Translated from *Uspekhi Khimii*, **51** 1225-1255 (1982) U.D.C. 541.543

The Possibility of Predicting the Retention Parameters in Gas-Liquid Chromatography

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Various methods for the calculation of retention parameters used in gas-liquid chromatography are critically examined in this review. They have been divided into four groups in accordance with their fundamental postulates. Attention has been concentrated on the physicochemical foundations of the methods considered, their generality, and the errors of the calculated quantities. The bibliography includes 325 references.

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INTRODUCTION

Like any other analytical method, analytical gas–liquid chromatography (GLC) involves qualitative and quantitative analyses. The physical detection methods and the fairly simple calculations from output data made it possible to solve, in the main, the problems of quantitative analysis. However, the problems of qualitative analysis have not so far been fully solved. The situation can be accounted for by the unsatisfactory level of development of the theory of solutions, which is mainly concerned with the concentration dependence of the solubility of spherical molecules[1,2] rather than by the deficiencies of the gas-chromatographic method. The experimental data on the properties of infinitely dilute non-electrolyte solutions, one of the components of which is highly volatile and the other is involatile, have become available only after the introduction of the GLC method and have not so far been examined with the theory of solutions.

The practice of qualitative analysis in GLC requires the creation of fairly simple and universal methods for the *a priori* calculation of the retention parameters of the substances to be separated (sorbates); such calculation is essential despite the availability of a fairly large number of auxiliary identification methods in GLC.[3] This is because each identification method yields an answer with some degree of uncertainty, which diminishes when data obtained by another, independent method, are resorted to.

Although more than 400 communications describing various methods for the *a priori* calculation of retention parameters in GLC have been published, their results have not so far been surveyed. The aim of the present review is to examine the *a priori* and correlation methods for the calculation of retention parameters in GLC and to discuss their physicochemical basis.

The physicochemical picture of retention in GLC is fairly complex[4] and is determined not only by solubility (liquid–gas equilibrium) but also by a number of adsorption processes at the interfaces. For a more unambiguous treatment of retention parameters, we shall examine below mainly systems where adsorption processes play a negligible role (non-polar systems or systems with low polarity). The questions of complex formation via hydrogen bonding are outside the framework of this review; its limited size also precludes the consideration of the influence of changes in the nature of the stationary phase on retention parameters. The data described are grouped in terms of the methodological principles of the approach to the calculation of retention parameters.

II. THE USE OF THE PRINCIPLE OF THE ADDITIVITY OF THE INCREMENTS IN THE MOLAR FREE ENERGY OF SOLUTION

The molar free energy of the gas–liquid phase transition ΔG_S (in the chromatographic literature it is usually referred to as the molar free energy of solution) is related to the gas–liquid partition coefficient K by the expression

$$\Delta G_S = -RT \ln K = -RT \ln V_N, \quad (1)$$

where V_N is the pure retention volume. The idea of employing the additivity of the molar free energy of solution in terms of groups of atoms in the sorbate molecule for the calculation of retention parameters is extremely attractive[5,6], although it is based solely on phenomenological observations[7]. A test of the applicability of this additivity principle to gas-chromatographic systems has been described in detail[7-13].

For monofunctional aliphatic compounds, it is possible to formulate an equation involving the number of methylene (n_{CH_2}) and methyl (n_{CH_3}) groups in the sorbate molecule and the energy F of the interaction of the atomic group with the stationary phase (the subscripts x, CH_2, and CH_3 denote the parameters of the functional group investigated and the methylene and methyl groups respectively):

$$\ln V_N = F_{CH_3} n_{CH_3} + F_{CH_2} n_{CH_2} + F_x. \quad (2)$$

The total number of carbon atoms in the sorbate molecule $n = n_{CH_3} + n_{CH_2}$. For $n > 5$, the last equation can be fitted by a linear relation of the type[14-16]:

$$\ln V_N = F_{CH_2} n_{CH_2} + F_x. \quad (3)$$

Eqn.(3) is used most widely in practical qualitative analysis in GLC although the error of the correlations in terms of the corresponding variables has been estimated in only a small number of publications[17-19]. In precise measurements of retention parameters, it was found that, even for the homologous series of n-paraffins in non-polar or weakly polar stationary phases, Eqn.(3) does not hold, and particularly marked deviations are observed in the case of stationary phases whose molecules contain cyclic groups of atoms[20-24]. However, despite the reliable data presented in the studies quoted above, reports are being published from time to time claiming a satisfactory linear relation between $\ln V_N$ and n (see, for example, the report of Wainwright et al.[25], who do not even indicate the errors of the calculated data and whose method of calculating the dead retention volume does not appear trustworthy).

Numerous publications have shown[26-29] that the slopes of the relations between $\ln V_N$ and n are not the same for different homologous series. In the presence of polar functional groups, both in the sorbate molecule and in the molecule of the stationary phase, the relation between $\ln V_N$ and n becomes non-linear[26,30]. Even when non-polar and weakly polar sorbates and stationary phases are used, the errors of calculations by Eqn.(3) for homologous series of sorbates are at least 3% [31] and the linearity of the relation between $\ln V_N$ and n holds only for a comparatively small number of members of homologous series. For example, the linear relation between I and n (I is the Kovàts retention index proportional to $\ln V_N$) holds only for two–three neighbouring homologues in the series of phenols [on a column with poly(phenylether)] and for the series of phenols, it is not even possible to find linear sections[32]. Some investigators[33] suggest that an empirical correction factor be introduced to correct the non-linearity of the relation between I and n, which converts Eqn.(3) into a semiparametric equation. When the methylsilicone elastomer OV-1 is used, the correlation coefficient for different homologous series varies in the range from 0.97 to 0.98, which is unacceptable for chromatographic measurements.

The number of carbon atoms in the sorbate molecule is by no means the only parameter which can be used to construct linear relations between the free energy of solution and the chemical composition of the molecule; attempts to set up correlations between $\ln V_N$ and I and the number of silicon[34], sulphur[35], nitrogen, and oxygen[36] atoms, phenyl groups[37], double bonds[38,39], and homogeneous *cis–trans* configurations[17,40] in sorbate molecules have been described. Parameters such as the equivalent chain length *Me*,[41,42] the steroid number R_{Mg} in the series of steroids[43,44], and the equivalent length of the carbon chain in the case of unsaturated aliphatic esters[45-48] have an analogous significance.

Eqn.(3) is not used solely for the interpolation or extrapolation of retention data for a selected homologous series; it also makes it possible to estimate the contribution of functional groups to the molar free energy of the interaction of the sorbate with the stationary phase. Thus the increments in $\ln V_N$ for a large number of functional groups (H, CH_3, C_2H_5, F, Cl, Br, I, OCH_3, CN, NO_2) in anilines, phenols, pyridines, aromatic hydrocarbons, cyclohexanes, and hexanes have been determined with the aid of an equation of type (3) using Carbowax 20M and Apiezon L as stationary phases[49].

In general, a functional group can be understood not only as a group containing heteroatoms but as any structural group distinguished both by the presence of multiple or aromatic bonds and by a non-linear arrangement of carbon atoms in space. In particular, for hydrocarbons, the presence of such structural groups in the molecule can be the cause of a change in the retention of the sorbate. In order to take into account the influence of individual structural groups as well as groups of carbon atoms linked by multiple bonds on the free energy of solution, it has been suggested[50] that the homomorphous factor H be calculated:

$$H = I_x - I_h, \qquad (4)$$

where the subscript h refers to a homomorphous paraffin, i.e. to a saturated hydrocarbon having the same carbon skeleton as the compound investigated.

The principal information obtained with the aid of Eqn.(4) characterises the influence of multiple bonds on retention parameters. The values of H have been determined in a number of studies[50-59] for non-polar and weakly polar stationary phases. On the other hand, similar measurements can be carried out also for polar sorbates, for example for alkylchlorosilanes[60] on weakly polar silicone stationary phases (PMS-100, E-301, SE-30, and DC-550); however, in such systems account must be taken of the length of the alkyl group in the member of the homologous series (the relation between I and n is non-linear). Since the considerations arising in the determination of the homomorphous factor H do not differ fundamentally from those used to determine F_x, the errors in the calculation of H by Eqn.(4) are also of the same order of magnitude. For example, the relative standard error s° is in the range 2–5% for aromatic hydrocarbons, alkyl sulphides, and ketones[61]. The contributions of aliphatic isoalkyl and unsaturated groups of atoms as well as sulphur atoms in metameric thiatridecanes have been determined[62].

Since the fundamental non-linearity of the relation between $\ln V_N$ and n has been demonstrated in numerous studies, a series of approaches have been devised, using specific mathematical modifications of Eqn.(3) to reconcile the calculated and experimental data with the aid of empirical parameters. For example, the following relation has been obtained in a series of studies by Golovnya and coworkers[62-69]:

$$I = k_1 + k_2 n + k_3/n, \qquad (5)$$

where k represent constants. It has been used to interpret retention data for n-alkyl sulphides[63], n-alkyl isoalkyl sulphides[64], alkyl vinyl, alkyl allyl, and alkyl propyl sulphides[65], thiophen, furan, and benzene derivatives[66], aliphatic di-isoalkyl sulphides[67], heterocyclic compounds[68], and di- tri-, and tetra-sulphides with an S–S bond[69] on four stationary phases (Apiezon M, silicone OV-17, Triton X-305, and PEG-1000).

The relevant considerations do not change fundamentally if the increments of the free energy of solution of the atomic groups of the sorbate are replaced by bond increments[70,71]. The assumption of the additivity of the values of ΔG_S for different bonds leads to the same computational errors as the hypothesis that the ΔG_S are additive with respect to atomic groups[72-75]. An attempt to take into account the influence of neighbouring bonds on the retention parameter for a selected bond has been made in a study[76] where the so-called bonding indices χ were used. However, in order to obtain linear relations, it was necessary to introduce a series of empirical parameters (for example, the distance A between the neighbouring bonds or methyl groups):

$$I = 200(\chi - 1.4142) + 100 + A^2. \qquad (6)$$

This equation has been used to calculate the retention parameters of isoalkanes[76]. The influence of neighbouring bonds and substituents on the increments in I for individual functional groups has been determined in a study[77] where mono- and di-alkylbenzenes were separated on squalane, Yukon LB-550X, and Yukon HB-280X at 100 °C; the average standard error of the calculation s was six retention index units.

The principle of additivity underlying Eqn.(3) is applicable primarily to monofunctional homologous series. When polyfunctional sorbates are considered, the additivity of the contributions of the functional groups to the molar free energy of solution holds only for substances where the functional groups are separated by a linear carbon chain consisting of at least three carbon atoms. In other cases account must be taken of the mutual influence of the carbon groups, which is expressed by the so-called second-order increments[54,55,59]. The magnitude of these corrections is so great that they cannot be neglected: for example, for paraffins with molecules containing three and four methyl side groups, they amount to 30 and 40 Kováts index units† respectively[76]. The second-order corrections are particularly large for very polar sorbates: thus for alcohols they vary in the range from 170 to 270 units. However, when weakly polar stationary phases such as methylpolysiloxanes or phenylmethylsiloxanes of the PPMS type are used, even the introduction of corrections of this kind does not reduce the errors of the calculation for polyfunctional sorbates below 4% and for a more polar stationary phase (SKTFT-50X) the error increases to 10%.

The non-additivity of the values of I in a homologous series is indicated by data presented in numerous publications. Thus, for the homologous series of isoparaffins on a series of stationary phases [tetracosane, squalane, dotriacontane, di(4-isopropylbenzyl)benzene and its analogues], the quantity I varies from 56 to 64 units[77], whereas the value required by theory is 100 units. According to the results of the same study[77], the increment in the retention index for alkylbenzenes varies from 102 to 95 for the homologous series investigated. Similar variations have been noted for n-alkynes on stationary phases of low polarity and, when polar stationary phases are used, the corresponding increments are in the range between 84 and 94 units.[78,79] The increment in the retention index in the homologous series is 90–95 units for dibasic acid esters[80], 50–125 units for alkylbiphenyls[81], 75–105 [82] and 60–100 units[83] for alkylbenzenes on three stationary phases of different polarity, and between 94 and 100 units for olefins[84].

Such phenomena indicate the need to seek more complex mathematical relations for the calculation of experimental retention parameters. Thus an equation of the type

$$I = k_1 + k_2 n + k_3 n^2 \qquad (7)$$

has been used[79] to calculate the retention indices of n-alkynes on a highly polar stationary phase—1,2,3-tris(2-cyanoethoxy)propane. However, no account was taken in the above study[79] of adsorption at the gas–liquid interface.

The data presented indicate a low accuracy of the calculation of retention parameters in homologous series using only one variable parameter—the number of carbon atoms in the molecule. Fairly large errors have also been observed after the introduction of second-order corrections taking into account the immediate environment of the functional groups. These failures are readily explicable in the analysis of the physicochemical basis of the relations employed. The molar free energy consists of two components: the molar heat of solution ΔH_S and the molar entropy of solution ΔS_S. If ΔH_S is treated to a first approximation as a quantity additive with respect to the atomic groups of the molecule, then ΔS_S is determined by the relative positions of the atomic groups rather than by their complete set. The greater the contribution of the entropy factor to the molar free energy of solution, the less applicable the principle of additivity to the description for the behaviour of the molar free energy of solution, i.e. to the calculation of $\ln V_N$ and I.

Despite the lack of a physicochemical basis, the principle of additivity is so simple and attractive that attempts to use it in the calculation of retention parameters have continued—mainly by increasing the number of empirical and semi-empirical parameters in the overall equation. Thus a multiparametric equation has been used[85] to describe the retention of diphenyl ether derivatives on weakly polar stationary phases. A three-parameter equation has been used[86] to describe the retention of aromatic ethers and their fluoroderivatives (taking into account the relative positions of the substituents).

One of the most fruitful approaches in the empirical calculation of retention in GLC involved the use of the principles of topological analysis[87,88]. According to this method, one must take into account the immediate environment of a given functional group–the first, second, third, etc. spheres. The reliability and accuracy of the calculation increase with increase in the number of surrounding spheres taken into account but at the same time there is also a sharp increase of the number of empirical parameters to be determined beforehand for the calculation, which requires in its turn the accumulation of extensive experimental data for the retention of the test compounds. Thus, in the calculation of the retention of alkanes with allowance for the influence of the first sphere of the environment, use is made of 14 parameters, while in the calculation with allowance for the influence of the second sphere the number of such parameters increases to 2000.[7] At the same time it has been shown that[7], even when 90 empirical parameters are used for C_4–C_8 olefins, the average standard deviation of the calculated data from experimental results is 11%.[7] The principles of the topological calculation of the retention indices of isoalkanes have been discussed[89]; the same method has been used[10] to calculate the retention parameters of 84 linear alkenes (up to tetradecane) on squalane using 25 empirical parameters. The average standard deviation of the calculated results from the experimental data is 3–4 units.

As a rule, in the topological analysis of experimental data and in the derivation of computational equations, computers are widely used because of the large number of calculations. For example, the DARC programme has been used in a series of investigations[87,91–93]; in calculations by means of this programme with 18 empirical topological constants, the average standard deviation from the experimental data for C_6–C_8 isoalkanes is 3.1 units[94] (one should bear in mind that the experimental data for 50 hydrocarbons must be used to calculate 17 topological parameters). With increase of the number of the empirical topological parameters to 23, the average standard deviation decreases by a factor of two. However, errors of such magnitude are characteristic solely of interpolation calculations; in the extrapolation of data the errors usually increase several times. The application of other computer programs leads to errors of the same order of magnitude[95–98].

Despite the considerable number of experimentally determined parameters for calculations in accordance with the topological scheme, the final result depends in many respects on the intuition of the investigator, who must choose correctly the test substances[76]. In order to increase the accuracy of the calculations and to reduce the required number of empirical parameters, the treatment has been restricted in certain studies to isotopological series of compounds, which reduces the error of the calculation almost by a factor of two[94]. Another (similar) characteristic of the sorbates—the degree of bonding—has been used also to calculate retention parameters[99]. The bonding indices have been employed to calculate the retention of polycyclic aromatic hydrocarbons[100],

† Henceforth for brevity the expression "Kováts index units" will be replaced by "units".

alcohols, ketones, and ethers on polar stationary phases[100] and of hydrocarbons, ethers, carbonyl compounds, and alcohols[102] on weakly polar stationary phases. It has been shown[102] that, whereas the employment of bonding indices for hydrocarbons has resulted in an error of calculation less than one unit, for oxygen-containing compounds the error is much greater (between 5 and 190 units). The errors can be reduced only by employing multiparametric equations.

The data described above permit certain conclusions. The principle of the additivity of the molar free energy of solution (for the determination of I, $\ln V_N$, and $\ln K$) does not hold even for members of a homologous series and can be used only for a preliminary estimation of the order of magnitude of the yields of the test components. The contribution of each functional group to the molar free energy of solution depends to a large extent on the influence of the neighbouring groups of atoms, which makes it necessary to resort to methods of topological analysis for a complete quantitative estimation of the interaction energy. The method of topological analysis as well as multiparametric equations with empirical constants can ensure a comparatively low error of the calculation (approximately 5–10 units), but such methods require a large number of preliminary experimental data. The greater the number of empirical constants used in the calculation, the greater the accuracy. The value of the data obtained by this approach is also reduced by the fact that they are of the interpolation type, the errors increasing appreciably on extrapolation of the equations to higher homologues. Consequently the methods employing the principle of additivity can be regarded only as a first approximation in the calculation of retention data and also as a convenient method of an abbreviated formulation of experimental information for homologous and isotopological series of sorbates.

III. CORRELATION BETWEEN THE RETENTION PARAMETERS AND THE PHYSICOCHEMICAL PROPERTIES OF SORBATES

Purely empirical methods based on the principle of additivity for the calculation of the retention characteristics require preliminary experimental studies if sufficiently accurate results are to be obtained. It is useful to attempt to diminish the set of predetermined parameters by introducing into the equations parameters related to the physicochemical properties of the substances to be separated. The retention parameters are related to the properties of the sorbates and of the stationary phase and their simplest correlations with the properties of sorbates merit particular attention.

The boiling point of the sorbate T_b is the characteristic most widely used for correlations, because it is one of the most readily available. The following relation has been postulated in a series of studies[103–109]:

$$\ln V_N = k_1 + k_2 T_b \ . \qquad (8)$$

Indeed the relative retention volume r can be expressed in terms of V_N and the activity coefficient γ:

$$r = V_{N_1}/V_{N_2} = \gamma_1 p_2^0/\gamma_2 p_1^0 \qquad (9)$$

where p^0 is the vapour pressure of the pure sorbate. Then

$$\ln r = \ln(\gamma_1/\gamma_2) + \ln(p_2^0/p_1^0) \ . \qquad (10)$$

According to Trouton's rule (a not altogether correct approximation), the molar entropy of evaporation ΔS_v at the boiling point of a given substance is constant, whereupon

$$RT \ln p^0 = k_3 - \Delta H_v \ , \qquad (11)$$

where ΔH_v is the molar heat of evaporation. Subject to a series of significant stipulations, the molar heat of evaporation can be replaced by the boiling point, which permits a reformulation of Eqn.(11):

$$\ln p^0 = k_4 + k_5 T_b \ . \qquad (12)$$

Finally, if it is assumed that γ_1/γ_2 is constant, we obtain an equation of type (8) linearly relating the boiling point of the sorbate to its retention.

All the assumptions made virtually reduce the applicability of the linear relation between the logarithm of the retention volume and the boiling point of the sorbate to the members of a single homologous series and even here the relation is considerably strained. This is indicated by data obtained for paraffins and olefins on non-polar stationary phases, i.e. for the most ideal solution; for this correlation, $s^0 = 2\%$.[104] The average standard error of the calculation for simple monofunctional compounds based on the linear relation between I and T_b amounts to 5 K when Apiezon L and Carbowax-20M are used as the stationary phases, the error increasing for the lowest members of the homologous series[110]. The relation holds accurately for isomeric hydrocarbons, which actually makes it possible to correct some boiling points of sorbates[111].

The use of the correlation between the boiling points of sorbates and their retentions can be recommended only for non-polar stationary phases. With increase of the polarity of the stationary phase, the correlations become non-linear[109,112,113]. To correct this disadvantage, various correction factors have been proposed. For example, the ratio z of the number of carbon atoms in the aromatic ring to the total number of carbon atoms in the molecule has been employed[113]. The equation derived is applicable to alkylbenzenes with Carbowax-1500 as the stationary phase:

$$I = 6.5 T_b + 7.66z - 305 \ . \qquad (13)$$

The average standard deviation of the data evaluated by this equation for C_7–C_{13} alkylbenzenes is 6.5 units. Particularly large deviations from the linear relation between I and T_b are observed in cases where there is steric hindrance to the interaction: for aromatic hydrocarbons[113–116], phenols[117], and heterocyclic compounds[118]. The claims that the deviations s for correlations of this kind involving a series of different classes of substances, including polar compounds, do not exceed one unit are rendered unreliable by all these factors[119–124].

As stated above, the similarity of the properties leads to a satisfactory correlation between I and T_b for isomeric compounds. The difference between Kováts indices for such compounds ΔI is linearly related to T_b:[125,126]

$$\Delta I = k \Delta T_b \ , \qquad (14)$$

but the proportionality coefficient k varies within wide limits. For example, Kováts and Vehroi[127,128] have found it to be 5, while Gastegnau and Villesot[129] obtained a value of 6.5.

Since the molar heat of evaporation varies somewhat with temperature, it has been suggested[130] that the column temperature T_c be taken into account by the relation

$$\ln V_g = k_1 + k_2 T_b/T_c \qquad (15)$$

where V_g is the specific retention volume. A family of parallel lines have been obtained in terms of the variables of this equation for hydrocarbons on the silicone elastomer E-301 and have been used to identify substances in homologous series[131–133], although more careful studies[134] indicate some curvature in relations of this kind.

The availability of the boiling points of many organic compounds has led to a large number of attempts to employ T_b as a parameter defining retention. For example, the temperature retention index has been proposed[133]. It is related to

the Kovats index in the following manner:

$$(\lg V_{Nx} - \lg V_{Nn})/(\lg V_{N(n+1)} - \lg V_{Nn}) = (T_{bx} - T_{bn})/(T_{b(n+1)} - T_{bn}), \quad (16)$$

where the subscript x refers to the test substance, n to the n-paraffin with n carbon atoms in the molecule, and $n+1$ to the n-paraffin with $n+1$ carbon atoms in the molecule.

By analogy, the following form of the index has been put forward[135]:

$$I_b = 100n + 100(\lg T_{bx} - \lg T_{bn})/(\lg T_{b(n+1)} - \lg T_{bn}) \quad (17)$$

and Shlyakhov et al. proposed yet another formulation[136]:

$$I^0 = (T_{bx} - T_{bn})/(T_{b(n+1)} - T_{bn}) + 100n . \quad (18)$$

The average discrepancy between I and I_ν is 16 units and even on non-polar sorbates such as isoparaffins this quantity is 5.1 units[134], which significantly reduces the value of such indices for practical GLS: however, some workers[135] believe that it is possible to employ the temperature retention index for hydrocarbons.

The molar volume of the sorbate $\overline{V}$ is also used to set up correlations with retention parameters. A linear relation between $\overline{V}$ and $\lg r$ has been established for a non-polar stationary phase[134,135], but, with increase of the polarity of the stationary phase, the correlation between these quantities disappears. A similar correlation has been found for alkynes[136]. The molar volumes of organic compounds are less readily available than the boiling points, which has been one of the main causes of the small popularity of such correlations. Furthermore, correlations of this kind are valid only for a limited number of systems.

The refractive index and the molar refraction characterise the ability of the sorbate to exhibit a dispersion interaction with the stationary phase. Correlations between these quantities and the retention parameters have been found in a number of studies, for example, for acid esters on a silicone stationary phase[137] and for hydrocarbons on phthalate esters[138]. In the latter case the discrepancy between the experimental and calculated data is on average 4 units. Correlations of the same type have been found for dimethylbiphenyls and xylenes[139], perhalogenoalkanes[140], and certain other classes of organic compounds[141,142]. The attempts to establish correlations between the retentions and the parachors of sorbates has been described[143].

It has been shown[143] that $\ln V_N$ is proportional to the quantity $(M - 170)^{1/3}$ for organoarsenic compounds on a silicone stationary phase (M is the molecular weight of the sorbate). By analogy with the Kovats retention indices, a molecular retention index has been proposed[144], using the molecular weights of the test substance and n-paraffins. In the presence of steric hindrance to intermolecular interaction, the correlation between the retention and the molecular weight disappears[145]. However, the molecular weight of the sorbate as well as its refractive index and molar refraction can be correlated solely with the energy of the dispersion interaction and for this reason the application of the above quantities is limited solely to non-polar systems, where the dispersion interaction plays the main role.

The orientational and inductive interactions of the sorbate with the stationary phase can be taken into account by resorting to the dipole moment of the molecule μ (the orientational interaction energy is proportional to the square of the dipole moment of the species). The following equation has been proposed[146,147] for the relation between the retention volume and the dipole moment of the sorbate molecule:

$$\ln V_N = k_1 + k_2\mu^2 . \quad (19)$$

However, the dipole moment enters into this equation with a power exponent of unity, which conflicts with the equation for the orientational interaction energy. A correlation between the retention characteristics and the molecular dipole moment of the sorbate has been found for xylidines[148], although such correlations have not been observed for oxygen-containing compounds[149]. The proportionality of the "polar" component of the retention volume to the square of the molecular dipole moment of the sorbate has been established for mononitro-derivatives of aromatic hydrocarbons[150]; on passing to dinitro-derivatives, the proportionality ceases to hold.

We believe that the use of the dipole moment of the entire molecule in the description of the intermolecular interaction in gas-chromatographic solutions is incorrect, since the orientational interactions in such solutions takes place between bond microdipoles[151]. A correlation between the retention and the dipole moment of the sorbate molecule is therefore hardly general. The same considerations apply also to another correlation parameter—the dielectric constant of the sorbate molecule[152,153]. An attempt to use the dispersion interaction as well as the orientational forces to characterise the retention has been made in a study[154] where the bonding parameter [the term $f(\chi)$] and the dipole moment were introduced into the equation

$$I = f(\chi) + k_1\mu^2 + k_2 . \quad (20)$$

The average discrepancy between the retention parameters calculated by this equation and found experimentally is 5–6 units.

The linear correlation postulated[155] between V_g and the viscosity of the sorbate has been tested for a series of dinitriles in polar stationary phases.

The size and shape of the molecule are taken into account by the Wiener three-parameter equation for the calculation of the Kovats indices of alkylbenzenes[156,157]. This approach is intermediate between the pure empirical calculation from the atomic group increments and the attempts to employ a definite physical parameter of the sorbate molecule.

Apart from the physical parameters of sorbate molecules, chemical characteristics such as the Hammett, Taft, Jaffé, and Palm constants have also been used to establish correlations with retention parameters. The Hammett–Taft constants are related to the ionisation potentials of molecules and are determined empirically from the reactivities of specific functional groups. In particular the Hammett constants characterise the energy of the hydrogen bond with phenols.

A relation was derived[158] for a pair of substituted phenols (subscripts 0 and x), which includes the Hammett constant σ, the constant k_1, and the activity coefficients of the phenol molecule (γ) and of a homomorphous molecule which does not form a hydrogen bond (γ^*):

$$\ln(\gamma_0/\gamma_x) = \ln(\gamma_0^*/\gamma_x^*) + k_1\sigma . \quad (21)$$

It follows from Eqn.(20) that, in order to ensure the linearity of the relation between the activity coefficients and the Hammett constants, the ratio γ_0^*/γ_x^* must be constant, i.e. Eqn.(21) is valid only for an isotopical series. As a rule, this is the case for isomeric compounds where the hydrogen bond energy makes a significant contribution to the overall intermolecular interaction energy. When a polyester stationary phase was used, a linear correlation between $\ln(\gamma_0^*/\gamma_x^*)$ and σ for phenols was observed with a correlation coefficient of 0.89 and an error s^0 of 3%.[158] This correlation coefficient for GLC data is extremely low, which indicates a low suitability of the correlation between the retention characteristics and the chemical constants for *a priori* calculations in GLC. A detailed thermodynamic analysis of the application

of Hammett–Taft contants in chromatographic calculations has been carried out[159-161].

The application of Hammett, Taft, and other constants is to some extent justified when there is a significant contribution of specific interactions (for example, hydrogen bonding) to the overall molecular interaction energy in the gas-chromatographic solution. There is hardly any physicochemical justification for the application of these constants in the calculation of the retention parameters of aromatic hydrocarbons and some of their derivatives. However, numerous attempts to find linear correlations of the type[139,162,170]

$$\ln r = k_1 + k_2\sigma \ , \qquad (22)$$

have in fact been made for such systems.

A more complex equation, containing a series of Hammett constants (σ_1, σ_2, and σ_3) has been proposed[49] for the retention parameters of derivatives of aromatic hydrocarbons on Apiezon L and Carbowax 20M:

$$\Delta\ln V_N = k_1\sigma_1 + k_2\sigma_2 + k_3\sigma_3 \ . \qquad (23)$$

The proportionality constants in this equation are found by regression analysis. The relative average standard deviation of the calculated data from experimental quantities was 1.5% for the system investigated. The comparatively high accuracy of the proposed computational method can be explained by the introduction into the equation of three constants with three proportionality coefficients: even without a physicochemical justification, the use of an empirical three-parameter equation can ensure approximately this accuracy of the calculation.

As already stated above, the application of Hammett type constants for the construction of correlations between the retention characteristics and the physicochemical properties of the sorbate is justified only for systems with a significant specific interaction. For the remaining systems (and these are the majority in GLC), one has to introduce a series of correction factors, including the interaction factor i, the resonance factor $\overline{R}$, and the Taft constant σ_0:[171]

$$\ln r = k_1(\sigma_0 + i\Delta\sigma\overline{R}) + k_2 \ . \qquad (24)$$

A number of studies[172-175], in which the characteristics of the steric hindrance to intermolecular interaction E_j, the contribution of the structural element of the sorbate molecule to the retention index I_i, and the empirical increment of the Kovats index for the selected structural group in the aliphatic compounds I_i^0 were used in the calculations, have been carried out on the application of the Taft constant to the calculation of the retention indices of bifunctional compounds (dihalogenoalkanes, halogenoepoxy-compounds, and ethers):

$$I_i = I_i^0 + k_1\sigma + k_2E_j \ . \qquad (25)$$

Correlations between the retention parameters of alkylbenzenes and the Taft constants have also been found in another study[176]. Correlations have also been established between the retention parameters of tri- and tetra-methylbenzenes and the Jaffé constants[177], between the retention parameters of aromatic hydrocarbons and their ionisation potentials[178,179], and between the retention parameters of a series of sorbates and the Palm constants and the Newman's rule of six[180,181]. The following equation was found to hold in the study of alkylpyridines on Carbowax-400, glycerol, Apiezon L, and dinonyl phthalate with a correlation coefficient of 0.99 and $s = 0.021\ln V_N$:[182]

$$\lg\frac{\gamma_0}{\gamma_x} = \lg\frac{\gamma_0^*}{\gamma_x^*} + k_1\sum\sigma_0 + k_2\sum E_s \ , \qquad (26)$$

where E_S is the steric Palm constant. The following equation has been derived[183] for the retention parameters of phenols on silicone OV-225 and neopentyl glycol adipate using the molecular refraction R_0 (I_{St}—data for the standard compound);

$$I = k_1I_{st} + k_2\sum\sigma + k_3\sum R_0 + k_4 \ . \qquad (27)$$

It has been suggested[184,185] that the mean square of the molecular radius be used in combination with the boiling point, or the molecular weight, or the density of the sorbate. The employment of such two-parameter correlations makes it possible to calculate the retention parameters for isoalkanes with s ranging from 1.3 to 5.5 units, the error of the calculation increasing with increase of the number of carbon atoms in the isoalkane molecule.

The single-parameter relations for the retention parameters presented above suffer from a very significant disadvantage: in their derivation it is postulated that the retention in GLC depends only on the properties of the sorbate, i.e. that the stationary phase should not make any contribution to the retention of the sorbate. Such neglect of the influence of the intermolecular interaction in gas-chromatographic solutions cannot fail to be reflected in the accuracy of correlation calculations of this kind. Only single-parameter relations describe the behaviour of the pure sorbate and not the properties of the solution and therefore such relations are at best useful for the description of the retention of small groups of sorbates with similar physicochemical properties using non-specific stationary phases (non-polar phases are best). An increase in the number of parameters in the correlation equation increases the accuracy of the calculation not so much because of the more complete allowance for all the intermolecular interaction factors in solutions as by virtue of the minimisation of the errors in the employment of a large number of empirical proportionality coefficients.

One of the successful trends in the use of two-parameter correlation equations has been developed by Dimov and coworkers[186-194], who postulated a correlation between the Kovats indices and the molar volume and the vapour pressure of the sorbate. In the derivation of correlation equations use is made of the Hildebrand–Scatchard theory of regular solutions, according to which a relation of the following type holds:

$$r = p_{12}^0\overline{V}_{21} \qquad (28)$$

(subscripts 12 and 21 show that the given quantity is the ratio of the corresponding characteristics of substances 1 and 2 being compared). According to this theory, for athermal solutions the free energy of solution is limited by the change in molar entropy on dissolution:

$$\Delta S_s^0 = -R\ln\overline{V}_{21} \ . \qquad (29)$$

The last two relations are based on the so-called physicochemical interaction indices (PCI). However, although two independent parameters of the sorbate were used in the calculations, the accuracy of the calculated data is far from being acceptable: for example, the mean square deviation of the PCI from the experimental values of I for isoparaffins on squalane was 7 units[186]. Such deviations are not surprising bearing in mind that solutions of isoalkanes in a paraffinic stationary phase can never be treated as athermal[195].

The significant errors in the calculation caused Dimov and coworkers to introduce a series of corrections, which are treated as corrections to the entropy of solution (more correctly this was an attempt to compensate for the deficiencies of the extremely simplified model of the gas-chromatographic solution). This correction (SN) was calculated from the following equation:

$$SN = k_1 + k_2X_1 + k_3X_2 + k_4X_3 + k_5X_4 + \ldots \ , \qquad (30)$$

where $X_1 = n_g$, $X_2 = n_{b\text{-}CH_3}/n_L$, $X_3 = (n_b + n_{CH_3})/(n_L + n - n_t)$, $X_4 = n_b n_{CH_3}/n_L(N - n_t)$, n_g is the number of possible conformations of the carbon chain of the molecule, n_b the number of n-butane units in the sorbate molecule, n_L the length of the n-paraffin chain, n_t the number of quaternary carbon atoms, and n the number of carbon atoms in the molecule.

Although Eqn.(30) involves the characteristics of the molecular structure of the sorbate, no justification for this is presented. Thus it reduces to a typical equation for correlations using the regression analysis of the experimental data. As was to be expected, the employment of additional five empirical proportionality coefficients made it possible to reduce the error of the calculation for isoalkanes on squalane to 1.4 units[191]; it must be emphasised that this error characterises interpolation calculations. When attempts were made to extrapolate the relations to higher homologues or isoalkanes with a larger number of carbon atoms in the molecule, the error increased severalfold (for practical GLC, the greatest difficulties arise precisely for alkanes with a large number of carbon atoms in the molecule, for which as a rule there are no published retention characteristics). For example, the employment of the relations obtained[191] in the extrapolation calculations of the parameters I of isoalkanes entails an error of approximately 5 units. The method of Dimov and coworkers has been used for the interpolation calculations of the Kováts indices for alkanes[192], alkylbenzenes[193], and cycloalkanes[194].

It has been suggested that the ratio $I_h/T_b\overline{V}$ (I_h are the retention indices of halogenoalkanes when the standard compounds used in the calculations are not n-alkanes, as for the Kováts indices, but the corresponding halogeno-n-alkanes) be employed for interpolation calculations[196]. For halogenoalkanes, this ratio is approximately constant, but, on passing to more polar sorbents, for example, alcohols on squalane[197], it becomes variable. On the other hand, when stationary phases of the type of Carbowax are used in the separation of n-alkyl alcohols, the above ratio again becomes constant. Thus a necessary condition for the constancy of the ratio is the similarity of the physicochemical properties of the sorbate and the stationary phases. However, even when this condition is observed, the attempt to apply $I/T_b\overline{V}$ as a characteristic of isoalkyl alcohols showed that it depends on the structure of the sorbate molecule[198].

An attempt at a thermodynamic justification of the preferential employment of the entropy factor for the calculation of the retention parameters of hydrocarbons has been made[199] using the Flory–Huggins equations. The free energy of mixing was treated[199] as the sum of the contributions of the entropy of mixing and the residual free energy of solution. Comparison of the calculated and experimental data for isoparaffins on Apiezon M showed that $s = 3$ units for this method. A formula has been proposed[134] for the retention index using the ratios of the molar volumes of the sorbate and the stationary phase. The error of the interpolation calculations using this retention index for C_6–C_8 isoparaffins (stationary phase—squalane) is 1.5 units and is close to the error of experimental data.

Unfortunately, even the two-parameter relations based on the properties of the pure sorbates do not permit the attainment of the required universality in calculations of the retention. It is not fortuituous that the method of calculation using eight additional empirical characteristics, which require the use of computers for the necessary calculations, was described in one of the latest communications by Dimov[200]. An example of the correlation equations proposed by Dimov for isoalkanes is given below[200]:

$$SN = 4.28 - 0.79n_r + 0.27n_i - 0.05n_d + \\ + 2.46n_{CH_3} + 1.50n_b - 2.21n + 0.57n_t \ , \qquad (31)$$

where n_t is the number of branches in the main carbon chain of the sorbate molecule, n_i the number of carbon atoms in the branches of the sorbate molecule, and n_d the number of methylene groups located between the branches of the carbon chain of the sorbate molecule.

Analogous equations have been derived with a series of empirical constants for olefins, cycloalkanes, and alkylbenzenes. In order to set up the necessary computer program, it is necessary to employ the experimental data for 17 to 20 hydrocarbons. The mean square deviation of the calculated data is approximately 2 units. It must be emphasised that all the calculations are of the interpolation type.

Takacs and coworkers[201–207] attempted to use not only the properties of the pure sorbate but also the characteristics of their interaction with the stationary phase for the derivation of correlation equations; this is undoubtedly an advance in the development of scientifically based methods for the calculation of retention in GLC. The properties of the pure sorbate are characterised by the sum of the atomic contribution I_a and the bond contribution I_b, while the interaction with the stationary phase is estimated in terms of the quantity I_i:

$$I = I_a + I_b + I_i + I_m + I_i \ , \qquad (32)$$

where I_m is the molecular index. The computational scheme postulates the additivity of all the increments of the equation, I_a is assumed to be 0.1 of the atomic weight of the given atom, and I_b is calculated by an iterative method from the experimental data using the number of bonds of the same type. The ratio of I_i and I_m was chosen in such a way that it is 25% of I at 100 °C and 25.5% at 50 °C.[201–209] Unfortunately, the correction for the influence of the stationary phase was assumed to be constant for all sorbates, which makes the above concept a variant of correlations with physicochemical properties of sorbates. The advantages of Takacs's method includes the endeavour to treat the retention parameters by resorting to molecular constants, excluding empirical characteristics of the individual sorbates such as the boiling point, the molecular weight, the refraction, etc.

In the calculation of the retention indices of the C_8–C_{10} isoparaffins on squalane the error of the calculation was 1.25 units,[205] which is comparable to the experimental error. In a later study[206] this error was as much as 2.7 units. An attempt has been made[210] to calculate the retention indices of olefins on squalane using the Takacs method; the average standard error (based on interpolation data) was then 16.7 units and for linear undecenes it was 14.5 units. The introduction of new corrections for the calculation of the Kováts indices made it possible to reduce the error to 3.7 units[208]. It has been found[208] that the ratio I_i/I_m is not the same for different sorbates; this to a large extent vitiates the Takacs equation. The large number of empirical parameters and the arbitrary nature of the derivation of the relations in the Takacs approach have been pointed out[211]. However, the approach itself has been applied in a number of subsequent studies. For example, a method has been described[209] for the calculation of I for alkylbenzene on Apiezon L, Carbowax-20M, diethylene adipate, and diethylene sebacate with the aid of a computer. The Kováts indices for alkanes have also been calculated[210].

An increase of the number of factors involved in the calculation is characteristic of many studies in which the retention indices of sorbates are related to physicochemical characteristics. A multifactor correlation equation for the specific retention volume, including the molecular weight of the sorbate M and the π-electron cloud density ρ_π, has been proposed[212,213]; the quantity E_S provides a measure of the steric hindrance to intermolecular interaction:

$$\ln V_g = k_1 M + k_2 \rho_\pi + k_3 E_s + k_4 \ . \qquad (33)$$

The coefficients of this equation are calculated by regression analysis from the experimental retention parameters. However, even this large number of empirical parameters does not enable one to obtain sufficiently accurate results in calculations by Eqn.(33); in the calculation of the V_g for polysubstituted aromatic hydrocarbons the error $s^0 = 25\%$ and can be reduced only by taking into account additional empirical corrections.

Thus the more complex the structure of the sorbate molecule, the greater the number of physicochemical characteristics which must be introduced into the equation for the calculation of retention characteristics. In practice it is impossible to isolate 1–2 dominant physicochemical parameters of the sorbate which would ensure a sufficiently high accuracy of the calculated data. The endeavour of some investigators to employ for this purpose the methods of factorial analysis[214-221], where the maximum number of sorbate parameters are introduced into the computational equations and then the characteristics which influence the retention parameters to the greatest extent are selected on the basis of experimental data, therefore appears to be quite natural.

Studies have shown[214] that the most important parameters of the sorbates are the molecular weight, the molar heat of evaporation, the molar refraction, and the constants of the equation of state. The molecular weight and the molar refraction characterise mainly the energy of dispersion interaction, while the remaining characteristics refer to the overall quantitative estimate of the energy of the interaction of the sorbate molecules with one another. Less important factors are the boiling point and the logarithm of the vapour pressure of the pure sorbate. Its density, dipole moment, vapour pressure, and dielectric constant are parameters for which the correlation with the retention characteristics is very weak. The smallest error of the calculation (approximately 5 units for butyric acid esters) is attained when one of two sets of sorbate parameters is used: (1) the boiling point, the van der Waals constants, the molar refraction, and the specific contribution of the ester group to the intermolecular interaction and (2) the boiling point, the van der Waals constants, the specific contribution of the ester group to the intermolecular interaction, and the number of carbon atoms in the molecule[220]. When an attempt was made to calculate the retention parameters of eighteen aliphatic acid esters on 25 stationary phases, it was shown[222] that the correlation of the results with five sorbate parameters ensures $s = 2.8$ units, an increase of one in the number of parameters employed reducing the error to 2.1 units.

A variant of factorial analysis has been used in studies[223, 224], where the retention factors P of alkylpyridines and ketones were calculated using a parameter proportional to the size of the sorbate molecule x_1, its polarity x_2, the characteristic of the steric environment of the functional groups x_3, and the number of pairs of vicinal alkyl groups x_4:

$$P = k_1 + k_2x_1 + k_3x_2 + k_4x_3 + k_5x_4 \ . \qquad (34)$$

A modification of this equation was presented in a subsequent study by the same workers[225], where the dipole moment of the sorbate molecule (μ) and the number of alkyl substituents in the α-position relative to the functional group (n_0) were used:

$$I = k_1 + k_2n + k_2\mu + k_3n_0 \ . \qquad (35)$$

The last equation was used to calculate the retention parameters of derivatives of aromatic hydrocarbons and pyridine on stationary phases such as Apiezon L, Carbowax 20M, silicone XE-60, and diethylene adipate; $s^0 = 3\%$ for phenols, $s = 56$ for anilines, $s = 14$ for alkylbenzenes, and s is up to 32 units for polar benzene derivatives. Such errors show that the last two equations yield only estimates.

Thus analysis of the attempt to use only the physicochemical characteristics of the sorbate without taking into account intermolecular interaction in gas-chromatographic solutions permits the conclusion that a more or less accurate calculation of retention parameters requires the employment of a number of empirical parameters together with the selected physicochemical constants, which is so large that the complexity of the calculations approaches that of the calculations using topological analysis. Thus the employment of only the characteristics of the sorbate does not lead to the solution of the problem of the calculation of retention parameters, because one then ignores the influence of the stationary phase on the intermolecular interaction in solution. The choice of one or several parameters of sorbates for the calculation of retention parameters can be justified only for a comparatively narrow range of substances and only for interpolation calculations.

The attempts at quantum-mechanical calculations of retention indices using the Hückel method of linear combinations of molecular orbitals are actually close to the above group of methods[226]:

$$I = k_1E + \sum k_2Q_i + k_3, \qquad (36)$$

where E is a dimensionless parameter which depends on the molar volume of the sorbate and the overall energy of the electrons in the molecule and Q_i is the effective charge on the ith atom of the sorbate molecule. The application of Eqn. (36) to the calculation of Kovats indices for cyclohexane derivatives on Apiezon L leads to $s = 14.5$ units. A reduction of the errors to 7–8 units is achieved when E is replaced by the sum of the indices referring to the σ- and π-electrons of the sorbate molecule[227]. The average deviation of the calculated data from the experimental results for 59 derivatives of cholestanyl acetate on SE-30 silicone is 5.7 units, the error increasing to 19.2 units on QF-1 silicone and to 39 units on more polar stationary phases. In calculations for narrow groups of sorbates, the error falls to 0.3 of a unit[226, 228]. The errors of calculations using quantum-mechanical data show that it is undesirable to employ characteristics of this kind: quantum-mechanical calculations for complex molecules are extremely laborious and the information obtained concerning the distribution of electron density in the molecule is only partly employed for calculations on the intermolecular interaction. Finally, the large number of what are essentially empirical parameters in the quantum-mechanical calculations for complex molecules of organic substances makes these methods similar to purely empirical procedures.

GLC practice has shown that the influence of the stationary phase on the retention must be taken into account in all methods for *a priori* calculations. Numerous instances have been described in the literature where a change in the nature of the stationary phase not only alters the relative retention parameters but also alters the sequence in which the substances are eluted from the column. Such phenomena are not reflected in any of the equations quoted in this section of the review. From this standpoint, it would appear to be useful to combine in the computational equations both the properties of the pure sorbates and the characteristics of the stationary phase. The latter quantities can be specified in terms of the Rohrschneider[229] or MacReynolds equations. When the three-parameter Rohrschneider equation is used, the error s in calculations for simple monofunctional sorbates is 12.6 units, while the application of the five-parameter Rohrschneider equation to the same systems lowers the error to 4.1 units. An intermediate error (6 units) has been obtained using the four-parameter Rohrschneider equation[230]. Similar correlations have been used[231] on 14 polysiloxane stationary phases for esters; the correct choice of test substances reduced the

error of the calculation from 6.7 to 4.7 units[232]. The constants of the MacReynolds equation proved to be less suitable for calculations than the corresponding constants of the Rohrschneider equation[233]: the errors for the three-parameter equation reached 30 units.

A series of column parameters and three–four constants of the sorbate have been used in the calculations of the values of I for alcohols, ethers, olefins, and aromatic and aliphatic hydrocarbons on Apiezon L, OV-25 silicone, and 5CP silar[234] with the column temperature programmed in the range from 25° to 250–300 °C. The MacReynolds constants, the molecular weight of the sorbate, its boiling point and molar volume were used. The discrepancies between the calculated and experimental data were 8–10 units.

An attempt to combine factorial analysis with the topological method has been described in a study[235], where the advantage of such combinations is emphasised. On the other hand, the influence of the stationary phase on the separation is taken into account by the appropriate choice of test substances, whose initial empirical constants are determined. The nature of these test substances must be as close as possible to that of the substances investigated.

Thus the data examined show that, only by resorting to the characteristics of the interaction of the stationary phase with the sorbate, can one devise an acceptable method for the calculation of the retention parameters of sorbates differing in physicochemical properties. The neglect of the influence of the stationary phase on the retention converts computational methods into specific procedures with extremely limited applications.

IV. THE POSSIBILITY OF USING THEORIES OF SOLUTIONS FOR THE CALCULATION OF RETENTION PARAMETERS

In contrast to the correlations between the retention parameters and the properties of pure sorbates, the application of the theory of non-electrolyte solutions makes it possible to relate the intermolecular interaction energy in solution to the retention parameter of the sorbate. From this standpoint, the employment of theories of solutions is extremely promising for *a priori* calculations of retention parameters. Unfortunately, the lack of a general theory of dilute non-electrolyte solutions or at least of a theory of gas-chromatographic solutions has largely retarded the application of individual variants of theories of solutions to practical calculations of retention parameters. Most of the theories of solutions employed model ideas which simplify unduly the picture of the intermolecular interaction in the gas-chromatographic solution.

Gas-chromatographic solutions have the following specific properties[151]: (a) the concentration of the solution is extremely low and as a rule ranges from 0.1 to 0.001%, (b) the sorbate molecule is much smaller than the molecule of the stationary phase and the intermolecular interaction therefore involves the entire sorbate molecule and part of the molecule of the stationary phase, and (c) the temperature of the stationary phase in the chromatographic column is usually closer to its melting point than to its boiling point, which makes it preferable to use the structure of the solid as an approximation to the structure of the stationary phase. The low concentrations of gas-chromatographic solutions suggest that the main type of interaction in them is that between the sorbate molecules and the surrounding molecules of the stationary phase. The concentration effects in dissolution play only a secondary role for gas-chromatographic solutions, whereas in the classical theories of solutions mainly concentration effects are investigated[1,2].

In comparing data obtained in the classical theory of solutions and the quantities characteristic of GLC, one should note that these two groups of data differ significantly: in the traditional theory of solutions the principal aim is to study the changes in the properties of substances on mixing (the liquid components are mixed), whereas in the study of gas-chromatographic solutions the main question is the alteration of the energy characteristics of the substance when it passes from the gas phase to the solution. The only thermodynamic quantity which has the same significance for the two approaches being compared is the activity coefficient γ and we shall therefore endeavour to confine ourselves to the consideration of attempts at calculations of this parameter.

Many theoretical concepts of the classical theories of non-electrolyte solutions are inapplicable, in principle, to gas-chromatographic solutions. These include all the theories which treat the liquid as a set of solid spherical particles. In view of the wide variety of gas-chromatographic systems consisting of molecules with comparatively complex conformations, only phenomenological theories of solutions can be used for gas-chromatographic calculations.

Since the model of the solid state constitutes the best approximation to the structure of the gas-chromatographic solution, theories treating the liquid as a quasi-crystal lattice have gained great popularity in GLC: each atomic group of the molecules of the stationary phase in the sorbate occupies one site in such a lattice. The ideas of Miller and Guggenheim[236,237] and of Flory and Huggins[238,239] constitute the basis of the equation which represents the excess free energy of solution, proportional to $\ln\gamma$, as the sum of $\ln\gamma^e$ (γ^e reflects the change in intermolecular forces on dissolution) and $\ln\gamma^s$ (this term characterises the entropy contribution due to the different dimensions of the molecules of the stationary phase and the sorbate)[240]. For low values of γ^e, these two parameters can be regarded as independent and then, neglecting the change in the energy of intermolecular forces on dissolution, one can formulate the following equation[241]:

$$\ln\gamma = \ln(1/r_1) + 6\ln\frac{6r_1}{5r_1+1} + \overline{F} \quad , \tag{37}$$

where r_1 is the ratio of the molar volumes of the sorbate and the stationary phase and F the interaction parameter consisting of the enthalpy ($\overline{F}_h$) and entropy components. The following relation is valid for athermal solutions:

$$-\Delta S_s^e/R = \ln(1/r_1) + 6\ln\frac{6r_1}{5r_1+1} + \overline{F}_s \quad , \tag{38}$$

where ΔS_s^e is the excess molar entropy of solution. In some cases $\overline{F}_s$ makes the main contribution to ΔS_s^e.[242] Eqn.(38) has been tested experimentally in relation to the retention parameters of paraffins and cycloparaffins on dinonyl phthalate[243].

A somewhat different form of the Flory–Huggins equation has been proposed for gas-chromatographic calculations[244]:

$$\ln\gamma = \ln r_1 + r_1 + 1 \quad . \tag{39}$$

The authors[244] point out the incorrectness of the representation of r_1 by the ratio of the molar volumes of the sorbate and the stationary phase and suggest that the ratio of the numbers of carbon atoms in the linear chains of the molecules of the sorbate and the stationary phase be used. If it is supposed that $\ln r_1 \ll r_1$, it is possible to derive the following correlation equation[245]:

$$\ln\gamma = k_1 + k_2 r_1 \quad . \tag{40}$$

The Flory–Huggins equation has also been used to calculate the retention parameters of C_1–C_6 alcohols on poly(ethylene glycol)-400;[246] the error s^0 in this method of calculation is 4%.

The Flory–Huggins ideas describe fairly satisfactorily the energy contributions associated with the difference between the sizes of the molecules of the stationary phase and the sorbate; unfortunately the problems of the calculation of $\overline{F}_S$ and $\overline{F}_h$ have been inadequately investigated to date. The Hildebrand–Scatchard theory for regular solutions can be applied to calculations of $\overline{F}_h$ using the so-called solubility parameter $\delta = [(\Delta H_v - RT)/V]^{0.5}$. When the latter is taken into account, Eqn.(36) can be formulated thus:

$$\ln \gamma = \ln(1/r_1) + 6 \ln \frac{6r_1}{5r_1 + 1} + \frac{\overline{V}^*}{RT}(\delta_1^2 - \delta_2^2)^2 , \qquad (41)$$

where $\overline{V}^*$ is the apparent molar volume of the sorbate.

In calculations of the retention parameters of C_5–C_7 isoparaffins, C_6–C_7 olefins, and cycloalkanes with the same number of carbon atoms in the molecule, the error is $s^0 = 1.8\%$.[243] However, the quantity $\overline{V}^*$ is to a large extent formal and all the factors contributing to the entropy of solutions are not reflected in Eqn.(41); furthermore, the need to determine the molar volumes and heats of evaporation increases the difficulty of the preliminary experiments required for calculations involving this equation.

Eqn.(41) is applicable only to systems in which the species are linked solely by dispersion forces. On the other hand, if orientational and inductive forces are manifested in the solution, it is necessary to introduce the corresponding corrections and the last term on the right-hand side of Eqn.(40) assumes the following form[246]:

$$\frac{\overline{V}^*}{RT}[(\delta_1^2 - \delta_2^2)^2 + (\omega_1^2 - \omega_2^2)^2 - f]$$

where

$$(\omega_1^2 - \omega_2^2)^2 = \frac{3.25 \cdot 10^7}{\overline{V}_1^2 RT}(\mu_1^2 \overline{V}_1 + \mu_2^2 \overline{V}_2) .$$

The quantity f is a correction for the negative deviation from Raoult's law. It is actually calculated as the discrepancy between the calculated and experimental data. When this equation is used for interpolation calculations of the retention parameters of hexenes on dimethylformamide, $s^0 = 6.7\%$.[247] The application of the modified Hildebrand–Scatchard equation to polar systems has been discussed in detail[248–250].

When the last equations are employed, there are certain difficulties associated with the necessity to determine the molar volumes of the sorbates and the stationary phase. In order to overcome these difficulties, it is suggested that these characteristics be calculated by indirect methods, for example, from the additive contributions of atomic groups[251] and from the solubility and viscosity[252,253]; it has also been suggested[254,255] that the effective molar volume be used as corrections for the surface tensions of the liquids.

The simplified ideas underlying the Hildebrand–Scatchard theory preclude the attainment of an acceptable accuracy in the calculation of gas-chromatographic retention characteristics for a wide range of compounds. It is difficult to expect that the two-parameter relation for the molar heat of solution as a function of ΔH_v and $\overline{V}$ will describe correctly the entire set of forces acting in a gas-chromatographic solution. The conversion of Eqn.(40) into three- and four-parameter modifications gives rise to only an apparent effect: it is known[214] that, when a three-parameter relation is available, the minimisation of the experimental proportionality coefficients can lead to fairly accurate interpolated data regardless of the nature of the correlation and the parameters employed for it.

It has also been suggested that the parameter $\overline{F}_h$ be evaluated as the mean (geometrical or arithmetical) of the energies of the sorbate and stationary phase molecules[256] or on the basis of Barker's theory[257,258]. The latter ideas have been used in a series of investigations[259–263] in which $\overline{F}_h$ was treated as the result of the interaction between the individual segments of the molecules, which gives the best description of the real pattern of the interaction in the gas-chromatographic solution. The authors[259–263] used the following equation:

$$\overline{F}_h = [q_1(u_1 - u_2)^2 E_i/kT]m_2^2 , \qquad (42)$$

where q_1 is the total number of points of contact, u_i the fraction of points of contact of type i for the given molecule, m_2 the mole fraction of the stationary phase in solution, and E_i the interaction energy. It has been postulated that E_i is independent of the medium surrounding the sorbate molecule. It has been shown[264] that the quantity $\overline{F}_h$ characterises the molar enthalpy of mixing. Barker's theory has also been used to calculate the retention parameters of alkanes[265–268], but no quantitative estimates of the accuracy of the method employed are indicated.

Prigogine's theory of solutions has been modified for gas-chromatographic systems[269]:

$$\overline{F}_h = h_1 k_i / 4RT, \quad \overline{F}_s = k_1(\lambda + k_i)^2/2R,$$
$$\lambda = 1 - (k_n/\overline{r})_2/(k_n/\overline{r})_1, \quad k_i = (\varepsilon_{22} - \varepsilon_{11})/\varepsilon_{22} , \qquad (43)$$

where $3k_n/\overline{r}$ is the number of external degrees of freedom of the molecular segment, k_i a constant proportional to the depth of the potential well for the 1–1 and 2–2 interactions of the substances and determined from the critical temperature and the volume of the hard spheres, h_1 the configurational enthalpy, k_n the configurational heat capacity, and ε the interspecies interaction potential. The quantity $k_n/\overline{r}$ can be determined directly. An empirical equation involving the number of segments in the sorbate molecule has been proposed for this purpose[269].

The activity coefficients of C_4–C_{10} n-alkanes in C_{22}–C_{36} n-paraffin stationary phases have been calculated to test Eqns.(43).[244] The experimental data showed that the ratio $k_n/\overline{r}$ increases linearly with the number of carbon atoms in the molecule of the stationary phase (the stationary phase is designated by subscript 2 and the sorbate by subscript 1). The authors[244] used the following equation for their calculations:

$$\overline{F} = 18(n_1 + 1)[1/(n_2 + 1) - 1/(n_1 + 1)]^2 \cdot E_i/kT . \qquad (44)$$

The configurational enthalpy and the parameter k_i were calculated from the formulae

$$h_1 = \Delta H_v + RT \qquad (45)$$

$$k_i = \frac{T_2^c \tilde{V}_2^{1/3}}{T_1^c \tilde{V}_1^{1/3}} - 1 \qquad (46)$$

where subscript c refers to the critical parameter and $\tilde{V}$ is the van der Waals volume.

The relative average standard deviation of the calculated quantities from the experimental data was 0.8%. According to the authors[244], the question of the influence of $\overline{F}_S$ on the retention parameters remained unelucidated in view of the inadequate accuracy of the experimental results. On the other hand, it has been claimed[270] that $\overline{F}$ is wholly determined by $\overline{F}_S$, while $\overline{F}_h$ has the greatest influence on the experimental error. In fact, however, the neglect or underestimate of the contribution of any of the components of $\overline{F}$ to the retention parameter distorts the real pattern of the intermolecular interaction in gas-chromatographic solutions, where the influences of the entropy and enthalpy of solution on the free energy of solution are comparable.

Prigogine's theory of solutions has been used[271] to describe the properties of solutions of benzene in polyphenyl stationary phases. The entropy of mixing was calculated on the basis of the lattice model of the liquid state and the energy

of the intermolecular forces was calculated using the theorem of corresponding states, although the latter employs a number of assumptions which are by no means correct.

The group method[271] operates, in conformity with its physical significance, also with two components of the free energy of the interaction of the sorbate with the stationary phase, namely the entropy component γ_S, calculated from the Flory–Huggins equation, and the group component γ_j, calculated from the equation

$$\gamma_j = n_{mj}(\lg\gamma_m - \lg\gamma_m^*) \quad , \qquad (47)$$

where n_{mj} is the number of groups k in the molecule j, γ_m the activity coefficient of the structural group k in solution, and γ_m^* the activity coefficient of group k in the pure solvent. After a series of simplifications, the following equation has been proposed for homologous series of sorbates, incorporating the constants of the interactions of individual structural groups[272]:

$$\lg\gamma = k_1 + k_2/(n_1 + k_3) + k_4k_5/n_1 + \\ + n_2/(k_5 + n_2) + k_6(k_5 - n_1)^2 \quad . \qquad (48)$$

All the constants in Eqn.(48) (from k_1 to k_6) are determined experimentally with the aid of test sorbates. The error of the calculated data is in this case 5–10%.

The relations for the calculation of the energy of intermolecular interaction by the method of the group theory have been examined in a general form[273,274]. It has been postulated that the interaction energy is additive with respect to the structural groups of the molecule in the stationary phase and the sorbate (the groups m_i^v and m_i^u respectively). For dilute binary solutions, the excess molar heat of solution is calculated from the equation

$$\Delta H_s^e = k_{12}s_1 \quad , \qquad (49)$$

where

$$k_{ij} = -\sum_{uv} k^{uv}(m_i^u/s_i - m_j^u/s_j)(m_i^v/s_i - m_j^v/s_j)s^us^v,$$

$$s_i = \sum m_i^u s^u, \; k^{uv} = \varepsilon^{uv} - 0.5(\varepsilon^{uu} + \varepsilon^{vv}) \quad .$$

Comparison of the calculated and experimental molar heats of solution of hydrocarbons of different classes shows that the average standard error of the calculation is 0.14 kJ mol^{-1}. It has been noted that the molar entropies of mixing of hydrocarbons calculated from the Flory–Huggins equation differ from the experimental values by a factor of 10–20. This shows that the description of the entropy of solution cannot be restricted to a single factor—the different dimensions of the molecules of the sorbate and the stationary phase. As shown in the next section, the entropy of solution consists of 4–5 main components, among which the factor associated with the differences between the dimensions of the molecules of the sorbate and the stationary phase is not the main one.

Calculations of the activity coefficients by the group method showed[274] that s^0 = 1.6% for acids in water, 4.5% for alcohols in water, 2.4% for alcohols in paraffins, 5% for ketones in paraffins, 5–8% for cycloalkanes in heptane, and 5–13% for paraffins and cycloalkanes in triethylene glycol. It is noteworthy that the errors of the calculation are smaller for extremely non-ideal systems such as those in alcohols and paraffins, while for solutions close to ideality (solutions of hydrocarbons in hydrocarbons) the errors of the calculation are large. This apparently indicates an unsuccessful choice of test substances for the determination of the empirical coefficients in the case of non-polar and weakly polar systems, while the final result of the calculation depends on the intuition of the investigator, as in factorial analysis. In the model of the group theory, the activity coefficients are calculated using a large number of empirical corrections introduced in the form of interaction coefficients and the effective cross-sections (encounter probabilities) of individual structural groups $s^{u,v}$. Despite this, the given model is closest to the approach based on the theory of group additivity and examined in Section II of this review. The errors themselves are also of the same order of magnitude as for the purely empirical methods for the calculation of retention parameters.

The application of the free volume theory to the calculation of the activity coefficients of spherical molecules has been described[275]. According to this theory, the potential energy of the liquid depends on the difference between its real volume and its calculated van der Waals volume. The introduction of a series of simplifying assumptions made it possible to calculate the activity coefficients of a number of molecules containing germanium, silicon, and titanium; the errors of the calculation proved to be smaller than those arising in the application of the Guggenheim and Hildebrand–Scatchard theories. A number of inorganic compounds have been investigated in a study[276,277] where the free volume theory was also used for the calculations.

The theory of conformal solutions[278], the theory of athermal solutions[278,279], and the theory of regular solutions[241] have also been used to calculate the retention parameters. The last two theories are more suitable for correlation calculations, because the concepts of athermal and regular solutions are invalid for real gas-chromatographic solutions.

The study of the statistical thermodynamics of solutions constitutes one of the trends in the theory of solutions, which are promising from the standpoint of their application to GLC: no model ideas, i.e. ideas simplifying the real picture of the interaction, are then put forward. The energy of the intermolecular interaction is calculated as the sum of the elementary functions of state of the molecules in solution: the intermolecular interaction energy of each conformation of the molecule and its statistical weight. However, the *a priori* determination of these parameters still encounters difficulties which cannot be overcome and which are associated with the inadequacy of our information about the real conformations and interactions of the molecules in solution. Nevertheless certain ideas on statistical thermodynamics have begun to be used in calculations of the relative retention; for example, the relative retentions of the stereoisomers of substituted cyclohexanoic acids have been calculated[280], with errors ranging from 0.1 to 1.5%, from the ratio of the partition functions based on the parameters of the rotational spectra of the molecules.

Analysis of the data described in this section permits certain conclusions concerning the possibility of employing the theories of solutions for the calculation of retention parameters in GLC. According to some results[151,269], three main factors contribute to the excess free energy of solution in GLC: (a) the geometrical effects arising as a consequence of the difference between the sizes of the molecules of the stationary phase and the sorbate (see the Flory–Huggins theory); (b) the energy effect associated with the energy of the intermolecular forces in solution ($\bar{F}_n$); (c) the structural effect associated with the change in the conformation of the molecule on dissolution and with the restriction of the number of degrees of freedom on passing from the gas to the liquid phase ($\bar{F}_s$). The effect (a) has been fairly thoroughly investigated and has been described mathematically, but its contribution does not always exceed 5–10% even to the entropy of solution. For the remaining two effects, the modern theories of dilute non-electrolyte solutions cannot provide an adequately accurate mathematical description, which is the reason why workers in the field of chromatography have been disappointed by the application of theories of solutions to the calculation of retention parameters in GLC. The significant model limitations (hard spheres, theorem of corresponding states, etc.) of solution theories preclude

their application to the description of the properties of a wide variety of gas-chromatographic systems. The introduction of additional empirical parameters lowers the value of solution theories to the level of the methods of empirical calculations of retention parameters.

V. SEMIEMPIRICAL CALCULATIONS OF THE MOLAR HEATS AND ENTROPIES OF SOLUTION

Most of the studies on the application of solution theories in calculations of retention parameters are associated with the evaluation of the activity coefficients, which are not in general direct retention characteristics: the calculation of activity coefficients requires (in the ideal case) the availability of data on the fugacity or (usually) the movement of the saturated sorbate vapour. At the same time the determination of thermodynamic functions for the phase equilibrium in gas-chromatographic systems does not require any information at all about the vapour pressure or fugacities of sorbates, i.e. such information in no way assists in the calculation of retention parameters. Furthermore, the molar free energy of solution (the free energy of the phase transition) as well as quantities proportional to it (I and $\ln V_N$) are hardly susceptible to calculation by additivity methods or methods involving the employment of correlations between the retention parameters and the physicochemical properties of the sorbates.

Consequently it is useful to seek a compromise, which combines the main advantages of the theoretical foundations of the intermolecular interaction, the solution theories, the correlations with physicochemical properties, and the additive contribution of individual atomic groups to the interaction energy. We believe that the application of these ideas is possible in the separate analysis of two main components of the molar free energy of solution—the molar heat of solution and the molar entropy of solution. A series of ideas in statistical thermodynamics and molecular physics can be related to each of these thermodynamic quantities, including the experience accumulated in the employment of the physicochemical characteristics of sorbates and stationary phases as well as purely empirical approximations.

In a series of studies of Sakharov and coworkers[281-288] gas-chromatographic solutions have been treated as quasi-crystalline lattices and the molar heats of solution ΔH_s have been treated as the sum of the energy of intermolecular forces and the work of formation of a hole within the solvent in which the sorbate molecule is accommodated. If the treatment is restricted to isomeric substances, then the molar heat of formation of the hole ΔH_h can be neglected for comparative calculations. The energy of intermolecular forces $\Delta H_s - RT$ can be quite correctly represented as the sum of the increments (ΔH_i) due to individual atoms (or groups of atoms) in the sorbate molecule. The energy of the intermolecular forces between the nth atom of the sorbate molecule and the stationary phase is calculated as the difference between the energy of the interaction of an isolated nth atom with the stationary phase E_n and the quantity E'_n reflecting the intermolecular shielding of the same atom in the sorbate molecule, i.e. ΔH_n represents the effective interaction of the nth atom with the stationary phase. It has been postulated[281-288] that the values of $\Sigma E'_n$ for isomeric compounds are identical and that $\Delta\Sigma E_n$ represents the difference between the molar heats of formation of these isomers (this claim is not altogether correct). Finally, it has been suggested that the molar entropy of solution is proportional to the molar heat of solution or, in other words, that the molar free energy depends solely on the molar heat of solution.

Linear correlations between $\ln r$ and the difference between the molar heats of formation of isomers have been found experimentally for C_4–C_7 alkanes and cycloalkanes using a non-polar stationary phase. This made it possible to formulate the following rule: "of two isomers with similar structure, the resonance and polar factors in the molecules of which are equal, the isomer with the greater (molar) heat of solution in the non-polar solvent has a smaller (molar) heat of formation"[281]. It is noteworthy that the suggested analogy between the energy of intermolecular forces in solution and the energy of formation of the molecule is formal, which is the reason for the considerable scatter of experimental points in many instances relative to the calculated relations. For example, the relations between the Kováts indices of isomeric olefins and their molar heats of formation[285] consist of a family of straight lines with different slopes and each straight line corresponds to a group of isomers with the same number of branches in the carbon chain around the double bond. Similar relations have been found for alkylbenzenes and certain other classes of compounds. The disadvantages of this concept include the correlation of the retention characteristics solely with the properties of the isomers being separated and the neglect of the influence of the stationary phase on the retention.

It is noteworthy that the approach of Sakharov and coworkers to the treatment of the intermolecular interaction in gas-chromatographic solutions has yet another positive aspect: attention is concentrated on the evaluation of the relative retention parameters r and I. Indeed, in GLC practice the main criterion of the selectivity of the stationary phase is the relative retention parameter which makes it possible to infer whether the separation of the relevant sorbates ($r \neq 1$) on a given stationary phase is possible and how difficult it is to achieve (the value of r and to some extent the value of V_N or V_g). The simplicity of the calculation of the relative retention parameters from experimental data, the low experimental error in the determination of these quantities, and their simplified theoretical treatment, where the effects of many factors cancel out made the relative retention parameters the most popular in GLC practice at the same time and, which is no less important, the most reproducible[289]. The principal thermodynamic relations between the relative retention parameters and the intermolecular interaction parameters are fairly simple (the superscript 0 denotes a relative molar thermodynamic function):

$$\Delta G_s^0 = -RT \ln r = \Delta H_s^0 - T\Delta S_s^0 \quad . \qquad (50)$$

It is therefore useful to describe briefly the semiempirical concept underlying the calculation of the relative molar thermodynamic functions of dissolution[290-292]. In this concept the gas-chromatographic solution is regarded as a quasi-crystalline lattice where each site is occupied by an atom (or atomic group incorporating all the chemically linked hydrogen atoms). Since the sorbate molecule is surrounded on all sides by the molecules of the stationary phase (infinitely dilute solution), the calculation of the intermolecular interaction in the given system reduces to the calculation of the energy of the interaction between the atomic groups of the sorbate molecules and the surrounding atomic groups of the stationary phase, and the relative positions of the molecules must be selected on the basis of the minimum potential energy of the system.

In conformity with the traditional ideas concerning the formation of a solution, the experimental molar heat of solution ΔH_S can be represented as the sum of the energy of the intermolecular forces between the sorbate molecule and the stationary phase E_i, the molar heat of formation of the hole, and the term RT reflecting the change in the energy of the

system on condensation of the ideal gas into the liquid phase:

$$\Delta H_s = E_i + \Delta H_h + RT \quad . \tag{51}$$

If the treatment is restricted to systems with dispersion interaction, the calculation of the energy of intermolecular forces is feasible. Sakharov[281] proposed the following equation for the energy of the dispersion interaction of the *i*th atom with the stationary phase:

$$U_d = -0.9 \int_{r_i+r_0}^{\infty} 0.75h\nu \frac{\alpha_i \cdot 4\pi r^2 \bar{\rho}}{r^6} dr = 0.9\pi h\nu \frac{\alpha_i \bar{\rho}}{(r_i + r_1)^3} \quad , \tag{52}$$

where α is the polarisability, $\bar{\rho}$ the density of the polarisability of the medium, i.e. of the stationary phase (the ratio of the molar refraction to the molar volume of the stationary phase), r_i the van der Waals radius of the *i*th atom, h the Planck constant, ν the average vibration frequency of the molecules of the stationary phase with the *i*th atom, and r_1 the average van der Waals radius of the functional groups of the stationary phase. Sakharov suggested that the quantity $D = \alpha_i/(r_i + r_1)^3$ be called the "dispersity" of the atom or atomic group and demonstrated, by analysing the literature data, a correlation between the Kováts index and the "dispersity".

A somewhat simpler relation between the dispersion interaction and the molar heats of solution in a non-polar stationary phase has been derived differently[290]. The dispersion interaction energy of a pair of fairly remote spherical particles (the distance between them is greater than the covalent radius) is described by an equation which includes the polarisabilities of the atomic groups of the sorbate (α_i) and the stationary phase (α_2):

$$U_d = -k\alpha_i\alpha_2\bar{r}^6 \quad . \tag{53}$$

When the interaction of atoms or atomic groups in a gas-chromatographic solution is considered, then Eqn.(53) is valid. On replacing the atomic polarisability by the atomic refraction R_0, we obtain the equation

$$D_n = R_{0i}R_{02}/(\bar{r}_i + \bar{r}_2)^6 \quad . \tag{54}$$

Indeed the linear correlation between ΔH_S and ΣD_n holds for a number of classes of non-polar and moderately polar compounds[293,294].

If the term $\bar{r}_1 + \bar{r}_2$ is represented as the sum of the van der Waals radii of an atom (or atomic group) in the sorbate and an atom (atomic group) in the stationary phase, then the values of D_S can be readily tabulated for all the atoms and atomic groups incorporating chemically bound hydrogen atoms[291]. The constants of the intramolecular shielding of the atoms or atomic groups of the sorbate can be readily calculated on the basis of the species constructed taking into account stereochemical ideas[295]. Thus the increments of the energy of the dispersion interaction of the atoms and atomic groups of the sorbate molecule with the medium (stationary phase) can be calculated from the molecular characteristics[290,291]. The quantity E_i is calculated as the sum of n increments due to the atomic groups of the molecule:

$$E_i = i \sum_n K_n D_n \quad , \tag{55}$$

where i is the normalising multiplier and K_n the coefficient of the intramolecular shielding of the atomic group of the sorbate. The normalising coefficient is calculated from the experimental molar heats of solution of n-paraffins and takes into account the influence of the real non-polar medium on the molar heat of solution. It varies non-linearly with the number of carbon atoms in the n-paraffin molecule, approaching exponentially a limiting value at $n > 7$.

Allowance for the work of formation of a hole in the gas-chromatographic solution is a difficult problem, whose solution depends on the real structure of the stationary phase. It has been suggested[283,296] that the work of formation of a hole in the solvent is proportional to the surface tension of the stationary phase and the surface area of the sorbate molecule. However, such hypotheses are valid only for a structureless stationary phase, which can be represented approximately as a system of randomly distributed small spherical molecules. The real stationary phases in GLC consist of an anisotropic medium with a distinct structure, which has been confirmed by X-ray diffraction studies[297]. For example, liquid paraffin stationary phases constitute a system of mutually oriented linear hydrocarbon chains, which migrate freely in parallel planes with a minimal energy expenditure. Therefore, if the accommodation of the sorbate molecule in a paraffin stationary phase requires merely a shift of a paraffin molecule in a parallel plane (longitudinal shift), then the work of formation of a hole is minimal; this applies to the dissolution of n-paraffins; the work of formation of a hole in n-paraffins is assumed to be zero in comparative calculations. On the other hand, when the structure of the stationary phase changes on dissolution, then the work of formation of the hole can no longer be neglected. For example, on dissolution of a branched isoparaffin in an n-paraffin stationary phase the molecules of the stationary phase move apart in a plane at right angles to their longitudinal axis (transverse shift). In the transverse shift of the molecules of the stationary phase the work of formation of a hole is proportional to the number of branches of the hydrocarbon chain of the sorbate molecule, although in the general case the relative positions of the branches also influence the work of formation of the hole[291,298].

In the chromatography of polar sorbates on non-polar or weakly polar stationary phases, a new factor appears—the concentration effect Δk,[299–304] which is due to the association of the molecules of the polar sorbate in the non-polar solvent, which occurs even at infinitesimal concentrations of the solution. The effect is particularly large for alcohols and other sorbates forming a hydrogen bond (approximately 14 kJ mol^{-1}); for the remaining polar sorbates, the energy of the concentration effect is approximately 3–6 kJ mol^{-1}.[301]

In the determination of the energy of intermolecular forces of polar sorbates in polar stationary phases account must be taken of the orientation interaction, which arises under the influence of the dipole moments of the functional groups of the stationary phase and the sorbates, which are determined by stereochemical factors. The bond microdipoles are partly shielded by the chemically linked atoms or atomic groups; apart from the bond microdipoles, the so-called secondary dipoles, formed by chemically non-linked atoms or atomic groups, participate in the orientation interaction. The contribution of the orientation interaction to the energy of the intermolecular forces can be determined solely by considering specific systems with allowance for the optimum relative positions of the molecules of the sorbate in the stationary phase. Examples of the determination of the extent of the orientation interaction in gas-chromatographic systems have been published[305–307].

The intermolecular forces in solutions of aromatic and other cyclic molecules must be calculated taking into account the relative spatial distribution of the molecules, the electronic effects of various substituents in the aromatic ring, and a number of other features characteristic of systems with steric hindrance to interaction. These questions have been discussed in detail[304,308–316].

The calculation of the relative molar entropy of solution for gas-chromatographic systems involves considerable difficulties. It follows from Section IV that the application of the

Flory–Huggins equation alone to the solution of this problem is inadequate. The difference between the molar entropies of the sorbate in the gas phase and in solution ΔS_S is determined by the following factors[317]. In the gas phase the entropy of the molecule includes the entropy of the rotational movement S_r [the sum of the entropies of the internal (S_{ri}) and external (S_{re}) rotational movements], the electronic entropy, the vibrational entropy, the nuclear components, and the translational entropy S_{tr}. On passing to the solution, the sorbate molecule loses some of its degree of freedom, i.e. the entropy decreases and the molar entropy of solution, calculated from gas-chromatographic data, is therefore always negative. The decrease of the entropy of sorbate molecules is determined primarily by the decrease in the rotational and translational entropies; as a consequence of the comparatively weak intermolecular forces in gas-chromatographic solutions, the remaining forms of the entropy of the sorbate molecules do not change on passing from the gas to the liquid phase.

Using the fundamental relations of statistical thermodynamics[318], it is possible to formulate the equation

$$\Delta S_{tr} = R \ln V^0 - k_1 , \qquad (56)$$

where V^0 is the molar volume of the ideal liquid related to the van der Waals molar volume of this liquid by the equation

$$RT \ln V^0 = R \ln M - R \ln \tilde{V} + k_2 . \qquad (57)$$

Eqn.(56) characterises the change in the translational entropy when the sorbate molecules pass from the gas to the liquid phase.

The so-called compensation effect[319], observed for many gas-chromatographic systems[320–323], makes a definite contribution to the entropy of solution. The essential feature of this effect consists in the linear relation between ΔS_S and ΔH_S for many simple systems, whose slope is an inverse function of temperature. The following equation is then obtained for the relative molar entropy of solution (the ratio for the sorbates x and r):

$$\Delta S_S^0 = \Delta H_S^0 T / k_1 + R \ln (M_x / M_r) - R \ln (\tilde{V}_x / \tilde{V}_r) + \Delta S_{re}^0 + \Delta S_{ri}^0 . \qquad (58)$$

For isomeric compounds, the values of $\tilde{V}$ are approximately the same. Calculations of the molar entropy of solution have been performed in a number of studies[308,324,325], where the influence of a change in the rotational entropy on ΔS_r was demonstrated.

The thermodynamic approach to the calculation of the molar heat and entropy of solution described above makes it possible not only to calculate the individual thermodynamic functions of solution but also to calculate, using their combination, the overall parameters of the selectivity of the stationary phase—the Kováts index and the relative retention, and the knowledge of the relative molar heats of solution makes it possible to calculate these quantities for any column temperature.

The given method makes it possible to obtain fairly accurately extrapolated retention parameters for extremely complex molecules. For example, the Kováts indices for C_9 and C_{10} isoparaffins on squalane have been calculated with an average standard error of 2.2 units[298]. Such an accuracy of extrapolation calculations is not ensured by any of the other methods considered in this review. The standard error of the calculation of the Kováts indices of C_7 and C_8 olefins on squalane by the same method proved to be 5.2 units, which is also the best result for such systems. In calculations of this kind, one introduces initially specific relations associated with the characteristics of the interaction of the individual structural groups of the sorbate molecules with the stationary phase and then these are used in the evaluation of the thermodynamic functions of solution, from which the Kováts indices are calculated.

Analysis of different investigations has shown that each group of methods has definite advantages and that at the present stage of the development of the theory of non-electrolyte solutions one cannot neglect any of these procedures.

When fairly extensive experimental data for test sorbates, grouped in specific series, are available, the optimum interpolated retention parameters can be calculated empirically by combining the methods of the topological and factorial analyses with the constants (for example, constants of the Rohrschneider type) for the stationary phase.

For interpolation calculations within narrow groups of sorbates with similar physicochemical properties, it is most rational to employ the correlations between the retention parameters and the physicochemical properties of the sorbates. The calculation of the thermodynamic functions of solution is possible only after a detailed analysis of the characteristics of the intermolecular interactions in the systems investigated. However, these are not only interpolation but also extrapolation calculations, which is particularly important for high-molecular-weight sorbates, whose retention parameters are usually unknown. The accuracy of the calculations using the fundamental functions of solution is highest among the methods considered.

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