

COULD MOLAR HEAT CAPACITY BE DERIVED FROM CHROMATOGRAPHIC DATA?

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SUMMARY

This paper, the latest in an established series on the alternative use of gas chromatographic data, is devoted to a possibility of deriving yet another thermodynamic magnitude from these data, the molar heat capacity, C_p . Traditionally, the molar heat capacity of a substance can be obtained directly by use of calorimeter [1]. Occasionally, however (e.g. when sufficient material is not available), this method can prove quite complicated. The question has thus been asked whether there are alternative possibilities of indirect measurement of this particular magnitude. In the work discussed in this paper we undertook this challenge by making an attempt to determine molar heat capacities for the three classes of compound, alkylbenzenes, aldehydes, and ketones, from simple chromatographic data originating from the capillary gas chromatography (CGC) and a set of specially devised mathematical models, complemented with appropriate statistical procedures.

INTRODUCTION

The general idea applied in this study has long been elaborated by our group and has been used in our earlier investigations. Stated simply, one must derive the relevant mathematical equations, on the basis of physicochemical and chromatographic assumptions and theories, and then to transform the fitting terms of the equations to obtain the thermodynamic magnitude of interest. In the first instance we successfully managed to determine the molar enthalpy of vaporization for a variety of different compounds and compound classes [2–4].

To determine the molar heat capacities, C_p , of the analytes investigated, we took into consideration three previously derived equations [4–6]:

$$r = A \exp\left(BV_m + C \frac{V_m}{T_B}\right) + const. \quad (1)$$

$$r_G = A \exp\left(BV_m + C\frac{V_m}{T_B}\right) + \text{const.} \quad (2)$$

$$\ln k = A + BV_m + C\left(\frac{V_m}{T_B}\right) \quad (3)$$

where r is the relative retention, r_G the non-reduced relative retention, k the retention factor, V_m the molar volume of the analyte, T_B its boiling point, and A , B , and C are physicochemically meaningful fitting terms of the equations.

The detailed derivation of eqs (1)–(3) has been described elsewhere and will not, therefore, be repeated here. These equations are the starting point of our current considerations. All three will be transformed in an analogous manner, because a physical magnitude of interest, the molar volume of the analytes (V_m), appears in each of these equations and will be substituted by one and the same expression.

THEORY

A simple yet classical way of defining the molar volume of a compound (V_m) is:

$$V_m = \frac{M}{d} \quad (4)$$

where M and d denote the molar weight and density of the compound, respectively.

The molar weight of a compound can also be given by the ratio of the molar heat capacity, C_p , to the specific heat capacity, c :

$$M = \frac{C_p}{c} \quad (5)$$

Combining eqs (4) and (5) gives:

$$V_m = \frac{C_p}{dc} \quad (6)$$

We also have at our disposal the Kopp and Neumann rule, according to which the molar heat capacity of a compound in the condensed

state is equal to the sum of the atomic heats of the individual atoms which constitute the compound. If we divide the molar heat capacity approximated in that way for a given compound by its molar weight, we obtain the specific heat capacity, which can be inserted in the denominator of eq. (6). The molar heat capacity present in the numerator of the same expression is the physical magnitude we are trying to obtain. It should, perhaps, be added that the Kopp and Neumann rule cannot be applied to the specific heat capacities of the elements in the sense that we cannot summarize them to obtain the specific heat capacities of our analytes, the magnitude of which must be introduced in eq. (6).

Let us return to eqs (1)–(3). These will now be re-written, although this time giving the complete physical description of the fitting terms B and C (the terms A and *const.* we leave as they are, because they are of no real importance in this study). Let us substitute eq. (6) for V_m in eqs (1)–(3) and, finally, let us rearrange the resulting relationships.

• **Equation (1):** $r = A \exp\left(BV_m + C\frac{V_m}{T_B}\right)$, $B = \frac{\overline{\Delta H^o}}{RT_c}$, $C = -\frac{\overline{\Delta H^o}}{R}$

where $\overline{\Delta H^o}$ is the enthalpy of vaporization of the analyte, recalculated per mole of a given congener (the mean value), T_c is the temperature of the column (analysis), and R the gas constant.

$$r = A \exp\left(\frac{\overline{\Delta H^o}}{RT_c} \cdot \frac{C_p}{dc} + \left(-\frac{\overline{\Delta H^o}}{R}\right) \frac{C_p}{dcT_B}\right) \quad (1a)$$

Let us rearrange the terms of the equation:

$$r = A \exp\left(\frac{\overline{\Delta H^o} C_p}{RT_c} \cdot \frac{1}{dc} + \left(-\frac{\overline{\Delta H^o} C_p}{R}\right) \frac{1}{dcT_B}\right) \quad (1b)$$

and re-write this equation in a simpler form:

$$r = A \exp\left(B\frac{1}{dc} + C\frac{1}{dcT_B}\right) \quad (1c)$$

where $B = \frac{\overline{\Delta H^{\circ} C_p}}{RT_c}$ and $C = -\frac{\overline{\Delta H^{\circ} C_p}}{R}$. It is apparent that the molar heat capacity, C_p (the magnitude that we are looking for) is present in the two terms B and C ; it can, consequently, be determined as follows:

$$C_p = \frac{BRT_c}{\Delta H^{\circ}} \text{ and } C_p = -\frac{CR}{\Delta H^{\circ}} \quad (7)$$

• **Equation (2):** $r_G = A \exp\left(BV_m + C\frac{V_m}{T_B}\right) + const.$, $B = \frac{\overline{\Delta H^{\circ}}}{RT_c}$, $C = -\frac{\overline{\Delta H^{\circ}}}{R}$

With this equation also let us perform the analogous transformations:

$$r_G = A \exp\left(\frac{\overline{\Delta H^{\circ}}}{RT_c} \cdot \frac{C_p}{dc} + \left(-\frac{\overline{\Delta H^{\circ}}}{R}\right) \frac{C_p}{dcT_B}\right) + const. \quad (2a)$$

$$r_G = A \exp\left(\frac{\overline{\Delta H^{\circ} C_p}}{RT_c} \cdot \frac{1}{dc} + \left(-\frac{\overline{\Delta H^{\circ} C_p}}{R}\right) \frac{1}{dcT_B}\right) + const. \quad (2b)$$

$$r_G = A \exp\left(B\frac{1}{dc} + C\frac{1}{dcT_B}\right) + const. \quad (2c)$$

where $B = \frac{\overline{\Delta H^{\circ} C_p}}{RT_c}$ and $C = -\frac{\overline{\Delta H^{\circ} C_p}}{R}$, and, again, let us determine the molar heat capacity of the compounds from these two terms:

$$C_p = \frac{BRT_c}{\Delta H^{\circ}} \text{ and } C_p = -\frac{CR}{\Delta H^{\circ}} \quad (7)$$

Now let us consider the last equation:

• **Equation (3):** $\ln k = A + BV_m + C\left(\frac{V_m}{T_B}\right)$, $B = \frac{\overline{\Delta H^{\circ}}}{RT_c}$, $C = -\frac{\overline{\Delta H^{\circ}}}{R}$

By an analogous procedure, analogous results are obtained:

$$\ln k = A + \frac{\overline{\Delta H^o}}{RT_c} \cdot \frac{C_p}{dc} + \left(-\frac{\overline{\Delta H^o}}{R} \right) \frac{C_p}{dcT_B} \quad (3a)$$

$$\ln k = A + \frac{\overline{\Delta H^o} C_p}{RT_c} \cdot \frac{1}{dc} + \left(-\frac{\overline{\Delta H^o} C_p}{R} \right) \frac{1}{dcT_B} \quad (3b)$$

$$\ln k = A + B \frac{1}{dc} + C \frac{1}{dcT_B} \quad (3c)$$

where $B = \frac{\overline{\Delta H^o} C_p}{RT_c}$ and $C = -\frac{\overline{\Delta H^o} C_p}{R}$. We finally obtain the two relationships:

$$C_p = \frac{BRT_c}{\overline{\Delta H^o}} \text{ and } C_p = -\frac{CR}{\overline{\Delta H^o}} \quad (7)$$

It worth noting that with each relationship the numerical values of the molar heat capacity from the respective fitting terms (B and C) are determined in exactly the same way. This suggests that the numerical results obtained by use of the three different relationships (and separately from terms B and C) should be similar, if the chromatographic conditions and the group of analytes investigated are kept exactly the same. It will be shown below that our intuition is correct.

Equations (1)–(3), introduced in this paper can also appear in a different form with the molar volume (V_m) replaced by the molar refraction (R_m). If we transform these relationships to obtain their final form, they become identical with eqs (1)–(3), respectively. Let us check just one example.

$$r = A \exp\left(BR_m + C \frac{R_m}{T_B} \right), \quad B = \frac{\overline{\Delta H^o}}{RT_c} \cdot \frac{n^2 + 2}{n^2 - 1}, \quad C = -\frac{\overline{\Delta H^o}}{R} \cdot \frac{n^2 + 2}{n^2 - 1} \quad (8)$$

where n is the refractive index of the given analyte. The molar refraction (R_m) is closely connected with the molar volume (V_m):

$$R_m = \frac{n^2 - 1}{n^2 + 2} \cdot V_m \quad (9)$$

Taking eq. (6) into account we obtain:

$$R_m = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{C_p}{dc} \quad (10)$$

Substitution of eq. (10) to eq. (8) gives:

$$r = A \exp \left(\frac{\overline{\Delta H^o}}{RT_c} \cdot \frac{n^2 + 2}{n^2 - 1} \cdot \frac{n^2 - 1}{n^2 + 2} \cdot \frac{C_p}{dc} + \left(-\frac{\overline{\Delta H^o}}{R} \cdot \frac{n^2 + 2}{n^2 - 1} \right) \frac{n^2 - 1}{n^2 + 2} \cdot \frac{C_p}{dcT_B} \right) \quad (8a)$$

and rearrangement of eq. (8a) gives the relationship:

$$r = A \exp \left(\frac{\overline{\Delta H^o} C_p}{RT_c} \cdot \frac{1}{dc} + \left(-\frac{\overline{\Delta H^o} C_p}{R} \right) \frac{1}{dcT_B} \right) \quad (8b)$$

If we define the respective fitting terms:

$$r = A \exp \left(B \frac{1}{dc} + C \frac{1}{dcT_B} \right), \quad B = \frac{\overline{\Delta H^o} C_p}{RT_c}, \quad C = -\frac{\overline{\Delta H^o} C_p}{R}, \quad (8c)$$

we finally extract from these fitting conditions the formulae already derived for determination of the molar heat capacity:

$$C_p = \frac{BRT_c}{\overline{\Delta H^o}} \quad \text{and} \quad C_p = -\frac{CR}{\overline{\Delta H^o}} \quad (7)$$

This final effect is indisputably clear—eq. (8c) is identical with eq. (1c), as also is the complete method for determination of the molar heat capacities of the compounds. A fully analogous outcome can also be obtained from the other two relationships.

The approach leading to determination of the molar heat capacities, C_p , of the compounds and presented in this section may seem somewhat complex and, therefore, the practical performance of the resulting relationships must be properly checked. In other words, one must ensure the proposed gas chromatographic strategy for obtaining the numerical values of C_p results in data which, if not very close, is at least in reasonable agreement with values obtained by other (e.g. direct) measurement techniques. Verification can only be achieved experimentally.

EXPERIMENTAL

Three groups of test analytes, alkylbenzenes, aldehydes, and ketones were tested by capillary gas chromatography. All these reagents were of GC standard purity grade (PolyScience Corporation, Niles, IL, USA and J.T. Baker, Deventer, The Netherlands).

Experiments were performed with a Fisons Instruments (Rodano/Milano, Italy) GC 8000 series capillary gas chromatograph with on-column injection and flame ionization detection. Isothermal chromatography was performed in the temperature range 323 to 423 K at 25 K intervals.

Analysis was performed on three different capillary columns (Agilent Technologies, Palo Alto, CA, USA, formerly J&W Scientific, Folsom, CA, USA), each of length, l , = 30 m, internal diameter, $i.d.$, = 0.32 mm, and stationary phase film thickness, d_f , = 1 μ m. Two low-polarity stationary phases, DB-1 (100% polydimethylsiloxane, polarity on the McReynolds scale 217) and DB-5 (95% polydimethylsiloxane + 5% phenyl, polarity 323) and one medium-polarity stationary phase, DB-Wax (100% polyethylene glycol, polarity 2188) were used.

Acquisition and immediate processing of the chromatographic data were performed by means of the computer program Chrom-Card for Windows 1.21 (CE Instruments, Milano, Italy). The programs Statistica 5.1. PL (StatSoft, Tulsa, OK, USA) and Matlab 6.5.0 (The MathWorks, Natick, MA, USA) were used for statistical analysis of the data. Excel (Microsoft Corporation, Redmont, WA, USA) was used for other computations.

RESULTS AND DISCUSSION

The aim of this study was not only determination of the molar heat capacity of the analytes, by means of the derived mathematical models, but also prediction of the retention of these analytes under the GC working conditions used.

In the first instance, however, the models ought to perform correctly in statistical terms, an indispensable precondition for reliable determination of the molar heat capacity of the compounds. This makes the issue of proper (i.e. chemometrically correct) statistical pretreatment of the experimental data of a paramount importance to the quality of the final result. The first step was proper selection of the experimental data sets. These data sets were chosen by the least median of squares (LMS) procedure, performed separately for each group of analytes. In this way outlier points were

eliminated. To enable application of the LMS procedure to the non-linear equations eqs (1c) and (2c), these relationships had first to be linearized.

Then, to derive numerical values of the fitting terms A , B , and C , and the statistical data also, which might enable evaluation of the fitting and predictive ability of the respective models, non-linear estimation by means of the quasi-Newton method was applied to the non-linear equations eqs (1c) and (2c) and the multiple regression procedure to eq. (3c).

Practical examples of the statistical treatment are given in Table I.

Table I

Statistical evaluation of the three mathematical models given by eqs (1c)–(3c) and the numerical values of the fitting terms (B and C), with their respective errors (n is the number of valid examples selected by the LMS procedure and r is the correlation coefficient). The test compounds were the aldehydes and the stationary phase was DB-1

Eq.	T_c (K)	$B \pm s_B$	$C \pm s_C$	n	RMS	% RMS	RMSCV	% RMSCV	r	Loss
1c	323	23.470 ± 0.106	-8932 ± 42	18	0.08	4.1	1.04	4.9	0.9988	0.783
	348	20.886 ± 0.025	-10456 ± 9	15	0.02	0.9	0.05	1.1	0.9999	0.007
	373	21.535 ± 0.220	-9325 ± 10	21	0.18	2.6	0.38	3.0	0.9933	1.208
	398	20.148 ± 0.200	-9596 ± 10	27	0.54	4.1	0.97	4.4	0.9957	3.174
	423	19.799 ± 0.003	-8802 ± 9	27	0.35	2.9	0.53	3.4	0.9952	0.995
2c	323	23.793 ± 0.109	-8563 ± 41	18	0.07	3.4	0.08	3.8	0.9987	0.101
	348	21.134 ± 0.027	-10130 ± 9	15	0.01	0.4	0.04	0.6	0.9998	0.004
	373	22.456 ± 0.220	-9329 ± 10	21	0.11	2.0	0.21	2.2	0.9939	0.915
	398	20.199 ± 0.001	-9544 ± 9	27	0.49	3.8	0.67	3.9	0.9957	2.657
	423	19.804 ± 0.001	-9820 ± 12	27	0.21	3.5	0.23	3.6	0.9951	1.175
3c	323	22.299 ± 0.539	-9237 ± 41	18	0.07	4.5	0.10	5.1	0.9987	X
	348	21.954 ± 0.196	-10243 ± 11	15	0.01	1.0	0.05	1.5	0.9997	
	373	22.408 ± 0.577	-9428 ± 8	21	0.12	3.4	0.16	4.1	0.9938	
	398	20.320 ± 0.258	-10025 ± 10	27	0.51	4.2	0.84	4.5	0.9956	
	423	20.398 ± 0.482	-9235 ± 13	27	0.12	2.2	0.11	2.5	0.9962	

The statistical term that gives evidence of the quality of fit of the derived model is the error of its fit to the data used for its construction, i.e. the root mean square error (RMS). Another statistical term, the root mean square error of cross-validation (RMSCV), characterizes the predictive power of the same model. RMSCV was evaluated for the independent test data by the validation method (in this work the leave-one-out approach). To achieve independent evaluation of the errors and to enable their comparison, the statistical data were standardized. All the data obtained are shown in Table I.

Statistics were also supplemented with the correlation coefficient, r , and, because some of our relationships are non-linear, with the loss function, which describes the amount of information lost in the course of fitting the curve to the measured data (this function was minimized by means of the least-squares method).

The numerical values of RMS and RMSCV ought to be as low as possible, because only then is evidence available of good fitting (%RMS) and of good predictive power (%RMSCV) of the model. The lowest possible loss function is also evidence of the good fit of the model.

From the data given in Table I it is apparent that the values of the standardized RMS and RMSCV errors do not exceed 5%, the values of the loss function are also low, and the high correlation coefficients ($r > 0.993$) clearly indicate that all three relationships applied to the examples selected (aldehydes, DB-1) and enabled good prediction of the retention of the analytes under these experimental GC conditions.

For the other chromatographic analyses the quality of the statistical data was similar to those shown in Table I. This enables us to deduce that with the aid of the equations tested in this study one can correctly predict the chromatographic behaviour of the analytes under any experimental conditions. In summary, the equations derived and discussed in this paper fulfil the first of the requirements stipulated herein, i.e. they enable prediction of retention.

Taking advantage of the opportunity, it might be worth taking a closer look at the numerical values, derived from the three equations scrutinized and obtained at analogous working temperatures. It is readily apparent that neither the respective statistical data nor the fitting terms differ too much among themselves. The reason is that in each instance we made use of the same database evaluated with aid of the same statistical procedure and, moreover, for each of the three evaluated equations the fitting terms B and C have exactly the same physical meaning. Consequently, final results (i.e. the molar heat capacity values) valid for a given working temperature and originating from each of the three equations are similar to one another. To make this conclusion more apparent and to confirm our intuition formulated in the *Theory* section, in Table II we present a selection of the numerical results (they refer to the example for which statistics were given in Table I).

If we compare molar heat capacity values (C_p) measured using identical working temperatures, we inevitably notice a striking similarity among them (although separately for those originating from term B and from term

Table II

Numerical values of molar heat capacity, C_p , for the aldehydes calculated by use of eqs (1c)–(3c), and the reference molar heat capacities derived by use of the Kopp and Neumann rule. For this example the stationary phase was DB-1. (The statistics for this example are given in Table I)

	T_c (K)					C_p ref. value	T_c (K)				
	323	348	373	398	423		323	348	373	398	423
	C_p (J mol ⁻¹ K ⁻¹) from term B						C_p (J mol ⁻¹ K ⁻¹) from term C				
<i>eq. (1c)</i>											
Propanal	145.53	114.24	166.80	140.73	151.82	126.76	171.47	164.33	193.63	168.40	159.56
Butanal	165.54	129.94	189.78	160.05	172.67	164.12	195.04	186.93	220.31	191.52	181.47
Pentanal	181.77	142.66	208.31	175.74	189.60	201.48	214.16	205.23	241.82	210.29	199.26
Hexanal	195.27	153.23	223.80	188.74	203.65	238.84	230.07	220.43	259.80	225.86	214.03
Heptanal	210.09	164.86	240.78	203.08	219.13	276.20	247.54	237.16	279.52	243.02	230.30
Octanal	226.75	177.96	259.92	219.23	236.53	313.56	267.16	256.00	301.74	262.33	248.59
Nonanal	241.03	189.17	276.25	233.02	251.42	350.92	283.98	272.12	320.69	278.84	264.24
Decanal	250.94	196.95	287.60	242.62	261.73	388.28	295.66	283.32	333.87	290.32	275.07
Undecanal	269.07	211.20	308.40	260.16	280.71	425.64	317.02	303.82	358.01	311.31	295.01
Dodecanal	278.59	218.67	319.35	269.34	290.60	463.00	328.25	314.56	370.73	322.30	305.41
<i>i</i> -Butanal	174.64	137.06	200.18	168.84	182.15	164.12	205.76	197.17	232.38	202.04	191.43
<i>i</i> -Pentanal	189.79	148.97	217.52	183.48	197.97	201.48	223.61	214.29	252.52	219.56	208.06
<i>eq. (2c)</i>											
Propanal	147.53	115.59	173.93	141.09	151.82	126.76	164.39	159.21	193.72	167.49	178.01
Butanal	167.81	131.48	197.90	160.45	172.67	164.12	187.00	181.10	220.41	190.48	202.46
Pentanal	184.26	144.36	217.22	176.18	189.61	201.48	205.33	198.83	241.92	209.15	222.31
Hexanal	197.95	155.05	233.37	189.22	203.66	238.84	220.58	213.55	259.91	224.63	238.78
Heptanal	212.98	166.82	251.08	203.60	219.13	276.20	237.32	229.77	279.64	241.70	256.93
Octanal	229.86	180.07	271.04	219.78	236.54	313.56	256.13	248.02	301.87	260.91	277.34
Nonanal	244.33	191.41	288.06	233.61	251.43	350.92	272.27	263.64	320.83	277.33	294.80
Decanal	254.38	199.29	299.91	243.23	261.74	388.28	283.46	274.49	334.02	288.75	306.88
Undecanal	272.76	213.71	321.59	260.82	280.72	425.64	303.94	294.35	358.17	309.63	329.13
Dodecanal	282.42	221.26	333.01	270.03	290.61	463.00	314.70	304.76	370.89	320.56	340.74
<i>i</i> -Butanal	177.03	138.69	208.74	169.27	182.16	164.12	197.27	191.02	232.48	200.95	213.57
<i>i</i> -Pentanal	192.39	150.73	226.83	183.94	197.98	201.48	214.38	207.61	252.62	218.37	232.13
<i>eq. (3c)</i>											
Propanal	138.27	120.07	173.56	141.93	156.41	126.76	177.32	160.99	195.79	175.93	167.41
Butanal	157.28	136.58	197.47	161.41	177.89	164.12	201.70	183.12	222.76	200.08	190.40
Pentanal	172.70	149.95	216.75	177.23	195.33	201.48	221.47	201.05	244.51	219.69	209.07
Hexanal	185.53	161.06	232.87	190.35	209.81	238.84	237.93	215.94	262.69	235.95	224.56
Heptanal	199.61	173.29	250.54	204.81	225.75	276.20	255.99	232.33	282.63	253.88	241.62
Octanal	215.44	187.05	270.45	221.09	243.69	313.56	276.28	250.79	305.09	274.06	260.82
Nonanal	229.00	198.83	287.44	235.00	259.03	350.9	293.68	266.58	324.26	291.30	277.24
Decanal	238.42	207.01	299.26	244.68	269.65	388.28	305.76	277.55	337.59	303.30	288.60
Undecanal	255.64	222.00	320.90	262.37	289.20	425.64	327.84	297.63	362.00	325.23	309.53
Dodecanal	264.70	229.84	332.29	271.63	299.39	463.00	339.45	308.16	374.85	336.71	320.44
<i>i</i> -Butanal	165.93	144.07	208.29	170.28	187.66	164.12	212.79	193.16	234.96	211.08	200.85
<i>i</i> -Pentanal	180.32	156.58	226.34	185.04	203.96	201.48	231.25	209.93	255.32	229.37	218.30

C). A good illustration is also given in Fig. 1, which shows that the experimental results are usually lower than those derived from the Kopp and Neumann rule (the only exceptions usually being the lower homologues). Better results are usually obtained by use of term *C* (for these results the error rarely exceeds 25%) than from *B*. Agreement between calculated and the experimental results is, however, not evidently better for the lower measurement temperatures, as might be expected because most of the physico-chemical constants appearing in the equations were determined at 293 K.

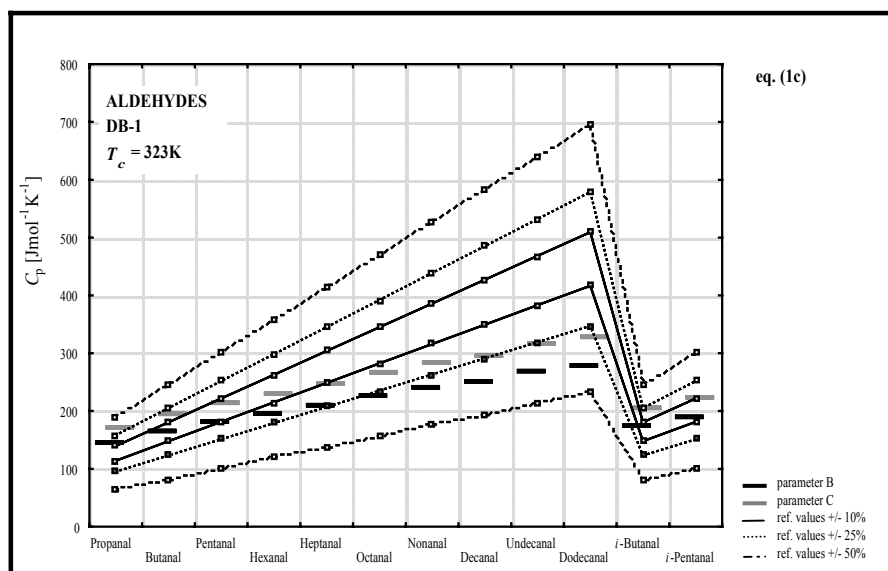


Fig. 1

Numerical values of the molar heat capacity, C_p , of aldehydes calculated on the experimental basis of chromatographic results from the fitting terms *B* and *C* for one of the tested relationships (eq. 1c), with the indicated ranges of the literature data. The stationary phase was DB-1

These observations and conclusions are also valid for the other experimental conditions used.

Let us again focus on numerical data taken from the literature and on the respective error limits. These data are the molar heat capacities and should better be called reference data, because they have never been cited in the literature in the form they are given in this paper. They were calculated for this study by use of the Kopp and Neumann rule (already mentioned in the *Theory* section) for each analyte separately. This procedure

consists in adding the atomic heats for all the atoms of the elements present in the structure of a given compound. Because we used selected alkylbenzenes, aldehydes, and ketones for our experiment we were making use of the atomic heats for three elements only, carbon, hydrogen, and oxygen. All the molar heat capacity (C_p) values given in this paper were derived from these data. The atomic heats for carbon (graphite), hydrogen, and oxygen are 8.53, 14.415, and 14.68 J mol⁻¹ K⁻¹, respectively [7].

The computed numerical values of C_p refer to standard conditions and are, of course, independent of the conditions used for gas chromatography. It is, moreover, readily apparent that, because of the procedure used, the values are identical for isomers.

It became clear to us there was strikingly good agreement between the molar heat capacities calculated by use of the Kopp and Neumann rule (our reference data) and data really originating from literature sources and derived by means of a variety of different measurement techniques (these

Table III

Comparison of reference molar heat capacity values, C_p , (J mol⁻¹ K⁻¹) obtained by use of the Kopp and Neumann rule and values taken from the literature for a selection of the test analytes

<i>Alkylbenzenes</i>	Reference data	Literature data ^a	
Benzene	137.67	136.1	
Toluene	175.03	162.0	
<i>o</i> -Xylene	212.39	188.8	
<i>m</i> -Xylene	212.39	183.3	
<i>p</i> -Xylene	212.39	183.8	
Ethylbenzene	212.39	185.9	
<i>Aldehydes</i>	Reference data	Literature data ^b	
Propanal	126.76	137.2	
Butanal	164.12	164.7	
Pentanal	201.48	189.2	
Hexanal	238.84	215.4	
<i>Ketones</i>	Reference data	Literature data ^a	Literature data ^b
Propanone	126.76	125	123.8
Butanone	164.12	162	159.2
Pentan-2-one	201.48		185.5
Hexan-2-one	238.84		214.8

^aAnalyte in condensed state, $T = 298.15$ K [7]

^bStationary phase DMPS, $T_c = 298$ K [8]

data are also subject to experimental and computational error). Evidence for this statement about good agreement is apparent from selected examples given in Table III. For this reason, in this study we used data calculated by use of the Kopp and Neumann rule as our reference data.

The average relative error of our calculated reference data compared with data taken from independent literature sources is approximately 7%, and even for some extreme values, i.e. for some alkylbenzenes, never exceeds 14%. Larger discrepancies observed for alkylbenzenes than for the other test analytes are most probably because of the aromatic nature of the carbon atoms in the molecules.

Taking into consideration the experimental error inevitably inherent in any chromatographic results, the numerous approximations contained in our models and their substantial complexity (these are equations with three independent variables), and the complex computational and statistical procedure we gave our reference values for the molar heat capacity (C_p) three error margins: $\pm 10\%$, $\pm 25\%$, and $\pm 50\%$. The choice of these margins, although arbitrary, was based on the following reasoning. Indirect derivation of thermodynamically valid experimental data (by means of CGC and of the assumed mathematical models) must be burdened by high experimental and computational error. For this reason even 100% error might seem understandable and acceptable. In these circumstances we agreed that error of 50% qualifies our results as acceptable whereas error half this (i.e. 25% error) was evidence of a very good outcome. The lowest discrepancy (10%) between the reference data and those from our research was regarded as excellent coincidence (because the reference data are also burdened with original experimental error).

Having explained the origin of the reference data, it is now time to focus on the experimental data, i.e. those derived from the fitting terms B and C . The molar heat capacity is calculated by use of eqs (1c)–(3c) in one and the same way, i.e. always using the terms given in eq. (7). The average magnitude $\overline{\Delta H^\circ}$ is assumed to be a constant in eqs (1)–(3), furnishing a unique numerical value for each individual group of congeneric analytes. If we really introduced the concept of averaging the enthalpy of vaporization for a given group of congeners to eqs (1c)–(3c), then for each analyte from this group chromatographed under these conditions we would obtain identical values of C_p . For the purpose of our current task, therefore, we slightly modified eqs (1c)–(3c) by replacing the average magnitude $\overline{\Delta H^\circ}$ with the magnitude ΔH° , unique for each separate analyte. ΔH° can

be obtained by dividing the molar enthalpy of vaporization of an analyte, ΔH_{vap} , by its molar volume. Only this procedure can guarantee different C_p values for the different analytes.

How can we obtain the individual numerical values of the enthalpy of vaporization, ΔH_{vap} , for each analyte considered in this study? These data can be derived from an equation published elsewhere [9]:

$$r_G = A \exp(BT_B) + \text{const.} \quad (11)$$

Of almost a dozen equations enabling derivation of ΔH_{vap} [4,10], eq. (11) proved the best performing and best at providing results most similar to the data available in the literature, hence we decided to make use of it in this study.

The chromatographic experiment was performed with three different stationary phases. An example of the data set obtained is given in Table IV. These results are valid for the least polar group of analytes, the alkylbenzenes, chosen specially to minimize intermolecular analyte–stationary phase-type interactions.

Again we confirmed our earlier observation that the calculated values of the molar heat capacity better resemble the reference data when derived from the low-polarity stationary phases than when derived from the more polar phases. The study also showed that intermolecular analyte–stationary phase-type interactions are responsible for elevation of the molar heat capacity values (Fig. 2).

We must now test the effect of the polarity of the analytes chromatographed on the same stationary phase on the outcome of our computations, i.e. on the numerical values of the molar heat capacity, C_p . To minimize the effect of intermolecular interactions we chose results from the least polar stationary phase, DB-1, for this discussion. The results obtained for the three types of analyte are shown in Table V.

If we consider the results given in Table V we notice the worst agreement between experimental and the reference C_p values for the most polar group of analytes, i.e. the ketones. For alkylbenzenes and aldehydes agreement is satisfactory and generally better when making use of the fitting term C than term B . For better visualization of these statements, one of the examples from Table V is also presented in a graphical form in Fig. 3.

It is apparent from the results of this study, viewed from several different directions, that the final results, i.e. the molar heat capacities (C_p) of the analytes, chromatographed under the given working conditions, can be regarded as satisfactory. One must keep in mind that the process used

Table IV

Numerical values of the molar heat capacity, C_p , of the alkylbenzenes, determined by use of eq. (1c) for the three stationary phases investigated, and the reference molar heat capacity values, derived from the Kopp and Neumann rule

	T_c (K)					C_p ref. value	T_c (K)				
	323	348	373	398	423		323	348	373	398	423
	C_p (J mol ⁻¹ K ⁻¹) from term B						C_p (J mol ⁻¹ K ⁻¹) from term C				
<i>DB-1</i>											
Benzene	150.60	190.24	292.37	212.48	197.24	137.67	192.50	229.91	278.18	198.57	253.13
Toluene	165.76	209.43	321.82	233.87	217.16	175.03	211.87	253.11	306.21	218.56	278.69
<i>o</i> -Xylene	173.15	218.80	336.24	244.28	226.80	212.39	221.32	264.43	319.92	228.29	291.06
<i>m</i> -Xylene	178.50	225.51	346.53	251.84	233.78	212.39	228.15	272.54	329.71	235.36	300.02
<i>p</i> -Xylene	179.39	226.63	348.25	253.09	234.96	212.39	229.28	273.89	331.36	236.52	301.54
Ethylbenzene	179.19	226.39	347.91	252.82	234.68	212.39	229.03	273.60	331.03	236.27	301.17
Cumene	195.44	246.93	379.44	275.70	255.95	249.75	249.80	298.43	361.03	257.65	328.47
<i>p</i> -Cymene	208.28	263.15	404.42	293.83	272.81	287.11	266.21	318.03	384.80	274.59	350.10
<i>n</i> -Propylbenzene	193.19	244.08	375.06	272.51	253.00	249.75	246.93	294.98	356.87	254.68	324.68
<i>n</i> -Butylbenzene	204.84	258.79	397.62	288.96	268.29	287.11	261.81	312.76	378.33	270.05	344.31
<i>n</i> -Hexylbenzene	227.08	286.89	440.90	320.38	297.45	361.83	290.24	346.72	419.51	299.41	381.72
<i>n</i> -Octylbenzene	246.88	311.93	479.30	348.29	323.35	436.55	315.55	376.98	456.04	325.49	414.96
<i>DB-5</i>											
Benzene	154.89	280.68	296.36	272.61	207.83	137.67	253.14	291.35	280.38	225.94	178.10
Toluene	170.47	308.98	326.27	300.08	228.81	175.03	278.61	320.73	308.69	248.71	196.09
<i>o</i> -Xylene	178.06	322.77	340.81	313.44	239.04	212.39	291.02	335.04	322.44	259.78	204.85
<i>m</i> -Xylene	183.54	332.69	351.30	323.14	246.32	212.39	299.98	345.33	332.36	267.82	211.09
<i>p</i> -Xylene	184.48	334.31	353.01	324.69	247.59	212.39	301.51	347.01	333.98	269.10	212.18
Ethylbenzene	184.26	334.01	352.66	324.36	247.31	212.39	301.14	346.71	333.65	268.84	211.94
Cumene	200.99	364.31	384.60	353.78	269.72	249.75	328.49	378.16	363.86	293.22	231.14
<i>p</i> -Cymene	214.19	388.29	409.95	377.06	287.51	287.11	350.06	403.05	387.85	312.51	246.39
<i>n</i> -Propylbenzene	198.66	360.02	380.14	349.65	266.60	249.75	324.69	373.70	359.65	289.80	228.47
<i>n</i> -Butylbenzene	210.64	381.77	403.15	370.78	282.68	287.11	344.25	396.28	381.42	307.30	242.25
<i>n</i> -Hexylbenzene	233.54	423.27	446.98	411.08	313.42	361.83	381.68	439.36	422.89	340.71	268.59
<i>n</i> -Octylbenzene	253.89	460.20	485.94	446.96	340.77	436.55	414.94	477.69	459.74	370.45	292.03
<i>DB-Wax</i>											
Benzene	247.15	361.96	320.23	268.54	244.37	137.67	303.72	339.30	264.71	334.74	293.86
Toluene	272.13	398.53	352.53	295.63	268.98	175.03	334.42	373.57	291.42	368.52	323.45
<i>o</i> -Xylene	284.17	416.27	368.18	308.80	280.95	212.39	349.22	390.20	304.35	384.93	337.85
<i>m</i> -Xylene	292.96	428.98	379.46	318.31	289.66	212.39	360.02	402.12	313.68	396.79	348.33
<i>p</i> -Xylene	294.34	431.12	381.41	319.84	291.08	212.39	361.72	404.13	315.29	398.69	350.03
Ethylbenzene	294.10	430.70	381.02	319.48	290.77	212.39	361.41	403.73	314.97	398.25	349.66
Cumene	320.81	469.72	415.53	348.50	317.17	249.75	394.24	440.30	343.49	434.42	381.40
<i>p</i> -Cymene	341.83	500.72	442.94	371.43	337.99	287.11	420.07	469.36	366.15	463.00	406.44
<i>n</i> -Propylbenzene	316.97	464.33	410.78	344.48	313.42	249.75	389.53	435.25	339.57	429.40	376.90
<i>n</i> -Butylbenzene	336.16	492.30	435.53	365.28	332.41	287.11	413.10	461.47	360.03	455.34	399.73
<i>n</i> -Hexylbenzene	372.66	545.89	482.89	404.93	368.55	361.83	457.97	511.71	399.18	504.76	443.18
<i>n</i> -Octylbenzene	405.23	593.42	524.94	440.20	400.64	436.55	497.98	556.26	433.94	548.72	481.78

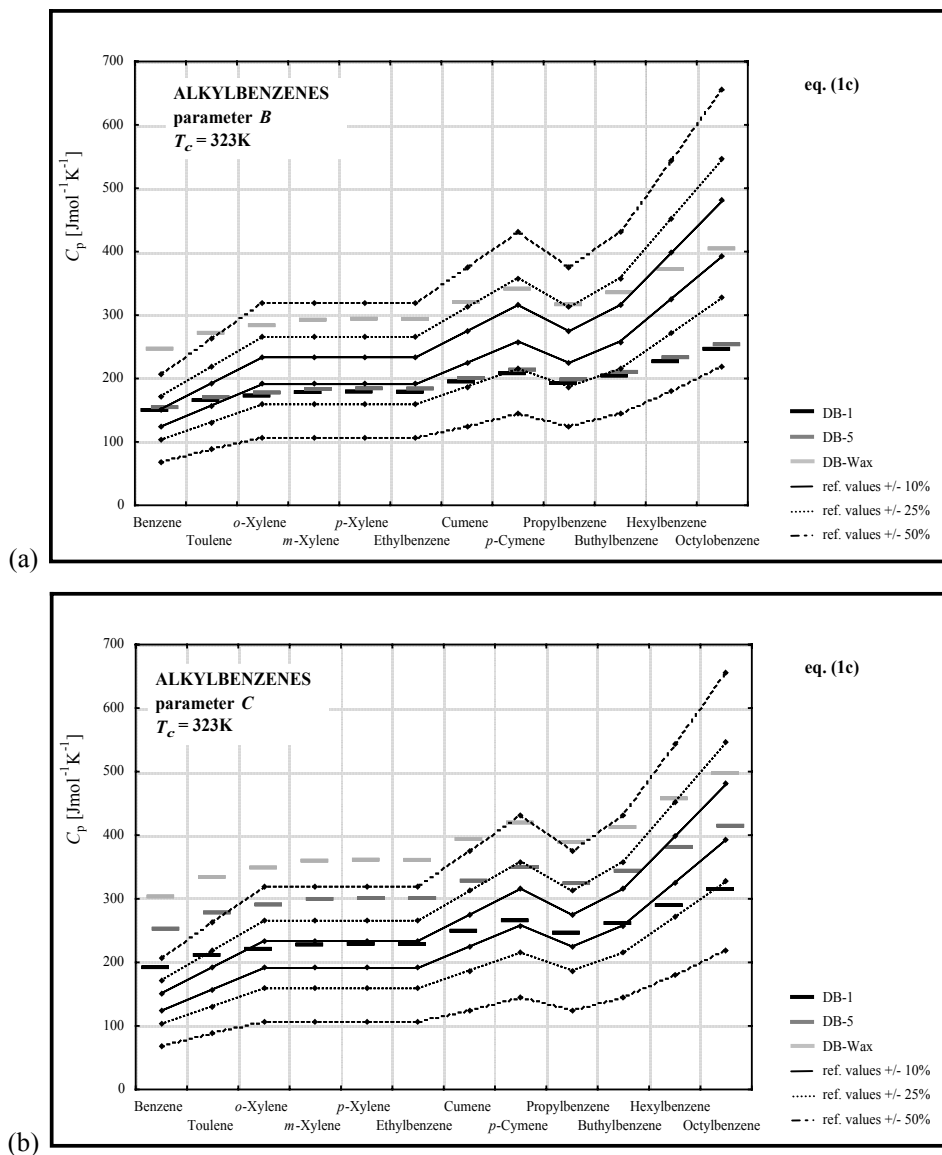


Fig. 2

Numerical values of the molar heat capacity, C_p , calculated for alkylbenzenes, at $T_c = 323\text{K}$, on different stationary phases, on the basis of experimental chromatographic results and use of the fitting terms B (a) and C (b) for one of the tested relationships, eq. (1c), and indicated ranges of the literature data

Table V

Numerical values of the molar heat capacity, C_p , determined for the three types of analyte on the same stationary phase, DB-1, by use of eq. (3c), and the reference molar heat capacity values, derived by use of the Kopp and Neumann rule

	T_c (K)					C_p ref. value	T_c (K)				
	323	348	373	398	423		323	348	373	398	423
	C_p (J mol ⁻¹ K ⁻¹) from term B						C_p (J mol ⁻¹ K ⁻¹) from term C				
<i>Alkylbenzenes</i>											
Benzene	155.00	190.89	298.56	218.74	208.02	137.67	180.60	220.71	257.52	171.19	223.28
Toluene	170.61	210.15	328.65	240.76	229.03	175.03	198.78	242.98	283.46	188.42	245.83
<i>o</i> -Xylene	178.21	219.55	343.36	251.48	239.19	212.39	207.64	253.85	296.16	196.81	256.74
<i>m</i> -Xylene	183.72	226.28	353.87	259.26	246.56	212.39	214.06	261.63	305.22	202.90	264.65
<i>p</i> -Xylene	184.63	227.41	355.63	260.55	247.81	212.39	215.12	262.93	306.74	203.91	265.98
Ethylbenzene	184.42	227.16	355.28	260.26	247.51	212.39	214.88	262.64	306.44	203.69	265.66
Cumene	201.15	247.78	387.48	283.82	269.94	249.75	234.36	286.48	334.21	222.12	289.74
<i>p</i> -Cymene	214.36	264.05	412.99	302.48	287.72	287.11	249.76	305.30	356.21	236.73	308.82
<i>n</i> -Propylbenzene	198.83	244.91	383.01	280.54	266.83	249.75	231.67	283.17	330.36	219.56	286.40
<i>n</i> -Butylbenzene	210.82	259.67	406.05	297.47	282.96	287.11	245.64	300.24	350.23	232.81	303.71
<i>n</i> -Hexylbenzene	233.71	287.87	450.24	329.82	313.71	361.83	272.31	332.84	388.34	258.12	336.72
<i>n</i> -Octylbenzene	254.09	313.00	489.46	358.55	341.02	436.55	296.06	361.89	422.17	280.61	366.04
<i>Aldehydes</i>											
Propanal		120.07	173.56	141.93	156.41	126.76	177.32	160.99	195.79	175.93	167.41
Butanal	157.28	136.58	197.47	161.41	177.89	164.12	201.70	183.12	222.76	200.08	190.40
Pentanal	172.70	149.95	216.75	177.23	195.33	201.48	221.47	201.05	244.51	219.69	209.07
Hexanal	185.53	161.06	232.87	190.35	209.81	238.84	237.93	215.94	262.69	235.95	224.56
Heptanal	199.61	173.29	250.54	204.81	225.75	276.20	255.99	232.33	282.63	253.88	241.62
Octanal	215.44	187.05	270.45	221.09	243.69	313.56	276.28	250.79	305.09	274.06	260.82
Nonanal	229.00	198.83	287.44	235.00	259.03	350.92	293.68	266.58	324.26	291.30	277.24
Decanal	238.42	207.01	299.26	244.68	269.65	388.28	305.76	277.55	337.59	303.30	288.60
Undecanal	255.64	222.00	320.90	262.37	289.20	425.64	327.84	297.63	362.00	325.23	309.53
Dodecanal	264.70	229.84	332.29	271.63	299.39	463.00	339.45	308.16	374.85	336.71	320.44
<i>i</i> -Butanal	165.93	144.07	208.29	170.28	187.66	164.12	212.79	193.16	234.96	211.08	200.85
<i>i</i> -Pentanal	180.32	156.58	226.34	185.04	203.96	201.48	231.25	209.93	255.32	229.37	218.30
<i>Ketones</i>											
Acetone	171.87	186.35	284.24	94.39	367.97	126.76	106.83	111.09	211.41	139.92	276.10
Butanone	195.76	212.22	323.79	107.51	419.13	164.12	121.68	126.51	240.83	159.37	314.48
Pentan-2-one	219.33	237.75	362.75	120.44	469.56	201.48	136.33	141.73	269.81	178.54	352.32
Hexan-2-one	237.61	257.54	392.95	130.46	508.59	238.84	147.69	153.53	292.27	193.40	381.60
Heptan-2-one	254.39	275.75	420.64	139.64	544.50	276.20	158.12	164.38	312.87	207.00	408.55
Octan-2-one	270.84	293.60	447.90	148.70	579.79	313.56	168.35	175.02	333.14	220.42	435.03
Nonan-2-one	288.64	312.91	477.44	158.49	618.00	350.92	179.41	186.53	355.12	234.95	463.70
Dodecan-2-one	329.85	357.61	545.51	181.10	706.14	463.00	205.03	213.18	405.75	268.46	529.84
Tridecan-2-one	346.53	375.70	573.19	190.28	741.93	500.36	215.39	223.96	426.33	282.07	556.69
Pentadecan-2-one	375.79	407.37	621.50	206.31	804.47	575.08	233.58	242.85	462.27	305.83	603.61

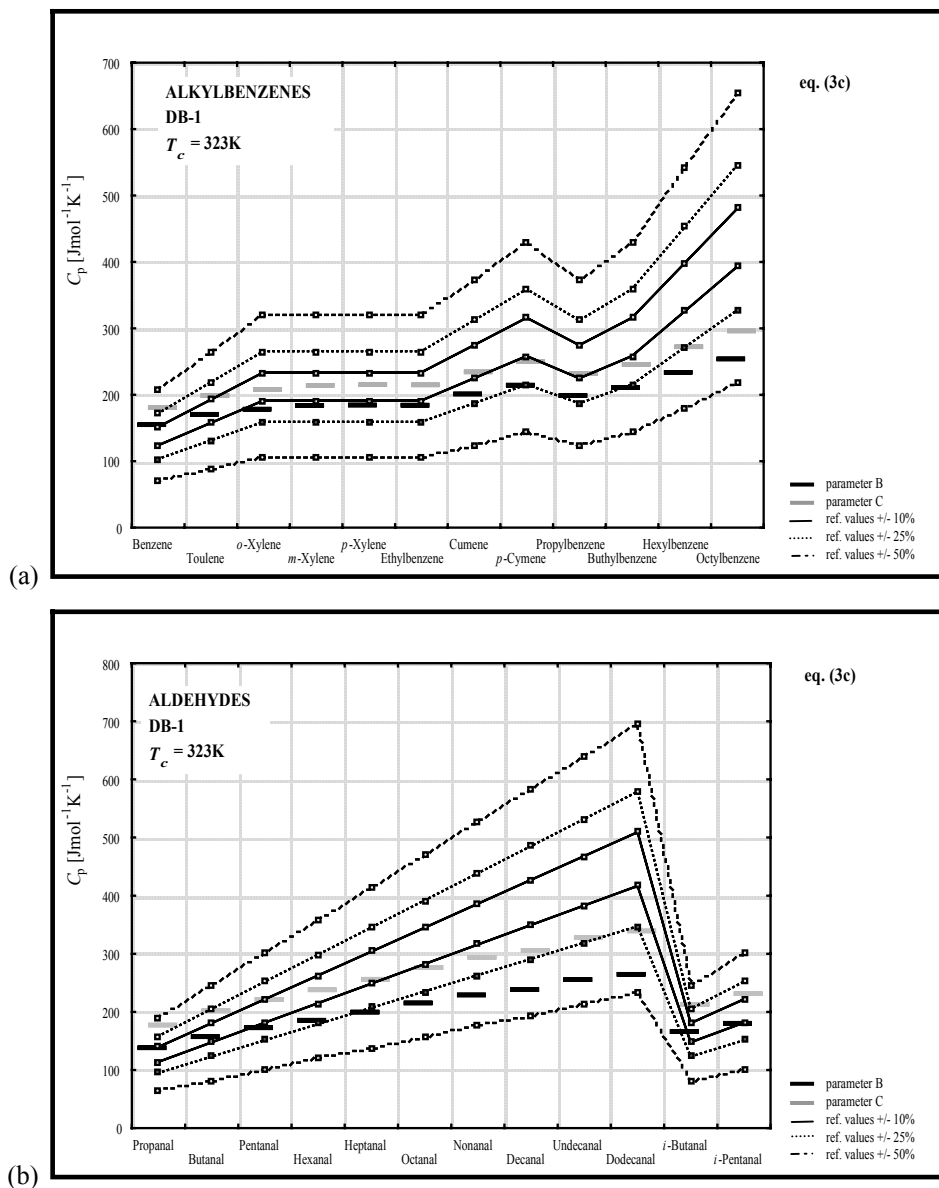


Fig. 3

Numerical values of the molar heat capacity, C_p , calculated for all three types of analyte, of different polarity (a, alkylbenzenes; b, aldehydes) on the basis of experimental chromatographic results with DB-1 as stationary phase, at $T_c = 323\text{K}$, and use of the fitting terms B and C from eq. (3c), with indicated ranges of literature data

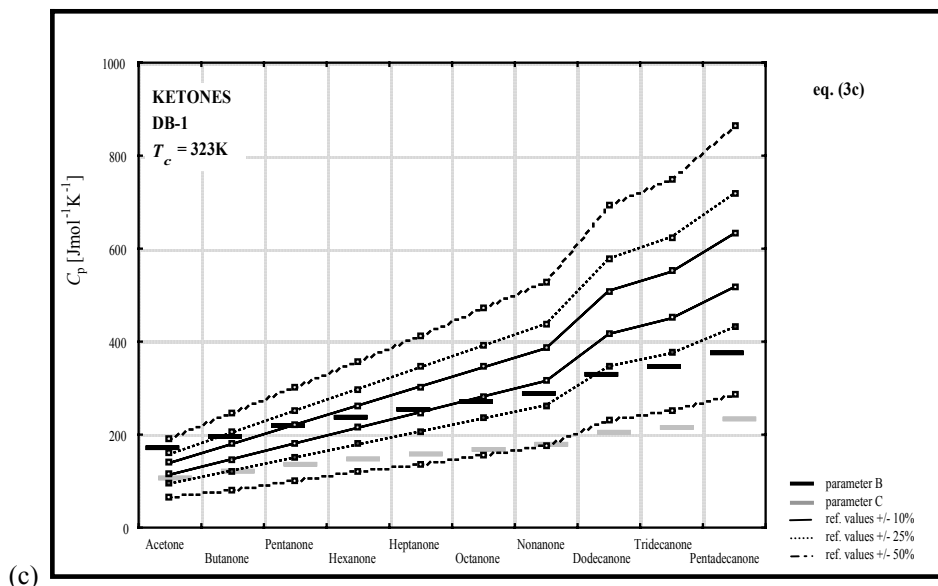


Fig. 3 (continued)

Numerical values of the molar heat capacity, C_p , calculated for all three types of analyte, of different polarity (c, ketones) on the basis of experimental chromatographic results with DB-1 as stationary phase, at $T_c = 323\text{ K}$, and use of the fitting terms B and C from eq. (3c), with indicated ranges of literature data

to derive them was complex and the intermediate stages thereof were burdened with several coarse simplifications, errors, and approximations. Now let us make a list of the major ‘traps’ on our way toward the ultimate result:

1. The reference values of the molar heat capacity were calculated by use of the approximate Kopp and Neumann rule (according to this rule isomeric aldehydes and ketones share, respectively, the same C_p values, although those derived from the independent experimental measurements show the expected differences). The reference values of the molar heat capacity are chromatographic-column-temperature-independent (whereas our experimental data originating from CGC were, of course, temperature-dependent).
2. The molar enthalpies of vaporization, ΔH_{vap} , crucial for calculation of the numerical values of ΔH° , were derived from eq. (11) and are inevitably burdened with error (which is usually within 10% although occasionally as much as 25%). Consequently, the numerical values of C_p are

indirectly burdened with analogous errors, the most acute cases being the alkylbenzenes and aldehydes chromatographed on DB-Wax and the ketones chromatographed on DB-1).

3. Imperfection of our model equations (because of simplifications, approximations, physical data valid for 293 K only, experimental errors, etc.) and a complicated computational and statistical procedure both contribute to enhancement of overall error in the final results.

CONCLUSIONS

- The three relationships tested enable prediction of the retention of the analytes under the chromatographic conditions used, as is proved by very good statistical data.
- For the three relationships applied to the assumed working conditions (i.e. when the group of test analytes, the stationary phase, and the column temperature are the same) final results, i.e. C_p values, are very similar.
- The proposed relationships enabled satisfactory estimation of the molar heat capacities of the analytes.
- The best agreement between obtained and the reference data was observed for alkylbenzenes and aldehydes; it was somewhat worse for the most polar group of test analytes, the ketones. Better results were obtained by use of low-polarity stationary phases than that of medium polarity, and by use of term C (which performs slightly better than B , although the observed differences are not very significant).
- There is no evident dependence of the quality of the results obtained on chromatographic working temperature. In other words, there was no confirmation from our experiment in support of the hypothesis that the best results originate from measurement at the lowest temperature (which might seem logical, because the reference molar heat capacity data were valid for 293 K).
- Good agreement of our experimental results with data obtained by use of the Kopp and Neumann rule gives evidence of the physicochemical soundness and satisfactory statistical performance of our novel models, despite their substantial complexity (the respective equations incorporate three independent variables, d , c , and T_B). Thus the derived models provide a convenient alternative to the long established calorimetric approaches and enable estimation of numerical values of the molar heat capacity from gas chromatographic data.

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