A Method to Estimate Critical Volumes

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Among the important correlating parameters used for the estimation of thermodynamic properties of substances via the corresponding states type of approach is the volume at the critical temperature V_c (Reid et, al.. 1977). Unfortunately, experimentally determined values for V_c are available for only a relatively few substances, and hence it is often necessary to estimate the critical volume. Various methods for doing this have been proposed, some of which require auxiliary data such as the critical temperature and/or the critical pressure which themselves are generally unknown. It would be advantageous to be able to obtain reasonable estimates for V_c using as small a number of parameters as possible, and in this category, several methods that employ only the chemical structure as input have been proposed.

1. The Lydersen (1955) method which estimates V_c by means of

$$V_c = 40 + \sum_i v_{li} \qquad (1)$$

where v_{li} is the contribution of each structural group to the critical volume. For this method, forty-one separate v_{li} contributions have been reported.

2. The Vetere (1976, 1977) method, which is given by

$$V_c = 33 + \left[\sum_i (v_{vi} M_i) \right]^{1.028} \qquad (2)$$

where v_{vi} is the structural contribution and M_i is the corresponding molecular weight. It is interesting to note that whereas Equation (1) is linear, Equation (2) is not. Vetere lists the values of forty-four separate group contributions.

3. The Fedors (1973) method, wherein V_c is given by

$$V_c = \sum_i v_{fi} \qquad (3)$$

where again v_{fi} are the separate contributions of each structural group, of which forty-four were evaluated.

We now wish to show that it is possible to estimate V_c much more simply using a combination of only eighteen atomic and structural contributions. These contributions v_i are listed in Table 1, and V_c is given by the linear expression

$$V_c = 26.6 + \sum_i v_i \qquad (4)$$

Superficially, Equations (1), (3), and (4) are very similar, but the great advantage of Equation (4) lies in the simplicity of the v_i values.

To compare the applicability of these various estimation procedures, we used the critical data listed in the compilation of Kudchadker et al. (1968). In order to obtain a fairer comparison, only data for those substances to which all estimation methods were applicable were used; the total number of such substances was 160. Excluded from the data base were about a dozen substances such as methane, the formate esters, nitromethane, etc., for which either the Lydersen or Vetere method or both were not applicable. The results of the comparison are shown in Table 2. As may be seen, the three methods yield about the same average error, that is, about 3%, but the new method is decidedly superior in the much smaller number of increments required to fit the 160 data points.

Table 1. Atomic and Structural Contributions to the Critical Volume

Atom	v_i cm³/mole	Structural feature	v_i cm³/mole
C	34.426	3-membered ring	−15.824
H	9.172	4-membered ring	−17.247
O	20.291	5-membered ring	−39.126
O (alcohols)	18.000	6-membered ring	−39.508
N	48.855	Double bond	5.028
N (amines)	47.422	Triple bond	0.7973
F	22.242	Each additional ring	
Cl	52.801	attached directly	
Br	71.774	to another ring	
I	96.402	(that is, biphenyl,	
S	50.866	naphthalene,	
		etc.)	35.524

$$V_c = 26.6 + \sum_i v_i$$

Table 2. Comparison of Critical Volume Estimation Methods

Method	Avg. % deviation*	Number of increments
Vetere	3.41	44
Lydersen	3.29	41
Present	3.15	18

* Equal to $\frac{100}{n} \sum \left| \frac{V_{c\,expt} - V_{c\,calc}}{V_{c\,expt}} \right|$ where n = number of substances, 160.

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