The Normal Boiling Points and Critical Constants of Saturated Aliphatic Hydrocarbons

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Several methods are available in the literature for the prediction of the critical constants of pure substances. Watson (*12*) has proposed an approach for the estimation of the critical temperature of a substance from its molecular weight, normal boiling point, and the corresponding liquid density. Riedel (*5, 6*) developed a procedure for the calculation of the critical temperature and pressure of any hydrocarbon from group contributions, the normal boiling point, and the molecular weight of the substance. This method was refined by Lydersen (*1*) who extended it to include the calculation of the critical volume. Thodos (*8, 9, 10, 11*) developed a procedure for the estimation of the van der Waals' constants of hydrocarbons of all types from structural considerations. The critical temperature, pressure, and volume of these substances can then be calculated through the use of established relationships between these quantities and the van der Waals' constants. Although the methods which utilize group contributions have proved to be of a high degree of accuracy in establishing critical constants, the application of these methods to saturated aliphatic hydrocarbons is frequently ambiguous because of the uncertainty of the correct pattern to be followed in the synthesis of the molecule. Therefore it would be desirable to develop an alternate procedure for the prediction of the critical constants of saturated aliphatic hydrocarbons from the structure of the molecule which does not possess the ambiguities of the existing methods.

The approach developed by Wiener (*13*) and Platt (*4*) for the calculation of the normal boiling points of saturated aliphatic hydrocarbons is capable of producing values of a high degree of accuracy. This method utilizes the following equation for the normal boiling point:

$$T_b = a\frac{w}{N^2} + bp + c \qquad (1)$$

The polarity number p is defined as the number of pairs of carbon atoms which are separated by three carbon-carbon bonds. The path number w is defined as the sum of the products of the number of carbon atoms on one side of each carbon-carbon bond of the molecule multiplied by those on the other side. For the normal paraffins the structural variables are

$$p_n = N - 3 \qquad (2)$$

and

$$w_n = \frac{1}{6}(N-1)(N)(N+1) \qquad (3)$$

In the present study the approach suggested by Wiener (*13*) and Platt (*4*) for the calculation of normal boiling points has been extended to include the calculation of the critical constants, T_c, P_c, v_c, and z_c, of saturated aliphatic hydrocarbons.

Table 1. Results of Comparisons Between Calculated and Experimental Boiling Points of Saturated Aliphatic Hydrocarbons

	Number	Average deviation °K.	Per cent
Propane	1	0.23	0.10
Butanes	2	0.25	0.24
Pentanes	3	0.19	0.06
Hexanes	5	0.19	0.06
Heptanes	9	0.59	0.16
Octanes	18	0.66	0.17
Nonanes	35	1.30	0.33
Decanes	75	2.87	0.66
Total	148		0.45

NORMAL BOILING POINTS

By the use of Equation (1) the normal boiling point of an isomeric aliphatic hydrocarbon T_{bi} can be related to the normal boiling point of the corresponding normal paraffin T_{bn} as follows:

$$T_{bn} - T_{bi} = a\left(\frac{w_n - w_i}{N^2}\right) + b(p_n - p_i) \qquad (4)$$

Wiener (*13*) and Platt (*4*) calculated the constants a and b of Equation (4) by the use of the normal boiling-point data then available in the literature for the aliphatic hydrocarbons through the octanes. The data currently available for the normal boiling points of all aliphatic hydrocarbons through the nonanes (*7*) were utilized in the present study to establish the constant a as the slope and constant b as the intercept of the straight line which resulted when the quantity $\Delta T_b/\Delta p$ was plotted against $\Delta(w/N^2)/\Delta p$.

As shown in Figure 1 the resulting relationship for the normal boiling point of any isomeric saturated aliphatic hydrocarbon is

$$T_{bi} = T_{bn} - 96.52\Delta\left(\frac{w}{N^2}\right) - 5.45\,\Delta p \qquad (5)$$

Platt (*3*) has proposed the following equation for the normal boiling points of the normal paraffins:

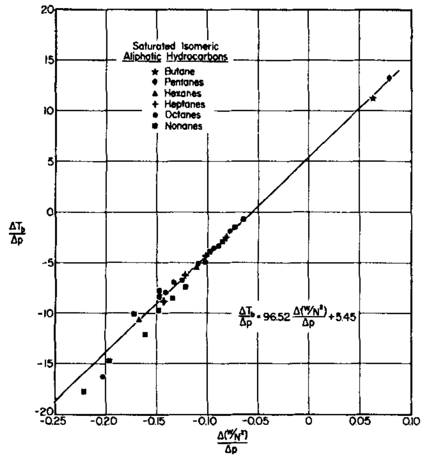


Fig. 1. Relationship between $\Delta T_b/\Delta p$ and $\Delta(w/N^2)/\Delta p$ for the saturated aliphatic hydrocarbons through the nonanes.

$$T_{bn} = 1{,}209.59 - \frac{1{,}162.91}{1 + 0.074189\, N^{0.85}} \tag{6}$$

Therefore Equations (5) and (6) can be used to calculate the normal boiling point of any aliphatic hydrocarbon from the structural variables p and w. In the calculation of boiling points from Equation (5), Equations (2) and (3) should be used to obtain p_n and w_n.

Equations (5) and (6) were used to calculate normal boiling points for all the saturated aliphatic hydrocarbons from propane through the decanes. The resulting deviations both in degrees and in per cent are presented in Table 1 for each isomeric group. The overall average deviation for 148 hydrocarbons was 0.45%. The larger deviations for the heavier hydrocarbons may result from the increased uncertainties in the experimental measurements for these substances.

CRITICAL TEMPERATURES

By the use of an analogous procedure the quantity $\Delta T_c/\Delta p$ calculated from experimental values of the critical temperatures of the saturated aliphatic hydrocarbons through the octanes (2) was plotted vs. $\Delta\left(\frac{w}{N^2}\right)/\Delta p$, as shown in Figure 2. The relationship obtained for the difference between the critical temperature of a normal paraffin and of an isomeric aliphatic hydrocarbon containing the same number of carbon atoms is

$$\Delta T_c = 109.25\Delta\left(\frac{w}{N^2}\right) + 9.61\Delta p \tag{7}$$

In order to calculate critical temperatures for the isomeric hydrocarbons from Equation (7) it is necessary to have a relationship for the critical temperature of the corresponding normal paraffin. Therefore it was assumed that a relationship of the form of Equation (1) could be developed for the critical temperature of a normal paraffin in which the constants a, b, and c were all independent of the number of carbon atoms in the molecule. The available values of the critical temperatures of the normal paraffins from propane through octane were utilized in conjunction with a least-squares procedure to determine the values of these constants. The resulting relationship for the critical temperature of a normal paraffin can be expressed as follows:

$$T_{cn} = 2321.7\frac{w_n}{N^2} - 363.17p_n - 660.98 \tag{8}$$

Equations (7) and (8) permit the calculation of the critical temperature of any saturated aliphatic hydrocarbon from its structural variables and the relationships of Equations (2) and (3).

CRITICAL PRESSURES

Similarly the quantity $\Delta P_c/\Delta p$ was calculated from the reported experimental values of the critical pressures of the saturated aliphatic hydrocarbons through the octanes (2) and was plotted against $\Delta\left(\frac{w}{N^2}\right)/\Delta p$ to produce the following relationship for the critical pressure difference $P_{cn} - P_{ci}$:

$$\Delta P_c = -6.667\,\Delta\left(\frac{w}{N^2}\right) + 0.283\Delta p \tag{9}$$

An approach similar to that utilized in the development of a relationship for the critical temperatures of normal paraffins was employed to obtain the following equation for the critical pressures of these substances:

$$P_{cn} = 47.39p_n - 294.64\frac{w_n}{N^2} + 174.21 \tag{10}$$

Thus the critical pressure of any saturated aliphatic hydrocarbon can be calculated from Equations (9) and (10) and the structural variables w, p, and N.

CRITICAL VOLUMES

The reciprocal of the critical volume $1/v_c$ had to be utilized in order to obtain an effective correlation for this property. By the use of the approach employed for the critical temperatures and pressures the following equations were developed from reported critical

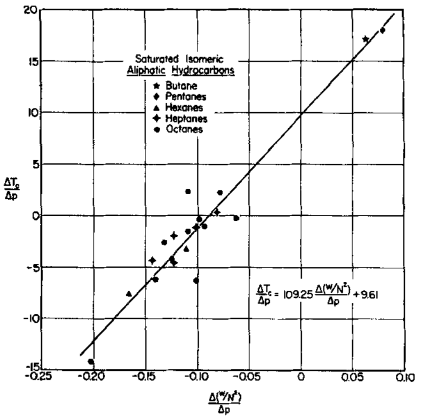


Fig. 2. Relationship between $\Delta T_c/\Delta p$ and $\Delta(w/N^2)/\Delta p$ for the saturated aliphatic hydrocarbons through the octanes.

volumes of the saturated aliphatic hydrocarbons through the octanes:

$$\Delta\left(\frac{1}{v_c}\right) = 2.84 \times 10^{-6}\,\Delta p - 5.604 \times 10^{-4}\,\Delta\left(\frac{w}{N^2}\right) \tag{11}$$

and

$$\frac{1}{v_{cn}} = 0.011719\,p_n - 0.070896\frac{w_n}{N^2} + 0.036497 \tag{12}$$

These equations permit the calculation of the critical volume of any saturated aliphatic hydrocarbon from the structural variables w, p, and N.

CRITICAL COMPRESSIBILITY FACTORS

Although the critical compressibility factor of a saturated aliphatic hydrocarbon can be calculated from the corresponding critical temperature, pressure, and volume, it would be desirable to have expressions from which this quantity could be calculated directly. Consequently the method used for the development of relationships for the other critical constants was employed to relate the critical compressibility factor to the structural variables. As for the critical volume, the reciprocal of the critical compressibility factor had to be employed in the development. The following equations resulted:

$$\Delta\left(\frac{1}{z_c}\right) = 0.5333\,\Delta\left(\frac{w}{N^2}\right) + 0.00951\,\Delta p \tag{13}$$

and

$$\frac{1}{z_{cn}} = 2.9375 + 0.1769\,p_n + 1.421\frac{w_n}{N^2} \tag{14}$$

TABLE 2. AVERAGE DEVIATIONS OF CRITICAL CONSTANTS FROM THIS STUDY AND COMPARISONS WITH OTHER METHODS

	No. of points	Average deviation, %			
		This study	Riedel (5,6)	Lydersen (1)	Thodos (9)
Critical temperature	37	0.55	0.80	0.60	0.51
Critical pressure	37	1.98	5.64	3.75	1.21
Critical volume	36	1.47	—	2.16	1.28
Critical compressibility factor	36	0.93	—	—	—

The critical compressibility factor of any saturated aliphatic hydrocarbon can be calculated from Equations (13) and (14).

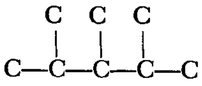
RESULTS AND CONCLUSIONS

The approach developed in this study for the calculation of the normal boiling point and the critical constants of a saturated aliphatic hydrocarbon is illustrated in the following example.

Example

Calculate the normal boiling point and critical constants of 2,3,4-trimethylpentane from its molecular structure.

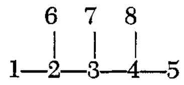
The path number can be easily calculated by representing the substance structurally:



For a bond joining a methyl group to a carbon atom the contribution to w is 1×7. There are five bonds of this type. For the other two bonds of the substance which have three carbon atoms on one side and five on the other the contribution of each bond is 3×5. Therefore the path number for this hydrocarbon becomes

$$w = 5(1 \times 7) + 2(3 \times 5) = 65$$

The polarity number can best be calculated by arbitrarily designating with a number each carbon atom in the above structural representation, as follows:



For this substance the following pairs of carbon atoms are separated by three carbon-carbon bonds:

14	25	64	75
17	28	67	78

Therefore for 2,3,4-trimethylpentane $p = 8$.

From Equations (2) and (3), the structural variables of the corresponding normal paraffin n-octane are

$$p_n = 8 - 3 = 5$$

and

$$w_n = \frac{1}{6}(8-1)(8)(8+1) = 84$$

Therefore

$$\Delta\left(\frac{w}{N^2}\right) = \frac{84-65}{8^2} = 0.2969$$

and

$$\Delta p = 5 - 8 = -3$$

From Equation (6) the normal boiling point of n-octane is found to be $T_{bn} = 398.91°\text{K}$. Therefore the normal boiling point of 2,3,4-trimethylpentane is calculated from Equation (5) to be

$$T_{bi} = 398.91 - 96.52\ (0.2969) - 5.45\ (-3) = 386.60°\text{K}.$$

This value should be compared with the experimental normal boiling point reported by Rossini et al. (7) for this substance, $T_{bi} = 386.63°\text{K}$.

The critical constants of n-octane are calculated from Equations (8), (10), (12), and (14) to be

$$T_{cn} = 569.24°\text{K}.$$

$$v_{cn} = 490.0 \text{ cc./g.-mole}$$

$$P_{cn} = 24.59 \text{ atm.}$$

$$z_{cn} = 0.2552$$

Therefore from Equations (7), (9), (11), and (13)

$$T_{ci} = 569.24 - 109.25\ (0.2969) - 9.61\ (-3) = 565.63°\text{K}.$$

$$P_{ci} = 24.59 + 6.667\ (0.2969) - 0.283\ (-3) = 27.42 \text{ atm.}$$

$$v_{ci} = 1/[1/490.0 + 5.604 \times 10^{-4}\ (0.2969) - 2.84 \times 10^{-6}\ (-3)] = 451.3 \text{ cc./g.-mole}$$

$$z_{ci} = 1/[1/0.2552 - 0.5333\ (0.2969) - 0.00951\ (-3)] = 0.2639$$

From the critical values reported by Kobe and Lynn (2) the following critical constants result for 2,3,4-trimethylpentane:

$$T_{ci} = 568.16°\text{K}.$$

$$v_{ci} = 446.2 \text{ cc./g.-mole}$$

$$P_{ci} = 27.6 \text{ atm.}$$

$$z_{ci} = 0.2640$$

Thus the critical constants calculated by the method developed in this study compare favorably with these values.

By the use of the method developed in this study critical constants were calculated for all the saturated aliphatic hydrocarbons from propane through the octanes and were compared with the corresponding reported values. The resulting deviations are presented in Table 2 and are compared with corresponding deviations resulting from the methods of Riedel (5, 6), Lydersen (1), and Thodos (9). It can be seen from Table 2 that the method of this study compares favorably with existing methods and is capable of producing reliable values of the critical constants of any saturated aliphatic hydrocarbon from only a knowledge of the molecular structure.

NOTATION

a, b = constants in Equation (1)
c = constant in Equation (1) for a given isomeric group
N = number of carbon atoms in the hydrocarbon
p = polarity number
P_c = critical pressure, atm.
T_b = normal boiling point, °K.
T_c = critical temperature, °K.
v_c = critical volume, cc./g.-mole
w = path number
z_c = critical compressibility factor

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