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MEASUREMENT OF HEATS OF VAPORIZATION BY MEANS OF A GAS CHROMATOGRAPH

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SUMMARY

The possibility of determining the heats of vaporization of substances of low volatility by depositing them on a chromatographic support and measuring with a flame-ionization detector the temperature dependence of the bleeding of the material at a fixed flow-rate of the carrier gas is demonstrated. The role of gas-phase non-ideality and liquid-phase compressibility effects is discussed. Hexadecane, octadecane and glycerol supported on Chromosorb W were used as model compounds. Employing a commercial analytical gas chromatograph, the relative standard deviation of the results was about 2%. Even at loadings as low as 0.1% the substrate vapour pressures and their temperature dependences were found to be virtually the same as those with the packings containing 10% of the substrate. About 3 mg of substrate was sufficient for the determination of its heat of vaporization.

INTRODUCTION

In spite of the limitations that stem from the great complexity of the chromatographic process, chromatography has proved to be very useful in solving many special physico-chemical problems. Detailed reviews on the non-analytical applications of chromatography have been published by Kobayashi *et al.*¹, Young² and Locke³. The most numerous and probably most important applications of that type are those in which gas chromatographic (GC) measurements are utilized in studying the properties of solutions and vapour-liquid (solid) systems. Papers devoted to GC studies of vapour pressures have been based mostly either on correlations with retention data⁴⁻⁶ or on the direct quantitative analysis of the gaseous phase of the system being studied⁷⁻¹⁰. Employing several methods independent of the use of the GC detector, Hawkes and Giddings¹¹ measured the vapour pressures of some liquids deposited on a chromatographic support and found them to be virtually equal to those of the bulk liquids if the loadings were higher than 2%.

In this work, we studied the possibility of determining heats of vaporization by depositing the liquid being investigated on a chromatographic support and measuring the temperature dependence of the bleeding of this material at a fixed flow-rate of the carrier gas with a flame-ionization detector. This method is especially suitable for measuring the heats of vaporization of substances of very low volatility, and both pure compounds and mixtures can be studied. In fact, this method can be looked upon as a variant of the original saturation method¹² for measuring vapour pressures.

THEORETICAL

On drawing a gas through a chromatographic packing with a volatile substrate, desorption frontal gas chromatography of the substrate occurs. Regarding the fine pattern of the packing, it can be considered that the effluent leaving the column is completely saturated with the vapour of the substrate until the desorption front of the latter starts to break through. Hence, within the region of the plateau of the frontal zone of a substrate i , the vapour-liquid system within the column is equilibrated, *i.e.*,

$$(f_i)_P = (f_i^0)_P \quad (1)$$

where $(f_i)_P$ and $(f_i^0)_P$ are the fugacity of substance i in admixture with the carrier gas and the fugacity of the liquid substance i , respectively, both at the overall pressure P and temperature T of the system (column). We are concerned with f_i^0 when P is equal to the saturation vapour pressure of substance i , *i.e.*, $(f_i^0)_{p_i^0}$. As $d \ln f_i^0 = (V_i^L/RT) dp$ at a given temperature, where V_i^L is the molar volume of liquid substance i and R is the perfect gas constant, we can write, provided that V_i^L can be assumed to be approximately constant within the limits of the experimental conditions:

$$(f_i^0)_{p_i^0} = (f_i^0)_P \exp [-V_i^L(P - p_i^0)/RT] \quad (2)$$

Combining eqns. 1 and 2 and introducing the fugacity coefficients of the vapour of component i in admixture with the carrier gas at the overall pressure P , $(\nu_i)_P$, and of the vapour of substance i alone at $P = p_i^0$, $(\nu_i^0)_{p_i^0}$, we obtain

$$p_i^0 = \frac{(\nu_i)_P}{(\nu_i^0)_{p_i^0}} \cdot p_i \exp [-V_i^L(P - p_i^0)/RT] \quad (3)$$

where p_i^0 is the saturation vapour pressure of substance i as it would be in the system at the given temperature in the absence of the carrier gas and p_i is the corresponding actual partial pressure of component i in the column effluent. In the arrangement employed, the final state of the gaseous phase in the equilibrated gas-liquid system (column) is determined by the conditions at the end of the column, and hence the T and P in eqn. 3 represent the column temperature and the pressure at the column outlet.

When employing a flame-ionization detector, the instantaneous response (amps) to the presence of the vapour of substance i in the column effluent, R_i , is given by¹³

$$R_i = a(\Sigma C_{eff})_i n_i \quad (4)$$

where α is the ionization efficiency (coulombs per gram-atom of paraffinic carbon), $(\Sigma C_{\text{eff}})_i$ is the number of effective carbon atoms in the molecule of substance i (gram-atoms of paraffinic carbon per mole)¹⁴ and n_i is the molar rate of introduction of substance i (mole/sec) into the detector. The quantity n_i is given by the concentration (moles per millilitre) of substance i in the effluent, c_i , and the volumetric rate of its introduction into the detector, v , i.e., $n_i = c_i v$. As $c_i = p_i/zRT$, where z is the compressibility factor of the effluent, eqn. 4 can be rewritten as

$$R_i = \alpha(\Sigma C_{\text{eff}})_i p_i v / zRT \quad (5)$$

On combining eqns. 3 and 5, we obtain

$$p_i^0 = R_i \frac{(v_i)_P}{(v_i^0)_{p_i^0}} \cdot \frac{zRT}{\alpha(\Sigma C_{\text{eff}})_i v} \cdot \exp[-V_i^L(P - p_i^0)/RT] \quad (6)$$

The quantities R and $(\Sigma C_{\text{eff}})_i$ are obviously constant under any circumstances. When working with a regulator of constant mass flow of the carrier gas and thermostating the column effluent, and if $p_i^0 \ll P$, then also v of the gas entering the detector and α are constant. Further, when assuming that $z = 1$, neglecting p_i^0 compared with P in the right-hand side of eqn. 6, and assuming that the variation of V_i^L with temperature is negligible within the experimental temperature range, we can write, with regard to the Clapeyron equation:

$$\Delta H_v = -\Delta z R \left[\frac{d \ln R_i}{d(1/T)} + \frac{d \ln [(v_i)_P / (v_i^0)_{p_i^0}]}{d(1/T)} - T - \frac{V_i^L P}{R} \right] \quad (7)$$

where ΔH_v is the heat of vaporization of component i at the column temperature T and Δz is the difference of the compressibility factors of component i in the gaseous mixture and in the liquid phase at the column temperature and P at the column outlet.

The expression $\ln [(v_i)_P / (v_i^0)_{p_i^0}]$ can be written as

$$\ln \frac{(v_i)_P}{(v_i^0)_{p_i^0}} = \frac{1}{RT} \left[\int_0^P \left(\bar{V}_i - \frac{RT}{P} \right) dP - \int_0^{p_i^0} \left(V_i - \frac{RT}{P} \right) dP \right] \quad (8)$$

\bar{V}_i is the partial molar volume of component i in the gaseous mixture and V_i is the molar volume of pure gaseous substance i . Employing the virial state equation truncated by the second term of the expansion, V_i and \bar{V}_i can be expressed, with some simplifying assumptions, by

$$V_i = (RT/P) + B_i \quad (9)$$

$$\bar{V}_i = (RT/P) + 2B_{im} - B_m \quad (10)$$

where B_i and B_m are the second virial coefficients of component i and of the carrier gas, m , respectively, and B_{im} is the cross-virial coefficient. Eqn. 10 holds when the concentration of component i in the mixture with the carrier gas is very low. Sub-

stituting for V_i and \bar{V}_i from eqns. 9 and 10 into eqn. 8 and integrating within the given limits, we obtain

$$\ln [(v_i)_P/(v_i)_{P^0}] = (2B_{im}P - B_mP - B_i p_i^0)/RT \quad (11)$$

Upon introducing the notation $2B_{im}P - B_mP - B_i p_i^0 = B^*$, we obtain

$$\frac{d \ln [(v_i)_P/(v_i)_{P^0}]}{d(1/T)} = \frac{1}{R} \left[B^* + \frac{1}{T} \cdot \frac{dB^*}{d(1/T)} \right] \quad (12)$$

where

$$\frac{dB^*}{d(1/T)} = 2P \cdot \frac{dB_{im}}{d(1/T)} - P \cdot \frac{dB_m}{d(1/T)} - \left[p_i^0 \cdot \frac{dB_i}{d(1/T)} + B_i \cdot \frac{dp_i^0}{d(1/T)} \right] \quad (13)$$

The B terms can be expressed by means of the constants a and b of the Van der Waals equation, thus obtaining¹⁵ $B_i = b_i - (a_i/RT)$, $B_m = b_m - (a_m/RT)$ and $B_{im} = b_{im} - (a_{im}/RT)$, where b_{im} and a_{im} are given by $b_{im} = [(\sqrt[3]{b_i} + \sqrt[3]{b_m})/2]^3$ and $a_{im} = \sqrt{a_i a_m}$. As $dp_i^0/d(1/T) = -p_i^0 \Delta H_v / \Delta z R$, according to the Clapeyron equation, eqn. 13 can be rewritten as

$$\frac{dB^*}{d(1/T)} = - \frac{(2a_{im} - a_m)P - [a_i + (B_i \Delta H_v / \Delta z)] p_i^0}{R} \quad (14)$$

and the combination of eqns. 7, 12, 13 and 14 gives

$$\Delta H_v = - \Delta z \left(R \cdot \frac{d \ln R_i}{d(1/T)} + \beta_1 P - \beta_2 p_i^0 - RT \right) \quad (15)$$

where $\beta_1 = 2 \left(B_{im} - \frac{a_{im}}{RT} \right) - \left(B_m - \frac{a_m}{RT} \right) - V_i^L$ and $\beta_2 = B_i \left(1 - \frac{\Delta H_v}{\Delta z RT} \right) - \frac{a_i}{RT}$.

Eqn. 15 provides for correcting the experimental data on $d \ln R_i / d(1/T)$ for the non-ideality of the gaseous phase and the compressibility of the liquid phase. If $p_i^0 \ll P$, then the term $\beta_2 p_i^0$ can be neglected and eqn. 15 simplified accordingly.

The procedure of treating the gas-phase non-ideality and liquid-phase compressibility effects in our case is, naturally, similar to that employed for correcting the partition coefficients^{16,17} and heats of sorption¹⁸ calculated from GC retention data.

EXPERIMENTAL

Chemicals

The model compounds chosen for the determination of ΔH_v by the method described were hexadecane (BDH, Poole, Great Britain), octadecane and glycerol (both from Lachema, Brno, Czechoslovakia). These substances were deposited, with no preliminary purification, on Chromosorb W, 30–60 mesh (Carlo Erba, Milan, Italy), dried at 150° for 3 h, employing the slurry method. The hexadecane and glycerol packings were each prepared at 10, 1 and 0.1% (w/w) loadings and the octadecane packings at a 10% (w/w) loading. Hexadecane and octadecane were deposited from

solutions in distilled pentane and glycerol from solutions in anhydrous distilled methanol. The solvents were evaporated from the packing materials under vacuum. A set of solutions of nonane (Baker Chemicals N.V., Deventer, The Netherlands) in carbon disulphide of concentrations in the range 10^{-8} – 10^{-5} g/ μ l were employed for testing the range of linearity of the detector used.

Apparatus

A Hewlett-Packard (Avondale, Pa., U.S.A.) Model 402 gas chromatograph with a flame-ionization detector was employed, coupled with an Infotronics (Shannon Airport, Ireland) 101 CRS integrator. In order to increase the accuracy of measuring the column temperature, a precisely calibrated iron–constantan thermocouple was suspended via one of the sample-inlet ports into the column oven, the reference temperature being 0° . The e.m.f. of the thermocouple was measured by means of an MT 100 digital voltmeter (Metra, Blansko, Czechoslovakia). The materials investigated were packed into 1-m long U-shaped glass columns of 3 mm I.D. The weights of the packings in the column were about 3 g, *i.e.*, 0.3, 0.03 and 0.003 g of the liquid were required for one determination with the 10, 1 and 0.1% packings, respectively. In each measurement, about a 10-cm length of the column at its outlet end was left unpacked in order to prevent the packing being heated by the detector.

Procedure

Each freshly prepared column was first kept at 100° until a steady response of the detector was achieved. The column-oven temperature was then increased in steps of about 4° while measuring the steady absolute response of the detector and reading the corresponding e.m.f. of the thermocouple. The temperature intervals of the measurement with hexadecane, octadecane and glycerol were about 60–120, 80–150 and 70–150 $^\circ$, respectively. The carrier gas was nitrogen, kept at a flow-rate of about 18 ml/min as measured at ambient temperature and pressure. The flow-rates of hydrogen and air were 30 and 430 ml/min, respectively.

The measurement of the detector response proper was carried out by means of the integrator; the integral of the response within a time interval of 200 sec was measured and divided by the time interval, thus obtaining the response in counts per second. These data were correlated with the corresponding column temperature according to the Antoine equation.

RESULTS AND DISCUSSION

The values of $\text{dln } R_i/\text{d}(1/T)$ were calculated from the equation $\text{dln } R_i/\text{d}(1/T) = 2.303 B T/(t + 230)^2$ where B is the slope of the line obtained by plotting $\log R_i$ against $1/(t + 230)$ and 230 is the Calingaert–Davis constant¹⁹ of the Antoine equation, T and t being the absolute and Celsius temperatures of the column, respectively.

The second virial coefficients were calculated from the constants a and b of the Van der Waals equation by using the above equations. The a and b values were calculated for hexadecane and octadecane from the contributions of the individual groups in the molecule according to Thodos²⁰ and for glycerol from the critical temperature and pressure ($a = 27 RT_c b/8$ and $b = RT_c/8P_c$). T_c and P_c were calculated with the equations²¹ $T_c = 1.027 T_b + 195$ and $P_c = 20.8 T_c/(V_c - 8)$, where T_b is

the absolute boiling temperature and $V_c = (0.377 \Sigma P_i + 11)^{1.25}$, ΣP_i being the sum of the atomic and structural parachor increments.

The values of V_i^L were calculated from $V_i^L \omega = V_i^{L_0} \omega^0$, where $V_i^{L_0}$ is the molar volume of the liquid at standard T and P and ω^0 and ω are the expansion factors at the standard and actual T and P , respectively, obtained from the generalized expansion diagram²². The values of Δz were calculated from $\Delta z = (\bar{V}_i - V_i^L)P/RT$, \bar{V}_i being obtained by eqn. 10. The ΔH_v and p_i^0 in $\beta_2 p_i^0$ (cf., eqn. 15) were estimated roughly by the Trouton²³ and Watson²² rules, employing $\Delta H_v^{T_b} = 21 T_b$ and $\Delta H_v = \varphi \Delta H_v^{T_b}$, where $\varphi = [(T_c - T)/(T_c - T_b)]^{0.38}$. Thus, p_i^0 was estimated from $\log p_i^0 = 4.6 \varphi [(T_b/T) - 1]$. This estimate is very inaccurate, especially with glycerol, but is acceptable owing to the insignificant role of the $\beta_2 p_i^0$ term.

The values of the individual quantities used for calculating the correction terms $\beta_1 P$ and $\beta_2 p_i^0$ are summarized in Tables I and II. Table III contains the values of $\beta_1 P$, $\beta_2 p_i^0$ and $100 [(\beta_1 P - \beta_2 p_i^0)/\Delta H_v]$, the last value showing the magnitude of the overall correction expressed as a percentage of ΔH_v obtained with the 10% packings. The relative unimportance of $\beta_2 p_i^0$ and the dependences of the correction terms on the type of substance and on temperature are apparent from the data in Table III.

TABLE I

INDIVIDUAL QUANTITIES USED IN CORRECTING THE GAS-PHASE NON-IDEALITY EFFECTS

a_i, a_m = constants a of the Van der Waals equation for compound i and the carrier gas, respectively ($\text{cm}^6 \cdot \text{atm} \cdot \text{mole}^{-2}$); a_{im} = cross-value of a for i and m ; R = gas constant ($\text{cm}^3 \cdot \text{atm} \cdot \text{deg}^{-1} \cdot \text{mole}^{-1}$); T = column temperature ($^{\circ}\text{K}$); B_i, B_m = second virial coefficients of compound i and the carrier gas, respectively ($\text{cm}^3 \cdot \text{mole}^{-1}$); B_{im} = cross-value of B terms for i and m .

Compound	t ($^{\circ}\text{C}$)	a_i/RT	a_m/RT	a_{im}/RT	$-B_i$	B_m	$-B_{im}$
Hexadecane	70	2497	49.36	351.1	2173	4.448	305.8
	80	2426	47.97	341.1	2103	5.625	295.8
	90	2359	46.65	331.8	2036	6.726	286.4
	100	2296	45.40	322.9	1973	8.274	277.5
	110	2236	44.21	314.4	1913	9.230	269.1
Octadecane	70	2988	49.36	384.1	2614	4.448	332.4
	80	2903	47.97	373.2	2529	5.625	321.6
	90	2824	46.65	362.9	2449	6.726	311.3
	100	2748	45.40	353.2	2374	8.274	301.6
	110	2676	44.21	344.0	2302	9.230	292.3
Glycerol	70	970.9	49.36	218.9	837.0	4.448	197.3
	80	943.4	47.97	212.7	809.6	5.625	191.1
	90	917.5	46.65	209.9	783.6	6.726	185.3
	100	892.9	45.40	201.3	759.0	8.274	179.7
	110	869.6	44.21	196.1	735.7	9.230	174.5

The data on the overall detector response (net response to compound i plus that produced by the hydrogen flame alone), R_{i0} , measured in units of integrator counts per second and plotted against $1000/(t + 230)$ for all of the materials investigated, are shown in Fig. 1. In our arrangement (electrometer output voltage 1 mV per $4 \cdot 10^{-12}$ A ionization current at full sensitivity setting, integrator count rate 4

TABLE II

INDIVIDUAL QUANTITIES USED IN CORRECTING THE GAS-PHASE NON-IDEALITY AND LIQUID-PHASE COMPRESSIBILITY EFFECTS

V_i, \bar{V}_i = molar volume of pure gaseous compound i and partial molar volume of gaseous compound i in mixture with the carrier gas, respectively ($\text{cm}^3 \cdot \text{mole}^{-1}$); V_i^L = molar volume of pure liquid compound i ($\text{cm}^3 \cdot \text{mole}^{-1}$); Δz = difference between the compressibility factors of compound i in admixture with the carrier gas and in the liquid state; $\Delta H_i^*, p_i^{0*}$ = estimates of the heat of vaporization ($\text{cal} \cdot \text{mole}^{-1}$) and saturation vapour pressure (atm) of compound i , respectively.

Compound	t ($^{\circ}\text{C}$)	V_i	\bar{V}_i	V_i^L	Δz	ΔH_i^*	p_i^{0*}
Hexadecane	70	25985	27542	304.4	0.967	15990	$1.117 \cdot 10^{-4}$
	80	26876	28382	307.8	0.969	15833	$2.361 \cdot 10^{-4}$
	90	27763	29220	310.1	0.970	15674	$4.759 \cdot 10^{-4}$
	100	28647	30057	312.4	0.971	15511	$9.175 \cdot 10^{-4}$
	110	29528	30894	314.9	0.973	15347	$1.698 \cdot 10^{-3}$
Octadecane	70	25544	27489	339.2	0.964	17317	$2.364 \cdot 10^{-5}$
	80	26450	28330	341.6	0.966	17161	$5.315 \cdot 10^{-5}$
	90	27350	29170	345.5	0.967	17001	$1.137 \cdot 10^{-4}$
	100	28246	30009	348.0	0.969	16839	$2.320 \cdot 10^{-4}$
	110	29139	30847	350.7	0.970	16674	$4.535 \cdot 10^{-4}$
Glycerol	70	27321	27759	76.33	0.983	16134	$9.482 \cdot 10^{-5}$
	80	28169	28691	76.90	0.987	15976	$2.627 \cdot 10^{-4}$
	90	29015	29422	77.48	0.985	15818	$4.090 \cdot 10^{-4}$
	100	29861	30252	78.07	0.985	15656	$7.933 \cdot 10^{-4}$
	110	30705	31082	78.66	0.986	15491	$1.477 \cdot 10^{-3}$

TABLE III

CORRECTIONS OF THE GAS-PHASE NON-IDEALITY AND LIQUID-PHASE COMPRESSIBILITY EFFECTS

P = column outlet pressure (atm); for β_1 and β_2 , see eqn. 15; for ΔH_V and p_i^{0*} , see Table II; ΔH_o = heat of vaporization as determined in this work (cf., Table IV).

Compound	t ($^{\circ}\text{C}$)	$-\beta_1 P$	$\beta_2 p_i^{0*}$	$-(\beta_1 P - \beta_2 p_i^{0*})$	$-\frac{100(\beta_1 P - \beta_2 p_i^{0*})}{\Delta H_o}$
Hexadecane	70	1540	5.174	1545	8.53
	80	1508	10.14	1518	8.43
	90	1475	18.96	1494	8.34
	100	1445	33.96	1479	8.30
	110	1416	58.18	1474	8.29
Octadecane	70	1691	1.438	1692	8.46
	80	1653	3.001	1656	8.33
	90	1619	5.965	1625	8.22
	100	1586	11.33	1597	8.12
	110	1555	20.62	1576	8.05
Glycerol	70	835.4	1.593	836.9	4.30
	80	814.4	4.070	810.5	4.18
	90	794.7	5.849	800.6	4.16
	100	776.5	10.49	786.9	4.12
	110	758.9	18.10	770.0	4.05

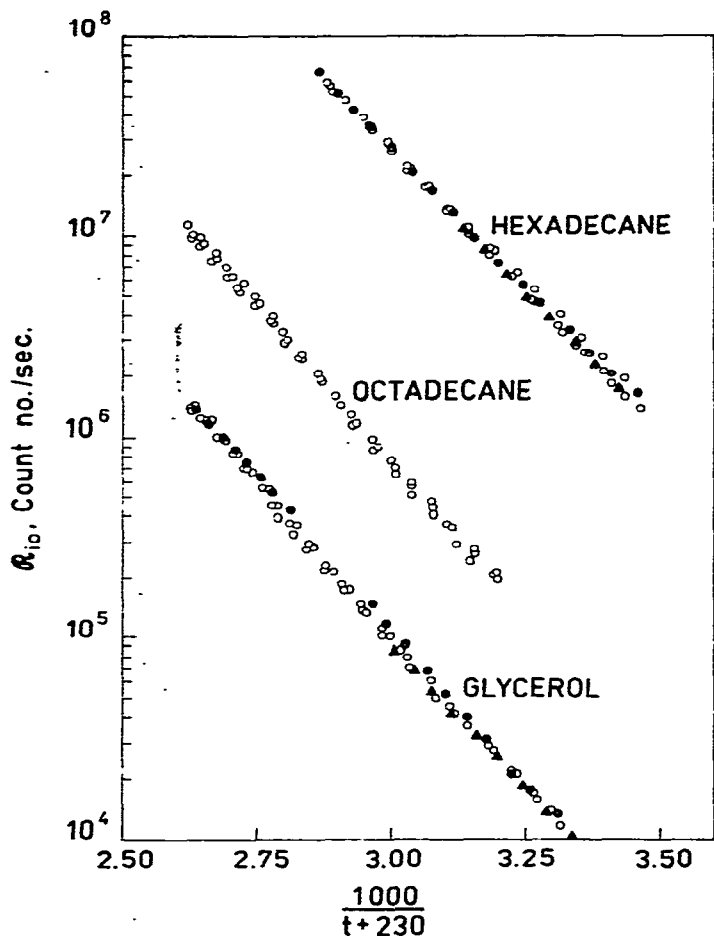


Fig. 1. Plots of the overall detector response versus $1000/(t + 230)$ for the hexadecane, octadecane and glycerol packings.

kHz/mV), a count rate of 1000 counts/sec corresponds to an ionization current of 10^{-12} A. Further, as the response produced by the hydrogen flame in the absence of compound i is constant under the conditions described above, then $d \log R_{i0}/d[1/(t + 230)] = d \log R_i/d[1/(t + 230)] = B$. The detector response was proved to be linear within a range of about $5 \cdot 10^{-12}$ – $5 \cdot 10^{-8}$ A, i.e., $5 \cdot 10^3$ – $5 \cdot 10^7$ counts/sec. With each of the 10% packings, three independent series of measurements (three different columns) were carried out at different times. The relative standard deviations of the determination of B with hexadecane, octadecane and glycerol were 2.6, 0.67 and 1.8%, respectively, the correlation coefficient being -0.999 in each instance. The results of these measurements are represented by the open circles in Fig. 1. The closed circles represent the results of the measurements with the 1% packings, and the triangles those results obtained with the 0.1% packings. With both the 1 and 0.1% packings the correlation coefficients were also -0.999 .

It can be seen from Fig. 1 that both the absolute values and the temperature dependences of the data obtained with the 1 and 0.1% packings agree well with the data measured with the corresponding 10% materials. Our results show that the vapour pressure of the substances deposited on Chromosorb W is virtually the same as that of the bulk liquids even at loadings as low as 0.1%. Only glycerol displays a slight deviation at this extremely low loading. These results are surprising, as they differ markedly from the findings of Hawkes and Giddings¹¹. We assume that this disagreement is due to the different types of chromatographic support used in the two studies.

Table IV shows the heats of vaporization at some selected temperatures, calculated from the data obtained with the 10% packings. The values of ΔH_v , $\Delta H'_v$ and $\Delta H''_v$ were calculated with both the $\beta_1 P$ and the $\beta_2 p_i^0$ terms taken into account, neglecting the $\beta_2 p_i^0$ term, and neglecting both correction terms, respectively. In Table V are given the ΔH_v values calculated from the data measured with the 1 and 0.1% packings. Except for the packings with 0.1% glycerol, these ΔH_v values coincide, within experimental error, with those obtained with the 10% packings.

TABLE IV

RESULTS OF THE MEASUREMENTS WITH THE PACKINGS CONTAINING 10% OF THE SUBSTRATES

$B = \text{dlog } R_i / \text{d}[1/(t + 230)]$; $\text{dln } R_i / \text{d}(1/T) = 2,303 \Delta zRB/[T(t + 230)]^2$; R_i = detector response; ΔH_v , $\Delta H'_v$ and $\Delta H''_v$ = heats of vaporization ($\text{cal} \cdot \text{mole}^{-1}$) calculated by taking into account both $\beta_1 P$ and $\beta_2 p_i^0$, neglecting $\beta_2 p_i^0$ and neglecting both $\beta_1 P$ and $\beta_2 p_i^0$, respectively.

Compound	t ($^{\circ}\text{C}$)	$-B$	$-\frac{\text{dln } R_i}{\text{d}(1/T)}$	ΔH_v	$\Delta H'_v$	$\Delta H''_v$
Hexadecane	70	2761.4 ± 72.3	8312	18116	18111	16622
	80		8242	18011	17965	16541
	90		8185	17917	17898	16467
	100		8121	17816	17783	16380
	110		8070	17769	17713	16335
Octadecane	70	3073.4 ± 20.7	9251	20000	19998	18368
	80		9173	19876	19873	18276
	90		9109	19762	19757	18191
	100		9039	19661	19650	18113
	110		8982	19570	19550	18041
Glycerol	70	3060.1 ± 53.5	9211	19475	19473	18652
	80		9133	19402	19398	18595
	90		9070	19242	19236	18453
	100		8999	19109	19099	18334
	110		8943	19029	19011	18262

Table VI gives some reference data on the ΔH_v of the compounds studied, calculated from published vapour pressure-temperature data^{24,25}. The Δt and C data in parentheses show the temperature intervals in which the vapour pressures were measured and the Antoine equation C constants employed in the calculation. In case (a) the C constants were taken from the book by Boublík *et al.*²⁴ and in case (b) they were calculated²⁶ for hexadecane and octadecane from $C = 271 - 7.6n$ and for glyc-

TABLE V

HEATS OF VAPORIZATION OF HEXADECANE AND GLYCEROL, MEASURED WITH THE PACKINGS CONTAINING 1 AND 0.1% OF THE SUBSTRATES

t (°C)	ΔH_v			
	Hexadecane		Glycerol	
	1%	0.1%	1%	0.1%
70	18087	18238	19420	17965
80	17981	18133	19348	17900
90	17887	18038	19187	17752
100	17787	17937	19056	17633
110	17742	17890	18976	17597

TABLE VI

REFERENCE DATA ON THE HEATS OF VAPORIZATION AT 70°, CALCULATED FROM PUBLISHED VAPOUR PRESSURE-TEMPERATURE DATA^{23,24} USING DIFFERENT ANTOINE EQUATION C CONSTANTS

(a) ref. 24; (b) ref. 26; (c) ref. 19.

Compound	ΔH_v at 70°			
	(a)	(b)	(c)	Average
Hexadecane ²⁴ ($t = 190-287^\circ$)	19523 ($C = 154.968$)	19944 ($C = 149.4$)	15705 ($C = 230$)	18391
Octadecane ²⁴ ($t = 175-317^\circ$)	21316 ($C = 155.492$)	23214 ($C = 134.2$)	17042 ($C = 230$)	20525
Glycerol ²⁵ ($t = 126-290^\circ$)	49326* ($C = 28.097$)	22072 ($C = 184.9$)	19781 ($C = 230$)	20926

* This value was not used in calculating the average.

erol from $C = 240 - 0.19 t_b$, where n and t_b are the number of carbon atoms in the molecule and the boiling temperature (°C), respectively. All of the data in Table VI obviously suffer from extrapolation errors; with glycerol in case (a) the C constant is evidently unsuitable for the extrapolation.

Table VII gives a comparison of the values of the second virial coefficients calculated by the method employed in this work²⁰ with those calculated according to the more rigorous Lennard-Jones model²⁷. The comparison was made for nonane,

TABLE VII

COMPARISON OF THE SECOND VIRIAL COEFFICIENTS OF NONANE CALCULATED ACCORDING TO THE LENNARD-JONES MODEL²⁷ AND IN THIS WORK FROM THE VAN DER WAALS CONSTANTS DETERMINED BY THE THODOS SCHEME²⁰

Method	Nonane, 70°		
	B_l	B_m	B_{lm}
Lennard-Jones ²⁷	-1019	4.448	-115.0
This work ²⁰	-891.5	-10.26	-139.6

as this is the highest hydrocarbon for which the Lennard-Jones constants necessary for calculating the B terms were available. Except for B_m , which is relatively unimportant in calculating β_1 (*cf.*, eqn. 15 and Table I), the agreement between the B values calculated by both methods is satisfactory. The value of B_{im} obtained by the method used in this work²⁰ is evidently much closer to the true value than that calculated from $B_{im} = (B_i + B_m)/2$.

CONCLUSIONS

As performed under the conditions described, the method proved suitable for the micro-determination of the heats of vaporization of substances of low volatility. With respect to the range of linearity of the response of the flame-ionization detector, the measurement can be carried out within ionization currents in the range *ca.* 10^{-12} – 10^{-7} A. However, as the flame-ionization detector is a destructive detector, the ionization current can be varied within wide limits by changing the flow-rate of the carrier gas at a given concentration of the component vapour in the effluent. Hence the applicability of the method can be extended to more volatile substances provided that the flow-rate is kept at an appropriately low value. This would, of course, necessitate some alterations in the expressions for correcting the gas-phase non-ideality effects. On calibrating the detector with the substance investigated, it is possible to convert the data on the detector response into the corresponding vapour pressures.

The precision of the determination of ΔH_v was about 2% of the value measured when employing a commercial analytical gas chromatograph. As the main sources of error are the fluctuations of the column temperature and the carrier gas flow-rate in the arrangement employed, the errors could be made appreciably smaller by using an apparatus designed specially for the purpose and provided with fine controls of the column temperature and the carrier gas flow-rate.

Compared with the so-called gas current method^{28,29}, for instance, the use of a gas chromatograph as described in this paper makes it possible to measure the heats of vaporization with amounts of sample about one order of magnitude smaller.

REFERENCES

- 1 R. Kobayashi, P. S. Chappellear and H. A. Deans, *Ind. Eng. Chem.*, 59 (1967) 63.
- 2 C. L. Young, *Chromatogr. Rev.*, 10 (1968) 129.
- 3 D. C. Locke, *Int. Lab.*, July/Aug. (1975) 13.
- 4 M. R. Hoare and J. H. Purnell, *Trans. Faraday Soc.*, 52 (1956) 222.
- 5 A. Rose and V. N. Schrodt, *J. Chem. Eng. Data*, 8 (1963) 9.
- 6 R. C. Duty and W. R. Mayberry, *J. Gas Chromatogr.*, March (1966) 115.
- 7 H. Mackle, R. G. Mayrick and J. J. Rooney, *Trans. Faraday Soc.*, 56 (1964) 115.
- 8 H. Mackle and R. T. B. McClean, *Trans. Faraday Soc.*, 60 (1964) 817.
- 9 A. Gianetto and M. Panetti, *Ann. Chim. (Rome)*, 50 (1960) 1713.
- 10 B. Kolb, *J. Chromatogr.*, 112 (1975) 287.
- 11 S. J. Hawkes and J. C. Giddings, *Anal. Chem.*, 36 (1964) 2229.
- 12 H. V. Regnault, *Anal. Chim.*, 15 (1845) 129.
- 13 J. Novák, *Advan. Chromatogr.*, 11 (1974) 1.
- 14 J. C. Sternberg, W. S. Gallaway and D. T. L. Jones, in N. Brenner, J. E. Callen and M. D. Weiss (Editors), *Gas Chromatography*, Academic Press, New York, 1962, p. 231.
- 15 J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1965, pp. 252 and 253.

- 16 D. H. Everett and C. T. H. Stoddart, *Trans. Faraday Soc.*, 57 (1961) 747.
- 17 D. H. Desty, A. Goldup, G. R. Luckhurst and W. T. Swanton, in M. Van Swaay (Editor), *Gas Chromatography 1962*, Butterworths, London, 1962, p. 67.
- 18 G. Blu, L. Jacob and G. Guiochon, *J. Chromatogr.*, 50 (1970) 1.
- 19 G. Calingaert and D. S. Davis, *Ind. Eng. Chem.*, 17 (1925) 1286.
- 20 G. Thodos, *AIChE J.*, 1 (1955) 165.
- 21 H. P. Meissner and E. P. Redding, *Ind. Eng. Chem.*, 34 (1942) 521.
- 22 K. M. Watson, *Ind. Eng. Chem.*, 35 (1943) 398.
- 23 J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1965, p. 283.
- 24 T. Boublik, V. Fried and E. Hála, *The Vapour Pressures of Pure Substances*, Elsevier, Amsterdam, London, New York, 1973, pp. 566 and 575.
- 25 T. E. Jordan, *Vapor Pressure of Organic Compounds*, Interscience, New York, London, 1954, p. 80.
- 26 E. Hála, J. Pick, V. Fried and O. Vilím, *Vapour-Liquid Equilibrium*, Pergamon Press, Oxford, 1967, p. 239.
- 27 J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1965, p. 1112.
- 28 J. A. Goff and J. B. Hunter, *J. Appl. Mech.*, 9 (1942) 21.
- 29 I. Wadsö, *Acta Chem. Scand.*, 14 (1960) 566.