REVIEW ARTICLES

PREDICTION OF THE PROPERTIES OF LIQUIDS AND GASES*

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By prediction we mean the listing of the thermodynamic and kinetic characteristics of a substance in the absence of macroscopic data, i.e., calculations based on the knowledge of the structure of the molecules, or at least of the structural formula of the substance. In accordance with this interpretation of the concept, prediction has to be the natural pragmatic consequence of the development of the molecular-kinetic theory, the direct and immediate result of revealing the nature of the gas—liquid state of a substance on the basis of the apparatus of statistical physics and information on the characteristics of the molecules. It is to the solution of this problem for the simplest type of object, viz., monatomic nonmetals, that the physics of liquids persistently moves.

The development of the physics of "simple liquids" was greatly helped by the use of computerized calculation methods, by "computer experiments." The methods of computer modeling greatly enrich the possibilities of theory, increase its yield of results, on the other hand, they create the feeling of a certain dissatisfaction on account of the deviation from the purely theoretical deductive path. One way or another, it cannot be denied that the basic properties of monatomic simple liquids have lately become ever better known and understood. The situation is much more complicated as regards the molecular physics of polyatomic liquids. Here it is not a priori obvious that it is possible to devise a theory ensuring the description of sufficiently broad classes of substances. In fact, there exists an enormous variety of compositions and structures of molecules multiplied by the existence of conformers, and there are complications due to the deformability of the interatomic bonds, the distribution of static charges, the nonadditivity of the interaction forces, not to speak of the additional complications such as the manifestation of the chemism of interaction. This abundance of complications and peculiarities naturally brings to mind the fact that the properties of polyatomic substances, too, have to be just as variegated, and that it is difficult to expect the existence of regularities that are sufficiently general. Such considerations generate pessimism whose extreme expression is the opinion that each substance has to have its own regularities and relationships that are uniquely its own.

To overcome this pessimism and skepticism is possible only with facts, with purposeful analysis of the empirical data, the search for really existing regularities. At present it is becoming more or less clear that in the properties of large classes of substances, a very limited amount of this variety of characteristics of the molecules is coming to the fore, that the behavior of a substance is determined by only some, the most fundamental qualities, and that the role and importance of the other details are secondary, as a rule. Below we will reveal the content of our assertions, and then we will turn to the works published in recent years and dealing with the development of the molecular-kinetic theory of polyatomic liquids, and we will examine the principal trends of the theoretical investigations.

A large group consists of works examining models of molecules that represent hard cores. It is no accident that these models arouse great interest. This is due chiefly to the important role of purely geometric factors in the physics of liquids and the corresponding important role ascribed to hard globular molecular models in the physics of simple monatomic liquids. Regardless of its extreme simplicity, it is a good basis for describing important aspects of the nature of liquids, chiefly their structure; the model of globular molecules is the zero approximation in the methods of the theory of perturbations [1].

The following were examined as models of polyatomic molecules: ellipsoids [2], spheroids [3-9], dumbbells [10-15] including asymmetric (heteroatomic) ones [16-19], systems of three,

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four, or five spheres [20]; there are works dealing with the generalization for convex bodies of arbitrary shape [21-23].

Works of this kind form some store for subsequent investigations in which the obtained results may serve as an indispensable element of the iteration procedure with which the "softness of the forces" of repulsion and the potential of attraction are taken into account. In this direction, only the first steps [24,25] have so far been made.

The second group of works deals with numerical calculations of the properties of substances for molecules that are coupled centers of forces. This model, the model of additive atom-atom interaction, was suggested in works by Van Laar [26], and later it found widespread application in crystal chemistry [27,28] and in the theory of adsorption [29]. In molecular physics, this model is only just beginning to gain recognition. Works of this kind include [30-41]. The calculations provide much interesting information but it is difficult to make generalizations because the calculations are limited by partial sets of parameters for concrete molecules.

Finally, we want to draw attention to yet another trend in some works where the complex nonpoint interaction potential of polyatomic molecules is replaced by the relatively simple model potential, the effective point potential whose shape to some extent takes into account the complexities of polyatomic interaction. In particular, works are known where the Kihara potential is used [31,42-46], and a number of works dealing with the application of the potential of a spherical shell ("blurred" on the sphere of the Lennard-Jones potential) [30, 47-53]; basically, these are works of ten years ago.

On the whole, the works with the above subjects helped chiefly to clear up details but so far they did not yield generalizations on whose basis it would have been possible successfully to develop a theory of polyatomic liquids that would be as general as possible. This is no accident. All the examined trends are the expression of activity on the basis of the a priori approach to the problem. This is logically faultless but it is not the optimum strategy. A more efficient way of devising a quantitative theory, or in any case, of quantitative calculation methods is a combination of the molecular-kinetic theory with those important heuristic consequences which follow from an analysis of the empirical material.

Now is the time to explain those concrete facts whose existence we so far only mentioned.

As is well known, an important apparatus of the methodology of empirical generalizations in applied physics is the theory of similarity. It in particular determines the forms of presenting the experimental material that yield a maximum of information and make it possible to extend information on single objects and processes to a large variety of similar ones. The theory of similarity makes it possible to draw conclusions about the unknown on the basis of the known, and proceeding from this, to determine the strategy of the investigations. In connection with the problem of the properties of a substance, it presents itself in the form of the theory of thermodynamic similarity which is an extension and a generalization on corresponding states [54-56].

One of the most important empirical regularities obtained by way of successive application of the theory of thermodynamic similarity is the so-called single-parameter law of corresponding states. The essence of this law is that the reduced dimensionless kind of the thermal equation of state of a normal substance depends only on one individual parameter, the determining criterion of thermodynamic similarity A [54-59]:

$$\Phi(\pi,\ \varphi,\ \tau,\ A) = 0, \tag{1}$$

$$\pi = P/P_{cr},\quad \varphi = V/V_{cr},\quad \tau = T/T_{cr}$$

(the fixed value of A corresponds to a group of thermodynamically similar substances). By normal substances we mean here nonassociated liquids and gases, i.e., substances whose molecules do not exhibit chemism in mutual interaction. These substances are all the hydrocarbons (alkanes, alkenes, alkynes, cyclanes, aromatic hydrocarbons) with all isomers and the halogen derivatives of all hydrocarbons, ethers (both simple and complex ones), and most low-atomic gases. Among the normal substances are also polar ones; the presence of a dipole moment in itself does not infringe the single-parametricity of the law of corresponding states. Deviations from the single-parameter law of corresponding states take place for liquids where quantum corrections (helium, hydrogen, partly neon) manifest themselves, and for compounds showing a tendency to association on account of the hydrogen bonds (alcohols, organic acids, water, etc.).

For a broad class of normal substances, the single-parameter law of corresponding states is correct in the entire region of the liquid–gas state of the substance, from moderately compressed gases to dense liquids under pressure, including the regions of metastable states. The accuracy with which (1) is fulfilled is determined by the accuracy to which the reduced π, φ, and τ values are known at present.

All that has been explained above provides grounds for viewing (1) as an important, very substantial and general empirical regularity. It would be difficult to overestimate its practical importance. Determination of the function (1) on the basis of information for several thoroughly studied substances ensures that the equations of state are obtained for each of the substances of the examined class. Tens of concrete methods of calculating the properties of liquids and gases on the basis of (1) can be found in [55,56].

To calculate the properties on the basis of (1), three initial values have to be specified. This follows from the circumstance that the three dimensional parameters T_{cr}, P_{cr}, and V_{cr}, and the fourth dimensionless parameter (similarity criterion $\mathbf{A}$) are uniquely correlated by the relationship

$$\frac{P_{cr} V_{cr}}{R T_{cr}} = f(\mathbf{A}), \tag{2}$$

following from the general tenets of the theory of similarity [55]; thus the number of independent characteristics is equal to three.

It is not mandatory to use the above-listed parameters as initial data. They can also be expressed through other magnitudes that are easier to determine. Among the elaborated algorithms, two should be pointed out; they are based on the most accessible empirical information. In the first one, the calculation is based on information on the normal boiling point, on one value of the pressure saturated vapor at a lower temperature, and on one value of the density at some arbitrary suitable temperature. The second algorithm is based on the knowledge of the boiling point and of two values of density at temperatures below the boiling point. Each of these algorithms ensures the calculation of the saturated vapor pressure, of the densities of coexisting phases (liquid, gas), of isothermal compressibility of a dense liquid, of the isotherms of a liquid and gas in the entire range of states, of the enthalpy of evaporation, of the surface tension, of isobaric and isochronous heat capacity of a liquid, of the thermal conductivity of a liquid, and of the viscosity of a gas. In fact, all the thermal and caloric properties and most kinetic properties of liquids and gases turn out to be accessible to calculations based on simple initial data [55,56].

The single-parameter law of the corresponding states (1) can serve as the basis of purely empirical methods of predicting properties if we use the relationships determining the initial parameters from information on the composition and structure (structural formula) of the corresponding molecules. In principle, it is possible, on the basis of (1) and using empirical methods, to determine the three critical parameters T_{cr}, P_{cr}, and V_{cr}; such methods are known, they can be found in [60]. In practice, the results of such calculations will be unsatisfactory because the function (2) is weak, and reliable information on the parameter $\mathbf{A}$ cannot be obtained in this way, whereas generally speaking, the role of $\mathbf{A}$ in (1) is considerable. The success of the empirical methods thus depends on the possibility of empirically determining the parameter $\mathbf{A}$. Such methods have not been worked out. Existing recommendations [60] suggest using information on the boiling point, i.e., information on the macroscopic characteristic of the substance. Thus prediction calculations on the basis of pure empiricism have not been worked out. Below we will demonstrate that resorting to molecular-kinetic model notions makes it possible to solve this problem. For this approach we will turn our attention to the fundamental importance of the single-parameter law of the corresponding states. Alone the existence of a law with fairly broad generality and high accuracy is a hopeful fact which enables us to view optimistically the possibility of devising a quantitative theory of multiatomic liquids. It indicates that, regardless of the deterring complexity of the interaction of multiatomic molecules, the quantitative description of these liquids at a level, satisfactory for practice, requires the knowledge of only three characteristics. One such general conclusion would be sufficient to enable us to speak of the great heuristic importance of the consequences of using methods of thermodynamic similarity for the conclusion of the expediency of enlisting experimental material for solving the problems of molecular physics, and conversely, of the importance of using the notions of molecular physics for the empirical regularities to make sense. However, we are in a position to obtain even more concrete, and therefore more valuable conclusions.

The concretization of the molecular-kinetic consequences of the existence of the single-parameter law of the corresponding states requires this regularity to be interpreted "at the molecular level." Leading here is the idea of Kamerling–Onnes about the mechanical similarity of a system of molecules as a sufficient condition of macroscopic, thermodynamic similarity. In viewing a system of molecules as the centers of forces (for multiatomic molecules, such a concept presupposes the introduction of an effective potential replacing the real noncentral interaction), thermodynamic similarity occurs on condition that the dimensionless form of the potential of the forces of intermolecular interaction is identical. This last is ensured by the potential function having two parameters. The single-parameter reduced equation of state describes the unidimensional variety of groups of similar substances, and this indicates the existence of the third parameter in the effective potential of interaction.

The conclusion about the three-parameter nature of the effective potential is general. It does not make it possible to judge which kind of potential is involved but it stimulates the search for this potential and draws attention in the first place to works using model three-parameter potentials (among them are the above-mentioned Kihara potentials of a spherical nucleus, and the potential of a spherical shell).

It is natural that the next step in the development of the foundations of the molecular-kinetic theory of polyatomic liquids has to be an investigation dealing with the problem of the effective potential. The results of systematizing the empirical factors and the consequences of using the methods of the theory of thermodynamic similarity come to our assistance here, too. It turns out that at this stage, too, we may assume the methodology based on close combination of the molecular-kinetic theory with the results of empirical generalizations to be optimal. The essence of the suggested approach consists in the following. As effective interaction potentials we examine potentials that are model potentials in the sense that their parameters are to a certain extent associated with the structural characteristics of the molecules (in the opposite case we are deprived of the possibility of devising a theory permitting the prediction of the properties of substances on the basis of information in the molecules). Among the model potentials are, e.g., the same Kihara potentials and the potentials of a spherical shell if the dimension of the nucleus in the first of them and of the shell in the second are correlated with the characteristic geometric dimensions of the molecules. As model potentials we may also class the potential of a "rectangular well" if the positions of the walls of the well are related to the corresponding dimensions of the molecules. For each of the examined potentials the macroscopic properties can be calculated by the known formula of the molecular-kinetic theory; this concerns in the first place the second virial coefficient, and the empirical formulas can be used for these properties for the purpose of comparing the parameters of the potential with the principal macroscopic parameters T_{cr}, V_{cr}, A. With the second virial coefficient, such an approach leads to the following chain of comparisons: structural characteristics of the molecules → parameters of the potential → parameters describing the dimensionless kind of temperature dependence of the second virial coefficient → critical parameters and the determining similarity criterion. As empirical generalization we may use the formulas suggested in [61]. The final result of such a chain is the correlation of the microparameters that is different for different potentials. This correlation can be related to those empirical dependences obtained by direct comparison of the "input" and "output" of the examined chain (details may be found in [55, 56]). Since there exist three independent parameters characterizing the individuality of the substance, there must exist three independent methods of verifying the potentials, three correlations of the micro- and macroparameters. The above-explained method of verifying the kind of interaction potentials, though important in itself, does not solve the question of which structural characteristics of the molecules in particular have to be used in the procedure under examination. Decisive here is the uniqueness of the correlation of the micro- and macroparameters in empirical systematization. In this case, considerations of a molecular-kinetic nature already help the empirical approach. The sequence of considerations is approximately the following. The successful development of the method of atom–atom potentials, mentioned at the beginning of the article, directs particular attention to the results of the application of this concept. The atom–atom interaction in averaging over all the possible mutual orientations of the molecules leads to a potential that is "smeared" over the spherical shells whose centers lie at the centers of the molecules. Rapid decrease of the interaction forces with increasing distance has the effect that at sufficiently small distances between molecules, the outer shells of such a model manifest themselves chiefly, and that that model of a spherical shell is correct in which the characteristic parameter has to be the

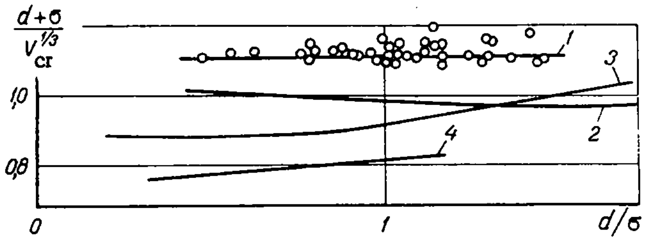

Fig. 1. Dependence of $\varphi = (d + \sigma)/V_{cr}^{1/3}$ on the ratio d/σ: 1) Eq. (3); 2, 3, 4) calculations of the potentials of a spherical shell, a Kihara and rectangular well, respectively. Dots indicate experimental data.

distance between the center of the molecule and the peripheral atom d/2. The second parameter σ in this model with the dimensionality of length characterizes the interaction of the peripheral atoms and determines the dimension of these atoms. This explains the selection of the two structural parameters d and σ as candidates for the role of the principal geometric characteristics of the molecules.

However, the above considerations are far from strict, they form only some kind of pattern of arguments, they are a kind of "suggestion." One way or another, it becomes clear that the parameters d and σ belong in fact to the important characteristics of the structure of molecules that manifest themselves in the macroscopic properties. Thus it was possible to reveal that the sum of these parameters determines the critical volume

$$d + \sigma = 1.111 V_{cr}^{1/3}, \tag{3}$$

and distinctly correlates the relationship with the macroscopic parameter A:

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

It was also possible to establish the third of the mentioned relationships of micro- and macroparameters. It has the form

$$C = \frac{T_{cr}^3}{P_{cr}^2} f(\mathbf{A}), \tag{5}$$

where

$$C = \sum_{i,k} c_{ik}, \tag{6}$$

and c_{ik} are the increments characterizing the additive interactions of the i-th atom of one molecule with the k-th atom of another molecule (they are coefficients of the formulas of dispersive interaction $u_{ik} = c_{ik}/r^6$), f is a known univalent function [55,56].

Then we examine each of relationships (3)-(5) as such and as the above-described way of approbation of concrete model effective potentials of interaction of polyatomic molecules.

Figure 1 shows the ratios $(d + \sigma)/V_{cr}^{1/3}$ in dependence on d/σ. Each dot in this graph corresponds to one substance. It can be seen that the dots are fairly closely grouped around the empirical straight line corresponding to Eq. (3). Relationship (3) turns out to be correct for molecules of very different shape and composition. This fact deserves thorough examination. Here empirical material provides food for molecular-kinetic thought.

Curves 2-4 in Fig. 1 illustrate the calculations of model potentials of a spherical shell, a Kihara and rectangular well, respectively. It can be seen that the potential of the spherical shell describes the examined dependence better than the others; the difference amounts to ∿10%.

Figure 2 illustrates the relationship (4). Here, too, each dot corresponds to a concrete substance. Equation (4) is represented by the straight line 1. The curves 2, 3, and 4 are the results of calculations of the potentials of a spherical shell, a Kihara and a rectangular well, respectively.

Figure 3 illustrates the complex $Y = T_{cr}^{3/2}/P_{cr}\sqrt{C}$ corresponding to Eq. (5), for hydrocarbons. (The question of optimum selection of c_{ik} will be discussed later.) It can be seen

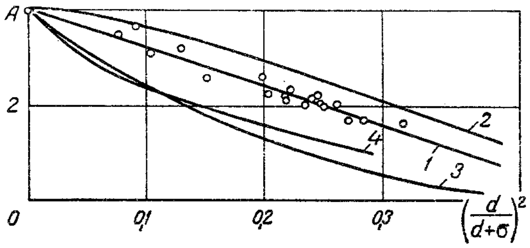

Fig. 2. Dependence of the determining criterion of thermodynamic similarity A on $[d/d + \sigma)]^2$: 1) Eq. (4); 2, 3, 4) calculations of the potential of a spherical shell, a Kihara and rectangular well, respectively. Dots indicate experimental data.

from the figure that a large amount of data for aliphatic and cyclic hydrocarbons (including all isomers) satisfies the dependence (5) with a scatter of ∿1%, i.e., with an accuracy equal to that of the experimental results.

The dependence obtained in Fig. 3 is represented by curve 1 in Fig. 4 in comparison with the results of the calculations of the potentials of a spherical shell (curve 2) and Kihara shell (curve 3).

Examination of the figures permits the conclusion that the relationships (3)-(5), on the one hand, fairly well approximate a large amount of empirical material, on the other hand, they are a convenient means of investigating quasispherical potentials. We want to point out that the approbation of potentials used here has little in common with the ordinary method consisting in comparing the quality of describing the temperature dependence of the second virial coefficient or the viscosity of the gases. The relatively low sensitivity of these means to the kind of potential would not make it possible to distinguish so accurately the effectiveness of using each of them. Now we are in a position to assert that the potential of a spherical shell as model potential describes the properties of a set of polyatomic substances better than the others. This conclusion is in agreement with the previously noted circumstance that the potential of a spherical shell corresponds more closely to the atom—atom additive interaction which is a successful zero approximation of the complex interaction of polyatomic molecules.

Later we will revert to each of the relationships (3)-(5), discuss some problems connected with their interpretation, and examine the various refinements and generalizations. Now we want to emphasize that the relationships (3)-(5), empirical in origin, and though prompted by some considerations at the "molecular level," nevertheless establish a correlation between the micro- and macrocharacteristics of a substance, and make it possible unambiguously to determine the critical parameters and criterion A from data on the composition and structure of the molecules. The values of the parameters σ and increments c_{ik}, indispensable for such calculations, were tabulated in [55,56]. If it is borne in mind that according to the above, the values of the critical parameters and of A suffice for calculations of the thermodynamic and a number of kinetic properties of liquids and gases, we have the full algorithm for predicting the properties of normal (nonassociated) substances.

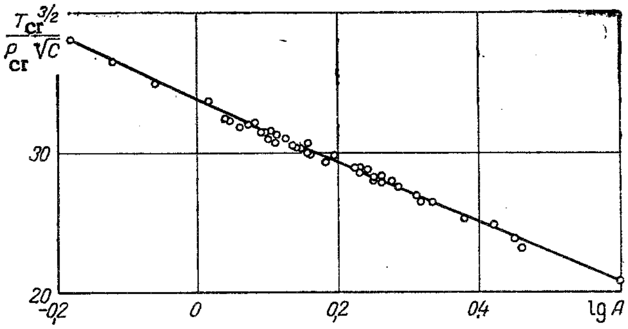

Fig. 3. Dependence of the complex $T_{cr}^{3/2}/P_{cr}\sqrt{C}$ on the logarithm of the determining criterion of thermodynamic similarity A for hydrocarbons.

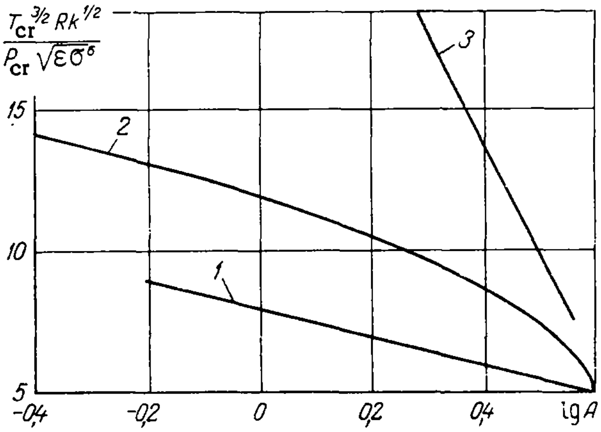

Fig. 4. Dependence of the complex $T_{cr}^{3/2}Rk^{1/2}/P_{cr}\sqrt{\varepsilon\sigma^6}$ on the logarithm of the determining criterion of thermodynamic similarity: 1) Eq. (8); 2, 3) calculations of the potentials of a spherical shell and a Kihara shell, respectively.

The first example of such a prediction — the calculation of the first representative of the Freon series (Freon 11) — was presented in [56]. The calculation was based on information on two structural characteristics of this substance (CCl_3F), the distance between the C and F atoms equal to 1.77 Å and the distance between the C and Cl atoms, viz. 1.44 Å (the angles between the bonds were taken as tetrahedral). The results of the prediction calculation were found to be very close to the experimental results for a variety of properties in a broad range of states. Table 1 presents the results of such calculations of the principal parameters of this substance, for the critical characteristics.

The second example of a calculation illustrates the possibilities of prediction that is not based on concrete structural characteristics but only on the knowledge of the structural formula of the substance. The calculations were carried out for the simplest representative of the Freons of the ethane series: Freon 116, hexafluoroethane (C_2F_6). For the values of the lengths of the bonds, the recommended mean values were taken from [63]. The results of the calculations of the critical characteristics are given in Table 2.

Undoubtedly, both examined examples belong to the successful ones. In [56] we emphasized that one should not expect such good coincidence with experiments in all cases. Here we will put the problem of the errors of prediction on a wider plane, as the problem of optimum methods of prediction. We will not only keep in mind the algorithm examined above, but also the possibilities of combining relationships (3)-(5) with other existing methods of empirical prediction estimates. We will combine discussion of this problem with a more detailed examination of each of the relationships (3) and (5), and explain some refinements obtained very recently. Along with the explanations we will also examine the calculation methods that use information on macroscopic properties but to a lesser extent than the previously elaborated methods. These new methods lie, so to speak, between the strict calculation methods and the methods of prediction. They use partly elements of the prediction procedure (information on the composition and on the structure of the molecules).

First we will turn out attention to relationship (5). We already noted above that Eq. (5) describes a set of experimental data for tens of hydrocarbons with an error of ∿1%, i.e., practically with the same accuracy which applies to the known critical data for this group of

TABLE 1. Results of Prediction and Calculations of the Principal Parameters of Freon-11

Parameter	Expt. [62]	Prediction	Method of calc.					
			1	2 (estim)	3	4	4′	5
T_{cr}, °K	471	472	470	479	466	470	470	468
P_{cr}, bar	44,1	44,3	44,1	42	42,5	44	46,3	43,7
V_{cr}, cm^3/mole	247	243	243	254	248	243	230	244
A	2,2	2,11	2,08	1,6	1,94	2,07	1,95	2,07

TABLE 2. Results of Predicting the Critical Parameters of Freon 116

Parameter	Prediction	Expt. [64, 65]
T_{cr}, °K	290	293
P_{cr}, bar	30,1	30,4
V_{cr}, cm³/mole	215	219—246
A	1,68	1,70

TABLE 3. Atomic Contributions of Fluorine $\sqrt{c_{FF}}$ in Different Compounds

Substance	$\sqrt{c_{FF}}$	Substance	$\sqrt{c_{FF}}$
CF_4	0,60	C_4F_8	0,61
C_2F_6	0,61	C_5F_{12}	0,64
C_3F_8	0,58	C_6F_{14}	0,58
C^4F_{10}	0,58	C_6F_6	0,63
		Mean	$0{,}60_3$

liquids. The increments c_{ik} given in [55,56] make it possible to carry out analogous calculations for haloid derivative hydrocarbons; the results of such calculations were examined in [56]. From the empirical point of view nothing better could be desired. Nevertheless, there was one circumstance which induced us to revert to this ratio and to raise once again the question of selecting the increments c_{ik}. In [56] we drew attention to the existence of considerable deviations from the known combination rule

$$c_{ik} = \sqrt{c_{ii}c_{kk}} \tag{7}$$

in the optimum set of increments thus found. Particularly large deviations occurred with the interaction H—F and H—Cl. For instance, the value of c_{HF} according to (7) should have been 0.20 instead of 0.59; the value of c_{HCl}, 0.71 instead of 1.35. Such differences cannot be reconciled with the existing theory of dispersion interaction [66]. The thought occurred that the difference betweeen c_{HF} and c_{HCl}, on the one hand, and the combination values, on the other, express the fact that most molecules containing the bonds CH, CF or CH, CCl are polar, and that the effective c_{HF} and c_{HCl} indirectly (and incompletely) take into account the dipole—dipole interaction of the corresponding molecules. To verify this, we determined the increments c_{ik} once again, limiting ourselves to the class of nonpolar and weakly polar substances. For the increments of interaction c_{CC} and c_{CH} we left the same values as in the previously used set. They were taken from the data on the adsorption of hydrocarbons on the surface of graphite [29]. For the increment of c_{HH} we took the value 0.166 corresponding to (7). This value is practically equal to the value taken in the potentials of Dashevskii [28] and Poltev [67]. (Previously we used $c_{HH} = 0.1$.) The change in this increment did not noticeably impair the scatter of the points with respect to the curve in Fig. 3 but it somewhat changed the function f(A). For a new set of increments, this function is approximated by the expression

$$f(\mathrm{A}) = 33.65 - 23.22\,\lg \mathrm{A} + 3.06\,(\lg \mathrm{A})^2. \tag{8}$$

Figures 3 and 4 illustrate this function in particular. The rms deviation of the points from (8) amounts to 0.9%, the maximum deviation (for one point) — to 2%. If relationship (7) is fulfilled for a new set of increments, it is possible to calculate the combination of the critical parameters $T_{cr}^{3/2}/P_{cr}$ for the hydrocarbons C_nH_m by the simple additive formula:

$$T_{cr}^{3/2}/P_{cr} = f(\mathrm{A})(1.136 + 0.4074\,m), \tag{9}$$

which is correct for saturated and cyclic hydrocarbons. For alkenes (hydrocarbons with double bonds) the number of carbon atoms with double bond (according to [56]) has to be preceded by the factor $\delta = 1.06$. For treble bonds, the corresponding factor is equal to 1.07, for the carbon of aromatic rings it is also equal to 1.07. These correction factors, taking the valency state of carbon into account, are close to those found by Avgul' et al. [29].

On condition that (7) is correct, a formula type (9) can be extended to apply to any nonassociated compound type $K_kL_lM_mN_n\ldots$, and in that case

$$T_{cr}^{3/2}/P_{cr} = f(\mathrm{A})(\sqrt{c_{kk}}\,k + \sqrt{c_{ll}}\,l + \sqrt{c_{mm}}\,m + \sqrt{c_{nn}}\,n + \ldots). \tag{10}$$

Verification of the relationship (10) for nonpolar haloid derivative hydrocarbons confirmed the correctness of the additive approximation, and made it possible to use (10) for determining the atomic contributions $\sqrt{c_{ii}}$. As an illustration of the accuracy of (10) we present Table 3 containing the values of $\sqrt{c_{FF}}$ obtained with the aid of (10) from the experimental data for different fluorine derivatives. In this table, unity of the second figure after the decimal point in the value of $\sqrt{c_{FF}}$ corresponds to approximately one percent of the

TABLE 4. Summary of Values

Atom	Ne	Ar	Kr	Xe	H	C	F	Cl	Br
$\sqrt{C}$	0,53	1,85	2,68	4,11	0,407	1,14	0,603	2,356	2,9

Atom	I	N	O	S	B	Ge	Si	Mo
$\sqrt{C}$	4,3	1,0	0,9	2,6	1,3	2,5	1,3	4,6

error in the magnitude of $T_{cr}^{3/2}/P_{cr}$. In Table 4 we present a summary of the values $\sqrt{c_{ii}}$ for different atoms obtained on the basis of (10). The values $\sqrt{c_{ii}}$ are given in $J \cdot m^6$(NTP)mole. It can be seen that the interaction energy of different atoms in the given list differs at equal distances; the differences amount to as much as two orders of magnitude.

The values of $\sqrt{c}$ for inert gases lie between the values obtained on the basis of the accurate and the approximate formulas of London [29,66]. From the values found on the basis of information on the second virial coefficient and the kinetic coefficients of diluted gases, they differ by 2-11% (from the lower limit of the interval of values of $\sqrt{c}$ from [68]). Table 4 provides food for thought concerning the correlation between the energy of dispersion interaction and the characteristics of the atoms.

Deviations from the additive formula (10), found for substances with relatively large values of the dipole moments (practically for $\mu > 1.2D$) correlate, as was to be expected, with the dimensionless magnitude characterizing the orientational interaction. This correlation has the form

$$\Delta C = 150 \frac{\mu^4}{T_{cr}}, \tag{11}$$

where ΔC is the difference between the calculations of C by the additive formula and the value $T_{cr}^3/(P_{cr}^2 f^2)$ (μ is in Debye units). For prediction calculations it is more convenient to use a somewhat different dimensionless complex and the formula

$$\frac{T_{cr}^3}{P_{cr}^2 f^2} = C + 2.8 \frac{\mu^4}{C} \left(\frac{V_{cr}}{100} \right)^2, \tag{12}$$

where

$$C = (\sqrt{c_{ii}}\, i + \sqrt{c_{kk}}\, k + \ldots)^2. \tag{13}$$

The second term in (12) contributes less than 1% to $T_{cr}^{3/2}/P_{cr}$ if

$$\frac{2.8\mu^4}{C^2} \left(\frac{V_{cr}}{100} \right)^2 < 0.02. \tag{14}$$

This occurs practically when $\mu < (1-1.5)D$. Inequality (14) provides a quantitative formulation of the term "weakly polar substances" concerning the description of properties. There exist only a few compounds to which (14) does not apply. In the case of haloid derivative hydrocarbons, e.g., this requires the simultaneous presence of H and F or H and Cl atoms.

If formula (12) is used for prediction, it does not greatly complicate the algorithm. The value of V_{cr} is determined at the first stage of calculating by Eq. (3). If the dipole moment is unknown, it can be estimated by the method of vector summing of the characteristic dipole moments of bonds [63], i.e., on the basis of information on the structure of the molecules or of the structural formula, taking the typical angles between bonds into account.

The accuracy of formula (12) and the quality of the calculations of the magnitude of $T_{cr}^{3/2}/P_{cr}$ were verified by calculations for fluoro- and chlorohydrocarbons with known values of A [55]. Calculations according to (12) and Table 4 using literature data for the dipole moments differ by 2.2% (standard deviation) from T_{cr} and P_{cr} found from experimental literature data. The magnitude of the scatter can be largely explained by errors of the data for the critical parameters. If we take it that the errors in the numerator and in the denominator of the ratio $T_{cr}^{3/2}/P_{cr}$ are of the same order of magnitude (which is close to the truth because accuracy of determining the critical temperatures is usually somewhat higher than the accuracy of determining the critical pressure), then a scatter of 2.2% corresponds to a mean error of temperature ∿1% and of pressure ∿1.5%.

The good results provided by formula (12) make it expedient to use it not only as an element of the algorithm for predicting properties, but also in calculations based on information on macroscopic properties. The use of (12) makes it possible to reduce the number of initial data indispensable for the calculations. Instead of three reference values needed for the above-mentioned calculation methods, two only will be needed. In accordance with this, one can imagine three basic sets of the simplest and most accessible initial data and correspondingly three calculation methods:

1) from the boiling point t_{boi} and another value of the vapor pressure (convenient at a temperature below the boiling point);
2) from two values of density at two different temperatures (possibly below the boiling point);
3) from the boiling point and a value of the density (at a temperature below the boiling point).

We will accompany the explanation of each of these methods with concrete examples. As the object we use Freon-11, CCl_3F, which serves as example in [56], and n-hexane, which was used as example in [55]. We will carry out the calculation up to the determination of the fundamental macroscopic magnitudes P_{cr}, V_{cr}, T_{cr}, and **A**. The algorithms of the calculations of the properties, basing themselves on these magnitudes, were explained in detail in [55], and the degree of agreement of these parameters with the experimental ones also characterizes unambiguously the accuracy of the calculations.

All the algorithms examined below have a basic element in common. In each of them, the calculations will amount to the determination of such a value of T_{cr} at which the complex $T_{cr}^{3/2}/P_{cr}$, determined with the aid of (12), is found to be equal to the same complex found by separate calculation: T_{cr} and P_{cr} (consequently, T_{cr} in such a procedure plays the role of the variable parameter). In fact, this means finding the point of intersection of the graphs of two functions: $\sqrt{cf[A(T_{cr})]}$ and $(T^{3/2}/P_{cr})(T_{cr})$. It is practically not mandatory to find the values of these functions for a large set of T_{cr}. For this purpose a fairly simple iteration procedure may be used.

Let us examine the first of the calculation procedures. The first step is based on using the following formula for the vapor pressure [55]:

$$\lg \frac{P^*}{P} = 3.9726 \lg \frac{T^*}{T} + \left(\frac{T^*}{T} - 1\right)\left(0.3252 + 0.40529 \frac{T^*}{T}\right). \tag{15}$$

Here P and T are parameters whose ratio to the critical parameters are unique functions of **A**. On the basis of (15) T* can be determined by:

$$T^* = \frac{T_1 T_2}{T_1 + T_2}\left[0.098805 + \sqrt{0.0097625 + 2.46737 \frac{T_2 + T_1}{T_2 - T_1}\left(\lg \frac{P_2}{P_1} - 3.9726 \lg \frac{T_2}{T_1}\right)}\right], \tag{16}$$

P* can be found directly from (15) after determining T*.

Then we have to specify the value of the critical temperature of zeroth approximation. For its selection it is convenient to use the approximate formula:

$$T_{cr}^{(0)} = \frac{T_{boi}}{0{,}64 - 0.7}, \tag{17}$$

the so-called Guldberg rule. The critical temperature determines the parameter **A** [55]:

$$\lg A = 1.1891 + 0{,}0481 \frac{T^*}{T_{cr}} - 0{,}6323 \left(\frac{T^*}{T_{cr}}\right)^2, \tag{18}$$

and substitution of $T_{cr}^{(0)}$ into (15) yields the critical pressure of the zeroth approximation, $P_{cr}^{(0)}$. Thereby $T_{cr}^{(0)3/2}/P_{cr}^{(0)}$ is determined. Substituting A, found by (18), into (8) yields the function f; calculation by increments c_{ik} on the basis of (13) and Table 4 makes it possible to determine that same complex $T_{cr}^{3/2}/P_{cr}$ proceeding from (12) if μ is known or determined from data on the dipole moments of the bonds [63]. If the value $T_{cr}^{3/2}/P_{cr}$, determined by the first method (we will henceforth call it the "direct" method), is larger than the result of calculation by the second method (we will henceforth call it the "additive" method in accordance with the principle of additive atom–atom interactions on which it is based), then the value of $T_{cr}^{(1)}$ of the subsequent approximation has to be increased in comparison with $T_{cr}^{(0)}$,

TABLE 5. Results of the Calculation of the Characteristics of n-Hexane

Parameter	Literature data [55]	Calc. method		
		1	2 (estimate)	3
T_{cr}, °K	508	508	503	508
P_{cr}, bar	30,3	30,7	30,0	30,7
V_{cr}, g/cm³	0,234	0,237	0,234	0,237
A	1,43	1,43	1,41	1,42

and conversely, $T_{cr}^{(1)}$ has to be taken smaller if the result of the direct calculation is smaller than that of the additive calculation.

Then the above-described procedure is repeated, and the subsequent, the second approximation is already found as the result of interpolating (or extrapolating) the two previous ones.

The critical volume and density can be calculated by a formula [69] concretizing relationship (2):

$$\frac{RT_{cr}}{P_{cr}V_{cr}} = 3.92-0.85\lg A. \tag{19}$$

We will carry out such a calculation for Freon-11. As initial data we use: $t_{boi} = 23.7°C$, and saturated vapor pressure at $t = 0°C$ is $P = 0.403$ bar (we used the same values previously [56]). The magnitudes thus found are compared with experimental data in Table 1.

Another example of a calculation is for n-hexane. The initial data in accordance with [55] are the following: $t_{boi} = 68.7°C$, $P = 121$ mm Hg at 20°C. The results of the calculations are presented in Table 5.

An analysis of the sensitivity of the examined calculation method, i.e., of the errors introduced by inaccuracies of stipulating the initial data, leads to the following results. If the boiling point, and consequently the second temperature at which the second value of the saturated vapor pressure is specified, is specified with an inaccuracy of 0.1°K, and these temperatures are scattered over ∿30°K, then the error of determining the critical temperature amounts to ∿0.1%, i.e., a fraction of one degree. It is thus fairly small, and in this respect the method under examination is close to the method of calculating by the aggregate of three initial parameters which was described in detail in [56].* Under the same conditions, the error of determining the critical pressure is 0.5%, for the parameter **A** it is ∿1.2%, for the critical volume 0.3%.

Let us now examine the second calculation method. Its algorithm can be represented in the following manner.

On the basis of the initial data described in [55], we can determine the magnitude

$$\zeta_0 = -\frac{1}{\rho}\frac{d\rho}{d\tau} \tag{20}$$

and then use the dependence

$$\zeta_0 = f(\mathbf{A}, \tau), \tag{21}$$

transforming it with respect to **A**:

$$\mathbf{A} = \mathbf{A}(\zeta_0, \tau). \tag{22}$$

The concrete form of the functions (21) and (22) can be obtained by differentiating Riedel's formula [69] for the dependence

$$\rho/\rho_{cr} = F(\tau, \mathbf{A}) \tag{23}$$

or some other formula, (6.2) from [55]. The function (22) can be used for determining **A** in selecting the zeroth approximation for T_{cr}. From the dependence (23) the critical density $\rho_{cr}^{(0)}$ can be found, and by formula (19) the critical pressure. After that we proceed like in the previous calculation method.

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*We use the opportunity to correct an error in [56]: for δT^* the article give the value 4°K, twice as much as it should be 2°K; correspondingly all the errors are increased by a factor of 2.

The described calculation procedure is usable but it is much less accurate than the first method. The basic reason for this is the relatively weak dependence of function (21) on **A**, and naturally, conversely, the strong dependence of (22) on ζ_0. As a result we find that small changes in ζ_0 have a considerable effect on the magnitude of **A** with fixed T_{cr}, and eventually they lead to appreciable errors in determining T_{cr}.

Taking all this into account, we cannot recommend the second method as a completely equivalent calculation method. Nevertheless, the initial set of data, together with information on the composition, is suitable for approximate calculations and estimates of the critical parameters.

In [55] we described a method of estimating the critical temperature and density by data on the values of the density at two temperatures below the boiling point. These estimates are based precisely on the fact that for organic liquids the dependence of the function (23) on **A** (for **A** from 1 to 2) is weak, and this makes it possible to use the simple approximate formula

$$\rho/\rho_{cr} = 3.95 - 1{,}95\tau. \qquad (24)$$

From (24) there follow the expressions for the critical density

$$\rho_{cr} = 0.253\left[\rho + T\,\frac{\rho_2 - \rho_1}{T_1 - T_2}\right] \qquad (25)$$

and temperature

$$T_{cr} = 0.493\left[\,T - \frac{\rho(T_2 - T_1)}{\rho_2 - \rho_1}\right. \qquad (26)$$

(as ρ and T, any of the specified pairs may be taken).

In the method of approximate calculation examined here, we may add the critical pressure and the parameter A to these two critical parameters. The recommended algorithm for the calculation is based on a formula which is obtained from (19), (5), and (8):

$$\lg \mathbf{A} = 3.7941 - 0.13889\varkappa - \sqrt{3.3985 + 0.22721\varkappa + 0.01929\varkappa^2}. \qquad (27)$$

where

$$\varkappa = \frac{T_{cr}^{1/2}M}{\rho_{cr}R\sqrt{C}}. \qquad (28)$$

If we determine $\varkappa$ on the basis of (25) and (26) and know C and M for a known composition of the molecule of the substance, we can find the parameter **A** on the basis of (27). The critical pressure is calculated by (19).

Let us examine examples of estimates. As initial data for Freon-11 we take: ρ = 1.5345 g/cm^3 at 0°C; ρ = 1.6223 g/cm^3 at –40°C [62]. The results of the calculation are presented in Table 1. The difference as against the experimental data for $T_{cr} \sim 1.7\%$ is typical of such a method [55].

The initial data for hexane are: ρ = 0.6772 g/cm^3 at 0°C; ρ = 0.6409 g/cm^3 at 40°C [70]. The results of the estimates are presented in Table 5.

The algorithm of the third calculation method is the following.

With the aid of (17) we find the critical temperature of the zeroth approximation of T_{cr}. On the basis of (24) we determine the coefficient of thermal expansion (20), and with its aid we convert the density specified at the temperature T to the density at the boiling point T_{boi}. Then we calculate the complex

$$K = T\rho/MP \qquad (29)$$

at P = 1 atm, and from the relationship

$$K = K(\tau,\ \mathbf{A}) \qquad (30)$$

we determine the parameter **A**. The function (30) in the form of the dependence

$$\tau^{-1} = f(\lg K,\ \lg \mathbf{A}) \qquad (31)$$

is here presented in the form of Table 6 which differs from the table in [55] chiefly by the values of τ^{-1} for the last row; it restores the previously found values [71] of these magnitudes because the procedure of smoothing by columns used in [55] led, as was found, to some

TABLE 6. Table of the Function (31)

—lgK	lg A				—lg K	lgA			
	0	0,1	0,2	0,3		0	0,1	0,2	0,3
0,7	1,947	2,010	2,074	2,139	1,7	1,670	1,717	1,763	1,810
0,9	1,895	1,954	2,014	2,075	1,9	1,612	1,6555	1,6985	1,741
1,1	1,841	1,8965	1,953	2,0105	2,1	1,554	1,6935	1,633	1,672
1,3	1,785	1,8375	1,8905	1,945	2,3	1,496	1,531	1,567	1,602
1,5	1,728	1,777	1,827	1,878	2,5	1,438	1,468	1,498	1,528

increase in the deviation from the most probable data. It should be mentioned here, however, that the table is based on a relatively small body of data because for encompassing the largest possible temperature interval, the sparse data of Young [72] on density were used. It seems desirable in future to refine the dependence (31).

The critical pressure can be found on the basis of the dependence

$$P/P_{cr} = F(T/T_{cr}, \mathbf{A}) \qquad (32)$$

for T = T_{boi}. As the dependence (32) we can use the table from [55] and one of the analytical approximations [55,56]. The further calculation procedure, like with the first method, consists in comparing the "direct" calculations of the complex $T_{cr}^{3/2}/P_{cr}$ with the "additive" ones on the basis of (5) and (8). For finding the critical density, either (19) may be used or a functional dependence type (23).

An analysis of the effect of an inaccuracy in specifying the initial data with the third calculation method under examination leads to the conclusion that the error in calculating the critical parameters depends on A and increases when we go over from compounds with few atoms to polyatomic ones. However, in the worst case, with an inaccuracy of 0.1°K in specifying the boiling point at T $\sim$ 300°K and $T_{cr} \sim$ 500°K, the error in determining T_{cr} will amount only to 0.6°K, which is comparable with the calculation error of the first of the examined new methods; the same conclusion is also obtained for the error of determining the critical pressure.

Let us examine examples of calculation by the third method. The initial data for Freon-11 are the following: t_{boi} = 23.7°C, ρ = 1.5345 g/cm³ at 0°C. A summary of the calculation results is contained in Table 1.

In the example of calculations for hexane, the initial data are as follows: t_{boi} = 68.7°C, ρ = 0.6594 g/cm³ at 20°C. The results are presented in Table 5. It can be seen from Tables 1and 5 that the deviations of the calculated data from the experimental ones exceed the above estimates of the errors due to inaccuracy of the initial data; this forces us to state that there exist inaccuracies in the algorithms themselves; we believe that their source is in the first place Table 6 which, as mentioned before, needs refinement.

With this we end the examination of (5) and of the practical consequences following from it. We will now turn to relationships (3) and (4) which correlate the geometry of the molecules with the macroscopic parameters, viz., the critical volume and the determining criterion of similarity **A**. Examples of prediction estimates of the critical volume on the basis of information on the structure for 17 chlorine- and fluorine-containing substances were provided by us in [73]; that same article also contained examples of the inverse calculations, the determination of structural characteristics from data on the critical volume. Here we will examine the question of the accuracy of such calculations.

The probable error of predicting the critical volume is determined by the extent to which relationship (3) is fulfilled. The scatter of the points in Fig. 1 relative to the straight line $(d + \sigma)/V_{cr}^{1/3} = 1.111$ for the 32 substances represented there amounts to 2.4% (standard deviation), which corresponds to a probable error of 7.2% in determining the critical volume. Part of this error may be ascribed to the inaccuracy of the experimental values of V_{cr}. If we take this error as equal to $\sim$3%, then with a view to the statistical independence of this contribution, the error of the prediction amounts to $\sim$6.5%. The second contribution to this error is the inaccuracy of the knowledge of the distance d, which on the average is also close to 3%. With a view to this error, the "pure" probable error of predicting V_{cr} on the basis of (3) amounts to 6.3%. This value can be reduced only by refining relationship (3), and by taking in more detail the effect of the shape and composition of the molecules into account. The first stage of work in this direction has to be an examination of the role of the atoms that are closest to the peripheral ones, and a calculation of the effect of the second shells in the model of the spherical shell.

The relatively large error in predicting the critical volume forces us to examine alternative methods of determining this magnitude on the basis of structural data. Historically the first was the method of additive calculation of the van der Waals parameter b suggested by Van Laar [26]. In fact, this is the method of calculating T_{cr}/P_{cr} which can also be used for V_{cr} on the basis of (19) in an algorithm that also includes the calculation of the parameter **A**. Calculations of b for 17 substances of those examined by us (for other substances, [26] did not contain the corresponding increments) yielded a standard error of 8.7%. The error of determining the critical volume for the same substances by our method amounted to 8.4%, i.e., on the average it was smaller, although the errors of the literature values of V_{cr} are higher than the errors of the data for b. The subsequent modification of the method of calculating b in the works by Riedel [74] and Forman and Todes (see [60]) improved the accuracy but the method became more cumbersome because a large number of structural details had to be taken into account, and this deprived the calculation procedure of the clarity that distinguished Van Laar's method. (Instead of additiveness, we now examine the quasiadditiveness of the magnitude $b^{3/4}$ which has no physical meaning.)

We will not dwell on these methods because we are in a position to examine the direct method of calculating V_{cr} suggested by Leadersen [60]. The method is fairly simple but more flexible than Van Laar's method because it takes into account the difference of the increments of atoms with different bonds and includes moreover some "free" term. Calculations by Leadersen's method cannot be carried out for the entire variety of substances examined by us. Calculations for the same 17 substances by Leadersen's method yield an error of 6.1%, which is 2% less than by calculations based on (3). At the present stage Leadersen's method is therefore preferable in the empirical approach to the selection of the optimum program of prediction. However, its applicability is limited to organic compounds; for inorganic substances, the method based on formula (3) has so far no equal.

Although relationship (3) is not the best for calculating the critical volume, its importance in principle and the practical consequences deserve close attention. The use of (3) for approbation of model potentials was examined above. However, this does not exhaust the role of (3). Below we will dwell on yet another important consequence of the relationship (3) which is associated with the simultaneous use of (3) and (4). But the examination of this equation will be preceded by an analysis of relationship (4).

The physical meaning of formula (4) is taking into account the spatial extension of polyatomic molecules. This extension, manifesting itself in the noncentral nature of the forces of interaction between the molecules, appears in the effective potential averaged over the orientations, in the form of a ratio of two geometric characteristics. Thus the ratio $[d/(d + \sigma)]^2$ plays the role of an "acentric factor." (This was the term Pitzer [57] used for the determining criterion of thermodynamic similarity introduced by him.) However, there is also another reason for the difference in behavior of polyatomic substances compared with monatomic ones: the role of the orientational dipole—dipole interaction. Regardless of the obviously physical difference of this effect, its macroscopic manifestation differs little from the manifestation of acentricity of interaction between polyatomic nonpolar molecules. This fact, revealed by analysis of the empirical material and molecular-statistical examination [55, 75-77], makes it reasonable to add an additional term to formula (4) taking the contribution of dipole interaction to the parameter **A** into account. The study of the data for a group of polar substances enables us to submit here a generalization of the relationship (4) in a form analogous to (12):

$$\mathbf{A} = 4 - 8\left(\frac{d}{d+\sigma}\right)^2 - 2.8\,\frac{\mu^4}{C^2}\left(\frac{V_{cr}}{100}\right)^2. \tag{33}$$

The condition, that the contribution of the "polar" term be small, is here, too, determined by inequality (14).

The standard deviation of the calculation results on the basis of (33) from the experimental results is ∿5%; such is the probable error of determining **A** whose considerable part is due to the inaccuracy of d. An error of 5% is not so large. In fact, it follows from the determination of **A** [55]

$$\mathbf{A} = 100\,\frac{P}{P_{cr}} \quad \text{for} \quad \frac{T}{T_{cr}} = 0.625$$

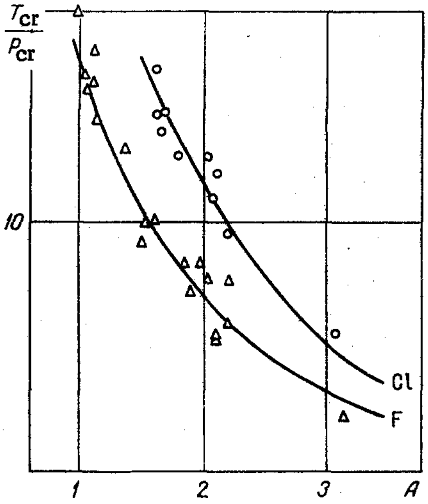

Fig. 5. Dependence of the ratio T_{cr}/P_{cr} on the parameter **A**.

and from the approximate formula

$$\lg \pi = \lg \frac{\mathbf{A}-2}{0.6}\left(1-\frac{1}{\tau}\right) \tag{34}$$

that if the inaccuracy of the critical temperature is 1% and of the critical pressure 1.5% (see above), then δ **A**/**A** $\sim$ 3%.

We will now examine the consequences of formula (3) and (4) for nonpolar substances. These formulas may be viewed as two equations containing the microscopic parameters d and σ. The solution of this system of equations yields a formula that makes it possible to determine each of these microscopic parameters through macroscopic magnitudes. It was precisely in this way that it was possible in [56] to establish that the effective parameters σ for hydrocarbon groups are practically equal. The exclusion of d from (4) with the aid of (3) determines more accurately the form of the function (33) on the basis of using the much greater variety of substances. Thus it is possible to include in the examination a large body of data for hydrocarbons for which the direct determination of d is made difficult by the presence of conformers. One of the important consequences of simultaneous examination of relationships (3) and (4), which we discuss here, is that the exclusion of d determines the correlation between the macroscopic parameters V_{cr} and **A** which is a family of functions determined solely by the parameter σ. In other words, we come to the conclusion that the field of the macroscopic magnitudes V_{cr} and **A**, which in principle are independent, has to consist of a number of discrete lines. This consequence of micro- and macrorelationships (3) and (4) permits direct macroscopic verification. It is expedient to carry it out by examining the values **A** and T_{cr}/P_{cr} (instead of V_{cr}) for substances containing F and Cl because the difference in the values of σ for F and Cl atoms is fairly large.

A comparison of these characteristics is presented in Fig. 5. The solid lines represent the results of calculations based on (3), (4), and (19) for $\sigma_F = 3.06$ and $\sigma_{Cl} = 3.55$. It can be seen that the examined set of substances is divided in effect into two groups depending on which atoms of the molecule are peripheral. The correlation of T_{cr}/P_{cr} and **A** is fairly strong. It illustrates the degree of reliability of the micro- and macrobonds discussed here. We want to point out that an analogous construction for hydrocarbons does not yield such a distinct picture. The reason is a shortcoming of the procedure itself, the lack of strictness in describing the hydrocarbon groups as structural units, and in consequence the lower "stability" of the values σ of the radicals CH_3, CH_2, and CH. As regards the correlation

$$P_{cr}/T_{cr} = F_\sigma(\mathbf{A}) \tag{35}$$

for molecules with peripheral atoms Cl and F, it deserves practical utilization.

The existence of relationship (35) makes it possible to reduce by one more the number of initial data in calculations when it is clear which is the peripheral atom in the corresponding molecules. Examples of groups of substances for which the corresponding calculations

TABLE 7. Calculations of Properties of Freon-218

Parameter	Literature source [55, 64]	Estimates on the basis of methods		
		4	4′	5
T_{cr}, °K	345	341	341	335
P_{cr}, bar	26,8	24,7	24,9	24,0
V_{cr}, g/cm³	0,628	0,628	0,630	0,622
A	1,43	1,27	1,33	1,25

could be intended are perfluoro- and perchlorocarbonates, perfluoro and perchloro silanes, and a number of Freons with more complex structure.

In accordance with the above, we can distinguish two calculation methods: one is based on the boiling point (fourth method) and one on the density (5th method). As an illustration we will examine the calculations for C_3F_8, perfluoropropane (Freon 218). We will also carry out calculations for Freon-11 so as to be able to compare the results with the previous ones, although it is clear that these calculations are only an additional illustration since we could know only on the basis of information of the structure permitting direct prediction that the peripheral atom in this substance is the chlorine atom.

In devising an algorithm for the calculation using (35), it is expedient to form a combination of (35) and (5):

$$T_{cr}/C = f^2(\mathbf{A})/F_\sigma^2(\mathbf{A}), \tag{36}$$

and then to find the inverse function

$$\mathbf{A} = A_\sigma(T_{cr}/C). \tag{37}$$

For substances with peripheral atoms of fluorine, this function can be well approximated by the formula

$$\mathbf{A} = 0.03 + 1.76\lg(T_{cr}/C). \tag{38}$$

For peripheral atoms of chlorine, a similar formula is suggested:

$$\mathbf{A} = 0.66 + 1.80\lg(T_{cr}/C). \tag{39}$$

Both (38) and (39) are correct for $1 < \mathbf{A} < 3$.

The algorithm of calculation by the fourth method is the following: first we calculate C on the basis of (12) from information on the composition of the substance. Then with the aid of (17) we select the critical temperature of the "zeroth" approximation of $T_{cr}^{(o)}$, and in accordance with (39), we determine the similarity criterion **A**.

The critical pressure of the zeroth approximation is found on the basis of formulas (36) and (5), i.e., with the aid of the ratio

$$P_{cr} = T_{cr}^{3/2}/\sqrt{C}f. \tag{40}$$

Knowing T_{cr}, P_{cr}, and **A** and using function (32), we can find the normal boiling point in this approximation. The found temperature is compared with the specified one. If the former is lower than the latter, the critical temperature has to be increased in the subsequent, the first approximation, if it is higher, it has to be reduced. The calculations are continued until the specified and the theoretical boiling points coincide; the critical density is found with the aid of (19).

An example of the calculations for C_3F_8 is given in Table 7. The boiling point, 37.5°C, was taken from [64], the calculations for Freon-11 are contained in Table 1 in the graph "calculation by the 4th method."

To characterize the sensitivity of the method under examination, we will show that indeterminacy in specifying the boiling point yields approximately double the error of determining the critical temperature. However, the real error with the method under examination may be much larger. With this algorithm, the "systematic" errors of calculation are determined chiefly by the accuracy of the ratios of type (35). If we proceed from the "methodical" error $\delta A/A \sim 5\%$ (such is the mean scatter of the points on the corresponding curves), then the error of determining the critical temperature is $\sim$0.5%, of the critical pressure $\sim$0.8%, of the critical density about 0.5%.

The algorithm for prediction estimates on the basis of data on the boiling point, suggested here, is not the only possible algorithm. An alternative method of calculation can be devised on the basis of Leadersen's empirical estimates for critical temperature and pressure [60]. The calculation procedure (we will call it method 4') looks as follows. Leadersen's method by increments is used to determine the magnitude of the ratio T/T_{cr}, and from this T_{cr} is found. Then we determine the critical pressure after Leadersen and on the basis of a ratio type (32). The results of such calculations for C_3F_8 and CCl_3F are given in Tables 1 and 7. For perfluoropropane, data are found that are close to the previously found ones, for Freon-11 the results of calculating the critical pressure and parameter A do not agree so well with the experiments. This circumstance is not surprising because calculations after Leadersen do not presuppose that it is known which of the atoms are peripheral. Owing to this, the method is more general but less accurate. We will yet revert to the use of calculations of the critical parameters after Leadersen, and then we will examine the second possible algorithm for calculations to estimate substances whose molecules contain known peripheral atoms. This, the fifth method to be examined, is based on data on the density of a liquid at one temperature.

The basic calculation procedure is analogous to the previous one. This is the selection of the critical temperature which ensures equality of the calculated and specified densities. Some complication compared with the fourth method is connected with the selection of the zeroth approximation for the critical temperature. Relationship (17) cannot be used here because the boiling point is unknown. In this case it is recommended to estimate the critical temperature by inverting formulas (38) and (39) and specifying the experimental value of the determining criterion **A**. For polyatomic substances this has to be selected near 1, for organic substances with few atoms near 2.

Examples of calculations are given in Tables 1 and 7. For Freon-218 the density was taken as 1.745 g/cm^3 at 200°K [50], for Freon-11 as 1.5345 g/cm^3 at 0°C [64].

The sensitivity of the fifth method is characterized by the fact that an indeterminacy of 0.1% in specifying the density causes an error of $\sim$1.3% in determining the critical temperature. An inaccuracy of 5% in calculating A by formulas (38) and (39) contributes substantially by up to 12% to the error of determining the critical temperature. It is no accident that the differences in the results of the calculation by this method in the examined examples are large. Thus, this method is less accurate than the fourth method, and its application is expedient only if there is no other information available.

With this we end the examination of the means of analyzing Eqs. (3) and (4) and revert to the procedure of predicting on the basis of only one structural datum.

We recall that Eqs. (3)-(5) with refinements (12) and (33) or without them ensure in principle prediction of the properties of substances belonging to the class of nonassociated ones. We noted previously, however, that for a narrower class of substances (for organic compounds), practically more accurate results can be obtained by employing simultaneously some purely empirical calculation methods. This conclusion was reached, in particular, in examining the calculation method of critical volume after Leadersen. Here we will examine other variants of such combined algorithms. In examining the fourth new calculation method we recalled the method of calculating the critical pressure after Leadersen. It is interesting to find out what yields better results: using Leadersen's empirical procedure for V_{cr} or for P_{cr}. To find the reply to this question, we will compare the calculated values of P_{cr} with the experimental data on 17 organic substances for which we can carry out simple calculations on the basis of our algorithm and of Leadersen's algorithm. The rms deviation of the data calculated after Leadersen from the experimental data was about 9%, which is much more than the value of 3.5% given in [64] and obtained for 172 substances. Such a difference is not surprising if it is borne in mind that among these many tens of substances, there are surely many hydrocarbons for which this kind of empirical procedure works much better.

Using the calculations to estimate critical pressure after Leadersen in combination with the calculations of the complex $T_{cr}^{3/2}/P_{cr}$ on the basis of (32) turns out to be particularly advantageous because this yields the critical temperatures with an error one third smaller than the error of P_{cr}, i.e., with an error of about 6%. An analogous combination of the complex $T_{cr}^{3/2}/P_{cr}$ with (19) and calculations of V_{cr} after Leadersen led to errors twice as large.

The above-explained notions concerning the optimum algorithms for prediction and errors of the respective calculations are based on our knowledge of the micro- and macrorelationships at a given instant. There are grounds to assume that these relationships will be made more accurate and the prediction procedures gradually improved.

The development of methods of predicting properties of substances brings us face to face with the solution of the inverse problem: the selection of substances with specified properties. To be more precise, what is involved is finding the structural formula of compounds whose properties would be extremely close to previously specified properties. Thus an important scientific and technical problem is involved. In [56] we noted some substantial aspects of the approach to its solution. This problem contains two substantial elements, two subprograms: the "macroscopic" one and the "microscopic" one. The object of the macroscopic program is to determine the minimum set of principal macroscopic parameters (critical characteristics and the determining similarity criterion); the microscopic program must ensure the computer search for the structural formulas whose characteristics provide the theoretical macroscopic parameters closest to the previously determined ones.

In principle, the realization of the macroscopic program should not involve much work. All we need here is conversion of the calculation program of the properties on the basis of the available macroscopic characteristics [55,56]. The microscopic program is more interesting and more complex. Here, one of the chief problems is devising algorithms for the purposeful variation of the structure and composition, a departure from the simple running through the possible formulas. Now, at the first stage of this work, the simplest and most accessible is the program of selecting the structures of halogen derivative hydrocarbons including bromine and iodine derivatives; fully realistic are the programs for silicon-organic substances, boron-base compounds, etc. The prospects of developing the examined trends of work seem very good.

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