Vapor Pressures of the Naphthenic Hydrocarbons

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A COMPREHENSIVE study of vapor pressures for the aliphatic (*22*, *23*) and aromatic (*5*) hydrocarbons has substantiated the value of the Frost-Kalkwarf equation (*8*) which can be expressed as follows:

$$\log P = A + \frac{B}{T} + C \log T + D\frac{P}{T^2} \tag{1}$$

A, B, C, and D of Equation 1 are constants required to define this exacting vapor pressure relationship for the region included between the triple and critical points. In this study, the previous work has been expanded to include the naphthenic hydrocarbons, so that the constants for Equation 1 would be established for all the basic types of hydrocarbons commonly encountered in petroleum technology.

Frost and Kalkwarf (*8*) have shown that the constant D is related to the pressure van der Waals' constant ,a, by the relationship:

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

where R is the gas constant. Applying a group contribution approach (*24*), the pressure and volume van der Waals' constants a and b for the naphthenic hydrocarbons have been calculated from their molecular structure. The value of a permits the calculation of D, and both constants a and b can be used to determine the critical temperature and pressure of the substance from the following relationships:

$$T_c = \frac{8a}{27\, Rb} \tag{3}$$

$$P_c = \frac{a}{27\, b^2} \tag{4}$$

Critical temperatures and pressures for the naphthenic hydrocarbons (*24*) are calculated from Equations 3 and 4. The reported values of the pressure van der Waals' constant a (*24*) are used to establish the constant D from Equation 2 in the following manner. When the pressure is expressed in millimeters of mercury and temperature in degrees Kelvin, the gas constant is $R = 62{,}630$ (cc.) (mm.)/(gram mole) (° K.). For cyclohexane, the reported value of $a = 21.729 \times 10^6$[(cc.)/(gram mole)]^2 atm. and from Equation 2

$$D = \frac{a}{2.303\, R^2} = \frac{(21.729 \times 10^6)(760)}{2.303\, (62{,}630)^2} = 1.84394\ (^\circ\text{K.})^2/\text{mm.}$$

Calculated values of D for the naphthenes are presented in Tables I and VI.

EVALUATION OF CONSTANTS *B* AND C

The constants B and C of Equation 1 were established from the experimental data following the method proposed by Sondak and Thodos (*23*) for the aliphatic hydrocarbons. This procedure utilizes all the available experimental vapor pressure data by associating them with a reliable vapor pressure point, arbitrarily selected. With constant D independently calculated from the molecular structure of the naphthene, constant A can be eliminated by the simultaneous solution of the two resulting linear equations to produce the relationship,

$$\frac{\log P/P_b - D(P/T^2 - P_b/T_b^2)}{\log T/T_b} = B\, \frac{(1/T - 1/T_b)}{\log T/T_b} + C \tag{5}$$

where B is the slope and C the intercept of the resulting straight line. Point (P, T) represents an experimental vapor pressure, while (P_b, T_b) is the selected reference point. This reference point does not have to be the same for the data of different investigators to produce the same values of B and C.

A typical representation of Equation 5 is given for cyclohexane in Figure 1 using the following moduli:

$$\text{Temperature modulus: } X = \frac{1/T - 1/T_b}{\log T/T_b}$$

$$\text{Vapor pressure modulus: } Y = \frac{\log P/P_b - D(P/T^2 - P_b/T_b^2)}{\log T/T_b}$$

These moduli represent the dependent and independent variables, respectively. The resulting relationship of Figure

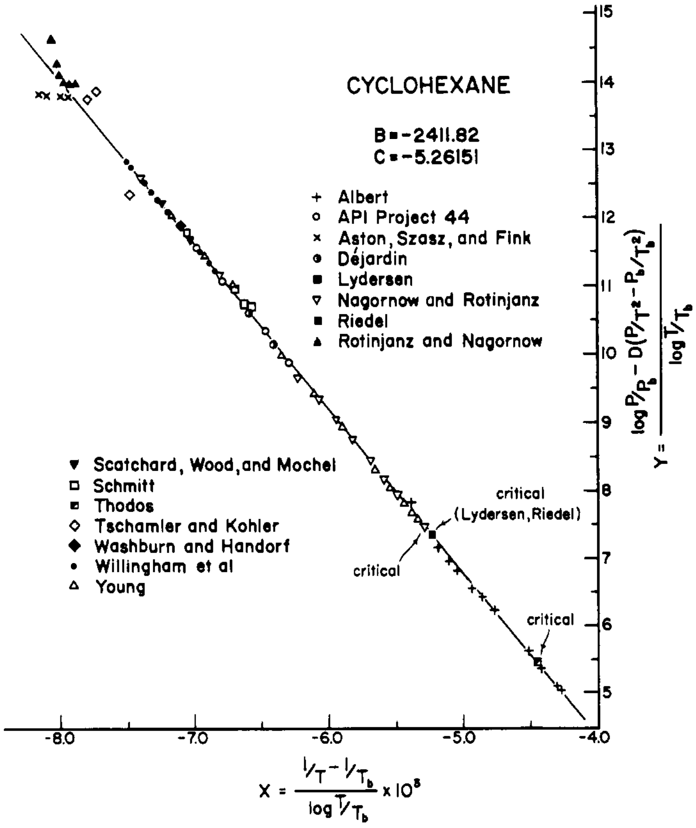

Figure 1. Relationship between vapor pressure and temperature moduli for cyclohexane

1 is linear, and the position of a point on this line depends on the reference point used. This is shown by the critical points resulting from the different reference points for the data of Lydersen (*10*), Nagornov and Rotinjanz (*12*), Riedel (*15, 16*), and Thodos (*24*).

The slope and intercept are calculated from two experimental points as $B = -2411.82$ and $C = -5.26151$. Following a similar procedure, values of B and C have been established for other naphthenic hydrocarbons and are presented in Table I. With constants B, C, and D defined, constant A is evaluated from a single experimental vapor pressure point. Values of the constant A for the naphthenes calculated from their normal boiling points are also presented in Table I.

Table I. Vapor Pressure Constants for the Frost-Kalkwarf Equation

(Determined from experimental values for naphthenic hydrocarbons)

	T_b, ° K.	A^a	B	C	D	References
Cyclopropane	240.30	19.55377	−1514.96	−4.35900	0.69722	(*10,15, 16, 19, 24*)
Cyclobutane	284.60	19.87545	−1813.84	−4.33901	1.03360	(*9, 10, 14–16, 24*)
Cyclopentanes						
Cyclopentane	322.427	21.62180	−2131.85	−4.83947	1.41701	(*2, 3, 4, 10, 11, 15–17, 24, 27*)
Methylcyclopentane	344.977	23.33397	−2361.19	−5.37845	1.83231	(*10, 15–17, 21, 24, 27*)
Ethylcyclopentane	376.631	24.71132	−2650.82	−5.74737	2.33282	(*7, 10, 15–17, 24*)
n-Propylcyclopentane	404.114	26.79758	−2975.29	−6.35629	2.88145	(*7, 10, 15–17, 24, 27*)
iso-Propylcyclopentane	399.584	24.84184	−2806.68	−5.74654	2.77851	(*7, 10, 15–17, 24, 27*)
n-Butylcyclopentane	429.725	29.51175	−3347.04	−7.16107	3.47242	(*10, 15–17, 24*)
n-Pentylcyclopentane	453.165	30.98588	−3624.28	−7.57552	4.10370	(*10, 15, 17, 18, 25*)
n-Hexylcyclopentane	476.165	32.90565	−3948.75	−8.12172	4.77359	(*10, 15, 17, 18, 25*)
n-Heptylcyclopentane	497.165	35.05692	−4281.69	−8.74494	5.48065	(*10, 15, 17, 18, 25*)
n-Octylcyclopentane	516.165	37.52712	−4615.88	−9.48157	6.22369	(*10, 15, 17, 18, 25*)
n-Nonylcyclopentane	535.165	38.63890	−4880.02	−9.77021	7.00161	(*10, 15, 17, 18, 25*)
n-Decylcyclopentane	552.365	41.65472	−5276.77	−10.66297	7.81279	(*10, 15, 17, 18, 25*)
n-Undecylcyclopentane	569.165	41.60325	−5417.44	−10.60690	8.65665	(*10, 15, 17, 18, 25*)
n-Dodecylcyclopentane	585.165	43.14884	−5709.37	−11.03338	9.53326	(*10, 15, 17, 18, 25*)
n-Tridecylcyclopentane	600.165	46.26459	−6100.50	−11.96468	10.44042	(*10, 15, 17, 18, 25*)
n-Tetradecylcyclopentane	614.165	49.33351	−6501.76	−12.87146	11.37898	(*10, 15, 17, 18, 25*)
n-Pentadecylcyclopentane	628.165	49.07559	−6606.64	−12.75924	12.34640	(*10, 15, 17, 18, 25*)
n-Hexadecylcyclopentane	641.165	49.17178	−6757.01	−12.74578	13.34436	(*10, 15, 17, 18, 25*)
1,1-Dimethylcyclopentane	361.011	22.93909	−2438.93	−5.20606	2.08444	(*7, 10, 15–17, 24*)
1,*cis*-2-Dimethylcyclopentane	372.697	24.08937	−2585.19	−5.55524	2.26426	(*7, 10, 15–17, 24*)
1,*trans*-2-Dimethylcyclopentane	365.034	27.25262	−2558.35	−5.74920	2.18500	(*7, 10, 15–17, 24*)
1,*cis*-3-Dimethylcyclopentane	364.890	24.05678	−2526.34	−5.56752	2.18500	(*7, 10, 15–17, 24*)
1,*trans*-3-Dimethylcyclopentane	363.938	24.05807	−2518.46	−5.57175	2.12254	(*7, 10, 15–17, 24*)
1-Methyl-1-ethylcyclopentane	394.687	24.94516	−2778.44	−5.79200	2.60794	(*7, 10, 15–17, 24*)
1-Methyl-*cis*-2-ethylcyclopentane	401.215	25.30853	−2857.58	−5.88413	2.80312	(*7, 10, 15–17, 24*)
1-Methyl-*trans*-2-ethylcyclopentane	394.365	25.68940	−2824.59	−6.03240	2.71707	(*10, 15–17, 24*)
1-Methyl-*cis*-3-ethylcyclopentane	394.565	25.43759	−2810.22	−5.95031	2.71707	(*10, 15–17, 24*)
1-Methyl-*trans*-3-ethylcyclopentane	393.965	24.96407	−2781.46	−5.79322	2.64927	(*10, 15–17, 24*)
1,1,2-Trimethylcyclopentane	386.894	23.51275	−2638.38	−5.34298	2.53658	(*7, 10, 15–17, 24*)
1,1,3-Trimethylcyclopentane	378.058	24.56944	−2626.82	−5.72382	2.45392	(*7, 10, 15–17, 24*)
1,*cis*-2,*cis*-3-Trimethylcyclopentane	396.165	23.81553	−2722.34	−5.41834	2.72989	(*9, 15–17, 24*)
1,*cis*-2,*trans*-3-Trimethylcyclopentane	390.665	25.08794	−2752.89	−5.85447	2.64469	(*9, 15–17, 24*)
1,*trans*-2,*cis*-3-Trimethylcyclopentane	383.365	24.57009	−2672.54	−5.70181	2.56050	(*9, 15–17, 24*)
1,*cis*-2,*cis*-4-Trimethylcyclopentane	391.165	24.00150	−2695.95	−5.49373	2.64469	(*9, 15–17, 24*)
1,*cis*-2,*trans*-4-Trimethylcyclopentane	389.896	23.80538	−2676.83	−5.43117	2.55966	(*7, 10, 15–17, 24*)
1,*trans*-2,*cis*-4-Trimethylcyclopentane	382.455	24.44177	−2663.69	−5.65683	2.49414	(*7, 10, 15–17, 24*)
Cyclohexanes						
Cyclohexane	353.903	23.09550	−2411.82	−5.26151	1.84394	(*1, 3, 6, 10, 12, 15–18, 20, 21, 24–28*)
Methylcyclohexane	374.099	23.55682	−2552.72	−5.28861	2.29888	(*10, 13, 15–17, 24, 27*)
Ethylcyclohexane	404.948	25.07528	−2863.15	−5.80546	2.84063	(*10, 15–17, 24, 27*)
n-Propylcyclohexane	429.659	26.96993	−3162.45	−6.35950	3.42855	(*7, 10, 15, 16, 24, 27*)
iso-Propylcyclohexane	427.728	26.17234	−3090.61	−6.11121	3.31857	(*7, 10, 15, 16, 24*)
n-Butylcyclohexane	454.112	28.64392	−3462.39	−6.83194	4.05694	(*7, 10, 15, 16, 24*)
iso-Butylcyclohexane	444.486	28.51905	−3359.33	−6.83407	3.94085	(*7, 10, 15, 16, 24*)
sec-Butylcyclohexane	452.500	27.71838	−3378.91	−6.54643	3.89070	(*7, 10, 15, 16, 24*)
tert-Butylcyclohexane	444.756	27.11408	−3257.14	−6.39101	3.73124	(*7, 10, 15, 16, 24*)
1,1-Dimethylcyclohexane	392.708	23.69567	−2672.32	−5.40567	2.57264	(*7, 10, 15–17, 24*)
1,*cis*-2-Dimethylcyclohexane	402.893	25.13860	−2837.50	−5.84523	2.76689	(*10, 15–17, 24, 27*)
1,*trans*-2-Dimethylcyclohexane	396.584	24.21392	−2730.74	−5.56525	2.68118	(*10, 15–17, 24, 27*)
1-*cis*-3-Dimenthylcyclohexane	393.253	24.42981	−2732.74	−5.63197	2.68118	(*10, 15–17, 24, 27*)
1,*trans*--3-Dimethylcyclohexane	397.615	24.37487	−2766.46	−5.59693	2.61380	(*10, 15–17, 24, 27*)
1,*cis*--4-Dimethylcyclohexane	397.486	24.78101	−2782.61	−5.73698	2.61380	(*10, 15–17, 24, 27*)
1,*trans*-4-Dimethylcyclohexane	392.516	24.11494	−2700.15	−5.53913	2.57264	(*10, 15–17, 24, 27*)
1,1,3-Trimethylcyclohexane	409.791	23.10375	−2766.55	−5.16171	2.97064	(*7, 10, 15, 16, 24*)

[a] Dimensions of constants A, B, C, and D are consistent and produce(at abs. temp., ° K.) vapor pressures in mm. of Hg.

RELATIONSHIP OF CONSTANT *B* AND MOLECULAR STRUCTURE

If no vapor pressure data are available for a naphthene other than the critical point and normal boiling point of the substance, an alternate procedure is required to calculate the constants of Equation 1. For the saturated aliphatic hydrocarbons, Sondak and Thodos (*23*) have found that the constant C could not be correlated with molecular structure or physical properties. But they have shown that for these hydrocarbons the constant B can be directly determined from the molecular structure using group contribution values, $\Delta(-B)$. Following a similar approach, Smith and Thodos (*22*) indicate that more accurate B values are obtained for both unsaturated and saturated aliphatic hydrocarbons if the group contributions, $\Delta(-B)^{0.88}$, are determined from molecular structure.

As a result of the previous work, group contributions, $\Delta(-B)^{0.88}$, were determined from the molecular structure of the alkylnaphthenic hydrocarbons investigated. The values of $(-B)^{0.88}$ were plotted against the number of carbon atoms present in the normal alkyl side chains for both monoalkyl cyclopentanes and cyclohexanes as shown in Figure 2. The resulting correlations are linear beyond the first methyl substitutions and produce a group contribution value of $\Delta(-B)^{0.88} = 107.16$ for each successive replacement of a hydrogen atom in a normal side chain by a methyl group. Similar group contribution values were established for the substitution of a methyl group for a hydrogen atom in isoalkyl side chains of naphthenes. These values of $\Delta(-B)^{0.88}$ depend of the type of structure of the carbon atom on which the substitution is made and on the nature of the adjacent carbon atoms. The different types of structure of these carbon atoms have been designated as follows:

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

These dependences are consistent with the results of the previous studies on the aliphatic (*22, 23*) and aromatic (*5*) hydrocarbons. The combined results of the present and previous studies have been utilized to produce the group contribution values $\Delta(-B)^{0.88}$ for naphthenes (Table II).

In Table II, the arrows point away from the type of carbon atom upon which the substitution is made and toward the types of adjacent carbon atoms. The method of calculating group contribution values involves the systematic substitution of methyl groups for hydrogen atoms starting with the basic naphthenic ring, to produce the final alkylnaphthene being considered. A definite order of substitution of these groups is required in the calculations as follows:

The longest normal side chain of the naphthene is first constructed.

Only methyl group substitutions are made on the carbon atoms of a normal side chain, substituting first from left to right for the upper hydrogen atoms and then from right to left for the lower hydrogen atoms of the side chain.

This process is continued by the addition of methyl groups to the previously substituted groups, continuing in the clockwise manner indicated above.

The results of this study indicate that the first methyl substitution depends on the size of the naphthene ring. Thus, the group contribution values obtained for this type of substitution were 79.93 for cyclopentane and 48.52 for cyclohexane, giving an average value of 64.22 which could be used for the initial methyl substitution. However, more precise values of the constant B for methylnaphthenes can be obtained by an alternate route. The ratio of the constant B and the normal boiling point, $-B/T_n$, obtained from the available data for methyl-, ethyl-, and n-propylcyclopentanes and cyclohexanes was found to have a different constant value for each of these alkylnaphthenes, as shown in Table III.

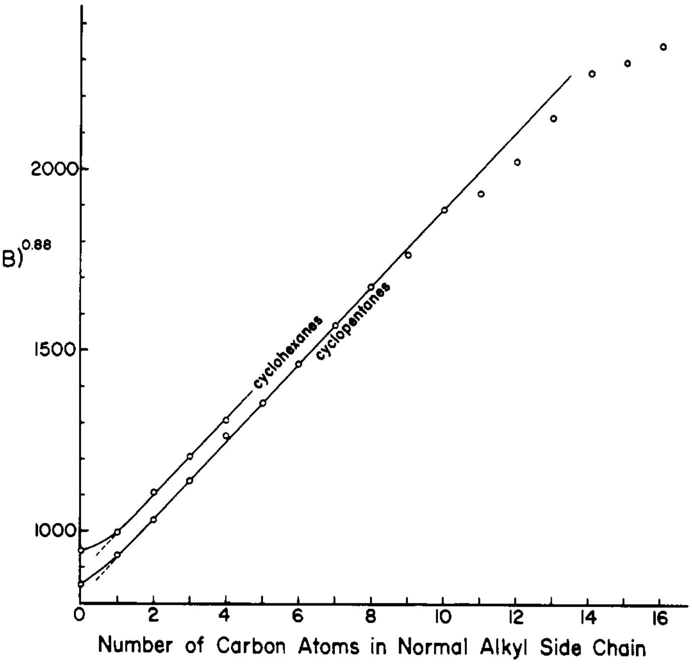

Figure 2. Relationships of $(-B)^{0.88}$ and number of carbon atoms present in the side chains of monoalkylcyclopentanes and cyclohexanes

For the methyl naphthenes, the following relationship between normal boiling point and ring size has been developed from the normal boiling points of methylcyclobutane, methylcyclopentane, and methylcyclohexane:

$$T_n = (495{,}100n_c - 263{,}700)^{2/5} \qquad (6)$$

where n_c represents the number of carbon atoms in the naphthenic ring. Therefore, since $-B/T_n = 6.8340$, constant B for methylnaphthenes can be related to n_c as follows:

$$(-B)^{0.88} = 5.426(495{,}100n_c - 263{,}700)^{0.352} \qquad (7)$$

Equations 6 and 7 were used to calculate the values of the constants B and normal boiling points presented in Table IV for the lighter methylnaphthenes. Thus B values for alkylnaphthenes can be calculated using the values $(-B)^{0.88}$ obtained from Equation 7 for the corresponding methylnaphthenes and adding the group contribution values $\Delta(-B)^{0.88}$ resulting from each subsequent methyl substitution. If normal boiling points are available for the corresponding ethyl- or n-propylnaphthene, the B value for either substance, obtained from its value of $-B/T_n$, could be used as the starting point in the calculations.

For the calculation of normal boiling points and B values for nonsubstituted naphthenes, the following expressions have been developed from data for cyclopropane, cyclobutane, cyclopentane, and cyclohexane:

$$T_n = (486{,}993n_c - 565{,}498)^{2/5} \qquad (8)$$

$$(-B)^{0.88} = (13{,}117n_c + 1538)^{0.607} \qquad (9)$$

Values calculated with Equations 8 and 9 are presented in Table IV for the light nonsubstituted naphthenes through cycloheptane.

Using Equations 7 and 9 and the group contribution values of Table II, the constant B of Equation 1 can be calculated for any naphthenic hydrocarbon from a knowledge of its molecular structure. The critical point and normal boiling point of the naphthene are then utilized to establish its A and C values. This method of calculating

Table II. Group Contribution Values, $\Delta(-B)^{0.88}$, for Substitution of Hydrogen Atoms by Methyl Groups in Naphthenic Rings and Their Alkyl Side Chains

Substitution in Naphthenic Ring

	First	Second	Third
2←2→2	64.22[a]	62.50	40.39
3←2→2		75.83	47.75
4←2→2			68.51
$2\leftarrow\underset{\underset{1}{\downarrow}}{3}\rightarrow 2$		33.95	

Substitutions in Alkyl Side Chains

2←1		3←1		4←1	
(107.16)		(99.88)		(94.79)	
1←2→2	(64.71)			2←2→2	(75.43)
1←2→3	(60.57)			2←2→3	(67.08)
$2\leftarrow\underset{\underset{1}{\downarrow}}{3}\rightarrow 1$	(52.17)			$4\leftarrow\underset{\underset{1}{\downarrow}}{3}\rightarrow 1$	(43.47)
$3\leftarrow\underset{\underset{1}{\downarrow}}{3}\rightarrow 1$	(49.33)			$2\leftarrow\underset{\underset{2}{\downarrow}}{3}\rightarrow 1$	(37.44)
$3\leftarrow\underset{\underset{1}{\downarrow}}{3}\rightarrow 2$	(35.79)			$3\leftarrow\underset{\underset{1}{\downarrow}}{3}\rightarrow 3$	(31.13)

[a] The group contribution value 64.22 represents average of values 79.93 and 48.52 resulting from methylcyclopentane and methylcyclohexane. A precise value of B for methylnaphthenes can be obtained directly from $-B/T_n = 6.8340$, where T_n is normal b.p., ° K. Group contributions in this table should be used for subsequent substitutions.

Table III. Values of Ratio, $-B/T_n$, for Methyl-, Ethyl-, and *n*-Propylnaphthenes

	T_n, ° K.	$-B$	$-B/T_n$	$(-B/T_n)_{av.}$
Methylcyclopentane	344.977	2361.19	6.8445	6.8340
Methylcyclohexane	374.099	2552.72	6.8236	
Ethylcyclopentane	376.631	2650.82	7.0382	7.0543
Ethylcyclohexane	404.948	2863.15	7.0704	
n-Propylcyclopentane	404.114	2975.29	7.3625	7.3614
n-Propylcyclohexane	429.659	3162.45	7.3604	

constants of Equation 1 is illustrated in this example: Calculate the vapor pressure constants of the Frost-Kalkwarf equation for 1-methyl-*cis*-2-ethylcyclopentane. The normal boiling point of this substance is presented in API Project 44 as 401.215° K. (*17*).

Calculation of Constant D. Using group contribution values, the van Waals' constants for this substance have been calculated (*24*) to be: $a = 33.032 \times 10^6$ (cc./gram mole)^2 atm.; $b = 199.08$ cc./gram mole. Using this value of a, D is calculated as follows:

$$D = \frac{a}{2.303\ R^2} = \frac{(33.032 \times 10^6)(760)}{2.303\ (62{,}630)^2} = 2.80312\ (°\ \mathrm{K.})^2/\mathrm{mm.}$$

Calculation of Constant B. The base group for 1-methyl-*cis*-2-ethylcyclopentane is methylcyclopentane, for which $(-B)^{0.88} = 928.67$ from Table IV. The introduction of a second methyl group in the ring involves a 3 ← 2 → 2 substitution, for which $\Delta(-B)^{0.88} = 75.83$ from Table II. The further addition of a methyl group to the second substituted methyl group to produce 1-methyl-*cis*-2-ethylcyclopentane involves a 3 ← 1 substitution for which $\Delta(-B)^{0.88} = 99.88$, from Table II. Therefore, for the complete molecular structure, $(-B)^{0.88}$ is

Methylcyclopentane (base group)	928.67
Second ring substitution (3 ← 2 → 2)	75.83
Side chain substitution (3 ← 1)	99.88
$(-B)^{0.88} =$	1104.38

Therefore constant $B = -2871.3$

Calculation of Constants A and C. From the values of the van der Waals' constants for this substance, the critical temperature and pressure can be calculated as follows:

$$T_c = \frac{8a}{27\ Rb} = \frac{8\ (33.032 \times 10^6)}{27\ (82.055)(199.08)} = 599.1°\ \mathrm{K.}$$

$$P_c = \frac{a}{27\ b^2} = \frac{33.032 \times 10^6}{27\ (199.08)^2} = 30.87\ \mathrm{atm.}\ (23{,}461\ \mathrm{mm.})$$

Substituting these values and the normal boiling point into Equation 1, the following two equations with unknowns A and C result:

$$\log 760 = A - \frac{2871.3}{401.215} + C \log 401.215 + 2.80312\ \frac{760}{(401.215)^2}$$

$$\log 23{,}461 = A - \frac{2871.3}{599.1} + C \log 599.1 + 2.80312\ \frac{23{,}461}{(599.1)^2}$$

These equations can be solved simultaneously to yield

$A = 25.63794$ and $C = -5.99753$

Therefore, the Frost-Kalkwarf vapor pressure equation for 1-methyl-*cis*-2-ethylcyclopentane is:

$$\log P = 25.63794 - \frac{2871.3}{T} - 5.99753 \log T + 2.80312\ \frac{P}{T^2} \qquad (10)$$

For this naphthenic hydrocarbon, the available reported vapor pressures (*17*) range from 10 to 1500 mm. A comparison between calculated and reported values is presented for six temperatures:

	Vapor Pressure, Mm.			Vapor Pressure, Mm.	
T, ° K.	Reported	Calcd.	T, ° K.	Reported	Calcd.
291.355	10	10.07	394.270	628.19	628.59
322.011	48.02	48.02	411.745	1000	999.2
369.771	300	300.46	428.565	1500	1497.7

These values produce an average deviation of 0.30% between reported and calculated values.

DISCUSSION OF RESULTS

To test the validity of the method developed in this study for the calculation of the Frost-Kalkwarf constants for naphthenes from the molecular structure and the normal boiling point of the substance, calculated vapor pressures have been compared with values reported in the literature for 34 naphthenes. The normal monoalkyl cyclopentanes up to and including *n*-hexadecylcyclopentane were selected for the comparisons in order to cover a full range of

Table IV. Calculated and Reported Normal Boiling Points and Constants B

	T_n, ° K.			
	Calcd.	Reported	$-B$	$(-B)^{0.88}$
Lighter Methylnaphthenes				
Methylcyclopropane	272.13	...	1859.44	753.55
Methylcyclobutane	311.80	311.8	2130.84	849.42
Methylcyclopentane	345.06	344.98	2358.14	928.67
Methylcyclohexane	374.10	374.10	2556.60	997.10
Methylcycloheptane	400.10	407.2	2734.28	1057.8
Lighter Unsubstituted Naphthenes				
Cyclopropane	240.3	240.3	1515.1	
Cyclobutane	285.9	284.6	1835.6	
Cyclopentane	322.6	322.4	2132.6	
Cyclohexane	353.9	353.9	2411.9	
Cycloheptane	381.5	391.2	2677.4	

Table V. Comparison of Calculated with Experimental Vapor Pressures for Representative Naphthenes

T, K.	Vapor Pressure, Mm. Experimental	Vapor Pressure, Mm. Calculated	% Deviation
Cyclopentane			
234.085	11.78	11.74	0.34
282.485	164.63	164.57	0.04
288.872	217.19	217.27	0.00
321.296	732.12	732.12	0.00
331.035	1,000.0	999.92	0.01
344.765	1,500.0	1,499.6	0.03
373.155	3,148.6	3,118.6	0.95
503.215	30,178	30,122	0.19
			Av. 0.20
n-Decylcyclopentane			
429.865	20.00	20.02	0.10
467.565	80.00	80.00	0.00
533.665	500.0	501.06	0.21
548.565	700.0	700.42	0.06
575.165	1,200	1,205.8	0.48
			Av. 0.17
Cyclohexane			
293.165	76.9	77.82	1.20
325.843	300.0	300.18	0.06
355.619	800.0	799.89	0.01
378.365	1,500.0	1,500.7	0.05
433.165	5,028.0	5,045.1	0.34
493.055	13,600	13,695	0.70
513.545	18,230	18,303	0.40
551.225	29,698	29,776	0.26
			Av. 0.38
1,1,3-Trimethylcyclohexane			
327.834	47.99	47.86	0.27
346.646	103.82	103.38	0.42
361.080	176.07	175.28	0.45
386.843	402.78	401.62	0.29
410.801	780.06	780.14	0.01
			Av. 0.29

molecular sizes. For the more complex molecular configurations, all of the available cyclohexanes were similarly analyzed.

For those hydrocarbons for which reported vapor pressures were available up to the critical point, at least eight values covering the full range were considered. If no vapor pressures were reported for the high pressure region of a naphthene, at least five points were included in the comparisons. Table V presents a comparison between experimental and calculated values for cyclopentane and cyclohexane up to the critical point, and for n-decylcyclopentane and 1,1,3-trimethylcyclohexane up to 1200 mm. and 780 mm. of mercury, respectively.

In Table VI the calculated constants A, B, C, and D are presented for the 34 naphthenes used in these comparisons, along with the resulting average deviation of each substance. The average deviation between calculated and reported vapor pressures was 0.78% for the 34 naphthenes.

In order to calculate vapor pressures of maximum accuracy from Equation 1 for a full range up to the critical point, the constants determined by the slope-intercept method should be used for those substances for which reliable vapor pressure data are available. Constants determined in this manner are presented in Table I for 55 naphthenic hydrocarbons. For naphthenes for which no vapor pressures are available, constants A, B, C, and D, calculated from only the molecular structure and the normal boiling point of the substance, give excellent results.

NOMENCLATURE

a = pressure van der Waals' constant, $(\text{cm}^3/\text{gram mole})^2$ atm.
A = vapor pressure constant, dimensionless

Table VI. Vapor Pressure Constants A, B, C, and D

(Calculated from molecular structure and normal boiling points of naphthenes and average deviations of resulting vapor pressures)

	A^a	B	C	D	Av. Deviation[b]
Normal Monoalkylcyclopentanes					
Cyclopentane	21.63300	−2132.5	−4.84313	1.41701	0.20
Methylcyclopentane	23.30490	−2358.1	−5.35911	1.83231	0.03
Ethylcyclopentane	24.56495	−2641.4	−5.70026	2.33282	0.23
n-Propylcyclopentane	26.51753	−2956.3	−6.26688	2.88145	0.22
n-Butylcyclopentane	28.63424	−3283.9	−6.88362	3.47242	0.10
n-Pentylcyclopentane	31.89612	−3691.4	−7.86244	4.10370	0.94
n--Hexylcyclopentane	32.72055	−3934.6	−8.06369	4.77359	0.44
n-Heptylcyclopentane	34.84353	−4264.9	−8.67833	5.48065	0.81
n-Octylcyclopentane	37.01223	−4586.5	−9.31275	6.22369	0.54
n--Nonylcyclopentane	39.14383	−4922.1	−9.92645	7.00161	0.50
n-Decylcyclopentane	41.62367	−5274.1	−10.65341	7.81279	0.17
n-Undecylcyclopentane	43.88342	−5616.0	−11.30786	8.65665	2.04
n-Dodecylcyclopentane	46.17530	−5960.3	−11.97208	9.53326	1.20
n-Tridecylcyclopentane	48.54342	−6307.1	−12.66101	10.44042	1.11
n-Tetradecylcyclopentane	51.00848	−6656.2	−13.38199	11.37898	2.31
n-Pentadecylcyclopentane	53.15275	−6989.2	−13.99872	12.34640	1.90
n-Hexadecylcyclopentane	55.82274	−7360.9	−14.77968	13.34436	0.79
Cyclohexanes					
Cyclohexane	23.14002	−2411.8	−5.27900	1.84394	0.38
Methylcyclohexane	23.61617	−2556.5	−5.40775	2.29888	0.46
Ethylcyclohexane	25.07871	−2863.4	−5.80654	2.84063	0.11
n-Propylcyclohexane	27.35196	−3189.6	−6.48059	3.42855	1.23
iso-Propylcyclohexane	25.49548	−3042.6	−5.89663	3.31857	0.72
n-Butylcyclohexane	29.25258	−3502.9	−7.02743	4.05694	0.38
iso-Butylcyclohexane	28.85502	−3383.8	−6.94016	3.94085	0.21
sec-Butylcyclohexane	28.03240	−3391.0	−6.65462	3.89070	0.61
tert-Butylcyclohexane	26.30541	−3197.8	−6.13602	3.73124	0.95
1,1-Dimethylcyclohexane	22.96516	−2655.6	−5.14048	2.57264	1.99
1,*cis*-2-Dimethylcyclohexane	23.89334	−2778.6	−5.42335	2.76689	0.72
1,*trans*-2-Dimethylcyclohexane	24.51495	−2778.6	−5.63466	2.68118	1.13
1,*cis*-3-Dimethylcyclohexane	24.42203	−2732.2	−5.62950	2.68118	0.30
1,*trans*-3-Dimethylcyclohexane	23.47981	−2732.2	−5.28575	2.61380	0.88
1,*cis*-4-Dimethylcyclohexane	23.50383	−2732.2	−5.29442	2.61380	1.40
1,*trans*-4-Dimethylcyclohexane	24.15620	−2732.2	−5.52356	2.57264	1.16
1,1,3-Trimethylcyclohexane	23.21592	−2774.2	−5.19750	2.97064	0.29
				Av.	0.78

Deviation % = $1/n \sum[(P_{\text{calcd.}} - P_{\text{lit.}})/P_{\text{lit.}}] \times 100$. [b] See footnote in Table I.

b = volume van der Waals' constant, cc./gram mole
B = vapor pressure constant, ° K.
C = vapor pressure constant, dimensionless
D = vapor pressure constant, (° K.)^2/mm.
n_c = number of carbon atoms in naphthenic ring
P = vapor pressure, mm.
P_b = reference vapor pressure, mm.
P_c = critical pressure, mm.
R = gas constant
T = absolute temperature, ° K.
T_b = reference temperature, ° K.
T_c = critical temperature, ° K.
T_n = normal boiling point, ° K.
X = temperature modulus, $\frac{1/T - 1/T_b}{\log T/T_b}$
Y = vapor pressure modulus, $\frac{\log P/P_b - D(R/T^2 - P_b/T_b^2)}{\log T/T_b}$

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Vapor Liquid Equilibria at Atmospheric Pressure

Binary Systems of Ethyl Acetate–Benzene, Ethyl Acetate–Toluene, and Ethyl Acetate–*p*-Xylene

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VAPOR-LIQUID equilibrium data at a pressure of 760 mm. of Hg were determined for the three binary systems, ethyl acetate-benzene, ethyl acetate-toluene, and ethyl acetate-*p*-xylene. The experimental results are given in Table I and the temperature *vs.* composition curves are shown in Figures 1, 2, and 3. The activity coefficients plotted in Figures 4, 5, and 6 show that the three systems are relatively symmetrical, and do not exhibit maxima or minima. Also, the molar volumes of the pure components have approximately the same values, so that any of the integrated forms of the Gibbs-Duhem equation is suitable to correlate the data. The van Laar equations have been chosen as most convenient to use. The activity coefficients were calculated from the equation

$$\gamma = y\pi / xp^0$$

and extrapolated to $x = 0$. The values of the van Laar constants so found were then adjusted for each binary mixture to give the curves most representative of all the experimental data. The constants used to calculate the curves in Figures 4, 5, and 6 are given in Table II, with values previously reported (*1*). These earlier values, calculated from total pressure data, are not satisfactory and give errors in the boiling points of binary mixtures of up to 5° and 0.8° C. for the systems ethyl acetate-benzene and ethyl acetate-toluene, respectively.

EXPERIMENTAL

Purity of Compounds. The chemicals used (C.P. grade) were redistilled. The distillates used in the equilibrium still had boiling ranges of not more then 0.025° C. The boiling points and refractive indices of the materials used are given in Table III.

Analysis of Samples. Binary compositions were found from refractive indices at 25° C. using a Zeiss-Abbé refractometer reading to four decimal places and giving an accuracy of analysis of ±0.08 mole %. In the calculation of activity coefficients according to the above equation, this variation in analysis can give a percentage change in γ_2 of ±2, ±0.75,