NOTATION

D = binary diffusion coefficient, sq.ft./hr.
E = plate efficiency
k = gas-side mass transfer coefficient, lb.moles/(hr.)(sq.ft.)(mole fraction)
m = moles of vapor in bubble, lb. moles
n = flux, lb.moles/(hr.)(sq.ft.)
N = number of transfer units
R = ratio of fluxes with and without interactions
S = area, sq.ft.
x = effective film thickness, ft.
X_j, X_c = mole fraction in liquid
y = mole fraction in gas

Greek Letters

γ = activity coefficient
δ_m = diffusional interaction term defined by Equation (4)
θ = time, hr.
ρ = molar density, lb.moles/cu.ft.
ϕ_o = diffusional interaction term defined by Equation (5)

Subscripts

A, B, C = species A, B, and C, respectively
b = binary value
i = interface
j = index which refers to species A or B
1, 2 = terminal points of diffusion path
I, II = entering and leaving plate, respectively

Superscripts

$*$ = equilibrium value
— = bulk mean value
$'$ = values at any vertical position on plate

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Critical Temperatures and Pressures of Organic Compounds

J. Charles Forman and George Thodos
The Technological Institute, Northwestern University, Evanston, Illinois

The approach presented for the prediction of critical temperatures and pressures for hydrocarbons from the van der Waals' constants *a* and *b* *(1)* has been extended to permit the estimation of these constants for other organic compounds. Analogously, contribution values for a number of functional groups have been established, and the majority were found to depend on the size of the organic molecule. Information presently available in the literature *(4)* has permitted the establishment of values for functional groups in organic compounds of the following types: alcohols, phenols, ethers, ketones, carboxylic acids and esters, amines, nitriles, and halides. These functional group contributions, in conjunction with the values previously developed for the hydrocarbons, now make possible the calculation of both van der Waals' constants from only structural considerations. Once these van der Waals' constants have been established, the critical temperature and pressure are readily calculated.

With the approach developed in this investigation critical temperatures and pressures for eighty-one organic compounds have been calculated and when compared with literature values produced average absolute deviations of 1.36% for the critical temperature and 2.82% for the critical pressure.

The use of van der Waals' constants has been presented at length for the calculation of the critical temperatures and pressures of hydrocarbons (*1, 5, 6, 7, 8*). The most recent investigation (*1*) is concerned with the establishment of the van der Waals' constants *a* and *b* for hydrocarbons of all classes. These earlier studies permit the calculation of these constants from structural considerations alone, without the necessity of utilizing any physical properties. The original work (*5, 6, 7, 8*) involves the successive building up of the molecular structure through the replacement of hydrogen by methyl groups along a definite prescribed pattern of substitution. The dependence upon a definite substitution pattern was later eliminated (*1*) through the introduction of structural group contributions, which when added together in any manner produced the van der Waals' constants directly. The latter approach has been selected for the extension of this method beyond the hydrocarbons to include organic compounds of other classes.

For a pure substance the critical temperature and pressure are related to the van der Waals' constants *a* and *b* by the relationships

$$T_c = \frac{8a}{27Rb} \qquad (1)$$

$$p_c = \frac{a}{27b^2} \qquad (2)$$

Conversely Equations (1) and (2) enable the calculation of the van der Waals' constants from available critical temperatures and pressures:

$$a = \frac{27R^2T_c^2}{64p_c} \qquad (3)$$

$$b = \frac{RT_c}{8p_c} \qquad (4)$$

Critical values found in the litera-

J. Charles Forman is now with Abbott Laboratories, North Chicago, Illinois.

TABLE 1. CONSTANTS FOR EQUATIONS WHICH ESTABLISH FUNCTIONAL GROUP CONTRIBUTIONS FOR ORGANIC COMPOUNDS

	Functional group	$\Delta a^{2/3} = \frac{m}{n} + k$		$\Delta b^{3/4} = \frac{s}{n} + t$	
		m	k	s	t
Alcohols	$-\text{OH}$	30,200	14,000	8.96	7.50
Phenols	$-\text{OH}$	0	8,500	0	4.19
Ethers (noncyclic)	$-\text{O}-$	14,500	6,500	0	3.26
Ethers (cyclic)	$-\text{O}-$	0	9,440	0	2.74
Ketones	$-\overset{\text{O}}{\overset{\|}{\text{C}}}-$	62,800	16,700	27.20	4.55
Carboxylic acids	$-\overset{\text{O}}{\overset{\|}{\text{C}}}\text{OH}$	142,670	16,730	66.80	5.10
Acid anhydrides	$-\overset{\text{O}}{\overset{\|}{\text{C}}}\text{O}\overset{\text{O}}{\overset{\|}{\text{C}}}-$	0	43,880	0	14.78
Esters					
Formates	$\text{H}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{O}-$	35,140	26,800	2.29	15.80
Others	$-\overset{\text{O}}{\overset{\|}{\text{C}}}\text{O}-$	37,430	25,500	−3.00	12.20
Amines					
Primary	$-\text{NH}_2$	4,800	18,900	0	10.15
Secondary	$-\overset{\text{H}}{\text{N}}-$	51,800	0	19.60	−1.10
Tertiary	$-\overset{\|}{\text{N}}-$	60,200	−4,300	29.20	−7.90
Nitriles	$-\text{CN}$	86,000	25,900	39.70	12.10
Aliphatic halides					
Fluorides	$-\text{F}$				
First carbon		2,420	12,240	−3.70	10.92
Second carbon		−38,500	4,510	−48.50	12.86
Third carbon		0	3,450	0	6.92
Chlorides	$-\text{Cl}$				
First carbon		0	22,580	0	11.54
Second carbon		66,000	−5,100	19.00	3.90
Third carbon		−60,250	29,100	−40.80	19.40
Fourth carbon		0	16,500	0	11.46
Bromides	$-\text{Br}$				
First carbon		−2,720	23,550	−4.35	11.49
Second carbon		0	20,860	0	5.37
Iodides	$-\text{I}$				
First carbon		0	33,590	0	13.91
Aromatic halides					
Fluoride	$-\text{F}$	0	4,210	0	7.22
Chloride	$-\text{Cl}$	0	17,200	0	10.88
Bromide	$-\text{Br}$	0	24,150	0	12.74
Iodide	$-\text{I}$	0	34,780	0	15.22

ture (*4*) permitted the calculation of van der Waals' constants for a number of classes of organic compounds and constitute the basis for the development of the group-contribution values of this study. When determined by the methods discussed below group-contribution values $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for various types of organic functional groups can be combined with the values for the rest of the organic molecule in any manner desired to give the van der Waals' constants a and b.

To maintain consistency with the work upon which this study is based, the exponents of the van der Waals' constants a and b were assumed to be 2/3 and 3/4 respectively. For the reasons underlying the use of these exponents, reference should be made to the parent article (*1*).

GENERAL CONSIDERATIONS

In the original article (*1*) group contributions were developed for the various types of carbon atoms present in hydrocarbons of all classes. These group contributions were found to be either independent of the size of the molecule or to vary linearly with the inverse number of carbon atoms. The same procedure was extended to this study and was found to correlate group contributions successfully for various types of organic compounds if the following two rules are adopted:

1. The total number of functional atoms is used to represent the size of an organic molecule. In this investigation a functional atom is defined as any atom present in the substance, excluding hydrogen. Thus in methanol $n = 2$, and in acetic acid $n = 4$.

2. Values are defined for the entire functional group in an organic compound. Thus the functional group contributions $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for the carboxylic-acid group represent the entire carboxylic portion of an acid molecule.

With these rules the results can be expressed in equations which produce the functional group contributions $\Delta a^{2/3}$ and $\Delta b^{3/4}$. These equations are of the basic form

$$\Delta a^{2/3} = \frac{m}{n} + k \tag{5}$$

$$\Delta b^{3/4} = \frac{s}{n} + t \tag{6}$$

The values of the constants for Equations (5) and (6) are summarized in Table 1 for the different types of organic compounds considered in this investigation.

The method of developing these constants for each class of organic compounds is discussed in the subsequent sections followed by illustrative examples.

ALCOHOLS

Critical temperatures and pressures for five primary alcohols permitted establishment of the functional group contributions, $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for the hydroxyl group in alcohols. These values were obtained by subtracting from the values of $a^{2/3}$ and $b^{3/4}$ for the substance, the contributions for that portion not representing the functional group. This portion contains only carbon and hydrogen atoms and is accounted for by the method already presented by Forman and Thodos (*1*). For example the ethanol molecule contains two carbon atoms and one oxygen atom; thus $n = 3$. Of the two carbon atoms one is type-1, and the other is type-2. Subtracting these values from the values of $a^{2/3}$ and $b^{3/4}$ for ethanol one gets values of $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for the hydroxyl functional group in this compound. This procedure was carried out for each alcohol for which experimental values of both critical temperature and pressure were available.

These contributions were found to vary with the size of the molecule in accordance with Equations (5) and (6).

Constants for the alcohol contributions were developed from data on primary alcohols. Since no reliable critical data are available for secondary and tertiary alcohols, this study cannot be reliably extended to these classes of compounds. With this limination Equations (5) and (6) may be used until data become available to check their validity.

Table 2. Deviations Resulting from This Study and that of Lydersen

	This investigation				Lydersen			
	No.	T_c % Dev.	No.	p_c % Dev.	No.	T_c % Dev.	No.	p_c % Dev.
Alcohols	7	1.74	5	4.50	7	1.07	5	3.67
Phenols	4	1.55	4	5.28	4	0.60	4	3.32
Ethers	5	0.84	5	1.48	5	0.41	5	2.69
Ketones	6	0.51	6	2.87	6	0.91	6	4.61
Carboxylic acids	6	1.04	2	1.30	6	0.88	2	7.16
Esters	10	0.85	10	1.76	10	0.58	10	3.81
Amines								
Primary	4	2.01	4	2.98	4	0.80	4	2.92
Secondary	4	2.64	4	6.78	4	0.62	4	7.26
Tertiary	3	2.91	3	1.45	3	0.51	3	4.14
Nitriles	5	0.84	5	2.68	5	0.73	5	3.87
Halides								
Fluorides	5	0.01	5	0.00	5	2.02	5	7.50
Chlorides	8	2.22	8	2.32	8	0.34	8	2.71
Bromides	4	0.00	3	0.00	4	1.72	3	6.45
Iodides	2	0.00	1	0.00	2	0.14	1	4.26
Fluorochloroalkanes	8	2.53	7	5.64	8	0.71	7	5.06
Total	81	1.36	72	2.82	81	0.80	72	4.39

PHENOLS

Group contributions for the phenolic hydroxyl group were obtained from data for phenol and the three isomeric cresols. These contributions were found to be constant at $\Delta a^{2/3} = 8{,}530$ and $\Delta b^{3/4} = 4.19$.

ETHERS

In the same manner as described above, data for four noncyclic ethers permitted establishment of functional group contributions for the oxygen group in noncyclic ethers.

Values of critical temperature and pressure for dioxane made possible the calculation of group contributions for the ether linkage in cyclic ethers. These values are $\Delta a^{2/3} = 9{,}440$ and $\Delta b^{3/4} = 2.74$. It should be noted that these values resulted from critical data on a single substance and therefore do not have the confidence factor possessed by the others. Additional experimental data are needed to corroborate these values.

KETONES

Functional group contributions for the carbonyl group in ketones were similarly obtained. More recent experimental data on several aliphatic ketones reported by Kobe, Crawford, and Stephenson (3) were included to obtain these contributions.

CARBOXYLIC ACIDS

An identical procedure was followed to produce group contributions for the carboxylic group in organic acids.

In addition, critical data for acetic anhydride permitted the calculation of the functional group contributions for the acid anhydride group, $-\overset{\text{O}}{\overset{||}{\text{C}}}-\text{O}-\overset{\text{O}}{\overset{||}{\text{C}}}-$. These were $\Delta a^{2/3} = 43{,}880$ and $\Delta b^{3/4} = 14.78$. Since these anhydride contribution values were obtained from a single substance, the same conservatism exists as pointed out for the cyclic ethers.

CARBOXYLIC ACID ESTERS

Critical data on four formates, three acetates, and three butyrates permitted establishment of group contribution values for the ester group. On correlation of the data, the formates were found to deviate from the other esters and were treated separately. This is a logical classification, since only formate esters contain the group $\text{H}\overset{\text{O}}{\overset{||}{\text{C}}}\text{O}-$, whereas other esters have hydrocarbon portions attached to both sides of the ester group, $-\overset{\text{O}}{\overset{||}{\text{C}}}\text{O}-$.

NITROGEN COMPOUNDS

Data from Kobe and Lynn (4) permitted the establishment of contributions for functional groups in amines and nitriles. For these classes of substances critical data were available for aromatic as well as aliphatic compounds. Analysis of these data showed that it made no difference whether the functional group was attached to an aliphatic or an aromatic hydrocarbon segment.

ORGANIC HALIDES

The method which successfully treated the classes of compounds already considered was found to apply to halides as long as only one halogen atom is attached to a carbon atom in the molecule. A complication arises with halides, since it is possible to substitute more than one halogen atom on a single carbon atom. This behavior is not ordinarily encountered with other noncarbon-containing functional groups. Thus only one hydroxyl group can be attached to a single carbon atom to produce an alcohol. An attempt to attach two hydroxyl groups to the same carbon atom will cause dehydration with the formation of a ketone. However since multisubstituted behavior does exist with halides, it was found that the second and further halogen attachments required an extension of the method which could take into account not only the size of the molecule but also the extent of substitution. An additional factor to be considered is the existence of mixed halides such as the Freons, which contain more than one type of halogen atom on the same carbon atom. Thus when more than one halogen exists on a single carbon atom, not only must the group contributions for succeeding halogen substitutions be considered differently, but also their order of introduction onto the carbon atom must be recognized.

The method which was adopted considers different group contributions for the first and succeeding halogen substitutions on a single carbon atom. Sufficient data were available to establish contributions for the first, second, and third fluoride per carbon and the first, second, third, and fourth chloride per carbon. Inadequate information exists for bromides and iodides; both critical temperatures and pressures were available for two aliphatic bromides and no aliphatic iodides. However only critical temperatures were available for methyl bromide and methyl iodide. To utilize this information, critical pressures were calculated by the method of Lydersen (2). With these values approximate group contributions were obtained for the first and second bromide per carbon and for the first iodide per carbon.

For mixed halides the contributions must be used in order of increasing atomic number. Thus when both fluorine and chlorine are attached to a single carbon atom, the fluoride contributions should be considered first, followed by chloride contributions after all fluorides have been accounted for. For example in a compound containing one fluorine and one chlorine atom on the same carbon a first fluoride contribution is considered first, followed by a second chloride contribution. The procedure to be followed is presented later in an illustrative example.

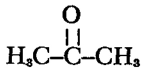
Critical data for fluoro-, chloro-, bromo-, and iodobenzene permitted calculation of functional group contributions, $\Delta a^{2/3}$ and $\Delta b^{3/4}$ for halide substitutions in aromatic compounds. The resulting values were found not to correlate with the first halogen per carbon contributions in aliphatic halides. This is not unexpected, since as with other types of functional groups only one halogen atom can be attached to a single carbon atom in the aromatic nucleus.

ILLUSTRATIVE EXAMPLES

To illustrate the procedure used in obtaining van der Waals' constants *a* and *b* by the method of this investigation the critical temperature and pressure will be calculated for two organic compounds. The first one, acetone, is a ketone and is representative of all classes of compounds except the aliphatic halides. The compound trifluorotrichloroethane represents a typical halogen compound and in addition is a mixed organic halide.

Acetone

Structure:



$$\mathrm{H_3C{-}\overset{\overset{O}{\|}}{C}{-}CH_3}$$

This ketone contains two type-1 (methyl group) carbons (*1*), and one carbonyl $(\overset{\overset{\text{O}}{\|}}{\text{–C–}})$ functional group. The number of functional atoms is 4. From the group contributions presented in Table 1 of the parent article (*1*) and calculated by means of Table 1 of this study, $a^{2/3}$ and $b^{3/4}$ are calculated as follows:

2 carbon atoms (type-1)	2(15,035)	2(11.453)
1 carbonyl group	32,400	11.35
	$a^{2/3} = 62{,}470$	$b^{3/4} = 34.256$

From these values the following calculated van der Waals' constants are produced:

$$a = 15.614 \times 10^6 \text{ (cc./g.-mole)}^2 \text{ atm.}$$

$$b = 111.26 \text{ cc./g.-mole}$$

to give the following values of critical temperature and pressure from Equations (1) and (2):

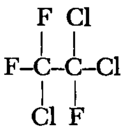
$$T_c = \frac{8(15.614 \times 10^6)}{27(82.055)(111.26)} = 506.8°\text{K.}$$

$$p_c = \frac{15.614 \times 10^6}{27(111.26)^2} = 46.7 \text{ atm.}$$

Kobe and Lynn (*4*) report values of 508.7°K. and 46.6 atm. for acetone.

Trifluorotrichloroethane (Freon-113)

Structure:



$$\mathrm{F{-}\overset{\overset{F}{|}}{\underset{\underset{Cl}{|}}{C}}{-}\overset{\overset{Cl}{|}}{\underset{\underset{F}{|}}{C}}{-}Cl} \qquad (n = 8)$$

In this compound there are two type-4 carbon atoms, two first fluorides (one per carbon), one second fluoride (on left-hand carbon), one second chloride (on right-hand carbon) and two third chlorides (one per carbon).

These contributions, when added together, produce values for $a^{2/3}$ and $b^{3/4}$ as follows:

Two type-4 carbons	2(3480)	2(−8.837)
Two first fluorides	2(12,550)	2(10.46)
One second fluoride	−300	6.80
One second chloride	3150	6.28
Two third chlorides	2(21,570)	2(14.30)
	$a^{2/3} = 78{,}050$	$b^{3/4} = 44.926$

These values produce the following van der Waals' constants

$$a = 21.801 \times 10^6 \text{ (cc./g.-mole)}^2 \text{ atm.}$$

$$b = 159.71 \text{ cc./g.-mole}$$

and the critical temperature and pressure from Equations (1) and (2) become

$$T_c = \frac{8(21.801 \times 10^6)}{27(82.055)(111.26)} = 492.9°\text{K.}$$

$$p_c = \frac{21.801 \times 10^6}{27(159.71)^2} = 31.7 \text{ atm.}$$

Critical values of 487.3°K. and 33.7 atm. are reported by Kobe and Lynn (*4*).

DISCUSSION

Critical temperatures and pressures were calculated for the eighty-one organic compounds of different classes available in the literature. Critical constants were also calculated for the same compounds by the method of Lydersen (*2*). The resulting deviations from comparison of calculated and experimental values by both methods are presented in Table 2. Of the eighty-one compounds examined, critical pressures were available for only seventy-five of them. In addition, excessive deviations were encountered for the critical pressures of two acids and one fluorochloroalkane. For the two acids, similarly large deviations were found for the critical pressures resulting from the Lydersen method. Since these substances do not conform to the normal pattern, they were eliminated in the calculation of average deviations.

It will be noted from Table 2 that the Lydersen method produces somewhat better values for the critical temperature, whereas the method of this study predicts better critical pressures. That the Lydersen method gives better critical temperatures is to be expected, since that method utilizes a physical property, the normal boiling point, in the calculation of the critical temperature. The method proposed by this investigation is independent in that no physical properties are required, and thus critical values can be calculated from structural considerations alone.

NOTATION

a = pressure van der Waals' constant, (cc./g.-mole)^2 atm.
b = volume van der Waals' constant, cc./g.-mole
k = constant in Equation (5)
m = constant in Equation (5)
n = total number of functional atoms in organic compound
p_c = critical pressure, atm.
R = gas constant, 82.055 (atm.) (cc.)/(g.-mole) (°K.)
s = constant in Equation (6)
t = constant in Equation (6)
T_c = critical temperature, °K.
Δ = difference

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