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Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

VAPOR PRESSURE DETERMINATION BY PRESSURE DSC

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Abstract

A new pressure DSC module (Mettler DSC27HP) and its abilities for vapor pressure determination in the range of subambient pressure to 7 MPa are presented. To compare the new to an established method, vapor pressures of caffeine, naphthalene and *o*-phenacetin have been determined both by pressure DSC and the Knudsen effusion cell method. These results, including the derived heats of evaporation and heats of sublimation, are compared to literature values.

Keywords: Knudsen effusion method, pressure DSC, steel ball method, vapor pressure determination

Introduction

The knowledge of exact vapor pressure data of a substance is of great importance for applications and manufacturing conditions [1–8]. From this data various parameters like heat of vaporization, rate of loss through vaporization during a process or behavior in heterogeneous reactions can be derived. This knowledge is of special interest with regard to process conditions and safety aspects. For this reason the demand for vapor pressure data is huge and a method to determine accurate vapor pressure data in short time is required. The Knudsen effusion method is the most extensively used method for vapor pressures below 100 Pa. The determination of exact vapor pressure data with this method is based on the mass loss of a sample at a constant temperature. It takes as much as a week for one substance to determine vapor pressure [9–11]. Another method that has been applied to determine vapor pressures is the steel ball method [12]. It is performed in a thermogravimetry set-up. An aluminum crucible closed with a steel ball forms a valve which opens when the inside pressure is higher than the outside pressure plus the pressure due to the mass of the ball [12]. With the new pressure DSC module [13, 14] the time for this procedure is much shorter, goes into a new

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pressure range and needs smaller samples. It uses the different boiling points at different pressures to determine vapor pressure. The three different methods are summarized in Table 1. However, only the Knudsen effusion and the pressure DSC method have been used in this work.

Table 1 Comparison of the different methods

	Knudsen effusion	steel ball valve	pressure DSC
Pressure range/Pa	$1\cdot10^{-3}$ to $1\cdot10^{-2}$	1 to $1\cdot10^{2}$	$0.1\cdot10^{6}$ to $7\cdot10^{6}$
Temperature range/K	200 to 2700	250 to 1100	300 to 1000

Experimental

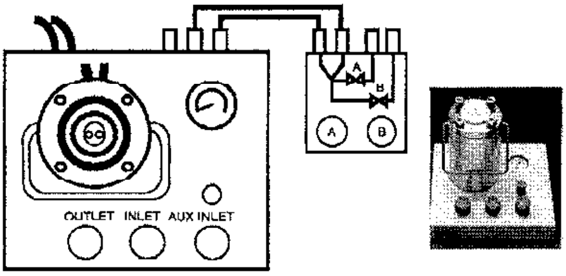
Materials

The origins and commercial purities of the samples are as follows: The caffeine sample was obtained from the United States Pharmacopeia USP as a melting point reference standard. Both naphthalene and *o*-phenacetin (1-Acetyl-*o*-phenetidin) originate as high purity samples from Cammenga [15]. The benzoic acid was taken from the Mettler melting point standard calibration kit.

Instrumentation

A Mettler TA8000 system with a DSC27HP measuring cell (Fig.1a) and a Knudsen effusion cell on a Mettlet TA1 thermobalance [11] have been used. Figure 1a shows a schematic view of the pressure DSC module with all connections and the position of the measuring cell within the pressure cylinder. The concentric circles symbolize the safety confinement, the pressure cylinder, silver oven and the measuring disk with the sample and reference position. The gas distributing box on the righthand side of Fig. 1a, is connected to the gas cylinder and facilitates fast filling and the connection of a precision pressure gauge. The height and width of the pressure DSC module (Fig. 1b) are about 32 cm requiring only little desk space.

The pressure DSC module measures thermal effects from room temperature to 900 K in variable gas atmospheres from ambient pressure up to 7 MPa. Subambient pressure measurements may be carried out as well, but need special instrumentation to control the pressure in the measuring cell. Gases like nitrogen, oxygen and carbon dioxide can be used to pressurize the measuring cell. Investigations of reactions with flammable, reactive or toxic gases as purge gas are carried out with controlled mass flow through an auxiliary inlet leading the purge gas near the sample. Thus a wide range of solid–gas or liquid–gas reactions could be investigated in addition to the vapor pressure measurements.



(a) (b)

Fig. 1 Top view (a) and picture (b) of the DSC27HP

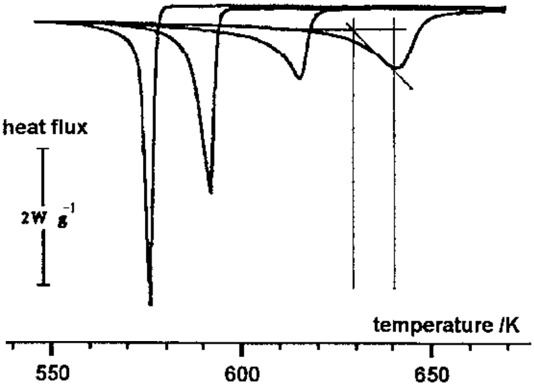


Fig. 2 Set-up for vapor pressure determination

The Mettler DSC27HP has different modes of operation. Figure 2 shows a scheme of the set-up applied for vapor pressure measurements. In the chosen set-up the pressure in the DSC cell is controlled by a precision gauge at the outlet of the instrument. A mass flow controller accurately monitors the purge gas flow, which was set to 50 ml min^{-1}.

Calculations

For the calculations of the heats of vaporization the Clausius–Clapeyron equation (Eq. 1) was applied, using the preset pressure and the temperature of maximum vaporization as parameters.

$$\log(p/\mathrm{Pa}) = -\frac{A}{TK} + B \qquad (1)$$

The peak temperature corresponds to the end of the vaporization of the material. Due to the fact that a one component system has a fixed temperature during

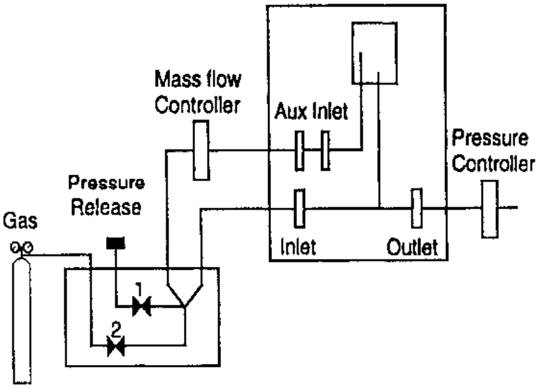


Fig. 3 DSC curves of *o*-phenacetin at 0.12, 0.15, 0.25 and 0.40 MPa nitrogen pressure

the vaporation process for a fixed pressure, this temperature can be used in the Clausius-Clapeyron equation. In Fig. 3 the original experimental data of *o*-phenacetin is shown as an example. The pressures are 0.12, 0.15, 0.25 and 0.40 MPa. The equilibrium vapor pressures in Knudsen effusion experiments were calculated according to the ideal Knudsen equation which is described in detail in the literature [1] .

Results and discussion

The heat of sublimation for caffeine (Fig. 4) above the solid-solid transition at 414 K was determined to be 112.55±2.24 kJ mol^{-1} (0.0005 to 0.1 Pa). The heat of sublimation is in good agreement with the literature value of Bothe and Cammenga [4, 5] who reported a value of 110.68±0.67 kJ mol^{-1} (0.03 to 0.33 Pa). The

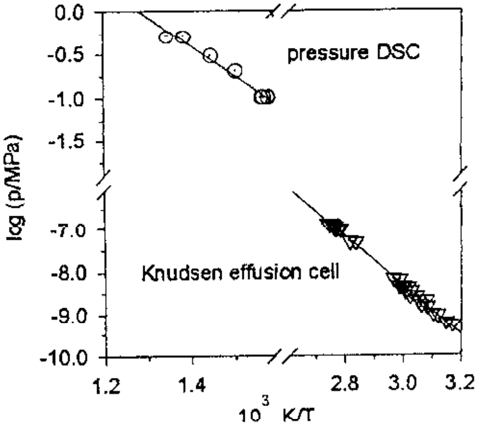


Fig. 4 Vapor pressure of solid and liquid caffeine. O – measured by pressure DSC; Δ – measured by Knudsen effusion cell

heat of vaporization by pressure DSC, determined as 64.90±2.85 kJ mol^{-1}, on the other hand, deviates significantly from the value of 75.01±0.71 kJ mol^{-1}, given by the same authors.

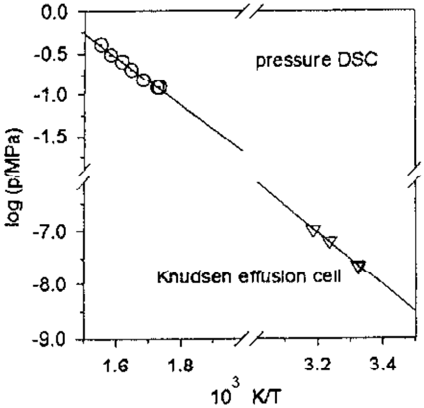


Fig. 5 Vapor pressure of solid and liquid *ortho*-phenacetin. O – measured by pressure DSC; ∇ – measured by Knudsen effusion cell

Ortho-phenacetin (Fig. 5) was measured as an example of a substance of pharmacologically active substance. The calculated heat of vaporization is 55.00±0.96 kJ mol^{-1} (0.12 to 0.40 MPa) and the heat of sublimation is 95.00±1.88 kJ mol^{-1}. Above 0.4 MPa and 470 K a competing reaction seems to occur.

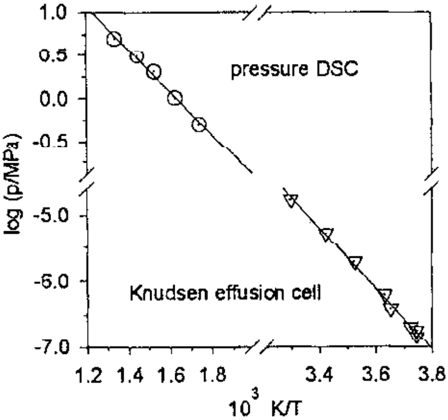


Fig. 6 Vapor pressure of liquid and solid naphthalene. O – measured by pressure DSC; ∇ – measured by Knudsen effusion cell

The measurements of naphthalene (Fig. 6) show good agreement with the values derived from data given in the literature [14]. The calculated heat of vaporization of 47.60±1.75 kJ mol^{-1} (0.1 to 5.0 MPa) is only slightly less than the literature value of 48.39 kJ mol^{-1} (350 Pa to 0.1 MPa). Sublimation with the Knudsen effusion cell leads to a value of 88.02±2.49 kJ mol^{-1} (0.14 to 17 Pa) for the heat of sublimation. Sabbah *et al.* [15] on the other hand determined a value of 69 to 72 kJ mol^{-1} depending on the rate of effusion. The much higher effusion rates in our measurements might be the reason for the differences. Benzoic acid was used to calibrate the orifice of the Knudsen effusion cell and measured in the pressure DSC.

Conclusions

The DSC27HP pressure cell proved to be a suitable instrument for vapor pressure determination of liquids in the range of ambient pressure to 7 MPa. The precision of the method is in the order of 2 to 4%, which is sufircient for many applications. Because there is no need for large amounts of material it is possible to obtain vapor pressure data in an early stage of developing new chemicals. This is of main interest in the evaluation of chemicals intended to be released into the environment, e.g. agro chemicals.

Appendix

Table 1 Caffeine Knudsen effusion cell experimental values

T/K	Mass loss rate/g s^{-1}	*p*/Pa	10^3 K/*T*
315.24	$1.472\cdot10^{-9}$	$5.459\cdot10^{-4}$	3.172
317.25	$1.694\cdot10^{-9}$	$6.304\cdot10^{-4}$	3.152
317.72	$1.658\cdot10^{-9}$	$6.174\cdot10^{-4}$	3.147
317.72	$1.667\cdot10^{-9}$	$6.205\cdot10^{-4}$	3.147
320.27	$2.583\cdot10^{-9}$	$9.655\cdot10^{-4}$	3.122
322.25	$2.754\cdot10^{-9}$	1.033·10–3	3.103
322.25	$2.750\cdot10^{-9}$	$1.031\cdot10^{-3}$	3.103
324.21	$3.944\cdot10^{-9}$	$1.483\cdot10^{-3}$	3.084
324.56	$5.611\cdot10^{-9}$	2.111·10–3	3.081
326.45	$4.299\cdot10^{-9}$	$1.622\cdot10^{-3}$	3.063
326.45	$4.306\cdot10^{-9}$	1.625·10–3	3.063
327.55	$5.410\cdot10^{-9}$	2.045·10–3	3.053
327.55	$5.417\cdot10^{-9}$	2.048·10–3	3.053
328.18	$7.028\cdot10^{-9}$	2.659·10–3	3.047
330.27	$8.861\cdot10^{-9}$	3.363·10–3	3.028
330.45	$7.002\cdot10^{-9}$	$2.659\cdot10^{-3}$	3.026
330.45	$7.000\cdot10^{-9}$	$2.658\cdot10^{-3}$	3.026
331.33	$1.131\cdot10^{-8}$	$4.298\cdot10^{-3}$	3.018

Table 1 Continued

T/K	Mass loss rate/g s^{-1}	p/Pa	10^3 K/T
332.25	$8.763\cdot10^{-9}$	$3.336\cdot10^{-3}$	3.010
332.35	$8.750\cdot10^{-9}$	$3.332\cdot10^{-3}$	3.009
332. 70	$1.189\cdot10^{-8}$	$4.529\cdot10^{-3}$	3.006
333 .75	$1.124\cdot10^{-8}$	$4.290\cdot10^{-3}$	2.996
333.75	$1.133\cdot10^{-8}$	$4.324\cdot10^{-3}$	2.996
334.51	$1.647\cdot10^{-8}$	$6.292\cdot10^{-3}$	2.989
334.65	$1.169\cdot10^{-8}$	$4.466\cdot10^{-3}$	2.988
334.65	$1.178\cdot10^{-8}$	$4.500\cdot10^{-3}$	2.988
337.05	$1.735\cdot10^{-8}$	$6.652\cdot10^{-3}$	2.967
337.05	$1.736\cdot10^{-8}$	$6.657\cdot10^{-3}$	2.967
352.27	$1.204\cdot10^{-7}$	$4.718\cdot10^{-2}$	2.839
354.85	$1.207\cdot10^{-7}$	$4.748\cdot10^{-2}$	2.818
359.26	$2.469\cdot10^{-7}$	$9.771\cdot10^{-2}$	2.783
359.26	$2.339\cdot10^{-7}$	$9.258\cdot10^{-2}$	2.783
359.54	$2.492\cdot10^{-7}$	$9.867\cdot10^{-2}$	2.781
360.95	$2.477\cdot10^{-7}$	$9.829\cdot10^{-2}$	2.770
361.34	$2.777\cdot10^{-7}$	$1.102\cdot10^{-1}$	2.767
361.95	$2.484\cdot10^{-7}$	$9.871\cdot10^{-2}$	2.763
362.04	$3.012\cdot10^{-7}$	$1.197\cdot10^{-1}$	2.762
362.73	$3.208\cdot10^{-7}$	$1.276\cdot10^{-1}$	2.757
362.73	$3.219\cdot10^{-7}$	$1.280\cdot10^{-1}$	2.757
363.29	$3.405\cdot10^{-7}$	$1.355\cdot10^{-1}$	2.753
364.15	$3.018\cdot10^{-7}$	$1.203\cdot10^{-1}$	2.746
364.75	$3.395\cdot10^{-7}$	$1.354\cdot10^{-1}$	2.742

Table 2 Caffeine pressure DSC experimental values

T/K	p/MPa	10^3 K/T
634.05	0.10	1.577
638.25	0.10	1.567
640.45	0.10	1.561
665.35	0.20	1.503
691.25	0.30	1.447
743.15	0.50	1.346
722.45	0.50	1.384

Table 3 *Ortho*-phenacetin Knudsen effusion cell experimental values

T/K	Mass loss rate/g s^{-1}	p/Pa	10^3 K/T
300.75	$2.229 \cdot 10^{-7}$	0.021	3.325
301.15	$2.448 \cdot 10^{-7}$	0.023	3.321
309.05	$6.661 \cdot 10^{-7}$	0.064	3.236
314.05	$1.086 \cdot 10^{-6}$	0.105	3.184

Table 4 *Ortho*-phenacetin pressure DSC experimental values

T/K	p/MPa	10^3 K/T
576.65	0.12	1.734
578.85	0.12	1.728
593.85	0.15	1.684
607.35	0.20	1.646
618.45	0.25	1.617
631.75	0.30	1.583
644.35	0.40	1.552

Table 5 Naphthalene Knudsen effusion cell experimental values

T/K	Mass loss rate/g s^{-1}	p/Pa	10^3 K/T
303.25	$3.790 \cdot 10^{-5}$	16.955	3.298
292.25	$1.220 \cdot 10^{-5}$	5.341	3.422
283.55	$4.380 \cdot 10^{-6}$	1.897	3.527
275.35	$1.430 \cdot 10^{-6}$	0.609	3.632
273.75	$3.590 \cdot 10^{-6}$	0.382	3.653
268.55	$4.960 \cdot 10^{-7}$	0.209	3.724
267.05	$1.360 \cdot 10^{-6}$	0.143	3.745
267.05	$4.290 \cdot 10^{-7}$	0.180	3.745

Table 6 Naphthalene pressure DSC experimental values

T/K	p/MPa	10^3 K/T
491.15	0.10	2.036
573.85	0.50	1.743
614.35	1.00	1.628
653.65	2.00	1.530
690.85	3.00	1.447
747.25	5.00	1.338

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