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## Comparison of methods for the determination of the polarity and selectivity of stationary phases in gas chromatography from a thermodynamic point of view

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### ABSTRACT

Different scales proposed for the evaluation of polarity and selectivity in gas chromatography as relative and absolute values were compared. It is shown that the scale including six parameters,  $\Delta G(X)$ ,  $\Delta G(Y)$ ,  $\Delta G(Z)$ ,  $\Delta G(U)$ ,  $\Delta G(S)$  and  $\Delta G(\text{CH}_2)$ , is more suitable and allows a unified system to be obtained for the polarity and selectivity of conventional stationary phases, organic and inorganic salts and polymer sorbents. The main equation for the calculation of the partial molar free energy of sorption,  $\Delta G$ , is simplified for capillary gas chromatography.

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### INTRODUCTION

Progress in gas chromatography (GC) has greatly increased the number of available stationary phases and sorbents. Some of these stationary phases have similar or identical chemical structures and sorption properties<sup>1,2</sup>. The main chromatographic suppliers usually offer up to 200 stationary phases with different properties<sup>3,4</sup>. In recent years, new groups of stationary phases, including organic salts<sup>5,6</sup> and crystal hydrates of inorganic salts<sup>7,8</sup>, have been described. Usually the selection of a suitable stationary phase for solving different problems is difficult and one needs a classification system suitable for comparison of stationary phases. The problem of a unified method for the selection and comparison of sorbents in GC still remains.

Many different approaches have been used to compare and classify different stationary phases and sorbents. All of them operate with the term "polarity". Polarity is used in GC to describe the ability of the sorbent to enter into different types of interactions with sorbates. The concepts of polarity and selectivity in GC are not

clearly defined and are interpreted in different ways by different investigators. In our opinion, GC polarity should be defined as the capacity of the sorbent for various intermolecular interactions: dispersive, inductive, orientative and donor-acceptor<sup>9</sup>.

The problem of polarity is still debated and many papers have been devoted to it. These can be divided into several groups. In some papers polarity is evaluated on the basis of relative parameters: values of retention indices of several test compounds<sup>1,2,10-16</sup>, sometimes in combination with the effective molecular weights of the sorbates<sup>17-19</sup>, or on the basis of the ratio of retention parameters of neighbouring *n*-alkanes<sup>20-23</sup>.

Evaluation of polarity utilizing thermodynamic values has often been undertaken. Such values are the excess free energy of sorption of a methylene unit in an *n*-alkane or any other monofunctional homologous series<sup>24-28</sup>; the partial molar free energy of sorption of a methylene unit itself<sup>29,30</sup> or divided on stationary phase density<sup>31</sup> [ $\Delta G(\text{CH}_2)$ ]; excess partial molar enthalpies<sup>32</sup> and partial molal free energies<sup>33</sup> of selected functional groups; and the six-parameter scale based on partial molar free energies of five test compounds and the methylene unit<sup>9,34-36</sup>.

In this paper we compare from the thermodynamic viewpoint different methods for the evaluation of polarity in order to reveal the physical meaning of some scales. We also consider the advantages and shortcomings of the thermodynamic polarity scales. The aim of this paper is to propose a convenient quantitative thermodynamic scale for the evaluation of stationary phase polarity that will be suitable for capillary GC.

There are great differences between the definition of a "polar substance" in physical chemistry and the concept of a polar sorbate and sorbent in chromatography. In physical chemistry "polarity" is a property of one individual substance. This property is associated with the dipole moment of a molecule. The ability of this molecule to interact with other molecules and the change in their properties during interaction is not considered. Hence compounds without dipole moments are termed non-polar. In chromatography some non-polar compounds from the physico-chemical viewpoint such as benzene, *p*-dinitrobenzene, pyrazine and 1,4-dioxane are assumed to be polar sorbates. The retention times of these compounds may increase owing to complex formation and donor-acceptor interactions with some stationary phases.

In chromatography, retention is determined primarily by the energy of intermolecular interactions between the analyte substances and the liquid stationary phases or adsorbents. The partial molar free energy of solution or adsorption is essentially a total of the energies of intermolecular interactions, both non-specific, determined by physical forces, and specific electron donor-acceptor interactions of a chemical nature. When all experimental conditions are equal, a polar sorbate is retained longer on a more polar than on a less polar column<sup>21</sup>.

It must be considered that the partial molar free energy of sorption is the result of all types of interactions. It is not possible to determine separately any part of it, dispersive, inductive, orientative or donor-acceptor. To evaluate the polarity one must use several test compounds which simulate the principal types of intermolecular interactions<sup>9</sup>. From this viewpoint we shall discuss some approaches to the evaluation of polarity in GC.

## EVALUATION OF POLARITY USING THE METHYLENE UNIT OF A HOMOLOGOUS SERIES

*n*-Alkanes are capable of dispersive and weak inductive interactions. In spite of this, *n*-alkanes are used predominantly for the determination of the polarity of stationary phases, *e.g.*, their ability to enter into all types of intermolecular interactions including orientation and donor-acceptor forces. *A priori* it is assumed that the decrease in the energy of dispersive interactions of the sorbents with *n*-alkanes is proportional to their ability to enter into other types of interactions.

In initial studies it was proposed to estimate the polarity of a sorbent by using the specific retention volumes of *n*-octane or the ratio of the retentions of two neighbouring homologues of any homologous series<sup>21</sup>. A similar approach was proposed by Chovin and Lebbe<sup>20</sup>. In their scale, the polarity of  $\beta,\beta'$ -oxydipropionitrile was considered to be equal to unity (polar reference stationary phase) and the polarity of squalane was considered to be equal to zero (non-polar reference phase). The polarity (*P*) of a phase of interest was then calculated as follows:

$$P_x = \frac{\log(t'_{n+1}/t'_n)_{\text{squ}} - \log(t'_{n+1}/t'_n)_x}{\log(t'_{n+1}/t'_n)_{\text{squ}} - \log(t'_{n+1}/t'_n)_{\beta,\beta'}} \quad (1)$$

where  $t'_{n+1}$  and  $t'_n$  are the adjusted retention times of *n*-alkanes with *n* + 1 and *n* carbon atoms, respectively, and squ,  $\beta,\beta'$  and *x* refer to the stationary phases squalane,  $\beta,\beta'$ -oxydipropionitrile and the tested stationary phase *x*, respectively. It was mentioned that the polarity of some stationary phases might be larger than 1. The existence of stationary phases with polarities lower than zero was not considered<sup>20</sup>.

In order to understand the physical meaning of eqn. 1, let us modify it in the following way:

$$P_x = \frac{2.3RT \log(t'_{n+1}/t'_n)_{\text{squ}} - 2.3RT \log(t'_{n+1}/t'_n)_x}{2.3RT \log(t'_{n+1}/t'_n)_{\text{squ}} - 2.3RT \log(t'_{n+1}/t'_n)_{\beta,\beta'}} \quad (2)$$

where *R* is the universal gas constant and *T* is the absolute temperature of the analysis. Eqn. 2 shows that the polarity in the scale of Chovin and Lebbe<sup>20</sup> is equivalent to the partial molar free energy of sorption of a methylene group for *n*-alkanes,  $\Delta G(\text{CH})_2$ , since  $\Delta G(\text{CH})_2$  may be calculated as follows:

$$\Delta G(\text{CH}_2) = -2.3RT \log(V_{g,n+1}/V_{g,n}) \quad (3)$$

where  $V_{g,n+1}$  and  $V_{g,n}$  are the specific retention volumes for *n*-alkanes with *n* + 1 and *n* carbon atoms, respectively.

If homologues are analysed under the same chromatographic conditions, eqn. 3 can be simplified to

$$\Delta G(\text{CH}_2) = -2.3RT \log(t'_{g,n+1}/t'_{g,n}) \quad (4)$$

As was demonstrated previously<sup>9</sup>,  $\Delta G(\text{CH}_2)$  is a measure of the capacity of a stationary phase for dispersive interactions.

Eqn. 2 can be transformed to the following equation using eqn. 3 or 4:

$$P_x = \frac{\Delta G(\text{CH}_2)_{\text{squ}} - \Delta G(\text{CH}_2)_x}{\Delta G(\text{CH}_2)_{\text{squ}} - \Delta G(\text{CH}_2)_{\beta, \beta'}} \quad (5)$$

In eqn. 5, the numerator is the difference in the capacity of  $n$ -alkanes for dispersive interactions with the stationary phase  $x$  and with squalane, while the denominator is the difference in the capacity of  $n$ -alkanes for dispersive interactions with the two reference stationary phases. Hence the scale of Chovin and Lebbe<sup>20</sup> really evaluates the possibility of stationary phases for dispersive interactions in relative units. On this scale a lower  $\Delta G(\text{CH}_2)$  value corresponds to a higher polarity  $P$ . Consequently, this scale ranks stationary phase according to their capacity for dispersive interactions with  $n$ -alkanes. The energy of dispersive interactions depends on the polarity of the stationary phase, but will change in a non-proportional manner with capacity for orientative and donor-acceptor interactions. This correlation is not as simple as was assumed previously<sup>20</sup>.

The scale of polarity  $\Pi_{\text{rel}}$ , based on a methylene group, was proposed by Sidorov<sup>22</sup>. The value of the polarity parameter  $t'_{\text{CH}_2}$  is defined as follows:

$$t'_{\text{CH}_2} = t'_{n+1}/t'_n \quad (6)$$

where  $t'_{n+1}$  and  $t'_n$  are the adjusted retention times of  $n$ -alkanes with  $n+1$  and  $n$  carbon atoms, respectively. On the basis of  $t'_{\text{CH}_2}$ , the relative polarity  $\Pi_{\text{rel}}$  for the studied stationary phase was calculated using the equation

$$\Pi_{\text{rel}} = 100 \cdot \frac{[\log(t'_{\text{CH}_2})_{\text{squ}} - \log(t'_{\text{CH}_2})_x]}{\log(t'_{\text{CH}_2})_{\text{squ}}} \quad (7)$$

Considering eqns. 4 and 6, we can easily transform eqn. 7 into

$$\Pi_{\text{rel}} = \frac{\Delta G(\text{CH}_2)_{\text{squ}} - \Delta G(\text{CH}_2)_x}{\Delta G(\text{CH}_2)_{\text{squ}}} \quad (8)$$

which is similar to eqn. 5. The main difference between the polarity scales in refs. 20 and 22 is that in the latter only one reference stationary phase, squalane, is used but the practical meaning of the two scales are the same. They reflect only the energy of dispersive interactions of a methylene unit with a sorbent in relative units.

The thermodynamic polarity scale proposed by Novak *et al.*<sup>24</sup> also utilizes the retention of a methylene unit for ranking of stationary phases, but does not include any reference stationary phase. According the concept of "reluctance", there are differences in properties between an ideal solution and a real solution of a sorbent in a stationary phase. These differences are minimal for the solution of an  $n$ -alkane in a hydrocarbon stationary phase such as squalane. It was accepted that more polar stationary phases have higher values of the excess Gibbs partial molar free energy of solution for  $n$ -alkanes. The measurement of the total excess Gibbs partial molar free energy of sorption of molecules is difficult, and therefore polarity was defined as the

excess Gibbs partial molar free energy of sorption for a methylene group,  $\Delta G^E(\text{CH}_2)^{24}$ . The values of  $\Delta G^E(\text{CH}_2)$  can be calculated using the equation

$$\Delta G^E(\text{CH}_2) = RT \ln [(V_{g,n}/V_{g,n+1})/(P_n^0/P_{n+1}^0)] \quad (9)$$

where  $V_{g,n+1}$  and  $V_{g,n}$  are the specific retention volumes and  $P_{n+1}^0$  and  $P_n^0$  are the saturated vapour pressures of two pure liquid homologues (with  $n+1$  and  $n$  carbon atoms, respectively) of any homologous series selected as test compounds.

To determine the values of the excess energies for sorption, one requires information about the vapour pressures of two test compounds at the temperature of the analysis, which are usually calculated by empirical equations of low precision. The accuracy in the determination of  $\Delta G^E(\text{CH}_2)$  values is generally poor.

It was assumed that the  $\Delta G(\text{CH}_2)$  value does not change for any series of homologues with  $n > 5$ , analysed on any stationary phase at any temperature. This assumption is not correct. Experimental data<sup>24</sup> show the differences in the values of the excess partial molar Gibbs free energies for sorption of homologous series. For example, on squalane  $\Delta G^E(\text{CH}_2) = -35$  kcal/mol for  $n$ -alkanes,  $-17$  kcal/mol for  $n$ -alkyl acetates and  $-23$  kcal/mol for  $n$ -alkanols. An investigation of surfactants as stationary phases demonstrated that for different series of homologues the  $\Delta G^E(\text{CH}_2)$  values may differ significantly. In some instances the excess partial molar Gibbs free energy for a methylene group in different homologous series may differ 5–6-fold<sup>26,27</sup>.

Let us compare the advantages of the scales of Novak *et al.*<sup>24</sup> and Chovin and Lebbe<sup>20</sup>. For this purpose we transform eqn. 9 into

$$\Delta G^E(\text{CH}_2) = -RT \ln (V_{g,n+1}/V_{g,n}) + RT \ln (P_{n+1}^0/P_n^0) \quad (10)$$

Thus, according to eqn. 3, one can obtain from eqn. 10 the equation

$$\Delta G^E(\text{CH}_2) = \Delta G(\text{CH}_2) + RT \ln (P_{n+1}^0/P_n^0) \quad (11)$$

The second term in eqn. 11 is proportional to the ratio of the saturated vapour pressures of two pure homologues. The ratio  $P_{n+1}^0/P_n^0$  does not depend on the type of stationary phase. Hence it becomes clear that the excess energy of sorption for a methylene group,  $\Delta G^E(\text{CH}_2)$ , and the partial molar Gibbs free energy of sorption,  $\Delta G(\text{CH}_2)$ , differ only by the constant, which depends on the vapour pressures of the test compounds and does not depend on the nature of the stationary phase. In general, the scales of Novak *et al.*<sup>24</sup> and Chovin and Lebbe<sup>20</sup> estimate the ability of a stationary phase for dispersive interactions with a methylene group.

Recently, Poole and co-workers<sup>29,30,37</sup> used the value of the partial molar Gibbs free energy of sorption for a methylene group,  $\Delta G(\text{CH}_2)$ , to measure the polarity of stationary phases and liquid organic salts. This scale, like the scale based on the excess partial molar Gibbs free energy of sorption for a methylene group<sup>24</sup>, does not use any reference stationary phase. The  $\Delta G(\text{CH}_2)$  value can be calculated easily and with high precision using, for example, eqn. 4. The  $\Delta G(\text{CH}_2)$  scale<sup>29,30</sup> utilizes the same *a priori* assumption that the decrease in energy of dispersive interactions on a polar phase is directly proportional to the capacity of that phase for polar interactions.

Of course, the  $\Delta G(\text{CH}_2)$  value is connected with the polarity of a stationary

TABLE I

ENERGETIC EQUIVALENTS OF A METHYLENE UNIT,  $\Delta G(\text{CH}_2)$ , AND RETENTION INDICES OF McREYNOLDS TEST COMPOUNDS<sup>1</sup> ON VARIOUS STATIONARY PHASES

Calculated using data in ref. 1.

Stationary phase	<i>b</i>	$-\Delta G(\text{CH}_2)$ (J/mol)	<i>I</i>				
			Benzene	2-Pentanone	1-Butanol	1-Nitropropane	Pyridine
Hallcomide M18 01	0.2844	2136	732	858	757	874	845
Pluronic P 85	0.2842	2135	712	676	708	803	828
Octoil S	0.2836	2130	854	980	874	1040	1034
Apiezon M	0.2833	2128	691	620	654	701	756
Polybutene 32	0.2832	2120	674	619	651	694	739
Diisooctyl adipate	0.2822	2120	731	777	753	856	839
Apiezon L	0.2821	2119	685	612	642	684	741
DEG stearate	0.2817	2116	726	764	743	841	828

phase but is not proportional to the energy of orientative and donor-acceptor interactions as was assumed in refs. 20-30. Really, the  $\Delta G(\text{CH}_2)$  values estimate only the ability of a stationary phase for dispersive interactions<sup>9</sup>. For some stationary phases the  $\Delta G(\text{CH}_2)$  values may be the same but their capacity for interactions with polar compounds may be different.

For example, in Table I are given eight stationary phases with similar values of  $\Delta G(\text{CH}_2)$ : hydrocarbons (Apiezon, polybutene), polyesters (Octoil S, DEG stearate) and amide (Hallcomide M18 01). One can see from Table I that the difference in the  $\Delta G(\text{CH}_2)$  values for the stationary phases may be less than 20 J/mol. At the same time, the difference in retention indices of test compounds may be more than 100 index units. These stationary phases cannot be considered to be identical or even similar. The data in Table I demonstrate that the ability of a stationary phase to undergo all types of interactions cannot be measured correctly by only one parameter, the  $\Delta G(\text{CH}_2)$  value. It is clear that there is no possibility of determining the chromatographic polarity of a stationary phase or sorbent using the chromatographic properties of only one type of molecule or fragment of molecule. In this instance it is impossible to evaluate by one parameter the ability of sorbent to undergo all types of intermolecular interactions with sorbates.

#### EVALUATION OF POLARITY USING RETENTION INDICES OF SEVERAL TEST SUBSTANCES

The polarity scale based on the sorption properties of several sorbents with different functional groups is more informative than those scales<sup>20-30</sup> based on only one parameter, the contribution of a methylene group to retention. For such scales of polarity one should select a number of test compounds simulating in the best way possible all intermolecular interactions: dispersive, orientative (dipole-dipole) and inductive interactions; and electron donor-acceptor interactions, including the capacity for hydrogen bonding.

This approach was used in well known classification schemes based on the

TABLE II

TEST COMPOUNDS USING FOR MEASUREMENT POLARITY ON THE McREYNOLDS SCALE

Definition	Test compound	Types of interaction tested
X	Benzene	Dispersive and $\pi$ -complex formation
Y	1-Butanol	Orientative with proton-donor and proton-acceptor capabilities <sup>a</sup>
Z	2-Pentanone	Orientative and proton-acceptor without proton-donor capability <sup>a</sup>
U	1-Nitropropane	High capability for orientative interactions (dipole moment, $\mu = 3.6D$ ), weak proton acceptor <sup>a</sup>
S	Pyridine	Weak orientative and strong proton acceptor <sup>a</sup>

<sup>a</sup> In combination with dispersive and orientative interactions.

retention indices of several test compounds proposed by Rohrschneider<sup>10</sup> and modified by McReynolds<sup>1</sup>. On this scale, polarity and selectivity may be described using five basic test compounds, benzene, 1-butanol, 1-nitropropane, 2-pentanone and pyridine. The polarity was measured by  $\Delta I$ . It was also assumed that the energy of dispersive interactions of a test compound determined on squalane is the same as that on any other stationary phase. In reality there must be differences in the dispersive interactions of test compounds with different stationary phases. However, on this scale<sup>10</sup>, this fact was not considered.

This classification system gained widespread popularity because about 200 widely used stationary phases were characterized using McReynolds constants<sup>1</sup>. Now about 400 stationary phases have been classified using this scale<sup>2-4,38,40</sup>. The principles of polarity and selectivity determination with this scale are reviewed elsewhere<sup>39,40</sup>.

Many criteria related to McReynolds constants have been recommended. For example, in catalogues of chromatographic suppliers and handbooks the sum of the first five constants,  $\sum_{i=1}^5 \Delta I_i$ , is often used to describe general polarity of stationary phases<sup>13,19,26,27,35,38</sup>. Similar to this parameter is the polarity index,  $CP^{3,15}$ , which can be calculated using the equation

$$CP = \frac{\sum_{i=1}^5 \Delta I_{\text{stat. phase}}}{\sum_{i=1}^5 \Delta I_{\text{OV-275}}} \cdot 100 \quad (12)$$

It is obvious that the scale based on the  $CP$  index, unlike the McReynolds scale, is restricted from both sides by squalane and OV-275.

Tarian *et al.*<sup>14</sup> recommended describing the polarity of a stationary phase using the parameter  $P_T$  which can be calculated as:

$$P_T = \frac{\sum_{i=1}^5 \frac{I_P - I_{sq}}{I_{sq}}}{5} \cdot 100 \quad (13)$$

TABLE III

COMPARISON OF McREYNOLDS CONSTANTS AND  $\sum \Delta I$ ,  $CP$  AND  $P_T$  CRITERIA FOR VARIOUS STATIONARY PHASES

Stationary phase	X	Y	Z	U	S	$\sum_{i=1}^5 \Delta I$	CP	$P_T$
OV-22	160	188	191	283	253	1075	25	33
Triton X-200	117	289	172	266	237	1081	26	34
Polypropylene glycol 2000	128	294	173	264	226	1085	26	34
Estinox	136	257	182	285	227	1087	26	34
Trimeric acid	94	271	163	182	378	1088	26	34
Pluracol-2010	129	295	174	260	227	1091	26	34
Poly 101	115	357	151	262	214	1099	26	34
Atpet 200	108	282	186	235	289	1100	26	35
Amin 220	117	380	181	293	133	1105	26	35
Maximum difference	64	198	40	101	255	30	1	2

To compare the informativity of the McReynolds scale with the scales obtained using eqns. 12 and 13, we considered data given as examples for eight stationary phases in Table III. It is seen that maximum difference in  $\sum_{i=1}^5 \Delta I_i$  values is less than 30 i.u. for all phases (see Table III), whereas the differences in  $CP$  values, calculated by eqn. 12, are less than 2 relative units. Consequently, stationary phases with similar values of  $\sum_{i=1}^5 \Delta I_i$  and  $CP$  are not interchangeable in practice. Obviously such parameters are less informative than the McReynolds constants. The  $\sum_{i=1}^5 \Delta I_i$ ,  $CP$ ,  $P_T$  and other similar parameters fail in the evaluation of the specific properties of a sorbent because of compensation effects.

In scales<sup>1,10-14</sup> which have a reference stationary phase (squalane, hydrogenated Apiezon, Apolan-87), polarity is evaluated simultaneously with the selectivity of a studied stationary phase in comparison with a reference stationary phase.

The problem of a reference stationary phase is eliminated in Evans and Haken's system of "selectivity indices"<sup>19</sup>. In this approach, the retention index of sorbate is divided into two parts, a dispersive index  $I_m$  and a selectivity index  $I^*$ :

$$I = I_m + I^* \quad (14)$$

The dispersive index may be calculated as the retention index of a hypothetical  $n$ -alkane with the same molecular mass as the sorbate:

$$I_m = \frac{M - 2.016}{0.14026} \quad (15)$$

where  $M$  is the molecular mass of the sorbate. The  $I_m$  value characterizes only the test



substance and is constant for any set of analytical conditions. The selectivity index  $I^*$  depends on the type of sorbate, sorbent and analytical conditions. There is some correlation between the selectivity indices of selected sorbates and the polarity of stationary phases<sup>19</sup>. However, the scale<sup>19</sup> which uses a hypothetical  $n$ -alkane molecular mass cannot be interpreted thermodynamically.

The retention index percentage contribution  $IP$  was introduced<sup>15</sup> to relate the solute retention index to the sum of ten retention indices corresponding to one stationary phase:

$$IP = \frac{100 I_P}{\sum_{P=1}^{10} I_i} \quad (16)$$

Using the  $IP$  parameter calculated from eqn. 16, most stationary phases were classified and separated into clusters containing groups of stationary phases with similar properties<sup>15</sup>.

The main disadvantage of scales<sup>1,10-19</sup> that use  $\Delta I$  and  $I$  values has been extensively discussed<sup>9,29,30,34,36,37</sup>. This disadvantage is connected with the great difference in the energetic equivalent of one index unit on different stationary phases<sup>9</sup>. The energetic equivalent of one index unit is calculated from

$$\Delta G_{i,u} = \Delta G(\text{CH}_2)/100 = -RT \ln(t'_{n+1}/t'_n) \quad (17)$$

where  $t'_{n+1}$  and  $t'_n$  are the adjusted retention times of two neighbouring homologues.

The values of the energetic equivalent of a retention index unit at the same column temperature may vary from  $-24$  to  $-5.2$  J/mol<sup>29</sup>. This means that for two stationary phases a sorbate may have the same retention index but a different energy of sorption<sup>9</sup>. This fact does not allow the interpretation of  $\Delta I$  values to find a physical meaning for polarity with such scales.

#### EVALUATION OF POLARITY OF SORBENTS USING $\Delta G'$ VALUES

Different approaches have been proposed for evaluating polarity from a thermodynamic point of view. Earlier we considered a thermodynamic scale of polarity based on the excess partial molar Gibbs free energy of sorption for a methylene group,  $\Delta G^E(\text{CH}_2)$  (ref. 24). It was also assumed that the polarity and selectivity of stationary phases can be defined in terms of the partial molar enthalpies of solution for certain functional groups, which were determined from the temperature dependence of the specific retention volumes of test compounds<sup>32</sup>. However, an evaluation of the capacity of stationary phases to retain polar substances without considering the entropy of sorption is not correct. Solution of polar compounds on polar stationary phases is accompanied not only by changes in the heat of solution but also with a decrease in the degree of freedom for the sorbate molecule. Neglecting the contribution of entropy can lead to a faulty conclusion.

This circumstance was considered by Reinbold and Risby<sup>32</sup>. The polarity of stationary phases was evaluated from the partial molal Gibbs free energies of sorption

for different functional groups<sup>33</sup>. This approach also is not correct, because the contribution of the same functional group in various molecules to the total energy of sorption may be different. The low informativity of  $\Delta G_{C=O}$  and  $\Delta G_{OH}$  parameters for the evaluation of the polarity of polyoxyethylene esters has been reported<sup>35</sup>.

Considering that five McReynolds test compounds adequately simulate the main types of intermolecular interactions (Table II), it was proposed to describe the polarity of sorbents using the partial molar Gibbs free energies of sorption for these compounds<sup>9,34</sup>. The capacity of the stationary phases for dispersive interactions on this scale was measured by a sixth parameter, the partial molar Gibbs free energy of sorption for a methylene group<sup>9,34</sup>.

The partial molar Gibbs free energy of solution for substances may be determined using the equation

$$\Delta G = -RT \ln(V_g T \rho / 273) \quad (18)$$

where  $V_g$  is the specific retention volume of the solute and  $\rho$  is the density of the stationary phase at the column temperature  $T$ <sup>41</sup>.

To simplify the problems relating to the determination of the specific retention volumes of all sorbates, it was recommended to calculate the partial molar Gibbs free energy of sorption using another equation:

$$\Delta G = RT \cdot \frac{(I - 100n)}{100} \cdot b + RT \ln \left( \frac{V_{gn} T \rho}{273} \right) \quad (19)$$

where  $I$  is the retention index of the solute,  $b$  the natural logarithm of the ratio of the specific retention volumes or adjusted retention times of  $n$ -alkanes eluted just before and after this solute,  $T$  the column temperature and  $V_{gn}$  the specific retention volume of an  $n$ -alkane with  $n$  carbon atoms<sup>34</sup>.

The measurement of the density of the stationary phase at the column temperature may be a problem in many instances. Therefore, it was recommended to use the value of  $\Delta G'$  calculated for each test substance using eqn. 20:

$$\Delta G' = \Delta G + RT \ln \rho \quad (20a)$$

$$\Delta G' = RT \left[ \frac{(I - 100n)}{100} \cdot b + \ln \left( \frac{V_{gn} T}{273} \right) \right] \quad (20)$$

Such an assumption in the calculation of the values of  $\Delta G'$  does not affect the overall picture for the evaluation of the polarity of stationary phases<sup>9,34</sup> in comparison with  $\Delta G$  values (eqn. 18), which give the correct evaluation of the polarity of the stationary phases.

The comparison of  $\Delta G(\text{CH}_2)$  and five values of  $\Delta G'$  for McReynolds test compounds permits the quantitative evaluation of the capacity of stationary phases for intermolecular interactions: dispersive, orientative and donor-acceptor.

The advantages of this scale<sup>9</sup> are the elimination of a reference stationary phase and the possibility of using retention indices and specific retention volumes of

*n*-alkanes from the literature. This method of calculating thermodynamic polarity is simple and may be used not only for stationary phases but also for adsorbents<sup>9</sup>. This scale was successfully used for the evaluation of the properties of ordinary stationary phases<sup>36</sup>. It was also used to investigate the ability of melted organic salts for undergo intermolecular interactions under gas chromatographic conditions<sup>6</sup>.

#### CALCULATION OF POLARITY USING ENERGETIC EQUIVALENTS OF RETENTION INDICES, $\Delta G(I)$ VALUES

It is well known that the partial molar free energy of sorption is related to the retention index by a very simple relationship:

$$\Delta G = A + BI \quad (21)$$

where *A* and *B* are constants under fixed chromatographic conditions<sup>42</sup>. The physical meaning of constant *B* was considered earlier<sup>43</sup>. It was demonstrated that *B* is the energetic equivalent of an index unit. Thus *BI* is the energetic equivalent of the retention index of a sorbate,  $\Delta G(I)$ . Consequently, eqn. 21 may be transformed to<sup>8,44</sup>

$$\Delta G = \Delta G_{i.u.}I + A = \Delta G(I) + A \quad (22)$$

Thus, using energetic equivalents of the retention indices [ $\Delta G(X)$ ,  $\Delta G(Y)$ ,  $\Delta G(Z)$ ,  $\Delta G(U)$ ,  $\Delta G(S)$ ] of test compounds it is possible to compare the capacity of a stationary phase to undergo different kinds of intermolecular interactions<sup>9</sup> but quantitative and correct evaluations are not possible because of different values of *A* in eqn. 22 for different stationary phases. On such a scale only the capacity for dispersive interactions may be measured quantitatively by a sixth parameter,  $\Delta G(\text{CH}_2)$  calculated according eqn. 3 or 4.

In Table IV are given the values for calculating the polarity of stationary phases, molten salts and polymer sorbents. The calculation of the capacity of sorbates for different types of interactions is rough because  $\Delta G(I) \neq \Delta G$ .

Using  $\Delta G(I)$  values for McReynolds test compounds, one can compare the properties of sorbents and stationary phases. It was mentioned previously that the retentions of sorbates on conventional stationary phases at 100°C and on porous polymers at 150–200°C are similar<sup>40</sup>. This assumption is confirmed by the  $\Delta G(I)$  values for test compounds given in Table IV. In all instances the energetic equivalents of the index values of test compounds on porous polymers are higher.

Recently a parameter similar to the energetic equivalent of a retention index was proposed for evaluating the selectivity of stationary phases and organic salts<sup>30</sup>, using the equation

$$I(P) = -2.3RT[(IB)_{\text{squ}} - (IB)_{\text{SP}}] + 2.3RT(A_{\text{squ}} - A_{\text{SP}}) \quad (23)$$

where  $A_{\text{squ}}$ ,  $A_{\text{SP}}$ ,  $B_{\text{squ}}$  and  $B_{\text{SP}}$  are constants that may be determined from the specific retention volumes of *n*-alkanes determined on squalane (squ) and the tested stationary phase (SP), respectively.

Considering eqn. 22, we transformed eqn. 23 to

$$I(P) = \Delta G(I)_{\text{squ}} - \Delta G(I)_{\text{SP}} + (A_{\text{squ}} - A_{\text{SP}}) \quad (24)$$

TABLE IV

CALCULATION OF POLARITY OF STATIONARY PHASES, ORGANIC SALTS AND POLYMER SORBENTS USING ENERGETIC EQUIVALENTS OF RETENTION INDICES OF TEST COMPOUNDS,  $\Delta G(I)$ , AT 120°C

The  $\Delta G(\text{CH}_2)$  and  $\Delta G(I)$  values were calculated using data from refs. 1, 6, 8, 27, 33 and 41.

Stationary phase	$-\Delta G(\text{CH}_2)$ (J/mol)	$-\Delta G(I)$ (J/mol)				
		Benzene	2-Pentanone	1-Butanol	1-Nitropropane	Pyridine
Butyl stearate	2191	15 211	15 321	15 167	16 746	16 877
Squalane	2172	14 185	12 817	13 620	14 163	15 184
Hallcomid M18	2149	15 731	18 438	16 268	18 782	18 159
Apolane 87	2140	14 429	12 844	13 487	14 215	15 499
Hallcomid M18 O	2136	15 856	18 592	16 455	19 041	18 464
Octyldecyl adipate	2130	15 593	16 381	15 891	18 000	17 745
Apiezon M	2128	14 560	13 028	13 666	14 518	15 731
Diocetyl sebacate	2125	15 411	16 113	15 624	17 686	17 473
Apiezon L	2119	14 520	12 973	13 608	14 499	15 707
DEG stearate	2116	15 177	16 574	15 515	16 828	18 839
Triton X-305	2111	19 320	22 318	19 869	24 070	23 838
Diocetyl phthalate	2097	15 629	16 280	16 301	18 629	18 168
Dexyl 400	2081	15 798	15 361	16 172	18 191	18 379
SKTFT-50	2058	14 947	15 071	17 171	18 900	17 932
PFMS-4	2058	15 627	15 194	15 997	17 994	18 180
Flexol 8N8	2053	15 381	17 332	16 244	18 729	18 030
Zinc stearate	2048	14 625	16 817	14 051	15 362	25 461
Silbor-1	1991	15 611	25 010	16 507	18 578	19 295
Versamid 940	1947	14 841	17 607	15 036	16 828	17 684
OV-7	1931	13 943	13 576	14 252	15 893	15 970
Diglycerol	1929	19 759	27 323	22 904	25 625	29 967
OV-11	1925	14 534	14 092	14 862	16 768	16 883
OV-3	1913	13 339	12 937	13 550	14 851	15 062
Tergitol NPX	1909	16 229	18 635	16 897	19 876	20 048
Triton X-100	1894	16 215	18 734	16 954	19 966	20 098
SE-30	1874	12 542	12 092	12 580	13 442	13 892
Sucrose acetate	1870	15 429	17 206	16 421	19 263	18 590
OV-101	1866	12 505	12 076	12 543	13 420	13 849
Silar 10C	1546	18 136	20 826	19 883	24 645	23 176
OV-1	1855	12 435	12 008	12 472	13 344	13 771
OV-22	1849	15 040	14 393	15 133	17 297	17 611
NPGA	1786	15 849	18 136	16 778	19 905	20 316
OV-225	1709	15 060	16 393	16 496	19 556	18 547
NPGS	1703	15 808	18 090	16 932	20 356	20 237
XE-60	1680	14 405	16 321	16 254	19 246	17 918
Carbowax 20M	1679	16 374	18 910	16 710	20 556	20 304
FFAP	1656	16 445	19 376	18 614	20 767	21 960
Carbowax 1000	1633	16 335	19 554	17 071	20 877	21 040
DEGA	1581	16 307	18 870	17 193	20 831	21 464
EGA	1573	16 112	18 393	17 009	20 565	20 958
TCEP	1338	16 675	19 364	18 454	22 482	21 599
Tetrabutylammonium picrate	1672	16 317	18 524	17 821	21 132	20 613
Tetrabutylammonium chloride	1588	16 245	28 394	16 849	22 566	21 136
KF · 2H <sub>2</sub> O sorbent <sup>a</sup>	440	2944	3947	4435	3687	3855
Porapak Q <sup>b</sup>	3457	21 328	20 982	22 503	22 607	23 021
Chromosorb 102 <sup>b</sup>	3187	19 825	19 379	20 813	21 837	21 228

<sup>a</sup> At 100°C.

<sup>b</sup> At 140°C.

One can see from eqn. 24 that the approach proposed by Poole *et al.*<sup>30,45</sup> is comparable to the  $\Delta G(I)$  scale<sup>8</sup> but needs a reference stationary phase, squalane. It is more complicated because it is based on assumptions about the linear dependence of the retention volumes of *n*-alkanes on the number of carbon atoms, which is under discussion<sup>46-48</sup>.

#### THERMODYNAMIC SELECTIVITY OF SORBENTS

The "selectivity" in GC, like polarity, is not clearly defined and is interpreted in different ways by different investigators. To characterize the selectivity of a sorbent this term is used in two ways: (1) to compare the capacity of an investigated sorbent to retain two sorbates (selectivity of one column); and (2) to compare capacity of two sorbents to retain one or several sorbates (selectivity of two columns). In the first instance the selectivity of the sorbents for a pair of sorbates X and Y can be calculated as the difference in their partial molar Gibbs free energies of sorption:

$$\delta(\Delta G)_{X,Y} = \Delta G_X - \Delta G_Y \quad (25)$$

It is better to measure the selectivity of a sorbent using the energetic equivalents of retention indices,  $\Delta G(I)$ . The partial molar Gibbs free energies of sorption are connected with the energetic equivalents of retention indices (see eqn. 17). Thus, considering that *A* is a constant for one sorbent under fixed analytical conditions, we obtain

$$\delta(\Delta G)_{X,Y} = \Delta G(I)_X - \Delta G(I)_Y \quad (26)$$

Let us consider the second case, the selectivity of two stationary phases, *i.e.*, their capacity to retain one substance *x*. The selectivity of two sorbents,  $S_1$  and  $S_2$ , with respect to one sorbate may be measured as the difference in their partial molar Gibbs free energies of sorption:

$$\delta(\Delta G)_{S_1,S_2} = \Delta G_{S_1} - \Delta G_{S_2} \quad (27)$$

Considering, that for different stationary phases 1 and 2 the value of the constant *A* is usually different, the use of energetic equivalents of retention indices,  $\Delta G(I)$ , in this instance gives only an approximate estimation of the selectivity of the compared columns. Consequently, quantitative measurements of selectivity for one column (see eqn. 26) and the approximate estimation of the selectivity for two columns can be carried out using  $\Delta G(I)$  values.

#### EVALUATION OF POLARITY AND SELECTIVITY OF STATIONARY PHASES IN CAPILLARY COLUMNS

Capillary columns are now widely used in GC and the determination of the polarity of stationary phases in this type of column is therefore required.

A thermodynamic approach to the polarity of capillary columns is also preferable. In this instance it is possible to use the partial molar Gibbs free energies of

sorption for several test compounds. For capillary columns, we have transformed the eqn. 18 for the calculation of  $\Delta G$  to a more convenient form.

Let us define some parameters for capillary columns. The volume of the empty part of the column without stationary phase will be termed the void volume or dead volume,  $V_0$ , and the total volume of the column is  $V$ .  $V_L$  is the volume of stationary phase in the column. These parameters are calculated using the following equations:

$$V = L\pi d^2/4 \quad (28)$$

$$V_0 = L\pi(d - 2d_f)^2/4 \quad (29)$$

$$V_L = L\pi[d^2 - (d - 2d_f)^2]/4 \quad (30)$$

where  $d$  is the diameter of the capillary column,  $d_f$  the film thickness of the stationary phase in the capillary column and  $L$  the length of the capillary column. On the other hand, the dead volume of the column can be determined from the carrier gas flow-rate,  $\omega$ , and the column dead time,  $t_0$ .

The specific retention volume of a sorbate X in GC is calculated using the equation

$$V_{g,X} = \frac{273t'\omega}{mT_r} \cdot j \left( 1 - \frac{P_{H_2O}^0}{P_0} \right) \quad (31)$$

where  $t'$  is the adjusted retention time of a solute X,  $\omega$  the carrier gas flow-rate (ml/min) measured at room temperature,  $T_r$ ,  $m$  the mass of stationary phase in the column,  $j$  the gas compressibility factor,  $P_{H_2O}^0$  the water vapour pressure at room temperature and  $P_0$  the inlet gas pressure. Considering the parameters in eqn. 31, one can reach the conclusion that some of them are not related to properties of the stationary phase, and the equation may be written as

$$V_{g,X} = \frac{273t'\omega}{mT_r} \cdot j\xi \quad (32)$$

where  $\xi$  is the correction for the pressure of water vapour at room temperature if carrier gas flow-rate was measured with a bubble flow meter;  $\xi = (1 - P_{H_2O}^0/P_0)$ .

The partial molar Gibbs free energy of sorption of a substance X may be calculated using the equation

$$\Delta G_X = -RT \ln \left( \frac{273t'\omega T_r j \xi}{273T_r m} \right) \quad (33)$$

We made some simplifications of eqn. 33 assuming that

$$\frac{1}{V_1} = \frac{\rho}{m} \quad (34)$$

and

$$\omega = V_0/t_0 \quad (35)$$

Thus, eqn. 33 may be transformed to

$$\Delta G = -RT \ln \left( \frac{t'}{t_0} \cdot \frac{V_0}{V_1} \cdot \frac{T}{T_r} \cdot j\xi \right) \quad (36)$$

The ratio of the adjusted retention time,  $t'$ , of a solute to the retention time of an unretained compound,  $t_0$ , is the capacity factor,  $k'$ , so the final expression for the calculation of the partial molar Gibbs free energy of sorption in capillary chromatography will be described by

$$\Delta G = -RT \ln \left( k' \cdot \frac{V_0}{V_1} - \frac{T}{T_r} \cdot j\xi \right) \quad (37)$$

Eqn. 37 provides an opportunity to calculate the energy of sorption using the capacity factor of a solute,  $k'$ . It is clear from eqn. 37 that to calculate the partial molar free energy of sorption of substance X it is necessary to determine the capacity factor,  $k'$ , and to measure accurately the experimental conditions (column temperature, room temperature, inlet and outlet pressure of carrier gas). As a rule, using modern chromatographic equipment it is not a problem to determine these parameters. The dead volume and the volume of stationary phase in the column may be calculated from values of the column length, inner diameter,  $d$ , and stationary phase film thickness,  $d_f$ , in the capillary column. These parameters are common characteristics of columns used in capillary GC. It is seen from eqn. 37 that the calculation of the partial molar free Gibbs energy of sorption for test compounds is simpler in capillary chromatography than for packed columns. One does not need to determine the density of the stationary phase under analytical conditions, the mass of stationary phase or the carrier gas flow-rate.

Eqn. 37 can be recommended for the determination of the polarity and selectivity of stationary phases in capillary GC on the basis of the partial molar Gibbs free energies of sorption  $\Delta G(X)$ ,  $\Delta G(Y)$ ,  $\Delta G(Z)$ ,  $\Delta G(U)$ ,  $\Delta G(S)$  and  $\Delta G(\text{CH}_2)$  of test compounds according to the scale given in ref. 9. This scale does not use any reference stationary phase and allows stationary phases to be ranked by all main types of intermolecular interactions. If necessary, the list of test compounds may be modified or expanded. The scale<sup>9</sup> also may be used to measure the selectivity of one capillary column for several sorbates or the selectivity of two capillary columns for one sorbate in accordance with eqn. 24 or 25.

The scale based on eqn. 37 can describe the specificity of any liquid stationary phase and is recommended for practical use. The quantitative thermodynamic measurement of polarity proposed here gives the opportunity to create a unified scale of liquid stationary phases of both organic and inorganic origin. The six-parameter thermodynamic scale, based on eqn. 18 or eqns. 19 and 37 is more informative than all previous scales proposed for the evaluation of the polarity of sorbents in GC.

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