CRITICAL CONSTANTS OF UNSATURATED ALIPHATIC HYDROCARBONS

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The van der Waals' constants a and b evaluated from structural considerations of the unsaturated aliphatic hydrocarbons are used to calculate the critical constants for these types of compounds. For these unsaturated hydrocarbons, both van der Waals' constants are calculated through the additive contribution of unsaturated bonds to the van der Waals' constants of the corresponding saturated aliphatic hydrocarbons calculated according to a method previously proposed (6).

With both van der Waals' constants available, the critical temperatures, pressures, and volumes for these types of compounds can be obtained.

By use of this approach, the critical temperatures, pressures, and volumes of several olefins, diolefins, and acetylenes have been calculated. These calculated values have been compared whenever possible with values reported in the literature to produce an average percentage deviation of 1.3 for the critical temperature, 3.0 for the critical pressure, and 1.5 for the critical volume. In this comparison questionable literature values have been included, and consequently the reported deviations present the worst possible expectation.

The prediction of the critical constants of the unsaturated aliphatic hydrocarbons is a subject that has received little attention in the past, primarily because of the lack of sufficient information from which a generalized approach could be established for the estimation of these critical values. Critical constants for a limited number of olefins, diolefins, and acetylenes are reported in the literature survey of Kobe and Lynn (3) and constitute the only data used in this study. From this information a method is developed that can be applied for the prediction of critical constants for the unsaturated aliphatic hydrocarbons only from a knowledge of the chemical structure of these compounds.

In a similar investigation dealing with saturated aliphatic hydrocarbons, Thodos (6) presents a method for estimating for this type of compound the pressure and volume van der Waals' constants a and b, respectively, which in turn are used to define the critical temperature and pressure of these substances through the relationships

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

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

The evaluation of the van der Waals' constants for the saturated paraffins becomes possible by taking into account the additive contribution of these constants involved in the successive replacement of hydrogen by methyl groups until the desired saturated hydrocarbon structure is obtained. In this connection the contributions of both van der Waals' constants a and b were found to be additive with $a^{0.626}$ and $b^{0.76}$. The extension of this approach into the field of the unsaturated aliphatic hydrocarbons considers the removal of hydrogen atoms for the formation of unsaturated double and triple bonds from the corresponding saturated paraffins to produce the van der Waals' constants a and b for these unsaturated compounds.

From the screened literature critical constants of Kobe and Lynn (3) the critical temperatures and pressures of all the olefins, diolefins, and acetylenes for which values were available were used to calculate the pressure and volume van der Waals' constants a and b from the expressions

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

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

Both van der Waals' constants resulting from Equations (3) and (4) are unique for the calculation of the critical temperatures and pressures; however, the use of the volume van der Waals' constant b in the theoretical relationship

$$v_c = 3b \tag{5}$$

produces critical volumes for these unsaturated aliphatic hydrocarbons that are not in agreement with the values reported in the literature (3). A similar behavior has been found for the saturated aliphatic hydrocarbons by Thodos (6), who modified Equation (5) in order to produce critical volumes consistent with those reported in the literature. Thus introduction of the empirical volume factor β enables Equation (5) to assume the modified form

$$v_c = 3\beta b \tag{6}$$

Equation (6) when applied to the normal paraffins produced volume factors β that were found to depend only on the number of carbon atoms present in the molecule. Furthermore, it was also found (6) that the ratio of the volume factors for the isomeric paraffins to those of the corresponding normal paraffins maintained the approximate value of 1.032 and proved to be independent of the degree of branching.

Volume factors for the limited number of monoolefins for which critical volumes are available have been calculated with Equation (6). These volume factor values β_u when referred to those of the corresponding saturated aliphatic hydrocarbons produced the following ratios:

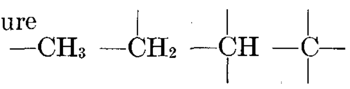
	$\frac{\beta_u}{\beta_s}$
Ethene	0.9429
Propene	0.9919
1-Butene	1.0090
2-Butene	0.9990
2-Methylpropene	0.9725
	0.9931

The average value of the ratio β_u/β_s with the exclusion of the value for ethene was found to be 0.9931 and is recommended for monoolefins. A similar treatment of the data for 1,3-butadiene and ethyne produced ratios of 0.9863 and 0.9609, respectively. As a result of this study, the following values for the volume factor ratios β_u/β_s are recommended:

	$\frac{\beta_u}{\beta_s}$
Monoolefins...............	0.9931
Diolefins..................	0.9863
Acetylenes................	0.9609

TREATMENT OF VAN DER WAALS' CONSTANTS

By means of an approach parallel to that carried out for the saturated aliphatic hydrocarbons (*6*), values of $a^{0.626}$ and $b^{0.76}$ were produced for the unsaturated hydrocarbons used in this investigation and were compared with the values of the corresponding saturated aliphatic hydrocarbons. This comparison was made in order to establish contributions involved in the removal of hydrogen atoms to produce unsaturated double and triple bonds. Contribution values $\Delta a^{0.626}$ and $\Delta b^{0.76}$ involved in the removal of hydrogen atoms to form unsaturated bonds were found to depend primarily on the nature of the carbon atoms involved before the removal of the hydrogen atoms. To differentiate between the different types of carbon atoms, the designation of Andersen, Beyer and Watson (*1*) has been used. Their method associates directly the type of carbon atom with the number of carbon-to-carbon bonds present in the saturated aliphatic hydrocarbon. Thus the following structures constitute the types of carbon atoms occurring with saturated paraffins:



Type	1	2	3	4
Structure	$-\text{CH}_3$	$\overset{\mid}{-\text{CH}_2}$	$\overset{\mid}{\underset{\mid}{-\text{CH}}}$	$\overset{\mid}{\underset{\mid}{-\text{C}-}}$

and represent the types of carbon atoms always encountered in the introduction of the first double or triple bond. The contribution values $\Delta a^{0.626}$ and $\Delta b^{0.76}$ associated with the introduction of a second double bond have been found to depend on the nature of the carbon atoms directly involved in the formation of the bond and the nature of the carbon atoms adjacent to them. The adjacent carbon atoms may be attached to a double bond that influences the contribution value associated with the introduction of the second unsaturated bond. This condition necessitates a somewhat different classification of carbon atoms, and consequently the following designation has been adopted:

Type	$\dot{3}$	$\dot{4}$
Structure	$\overset{H}{=\text{C}-}$	$=\text{C}=$

The contribution values $\Delta a^{0.626}$ and $\Delta b^{0.76}$ resulting from the literature data are limited in number and do not as such represent all the possible cases that can arise. In order to present a larger number of combination types, the available information was extrapolated and interpolated as well as possible to produce the average contribution values reported in Table 1.

CALCULATION OF CRITICAL CONSTANTS

To illustrate the use of the method proposed in this investigation, the critical temperatures, pressures, and volumes of 1-butene, 1, 3-butadiene, and 1-butyne will be considered. For each of these substances, van der Waals' constants a and b must be produced, from which the critical temperature, pressure, and volume can be calculated. The van der Waals' constants for these unsaturated hydrocarbons can be calculated from the van der Waals' constants of the corresponding saturated paraffins. Thus from the work of Thodos (*6*) for *n*-butane, $a^{0.626} = 29{,}379$, $b^{0.76} = 37.137$, and $\beta_s = 0.7314$.

1-Butene

n-butane	29,379	37.137
from Table 1, first double bond (1-2)..........	— 1,518	— 1.940
	$a^{0.626} = 27{,}861$;	$b^{0.76} = 35.197$

$a = 12.603 \times 10^6$ (cc./g.mole)^2 atm., $b = 108.36$cc./g. mole

$$T_c = \frac{8a}{27\,Rb} = \frac{8\,(12.608 \times 10^6)}{27\,(82.055)\,(108.36)} = 420.1°\text{K.}$$

$$p_c = \frac{a}{27\,b^2} = \frac{12.608 \times 10^6}{27\,(108.36)^2} = 39.77 \text{ atm.}$$

for monoolefins: $\beta_u/\beta_s = 0.9931$; therefore, $\beta_u = 0.9931(0.7314) = 0.7264$

$$v_c = 3\beta_u = 3(0.7264)\,(108.36) = 236.1 \text{ cc. g. mole}$$

Kobe and Lynn (*3*) report for 1-butene critical values of 419.6°K., 39.7 atm., and 239.7 cc./g. mole.

1,3-Butadiene

n-butane	29,379	37.137
from Table 1,; first double bond (1-2)..........	— 1,518	— 1.940
second double bond ($1\text{-}2 \rightarrow \dot{3}$).....................	— 792	— 1,549
	$a^{0.626} = 27{,}069$;	$b^{0.76} = 33.648$

$a = 12.041 \times 10^6$ (cc./g. mole)^2 atm., $b = 102.13$ cc./g. mole

$$T_c = \frac{8a}{27\,Rb} = \frac{8\,(12.041 \times 10^6)}{27\,(82.055)\,(102.13)} = 425.7°\text{K.}$$

$$p_c = \frac{a}{27\,b^2} = \frac{12.041 \times 10^6}{27\,(102.13)^2} = 42.76 \text{ atm.}$$

for diolefins: $\beta_u/\beta_s = 0.9863$; therefore, $\beta_u = 0.9863(0.7314) = 0.7214$

$$v_c = 3\beta_u b = 3(0.7214)\,(102.13) = 221.0 \text{ cc./g. mole}$$

Kobe and Lynn (*3*) report for 1, 3-butadiene critical values of 425.2°K., 42.7 atm. and 220.8 cc./g. mole.

1-Butyne

n-butane	29,379	37.137
from Table 1, triple bond (1-2)................	— 942	— 3.260
	$a^{0.626} = 28{,}437$;	$b^{0.76} = 33.877$

$a = 13.027 \times 10^6$ (cc./g. mole)^2 atm., $b = 103.04$ cc./g. mole.

$$T_c = \frac{8a}{27\,Rb} = \frac{8\,(13.027 \times 10^6)}{27\,(82.055)\,(103.04)} = 456.5°\text{K.}$$

$$p_c = \frac{a}{27\,b^2} = \frac{13.027 \times 10^6}{27\,(103.04)^2} = 45.44 \text{ atm.}$$

for acetylenes: $\beta_u/\beta_s = 0.9609$; therefore $\beta_u = 0.9609(0.7314) = 0.7028$

$$v_c = 3\beta_u b = 3\,(0.7028)\,(103.04) = 217.2 \text{ cc./g. mole.}$$

Kobe and Lynn (*3*) report for 1-butyne a critical temperature of 463.7°K. and no critical pressure and volume.

TABLE 2.—CALCULATED VAN DER WAALS' CONSTANTS AND COMPARISON OF CALCULATED AND REPORTED CRITICAL TEMPERATURES, PRESSURES AND VOLUMES FOR SOME OLEFINS, DIOLEFINS, AND ACETYLENES

	Calculated van der Waals' Constants				Calculated			Literature (3)			Percentage deviation		
	$a^{0.626}$	$b^{0.76}$	a (cc./g. mole)^2 atm.	b cc./g. mole	T_c, °K.	p_c, atm.	v_c, cc./g. mole.	T_c, °K.	p_c, atm.	v_c, cc./g. mole	T_c	p_c	v_c
Olefins													
Ethene..........	14,633	21.742	4.507×10^6	57.49	283.1	50.51	129.9	283.1	50.5	123.6	0.00	−0.02	−5.10
2-Methylpropene......	27,790	35.234	12.556	108.51	417.8	39.50	244.0	417.9	39.5	238.7	0.02	0.00	2.22
3-Methyl-1-butene	33,122	41.076	16.620	132.73	452.2	34.94	293.0	464.8	33.9	......	2.71	−3.07	
1-Dodecene........	79,197	88.685	66.898	365.56	660.8	18.54	680.2						
1-Eicosene........	130,533	142.173	148.62	680.38	788.8	11.89	1049						
Diolefins													
1, 3-Butadiene........	27,069	33.648	12.040	102.13	425.7	42.76	221.0	425.2	42.7	220.8	−0.12	−0.14	−0.11
1, 4-Pentadiene........	32.760	39.943	16.330	127.98	460.7	36.92	271.9						
1, 5-Hexadiene........	39,177	46.629	21.732	156.90	500.2	32.70	327.1	507.6	....	....	1.46		
Acetylenes													
Ethyne..........	14,431	19.992	4.408	51.48	309.2	61.61	112.5	309.2	61.6	112.7	0.00	−0.02	0.19
Propyne..........	22,020	27.191	8.658	77.16	405.2	53.86	165.7	401.2	52.8	....	−1.00	−2.01	
											1.30*	2.99*	1.50*
											0.78†	0.63‡	0.90**

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*All deviations included in average value.

†Deviations of propadiene and 2-butyne not included.

‡Deviations of 1-pentene, 2-pentene, and 2-methyl-2-butene not included.

**Deviation of ethene not included.

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TABLE 1.—CONTRIBUTION VALUES, $\Delta a^{0.626}$ AND $\Delta b^{0.76}$, INVOLVED IN THE REMOVAL OF HYDROGEN ATOMS FROM SATURATED ALIPHATIC HYDROCARBONS TO PRODUCE UNSATURATED BONDS

	$\Delta a^{0.626}$	$\Delta b^{0.76}$
A. First double bond		
1–1	−1,941	−2.126
2–1	−1,518	−1.940
2–2	—1,204	—2.123
3–1	— 801	−1.692
3–2	— 561*	−1.858*
B. Second double bond		
3–1	— 610*	−1.158*
$\dot{3}$–1	— 713*	−1.814*
3–2	— 428*	−1.811*
$\dot{3}$–2	— 670*	−1.978*
$\dot{3}$–3	— 637*	−2.142*
$\dot{3}\leftarrow$2–1	— 792	−1.549
$\dot{3}\leftarrow$2–2	— 610*	−1.68*
$\dot{4}\leftarrow$2–1	— 750*	−1.615
C. Triple bond		
1–1	−2,143	−3.876
1–2	— 942	−3.260
2–2	— 628*	−3.443*

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*Estimated values.

Arrow points away from the carbon atoms involved in the formation of unsaturate bonds and toward the type of carbon atoms adjacent to them.

COMPARISON OF RESULTS

Following a similar approach, the critical temperatures, pressures, and volumes of forty-four unsaturated hydrocarbons, including olefins, diolefins, and acetylenes, have been calculated and appear in Table 2, where the calculated values are compared with those available in the literature (*3*) to produce average absolute deviations of 1.3% for the critical temperature, 3.0% for the critical pressure, and 1.5% for the critical volume. In these comparisons questionable literature values have been included and consequently the foregoing deviations present the worst possible expectation.

In order to compare the validity of the present method, critical values have been calculated by the methods of Riedel (*4, 5*) and Lydersen (*2*). Riedel utilizes a method involving group contributions and the molecular weight to calculate the critical pressure (*4*) and the normal boiling point to establish the critical temperature (*5*). Lydersen (*2*) refines the method of Riedel(*4, 5*) and extends his work to include the critical volume. Critical values for the unsaturated aliphatic hydrocarbons, for which literature data are available and appear in Table 2, have been calculated by these methods and compared to produce the following average percentage deviations:

Critical value	(*4,5*)	(*2*)	This work
Temperature	1.53	1.71	1.30
Pressure	3.58	3.70	2.99
Volume	....	1.97	1.50

The comparisons in the present investigation appearing in Table 2 point to significant deviations of critical temperature for propadiene and 2-butyne, of critical pressure for the pentenes and 2-methyl-2-butene, and of critical volume for ethene. If the deviations for these compounds are not included in the over-all average values, the deviations become 0.78% for the critical temperature, 0.63% for the critical pressure, and 0.90% for the critical volume.

NOTATION

a = pressure van der Waals' constant, (cc./g. mole)^2 atm.
b = volume van der Waals' constant, cc./g. mole
p_c = critical pressure, atm.
R = gas constant, 82.055 (atm.) (cc.) / (g. mole) (°K.)
T_c = critical temperature, °K.
v_c = critical volume, cm./g. mole
β_s = volume factor for saturated aliphatic hydrocarbons
β_u = volume factor for unsaturated aliphatic hydrocarbons

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CRITICAL CONSTANTS OF SATURATED ALIPHATIC HYDROCARBONS

Through the use of group contributions the van der Waals' constants, *a* and *b*, were estimated for a number of saturated aliphatic hydrocarbons from a knowledge of the chemical structure of these compounds and were used to define the critical temperature and pressure of these substances.

By the use of methane as the base group, both van der Waals' constants were estimated for a number of saturated aliphatic hydrocarbons of considerable size and complexity through the additive contribution of methyl groups in the seccessive substitution of hydrogen until the desired structure of the substance was obtained. For the normal saturated hydrocarbons these contributions were found to be additive for the evaluation of $a^{0.626}$ and $b^{0.76}$ up through *n*-octane, and these exponents have been assumed to apply in the scaling up of larger normal and isomeric hydrocarbon molecules for which experimental data are lacking.

The volume van der Waals' constant *b* alone serves to define the critical volume of these compounds through the expression $v_c = 3\,\beta\,b$, where β represents a factor which has been found to depend on the size and arrangement of the molecule.

By following this procedure the critical temperatures, pressures and volumes of the normal saturated hydrocarbons through eicosane ($C_{20}H_{42}$), inclusive, and all the isomeric hydrocarbons up to and through the nonanes were calculated and compared, whenever possible, with values already available in the literature with an agreement of 0.43% for the estimation of the critical temperature, 0.69% for the critical pressure, and 0.86% for the critical volume. A combined consideration of these average deviations points to the estimation of the critical constants of the aliphatic saturated hydrocarbons with an average error of 0.7%.

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The ever-present problem of the prediction of the critical constants of substances has received considerable attention from a number of investigators. For the estimation of the critical values some of the common physical properties of a substance such as density, normal boiling point, molecular weight, and surface tension have been used as correlating variables. When information is available, these properties prove satisfactory for estimating the critical constants for a

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