



Determination of vaporization enthalpies of simple organic molecules by correlations of changes in gas chromatographic net retention times

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Abstract

A technique is described for determining vaporization enthalpies $\Delta_f H_m(298\text{ K})$ of organic compounds by high resolution gas chromatography. The technique correlates changes in net retention times of compounds whose $\Delta_f H_m(298\text{ K})$ are known with those of the compound(s) of interest. The best results are obtained when the reference compounds are structurally similar and in the same chemical family. Application to hydrocarbons and various hydrocarbon derivatives containing one functional group is documented in this report. Comparison with literature values of 102 compounds resulted in a standard deviation of 1.27 kJ mol^{-1} . In most cases, the difference between the literature value and the value from our results is within the normal errors associated with vaporization enthalpy determinations. A linear correlation between the logarithms of experimental vapor pressure and reciprocal retention time was also observed for the compounds studied.

Keywords: GC; Heat of vaporization; Retention time; Vapour pressure

1. Introduction

Gas chromatography has been frequently used to measure thermodynamic properties of solutions, and a number of investigators have measured vaporization enthalpies of pure materials indirectly by this technique. The most detailed vaporization enthalpy studies are those of Peacock and Fuchs, who used gas chromatography to measure enthalpies of transfer from solution to vapor [1,2] and combined

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these results with solution calorimetry to correct for the heat of solution of the solute in the stationary phase of the column [2]. Although differences between literature and experimental vaporization enthalpies were observed, it was possible to obtain accurate vaporization enthalpies by correlating the observed vaporization enthalpies with literature values. The equation resulting from the correlation was used to correct other observed vaporization enthalpies obtained by this combined calorimetric–gas chromatographic technique. This procedure has been demonstrated on liquids boiling over a wide range of temperatures and containing a variety of functional groups [2].

We report some simple modifications of this technique that eliminate the need for the calorimetric measurements and generally simplify the experimental aspects of the experiment. As described by Fuchs and others [1,2], a plot of $\ln(1/t_r)$ vs. $1/(T/K)$, where t_r is the retention time corrected for the dead volume (retention time of a compound less the retention time of an unretained reference), results in a straight line, whose slope when multiplied by the gas constant affords $\Delta_{\text{sol}}^{\circ}H_m$. We have found that, in cases where compounds are properly selected with regards to molecular structure, plotting $\Delta_{\text{sol}}^{\circ}H_m$ against the known vaporization enthalpy at temperature T , $\Delta^{\circ}H_m(T)$, also affords a straight line. The equation of this line can subsequently be used to evaluate the unknown vaporization enthalpy of any structurally related material provided that the unknown is analyzed at the same time as the standards. We have applied this procedure in a systematic manner, and have found that this technique is capable of reproducing the resulting $\Delta^{\circ}H_m(298)$ of a compound generally within the experimental error limits associated with the vaporization enthalpy of the standards. Hydrocarbons, and also hydrocarbon derivatives containing single and multiple functional groups, have been examined in separate studies. This report focuses on the results obtained on hydrocarbons and hydrocarbon derivatives containing a single substituent.

2. Experimental

2.1. Instrumentation

All the determinations described here were performed on a Hewlett-Packard Model 5890 Series II Gas Chromatograph equipped with a split/splitless capillary injection port and a flame ionization detector (FID). No additional modifications were necessary. Retention times, in minutes, were recorded to three decimal places by means of a Hewlett-Packard Model 3396A integrator/plotter.

The chromatographic columns employed, unless otherwise stated, were a 30 m \times 0.32 mm DB-5 (from J and W Scientific) and a 60 m DB5-MS capillary column with a 0.25 μm film thickness. A 60 m \times 0.25 mm \times 0.20 μm SP-2331 fused silica capillary column was also used for some experiments. Helium was used as the carrier gas, with column head pressures of 2.5, 5, 10, 25 or 30 psi as noted. Although in principle these determinations should be possible on either packed or capillary columns, all of our experiments were performed on a capillary column.

Analyses were performed using a split injection ratio of $\approx 100:1$. A split injection was used to keep sample loading to a minimum, thereby also minimizing solute–solute interactions and increasing the accuracy of the retention time measurement. Standard injection size was 1 μl . Sample purity is not an issue using this technique, as the chromatography can generally separate the impurity from the compound of interest. Temperature control was provided by the instrument. The column temperature was monitored independently using a Kluge 51 K/J thermometer. Constant temperature was maintained within $\pm 0.1^\circ\text{C}$. The detector and injector were maintained at 250 and 200 $^\circ\text{C}$ respectively for all experiments.

2.2. Procedure

A small amount of sample is added to ≈ 1 ml of a volatile solvent such as carbon tetrachloride, methylene chloride or methanol. In cases where the solvent had a retention time causing it to interfere with the analysis, we used higher boiling solvents such as dodecane. Several standards of similar functionality to that of the target and whose vaporization enthalpies bracket the compound of interest were chosen. If the solvent is retained at the temperatures to be studied, a small amount of an unretained compound is added; e.g. methane, butene, etc., is bubbled into the solution. The non-retained standard used in each experiment in Tables 2–4 is noted following the numerical identification of each mixture unless otherwise indicated. Isothermal gas chromatograms were obtained over a 50 $^\circ\text{C}$ range at least every 10 K. The net retention time t_r was calculated for each compound by subtracting the retention time of the unretained compound. A plot of $\ln(1/t_r)$ vs. $1/(T/\text{K})$ for each compound results in a straight line that gives $\Delta_{\text{sol}}^{\text{g}}H_m$ when the slope is multiplied by the gas constant R . We have observed that the quality of the correlation coefficient is a good indication of whether the unretained compound is truly unretained at the temperature of the experiment. A correlation coefficient of < 0.99 obtained from a plot of $\ln(1/t_r)$ vs. $1/T$ is usually an indication of some retention (see Table 3, column 7). A second plot of $\Delta_{\text{sol}}^{\text{g}}H_m$ against $\Delta_f^{\text{g}}H_m(\text{lit})$ also results in a straight line if the standards are properly chosen. The vaporization enthalpy of the unknown is calculated from the equation of the line obtained in the second correlation.

More than one unknown can be determined in the same mixture providing that the compounds can be separated by the chromatography. We have measured as many as seven target compounds and five standards in the same mixture. The method is thus a very fast means of making determinations when several compounds of the same family and similar volatility are to be measured.

Capillary column injection ports are generally isobaric and this results in a decrease in flow rate as the helium viscosity increases with increasing column temperature. This effect is apparent in the retention times listed for carbon tetrachloride in Tables 1 and 2. Because the standards are analyzed at the same time as the targets and thus experience the same flow rate change, correction for this effect is not necessary. It is also significant to point out that, although $\Delta_{\text{sol}}^{\text{g}}H_m$ is evaluated at the average temperature T_M , the correlation with experimental values can be at any temperature. This correlation yields results directly applicable to the temperature

Table 1
GC retention times (in minutes) of various hydrocarbons vs. temperature

Compound ^a	Temperature/°C					
	150	160	170	180	190	200
Mix 1						
CCl ₄ ^b	2.053	2.071	2.099	2.120	2.153	2.178
Decane	2.554	2.464	2.412	2.373	2.360	2.349
Dodecane	3.488	3.145	2.920	2.757	2.656	2.580
Tetradecane	5.943	4.848	4.132	3.635	3.305	3.067
Pentadecane	8.392	6.489	5.264	4.430	3.875	3.484
Hexadecane	12.335	9.068	7.000	5.624	4.713	4.085
Octadecane	28.852	19.452	13.741	10.095	7.752	6.195
Compound ^a	Temperature/°C					
Mix 2	100	110	120	130	140	150
CCl ₄ ^b	1.900	1.928	1.950	1.976	2.002	2.032
Isooctane ^c	2.155	2.128	2.114	2.111	2.113	2.125
1-Octene	2.440	2.337	2.272	2.232	2.207	2.198
<i>p</i> -Xylene	2.917	2.692	2.542	2.441	2.372	2.330
<i>o</i> -Xylene	3.106	2.830	2.646	2.520	2.434	2.380
(+)-Limonene	4.825	4.025	3.500	3.140	2.894	2.725
Dodecane	10.445	7.624	5.880	4.744	4.000	3.502

^a Compounds are listed in order of increasing retention time; DB-5 column, 10 psi. ^b Unretained reference. ^c Only the first four temperatures were used.

as determined by the standards. Additional details regarding the effect of heat capacity corrections on these results will be reported separately.

2.3. Compounds

Systematic nomenclature for some of the common names of substances given in Tables 1-4 is as follows. (+)-Limonene: (*R*)(+)-4-isopropenyl-1-methyl-1-cyclohexene; *trans*-stilbene: *trans*-1,2-diphenylethene; adamantane: tricyclo[3.3.1.1^{2,6}]decane; methyl palmitate: methyl hexadecanoate; methyl oleate: methyl *cis*-9-octadecenoate; mesityl oxide: 4-methyl-3-penten-2-one; camphor: (±)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-one; norcamphor: (±)-bicyclo[2.2.1]heptan-2-one; thymol: 2-isopropyl-5-methylphenol; 2-picoline: 2-methylpyridine; 2,6-lutidine: 2,6-dimethylpyridine; 2,4,6-collidine: 2,4,6-trimethylpyridine. All compounds were purchased from Aldrich Chemical Company or Fisher Scientific.

3. Results and discussion

Table 1 illustrates the application of this technique to a series of hydrocarbons at two different temperatures. Fig. 1 illustrates a typical chromatogram of the hydro-

carbons of mix 1. This mixture contains a homologous set of *n*-alkanes similar to those examined by Fuchs et al., but the hydrocarbons of mix 2 are structurally more diverse. A plot of $\ln(1/t_r)$ for each compound as a function of $1/T$ gives a straight line from which $\Delta_{\text{sol}}^{\text{g}}H_m$ is obtained. These results are shown in Fig. 2 and the slopes of the lines are listed in the second column of Table 2. In a second series of correlations, plotting $\Delta_{\text{sol}}^{\text{g}}H_m$ for each compound in Table 2 against each respective known $\Delta^{\text{f}}H_m(298)$ gives the results shown in Fig. 3. The data in the two lines correspond to two experiments conducted on the same column with the same column head pressure but different temperature ranges. The equation of the line obtained by least squares for the *n*-alkanes of Table 1, mix 1, is characterized by a correlation coefficient of 0.9999 and is given by Eq. (1); Eq. (2) and a correlation coefficient of 0.9960 summarize the similar results obtained for the hydrocarbons of mix 2.

Mix 1

$$\Delta^{\text{f}}H_m(298)_{\text{calcd}} = (1.457)\Delta_{\text{sol}}^{\text{g}}H_m - 1.31 \quad (1)$$

Mix 2

$$\Delta^{\text{f}}H_m(298)_{\text{calcd}} = (1.30)\Delta_{\text{sol}}^{\text{g}}H_m + 0.59 \quad (2)$$

Column 5 of Table 2 gives the vaporization enthalpy of each respective compound as calculated from Eqs. (1) and (2). The results for *n*-dodecane, a compound used in both series of experiments, are included to illustrate the precision of this method. A reliable vaporization enthalpy at 298 K is not available for octadecane. Antoine constants describing the vapor pressure–temperature relationship from 318 to 361 K are available [6], and transformation of the vapor pressure/temperature data using a 30 K temperature range results in a $\Delta^{\text{f}}H_m(333 \text{ K})$ of 84.31 kJ mol⁻¹. The heat capacity $C_p(l)$ of liquid octadecane was estimated by a group method [7] and the following relationship was used to correct vaporization enthalpies to 298 K [8]:

$$\Delta^{\text{f}}C_p\Delta T = [10.28 + 0.26C_p(l)](T - 298) \quad (3)$$

This resulted in a vaporization enthalpy of 89.92 kJ mol⁻¹, in good agreement with the value reported in Table 2.

The linear relationship observed between $\Delta_{\text{sol}}^{\text{g}}H_m$ and $\Delta^{\text{f}}H_m$ suggests an easy method for obtaining the vaporization enthalpy of an unknown as illustrated for octadecane if the vaporization enthalpies of several structurally related compounds are available. The accuracy of the results depends on the accuracy of the vaporization enthalpies of the reference standards. We have chosen to illustrate this procedure on the linear alkanes because accurate data which have been critically reviewed [5] are available for these compounds. However, we have found that this correlation gives satisfactory results on all the hydrocarbons we have examined.

A study of the effect of temperature on the quality of the correlations is illustrated by the results reported for mix 3 (Table 2). Analysis of the same mixture over the temperature ranges 40–78 and 80–120°C gives similar $\Delta^{\text{f}}H_m(298 \text{ K})$ values. These similar results are obtained under conditions where the retention times vary significantly. We conclude from these results that, provided that both

Table 2
Vaporization enthalpies of hydrocarbons at 298 K

Compound	Slope	$\Delta_{\text{exp}} H_{\text{m}}^{\circ}$	$\Delta_f H_{\text{m}}^{\circ}(\text{lit})^{\text{a,b}}$ (298 K)	$\Delta_f H_{\text{m}}^{\circ}(\text{calc})$	Difference (%)	Correlation of $\ln(1/t_r)$ vs. $1/T$
Mix 1: temperature range of experiments 150–200°C, DB-5 column, 10 psi						
Decane	–4302.97	35.77	51.38	51.46	0.17	0.9999
Dodecane	–5093.11	42.34	61.25	61.16	–0.15	0.9999
Tetradecane	–5908.40	49.12	71.30 ^c	71.16	–0.20	0.9999
Pentadecane	–6321.09	52.55	76.11 ^c	76.22	0.15	0.9999
Hexadecane	–6743.83	56.07	81.38	81.41	0.03	0.9999
Octadecane	–7594.36	63.14	NA ^d	91.84		0.9999
Mix 2: temperature range of experiments: 100–150°C, DB-5 column, 10 psi						
Isooctane	–3170.61	26.36	35.10	34.89	–0.74	0.9998
1-Octene	–3704.08	30.79	40.58	40.60	0.05	0.9999
p-Xylene	–3865.12	32.13	42.38	42.34	–0.09	0.9999
o-Xylene	–3915.45	32.55	43.43	42.89	–1.24	0.9999
(+)-Limonene	–4539.51	37.74	48.12	49.63	3.14	0.9999
Dodecane	–5551.08	46.15	61.25	60.65	–1.13	0.9999
Mix 3: A, temperature range of experiments 40–78°C, DM-5MS column, 25 psi, methane B, temperature range of experiments 80–120°C, DB-5MS column, 25 psi, methane						
I-Octene						
A:	–4095.25	34.02	40.58	40.63	0.12	0.9999
B:	–3749.37	31.17	40.58	40.29	–0.68	0.9999
p-Xylene						
A:	–4303.5	35.77	42.38	42.59	0.50	0.9999
B:	–3979.35	33.05	42.38	42.72	0.74	0.9999
o-Xylene						
A:	–4370.22	36.32	43.43	43.22	–0.47	0.9999
B:	–4043.59	33.60	43.43	43.39	–0.14	0.9999
n-Decane						
A:	–5221.05	43.39	51.38	51.25	–0.25	0.9999
B:	–4824.73	40.12	51.38	51.51	0.21	0.9999
Naphthalene (c)						
A:	–5534.21	45.98	[53.3] ⁱ	54.18		0.9999
B:	–5261.83	43.76	[53.3] ⁱ	56.02		0.9999

Table 3
Vaporization enthalpies of monosubstituted compounds^{a,b}

Compound	Slope	$\Delta_{\text{sub}}H_m$	$\Delta fH_m(\text{lit})^b$ (298 K)	$\Delta fH_m(\text{calc})$	Difference (%)	Correlation of $\ln(1/r_s)$ vs. $1/T$
Acids						
Mix 7: temperature range of experiments 80–120°C, DB-5MS column, 25 psi, methane						
Propionic acid	-3927.31	32.65	54.81 ^c	54.88	0.13	0.9989
Butanoic acid	-4505.89	37.46	58.16	60.73	4.41	0.9995
Pentanoic acid	-5013.45	41.68	69.45	65.85	-5.18	0.9997
Hexanoic acid	-5548.75	46.13	71.13	71.26	-0.18	0.9997
Benzoic acid	-6303.19	52.40	[72.00] ⁿ	78.87	0.9999	0.9999
Heptanoic acid	-5987.25	49.75	75.73	75.65	-0.10	0.9999
Octanoic acid	-6537.77	54.35	80.33	81.24	-1.13	0.9998
Alcohols						
Mix 8: temperature range of experiments 100–150°C, DB-5 column, 10 psi, methanol						
<i>n</i> -Hexanol	-3895.32	32.38	61.59	61.49	-0.17	0.9997
<i>n</i> -Heptanol	-4363.36	36.28	66.82	66.40	-0.63	0.9998
<i>n</i> -Octanol	-4861.60	40.42	70.96	71.62	0.93	0.9998
<i>n</i> -Nonanol	-5349.77	44.48	76.86	76.74	-0.16	0.9999
<i>n</i> -Decanol	-5827.88	48.45	81.5	81.74	0.29	0.9999
<i>n</i> -Undecanol	-6305.99	52.43	[81.4] ^h	86.76	0.9999	0.9999
<i>n</i> -Dodecanol	-6779.06	56.36	91.96	91.71	-0.27	0.9999
Mix 9: temperature range of experiments 50–100°C, DB-5 column, 10 psi, methanol						
<i>i</i> -Butanol	-2687.47	22.34	46.74	45.35	-2.97	0.9991
<i>n</i> -Propanol	-3110.22	25.86	47.49	49.23	3.66	0.9991
2-Methyl-2-butanol	-3251.13	27.03	50.17	50.53	0.72	0.9998
<i>n</i> -Butanol	-3467.54	28.83	52.43	52.52	0.17	0.9998
2-Pentanol	-3588.32	29.83	54.22	53.63	-1.09	0.9998
3-Methyl-1-butanol	-3764.47	31.30	55.65	55.25	-0.72	0.9998
<i>n</i> -Pentanol	-3995.97	33.22	56.90	57.38	0.84	0.9999
<i>n</i> -Hexanol	-4458.98	37.07	61.59	61.64	0.08	0.9998
<i>n</i> -Heptanol	-4987.42	41.46	66.82	66.49	-0.49	0.9998

Mix 10: temperature range of experiments 50-100°C, DB-5 column, 10 psi, methanol					
2-Propen-1-ol	-2984.4	24.81	47.28	47.26	0.9995
2-Methyl-2-propen-1-ol	-3422.24	28.45	NA ^a	51.86	0.9998
n-Pentanol	-3985.91	33.14	56.90	57.79	0.9998
Cyclopentanol	-3915.45	32.55	57.49	57.05	0.9998
Cyclohexanol	-4318.07	35.90	62.01	61.28	0.9999
1-Ethynyl-1-cyclopentanol	-4393.56	36.53	NA ^a	62.08	0.9999
2-Methylcyclohexanol	-4514.34	37.53	63.22	63.34	0.9999
3-Methylcyclohexanol	-4720.68	39.25	65.31	65.51	0.9999
4-Methylcyclohexanol	-4755.91	39.54	65.90	65.88	0.9999
Benzyl alcohol	-5103.17	42.43	[61.5] ^a	69.53	0.9999
Aldehydes					
Mix 11: temperature range of experiments 40-80°C, DB-SMS, 25 psi, methane					
Isobutyraldehyde	-2962.52	24.63	31.51	32.26	0.9999
Butanal	-3058.96	25.43	33.68	33.18	0.9997
Pentanal	-3591.59	29.86	38.79 ^c	38.28	0.9998
Heptanal	-4672.60	38.84	47.70	48.66	0.9999
Benzaldehyde	-4715.20	39.20	49.79	49.08	0.9999
Octanal	-5209.14	43.31	[44.3] ^a	53.80	0.9999
Nonanal	-5741.48	47.73	[53.3] ^m	58.91	0.9999
Amines, primary					
Mix 12: temperature range of experiments 50-100°C, DB-SMS column, 25 psi, methane					
1-Butylamine	-3178.70	26.40	35.56	35.62	0.9998
1-Hexylamine	-4218.56	35.06	45.19 ^c	45.01	0.9998
1-Heptylamine	-4761.23	39.58	49.79 ^c	49.91	0.9998
1-Octylamine	-5281.78	43.89	[53.14] ^u	54.58	0.9998
Bromides					
Mix 13: temperature range of experiments 50-90°C, DB-5 column, 10 psi, 1-butene					
2-Bromopropane	-3021.97	25.12	30.21	30.63	0.9999
1-Bromobutane	-3628.47	30.17	36.69	36.37	0.9999
2-Bromopentane	-3855.02	32.05	[37.9] ^j	38.51	0.9999
1-Bromopentane	-4103.6	34.12	41.09	40.87	0.9999
1-Bromohexane	-4591.92	38.18	45.61	45.49	0.9999
1-Bromoheptane	-5091.8	42.33	50.21	50.22	0.9999
1-Bromooctane	-5602.48	46.58	54.81	55.05	0.9999

Table 3 (continued)

Compound	Slope	$\Delta_{\text{exp}} H_m$	$\Delta_f H_m$ (lit) ^b (298 K)	$\Delta_f H_m$ (calc)	Difference (%)	Correlation of $\ln(1/t_r)$ vs. $1/T$
Chlorides						
Mix 14: temperature range of experiments 40-80°C, DB-5 column, 10 psi, 1-butene						
2-Chloro-2-methylpropane	-3038.04	25.25	29.0	28.59	-1.41	0.9998
1-Chloro-3-methylbutane	-3949.61	32.84	36.82	38.13	3.56	0.9992
1-Chloropentane	-4012.36	33.36	38.20	38.79	1.54	0.9996
Chlorobenzene	-4156.58	34.56	40.29	40.30	0.02	0.9999
Chlorocyclohexane	-4301.53	35.76	43.51	41.82	-3.88	0.9999
1-Chloroheptane	-4882.58	40.59	47.70 ^c	47.90	0.42	0.9999
Disulfides						
Mix 15: temperature range of experiments 110-160°C, DB-5 column, 10 psi, carbon tetrachloride						
Ethyl disulfide	-3923.15	32.62	45.19	44.82	-0.08	0.9998
Isopropyl disulfide	-4316.07	35.88	[51.09] ^d	49.32		0.9998
<i>t</i> -Butyl disulfide	-4709.38	39.15	53.14	53.83	-1.29	0.9998
Dibutyl disulfide	-5606.62	46.61	64.43	64.11	-0.05	0.9998
Esters						
Mix 16: temperature range of experiments 40-80°C, DB-5 column, 10 psi, 1-butene						
Ethyl ethanoate	-3759.72	31.26	35.10	35.04	-0.17	0.9983
Isopropyl ethanoate	-3944.01	32.79	37.20	37.04	-0.44	0.9996
Butyl ethanoate	-4505.39	37.46	43.51	43.12	-0.90	0.9998
Methyl hexanoate	-4973.31	41.35	46.44	48.19	3.76	0.9997
Methyl heptanoate	-5466.42	45.45	50.21	53.53	6.61	0.9997
Phenyl ethanoate	-5423.13	45.09	55.23	53.06	-3.93	0.9998
Methyl benzoate	-5452.57	45.33	55.65	53.38	-4.08	0.9998
Mix 17: temperature range of experiments 40-90°C, DB-5 column, 10 psi, 1-butene						
Methyl propanoate	-3032.70	25.21	[36.4] ^e	28.85		0.9966
<i>n</i> -Propyl ethanoate	-3855.44	32.05	[38.8] ^f	37.65		0.9999
Methyl trimethylacetate	-3863.58	32.12	NA ^g	37.73		0.9999
Butyl ethanoate	-4330.45	36.00	43.51	42.72	-1.82	0.9999
Methyl hexanoate	-4811.74	40.00	46.44	47.86	3.06	0.9999

Methyl heptanoate	44.29	50.21	53.37	0.9999
Phenyl ethanoate	44.44	55.23	53.31	0.9999
Methyl benzoate	44.46	55.65	53.78	0.9999
Mix 18: temperature range of experiments 160–200°C	44.10°C, DB-5 column, 10 psi, 1-butene	50.21	53.72	0.9999
Methyl heptanoate	35.35	55.23	53.58	0.9999
Phenyl acetate	35.35	55.65	54.71	0.9999
Methyl benzoate	35.48	72.38	70.58	0.9999
Methyl undecanoate	48.63	87.86	88.75	0.9999
Methyl pentadecanoate	63.66	[105.1] ¹	93.17	0.9999
Methyl palmitate	66.71	[108.5] ^p	99.58	0.9999
Methyl oleate	71.			0.9999
Ethers				
Mix 19: temperature range of experiments 80–120°C	30.13	36.15	36.47	0.9991
Butyl vinyl ether	30.36	46.86	45.33	0.9994
Anisole	36.41	49.79	51.41	0.9992
Diisomyl ether	41.50	64.02 ^c	63.50	0.9978
Dihexyl ether	50.52	66.94	67.05	0.9993
Diphenyl ether	52.			
Iodides				
Mix 20: temperature range of experiments 40–80°C	30.13	35.40	36.99	0.9990
<i>t</i> -Butyl iodide	30.32	38.49 ^c	37.86	0.9997
2-Iodobutane	32.34	40.58 ^c	39.66	0.9998
1-Iodobutane	34.36	[43.2] ^v	42.22	0.9998
1-Iodo-3-methylbutane	36.40	47.70 ^c	47.40	0.9999
Iodobenzene	40.47	47.28	48.32	0.9999
Iodocyclohexane	40.37	45.19	44.39	0.9999
1-Iodopentane	37.45			
Mix 21: temperature range of experiments 40–80°C	26.02	31.71	31.71	0.9998
Iodoethane	26.28	34.09	34.01	0.9999
2-Iodopropane	28.32	38.49 ^c	38.82	0.9997
2-Iodobutane	32.34	40.58 ^c	40.33	0.9998
1-Iodobutane	34.			
Ketones				
Mix 22: temperature range experiments 70–110°C	32.46	[42.2] ^w	44.82	0.9999
Mesityl oxide	32.			

Table 3 (continued)

Compound	Slope	$\Delta_{\text{calc}}^{\circ}H_m$	$\Delta_f H_m$ (lit) ^b (298 K)	$\Delta_f H_m$ (calc)	Difference (%)	Correlation of $\ln(I/I_c)$ vs. $1/T$
Cyclohexanone	-4126.76	34.31	45.19	46.67	3.28	0.9999
4-Heptanone	-4267.92	35.48	[46.0] ^a	47.84		0.9999
Cycloheptanone	-4605.49	38.29	51.88	50.66	-2.35	0.9999
2-Octanone	-4835.53	40.20	[50.8] ^y	52.57		0.9999
Acetophenone	-4938.95	41.06	56.07	53.44	-4.69	0.9999
Cyclooctanone	-5032.29	41.84	54.39	54.22	-0.31	0.9999
Camphor	-5145.01	42.77	[45.0] ⁱ	55.15		0.9999
1-Phenyl-2-propanone	-5258.58	43.72	53.56	56.10	4.74	0.9999
Mix 23: temperature range of experiments 70-110°C, DB-5MS column, 25 psi, methane						
Cyclohexanone	-4100.93	34.06	45.20	46.94	3.89	0.9999
2-Heptanone	-4319.13	35.90	47.28 ^c	48.45	2.47	0.9998
Norcamphor	-4484.71	37.28	[45.6] ^q	49.58		0.9999
Cycloheptanone	-4633.77	38.49	51.88	50.63	-2.46	0.9999
Acetophenone	-4942.57	41.09	56.07	52.72	-5.96	0.9998
Cyclooctanone	-5061.03	42.05	54.39	53.55	-1.70	0.9999
Camphor	-5201.06	43.22	[45.0] ^v	54.52		0.9999
1-Phenyl-2-propanone	-5275.06	43.85	53.56	55.02	2.71	0.9998
6-Undecanone	-6257.66	52.01	60.67	61.76	1.79	0.9999
Mix 24: temperature range of experiments 70-110°C, SP-2331 column, 25 psi, methane						
2-Heptanone	-4276.73	35.52	47.28 ^c	46.11	-2.49	0.9998
Cyclohexanone	-4289.21	35.65	45.20	46.23	2.30	0.9999
Norcamphor	-4813.89	39.99	[45.6] ^q	51.46		0.9993
Cycloheptanone	-4857.62	40.38	51.88	51.88	0.00	0.9999
Acetophenone	-5460.55	45.40	56.07	57.91	3.25	0.9999
Cyclooctanone	-5104.67	42.43	54.39	54.35	-0.09	0.9998
Camphor	-5113.16	42.47	[45.0] ⁱ	54.43		0.9999
6-Undecanone	-5575.23	46.32	60.67	59.04	-2.70	0.9999
Nitro compounds						
Mix 25: temperature range of experiments 40-80°C, DB-5 column, 10 psi, 1-butene						
Nitromethane	-3316.15	27.57	38.41	37.23	-3.07	0.9999

2-Nitropropane	-4042.49	33.61	41.30	43.93	6.37	0.9991
1-Nitropropane	-4042.84	33.61	43.51	43.93	0.97	0.9997
1-Nitrobutane	-4370.81	36.34	48.53	46.96	-3.24	0.9998
Nitrobenzene	-5190.37	43.15	54.81	54.52	-0.53	0.9999
Phenols						
Mix 26: temperature range of experiments 120–160°C, DB-5MS column, 25 psi, methanol						
Phenol	-4248.77	35.32	59.12 ^a	58.83	-0.50	0.9999
<i>m</i> -Cresol	-4709.89	39.16	61.71	62.49	1.26	0.9999
2-Ethylphenol	-4958.98	41.23	63.60	64.46	1.35	0.9999
2,4-Dimethylphenol	-4971.43	41.33	65.90	64.56	-2.04	0.9999
Thymol	-5714.39	47.51	[71.8] ^r	70.45		0.9999
2-Naphthol	-6441.88	53.56	[76.7] ^s	76.22		0.9999
Pyridines						
Mix 27: temperature range of experiments 50–100°C, DB-5 column, 10 psi, 1-butene						
Pyridine	-3566.37	29.65	40.21	40.40	-0.47	0.9998
2-Picoline	-3974.21	33.04	42.68	43.56	-2.06	0.9998
4-Picoline	-4121.63	34.27	45.19	44.70	1.08	0.9998
2,6-Lutidine	-4337.68	36.06	46.02	46.37	-0.76	0.9999
2,4-Lutidine	-4478.7	37.23	47.70	47.46	0.50	0.9999
2,3-Lutidine	-4501.56	37.42	48.95	47.64	2.68	0.9998
3,5-Lutidine	-4635.44	38.54	50.21	48.68	3.05	0.9998
2,4,6-Collidine	-4837.24	40.21	48.12 ^c	50.24	-4.41	0.9998

^a All enthalpies in kJ mol⁻¹. ^b All data from Ref. [4] unless stated otherwise; values in brackets are included for purposes of comparison only. ^c Ref. [5]. ^d Vaporization enthalpy 43.80 kJ mol⁻¹ (392 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ^e Vaporization enthalpy 35.87 kJ mol⁻¹ (308 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ^f Vaporization enthalpy 38.15 kJ mol⁻¹ (327 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ^g Vaporization enthalpy 43.44 kJ mol⁻¹ (308 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ^h Vaporization enthalpy 68.6 kJ mol⁻¹ (406 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ⁱ Sublimation enthalpy 51.8 [10]; fusion enthalpy 6.82 kJ mol⁻¹ [14]. ^j Vaporization enthalpy 37.47 kJ mol⁻¹ (304 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ^k Vaporization enthalpy 84.43 kJ mol⁻¹ (426 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ^l Vaporization enthalpy 61.5 kJ mol⁻¹ (303 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ^m Vaporization enthalpy 51.16 kJ mol⁻¹ (321 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ⁿ Sublimation enthalpy 89.3 [10]; fusion enthalpy 17.31 kJ mol⁻¹ [15]. ^o Vaporization enthalpy 57.38 kJ mol⁻¹ (329 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ^p Vaporization enthalpy 83.0 kJ mol⁻¹ (443 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ^q Sublimation enthalpy 49.0 [10]; fusion enthalpy 3.39 kJ mol⁻¹ [12]. ^r Sublimation enthalpy 89.1 [10]; fusion enthalpy 17.26 kJ mol⁻¹ [12]. ^s Sublimation enthalpy 94.2 [10]; fusion enthalpy 17.5 kJ mol⁻¹ [12]. ^t Not available. ^u Vaporization enthalpy 50.8 kJ mol⁻¹ (323 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ^v Vaporization enthalpy 43.5 kJ mol⁻¹ (285 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ^w Vaporization enthalpy 41.5 kJ mol⁻¹ (328 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ^x Vaporization enthalpy 45.5 kJ mol⁻¹ (319 K) [6]; corrected to 298 K using Eq. (3) [7,8]. ^y Vaporization enthalpy 49.8 kJ mol⁻¹ (332 K) [6]; corrected to 298 K using Eq. (3) [7,8].

Table 4
Mixed functional groups, constant hydrocarbon structure

Compound	Slope	$\Delta_{\text{sol}}^{\circ}H_m$	$\Delta_f H_m$ (lit) ^b (298 K)	$\Delta_f H_m$ (calc)	Difference (%)	Correlation of $\ln(1/r_i)$ vs. $1/T$
Mix 28 ^{a,d} : temperature range of experiments 80-120°C, DB-5MS column, 25 psi, methanol						
Chlorobenzene	-3842.49	31.92	40.29	40.90	1.51	0.9999
Bromobenzene	-4132.86	34.35	43.93	45.27	3.04	0.9996
Aniline	-4464.31	37.11	55.65 ^c	50.23	-9.74	0.9995
Benzonitrile	-4494.56	37.36	52.30	50.68	-3.10	0.9995
Iodobenzene	-4538.09	37.70	47.70	51.29	7.52	0.9998
Phenol	-4734.97	39.33	[59.1] ^h	54.22		0.9993
Nitrobenzene	-4876.19	40.50	54.81	56.32	2.76	0.9997
Benzoic acid	-6034.59	50.17	[78.9] ^f	73.71		0.9986
Benzamide	-6263.38	52.05	[79.1] ^g	77.09		0.9997
Mix 29 ^{a,e} : temperature range of experiments 40-80°C, DB-5MS column, 25 psi, methane						
Diethylamine	-3074.50	25.52	31.21	29.04	-6.96	0.9998
3-Pentanone	-3510.25	29.16	38.49	35.60	-7.53	0.9982
Ethyl propionate	-3643.96	30.29	39.12	37.61	-3.87	0.9984
Diethyl sulfide	-3856.02	32.05	35.90	40.79	13.64	0.9999
Diethyl disulfide	-4536.33	37.70	45.19	51.04	12.93	0.9999
Diethyl sulfone	-5540.41	46.02	70.29	66.15	-5.91	0.9998

^a All enthalpies in kJ mol⁻¹. ^b All data from Ref. [4] unless stated otherwise. ^c Ref. [5]. ^d Methanol used as non-retained reference. ^e Methane used as non-retained reference. ^f As evaluated in mix 7. ^g Sublimation enthalpy 96.9 mol⁻¹ (333.5 K) [6]; corrected to 298 K (97.47 kJ mol⁻¹ [7]); fusion enthalpy 18.4 kJ mol⁻¹ [15]. ^h Vaporization enthalpy 57.36 kJ mol⁻¹ (329 K); corrected to 298 K using Eq. (3) [7,8].

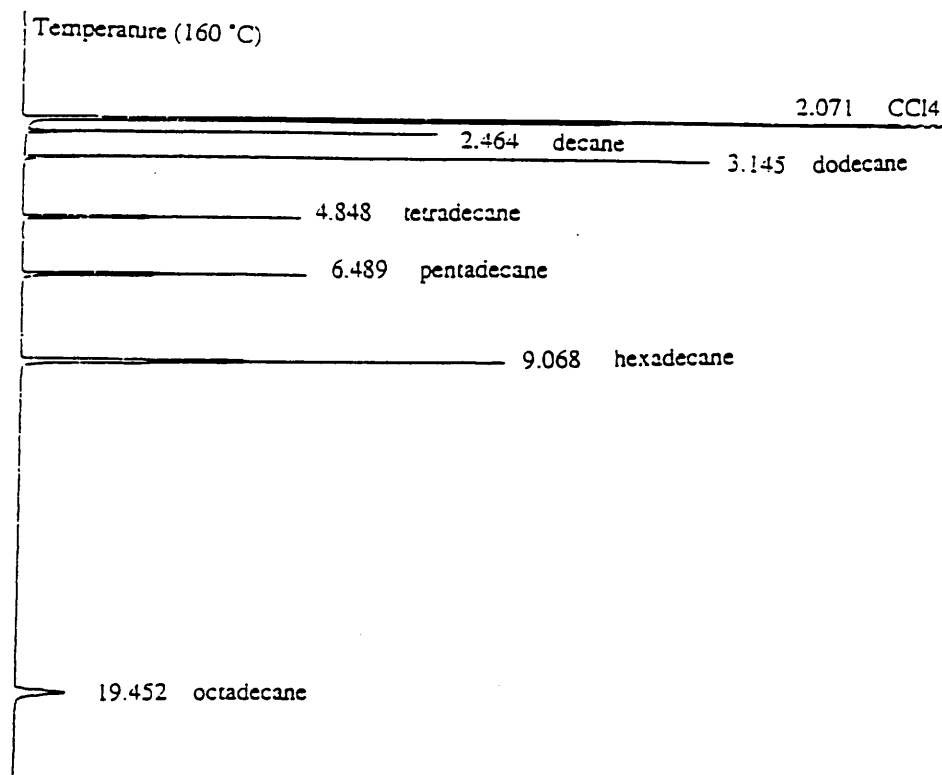


Fig. 1. A typical gas chromatogram obtained for mix 1 at 160°C; intensity vs. time (in min).

knowns and unknowns are analyzed simultaneously and accurate t_r values can be measured, the measured vaporization enthalpy is not highly dependent on the temperature range selected for study. The choice of temperature range does play an important role in one respect, however. The magnitude of the corrected retention time is significantly affected by temperature. For volatile compounds with short retention times, uncertainties in the measurement of t_r can become significant in relation to the magnitude of t_r , resulting in an increase in the error associated with $\Delta_{\text{sol}}^{\text{g}}H_m$. Although it is possible to run chromatograms below ambient temperature to increase retention times, we have not tested this approach, and this has limited the size of the molecules we have examined at this end of the scale.

To determine the role that column selection plays in the correlations for hydrocarbons, we have compared the results obtained for the components of mix 1 (DB-5 capillary column, 150–200°C) with those obtained on a more polar column (SP-2331 capillary column, 90–140°C) for mix 4. The lower temperatures used for experiments on the more polar column were necessitated by shorter retention times. Very little difference is observed between the two sets of vaporization enthalpies evaluated by the correlation.

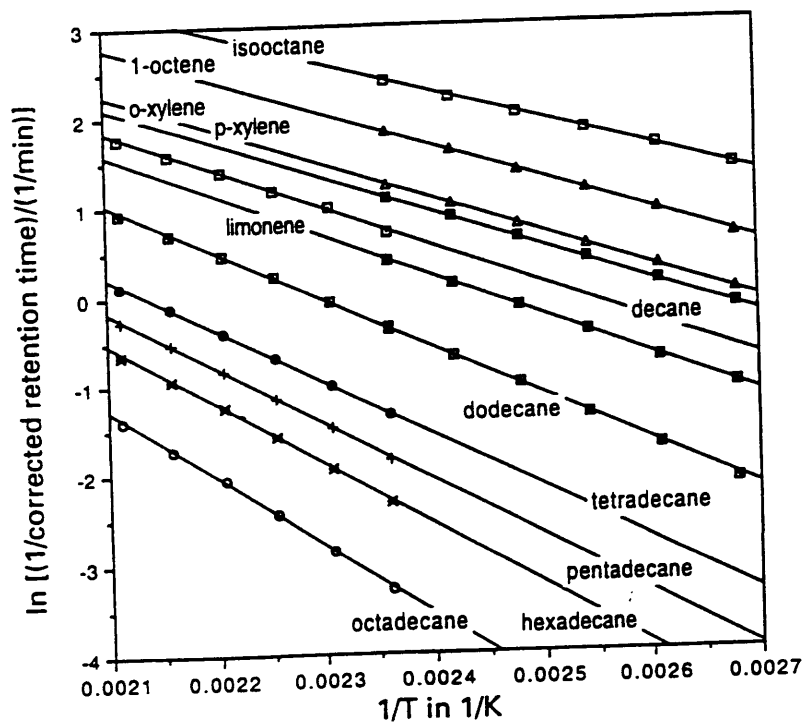


Fig. 2. A natural logarithm plot of reciprocal corrected retention time against reciprocal temperature (in 1/K).

The results obtained for naphthalene in mix 3 also bear mentioning. Naphthalene, m.p. 80.4°C, is a solid over the temperature range 40–78°C. The results obtained below and above 80°C are within 2 kJ mol⁻¹ of each other and are in reasonable agreement with a $\Delta_f H_m(298)$ of 53.3 kJ mol⁻¹, calculated from the difference between the sublimation enthalpy at 298 K (72.4 kJ mol⁻¹ [10]) and the fusion enthalpy (19.1 kJ mol⁻¹ [12]). This suggests that the GC correlation method can be also used to measure vaporization enthalpies $\Delta_f H_m$ of solids. The analyses of some additional solids can be found in Tables 2 and 3; solid compounds can be located by the (c) following their name. $\Delta_f H_m(\text{lit})$ values for most solids were calculated from differences in sublimation and fusion enthalpies [9,10]. These compounds and those for which the literature $\Delta_f H_m(298)$ values are enclosed by brackets (column 4 of Tables 3 and 4) were not used in the correlations but are included for purposes of comparison. For some of these compounds it was necessary to calculate vaporization enthalpies at 298 K from the Antoine constants measured at higher temperatures and to correct the resulting vaporization enthalpies for heat capacity differences over this temperature range. The values for most of these compounds were also not included in the correlations because the data have not been critically reviewed. Only for octadecane (mix 4), eicosane (mix 5) and phenol (mixes 26 and 28) were non-reviewed values used. The value used for octadecane in mix 4 was evaluated in mix 1 and the value

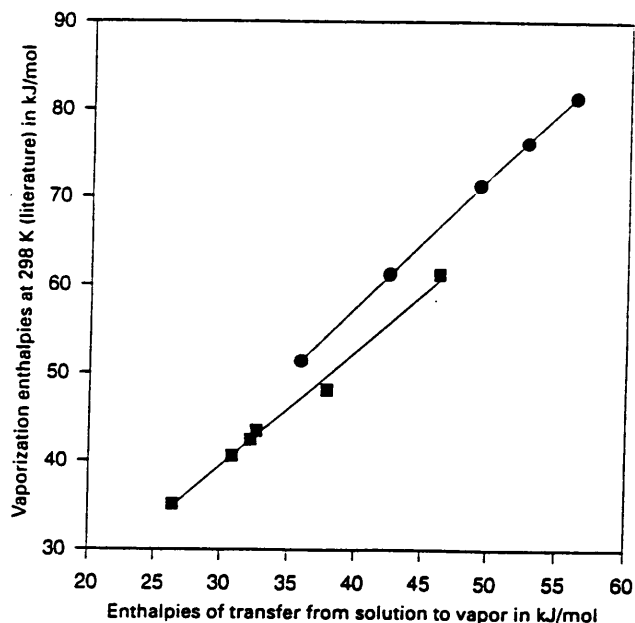


Fig. 3. A correlation of literature vaporization enthalpies at 298 K of the hydrocarbons of Table 2 against vaporization enthalpies of transfer from solution to vapor: ■. mix 1, line from Eq. (1); ●. mix 2, line from Eq. (2).

for eicosane was evaluated from the Antoine constants [6]. All were used because reliable vaporization enthalpy data were not available for compounds of similar volatility. The results for these mixtures should be treated accordingly.

In order to test the generality of the procedure just outlined to evaluate vaporization enthalpies of hydrocarbon derivatives, we examined several series of mixtures, each series characterized by a common functional group. The results of these experiments are summarized in Table 3. This grouping together by functionality was suggested by the results obtained on hydrocarbons and the results from a series of experiments in which the hydrocarbon portion of the molecule was held constant and the functional group was varied. These results are discussed below.

Linear correlations are observed between $\Delta_{\text{sol}}^{\text{g}}H_m$ and $\Delta^{\text{f}}H_m(\text{lit})$ for a wide range of simple organic molecules when the functional group is held constant and the hydrocarbon portion of the molecule is allowed to vary. A selection is represented in Table 3, which includes most common functional groups: organic acids (mix 7), alcohols (mixes 8–10), aldehydes (mix 11), primary amines (mix 12), bromides (mix 13), chlorides (mix 14), disulfides (mix 15), esters (mixes 16–18), ethers (mix 19), iodides (mixes 20 and 21), ketones (mixes 22–24), nitro compounds (mix 25), phenols (mix 26) and pyridines (mix 27). It appears from the correlations that the nature and location of the functional group in the molecule are not very important provided that compounds of similar composition are compared. Compounds containing quaternary carbon atoms, such as *t*-butanol and 2-methyl-2-pentanol (mix

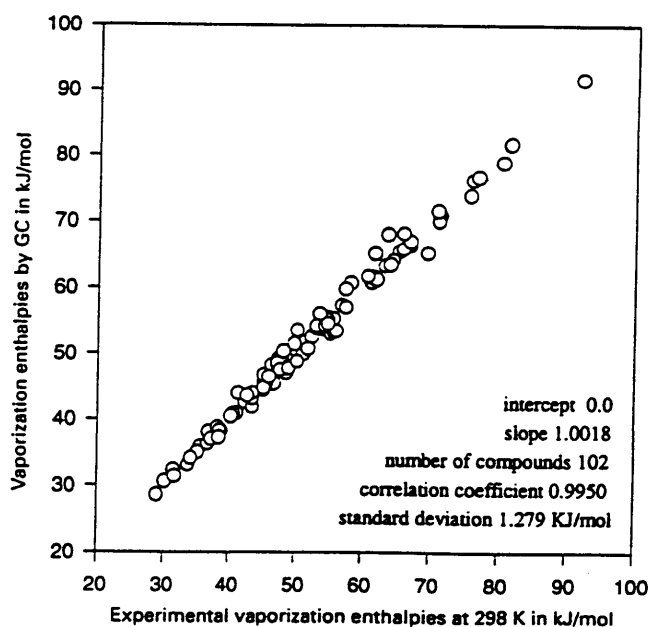


Fig. 4. A correlation of vaporization enthalpies of the compounds in Tables 2 and 3 evaluated by gas chromatography to experimental vaporization enthalpies at 298 K.

9), are correlated by this approach as well as other compounds that form strong hydrogen bonds. The results for the ketones (mixes 22 and 23) obtained on two different columns suggest that, although $\Delta_{\text{sol}}^{\text{v}} H_m$ values are dependent on the nature of the stationary liquid phase of the column, the vaporization enthalpies obtained by correlation are not significantly affected.

A measure of the quality of the correlation can be obtained by examining the results of Fig. 4. The parameters of the line obtained by a least squares treatment with the intercept forced to pass through the origin are given in the figure. A standard deviation of 1.28 kJ mol^{-1} was observed between literature and correlated gas chromatographic values. Calculated and experimental vaporization enthalpies are correlated by a coefficient of 0.9950. The equation of the line without this restriction was not significantly different. Compounds for which values are shown in brackets in Tables 2 and 3 were not included in the correlation, and those used frequently as standards were included only once.

The results obtained from Tables 2–4 suggest that the quality of the correlation is not extremely sensitive to the structure of the hydrocarbon portion of the molecule provided that the functional group is maintained constant. The results from studies in which the hydrocarbon portion of the molecule was held constant and the functional group was allowed to vary as mentioned above are tabulated in Table 4 for mixes 28 and 29 and shown in Fig. 5. Although data for far fewer compounds are available in this case, there appears to be more scatter between calculated and experimental results. A standard deviation of 3.57 kJ mol^{-1} was

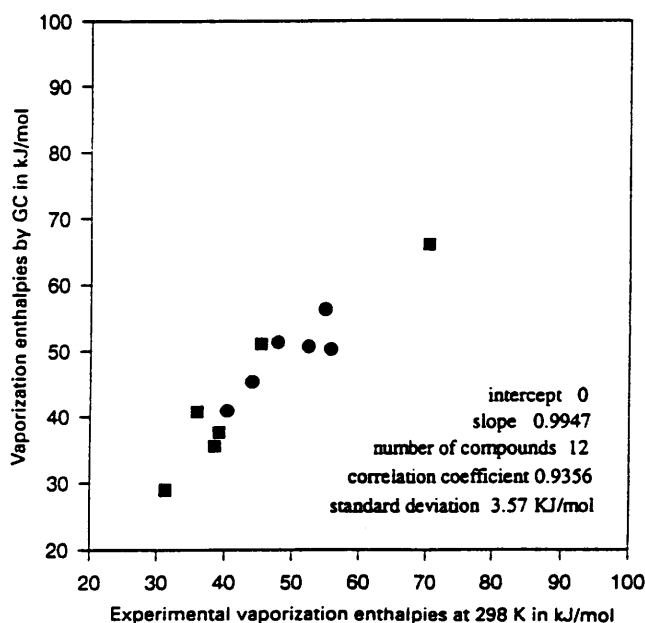


Fig. 5. A correlation of vaporization enthalpy of the compounds in Table 4 evaluated by gas chromatography to experimental vaporization enthalpies at 298 K; squares, $\text{CH}_3\text{CH}_2\text{-X-CH}_2\text{CH}_3$; circles, Ph-X.

observed between literature and gas chromatographic vaporization enthalpies of the 12 compounds examined. The values enclosed in brackets in Table 4 were not included in the correlation. These results are very similar to those observed in previous modeling studies. $\Delta_f H_m(298)$ values for compounds containing a single functional group are far more sensitive to the nature of the group than to the location of the group in the molecule [18].

In addition to obtaining vaporization enthalpies by this technique, gas chromatographic retention times can be correlated to experimental vapor pressures [19]. Correlation of the logarithm of reciprocal corrected retention time with the logarithm of the experimental vapor pressure for 99 of the 102 compounds listed in Tables 2–4 gave the results shown in Fig. 6. Experimental vapor pressures were obtained from the reported Antoine constants [6] evaluated at temperatures consistent with both retention time measurements and range of applicability. The results reported in Fig. 6 are vapor pressures evaluated at several different temperatures, and are intended to illustrate the quality of the correlation that can be obtained. Exclusion of the data associated with the filled circles results in a linear correlation described by the constants in Fig. 6. The standard deviation of the mean is 0.45 natural logarithm units, which corresponds to an uncertainty of 1.57 kPa. The filled circles represent the results obtained for the carboxylic acids of mix 7. It appears that, although the logarithms of vapor pressure and reciprocal retention time of the carboxylic acids do not correlate well with the results obtained for other functional

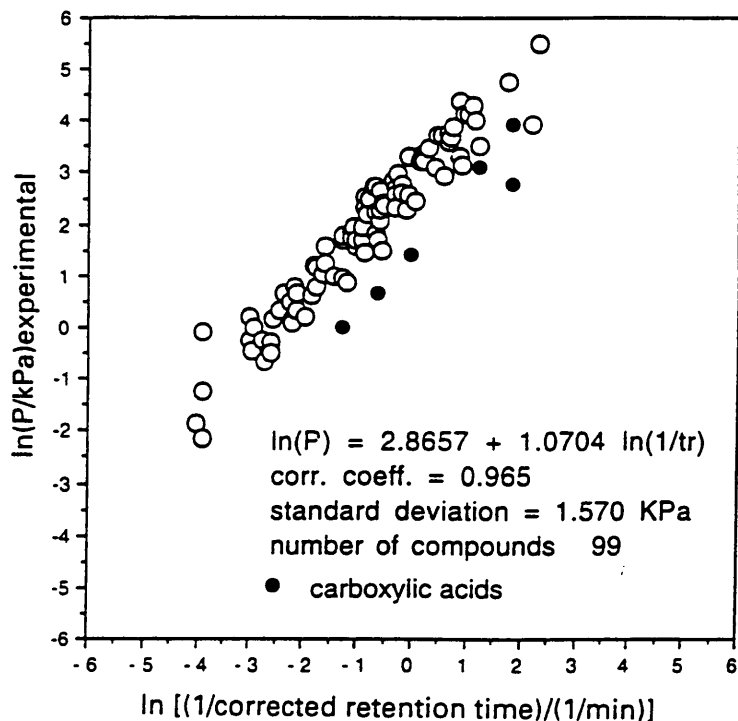


Fig. 6. A correlation of logarithm of experimental vapor pressure against the logarithm of reciprocal retention time.

groups, they do correlate amongst themselves. This emphasizes the importance of the proper selection of standards in using this technique to evaluate the vapor pressure of an unknown. Similar gas chromatographic correlations have been used by environmental chemists to evaluate the vapor pressures of polyaromatic and polychlorinated hydrocarbons [19,20].

4. Summary

The gas chromatographic technique described here appears to be an accurate means of determining vaporization enthalpies of simple molecules. At present, we have demonstrated its application for determining vaporization enthalpies and vapor pressures of hydrocarbons and simple hydrocarbon derivatives. The advantages of this method are its speed and accuracy and small sample sizes required. In addition, whereas most thermochemical measurements require purities in excess of 99%, there is no minimum purity requirement for this method.

The foremost limitation of this method is that the results are entirely dependent upon the choice of standards and the reliability of their vaporization enthalpies and vapor pressures. An additional concern to those interested in using this method is

the need to document the stability of the compounds being studied under the conditions of chromatography. The model we have used in selecting appropriate standards is very similar to a model developed to predict vaporization enthalpies. Vaporization enthalpies of hydrocarbons and hydrocarbon derivatives containing the same functional group can be evaluated to a very good approximation by means of the nature of the functional group and the carbon count [18]. The location of the functional group in the molecule plays a more significant role in more highly substituted compounds. The evaluation of vaporization enthalpies of more complex molecules, the effects of heat capacity corrections and a discussion of the factors influencing the success of the correlation will be the focus of a future report.

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