Critical Constants of the Naphthenic Hydrocarbons

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Group-contribution values are presented and, together with those already developed for the aliphatic hydrocarbons (*10, 11*), make possible the evaluation of both van der Waals' constants for the naphthenic hydrocarbons. These constants can be used to produce the critical temperatures, pressures, and volumes of these compounds entirely from a knowledge of their chemical structure.

Critical constants have been calculated for several naphthenes, and from a comparison of them with the constants resulting from the methods of Riedel (*5, 6*) and Lydersen (*3*) it was found that the critical constants calculated by these three methods were in fair agreement for naphthenes having short alkyl side chains and progressively deviated from each other as the chains were permitted to lengthen. An appraisal has been made on five naphthenes along the lines proposed by Sondak and Thodos (*9*) in order to see whether these calculated critical constants properly represent the vapor-pressure function resulting from vapor-pressure data found in the literature for these hydrocarbons.

Critical constants have been produced for more than fifty naphthenes, for which vapor-pressure data are available in the literature, and will be used in a separate, comprehensive vapor-pressure study for hydrocarbons of this type.

Information available in the literature on the critical constants of the naphthenic hydrocarbons is limited to the simpler cyclopentanes and cyclohexanes of the series. Frequently occasions arise that demand reliable critical constants for naphthenic hydrocarbons for which critical values are not available. Consequently this study was directed and limited to the development of a method capable of predicting critical constants for this type of compound and involved an extension of the background already presented for the aliphatic hydrocarbons (*10, 11*). For the aliphatic hydrocarbons and the present study on naphthenes, the van der Waals' constants have been used as the basic quantities necessary to define the critical constants. From an analysis of data available in the literature on the critical constants of naphthenes, group-contribution values have been developed and, together with those already available for the aliphatic hydrocarbons (*10, 11*), now make possible the extension of this limited background to the calculation of critical temperatures, pressures, and volumes for naphthenes having involved molecular structures and high molecular weights.

The pressure and volume van der Waals' constants a and b for only ten naphthenes, for which critical constants are presented in the literature (*4, 7*), have been used to produce the fundamental background for this study through the basic relationships

$$a = \frac{27R^2T_c^2}{64p_c} \qquad (1)$$

$$b = \frac{RT_c}{8p_c} \qquad (2)$$

where

a = pressure van der Waals' constant
b = volume van der Waals' constant
p_c = critical pressure
R = gas constant
T_c = critical temperature

The van der Waals' constants resulting from the critical temperatures and pressures of these ten naphthenic hydrocarbons are presented in Table 1. Although these constants are specific to these few naphthenes, these values have proved useful in extending this limited background to the formulation of generalized relationships and group-contribution values that become applicable to naphthenic hydrocarbons in general.

CRITICAL TEMPERATURES AND PRESSURES

Normal Cycloparaffins

For the only two naphthenes having no alkyl side chains for which critical values are available in the literature (*4, 7*), interesting and consistent relationships have been found to exist when their van der Waals' constants are divided by those of the corresponding normal paraffins. For example, the ratio of values for the pressure van der Waals' constant, a, for cyclopentane and normal pentane becomes

$$\frac{16.699 \times 10^6}{18.824 \times 10^6} = 0.8871$$

and that for cyclohexane and normal hexane becomes

$$\frac{21.729 \times 10^6}{24.503 \times 10^6} = 0.8868.$$

Similarly, for the volume van der Waals' constant, b, these ratios become

$$\frac{117.83}{114.70} = 0.8143$$

and

$$\frac{141.84}{174.22} = 0.8141$$

respectively. The values of these ratios strongly point to the existence of a generalized relationship involving the van der Waals' constants of the cyclized normal paraffins and those of the corresponding normal paraffins. If the average values of the ratios for cyclo-

Table 1. Critical Constants of Naphthenes Available in the Literature and van der Waals' Constants Calculated from Them

	Critical constants (4, 7)			van der Waals' constants			
	T_c, °K.	p_c, atm.	v_c, cc./ g.-mole	a, (cc./ g.-mole)^2 atm. $\times 10^{-6}$	b, cc./ g.-mole	$a^{0.626}$	$b^{0.76}$
Cyclopentane	511.765	44.55	259.7	16.699	117.83	33,220	37.511
Methylcyclopentane	532.775	37.364	318.8	21.579	146.26	39,003	44.207
Ethylcyclopentane	569.465	33.526	374.7	27.476	174.22	45,372	50.494
1,1-Dimethylcyclopentane	555	35	350.6	24.550	161.18	42,284	47.594
1, cis-2-Dimethyl-cyclopentane	565	34	363.6	26.669	170.45	44,533	49.661
1, trans-2-Dimethyl-cyclopentane	555	34	363.6	25.734	167.43	43,549	48.991
1, cis-3-Dimethyl-cyclopentane	555	34	363.6	25.734	167.43	43,549	48.991
1, trans-3-Dimethyl-cyclopentane	555	35	350.6	24.998	162.65	42,765	47.924
Cyclohexane	553.165	40.0	308.3	21.729	141.84	39,174	43.189
Methylcyclohexane	572.265	34.32	344.5	27.104	171.03	44,986	49.790

pentane and cyclohexane are assumed to be general, then the van der Waals' constants for normal cycloparaffins of any ring size can be calculated from those of the corresponding normal paraffins through the relationships

$$a_c = 0.8870a_n \quad (3)$$

and

$$b_c = 0.8142b_n \quad (4)$$

where the subscripts c and n refer to the normal cycloparaffin and normal paraffin, respectively. Although Equations (3) and (4) can be used directly to calculate van der Waals' constants for the normal cycloparaffins, their equivalent form by raising each expression to a convenient exponent will prove more advantageous for computational purposes. The details justifying this procedure will be borne out in a later discussion, in which it will be shown that the proper exponent for Equation (3) is 0.626 and that for Equation (4) becomes 0.76.

Methyl Naphthenes

Using an approach similar to that outlined for the normal cycloparaffins, the author referred the van der Waals' constants appearing in Table 1 for methylcyclopentane and methylcyclohexane to those of their respective normal paraffins (*11*). Thus the ratio of the pressure van der Waals' constants for methylcyclopentane and normal hexane becomes $(21.579 \times 10^6)/(24.503 \times 10^6) = 0.8807$ and that for methylcyclohexane and normal heptane becomes $(27.104 \times 10^6)/(30.690 \times 10^6) = 0.8830$. Similarly, the ratios for the volume van der Waals' constants become $146.26/174.22 = 0.8395$ and $171.03/205.20 = 0.8335$, respectively. Although the agreement of these ratios was not so close as that found to exist for the normal cycloparaffins, the average values of these ratios may be assumed to represent the general case involving the cyclization of a normal paraffin to produce the corresponding methyl naphthene. For this case the following expressions can be assumed to apply:

$$a_c = 0.8818a_n \quad (5)$$

and

$$b_c = 0.8365a_n \quad (6)$$

Although similar generalized expressions for alkyl naphthenes having longer side chains could prove valuable, the information available from Table 1 does not justify an extension of this type of analysis. Equations (5) and (6) are presented for completeness but have not been used in this investigation in the calculation of van der Waals' constants for methyl naphthenes. Instead the more generalized approach adopted in this study and involving group contributions has been used for the calculation of these constants; it considers the replacement of a hydrogen atom by a methyl group from the corresponding normal cycloparaffin.

Group-contributions Values

Differences of the van der Waals' constants, Δa and Δb, obtained from hydrocarbons having similar structures but differing in molecular dimensions by a single methyl group can be produced for the naphthenes appearing in Table 1. Although these differences as such may prove expedient for the calculation of van der Waals' constants, their use must be limited to the type of naphthenes appearing in Table 1 and having no more than two carbon atoms in an alkyl side chain. For naphthenes having alkyl side chains consisting of more than two carbon atoms, the reliability of these group-contribution values becomes doubtful and less exacting with increasing chain lengths. Because of these limitations, in the search for a more consistent pattern to follow, the general behavior of the van der Waals' constants for these naphthenic hydrocarbons was assumed to follow that of the aliphatic hydrocarbons (*10, 11*). For the saturated aliphatic hydrocarbons additive group contributions have been found to exist in the replacement of a hydrogen atom by a methyl group when the van der Waals' constants a and b are raised to the 0.626 and 0.76 powers, respectively.

With this arrangement Equations (3) and (4) have been modified to define the van der Waals' constants of the normal cycloparaffins in terms of those of the corresponding normal paraffins through the relationships

$$a_c^{0.626} = 0.928a_n^{0.626} \quad (7)$$

$$b_c^{0.76} = 0.8555b_n^{0.76} \quad (8)$$

Equations (7) and (8) are not necessary for the development of van der Waals' constants but prove useful for computational purposes. However, Equations (3) and (4) or their equivalent Equations (7) and (8) are significant in these studies because through them it becomes possible to calculate both van der Waals' constants for the normal cycloparaffins and thus to establish the basic value for the ring required for these naphthenic hydrocarbons. For a limited number of normal cycloparaffins, both van der Waals' constants have been calculated with Equations (7) and (8) from the constants $a^{0.626}$ and $b^{0.76}$ of the corresponding normal paraffins (*11*). With both van der Waals' constants available, the critical temperatures and pressures were produced for these naphthenes from the following basic relationships:

$$T_c = \frac{8a}{27Rb} \quad (9)$$

$$p_c = \frac{a}{27b^2} \quad (10)$$

and are presented in Table 2 from cyclopropane through cyclodecane, inclusive.

The van der Waals' constants a and b for the naphthenes appearing in Table 1 have been raised to the 0.626 and 0.76 powers, respectively, and are also included in this table. From these calculated values, the differences resulting for hydrocarbons having similar molecular structures but differing by a methyl group have been defined as group contributions and are designated as $\Delta a^{0.626}$ and $\Delta b^{0.76}$. These group contributions can be interpreted to be the result involving the replacement of a hydrogen atom by a methyl group. The average differences produced from the analysis of the values presented in Table 1 appear as the recommended group contributions, $\Delta a^{0.626}$ and $\Delta b^{0.76}$, in Table 3.

The first replacement of hydrogen by a methyl group to produce the corresponding methylcycloparaffin has been found to have the average values $\Delta a^{0.626} = 5{,}798$ and $\Delta b^{0.76} = 6.648$. Consequent replacements of hydrogen atoms from the nucleus by methyl groups to produce polymethylnaphthenes must be associated with the

positions involved in these secondary substitutions. For this study, only values for the second methyl substitution are available, and these are presented in Table 3 for the cases involving the different types of substitution. Since these data are limited to the formation of dimethylcyclopentanes, further substitutions in the naphthenic ring to produce alkylnaphthenes having more than two methyl groups become somewhat speculative. For lack of better information, the group-contribution values for the second methyl substitution are recommended for the calculation of van der Waals' constants of naphthenes having more than two methyl groups. For this case, the substitutions may be carried out in a clockwise direction with reference being placed always on the methyl group immediately preceding the one involved directly in the substitution.

The replacement of the hydrogen atom on a methyl side chain by a methyl group to produce an ethyl side chain involves group-contribution values $\Delta a^{0.626} = 6{,}369$ and $\Delta b^{0.76} = 6.287$. For this substitution the notation C ← 1 has been adopted, in which the arrow points away from the type of carbon atom on which the substitution is made and toward the type adjacent to it. In this case C represents the naphthenic ring, and the designation 1 indicates the presence of a single carbon-to-carbon bond on the carbon atom on which the methyl substitution is made. The classification of types of carbon atoms is consistent with that of Andersen, Beyer and Watson (*1*), who associate the type of carbon atom with the number of carbon-to-carbon bonds. Thus, for the saturated aliphatic hydrocarbons, the following types of carbon atoms are possible:

Type	1	2	3	4
Structure	$-CH_3$	$-CH_2-$	$-CH<$	$-C<$

To produce van der Waals' constants for alkyl naphthenes of side chains having more than two carbon atoms each, the group-contribution values for the aliphatic hydrocarbons (*10, 11*) are recommended.

With Equations (7) and (8) and the group-contribution values presented in Table 3, van der Waals' constants for the naphthenic hydrocarbons presented in Table 1 have been calculated and, when used with Equations (9) and (10), they produced the corresponding critical temperatures and pressures for these hydrocarbons. These calculated critical values are presented in Table 4.

In addition to the naphthenes appearing in Table 1, van der Waals' constants and critical temperatures, pressures, and volumes have been calculated for fifty-two alkylcyclopentanes and cyclohexanes. These calculated van der Waals' constants along with the calculated critical temperatures, pressures, and volumes are presented in Table 4 and include all the normal monoalkylcyclopentanes through *n*-hexadecylcyclopentane and a number of cyclopentanes and cyclohexanes having two and three alkyl side chains.

Table 2. Calculated van der Waals' Constants and Critical Constants Resulting from Them for Some Normal Cycloparaffins

	Calculated van der Waals' constants			Calculated critical constants		
	$a_c \times 10^{-6}$	b_c	β_c	T_c, °K.	p_c, atm.	v_c, cc./g.-mole
Cyclopropane	8.216	72.94	0.7649	406.7	57.20	167.4
Cyclobutane	12.180	94.71	0.7512	464.4	50.29	213.4
Cyclopentane	16.698	117.75	0.7374	512.1	44.60	260.5
Cyclohexane	21.729	141.93	0.7237	552.8	39.95	308.1
Cycloheptane	27.243	167.17	0.7100	588.4	36.10	356.1
Cycloöctane	33.210	193.34	0.6963	620.2	32.90	403.9
Cyclononane	39.605	220.39	0.6825	648.9	30.20	451.2
Cyclodecane	46.414	248.29	0.6688	675.0	27.88	498.2

Example

As an illustration of the application of this method, the critical temperature and pressure for 1, cis-2, cis-4-trimethylcyclopentane are presented. In order to calculate both van der Waals' constants for this particular hydrocarbon, it is necessary to produce the values of $a^{0.626}$ and $b^{0.76}$ for the base group cyclopentane from the corresponding values for *n*-pentane. From the related work dealing with the saturated aliphatic hydrocarbons (*11*), for *n*-pentane, $a^{0.626} = 35{,}796$ and $b^{0.76} = 43.823$. Therefore, with Equations (7) and (8), the van der Waals' constants for cyclopentane become $a^{0.626} = 0.928\ (35{,}796) = 33{,}219$ and $b^{0.76} = 0.8555\ (43.823) = 37.491$.

A. Base group—cyclopentane	33,219	37.491
B. First methyl substitution	5,798	6.648
C. Second methyl substitution, cis (1,2)	5,530	5.454
D. Third methyl substitution, cis (1,3)	4,546	4.784
	$a^{0.626} =$ 49,093	$b^{0.76} =$ 54.377

$a = 31.163 \times 10^6$ (cc./g.-mole)^2 atm.
$b = 192.06$ cc./g.-mole

Substituting the calculated values of a and b in Equations (9) and (10) yields

$$T_c = \frac{8a}{27Rb} = \frac{8(31.163 \times 10^6)}{27(82.055)(192.06)}$$

$$= 585.9°\text{K.}$$

$$p_c = \frac{a}{27b^2} = \frac{31.163 \times 10^6}{27(192.06)^2}$$

$$= 31.29 \text{ atm.}$$

For 1, cis-2, cis-4-trimethylcyclopentane critical constants are not available in the literature, and consequently no direct comparisons can be made.

Critical Volume

It has been shown that the critical volumes of the aliphatic hydrocarbons (*10, 11*) can be defined in terms of the volume van der Waals' constant, b, through the relationship

$$v_c = 3\beta b \qquad (11)$$

where β represents a volume factor that has been found to depend on the total number and orientation of the carbon atoms present in the hydrocarbon. Specifically for the normal and branched-chain paraffins (*11*), the volume factor has been found to be, respectively,

$$\beta_n = 0.7849 - 0.01337n_c \qquad (12)$$

and

$$\beta_i = 0.8100 - 0.0138n_c \qquad (13)$$

where n_c represents the total number of carbon atoms present in the saturated aliphatic hydrocarbon.

With the critical volumes of the naphthenes appearing in Table 1 and the corresponding volume van der Waals' constants, b, volume factors, β, were calculated through the use of Equation (11) for all the naphthenic hydrocarbons presented in this table. An examination of these values reveals the ratios of volume factors for cyclopentane to *n*-pentane and cyclohexane to *n*-hexane to be 1.0258 and 1.0281, respectively. Since these ratios are nearly the same, a strong inference exists that the ratio of volume factors of the normal cycloparaffins to those of the corresponding normal paraffins is constant and may be taken to be equal to 1.027, the average of the values 1.0258 and 1.0281. Consequently, the volume factor for unsubstituted naphthenes can be defined in terms of the volume factor of the corresponding normal paraffins, β_n, as

$$\beta_c = 1.027\beta_n \qquad (14)$$

Upon substitution of Equation (12) into Equation (14), the volume factor, β_c, for unsubstituted naphthenes becomes

$$\beta_c = 0.8061 - 0.01373n_c \qquad (15)$$

where n_c represents the total number of carbon atoms present in the ring.

A review of the volume-factor values for the naphthenic hydrocarbons having alkyl side chains indicates that a constant-value contribution exists for each carbon atom attached to the cycloparaffinic nucleus. Thus, for methyl naphthenes, the volume factor, β_{cs}, becomes

$$\beta_{cs} = \beta_c - 0.00785\alpha \qquad (16)$$

where α represents the total number of methyl groups attached to the naphthenic ring. By combination of Equations (15) and (16), the volume factor for methyl naphthenes, β_{cs}, becomes

$$\beta_{cs} = 0.8061 - 0.01373n_c - 0.00785\alpha \qquad (17)$$

An extension of this background to include alkyl naphthenes having both normal and branched side chains through the use of Equations (12) and (13) produces the following generalized expression for the volume factor:

$$\beta_{cs} = 0.8061 - 0.01373n_c - 0.00785(\alpha_n + \alpha_i) - 0.01337(n_{cn}' - \alpha_n) - 0.0138(n_{ci}' - \alpha_i) \qquad (18)$$

where

β_{cs} = volume factor of alkyl naphthenes

α_n, α_i = total number of normal and branched side chains, respectively, attached to naphthenic nucleus

n_c = total number of carbon atoms in ring

n_{cn}', n_{ci}' = total number of carbon atoms present in normal and branched side chains, respectively

Example

To illustrate the use of this method, the calculation of the critical volume for 1, cis-2, cis-4-trimethylcyclopentane is presented. This alkyl naphthene contains three methyl groups attached to the cyclopentane nucleus, and therefore Equation (17) becomes applicable. For this case $n_c = 5$, $\alpha = 3$, and therefore

$$\beta_{cs} = 0.8061 - 0.01373(5) - 0.00785(3) = 0.7139$$

The volume van der Waals' constant, b, for this compound has been found to be $b = 192.06$ cc./g.-mole. Therefore $v_c = 3(0.7139)(192.06) = 411.3$ cc./g.-mole.

By use of Equation (18), volume factors have been calculated for all the naphthenic hydrocarbons presented in Table 1. These values, together with the calculated van der Waals' constants, produced with Equation (11) the critical volumes for these naphthenic hydrocarbons. Similarly, critical

Table 3. Methyl Group Contributions $\Delta a^{0.626}$ and $\Delta b^{0.76}$ Involved in the Replacement of Hydrogen Atoms by Methyl Groups from Naphthenic Nuclei and Alkyl Side Chains

	$\Delta a^{0.626}$	$\Delta b^{0.76}$
First methyl substitution	5,798	6.648
Second methyl substitution		
(1,1)	3,281	3.387
cis (1,2)	5,530	5.454
trans (1,2)	4,546	4.784
cis (1,3)	4,546	4.784
trans (1,3)	3,762	3.717
cis (1,4)	3,762	3.717
trans (1,4)	3,281	3.387
Methyl group substitutions on side chains		
$C \leftarrow 1$	6,369	6.287
$2 \leftarrow 1$	6,417	6.686

Note: C represents a cycloparaffinic nucleus

For the introduction of more than two methyl groups in the naphthenic nucleus, the values listed for second methyl substitution are recommended. For these cases the substitutions should be carried out in a clockwise direction with position reference being placed on the methyl group immediately preceding the one involved in the substitution.

A more extensive list of methyl group contributions involving the substitution of hydrogen atoms in alkyl carbon atoms can be found elsewhere (*11*).

Table 4. Calculated van der Waals' Constants and Critical Values for Several Cyclopentanes and Cyclohexanes

	van der Waals' constants			Critical temperature, °K.			Critical pressure, atm.			Critical volume, cc./g.-mole	
	a, (cc./g.-mole)^2 atm. $\times 10^{-6}$	b, cc./g.-mole	Volume factor, β	Lydersen (*3*)	Riedel (*6*)	This investigation	Lydersen (*3*)	Riedel (*5*)	This investigation	Lydersen (*3*)	This investigation
Cyclopentanes											
Cyclopentane	16.698	117.75	0.7374	513.6	512.6	512.1	44.16	43.83	44.60	262.5	260.5
Methylcyclopentane	21.592	145.96	0.7296	535.8	534.8	534.2	37.66	37.66	37.54	319.0	319.5
Ethylcyclopentane	27.490	173.91	0.7162	570.5	569.8	570.8	33.11	32.99	33.66	374.0	373.7
n-Butylcyclopentane	40.919	237.00	0.6895	622.5	620.1	623.4	26.68	26.46	26.98	484.0	490.2
n-Octylcyclopentane	73.340	375.66	0.6360	696.8	681.9	705.0	19.17	18.91	19.25	704.0	716.8
n-Dodecylcyclopentane	112.34	528.08	0.5825	751.6	712.8	768.2	14.96	14.72	14.92	924.0	922.8
n-Hexadecylcyclopentane	157.25	691 94	0.5290	798.0	724.5	820.6	12.27	12.05	12.16	1,144	1,098
1, 1-Dimethylcyclopentane	24.563	160.87	0.7218	559.9	546.2	551.4	34.62	32.99	35.16	359.0	348.4
1, cis-2-Dimethylcyclopentane	26.682	170.15	0.7218	565.2	563.8	566.3	32.80	32.99	34.13	375.5	368.4
1, trans-2-Dimethylcyclopentane	25.748	167.13	0.7218	553.6	552.2	556.3	32.80	32.99	34.14	375.5	361.9
1, cis-3-Dimethylcyclopentane	25.748	167.13	0.7218	553.4	552.0	556.3	32.80	32.99	34.14	375.5	361.9
1, trans-3-Dimethylcyclopentane	25.011	162.34	0.7218	551.9	550.6	556.3	32.80	32.99	35.15	375.5	351.5
1, 1, 2-Trimethylcyclopentane	29.891	185.60	0.7139	586.0	571.5	581.5	30.47	29.36	32.14	415.5	397.50
Cyclohexanes											
Cyclohexane	21.729	141.93	0.7237	553.9	553.0	552.8	40.36	39.92	39.95	307.0	308.1
Methylcyclohexane	27.090	171.34	0.7159	571.5	570.3	570.9	34.83	34.70	34.18	363.5	368.0
n-Butylcyclohexane	47.807	265.34	0.6051	649.3	645.0	650.6	25.18	24.93	25.15	528.5	537.8
1, 1-Dimethylcyclohexane	30.316	186.82	0.7080	599.2	584.4	586.0	32.16	30.69	32.17	403.5	396.8
1, cis-3-Dimethylcyclohexane	31.595	193.30	0.7080	587.4	585.2	590.2	30.63	30.69	31.32	420.0	410.6

Complete table is available from the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., as document 5057, obtainable for $1.25 as microfilm or photoprint.

volumes have been calculated for the naphthenic hydrocarbons presented in Table 4 and, together with the critical temperatures and pressures already presented, completely define the critical constants for these compounds.

COMPARISON OF RESULTS

With the exception of the critical constants for the ten naphthenes used in this study, no experimental data are available in the literature to compare the reliability of values calculated by this method. Furthermore, a comparison of calculated values with those already available for the ten naphthenes used in this investigation appears unjustifiable in view of the fact that the critical constants of these hydrocarbons have been used to produce the group-contribution values for these naphthenes. Because of these limitations direct comparisons of calculated values and the critical constants found in the present literature will have no significance.

In order to appraise the information resulting from these studies, however, a comparison of the critical constants obtained from the present method and those produced by the methods of Riedel (*5, 6*) and Lydersen (*3*) has been carried out for more than fifty naphthenes including several alkyl cyclopentanes and cyclohexanes. For the calculation of the critical temperature both Riedel and Lydersen require the use of the normal boiling point of the substance and for the critical pressure the molecular weight. The critical constants resulting for these naphthenes are presented in Table 4. From these comparisons, it was found that the critical constants resulting from the methods of Riedel and Lydersen are in good agreement with those produced by the present method for naphthenes having short alkyl side chains. With increasing chain lengths, the critical values resulting from these methods were found to deviate progressively. For example, the critical temperature and pressure for *n*-hexadecylcyclopentane calculated by the method of Riedel were 724.5°K. and 12.05 atm., by that of Lydersen 798.0°K. and 12.27 atm., and the present method produced 820.6°K. and 12.16 atm. For the naphthenes considered in this investigation, the foregoing discrepancies represent the maximum deviations and were found to correlate with the length of the alkyl side chain. Similar comparisons for *n*-dodecylcyclopentane give rise to the following values: Riedel, 712.8°K. and 14.72 atm.; Lydersen, 751.6°K. and 14.96 atm.; present method, 768.2°K. and 14.92 atm. It is obvious from this comparison that these discrepancies become smaller with decreasing lengths of the alkyl side chains. Nonetheless, these differences were significant enough to justify a further study for the selection of the method producing dependable values.

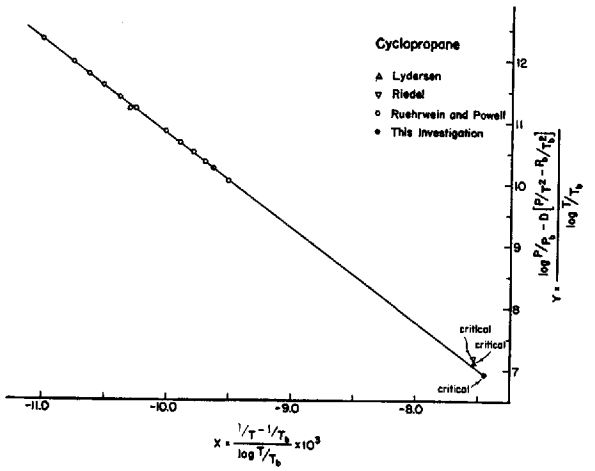

Fig. 1. Relationship of Y vs. X for cyclopropane.

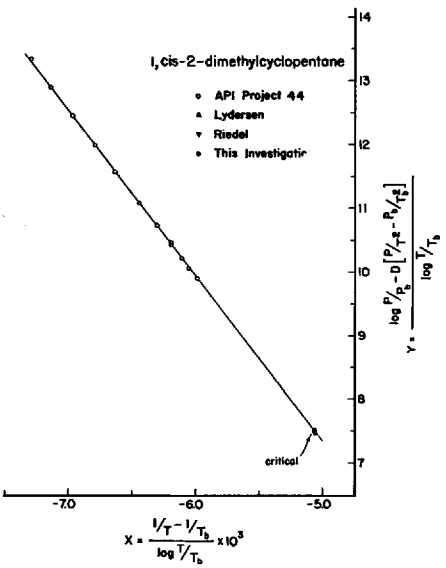

Fig. 2. Relationship of Y vs. X for 1, cis-2-dimethylcyclopentane.

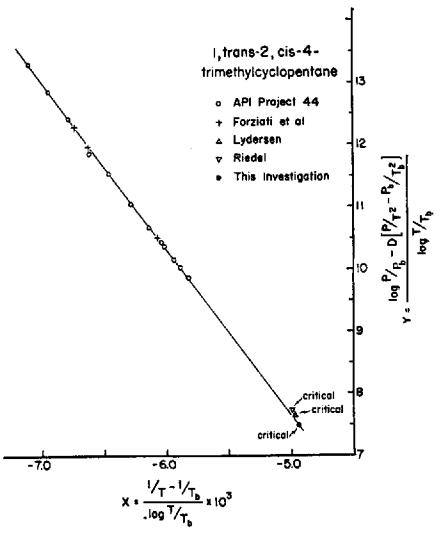

Fig. 3. Relationship of Y vs. X for 1, trans-2, cis-4-trimethylcyclopentane.

Since no critical constants are available in the literature to appraise the results produced by these methods, an indirect approach has been instituted in order to discriminate among the methods utilized to produce these critical constants. This approach considers a detailed analysis of existing vapor-pressure data found in the literature as proposed by Sondak and Thodos (*9*), in which the calculated critical values are considered in order to see whether they actually represent the vapor-pressure behavior of each respective hydrocarbon. This analysis considers the resolution of the complicated vapor-pressure function represented by the expression (*9*)

$$\log P = A + \frac{B}{T} + C \log T + D \frac{P}{T^2} \quad (19)$$

where (P, T) represents a vapor-pressure point, and A, B, C, and D are specific vapor-pressure constants into a straight line through the use of the vapor-pressure–temperature modulus,

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

and temperature modulus,

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

The slope of the straight line is equal to the vapor-pressure constant B; whereas its intercept becomes equal to constant C. In these moduli (P, T) represents any vapor-pressure point; whereas (P_b, T_b) is any arbitrarily selected reference vapor-pressure point. Constant D is related to the pressure van der Waals' constant, a, through the relationship $D = a/2.303\ R^2$.

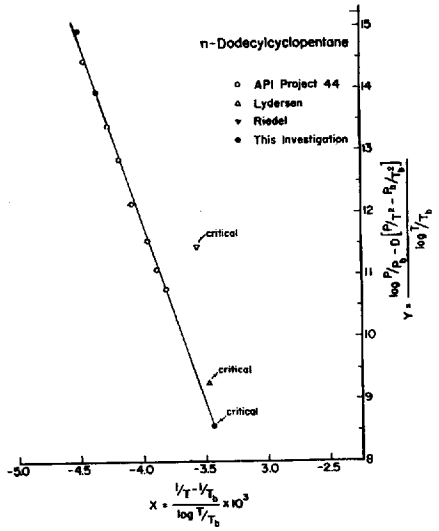

Fig. 4. Relationship of Y vs. X for n-dodecylcyclopentane.

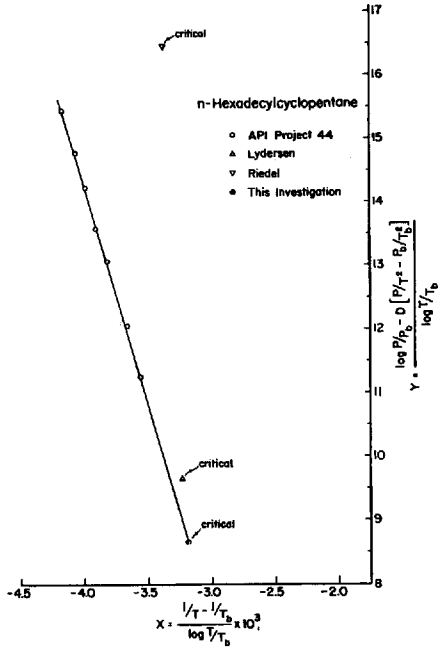

Fig. 5. Relationship of Y vs. X for n-hexadecylcyclopentane.

For the saturated aliphatic hydrocarbons, Sondak and Thodos (*9*) have shown that a plot of the moduli Y vs. X on rectilinear coordinates produces straight-line relationships for vapor-pressure data included between the triple and critical points. Through the use of this scheme, the accuracy of vapor-pressure data can be critically reviewed once the pressure van der Waals' constant, a, of the substance becomes available. In this analysis, vapor-pressure points which give rise to moduli Y and X, which scatter, are considered highly questionable. Conversely, it follows that vapor-pressure values producing moduli Y and X, which give rise to a continuous relationship, properly represent the vapor-pressure function of the substance and are considered reliable.

In this treatment the critical constant represents the end of the vapor-pressure function and as such should represent the terminal point of the resulting straight line, Y vs. X, when the same reference point (P_b, T_b) is used to produce these moduli Y and X.

An appraisal of the validity of the critical constants calculated by the present method and also by that of Riedel (*5*, *6*) and Lydersen (*3*) has been carried out for five arbitrarily selected naphthenes, for which this analysis has been used to verify that these calculated critical values properly represent the vapor-pressure functions of these naphthenes. In this treatment the vapor-pressure data available in the literature for cyclopropane (*8*), 1, cis-2-dimethylcyclopentane (*7*), 1, trans-2, cis-4-trimethylcyclopentane (*2*, *7*), n-dodecylcyclopentane (*7*), and n-hexadecylcyclopentane (*7*) have been used to produce the moduli Y and X, which when plotted produce the straight-line relationships presented in Figures 1 to 5, inclusive. The naphthenes cyclopropane to n-hexadecylcyclopentane have been selected in order to cover the extent of molecular dimension; while 1, trans-2, cis-4-trimethylcyclopentane was chosen to represent the more complex structures involving more than two methyl group substitutions in the ring.

The critical values resulting from the methods of Lydersen, Riedel, and this study have been found to represent satisfactorily the vapor-pressure functions for cyclopropane; 1, cis-2-dimethylcyclopentane; and 1, trans-2, cis-4-trimethylcyclopentane as indicated in Figures 1, 2, and 3. However, for n-dodecylcyclopentane and n-hexadecylcyclopentane only the critical constants resulting from the present investigation were found to be an extension of the straight line representing the vapor-pressure functions of these naphthenes. This is indicated in Figures 4 and 5. In view of these findings, the present method offers some distinct advantages, particularly for the calculation of critical constants involving alkyl naphthenes having side chains of considerable length.

Critical constants have been calculated by the present method and the methods of Lydersen (*3*) and Riedel (*5*, *6*) for all the naphthenes for which vapor-pressure data are available in the literature (*2*, *7*) and are presented in Table 4. Comparisons of these critical constants will be made in a separate comprehensive study of vapor pressures for the naphthenic hydrocarbons presented in Table 4 along the same paths outlined for the five naphthenes treated in detail in this study.

NOTATION

a = pressure van der Waals' constant, (cc./g.-mole)^2 atm.
A, B, C, D = constants for vapor-pressure equation
b = volume van der Waals' constant, cc./g.-mole
n_c = number of carbon atoms in saturated aliphatic hydrocarbon or naphthenic nucleus
n_{cn}' = total number of carbon atoms in normal alkyl side chains
n_{ci}' = total number of carbon atoms in branched alkyl side chains
P = vapor pressure
p_c = critical pressure, atm.
R = gas constant, 82.055 (atm.)(cc.)/(°K.)(g.-mole)
T = temperature, °K.
T_c = critical temperature, °K.
v_c = critical volume, cc./g.-mole
X = temperature modulus, $(1/T - 1/T_b)/\log T/T_b$
Y = vapor-pressure–temperature modulus,

$$\frac{\log P/P_b - D(P/T^2 - P_b/T_b^2)}{\log T/T_b}$$

Greek Letters

α = total number of methyl groups attached to the ring
α_n = total number of normal alkyl chains attached to the ring
α_i = total number of branched alkyl chains attached to the ring
β = volume factor
β_c = volume factor for unsubstituted cycloparaffins
β_{cs} = volume factor for alkyl naphthenes
Δ = difference

Subscripts

c = cyclic
n = normal

LITERATURE CITED

1. Anderson, J. W., G. H. Beyer, and K. M. Watson, *Natl. Petroleum News, Tech Sec.*, **36**, R476 (July 5, 1944).
2. Forziati, A. F., W. R. Norris, and F. D. Rossini, *J. Research Natl. Bur. Standards*, **43**, 555 (1949).
3. Hougen, O. A., K. M. Watson, and R. A. Ragatz, "Chemical Process Principles," pp. 87–95, John Wiley and Sons, New York (1954).
4. Kobe, K. A., and R. E. Lynn, Jr., *Chem. Rev.*, **52**, 117 (1953).
5. Riedel, L., *Z. Elektrochem.*, **53**, 222 (1949).
6. ———, *Chem. Ing. Tech.*, **24**, 353 (1952).
7. Rossini, F. D., K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, *Am. Petroleum Inst., Project* 44, Carnegie Press, Pittsburgh, (1953).
8. Ruehwein, R. A., and T. M. Powell, *J. Am. Chem. Soc.*, **68**, 1063 (1946).
9. Sondak, N. E., and George Thodos, *A.I.Ch.E. Journal*, **2**, 347 (1956).
10. Thodos, George, *op. cit.*, **1**, 165 (1955).
11. *Ibid.*, p. 168 (1955).