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System of Retention Indices and Its Physicochemical Application

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The system of retention indices widely used in gas chromatography is reviewed. Methods of calculating indices are examined, their accuracy and reproducibility, and the effect on the index of parameters of the gas-chromatographic experiment (temperature, pressure, velocity of carrier gas, and quantity of stationary phase in the column). Systems resembling retention indices are described, problems of polarity, selectivity, and effectiveness of separation are discussed, and the physicochemical application of indices to calculate various thermodynamic functions is considered. A list of 252 references is included.

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I. INTRODUCTION

Choice of the best mode of expressing retention data has hitherto been one of the highly debated problems of gas chromatography[1-5].

The use of retention parameters in the form of absolute units, e.g. as the specific volume retained, is not generally accepted, since change in the sorbent during prolonged use, inadequate accuracy in measuring the speed of the carrier gas and the pressure at the inlet to the column, and also unsatisfactory reproducibility of the column temperature lead to uncompensated errors[2-4]. Furthermore, this determination is very laborious[6]. Relative retention volumes, which are less dependent on the conditions of analysis, can be determined more simply and with sufficient accuracy[1,7,8]. However, this method requires a multiplicity of standards, which in fact makes correlation between different publications impossible[2,3].

These difficulties in determining universal gas-chromatographic characteristics led Kováts[9,10] to introduce retention indices. In the opinion of many investigators this system is the most systematic and convenient for generalising retention data. Several reviews have been published[2,3,11-14], and a large number of original papers, mainly concerned with the use of retention indices for identification purposes. The aim of the present Review is to give a comprehensive survey of indices as retention parameters and to reveal the main fields of and prospects for application of this system in physicochemical calculations. This permits an approach both to certain analytical problems (identification of substances, choice of selective stationary phases, selection of conditions of separation) and to several physicochemical problems (study of structure, determination of physicochemical properties from chromatographic data, and investigation of interactions in solution).

II. METHODS OF CALCULATION OF RETENTION INDICES

The elution maxima of individual members of the homologous series of n-alkanes form the fixed points of the system of indices. In the original definition of retention indices[9] Kováts proposed to use only n-alkanes with an even number of carbon atoms. He assumed that an appreciable difference in chromatographic behaviour would be observed in the successive identification of all the members of a homologous series. However, this limitation was subsequently removed[15], and the retention index came to be determined by means of the equation

$$I = 100\frac{\lg V_X - \lg V_n}{\lg V_{n+1} - \lg V_n} + 100n \qquad (1)$$

provided that $V_n \leqslant V_X \leqslant V_{n+1}$, where V_X, V_n, and V_{n+1} are the corrected retention volumes of the test substance and of the standard n-alkanes containing n and $n+1$ carbon atoms respectively. It follows from Eqn. (1) that any absolute or relative (reduced to the same standard) retention parameters[2,3,8,15], corrected for the dead space, or the corresponding distances on the chromatogram, can be used as initial parameters for calculating retention indices.

The linear dependence of the logarithm of the retention volume of an n-alkane on the number n of carbon atoms[2,3,16-18]

$$\lg V_n = a + bn \qquad (2)$$

where b depends solely on temperature and on the properties of the stationary phase[19-21], will yield the simpler equation

$$I = 100\frac{\lg V_X - \lg V_n}{b} + 100n \qquad (3)$$

for calculating retention indices[2]. Calculation of retention indices by means of Eqn. (3) is based on a "theoretical" series constructed from 3 or 4 experimental retention times for normal hydrocarbons having $n \geqslant 6$.

In work with capillary columns the gas-dynamic pulse at the start of an experiment produces an appreciable scatter in the values of I calculated by means of Eqn. (3).[22] It was suggested that the reproducibility could be improved by calculating initially the relative retention $V_{X,\,st}$ and then converting it into the retention index by means of the equation

$$I = 100\frac{\lg (V_{X,\,st} \cdot V_{st,\,n})}{b} + 100n\,. \qquad (4)$$

Preliminary determinations had been made of b and of the relative retention of the standard with respect to n-alkanes $V_{st,n}$.

Graphical methods [23-25], nomograms [26-28], and a special slide-rule [15] have been suggested to simplify calculations of retention indices. Computer programmes have also been written for calculating indices [29-31].

Not only n-alkanes but any other components whose indices under the given conditions are known (I_1 and I_2) can be used to determine the retention indices of unknown components. The Kováts formula then becomes [25]

$$I_X = (I_2 - I_1)\frac{\lg V_X - \lg V_1}{\lg V_2 - \lg V_1} + I_1 . \quad (5)$$

Equation (5) is advantageous for prolonged analyses, e.g. when a capillary column is used, since it is unnecessary to reuse the standard n-alkanes. Furthermore, formula (5) may find application for calculating retention indices on polar stationary phases if Eqn. (2) does not apply.

Theoretical Calculation

Cases quite often arise in analytical practice when it is necessary to calculate retention indices theoretically. Linear equations are very often used for this purpose, relating retention indices with the number of carbon atoms in the molecule or with the boiling point, or else the calculation is based on the difference in retention indices on columns differing in polarity [32-54]. Such an approach underlies the standard-free identification of substances. In several cases relations of this type give only a first approximation to the index, owing to departures from linearity.

Retention indices can be determined additively from structural increments [11,14,32-40,44,47,55-68]. According to Tatevskii's theory [69] additivity calculations are based on the general relation [70]

$$\lg L = \sum_{i,j}^{k} n_{i,j}\Gamma_{i,j} \quad (6)$$

where L is the elution characteristic, $\Gamma_{i,j}$ the contribution of the structural unit, and $n_{i,j}$ the number of structural units in the molecule. Temperature coefficients of retention indices are sometimes used in calculating the latter from structural increments [71-74]. The validity and practical application of additivity calculations have been shown by many workers [10,32-42,45,75-84], but there is no doubt about their approximate character.

Retention indices for solutions that are nearly ideal can be calculated from the vapour pressures of the components at the temperature of the column [85]:

$$I_{p^0} = 100\frac{\lg p^0_X - \lg p^0_n}{\lg p^0_{n+1} - \lg p^0_n} + 100n \quad (7)$$

where p^0_X, p^0_n, and p^0_{n+1} are the vapour pressures of the test substance X and the standard hydrocarbons containing n and $n+1$ carbon atoms respectively. Tourres [86] showed that in non-polar systems I_{p^0} and the experimental I have almost the same temperature dependence, since the variation of the activity coefficients with temperature can be neglected in this case [87]. With the vapour pressure at various temperatures (and hence I_{p^0}) known, therefore, it is possible to predict both the behaviour of substances and their degree of separation. The so called standard retention index I_{st} [88], calculated from the boiling points by means of the formula

$$I_{st} = 100\frac{\lg T_{bp(X)} - \lg T_{bp(n)}}{\lg T_{bp(n+1)} - \lg T_{bp(n)}} + 100n \quad (8)$$

must be regarded as a particular case of I_{p^0}.

A more exact equation for calculating retention indices of hydrocarbons on non-polar stationary phases, proposed by Dimov and Shopov [89,90], involved the molar volumes:

$$I_{p^0,v^0} = 100\frac{\ln\left(\frac{p^0_X v^0_X}{p^0_n v^0_n}\right) - \left(\frac{v^0_X - v^0_n}{v^0_1}\right)}{\ln\left(\frac{p^0_{n+1} v^0_{n+1}}{p^0_n v^0_n}\right) - \left(\frac{v^0_{n+1} - v^0_n}{v^0_1}\right)} + 100n \quad (9)$$

where v^0_X, v^0_n, v^0_{n+1}, and v^0_1 are the molar volumes of the substance X, the normal hydrocarbons containing n and $n+1$ carbon atoms, and the stationary phase respectively. A thermodynamic proof of Eqn. (9) has been given by Hammers and de Ligny [91]. However, the "physicochemical indices" obtained in this way differ to some extent from the experimental values I. Conversion from I_{p^0,v^0} to I requires the introduction of corrections equal to the mean difference between I and I_{p^0,v^0} for hydrocarbons of the same class [92].

Unfortunately, theoretical calculation of retention indices by means of Eqns. (7)-(9) is possibly only for hydrocarbons and non-polar stationary phases, which considerably diminishes the significance of these relations.

Thus the foundation of the gas-chromatographic study of real systems remains as before the experimental determination of the retention index by means of Eqns. (1) and (3).

III. PARAMETERS RESEMBLING RETENTION INDICES

The indices I_{p^0}, I_{st}, and $I_{p^0v^0}$ discussed in Section II (Eqns. 7-9) are completely analogous to the Kováts index. Retentions are replaced by physicochemical constants.

The Kováts indices were followed by several similar scales, but these found limited application in gas chromatography. Examples are the "methylene unit" [93-95], which is identical with the retention index divided by 100, the "effective molecular weight" [79,96-98], where the molecular weights of n-alkanes are used as fixed points on the scale, and the "carbon numbers" [99,100] ("equivalent chain length" [101]), which are convenient for the analysis of aliphatic acids and their methyl esters. All these systems, being particular cases of the general Kováts system, possess closely similar properties. The mathematical equivalence of the above systems was shown by Guerin and Banks [102].

In several cases, e.g. in high-temperature gas-chromatographic analyses or with the use of strongly polar phases, n-alkanes are not always convenient as standard substances [103]. Swoboda [104], without changing the general construction of the Kováts system, proposed that the standards should be chemically similar to the test compounds. Thus "steroid numbers" [93-95] proved convenient in the gas-chromatographic analysis of steroids, the "phenyl number" [105] in the chromatography of linear polyphenyls, and the "siloxane index" [106-108] for the identification of organosilicon derivatives. An analogous system was proposed for the characterisation of high-boiling (up to 500 °C and above) fused aromatic and heteroaromatic compounds, where comparisons are based on polyacene hydrocarbons—benzene, naphthalene, anthracene, tetracene, etc. [109]

A rational generalisation of these systems is the dimensionless parameter φ[110]. Standard compounds belonging to the same homologous series as the test substance are used in calculating φ:

$$\frac{\lg V_{g\,X} - \lg V_{g1}}{\lg V_{g2} - \lg V_{g1}} = \varphi = \frac{T_{bp(X)} - T_{bp(1)}}{T_{bp(2)} - T_{bp(1)}} \qquad (10)$$

where V_gX, V_{g1}, V_{g2}, $T_{bp(X)}$, $T_{bp(1)}$, and $T_{bp(2)}$ are the retention volumes and the boiling points of the related compounds (X unknown, and *1* and *2* known). The parameter φ was shown to be constant, independent of the temperature of the analysis and the composition of the stationary phase. However, it cannot be recommended for the identification of complicated mixtures, comprising substances belonging to different homologous series, owing to ambiguity in the choice of standards and the absence of a natural "zero point". Retention indices have an undoubted advantage in this respect.

In order to avoid comparatively laborious stages in determining the "dead space" and taking logarithms in calculating Kováts indices, it was suggested that an "arithmetic index"[111-113] should be calculated by means of the equation

$$I_A = 100\,\frac{t_X - t_n}{t_{n+1} - t_n} + 100n \qquad (11)$$

where t_X, t_n, and t_{n+1} are uncorrected retention times for the test substance X and the standard n-alkanes. Equation (11) is sometimes written without the coefficients 100.[111,112,114] The arithmetic index has been used to estimate partition and activity coefficients[114]. However, the usefulness of the arithmetic index as a retention parameter is debatable[113,115,116], since no thermodynamic interpretation has yet been found. The theoretical possibility of the graphical conversion of I_A into I has been established[114]. An equation has recently been deduced[117] linking the arithmetic index with the retention index:

$$\frac{I - 100n}{100} = \frac{\lg\left[1 + \frac{I_A - 100n}{100}(D-1)\right]}{\lg D} \qquad (12)$$

where

$$D = \frac{t_{n+1} - t_n}{t_n - t_{n-1}}$$

t_{n-1}, t_n, and t_{n+1} being uncorrected retention times of successive n-alkanes. Furthermore, D = antilog b, where b is the coefficient in Eqn. (2). A thermodynamic basis for I_A may, perhaps, be found by the application of Eqn. (12).

IV. ACCURACY AND REPRODUCIBILITY OF RETENTION INDICES

For a long time the accuracy and the reproducibility of retention indices remained an open question. In connection with the increasing importance of gas chromatography in qualitative analysis and physicochemical research, interest has arisen during recent years in the precise measurement of retention parameters[23,118-124]. These aspects of retention indices calculated by means of Eqn. (1) can be extended equally to the simpler equation (3), since the two equations give values of comparable accuracy[17].

Tests of the reproducibility of indices determined on standard instruments in different laboratories[125] gave a standard deviation of ±1 on squalane and dinonyl phthalate and ±3 on [polyethylene glycol] PEG-400; the divergence in the indices on a polar stationary phase depends on the size of the sample of n-alkanes introduced into the chromatograph. It was shown later[126] that reproducible retention indices can be obtained even on such a polar phase as oxy-$\beta\beta'$-dipropionitrile if the samples of n-alkanes used in solution are 0.002–0.007 μl, when the linear portion of the partition isotherm is reached.

Loewenguth[127] gave a similar statistical assessment of the reproducibility of retention indices. Reproducibility is influenced mainly by the accuracy with which retention times and column temperatures are measured. The latter factor is especially significant in the analysis of compounds with a large temperature coefficient of the index dI/dT. Kaiser[23] reaches the same conclusion.

The first precision measurements of retention indices were made on ordinary and deuteriated squalane, with a maximum discrepancy of 0.06.[16,128] Schomburg et al.[129] used an on-line computer to measure retention indices with a reproducibility of ±0.03–0.05. Cramers et al.[130] achieved the same reproducibility (±0.03) without using an electronic computer. Analysis of these results showed that, in order to obtain reproducible retention indices, careful attention should be paid to measuring and stabilising the temperature of the thermostat; an inert material of uniform grain size should be used as solid support; the length and diameter of the column, the effectiveness of separation of the mixture, the rate of flow of the carrier gas, and the inlet and outlet pressures to and from the column must be taken into account; and the retention times of test substances and standard n-alkanes must be measured accurately[119].

Whereas the reproducibility of retention indices can be judged from how well the calculated values of I converge in a series of experiments, it is a more complicated task to determine the accuracy of the calculation of indices. A rigorous approach to this problem based on the principles of mathematical statistics was first made by Takács and Králik[131,132]. A solution of the problem was obtained independently by Uhdeova[118], but only in general form.

Analysis of the extended error formula deduced by Takács and Králik (called the Erdey equation) showed that the accuracy with which retention indices are determined depends on the absolute retention times of the test substance t_X, the n-alkanes t_n and t_{n+1}, and the unsorbed gas t_M, as well as the arithmetic mean errors of their determination. With a favourable choice of chromatographic conditions, when t_n, t_X, $t_{n+1} \gg t_M$, errors in the determination of the "dead space" can be neglected. From this the important conclusion can be drawn that, in the determination of retention indices, direct measurement of t_M can be replaced by indirect calculation, e.g. by use of the equation of Peterson and Hirsch[133]. For squalane the determination of t_M with respect to methane and hydrogen and by the Peterson–Hirsch method[133] was shown by Cramers et al.[130] to give identical results, with a reproducibility of the index of ±0.03.

Thus indices can be obtained with a minimum error. It is also noteworthy that the precision measurement of other retention parameters has not been studied so thoroughly, and this constitutes an indubitable advantage of the Kováts system of indices.

V. TEMPERATURE DEPENDENCE OF RETENTION INDICES AND ITS USE IN GAS CHROMATOGRAPHY WITH TEMPERATURE PROGRAMMING

In the early gas-chromatographic investigations Kováts and Wehrli [9,10] established a linear correlation between the index and the temperature of the analysis. They proposed that three parameters—(*a*) the index at the given temperature, (*b*) the temperature coefficient $10dI/dT$ for a 10 deg change in temperature, and (*c*) the temperature limits within which the indices were measured—should be stated to express the temperature dependence of retention indices. The temperature dependence was subsequently studied by many investigators [3,15,71,76,78,85,87,134-141]. The relation was found to be hyperbolic over a wide temperature range [78,134].

Allowing for the temperature dependence of the corrected retention volume [142], Takács et al. [12,142-144] showed by rigorous mathematics that the temperature dependence of retention indices obeys a hyperbolic equation with three constants, resembling Antoine's equation

$$I_{(T)} = A + \frac{B}{T + C} \qquad (13)$$

where A, B, and C depend on the properties of the test substance and the stationary phase. Experimental verification of Eqn. (13) is accomplished by means of an electronic computer [145,146]. The hyperbola (13) is usually essentially linear in the gas-chromatographic temperature range [143]. Fig. 1 shows the general form of the temperature dependence of the retention index of propan-1-ol on PEG-400.

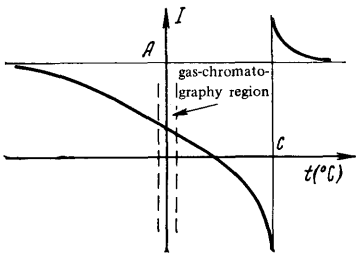


Figure 1. General form of temperature dependence of retention index of propan-1-ol for the phase PEG-400. [143]

The temperature coefficient dI/dT is an important characteristic of the substance and the stationary phase, and can be used for identification purposes [72,140,147]. In several investigations [73,87] the coefficient $dI/d(1/T)$ has been used to establish structure. The differential dI/dT was employed [148,149] to calculate the equivalent isothermal index in the case of linear temperature programming. If at least one component in a solute–stationary phase system is polar, the sign of the differential will depend on the properties of the system for the individual case [91,150-153].

Study of the temperature dependence of the retention indices of various hydrocarbons [71,86,87,91,154] showed that the coefficient is affected by the number and the steric arrangement of the side-chains in the molecule. Hammers and de Ligny [91] gave a rigorous thermodynamic basis to the coefficient dI/dT, and established that its magnitude is determined by the free energy and the entropy of vaporisation of the substance undergoing analysis.

The temperature dependence of retention indices has been examined thermodynamically for ideal solutions [155]. The general dependence of the index on the temperature and the enthalpies and entropies of vaporisation was shown for three simple hypotheses—(i) that the enthalpy of evaporation of n-alkanes is constant, (ii) that the enthalpy decreases linearly with rise in temperature, and (iii) that the enthalpy varies in conformity with the Thiesen (Watson) equation [156]—among which the third assumption gives the best agreement between calculated and experimental indices.

The Kováts index has proved a convenient retention parameter not only in isothermal but also in temperature-programmed gas chromatography. An equation has been proposed for calculations [105,135,136,157-159], based on a nearly linear dependence of the elution temperature of n-alkanes on the number of carbon atoms:

$$I_{\text{tpr}} = 100\frac{T_{r_X} - T_{r_n}}{T_{r_{n+1}} - T_{r_n}} + 100n \qquad (14)$$

where I_{tpr} is the retention index of the test substance with temperature programming, and $T_{r}X$, $T_{r}n$, and $T_{r,n+1}$ are the retention temperatures of the test substance and of n-alkanes containing n and $n + 1$ carbon atoms respectively. A theoretical deduction of Eqn. (14) has recently been achieved by Takemura [160] on the basis of his previously established [161,162] linear relation between the isothermal relative retention and the relative retention with temperature programming.

The index calculated by means of formula (14) usually differs from, but is quite close to, the isothermal index at some equivalent temperature T_{eq}. Thus Guiochon [135,136] found that programmed indices agree best with the isothermal value at 20 deg below the retention temperature. Habgood and Harris showed [157] that, with cyclic hydrocarbons, the indices with temperature programming correspond to the isothermal values at a temperature 30–50 deg below T_r. Giddings [163] proposed the correlation equation $T_{\text{eq}} = 0.92T_r$.

The opinion has become established among specialists in this field that, with temperature programming, the retention index varies little with quite a wide choice of analysis conditions—initial temperature, rate of programming, and speed of carrier gas [135,136,157,158,163].

The experimental conditions have an appreciable effect on the index with programming, especially when substances showing a large temperature coefficient are analysed on polar phases [148,149]. An equation was deduced to allow for the experimental parameters—rate of linear programming β, temperature coefficient of index dI/dT, and retention temperature of substance T_r:

$$I_{T_0/\beta} = I_{T_0} + \frac{\beta T_r}{2} \cdot \frac{dI}{dT} . \qquad (15)$$

Comparison of the calculated equivalent isothermal indices I_{T_r-20}, $I_{0.92T_r}$ and $I_{T_0/\beta}$ showed that $I_{T_0/\beta}$ will give the best agreement with the experimental value I_{tpr} [148,149]. This is because $I_{T_0/\beta}$ takes into account not only T_r but also the conditions of the programmed experiment (T_0, β, t). The equivalent isothermal index $I_{T_0/\beta}$ has been used with linear temperature programming for the qualitative analysis of monocarbonyl compounds in the volatile components of certain foodstuffs [164,165]. Robinson and Odell [88] extended

the mathematical approach[148,149] to non-linear temperature programming (with the temperature raised in steps), and suggested that the mean temperature of the elution and the temperature coefficient of the index should be taken into account in calculating retention indices.

Erdey et al.[12,166,167] integrated Eqn. (13) from the initial temperature T_0 to the retention temperature T_r, and obtained a general equation for the equivalent isothermal index in temperature-programmed gas chromatography:

$$I_{eq} = A + \frac{2.3B \cdot \lg\left(\frac{T_r + C}{T_0 + C}\right)}{T_r - T_0} \qquad (16)$$

where A, B, and C are the constants in Eqn. (13) determined from the isothermal indices measured at three different temperatures[143]. If these constants are known, I_{eq} can be calculated by means of (16) without the need to chromatograph n-alkanes. Because the computation of A, B, and C is laborious, the determination of I_{eq} by means of Eqn. (16) is extremely complicated.

Formulae (15) and (16) are essentially similar, although the former was deduced on the hypothesis of a linear temperature dependence of retention indices, and the latter from a hyperbolic dependence. Because the hyperbola usually has a linear section in the gas-chromatographic temperature range[143], Eqns. (15) and (16) should give the same calculated result. Erdey et al.[167] found that equivalent isothermal indices calculated by means of the two equations for benzene and PEG-1500 as stationary phase differed at most by ±1. From a practical point of view, therefore, use of the simpler equation (15) is to be preferred, despite its less general character.

Thus the temperature dependence of retention indices obeys in general a hyperbolic law, although the hyperbola usually has a linear section in the gas-chromatographic temperature range. This enables retention indices at different temperatures to be handled very simply, and validates the use of the temperature coefficient dI/dT. It also presents greater opportunities for the widespread use of Eqn. (15) in gas chromatography with linear programming of temperature.

VI. EFFECT OF THE INDEX OF PARAMETERS OF GAS-CHROMATOGRAPHIC EXPERIMENT

The principles of classical equilibrium chromatography, when the temperature of analysis T, the speed of the carrier gas w, the input pressure to the column p_i, and the pressure drop factor j_2^3 are constant, are generally used in calculating retention indices, as with other retention parameters[131]. Under these conditions the fall in pressure in the column and the speed of the carrier gas in numerator and denominator of Eqns. (1) and (3) cancel out, with small variations in T, w, and p_i partly or completely balanced out. This forms the basis for the conclusion that the system of indices is stable with respect to experimental conditions[2,3,15,168]. Nevertheless, it is useful to examine the effect of various experimental variables on the retention index.

1. Retention Index and Speed of Carrier Gas

Guerin and Banks[102] found that the constant b in Eqn. (3) is unaffected by changing the speed of the carrier gas from 40 to 200 ml min^{-1}.

Equation (1) was transformed[169,170] to contain rates of flow of the carrier gas w (instead of specific retention volumes) and the constants in the equation for the dependence of retention time on w. Changing the speed of the carrier gas from 1 to 500 ml min^{-1} left the indices almost unchanged. This enables retention indices to be used to identify components in gas chromatography with programming of the gas flow.

2. Retention Index and Pressure in System

Two main factors—considerable non-ideality of the gas phase and solubility of the carrier gas in the stationary phase—complicate the interpretation of retention indices and the calculation of thermodynamic functions from chromatographic data obtained at high pressures[54]. Vigdergauz and Semkin[171-173] demonstrated the effect of non-ideality of the gas at high pressures on the retention indices of hydrocarbons. They showed that changing from helium to carbon dioxide and raising the pressure in the column to 15 atm are accompanied by changes in the retention indices, and in some cases even the sequence in which substances are eluted may change. Retention indices at high pressures have been used for the calculation of second virial coefficients[54,171-173].

Unfortunately, the effect of increased pressure on retention characteristics, including Kováts indices, has still been comparatively little studied.

3. Retention Index and Quantity of Stationary Phase in Column

The relative retention volumes of polar substances (in relation to non-polar substances) are strongly dependent on the proportions of highly polar stationary phases when these are below 5%.[174] This makes it difficult to identify components of a mixture by means either of relative retention volumes or of retention indices. Kováts[15] recommended working at high proportions of the stationary phase in order to obtain good reproducibility of the retention indices. However, this diminishes the efficiency of the column, the height of a theoretical plate is considerably more strongly dependent on the speed of the carrier gas, and the duration of the analysis increases[175]. In order to achieve maximum separating power with a chromatographic column, therefore, the optimum quantity of stationary phase must be taken. With diatomites this varies within 5–10% of the total weight of sorbent[176].

In the analysis of unsaturated and substituted methyl esters of C_{16}–C_{18} acids on the non-polar stationary phases Apiezon L and SE-30 the retention indices are almost independent of the quantity of the stationary phase on the solid support, whereas a very considerable variation is found on the polar polyethylene glycol succinate[177]. The chromatography of polar substances shows that the nature of the adsorbent has an appreciable effect on the index. Thus the retention indices of alcohols on squalane columns become smaller when Chromosorb V is replaced by Chromosorb G[179].

Bonastre et al.[178] obtained an equation for calculating retention indices that took into account adsorption phenomena in the column:

$$I = 100\,\frac{\lg\dfrac{\left|V_g^{\infty} + \dfrac{h}{\Pi} + \hbar\left(\dfrac{1}{\Pi} - \dfrac{1}{10}\right)\right|_x}{\left|V_g^{\infty} + \dfrac{h}{\Pi} + \hbar\left(\dfrac{1}{\Pi} - \dfrac{1}{10}\right)\right|_n}}{\lg\dfrac{\left|V_g^{\infty} + \dfrac{h}{\Pi} + \hbar\left(\dfrac{1}{\Pi} - \dfrac{1}{10}\right)\right|_{n+1}}{\left|V_g^{\infty} + \dfrac{h}{\Pi} + \hbar\left(\dfrac{1}{\Pi} - \dfrac{1}{10}\right)\right|_n}} + 100n \qquad (17)$$

where V_g^∞ is the specific retention volume with maximum possible percentage impregnation Π, and the coefficient h and $\hbar$ represent adsorption on the film of stationary phase and on the solid support respectively. With the standard n-alkanes $\hbar \simeq 0$. With PEG-20 000 and thio-ββ-dipropionitrile as the stationary phases, polytetrafluoroethylene and Chromosorb P as solid supports, and a large number of substances belonging to various classes these workers showed that the retention indices increase with increase in the degree of impregnation Π, in conformity with Eqn. (17), and approach their limiting values I^∞. It was found also that the constant $\hbar$ can be substantially diminished by the use of inert supports. A generalised equation for the retention volume in gas-liquid chromatography which in addition to solution in the stationary phase takes into account adsorption at its interfaces with the carrier gas and adsorbent has also been proposed [180,181].

On the whole it can be accepted that retention indices are extremely stable over a wide range of rates of flow of the carrier gas at column pressures that are usual in analytical gas chromatography. However, the quantity of stationary phase in the column (especially one of high polarity) has an appreciable effect on the index. In order to obtain reproducible indices, therefore, inert solid supports must be used, the same quantity of stationary phase (not less than 5–10 wt.%), and with highly polar phases minimum samples of the standard n-alkanes in order to reach the linear portion of the partition isotherm.

VII. CHARACTERISATION OF STATIONARY PHASES AND COLUMNS BASED ON RETENTION INDICES (POLARITY, DONOR AND ACCEPTOR POWER, SELECTIVITY, EFFECTIVENESS OF SEPARATION)

Problems of forecasting the chromatographic value of stationary phases and columns from the theory of dissolution and the physicochemical properties of solute and solvent have been solved during recent years [4,176,182,183]. In order to make a preliminary estimate of retention parameters, many attempts were undertaken to relate them to the thermodynamic, electrical, and geometric properties of stationary phases. Many groups of substances exhibit a certain dependence of the relative retention parameters on the electrical characteristics (dipole moment, dielectric constant, polarisability, refraction) of the stationary phase or of the separable components) [184–189].

Polarity

The terms "polar", "weakly polar", "non-polar", etc. are too inexact to characterise stationary phases. As Kováts showed [15], the concept of "polarity" is convenient, and in some cases sufficient, to describe many effects, but it cannot be expressed by a single parameter.

The polarity of stationary phases determined from retention characteristics is ultimately a function of the cohesion potential: i.e. it depends on the contribution by orientation, induction, and dispersion forces. Together with these, donor–acceptor interactions are especially important in gas chromatography [190]. The energy of van der Waals interaction, except for the dispersion component, depends on the temperature, so that polarity is also a function of temperature [188,191].

Rohrschneider [192] originally proposed a graphical method, in which the stationary phases were arranged along the horizontal axis with the polarities 0 and 100 assigned to squalane and oxy-ββ′-dipropionitrile respectively, which enabled stationary phases to be characterised by appropriate polarity indices. Almost the same approach to classifying phases was being followed by several other workers [191,193–205], except that the standard substances used were not butadiene and butane, but methanol and butane, acetylene and ethane, benzene and hexane, two n-alkanes, etc. Sakharov has shown [185,206] that all these methods derive from the general relation

$$\lg V = B_1 \lg V_{st} + B_2 \qquad (18)$$

where V and V_{st} are the retention volumes of the substance and the standard respectively, B_1 is a constant representing the polarity of the substance undergoing analysis, B_2 is another constant, and $\lg V_{st}$ measures the polarity of the stationary phase. However, the considerable uncertainty in the choice of standard substances imposes considerable limitations on this method.

The system of retention indices provides a more convenient form for expressing differences in the character of stationary phases. This assignment is based on the difference between the interaction of the substance with the test phase and with a phase which is by definition regarded as non-polar (squalane, Apiezon).

Wehrli and Kováts [10,15] suggested measuring the difference ΔI between the retention indices for compounds of general formula RX, where R is a hydrocarbon radical containing six or more carbon atoms, and X a functional group. Since $\Delta I = 0$ when X = H, the proposed scale begins at zero. It is termed the "dispersion of retention" of the stationary phase.

Developing this idea, Rohrschneider [207–210] suggested that the polarity of the column depends not only on the nature of the stationary phase but also on the type of substance analysed. The polarity of a stationary phase must therefore be assessed simultaneously with respect to a whole group of compounds possessing diverse donor–acceptor properties. This is a more rigorous approach to solving the problem. Rohrschneider originally proposed one- and three-term equations, but these did not find wide application. Later he worked out a general five-term polarity system, which has been recommended for the widest use in gas chromatography [211–213]. The general equation is

$$\Delta I = ax + by + cz + du + es \qquad (19)$$

where a, b, c, d, and e are polarity factors of the stationary phase, and x, y, z, u, and s are polarity factors of the substances undergoing analysis. Having determined the polarity factors of 22 stationary phases with respect to the compounds adopted as standards (benzene, ethanol, butan-2-one, nitromethane, and pyridine) and those of 30 substances, Rohrschneider calculated 660 indices with errors not exceeding 4–6. Accurate measurements have shown that the values of the Rohrschneider constants depend on the size of sample introduced [214], so that this size must be indicated when such constants are published.

Without changing Rohrschneider's general concept, McReynolds [215] suggested a different list of standards—including benzene, butanol, pentan-2-one, nitropropane, pyridine, and five other substances for solving particular problems—which are more convenient experimentally. McReynolds compiled a table of differences in retention indices of ten test substances for various stationary phases. The list of stationary phases comprises approximately 200 items.

Takács et al. [212,213] has recently shown, by rearranging Eqn. (19), that the interaction between test substances and

stationary phases can be characterised not only by the difference between but also by the ratio of the indices. They obtained the equation

$$I_X^P = I_X^S \sum_{i=1}^{5} f_i s_i \qquad (20)$$

where I_X is the isothermal retention index of the substance X, the letters P and S represent a polar stationary phase and squalane respectively, $f_i = I^P/I^S$ is the ith polar factor, i is the serial number of Rohrschneider's or McReynolds' standard substance, and

$$\frac{a}{100}\cdot\frac{I_1^S}{I_X^S} = s_1;\ \frac{b}{100}\cdot\frac{I_2^S}{I_X^S} = s_2;\ \cdots\ \frac{e}{100}\cdot\frac{I_5^S}{I_X^S} = s_5$$

are specific factors for the substance, characterising the molecular structure and the interaction potential. Equation (20) represents more accurately the effect of the specific factors s_i for substances and gives better agreement between calculated and experimental values of the index than does Eqn. (19).

Another proposed method for determining the polarity of a stationary phase is based on the equation [85,178,216]

$$P = (k^0 - k)\cdot 10^5 = 10^3 \lg(\gamma_{n+1}^{\infty}/\gamma_n^{\infty}) \qquad (21)$$

in which γ_n^{∞} and γ_{n+1}^{∞} are the activity coefficients of the n-alkanes containing n and $n+1$ carbon atoms. The quantities k^0 and k are related to the retention indices I_1 and I_2 of two substances by indices $I_{p_{(1)}^0}$ and $I_{p_{(2)}^0}$ computed from the vapour pressures (Eqn. 7) and by the relative activity coefficient $\gamma_{1,2}^{\infty}$:

$$\lg\gamma_{1,2}^{\infty} = k^0(I_{p_{(1)}^0} - I_{p_{(2)}^0}) - k(I_1 - I_2). \qquad (22)$$

Bonastre et al. [178] then suggested that, to allow for adsorption phenomena on the surface of the adsorbent and the stationary phase, indices should be calculated by means of Eqn. (17) and k replaced by k^{∞}, corresponding to the largest proportion of stationary phase. In this case the polarity computed by means of formula (21) will then be determined almost entirely by the dissolution of the substance in the stationary phase, which is more accurate.

Comparison of the Chovin–Lebbe [193-195,201,202] and the Bonastre–Grenier [85,178,216] methods for determining the polarity of stationary phases shows that physically the former consists in measuring the constant b (Eqn. 2), which is equal to the increment of the partial molar free energy of sorption per methylene group $\Delta G_{s,CH_2}$ in an n-alkane [19]. Thus in this method the polarity is estimated solely from the dispersion component of the total interaction potential, and increase in polarity correlates with a decrease in b. In contrast Bonastre and Grenier assess polarity not on the basis of the above increment but on $\Delta G^E_{CH_2}$, which measures the departure of the system from Raoult's law. The more the ratio $\gamma_{n+1}^{\infty}/\gamma_n^{\infty}$ in Eqn. (21) differs from unity, and hence $\Delta G^E_{CH_2}$ from zero, the more polar is the stationary phase. Strictly speaking, however, Eqn. (21) defines not the polarity but the selectivity of the stationary phase with respect to the n-alkanes, since, apart from a constant (2.3 RT), the logarithm of the relative activity coefficient is the "empirical" selectivity—the difference between the partial molar excess (free) energies of sorption [17,183].

Kováts and Weisz [217] also used retention indices to examine the polarity of stationary phases. If the total free energy of dissolution is determined by the work of separation (the energy of a hole), by a dispersion term, by a polar term, and by the energy of donor–acceptor interaction, the sum of the last two terms is proportional to the difference between the retention indices of the test substance on the column with a given solvent and a standard non-polar phase.

Thus a survey of published information shows that Rohrschneider's method, with the standard compounds proposed by McReynolds, is the most widely used at the present time for assessing the polarity of stationary phases.

Donor and Acceptor Power

Using Brown's triangular method [218], Guiochon et al. [61,219] showed that retention indices could be employed to assess such important properties of a phase as its donor and acceptor power. The method involves constructing a triangular diagram, on which are plotted the normalised retention indices of an electron acceptor (1,4-dioxan), an electron donor (1,1,2-trichloroethane), and a neutral compound (n-decane). Use of a triangular diagram provides a simple and graphic procedure for assessing the donor and acceptor power of a stationary phase, but the method has no significant advantages over Rohrschneider's system.

Selectivity

The selectivity of a stationary phase in gas–liquid chromatography is a static characteristic independent of kinetic factors, e.g. plate height [220]. It is measured [4,182,183,220] by the relative activity coefficient or by the difference in the free energies of mixing $\Delta\Delta G^E_{i,j}$. In this connection retention indices provide the most rational system, since they represent the relative retention with n-alkanes as a scale of standards of the same type. Several equations have been suggested [17,20,21,221] for estimating the selectivity of a stationary phase from retention indices:

$$\lg\alpha_{i,j} = \frac{b\,\delta I_{i,j}}{100} = -\lg(\gamma_{i,j}^{\infty} p_{i,j}^0) \qquad (23)$$

$$\Delta\Delta G_{i,j}^E = -2.3RT\left(\frac{b\,\delta I_{i,j}}{100} + \lg p_{i,j}^0\right) \qquad (24)$$

$$\Delta\Delta H_{i,j}^E = -2.3RT\left[\frac{\delta I_{i,j}}{100}\cdot\frac{\partial b}{\partial 1/T} + \frac{b}{100}\cdot\frac{\partial(\delta I_{i,j})}{\partial 1/T} + \cdot\frac{1}{2.3p_{i,j}^0}\frac{\partial p_{i,j}^0}{\partial 1/T}\right] \qquad (25)$$

$$\Delta\Delta S_{i,j}^E = \frac{\Delta\Delta H_{i,j}^E - \Delta\Delta G_{i,j}^E}{T} \qquad (26)$$

where $\alpha_{i,j}$ is the separation factor, $\Delta\Delta G^E_{i,j}$, $\Delta\Delta H^E_{i,j}$, and $\Delta\Delta S^E_{i,j}$ are the differences between the free energies, enthalpies, and entropies of mixing, b is a constant in Eqn. (2), $\delta I_{i,j} = I_i - I_j$ is the difference between the retention indices of two substances, $p^0_{i,j}$ is the relative vapour pressure with the column at temperature T°K, and i and j are the compounds under examination.

Equations (23)–(26) have enabled a successful choice to be made of selective columns for the analysis of carbonyl [222] and sulphur-containing compounds [17,20,21,221,223]. In the latter case eleven stationary phases were examined, for which values of $\Delta\Delta G^E_{i,j}$ were calculated by means of Eqn. (24) using n-hexanethiol, dipropyl sulphide, and diethyl disulphide as examples (results in Table). The maximum values of this difference were obtained for columns containing oxy-$\beta\beta'$-dipropionitrile, polyethylene glycols (PEG), and Triton X-305. It was found that oxy-$\beta\beta'$-dipropionitrile, previously regarded as the most

selective column for all sulphur-containing compounds[224], was not selective in the separation of thiols and sulphides (as $\Delta\Delta G^{E}_{2,1} \simeq \Delta\Delta G^{E}_{3,1}$—see Table), but was convenient in the separation of thiols and disulphides, and also of sulphides and disulphides.

Values $\Delta\Delta H^{E}_{i,j}$ and $\Delta\Delta S^{E}_{i,j}$ have been calculated by means of Eqns. (25) and (26) in order to reveal the nature of the selectivity of phases. It is found, for example, that the enthalpy factor predominates in the separation of dipropyl sulphide from diethyl disulphide on PEG-1000, but the entropy factor with hexanethiol and diethyl disulphide[17, 20, 21, 221].

Differences in partial molar free energies of mixing, calculated by means of Eqn. (24), of certain organosulphur compounds on various stationary phases[17, 40].

Stationary phase (at 60°C)	$\Delta\Delta G^{E}_{2,1}$	$\Delta\Delta G^{E}_{3,1}$	Stationary phase (at 60°C)	$\Delta\Delta G^{E}_{2,1}$	$\Delta\Delta G^{E}_{3,1}$	Stationary phase (at 130°C)	$\Delta\Delta G^{E}_{2,1}$	$\Delta\Delta G^{E}_{3,1}$
SE-30	—60	—100	Tritolyl phosphate	140	220	Apiezon M	10	20
Apiezon M	—70	—100	Triton X-305	200	330	Silicone DS-550	70	60
Silicone DS-200	—70	—120	PEG-1000	250	390	Triton X-305	220	290
Dinonyl phthalate + 5% diphenylamine	5	60	Oxy-ββ′-dipropionitrile	390	380	PEG-20000	260	370
Dinonyl phthalate	10	60						

Note. $\Delta\Delta G^{E}_{2,1}$ = difference between free energies of mixing of hexanethiol and diethyl disulphide.
$\Delta\Delta G^{E}_{3,1}$ = difference between free energies of mixing of dipropyl sulphide and diethyl disulphide.
Values of $\Delta\Delta G^{E}_{i,j}$ given in cal mole^{-1}.

Thus it has been shown experimentally that Eqns. (23)–(26) are extremely convenient for estimating the selectivity of stationary phases.

Effectiveness of Separation

The practical value of a chromatographic column is always determined by the fundamental possibility of separation and the time required for this separation. The effectiveness of separation is usually understood to refer to the blurring of the peak during the analysis[225].

Kováts[9] deduced the relation

$$\delta I \simeq 5\delta T_{bp} \qquad (27)$$

for the difference between the indices of two substances, from which can be estimated the minimum difference in boiling points necessary for the separation of isomers on non-polar stationary phases. However, Eqn. (27) is apparently not general in character, for it has recently been shown[51] with branched C_9 and C_{10} alkenes that the proportionality constant may differ considerably from 5, and assume values from 1.8 to 13.9.

A suggested criterion of separation R was determined by the ratio of the distance between the peak maxima to the sum of their half-widths at the base[226].

Instead of R Strickler and Kováts[19] used the $N\sigma$ criterion —the distance between the two separable substances expressed in σ-units (where σ is the half-width at the level of the point of inflection): separation does not occur if the distance between the peaks is equal to or less than 2σ. The 4σ criterion corresponds to adequate separation, and the 6σ criterion to almost complete separation. These workers compared the $N\sigma$ criterion with the difference between the retention indices of the separable substances δI, with the free energy of evaporation of the substances from the stationary phase per methylene group $\Delta G_{e(CH_2)} = b$—see Eqn. 2), and with the number of theoretical plates N_t:

$$\delta I = \frac{N\sigma\Phi}{\sqrt{N_t}}\left(1 + \frac{1}{k_i}\right) \qquad (28)$$

where k_i is the reduced retention time relative to the dead time, and

$$\Phi = \frac{100RT}{\Delta G_{e\,(CH_2)}}.$$

Struppe[227] proposed the use of a quantity Z which allowed for the progressive broadening of the peak on the chromatogram. In general, however, the calculation of this parameter is extremely complicated. From an analysis of values of Z this author concluded that, when highly efficient capillary columns are used, identification is possible only from the retention indices.

Ettre and Billeb[228] deduced an equation linking the difference in retention indices with the number of effective plates N_{eff} and the separation criterion R:

$$\delta I = \text{const} \cdot \lg \frac{\sqrt{N_{eff}}}{\sqrt{N_{eff}} - 4R} \qquad (29)$$

where the constant is $100/\lg(t_{R(n+1)}/t_{R(n)})$.

Rohrschneider showed[229] that R can be calculated from the difference between the retention indices by means of the equation

$$R = \frac{\delta I}{1.6998_I} \qquad (30)$$

where θ_I is the width of the peak at mid-height (in index units). He used an equation relating the logarithm of the relative retention to the difference in molar free energies of sorption to assign a rigorous thermodynamic meaning to the criterion R. He demonstrated also[230] that the effectiveness of separation depends on the polarity of the stationary phase expressed as in Eqn. (19).

In conclusion we note that the separation criterion R is used in gas chromatography far more often than are $N\sigma$ and Z, because R is most simply related to data obtained directly from a chromatogram. In order to estimate effectiveness of separation from retention indices, therefore, Eqn. (30) must evidently be used.

VIII. APPLICATION OF RETENTION INDICES IN THE CALCULATION OF PHYSICOCHEMICAL PARAMETERS

Tourres[86], as well as Bonastre and Grenier[85, 216], established the relation

$$I = 100\frac{\lg p^0_n - \lg p^0_X + \lg(\gamma^{\infty}_n/\gamma^{\infty}_X)}{\lg p^0_n - \lg p^0_{n+1} + \lg(\gamma^{\infty}_n/\gamma^{\infty}_{n+1})} + 100n \qquad (31)$$

between the relative activity coefficient, the vapour pressure, and the retention index, and used it to predict retention indices and to assess the polarity of stationary phases.

Vigdergauz and Semkin have recently suggested[54, 171–173] that retention indices at two elevated pressures P_1 and P_2 should be used to determine the mixed second virial coefficient B_{12}:

$$\frac{\Delta I}{\Delta P} = \frac{(I_1 - 100n)(\beta_{n+1} - \beta_n) - 100(\beta_X - \beta_n)}{-b_2} \qquad (32)$$

where $\Delta P = P_2 - P_1$, $\Delta I = I_2 - I_1$ measured at pressures

P_2 and P_1 in the column, $\beta_i = (2B_{12i} - v_i^\infty)/2.303RT$ $(i = x, n, n+1)$, v_i^∞ is the molar volume of the liquid sorbate, and $b_2 = \lg(V_{g(n+1)_2}/V_{g(n)_2})$ is the logarithm of the relative retention volume of adjacent n-alkanes at pressure P_2. Calculation of B_{12} by means of Eqn. (32) is assumed to give more accurate results than its determination from the retention volumes.

Martynov and Vigdergauz [54] suggested a method for determining the density of alkanes at 20°C from the retention indices on squalane.

The most obvious though approximate method for determining the properties of substances is based on the relation, widely used in practical analysis, between the index or the logarithm of the relative retention and the boiling point, the number of carbon atoms in the molecule, or the logarithm of the vapour pressure [32-54, 59, 231-238].

Martin showed [239] that the free energy of sorption can be estimated by summing the structural increments for the molecule. Additivity of the retention index follows as a particular case [10, 56, 182, 240, 241]. The possibility thus appears of determining chromatographically the properties of compounds differing e.g. in quantity of substituents, number of multiple bonds, skeletal structure, etc.

Thermodynamic Nature of Index

Kováts [9] made the first attempt to find a thermodynamic basis for the retention index. Using the relation between the relative retention and the difference between the molar free energies of evaporation of the test substance and of the standard n-alkane $\Delta G_{e,X}$ and $\Delta G_{e,n}$, he established that

$$I = 100\frac{\Delta G_{e_X} - \Delta G_{e_n}}{\Delta G_{e\,(CH_2)}} + 100n\,. \qquad (33)$$

Comparison with Eqn. (3) shows that the constant b has a quite definite thermodynamic significance: it is the increment of the free energy of evaporation (dissolution) per methylene group [9, 17, 19, 91, 155, 242]. Kováts [9] obtained values of approximately 500 and 460 cal mole^{-1} for $\Delta G_{e(CH_2)}$ for Apiezon L and the Emulphor O respectively. He pointed out that, in the thermodynamic interpretation of retention indices, the free energies not only result from dissolution but also contain a contribution due to adsorption on the solid support and on the surface of the stationary phase.

Kováts and Weisz [217] showed later that the index measures the retention of a component on the scale of the standard chemical potentials of the n-alkanes:

$$I = 100\frac{\Delta\mu_X - \Delta\mu_n}{\Delta\mu_{n+1} - \Delta\mu_n} + 100n \qquad (34)$$

where $\Delta\mu_X$, $\Delta\mu_n$, and $\Delta\mu_{n+1}$ are the differences, between an ideal dilute solution and the ideal gas state, in the standard chemical potentials of the compound and of the n-alkanes. Formula (34) is most often written in terms of the Gibbs function [17, 20, 21, 91, 155, 242] or the free energy [54, 243].

Bach et al. [244] have recently used relations connecting the logarithm of the relative retention time with the thermodynamic functions of dissolution, Trouton's rule† and Klages' equation; these establish that the square of the boiling point is an additive function for homologues, to give an original thermodynamic proof of the system of retention indices.

†According to this rule the molar heat of evaporation of a non-associated liquid at its boiling point and atmospheric pressure is directly proportional to the absolute boiling point.

Thermodynamic Functions of Sorption

For a long time retention indices, because of their quite complicated thermodynamic interpretation (Eqn. 34), were not used in calculating the thermodynamic functions of the fundamental process in gas–liquid chromatography. It was found experimentally that the index varies linearly with the change in the molar free energy of sorption, and can serve as a measure of the latter when different substances are being compared [242].

The first systematic investigation of the thermodynamic application of retention indices [17, 20, 21, 221, 245, 246] led to deduction of the equations

$$\lg K_X = \frac{(I-100n)\lg\left(\frac{t_{R_{n+1}}}{t_{R_n}}\right)}{100} + \lg\frac{V_{g_n}^0 T\rho}{273}\,, \qquad (35)$$

$$\Delta G_{s_X} = -2.3RT\lg K_X\,, \qquad (36)$$

$$\Delta\Delta G_{s_X,\,n} = -0.023RT(I-100n)\lg\frac{t_{R_{n+1}}}{t_{R_n}}\,, \qquad (37)$$

$$\Delta H_{s_X} = \Delta H_{s_n} - 0.023R\left[\lg\left(\frac{t_{R_{n+1}}}{t_{R_n}}\right)\cdot\frac{\partial I}{\partial 1/T} + (I-100n)\frac{\partial}{\partial 1/T}\lg\left(\frac{t_{R_{n+1}}}{t_{R_n}}\right)\right], \qquad (38)$$

$$\frac{(I-100n)}{100}\lg\left(\frac{t_{R_{n+1}}}{t_{R_n}}\right) = \frac{-\Delta H_{s_X} + \Delta H_{s_n}}{2.3RT} + \frac{\Delta S_{s_X} - \Delta S_{s_n}}{2.3R}\,, \qquad (39)$$

enabling determinations to be made of partition coefficients K and partial molar enthalpies ΔH_s, entropies ΔS_s, and free energies ΔG_s of sorption (it is advisable to calculate excess thermodynamic functions and estimate the selectivity of chromatographic columns by means of Eqns. 23–26). In the above equations t_{R_n} and $t_{R_{n+1}}$ are the corrected retention times of the n-alkanes, and ρ is the density of the stationary phase. If $n \geqslant 6$, we can replace $\lg(t_{R_{n+1}}/t_{R_n})$ by the constant b of Eqn. (2). [17, 18] An equation analogous to (38) has since been published by other workers [91, 247, 248].

Since the dependence of $(I - 100n)b/100$ on $1/T$ (°K^{-1}) conforms closely to a linear law (Fig. 2), the calculation of enthalpies and entropies of sorption, as well as of separation factors, is considerably simplified by the graphical interpretation of Eqn. (39). [17, 20, 221]

The proposed method of calculating thermodynamic functions is simple and makes rather smaller demands on the experimental apparatus than does the classical method, based on the measurement of specific retention volumes. Thus it becomes unnecessary to measure the quantity of "active" phase in the column, the space velocity of the carrier gas, and the drop in pressure. Provided that $\Delta H_{s,n}$ and $\Delta S_{s,n}$ are known, neither the density nor the molecular mass of the stationary phase need be known in order to calculate $\Delta H_{s,X}$ and $\Delta S_{s,X}$ by means of Eqns. (38) and (39). With stationary phases that form athermal solutions with alkanes (hydrocarbons, phthalic esters, etc.), moreover, the tabulated value of the latent heat of evaporation can be used [243] instead of the standard function $\Delta H_{s,n}$.

With substances having retention indices exceeding 600, as mentioned above, $\lg(t_{R_{n+1}}/t_{R_n})$ can be replaced by the constant b in Eqn. (2), which expresses the linear dependence of the logarithm of the corrected retention volume of n-alkanes on the number of carbon atoms in the molecule. However, the legitimacy of using a linear equation has

hitherto been a controversial matter in gas–liquid chromatography. Several workers proposed non-linear equations to describe the gas-chromatographic behaviour of straight-chain hydrocarbons[203, 249, 250]. The accuracy of known equations has been assessed statistically by the use of regression analysis[17,18]. Experimental data on the retention of n-alkanes have been taken from McReynolds' tables[152] for thirteen stationary phases of varying polarity. The calculations were made on an electronic computer. The best of the non-linear equations, suggested by Sakharov and Voskov[250], has an accuracy of around 0.2% in $\lg V_g^0$, while that of the linear equation (2) is 0.8%. Thus the linear approximation provides quite satisfactory accuracy, and can be used in gas–liquid chromatography for various calculations and correlations, including the calculation of thermodynamic functions from retention indices.

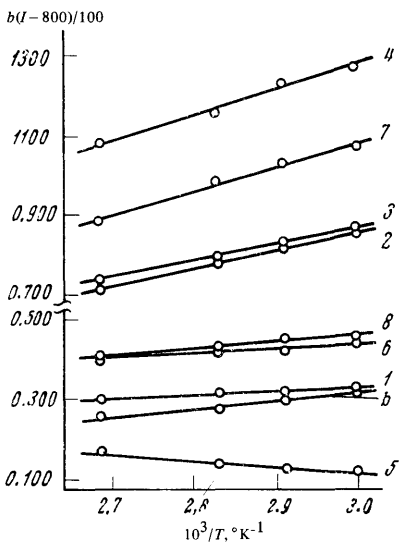


Figure 2. Dependence of $b(I - 800)/100$ on reciprocal of the temperature for the phase PEG-1000 [20] and the compounds: 1) $(C_2H_5)_2S$; 2) $(n\text{-}C_3H_7)_2S$; 3) $(CH_3S)_2$; 4) $(C_2H_5S)_2$; 5) $n\text{-}C_3H_7SH$; 6) $n\text{-}C_4H_9SH$; 7) $n\text{-}C_6H_{13}SH$; 8) C_6H_6.

The accuracy with which thermodynamic characteristics can be calculated from retention indices has been estimated[17,251]. Mathematical statistics have been used to deduce formulae for the standard deviation of the determination of thermodynamic functions by means of Eqns. (23)–(26) and (35–39). The accuracy of the calculation is comparable with that for the calculation of the same functions from specific retention volumes. Other work[243,252] has shown the fundamental possibility of determining thermodynamic functions from retention indices by extrapolation and interpolation.

Thus both experimental and theoretical results indicate that, among the gas-chromatographic retention parameters that are currently available, the system of indices is most generally applicable, is highly accurate and reproducible, and provides adequate information on stationary phases and chromatographic columns. The system of retention indices has a great advantage in analyses with programming of the temperature or the velocity of the carrier gas, as well as when high pressures are used. It is convenient also for the calculation of physicochemical quantities characterising the process of sorption in gas chromatography.

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