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Thermodynamic Treatment of the Polarity and the Selectivity of Sorbents in Gas Chromatography

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Existing methods for assessing the polarity and the selectivity of sorbents in gas chromatography are examined. The recently developed thermodynamic treatment of the polarity and the selectivity of stationary phases is shown to have several advantages over the Rohrschneider-McReynolds system. Attention is paid mainly to the quantitative characterisation of the energy of sorbate-sorbent intermolecular interactions on the basis of retention indices. A universal system is proposed for assessing polarity and selectivity in gas chromatography in terms of the energy of intermolecular interaction.
A list of 83 references is included.

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I. INTRODUCTION

The widespread use of gas-chromatographic methods of analysis in science and technology makes it necessary to assess as fully as possible the properties of stationary phases and adsorbents, which would permit the choice of optimum conditions for analysis. The problem of classifying stationary phases in gas chromatography and assessing their polarity and selectivity has already been the subject of research for more than twenty years. Empirical methods for such assessment have been surveyed[1].

Before passing to a thermodynamic consideration of the problem of polarity and selectivity, we shall briefly consider existing methods of determination. According to Littlewood polarity is determined by the enhanced affinity of the given substance for a polar compound ("the stationary phase is the more polar the longer it retains a polar substance in comparison with the retention of a non-polar substance"[2]). The polarity of a compound is attributed to the presence of a dipole moment; the magnitude of the orientation (dipole–dipole) interaction is regarded as decisive in assessing the polarity of a stationary phase[3,4]. Several attempts have been made to relate polarity to the electrostatic and structural properties of stationary phases and substances analysed. Careful analysis of these results[5-7] has shown that only when both structures are comparatively simple, while the proportion of polar groups in the stationary phase is not too large, do relative retentions clearly depend on polarisability, the dipole moments of the interacting molecules, and the dielectric constant of the stationary phase. It is especially difficult to establish any dependence with stationary phases and compounds whose molecules have no dipole moment but are capable of forming hydrogen bonds (such stationary phases are usually regarded as polar[8,9]). Substances that have no dipole moment but are capable of complex formation are retained better by polar than by non-polar phases. The results that have accumulated have made it necessary to interpret the polarity of stationary phases somewhat more broadly, as the capability of such phases for electron-donor–acceptor interaction with a substance being analysed[10].

Numerous attempts have been made to assess the polarities of stationary phases, adsorbents, and carriers empirically in terms of the retention of polar and non-polar substances. Kovats and Wehrly developed[11,12] the idea of estimating the polarities of stationary phases from the retention indices I of a series of compounds of general formula RX, where R represents an n-alkyl radical containing at least six carbon atoms, and X various functional groups. Selectivity was measured by the difference ΔI between the retention indices for each of the substances RX on the given stationary phase and on Apiezon L. The range of ΔI values was termed the "retention dispersion". Despite the great quantity of information which this parameter gave on the ability of stationary phases to retain substances containing various functional groups, it did not become widely used because of the large amount of experimental work required. Bayer[13] suggested that selectivity could be determined from the relative retention of two substances having similar boiling points, one of these compounds being an n-alkane. Rohrschneider[14] used the relative butane–butadiene retention to assess polarity; he chose squalane and oxy-$\beta\beta'$-dipropionitrile as extreme points of the polarity scale, with that for squalane equated to zero. Later suggestions for determining the polarity of stationary phases have included the use of two[15-19], three[20-23], and five[24] compounds.

The well known Rohrschneider–McReynolds system[25-27] has become the most widely used, in which the main compounds for testing stationary phases are benzene, butanol, pentan-2-one, nitropropane, and pyridine, supplemented by 2-methylpentan-2-ol, 1-iodobutane, oct-2-yne, 1,4-dioxan, and *cis*-hydrindane. The indices I for the first five test compounds serve for the assessment of polarity, and the differences ΔI for assessing the selectivity of stationary phases.

It is interesting that the suggestion has been made repeatedly that the polarity of stationary phases should be assessed from the relative retention of adjacent n-alkane homologues[28-31]. It was first proposed[28] that the polarity should be defined by

$$\lg \alpha = \lg V_{g(n+1)} - \lg V_{gn},$$

where $V_{g(n+1)}$ and V_{gn} are the retention volumes of n-alkanes containing respectively $n+1$ and n carbon atoms. It was assumed that the more polar the stationary phase the shorter the retention time of n-alkanes. The one-sidedness of assessing the polarity of stationary phases with respect to n-alkanes has been stressed[32,33].

The problem of determining the polarity of stationary phases in terms of the differential molar free energy per mole of methylene groups in n-alkanes has been discussed[34-36]. Developing these ideas, Novak suggested[10] that the polarity should be determined from the excess energies of mixing of a mole of methylene groups. He obtained these values by measuring the retention times of acetates forming a homologous series and the vapour pressures of the homologues at the analysis temperature and a pressure of 1 atm. The idea of assessing the polarity of stationary phases solely on the basis of the change in the retention parameters of n-alkanes or their thermodynamic characteristics is somewhat illogical, since this involves an attempt to determine polarity by testing compounds for which polar interactions with stationary phases are uncharacteristic. The decrease in energy of dispersion interaction during analysis on a polar phase is thus assumed to be directly proportional to the capacity of the phase for polar interactions. This hypothesis requires proof: it cannot be assumed *a priori*. In any case the polarity scale based on capacity for dispersion interaction is uninformative. It has been suggested[36,37] that the polarity and the selectivity of stationary phases should be estimated from the differential molar enthalpies of the dissolution of compounds containing a series of functional groups. Enthalpies were determined from the temperature dependence of the specific retention volume of the test substances. However, an approach to the assessment of ability to retain polar substances that disregards the change in entropy is not rigorous. The analysis of polar substances on polar stationary phases involves not only a change in the heat of dissolution but also a decrease in the degree of freedom of the molecule analysed, so that retention is determined by the overall differential molar free energy of dissolution. Neglect of the entropy contribution may lead to erroneous conclusions. The need to allow for the entropy contribution in assessing polarity has been noted[38,39] with the suggestion that the polarity of stationary phases should be estimated from the energy contributions by various functional groups.

A tendency has appeared recently for the concepts of "polarity" and "selectivity" to be equated[40,41], which introduces still greater confusion into an understanding of the physical significance of these terms. Thus the concept of polarity and selectivity in gas chromatography has hitherto remained indeterminate. Inspection of published results reveals ambiguity in the treatment of this concept.

The present Review is concerned mainly with the thermodynamic assessment of polarity and selectivity. These concepts are interpreted in terms of various types of intermolecular interactions governing retention in gas chromatography. Systematic regard for the thermodynamic characteristics of processes involved in the interaction between the sorbent and the substances undergoing analysis enables a simple method to be recommended for the quantitative estimation of polarity and selectivity from thermodynamic quantities.

II. INTERMOLECULAR INTERACTIONS GOVERNING RETENTION IN GAS CHROMATOGRAPHY

Retention in chromatography is determined mainly by the energy of intermolecular interactions between the substances undergoing analysis and the stationary liquid phase or the adsorbent. The differential molar free energy of dissolution or adsorption is the sum of the energies of the intermolecular interactions—non-specific, due to physical forces, and specific electron-donor–acceptor interactions, which are chemical in nature.

Physical forces of interaction between two molecules (van der Waals forces) comprise dispersion, induction, and orientation interactions, the total energy of which is for diatomic molecules 1–3 kcal mole^{-1}.[42] The energy of dispersion interaction to the London approximation E_d is the main component of the physical forces:

$$E_d = -\frac{3}{2}\frac{\pi h}{R^6}\alpha_1\alpha_2\frac{J_1 \cdot J_2}{J_1 + J_2}, \quad (1)$$

where α is the static polarisability of the molecules, the J are their ionisation potentials, and R is the intermolecular distance.

If the molecules have non-zero dipole moments μ_1 and μ_2, the contribution of the energy of orientation interaction E_0 may be very substantial:

$$E_0 = -\frac{2}{3kTR^6}\mu_1^2\mu_2^2, \quad (2)$$

where k is Boltzmann's constant and T K is the temperature. In some cases E_0 may reach 50% of the energy of the physical forces[42-44].

The energy of induction interaction E_i usually introduces a small fraction to the total energy; it is expressed by the Debye formula[43]

$$E_i = -\frac{1}{R^6}(\mu_1^2\alpha_2 + \mu_2^2\alpha_1). \quad (3)$$

Thus the energy of the physical forces of interaction of the molecules depends on their static polarisability α, ionisation potentials J, and dipole moments μ. The polarisability can be calculated by means of the formula[42]

$$\alpha = \frac{3}{4}\frac{MR_\infty}{\pi N} \approx \frac{3}{4}\frac{MR_D}{\pi N}.$$

Since $n_\infty^2 \cong 1.1 n_D^2$, we find that

$$\alpha = \frac{3}{4\pi N}\frac{n_D^2 - 1}{n_D^2 + 2}\tilde{V}_m \quad (4)$$

where MR_D is the molecular refraction for the sodium D-line, MR_∞ the molecular refraction for light of zero frequency[42], i.e. at infinite wavelength, n_D the refractive index for the sodium D-line, N Avogadro's number, and $\tilde{V}_m$ the molar volume. We shall examine the cases encountered in gas chromatography.

1. In the analysis of a non-polar molecule (subscript "T") on a non-polar stationary phase (subscript "Ph") the differential molar free energy of dissolution is determined by the energy of dispersion interaction: i.e. $E = E_d$. Hence the greater the molecular refraction the more strongly will the substance be retained by the column sorbent. This was first verified experimentally by Littlewood[2].

2. In the analysis of a non-polar substance on a polar phase or of a polar substance on a non-polar phase the interaction energy is determined by the sum of the contributions:

$$E = E_d + E_i; \quad (5)$$

in which E_i, calculated by means of Eqn.(3), will have a single component. If the dipole moment of the test substance $\mu_T = 0$, we have

$$E_i = -\frac{1}{R^6}\mu_{Ph}^2\alpha_T; \quad (6)$$

if, however, $\mu_{Ph} = 0$, then

$$E_i = -\frac{1}{R^6}\mu_T^2\alpha_{Ph}. \quad (7)$$

It must be borne in mind that, if the substance is capable of donor–acceptor interaction (DA) with the stationary phase, the energy of such specific interaction is added:

$$E = E_d + E_i + E_{DA}. \quad (8)$$

For example, benzene and *p*-dinitrobenzene have zero dipole moments, but with several polar phases they give π-complexes; the donor–acceptor interaction energy of aromatic hydrocarbons with the ether groups of polyethylene glycols (PEG) reaches ~1.8 kcal mole^{-1},[45] and must be taken into account.

3. In the analysis of a polar substance on a polar stationary phase all types of physical interaction occur, and interactions of chemical nature—complex formation, hydrogen bonding, etc.—are often added. The total interaction energy is

$$E = E_d + E_i + E_o + E_{DA}. \quad (9)$$

The concept of physical interactions has been developed and tested experimentally for diatomic molecules. Applied to gas chromatography, therefore, it merely enables us to understand on what the energy of physical forces of interaction depends, what is the contribution by each component to the total free energy. It makes possible prediction of the sequence in which substances of similar structure are eluted from a column in the absence of specific donor–acceptor interactions with the sorbent. Actually, the interaction energy is considerably greater, and an accurate calculation must take into account the influence on the test molecule of the surrounding medium, the molecular weight, the number of contacts with the stationary phase, etc; an attempt can be made to use for this purpose one of the theories of solutions[46,47]. Experimental data indicate that the energy of interaction of non-specific physical forces in gas–liquid chromatography may reach ~10 kcal mole^{-1}. When the methyl ester of an aliphatic acid containing 24 carbon atoms undergoes analysis on SE-30, for example, the differential molar free energy is 8.34 kcal mole^{-1}.[48]

The differential molar free energy of sorption, which determines the retention of a substance in a column, is in general the sum of energies of both physical and chemical types of interaction; this sum is determined solely by experiment. According to views developed by Zhukhovitskii, furthermore, the free energy probably includes also the energy consumed by the substance in penetrating the stationary phase[3,5,49,50]. The contribution by the energy of donor–acceptor interactions, which are chemical in nature, may be significant in the analysis of polar substances on polar stationary phases. Such interactions probably involve at least partial delocalisation of electrons and the formation of electron-donor–acceptor bonds. The energy of weak donor–acceptor interactions usually varies in the range 1–3 kcal mole^{-1}. In the case of hydrogen bonds it may reach 3–8 kcal mole^{-1}.[51,52]

Experimental investigation of donor–acceptor interactions began at the start of the 1960s. The properties of many such interactions and their energies of formation have been given in a monograph[53]. Several determinations of the energy of weak hydrogen bonds have been made by the methods of infrared spectroscopy and gas chromatography[54,55]. There is no doubt that donor–acceptor interactions occur widely. Published data[56] enable us to assess between what classes of substances they are possible and what is the heat of formation of the complexes. Benzene, for example, is active in forming complexes with aromatic compounds—benzene, phenol, aniline—and also with dioxan and hydrogen cyanide. Complex formation of similar type probably occurs in the analysis of benzene and other aromatic compounds on silicone phases containing phenyl and nitrile groups, as well as on phases containing ether groups (polyethylene glycols, Tritons, Carbowaxes, etc.). Complex formation with alcohols can occur during analysis on stationary phases containing nitrile and ester groups. During gas-chromatographic analysis the energy contribution by donor–acceptor interactions to the free energy may be substantial[45,51–56].

Thus the differential molar free energy of dissolution of a substance in a stationary phase is the sum of non-specific energies of intermolecular interactions amounting to ~1–10 kcal mole^{-1}, due to physical forces, and the energy of specific donor–acceptor interactions of chemical nature, including hydrogen bonding (~1–8 kcal mole^{-1}).

III. THERMODYNAMIC TREATMENT OF THE POLARITY AND SELECTIVITY OF STATIONARY PHASES AND ADSORBENTS IN GAS CHROMATOGRAPHY

It has already been remarked that the concepts of polarity and selectivity are very indefinite in gas chromatography, and are interpreted differently by different investigators[2–40]. In the opinion of the Reviewers gas-chromatographic polarity must be interpreted as *the capacity of a sorbent for various types of intermolecular interactions,* which is assessed from the differential molar free energy respectively of dissolution and of adsorption ΔG and ΔG_A in gas–liquid and gas–adsorption chromatography: the higher is ΔG, the more polar the sorbent. The selectivity of two comparable stationary phases or adsorbents represents *the difference in ability to retain* the compound analysed, and is expressed quantitatively by the difference in excess energies of mixing $\delta(\Delta G^E)$[57]: the greater the value of $\delta(\Delta G^E)_{2,1}$, the greater the selectivity of sorbent *2* in comparison with *1*.

The polarity of a sorbent cannot be assessed by analysing only one substance, since it is impossible to choose a compound capable of all types of intermolecular interactions on contact with the sorbent. A series of test substances must be selected that model possible intermolecular interactions most closely and completely. They should include those that will reveal the capacity of the sorbent for dispersion, orientation (dipole–dipole), and induction interactions, and permit determination of electron-donor–acceptor properties, as well as the ability to form hydrogen bonds.

Determination of the polarity of stationary phases or adsorbents requires the use, not of a single scale for one test substance, but of a set of scales for all the test substances. The reason is that each sorbent has a different capacity for intermolecular interactions during an analysis, and it is advisable to compare all free energies for all test substances. But the sum of the values

$$\sum_1^i \Delta G_i,$$

like the sum[24,58]

$$\sum_{i=1}^{i} \Delta I_i,$$

does not indicate individual features of a sorbent because of possible compensation effects. For example, a stationary phase with a large energy of dispersion interaction and hence a small energy of orientation interaction may have the same sum

$$\sum_{i=1}^{i} \Delta G_i,$$

as a phase having moderate energies of dispersion and electron-donor–acceptor interactions; therefore assessing polarity from the sum of the differential molar free energies of dissolution of all the test substances will not enable the optimum phase to be chosen for separating a specific mixture.

In every case the experimenter who has a mixture of compounds should envisage the intermolecular interactions of which they are capable, and then select a stationary phase or an adsorbent that will realise these possibilities. If, for example, compounds having a large dipole moment, unsaturated or hydroxylated, are to be separated, polarity scales are to be compared on the basis of free-energy values for substances that test the capacity of stationary phases for orientation interaction, π-complex formation, and hydrogen bonding.

The choice and the number of test substances have been the subject of study by many investigators for more than a decade[20-27]. The difficulty is that it is impossible to select test substances capable of only a single type of interaction—orientation, induction, or donor–acceptor interaction—for usually two or more types function simultaneously. Researches to find the necessary and sufficient number of test substances, made by Tacats[59], Hartkops[60], and de Clercq[61] with mathematical assessment of the weighting of each of a long series of proposed substances used to characterise stationary phases, have shown that Rohrschneider and McReynolds' five compounds are quite sufficient to assess the polarity of stationary phases in gas–liquid chromatography. Other substances will give little additional information on the properties of sorbents.

In the Reviewers' opinion the assessment of polarity can usefully be expressed in terms of six parameters[62-64] based on the differential molar free energies of dissolution ΔG^{CH_2} of a methylene unit of an n-alkane (or of a methyl ester of an aliphatic acid) and the five well known test substances[24,27,58]—benzene (x), butan-1-ol (y), pentan-2-one (z), 1-nitropropane (u), and pyridine (s)—which model the chief types of intermolecular interactions with stationary phases during analysis (Table 1). Some changes in this list of test substances may be required to estimate the polarity of adsorbents in gas–adsorption chromatography, but at present this is difficult to verify, since sufficient published data are not available.

If gas-chromatographic polarity is regarded as the capacity of sorbents for various intermolecular interactions (physical and chemical in nature) with substances undergoing analysis, it can be determined numerically from the differential molar free energies of sorption of the test substances. Retention of a compound in a column is always due to intermolecular forces of interaction. On this view there are in gas chromatography no stationary phases or adsorbents that are absolutely incapable of intermolecular interactions. In the old terminology non-polar solvents are those that are capable mainly of dispersion interaction with a substance to be analysed. Such stationary phases include, for example, squalane, Apiezons, Kovats' hydrocarbon, etc. These phases are characterised by large differential molar free energies of dissolution of the methylene group. According to the thermodynamic treatment of polarity they possess a large "dispersion polarity"[62]. Stationary phases and adsorbents that possess a minimal capacity for all types of intermolecular interactions, i.e. that have minimal values of ΔG for all test substances, must be included among non-polar sorbents[63,64].

Thus the thermodynamic interpretation of gas-chromatographic polarity attributes to this term a quite different significance from that accepted hitherto. Such a definition of polarity makes it easy to avoid the ambiguity in understanding the nature of sorption forces in gas chromatography and brings published results into an orderly system, avoiding the confusion that had arisen from a different interpretation of this concept.

The energy of the dispersion, orientation, induction, and donor–acceptor interactions responsible for the retention of a substance in a column depends on the temperature of analysis. Hence the polarity, defined by the energy of intermolecular interaction, will also depend on the temperature. Therefore the polarities of different stationary phases and adsorbents can be compared only under isothermal conditions at the same analysis temperature by comparing values of ΔG or specific retention volumes. It is incorrect to determine the polarities of different sorbents from the retention indices, and the selectivities from ΔI, as is widely done at the present time for stationary phases[58], since the energy value of an index unit changes from one sorbent to another (see Section IV). As a consequence, different sorption energies correspond to the same values of the retention index or of ΔI.

Recent publications have suggested[38,39] that the polarities of stationary phases should be determined from the differential molar free energies of dissolution of functional groups—hydroxyl, formyl, carbonyl, formyloxy, acetoxy, oxy—for homologous series of organic compounds. Firstly the dependence of the specific retention volume on the reciprocal of the temperature is plotted from two or three points, ΔH and ΔS are determined graphically, the total energy of dissolution ΔG is calculated, and then the energy contributions by individual fragments of the molecules, including functional groups, are determined[39]. However, the authors disregard the effect of the position of a functional group in a molecule on its energy contribution. For example, the contribution by a carbonyl group is greater in the homologous series of alkan-2-ones than in alkan-3- and -4-ones[65]; the same applies to the oxy-group, which is analogous to the thio-group[66] in its gas-chromatographic behaviour. Hence the estimation of polarity from the contributions by various functional groups[39] is quite complicated and does not give a true picture because of inaccurate calculation and a simplified treatment of the results.

Thus in the strict thermodynamic sense the capacity of a sorbent for various intermolecular interactions with a substance undergoing analysis (its polarity) is determined by the differential molar free energies of sorption. Selectivity represents a difference in the capacity of comparable sorbents for intermolecular interactions with the substance analysed, and is determined by the quantity $\delta(\Delta G^E)$.

IV. UNIVERSAL SYSTEM FOR ASSESSING POLARITY AND SELECTIVITY OF STATIONARY PHASES

1. Assessment of Polarity

Before considering a universal system for assessing the polarity of sorbents in gas chromatography we can usefully examine in greater detail the Rohrshchneider–McReynolds estimation of the polarity and selectivity of stationary phases[24-27,58], which has been widely used by research workers. By now more than 200 stationary phases have been classified according to this system[27,58], which diminishes the number of experiments in the selection of stationary phases for gas–liquid chromatography.

A detailed account of the principle underlying the characterisation of stationary phases will be found in a review[1]. According to Rohrschneider polarity and selectivity are characterised by five ΔI values, each the difference between the retention indices of a standard test substance x, y, z, u, or s (Section III) on the given stationary phase and on squalane regarded as a phase of "zero polarity".

In order to describe theoretically the relation between the ΔI values and the thermodynamic characteristics of the gas-chromatographic process Rohrschneider suggested the empirical equations[24]

$$\lg V_g = -\Delta G + \text{const}, \qquad (10)$$

$$-\frac{\Delta G^{CH_2}}{100} = B = b/100, \quad (11)$$

$$\Delta I = I_{Ph} - I_{Ph_1} = 100\frac{\Delta G_{Ph} - \Delta G_{Ph_2}}{\Delta G^{CH_2}_{Ph}}, \quad (12)$$

in which b is the coefficient in the dependence of the logarithm of the specific retention volume of an n-alkane on the number of carbon atoms

$$\lg V_{gn} = a + bn, \quad (13)$$

or

$$b = \lg V_{g(n+1)} - \lg V_{gn}; \quad (14)$$

$\Delta G^{CH_2}_{Ph}$ is the differential molar free energy of dissolution of a methylene group of the n-alkane in Ph, the polar phase, I_{Ph} and I_{Ph_1} are the retention indices of the substance on the phases Ph and Ph_1, the latter representing squalane, and ΔG_{Ph_0} is the energy of dissolution in the polar phase Ph of the hypothetical hydrocarbon containing $n = I_{Ph_1}/100$ carbon atoms.

Equation (10) shows the dependence of the specific retention volume V_g on the differential molar free energy of dissolution ΔG. Equation (11) represents the dependence of the differential molar free energy of dissolution of a methylene unit of an n-alkane ΔG^{CH_2} on the coefficient b. According to the fundamental empirical equation (12) the quantity ΔI is directly proportional to the difference between the free energies of dissolution on the given phase Ph and the phase of "zero polarity" Ph_1. Actually, Eqn.(10) is valid only when specific volumes of substances V_g are compared on the same stationary phase at the same temperature. According to other workers[67]

$$\Delta G = -2.3RT \lg \frac{V_g T\rho}{273}, \quad (15)$$

$$\lg V_g = -\frac{\Delta G}{2.3RT} - \lg \frac{T\rho}{273}, \quad (16)$$

where ρ is the density of the stationary phase at the analysis temperature T K. Hence Eqn.(16)—not Eqn.(10) as in Ref.24—must be used to classify different stationary phases.

A rigorous deduction of Eqns.(11) and (12) could be made after the relation between the retention index and the free energy ΔG had been established. In 1971 Golovnya and Arsen'ev showed[68] that

$$\Delta G = -2.3RT\left[\frac{I - 100n}{100}b + \lg\frac{V_{gn}T\rho}{273}\right], \quad (17)$$

which revealed discrepancies in Rohrschneider's thermodynamic treatment of ΔI and also ΔG^{CH_2}. Thus, when we use Eqn.(17) to express the differential molar free energies of dissolution of two n-alkane homologues ΔG_{n+1} and ΔG_n and take their difference, we obtain[62]

$$\Delta G^{CH_2} = -2.3RTb. \quad (18)$$

Hence calculation of the differential molar free energy of dissolution of a methylene unit of an n-alkane, or other homologous compounds in which the difference in the index per methylene unit is 100, requires the use of Eqn.(18), not Eqn.(11), which is not even dimensionally correct.

Use of Eqn.(17) to compare the gas-chromatographic behaviour of a given substance on the two phases Ph and Ph_0 yields for the difference in the differential molar free energies of dissolution the expression[63]

$$\delta(\Delta G)_{Ph,\,Ph_0} = \Delta G_{Ph} - \Delta G_{Ph_0} = \quad (19)$$
$$= \frac{1}{100}(I_{Ph}\Delta G^{CH_2}_{Ph} - I_{Ph_0}\Delta G^{CH_2}_{Ph_0}) - 2.3RT(a_{Ph} - a_{Ph_0}) + 2.3RT\lg \rho_{Ph}/\rho_{Ph_0},$$

where a_{Ph} and a_{Ph_0} are determined for n-alkanes by the application of Eqn.(13) to analytical results on these phases. Equation (19) shows that the difference in the free energies of dissolution in the two phases is a complicated function of the indices I_{Ph} and I_{Ph_0}, which is not consistent with the empirical equation (12) previously used to assess the polarity and the selectivity of stationary phases[24-27,58]. Analysis of Eqn.(19) reveals that the free-energy difference cannot be directly proportional to ΔI. The same conclusion can be reached by using the well known relation[44,48,69] $\Delta G = A + BI$ to express ΔI. The resulting formula

$$\Delta I_{Ph,\,Ph_0} = \frac{\Delta G_{Ph} - A_{Ph}}{\Delta G^{CH_2}_{Ph}} - \frac{\Delta G_{Ph_0} - A_{Ph_0}}{\Delta G^{CH_2}_{Ph_0}},$$

is not equivalent to Rohrschneider's equation (12). The Rohrschneider–McReynolds assessment of polarity distorts the real picture more strongly the greater the difference in the gas-chromatographic behaviour of n-alkanes on the stationary phases under comparison, and hence the difference in the quantities $\Delta G^{CH_2}_{Ph}$ and $\Delta G^{CH_2}_{Ph_0}$.

It follows from Eqn.(19) that the energy value of one index unit differs on different stationary phases. Therefore the same index on different stationary phases corresponds to different free energies. The energetic importance of unit retention index on a given stationary phase can be determined by means of Eqn.(18), since ΔG^{CH_2} correspond to 100 index units (i.u.), and $\Delta G_{i.u.} = \Delta G^{CH_2}/100 = -0.023RTb$ cal mole^{-1} is the energy value of one index unit. According to the thermodynamic treatment (Section III) the polarity of a stationary phase must be determined from ΔG values calculated from retention indices by means of Eqn.(17).[63] At the present time it is probably advisable to use the compounds listed in Table 1 as test substances for the assessment of polarity.

Table 1. Test species for assessment of phase polarities.

Species	Type of interaction with sorbent tested*
Methylene in n-alkane or methyl aliphatic ester	dispersion
Benzene	π-complex formation
Butan-1-ol	hydrogen bonding with electron-donor groups
Pentan-2-one (weak electron-donor)	donor–acceptor complex formation
1-Nitropropane	orientation, since dipole moment $\mu = 3.6$; donor–acceptor complex formation
Pyridine (base)	hydrogen bonding with hydrogen donors; donor–acceptor complex formation

*Only the retention of methylene groups is determined by the energy of dispersion interaction. Retention of the remaining test species, unfortunately, depends on the character of the sorbent as a consequence of the total energy of the dispersion, orientation, induction, and donor–acceptor interactions (Section II); the type of interaction which they test is a component of the total energy of sorption.

The capability of a sorbent for dispersion interaction with a substance undergoing analysis is determined from the differential free energy of sorption of a methylene group ΔG^{CH_2} in the homologous series of n-alkanes, or in methyl esters of aliphatic acids in the case of very polar sorbents.

It has recently been established[70] that these esters have a homologous difference of 100 index units per methylene group even on such polar phases as Silar 5CP and Silar 10C,[70] whereas the series of alkyl acetates suggested previously for this purpose[10] exhibits a variation in the homologous difference with the polarity of the phase, as follows from a comparison of the indices for homologues tabulated in Ref.71. Hence acetates cannot be recommended as test substances for the classification of sorbents according to their ΔG^{CH_2} values.

As example of the assessment of dispersion polarity Table 2 lists values of ΔG^{CH_2} for several stationary phases, calculated by means of Eqn.(18).[63] Comparison of the capacities of these phases for dispersion interaction, assessed from the ΔG^{CH_2} values (Table 2) shows that SE-30, which is non-polar in the old terminology, is less capable of dispersion interaction than are the moderately polar OV-17 and Chalcomide M-18 OL, and is close to the more polar Triton X-305. Hence the decrease in the capacity for dispersion interaction is not proportional to the increase in polarity of the stationary phases[62,63]. Maximum dispersion polarity, i.e. capacity for dispersion interaction with a substance, is exhibited by such phases as squalane, the Kovats hydrocarbon $C_{87}H_{176}$,[72] and the Apiezons. The greatest dispersion polarity among the stationary phases in Table 2 is exhibited by squalane, which has the highest free energy of dissolution of n-alkanes.

Table 2. "Dispersion polarity"* of some stationary phases at 120 °C, estimated from the differential molar free energies of dissolution of a methylene unit of an n-alkane ΔG^{CH_2}.[63]

Stationary phase	b	$-\Delta G^{CH_2}$, cal mole^{-1}	Stationary phase	b	$-\Delta G^{CH_2}$, cal mole^{-1}
Squalane	0.2891	520	SE-30	0.2495	449
Dioctyl sebacate	0.2862	514	SE-31	0.2485	447
Chalcomide M-18 OL	0.2844	511	Igepal CO-880	0.2414	434
$C_{87}H_{176}$	0.2841	511	Triton X-305	0.2404	432
Apiezon M	0.2833	510	Pluroonic F-88	0.2362	425
Apiezon L	0.2821	507	Quadrol	9.2353	423
Dioctyl phthalate	0.2792	502	PEG-4000	0.2238	403
Flexol 8N8	0.2733	491	Carbowax-20M	0.2235	402
Castorwax	0.2684	483	PEG-600	0.2180	392
Tritolyl phosphate	0.2630	473	Carbowax-1000	0.2174	391
Ucon LB 1715	0.2603	468	DEGA	0.2105	379
Poly-Tergent J-300	0.2598	467	EGA	0.2091	376
Oronite N1W	0.2576	463	Zonyl-E7	0.2083	375
Diglycerol	0.2568	461	XF-1150	0.2053	369
OV-17	0.2551	459	Silar 10C	0.1960	353
SE-52	0.2548	458	Tris-CEP	0.1787	322

*Results from Ref.63 supplemented by calculations of ΔG^{CH_2} for several stationary phases taken from tables[27,71].

The capacity of stationary phases for other types of intermolecular, including dispersion, interaction is determined from the differential molar free energies of dissolution of the five test substances (Table 1), which are calculated by means of Eqn.(17). Indices of the test substances, specific retention volumes V_{gn} of n-alkanes, and values of the coefficient b, which are required for the calculation, can be taken from Reynolds' tables[27,71]. Density data for stationary phases at the temperature of analysis cannot usually be found in the literature, and must be determined specially. If the density ρ is unknown, values of ΔG can be calculated[63] to within 10% by means of the formula

$$\Delta G + 2.3RT \lg \rho = -2.3RT\left[\frac{I - 100n}{100} b + \lg \frac{V_{gn}T}{273}\right]. \qquad (20)$$

This does not affect the general picture in the estimation of polarity.

Table 3 gives as example the estimation of polarity for several stationary phases from the ΔG values of the five test substances[63]. Comparison of ΔG^{CH_2} and of the five ΔG values permits numerical assessment of the capacity of the stationary phases for intermolecular interactions—dispersion, orientation, induction and donor—acceptor—including hydrogen bonding. The larger the value of ΔG for a given test substance the greater the capacity of the phase for those intermolecular interactions that are tested by this substance (Table 1). Thus in the thermodynamic treatment of polarity the most polar stationary phase will be that exhibiting the highest ΔG values for every test substance among comparable stationary phases, and the most non-polar that with which all five ΔG values are least. Inspection of Table 3 on this basis indicates SE-30 to be the most non-polar, and Oronite N1W the most polar. Table 3 indicates also that each stationary phase has its individual features. For example, the retention of alcohols on Oronite N1W, Poly-Tergent J-300, and Chalcomide M-18 OL, and that of organic bases on Oronite N1W, are greater than on polyethylene glycols. Aromatic compounds are retained most strongly by Oronite N1W, dioctyl sebacate, Chalcomide M-18 OL, Flexol 8N8, and Poly-Tergent J-300 (Table 3). The contribution of dispersion interaction to the total ΔG value can be determined as in Ref.62.

Table 3. Polarities* of some stationary phases at 120 °C.[63]

Stationary phase	$-(\Delta G + 2.3RT \lg \rho)$, cal mole^{-1}				
	benzene	butan-1-ol	pentan-2-one	1-nitropropane	pyridine
Apiezon L	2820	2450	2600	2820	3110
Apiezon M	2820	2460	2610	2810	3100
Dioctyl sebacate	3250	3420	3300	3800	3750
Chalcomide M-18 OL	3220	3870	3360	3980	3840
Dioctyl phthalate	3050	3200	2310	3770	3660
Flexol 8N8	3110	3530	3270	3860	3690
Castorwax	3060	3510	3260	3640	3950
Tritolyl phosphate	2910	3320	3140	3840	3710
Ucon LB 1715	2890	3360	2990	3550	3580
Poly-Tergent J-300	3080	3710	3240	3930	3950
Oronite NIW	3840	4400	3980	4690	4710
Diglycerol	930	2730	1680	2330	3360
SE-52	2580	2470	2610	2870	2950
SE-30	2530	2410	2540	2740	2850
SE-31	2540	2430	2560	2760	2870
Igepal CO-880	2910	3510	3020	3870	3830
Triton X-305	2650	3260	2760	3620	3570
Pluronic F-88	2950	3530	3020	3880	3810
PEG-4000	2860	3520	2960	3890	3830
Carbowax 20M	2870	3470	2950	3870	3810
PEG-600	2810	3670	3020	3910	3990
Carbowax 1000	2860	3630	3030	3940	3980
DEGA	2460	3080	2680	3550	3700
EGA	2450	2980	2650	3510	3540
Zonyl E-7	2220	2500	3040	3440	3300
XF-1150	2450	3000	2960	3780	3440
Quadrol	2380	3620	2870	3460	3730

*Results from Ref.63 supplemented by calculation for stationary phases from Refs.27 and 71.

The system proposed[62-64] for assessing polarity from the ΔG^{CH_2} values and the five ΔG values of the Rohrschneider–McReynolds test substances is universally applicable. It does not require the "zero polarity" phase necessary in other methods for estimating the polarity of stationary phases[24,27,58], and can be extended to determination of the polarity of adsorbents in gas chromatography if values are included for

the differential molar free energies of adsorption ΔG_A of the test substances. The polarity of adsorbents can be calculated by means of the equations[63]

$$\Delta G_A^{CH_2} = -2.3RTb_A = -2.3RT\,[\lg V_{g(n+1)} - \lg V_{gn}], \quad (21)$$

$$\Delta G_A = -2.3RT\left[\frac{I-100n}{100}\,b + \lg V_{gn} - \lg RTS\right], \quad (22)$$

$$\delta(\Delta G)_{A_1A_2} = \frac{1}{100}(I_{A_1}\Delta G_{A_1}^{CH_2} - I_{A_2}\Delta G_{A_2}^{CH_2}) - 2.3RT\,(a_{A_1} - a_{A_2}) + 2.3RT \lg S_{A_1}/S_{A_2}, \quad (23)$$

in which a is the constant and b the coefficient in the relation $\lg V_{gn} = a + bn$ for n-alkanes analysed on an adsorbent A, where $b_A = \lg V_{g(n+1)} - \lg V_{gn}$, while I_{A_1} and I_{A_2} are the retention indices of the substance on adsorbents A_1 and A_2, with $\Delta G_{A_1}^{CH_2}$ and $\Delta G_{A_2}^{CH_2}$ the differential molar free energies of adsorption of a methylene unit in n-alkanes on these adsorbents, and S_{A_1} and S_{A_2} (in $cm^2\ g^{-1}$) their specific surfaces.

The single method of using free energies of sorption for quantitative assessment of the capability of stationary phases and adsorbents for intermolecular interactions with substances undergoing analysis makes it possible to characterise every sorbent individually.

2. Assessment of Selectivity

The term "selectivity" is widely used in gas chromatography, but it is often applied without regard to its thermodynamic basis, consequently with different and occasionally incorrect interpretations. For example, selectivity and column efficiency have been identified in one book[74]. Several papers regard selectivity as synonymous with polarity[38,40] or as the ability to separate two substances of closely similar boiling points, and distinguish three types of selectivity defined in different ways[75].

Actually the separating ability of a column is a result of its selectivity and efficiency. The former depends solely on the equilibrium characteristics in the sorbent–gas system; it indicates the difference in retention of the substances undergoing analysis, and is assessed in terms of the relative retention. Selectivity can be expressed quantitatively in terms of thermodynamic quantities. Efficiency depends on kinetic processes occurring in the column and influencing the peak widths; it is estimated as the height of a theoretical column H. It follows from van Deemter's rate theory[76] that H depends on the velocity of the carrier gas, diffusion, and resistance to mass exchange. The separation of two substances depends both on the selectivity and on the efficiency of the column, and is measured by the separation factor R,[43] which includes the distance d between the retention times of the substances and the widths w of their peaks:

$$R = 2d/(w_1 + w_2). \quad (24)$$

It is evident from this formula that the larger is d the higher the selectivity, and that the wider the peaks the lower the efficiency and hence the overall separation.

A thermodynamic examination of comparable gas-chromatographic processes will help to introduce complete clarity into an understanding of selectivity, which is used in two cases—to compare the abilities of (i) a given sorbent to retain two substances, and (ii) two sorbents to retain a given substance—as a characteristic of the properties of a sorbent. Both cases have been considered in terms of thermodynamics, and selectivity has been determined quantitatively from differences in differential molar free energy of mixing $\delta(\Delta G^E)$.[57,77]

The selectivity of a stationary phase in the separation of two substances is defined by the factor

$$\alpha_{ij} = \frac{\gamma_j^\infty p_j^0}{\gamma_i^\infty p_i^0} = (e^{\Delta G_j^E/RT}/e^{\Delta G_i^E/RT})\frac{p_j^0}{p_i^0}, \quad (25)$$

in which γ_i^∞ and γ_j^∞ are the activity coefficients of substances i and j at infinite dilution, p_i^0 and p_j^0 are their saturated vapour pressures under 1 atm at the column temperature, and ΔG_i^E and ΔG_j^E their excess free energies of mixing on the given stationary phase. After rearranging Eqn.(25) we obtain a quantitative assessment of the selectivity of a stationary phase in terms of the difference in excess free energies of dissolution of the two substances:

$$\delta(\Delta G^E)_{ij} = \ln \alpha_{ij} = \Delta G_i^E - \Delta G_j^E. \quad (26)$$

Since[68,77-79]

$$\delta(\Delta G^E)_{ij} = 2.3RT \lg \gamma_i/\gamma_j. \quad (27)$$

the selectivity of a given stationary phase with respect to two substances, i.e. the difference in its ability to retain them at a given temperature, is determined by the difference in the excess energies of mixing: it can be found from the polarity expressed in terms of ΔG by means of the equation[63,64]

$$\delta(\Delta G^E)_{ij} = \delta(\Delta G)_{ij} - 2.3RT \lg p_i^0/p_j^0. \quad (28)$$

The calculation of selectivity by means of this formula requires knowledge of the vapour pressures of the pure substances p_i^0 and p_j^0 under 1 atm at the analysis temperature. When the polarity of the phase expressed in free energies is unknown, the first term in Eqn.(28) can be calculated from the difference in the retention indices of i and j by means of the equation[44]

$$\delta(\Delta G)_{ij} = -2.3RTb\frac{\delta I_{ij}}{100}. \quad (29)$$

It follows from (28) and (29) that the selectivity of one stationary phase with respect to substances i and j can be calculated by means of the formula[63,64]

$$\delta(\Delta G^E)_{ij} = -2.3RT\left[b\frac{\delta I_{ij}}{100} + \lg p_i^0/p_j^0\right]. \quad (30)$$

The second case—the selectivity of two stationary phases Ph_2 and Ph_1 with respect to a given substance a—is expressed quantitatively by the formula[77]

$$\delta(\Delta G^E)_{Ph_2Ph_1} = 2.3RT \lg \gamma_{Ph_2}/\gamma_{Ph_1}, \quad (31)$$

in which γ_{Ph_2} and γ_{Ph_1} are the activity coefficients of i at infinite dilution in the two phases. Recently it has been shown[63,64] that selectivity can easily be determined quantitatively from the polarities of the phases expressed in terms of free energies. Thus at a given temperature the excess energy of i on the phases will be given by the classic equations

$$\Delta G_{Ph_2}^E = \Delta G_{Ph_2} + \Delta G_e, \quad (32)$$

$$\Delta G_{Ph_1}^E = \Delta G_{Ph_1} + \Delta G_e, \quad (33)$$

where ΔG_e is the differential molar free energy of evaporation of the pure substance i under 1 atm at the analysis temperature, and ΔG_{Ph_2} and ΔG_{Ph_1} are the differential molar free energies of dissolution of i in the phases Ph_2 and Ph_1. From (33) and (32) we obtain for selectivity the thermodynamic formula

$$\delta(\Delta G^E)_{Ph_2Ph_1} = \Delta G_{Ph_2} - \Delta G_{Ph_1} = \delta(\Delta G)_{Ph_2Ph_1}. \quad (34)$$

Thus the selectivity of two stationary phases towards a substance analysed at a given temperature is determined quantitatively from the difference in its free energies of

dissolution on the phases and can be calculated from a table of estimated polarities of stationary phases (Table 3).

A single system for assessing selectivity can be obtained by selecting one of the stationary phases as reference, which should satisfy certain requirements. According to the thermodynamic treatment of polarity and selectivity the reference phase should have minimal ΔG values for all test substances and minimal differences between them: i.e.it should have minimal selectivity. Furthermore, it should be chemically homogeneous and should withstand high temperatures. These demands are met neither by squalane (whose disadvantages, including irreproducibility of the indices, have been criticised by Ettre[1] and by Supina[80]) nor by the hydrocarbon 24,24-diethyl-19,29-dioctadecylheptatetracontane, proposed by Kovats[72,73] to replace squalane, as is evident from Table 4.

Table 4. Choice of reference phase for assessing the selectivity of stationary phases on the thermodynamic criterion[64] $\delta(\Delta G)_{max}$.

Phase	Retention index for test cpd.*					ΔI_{max}	Energy of 1 i.u., cal mole^{-1}	$-\delta(\Delta G)_{max}$,
	benzene	butan-1-ol	pentan-1-ol	nitropropane	pyridine			
Squalane	653	590	627	652	699	109	—5.20	567
$C_{87}H_{176}$	674	600	630	664	724	124	—5.11	634
SE-30	668	643	671	716	740	97	—4.49	435
Hydrogenated Apiezon-30	671	599	632	667	736	137	—	—

*Underlining denotes indices of compounds for which ΔI_{max} and $\delta(\Delta G)_{max} = -0.023RTb\Delta I_{max}$ have been calculated.

Recently a comparison has been made[73] of the phases—hydrogenated Apiezon M, the hydrocarbon $C_{87}H_{176}$, and SE-30—with respect to their ability to reproduce the retention indices of the five test-substances, with the aim of seeking a null phase for the determination of selectivity by the Rohrschneider–McReynolds method. Prolonged operation over the range 120–200 °C showed that the indices at 120 °C remained almost unchanged for a year on SE-30, in contrast to the Kovats hydrocarbon. Since the reference phase should possess outstanding reproducibility of indices, and also satisfy the thermodynamic criterion, i.e.have a minimal difference in the free energies of dissolution of the test substances, we have made an estimate of ΔG values. Table 4 lists indices of the test substances for the four phases proposed as reference phases[27,72,73], the energy value of one index unit on each of the stationary phases, and values of the differences $\delta(\Delta G)_{max}$ in the free energies of dissolution of two substances, one of which is retained the longest in the column, whereas the other is eluted first from the column. Among the four stationary phases compared the Kovats hydrocarbon has the maximum selectivity and is therefore least suitable as reference phase for the assessment of selectivity. Minimal selectivity is exhibited by SE-30, which is recommended as reference phase[63,64].

A quantitative assessment of the selectivity of a stationary phase for a given test substance is a measure of its specific interaction with the latter in comparison with SE-30. Table 5 shows as example the selectivities of several stationary phases in terms of $\delta(\Delta G^E)_{Ph,SE}$. It includes for comparison selectivity estimates according to McReynolds[27] based on ΔI values†. It is evident that the former method of assessment is far more informative. As example we compare two phases—Triton X-305 and Igepal CO-880—that are identical on the Rohrschneider–McReynolds view, since their ΔI values differ by 20 index units: actually they exhibit differences in practical gas chromatography, which can be clearly traced in the $\delta(\Delta G^E)$ data, for Igepal CO-880 is three times as selective as Triton X-305 towards aromatic compounds, and twice as selective in the separation of carbonyl compounds. Although the Rohrschneider–McReynolds method shows identity of XF-1150 and Carbowax-20M in the separation of aromatic compounds, alcohols, and amines, the $\delta(\Delta G)_{Ph,SE}$ values indicate that the latter phase has an advantage for the separation of all three classes of compounds. The phases EGA and XF-1150 are also identical according to their ΔI values in the analysis of carbonyl compounds and nitroderivatives, whereas the $\delta(\Delta G^E)$ values indicate that XF-1150 is four times as selective towards the former compounds, and 50% more selective towards the latter, which is confirmed by experiment[63]. Another pair—tritolyl phosphate and Poly-Tergent—have the same selectivity in the separation of aromatic compounds and amines according to ΔI data, but differ sharply according to the $\delta(\Delta G^E)$ values. The choice of optimum conditions for gas-chromatographic analysis of a mixture on the basis of the latter type of data has been described in detail[81] for analysis of a mixture of saturated and unsaturated aldehydes and ketones.

Table 5. Comparison of selectivities of stationary phases based on $\delta(\Delta G^E)_{Ph,SE-30}$ values and on McReynolds constants (at 120 °C).[63]

$-\delta(\Delta G^E)_{Ph,SE-30}$, cal mole^{-1}					Stationary phase	$\Delta I_{Ph,squalane}$				
benzene	butan-1-one	pentan-2-one	nitropropane	pyridine		benzene	butan-1-one	pentan-2-one	nitropropane	pyridine
290	40	60	80	260	Apiezon M	31	22	15	30	40
290	50	70	70	250	Apiezon L	32	22	15	32	42
720	1010	760	1060	900	Dioctyl sebacate	72	168	108	180	123
690	1460	820	1240	990	Chalcomide M-18 OL	89	280	143	239	165
520	790	670	1030	810	Dioctyl phthalate	92	186	150	236	167
580	1120	730	1120	840	Flexol 8N8	96	254	164	260	179
530	1100	720	900	1100	Castorwax	108	265	175	229	246
380	910	600	1100	860	Tritolyl phosphate	176	221	250	374	299
360	960	450	810	730	Ucon LB 1715	132	297	180	275	235
550	1300	700	1190	1800	Poly-Tergent J-300	168	366	227	350	308
1310	1990	1440	1950	1860	Oronite N1W	185	370	242	370	327
50	60	70	130	100	SE-52	32	72	65	98	67
10	20	20	20	20	SE-31	16	54	45	65	43
380	1100	480	1130	980	Igepal CO-880	259	461	311	482	426
120	850	220	880	720	Triton X-305	262	467	314	488	430
420	1120	480	1140	960	Pluronic F-88	262	461	306	483	419
330	1110	420	1150	980	PEG-4000	325	551	375	582	520
340	1060	410	1130	960	Carbowax 20M	322	536	368	572	510
280	1260	480	1170	1140	PEG-600	350	631	428	632	605
330	1220	490	1200	1130	Carbowax 1000	347	607	418	629	589
—70	670	140	810	850	DEGA	378	603	460	665	658
—80	570	110	770	690	EGA	372	576	453	655	617
—310	90	500	700	450	Zonyl E-7	223	359	468	549	465
—80	590	420	1040	590	XF-1150	308	520	470	669	528
—150	1210	330	720	880	Quadrol	214	571	357	472	489

†It has already been mentioned that comparison based on values of $\Delta I = I_{Ph} - I_{sql}$ is incorrect because of different energy equivalents of an index unit of different stationary phases (Section IV).

The above results provide clear evidence that the proposed thermodynamic assessment of the selectivity of stationary phases[63,64] is definitely superior to the McReynolds system and reveals most fully the gas-chromatographic possibilities of a sorbent. It can be extended to gas-adsorption chromatography, since Eqns.(30)–(34) for estimating selectivity from $\delta(\Delta G^E)$ data are still valid[63].

Thus the rigorous thermodynamic treatment of polarity and selectivity in gas chromatography and the availability of equations enabling these properties of sorbents to be determined from thermodynamic functions quantitatively in terms of retention indices enable a single, universally applicable system to be constructed, which will make it possible to find the optimum form of gas-chromatographic analysis to solve a specific problem.

V. CALCULATION OF ENERGY CONTRIBUTIONS BY FRAGMENTS OF MOLECULE ANALYSED

The use of retention indices as gas-chromatographic parameters makes it possible for a qualitative analysis to yield also data for thermodynamic calculation of the contributions, by individual groups in the compounds analysed, to the differential molar free energy of dissolution. For this purpose the formula

$$\delta(\Delta G) = -2.3RTb\frac{\delta I_{ij}}{100}, \qquad (35)$$

is used[44], in which δI_{ij} is the difference between the retention indices of two comparable compounds analysed under the same conditions. Equation (35) has been employed in a comparison of the methyl esters of aliphatic and monounsaturated acids i and j to determine the change in free energy of dissolution on introduction of a double bond into the molecule. On the non-polar phase SE-30 the presence of a double bond diminishes this free energy by 80–120 cal mole^{-1}, but on a polar phase (Silar 5CP) an average increase of 80 cal mole^{-1} is evident at 200 °C.[48]

In analogous heteroatomic compounds the replacement of oxygen by sulphur increases the differential molar free energy of dissolution by 1020 ± 30 cal mole^{-1} independently of the character of the stationary phase[44]. Such an increase is observed on passing from aliphatic ethers, furan, oxolan, dioxan, and their substituted derivatives to sulphides, thiophens, thiolans, and dithians[44]. Calculation based on the application of formula (35) to the difference in retention indices between sulphur- and oxygen-containing compounds of analogous structure indicates that on the non-polar Apiezon M and the polar polyethylene glycol 1000 the retention of both types of compounds is a consequence mainly of dispersion interaction[44].

Equation (35) can be used also to determine the contribution by a functional group in metameric compounds, i.e. compounds of the same class containing the same number of carbon atoms but differing in the position of the functional group. This would indicate whether it is legitimate to assume, when the contribution by a functional group to the free energy of dissolution of one homologous series is known, that this contribution will be the same in another homologous series. We have used earlier results on thiatridecane metamers[82] to trace the variation in the energy contribution by the functional thio-group as it moves deep into an unbranched aliphatic chain[84]. If the contributions to the free energy ΔG by fragments of a molecule are additive[10] the metameric sulphides should be described by the single equation

$$\Delta G = 2\Delta G^{CH_3} + (n-2)\Delta G^{CH_2} + \Delta G^{-S-}. \qquad (36)$$

Analysis of the results[82] shows that the energy contributions ΔG^{CH_3} and ΔG^{CH_2} of the metamers are the same, whereas ΔG^{-S-} changes, decreasing as the sulphur atom moves along the chain. This is readily seen from Table 6, which gives the differences in free energy of dissolution of the thiatridecane metamers relative to 2-thiatridecane. As the sulphur atom is displaced from position 2 to position 7 ($K = 2$ and 7 respectively), the differential molar free energy of dissolution diminishes by 234 and 308 cal mole^{-1} on Apiezon M and polyethylene glycol 1000 respectively. Hence additive equations analogous to (36) can be used only for specific homologous series. The position of a functional group in the molecule must be indicated in a statement of the contribution by the group.

Table 6. Retention indices I and free energies of dissolution ΔG of metameric thiatridecanes on Apiezon M and on PEG-1000 at 130 °C.

K*	Apiezon M at 130°C				PEG-1000 at 130°C			
	I metamer	$-\Delta G$ metamer, cal mole^{-1}	$-\delta(\Delta G)_{2,\,K>2}$** cal mole^{-1}	energy per S, cal mole^{-1}	I metamer	$-\Delta G$, metamer cal mole^{-1}	$-\delta(\Delta G)^{*}_{2,\,K>2}$ cal mole^{-1}	energy per S, cal mole^{-1}
2	1520	6831	0	—1595	1757	5783	0	—2173
3	1493	6696	135	—1460	1710	5600	183	—1990
4	1481	6636	195	—1400	1692	5530	253	—1920
5	1477	6616	215	—1380	1684	5499	284	—1889
6	1475	6606	225	—1370	1681	5487	296	—1877
7	1473	6597	234	—1360	1678	5475	308	—1865

*Position of sulphur in metameric thiatridecane, $2 \leq K \leq 7$.
**$\delta(\Delta G)$ is the difference in free energies of dissolution between 2-thiatridecane and the metamer in which the position of the sulphur atom is $K > 2$.

Table 7. Contributions per methylene group ΔI^{CH_2} and ΔG^{CH_2} in various homologous series[65,82,83].

Homologues	Phase	T, °C	ΔI^{CH_2}	$-\Delta G^{CH_2}$, cal mole^{-1}
Nonane-octane	Apiezon M	130	100	498
Nonane-octane	PEG-1000	130	100	389
Nonane-octane	Apiezon M	125	100	503
Nonane-octane	PEGA	125	100	375
Nonane-octane	XF-1150	125	100	359
Nonane-octane	oxy-ββ'-dipropionitrile	50	100	449
Nonanal-octanal	Apiezon M	125	100	503
Nonanal-octanal	PEGA	125	100	375
Nonan-2-one-octan-2-one	Apiezon M	125	100	503
Hexane-1,6-dithiol-pentane-1,5-dithiol	Apiezon M	130	103	513
	PEG-1000	130	97	377
Octan-1-ol-heptan-1-ol	PEG-1000	130	108	420
Hept-2-enal-hex-2-enal	XF-1150	125	112	402
Hept-2-enal-hex-2-enal	oxy-ββ'-dipropionitrile	50	84	377
Heptan-2-one-hexan-2-one	oxy-ββ'-dipropionitrile	50	83	373

Previous results[65,82,83] can be used to calculate the energy contribution by a methylene unit in various homologous series analysed under identical conditions. Table 7 shows that $\Delta I^{CH_2} = 100$ does not apply to all homologous series: it is observed only with straight-chain aldehydes and methyl ketones on Apiezon M and PEGA, whose differential molar free energy for dissolution of a methylene group is the same as with n-alkanes. For homologous series in which

$\Delta I^{CH_2} = 100$, Eqn.(35) can be used to calculate the energy contribution due to specific interaction of the functional group with the stationary phase, from the difference between the retention indices of the given substance and the n-alkane containing the same number of carbon atoms. For αβ-unsaturated aldehydes on XF-1150 and on oxy-ββ′-dipropionitrile $\Delta I^{CH_2} \neq 100$ and ΔG^{CH_2} differs substantially from the values obtained for n-alkanes (Table 7). A similar pattern is observed for dithiols and other compounds.

Hence the energy contribution whether of a methylene or of a functional group depends on the homologous series and the character of the stationary phase. It is thus inadvisable to use energetic contributions to the free energy of dissolution of functional groups, to estimate the polarity of a stationary phase[39], in isolation from the total differential molar free energy of dissolution of the test substance.

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