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## THERMODYNAMIC CRITERION FOR THE IDENTIFICATION OF SULPHUR-CONTAINING COMPOUNDS BY GAS CHROMATOGRAPHY

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### SUMMARY

A thermodynamic criterion,  $\Delta Q$ , is proposed which permits reliable identification of the functional groups of aliphatic compounds by gas chromatographic analysis on stationary phases of different polarities. The advantages of such a criterion in those cases where the method based on  $\Delta I$  values fails are demonstrated.

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### INTRODUCTION

The identification of trace organic substances present in complex mixtures of unknown composition is of particular interest, for example, in the analysis of odour condensates of biological objects, of environmental pollutants and the degradation products of various polymeric materials<sup>1,2</sup>. Data obtained by gas chromatographic-mass spectrometric (GC-MS) analysis of such samples separated on one column may be insufficient for identification of the individual compounds. In order to characterize a substance it is necessary to obtain the GC parameters on different sorbents. The sorption properties of compounds are closely related with their structures.

Any homologous series of aliphatic organic compounds, including *n*-alkanes, is known to be characterized by a non-linear change in the logarithm of the specific retention volumes or retention indices with increasing carbon number<sup>3-5</sup>. An especially strong deviation from linearity is observed for the first five or six members of series having the general formula  $R_nX$  where X is a functional group and  $R_n$  is the *n*-radical  $C_nH_{2n+1}$ . The polarity of the analyzed compound, the nature of its functional group, the column temperature and the polarity of the stationary phase determine the extent of this non-linear region. The reason for the deviation of the retention parameters  $\log V_g$  and  $I$  from the linear dependence for the first few homologues is not yet clear.

Based on the thermodynamics of the GC separation process and on the dependence of the retention index on the partial molar free energy of sorption, we have tried to determine the reasons for the non-linear behaviour and to elucidate the rôles of column temperature and stationary phase polarity<sup>6,7</sup>. It was found that the energy contribution per  $CH_2$  group,  $\Delta G^{CH_2}$ , is not constant but changes with the increasing

carbon number,  $m$ , in any homologous series. This behaviour is observed on both polar and non-polar stationary phases and at different temperatures of analysis. However, in the  $n$ -alkanes the dependence of  $\Delta G^{\text{CH}_2}$  on  $m$  is quite different. We concluded that the inconstancy of  $\Delta G^{\text{CH}_2}$  reflects the interactions between the  $\text{CH}_3$  group and functional X group or between two neighbouring  $\text{CH}_3$  groups<sup>6,7</sup>.

The inconstancy of  $\Delta G^{\text{CH}_2}$  is the reason for the non linear dependence of  $I$  on  $m$  observed especially for the first members of any homologous series. The resulting inconstancy of  $\Delta I$  for members of given homologous series may lead to erroneous identification. Members of different homologous series can have the same values of  $\Delta I$  (see Table I). In this case,  $\Delta I$  cannot help in the identification, and we employ a thermodynamic criterion,  $\Delta Q$ , to identify the nature of the functional group and the carbon number of the  $n$ -alkyl radical of the substances under investigation. This means that we compare not only retention indices but also their energy equivalents. For example, this thermodynamic criterion has been used for the identification of aliphatic amines in a mixture of thirteen homologous series<sup>8</sup>.

In the present paper we compare the results of application of  $\Delta Q$  and  $\Delta I$  to the identification of the functional groups of aliphatic compounds. The advantages of the thermodynamic criterion in the identification of sulphur-containing compounds having the same  $\Delta I$  values are demonstrated.

## EXPERIMENTAL

Retention indices of sulphur-containing compounds were obtained on a Pye Unicam 104 gas chromatograph equipped with a flame ionization detector and glass column (210 × 0.4 cm). The four columns contained 5% Apiezon M (Associated Electrical Industries, U.K.), Triton X-305 (Schuchardt, F.R.G.) or Carbowax 1000 (Austrowaren, Austria) on Chromosorb W AW DMCS (80–100 mesh). High purity grade argon was employed as carrier gas. The temperature of analysis was 130°C.

The preparation of the sulphur-containing compounds and GC conditions were detailed previously<sup>9–12</sup>.

## RESULTS AND DISCUSSION

In the Kováts retention index system the difference in  $\log V_{g,n}$  for any two neighbouring  $n$ -alkanes is equal to 100 index units (i.u.)<sup>13,14</sup>. Thus, the energy equivalent to one index unit,  $\Delta G_{i.u.}$ , is calculated by:

$$\Delta G_{i.u.} = \Delta G^{\text{CH}_2}/100 = -0.023RT (\log V_{g,n+1} - \log V_{g,n}) \quad (1)$$

The dependence of the specific retention volume on the number of carbon atoms,  $n$ , is described most accurately by<sup>15</sup>

$$\log V_{g,n} = a + bn + \frac{c}{n+d} \quad (2)$$

where  $a$ ,  $b$ ,  $c$  and  $d$  are coefficients which depend on the stationary phase and the analysis temperature.

Taking into account eqn. 1, we can write the change in the energy equivalent to one index unit on increasing the length of the carbon chain of  $n$ -alkanes in the form

$$\Delta G_{i,u.} = -0.023 RT \left[ b - \frac{c}{(n+d)(n-1+d)} \right] \quad (3)$$

where  $b$ ,  $c$  and  $d$  are the same coefficients as those of eqn. 2. Eqn. 3 shows that  $\Delta G_{i,u.}$  tends to  $-0.023 RTb$  for large values of  $n$ , i.e., to a constant value for high-molecular-weight homologues.

The definition of the retention index as a relative parameter suggests that any substance  $i$  with retention index  $I_i$  may be considered as a hypothetical  $n$ -alkane with a fractional number of carbon atoms,  $n_i = I_i/100$ . In this case the specific retention volume of the substance,  $V_{g,i}$ , obeys the equation

$$\log V_{g,i} = a + bI_i/100 + c/(I_i/100 + d) \quad (4)$$

where the coefficients  $a$ ,  $b$ ,  $c$  and  $d$  are equal to those in eqn. 2 obtained for  $n$ -alkanes. Eqn. 4 allows us to calculate  $V_{g,i}$  of any substance from the value of  $I_i$  and the specific retention volumes of  $n$ -alkanes analyzed under the same GC conditions<sup>16</sup>.

The energy equivalent to one index unit of any substance with the retention index,  $I_i$ , on the scale for the  $n$ -alkanes is determined by:

$$\Delta G_{i,u.} = -0.023RT \left[ b - \frac{c}{(I_i/100 + d)(I_i/100 - 1 + d)} \right] \quad (5)$$

where  $b$ ,  $c$  and  $d$  are the coefficients in eqn. 2. Thus,  $\Delta G_{i,u.}$  depends on the two  $n$ -alkanes used for calculation of the retention index. This means that substances with different retention indices obtained under the same conditions may have different energy equivalents, and therefore  $\Delta G_{i,u.}$  can be used for identification in complicated cases. For example, on Apiezon M and Carbowax 1000 the retention indices of  $C_2H_5SH$  are equal to 517 and 753 respectively, and those of  $CH_3SC_{12}H_{25}$  are 1620 and 1857 under the same conditions. It is not difficult to see that  $\Delta I = I^{Carb} - I^{Ap}$  has the same value for each compound. Therefore, these compounds cannot be distinguished by use of  $\Delta I$ , but can be identified by their energy equivalents.

On Carbowax the specific retention volumes for  $n$ -alkanes analyzed under the same GC conditions obey the equation:

$$\log V_{g,n} = -0.2410 + 0.2047n - \frac{4.7888}{n + 2.5} \quad (6)$$

According to eqn. 5, the energy equivalent to one index unit for any substance analyzed under these conditions is:

$$\Delta G_{i,u.} = -0.023RT \left[ 0.2047 + \frac{4.7888}{(I_i/100 + 2.5)(I_i/100 - 1 + 2.5)} \right] \quad (7)$$

For  $C_2H_5SH$  and  $CH_3SC_{12}H_{25}$  we obtain values of 4.74 and 3.98, respectively. Thus, even on the same stationary phase the energy equivalent to one index unit is different for substances which have different retention indices.

The total energy equivalent of the retention index can be calculated on any stationary phase:

$$\Delta G_I = I \cdot \Delta G_{i.u.} \quad (8)$$

On Carbowax the energy equivalent of the retention index for  $C_2H_5SH$  is  $\Delta G_{I(x)}^{Carb} = 7.53 \cdot 4.74 = 3569.22$  cal/mol; for  $CH_3SC_{12}H_{25}$ ,  $\Delta G_{I(y)}^{Carb} = 7390.9$  cal/mol. On Apiezon, for these compounds  $\Delta G_{I(x)}^{Ap} = 3050.3$  cal/mol and  $\Delta G_{I(y)}^{Ap} = 8326.8$  cal/mol. The differences between the energy equivalents,  $\Delta Q$ , are  $\Delta Q_x = -518.9$  cal/mol for  $C_2H_5SH$  and  $\Delta Q_y = 935.6$  cal/mol for  $CH_3SC_{12}H_{25}$ . Thus, these compounds can be identified from their  $\Delta Q$  values.

This means that the  $\Delta Q$  values of a substance on two stationary phases gives more information about the structural characteristics of the molecule than does  $\Delta I$ . To establish the nature of the functional group we suggest the use of the quantity  $\Delta Q^{P_1 P_2}$ , the energy equivalent of the difference in the retention indices,  $\Delta I$ , on polar and non-polar phases

$$\Delta Q^{P_1 P_2} = P_1 \cdot \Delta G_{i.u.}^{P_1} - P_2 \cdot \Delta G_{i.u.}^{P_2} \quad (9)$$

where  $P_1$  and  $P_2$  are the retention indices of the substance on the phases  $P_1$  and  $P_2$ , respectively;  $\Delta G_{i.u.}^{P_1}$  and  $\Delta G_{i.u.}^{P_2}$  are the energies equivalent to one index unit as calculated by eqn. 5 for the stationary phases  $P_1$  and  $P_2$ , respectively.

Calculation of  $\Delta Q$  enables one to take into account the non-linear variation of the dispersion energy with increasing carbon number in the homologous series  $R_mX$  and to gain a deeper insight into the specific features of the functional group  $X$ . The dispersion energy is the main contribution to the free energy of interaction of a substance with the stationary phase<sup>17</sup>. Thus, investigation of the variation of the dispersion energy on different stationary phases yields comprehensive information on the energy contribution of the functional group and its specific interaction with the stationary phase.

To confirm that  $\Delta Q$  is superior to  $\Delta I$  as a measure of the energy of interaction of the functional group  $X$  with the stationary phase, we have compared the dependences of  $\Delta I$  and  $\Delta Q$  on the carbon number,  $m$ , for 25 homologous series  $R_mX$ , where  $R_m$  is the  $n$ -alkyl radical  $C_mH_{2m+1}$  and  $X$  is a sulphide or disulphide group. The results obtained show that on all phases  $\Delta I$  varies non-linearly with increasing  $m$  for any homologous series. Figs. 1 and 2 show plots of  $\Delta I$  vs.  $m$  for eight homologous series of sulphur-containing compounds:  $CH_3SR_m$ ,  $C_2H_5SR_m$ ,  $C_3H_7SR_m$ ,  $C_4H_9SR_m$ ,  $C_5H_{11}SR_m$ , iso- $C_3H_7SR_m$ , iso- $C_4H_9SR_m$  and iso- $C_5H_{11}SR_m$ . The phases are Carbowax 1000 (Carb) and Apiezon M (Ap). It is seen that in each homologous series the values of  $\Delta I^{Carb, Ap}$  are dependent on the carbon number. Such curves may coincide, e.g., the values of  $\Delta I$  for  $C_4H_9SR_m$  and  $C_5H_{11}SR_m$  are equal to within  $\pm 1$  i.u. for all homologues.

For all homologous series studied the values of  $\Delta I$  are not constant; the curves intersect. The total scatter of  $\Delta I$  values for a given functional group may be as high

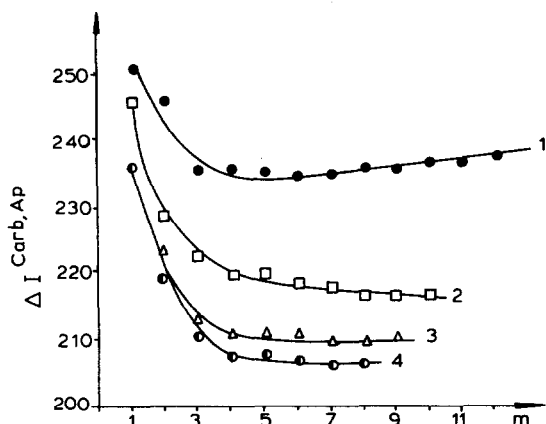


Fig. 1. The difference in retention indices,  $\Delta I$ , on Carbowax 1000 and Apiezon M at 130°C vs. the carbon number,  $m$ , for homologous series of aliphatic compounds. Curves: 1,  $\text{CH}_3\text{R}_m$  (●); 2,  $\text{C}_2\text{H}_5\text{SR}_m$  (□); 3,  $\text{C}_3\text{H}_7\text{SR}_m$  (△); 4,  $\text{C}_4\text{H}_9\text{SR}_m$  (○) and  $\text{C}_5\text{H}_{11}\text{SR}_m$  (◐).

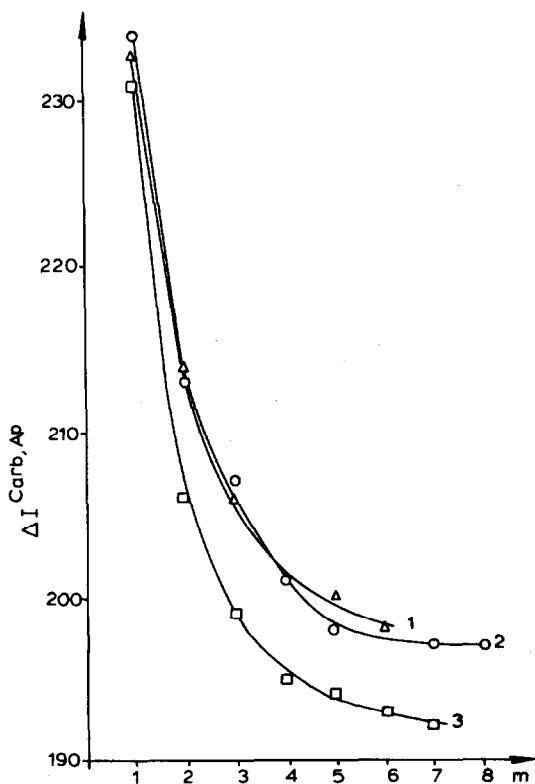


Fig. 2. The difference in retention indices,  $\Delta I$ , on Carbowax 1000 and Apiezon M at 130°C of iso-alkyl sulphides vs. the carbon number. Curves: 1, iso- $\text{C}_5\text{H}_{11}\text{SR}_m$  (△); 2, iso- $\text{C}_3\text{H}_7\text{SR}_m$  (○); 3, iso- $\text{C}_4\text{H}_9\text{SR}_m$  (□).

TABLE I

$\Delta I$  VALUES OF 25 HOMOLOGOUS SERIES OF SULPHUR-CONTAINING COMPOUNDS ON THREE STATIONARY PHASES AT 130°C

In all series  $R_mX$ ,  $m = 1-8$ , except for mercaptans for which  $m = 2-8$ ; retention indices as published<sup>9-12</sup>.

No.	Functional group, X	$\Delta I^{Carb, Ap}$	$\Delta I^{Carb, Tr}$	$\Delta I^{Tr, Ap}$
1	HS-	237-234	57-52	185-178
2	CH <sub>3</sub> S-	251-235	64-54	187-179
3	C <sub>2</sub> H <sub>5</sub> S-	246-217	59-49	184-167
4	C <sub>3</sub> H <sub>7</sub> S-	236-210	54-49	185-160
5	C <sub>4</sub> H <sub>9</sub> S-	236-206	55-48	181-157
6	C <sub>5</sub> H <sub>11</sub> S-	236-206	55-48	180-156
7	iso-C <sub>3</sub> H <sub>7</sub> S-	234-197	62-50	172-147
8	iso-C <sub>4</sub> H <sub>9</sub> S-	231-192	69-48	162-144
9	sec.-C <sub>4</sub> H <sub>9</sub> S-	230-192	62-49	168-143
10	tert.-C <sub>4</sub> H <sub>9</sub> S-	214-174	58-48	156-126
11	iso-C <sub>5</sub> H <sub>11</sub> S-	233-198	62-51	171-147
12	sec.-C <sub>5</sub> H <sub>11</sub> S-	223-181	60-45	163-134
13	tert.-C <sub>5</sub> H <sub>11</sub> S-	218-177	61-47	157-130
14	CH <sub>3</sub> SS-	354-321	85-76	271-245
15	C <sub>2</sub> H <sub>5</sub> SS-	337-305	78-72	259-232
16	C <sub>3</sub> H <sub>7</sub> SS-	328-294	76-71	252-223
17	C <sub>4</sub> H <sub>7</sub> SS-	322-288	76-70	246-218
18	iso-C <sub>3</sub> H <sub>7</sub> SS-	315-269	72-62	243-207
19	iso-C <sub>4</sub> H <sub>9</sub> SS-	307-268	71-67	236-199
20	CH <sub>3</sub> C(O)S-	401-364	92-81	309-282
21	C <sub>2</sub> H <sub>5</sub> C(O)S-	376-332	80-75	296-257
22	C <sub>3</sub> H <sub>7</sub> C(O)S-	363-322	80-75	283-247
23	CH≡CS-	499-470	114-109	385-361
24	CH <sub>2</sub> =CHS-	302-268	77-64	227-204
25	CH <sub>2</sub> =CHCH <sub>2</sub> S-	304-277	80-70	224-207

as 40 i.u. (see Table I). Hence, the use of  $\Delta I$  for identification may lead to errors.

The energy equivalent of the difference in retention indices,  $\Delta Q^{P_1P_2}$ , was calculated by eqns. 9 and 5 for the same homologous series and stationary phases (Carb and Ap). The results reveal a linear dependence of  $\Delta Q$  on  $m$  (Figs. 3 and 4), starting with first homologue of any series. Each series  $R_mX$  has its own straight line

$$\Delta Q^{P_1P_2} = (\alpha + \beta m) \cdot \text{cal/mol} \quad (10)$$

where the coefficients  $\alpha$  and  $\beta$  are determined by the GC conditions and by the functional group of the series. A linear dependence is observed for all 25 investigated series of sulphur-containing compounds on stationary phases of different polarities. Thus the linear dependence of  $\Delta Q$  on the carbon number  $m$  may be proposed as a thermodynamic characteristic of the functional group of a series. The advantages of such a thermodynamic criterion for the structure is clearly seen from a comparison of Fig. 1 and 3, 2 and 4. While in Fig. 1 the curves for the series C<sub>4</sub>H<sub>9</sub>SR<sub>m</sub> and C<sub>5</sub>H<sub>11</sub>SR<sub>m</sub> almost coincide (with respect to  $\Delta I$ ), in Fig. 3 they are separated (with respect to  $\Delta Q^{Carb, Ap}$ ) by 125 cal/mol. A similar situation is found when  $\Delta Q$  and  $\Delta I$

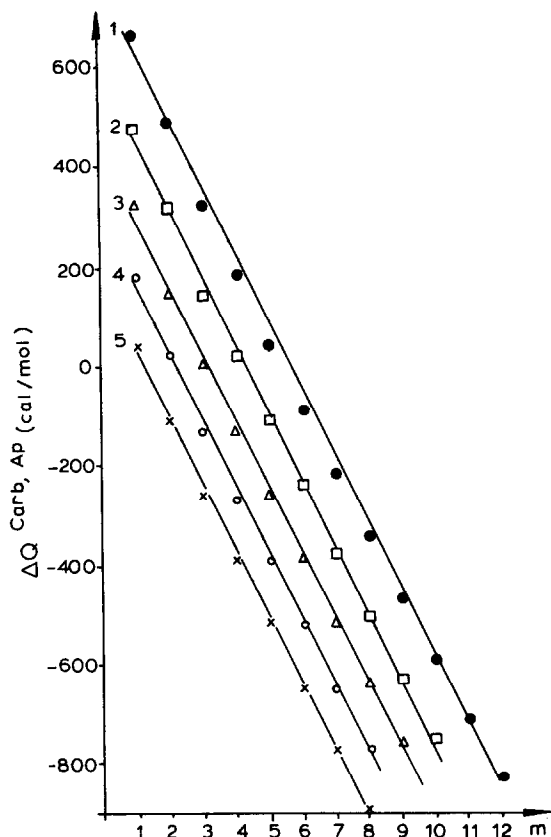


Fig. 3. The energy equivalent,  $\Delta Q$ , on Carbowax 1000 and Apiezon M at 130°C vs. carbon number,  $m$ , for five homologous series. Curves: 1,  $\text{CH}_3\text{SR}_m$  (●); 2,  $\text{C}_2\text{H}_5\text{SR}_m$  (□); 3,  $\text{C}_3\text{H}_7\text{SR}_m$  (△); 4,  $\text{C}_4\text{H}_9\text{SR}_m$  (○); 5,  $\text{C}_5\text{H}_{11}\text{SR}_m$  (×).

are determined on Triton X-305 and Ap: the series are distinctly separated only with respect to  $\Delta Q^{\text{Tr,Ap}}$ . For instance, for the fifth homologue of this series,  $\Delta I^{\text{Tr,Ap}}$  is equal to 159 i.v. while the values of  $\Delta Q^{\text{Tr,Ap}}$  for the same substance are equal to -309 and -380 cal/mol, *i.e.*, they differ by 71 cal/mol, quite sufficient to identify the functional group. The advantage of using  $\Delta Q$  is also seen with homologous iso-aliphatic compounds. Figs. 2 and 4 show the corresponding plots (data from refs. 9-12) of  $\Delta I$  and  $\Delta Q$  for the homologous series: iso- $\text{C}_3\text{H}_7\text{SR}_m$ , iso- $\text{C}_4\text{H}_9\text{SR}_m$  and iso- $\text{C}_5\text{H}_{11}\text{SR}_m$ . As is seen from Fig. 4, the curves of  $\Delta Q^{\text{Carb,Ap}}$  do not intersect and are described by straight lines which restore the "natural order" of the series: iso- $\text{C}_3\text{H}_7\text{SR}_m$ , iso- $\text{C}_4\text{H}_9\text{SR}_m$ , iso- $\text{C}_5\text{H}_{11}\text{SR}_m$ .

Thus, whereas comparison of the  $\Delta I$  values of homologous series may lead to erroneous identification, use of the thermodynamic criterion,  $\Delta Q$ , ensures separation of such series, even for compounds which have equal  $\Delta I$  values.

Table II lists the coefficients of eqn. 10 used for determining  $\Delta Q^{\text{P}_1\text{P}_2}$  and also the mean square deviations,  $s$ , of values calculated from the experimental data. It is seen that for all series  $\Delta Q^{\text{P}_1\text{P}_2}$  depends linearly on  $m$  ( $s \geq 15$  cal/mol). Somewhat

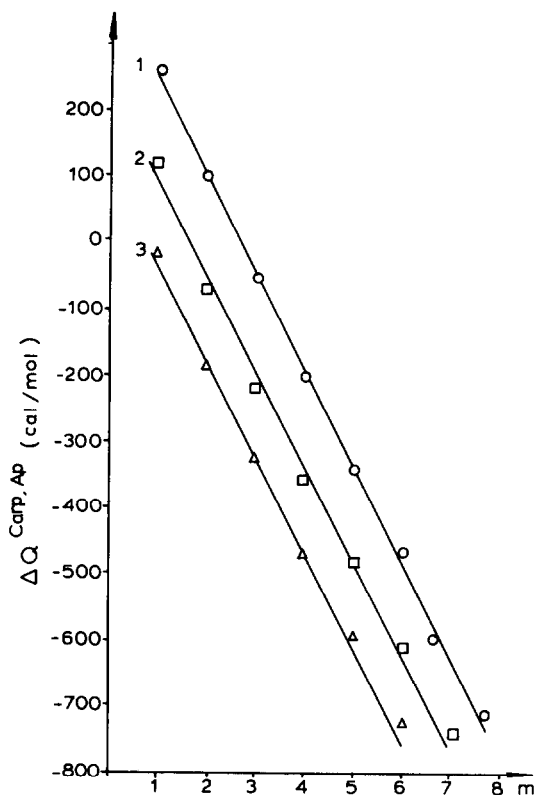


Fig. 4. The energy equivalent vs. the carbon number,  $m$ , for iso-alkyl sulphides on Carbowax 1000 and Apiezon M at 130°C. Curves: 1, iso-C<sub>3</sub>H<sub>7</sub>SR<sub>m</sub> (○); 2, iso-C<sub>4</sub>H<sub>9</sub>SR<sub>m</sub> (□); 3, iso-C<sub>3</sub>H<sub>11</sub>SR<sub>m</sub> (△).

larger errors (up to 22 cal/mol) can be explained by inaccurate values of the retention indices for the first homologues of these series on Apiezon M (Ap) at 130°C. Nevertheless, this does not hinder correct identification of the functional group.

An analysis of the coefficients of the equations describing  $\Delta Q^{P_1 P_2}$  as a function of  $m$  leads to the following conclusions. The coefficients  $\alpha$  and  $\beta$  depend on the functional group of a homologous series and on the stationary phases.  $\alpha$  has different values for almost all the compounds studied (see Table II). Seemingly, this coefficient best reflects the specific features of the functional groups of the homolog series, while  $\beta$  has similar values for many series. If the functional group includes a branched radical R<sub>1</sub>, this influences the coefficients  $\alpha$  and  $\beta$ . For example, for sulphur-containing compounds of the general formula R<sub>1</sub>SR<sub>m</sub>,  $\alpha = 335.4$  when R<sub>1</sub> = iso-C<sub>3</sub>H<sub>7</sub> and  $\alpha = 275.3$  when R<sub>1</sub> = *n*-C<sub>3</sub>H<sub>7</sub>; the values of  $\beta$  are 133.4 and 126.9, respectively. It is worth nothing that the coefficients  $\alpha$ , calculated for one substance on different pairs of stationary phases P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub>, are related by:

$$\alpha^{P_1 P_3} = \alpha^{P_1 P_2} + \alpha^{P_2 P_3} \quad (11)$$

This is caused by the linear relationships between  $\Delta Q$  and the carbon number in any



TABLE II

COEFFICIENTS OF EQN. 10 USED FOR CALCULATING THE THERMODYNAMIC EQUIVALENT,  $\Delta Q$ , OF SULPHUR-CONTAINING COMPOUNDS OF DIFFERENT HOMOLOGOUS SERIES

$s$  = Mean-square deviation of the calculated  $\Delta Q$  values from the experimental data;  $m$  = carbon number of the  $n$ -radical  $R_m = C_mH_{2m+1}$ .

Functional group, X	$\Delta Q^{Carb,Ap}$	$s$	$\Delta Q^{Carb,Tr}$	$s$	$\Delta Q^{Tr,Ap}$	$s$
HS-	716.2-130.3 $m$	10	317.2-58.0 $m$	6	426.9-75.4 $m$	4
CH <sub>3</sub> S-	582.8-127.4 $m$	11	228.8-52.3 $m$	6	366.8-76.5 $m$	8
C <sub>2</sub> H <sub>5</sub> S-	444.1-130.7 $m$	7	203.8-56.1 $m$	5	235.4-74.0 $m$	5
C <sub>3</sub> H <sub>7</sub> S-	275.1-126.9 $m$	5	134.0-53.0 $m$	5	141.1-73.9 $m$	6
C <sub>4</sub> H <sub>9</sub> S-	162.2-130.3 $m$	17	79.5-53.0 $m$	3	81.1-77.0 $m$	21
C <sub>5</sub> H <sub>11</sub> S-	27.5-128.2 $m$	14	21.2-51.2 $m$	4	4.2-76.6 $m$	18
iso-C <sub>3</sub> H <sub>7</sub> S-	335.1-133.4 $m$	9	189.9-56.3 $m$	4	144.8-77.1 $m$	9
iso-C <sub>4</sub> H <sub>9</sub> S-	186.1-133.5 $m$	8	122.8-55.0 $m$	15	63.3-78.6 $m$	7
sec.-C <sub>4</sub> H <sub>9</sub> S-	195.9-134.4 $m$	11	130.1-55.7 $m$	5	67.2-79.0 $m$	7
tert.-C <sub>4</sub> H <sub>9</sub> S-	251.4-140.4 $m$	13	149.9-53.1 $m$	4	100.0-87.0 $m$	11
iso-C <sub>5</sub> H <sub>11</sub> S-	80.0-135.3 $m$	17	74.9-55.0 $m$	3	0.8-79.4 $m$	19
sec.-C <sub>5</sub> H <sub>11</sub> S-	55.2-133.8 $m$	22	38.0-46.6 $m$	8	17.2-87.3 $m$	8
tert.-C <sub>5</sub> H <sub>11</sub> S-	99.2-139.2 $m$	10	99.5-55.5 $m$	3	0.2-83.7 $m$	10
CH <sub>3</sub> SS-	663.6-145.0 $m$	8	146.6-53.1 $m$	4	517.0-91.9 $m$	7
C <sub>2</sub> H <sub>5</sub> SS-	480.3-137.1 $m$	16	98.8-51.5 $m$	9	381.5-85.6 $m$	14
C <sub>3</sub> H <sub>7</sub> SS-	342.9-139.1 $m$	6	43.1-48.9 $m$	9	299.6-90.1 $m$	12
C <sub>4</sub> H <sub>9</sub> SS-	208.1-139.4 $m$	6	-17.8-47.0 $m$	3	225.9-92.4 $m$	9
iso-C <sub>3</sub> H <sub>7</sub> SS-	349.5-142.4 $m$	5	93.4-58.8 $m$	14	256.1-83.6 $m$	16
iso-C <sub>4</sub> H <sub>9</sub> SS-	187.8-137.1 $m$	10	-8.8-43.7 $m$	2	198.8-93.9 $m$	9
CH <sub>3</sub> C(O)S-	868.5-129.4 $m$	12	200.6-53.1 $m$	4	668.0-76.3 $m$	9
C <sub>2</sub> H <sub>5</sub> C(O)S-	704.4-141.9 $m$	10	147.3-54.2 $m$	10	557.1-87.7 $m$	21
C <sub>3</sub> H <sub>7</sub> C(O)S-	502.4-131.9 $m$	20	86.2-50.4 $m$	8	416.3-81.5 $m$	5
CH≡CS-	1229.7-131.5 $m$	19	244.2-53.2 $m$	8	985.4-78.3 $m$	22
CH <sub>2</sub> =CHS-	663.0-134.0 $m$	11	249.6-59.8 $m$	4	393.3-76.0 $m$	6
CH <sub>2</sub> =CHCH <sub>2</sub> S-	598.0-133.5 $m$	18	199.1-54.6 $m$	5	391.0-83.0 $m$	13

series on any stationary phase. The slope of straight lines described by eqn. 10,  $\beta$ , depends on the difference in polarities of the phases. For instance, in the calculation of  $\Delta Q$ , this coefficient varies from 127 to 145 for  $P_1$  = Carbowax and  $P_2$  = Ap, from 74 to 92 for Triton (Tr) and Ap and from 43 to 60 for Carb and Tr. Hence, the more similar are the polarities of the stationary phases compared, the smaller are  $\Delta Q$  and  $\beta$  for the same series of homologues.

Thus, there is a distinct correlation between the energy equivalent,  $\Delta Q^{P_1P_2}$ , and the nature of the functional group in homologous series and also the polarities of the stationary phases  $P_1$  and  $P_2$ . The results obtained show that the thermodynamic criterion is promising for quantitative description of the variation in sorption free energy in homologous series and also for the estimation of the influence of the functional group on the homologue-phase interaction energy.

The results show that the dependence of  $\Delta Q^{P_1P_2}$  on  $m$  reveals not only the nature of the functional group of a homologous series, but also gives the carbon number in the  $n$ -radical  $C_mH_{2m+1}$  of the homologous series  $C_mH_{2m+1}X$ . The dependence is suggested as a criterion for identifying components in complex mixtures of

TABLE III

## INITIAL DATA FOR IDENTIFICATION OF SUBSTANCES N1 AND N2

The coefficients were calculated by eqn. 2 for *n*-alkanes.

Coefficient of eqn. 6	Stationary phase		
	Carbowax 1000	Triton X-305	Apiezon M
<i>b</i>	0.2047	0.2281	0.2675
<i>c</i>	-4.7888	-2.6434	-4.908
<i>d</i>	2.5	2.375	5.0
Substance	Retention index		
N1	1463	1387	1142
N2	1113	1061	893

aliphatic compounds belonging to different homologous series. In order to demonstrate the new identification method, we have chosen two values of  $\Delta Q$ ,  $-51.4$  and  $-81.4$  cal/mol, belonging to different compounds in which the functional groups cannot be identified by  $\Delta I$ . Let these compounds be denoted by N1 and N2, respectively, and we assume that N1 and N2 may belong to any homologous series among those listed in Table II. The identification procedure requires, as the initial data: (1) the retention indices of the compounds on any three stationary phases at the same column temperature; (2) the retention parameters of *n*-alkanes, for calculating the coefficients in eqns. 2 and 5. Table III lists these data for compounds N1 and N2.

Using these data, we obtain  $\Delta Q^{P_1 P_2}$  from eqn. 9 taking due account of eqn. 5; the results are presented in Table IV. Once the values of  $\Delta Q$  are known we can find values of *m* on each pair of stationary phases:

$$m_{\text{calc}} = \frac{\Delta Q^{P_1 P_2} - \alpha}{\beta} \quad (12)$$

If the compounds are identified correctly, the calculated values of *m* ( $m_{\text{calc}}$ ) must coincide for the same substance, independent of the stationary phases chosen. Since *m* is the carbon number, the calculated value must be a positive integer. Moreover, if the substance in question belongs to a given series  $R_m X$ , then  $m_{\text{calc}}$  must be equal to its carbon number *m* in the homologous series. This leads to the following identification criteria.

The compound analyzed belongs to a given series if three conditions are ful-

TABLE IV

ENERGY EQUIVALENTS,  $\Delta Q^{P_1 P_2}$ , USED FOR IDENTIFICATION OF SUBSTANCES N1 AND N2

Substance	$-\Delta Q^{\text{Carb.Tr}}$ (cal/mol)	$-\Delta Q^{\text{Carb.Ap}}$ (cal/mol)	$\Delta Q^{\text{Tr.Ap}}$ (cal/mol)
N1	116.9	51.4	65.5
N2	22.9	81.4	58.5

TABLE V  
IDENTIFICATION OF COMPOUNDS N1 AND N2 BY THREE-STEP CALCULATION  
 $\Delta Q$  values taken from Table IV.

Functional group X	$m_{calc. for N1}$		$m_{calc. for N2}$	
	$\Delta Q^{Tr, AP}$ = 65.5 cal/mol	$\Delta Q^{Carb, Tr}$ = -116.9 cal/mol	$\Delta Q^{Tr, AP}$ = 58.5 cal/mol	$\Delta Q^{Carb, AP}$ = -81.4 cal/mol
1 HS-	4.8	7.5	6.4	
2 CH <sub>3</sub> S-	3.9	6.6	5.6	
3 C <sub>2</sub> H <sub>5</sub> S-	2.3		3.9	4.0
4 C <sub>3</sub> H <sub>7</sub> S-	1.0	4.7	2.7	
5 C <sub>4</sub> H <sub>9</sub> S-	0.2		1.8	1.9
6 C <sub>3</sub> H <sub>11</sub> S-	-0.8		0.8	1.9
7 iso-C <sub>3</sub> H <sub>7</sub> S-	1.0	5.4	2.6	
8 iso-C <sub>4</sub> H <sub>9</sub> S-	0		1.5	
9 sec-C <sub>4</sub> H <sub>9</sub> S-	0		1.6	
10 tert.-C <sub>4</sub> H <sub>9</sub> S-	0.4		1.8	3.2
11 iso-C <sub>3</sub> H <sub>11</sub> S-	-0.8		0.7	
12 sec.-C <sub>3</sub> H <sub>11</sub> S-	-0.6		0.9	1.3
13 tert.-C <sub>3</sub> H <sub>11</sub> S-	-0.8		0.7	
14 CH <sub>3</sub> SS-	4.9	5.0	6.3	
15 C <sub>2</sub> H <sub>5</sub> SS-	3.7		5.1	2.4
16 C <sub>3</sub> H <sub>7</sub> SS-	2.6		4.0	1.3
17 C <sub>4</sub> H <sub>9</sub> SS-	1.7		3.1	0.1
18 iso-C <sub>3</sub> H <sub>7</sub> SS-	2.3		3.8	2.0
19 iso-C <sub>4</sub> H <sub>9</sub> SS-	1.4		2.7	
20 CH <sub>3</sub> C(O)S-	7.9	6.0	9.5	3.1
21 C <sub>2</sub> H <sub>5</sub> C(O)S-	5.6		7.0	
22 C <sub>3</sub> H <sub>7</sub> C(O)S-	4.3		5.8	
23 CH≡CS-	11.7		13.3	
24 CH <sub>2</sub> =CHS-	4.3		5.9	
25 CH <sub>2</sub> =CHCH <sub>2</sub> S-	3.9	5.8	5.4	5.5

filled for the value  $m_{\text{calc}}$  obtained from  $\Delta Q$ : (1)  $|m_{\text{calc}} - m| < 0.3$ , where  $m$  is an integer, (2)  $m_{\text{calc}}$  cannot be negative, (3)  $m_{\text{calc}}$  must have the same value for two or three pairs of stationary phases.

Let us now identify substances N1 and N2, using the above criteria. First of the three values of  $\Delta Q$  for different pairs of stationary phases (see Table IV) we choose those values which correspond to the phases Triton and Apiezon. Compounds N1 and N2 may belong to any of the series listed in Table II, therefore we calculate  $m_{\text{calc}}$  using eqn. 12 and the coefficients  $\alpha$  and  $\beta$  for all the equations listed in Table II. The values of  $m_{\text{calc}}$  thus obtained are present in Table V. An analysis of the data in this Table shows that out of 25 series we should select after the first step 11 series for N1 and 7 series for N2, since only in these cases does  $|m_{\text{calc}} - m| < 0.3$ ; in the remaining cases  $m_{\text{calc}}$  is either fractional (condition is not satisfied) or negative.

In the second step, from the indices of compounds N1 and N2 taken from Table III we calculated the values of  $\Delta Q^{\text{Carb,Tr}}$  which are equal to  $-116.9$  and  $-22.9$  cal/mol, respectively. These values are then substituted into the remaining 11 equations for N1 and the 7 equations for N2. The results of the calculation are listed in Table V. Again, we discard negative and fractional values of  $m_{\text{calc}}$  and also those homologous series for which  $m_{\text{calc}}$  values obtained in the two steps do not coincide. Hence, the results of the two identification steps reveal only one possibility: compound N1 belongs to the series  $\text{CH}_3\text{SSR}_m$ ; it may be methyl *n*-amyl disulphide ( $m = 5$ ). Compound N2 belongs to the series  $\text{C}_2\text{H}_5\text{SR}_m$  ( $m = 4$ ) or  $\text{C}_4\text{H}_9\text{SR}_m$  ( $m = 2$ ). It may be ethyl *n*-butyl sulphide.

In the third step we verify the identification. Let us consider the last values of  $\Delta Q^{\text{Carb,Ap}}$ . By use of eqn. 12 we obtained  $m_{\text{calc}} = 4.9$  for compound N1 of the series  $\text{CH}_3\text{SSR}_m$ ; for N2 we have two values;  $m_{\text{calc}} = 1.9$  or  $4.0$  (see Table V, third step). Thus, the identity of compound N1 is confirmed as the fifth homologue of the series  $\text{CH}_3\text{SSR}_m$  because the  $m_{\text{calc}}$  values obtained from  $\Delta Q^{\text{Carb,Tr}}$ ,  $\Delta Q^{\text{Carb,Ap}}$  and  $\Delta Q^{\text{Tr,Ap}}$  are equal to 5.0, 4.9 and 4.9, respectively. For compound N2 we have  $m_{\text{calc}} = 3.9$ , 4.0 and 4.0 for the series  $\text{C}_2\text{H}_5\text{SR}_m$  and 1.8, 1.9 and 1.9 for  $\text{C}_4\text{H}_9\text{SR}_m$ . Thus, it can only be ethyl *n*-butyl sulphide.

## CONCLUSIONS

The energy equivalent,  $\Delta Q$ , is proposed for quantitative estimation of the difference in interaction energies of functional groups with different stationary phases. The dependence of  $\Delta Q$  on the carbon number,  $m$ , has been shown to be linear, starting with the first member in any aliphatic series  $\text{R}_m\text{X}$ .

The advantages of this thermodynamic criterion for identifying substances where methods based on  $\Delta I$  values fail have been demonstrated. It is shown that the use of this criterion enables identification of the functional group X and the number of carbon atoms in the alkyl radical  $\text{R}_m$ .

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