

ON THE APPROXIMATE CALCULATION OF CRITICAL VOLUMES OF LIQUIDS

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In a previous paper a method for the approximate calculation of critical pressures of liquids [1] was published. Modifying this method it is possible to calculate critical volumes V_c of liquids simply, but with sufficient accuracy.

For the calculation of critical volumes of liquids some general methods are known. One part of these methods employ for calculating critical volumes, molecular volumes measured at the absolute zero V_0 , at the melting point V_m , at reduced temperature 0.6, $V_{0.6}$ resp. at the normal boiling point V_b . So according to HERZ [2] resp. FERGUSON and KENNEDY [3] correlations are valid for critical volumes which are to a certain extent, analogous to the rule of GULDBERG and GUYE:

$$\frac{V_c}{V_b} = \text{const. resp.}$$

$$\frac{V_c}{V_{0.6}} = \text{const.}$$

But according to PORLEZZA [4] $V_0 + V_m + V_b \approx V_c$. This is "the rule of four volumes".

Another part of approximative methods for the calculation of critical volumes operates by summarizing atomic and bond increments or starts out from quantities which may be set up from increments. Such critical volumes are to be calculated according to SCHUSTER [5], RIEDEL [6], LYDERSEN [7] and BAKOS [8], from atomic group and bond increments.

Critical volumes may be calculated according to other methods indirectly from atomic and bond increments. These, according to THODOS [9], critical volumes are direct proportional to the volume-correction of van der Waals' equation of state (see e.g. [10]) which is according to VAN LAAR [11] an additive quantity.

Critical temperatures are, according to SUGDEN [12], HERZOG [13] resp. BAKOS [8] linear functions of the parachor \bar{P} resp. to the molecular refraction

\bar{R} . According to the correlations generally employed of REDDING and MEISSNER [14]

$$V_c = (0.377 \bar{P} + 14.0)^{1.25}$$

But according to MEISSNER [15]

$$V_c = 0.55 (1.5 \bar{P} + 9 - 4.34 \cdot \bar{R})^{1.155}$$

The use of the third part of the methods for the approximate calculation of critical volumes presumes the knowledge of critical temperatures T_c and of critical pressures p_c , further also that of the parachor.

So according to HERZOG [13]

$$V_c = C \cdot \bar{P} p_c^{-0.25} = C' \bar{P}^{1.2} \cdot T_c^{-0.3}$$

where C and C' are constants. According to the general gas law of Boyle, Mariotte and Gay-Lussac and according to van der Waals' equation of state resp. according to WÖHL [16]

$$\frac{p_c V_c}{T_c} = \text{const.}$$

From the above equations, these which assume the additivity of critical volumes are only very approximative ones, but in corrected forms [6], [7], [8] operate with an extensive table of increments. The disadvantage of the calculation employing other physical quantities is that these quantities are calculated by approximate methods, too, and calculated values of critical volumes may be incorrect in connection with accumulation of errors.

Therefore, it seemed be advantageous to look for a not very complicated, but sufficiently accurate correlation containing few empirical constants. Since critical volumes are, in homologous series, not strictly additives and are according to BAKOS functions approximately of second degree of number of carbon atoms, we have tried — as a generalisation of this — to approximate the correlation of critical volumes and number of carbon atoms with a power law of degree not fixed in advance. In other terms we have looked for a correlation between the logarithmic values of critical volumes and logarithmic values of number of carbon atoms. Studying the most general form of correlations of this kind we have intended to determine the constants of equation

$$\log V_c = a \log (n + b) + c \quad (1)$$

and the accuracy to be obtained by equation (1). Constant b of equation (1) has been determined by substituting different integer numbers, then plotting the connected logarithmic values of critical volumes and numbers of carbon atoms and searching for the value of b to which fall the connected points on a straight line. After the determination of b the value of a and c was determined by the "zero-sum" method [17]. It would have been more correct

Table 1

	measured V_c calculated		δ	%
	ml./g.-mole			
methane	99	102.3	+3.3	3.3
ethane	148	148.7	+0.7	0.5
propane	200	198.6	-1.4	0.7
n-butane	255	251.7	-3.3	1.3
n-pentane	311	307.3	-3.7	1.2
n-hexane	368	365.6	-2.4	0.7
n-heptane	426	425.8	-0.2	0.0
n-octane	490	487.2	-2.8	0.6
n-nonane	552.7	552.5	-0.2	0.0
n-decane	618.6	618.6	\pm 0.0	0.0
n-undecane	683.1 [19]	687.1	+4.0	0.6
n-dodecane	755.3 [19]	755.1	+0.1	0.0
cyclobutane	214*	212.7	-1.3	0.6
cyclopentane	260	260.1	+0.1	0.0
cyclohexane	308	309.6	+1.6	0.5
cycloheptane	362	361.0	-1.0	0.3
cyclooctane	414*	414.2	+0.2	0.0
cyclononane	468*	469.0	+1.0	0.2
benzene	260	262.3	+0.3	0.1
toluene	316.3 [20]	313.3	-3.0	1.0
ethylbenzene	374	369.5	-4.5	1.2
n-propylbenzene	430	430.7	+0.7	0.2
n-butylbenzene	498	497.1	-0.9	0.2
methanol	118	118.0	\pm 0.0	0.0
ethanol	167	167.0	\pm 0.0	0.0
n-propanol	220	218.6	-1.4	0.7
n-butanol	270.7*	272.4	+1.7	0.6
methylformate	172	173.9	+1.9	1.1
methylacetate	228	227.4	-0.6	0.3
ethylformate	229	227.4	-1.6	0.7
methylpropionate	281.7	285.3	+3.6	1.3
ethylacetate	286	285.3	-0.7	0.2
propylformate	285	285.3	+0.3	0.1
methyl-n-butyrate	340	347.3	+7.3	2.1
ethylpropionate	352.5	347.3	-5.2	1.5
propylacetate	345	347.3	+2.3	0.7
ethyl-n-butyrate	420.9	413.0	-7.9	1.9
methyl-n-valerate	416.3	413.0	-3.3	0.8

* Calculated by other approximative methods.

to take the value of b determined by the method discussed above as an approximate value and to determine its correct value by the method of least squares employed to non-linear forms of equations, (see e.g. [18]). But with regard to the accuracy of measured data and to deviations of data issuing from different sources this calculation seemed to be unnecessary.

The logarithmic values of critical volumes in different homologous series can be calculated by equations as follow:

n-paraffins: $\log V_c = 1.2974 \log (n + 2) + 1.3912$

cycloparaffins: $\log V_c = 1.4041 \log (n + 2) + 1.3131$

n-alkylbenzenes: $\log V_c = 2.235 \log (n + 6) + 0.0192$

aliphatic n-alcohols: $\log V_c = 1.2068 \log (n + 2) + 1.4961$

esters: $\log V_c = 1.2589 \log (n + 2) + 1.4775$

In table 1. values of critical volumes calculated by the above method resp. measured and those differences δ are presented. Critical volumes are mainly from the compilation of BAKOS [8].

Differences of calculated and measured data generally do not surpass the errors of measurements or at least the differences of values published by different authors. The mean of differences calculated from data of 38 compounds is 2.0 ml./g-mole i.e. 0.66%, which may be taken as being sufficient since critical volumes of compounds listed in table 1. can be calculated by the method of BAKOS with an error of about 1.4%.

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Summary

The logarithmic values of critical volumes in the homologous series of n-paraffins, cycloparaffins, n-alkylbenzenes, aliphatic n-alcohols and esters can be calculated from the number of carbon atoms by equations of type (1).

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