

Mathematical Models of Solute Retention in Gas Chromatography as Sources of Thermodynamic Data. Part I. Methyl *n*-Alkyl Ketones as the Test Analytes

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Abstract

Although gas chromatography (GC) is mainly used for analytical and preparative separation of complicated mixtures and then identification of the separated components, it can also be used as a relatively simple tool for the determination of physicochemical (including thermodynamic) properties. In this study, we discuss three different retention models devised specially for GC. They are tested for a homologous series of methyl *n*-alkyl ketones chromatographed on stationary phases of low and medium polarity at several different isothermal temperatures. The statistical performance of each model is excellent, which makes them a convenient tool for the evaluation of analyte retention under the given working conditions. They can also be used for the determination of the numerical values of thermodynamic properties (e.g., the enthalpy of vaporization of the analytes and the standard molar chemical potential of the partitioning of one methylene group ($-\text{CH}_2-$) between the stationary and mobile phases).

Introduction

In addition to analytical and preparative applications, gas chromatography (GC) can be employed in physicochemical studies. The simplicity of this technique, its relative rapidity, and the low cost of reagents and equipment enable the easy collection of a considerable amount of experimental data, which can then be processed statistically. The use of GC to procure physicochemical (including thermodynamic) data is possible only when strict and repeatable measurement conditions are used, because these secure the high precision of the retention measurements. These data can then be compared with results obtained by the use of other, independent, techniques; satisfactory agreement is usually observed. The use of GC to determine thermodynamic data is a long-established procedure (1–15).

Several new and original retention models have recently been devised as a result of coupling general physicochemical ap-

proaches with thermodynamic and chromatographic models (and it is worthwhile to note that these are not empirical models) (16–22). These models take the form of mathematical equations, the terms of which have clearly defined physical meaning, thus enabling the calculation of thermodynamic properties. The same models can also be used to predict solute retention data. All of these new and original retention models are based on a set of common and simple assumptions.

For analytes and stationary phases of low polarity, retention of an analyte (which in fact depends on its partitioning between the stationary and mobile phases) can be approximated by two physical processes that are the reverse of each other, vaporization and solution.

Transfer of an analyte from the liquid stationary phase to the gaseous mobile phase is similar to (although not identical with) the process of vaporization of the pure liquid analyte.

Vaporization of liquids is adequately described by Trouton's rule, and the entropy of vaporization is almost the same for the vast majority of liquids (approximately $85 \pm 3 \text{ J mol}^{-1}\text{K}^{-1}$).

Because vaporization and solution are reverse processes, their respective thermodynamic characteristics for low-polarity solutes analyzed on low-polarity stationary phases are equal in absolute magnitude, but with an opposite sign.

The models discussed do not reflect intermolecular interactions and, therefore, perform better with chromatographic systems in which interactions are exclusively weak and nonspecific.

Detailed derivation of the ten new models of analyte retention (which were rigorously tested by the chromatography of low-polarity analytes (alkylbenzenes) on low (or very exceptionally medium) polarity stationary phases) is given elsewhere (16–22). The statistical and thermodynamic verification of these models resulted in sufficient confirmation of their correctness. Such chromatographic systems are very convenient for the investigation of physicochemical processes, because of the weak yet durable dispersive interactions that occur between the analytes and stationary phases and because specific interactions are practically absent. Because in the course of retention the analyte is partitioned between the stationary and mobile phases, we can assume that in this process a sequence of thermodynamic equi-

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libria of the type vaporization \leftrightarrow solution is established and that transfer of an analyte from the low-polarity stationary phase to the gaseous mobile phase is energetically very similar to (although not identical with) vaporization of the molecules of this analyte from its own liquid bulk phase. The reverse process (i.e., solution) is fully analogous, although in the opposite direction. With increasing stationary-phase polarity the process of solute retention cannot be approximated by a sequence of vaporization \leftrightarrow solution steps, because under such conditions specific interactions between the analyte and the stationary phase can no longer be neglected. It can be generally stated that the performance of the models (which neglect intermolecular interactions) is usually worse for these systems, in which interactions are not only nonspecific, but also specific.

Further verification of these models by the use of consecutive members of groups of test analytes will result in their classification as general or "local" (i.e., only useful for selected groups of analytes) and, consequently, in the exact definition of their areas of usefulness as precise tools for collecting thermodynamic data.

Three investigated physicochemical models of solute retention in GC

Of the ten new GC models presented elsewhere (16–22), in this study we focus on the three that perform the best for our medium-polarity analytes (i.e., methyl *n*-alkyl ketones). These models will be introduced in the forthcoming sections and tested for their performance in predicting solute retention and deriving thermodynamic data.

Model I ($r = A \exp(BT_B) + \text{constant}$)

The derivation of Model I has been presented in reference 16. The assumptions and an outcome of this particular approach will be briefly summarized. The essential physicochemical magnitudes referring to the chromatographic process are the relative retention time:

$$r = \frac{t_R}{t_{R(st)}} \quad \text{Eq. 1}$$

and the retention factor (k):

$$k = \frac{t_R - t_M}{t_M} \quad \text{Eq. 2}$$

where r denotes the relative retention; t_R and $t_{R(st)}$ are the retention times of a given analyte and the standard compound (min), respectively; and t_M is the column hold-up time (min).

The retention factor has its thermodynamic interpretation as well, namely:

$$k = K\beta \quad \text{Eq. 3}$$

which can also be given in a logarithmic form as:

$$\ln k = \ln(K\beta) = \ln K + \ln \beta \quad \text{Eq. 4}$$

where K is the thermodynamic constant of the partitioning of an i th analyte between the stationary and mobile phase and β is the phase ratio.

However, it is also well-known that:

$$\ln K = \frac{\Delta\mu_p}{RT_c} \quad \text{Eq. 5}$$

where $\Delta\mu_p$ is the standard chemical potential of the partitioning of this analyte between the stationary and mobile phase, R is the universal gas constant (8.314 J mol⁻¹K⁻¹), and T_c is the working (i.e., column) temperature (K).

If we substitute equation 5 into 4 and then additionally make use of equations 1 and 2, then we will obtain the following relationship:

$$\ln \frac{rt_{R(st)} - t_M}{t_M} = \frac{\Delta\mu_p}{RT_c} + \ln \beta \quad \text{Eq. 6}$$

For the process of vaporization (which is in fact involved in the partitioning of an analyte between the stationary and mobile phase) the following regularity is observed:

$$\Delta\mu_p = \Delta H_{vap} - T_c \Delta S_{vap} \quad \text{Eq. 7}$$

where ΔH_{vap} and ΔS_{vap} are the enthalpy and entropy, respectively, of its vaporization.

Utilizing Trouton's rule:

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_B} = \text{constant} = 85 \text{ (J mol}^{-1} \text{K}^{-1}) \quad \text{Eq. 8}$$

we can transform equation 7 into the following form:

$$\Delta\mu_p = \Delta S_{vap} T_B - \Delta S_{vap} T_c = \Delta S_{vap} (T_B - T_c) = 85(T_B - T_c) \quad \text{Eq. 9}$$

where T_B is the boiling point of an i th analyte (K).

Substituting equation 9 into 6, we obtain the following relationship:

$$\ln \frac{rt_{R(st)} - t_M}{t_M} = \frac{85(T_B - T_c)}{RT_c} + \ln \beta \quad \text{Eq. 10}$$

Upon performing all necessary transformations, the following final form of the equation is obtained:

$$r = \frac{t_M \beta}{t_{R(st)}} \exp\left(-\frac{85}{R}\right) \exp\left(\frac{85 T_B}{RT_c}\right) + \frac{t_M}{t_{R(st)}} \quad \text{Eq. 11}$$

which of course can also be written in a simpler way:

$$r = A \exp(BT_B) + \text{constant} \quad \text{Eq. 12}$$

where:

$$A = \frac{t_M \beta}{t_{R(st)}} \exp\left(-\frac{85}{R}\right) \quad \text{Eq. 13}$$

$$B = \frac{85}{RT_c} \quad \text{Eq. 14}$$

$$\text{constant} = \frac{t_M}{t_{R(st)}} \quad \text{Eq. 15}$$

Model II ($I = C + DT_B$)

Model II was first introduced and extensively discussed in references 17 and 18. Its abbreviated derivation can start from the fol-

lowing and well-known relationship, which describes the Kováts retention index (I):

$$\frac{I}{100} = \frac{\Delta\mu_{p(i)} - \Delta\mu_{p(z)}}{\Delta\mu_{p(z+1)} - \Delta\mu_{p(z)}} + z \quad \text{Eq. 16}$$

where $\Delta\mu_{p(i)}$, $\Delta\mu_{p(z)}$, $\Delta\mu_{p(z+1)}$, and $\Delta\mu_{p(-CH_2-)}$ are the standard chemical potentials of the partitioning of the i th analyte, n -alkane with z carbon atoms, n -alkane with $(z+1)$ carbon atoms, and one methylene group ($-CH_2-$), respectively, between the stationary and mobile phase.

Besides, we know from the multiple empirical studies that with simply structured molecules (e.g., those that lack double or triple bonds) the respective chemical potentials are structurally additive. Thus:

$$\Delta\mu_{p(z+1)} - \Delta\mu_{p(z)} = \Delta\mu_{p(-CH_2-)} \quad \text{Eq. 17}$$

Substituting equation 17 into 16, we obtain:

$$\frac{I}{100} = \frac{\Delta\mu_{p(i)} - \Delta\mu_{p(z)}}{\Delta\mu_{p(-CH_2-)}} + z = \frac{\Delta\mu_{p(i)}}{\Delta\mu_{p(-CH_2-)}} - \frac{\Delta\mu_{p(z)}}{\Delta\mu_{p(-CH_2-)}} + z \quad \text{Eq. 18}$$

Assuming great structural similarity between the methylene ($=CH_2$) and methyl ($-CH_3$) groups, we can further accept that the chemical potentials for these two functionalities are practically equal. If we apply this general rule to the homologous series of n -alkanes utilized for the determination of the magnitude I , we obtain the following dependence:

$$\frac{\Delta\mu_{p(z)}}{\Delta\mu_{p(-CH_2-)}} \cong z \quad \text{Eq. 19}$$

Substituting equation 19 into 18 and making all of the necessary transformations, we obtain the relationship:

$$\frac{I}{100} = \frac{\Delta\mu_{p(i)}}{\Delta\mu_{p(-CH_2-)}} \quad \text{Eq. 20}$$

Keeping in mind the validity of equations 7–9 and substituting equation 9 into 20, we finally obtain the following relationship (which can optionally be written in two different ways):

$$\frac{I}{100} = \frac{85(T_B - T_c)}{\Delta\mu_{p(-CH_2-)}} \quad \text{Eq. 21}$$

or

$$\frac{I}{100} = \frac{100 \cdot 85}{\Delta\mu_{p(-CH_2-)}} T_B - \frac{100 \cdot 85 T_c}{\Delta\mu_{p(-CH_2-)}} \quad \text{Eq. 22}$$

Obviously, equation 22 can also be written in a simpler form:

$$I = C + DT_B \quad \text{Eq. 23}$$

where

$$C = - \frac{100 \cdot 85 T_c}{\Delta\mu_{p(-CH_2-)}} \quad \text{Eq. 24}$$

$$D = \frac{100 \cdot 85}{\Delta\mu_{p(-CH_2-)}} \quad \text{Eq. 25}$$

Model III ($r = E \exp(FR_m + G(R_m/T_B)) + \text{constant}$)

Model III was first introduced in reference 22. At the initial stages its derivation was fully analogical to that of Model I (see equations 1–8). Substituting equation 8 into 7, we obtain the relationship:

$$\Delta\mu_p = \Delta H_{vap} - T_c \frac{\Delta H_{vap}}{T_B} \quad \text{Eq. 26}$$

Then, we make an additional assumption that with a set of congeneric or homologous analytes, the ΔH_{vap} values are proportional to their respective molar volumes (V_m), thus the magnitude (ΔH°) can be viewed as the proportionality coefficient. In physicochemical terms, ΔH° is the enthalpy of vaporization of the volume unit of any given analyte from the homologous series discussed:

$$\Delta H_{vap} = \Delta H^\circ V_m \quad \text{Eq. 27}$$

Moreover, in our derivation we also make use of the classical relationship describing the molar refraction (R_m) of the i th analyte as a function of its unitless refraction index (n) and molar volume (V_m):

$$R_m = \left(\frac{n^2 + 2}{n^2 - 1} \right) V_m \quad \text{Eq. 28}$$

Substituting equation 28 into 27 and then introducing the relationship obtained in equation 26, we finally get the following dependence:

$$\Delta\mu_p = \Delta H^\circ \left(\frac{n^2 + 2}{n^2 - 1} \right) R_m - T_c \frac{\Delta H^\circ \left(\frac{n^2 + 2}{n^2 - 1} \right) R_m}{T_R} \quad \text{Eq. 29}$$

Substituting equation 29 into 6, we obtain the following relationship:

$$\ln \frac{rt_{R(st)} - t_M}{t_M} = \frac{\Delta H^\circ \left(\frac{n^2 + 2}{n^2 - 1} \right) R_m - T_c \frac{\Delta H^\circ \left(\frac{n^2 + 2}{n^2 - 1} \right) R_m}{T_B}}{RT_c} + \ln \beta \quad \text{Eq. 30}$$

which after necessary transformations results in the following form:

$$r = \frac{t_M \beta}{t_{R(st)}} \exp \left(\frac{\Delta H^\circ}{R} \left(\frac{n^2 + 2}{n^2 - 1} \right) R_m - \frac{\Delta H^\circ}{R} \left(\frac{n^2 + 2}{n^2 - 1} \right) \frac{R_m}{T_B} \right) + \frac{t_M}{t_{R(st)}} \quad \text{Eq. 31}$$

Equation 31 can also be written in a simpler form:

$$r = \exp \left(FR_m + G \frac{R_m}{T_B} \right) + \text{constant} \quad \text{Eq. 32}$$

$$E = \frac{t_M \beta}{t_{R(st)}} \quad \text{Eq. 33}$$

$$F = \frac{\Delta H^\circ}{RT_c} \cdot \frac{n^2 + 2}{n^2 - 1} \quad \text{Eq. 34}$$

$$G = \frac{\Delta H^\circ}{R} \cdot \frac{n^2 + 2}{n^2 - 1} \quad \text{Eq. 35}$$

Table I. Characteristics of the Stationary Phases Used*

Composition		Polarity [†]
DB-1	100% Polydimethylsiloxane	217
DB-5	95% Polydimethylsiloxane + 5% phenyl	323
DB-Wax	100% Poly(ethylene glycol)	2188

* All columns were manufactured by J&W and have the same dimensions (30-m × 0.32-mm i.d., $d_i = 1 \mu\text{m}$).
[†] Sum of the first five McReynolds constants.

Table II. The Numerical Values of Estimates of the Equation Parameters (*B*) and the Regression Parameters (Number of Measurements (*N*), *R*, and *R*²) for the Measurement Temperatures and Stationary Phases Investigated for Model I

<i>T_c</i> (K)	constant	<i>B</i>	Final loss*	<i>N</i>	<i>R</i>	<i>R</i> ² (%)
DB-1						
348	0.18	0.0338	0.0024	21	0.99996	99.993
373	0.34	0.0300	0.0010	21	0.99997	99.993
DB-5						
348	0.20	0.0342	0.0022	21	0.99997	99.993
373	0.37	0.0301	0.0012	21	0.99996	99.991
DB-Wax						
348	0.22	0.0175	1.5552	24	0.98930	97.872
373	0.26	0.0175	1.3762	27	0.99370	98.744

* Calculated by means of the least squares method.

Table III. The ΔH_{vap} Values Calculated from the Fitting Parameter (*B*) for the Working Conditions Given in Table II and Data Taken from the Literature for Model I*

Analyte [†]	ΔH_{vap} (kJ/mol)						Data taken from the literature (kJ/mol)				
	Experimental results										
	DB-1		DB-5		DB-Wax						
	348	373	348	373	348	373	$-\Delta H_{\text{sol}}^{\ddagger, \$}$	$ \Delta H_{\text{sol}}^{\circ} ^{**}$	$\Delta H_{\text{vap}}^{\dagger\dagger}$	$-\Delta H_{\text{sol}}^{\ddagger\ddagger}$	$\Delta H_{\text{vap}}^{\S\S}$
C ₃	32.19	30.62	32.57	30.72	16.67	17.86	23.88	26.71		29.03	27.81
C ₄	34.49	32.81	34.89	32.92	17.86	19.14	27.50	31.54		31.73	31.30
C ₅	36.71	34.92	37.14	35.04	19.00	20.37	31.05	35.03		34.35	34.87
C ₆	39.19	37.28	39.65	37.41	20.29	21.75	35.85	39.06		37.85	39.62
C ₇	41.48	39.46	41.97	39.59	21.48	23.02	40.79	44.51	47.28	41.12	43.14
C ₈	43.58	41.46	44.10	41.60	22.56	24.19	44.47	48.31	50.80	43.91	47.04
C ₉	45.81	43.58	46.35	43.73	23.72	25.42	48.68	52.62		46.94	50.94
C ₁₂	50.82	48.34	51.42	48.51	26.31	28.20	61.33	65.55		56.03	62.63
C ₁₃	52.43	49.88	53.05	50.05	27.15	29.10	65.55	69.87		59.06	66.53
C ₁₅	55.46	52.76	56.12	52.94	28.72	30.78	73.98	78.49		65.12	74.33

* Italics denote numerical values extrapolated by use of the regression equation relating ΔH_{vap} to the number of carbon atoms in the analyte molecule.

[†] Symbols denoting the number of carbon atoms in the molecule of a given homologous analyte.

[‡] ΔH_{sol} , enthalpy of solution.

[§] HP-1 column ($\Sigma = 222$). $T_c = 323$ –83 K (24). The sign Σ denotes the sum of the five McReynolds constants.

** Absolute numerical value of $\Delta H_{\text{sol}}^{\circ}$. HP-1 column ($\Sigma = 222$). $T_c = 298$ K (25).

^{††} DB-5MS column ($\Sigma = 323$). $T_c = 343$ –83 K (12).

^{†††} HP-Innowax column ($\Sigma = 2308$). $T_c = 323$ –83 K (24).

^{§§} $T_c = 353$ K (24).

Experimental

The performance of the three retention models was tested for a homologous series of methyl *n*-alkyl ketones (GC standards purchased from PolyScience Corporation, Niles, IL). *n*-Alkanes (purchased from PolyScience Corporation as GC standards and from E. Merck (Darmstadt, Germany) and J.T. Baker (Deventer, Holland) as compounds of GC purity grade) were used as reference compounds for the determination of the retention indices.

Solutions (1 $\mu\text{L}/\text{mL}$) of the analytes were prepared in acetone and those of the standards in *n*-hexane. The retention times of the analytes were measured by using a Fisons Instruments GC 8000 series capillary GC. Samples (0.2 μL) were injected on-column, and helium (99.9999% purity) was used as the carrier gas at a flow rate of 1.35 mL/min. Detection was performed by flame ionization (220°C detector temperature). Heptan-2-one (C₇) was selected as the standard for the calculation of *r*.

Experiments were performed at temperatures from 323 to 423 K (in 25-K intervals) for the three different stationary phases (of different polarity) listed in Table I. All of the retention data were measured under isothermal conditions.

Collection and processing of the chromatographic data were carried out using the computer program Chrom Card 2.0 (Fisons Instruments). The raw results and the necessary physicochemical data are all given elsewhere (22,23). The statistical performance of the models was examined with the aid of the program Statistica 5.1 PL (StatSoft Polska, Cracow, Poland).

Results and Discussion

For further verification of the models (described elsewhere)

(16–22) and to expand their range of applicability, they had to be tested on a sufficiently wide type of analytes. For the purpose of this study we employed a homologous series of medium-polarity methyl *n*-alkyl ketones and stationary phases with a wider range of polarity (the phases differed in polarity by a factor of approximately ten on the McReynolds scale).

Models giving good statistical and thermodynamic performance with our test analytes were listed earlier. Although our study was carried out at five different temperatures, the results presented in this study were obtained only at the temperatures at which model performance was the best.

Model I

Model I (Table II) assumes the form of an exponential equation and describes the relationship between the *r* value of the analyte and its T_B . Elevated numerical values of *R*, and consequently also of its second power (R^2), and the really negligible values of final

losses are evidence of the excellent statistical performance of this model and, therefore, of its suitability for the prediction of the analytes' retention. On the basis of these premises the model can be used to distinguish upon its performance between different stationary phases.

The thermodynamic magnitude, which can be derived from Model I, is the molar ΔH_{vap} . This particular property does not appear explicitly in the model, but Trouton's rule states that:

$$85 = \Delta S_{vap} = \frac{\Delta H_{vap}}{T_B} \quad \text{Eq. 36}$$

By the use of equation 15, ΔH_{vap} can be calculated as equal to $BRT_c T_B$. The resulting numerical values of ΔH_{vap} are given in Table III and compared with data taken from the literature and with those extrapolated by the use of linear regression, which relates the enthalpy of vaporization with the number of carbon atoms in the molecule of the analyte (as denoted by the italics). This comparison gives evidence that the model can be successfully applied to the determination of the numerical values of ΔH_{vap} for methyl *n*-alkyl ketones chromatographed on low-polarity stationary phases.

Model II

Model II is a simple linear model relating *I* and T_B . The regression data (Table IV) (i.e., *R* and the Fisher–Snedecor test value (*F*), and also the confidence value for the *F* value (*p*) and the standard error of estimation (*SD*)) prove that this model is particularly useful for the prediction of analyte retention. Similarly to Model I, the best results were again obtained for the low-polarity stationary phases (DB-1 and DB-5). Seemingly high numerical values of *SD* are in fact quite insignificant when compared with the numerical values of the *I* values, which are approximately 10^2 to 10^3 (expressed in dimensionless units).

This linear model enables the determination of the two thermodynamic magnitudes, $\Delta\mu_{p(-CH_2-)}$, and ΔH_{vap} .

$\Delta\mu_{p(-CH_2-)}$ can be easily derived from terms *C* or *D*. Because *D* is simpler than *C* (it contains fewer physical magnitudes), it is recommended that $\Delta\mu_{p(-CH_2-)}$ be calculated from *D*. The results

Table IV. Numerical Values of the Fitting Parameters (*D*) of the Equations (with the Respective Errors) and the Regression Parameters (Number of Measurements (*N*), *R*, *F*, *SD*, and *p) for Model II**

T_c (K)	$D \pm s_D^\dagger$	<i>N</i>	<i>R</i>	<i>F</i>	<i>SD</i>
DB-1					
348	4.14 ± 0.02	21	0.9998	51166.1	3.9125
373	4.28 ± 0.03	18	0.9997	25050.1	4.5554
DB-5					
348	4.28 ± 0.03	21	0.9996	24110.6	5.8878
373	4.20 ± 0.04	18	0.9991	9187.8	7.3844
DB-Wax					
348	4.42 ± 0.24	24	0.9683	330.8	70.2505
373	3.72 ± 0.11	24	0.9898	1066.7	34.2164

* In each case, $p < 0.0000$.
[†] s_D , standard deviation.

Table V. $\Delta\mu_{p(-CH_2-)}$ Calculated by the Fitting Parameters (*D*) for the Chromatographic Conditions Given in Table IV and Data Taken from the Literature

Analyte*	$\Delta\mu_{p(-CH_2-)} \text{ (kJ/mol)}$											
	Experimental results						Data taken from the literature (kJ/mol)					
	DB-1		DB-5		DB-Wax							
	$T_c \text{ (K)}$											
	348	373	348	373	348	373	348	373	348	373	348	373
<i>C</i> ₃ – <i>C</i> ₁₅	2.05	1.99	1.99	2.02	1.92	2.28	2.11 [†]	1.96 [†]	2.15 [§]	1.98 [§]	1.72 ^{††}	1.61 ^{††}
								2.18 [‡]	1.84 ^{**}	1.76 ^{**}		1.64 ^{††}

* Symbols denote the number of carbon atoms in the molecule of a given homologous analyte.
[†] OV-101 ($\Sigma = 229$) (5). The sign Σ denotes the sum of the five McReynolds constants.
[‡] PDMS (17).
[§] OV-3 ($\Sigma = 423$) (5).
^{**} SE-54 ($\Sigma = 337$) (5).
^{††} Carbowax 20M ($\Sigma = 2308$) (5).
^{††} PEG 20M ($\Sigma = 2308$) (18).

obtained can then be used for the determination of ΔH_{vap} by the use of the following equation (17):

$$\Delta H_{vap(i)} = \frac{I(i)}{100} \Delta \mu_{p(-CH_2-)} + 85T_c \quad \text{Eq. 37}$$

The numerical values of $\Delta \mu_{p(-CH_2-)}$ (Table V) are in good agreement with those taken from the literature (as usual, the greatest discrepancies are observed for the most polar stationary phase), whereas the experimentally obtained ΔH_{vap} values (Table VI) are slightly higher than those taken from the literature.

Model III

The opposite situation is observed for the last model discussed: the numerical values of ΔH_{vap} are slightly higher than those taken from the literature (Table VII). The experimental values of the enthalpy of vaporization are derived from the F term of the exponential equation. F includes one magnitude (ΔH°), which denotes the enthalpy of vaporization recalculated for unit volume of a congeneric compound (i.e., for 1 mL thereof). It has the same numerical value for each analyte from a given series, and multiplication by the molar volume of the homologue gives the molar ΔH_{vap} value (equation 27).

Although it was theoretically possible to determine ΔH_{vap} from G also, the error in this term was higher than that in F (as shown by preliminary statistical classification of Model III involving its linearization). This is most probably the reason why the enthalpy derived from G occasionally assumed negative values, even though ΔH° refers to the energy-consuming vaporization process and ought, therefore, to have positive values only.

The best agreement between the experimental results and those taken from literature was observed for the least polar sta-

tionary phase at the lowest measurement temperature (323 K). Table VIII contains some strikingly high R and R^2 values and extremely low final losses; we therefore used these conditions as our sole example. Use of a low-polarity stationary phase contributes markedly to the elimination of at least some of the unwanted intermolecular interactions, which are not taken into account in the model. The good performance of Model III at 323 K results from the relatively small discrepancy between our working temperature and that used to measure the physico-chemical data employed in the model (i.e., the refractive indices and densities of the analytes) (20°C, 293 K). Obviously, with changing measurement temperature the values of these two physical magnitudes change slightly, and assumption of their thermal stability is, therefore, an evident simplification, generating additional error. The higher the temperature used for GC, the greater the resulting errors; this results in a deterioration of the agreement between the data derived from Model III and those originating from different sources. In spite of this, the model can still be used to estimate analyte retention.

In spite of the different forms of the three models investigated and the different magnitudes used for the description of the retention data, each model serves its purpose well with regard to the analysis of the methyl *n*-alkyl ketones, enabling the prediction of their retention and the thermodynamic properties ΔH_{vap} and $\Delta \mu_{p(-CH_2-)}$. It is, however, worthy to note that the best results are consistently obtained on the low-polarity stationary phases (DB-1 and DB-5), for which there are no effective intermolecular interactions, than on the medium-polarity stationary phase (DB-Wax), which can interact with the analytes not only through nonspecific interactions, but also through specific interactions.

The focus again should be put upon the numerical values of

Table VI. ΔH_{vap} Values Calculated from the $\Delta \mu_{p(-CH_2-)}$ Values in Table V for the Chromatographic Conditions Given in Table IV and Data Taken from the Literature for Model II*

Analyte [†]	ΔH_{vap} (kJ/mol)						Data taken from the literature (kJ/mol)				
	Experimental results										
	DB-1		DB-5		DB-Wax						
	348	373	348	373	348	373	$-\Delta H_{sol}^{*,§}$	$ \Delta H_{sol}^{\circ} ^{**}$	$\Delta H_{vap}^{††}$	$-\Delta H_{sol}^{**}$	$\Delta H_{vap}^{§§}$
	T_c (K)										
C ₃	39.44		39.26	40.89	41.53		23.88	26.71		29.03	27.81
C ₄	41.45	43.06	41.48	44.01	47.58	53.11	27.50	31.54		31.73	31.30
C ₅	43.15	45.08	43.41	45.71	48.53	54.86	31.05	35.03		34.35	34.87
C ₆	45.38	47.04	45.32	47.69	49.76	56.74	35.85	39.06		37.85	39.62
C ₇	47.38	49.02	47.33	49.79	51.06	59.51	40.79	44.51	47.28	41.12	43.14
C ₈	49.40	50.97	49.30	51.76	53.28	61.26	44.47	48.31	50.80	43.91	47.04
C ₉	51.29	52.99	51.28	53.79	57.14	64.73	48.68	52.62		46.94	50.94
C ₁₂					58.87	66.85	61.33	65.55		56.03	62.63
C ₁₃						68.25	65.55	69.87		59.06	66.53

* Italics denote numerical values extrapolated by use of the regression equation relating ΔH_{vap} to the number of carbon atoms in an analyte molecule.

† Symbols denote the number of carbon atoms in the molecule of a given homologous analyte.

‡ ΔH_{sol} , enthalpy of solution.

§ HP-1 column ($\Sigma = 222$). $T_c = 323\text{--}83$ K (24). The sign Σ denotes the sum of the five McReynolds constants.

** Absolute numerical value of ΔH_{sol}° . HP-1 column ($\Sigma = 222$). $T_c = 298$ K (25).

†† DB-5MS column ($\Sigma = 323$). $T_c = 343\text{--}83$ K (12).

‡‡ HP-Innowax column ($\Sigma = 2308$). $T_c = 323\text{--}83$ K (24).

§§ $T_c = 353$ K (24).

ΔH_{vap} taken from the literature. The most frequently encountered enthalpy is that of solution (ΔH_{sol})—only occasionally do we encounter enthalpy of vaporization data. According to our basic assumption, for low-polarity solutes the absolute values of these two enthalpies are equal but they are of opposite signs (i.e., $-\Delta H_{sol} \approx \Delta H_{vap}$). This assumption was based on the fact that vaporization and solution are reverse processes and, therefore, their absolute enthalpies should be equal. In gas-liquid chromatography thermodynamic equilibrium is attained for the partitioning of an analyte between the liquid stationary phase and the gaseous mobile phase (which for low-polarity stationary phases can be approximated by the thermodynamic equilibrium between the processes of vaporization and solution of the pure analyte). The experimental enthalpies of vaporization and solution of the analytes, taken from the literature, originate from measurements conducted on stationary phases similar to (although not identical with) those employed in our investigations, and also at somewhat different measurement temperatures. Assumption of a relatively wide range of temperatures, for which the thermodynamic

behavior of the investigated chromatographic systems can be regarded as stable, enables a convenient comparison of the experimental results with those taken from the literature. Discrepancies among data originating from the different reference sources can be interpreted in favor of the results derived with the aid of the retention models studied in this work.

Conclusion

By the use of a group of medium-polarity analytes it was proved that each of the three retention models enables the prediction of retention in the capillary GC and estimation of the thermodynamic properties ΔH_{vap} and $\Delta \mu_{p(-CH_2-)}$.

Because of the different physicochemical nature of the used analytes and stationary phases, the quality of the statistical fits obtained varied considerably as did that of the respective thermodynamic data (thus the models considered can help to classify stationary phases according to their polarity).

The best agreement between the models and the investigated phenomena was observed when intermolecular interactions between the analyte and the stationary phase were least pronounced (i.e., for the low-polarity stationary phases DB-1 and DB-5). The performance of the models was worst for the medium-polar stationary phase DB-Wax.

The thermodynamic properties (i.e., ΔH_{vap} and $\Delta \mu_{p(-CH_2-)}$), determined by the use of Models I–III, are in good agreement with data taken from the literature, and with each model the best performance was observed for the least polar stationary phase.

Capillary GC is an efficient alternative (comparable with microcalorimetric techniques) for the derivation of thermodynamic data, if a suitable retention model is employed.

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Table VII. ΔH_{vap} Values Calculated from the Fitting Parameter (F) for the Working Conditions Given in Table VIII and Data Taken from the Literature for Model III*

Analyte [†]	ΔH_{vap} (kJ/mol)		Data taken from the literature (kJ/mol)	
	Experimental results			
	$T_c = 323$ K	$-\Delta H_{sol}^{*,§}$	$ \Delta H_{sol}^o ^{**}$	$\Delta H_{vap}^{opt††}$
C ₃	17.19	23.88	26.71	27.81
C ₄	21.24	27.50	31.54	31.30
C ₅	25.46	31.05	35.03	34.87
C ₆	29.76	35.85	39.06	39.62
C ₇	34.14	40.79	44.51	43.14
C ₈	38.09	44.47	48.31	47.04
C ₉	42.39	48.68	52.62	50.94
C ₁₂	55.47	61.33	65.55	62.63
C ₁₃	59.50	65.55	69.87	66.53

* Italics denote numerical values extrapolated by means of the regression equation relating ΔH_{vap} to the number of carbon atoms in an analyte molecule.

[†] Symbols denoting the number of carbon atoms in the molecule of a given homologous analyte.

[§] ΔH_{sol} , enthalpy of solution.

[§] HP-1 column ($\Sigma = 222$). $T_c = 323$ –83 K (24). The sign Σ denotes the sum of the five McReynolds constants.

** Absolute numerical value of ΔH_{sol}^o . HP-1 column ($\Sigma = 222$). $T_c = 298$ K (25).

†† $T_c = 353$ K (24).

Table VIII. Numerical Values of the Estimates of the Equation Parameters (F) and the Regression Parameters (Number of Measurements (N), R , and R^2) for the Measurement Temperatures and Stationary Phases Selected for Model III

T_c (K)	constant	F	Final loss*	N	R	R^2 (%)
DB-1						
323	0.07	0.2540	0.0007	18	0.99997	99.994

* Calculated by means of the least squares method.

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