Critical Temperatures and Pressures of Hydrocarbons

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A method has been developed for the calculation of van der Waals' constants both *a* and *b* for hydrocarbons usually encountered, including the aliphatic, naphthenic, and aromatic types. With these constants critical temperatures and pressures can be calculated directly.

Methods recently made available (*12, 13, 14, 15*) allow the calculation of these constants through the use of substitution values involving the replacement of hydrogen atoms by methyl groups in a definitely prescribed pattern. In this study van der Waals' constants are directly calculated from a consideration only of the molecular structure of the hydrocarbon. This approach has become possible through the assignment of group contributions to different types of carbon atoms, which can be combined in any manner to produce the van der Waals' constants representative of the molecular structure of the hydrocarbon.

Several methods have been presented which permit the evaluation of critical constants of organic compounds (*2, 4, 5, 7, 8, 9, 12* to *17*). For their successful application most of these methods require certain physical properties of the substances; for example, the method of Watson (*17*) requires the use of the normal boiling point and corresponding liquid density, that of Wan (*16*) utilizes molar refraction for the calculation of the critical temperature, Meissner and Redding (*7*) and Herzog (*4*) introduce the use of the parachor in conjunction with the normal boiling point for the calculation of critical constants of a number of hydrocarbons, and density and viscosity measurements are required for the calculation of the critical density according to Boas (*2*).

The first attempt to eliminate the use of physical properties was that of Riedel (*8, 9*), later extended and improved by Lydersen (*5*). These methods are fundamentally alike and permit the calculation of critical constants from structural-group contributions and only the normal boiling point. In their attempts, Riedel and Lydersen minimized the dependence of critical-constant calculations on physical properties and chose to use the normal boiling point, which is usually readily available. Although their methods constitute an improvement, they are not completely independent of physical properties and, in addition, do not permit differentiation between structural isomers.

The calculation of critical constants without recourse to physical properties was introduced by Thodos and was applied to several classes of hydrocarbons (*12* to *15*). His method utilizes substitution values for the calculation of van der Waals' constants, which in turn permit the calculation of the critical temperature, pressure, and volume. To produce these van der Waals' constants, a successive building up of the molecular structure is employed involving the replacement of hydrogen by methyl groups along a definite prescribed pattern of substitutions, which must be rigorously adhered to in order to produce reliable values. Unless this replacement procedure is carefully followed over the entire course of structural development, considerable confusion can result.

This investigation was undertaken to develop a method for calculating van der Waals' constants which would not require recourse to a pattern for building molecular structures.

FUNDAMENTAL RELATIONSHIPS

As utilized previously (*12* to *15*), the van der Waals' constants a and b are again employed as the fundamental basic quantities with which critical temperatures and pressures can be calculated from the relationships

$$T_c = \frac{8a}{27Rb} \tag{1}$$

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

Conversely, from the simultaneous solution of Equations (1) and (2), the van der Waals' constants can be evaluated from available critical temperatures and pressures:

$$a = \frac{27R^2T_c^2}{64p_c} \tag{3}$$

$$b = \frac{RT_c}{8p_c} \tag{4}$$

By means of Equations (3) and (4), both van der Waals' constants were evaluated from the literature data on seventy-five saturated and unsaturated aliphatic, naphthenic, and aromatic hydrocarbons and constitute the basic values for the development of the method presented here.

Earlier attempts to relate the van der Waals' constants with structure have produced a linear relationship with the number of carbon atoms of the normal paraffins for values of $a^{0.626}$ and $b^{0.76}$ (*13*). The exponents 0.626 and 0.76 have been assumed valid for other types of hydrocarbons (*12* to *15*) and have been applied successfully to produce van der Waals' constants for saturated and unsaturated aliphatic, naphthenic, and aromatic hydrocarbons.

A reconsideration of the exponents for both van der Waals' constants indicated essentially the same linear relationship for values of $a^{2/3}$ and $b^{3/4}$, and accordingly these exponents have been adopted in this study in place of the awkward previous values, $a^{0.626}$ and $b^{0.76}$. The approach adopted here for the determination of values of a and b is entirely different from that utilized previously. The concept of substitution values has been discarded, and in its place a method has been devised utilizing group contributions specific to various types of carbon atoms. These group contributions are added to produce the van der Waals' constants of the hydrocarbon from its structure alone and do

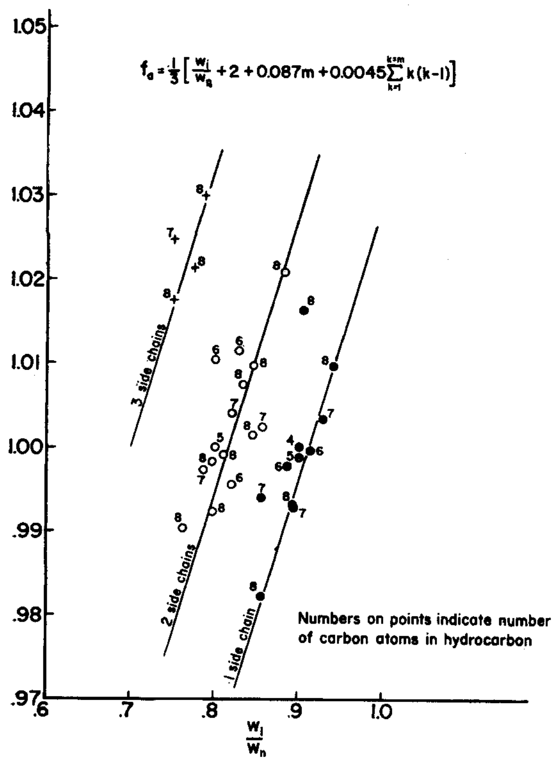


Fig. 1. Relationship of isomer factor, f_a, and Wiener number ratio.

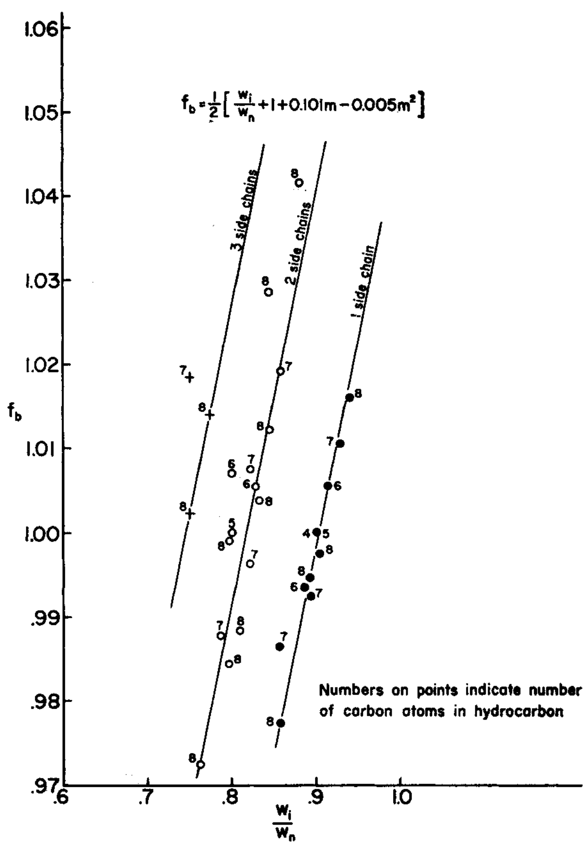
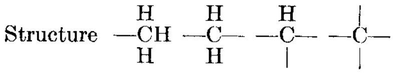


Fig. 2. Relationship of isomer factor, f_b, and Wiener number ratio.

not involve the replacement procedures adopted in the earlier work.

SATURATED ALIPHATIC HYDROCARBONS

The paraffins represent the largest group of hydrocarbons for which experimental data are available and consequently were used as the basis of study for the aliphatic series. In this study the notation of Andersen, Beyer, and Watson (*1*) was used to differentiate types of carbon atoms. For the saturated aliphatic series four different types of carbon atoms are possible:



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

and can be recognized by the number of carbon-carbon (as contrasted with carbon-hydrogen) bonds.

The basis of analysis was the establishment of constant group-contribution values of $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for the type-2 methylene-group carbon by taking the difference in $a^{2/3}$ and $b^{3/4}$ of normal paraffins differing in size by a single methylene group. For the normal paraffins between *n*-octane and *n*-butane, these differences are essentially constant and their average values

$$\Delta a^{2/3} = 13{,}678 \quad \text{and} \quad \Delta b^{3/4} = 6.262$$

have been taken as the contribution for the type-2 carbon.

The normal paraffins were also used to establish the group contributions for the type-1 (methyl group) carbon. Subtracting the contribution of the methylene groups in each normal paraffin established the contribution due to the two end methyl groups, and when this was divided by two it produced the methyl-group contribution in each compound. For the van der Waals' constant *a*, these group contributions were not constant and decreased with the size of the molecule. The variation of $\Delta a^{2/3}$ for the type-1 carbon can be expressed as a function of the total number of carbon atoms in the molecule *n* as

$$\Delta a^{2/3} = \frac{2168}{n} + 14{,}493 \tag{5}$$

On the other hand, the methyl-group contribution for *b* was found to be constant as $\Delta b^{3/4} = 11.453$.

The isomeric paraffins, in conjunction with the above-determined group contributions for types-1 and -2, permitted the establishment of the group contributions for types-3 and -4 carbons. Fortunately, almost all the isomeric hydrocarbons available contained either type-3 or type-4 carbons, but not both. This situation permitted the direct evaluation of these group contributions, which were also found to be dependent on the number of carbon atoms in the molecule. The average values for $\Delta a^{2/3}$ and $\Delta b^{3/4}$ within each isomeric group (that is, octanes, heptanes, hexanes, etc.) similarly were found to vary as follows with the total number of carbon atoms in the compound:

Type-3 ($n \geqq 5$)

$$\Delta a^{2/3} = \frac{27{,}560}{n} + 5677 \tag{6}$$

$$\Delta b^{3/4} = \frac{23.55}{n} - 3.824 \tag{7}$$

Type-4

$$\Delta a^{2/3} = \frac{36{,}013}{n} - 1022 \tag{8}$$

$$\Delta b^{3/4} = \frac{52.00}{n} - 15.337 \tag{9}$$

For convenience, values of group contributions for both $\Delta a^{2/3}$ and $\Delta b^{3/4}$ have been calculated for paraffin hydrocarbons up to $n = 15$ and are presented in Table 1 for the four types of carbon atoms.

Up to this point the adopted procedure fails to differentiate between isomeric hydrocarbons containing the same types of carbon atoms but differing in structural arrangement. For example, 2-methylheptane, 3-methylheptane, 4-methylheptane, and 3-ethylhexane produce the same calculated van der Waals' constants, since they contain the same number of types-1, -2, and -3 carbon atoms.

In order to account for these isomeric differences, van der Waals' constants calculated with the group contributions from Table 1 were divided into the corresponding constants resulting from the critical values in the literature to produce

Table 1. Group Contributions, $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for the Saturated Aliphatic Hydrocarbons

	Type-1		Type-2		Type-3		Type-4	
n	$\Delta a^{2/3}$	$\Delta b^{3/4}$	$\Delta a^{2/3}$	$\Delta b^{3/4}$	$\Delta a^{2/3}$	$\Delta b^{3/4}$	$\Delta a^{2/3}$	$\Delta b^{3/4}$
1								
2	15,577	11.453						
3	15,216	11.453	13,678	6.262				
4	15,035	11.453	13,678	6.262				
5	14,927	11.453	13,678	6.262	11,189	0.886	6,181	− 4.937
6	14,854	11.453	13,678	6.262	10,270	0.101	4,980	− 6.670
7	14,803	11.453	13,678	6.262	9,614	−0.460	4,123	− 7.909
8	14,764	11.453	13,678	6.262	9,122	−0.880	3,480	− 8.837
9	14,734	11.453	13,678	6.262	8,739	−1.207	2,979	− 9.559
10	14,710	11.453	13,678	6.262	8,433	−1.469	2,579	−10.337
11	14,690	11.453	13,678	6.262	8,182	−1.683	2,252	−10.160
12	14.674	11.453	13,678	6.262	7,974	−1.862	1,979	−11.004
13	14,660	11.453	13,678	6.262	7,797	−2.012	1,748	−11.337
14	14,648	11.453	13,678	6.262	7,646	−2.142	1,550	−11.623
15	14,638	11.453	13,678	6.262	7,514	−2.254	1,379	−11.870

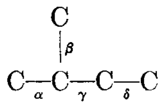
the isomer factors defined by the expressions

$$a_{actual}^{2/3} = f_a a_{group}^{2/3} \qquad (10)$$

and

$$b_{actual}^{3/4} = f_b b_{group}^{3/4} \qquad (11)$$

Attempts to correlate the isomer factors f_a and f_b proved successful when the Wiener number ratio w_i/w_n was used as the correlating variable. The Wiener number w is defined as "the sum of distances between any two carbon atoms in the molecule in terms of carbon-carbon bonds" (*18*). This is calculated by multiplying the number of carbon atoms on one side of each carbon-carbon bond by the number of carbons on the other side of the bond and then adding all the contributions from each carbon-carbon bond in the molecule; for example, for the compound 2-methylbutane, the procedure is as follows



$$\alpha = 1 \times 4 = 4$$
$$\beta = 1 \times 4 = 4$$
$$\gamma = 3 \times 2 = 6$$
$$\delta = 4 \times 1 = 4$$
$$w = 18$$

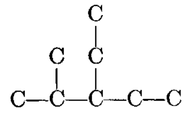
The Wiener number ratio w_i/w_n is defined as the quotient of the Wiener number of the isomeric hydrocarbon and the corresponding normal paraffin (that is, with the same number of carbon atoms). Figures 1 and 2 represent the resulting correlation, in which the number of side chains m in the isomer is the third correlating parameter. The variation of f and w_i/w_n can be expressed linearly for each group having the same number of side-chain constituents. The linear relationships can be collectively expressed as follows:

$$f_a = \frac{1}{3}\left[\frac{w_i}{w_n} + 2 + 0.087m + 0.0045 \sum_{k=1}^{k=m} k(k-1)\right] \qquad (12)$$

$$f_b = \frac{1}{2}\left[\frac{w_i}{w_n} + 1 + 0.101m - 0.005m^2\right] \qquad (13)$$

As an example, the critical temperature and pressure of 2-methyl-3-ethylpentane are calculated by the procedure adopted in this study:

Structure



Calculation of $a_{group}^{2/3}$ and $b_{group}^{3/4}$

The isomer 2-methyl-3-ethylpentane contains a total of eight carbon atoms ($n = 8$) and also two side chains ($m = 2$). In this hydrocarbon there are four type-1, two type-2, and two type-3 carbon atoms. From the group-contribution values presented in Table 1, $a_{group}^{2/3}$ and $b_{group}^{3/4}$ are calculated as follows:

Number					
4	Type-1	4(14,764) =	59,056	4(11.453) =	45.812
2	Type-2	2(13,678) =	27,356	2(6.262) =	12.524
2	Type-3	2(9,122) =	18,244	2(−0.880) =	−1.760
		$a_{group}^{2/3}$ =	104,656	$b_{group}^{3/4}$ =	56.576

Calculation of Isomer Correction

By the procedure already developed, the Wiener numbers are calculated to be for

2-methyl-3-ethylpentane,	$w_i = 67$
n-octane,	$w_n = 84$

The Wiener-number ratio becomes $w_i/w_n = 67/84 = 0.798$. Substituting this value and $m = 2$ into Equations (12) and (13) yields the isomer corrections

$$f_a = \frac{1}{3}\left[0.798 + 2 + 0.087(2) + 0.0045 \sum_{k=1}^{k=2} k(k-1)\right] = 0.9940$$

$$f_b = \tfrac{1}{2}[0.798 + 1 + 0.101(2) - 0.005(2)^2] = 0.9900$$

Calculated van der Waals' Constants and Critical Temperature and Pressure

The calculated values given above are substituted into Equations (10) and (11) to produce the following actual van der Waals' constants:

$$a_{actual}^{2/3} = 0.9940(104{,}656) = 104{,}028$$

$$b_{actual}^{3/4} = 0.9900(56.576) = 56.010$$

From these values, the following calculated van der Waals' constants are produced:

$$a = 33.552 \times 10^6 (\text{cc./g.-mole})^2 \text{ atm.}$$

$$b = 214.30 \text{ cc./g.-mole}$$

to give the following critical temperature and pressure from Equations (1) and (2):

$$T_c = \frac{8(33.552 \times 10^6)}{27(82.055)(214.30)} = 565.4°\text{K.}$$

$$p_c = \frac{33.552 \times 10^6}{27(214.30)^2} = 27.06 \text{ atm.}$$

Kobe and Lynn (*6*) report values of 568.2°K. and 27.4 atm. for 2-methyl-3-ethylpentane.

Similarly, the critical temperatures and pressures for the thirty-nine saturated aliphatic hydrocarbons used in this study were calculated, and they produced average over-all absolute deviations of 0.61% for the critical temperature and 1.06% for the critical pressure.

UNSATURATED ALIPHATIC HYDROCARBONS

Both critical constants available in the literature for nine monoolefins, one diolefin, and two acetylenes were used to calculate the van der Waals' constants for these unsaturated aliphatic hydrocarbons. Differences of these van der Waals' constants $a^{2/3}$ and $b^{3/4}$ and those of the corresponding paraffin hydrocarbons were accepted as representative of the particular type of unsaturation present. Thus, these differences represent the removal of a hydrogen from each of two adjacent carbon atoms to produce the corresponding olefinic linkage and the removal of two hydrogens from each of two adjacent carbons to produce the acetylenic triple bond.

The principle utilized in this method has been used previously (*12*) and was adopted here since the literature data on the unsaturated aliphatics were limited and did not permit an extensive treatment for the establishment of group contributions specific to unsaturated carbon atoms in a manner similar to that already developed for the paraffins. If extensive data had been available for isomeric unsaturated hydrocarbons, a method of analysis similar to that used above could have been developed. Since this was not the case, the extensive background of group contributions and isomer corrections developed for the paraffinic hydrocarbons, when combined with these difference contributions for unsaturated linkages, should produce reliable van der Waals' constants.

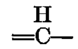
The difference contributions $\Delta a^{2/3}$ and $\Delta b^{3/4}$ are characterized by the type of saturated carbon atoms existing before the introduction of the unsaturated linkage; for example, the difference contribution for the establishment of the double bond in ethylene is designated as 1-1 since both carbon atoms of the corresponding paraffin, ethane, were of type-1. Likewise, the double bond in 1-butene and other end-of-chain olefins was designated as 2-1. Other types of differences are 2-2, 3-1, 3-2, and 3-3 contributions. Difference contributions accounting for *cis* and *trans* forms of the olefinic linkages cannot be included until reliable critical values become available for these structural isomers.

TABLE 2. DIFFERENCE CONTRIBUTIONS FOR THE CALCULATION OF VAN DER WAALS' CONSTANTS OF UNSATURATED ALIPHATIC HYDROCARBONS

	$\Delta a^{2/3}$	$\Delta b^{3/4}$
First double bond		
1—1	−3,868	−2.021
2—1	−3,154	−1.895
2—2	−2,551	−2.009
3—1	−1,548	−1.706
3—2	− 928	−1.820
3—3	− 540	−1.930
Second double bond		
3—1	− 828	−1.259
3—2	− 496	−1.343
3_u—1	−1,332	−1.745
3_u—2	−1,324	−1.862
3_u—3	−1,316	−1.979
3_u←2—1	−1,687	−1.399
3_u←2—1	− 910	−1.485
Triple bond		
1—1	−4,269	−3.680
1—2	−1,934	−3.008
2—2	−1,331	−3.122

NOTE: Arrow points away from the carbon atom involved in the formation of unsaturated bonds and toward the type of carbon atom adjacent to it (to be used in conjugated systems only).

The introduction of a second double bond to form diolefins necessitated the definition of an additional type of carbon atom to account for existing adjacent and conjugated unsaturation. An extension of the Andersen, Beyer, and Watson nomenclature (*1*) suggests the designation of the following additional type of carbon atom:

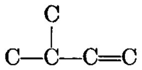
Type	Structure
3_u	 $\overset{H}{=C-}$

which must already be present before the introduction of the second bond.

The development of difference contributions for the triple bond is identical to that already presented for the first double bond and includes types 1-1, 1-2, and 2-2.

Because the data were limited, it became necessary to utilize the available information generally, in order to produce as many difference contributions as possible. Considerable interpolation and extrapolation of the available difference contributions was found necessary to produce the values presented in Table 2.

As an illustration of the procedure, the calculation of the critical temperature and pressure for 3-methyl-1-butene (isoamylene) is presented:

structure 

$$\overset{\overset{C}{|}}{C-C}-C=C$$

Calculation of van der Waals' Constants and Critical Temperature and Pressure

Values of $a^{2/3}$ and $b^{3/4}$ for the corresponding paraffin, 2-methylbutane, have been calculated by the method presented in the previous section:

2-methylbutane	69,370	41.320
Difference contribution, first double bond (2–1)	−3,154	−1.895
	$a^{2/3}$ = 66,216	$b^{3/4}$ = 39.425

a = 17.033 × 10^6 (cc./g.-mole)^2 atm.

b = 134.19 cc./g.-mole

Substituting these values into Equations (1) and (2) yields the following calculated critical temperature and pressure:

$$T_c = 458.3°\text{K. and } p_c = 35.03 \text{ atm.}$$

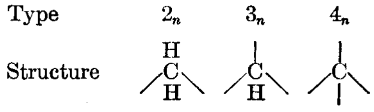
Kobe and Lynn (*6*) report values of 464.8°K. and 33.9 atm.

In the same way critical temperatures and pressures have been calculated for several unsaturated aliphatic hydrocarbons, including all those used in this investigation. This group includes values calculated for hydrocarbons for which only the critical temperature is presented in the literature. Altogether, critical temperatures have been calculated for eleven monoolefins, three diolefins, and five acetylenes, for which critical temperatures are reported. For these the over-all average deviation was 1.21% for the critical temperature. The comparison of critical pressures was limited to nine monoolefins, one diolefin, and two acetylenes used to produce the difference contributions. In these comparisons excessive deviations were noted for an undefined pentene and 2-pentene. If these two values are disregarded, the average absolute deviation becomes 1.37% for the critical pressure. The average critical-temperature deviation for the remaining ten compounds is 0.53%.

NAPHTHENIC HYDROCARBONS

Group contributions $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for the carbons in naphthenic rings were developed from data on cyclopentanes and cyclohexanes. Differences of $a^{2/3}$ and $b^{3/4}$ between cyclohexane and cyclopentane produced values which were taken as the group contributions for the group–CH_2– in a naphthenic ring. When these contributions were used to construct the cyclopentane and cyclohexane molecules, the additional values of $\Delta a^{2/3}$ = 2,658 and $\Delta b^{3/4}$ = 9.073 were necessary to duplicate the van der Waals' constants derived from critical values. Therefore, these values contribute to the formation of naphthenic rings and have been designated as the *naphthenic-ring contributions.*

To obtain group contributions for type-3 and -4 carbon atoms in naphthenic rings, the previously outlined method for paraffin hydrocarbons was applied to the alkyl side chains of substituted naphthenes. These alkyl group contributions, combined with the values calculated above, permitted calculation of the type-3 and -4 group contributions. In order to differentiate these carbon atoms from types present in other classes of hydrocarbons, the notation of Andersen, Beyer, and Watson was extended to include the carbon atoms present in naphthenic rings, as follows:

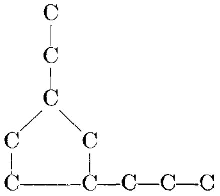


The group-contribution values resulting from this study are summarized in Table 3.

Additional data (*10*) on five disubstituted cyclopentanes permitted the establishment of position contributions of the *cis* and *trans* type for 1,2 and 1,3 disubstituted naphthenes. Lack of further data on disubstituted naphthenes prevents an extension of these position contributions beyond the 1,2 and 1,3 types presented in Table 3. For substitutions involving other position types the 1,3 position contribution can be used. Further lack of data prevents a rigorous analysis of position contributions for polysubstituted hydrocarbons. Until such data become available, the 1,2 and 1,3 position contributions can be applied in multiple sequence. These position contributions are also presented in Table 3.

Table 3, in conjunction with Tables 1 and 2, makes possible the establishment of van der Waals' constants for alkyl naphthenes with side chains of considerable size and complexity. In order to establish the values for the alkyl side chains, the total number of carbon atoms in the alkyl naphthene must be used to obtain the group-contribution values from Table 1. To illustrate this method, the critical temperature and pressure of 1-ethyl-3, *cis*-*n*-propylcyclopentane are calculated as follows:

Structure



A. Naphthenic Ring				
Three Type-2_n carbons	3(12,535) =	37,605	3(5.338) =	16.014
Two Type-3_n carbons	2(9,910) =	19,820	2(0.023) =	0.046
Naththenic-ring contribution		2,658		9.073
Position contribution, *cis*-1, 3		−2,525		−1.493
B. Ethyl Side Chain (n = 10)				
One Type-1 carbon		14,710		11.453
One Type-2 carbon		13,678		6.262
C. n-Propyl Side Chain (n = 10)				
One Type-1 carbon		14,710		11.453
Two Type-2 carbons	2(13,678) =	27,356	2(6.262) =	12.524
	$a^{2/3}$ =	128,012	$b^{3/4}$ =	65.332

$$a = 45.801 \times 10^6 (\text{cc./g.-mole})^2 \text{ atm.}$$

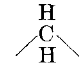
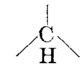
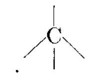
$$b = 263.12 \text{ cc./g.-mole}$$

From Equations (1) and (2)

$$T_c = \frac{8(45.801 \times 10^6)}{27(82.055)(263.12)} = 628.6°\text{K.} \qquad p_c = \frac{45.801 \times 10^6}{27(263.12)^2} = 24.50 \text{ atm.}$$

Critical constants are not available for this hydrocarbon, and consequently no direct comparisons can be made.

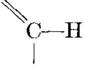
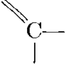
Table 3. Group and Position Contributions, $\Delta a^{2/3}$ and $\Delta b^{3/4}$, for Naphthenic Rings

Type	Structure	$\Delta a^{2/3}$	$\Delta b^{3/4}$
A. Group contributions			
2_n		12,535	5.338
3_n		9,910	0.023
4_n		2,066	−8.094
Naphthenic-ring contribution		2,658	9.073
B. Position contributions			
cis-1,2		− 427	−0.866
-1,3		−2,525	−1.493
trans-1,2		−2,525	−1.493
-1,3		−4,195	−2.494

This procedure was applied to the calculation of critical temperatures and pressures of the ten available naphthenic hydrocarbons (*6*, *10*). Average absolute deviations of 0.11% for the critical temperature and 0.20% for the critical pressure were obtained, but these low deviations should not be construed as representative of this class of compounds since the group contributions presented in Table 3 were established directly from these hydrocarbons.

AROMATIC HYDROCARBONS

The same type of analysis was applied to cover the aromatic series or the remaining class of hydrocarbons, including polynuclear aromatics and alkyl derivatives of benzene and polynuclear compounds. In this connection, the notation of Andersen, Beyer, and Watson (*1*) was further extended to define the following additional types of carbon atoms specific to the aromatic series:

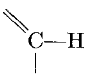
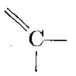
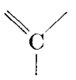
Type	3_a	4_a
Structure		

Group contributions for the type-3_a carbon were directly obtained by dividing by six the van der Waals' constants $a^{2/3}$ and $b^{3/4}$ for benzene. Because aromatic rings consist of six carbon atoms, no ring contribution is necessary. With the group contributions for type-3_a as a basis, in conjunction with the contributions due to alkyl side chains, the group-contribution values for the type-4_a carbon were established from the monoalkyl benzenes. As pointed out for alkyl-naphthenic hydrocarbons, the total number of carbon atoms in the alkyl benzene must be used to obtain group contribution values from Table 1 for the alkyl side chains.

Position contributions for polysubstituted aromatic hydrocarbons were obtained by using the group-contribution values of the type-3_a and -4_a carbons already established, in conjunction with the values of the alkyl side chains. Position-contribution values of the types 1-2, 1-3, 1-4, 1-5, and 1-6 were established. These position types designate the location of the side chains with reference to the carbon atoms in the aromatic nucleus. In using these position contributions, any convenient side chain can be selected as a reference point. The ring is then traversed in a clockwise or counterclockwise direction, any side-chain constituents being accounted for along the path until the reference point is reached again. Thus for *o*-xylene, two position contributions are utilized: the 1-2 contribution for the immediately adjacent methyl group and the 1-6 contribution continuing from the second methyl group back to the starting point. Likewise, *m*-xylene requires a 1-3 and a 1-5 position contribution, and *p*-xylene utilizes two 1-4 contributions. A similar procedure is followed for polyalkyl benzenes.

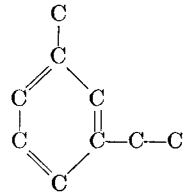
In order to construct polynuclear aromatic hydrocarbons, fused bridge carbons must be used to join the aromatic nuclei. This carbon atom is of type 4 and for purposes of differentiation has been designated as type-4_p. The critical temperature and pressure reported by Schröer (*11*) for naphthalene made possible the establishment of this group-contribution value. Group-contribution values for this type of carbon were produced from the van der Waals' constants $a^{2/3}$ and $b^{3/4}$ for naphthalene through the subtraction of eight type-3_a carbons. The resulting difference when divided by two produced the type-4_p group contribution. All these group and position contributions for the aromatic series are presented in Table 4.

Table 4. Group and Position Contributions, $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for Aromatic Rings

Type	Structure	$\Delta a^{2/3}$	$\Delta b^{3/4}$
A. Group contributions			
3_a		11,646	5.991
4_a		11,144	1.043
4_p		11,561	1.634
B. Position contributions			
1–2		−830	−1.253
1–3		−1,597	−0.806
1–4		155	0.212
1–5		279	0.254
1–6		488	0.525

As an illustration of the application of this method, the procedure for calculating the critical temperature and pressure for 1-methyl-3-ethylbenzene becomes

Structure



A. Aromatic Ring		
Four Type-3_a carbons	4(11,646) = 46,584	4(5.991) = 23.964
Two Type-4_a carbons	2(11,144) = 22,288	2(1.043) = 2.086
Position contributions:		
1–3	−1,597	−0.806
1–5	279	0.254
B. Methyl Side Chain (n = 9)		
One Type-1 carbon	14,734	11.453
C. Ethyl Side Chain (n = 9)		
One Type-1 carbon	14,734	11.453
One Type-2 carbon	13,678	6.262
	$a^{2/3}$ = 110,700	$b^{3/4}$ = 54.666

$$a = 36.832 \times 10^6 (\text{cc./g.-mole})^2 \text{ atm.}$$

$$b = 207.47 \text{ cc./g.-mole}$$

From Equations (1) and (2)

$$T_c = \frac{8(36.832 \times 10^6)}{27(82.055)(207.47)} = 641.0°\text{K.}$$

$$p_c = \frac{36.832 \times 10^6}{27(207.47)^2} = 31.69 \text{ atm.}$$

Kobe and Lynn (*6*) report critical values of 636.2°K. and 31 atm. for 1-methyl-3-ethylbenzene.

In the same way the critical temperatures and pressures of nineteen aromatic hydrocarbons for which data were available were calculated, and they produced over-all average-absolute deviations of 0.43% for the critical temperature and 2.29% for the critical pressure. In these comparisons questionable literature values have been included, and consequently these deviations represent conservative expectations. This is further substantiated from the excellent agreement resulting from the comparison of actual and calculated critical values for diphenyl and diphenylmethane. Critical constants for these hydrocarbons were obtained from Guye and Mallet (*3*) and were not utilized for the establishment of group contributions presented in Table 4; yet for both hydrocarbons the average deviation was found to be less than 0.5% for the critical temperature and pressure.

CONCLUSIONS

The method of this investigation has been applied to the calculation of critical temperature and pressure of a number of hydrocarbons of all classes. The resulting calculated critical values have been compared with those in the literature to produce the following results:

		Deviation	
	Number	T_c, %	p_c, %
Saturated aliphatics	36	0.61	1.06
Unsaturated aliphatics	10	0.53	1.37
Naphthenes	10	0.11	0.20
Aromatics	19	0.43	2.29
	75	0.49	1.30

In view of these results, it is felt that this method is capable of producting critical values with an expectancy of less than 1% deviation for the critical temperature and less than 2% for the critical pressure.

Critical constants for these hydrocarbons have been produced by the methods of Riedel (*8, 9*) and Lydersen (*5*) and have been presented elsewhere (*12* to *15*). Comparisons of the critical values resulting from these methods have been made with literature values and were found to be in good agreement with the results of this investigation. Specifically, the over-all deviations resulting from this study were found in general to be somewhat less than those resulting from the methods of Riedel and Lydersen.

It should be noted that the exponents applied to the van der Waals' constants a and b for the saturated aliphatic hydrocarbons were adapted to those of the unsaturated, naphthenic, and aromatic hydrocarbons. This approach was adopted since the data on these classes of hydrocarbons are not sufficiently extensive for individual investigation. Because of these limitations and in order to make this pattern consistent throughout, the general behavior of the van der Waals' constants for the other classes of hydrocarbons was assumed to follow that of the saturated aliphatics. The validity of this assumption is borne out by the good agreement found to exist for classes of hydrocarbons other than the saturated aliphatics.

NOTATION

a = pressure van der Waals' constant, (cc./g.-mole)^2 atm.
b = volume van der Waals' constant, cc./g.-mole
f_a = isomer factor for pressure van der Waals' constant, Equation (10)
f_b = isomer factor for volume van der Waals' constant, Equation (11)
m = number of side chains in isomeric paraffin
n = total number of carbon atoms in hydrocarbon
p_c = critical pressure, atm.
R = gas constant, 82.055 (atm.)(cc.)/(g.-mole)(°K.)
T_c = critical temperature, °K.
w_i = Wiener number for isomeric paraffins
w_n = Wiener number for normal paraffins
Δ = difference

Subscripts for types of carbon atoms

a = for aromatic ring carbons
n = for naphthenic ring carbons
p = for polynuclear aromatic bridgehead carbons
u = for unsaturated aliphatic hydrocarbons

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