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APPLICATIONS OF THERMOGRAVIMETRY FOR VAPOR PRESSURE DETERMINATION

H. G. WIEDEMANN
Mettler Instrumente, A. G., Greifensee (Switzerland)

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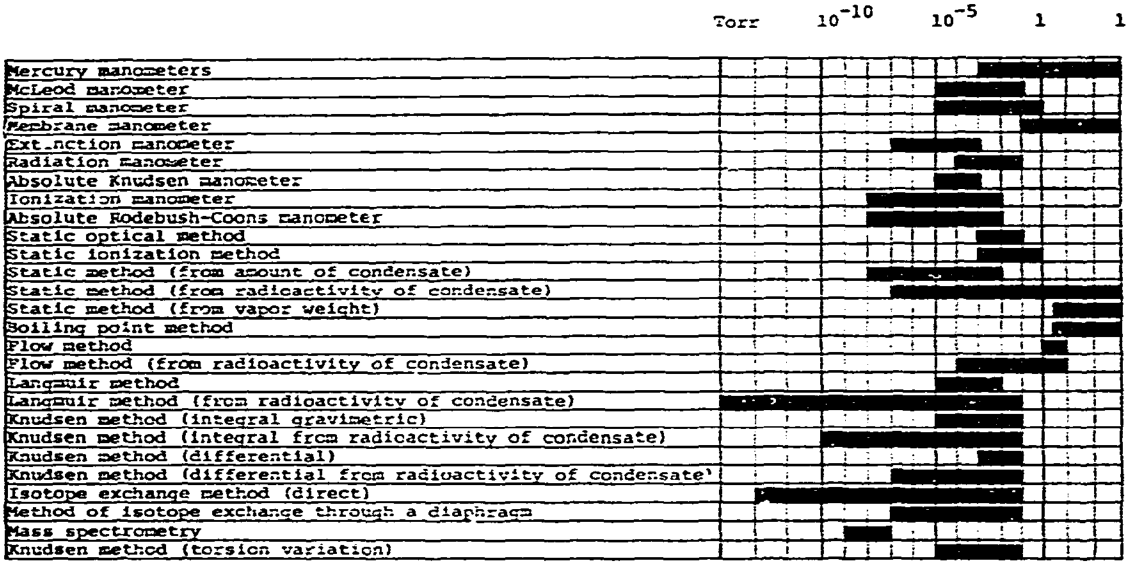
INTRODUCTION

Nesmeyanov[1] has reviewed some of the current methods for the determination of vapor pressures together with the pressure ranges over which these methods can be applied (Table I). One of these is the Knudsen effusion method[7,8], used for the measurement of low vapor pressures in the range from 10^0 to 10^{-5} torr, and involves measurement of the rate of loss of molecules of the evaporating substance leaving the opening of an effusion cell. A series of recent papers[10–12,18,19] describes the adaptation of this method to a thermobalance in which the normal TG sample holder is replaced by an effusion cell. This procedure allows measurement of the loss in weight of an evaporating substance due to the exit of its molecules through a calibrated orifice. Measurements are made under isothermal conditions, with weight loss being recorded as a function of time simultaneously with sample temperature, and with

TABLE I

MONOGRAM SHOWING THE SENSITIVITY OF THE VARIOUS METHODS FOR MEASURING VAPOR PRESSURE



pressure measured outside the effusion cell. Morawietz and Roeder[13] used this method for the determination of the vapor-phase of the potassium–mercury melt, and detected formation of intermetallic compounds of the HgK_3 type. Similarly, Hoenig *et al.*[15] have studied the evaporation of gadolinium carbide in the temperature range 1300–1800°C.

In the organic field, this same method was used successfully by Cordes *et al.*[10] for the vapor pressure measurement of such aromatic complexes as chromium-dibenzene and chromium-hexacarbonyl. The present work demonstrates the extent to which a vacuum thermobalance can be used for routine vapor pressure measurements of organic compounds.

APPARATUS

Measurements were made using the Mettler Thermoanalyzer. This apparatus has been described earlier[9] and, therefore, only special details relating to these measurements will be presented.

Fig. 1 shows schematically the most important components of the instrumentation. The thermobalance, D, is located in a tank thermostatically controlled at 25°C.

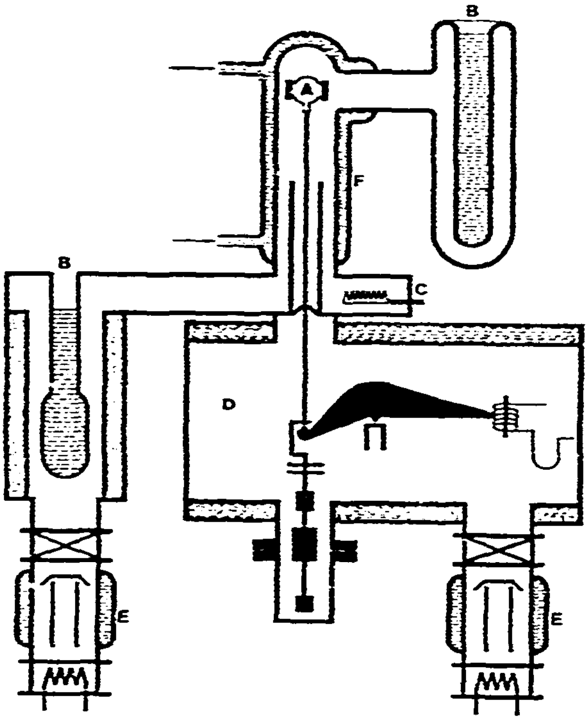


Fig. 1. Schematic drawing of experimental equipment. A, Knudsen cell; B, Cold trap; C, Ionization gauge; D, Balance and housing; E, Diffusion pumps; F, Thermostatically controlled reaction chamber.

The vacuum of 10^{-6} torr required for these measurements is obtained by a built-in system of which only the two diffusion pumps (E) are shown. Two different types of furnaces were used for these measurements. The furnace, F, hooked on to the balance, consisted of a double-walled glass container through which liquids such as ethylene glycol, water and mixtures of glycerin and water could be cirulated from a thermostat, according to the temperature range desired (−20°C to +150°C). Cold trap, B, was filled with liquid nitrogen or other refrigerant. Molecules leaving the Knudsen cell, A, pass through the opening into the cold trap where the majority are condensed, thus avoiding any condensation on the rod supporting the Knudsen cell.

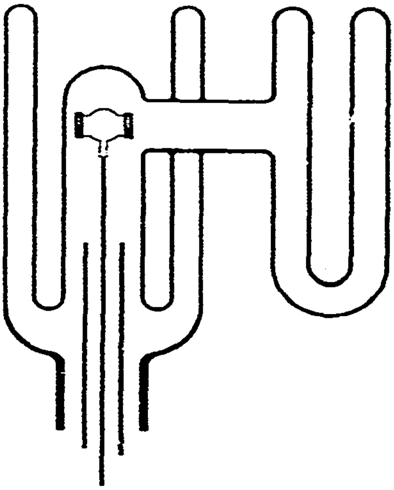


Fig. 2. Double cold trap for measurements with cooling baths from −20° to −90°C.

Fig. 2 shows another "furnace" used for measurements below −20°C. The Dewar flask housing the Knudsen cell was filled with different coolants, such as; carbon tetrachloride–solid carbon dioxide (−23°C), ethyl alcohol–solid carbon dioxide (−78°C), etc., while the cold trap was filled with liquid nitrogen. These coolant temperatures were reproducible to ±1°C. Ionization gauge, C, (see Fig. 1) controlled and recorded the pressure in the furnace compartment during the measurements.

Knudsen cell

Fig. 3 shows a photograph and a schematic cross-section of the Knudsen cell employed. The body, A, of this cell is made of aluminum. The lower part of the cell is fixed to a 4-hole alumina capillary tube connected to the balance. A copper–constantan thermocouple, E, brought into the cell through a vacuum-tight connection, directly measures either the temperature of the sample, F, or the temperature of the vapor phase just above the sample. A second thermocouple, D, (Pt–Pt/10% Rh) is located outside the cell and serves to control temperature in the furnace compart-

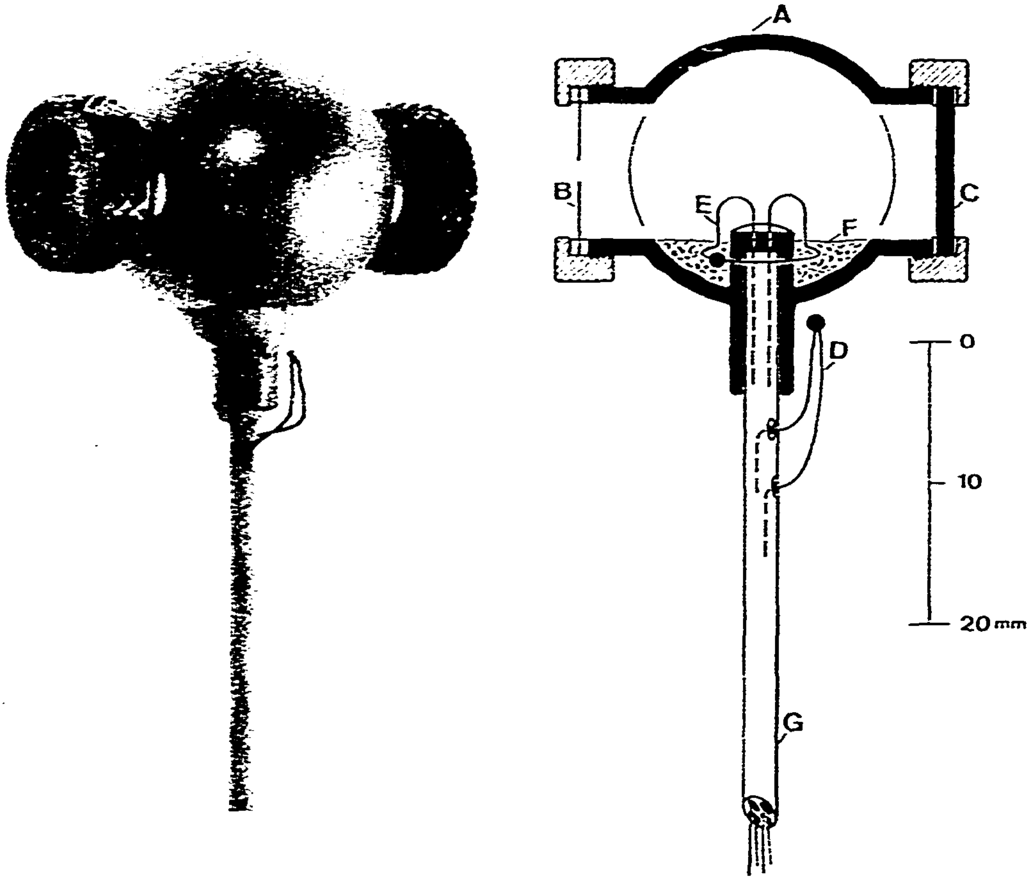


Fig. 3. The effusion cell.

ment. The orifice, B, is made of a 0.01 mm thick Cr–Ni foil into which a hole is punched. A screw cover pemits ready exchange of orifices with various hole diameters (1, 2 and 3 mm). A second opening was used for sample introduction and both screw covers sealed on Teflon rings. Sample volumes of ≤ 1.5 cm^3 can be studied at working temperatures from -100° to $+200\,^\circ$C.

For some measurements a Pyrex glass cell having a sphere diameter of approximately 15 mm was used. In this case the substance was introduced through the orifice and the copper–constantan thermocouple inserted through a vacuum-tight inlet at the bottom in order to measure the sample temperature.

CALCULATIONS

The Knudsen vapor pressure of four different organic compounds was studied: *p*-chlorophenyl-*N'*,*N'*-dimethyl urea (Monuron, a herbicide), *p*-phenacetin, anthracene and benzoic acid. Sublimation was studied in the temperature range of 250–400 °K, *i.e.* well below their respective melting points.

Equilibrium vapor pressures were calculated according to the ideal Knudsen Eqn. (1)

$$p = \frac{\Delta m}{\Delta t} \times \frac{1}{q} \sqrt{\frac{2\pi RT}{M}} \tag{1}$$

where p = vapor pressure in dyne cm^{-2} (1 dyne cm^{-2} = 0.750062 torr), $R = 8.314 \times 10^7$ erg $^\circ\text{C}^{-1}$ mole^{-1}, q = orifice area in cm^2, $\Delta m/\Delta t$ = rate of weight loss in g sec^{-1}, T = temperature in °K, and M = molecular weight of the specimen in g.

For each of three sets of data (anthracene, phenacetin, monuron) three separate curves were fitted:

$$\ln p = B + \frac{A_1}{T} \tag{2}$$

$$\ln p = B + \frac{A_1}{T} + A_2 \ln T \tag{3}$$

$$\ln p = B + \frac{A_1}{T} + A_2 \ln T + A_3 T \tag{4}$$

It was found in each case that Eqn. (2) gave a satisfactory fit to the data[3]. The standard errors of the estimated values of A and B were also calculated. The correlation coefficient, r (r^2 = the proportion of the variance of ln p accounted for by the fitted regression) was as follows for Eqn (2): for anthracene $r = 0.9988$, for phenacetin $r = 0.9995$, and for monuron $r = 0.9976$. When extra terms were included, no significant improvement in r was found so that Eqn. (2) was accepted as an appropriate fit to the data given in Table II and shown in Fig. 4.

Vapor pressure curves for small temperature ranges can thus be approximated using Eqn. (2); however for larger temperature ranges Eqn. (4) is used. The value of the product $4.574A$ corresponds directly to the heat of sublimation (ΔH_s) for measurements below the melting point, and to the heat of vaporization (ΔH_v) for measurements which have been made at temperatures above the melting point. If measurements are made over a narrow temperature range on both sides of the melting point, then since the temperature dependence of ΔH_s and ΔH_v can be neglected over small temperature ranges, $(\Delta H_s - \Delta H_v)$ corresponds to the heat of fusion, ΔH_f. Fig. 5 shows this method of obtaining ΔH_f using the experimental values of vapor pressure, for the case of benzoic acid.

EXPERIMENTAL

The mean value of the orifice diameter in the Knudsen cell was determined by use of a microscope with ocular micrometer and the corresponding area was calulated prior to making the effusion measurements.

The Knudsen cell made from aluminum was unsuitable for use with the halogenated organic compounds studied, since these appeared to decompose during the

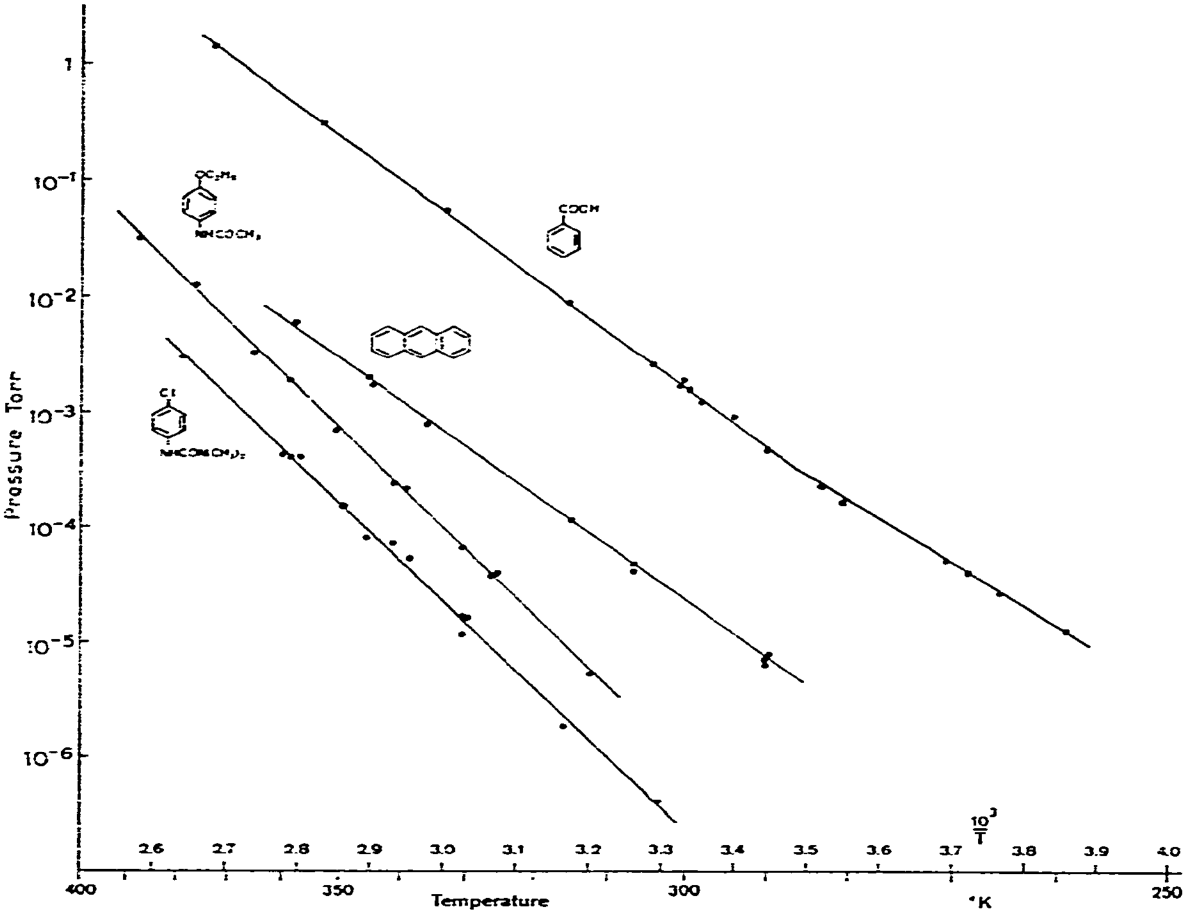


Fig. 4. Knudsen vapor pressure of different compounds at 250°–400°K. Monuron, *p*-phenacetin, anthracene, benzoic acid.

test. Therefore a Pyrex cell having the same features as the aluminum cell was used. Since, for mechanical stability, the glass cell could not be made with a wall thickness of 0.01 mm, the orifice area was determined by calibration against the known vapor pressure of benzoic acid[21,22]. From the rate of vaporization of benzoic acid at different temperatures the orifice area could be determined using Eqn. (5)

$$q = -\sqrt{\frac{2\pi RT}{M}} \times \frac{g}{p} = -K\sqrt{\frac{Tg}{p}} \tag{5}$$

where q = orifice area in cm^2, p = vapor pressure in torr, g = rate of weight loss in g sec^{-1}, and R, T and M have the usual meanings. This Eqn. can be simplified by combining several values into a constant, K. The mean value of the orifice area of the glass cell (Fig. 6) was found to be 1.93×10^{-2} cm^2 (Table III).

The wall thickness of the Pyrex cell and the form factor are automatically taken into account by determining the orifice area this way. Clausing has described investigations of this nature[16, 17]on a wide variety of materials. It is necessary that the

TABLE II

VAPOR PRESSURES OF THE MEASURED COMPOUNDS

Sample	*Temp.* (°*K*)	*Weight loss* (*g/sec*)	*Pressure* (*torr*)	log $p = B - A/T$
Monuron[4]	303.5	1.333×10^{-9}[a]	4.00×10^{-7}	$A = 5988.39 \pm 275.751$
Sandoz AG, Basel	316.0	5.972×10^{-9}[a]	1.83×10^{-6}	
MW = 198.6	329.8	5.741×10^{-9}	1.62×10^{-5}	
	330.6	3.667×10^{-8}	1.15×10^{-5}	$B = 13.3052$
	330.6	5.889×10^{-9}[a]	1.66×10^{-5}	
	338.8	1.857×10^{-8}	5.29×10^{-5}	$\Delta H_s = 27.4$ kcal mole^{-1}
	341.4	2.479×10^{-8}	7.09×10^{-5}	
	345.7	2.472×10^{-7}	7.91×10^{-5}	
	349.5	5.278×10^{-8}[a]	1.53×10^{-4}	
	357.0	1.222×10^{-6}	3.97×10^{-4}	
	358.7	1.233×10^{-6}[a]	4.02×10^{-4}	
	360.2	1.288×10^{-6}[a]	4.21×10^{-4}	
	379.1	9.914×10^{-7}	2.99×10^{-3}	
p-Phenacetin[20]	312.4	1.823×10^{-9}	5.25×10^{-6}	$A = 6036.09 \pm 142.466$
(*p*-Acetophenetidide)	325.4	1.333×10^{-8}	3.92×10^{-5}	
MW = 179.21	326.3	1.278×10^{-8}	3.76×10^{-5}	$B = 14.0852$
	330.7	2.190×10^{-8}	6.49×10^{-5}	
	339.3	7.014×10^{-8}	2.15×10^{-4}	$\Delta H_s = 27.6$ kcal mole^{-1}
	341.3	7.937×10^{-8}	2.39×10^{-4}	
	350.9	2.569×10^{-7}	7.85×10^{-4}	
	358.9	6.074×10^{-7}	1.88×10^{-3}	
	365.4	1.037×10^{-6}	3.23×10^{-3}	
	376.5	3.935×10^{-6}	1.25×10^{-2}	
	387.8	9.785×10^{-6}	3.14×10^{-2}	
Anthracene for scintillation[2]	290.1	2.778×10^{-9}	7.74×10^{-6}	$A = 4397.60 \pm 163.754$
Merck AG, Darmstadt	290.6	2.258×10^{-9}	6.29×10^{-6}	
MW = 178.24	290.6	2.529×10^{-9}	7.05×10^{-6}	$B = 10.0216$
	304.9	1.441×10^{-8}	4.11×10^{-5}	
	304.9	1.633×10^{-8}	4.66×10^{-5}	$\Delta H_s = 20.1$ kcal mole^{-1}
	304.9	1.667×10^{-8}	4.76×10^{-5}	
	315.1	3.944×10^{-8}	1.15×10^{-4}	
	336.2	2.571×10^{-7}	7.71×10^{-3}	
	344.8	6.050×10^{-7}	1.67×10^{-3}	
	345.5	6.444×10^{-7}	1.96×10^{-3}	
	358.0	1.911×10^{-6}	5.91×10^{-2}	
Benzoic acid[21,2,6]	290.4	1.24×10^{-7}	4.60×10^{-4}	$A = 4530.02 \pm 80.988$
B. D. H. Analar	294.4	2.25×10^{-7}	8.86×10^{-4}	
MW = 122.12	298.3	3.20×10^{-7}	1.20×10^{-3}	$B = 12.2937$
	299.8	3.89×10^{-7}	1.54×10^{-3}	
	300.5	4.59×10^{-7}	1.83×10^{-3}	$\Delta H_s = 20.7$ kcal mole^{-1}
	301.1	4.15×10^{-7}	1.65×10^{-3}	
	304.4	6.67×10^{-7}	2.53×10^{-3}	
	315.5	2.28×10^{-6}	8.80×10^{-3}	

[a] Orifice diameter 3 mm. For other measurements, orifice diameter 1 mm.

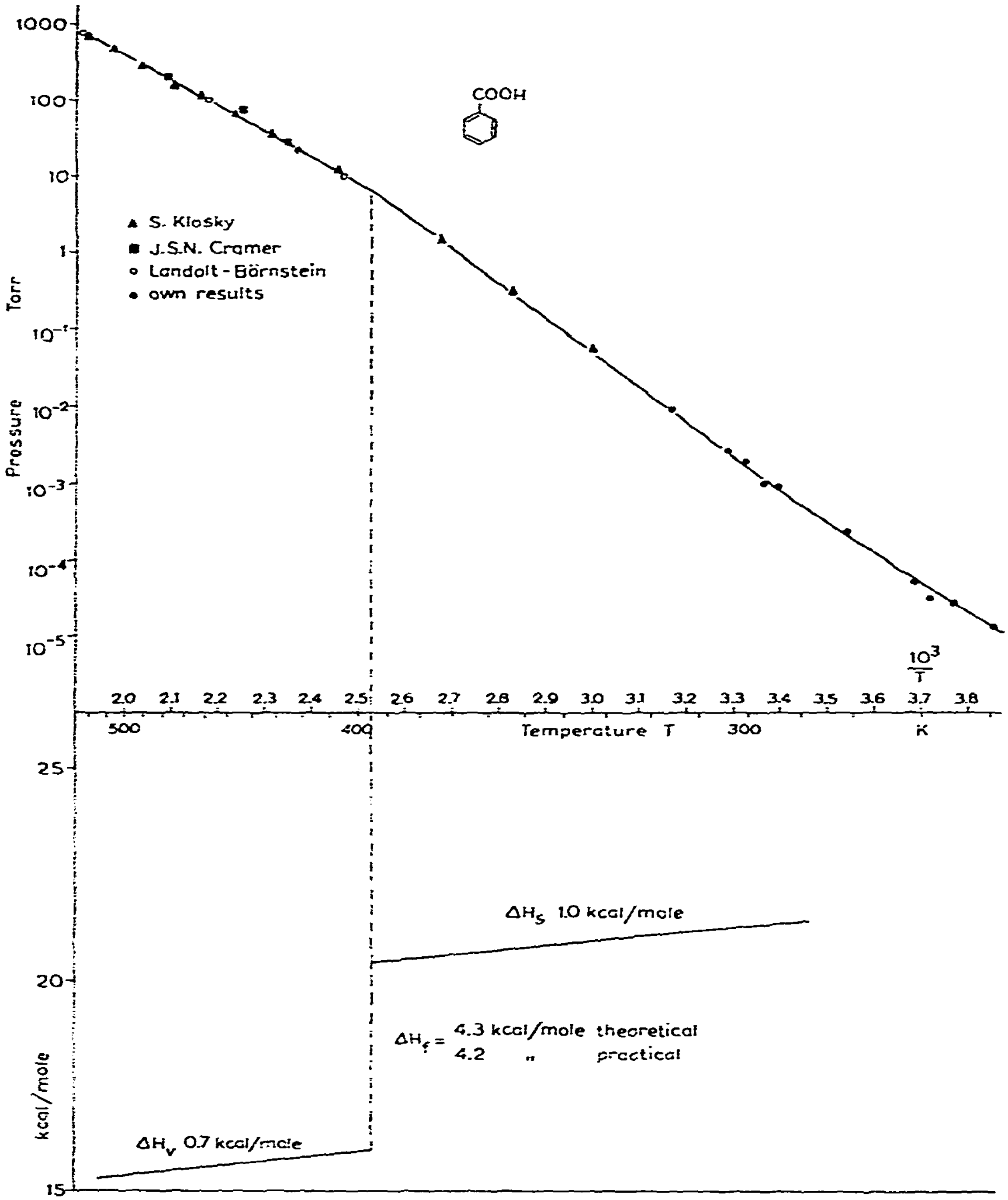


Fig. 5. Determination of heat of sublimation, ΔH_s, heat of vaporization, ΔH_v, and the heat of fusion, ΔH_f, from the vapor pressure curve of benzoic acid.

mean free path of the molecules is larger than the orifice diameter in order to employ the Knudsen formula. Thus, the highest measurable pressure is between 10^0 and 10^{-1} torr for an orifice diameter of 0.1 mm, depending upon molecular weight.

The lowest vapor pressure to be determined by this method depends on several

TABLE III

ORIFICE CALIBRATION OF THE KNUDSEN CELL

Temp. (°*K*)	*Pressure (Torr)* *Benzoic acid*	$\Delta m/\Delta t \times 10^7$ ($g\ sec^{-1}$)	*Orifice area* $a \times 10^2$ (cm^2)
293.36	6.6×10^{-4}	4.929	1.984
293.56	6.8×10^{-4}	4.956	1.937
293.36	6.7×10^{-4}	4.725	1.874

Mean value of $q = 1.93 \times 10^{-2}$ cm^2.

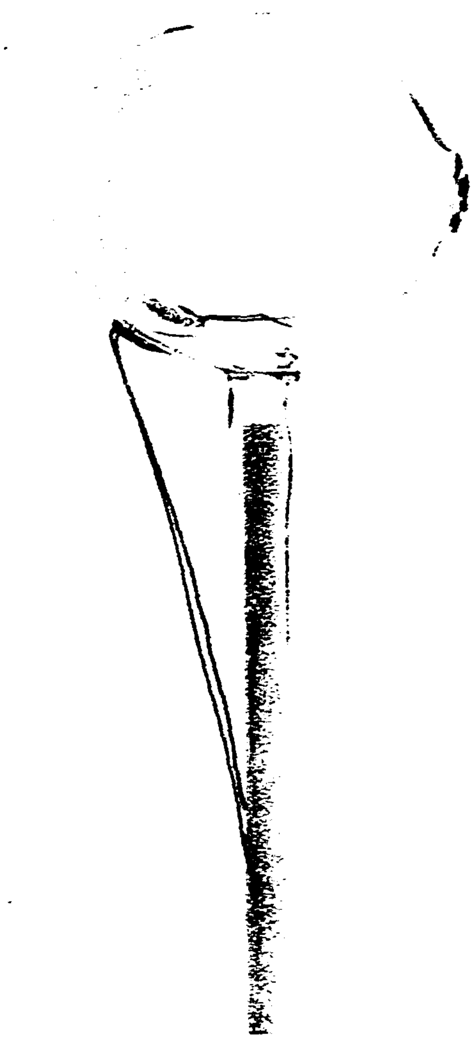


Fig. 6. Pyrex effusion cell.

factors including orifice diameter. Since effusion rate is very small at low pressures, a larger orifice diameter is required. Orifice diameters of 3–5 mm are needed for vapor pressures of 10^{-4}–10^{-6} torr, since the mean free path is about 1m under these conditions. Thus, the range over which measurements can be made using this method depends on the sensitivity and reproducibility of the balance, *i.e.* for an effusion rate of 10^{-9} g sec^{-1}, corresponding to a pressure of 10^{-6} torr, and for a test lasting 10–20 h, the maximum drift of the balance should not be more than $\pm 5\ \mu g$ ($\sim 5\%$). Furthermore, the vacuum outside the effusion cell is important. In general, this pressure should be about an order of magnitude below the vapor pressure to be determined in order to ensure effusion of the molecules. This external pressure is monitored and recorded continuously. The cold trap near the orifice of the Knudsen cell serves to condense the vaporized compound and assists in stabilizing the external pressure. Maintaining the temperature of the sample and effusion cell constant is the most important requirement for such measurements. Since the change of a few tenths °C will alter the vaporization rate and lead to erroneous measurements, the sample temperature thermocouple was placed close to the sample under investigation

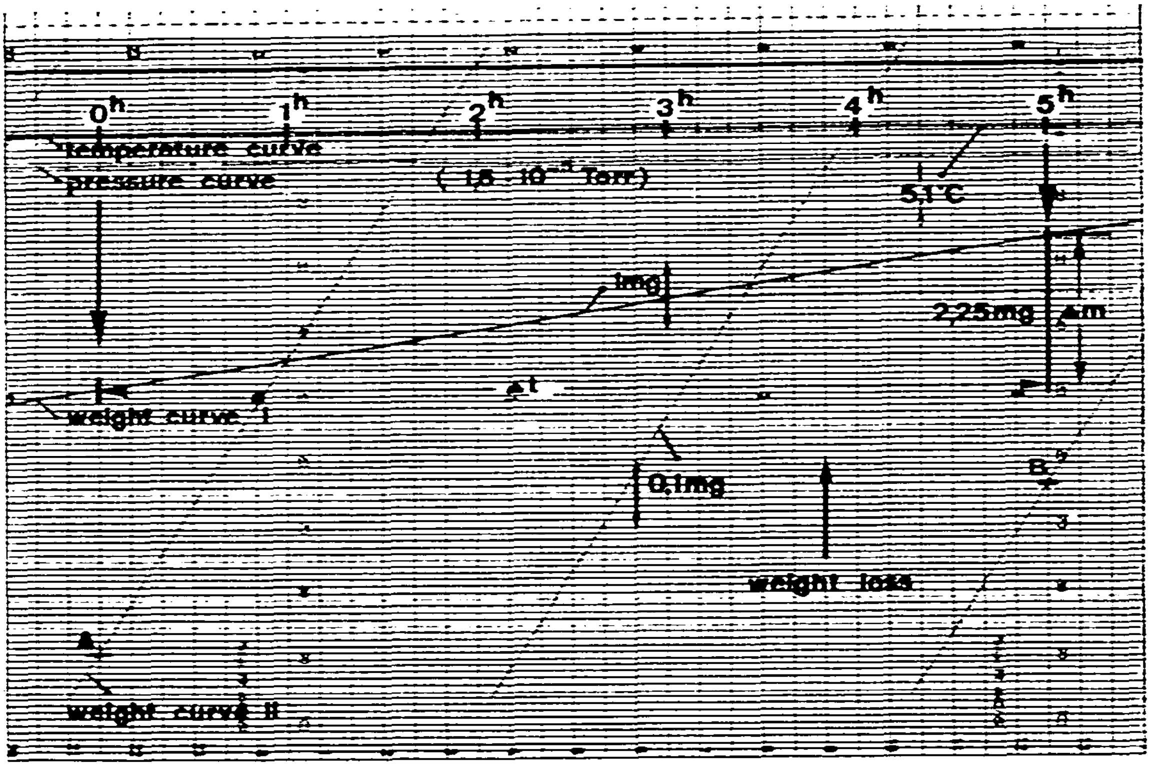


Fig. 7. Original diagram of a vapor pressure measurement weight loss produced by effusion of benzoic acid vapor leaving the cell through a calibrated orifice (7.147×10^{-3} cm^2) under isotherm conditions (17.28°C), recorded as a function of time simultaneously with sample temperature and pressure outside the cell.

and the temperature was maintained constant by use of a thermostatically controlled liquid bath.

A sample weight of about 500 mg was used in the Knudsen cell for each test, and materials were sublimed several times, and degassed on the balance under high vacuum, before effusion measurements.

Fig. 7 shows an original diagram of a run with benzoic acid at 17.28 °C, after establishing equilibrium conditions. One small division corresponds to 0.5 °C, showing that the temperature was kept constant to ± 0.1 °C over the test time of 6 h. Similarly, the pressure was nearly constant at 1.5×10^{-5} torr. The two weight traces, recorded at different sensitivities, show a constant rate of weight loss. The total measured effusion of benzoic acid was 2.25 mg after 6 h, corresponding to an effusion rate of 10^{-7} g sec^{-1}.

If the effusion rate appears to be non-linear, this may be due to: (*i*) equilibrium conditions have not yet been reached, (*ii*) the substance is not pure or has started to decompose, (*iii*) the sample is completely vaporized.

RESULTS AND DISCUSSION

Fig. 4 and Table II show that this measurement technique is applicable over the pressure range 10^{0}–10^{-6} torr, with the available instrumentation. Comparison with established values is relatively difficult, since very little data for the vapor pressure of organic compounds have been published for this pressure range. Values for benzoic acid, known to about 10^{-2} torr, are in good agreement with present measurements; however the new data deviate from the available information for monuron[4] and anthracene[19].

The vapor pressure curve of benzoic acid shows a deviation from linearity in the pressure range 10^{-4}–10^{-5} torr, possibly due to association or dimerization of the benzoic acid molecules. An attempt to verify this suggestion will be made using simultaneous mass spectrometric measurements.

CONCLUSION

Results of these measurements demonstrate this method for vapor pressure measurements in the range 10^{0}–10^{-6} torr will produce useful results in a comparatively short time. Further tests are underway in different temperature ranges.

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