data to estimate the critical density. The critical volumes produced by both methods are presented in Table 3 along with the available literature values. They

TABLE 3.—COMPARISON OF CALCULATED CRITICAL VOLUMES OBTAINED BY THE METHOD OF BOAS (*2*) AND THE PRESENT INVESTIGATION FOR SOME NORMAL PARAFFINS

	Calculated critical volumes, cc./g.-mole		
	Literature (*7*)	Boas (*2*)	This Investigation
Pentane	310.99	305.98	311.42
Hexane	368.25	366.68	368.47
Heptane	426.38	424.58	425.71
Octane	490.21	484.60	482.80
Nonane		544.59	539.56
Decane		604.67	595.59
Undecane		665.39	650.63
Dodecane		725.74	704.66

TABLE 4.—CALCULATED VAN DER WAALS' CONSTANTS AND COMPARISON OF CALCULATED AND REPORTED CRITICAL TEMPERATURES, PRESSURES, AND VOLUMES FOR THE LIGHT SATURATED ALIPHATIC HYDROCARBONS

	Calculated van der Waals' constants				Calculated critical constants			Literature values (7)			Percentage deviation		
	$a^{0.626}$	$b^{0.76}$	a (cc./g.-mole)^2 atm.	b cc./g.-mole	T_c, °K.	p_c, atm.	v_c, cc./g-mole	T_c, °K.	p_c, atm.	v_c, cc./g.-mole	T_c	p_c	v_c
n-Pentane	35,796	43.823	18.816×10^6	144.58	469.9	33.33	311.42	469.8	33.3	310.99	−0.02	−0.09	−0.14
2, 2-Dimethylpropane	33,486	42.743	16.914	139.92	436.5	32.00	311.04	433.8	31.6	303.15	−0.62	−1.27	−2.60
n-Hexane	42,213	50.509	24.486	174.29	507.3	29.86	368.47	507.9	29.9	368.25	0.12	0.14	−0.06
2, 2-Dimethylbutane	39,215	47.471	21.768	160.63	489.4	31.24	350.48	489.4	30.7	366.68	0.00	−1.76	4.42
n-Heptane	48,630	57.195	30.696	205.27	540.0	26.98	425.71	540.2	27.0	426.38	0.04	0.07	0.16
3-Methylhexane	47,078	55.172	29.147	195.77	537.6	28.17	418.99	535.6	28.1	417.50	−0.37	−0.25	−0.36
2, 2, 3-Trimethylbutane	44,197	51.862	26.350	180.46	527.3	29.97	386.22	531.5	29.75	394.49	0.79	−0.74	2.10
n-Octane	55,047	63.881	37.420	237.40	569.2	24.59	482.80	569.4	24.6	490.21	0.04	0.04	1.51
4-Methylheptane	53,495	61.858	35.747	227.57	567.2	25.56	477.62	563.2	25.6	475.92	−0.71	0.16	−0.36
2, 5-Dimethylhexane	52,735	62.267	34.940	229.55	549.6	24.56	481.78	550.0	24.6	481.94	0.07	0.16	0.03
2, 2, 4-Trimethylpentane	50,893	60.036	33.010	218.78	544.8	25.54	459.18	544.1	25.4	470.04	−0.13	−0.16	2.31

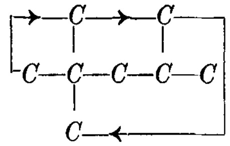
TABLE 5.—CALCULATED VAN DER WAALS' CONSTANTS AND CRITICAL TEMPERATURES, PRESSURES, AND VOLUMES FOR SOME OF THE HEAVIER SATURATED ALIPHATIC HYDROCARBONS

	Van der Waals' constants		Calculated critical constants		
	a (cc./g.-mole)^2 atm	b cc./g.-mole	T_c, °K.	p_c, atm.	v_c, cc./g.-mole
Nonanes					
n-Nonane	44.625×10^6	270.62	595.4	22.57	539.6
3-Ethylheptane	42.069	254.31	597.3	24.09	523.2
2, 5-Dimethylheptane	41.526	256.44	584.7	23.39	527.6
4, 4-Dimethylheptane	40.200	245.44	591.4	24.72	505.0
2, 2, 3-Trimethylhexane	39.054	238.24	591.9	25.48	490.2
2, 3, 5-Trimethylhexane	40.109	248.55	582.7	24.04	511.4
2, 2, 4, 4-Tetramethylpentane	37.876	240.40	568.9	24.27	494.6
Normal saturated hydrocarbons					
n-Decane	52.298	304.87	619.4	20.84	595.6
n-Pentadecane	97.052	489.30	716.2	15.02	857.8
n-Eicosane	151.40	692.47	789.5	11.69	1075

show good agreement through *n*-octane. For the normal paraffins above *n*-octane, no absolute comparisons can be made with the calculated critical volumes because of the lack of literature values. The method of Boas(*2*) produces for these heavier hydrocarbons critical volumes that are somewhat higher than those predicted by the present method.

ILLUSTRATION A

In order to illustrate the utility of the proposed method, van der Waals' constants *a* and *b* are calculated for 2, 2, 4-trimethylpentane, from which all the critical constants are evaluated. Beginning with methane, the van der Waals' constants are calculated by the successive substitutions on methane to produce *n*-pentane, and then side chain substitutions are made in the order of 2, 4, and 2 as outlined below:



Methane-base group	9509	17.371
Primary methyl substitution	7065	6.497
Secondary methyl substitutions		
$1 \leftarrow 1$	6388	6.583
$2 \leftarrow 1$	6417	6.686
$2 \leftarrow 1$	6417	6.686
$1 \leftarrow 2 \rightarrow 2$	5261	5.879
$2 \leftarrow 2 \rightarrow 1$	5261	5.879
$1 \leftarrow 3 \rightarrow 2$ $\downarrow$ 1	4575	4.455
	$a^{0.626} = 50{,}893$	$b^{0.76} = 60.036$

$a = 33.010 \times 10^6$ (cc./g.-mole)^2 atm. $b = 218.78$ cc./g.-mole

from Equation (3) $$T_c = \frac{8a}{27Rb} = \frac{8 \times 33.010 \times 10^6}{17 \times 82.055 \times 218.78} = 544.8^\circ \text{ K.}$$

and Equation (4) $$p_c = \frac{a}{27b^2} = \frac{33.010 \times 10^6}{27\ (218.78)^2} = 25.54 \text{ atm.}$$

The volume factor β_i for this hydrocarbon becomes through the use of Equation (10)

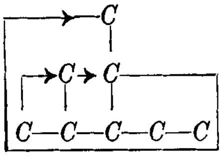
$$\beta_i = 0.8100 - 0.0138\ (8) = 0.6996$$

By use of Equation (7) the critical volume of this isometric paraffin becomes $v_c = 3(0.6996)\ (218.78) = 459.2$ cc./g.-mole.

Kobe and Lynn(*7*) report for 2, 2, 4-trimethylpentane critical values of 544.1°K., 25.4 atm., and 470.0 cc./g.-mole.

ILLUSTRATION B

The evaluation of van der Waals' constants *a* and *b* and the corresponding calculated critical temperature, pressure, and volume is presented for 2-methyl-3-ethylpentane in order to illustrate a case in which a methyl substitution is made on an already substituted methyl group. The order of methyl group substitutions will be along the following pattern:



Methane—base group	9509	17.371
Primary methyl substitution	7065	6.497
Secondary methyl substitutions		
$1 \leftarrow 1$	6388	6.583
$2 \leftarrow 1$	6417	6.686
$2 \leftarrow 1$	6417	6.686
$1 \leftarrow 2 \rightarrow 2$	5261	5.879
$3 \leftarrow 2 \rightarrow 2$	4758	3.882
$3 \leftarrow 1$	5742	5.450
	$a^{0.626} = 51{,}557$	$b^{0.76} = 59.034$

$a = 33.702 \times 10^6$ (cc./g.-mole)^2 atm. $b = 214.00$ cc./g.-mole

$$T_c = \frac{8a}{27Rb} = \frac{8 \times 33.702 \times 10^6}{27 \times 82.055 \times 214.00} = 568.6° \text{ K.}$$

$$p_c = \frac{a}{27b^2} = \frac{33.702 \times 10^6}{27\ (214.00)^2} = 27.26 \text{ atm.}$$

The volume factor, β_i, for 2-methyl-3-ethylpentane is the same as that calculated for 2,2,4-trimethylpentane presented in illustration *A*. Therefore the critical volume of 2-methyl-3-ethylpentane becomes

$v_c = 3(0.6996)\ (214.00) = 449.12$ cc./g.-mole.

Kobe and Lynn (*7*) report for 2-methyl-3-ethylpentane critical values of 568.2°K., 27.4 atm., and 449.68 cc./g.-mole.

A direct comparison of critical temperatures, pressures, and volumes calculated by this method and those reported by Kobe and Lynn (*7*) is presented in Table 4.* In this table are also included the calculated van der Waals' constants a and b resulting from the present group contribution method and the $\Delta a^{0.626}$ and $\Delta b^{0.76}$ values appearing in Table 2. As a result of these comparative studies on thirty-eight saturated aliphatic hydrocarbons for which literature values are available, an average percentage deviation for the critical temperature of 0.43, for the critical pressure of 0.69, and for the critical volume of 0.86 was found to exist. In view of these percentage deviations, it is safe to assume that the critical temperature, pressure, and volume for the saturated aliphatic hydrocarbons can be estimated by the proposed method with an average deviation of 0.7%.

A comparison of the proposed method with a similar scheme of Riedel (*10, 11*) has been carried out. The method of Riedel (*11*) utilizes group contributions and the normal boiling point of the substance to predict the critical temperature. For the thirty-eight saturated aliphatic hydrocarbons studied, the average deviation for the prediction of the critical temperature amounts to 0.74%. For the estimation of the critical pressure Riedel (*10*) is able to treat adequately the normal paraffins, but because of inconsistencies is unable to account properly for the critical pressures of branched chain paraffins. Despite this limitation, Riedel proposes the use of a common group contribution for the different types of carbon atoms existing in the aliphatic saturated hydrocarbons to produce with the aid of the molecular weight, critical pressures for branched chain paraffins. For the thirty-eight compounds investigated, the critical pressures calculated by the method of Riedel gave an average deviation of 5.78%.

Hougen, Watson, and Ragatz (*6*) present the method of Lydersen which has been used to calculate all the critical constants of the paraffins for which literature data are available. Lydersen improves on the method of Riedel by producing refined group contributions to predict both the critical temperature and pressure of substances and extends this work to include the critical volume. A careful study of the thirty-eight paraffins treated above produced critical temperatures, pressures, and volumes that showed an average deviation of 0.50, 3.82 and 2.03% respectively. A review of the results produced by the method of Lydersen shows that the critical temperatures can be evaluated with a high degree of precision and the greatest uncertainty lies in the estimation of the critical pressure.

For completeness, the critical constants of all the saturated nonanes and the normal saturated hydrocarbons from n-decane through n=eicosane inclusive, have been calculated and are presented in Table 5* along with the corresponding calculated van der Waals' constants. For these hydrocarbons no comparisons can be made since the literature does not present the reliable experimental values needed.

NOTATION

a = pressure van der Waals' constant, (cc./g.-mole)^2, atm.
b = volume van der Waals' constant, cc./g.-mole
m, n = arbitrary constants ($m = 0.626$, $n = 0.76$)
n_c = number of carbon atoms in saturated aliphatic hydrocarbon
p = pressure, atm.
p_c = critical pressure, atm.
R = gas constant, 82.055 (atm.) (cc.) / (K.°) (g.-mole)
T = temperature, °K.
T_c = critical temperature, °K.
v = molar volume, cc./g.-mole
v_c = critical volume, cc./g.-mole
β = volume factor
β_i = volume factor for isomeric paraffins
β_n = volume factor for normal paraffins
Δ = change in the substitution of hydrogen by a methyl group

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* See footnote on page 168.