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Ebulliometric apparatus for the measurement of enthalpies of vaporization

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Abstract

A differential ebulliometric apparatus of the Swietoslawski type requiring ca. 10 cm^3 of sample is described. The application of this apparatus to the determination of enthalpies of vaporization was tested with cyclohexane and ethanol. The values obtained at 298.15 K were 33.1 ± 0.5 kJ mol^{-1} and 42.3 ± 0.5 kJ mol^{-1}, for cyclohexane and ethanol, respectively, in good agreement with the corresponding values in the literature.

Keywords: Cyclohexane; Ebulliometer; Ethanol; Heat of vaporization

1. Introduction

To discuss the relations between energetics, structure, and reactivity of molecules, it is often necessary to know the standard enthalpy of formation of a compound in the ideal gas state, $\Delta_f H_m^\circ(g)$ [1–3]. For compounds which are liquids at the reference temperature of 298.15 K, $\Delta_f H_m^\circ(g)$ is calculated using

$$\Delta_f H_m^\circ(g) = \Delta_f H_m^\circ(l) + \Delta_l^g H_m^\circ \qquad (1)$$

where $\Delta_f H_m^\circ(l)$ is the standard molar enthalpy of formation in the liquid state (determined by calorimetric methods) and $\Delta_l^g H_m^\circ$ is the standard molar enthalpy of vaporization. The availability of a large and reliable $\Delta_l^g H_m^\circ$ data bank is, therefore,

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of major importance for the above mentioned studies and for many other applications [4].

The determination of the enthalpy of vaporization of pure substances using experimental vapour pressure–temperature data and the Clausius–Clapeyron equation [5] is frequently used, because of its simplicity compared with calorimetric measurements [1,4,6]. The accuracy of the $\Delta_l^g H_m^\ominus$ values derived by the former method strongly depends on the reliability of the measured vapour pressure-temperature data and on the choice of an adequate method of calculation [4,6].

In this paper, an ebulliometric apparatus operating in the range ca. 30–100 kPa pressure is described, and its application to the determination of enthalpies of vaporization is tested using cyclohexane and ethanol.

2. Experimental

Cyclohexane (Aldrich, 99.9+%, HPLC grade) was used without further purification. Ethanol (Merck, >99.8%) was predried over CaH_2, dried over small slices of sodium and distilled under argon U atmosphere. Distilled and deionized water from a Millipore system (conductivity ≤ 0.1 μs cm^{-1}) was used as reference for the determination of vapour pressures.

The apparatus used in this work (Figs. 1 and 2) is similar to that developed by Osborn and Douslin [7] and requires about 10 cm^3 of sample. Each ebulliometer (1,

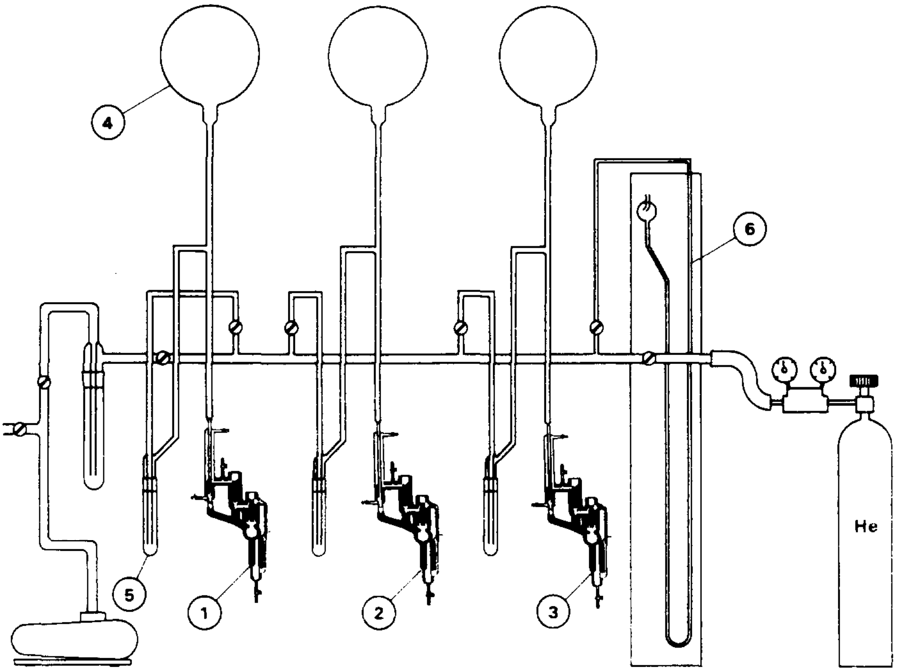

Fig. 1. Differential ebulliometer apparatus: (1), (2) and (3) ebulliometers, (4) 6 dm^3 ballast, (5) liquid nitrogen trap, (6) mercury manometer.

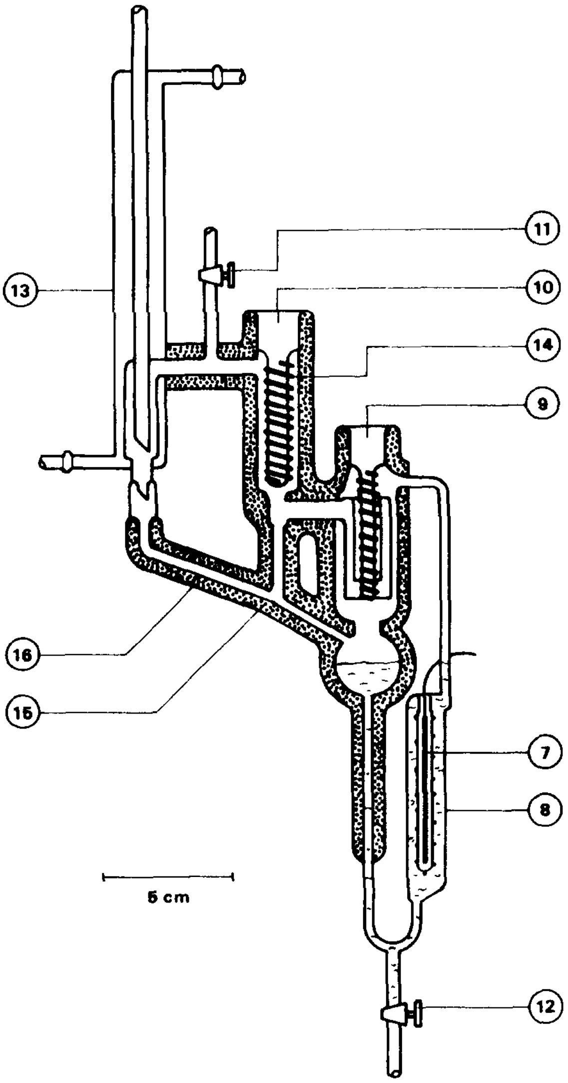

Fig. 2. Ebulliometer: (7) resistance heater, (8) boiler, (9) boiling temperature well, (10) condensation temperature well, (11) and (12), Young PTFE O-ring taps, (13) condenser, (14) glass spiral, (15) glass wool insulation, (16) aluminium foil cover.

2, and 3, Fig. 1) is connected to a common vacuum/helium line that includes three 6 dm^3 ballasts, 4, three liquid nitrogen traps, 5, and a mercury manometer, 6. The resistance heater 7 (Fig. 2) is inserted in a re-entrant well in the boiler, 8, with copper threads as the heat transfer medium. The inner surface of the well, in contact with the sample, is covered with sintered glass powder, to promote a bump-free boiling. The temperatures of the boiling liquid and of the condensing vapour are measured in wells 9 and 10, respectively, by use of 100 Ω platinum resistance thermometers (immersed in silicone oil) calibrated in the temperature range 298–353 K against a quartz thermometer (Hewlett-Packard 2804A). The resistances of the platinum thermometers are measured, in a four wire configuration, with a PC containing an ACPC-16-8 data acquisition board, and a T51 terminal panel with a current set resistor of 20 kΩ, from Strawberry Tree Inc. This temperature measuring device has a resolution of ±0.005 K and an accuracy better than ±0.1 K.

The apparatus, containing water in ebulliometer 2 (Fig. 1), was evacuated and filled with helium (Ar Líquido N45; purity >99.995%). To avoid exposure to atmosphere, the sample under study was transferred, under helium pressure, from a Schlenk tube into ebulliometer 1 (Fig. 1), through a Young PTFE O-ring tap (11, Fig. 2). The sample and the water used as reference were boiled under reflux after approximately adjusting the pressure of helium in the system with the mercury manometer 6. The third ebulliometer, which can be employed for a second reference or for a different sample, was not used in these experiments. The average output of each platinum resistance thermometer during 10 s was measured as a function of time until stable temperature readings were obtained. The temperature readings were then collected for 10 min and, for each thermometer, the average of the values acquired by the computer in that time period was calculated. Differences $\leq \pm 0.1$ K between the boiling and the condensation temperatures of the liquids under study, at constant pressure, were observed during the experiments. These temperatures, however, are substantially independent of the boiling rate as observed by considerably changing the heater power. The average of the boiling and condensation temperatures was taken as the equilibrium boiling temperature of the liquid at that pressure. The vapour pressure of the sample at a given temperature was calculated from the measured boiling temperature of the water, using the IAPWS ITS-90 approved vapour pressure equation of water [8]

$$p/\mathrm{kPa} = p_c \exp\left[\frac{T}{T_c}(a_1\tau + a_2\tau^{1.5} + a_3\tau^3 + a_4\tau^{3.5} + a_5\tau^4 + a_6\tau^{7.5})\right] \qquad (2)$$

where $\tau = 1 - T/T_c$, $T_c = 647.096$ K, $p_c = 22\,064$ kPa, $a_1 = -7.85951783$, $a_2 = 1.84408259$, $a_3 = -11.7866497$, $a_4 = 22.6807411$, $a_5 = -15.9618719$, $a_6 = 1.80122502$.

3. Results and discussion

The vapour pressure–temperature data shown in Tables 1 and 2 were fitted to Eq. (3)

$$\ln(p/\mathrm{Pa}) = A + \frac{B}{T} + C \ln T + DT^E \qquad (3)$$

using the least-squares method; the residuals, $\Delta \ln p = (\ln p_{\mathrm{exp}} - \ln p_{\mathrm{calc}})/\ln p_{\mathrm{calc}}$, are also presented in Tables 1 and 2. The values obtained for the constants A, B, C, D and E are given in Table 3. Figs. 3 and 4 show a comparison of the vapour pressure data measured in this work with the corresponding values recommended in Ref. [9].

Table 1
Vapour pressures of cyclohexane and residuals of Eq. (3)

T/K	p/kPa	$100 \times \Delta \ln p$	T/K	p/kPa	$100 \times \Delta \ln p$
312.9	24.253	0.0238	324.6	38.231	0.0047
313.7	25.064	0.0059	325.2	39.019	0.0038
315.1	26.484	0.0020	326.4	40.856	0.0056
315.8	27.206	0.0186	327.2	42.045	0.0047
316.8	28.333	−0.0029	327.9	42.929	−0.0291
317.7	29.354	−0.0039	328.0	43.235	0.0009
318.5	30.197	−0.0107	329.0	44.703	−0.0047
319.6	31.464	−0.0183	329.9	46.254	−0.0130
319.8	31.831	−0.0029	330.9	48.223	0.0584
320.7	32.889	−0.0135	331.8	49.582	0.0055
321.1	33.423	0.0019	332.7	51.011	0.0000
321.5	33.921	−0.0173	333.4	52.370	0.0028
322.1	34.724	0.0057	334.5	54.339	0.0037
323.1	35.936	−0.0002	335.5	56.258	0.0009
323.3	36.337	0.0000			

Table 2
Vapour pressures of ethanol and residuals of Eq. (3)

T/K	p/kPa	$100 \times \Delta \ln p$	T/K	p/kPa	$100 \times \Delta \ln p$
309.0	14.354	0.0006	330.4	41.378	−0.0132
312.6	17.366	0.0297	330.5	41.652	−0.0038
313.1	17.796	0.0109	330.7	42.007	−0.0047
315.9	20.127	−0.2432	331.7	43.928	−0.0149
318.2	23.098	−0.0020	332.8	46.042	−0.0047
319.4	24.463	−0.0089	333.6	47.791	−0.0093
319.9	25.079	0.0009	333.7	47.921	−0.0148
320.5	25.926	−0.0010	334.4	49.712	0.0028
321.0	26.505	0.0088	335.1	51.139	−0.0157
322.2	28.181	−0.0009	336.2	53.729	−0.0073
323.2	29.578	0.0078	336.4	54.046	−0.0083
323.7	30.306	0.0029	336.6	54.513	−0.0128
325.0	32.135	0.0106	337.7	57.331	−0.0109
325.3	32.630	−0.0029	338.2	58.624	0.0082
326.0	33.806	0.0084	338.6	59.653	−0.0136
326.1	33.830	−0.0019	339.2	61.126	−0.0109
326.6	34.683	0.0096	340.7	65.212	−0.0135
328.1	37.127	−0.0038	342.1	69.279	−0.0144
338.2	37.410	−0.0019	343.1	72.063	−0.0021
328.4	37.733	−0.0085			

The enthalpies of vaporization of cyclohexane and ethanol (Table 3) at T_m (the average of the highest and lowest temperature of the experiments) and at 298.15 K, were derived from

$$\Delta_l^g H_m^\circ = ZRT^2 \frac{d \ln p}{dT} \tag{4}$$

Table 3
Parameters of Eq. (3), second virial coefficients, compressibility factors and enthalpies of vaporization for cyclohexane and ethanol

	Cyclohexane	Ethanol
A	71.1211	59.817
B	−6106.3	−6614.6
C	−7.3181	−5.0417
D	$(1.7161)\times10^{-3}$	$(6.9815)\times10^{-7}$
E	1.0	2.0
T_m/K	324.20	326.05
$B(T_m)$/(dm^3 mol^{-1})	−1.341	−1.973
B(298.15 K)/(dm^3 mol^{-1})	−1.724	−2.935
$Z(T_m)$	0.981	0.975
Z(298.15 K)	0.991	0.991
$p(T_m)$/Pa	37581.9	33798.5
p(298.15 K)/Pa	12791.6	33740.5
d ln p/dT, T_m	0.0372	0.0472
d ln p/dT, 298.15 K	0.0459	0.0579
$\Delta_l^g H_m^\ominus(T_m)$/(kJ mol^{-1})	31.9	40.7
$\Delta_l^g H_m^\ominus$(298.15 K)/(kJ mol^{-1})	33.1[a]	42.4[a]
	33.1[b]	42.1[b]

[a] Calculated from Eq. (4). [b] Calculated from Eq. (8).

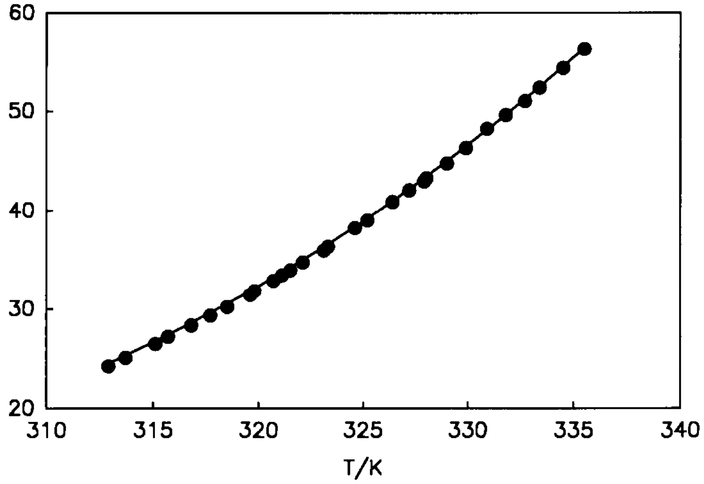

Fig. 3. Vapour pressures of cyclohexane as a function of the temperature: (●) this work; (——) Ref. [9].

where Z is the compressibility factor of the gas, R is the gas constant (8.31451 J K^{-1} mol^{-1}) and T is the absolute temperature. The compressibility factors for cyclohexane and ethanol (Table 3) were calculated from

$$Z = 1 + \frac{Bp}{RT} \tag{5}$$

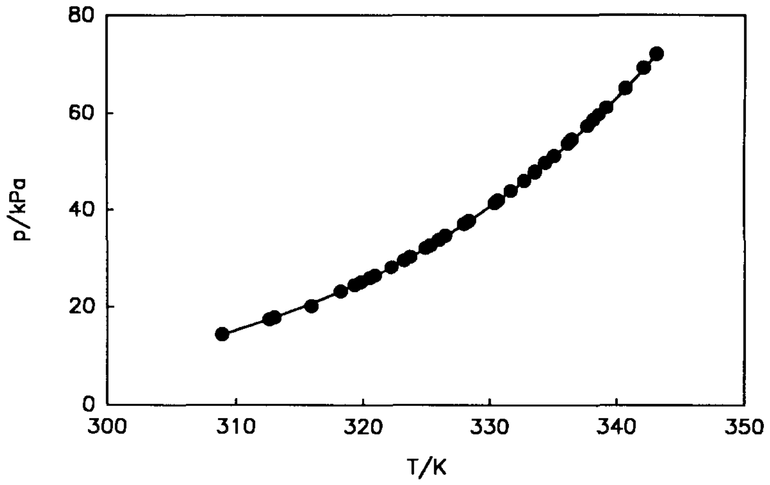

Fig. 4. Vapour pressures of ethanol as a function of the temperature: (●) this work; (——) Ref. [9].

where B represents the second virial coefficient at the temperature T. The values of B for C_6H_{12} and C_2H_6O (Table 3) were obtained from Eqs. (6) and (7), respectively

$$B(C_6H_{12})/(\mathrm{dm^3\,mol^{-1}}) = -33.482 + 0.26482T - 8.1584 \times 10^{-4}T^2 + 1.1315 \times 10^{-6}T^3 - 5.9022 \times 10^{-10}T^4 \tag{6}$$

$$B(C_2H_6O)/(\mathrm{dm^3\,mol^{-1}}) = 29.894 - 0.38536T + 1.3631 \times 10^{-3}T^2 - 1.4751 \times 10^{-6}T^3 \tag{7}$$

which were derived from polynominal fits of the data given in Ref. [10].

As a test of the internal consistence of our results, the enthalpies of vaporization of cyclohexane and ethanol at 298.15 K were also calculated from

$$\Delta_l^g H_m^\ominus(298.15\ \mathrm{K}) = \Delta_l^g H_m^\ominus(T_m) + \int_{T_m}^{298.15} [C_{p,m}^\ominus(g) - C_{p,m}^\ominus(l)]\,dT \tag{8}$$

using the $\Delta_l^g H_m^\ominus(T_m)$ values obtained from Eq. (4) and the heat capacities of liquid and gaseous cyclohexane and ethanol given by Eqs. (9–12) [9,11]

$$C_{p,m}^\ominus(C_6H_{12}, l)/(\mathrm{J\,mol^{-1}\,K^{-1}}) = -2.2060 \times 10^2 + 3.1183T - 9.4216 \times 10^{-3}T^2 + 1.0687 \times 10^{-5}T^3 \tag{9}$$

$$C_{p,m}^\ominus(C_6H_{12}, g)/(\mathrm{J\,mol^{-1}\,K^{-1}}) = -52.107 + 0.5995T - 2.3071 \times 10^{-4}T^2 \tag{10}$$

$$C_{p,m}^\ominus(C_2H_6O, l)/(\mathrm{J\,mol^{-1}\,K^{-1}}) = 94.560 - 0.0562T - 3.29 \times 10^{-4}T^2 + 2.3980 \times 10^{-6}T^3 \tag{11}$$

$$C_{p,m}^\ominus(C_2H_6O, g)/(\mathrm{J\,mol^{-1}\,K^{-1}}) = 6.2977 + 0.2315T - 1.1854 \times 10^{-4}T^2 + 2.2210 \times 10^{-8}T^3 \tag{12}$$

The results obtained (Table 3) are in good agreement with the $\Delta_l^g H_m^\ominus(298.15\ \mathrm{K})$ values calculated from Eq. (4).

The mean value of the enthalpies of vaporization of cyclohexane at 298.15 K in Table 3 is 33.1 ± 0.5 kJ mol^{-1}, where the uncertainty quoted is the estimated overall error of the determination. This value is in good agreement with the mean of all calorimetric results for $\Delta_l^g H_m^\ominus(C_6H_{12}, 298.15\ \mathrm{K})$ listed in Ref. [4] (32.98 ± 0.02 kJ mol^{-1}) and with the value $\Delta_l^g H_m^\ominus(C_6H_{12}, 298.15\ \mathrm{K}) = 33.0 \pm 1.1$ kJ mol^{-1}, recommended in Ref. [12].

In the case of ethanol, $\Delta_l^g H_m^\ominus(C_2H_6O, 298.15\ \mathrm{K}) = 42.3 \pm 0.5$ kJ mol^{-1} is derived from the results in Table 3. This value is also in good agreement with the mean of all calorimetric results for $\Delta_l^g H_m^\ominus(C_2H_6O, 298.15\ \mathrm{K})$ listed in Ref. [4] (42.30 ± 0.04 kJ mol^{-1}) and with the value $\Delta_l^g H_m^\ominus(C_2H_6O, 298.15\ \mathrm{K}) = 42.3 \pm 0.6$ kJ mol^{-1}, recommended in Ref. [12].

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