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Note

ENTHALPY OF VAPORIZATION OF *n*-HEPTACOSANE AND *n*-NONACOSANE FROM THEIR VAPOUR PRESSURE DETERMINATIONS

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In our previous work [1] the vaporization enthalpies of a homologous series of some *n*-alkanes were determined. In order to continue this series, the vaporization of other two compounds, *n*-heptacosane and *n*-nonacosane, was studied and the results obtained are reported in this note. Apart from obsolete data based on old experimental determinations [2] and some vapour pressure values of *n*-heptacosane obtained by Morecroft [3] employing the Knudsen method, apparently at present no other vapour pressures and vaporization enthalpies of these compounds are available in literature.

The samples of *n*-heptacosane and *n*-nonacosane (supplied by Aldrich Chemie) used were 99.5% pure with impurities probably due to homologous species. The vapour pressures of these compounds were measured by the

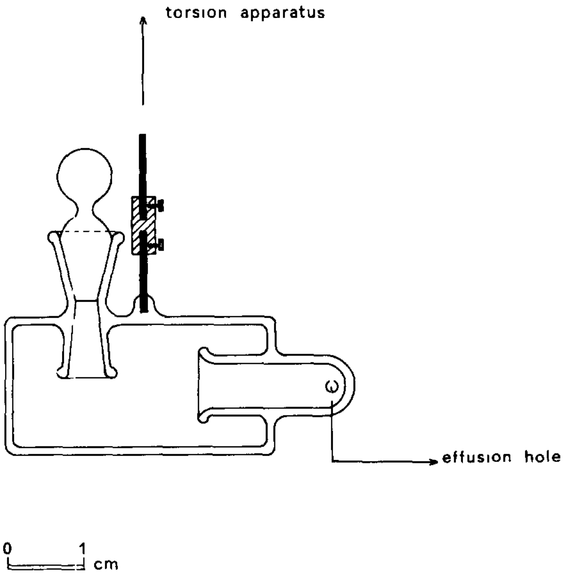

Fig. 1. Torsion effusion cell.

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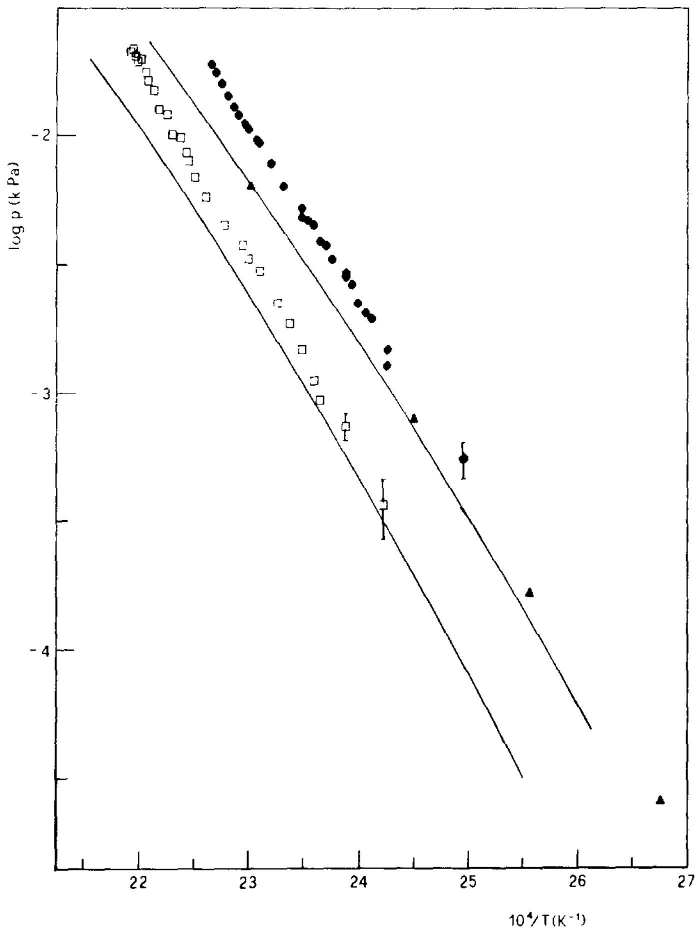

Fig. 2. Vapour pressures of *n*-heptacosane (●) and *n*-nonacosane (□): ———, selected TRC data [2]; ▲, Morecroft's values [3].

torsion method employing the assembly described in a previous paper [4]. A drawing of the Pyrex effusion cell used is given in Fig. 1, the shape being designed to prevent during the experiment the overflow of the samples that appreciably wet the glass. The instrument constant was determined experimentally by vaporizing two standard compounds from the relation $K = p_t/\alpha_i$ where α_t is the experimental torsion angle measured at a given temperature and p_t the corresponding vapour pressure value selected from the literature (naphthalene [5] and urea [6]) at the same temperature. In Fig. 2 our experimental vapour pressure values and those reported in literature are plotted as log p vs. $1/T$. The data were treated by least squares and the linear log p vs. $1/T$ equations obtained are presented in Table 1, where the errors are estimated considering the major source of uncertainty to be that associated with the instrument constant. In the same table are also reported the equations found from transpiration measurements in the previous work

TABLE 1

Vapour pressures of *n*-alkanes

Compound	Method	Temperature range (K)	$\log[p(\mathrm{kPa})] = A - B/T$	
			A	B
n-Tetracosane	transpiration	451 –497	8.76 ± 0.50	4501 ± 250
n-Pentacosane	transpiration	461 –498	9.16 ± 0.60	4745 ± 300
n-Hexacosane	transpiration	455.5–519	9.93 ± 0.50	5168 ± 200
n-Heptacosane	torsion	401 –441.5	12.48 ± 0.40	6103 ± 150
n-Octacosane	transpiration	473 –515	10.02 ± 0.40	5385 ± 150
n-Nonacosane	torsion	423 –456.5	13.84 ± 0.40	7161 ± 150

[1]. The results obtained in the present work seem to be in disagreement with the trend found in the previous work, but considering the different pressure ranges covered in these researches and that the *n*-alkanes exhibit [2] a temperature dependence of their vaporization enthalpies (which increase as the temperature decreases), the disagreement is not so marked.

Following Thomson's procedure [7] and assuming the boiling temperatures to be "free from error" points (695.1 K and 713.8 K for *n*-heptacosane and *n*-nonacosane respectively) the vapour pressures of these compounds were used to obtain the constants of Antoine's equation. In this way the following constants for *n*-heptacosane and *n*-nonacosane respectively are obtained: $A = 5.96$ and 5.40; $B = 2017$ and 1680 and $C = 88$ and 53.

From these constants, and the known heat of fusion of *n*-heptacosane ($\Delta_{\mathrm{fus}}H^{\ominus}_{332} = 60.2$ kJ mol^{-1} [8]), the standard sublimation enthalpy, $\Delta_{\mathrm{sub}}H^{\ominus}_{298} = 351$ kJ mol^{-1}, was derived from the equation

$$\Delta_{\mathrm{sub}}H^{\ominus}_{298} = \Delta_{\mathrm{fus}}H^{\ominus}_{332} + B \times 2.3R[T/(C+t)]^2$$

where R is the gas constant and T and t represent the melting point expressed in kelvins and degrees Celsius respectively.

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