METHODS FOR PREDICTING PROPERTIES OF LIQUIDS AND GASES

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Predictive methods, i.e., calculation of the properties of substances from information on the molecular structure, include two stages: 1) determination of the basic macroscopic parameters from the structural data; 2) calculation of the properties from the set of macroscopic parameters obtained. Application of the methods of thermodynamic similarity revealed that for a class of normal (nonassociated) substances, the list of independent macroscopic parameters contains three quantities, which are most conveniently chosen as follows: the critical volume V, the critical temperature T, and A, the determining criterion of thermodynamic similarity, a dimensionless characteristic of the individuality of a substance in the single-parameter law of corresponding states [1]. Algorithms for calculating thermodynamic and partly kinetic properties of liquids and gases based on these parameters are described in [1-3]. Relations that permit estimating the macroscopic parameters from information on molecular structure are examined in [4] and, in part, in [1-3]. This paper is concerned with refining and extending these relations and thereby completing and improving the methodological foundations of predicting the properties of substances. In this review, a number of papers on this subject are summarized. The information contained therein is synthesized, a modern algorithm for predicting properties is formulated, and the prospects for further development of this problem are discussed. The possibilities of forecasting properties at the given, new stage are illustrated by specific examples for random choice of substances.

The problem of the relationship between microscopic (molecular) characteristics and macroscopic (thermodynamic and kinetic) parameters has two basic aspects. The first of these, a purely structural aspect, is the interpretation of the parameters listed above in terms of the structural—molecular data. The second aspect, the dynamic aspect, is the determination of the form of the effective model three-parameter interaction potentials of polyatomic molecules, which replace the actual complicated acentric interactions; model potentials are understood here to mean parameters which can be related to the structural characteristics of the molecular models. Both aspects are interrelated and their combined study enriches each of them [5]. Here, however, we shall limit ourselves to an examination of primarily only the structural aspect of the problem, since the algorithm for predicting properties is based precisely on it.

The first of the examined micro- and macrorelationships involves interpretation of the critical volume. This quantity must correspond to the characteristic molecular volume and, correspondingly, to the characteristic molecular size. In [1-4], the following quantity appeared as such a dimension:

$$l = d + \sigma, \tag{1}$$

where d is twice the distance from the center of mass of the molecules to the center of the most distant atom and σ is the diameter of the latter.

The relation between the critical volume and the characteristic size had the following form in [1-4]

$$V_{1c} = 0.73 l^3 \tag{2}$$

(l is in Å). The values of σ, which optimize this relation, are given in Table 1 (the value of σ for Br in this table is changed from that in [2] by 4%). In the dynamic interpretation of (2), σ plays the role of the interaction constant for the corresponding atoms interacting with one another and characterizes the distance to the minimum in the potential. For this reason, it is not accidental that the set of σ in Table 1 is close to the series of data in the literature (see [2]).

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TABLE 1

Atom	H	F	Cl	Br	I	C
σ, Å	2,63	3,06	3,55	3,76	4,0	3,4

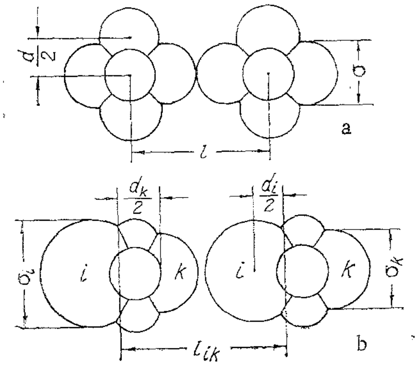

Fig. 1. Determination of the characteristic size of polyatomic molecules.

For nearly spherical molecules, Eq. (2) agrees well with the actual data [2-4] and for molecules with a more complicated shape, a generalization is required. This generalization, performed in [6], is based on the interpretation of the quantity l as the distance between the centers of the molecules when the peripheral atoms touch along the line connecting the centers (Fig. 1a). The generalizing formula for unsymmetrical molecules must include the possibility of contact of different atoms at the periphery with one another (Fig. 1b). The corresponding values of l must be averaged with weighting factors $\varkappa_{ik}$, which account for the possibility of contacts between atom i on one molecule and atom k on another. The general expression for the effective size l has the form

$$\bar{l} = \frac{\sum_{i,k} l_{ik}\varkappa_{ik}}{\sum_{i,k} \varkappa_{ik}}. \tag{3}$$

The factors $\varkappa_{ik}$ in [6] were taken as the product of the steric factors $\varkappa_i$:

$$\varkappa_{ik} = \varkappa_i \varkappa_k, \tag{4}$$

where

$$\varkappa_i \equiv \frac{\sigma_i^2}{(d_i + \sigma_i)^2} \equiv \frac{\sigma_i^2}{l_i^2}. \tag{5}$$

The quantities $\varkappa_i$ are proportional to the solid angles at which the atoms are "visible" from the center of the molecule. An important property of the factors $\varkappa_i$ is the fact that for compact molecules their sum is close to unity

$$\sum_i \varkappa_i \sim 1. \tag{6}$$

In forming l_{ik} and $\varkappa_i$ it is important to understand exactly what is meant by the center of the molecule. The use of the center of mass for this purpose is fundamentally incorrect since the atomic masses, which characterize the dynamics, should not enter into the definition of a purely geometric characteristic such as the volume. A more reasonable approach would be to eliminate completely the idea of a "center." However, the scheme used in [6], generalizing the relation for quasispherical molecules, actually originates from such a concept. From the different schemes examined in [6], the best results are obtained from the following definition of the center:

$$\vec{R}=\frac{\sum_i \vec{r}_i\sigma_i^3}{\sum_i \sigma_i^3}, \tag{7}$$

where $\vec{r}_i$ is the radius vector of the i-th atom. According to (7), the center of the molecule is determined as the center of mass of the corresponding figure, all atoms of which are uniformly filled with a uniform substance.

It is convenient to use Eq. (3) together with the approximation

$$l_{ik}=\frac{l_i+l_k}{2}\simeq l_i^{1/2}l_k^{1/2}, \tag{8}$$

which is valid when l_i and l_k – the distances from the center of the molecule to the i-th and k-th atoms – differ relatively little from one another (the choice of the center of the molecules described ensures this). After substituting (8) and (4), Eq. (3) assumes the form

$$\bar{l}=\left(\frac{\sum_i l_i^{1/2}\varkappa_i}{\sum_i \varkappa_i}\right)^2. \tag{9}$$

This relation extends Eq. (2) to a wide class of substances with molecules of diverse shapes. The more exact equation (2), in this case, has the form

$$V_c=0.792\bar{l}^3. \tag{10}$$

(The difference between the factor in (10) and the same factor in (2) is related to the fact that in the latter equation, the quantity entering for l is on the average somewhat smaller than that given by (9), the distance to the most distant peripheral atom.)

In formulating an algorithm for predicting properties based on (9), the following refinements must be made. This equation was derived for compact molecules, for which the concept of "peripheral atoms" is completely clear and unique. As a practical definition of the concept "compact," in this case, the following is proposed in [6]:

$$\sum_i \varkappa_i > 0.9. \tag{11}$$

However, in a number of cases, for example, for halide derivatives of ethylene, the inequality (11) is not valid. This can be interpreted as the "relative accessibility" of carbon atoms for contacts. A generalization of Eq. (9) is proposed in [6] to the case of noncompact molecules, based on the introduction of steric factors of the following form for "internal," partially "shaded" atoms:

$$\varkappa_i=\varkappa_i^0-\sum_k \varkappa_k=\frac{\sigma_i^2}{l_i^2}-\sum_k \varkappa_k, \tag{12}$$

where $\varkappa_k$ are the steric factors of the "shading" atoms. Equation (12) is useful for $\varkappa \sim 0{,}7$ - 0.8.

A different approach to calculation of the critical volume of "noncompact" atoms, namely, introduction of an additional factor into Eq. (10) that depends on $\sum_i \varkappa_i$, is also possible. Thus, for tetrahedral molecules (halide derivatives of eight elements of the fourth group of the periodic system, 15 substances) the following equation can be proposed:

$$V_c=\frac{0.792}{1+5\left(1-\sum_i \varkappa_i\right)^2}\,l^3. \tag{13}$$

TABLE 2. Increments to the Critical Volume according to [8], cm^3/mole

Atom	Compound		
	alkanes	alkenes	aromatic
H	8,64	8,9	8,9
F (single atom)	24,5	20,9	22,5
F (several atoms, bound to a single C atom)	21,8	20,3	—
Cl	50,2	49,3	48,9
Br	64,2	63,1	62,4
I	82,3	81,7	80,6
C	61,7 (methane) 50 (ethane and successive compounds	48,2	36,0

TABLE 3. Results of Calculation of the Critical Volume of Halide Derivatives of Methane Using Different Methods

Substance	$\sum_i \varkappa_i$	V_C, cm^3/mole				
		expt.	calc. accord. to			
			(10), (15)	Lidersen	Bowles	Okhotsimskii
CH_3F	1,16	105	105	113	107	112
CH_3Cl	1,08	138	135	144	138	138
CH_3Br	1,04	150	153	165	156	150
CH_3I	1,00	175	176	190	185	170
CH_2F_2	1,16	121	118	131	132	123
CH_2Cl_2	1,04	178	181	193	184	179
CH_2Br_2	1,00	208	217	235	221	207
CH_2ClBr	1,03	194	197	214	203	193
CHF_3	1,15	133	133	145	139	133
$CHCl_3$	1,03	228	228	238	231	221
CHF_2Cl	1,09	167	164	176	170	164
$CHFCl_2$	1,05	197	198	207	200	195
CF_4	1,14	143	149	153	153	145
CCl_4	1,00	277	282	277	277	262
CF_3Cl	1,09	180	181	184	186	175
CF_2Cl_2	1,05	217	213	215	216	206
$CFCl_3$	1,02	248	249	246	247	237
CF_2ClBr	1,04	232	230	236	235	220
CF_3Br	1,06	200	198	205	204	189
Av. deviation			1,6%	7%	4,3%	3,2%

Together with the basic equation (9), it is interesting to examine the more general relation

$$\bar{l} = \left(\frac{\sum_i l_i^n \varkappa_i}{\sum_i \varkappa_i} \right)^{1/n}. \tag{14}$$

For most cases, when l_i do not differ by very many factors, the difference between (14) and (19) constitutes fractions of a percent for n varying from 1/2 to 3. Of special interest is the case n = 2, when

$$\bar{l} = \left(\frac{\sum_i \sigma_i^2}{\sum_i \varkappa_i} \right)^{1/2}. \tag{15}$$

Calculations using Eq. (15) require a knowledge not so much of the structure of the molecule as its composition, since the structure is important only for determining the denominator in this equation, while the latter, according to (6), is close to unity for compact molecules and is nearly independent of the choice of the center of the molecule. (Equation (15) suggests a different interpretation of the parameter $\sum_i \varkappa_i$. It characterizes the difference between the volume defined according to the area of the surface and the volume as such. From here, $\sum_i \varkappa_i$ can be interpreted as a form factor of the molecule. Deviation from the spherically symmetrical form will decrease the form factor.) Some variants of the scheme for determining the critical volume based on (15) are examined in [6].

Another particular case of Eq. (14), for n = 3, is interesting in that the critical volume in this case is defined as the additive sum of contributions from separate atoms $l_i\sigma_i^2$ (the volumes of the cones with vertices at the center of the molecule). Here we approach the scheme of an additive, incremental method for calculating the critical volume.

There are several methods for incremental calculation of critical volumes of empirical origin [7]. We shall examine them below when comparing with alternative methods, starting from a calculation of the intrinsic volume of the molecule. This method is based on the fact that the molecular and critical volumes are proportional to one another, i.e., on the generalization of Eq. (10). Variants of the incremental calculation of molecular and corresponding critical volume are examined in [8]. The test of these variants include the differences in the bond lengths between atoms in various types of compounds. The corresponding increments are presented in Table 2.

The results of calculations based on Eq. (15), calculations using Lidersen's method (recommended in [7] as the best method), Bowles' method (this method is given as the best empirical method), and Okhotsimskii's method [8] are compared with the experimental data in Table 3 for halide derivatives of methane. Table 3 also presents the values of $\sum_i \varkappa_i$, illustrating relation (6). It can be verified that the algorithms recommended here for predicting the critical volume, based on Eq. (9) and (15), and incremental methods of type [8] give results whose accuracy is several times higher than that achieved at the previous stage (in [4], the error was estimated as 6-7%).

The method for predicting the critical volume was further developed by analyzing the revised and refined data for V_c of a large number of substances. This work was based on the relation between the reduced orthobaric volume $\varphi = V/V_c$ and the compressibility factor $z \equiv PV/RT$ on the saturation curve. It was noted in [1, 9] that the dependence $\varphi(z)$ has practically no determining similarity criterion A and is very steep, which makes it convenient for determining φ and, thus, the critical volume. To approximate the function $\varphi(z)$, it is convenient to use the equation

$$\frac{V}{V_c} = \frac{1.169 + 1.792(-\lg z)}{6{,}444(-\lg z) - 1}. \tag{16}$$

It was obtained by analyzing the data for many tens of quite well-studied substances and was checked again according to the values of V_c, recommended as the most reliable for hydrocarbons in [10]. Calculations of V_c according to experimental data on P and V on the saturation curve give values of V_c that are reproduced within 0.5% for $-\log z$ varying over a range of five orders of magnitude (from $-\log z = 1.1$-6) and for values of the parameter A from 1 to 2.5. A more detailed analysis of the corresponding dependence permits refining (16) by introducing a correction factor f(z, A), which decreases the probable error in determining V_c by another factor of 2. Here, we are talking not only about the error determined by the reproducibility of the values of V_c for different $-\log z$ but also on the absolute error, since the statistical averaging of the most reliable experimental values of V_c increases the accuracy of the calculation by a factor $\sim\sqrt{N}$, where N is the number of substances used in determining the function $\varphi(z)$. Thus, it is possible to obtain data for V_c, whose error is considerably lower than in most cases and permits discussing at a higher level the problem of the relation between the structure of the molecules and the critical volume.

One specific application of this investigation is determination of the characteristics of variation of V_c for isomers of limiting hydrocarbons. For example, it is possible to establish clearly that V_c for 2-methyl isomers of normal alkanes is appreciably higher than V_c of 3-methyl isomers. The simple incremental computational scheme does not permit including other analogous facts as well. At the same time, we can propose an elementary improved scheme, which can take into account details in the behavior of V_c of branched hydrocarbons. The improvement reduces to introducing a separate increment for the groups C_2H_5. (To de-

TABLE 4. Increments of Critical Volume for Alkanes, Alkenes, and Their Halide Derivatives

Radical	$\mathrm{CH_3}$	$\mathrm{CH_2}$	CH	C	$\mathrm{C_2H_5}$	$\underset{\vert}{\overset{\vert}{\mathrm{HC}}}-\underset{\vert}{\overset{\vert}{\mathrm{CH}}}$	$-\underset{\vert}{\overset{\vert}{\mathrm{C}}}-\underset{\vert}{\overset{\vert}{\mathrm{CH}}}$	$\mathrm{CH_2}=\overset{\vert}{\mathrm{CH}}$	$\mathrm{CH_2}=\underset{\vert}{\overset{\vert}{\mathrm{C}}}$	cis $\underset{\vert}{\overset{\mathrm{H}}{\mathrm{C}}}=\underset{\vert}{\overset{\mathrm{H}}{\mathrm{C}}}$	trans $\underset{\mathrm{H}}{\overset{\vert}{\mathrm{C}}}=\underset{\vert}{\overset{\mathrm{H}}{\mathrm{C}}}$	$\underset{\vert}{\overset{\vert}{\mathrm{C}}}=\underset{\vert}{\overset{\mathrm{H}}{\mathrm{C}}}$	$\underset{\vert}{\overset{\vert}{\mathrm{C}}}=\underset{\vert}{\overset{\vert}{\mathrm{C}}}$	$-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-\mathrm{O}-$	$\mathrm{H}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-\mathrm{O}$	F	C	Br
ΔV_C	73,1	57,4	35,8	15,1	126,5	65,6	40,8	109,2	86,3	89,7	92,7	68,9	42,1	81	98,2	32,5	65,6	77,9

TABLE 5. Increments of Critical Volume of Cyclical Hydrocarbons

In rings	ΔV_C				
	$\mathrm{CH_2}$	CH	C	$\mathrm{C_2H_2}$ cis	$\mathrm{C_2H_2}$ trans
C_3	55,3	39,3	20	74	78,5
C_4	53,3				
C_5	51,5			67,6	75,6
C_6					

scribe V_C in detail for multiply branched isomers, it is useful to introduce increments of of the groups $\underset{\vert}{\overset{\vert}{\mathrm{HC}}}-\underset{\vert}{\overset{\vert}{\mathrm{CH}}}$ and $\underset{\vert}{\overset{\vert}{\mathrm{HC}}}-\underset{\vert}{\overset{\vert}{\mathrm{C}}}-$) . The use of the set of increments, presented in Table 4, permits describing the critical volumes of 43 alkanes from C_2 to C_9, inclusively, with mean-square error (compared to that found using Eq. (16)) of 0.4%. (Calculations for the same block of data using Lidersen's method give 1.6%.) An analogous analysis for alkenes permits distinguishing differences in cis- and trans isomers of groups C_2H_2 and so on, which makes it useful to introduce separate increments for radicals connected by a double bond. The set of values of ΔV_C from Table 4 permitted reproducing the value of the critical volume of 67 alkenes from C_3 to C_{11} with an average error of 0.65% (1.7% according to Lidersen). For cyclical hydrocarbons from C_3 to C_6, it is necessary to introduce nine increments, taking into account the number of atoms in a ring (Table 5); with the help of this set, the V_C for 60 substances are described with an error of 0.55% (2.4% according to Lidersen).

The second element of the scheme for predicting properties is calculation of the determining similarity criterion. The following equation was used in [1-3] for this purpose:

$$\mathbf{A} = 4 - 8\left(\frac{d}{d+\sigma}\right)^2. \tag{17}$$

This computational method gives completely satisfactory results for quasispherical molecules. For molecules with a complicated shape, it is necessary to refine and extend this relation, which would take into account the role of all (and not the most distant, as in (17)), atoms at the periphery. One of the variants for such a generalization is described in [6]. Here we shall examine a more general approach to the problem. We shall rewrite Eq. (17) in the form

TABLE 6. Atomic and Group Increments n_i^* for Calculations of the Determining Criterion of Thermodynamic Similarity

Atoms, groups	n^*	Atoms, groups	n^*
F, Cl, Br, I, CH_4	1	$-\overset{\mid}{\underset{\mid}{CH_2}}$	0,85
CH, CH_3	1	$-\overset{\mid}{\underset{\mid}{C}}H$ in cyclanes	
CH_2	1,30	$-\overset{\mid}{\underset{\mid}{C}}-$ in alkanes	0,15
$=CH_2$ in alkenes	1	$-\overset{O}{\overset{\Vert}{C}}-O-H$	4
$=\overset{\mid}{\underset{\mid}{C}}$ in alkenes and in aromatic rings	1	$-\overset{O}{\overset{\Vert}{C}}-O-CH_3$,	6
$=\underset{\mid}{C}-H$ in aromatic rings	0,85	$-\overset{O}{\overset{\Vert}{C}}-O-\overset{H_2}{C}-$,	6
		$-\overset{O}{\overset{\Vert}{C}}-O-\overset{H}{\overset{\mid}{\underset{\mid}{C}}}-$	6

$$A = 4 - 8(1 - \varkappa^{1/2})^2, \quad \varkappa \equiv \frac{\sigma^2}{(d+\sigma)^2}. \tag{18}$$

We shall average the quantity $\varkappa^{1/2}$ starting from the fact that the quantities $\varkappa_i^{1/4}\varkappa_k^{1/4}$ correspond to contacts between atoms i and k of the molecules. Using for the weighting factors, describing the probabilities of these contacts, as above, the ratio $\dfrac{\varkappa_i\varkappa_k}{\sum\limits_{i,k}\varkappa_i\varkappa_k}$, we obtain

$$\overline{\varkappa^{1/2}} = \left(\frac{\sum\limits_{i=1}^{n}\varkappa_i^{5/4}}{\sum\limits_{i=1}^{n}\varkappa_i}\right)^2. \tag{19}$$

In view of the relatively small difference between the quantities $\varkappa_i$, this equation differs very little from the following one:

$$\overline{\varkappa^{1/2}} = \left(\frac{\sum\limits_{i=1}^{n}\varkappa_i}{n}\right) \tag{20}$$

Thus, the generalization of Eq. (17) is the expression

$$A = 4 - 8\left[1 - \left(\frac{\sum\limits_{i=1}^{n}\varkappa_i}{n}\right)^{1/2}\right]^2 \tag{21}$$

Taking into account (6), we see that the quantity n, which is the number of peripheral atoms in the molecule, plays the main role in the equation. This result is explained by a number of previously established facts [1]: the thermodynamic similarity of halide derivatives of methane, freons in the ethane series, identity of A for halide derivatives of benzene, etc. In the general case, we can include the correlation between the factor $\sum\limits_{i=1}^{n}\varkappa_i$ and n and examine the dependence

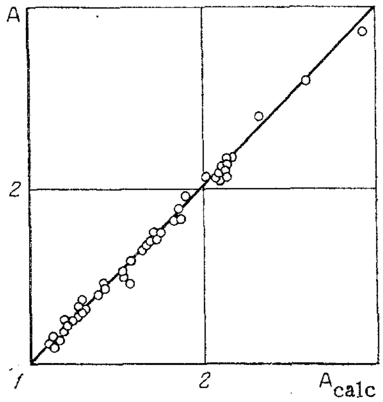

Fig. 2. Check of the computational results for the determining criterion for thermodynamic similarity.

TABLE 7. Values $\sqrt{C}$ for Inert Gases

Element	$\sqrt{C}$, $(J^{1/2}\cdot nm^{1/3})/mole^{1/2}$			
	according to (30)	based on the theory of dispersion forces		
		[11]	[12]	[13]
He	0,27	0,28	0,29	0,29
Ne	0,55	0,53	0,60	0,61
Ar	1,92	1,83	1,93	1,97
Kr	2,78	2,54	2,73	2,77
Xe	4,23	3,77	3,94	4,16
Rn	5,8			

$$A = A(n). \tag{22}$$

Analysis of this dependence leads to the conclusion that the function (22) can be universal and single-valued, if instead of the number of atoms at the periphery n we use the sum of several structural increments of atoms:

$$n = \sum_{i=1}^{n} n_i^*. \tag{23}$$

In this sum, most atoms have $n^* = 1$, but hydrocarbons in the groups CH, CH_2 and CH_3 must also be assigned values close to unity. The increments n_i* are summarized in Table 6.

The equation for calculating A has the form

$$A = \frac{1}{n^{*1/2}} \frac{3.963 - 0.9236n^* + 0.06779n^{*2}}{1 - 0.24825n^* + 0.01932n^{*2}} - 1.4\frac{\mu^2}{C}\left(\frac{V_c}{100}\right). \tag{24}$$

The second term in this equation takes into account the contribution of dipole–dipole interactions; here μ is the dipole moment in Debye units (in principle, it can be determined from the structural data, according to the vector incremental scheme); C is the dispersion interaction constant. The last quantity can, in principle, be found by adding the atomic increments (see below). On the whole, Eq. (24) makes it possible to determine the similarity criterion A (for $A \geqslant 1$) based on a knowledge of the structural equation of the substance.

The quality of these calculations can be judged from Fig. 2, which compares the computed and tabulated values of A for 50 weakly polar substances (hydrocarbons and their halide derivatives). The mean square deviation is 2%. This is 2.5 times less than the error in calculating A, achieved at the preceding stage of this work [4], and it is close to the error in determining A from thermodynamic data. Moreover, the improved computational method encompasses a much larger number of substances.

The third element of the scheme for predicting properties of substances is calculation of the critical temperature. This calculation is based on the relation expressing the com-

TABLE 8. Values of the Square Root of the Intermolecular Interaction Constant

Substance	According to (29)	According to (30)	According to (31)	[12, 13]
H_2	0,82		0,83	0,83
N_2	2,0	1,9	1,9	2,0
O_2	1,8	1,8	1,8	2,1
Cl_2	4,8	4,6	4,4	
CO_2	2,9	2,7	3,0	
CH_4	2,77	2,78	2,60	2,94
NH_3	2,2		2,1	
HCl	2,83	2,93	2,59	
HBr	3,76	3,54	3,3	
Hf	4,9	4,9	4,7	
CF_3Br	6,3	6,3	5,6	

TABLE 9. Summary of Values of $\sqrt{c_i}$

Element	H	B	C	$C_=$	N
$\sqrt{c_i}$, $(J^{1/2}\cdot nm^3)/mole^{1/2}$	0,41	1,3	(1,14)	1,27	1,0

O	F	Al	Si	P	Cl	Ge	As
0,9	0,60	2,7	2,0	2,7	2,42	3	3,0

Se	Br	Zr	Nb	Mo	In	Sn	Te
3,2	3,35	3,6	5,1	4	(6)	4,4	5

I	Hf	Ta	W	Tl	Pb	Bi	U
4,9	3,5	(5)	4	(6)	(4)	6,2	4,7

plex of critical characteristics $T_cV_c^2$ in terms of the dispersion interaction constant, i.e., the coefficient in front of r^{-6} in the Van der Waals interaction potential:

$$-U = \frac{C}{r^6}. \tag{25}$$

According to the theory of thermodynamic similarity, the ratio $T_cV_c^2$ must be a universal function of the determining similarity criterion [1-3]:

$$\frac{T_cV_c^2}{C} = f(A). \tag{26}$$

It was shown in [4] by analyzing actual data that the quantity C can be determined based on the scheme of additive atomic interactions according to which

$$C = \sum_{i,k} c_{ik}, \tag{27}$$

where c_{ik} is the parameter of the dispersion interaction of the i-th and k-th atoms. In addition to this, we can invoke the combinative rule

$$c_{ik} = c_i^{1/2}c_k^{1/2}, \tag{28}$$

where $c_i \equiv c_{ii}$, $c_k \equiv c_{kk}$. In this case,

$$C = \left(\sum \sqrt{c_i}\right)^2. \tag{29}$$

TABLE 10. Results of Predicting the Basic Macroscopic Parameters

Substance	Formula	T_C K		P_C, MPa		V_C, cm³/mole			A	
		prediction	from literature data	prediction	from literature data	prediction	from literature data	calc. accord. to (16)	prediction	from literature data
2-Methylheptane	C_8H_{18}	561	559,6*) [19]	2,51	2,48 [19]	480,7	488 [17]	481,3	1,13	1,10 [1]
2,3-Dimethyl 2-pentane	C_7H_{14}	558		3,33		387,6		388,9	1,42	
4,4-Dimethyl 1-pentane	C_7H_{14}	491		2,72		401,0		401,7	1,61	
Isopropylenecyclobutane	C_7H_{12}	533		3,35		355,5		359,2	1,73	
Freon-11	$CFCl_3$	468	471 [19]	4,33	4,37 [22]	246	248 [19]	247	2,13	2,10 [1]
Methyl iodide	CH_3I	535	528 [19]	7,07		176		175	2,76	
1,2,5-Tribromopropane	$C_3H_5Br_3$	694		3,98		384			1,5	
Methylisobutyrate	$C_5H_{10}O_2$	563	541 [19]	3,58	3,39 [19]	336	339 [19]		1,03	
Bismuthbromide	$BiBr_3$	1173	1220 [18]	8,69	8,40 [30] 9,10 [18]	304	302 [18]		1,88	
Silicon tetrabromide	$SiBr_4$	642	663 [18]	3,77	4,00 [18]	381	382 [18]		1,72	

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*The value of T_k in [17] contains a misprint, which is repeated in [1]; in [1], a corresponding change was made in the value of A.

Equation (26) in the generalized and simultaneously corrected equation has the form

$$\left(\sum_i \sqrt{c_i}\right)\left[1 + 1.4\left(\frac{\mu}{\sum_i c_i}\right)^4\left(\frac{V_C}{100}\right)^2\right] = \frac{T_C^{1/2} V_C \cdot 10^{-3}}{0.709 - 0.3583 \lg A}. \qquad (30)$$

The term in the brackets describes the contribution from the polarity of the molecule; for $\mu > 1$-1.5 D, the corresponding correction, as a rule, does not exceed 1%. All quantities V_h, A, μ, $\sum_i c_i$ entering into (30) are determined from information on the molecular structure, which permits finding T_C, i.e., the third of the set of basic macroscopic quantities, likewise from structural data.

In discussing the data concerning the quantities C, it is interesting to clarify the extent to which the values c_i of the elements found from the data on the critical parameters based on (30) agree with the calculations based on the theory of dispersion forces. This is conveniently checked for inert gas atoms. The results of this comparison, presented in Table 7, verify that the values of the increments of the atomic interaction obtained from the thermodynamic data characterize the real magnitudes of the potential of the dispersion forces. Analogous comparisons for other elements confirm this result.

Finally, the data presented in Table 8 permits verifying simultaneously the validity of the principle of additive composition (29) and the agreement with results of semiempirical estimates based on the theory of dispersion forces. The first column in the table contains the results of determining $\sqrt{C}$ based on the additive composition of atomic increments, obtained as optimum increments for a large set of polyatomic molecules, and the second column presents the results of determining $\sqrt{C}$ from Eq. (30) based on information on the critical parameters and A, and the third column presents the calculations based on the approximate London equation

TABLE 11. Results of Predicting the Properties of 2-Methylheptane

T, K	P		ρ, g/cm³		L, kJ/mole			σ, 10^{-3} N/m	
	prediction	[16]	prediction	(16)	prediction using (37)	prediction using (38)	[16]	prediction	[16]
233,15		—		—	41,6	42,5	42,9	22,8	22,7
253,15	1,06	1,07 mm		—	41,4	41,8	42,4	21,0	20,7
273,15	1,7	4,6	0,718	0,714	40,7	41,5	40,9	19,0	18,8
293,15	16,2	15,6	0,702	0,698	40,1	39,9	40,3	17,0	16,8
333,15	45	44	0,686	0,682	38,6	39,2	38,8	15,1	14,9
333,15	110	107	0,668	0,665	37,3	37,5	37,6	13,4	12,9
353,15	235	231	0,650	0,648	35,9	36,3	36,2		—
373,15	456	451		—	34,3	34,9	34,8		
393,15	0,109	0,108MPa			32,8	33,5	33,3		
413,15	0,184	0,182			31,2	31,9	31,9		
433,15	0,293	0,291			29,6	30,2	30,4		
453,15	0,447	0,442			28,0	28,3	29,0		
473,15		—			26,3	26,1	27,5		

$$\sqrt{C}=\frac{\sqrt{3}}{2}\sqrt{IR}, \tag{31}$$

where I is the ionization potential, R is the atomic refraction, and the last column contains the calculations from [12, 13].

Confidence in the fact that the values of the atomic increments c_i are not merely empirical parameters but characterize the atomic interaction potentials stimulated the search for the laws determining the dependence of c_i on the position of elements in the periodic system and determination of the values of $\sqrt{c_i}$ of almost all elements. The results of this work are shown in Table 9. Values obtained from characteristic variations of $\sqrt{c_i}$ in groups and periods of Mendeleev's system are enclosed in parentheses. The values of $\sqrt{c_i}$ for carbon are also enclosed in parentheses since it is this value that was used as a basis for finding the set of increments; this value was taken from [14]. The symbol $C_=$ indicates carbon in substances with a double bond and aromatic compounds. The difference between the corresponding increment and the increments in compounds with saturated bonds is explained by the difference in the electronic states; the magnitude of the ratio $C_C/C_{C_=}$ agrees with the estimates in [14].

With this we complete the exposition of the foundation of the techniques for predicting properties. We emphasize that these methods for determining V_c, A, and T_c make it possible to find the initial set of data for the calculation of the properties, using information on the structure of molecules (using equations of type (9) for determining the critical volume) or using the structural formula (with the incremental method for calculating V_c).

Below we present and discuss examples of the use of the algorithm presented. In order that the corresponding calculations be sufficiently representative, we shall examine ten substances chosen randomly* from 576 substances, for which information on properties was available in widely used handbooks [15-19]. The substances presented include: four hydrocarbons up to C_9 (from a block of 216 substances), two halide derivatives of hydrocarbon (from 180 substances), two organic substances from a group including simple and complex esters, ketones, sulfides, etc. (72 substances in all), and two inorganic compounds (from a block of 108 substances). The list of substances and results of prediction of the basic macroscopic parameters are presented in Table 10. We shall discuss the table.

The calculations of the critical pressure P_c were performed using the equation

$$z_c\equiv\frac{P_cV_c}{RT_c}=0.2563+0.0535\lg A, \tag{32}$$

obtained by generalizing the most reliable information on the critical parameters, in particular, based on data recommended in [10]. For 2-methylheptane, the accuracy of the prediction

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*The choice was made at a conference in the Division of Molecular Physics in the Physics Department of the Moscow University on November 13, 1981.

TABLE 12. Results of Prediction

Substance	Formula	T_{boil} K		ρ_{20}, g/cm^3	
		prediction	accord. to literature data	prediction	accord. to literature data
2,3-Dimethyl-2-heptane	C_7H_{14}	374	371 [16]	0,740	0,729 [16]
4,4-Dimethyl-1-pentane	C_7H_{14}	332	345 [16]	0,682	0,683 [16]
Isopropylidenecyclobutane	C_7H_{12}	358	380 [16]	0,778	0,782 [16]
Methyl iodide	CH_3J	313	315 [16]	2,24	2,28 [28]
1,2,3-Tetrabromopropane	$C_3H_5Br_5$	455	493 [17[	2,35	2,24 [28]
Methylisobutyrate	$C_5H_{10}O_2$	382	366 [17]	0,90	0,89 [28]
Bismuth bromide	$BiBr_3$	703	734 [18]	4,03	At T_{boil} 4,05 [18]
Silicon tetrabromide	$SiBr_4$	418	426 [18]	2,40	2,37 [18]

of the critical volume exceeds the accuracy of the experimental data. This can be verified by examining Table 11, which contains the results of calculations of the vapor pressure, density, heat of vaporization, and surface tension. The vapor pressure is calculated using the equation from [1]:

$$\lg\frac{P^*}{P} = 3.9726\lg\frac{T^*}{T} + \left(\frac{T^*}{T} - 1\right)\left(0.3252 + 0.40529\frac{T^*}{T}\right). \tag{33}$$

The quantity T* is determined from the equation [1]†

$$\frac{T^*}{T_c} = 0.03803 + \sqrt{1.882 - 1.5815\lg A}. \tag{34}$$

The value of P* was found from (33) for $T = T_c$. Equation (16) was used to calculate the density, while the complex z was found from the relation:

$$-\lg z = \left[\frac{(0.7943\tau)^n}{0.654} + 0.05\right]^{-1}, \tag{35}$$

where

$$\tau = T/T_c,\ n = 2.314 - 0.766\lg A \quad (\text{see } [9]). \tag{36}$$

To calculate the heat of vaporization L, two equations were used:

$$\frac{L}{T} = (55 - 18.2\lg A)\frac{1-\varphi^2}{4\varphi - 1} \tag{37}$$

(L is in J/mole (see [20])) and

$$\frac{L}{RT} = -(11.6319 - 3.94536\lg A)(\lg z)(0.44933 + 0.019732\lg z)\left[1 - \left(\frac{z}{z_c}\right)^{1.66}\right] \tag{38}$$

(see [9]). The surface tension was calculated using Muratov's method [21]. The following equations were used:

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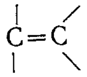
†In (34), a misprint in the value of the first coefficient in the radical in [1] is corrected.

$$\frac{\sigma}{\sigma_{0,6}} = 1.1239(1-\tau) + 9.116(1-\tau)^2 - 29.0038(1-\tau)^3 + 51.1109(1-\tau)^4 - 35.105(1-\tau)^5, \tag{39}$$

where

$$\sigma_{0,6} = \sigma^* R^{1/3} P_c^{2/3} T_c^{1/3}, \tag{40}$$

$$10^8\sigma^* = 7.56938 - 2.57629\,A + 0.711868\,A^2 - 0.07567\,A^3. \tag{41}$$

For most substances, we can compare the minimum empirical information with the calculation. The results of this comparison are presented in Table 12. Comparison of the properties of two isomers of heptane indicates that the predictive scheme examined describes completely satisfactorily the appreciable role of isomerization. The case of isopropylene cyclobutane is among the worst of the hydrocarbons, since the increment of the group  $\overset{|}{\underset{|}{C}}=\overset{/}{\underset{\backslash}{C}}$ for cyclical hydrocarbons is not separated in the computational scheme; for this reason, V_c was determined using Lidersen's method. In spite of this, the results of the predictive calculations can be viewed as being satisfactory in this case as well.

In calculating the properties of CCl_3F, it was possible to use the detailed information on the structure of the molecule contained in [23]. The critical volume was calculated using Eqs. (10) and (14); the refinement of the value of $\sum_i \varkappa_i$ compared to Table 3 was 1.029. The vapor pressure and density were calculated using Eqs. (32)-(36). To determine the vapor density, the equation in [3] was used:

$$\lg\left(1 - \frac{PV_n}{RT}\right) = 0.094\lg A + 0.254 - (0.705 - 0.0668\lg A)(-\lg z). \tag{42}$$

From the data on the vapor density, the variable

$$z^* \equiv \rho_v/\rho_l \tag{43}$$

was determined and with its help the dimensionless isothermal compressibility was calculated:

$$\mathcal{P} \equiv \frac{\beta_T RT}{V}, \tag{44}$$

where $\beta_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$. The calculation was performed using the equation in [24]:

$$\mathcal{P} = \frac{0.665 + 0.055(\lg z^*)^2}{(\lg z^*)^2(1 - \lg z^*)}. \tag{45}$$

In its turn, the values of $\mathcal{P}$ permitted determining the surface tension σ using the equation in [25]

$$\frac{31\mathcal{P}^{1/2}(1+\tilde{\sigma})}{f_A(35-\tilde{\sigma})} = 1, \tag{46}$$

where

$$\tilde{\sigma} \equiv \sigma/\sigma^*,\ \sigma^* \equiv k^{1/3} P_c^{2/3} T_c^{1/3} \tag{47}$$

(k is Boltzmann's constant);

$$f_A = 1.027 - \frac{0.17\lg A}{1 + 2\lg A}. \tag{48}$$

The computed values of σ in this case are close to those found using Muratov's method.

The viscosity of CCl_3F vapor was calculated using Chusov's equation

$$\frac{\eta}{\eta_c^0} = \frac{3\tau^{3/2}}{1 + 2\tau^{0.91}} \tag{49}$$

TABLE 13. Results of Predicting the Properties of Freon-11

T, K	P, MPa		ρ_l, g/cm^3		ρ_v, g/cm^2		L, J/g		$\sigma \cdot 10^{-3}$ N/m		η, μP	
	prediction	[15]	prediction	[15]	prediction	[15]	prediction	[15]	prediction	[15,27]	prediction	[15]
213,15	0,0013	0,0013	1,67	1,67	—	—	205	211	29,9	29,3		—
233,15	0,0055	0,0052	1,63	1,62	0,00039	0,00036	199	204	26,5	26,5		—
253,15	0,017	0,016	1,58	1,58	0,0011	0,0010	193	197	23,4	23,8	98	100
273,15	0,043	0,040	1,53	1,53	0,0026	0,0025	187	190	20,5	21,1	106	107
293,15	0,093	0,090	1,48	1,49	0,0055	0,0052	180	183	17,8	18,3	114	113
313,15	0,18	0,18	1,43	1,44	0,010	0,010	172	177	15,3	15,8	121	119
333,15	0,33	0,32	1,38	1,39	0,018	0,017	165	167	13,0	13,4	129	124
353,15	0,54	0,53	1,32	1,33	0,029	0,027	155	158	10,7	11,0	136	130
373,15	0,86	0,84	1,27	1,28	0,046	0,043	145	147	8,64	8,76	143	135
393,15	1,29	1,25	1,22	1,21	0,070	0,066	140	135	6,57	6,57		—
413,15	1,9	1,8										
433,15	2,6	2,5										
453,15	3,5	3,4										

and the relation

$$\frac{\eta_c^0 T_c^{1/6}}{M^{1/2} P_c^{2/3}} = 3.43 \tag{50}$$

(see [1]).

The results of the calculations, presented in Table 13, convincingly indicate the great possibilities of the predictive methods.

In calculating the properties of CH_3I, it is necessary to include the dipole moment. For μ we used the value 1.8 D, characteristic for CH_3I compounds. The contribution of the dipole moment to the determining similarity criterion was 0.15% and 1.6% in the sum of increments $\sqrt{C}$. The critical volume was calculated using Eq. (14). The value of $\sum_i \varkappa_i$ in accordance with Table 1 is set equal to 1.00. The results of the calculations are given in Table 12.

In calculating the properties of C_3H_5Br, we encountered one of the worst situations. The calculations of the critical volume are not as accurate as for most other substances. Optimization of the increments $\sqrt{C_i}$ based on (16) of halide derivatives of hydrocarbons has not yet been done and the set of increments at the end of Table 4 is still based on a quite small number of data. For the same reason, the increments $\sqrt{C_i}$, n^* are less accurate as well. Uncertainty due to the contribution of the dipole moment is added to this. For a priori, predictive calculations, it is possible to start from values of μ for the C—Br bond (2.04 D[29]). However, the result of vector composition of these three moments requires a knowledge of an assortment of conformations. Depending on the rotation of the molecular groups, the resulting dipole moment of the molecule can vary from 0 to 2.3 D. In the estimates we used $\mu \sim 2$ D. The results of the predictive estimates in Table 12, as we can see, are not nearly as accurate as calculations for other substances (8% for T_{boil}, 3% for ρ_{20}). The conditions are also not the best for methylisobutyrate, since the value of the determining similarity criterion is near the limit of validity of Eq. (24), and the increments n, $\sqrt{C}$, and ΔV_c were determined from a not very large number (about 10) of relatively well studied complex esters. As follows from Tables 10 and 12, the critical temperatures and the temperature of normal boiling are determined here to within 4% and the density to within 1%.

In estimating the properties of $BiBr_3$, it turned out that the data required for the calculation on the parameter σ of bismuth are absent. (Bismuth is located at the apex of a pyramid in this molecule.) We were able to get out of this difficulty by using the correlation between σ and the covalent radii r of the elements:

$$\sigma = 2.23 + 1.33r. \tag{51}$$

The structural data required to calculate V_c were taken from [31]. The considerable uncertainty in these calculations is introduced by the absence of information on the dipole moment of the $BiBr_3$ molecule. We used μ = 4 D based on data for compounds of other elements in group

V of the periodic system. The need to draw upon this additional information is, of course, a shortcoming of these calculations. Taking into account what has been said above, the agreement between the predicted and experimental data for $BiBr_3$ must be viewed as being completely satisfactory. The critical volume of $SiBr_4$ was calculated based on structural data in [31] using Eq. (13) and the parameter A was found directly from Eq. (17).

Let us summarize what has been said above. From an analysis of the results of predicting a random set of substances, we reach the conclusion that the algorithms described provide in all cases a determination of the basic macroscopic parameters, sufficient for estimating thermodynamic properties. For hydrocarbons and halide derivatives, the results of the calculations in many cases are close in accuracy to the experimental data, and for inorganic substances, the error of the calculation of characteristic temperatures and volumes is a small percentage. Further improvement of the predictive method examined here presumes that the tables of increments will be refined and expanded, which must permit making predictions from the structural formula of the substance only (including also inorganic compounds). We can point out, in particular, one of the specific paths for refining the increments $\sqrt{c}$, free of the inaccuracies in the knowledge of the critical temperatures T_C. It is based on the analysis of the relation between the dimensionless complexes $(T^{1/2}M)/(\rho\sqrt{C})$ and z. We can verify that this dependence is well approximated by the equation

$$\sqrt{C} = \frac{T^{1/2}M}{\rho} (\lg z)^{1/2} f_1 f_2, \tag{52}$$

where

$$f_1 = 340.7 - 202 \lg \mathbf{A}, \; af_2 = f_2(z) \tag{53}$$

with $-\log z$ varying from 2.3 to 4 differs from 1 by not more than 0.5%. A relation of the type (52) thereby permits finding $\sqrt{C}$ from the minimum in the empirical data. The use of (52) together with (16) can greatly supplement and refine the tables required for making predictions.

On the whole, we have every reason to believe that even at its present level, the scheme for predicting the properties of normal (nonassociated) substances) can find broad practical application for estimating the properties of new products of chemical technology, heat carriers, heat storage substances, cooling agents, etc. The development of these methods makes realistic the practical fruition of the inverse problem: the program for selecting substances with properties that are closest to chosen properties.

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