Vapor Pressures: Unsaturated Aliphatic Hydrocarbons

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Vapor-pressure data available in the literature for olefins, diolefins, and acetylenes have been used to establish the constants of the Frost-Kalkwarf equation (9). This equation requires the establishment of constants *A, B, C,* and *D* and defines accurately the vapor-pressure function over the complete range included between the triple point and the critical point. Constant *D* has been shown to be equal to $a/2.303R^2$. Both van der Waals' constants can be predicted from the molecular structure *(33),* thus enabling the calculation of the critical temperatures and pressures for these unsaturated hydrocarbons. Constant *B* has been found also to depend on the molecular structure of these hydrocarbons.

The normal boiling point of an aliphatic hydrocarbon in conjunction with its critical point and the values *B* and *D* calculated from structural considerations permit the calculation of constants *A* and *C*. All four vapor pressure constants were calculated for twenty-seven monoolefins, nine diolefins, and five acetylenes for which reliable vapor-pressure data are presented in the literature. Comparisons between calculated values and values reported in the literature produced an average percentage deviation of 0.63 for the monoolefins, 2.65 for the diolefins, and 1.13 for the acetylenes. For the forty-one unsaturated aliphatic hydrocarbons considered in this investigation the average deviation was 1.14% for the randomly selected points of comparison.

The vapor-pressure behavior of the saturated aliphatic hydrocarbons has been studied extensively for the normal- and branched-chain paraffins (*32*). In order to reproduce the vapor-pressure function accurately for these compounds the Frost-Kalkwarf equation (*9*)

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

has been applied because of its inherent accuracy over the range included between the triple and critical point. The constants *A*, *B*, *C*, and *D* have been calculated for the light normal paraffins, from methane through *n*-dodecane by Perry and Thodos (*24*) who used four reliable vapor pressures, which included the normal boiling points and the critical points of these hydrocarbons. Their approach produced an average deviation of 0.27%, when the experimental points used in establishing the vapor-pressure constants are properly distributed over the entire vapor-pressure function. Reliable data in the high-pressure region are available for a limited number of compounds. Consequently accurate vapor-pressure constants can be properly established only for this limited number of hydrocarbons. Because of these limitations Sondak and Thodos (*32*) extended their studies to permit the prediction of these vapor-pressure constants from only a single vapor-pressure measurement and a knowledge of the molecular structure of the saturated aliphatic hydrocarbon. Thus experimental data over the entire vapor-pressure range are no longer necessary.

From molecular-structure considerations both van der Waals' constants *a* and *b* can be calculated (*33, 34*) for the saturated and unsaturated aliphatic hydrocarbons. These van der Waals' constants define the critical temperature and pressure. As pointed out by Frost and Kalkwarf (*9*) the pressure van der Waals' constant *a* establishes the constant D, as $a/2.303\ R^2$.

For the saturated aliphatic hydrocarbons attempts to correlate constant *C* with the molecular structure have proved unsuccessful. However constant *B* can be predicted from the molecular structure of the saturated aliphatic hydrocarbons (*32*). In this connection the constant *B* was found to be

$$-B = B_o + \Sigma\Delta B \qquad (2)$$

To produce the necessary reference values to be used with the unsaturated aliphatic hydrocarbons the following relationship should be used:

$$[-B]^{0.88} = [B_o]^{0.88} + \Sigma[\Delta B]^{0.88} \qquad (3)$$

Equation (3) also produces reliable values of *B* for the vapor pressures of saturated hydrocarbons.

ESTABLISHMENT OF CONSTANTS B AND C FROM VAPOR-PRESSURE DATA

In order to establish the constants *B* and *C* represented by Equation (1) from reported vapor-pressure data the approach used for the saturated aliphatic hydrocarbons (*32*) was adopted in this investigation. With constant *D* determined from the pressure van der Waals' constant *a* (*33*), a single-reference vapor-pressure point suffices to transform Equation (1) into the linear function

$$\frac{\log P/P_b - D\,[P/T^2 - P_b/T_b^2]}{\log T/T_b} = B\frac{1/T - 1/T_b}{\log T/T_b} + C \qquad (4)$$

in which constant *B* becomes the slope and constant *C* the intercept for the variables $Y = [\log P/P_b - D(P/T^2 - P_b/T_b^2)]/\log T/T_b$ and $X = [1/T - 1/T_b]/\log T/T_b$. In these studies the normal boiling point has been arbitrarily chosen as the reference point (P_b, T_b).

A typical relationship of *Y* vs. *X* is presented in Figure 1 for 1, 3-butadiene and covers the range of vapor pressures from 0.520 mm. of mercury at 164.245°K. to the critical point of 425.165°K. and 32,420 mm. of mercury. In this plot *Y* is a linear function of *X* and consequently substantiates the validity of Equation (1). Two arbitrarily well-selected points (*Y, X*) establish the slope *B* and intercept *C*. With constants *B*, *C*, and *D* known the normal boiling point suffices to determine constant *A*. This procedure was carried out for the unsaturated aliphatic hydrocarbons for which reliable vapor-pressure data were available and included 27 monoolefins, 10 diolefins, and 5 acetylenes. In the group of diolefins the data for propadiene obtained from different sources were found to be contradictory, and consequently the constants resulting from them are not reliable. Values of *B* and *C* produced by this procedure are summarized in Table 1 for all the unsaturated aliphatic hydrocarbons investigated. The values for constant *D* resulting from the pressure van der Waals' constant *a* are also summarized in this table along with the values of constant *A*. These four constants, *A*, *B*, *C*, and *D*, summarized in Table 1 are representative of the vapor-pressure data used in this study and should be used for the hydrocarbons presented in this table.

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TABLE 1. VAPOR-PRESSURE CONSTANTS FOR EQUATION.

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

Vapor-pressure constants obtained from comprehensive treatment of literature vapor-pressure data

	A	*-B*	*-C*	*D*	References
Monoolefins					
Ethene (ethylene)	17.13307	997.69	3.75709	0.38247	*5,8,14,16,26,33,36*
Propene (propylene)	19.13914	1404.59	4.26637	0.70426	*16,19,25,26,27,33,35*
1-Butene	21.10164	1741.32	4.82539	1.06992	*2,4,7,16,23,26,33*
2-Butene (cis)	22.04211	1858.82	5.10124	1.08927	*15,16,26,29,33*
2-Butene (trans)	20.80838	1777.27	4.69816	1.08927	*10,15,16,26,33*
2-Methylpropene	20.98074	1732.08	4.78547	1.06560	*3,6,16,26,28,33*
1-Pentene	22.39924	2032.28	5.16858	1.48982	*26,33*
2-Pentene (cis)	23.43136	2141.77	5.48099	1.51171	*26,33*
2-Pentene (trans)	22.96909	2115.69	5.32577	1.51171	*26,33*
2-Methyl-1-Butene	22.87410	2072.44	5.31356	1.45952	*26,33*
3-Methyl-1-Butene	21.53718	1916.60	4.91755	1.41039	*26,33*
2-Methyl-2-Butene	22.48491	2111.07	5.15025	1.47607	*16,26,33*
1-Hexene	24.16844	2350.64	5.66574	1.95969	*26,33*
1-Heptene	25.90236	2659.36	6.15555	2.47607	*17,26,33*
1-Octene	27.94965	2989.80	6.74267	3.03649	*26,33*
1-Nonene	29.80875	3305.67	7.27090	3.63841	*26,33*
1-Decene	31.65642	3616.05	7.79829	4.28021	*26,33*
1-Undecene	34.22903	3972.11	8.55951	4.96020	*26,33*
1-Dodecene	36.50519	4309.82	9.22339	5.67702	*26,33*
1-Tridecene	38.28717	4616.75	9.72614	6.42931	*26,33*
1-Tretradecene	40.86631	4975.21	10.48509	7.21656	*26,33*
1-Pentadecene	43.47018	5332.21	11.25312	8.03666	*26,33*
1-Hexadecene	45.25564	5634.61	11.75800	8.89002	*26,33*
1-Heptadecene	48.23626	6019.22	12.64332	9.77427	*26,33*
1-Octadecene	53.84430	6601.56	14.35501	10.69076	*26,33*
1-Nonadecene	54.60122	6840.82	14.52527	11.63611	*26,33*
1-Eicosene	58.87737	7341.11	15.80560	12.61201	*26,33*
Diolefins					
Propadiene	20.83333	1539.42	4.84117	0.66718	*16,18,26,33*
1,2-Butadiene	16.99020	1703.56	3.31016	1.02911	*26,33*
1,3-Butadiene	20.83612	1751.11	4.71334	1.02172	*11,26,30,33*
1,2-Pentadiene	21.99446	2147.04	4.94443	1.44357	*26,33*
1, cis 3-Pentadiene	23.49831	2204.65	5.46820	1.44764	*26,33*
1, trans 3-Pentadiene	22.31993	2128.84	5.08134	1.44764	*26,33*
1,4-Pentadiene	22.42851	2018.33	5.17484	1.38578	*16,26,33*
2,3-Pentadiene	25.49527	2347.77	6.11106	1.46521	*26,33*
3-Methyl-1,2-Butadiene	23.33390	2165.17	5.42913	1.36728	*26,33*
2-Methyl-1,3-Butadiene	21.78369	2042.25	4.93139	1.36914	*26,33*
Acetylenes					
Ethyne (acetylene)	18.37039	1188.90	4.03099	0.37407	*20,33,36*
Propyne	22.94034	1759.46	5.43367	0.73472	*13,22,33*
1-Butyne	25.47789	2051.26	6.25296	1.10548	*21,22,33*
2-Butyne	23.63336	2141.67	5.50057	1.12508	*12,22,33*
1-Pentyne	25.37711	2278.47	6.10440	1.53013	*22,33*

ESTABLISHMENT OF CONSTANT B FROM MOLECULAR STRUCTURE

The differences of constant *B*, Δ*B* for the monoolefins and corresponding saturated hydrocarbons were not found to be constant but increased with the number of carbon atoms present in the hydrocarbon. For instance these differences were found to be 72.90 for ethylene and ethane, 109.56 for 1-octene and *n*-octane, and 155.45 for 1-dodecene and *n*-dodecane. The ratios of *B* constants for the normal monoolefins having the double bonds in the 1-position to that of the corresponding normal paraffins were found to be essentially constant and equal to 0.968 for all the hydrocarbons from 1-pentene to 1-pentadecene, inclusive. However this behavior was not found to exist for the branched monoolefins and consequently did not present a general pattern capable of predicting constant *B* for monoolefins of all types.

Values of constant *B* for all the normal monoolefins having the double bond present in the 1-position, when plotted against the number of carbon atoms present in these hydrocarbons, produced an elongated S-shaped curve. This relationship exhibited a reversal of curvature above 1-butene and extended through 1-eicosene. In the related work of Sondak and Thodos (*32*) dealing with the saturated aliphatic hydrocarbons constant *B* was found to vary linearly with the number of carbon atoms present in the molecule since no definite trend existed for the heavier hydrocarbons. However in view of the definite curved behavior found to exist in this investigation for these normal monoolefins an S-shaped curve was assumed to apply to the corresponding correlation of Sondak and Thodos (*32*) dealing with the normal paraffins. For these monoolefins and normal paraffins straight-line relationships resulted when $[-B]^{0.88}$ was related to n_c, the number of carbon atoms present in the molecule inclusive in the range between 1-butene to 1-eicosene and *n*-butane to *n*-eicosane, respectively. These relationships are presented in Figure 2 for the normal paraffins and the corresponding monoolefins of 1-position. An extension of the linear portion of these relationships produces a common intercept of 278 for these straight lines which can be expressed analytically as

$$[-B_s]^{0.88} = 111.68\, n_c + 278 \qquad \text{(normal paraffins)} \qquad (5)$$

and

$$[-B_u]^{0.88} = 108.40\, n_c + 278 \qquad \text{(normal monoolefins of 1-position)} \qquad (6)$$

From Equations (5) and (6)

$$\frac{[-B_s]^{0.88} - [-B_u]^{0.88}}{n_c} = 3.28 \qquad (7)$$

The value of 3.28 of Equation (7) is characteristic of the contribution involved in the formation of a double bond on the end carbon atom of a normal paraffin. In order to expand this background to include other types of substitutions it becomes necessary to differentiate between the different types of carbon atoms involved in the formation of the unsaturated bond. The classification of Andersen, Beyer, and Watson (*1*) has been adopted and associates the type of carbon atom with the number of carbon-to-carbon bonds attached to it. Thus the following types of carbon atoms are possible for the saturated aliphatic hydrocarbons:

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

When one uses this classification, the contribution involved in the formation of a double bond in the 1-position becomes a 1-2 type of substitution for which the contribution value is 3.28. To produce contribution values for other types of substitutions involving the formation of a double or a triple

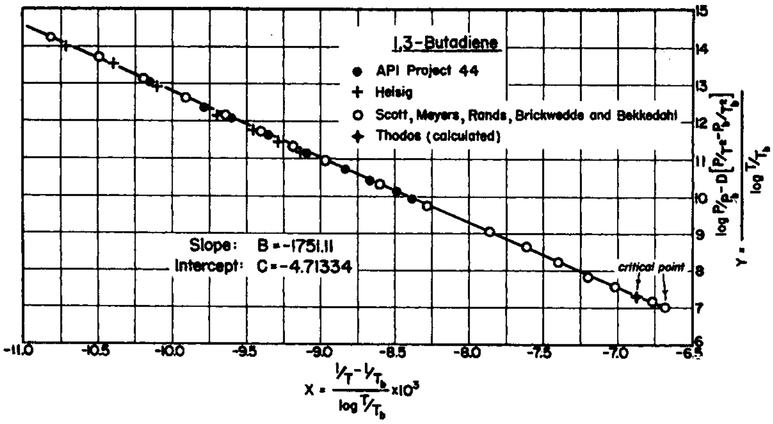

Fig. 1. Typical linear relationship of Y vs. X for 1,3-butadiene.

bond the following generalized expression

$$\gamma = \frac{[-B_s]^{0.88} - [-B_u]^{0.88}}{n_c} \tag{8}$$

has been used. For these types of substitutions values of γ have been calculated with Equation (8) from the values of constant B presented in Table 1 for several monoolefins and monoacetylenes and from the values of constant B for the corresponding saturated aliphatic hydrocarbons (32). These average contribution values are presented in Table 2 and are found to depend on the nature of the unsaturated bond produced and on the types of carbon atoms associated in its formation.

A comparable detailed analysis of constant B for the diolefins did not produce consistent results for the ratios of this value and that of the corresponding monoolefins and saturated aliphatic hydrocarbons. In addition the differences produced between constant B for the diolefins and the corresponding monoolefins and saturated aliphatic hydrocarbon varied and did not show any definite pattern. However upon application of Equation (8) consistent contribution values of γ were possible for the second double-bond formation when the corresponding monoolefin was used as the reference hydrocarbon. In view of this behavior Equation (8) can be expressed in the more generalized form

$$\gamma = \frac{[-B_r]^{0.88} - [-B]^{0.88}}{n_c} \tag{9}$$

For the second double-bond substitution, contribution values are also presented in Table 2.

Values of $[-B]^{0.88}$ for the saturated aliphatic hydrocarbons can be calculated from methyl-group contributions $\Delta[-B]^{0.88}$ established from the comprehensive analysis of constant B values for these compounds (32). From this comprehensive study group-contribution values of $\Delta[-B]^{0.88}$ have been produced for various types of substitutions, and the average values are presented in Table 3. With the base group value $[-B]^{0.88}$ for methane and the group contribution values $\Delta[-B]^{0.88}$ presented in Table 3 it now becomes possible through the successive substitution of hydrogen atoms by methyl groups to produce the vapor-pressure constant B for saturated aliphatic hydrocarbons of any size and degree of complexity. In making these substitutions the procedure proposed by Sondak and Thodos (32) has been adopted in this work and considers the replacement of hydrogen atoms by methyl groups from the longest normal paraffinic chain present in the hydrocarbon, beginning from the left end of the normal paraffin and making these substitutions always in a clockwise direction. These values of B are a requirement for the calculation of the value of B of the corresponding unsaturated aliphatic hydrocarbons. Therefore from the molecular structure the group contribution values $\Delta[-B]^{0.88}$ and the substitution values permit the evaluation of constant B for γ unsaturated hydrocarbons.

ESTABLISHMENT OF CONSTANTS A, C, AND D

Molecular structure considerations permit the evaluation of the van der Waals' constants a and b for unsaturated hydrocarbons (33). Since Frost and Kalkwarf (9) have shown that the constant D is related to the pressure van der Waals' constant a through the relationship

$$D = \frac{a}{2.303\,R^2} \tag{10}$$

Constant D now can be predicted from a knowledge of the molecular structure of these hydrocarbons. Following this approach, one can calculate values of D from molecular structural considerations for the unsaturated aliphatic hydrocarbons presented in Table 1. Since both van der Waals' constants can be calculated from the molecular structure of these compounds (33), these values can be used to define the critical temperatures and pressures of these substances through the relationships

$$T_c = \frac{8\,a}{27\,R\,b} \tag{11}$$

$$P_c = \frac{a}{27\,b^2} \tag{12}$$

Various attempts to correlate the constants C of these unsaturated hydrocarbons failed to present a consistent pattern capable of reproducing these values with the accuracy required by the general vapor-pressure equation. If the prediction of accurate values of constant C were possible from molecular structure, then the calculated critical point would suffice to define constant A. Unfortunately inasmuch as the accurate prediction of constant C was not possible, it became necessary to associate with the calculated critical point one reliable vapor-pressure point in order to define the vapor-pressure function in its entirety. For the sake of convenience this vapor-pressure point has been selected to be the normal boiling point. Therefore the normal boiling point and calculated critical point now permit the calculation of constants A and C, and thus with the predicted values of B and D allow a definition of the complete vapor-pressure function of the unsaturated aliphatic hydrocarbons.

TABLE 2. CONTRIBUTION VALUES γ FOR THE FORMATION OF UNSATURATED BONDS IN ALIPHATIC HYDROCARBONS

First double bond	γ
1-1	13.94
1-2	3.28
1-3	-6.34
2-2 (cis)	-5.57
2-2 (trans)	-1.00
2-3	-8.44
3-3	-12.40
Second double bond	
1-2	0.74
1-3	-12.70
2-2 (cis)	-12.10
2-2 (trans)	-6.80
2-3	-12.87
3-3	-17.53
First triple bond	
1-1	-22.39
1-2	-25.98
2-2	-33.11

APPLICATION OF PRESENT METHOD

In order to apply the method proposed in this investigation the calculation of vapor pressures for 1-butene and 1,3-butadiene will be considered. These hydrocarbons have normal boiling points of 266.905° and 268.752°K. respectively. With only this information the vapor-pressure constants are calculated as follows:

The van der Waals' constants a and b for these hydrocarbons have been calculated by Thodos (*33*) to be

	a (cc./g.-mole)^2 atm.	b cc./g.-mole
1-Butene	12.608×10^6	108.36
1,3-Butadiene	12.040×10^6	102.13

From Equations (11) and (12) the critical temperatures and pressures are calculated to be:

1-Butene:

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

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

1,3-Butadiene:

$$T_c = \frac{8\ (12.040 \times 10^6)}{27\ (82.055)\ (102.13)} = 425.7°\text{K.}$$

$$p_c = \frac{12.040 \times 10^6}{27\ (102.13)^2} = 42.76 \text{ atm.}$$

Constant D

Vapor-pressure constants D are calculated from Equation (10) to be

1-Butene:

$$D = \frac{(12.608 \times 10^6)\ 760}{2.303 (82.055 \times 760)^2} = 1.06992\ (°\text{K.})^2/\text{mm.}$$

1,3-Butadiene:

$$D = \frac{(12.040 \times 10^6)\ 760}{2.303\ (82.055 \times 760)^2} = 1.02172\ (°\text{K.})^2/\text{mm.}$$

Constant B

To calculate constant B for 1-butene it becomes necessary first to establish constant B for the reference substance, n-butane. Similarly to calculate constant B for 1,3-butadiene the value of constant B for 1-butene is used as the reference.

Establishment of Constant B for n-Butane

(a)	Base group - methane	265.19
(b)	Primary methyl group substitution on methane	198.33
(c)	Secondary methyl group substitutions:	
	$1 \leftarrow 1$	145.57
	$1 \leftarrow 2$	111.68
	$[-B]^{0.88} =$	720.77

With the value of $[-B]^{0.88} = 720.77$ for n-butane the corresponding value of B for 1-butene can be calculated from Equation (9). In this case $\gamma = 3.28$ for a 1-2 double-bond substitution. Therefore for 1-butene the value of constant B becomes

$$[-B]^{0.88} = 720.77 - 3.28\ (4) = 707.65$$

or

$$B = -1731.52 \text{ (1-butene)}$$

The value of constant B for 1,3-butadiene can also be obtained from Equation (9), in which the value of the reference substance is that of 1-butene. In this case the value of $\gamma = 0.74$ for the second double-bond substitution of the 1-2 type. Consequently constant B for 1,3-butadiene becomes

$$[-B]^{0.88} = 707.65 - 0.74\ (4) = 704.69$$

or

$$B = -1723.17 \text{ (1,3-butadiene)}$$

Constants A and C

In order to calculate constants A and C the critical point and normal boiling point are used in conjunction with the calculated values B and D. This procedure produces two linear equations that can be solved algebraically to establish these constants. Thus for 1-butene

$$\log (39.77 \times 760) = A - \frac{1731.52}{420.1}$$

TABLE 3. METHYL-GROUP CONTRIBUTION VALUES $\Delta[-B]^{0.88}$ FOR THE SATURATED ALIPHATIC HYDROCARBONS

Base group value: methane, $[-B]^{0.88} = 265.19$

Methyl-group contribution in the replacement $\Delta[-B]^{0.88}$ of hydrogen from methane 198.33

Methyl-group contributions in the replacement of hydrogen from saturated aliphatic hydrocarbons

1←1	145.57
2←1	111.68
3←1	102.21
4←1	89.47
1←2→1	83.01
1←2→2	64.68
1←2→3	56.26
2←2→2	75.43
2←2→3	66.23
1←3→1 ↓ 1	65.77
2←3→1 ↓ 1	52.17
3←3→1 ↓ 1	64.14
3←3→2 ↓ 1	35.79
4←3→1 ↓ 1	43.47
2←3→2 ↓ 1	39.77
3←3→3 ↓ 1	31.13

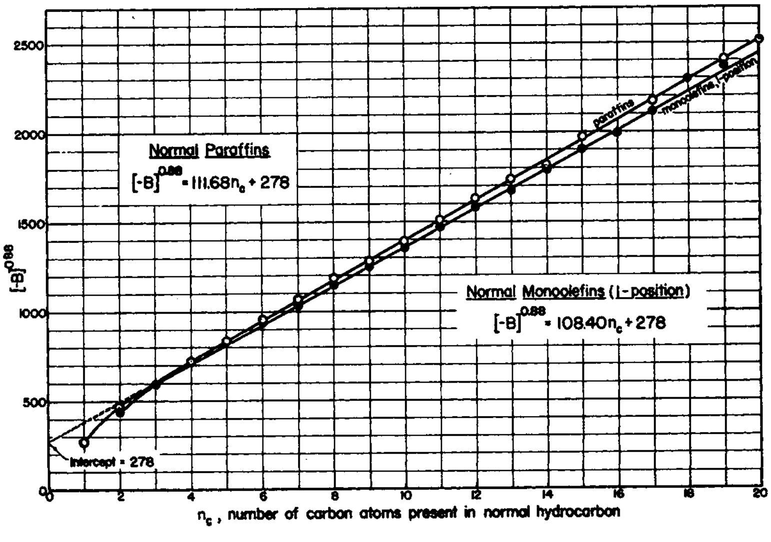

Fig. 2. Relationships of $[-B]^{0.88}$ vs. n_c, the number of carbon atoms present in the normal paraffinic and monoolefinic (1-position) hydrocarbons.

$$+ C \log 420.1 + 1.06992 \frac{39.77 \times 760}{(420.1)^2}$$

and

$$\log (760) = A - \frac{1731.52}{266.905}$$

$$+ C \log 266.905 + 1.06992 \frac{760}{(266.905)^2}$$

from which A and C are calculated to be $A = 20.91006$ and $C = -4.76156$. Similarly for 1,3-butadiene constants A and C become

$$\log (42.76 \times 760) = A - \frac{1723.17}{425.7}$$

$$+ C \log 425.7 + 1.02172 \frac{42.76 \times 760}{(425.7)^2}$$

and

$$\log (760) = A - \frac{1723.17}{268.752}$$

$$+ C \log 268.752 + 1.02172 \frac{760}{(425.7)^2}$$

from which A and C are calculated to be $A = 20.29240$ and $C = -4.53232$.

Vapor-Pressure Equations

With constants A, B, C, and D established the vapor-pressure function in its entirety can be defined as

1-butene:

$$\log P = 20.91006 - \frac{1731.52}{T}$$

$$- 4.76156 \log T + 1.06992 \frac{P}{T^2}$$

1,3-butadiene:

$$\log P = 20.29240 - \frac{1723.17}{T}$$

$$- 4.53232 \log T + 1.02172 \frac{P}{T^2}$$

For 1-butene Beattie and Marple (*4*) report a vapor pressure of 21,116 mm. Hg. at 398.165°K. For this temperature the vapor pressure of 1-butene is calculated to be

$$\log P = 20.91006 - \frac{1731.52}{398.165}$$

$$- 4.76156 \log 398.165$$

$$+ 1.06992 \frac{P}{(398.165)^2}$$

which reduces directly to

$\log P = 4.18097 + 0.00675 \times 10^{-3} P$
By trial and error P is found to be 21,037 mm. Hg.

For 1,3-butadiene Scott *et al.* (*30*) report a vapor pressure of 22,400 mm. Hg. at 403.165°K. For this temperature the vapor pressure of 1,3-butadiene is calculated to be

$$\log P = 20.29240 - \frac{1723.17}{403.165}$$

$$- 4.53232 \log 403.165$$

$$+ 1.02172 \frac{P}{(403.165)^2}$$

which reduces directly to

$\log P = 4.20942 + 0.00629 \times 10^{-3} P$
By trial and error P is found to be 22,405 mm. Hg.

VALIDITY OF PRESENT METHOD

Vapor-pressure constants A, B, C, and D have been calculated along the lines prescribed in the preceding sections and are presented elsewhere (*31*) for the unsaturated aliphatic hydrocarbons studied in this investigation. In order to establish the precision with which these calculated constants can reproduce the actual vapor-pressure function, equilibrium vapor pressure and temperature values obtained from the literature were randomly selected. For these equilibrium temperatures vapor pressures were calculated and compared with the values reported in the literature. Because of the transcendental nature of the general vapor-pressure equation due to the term $D(P)/(T^2)$ a trial-and-error procedure became necessary for the calculation of these vapor-pressure values.

Extensive comparisons between calculated and vapor pressures available in the literature have been made for the hydrocarbons presented in Table 1. The deviations cover the available vapor-pressure range on which these comparisons were made and consider the random selection of points included in these ranges. The ranges investigated varied and extended up to the critical point for those hydrocarbons for which literature data were available. Comparisons of calculated and literature vapor pressures for some typical unsaturated aliphatic hydrocarbons are presented elsewhere (*31*).

For the twenty-seven monoolefins for which vapor-pressure data are available in the literature the average absolute deviation was found to be 0.63%, whereas for the nine diolefins examined this deviation became 2.65%, and for the five acetylenes this deviation was 1.13%. For the forty-one unsaturated aliphatic hydrocarbons studied in this investigation the average deviation was 1.14%.

NOTATION

a = pressure van der Waals' constant (cc./g.-mole)^2 atm.
A = vapor-pressure constant, dimensionless
b = volume van der Waals' constant, cc./g.-mole
B = vapor pressure constant, °K.
B_o = vapor-pressure constant for base group methane, dimensionless
B_r = vapor-pressure constant for reference substance, dimensionless
B_s = vapor-pressure constant for saturated aliphatic hydrocarbon, dimensionless
B_u = vapor-pressure constant for monoolefins and monoacetylenes, dimensionless
C = vapor-pressure constant, dimensionless
D = vapor-pressure constant, (°K.)^2/mm. Hg
n_c = total number of carbon atoms present in the aliphatic hydrocarbon
p_c = critical pressure, atm.
P = vapor pressure, mm. Hg
P_b = atmospheric pressure, 760 mm. Hg
R = gas constant, 82.055 (cc.) (atm.)/(g.-mole) (°K.)
T = absolute temperature, °K. (273.165 + t°C.)
T_b = normal boiling point, °K.
T_c = critical temperature, °K.
$X = \left[\frac{1}{T} - \frac{1}{T_b}\right] / \log \frac{T}{T_b}, \frac{1}{°K.}$
$Y = \left[\log \frac{P}{P_b} - D\left(\frac{P}{T^2} - \frac{P_b}{T_b^2}\right)\right] / \log \frac{T}{T_b}$, dimensionless
γ = contribution value for formation of unsaturated bonds
ΔB = methyl-group contribution in the replacement of a hydrogen atom from aliphatic hydrocarbons, dimensionless

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Extractive Reaction: Batch- and Continuous-Flow Chemical-Reaction Systems, Concentrated Case

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The theory of extractive reaction is extended to concentrated solutions where the distribution coefficients are no longer constant and where important changes in phase volumes may occur. The methods developed are applicable to simple or complex reactions of any order. Two- and one-solvent systems are treated, and convenient graphical methods are developed and illustrated with numerical examples.

The yield of many reversible and irreversible reactions can be increased by the deliberate, controlled addition to the reaction system of an immiscible, extractive solvent phase (*8*). Such processes, which we have labeled *extractive reactions*, encompass several unit operations. They have often been used in industrial and laboratory practice without the common character of these apparently different operations being recognized. For example, for many years simultaneous reaction and distillation have been used to shift the equilibrium of such reactions as esterification and ester exchange (*1, 2, 6*). It will be seen here that the yield of other types of reactions, for example $A \rightarrow B \begin{smallmatrix} \nearrow C \\ \searrow D \end{smallmatrix}$, can likewise be increased over single-phase processes. Gas-absorption operations with simultaneous chemical reaction have been and continue to be the subject of numerous publications (9). Hofmann (*5*), for example, has recently shown how the conversion of pentosane to furfural can be increased by adding a solvent to the reacting system.

In a preceding paper two-solvent, two-phase extractive reactions occurring in batch or continuous stirred-tank reactor (CSTR) systems were considered, and complete analytical solutions were obtained for cases where the concentrations of the reactants are so low that the ratio of the two phases and the partition coefficients is constant (*8*).

The more complex problems of high concentrations and of reactions of any order are examined here. The limiting case of one-solvent systems is also considered, and convenient graphical solutions based on ternary equilibrium diagrams are developed.

Homogeneity within each phase and physical equilibrium between the two phases are, as before, assumed to result from sufficient agitation. Thus rates of mass transfer are herein considered not to affect the over-all rates of the reaction processes. Reaction is considered to occur in only one phase, no reaction occurs at the interface, and isothermal conditions prevail (*8*).

CONCENTRATED TWO-SOLVENT, TWO-PHASE SYSTEMS

Batch Systems

Consider a two-solvent, two-phase extractive-reaction batch process in

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