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THE CONSTRUCTION, TESTING AND USE OF A NEW KNUDSEN EFFUSION APPARATUS

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ABSTRACT

The construction of a new Knudsen effusion apparatus for measuring vapour pressures of organic and organometallic solids as a function of temperature and the subsequent calculation of enthalpies of sublimation are described. The new apparatus enables the simultaneous operation of three different effusion cells, reducing, considerably, the time necessary for the study of each compound.

The performance of the apparatus was checked by measuring, as a function of temperature, the vapour pressure of benzoic acid (between 307.15 and 314.15 K) and ferrocene (between 292.27 and 300.01 K), from which their standard molar enthalpies of sublimation, at 298.15 K, were derived: benzoic acid, $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{298.15}^{\ominus} = 89.25 \pm 0.85$ kJ mol^{-1}; ferrocene, $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{298.15}^{\ominus} = 72.39 \pm 1.00$ kJ mol^{-1}.

INTRODUCTION

The Knudsen effusion method is one of the most accurate methods for measuring vapour pressures of solids mainly in the range 0.1–1 Pa.

The theoretical background of the method is the Kinetic Theory of Gases, from which Knudsen [1,2] derived an expression for the slow isothermal flow of vapours through orifices.

In practice, the crystalline sample is placed at the base of a cylindrical cell (Knudsen cell). Through a hole located coaxially at the top of the cell, the vapour effuses into the vacuum outside the cell. The loss of mass m during time t is determined by weighing the effusion cell before and after the measurement. The mass loss is related to the vapour pressure by

$$m/t = p_k A_0 W_0 (M/2\pi RT)^{1/2} \tag{1}$$

where p_k is the vapour pressure near the orifice, A_0 is the area of the hole, M is the molecular weight of the effusing vapour, T is the absolute temperature, R is the gas constant, and W_0 is the Clausing probability factor [3], which can be calculated using the expression

$$W_0 = \frac{1}{1 + (3l/8r)} \tag{2}$$

where l is the length and r the radius of the hole.

KNUDSEN EFFUSION APPARATUS

Vacuum system

The experimental technique requires that the vacuum outside the cell (about 10^{-3} Pa) be achieved quickly, so that the beginning of an experiment can be registered with sufficient accuracy.

The pumping system, which is represented in Fig. 1, consists of one rotary vacuum pump (Edwards, model ED 200), which is used both for pre-evacuating the system and for backing the oil diffusion pump (Edwards, model E04), connected to a liquid nitrogen trap (Edwards, CT 100). A Pirani gauge (model PR 10) connected to a Pirani head gauge (model 11) is used for leak detection and for measuring the vacuum in the system during the pre-evacuation process. A Penning gauge (CP 25) connected to a Penning gauge head (model 8) is used to measure the vacuum maintained in the system throughout the effusion process. Figure 2 shows some details of the vacuum line, which is connected to the pumping system through a glass cold trap. The vacuum line consists essentially of three Pyrex tubes, each of internal diameter 43 mm and length 270 mm. Each tube is protected by a Pyrex cold finger, which can be filled with liquid nitrogen, and contains a cell holder. The cell holders are aluminium blocks of length 45 mm, which fit closely into the Pyrex tubes. The effusion cells fit tightly into cylindrical cavities in the aluminium blocks, these cavities being each of diameter 21 mm and depth 17 mm. Close-fitting contacts are important for the rapid

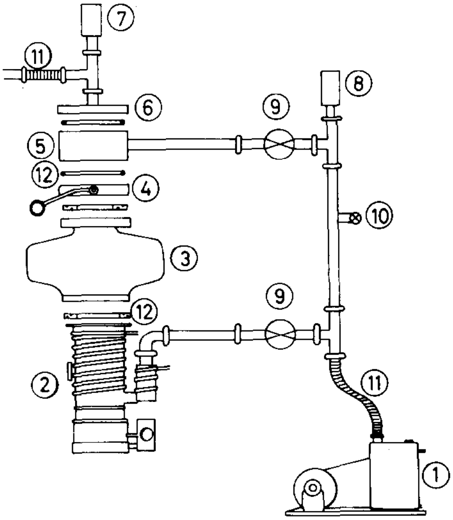

Fig. 1. Pumping system: 1, rotary pump; 2, oil diffusion pump; 3, liquid nitrogen trap; 4, butterfly valve; 5, spacer; 6, coupling; 7, Penning gauge; 8, Pirani gauge; 9, speedivalves; 10, needle valve; 11, flexible pipes; 12, flanges.

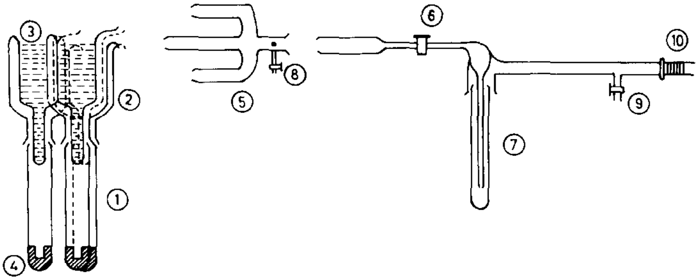

Fig. 2. Some details of the glass vacuum line: 1, glass holders with aluminium blocks for holding the effusion cells; 2, cold fingers; 3, liquid nitrogen; 4, aluminium block; 5, glass adaptor; 6, 8 and 9, glass taps; 7, liquid nitrogen trap; 10, flexible pipe.

establishment of thermal equilibrium. All Quick-fit glass joints are sealed with Edwards high vacuum silicone grease, and the metal-to-metal joints are sealed using "O-rings" lubricated with Apiezon L grease.

Effusion cells

The effusion cells, made of aluminium, are cylinders of internal diameter 20 mm and depth 23 mm. On the top of the cylinder a brass lid, with a hole of diameter 10 mm, is attached by means of a fine-pitched screw thread. A thin brass foil (thickness 0.049 mm), with the effusion hole at the centre, is soldered over the hole of each lid. The effusion holes in the brass foil were at first made using very fine drills, but the orifices obtained by this technique presented ragged edges when observed through the microscope (Fig. 3a), and consequently it was impossible to measure their lengths with accuracy. In order to overcome this problem, a new technique has been developed, based on chemical corrosion of the brass foil: the holes are made using "ALFAC-electro" printed circuit symbols, with orifices of the required diameter. The printed circuit symbol is placed on the brass foil and the remaining area

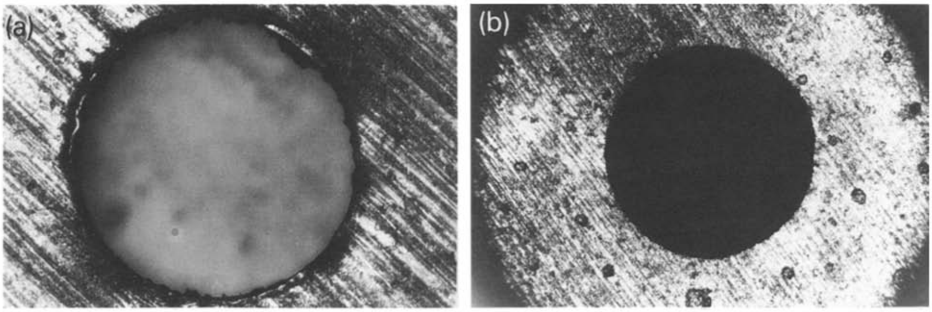

Fig. 3. Microphotographs of effusion orifices: (a) orifice made by drilling; (b) orifice made by electrochemical corrosion.

conveniently protected. The brass foil is then immersed in a saturated iron(III) chloride solution for an appropriate period of time (3–4 h). By this technique we obtain well defined orifices without ragged edges (Fig. 3b). These orifices can then be microphotographed, and their area and length determined by photographic projections, with 250–300 times amplification.

Constant temperature bath

The constant temperature bath consists of a glass tank containing 50 dm^3 of water, surrounded by insulating material and enclosed in a wooden box. Efficient stirring is achieved by means of a stirrer (2200 r.p.m.) with a three-blade propeller. The hot and cold sources of the temperature control system, regulated by means of a Tronac PTC 40 controller with an accuracy of ±0.001 K, are, respectively, an immersion electrical heater (100 W) and a copper cooling coil. Water flows through the cooling coil from a secondary thermostatic bath, the temperature of which is maintained by a Grant thermostatic head at 0.5 K below the temperature of the main bath. The temperature of the main bath is measured using Amarell mercury thermometers, graduated to 0.01 K, calibrated by Eichamt Wertheim (F.R.G.). The bath is easily moved up and down by means of a screw-jack structure.

EXPERIMENTAL TECHNIQUE

An effusion experiment consists of a measurement of the amount of sample sublimed (measurement of mass lost) during a known effusion time period, at a constant and known temperature, in order to calculate the vapour pressure of the sample at that temperature.

The apparatus was tested with samples of benzoic acid (BDH, thermochemical standard) and ferrocene (Janssen Chimica), both previously resublimed under vacuum and finely ground. The samples were introduced into the three cells until the surface was about 2 cm from the top, and then compressed inside the cell, so as to obtain a good thermal contact and a flat surface with no solid on the walls above the sample. The cells were closed by screwing down the lids, weighed on an analytical balance (Mettler H54) with an accuracy of ±0.01 mg, and fitted into the aluminium blocks of the cell holders. The holders were connected to the three cold fingers and immersed to about 12 cm depth in the thermostatic bath. The taps or valves numbered 4, 14, 15, 16 and 17 in Fig. 4 were then closed, and those numbered 10 and 13 opened. The pumps were switched on, and the trap of the diffusion pump filled with liquid nitrogen. After half an hour, temperature equilibrium was assumed to have been achieved between the sample and the bath, and the system was then evacuated by opening tap 15. This tap was closed again after the pressure had reached 1 Pa; valve 4 was then opened and valve 10

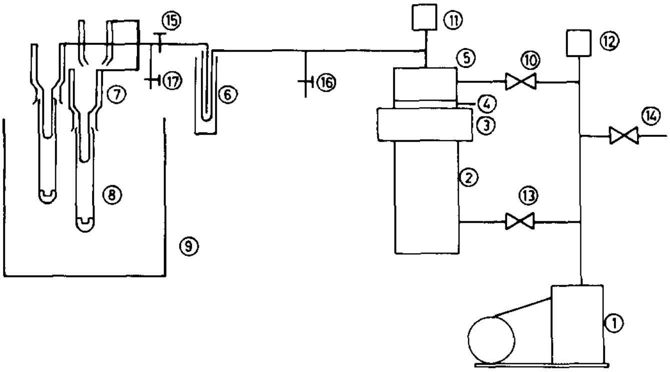

Fig. 4. General scheme of the apparatus: 1, rotary pump; 2, oil diffusion pump; 3, liquid nitrogen trap; 4, butterfly valve; 5, spacer; 6, liquid nitrogen trap; 7, cold fingers; 8, glass holder; 9, thermostatic bath; 10 and 13, speedivalves; 11, Penning gauge; 12, Pirani gauge; 14, needle valve; 15, 16 and 17, glass taps.

closed; the trap (6) and the three cold fingers (7) were filled with liquid nitrogen, and tap 15 was reopened, starting the effusion time period. After 1 min the vacuum would reach about 10^{-3} Pa. After a convenient period of time (3–6 h, depending on the hole size, the temperature and the compound), tap 15 was closed and tap 17 opened gently to the atmosphere. This was considered the ending of the effusion time period. The cells, after cooling to room temperature in a desiccator, were weighed to within ± 0.01 mg.

The hardest vacuum reached during an experiment was about 7×10^{-5} Pa. Bath temperatures (readings on the mercury thermometers immersed in the main bath) before, during and after each experiment were usually in agreement to within ± 0.001 K.

CALCULATION METHOD

The vapour pressure p_k measured by a Knudsen effusion experiment can be calculated using eqn. (1), but the equilibrium pressure p_{eq} can differ from the calculated p_k value. Whitman [4] and Motzfeldt [5] have shown that p_{eq} and p_k are related through the equation

$$p_{eq} = p_k\left[1 + \frac{W_0 A_0}{A_s}\left(\frac{1}{\alpha} + \frac{1}{W_c} - 2\right)\right] \tag{3}$$

where W_0 is the Clausing probability factor of the orifice, W_c is the cell probability factor, A_0 is the area of the orifice, A_s is the area of the cross-section of the cell, and α is the condensation coefficient, which is a characteristic of the particular compound.

For a cell of length equal to its diameter, which was the case for our cells, $W_c = 0.5$ [6]; so eqn. (3) can be written as

$$p_{eq} = p_k(1 + W_0 A_0/\alpha A_s) \tag{4}$$

By applying eqn. (4) it is possible to calculate the values of p_{eq} for different orifices and similar experimental conditions: a plot of p_k vs. $(p_k W_0 A_0)$ should give a straight line with p_{eq} as the intercept. The value of the condensation coefficient α can also be calculated, from the slope of the straight line. Using three different orifices in each experiment, p_{eq} and α were calculated by this method, but, as has also been reported elsewhere [6], accurate values of α or p_{eq} were not obtained. When α is close to unity, the differences between the measured p_k values obtained for different effusion holes are much smaller than the associated experimental errors, provided the holes do not vary greatly in size. On the other hand, the use of holes of similar sizes is convenient, because, as Winterbottom and Hirth have reported [7], the surface diffusion increases as the radius of the hole decreases, and also because the possibility of kinetic diminution of the vapour pressure in the neighbourhood of the hole will increase with its radius. Other factors may also cause considerable error in the measured vapour pressures. Thus, for example, the existence of small leaks in the cell is very inconvenient if the effusion hole has a small size, since the calculated vapour pressure will be considerably higher than the true value; on the other hand, very large holes can yield considerably lower values for the vapour pressures, owing to self-cooling of the sample.

In the case of a small condensation coefficient these effects can be enhanced, resulting in an even smaller calculated coefficient, together with a larger calculated equilibrium vapour pressure. This seems to be the case for our experimental results for ferrocene, as will be discussed below.

To calculate the sublimation enthalpy, the experimental results are fitted to the integrated Clausius–Clapeyron equation

$$\ln p = -\frac{\Delta_{cr}^{g} H_T^{\ominus}}{RT} + C \tag{5}$$

The slope of the straight line obtained by plotting $\ln p$ vs. $1/T$ is $-\Delta_{cr}^{g} H_T^{\ominus}/R$. The enthalpy of sublimation calculated by this method is referred to the mean temperature T of the experimental temperature range of the different experiments. The values obtained in this way were corrected to 298.15 K using

$$\Delta_{cr}^{g} H_{298.15}^{\ominus} = \Delta_{cr}^{g} H_T^{\ominus} + \int_T^{298.15} \Delta_{cr}^{g} c_p^{\ominus} \, dT \tag{6}$$

For benzoic acid we used the data of Furukawa et al. [8] and Stull et al. [9] for the solid and the vapour, respectively, to obtain

$$\Delta_{cr}^{g} c_p^{\ominus} = (-0.1211\, T - 7.248) \text{ J K}^{-1} \text{ mol}^{-1} \tag{7a}$$

TABLE 1

Areas and Clausing factors of the cell effusion holes

	Hole number					
	1	2	3	4	5	6
Area (mm^2)	0.841	1.04	1.16	0.754	0.813	0.862
W_0	0.966	0.969	0.971	0.964	0.965	0.966

For ferrocene we used the data of Jans and Gjaldbek [10] and Lippincott and Nelson [11] for the solid and the vapour, respectively, to obtain

$$\Delta_{\mathrm{cr}}^{\mathrm{g}} c_p^{\ominus} = (-0.1592\ T + 13.99)\ \mathrm{J\ K^{-1}\ mol^{-1}} \tag{7b}$$

RESULTS AND DISCUSSION

Vapour pressure measurements for benzoic acid were made between 307.150 and 314.150 K, using holes designated 1, 2 and 3; for ferrocene the measurements were made between 298.270 and 300.010 K, using holes

TABLE 2

Experimental results for benzoic acid

Exp.	T (K)	t (s)	Sublimed mass (mg)			Vapour pressure, p_k (Pa)		
			m_1	m_2	m_3	p_1	p_2	p_3
8	307.150	18300	12.84	16.88	18.48	0.3131	0.3318	0.3250
9	307.150	16200	11.82	14.72	16.01	0.3255	0.3268	0.3180
10	307.150	16200			16.21			0.3220
15	308.150	18000	14.18	18.10	19.72	0.3521	0.3623	0.3531
16	308.150	21480	17.40	21.59		0.3620	0.3621	
17	309.150	19800	17.93	21.95	24.72	0.4054	0.4000	0.4031
18	309.150	18180	16.21	20.16	22.07	0.3991	0.4002	0.3919
6	310.155	19680	19.68	24.95	27.03	0.4484	0.4582	0.4442
7	310.155	18000	18.08	22.87	25.24	0.4503	0.4592	0.4535
1	311.164	24480	27.40			0.5027		
2	311.164	14687	16.51		23.18	0.5048		0.5112
3	311.164	27000	30.62			0.5093		
4	311.164	18000		25.30	28.26		0.5089	0.5085
5	311.164	19800		28.02			0.5123	
19	312.150	19680	24.21	30.39	33.16	0.5533	0.5599	0.5466
20	312.150	19200	23.37	28.99	31.84	0.5475	0.5475	0.5380
13	313.150	16080	22.80	28.42	31.31	0.6388	0.6419	0.6327
14	313.150	17460	24.61	30.80	33.92	0.6350	0.6407	0.6313
11	314.150	18420	28.52	35.13	38.35	0.6987	0.6938	0.6776
12	314.150	15480	23.89	30.41	32.63	0.6964	0.7146	0.6860

TABLE 3

Experimental results for ferrocene

Exp.	T (K)	t (s)	Sublimed mass (mg)			Vapour pressure, p_k (Pa)		
			m_4	m_5	m_6	p_4	p_5	p_6
5	292.270	13500	20.55	21.35	22.67	0.5999	0.5774	0.5776
6	292.270	14940	22.26	23.16	24.22	0.5872	0.5660	0.5577
9	294.078	13620	24.81	25.61	27.20	0.7201	0.6887	0.6892
10	294.078	14040	25.29	26.63	27.87	0.7122	0.6947	0.6850
15	295.145	14280	28.68	30.33	31.68	0.7954	0.7794	0.7670
16	295.145	14640	29.65	31.24	33.25	0.8021	0.7830	0.7852
17	296.570	15720	36.07	38.67	40.37	0.9110	0.9048	0.8900
18	296.570	12000	27.22	28.55	30.27	0.9006	0.8752	0.8743
7	297.080	15600	38.06	39.61	40.75	0.9694	0.9347	0.9060
8	297.080	12600	30.48	31.69	32.65	0.9612	0.9259	0.8988
1	298.202	14400	37.67	40.25		1.042	1.031	
2	298.202	18120	46.96	51.09		1.032	1.040	
3	298.202	12300			36.72			1.037
4	298.202	11700			35.38			1.051
13	299.117	12600	36.36	38.48	39.26	1.151	1.128	1.084
14	299.117	13200	38.48	41.55	41.81	1.162	1.163	1.103
11	300.010	12840	41.63	44.28	46.03	1.294	1.275	1.249
12	300.010	11400	37.40	39.35	40.96	1.310	1.277	1.252

designated 4, 5 and 6. The thickness of each hole was 0.049 mm, and their areas and corresponding Clausing factors W_0 are given in Table 1.

The experimental results for benzoic acid and ferrocene are listed in Tables 2 and 3, respectively, and from these data were obtained plots of $\ln p = f(1/T)$ for each hole and also for the global treatment of all the experimental data with the three orifices (Figs. 5 and 6). Fitting of the experimental data from Tables 2 and 3 to the Clausius–Clapeyron equation was done using a least-squares computer program. The results obtained (individual holes and global treatment) for benzoic acid and ferrocene are listed in Tables 4 and 5, respectively. These tables also include calculated values for the enthalpies of sublimation under the different experimental conditions used. The standard deviations associated with the values of the sublimation enthalpies were derived from the least-squares computer treatment for the calculation of the slope of $\ln p = f(1/T)$.

In the case of ferrocene, from the plots of p_k vs. $(p_k W_0 A_0)$ for the different experimental temperatures, a value of 1.42 Pa is calculated for the equilibrium vapour pressure p_{eq} at 298.15 K, and a mean value of 7×10^{-3} for the condensation coefficient α. Looking at values from the literature for vapour pressure at 298.15 K (Table 7), one can see that these are smaller than the calculated values for the equilibrium pressure, and that the mean of the literature values (excluding those of refs. 30 and 34, and the second value

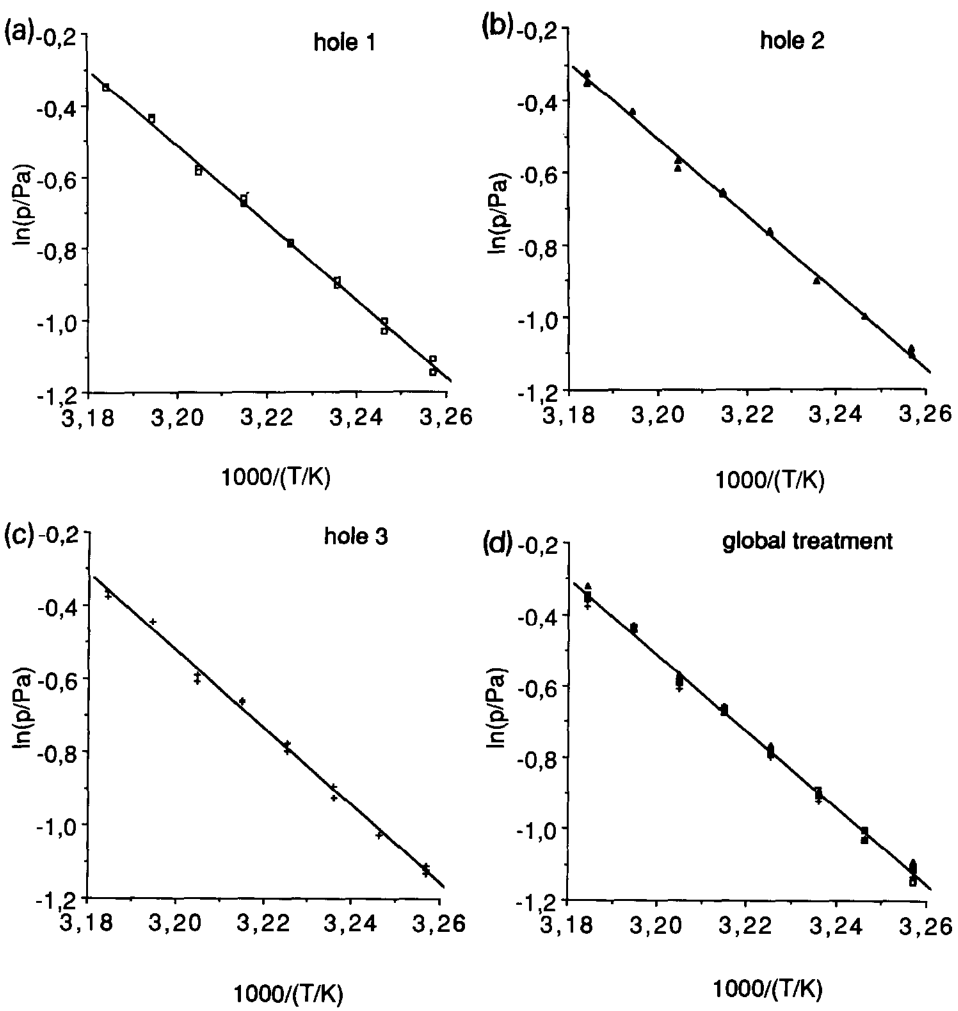

Fig. 5. Plots of ln $p = f(1/T)$ for benzoic acid.

of ref. 28, which seem to low) is about 1.02 Pa, which is very close to our mean p_k value of 1.04 Pa. The value 1.16 Pa [32] obtained by a static measurement also confirms our assumptions that the values of p_{eq} calculated from the plots for ferrocene are greater than the real equilibrium values. This is probably due to diffusion processes inside the effusion cells, leading to an apparent condensation coefficient smaller than the real one. In the subsequent calculations, we assume that the mean of our measured p_k values is close to the equilibrium vapour pressure.

For benzoic acid, our results show no clear tendency of variation of p_k values with the size of the effusion holes, which might mean that the difference among the measured p_k values is masked by experimental error; this is in agreement with the situation in which the condensation coefficient

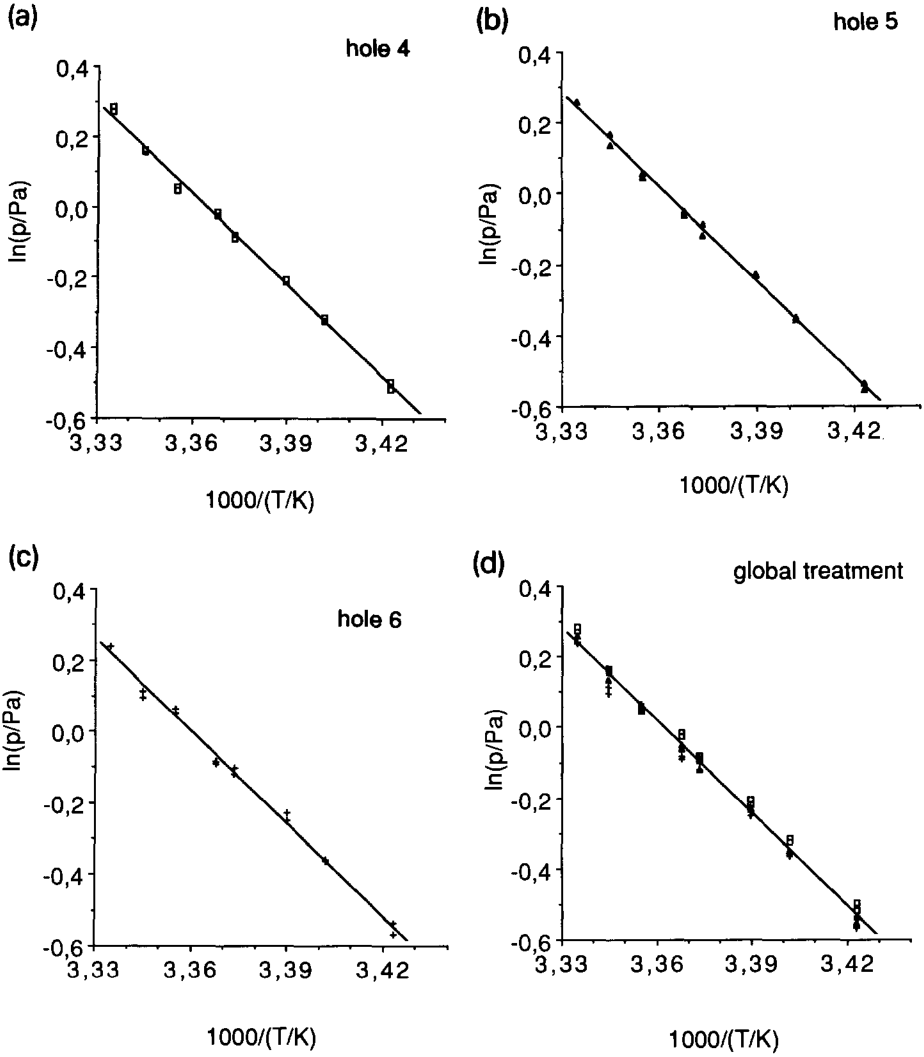

Fig. 6. Plots of ln $p = f(1/T)$ for ferrocene.

TABLE 4

Parameters of the equation $[\ln(p/\mathrm{Pa}) = a - b/(T/\mathrm{K})]$ for benzoic acid

	a	b	Correlation coefficient	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H^{\ominus}_{310.65}$ (kJ mol^{-1})
Hole 1	34.1114 ± 0.4654	10828.0 ± 144.6	0.9986	90.02 ± 1.20
Hole 2	33.4959 ± 0.5308	10633.3 ± 164.8	0.9983	88.41 ± 1.37
Hole 3	33.1972 ± 0.5943	10545.9 ± 184.6	0.9978	87.68 ± 1.53
Global treatment	33.6009 ± 0.3297	10668.9 ± 102.4	0.9978	88.70 ± 0.85

TABLE 5

Parameters of the equation $[\ln(p/\mathrm{Pa}) = a - b/(T/\mathrm{K})]$ for ferrocene

	a	b	Correlation coefficient	$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{296.14}^{\ominus}$ (kJ mol^{-1})
Hole 4	28.9211 ± 0.5132	8604.7 ± 152.2	0.9978	71.54 ± 1.27
Hole 5	29.9008 ± 0.4229	8901.9 ± 125.4	0.9986	74.01 ± 1.04
Hole 6	29.0619 ± 0.6201	8657.6 ± 183.9	0.9968	71.98 ± 1.53
Global treatment	29.2946 ± 0.3687	8721.4 ± 109.4	0.9964	72.51 ± 0.91
Calculation for $P = P_{\mathrm{eq}}$	27.9820 ± 0.3460	8238.7 ± 102.6	0.9995	68.50 ± 0.85

is close to unity, and so the measured vapour pressure values p_k are equal, within experimental error, to the equilibrium vapour pressure p_{eq}.

For both benzoic acid and ferrocene, values of the enthalpies of sublimation were calculated considering the results of each cell, and also by an overall treatment of the experimental results obtained with the three cells. These results are reported in Tables 4 and 5, for benzoic acid and ferrocene, respectively. The enthalpy of sublimation is taken, in both cases, as the value calculated by the overall treatment of the experimental results of the three cells.

Tables 6 and 7 show values published in the last three decades for the standard molar enthalpies of sublimation and vapour pressure, at 298.15 K, of benzoic acid and ferrocene, respectively. In cases where the enthalpy of sublimation at 298.15 K was not reported, its value has been calculated by the present authors, using eqn. (6). The vapour pressures at 298.15 K were calculated using the variously reported vapour pressure equations when the experimental temperature ranges included that temperature. For extrapolations, the Clarke and Glew equation [12] was used:

$$R \ln(p/p^{\ominus}) = -\Delta_{\mathrm{cr}}^{\mathrm{g}} \Delta G_{\theta}^{\ominus}/\theta + \Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\theta}^{\ominus}(1/\theta - 1/T) + \Delta_{\mathrm{cr}}^{\mathrm{g}} c_p^{\ominus}\{(\theta/T) - 1 + \ln(T/\theta)\} \qquad (8)$$

where $p^{\ominus}$ is a standard reference pressure of 1 Pa, and θ is a reference temperature. For $\Delta_{\mathrm{cr}}^{\mathrm{g}} c_p^{\ominus}$ we used the values reported above.

For benzoic acid, the standard molar enthalpy of sublimation at 298.15 K determined in the present work (89.25 ± 0.85 kJ mol^{-1}) agrees, within experimental error, with the value of 89.7 ± 0.5 kJ mol^{-1} recommended by Cox [20] in 1974. It also agrees with the mean of the literature values (excluding that of ref. 16), 89.98 kJ mol^{-1}, and also with the results reported by Murata et al. [24], who state that the correct value lies between 89.3 ± 0.3 and 88.9 ± 0.3 kJ mol^{-1}, considering that the degree of dissociation of the dimer species at 298.15 K can be between 0.997 and 1.000, respectively. The value of the vapour pressure at 298.15 K also agrees, within experimental

TABLE 6

Enthalpies of sublimation and vapour pressures at 298.15 K of benzoic acid

Ref.	Year	Investigators	Method	Temp. range (K)	T (K)	$\Delta_{cr}^{g} H_T^{\ominus}$ (kJ mol^{-1})	$\Delta_{cr}^{g} H_{298.15}^{\ominus}$ (kJ mol^{-1})	Vapour pressure at 298.15 K (Pa)
13	1965	Davies and Kybett	Mass loss effusion [a]	291–307	299	90.9	90.9	0.094
14	1969	Chastel et al.	Calvet microcalorimetry		298	89.7 ±0.6	89.7 ±0.6	
15	1971	Ashcroft	Thermogravimetry	299–329	314	89.1	89.8 [b]	
16	1971	Beech and Lintonbon	D.S. calorimetry	420–480		100 ±5		
17	1972	Morawetz	Triplet calorimetry		298	89.50±0.17	89.50±0.17	
18	1973	Malaspina et al.	Calvet microcalorimetry	338–383	360	86.0 ±0.3	88.9 ±0.3 [b]	
			Mass loss effusion	338–383	360	86.2 ±0.3	89.1 ±0.3 [b]	0.143
19	1973	de Kruif and Oonk	Thermal conductivity manometry	297–311	304	88.1 ±0.2	88.4 ±0.2 [b]	
20	1974	Cox	RECOMMENDED VALUE				89.7 ±0.5	
21	1975	Van Ginkel et al.	Mass loss effusion	294–331	312.6	92.5 ±0.4	93.2 ±0.4 [b]	0.104
22	1975	de Kruif et al.	Torsion effusion	293–318	306	88.5 ±2	88.3 ±2 [b]	
23	1980	de Kruif	Torsion mass loss effusion	296–317	308	90.0 ±1	90.4 ±1 [b]	
24	1982	Murata et al.	Calvet microcalorimetry	320–370			(88.9–89.3)±0.3	
25	1982	Colomina et al.	Mass loss effusion	293–313	303.4	90.35±0.13	90.6 ±0.2	0.110
26	1982	de Kruif and Blok	Diaphragm manometry	316–391	353.2	89.45±0.05	92.11±0.25	0.105
27	1988	Torres-Gómez et al.	D.S. calorimetry		335	87.45±0.34	89.23±0.95	
	1990	Present work	Mass loss effusion	307–314	310.6	88.70±0.85	89.25±0.85	0.113

[a] Hiby and Pahl factor [35].

[b] Calculated in the present work from $\Delta_{cr}^{g} H_T^{\ominus}$, using eqn. (6).

TABLE 7

Enthalpies of sublimation and vapour pressures at 298.15 K of ferrocene

Ref.	Year	Investigators	Method	Temp. range (K)	T (K)	$\Delta_{cr}^{g} H_T^{\ominus}$ (kJ mol^{-1})	$\Delta_{cr}^{g} H_{298.15}^{\ominus}$ (kJ mol^{-1})	Vapour pressure at 298.15 K (Pa)
28	1962	Edwards and Kington	Mass loss effusion	295 –303	299.3	76.59	76.57 ± 0.13	0.963
			Mass loss effusion [a]	295 –303	299.3	73.32	73.35 ± 0.42	0.910
			Thermal conductivity Manometry	295 –302	298.5	72.38 ± 1.26	72.38 ± 1.26	
29	1969	Andrews and Westrum	Mass loss effusion	293 –306	299.2	72.67	72.73 ± 0.54	0.965
30	1980	Calado et al.	Mass loss effusion [a]	297.5–303	299.6	72.60 ± 1.36	72.60 ± 1.36 [b]	0.907
31	1981	Pelino et al.	Torsion effusion	288 –353	320.5	72.84 ± 0.88	74.0 ± 2.0	1.04
32	1983	de Kruif et al.	Torsion effusion	277 –297	289.4	75.90 ± 0.69	75.61 ± 0.69 [b]	1.01
			Mass loss effusion	277 –297	289.5	73.39 ± 0.12	73.10 ± 0.12 [b]	0.970
			Diaphragm manometry	329.5–360	346.6	70.45 ± 0.23	72.26 ± 0.23 [b]	1.16
33	1988	Torres-Gómez et al.	Mass loss effusion	278 –309	293.6	72.07 ± 0.36	71.92 ± 0.36 [b]	1.04
34	1989	Minas da Piedade	Mass loss effusion [a]	294 –302	298.1	70.3 ± 1.0	70.3 ± 1.0	0.858
	1990	Present work	Mass loss effusion	292 –300	296.1	72.51 ± 1.00	72.39 ± 1.00	1.04

[a] Hiby and Pahl factor [35].

[b] Calculated in the present work from $\Delta_{cr}^{g} H_T^{\ominus}$, using eqn. (6).

error, with the literature values (excluding the high value by Malaspina et al. [18]).

For ferrocene, the standard molar enthalpy of sublimation at 298.15 K determined in the present work (72.39 ± 1.00 kJ mol^{-1}) also agrees with the mean of the literature values, 72.48 kJ mol^{-1} (when we exclude the first values of refs. 28 and 32, which seem rather high when compared with the other values reported by those authors).

The results obtained in the present test of the new Knudsen effusion apparatus with compounds as different as benzoic acid (the classical standard) and ferrocene (a standard more appropriate for the study of organometallic compounds) give us confidence in this apparatus, which has the considerable advantage of enabling the simultaneous operation of three different effusion cells, thus reducing the long time otherwise required for such studies.

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