Physical Constants of Organic Liquids

A Nomograph for Estimating Physical Constants of Normal Paraffins and Isoparaffins

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THE STRUCTURAL variation in the physical properties of hydrocarbon liquids has long been investigated, and many empirical and semiempirical methods have been proposed for correlating the various properties of hydrocarbon liquids with the structural formula of compounds. The Egloff equation (*3*) for the normal boiling point of normal paraffins is a typical example. A comprehensive review of these methods may be found in the recent article by Greenshields and Rossini (*7*).

The values of the physical properties of normal paraffins can be evaluated with sufficient accuracy, but the interrelationships among the evaluation methods for different properties have not yet been fully investigated. The present study provides a systematic description of various properties of paraffin hydrocarbons on the basis of the statistical theory of liquids.

A set of equations is derived for three critical constants (temperature, pressure, and volume), the vapor pressure *vs.* temperature relationship, and the heat of vaporization of normal paraffin liquids on the basis of the recently proposed hole theory of chain molecular liquids (*8*), and the derived equations are arranged in a nomographic form by introducing some empirical correction.

The isomeric variation in the physical properties of isoparaffins was studied. By introducing the "effective carbon number," a new structural constant depending on both the number and relative position of side chains, the equations and nomograph are applied to isoparaffins.

The equations and nomograph can reproduce the available data for paraffin hydrocarbons. Except for an attempt by Wiener (*15*), no method has been proposed so far for the quantitative prediction of the vapor pressure *vs.* temperature relationship from the structural formula. Therefore, this method, which permits a rapid evaluation only from the structural formula, should prove convenient for chemical engineering purposes.

THEORETICAL

The liquid is assumed, in the theory, to be a mixture of molecules and holes. A molecule consists of repeating chain elements and occupies some consecutive cells, the number of which is denoted by x, and a hole is identical with an empty cell. The volume, τ, of a cell is assumed to be almost the same as that of a chain element, and the multiple occupation of a cell by more than two elements is completely excluded because of the repulsive force between them. If the Flory expression (*4*) is employed for the mixing entropy of this system, some simple calculations produce the following expressions for the pressure, P, and the chemical potential, μ.

$$P = -\frac{kT}{\tau}\left[\ln\left(1 - \frac{x\tau}{v}\right) + (x-1)\frac{\tau}{v}\right] - \frac{z}{2\tau}(\epsilon - Ts)\left(\frac{x\tau}{v}\right)^2 \qquad (1)$$

$$\mu = f + kT\left[\ln\left(\frac{x\tau}{v}\right) - x \times \ln\left(1 - \frac{x\tau}{v}\right) - (x-1)\right] + \frac{zx}{2}(\epsilon - Ts)\left(1 - 2\frac{x\tau}{v}\right) \qquad (2)$$

Here k represents the Boltzmann constant, T the absolute temperature, v the volume occupied by a molecule, and z the number of the nearest neighbor cells. ϵ and s are the energy part and the entropy part of the interaction free energy between two chain elements, respectively, and both are assumed to be independent of the temperature. f is the free energy related to the intramolecular degrees of freedom.

If the temperature, T, is lower than a critical value, T_c, the equation of state 1 describes an S-shape of the van der Waals type in the P *vs.* v diagram and indicates the coexistence of two phases—i.e., liquid and vapor phases. Hence, substituting Equation 1 into the well-known conditions,

$$(\partial P/\partial v)_{T_c} = 0 \text{ and } (\partial^2 P/\partial v^2)_{T_c} = 0 \qquad (3)$$

produces

$$\frac{1}{T_c} = \left(\frac{k}{z\epsilon} + \frac{s}{\epsilon}\right) + \frac{2k}{z\epsilon}\left(\frac{1}{x^{1/2}} + \frac{1}{2x}\right) \qquad (4)$$

$$v_c = \tau(x + x^{3/2}) \qquad (5)$$

$$P_c = \frac{kT_c}{\tau}\left[\ln\left(1 + \frac{1}{x^{1/2}}\right) - \frac{1}{x^{1/2}} + \frac{1}{2x}\right] \qquad (6)$$

where T_c is the critical temperature, v_c is the critical volume per molecule, and P_c is the critical pressure.

The conditions for equilibrium between liquid and vapor phases are expressed by stipulating equality of the pressure and the chemical potential in two phases—it is

$$P(T, v) = P(T, v') \text{ and } \mu(T, v) = \mu(T, v') \qquad (7)$$

where the prime is the designation for the more concentrated liquid phase. If temperature T is specified, the other two variables, v and v', are fixed by the two simultaneous Equations 7, and the vapor pressure is expressed in terms of T so that $P(T, v) = P[T, v(T)]$. However, the equations cannot be solved explicitly because of mathematical difficulty, and we are obliged to restrict ourselves to the special case mentioned below.

If the temperature is not so high that the vapor phase is regarded as an ideal gas, an approximate solution of Equation 7 is

$$\ln P = \left[\ln\left(\frac{kT}{x\tau}\right) - 1\right] + x\left(1 + \frac{zs}{2k}\right) - x\left(\frac{z\epsilon}{2kT}\right) \qquad (8)$$

though the derivation (*8*) is not reproduced here. The molar heat of vaporization, Λ, is given by the Clapeyron equation

$$\Lambda = RT^2(d \ln P/dT) \qquad (9)$$

Therefore,

$$\Lambda = N(z\epsilon/2)\,x + RT \qquad (10)$$

where R denotes the gas constant and N, Avogadro's number.

Finally, if the vapor pressure is expressed in terms of atmospheres, ln P becomes zero at the normal boiling point, T_b^0, and Equation 8 can be readily rewritten into

$$\frac{1}{T_b^0} = \left(\frac{2k}{z\epsilon} + \frac{s}{\epsilon}\right) + \frac{2k}{z\epsilon}\left[\ln\left(\frac{kT_b^0}{x\tau}\right) - 1\right]\frac{1}{x} \qquad (11)$$

As was briefly stated previously (*8*), these equations can favorably reproduce the observed variations in the physical constants of the normal paraffins with the carbon number n, provided that an empirical relation

$$x = n^{2/3} \tag{12}$$

is assumed. In addition, the present theory is also applicable to other homologous compounds without any essential alterations.

COMPARISON WITH EXPERIMENTAL DATA

Normal Boiling Point. The combination of Equations 11 and 12 yields

$$\frac{1}{T_b^0} = \frac{C}{D} + \left(\frac{B}{D}\right)\frac{1}{n^{2/3}} \tag{13a}$$

or

$$\frac{n^{2/3}}{T_b^0} = \frac{B}{D} + \frac{C}{D}\,n^{2/3} \tag{13b}$$

with the abbreviated notations,

$$B = \ln(kT_b^0/n^{2/3}\tau) - 1$$
$$C = 1 + (zs/2k) \text{ and } D = z\epsilon/2k \tag{13c}$$

Because the ratio $T_b^0/n^{2/3}$ does not appreciably depend on n, factor B is practically regarded as a constant independent of n. Figure 1 proves this statement, where the experimental data of $n^{2/3}/T_b^0$ (dots) fall on a line, though a slight deviation is observed in the range of n higher than 20. Thus,

$$n^{2/3}/T_b^0 = 0.007840 + 0.0005514\,n^{2/3} \tag{14a}$$

or

$$T_b^0 = \frac{127.55\,n^{2/3}}{1 + 0.07033\,n^{2/3}} (^\circ \text{K.}) \tag{14b}$$

which indicate that $C/B = 0.07033$.

The values of T_b^0 evaluated by this equation are shown in Table I in comparison with the observed values. Also shown are the values calculated by Equation 15, Egloff's equation (*3*), and Varshni's equation (12), Equation 16, for comparison.

$$T_b^0 = 745.42\log(n + 4.4) + 416.32 \tag{15}$$

$$T_b^0 = \left(\frac{21720\,n - 11820}{1 + 0.000283\,n^2}\right)^{1/2} \tag{16}$$

Vapor Pressure vs. Temperature Relationship. Substituting Equation 12 and the abbreviated notations B, C, and D defined by Equation 13c into Equation 8 produces

$$\frac{n^{2/3}}{T} = \frac{1}{D}\left[B - \ln P - \ln\left(\frac{T_b^0}{T}\right)\right] + \frac{C}{D}\,n^{2/3} \tag{17}$$

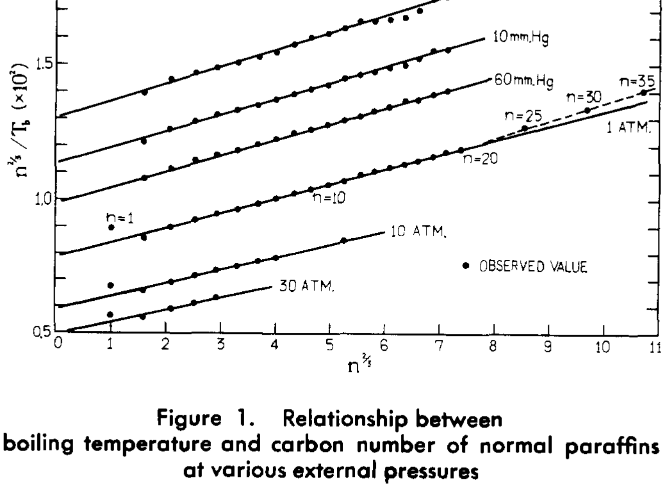


Figure 1. Relationship between boiling temperature and carbon number of normal paraffins at various external pressures

Table I. Boiling Temperature of Normal Paraffins at Various External Pressures[a]

Carbon Number, n	Compound	Normal Boiling Point, T_b^0, ° C.							General Boiling Point, T_b, ° C.							
			Eq. 14b		Eq. 15		Eq. 16		P = 1 Mm. Hg.		P = 100 Mm. Hg.		P = 1500 Mm. Hg.		P = 5 Atm.	
		Obsd.	Calcd.	Δ[b]	Calcd.	Δ[b]	Calcd.	Δ[b]	Obsd.	Eq. 21	Obsd.	Eq. 21	Obsd.	Eq. 21	Obsd.	Eq. 21
1	Methane	−161.5	−154.0	+ 7.5	−143.6	+ 17.9	−173.7	−12.2	. . .	−200.7	−181.5	−175.3	−152.5	−144.1	−138.3	−126.8
2	Ethane	−88.6	−91.1	−2.5	−88.5	+ 0.1	−95.5	−0.9	−159.5	−160.9	−119.3	−122.7	−75.0	−76.4	−52.8	−51.2
3	Propane	−42.1	−41.7	+ 0.4	−41.5	+ 0.6	−42.5	−0.4	−128.9	−129.0	−79.3	−81.0	−25.4	−23.7	+ 1.4	+ 7.2
4	*n*-Butane	−0.5	+ 0.2	+ 0.7	−0.6	−0.1	−0.1	+ 0.4	−101.5	−101.5	−44.2	−45.6	+ 18.9	+ 20.6	50.0	55.8
5	*n*-Pentane	+ 36.1	36.1	0	+ 35.9	−0.2	+ 36.8	+ 0.7	−76.6	−77.1	−12.6	−14.4	57.6	59.1	92.4	97.9
6	*n*-Hexane	68.7	68.6	−0.1	68.6	−0.1	69.3	+ 0.6	−53.9	−54.9	+ 15.8	+ 13.7	92.1	93.4	131.7	135.3
7	*n*-Heptane	98.4	98.0	−0.4	98.3	−0.1	98.7	+ 0.3	−34.0	−34.6	41.8	39.3	123.4	124.4	165.7	168.8
8	*n*-Octane	125.7	124.9	−0.8	125.6	−0.1	125.6	−0.1	−14.0	−15.7	65.7	62.9	152.1	152.8	196.2	199.4
9	*n*-Nonane	150.8	149.9	−0.9	150.6	−0.2	150.5	−0.3	+ 1.4	+ 1.9	87.9	84.9	178.5	179.0		
10	*n*-Decane	174.1	173.1	−1.0	174.0	−0.1	173.7	−0.4	16.5	18.5	108.6	105.4	202.9	203.3		
11	*n*-Undecane	195.9	194.9	−1.0	195.6	−0.3	195.4	−0.5	32.7	34.2	127.9	124.7	225.7	226.0		
12	*n*-Dodecane	216.3	215.3	−1.0	216.1	−0.2	215.8	−0.5	47.8	49.2	146.1	142.9	247.1	247.3	300.0	300.4
13	*n*-Tridecane	235.5	234.6	−0.9	235.2	−0.3	234.9	−0.6	59.4	57.0	162.3	160.2	267	267.4		
14	*n*-Tetradecane	253.6	252.8	−0.8	253.3	−0.3	253.0	−0.6	76.4	76.9	178.3	176.6	286	286.4		
15	*n*-Pentane	270.7	270.2	−0.5	270.4	−0.3	270.1	−0.6	91.6	89.9	193.8	192.2	304	304.4		
16	*n*-Hexadecane	287.1	286.7	−0.4	286.7	−0.4	286.3	−0.8	105.8	102.4	208.3	207.2	320.6	321.5		
17	*n*-Heptadecane	302.6	302.4	−0.2	302.2	−0.4	301.6	−1.0	115.0	114.4	222.8	221.5	336	337.8		
18	*n*-Octadecane	317.4	317.5	+ 0.1	316.9	−0.5	316.1	−1.3	119.6	125.9	235.2	235.2	351	353.4		
19	*n*-Nonadecane	331.6	331.9	+ 0.3	331.1	−0.5	329.9	−1.7	133.2	137.1	248	248.4	365	368.3		
20	*n*-Eicosane	345.1	345.8	+ 0.7	344.7	−0.4	342.9	−2.2	. . .	147.8	260	261.1	379	382.6		

[a] Observed values, Egloff (*2*), Rossini (*10*), Stull (*11*). [b] $\Delta \equiv T_b^0(\text{calcd.}) - T_b^0(\text{obsd.})$.

after some rewritings, which correlates vapor pressure P with temperature T, or boiling point T with external pressure P. However, to calculate the boiling point, T_b ($\equiv T$), it is desirable to write Equation 17 in a more convenient form.

First is the term $\ln (T_b^0/T_b)$ [$\equiv \ln (T_b^0/T)$] neglected in the right-hand side of Equation 17,

$$\frac{n^{2/3}}{T_b} = \frac{1}{D} (B - \ln P) + \frac{C}{D} n^{2/3} \tag{18}$$

This equation will predict the "zeroth approximation" of the boiling point, T_b. Then combining Equation 18 with Equation 13,

$$T_b^0/T_b = 1 - \left(\frac{\ln P}{B + C n^{2/3}}\right) \tag{19a}$$

hence,

$$\ln\left(\frac{T_b^0}{T_b}\right) = - \frac{\ln P}{B} \left(1 - \frac{C}{B} n^{2/3} + \ldots\right) - \frac{1}{2} \left(\frac{\ln P}{B}\right)^2 \left(1 - 2 \frac{C}{B} n^{2/3} + \ldots\right) + \ldots \tag{19b}$$

According to Equation 14b and the expression for the heat of vaporization given below, C/B and B are estimated to be 0.07 and 7.5, respectively. Therefore, in the double expansion of Equation 19b, the terms with higher powers of $(C/B)\ n^{2/3}$ and $(1/B) \times \ln P$ are not expected to be significant, except some leading terms, in so far as both n and $\ln P$ are not too large. Then, substituting Equation 19b in Equation 17 gives

$$n^{2/3}/T_b = [(B/D) + \beta_1 \ln P + \beta_2 (\ln P)^2 + \ldots] + [(C/D) + \gamma_1 \ln P + \ldots]\, n^{2/3}, \tag{20}$$

where β_1, β_2, and γ_1 are constants independent of P and n.

Equation 20 indicates that the ratio $n^{2/3}/T_b$ changes its values linearly with $n^{2/3}$ at any given pressure. This is proved by the experimental data (Figure 1), and

$$n^{2/3}/T_b = [0.007840 - 0.00215 \times \log P - 0.00010 \times (\log P)^2] + (0.0005514 - 0.000011 \times \log P)\, n^{2/3} \tag{21}$$

Of course, this equation is reduced to Equation 14a in the special case that $P = 1$ atm. Table I illustrates the experimental test of Equation 21, where a satisfactory agreement is obtained over wide ranges of pressure—i.e., from very low pressure to about 5 atm.

Heat of Vaporization. The substitution of Equation 21 in Equation 9 yields

$$\Lambda = \frac{2128\, n^{2/3}}{1 + 0.00512\ n^{2/3} + 0.0930 \times \log P} \left(\frac{\text{cal.}}{\text{mole}}\right) \tag{22}$$

Table II gives values of Λ at the normal boiling point and 25° C. which were evaluated by using Equations 21 and 22. The agreement between the evaluated and observed values is generally good, but an appreciable discrepancy is found in Λ_{25} for the lower members than propane. For this discrepancy, it should be remembered that at 25° C. the vapor pressure of the compounds reaches 10 or more atmospheres which are above the limit of application of Equation 21.

To make another test of the validity of rewriting Equations 17 to 21, substituting Equations 12, 13, and 14 in Equation 10 produces

$$\Lambda^0 = RDn^{2/3}\, \frac{1 + (1/B) + (C/B)\, n^{2/3}}{1 + (C/B)\, n^{2/3}} \tag{23}$$

Then, comparing with the experimental data,

$$B = 7.463,\ C = 0.5426, \text{ and } D = 952 \text{ degrees}$$

$$\Lambda^0 = 2146\ n^{2/3} \left(\frac{1 + 0.06202\, n^{2/3}}{1 + 0.07033\, n^{2/3}}\right) \left(\frac{\text{cal.}}{\text{mole}}\right) \tag{24}$$

As shown in Table II, both Equations 22 and 24 predict almost the same value for Λ^0. This seems to prove the correctness of the approximations adopted in the derivation of Equation 21.

The Trouton ratio, Λ^0/T_b^0, is obtained as

$$\frac{\Lambda^0}{T_b^0} = 16.68 \left(\frac{1 + 0.07033\, n^{2/3}}{1 + 0.00512\, n^{2/3}}\right) \left(\frac{\text{cal.}}{\text{mole-degree}}\right) \tag{25}$$

which represents a gradual increase of the ratio with increasing n. A test of this equation is also given in Table II.

Critical Constants. Combining Equation 5 with Equation 12, and making comparison with the experimental data gives the following expression for critical volume,

$$V_c = 0.0412\, (n^{2/3} + n)\ (\text{cc./mole}) \tag{26}$$

which gives a good approximation for V_c as shown in Table III.

For the critical temperature, T_c, the following relationship is obtained from Equations 4 and 12:

$$\frac{1}{T_c} = A' + B' \left(\frac{1}{n^{2/3}} + \frac{2}{n^{1/3}}\right) \tag{27}$$

where A' and B' are constants. In this case, however, a more simple equation,

$$\frac{1}{T_c} = 0.000702 + \frac{0.004192}{n^{2/3}} \tag{28}$$

is recommended for quantitative purposes, though Equation 27 itself can be used for a rough evaluation of T_c (*8*). A comparison of Equation 28 with experimental data is shown in Table III, where two recent observations for *n*-decane and *n*-dodecane (*5*) are adopted. For higher members than dodecane for which no observation is available, Equation 28 predicts the values fairly close (average 2.3° C. lower) to the recent estimates of Francis (*5*), but much higher than the API estimates (*10*).

The combination of Equation 28 with 14b yields

Table II. Latent Heat of Vaporization and Trouton's Ratio of Normal Paraffins

Carbon Number, n	Compound	Λ^0 at Normal Boiling Point[a]			Λ_{25} at 25° C.[a]		Trouton's Ratio	
		Obsd.[b]	Eq. 22	Eq. 24	Obsd.[b]	Eq. 22	Obsd.[b]	Eq. 25
1	Methane	1.955	2.117	2.117	...	...	17.51	17.76
2	Ethane	3.517	3.351	3.350	...	...	19.06	18.40
3	Propane	4.487	4.380	4.378	3.605	4.03	19.42	18.92
4	*n*-Butane	5.352	5.294	5.292	5.035	5.12	19.63	19.39
5	*n*-Pentane	6.160	6.130	6.127	6.316	6.22	19.92	19.82
6	*n*-Hexane	6.896	6.910	6.906	7.540	7.42	20.17	20.22
7	*n*-Heptane	7.575	7.644	7.639	8.735	8.64	20.38	20.59
8	*n*-Octane	8.214	8.341	8.336	9.915	9.92	20.59	20.95
9	*n*-Nonane	8.82	9.008	9.001	11.099	11.28	20.80	21.29

[a] Latent heat of vaporization, kcal./mole.
[b] Rossini (*10*).

Table III. Critical Constants of Normal Paraffins

Carbon Number, n	Compound	Critical Temperature T_c, ° K.		Critical Pressure, P_c, Atm.		Critical Volume, V_c, Cc./Mole	
		Obsd.[a]	Eq. 28	Obsd.[b]	Eq. 32	Obsd.[b]	Eq. 26
1	Methane	190.7	204.4	45.8	68.9	0.099	0.0824
2	Ethane	305.4	299.2	48.2	50.4	0.148	0.148
3	Propane	370.0	368.1	42.0	41.4	0.200	0.209
4	n-Butane	425.2	422.8	37.5	35.6	0.255	0.269
5	n-Pentane	469.8	468.4	33.3	31.6	0.311	0.326
6	n-Hexane	507.9	507.4	29.9	28.5	0.368	0.383
7	n-Heptane	540.2	541.4	27.0	26.1	0.426	0.439
8	n-Octane	569.4	571.4	24.6	24.1	0.486	0.494
9	n-Nonane	...	598.4	22.5	22.4	0.543	0.549
10	n-Decane	621.4	623.1	20.8	21.0	0.602	0.603
11	n-Undecane	...	645.6	19.2	19.8	0.660	0.657
12	n-Dodecane	664.7	666.2	17.9	18.7	0.718	0.710
13	n-Tridecane	...	684.9	...	17.8	...	0.763
14	n-Tetradecane	...	702.7	...	16.9	...	0.816
15	n-Pentadecane	...	718.9	...	16.2	...	0.869
16	n-Hexadecane	...	734.2	...	15.5	...	0.921
17	n-Heptadecane	...	748.5	...	14.8	...	0.973
18	n-Octadecane	...	762.2	...	14.3	...	1.03
19	n-Nonadecane	...	774.6	...	13.7	...	1.08

[a] Francis (*6*); Rossini (*10*). [b] Rossini (*10*).

$$T_b^0/T_c = 0.5344 + 0.0004073\ T_b^0 \qquad (29)$$

This equation represents a gradual increase in the ratio T_b^0/T_c with increasing n, and was proposed by Varshni (*12*).

The substitution of Equation 12 in Equation 6 leads to

$$\frac{P_c}{T_c} = \frac{k}{\tau}\left[\ln\left(1 + \frac{1}{n^{1/3}}\right) - \frac{1}{n^{1/3}} + \frac{1}{2n^{2/3}}\right] \qquad (30)$$

which is roughly supported by the experimental data as shown in Figure 2. But, in this case too, the following relation is more favorable than Equation 30.

$$\frac{P_c}{T_c} = \frac{0.337}{n}\left(\frac{\text{atm.}}{\text{degree}}\right) \qquad (31)$$

Thus,

$$P_c = \frac{80.37}{n^{1/3}\,(1 + 0.1675\, n^{2/3})}\ \text{atm.} \qquad (32)$$

Table III proves this statement.

Limit of Application of Theory. The equations presented here are extensive and accurate enough for practical purposes so far as members of the normal paraffins lower than eicosane are concerned and when the vapor pressure does not exceed about 5 atm. The empirical relation that $x = n^{2/3}$ proved very effective under the conditions mentioned above, though slight modifications had to be made to obtain the recommended equations of T_c and P_c.

For the higher members than eicosane, however, the $n^{2/3}$ rule becomes unsatisfactory for quantitative purposes. In Table IV is an example, where the normal boiling point, T_b^0, evaluated by Equation 14b is compared with the observed values collected by Rossini and others (*10*). The table shows that the error of Equation 14b is always positive; therefore, it may be diminished by adjusting x to a value smaller than $n^{2/3}$. Such an adjustment of x seems to be natural from the theoretical point of view, for the

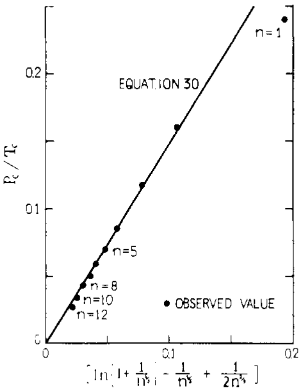


Figure 2. Experimental test of Equation 30 for critical pressure of normal paraffins

Table IV. Normal Boiling Temperature of Normal Paraffins of High Molecular Weight

Carbon Number, n	Compound	Selected Values (*10*)	Normal Boiling Point, T_b^0, ° C.			
			Eq. 14b	Eq. 15, (*3*)	Eq. 16, (*12*)	(*11*)
21	n-Heneicosane	355.1	359.1	357.7	355.3	350.5
22	n-Docosane	367.0	372.0	370.2	367.0	376.0
23	n-Tricosane	378.3	384.4	382.3	378.1	366.5
24	n-Tetracosane	389.2	396.3	393.8	388.7	386.4
25	n-Pentacosane	399.7	407.7	405.0	398.6	390.3
26	n-Hexacosane	409.7	419.0	415.9	408.1	399.8
27	n-Heptacosane	419.4	430.3	426.3	417.0	410.6
28	n-Octacosane	428.7	440.3	436.5	425.4	412.5
29	n-Nonacosane	437.7	450.4	446.5	433.4	421.8
30	n-Triacontane	446.4	460.2	455.8	440.9	...
35	n-Pentatriacontane	486	505.6	499.8	472.3	...
40	n-Tetracontane	520	545.3	538.5	494.8	...
50	n-Pentacontane	...	612.5	604.2	520.0	...

flexibility of the molecular chain generally increases with n and shortens the effective chain length.

For high pressure regions, the analytical expression can not be derived for the vapor pressure due to mathematical difficulties. But fortunately, Equation 32 of the critical pressure may be easily solved by making an empirical interpolation to give the vapor pressure value in the intermediate region, from about 5 atm. to critical pressure.

NOMOGRAPH

The basic equation for the nomograph is Equation 21, which may be rewritten as

$$f(T) + g(n) \times h(P) = \phi(P) \qquad (33a)$$

with

$$\begin{aligned} f(T) &= 1/T, \qquad g(n) = 1/n^{2/3} \\ h(P) &= -0.007840 + 0.00215 \times \log P + 0.00010\,(\log P)^2, \\ \phi(P) &= 0.0005514 - 0.000011 \times \log P \qquad (33b) \end{aligned}$$

This type of equation can be readily represented in a nomogram, (Figures 3a and b).

The deviation of Equation 21 from experimental data, however, is not negligible in some cases, and some empirical corrections are required to obtain a precise agreement between the predicted and experimental values. For example, if n is unity in Equation 21, the calculated value of the boiling point of methane becomes larger than the experimental value, irrespective of the external pressure. This particular deviation in methane must be due to the difference of symmetry in molecular shape between methane and other members, and can be eliminated by assigning for n a value smaller than unity. Similar correction of n is also required for the higher members than eicosane. This may arise from the increasing flexibility of the molecular chain with n. Thus the n-axis shown in Figures 3a and b, is obtained sliding the n scale from $1/n^{2/3}$ to a corrected scale.

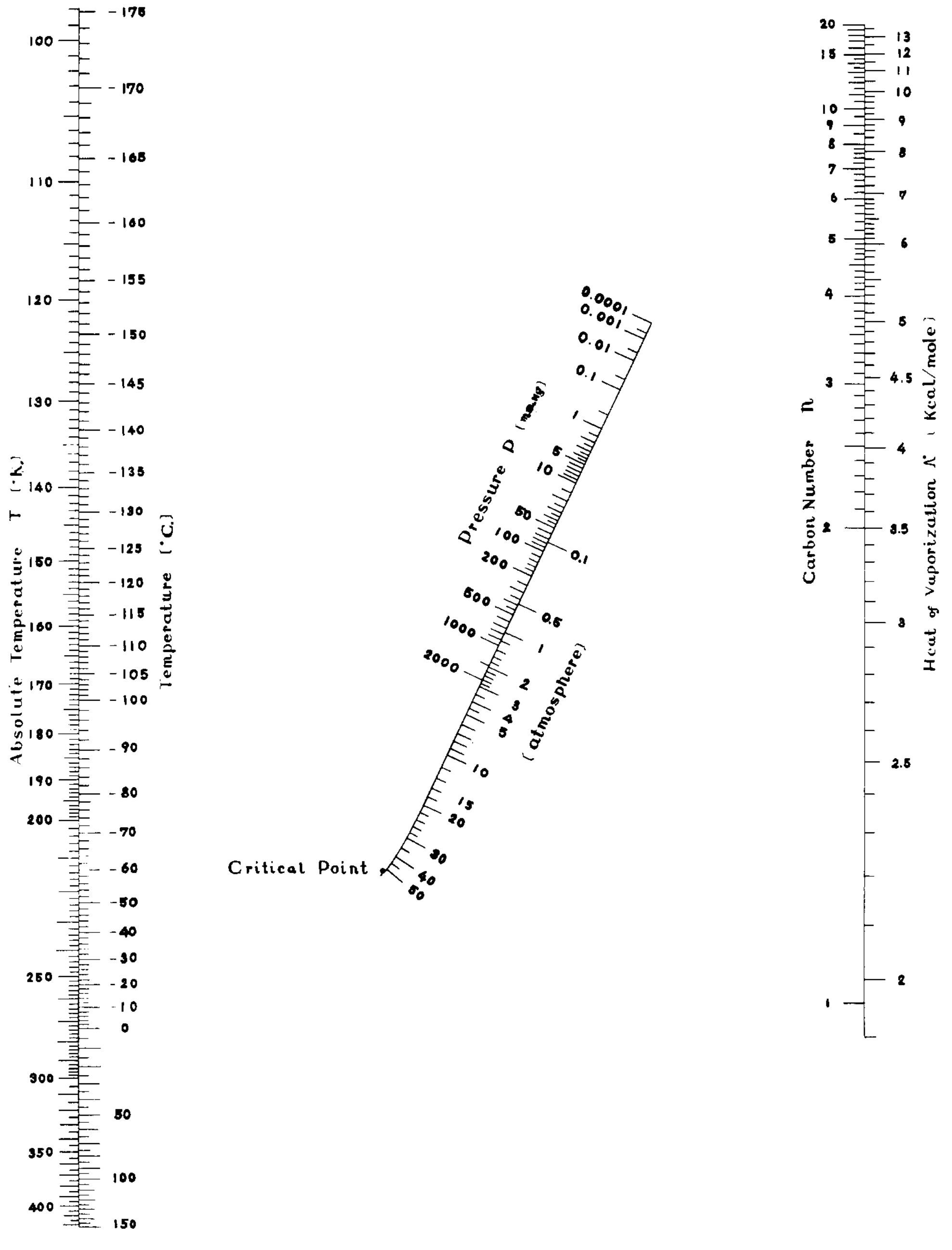


Figure 3a. Nomograph for estimating critical constants, heat of vaporization, and boiling points from — 175° to 150° C.

The pressure scale from 5 atm. to the critical pressure where Equation 21 does not hold can be completed by using the experimental data of boiling point of methane and ethane at high pressures as reference.

As is easily seen from the form of Equation 28, the critical point can be represented by a point in this nomogram. Furthermore, according to Meyer and van der Wyk (*9*), the melting point, T_m, of normal paraffins can be favorably given by

$$1/T_m = 0.002395 + 0.0171/(n - 1) \qquad (34)$$

This equation is different in form from Equation 14 of the normal boiling point or Equation 28 of the critical point, and therefore the melting point cannot be represented by one point in the nomogram. For practical purposes, however, that two points denoted by *A* and *B* in the nomogram are very effectively applied to read the melting point of the compounds with the carbon number of 13 to 25 and with that of 26 to 70, respectively.

For convenience, two nomograms of the same type are presented here: Figure 3a, covers the temperature range between – 175° and 150° C. and Figure 3b, covers the range of 0° to 550° C. Using these two figures, one can read with sufficient accuracy the normal and general boiling points, vapor pressure at every temperature, melting point, critical temperature, critical pressure, and heat of vaporization at the normal boiling point. Furthermore, if the evaluated values of T_c, T_b^0, and Λ^0 are substituted in the Watson equation (*13*),

$$\log \Lambda = \log \Lambda^0 + 0.38 \log [(T_c - T)/(T_c - T_b^0)] \qquad (35)$$

the heat of vaporization, Λ, is easily evaluated as functions of the temperature. Table V gives the values of various properties evaluated by the nomogram in comparison with

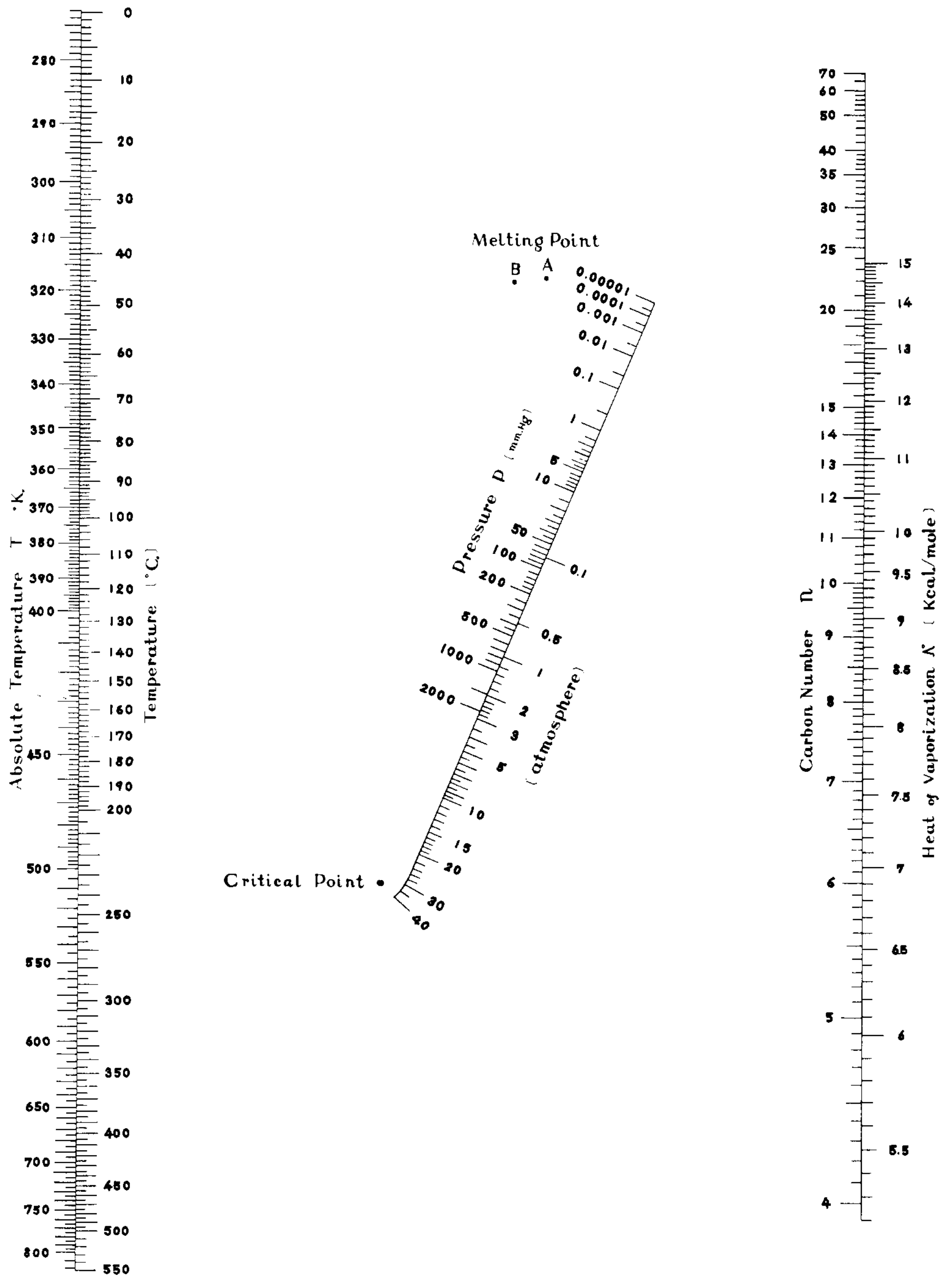


Figure 3b. Nomograph for estimating critical constants, heat of vaporization, and boiling points from 0° to 550° C.

Table V. Comparison of Values Read on Nomograph with Experimental Data[a]

Carbon Number, n	Compound	Boiling Point, T_b ° C.				Heat of Vaporization Λ, Kcal./Mole				Critical Constant				Melting Point	
		1 Atm.		10 Atm.		At T_b^0		At 25° C.		T_c (° K)		P_c(Atm.)		T_m, ° C.	
		Obsd.	Fig. 3	Obsd.	Fig. 3	Obsd.	Fig. 3	Obsd.	Eq. 35 Fig. 3	Obsd.	Fig. 3	Obsd.	Fig. 3	Obsd.	Fig. 3
		Carbon Number Less Than 20													
1	Methane	−161.5	−162.2	−124.8	−127.0	1.955	1.96	...	...	190.7	191.5	45.8	...		
5	*n*-Pentane	+ 36.1	+ 35.6	+ 124.7	+ 126	6.160	6.09	6.316	6.11	469.8	469	33.04	33		
8	*n*-Octane	125.7	125	235.8	233	8.214	8.21	9.915	9.77	569.8	570	24.66	25		
12	*n*-Dodecane	216.3	215	345.8	339	10.44	10.45	14.647	13.84	664.7	662	18.59	19		
15	*n*-Pentadecane	270.7	270	...	400	11.8	11.91	18.20	16.70	...	714	15.75	16	9.9	11.7
20	*n*-Eicosane	345.1	343	...	483	13.8	13.8	...	...	...	780	...	13	36.6	35.5

Carbon Number More Than 21

Carbon Number, n	Compound	Normal Boiling Point, T_b^0, ° C.		Boiling Point, T_b ° C.				Melting Point, T_m ° C.	
				15 Mm. Hg.		3 Mm. Hg.			
		Obsd.	Fig. 3	Obsd.	Fig. 3	Obsd.	Fig. 3	Obsd.	Fig. 3
21	*n*-Heneicosane	355.1	357	215	214	179.8	178	40.4	40.3
25	*n*-Pentacosane	399.7	403	259	255			53.5	54
30	*n*-Triacontane	446.4	446			258.5	250	65.5	65
35	*n*-Pentatriacontane	486	488			292.3	283	74.5	74
43	*n*-Tritetracontane		538			332.0	328	84.5	85
50	*n*-Pentacontane							92.1	92
70	*n*-Heptacontane							105.3	106

[a] Egloff (*2*), Francis (*5*), Rossini (*10*), Stull (*11*).

the experimental data. In every case concerned the agreement between the evaluated and experimental values is fairly close, and Figures 3a and b are useful for the rapid evaluation of the physical constants of normal paraffins.

ISOPARAFFINS

Isomeric variation in the physical properties of isoparaffins has been investigated (*1, 7, 14, 15*).

EFFECTIVE CARBON NUMBER

The isoparaffins are nothing but branched-chain molecules consisting of the same chain elements as in the normal paraffins, and the basic Equations 1 and 2 are applicable to branched-chain molecules as well as to linear chain molecules, because the Flory expression for the mixing entropy on which this theory was based is by no means affected by the presence of side chains. This suggests that the nomograph would be applicable to isoparaffins with slight modification. A new structural constant, the "effective carbon number," is introduced for this purpose.

Let us first investigate the vapor pressure *vs.* temperature relationship of an isoparaffin—for example, 2-methylpropane. The observed values of general boiling points T_b of this compound are given in Table VI as functions of the external pressure. Using these data and the nomogram (Figures 3a and b) values of n can be read at each intersection of the n axis and the lines connecting two points that $T_b = -109.2$° C. and $P = 1$ mm. of mercury, −86.4° C. and 10 mm. of mercury, −54.1° C. and 100 mm. of mercury and so on, and the n values given in Table VI are obtained at each attempt. The n values all coincide with one another, and the mean value 3.72 of n can give a satisfactory approximation for general boiling points and heat of vaporization, Λ^0, at normal boiling point, the critical temperature, T_c, and critical pressure P_c, as shown in Table VI. A similar test is given for another example, 2,2-dimethylbutane, in the same table. Thus, the n value, 3.72 for 2-methylpropane or 5.41 for 2,2-dimethylbutane, can represent the properties of each compound as well as does the true carbon number of n-paraffins. Hereafter, the n value is called effective carbon number of isoparaffins and is denoted by n^*.

The effective carbon number, n^*, of isoparaffins is always smaller than the number of carbon atoms. This may be interpreted in terms of a decrease in the contribution of branched carbon atoms to the intermolecular potential due to a screening effect of the neighboring carbon atoms. The authors believe, therefore, the n^* must be correlated with the structural arrangement of carbon atoms by a proper relationship, though the theoretical derivation of the relationship will be a formidably difficult problem.

In this connection, Wiener (*14*) has suggested that the isomeric variation in the normal boiling point, T_b^0, can be expressed in terms of two structural parameters, the path number, w, and the polarity number, p, which can be calculated from structural formula. The path number, w, was defined as the total number of bonds between all pairs of carbon atoms and the polarity number, p, was defined as the total number of pairs of carbon atoms three bonds apart.

For normal paraffins, these structural parameters are given as

$$w(\text{normal}) = (n-1)\,n(n+1)/6 \tag{36}$$

$$p(\text{normal}) = n - 3 \tag{37}$$

If

$$\Delta w = w(\text{normal}) - w(\text{isomer}) \tag{38}$$

and

$$\Delta p = p(\text{normal}) - p(\text{isomer}) \tag{39}$$

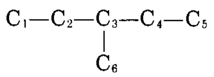
the Wiener equation of the isomeric variation in the normal boiling point T_b^0 is expressed as

$$\Delta T_b^0 = T_b^0(\text{normal}) - T_b^0(\text{isomer}) = 98\ (\Delta w/n^2 + 5.5\ \Delta p \quad (40)$$

Now, to correlate the effective carbon number n^* with the structural formula, we also adopt the Wiener parameters mentioned above and find that n^* can be favorably given as

$$\Delta n \equiv n - n^* = 3.4 \times (\Delta w/n^2) + 0.18\ \Delta p \quad (41)$$

The use of Equation 41 may best be illustrated by an example. For the n^* of 3-methylpentane,



$$C_1{-}C_2{-}\underset{\substack{|\\C_6}}{C_3}{-}C_4{-}C_5$$

There are six carbon atoms in 3-methylpentane; therefore $n = 6$. The w may be computed by Wiener's short method or by multiplying the number of carbon atoms on one side of a bond by the number on the other side and summing the products for all bonds. Thus the product for bond $C_1{-}C_2$ is $1 \times 5 = 5$; for $C_2{-}C_3$, $2 \times 4 = 8$; for $C_3{-}C_4$, $2 \times 4 = 8$; for $C_4{-}C_5$, $1 \times 5 = 5$; for $C_3{-}C_6$, $1 \times 5 = 5$. Therefore $w(\text{isomer}) = 5 + 8 + 8 + 5 + 5 = 31$. Pairs of carbon atoms three bonds apart are C_1C_4, C_1C_6, C_2C_5, and C_5C_6; therefore $p(\text{isomer}) = 4$. On the other hand, substituting $n = 6$ into Equations 36 and 37 gives $w(\text{normal}) = 35$ and $p(\text{normal}) = 3$. Thus, substituting these values in Equations 38, 39, and 41, one obtains $n^* = 5.80$, which is to be compared with 5.82 obtained by combining use of the nomogram and the observed value 63.3° C. of the normal boiling point.

Table VI. Effective Carbon Number of Some Isoparaffins Read on the Nomogram,

(Figures 3a or b, using various experimental data)

	Boiling Temp. T_b ° C.,						Heat of Vaporization, Λ^0, Kcal./Mole	Critical Constant	
	1 Mm. Hg.[a]	10 Mm. Hg.[b]	100 Mm. Hg.[b]	760 Mm. Hg.[b]	1500 Mm. Hg.[b]	20 Atm.[a]		T_c, ° K.	P_c (Atm.)
				2-Methylpropane					
Obsd.	−109.2	−86.4	−54.1	−11.7	+7.1	99.5	5.089	408.2	36
n^*	3.71	3.71	3.71	3.72	3.73	3.70	...	...	...
Fig. 3[c]	−109.0	−86	−54	−11	+8	100	5.05	407	37
				2,2-Dimethylbutane					
Obsd.	−69.3	−41.5	−2.0	+ 49.7	72.8	...	6.355	489.4	30.7
n^*	5.31	5.33	5.38	5.41	5.42	...	...	...	...
Fig. 3[d]	−68	−40	−1	+ 49.2	72.4	185	6.45	484	31

[a] Stull (*11*).
[b] Rossini (*10*).
[c] Nomogram values, $n^* = 3.72$ instead of true carbon number.
[d] Nomogram values, $n^* = 5.41$ instead of true carbon number.

The values of n^* calculated by Equation 41 are shown in the fourth column of Table VII in comparison with the observed value of n^* which are obtained in Figures 3a or b as the intersection of the n scale and the connected line between the point of 1 atm. on the P scale and the observed value of the normal boiling point. The maximum deviation of $n^*_{\text{calcd.}}$ from $n^*_{\text{obsd.}}$ is 4.6% and the average deviation does no exceed 1.5%.

COMPARISON WITH EXPERIMENTAL DATA

If n^* is used instead of n, Equations 1 to 35 can be applied to isoparaffins too. However, calculation of $n^{2/3}$ which appears in the equations is somewhat laborious for practical purposes. Thus, the nomogram is recommended.

The method of using the nomogram is similar to that in the case of normal paraffins. The properties which can be evaluated from this nomogram are the general boiling points as functions of the external pressure, critical temperature, critical pressure, and heat of vaporization at normal boiling point. The heat of vaporization at any given temperature can be evaluated by using the Watson equation (*13*).

$$\log \Lambda = \log \Lambda^0 + 0.38 \log \frac{T_c - T}{T_c - T_b^0} \quad (42)$$

However, the melting point of isoparaffins cannot be evaluated by using point *A* or *B* in the nomogram, for the symmetry of molecular shape has an appreciable effect on the melting point.

Table VII shows the evaluated values of various properties of 66 isoparaffins from C_4H_{10} to C_9H_{20} in comparison with experimental data (*5, 6, 10*). The agreement between them is generally satifactory. For instance, in the case of Λ^0, the maximum deviation is 3.5% and average deviation is 1.2% for these 66 isoparaffins. This is to be compared with the maximum deviation of 5% and average deviation of 2% obtained by the method of Chu and others (*1*).

For isoparaffins higher than $C_{10}H_{22}$, fragmentary data have been accumulated by Egloff (*2*): The normal boiling points of 58 isoparaffins from $C_{10}H_{22}$ to $C_{12}H_{26}$ are also evaluated by the method described above. Although the results are not given here, the average deviation of the evaluated values from the literature values is about ±3.3° C. and the maximum deviation is 10° C. for 2,4-dimethylnonane.

DISCUSSION

As is shown in Table VII, introducing the effective carbon number n^* seems to be appropriate for evaluating the physical properties of isoparaffins. Assuming that n^* is regarded as characteristic of the structural arrangement of carbon atoms in the molecule appears correct at least as the first approximation. However, slightly different values of n^* are to be assigned for each property to obtain the closest agreement with the observed values. For instance, detailed examination of boiling point data often leads to a gradual increase of n^* with increasing temperature. Although the increase is negligible in most cases, there is a general tendency that the more compact the structural arrangement of carbon atoms becomes, the more the n^* depends on the temperature—e.g., 2,2,3,3-tetramethylbutane. This observation may offer an interesting problem concerning the molecular structure of hydrocarbons.

Table VII. Comparison of Values of Various Physical Properties Read on Nomogram with Experimental Data[a]

Carbon Number, n	Compound	Effective Carbon Number, n^*		Boiling Temperature, T_b ° C.						Heat of Vaporization λ, (Kcal./Mole at				Critical Constant			
				10 Mm. Hg.		760 Mm. Hg.		1500 Mm. Hg.		T_b^0		25° C.		T_c, ° K.		P_c, atm.	
		T_b^0 obsd.	from Eq. 6	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
4	2-Methylpropane	3.72	3.61	−86.4	−89	−11.7	−15	7.1	3	5.089	4.96	4.570	4.38	408.2	401	36	38
5	2-Methylbutane	4.76	4.73	−56.9	−58	+27.8	+26.5	49.2	48.2	5.842	5.88	5.878	5.95	461.0	457	32.9	35
	2,2-Dimethylpropane	4.27	4.10	. . .	. . .	9.5	3.0	29.9	24.0	5.438	5.36	5.205	5.33	433.8	428	31.6	37
6	2-Methylpentane	5.73	5.72	−32.1	−32	60.3	59.6	83.4	83.1	6.626	6.71	7.138	7.22	498.1	497	30	30
	3-Methylpentane	5.82	5.82	−30.1	−30	63.3	62.6	86.6	86.7	6.578	6.78	7.235	7.35	504.4	500	30.8	30
	2,2-Dimethylbutane	5.41	5.34	−41.5	−41	49.7	47.0	72.8	70.2	6.355	6.38	6.617	6.70	489.4	482	30.7	32
	2,3-Dimethylbutane	5.66	5.61	−34.9	−35	58.0	55.8	81.3	79.2	6.595	6.62	6.960	7.10	500.4	492	31.0	31
7	2-Methylhexane	6.71	6.72	−9.1	−10	90.0	89.5	114.8	115	7.35	7.42	8.318	8.40	531.1	531	27.2	27
	3-Methylhexane	6.77	6.76	−7.9	−9	91.9	91.0	116.7	116	7.42	7.46	8.385	8.45	535.6	533	28.1	27
	3-Ethylpentane	6.83	6.81	−6.8	−8	93.5	92.2	118.5	118	7.44	7.47	8.419	8.48	540.8	534	28.6	27
	2,2-Dimethylpentane	6.34	6.31	−18.6	−19	79.2	77.8	103.8	103	6.98	7.12	7.751	7.91	520.9	518	28.4	28
	2,3-Dimethylpentane	6.70	6.67	−10.3	−12	89.8	88.5	114.8	114	7.30	7.38	8.184	8.34	537	530	29.2	28
	2,4-Dimethylpentane	6.38	6.45	−17.0	−16	80.5	81.5	104.9	107	7.10	7.22	7.860	8.07	521.7	522	27.4	28
	3,3-Dimethylpentane	6.58	6.53	−14.4	−14	86.1	84.0	111.3	109	7.07	7.29	7.892	8.18	536	526	. . .	28
	2,2,3-Trimethylbutane	6.40	6.39	−18.8	−17	80.9	80.0	105.9	105	6.94	7.18	7.657	8.00	531.5	521	29.8	28
8	2-Methylheptane	7.73	7.73	+ 12.3	+ 13.0	117.6	117	143.8	144	8.03	8.04	9.483	9.45	561	562	24.8	25
	3-Methylheptane	7.78	7.76	13.3	13.6	118.9	118	145.2	145	8.14	8.07	9.520	9.51	565	563	25.6	25
	4-Methylheptane	7.74	7.70	12.4	12.5	117.7	117	143.9	143	8.100	8.02	9.482	9.45	563	562	25.6	26
	2,2-Dimethylhexane	7.31	7.31	3.1	4.8	106.8	107	132.8	133	7.73	7.77	8.912	9.03	552	550	25.6	26
	2,3-Dimethylhexane	7.65	7.62	9.9	10.8	115.6	114	142.0	141	8.02	7.97	9.271	9.34	566	558	26.6	26
	2,4-Dimethylhexane	7.41	7.49	5.2	8.5	109.4	111	135.5	138	7.82	7.88	9.026	9.19	555	555	25.8	26
	2,5-Dimethylhexane	7.40	7.47	5.3	8.0	109.1	111	135.0	137	7.84	7.87	9.048	9.19	550.0	555	25.0	26
	3,3-Dimethylhexane	7.51	7.46	6.1	7.7	112.0	110	138.4	137	7.82	7.86	8.971	9.15	564	555	27.2	26
	3,4-Dimethylhexane	7.74	7.69	11.3	12.4	117.7	117	144.2	143	8.02	8.01	9.315	9.44	571	562	27.4	25
	3-Ethylhexane	7.77	7.72	12.8	12.8	118.5	117	144.9	144	8.19	8.03	9.475	9.45	567	562	26.4	25
	2,2,3-Trimethylpentane	7.43	7.42	3.9	6.8	109.8	109	136.4	136	7.69	7.84	8.823	9.12	567	554	28.2	27
	2,2,4-Trimethylpentane	7.03	7.04	−4.3	−3	99.2	99	125.2	125	7.410	7.62	8.396	8.75	544.1	543	25.5	26
	2,3,3-Trimethylpentane	7.62	7.55	6.9	9.5	114.8	112	141.7	139	7.78	7.93	8.895	9.28	576	558	29.0	26
	2,3,4-Trimethylpentane	7.57	7.53	7.1	9.2	113.5	112	140.0	139	7.810	7.92	9.012	9.26	568	557	27.6	27
	2-Methyl-3-ethylpentane	7.65	7.64	9.5	11.5	115.6	115	142.2	142	7.96	7.98	9.207	9.37	568	560	27.4	26
	3-Methyl-3-ethylpentane	7.76	7.66	9.9	11.8	118.3	116	145.3	142	7.91	8.00	9.080	9.40	578	561	28.9	25
	2,2,3,3-Tetramethylbutane	7.30	7.34	13.2	5.3	106.3	107	133.0	133	7.56	7.80	Solid	9.05	(564)	552		27
9	2-Methyloctane	8.71	8.75	32	33.4	143.3	144	171	171	8.76	8.66	10.67	10.55		591		23
	3-Methyloctane	8.75	8.74	33	33.2	144.2	144	172	171	8.79	8.65	10.69	10.54		591		23
	4-Methyloctane	8.69	8.68	32	32.2	142.5	142	170	170	8.75	8.62	10.69	10.49		588		23
	3-Ethylheptane	8.70	8.69	32	32.3	143.0	142	171	170	8.78	8.62	10.71	10.48		589		23
	4-Ethylheptane	8.67	8.60	31	30.7	141.2	140	169	168	8.76	8.58	10.71	10.40		587		23
	2,2-Dimethylheptane	8.23	8.33	23	25.5	132.7	133	160	161	8.31	8.41	10.10	10.11		580		24
	2,3-Dimethylheptane	8.62	8.60	29	30.7	140.5	140	168	168	8.63	8.58	10.46	10.40		587		23
	2,4-Dimethylheptane	8.32	8.42	24	27.3	133	135	160	163	8.45	8.46	10.25	10.19		582		24
	2,5-Dimethylheptane	8.43	8.51	26	28.8	136	138	163	165	8.51	8.52	10.25	10.30		584		24

2,6-Dimethylheptane	8.41	8.50	26	28.7	135.2	138	163	165	8.49	8.52	10.24	10.30		584	24
3,3-Dimethylheptane	8.49	8.44	26	27.7	137.3	136	165	164	8.44	8.47	10.19	10.21		583	24
3,4-Dimethylheptane	8.70	8.62	29	31.0	140.6	141	168	168	8.69	8.59	10.48	10.44		587	23
3,5-Dimethylheptane	8.43	8.52	26	29.2	136.0	139	163	166	8.52	8.53	10.27	10.34		585	24
4,4-Dimethylheptane	8.51	8.35	24	26.0	135.2	134	163.0	161	8.45	8.42	10.19	10.12		582	24
2-Methyl-3-ethylhexane	8.55	8.53	27	29.6	138.0	139	165.6	166	8.60	8.53	10.48	10.34		585	24
2-Methyl-4-ethylhexane	8.43	8.44	24	27.7	133.8	136	161	164	8.52	8.47	10.27	10.21		583	24
3-Methyl-3-ethylhexane	8.70	8.54	27	29.9	140.6	139	169	167	8.54	8.54	10.28	10.35		586	23
3-Methyl-4-ethylhexane	8.70	8.63	29	31.3	140.4	141	168	168	8.70	8.59	10.50	10.44		587	23
2,2,3-Trimethylhexane	8.36	8.36	23	26.2	134	134	161	161	8.31	8.43	10.02	10.13		582	24
2,2,4-Trimethylhexane	8.07	8.09	17	20.5	126.5	127	154	154	8.13	8.25	9.69	9.84		573	24
2,2,5-Trimethylhexane	7.99	8.08	16.2	20.2	124.1	127	151.1	154	8.07	8.25	9.601	9.84	569.9	573	24
2,3,3-Trimethylhexane	8.36	8.46	25	27.9	137.7	136	166	164	8.31	8.48	10.09	10.23		583	24
2,3,4-Trimethylhexane	8.59	8.54	27	29.9	139.0	139	167	167	8.53	8.54	10.26	10.34		586	23
2,3,5-Trimethylhexane	8.26	8.35	21	26.0	131.3	134	159	161	8.32	8.42	9.900	10.12		582	24
2,4,4-Trimethylhexane	8.25	8.18	19.9	22.4	130.6	129	158.3	157	8.20	8.31	9.76	9.92		577	24
3,3,4-Trimethylhexane	8.55	8.56	27	30.1	140.5	139	169	167	8.40	8.55	10.11	10.36		586	23
3,3-Diethylpentane	8.84	8.74	30.7	33.2	146.2	144	174.9	171	8.60	8.65	10.36	10.54		591	23
2,2-Dimethyl-3-ethylpentane	8.35	8.38	22	26.5	133.8	134	162	162	8.32	8.44	10.04	10.14		582	24
2,3-Dimethyl-3-ethylpentane	8.67	8.65	28	31.7	142	141	171	169	8.44	8.60	10.17	10.45		587	23
2,4-Dimethyl-3-ethylpentane	8.46	8.46	24	27.9	136.7	136	165	164	8.46	8.48	10.26	10.23		583	24
2,2,3,3-Tetramethylpentane	8.60	8.48	26.1	28.5	140.3	137	168.9	165	8.43	8.50	9.80	10.27		584	24
2,2,3,4-Tetramethylpentane	8.32	8.29	20.9	24.6	133.0	132	161.1	159	8.19	8.38	9.80	10.05		579	24
2,2,4,4-Tetramethylpentane	7.91	7.66	12.5	11.7	122.3	115	149.9	143	7.85	8.00	9.11	9.38		561	25
2,3,3,4-Tetramethylpentane	8.65	8.57	27.2	30.3	141.6	140	170.1	167	8.35	8.55	9.98	10.38		586	23

[a] Data obtained from Rossini (*10*) and Francis (*5, 6*).

Following the suggestion first proposed by Wiener, an empirical equation was presented which correlates n^* with two structural parameters, the path number and the polarity number. As shown in the third and fourth columns of Table VII, Equation 41 agreed with $n^*_{\text{obsd.}}$ in spite of the simplicity in form. However, it is also a matter of course that a more elaborate equation containing more than two structural parameters should lead to a more close approximation for n^*. Examples of such additional parameters may be found in a recent article by Greenshields and Rossini (*7*).

NOMENCLATURE

f = free energy related to intramolecular degrees of freedom
k = Boltzmann constant
N = Avogadro number
n = carbon number of paraffin hydrocarbons
n^* = effective carbon number
Δn = $n - n^*$
P = pressure
P_c = critical pressure
p = polarity number
Δp = p(normal) − p(isomer)
R = gas constant
s = entropy part of the interaction free energy between two chain elements
T = absolute temperature
T_b = general boiling point
T_b^0 = normal boiling point
ΔT_b^0 = T_b^0(normal) − T_b^0(isomer)
T_c = critical temperature
T_m = melting point
v = volume occupied by a molecule
V_c = critical volume
v_c = critical volume per molecule
w = path number
Δw = w(normal) − w(isomer)
x = number of consective cells occupied by a molecule
z = number of the nearest neighbor cells
ϵ = energy part of the interaction free energy between two
= chain elements
Λ = molar heat of vaporization, cal./mole
Λ^0 = molar heat of vaporization at normal boiling point, cal./mole
μ = chemical potential
τ = volume of cell

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