

VAPOUR PRESSURE OF SOME LOW-VOLATILE HYDROCARBONS DETERMINED BY THE EFFUSION METHOD

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A new apparatus has been described for the determination of vapour pressures lower than 10^{-2} Torr by Knudsen's effusion method. The rate of effusion is measured *in situ* by means of quartz spiral weights in an arrangement enabling a defined sample temperature to be maintained. The effectivity of sample thermostating is controlled by simultaneous measurements in the classical arrangement when the sample is weighed outside the system before and after effusion. A comparison of preliminary results obtained by both procedures using cells with orifices of different sizes allowed experimental conditions to be found which guarantee a defined temperature, and also an appropriate equation to be chosen for vapour pressure calculations. The function of the device was verified by measuring the vapour pressure of benzophenone. Measurements were also performed with diphenyl, 2,2'- and 3,3'-ditolyl and 1,3-diphenylbutane at several temperatures in the region from 10°C to 35°C. The temperature dependence thus obtained was expressed in terms of the Clausius-Clapeyron equation.

The data on the vapour pressures of low-volatile compounds can be useful both in practice and for theoretical purposes. They can be used, *e.g.*, to estimate if the liquid phase in gas-liquid chromatography or the polymer softener is sufficiently resistant against evaporation, or they can serve as a basis for separation of compounds by molecular distillation. The data are also desirable for the thermodynamics of oligomeric models of macromolecular compounds which are very interesting from the theoretical viewpoint. An improvement of the respective measuring methods is important also with respect to their future application to mixtures of low-volatile compounds and their thermodynamics.

One of the suitable methods of determination is Knudsen's effusion method¹. It is used within a broad range of pressures from 10^{-2} to 10^{-8} Torr; it is also comparatively easy from the experimental viewpoint; the calibration constants of the device hold for all compounds under investigation. When using this method, however, one should be careful to observe the experimental conditions under which the equations used are valid and the sample can be maintained at a defined temperature.

This paper describes a new arrangement of the effusion method based on weighing *in situ* with a satisfactory thermostating of the sample. A comparison with the results obtained in the classical arrangement (which was more time-consuming, but with a more perfect thermostating) and measurements with different sizes of the effusion orifice permitted suitable experimental conditions to be defined.

If saturated vapour effuses from a cell having an area of a at a temperature T , the equilibrium vapour pressure P_K can be calculated from the rate of the weight loss G of the compound closed in the cell by using the original Knudsen's relationship

$$P_K = G(2\pi RT/M)^{1/2} a^{-1}, \quad (1)$$

where M is the molar mass of the compound and R is the gas constant. Equation (1) is valid assuming that: *a*) there are no recoils from the walls of the orifice (the assumption is fulfilled if $2r \gg l$, where $2r$ is the diameter of the orifice, l is the thickness of the walls); *b*) the flow of vapour of the compound is molecular (this holds for $2r < \lambda$; λ is the mean free path of the molecules), *c*) inside the cell there is a corresponding equilibrium vapour pressure (*i.e.* for $a \ll A$; A is the effective evaporation area), *d*) the cell with the compound is isothermal, *e*) there is no back flow from the surroundings of the cell and *f*) contribution of surface migration to the effusion flux is negligible.

Eq. (1) was modified by a number of authors for experimental conditions so as to describe the dependence of G on vapour pressure even if not all the above assumptions are fulfilled. If it does not hold that $2r \gg l$, the equilibrium pressure P_C can be calculated from Eq. (1) by introducing the so-called Clausing's² coefficient W_2 for an orifice according to

$$P_C = P_K/W_2. \quad (2)$$

The transmission coefficient W_2 expresses the probability that a molecule that enters the hole will pass through it irrespective of recoils from the walls of the orifice that may occur here. Clausing's calculations² were summarized in a table giving the values of W_2 depending on l/r for a cylindrical tube (here, a cylinder-shaped orifice). The same dependence was expressed analytically by De Marcus^{3,4} and verified by statistical modelling of the particle motion by the Monte Carlo method⁵. If the orifice is conical, W_2 is moreover a function of the apex angle^{6,7}.

The above calculations of Clausing's coefficient were made on the assumption that the vapour flow is molecular, *i.e.* that the effect of mutual molecular collisions is negligible. The highest pressure under which this assumption is fulfilled is characterized by the critical Knudsen's number Kn_{min} where $Kn = \lambda/2r$. Experiments^{8,9} showed that during passage through the cylindrical orifice having $l \ll 2r$, Kn_{min} is 5 to 10, for $l/2r < 5$, Kn_{min} is 1 to 5. The effusion process for $Kn < Kn_{min}$ has so far been described quantitatively¹⁰ only for the near transition region between the molecular and viscous flows. The vapour pressure P_s involving a correction for binary collision of molecules is in this flow region and for $W_2 \rightarrow 1$ given by

$$P_s = P_C[1 + (0.13/Kn)]^{-1}. \quad (3)$$

Eq. (2) was also modified by Motzfeld¹¹ for a case when the ratio $f = a/A$ is not sufficiently small. He based his reasonings on the assumption that the vapour pressure that exists even immediately above the level of the condensed phase is not an equilibrium one and further decreases toward the orifice level. From flux balance in both directions in the level of the orifice and of the condensed phase he obtained for the equilibrium pressure P_M

$$P_M = P_C\{1 + fW_2[(1/\alpha) + (1/W_1) - 2]\}, \quad (4)$$

where W_1 again is Clausius' coefficient, this time related to the cell, so that it is the function of the ratio of its height L to the radius R ; α is the condensation or Langmuir's¹² coefficient (*i.e.* fraction of molecules which condensate on falling on the surface of the condensed phase).

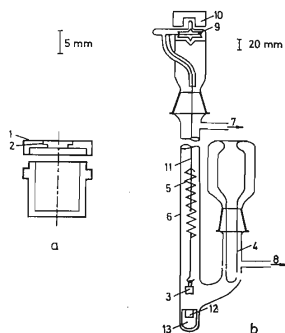
The value of Motzfeld's coefficient P_M/P_C agreed well with those calculated by the Monte Carlo method¹³.

Trying to explain the discrepancies between experiments and theory, Winterbottom and Hirth¹⁴⁻¹⁶ made a plausible assumption that during effusion experiments surface diffusion flow is also operative besides the effusion flow. The total transmission coefficient W is then a function of L, R, l, r, T, P and of quantities characterizing the sorption and diffusion properties of the cell and the compound under investigation. Since the sorption and diffusion coefficients are not known as a rule, the equations derived for effusion with simultaneous surface diffusion have a limited use only. They are useful for qualitative conclusions concerning the possibility of limitation of the contribution of surface diffusion. This contribution increases for instance with decreasing r and l and is more operative in the case of a conical orifice than in the case of a cylindrical one (for the same r, l).

Besides errors that may arise by neglecting the above corrections another quite important error must be borne in mind, whose source lies in an insufficient temperature control. The heat lost by the sample by evaporation must be compensated for so that isothermal conditions at a defined temperature are maintained. If the cell containing the sample is suspended in a vacuum, radiation is the only important mode of heat exchange; this, however, can be sufficient at high temperatures only, for instance during measurements of the pressure of metal vapours. This fact must be borne in mind for each measurement performed at usual temperatures; therefore we developed an arrangement providing heat exchange by conduction.

EXPERIMENTAL PART

Compounds. Benzophenone produced by L. Light & Co. Ltd., Colnbrook, England, was recrystallized. Preparation and characteristics of the aromatic hydrocarbons used are described in ref.¹⁷.



Apparatus and procedures. The loss rate of the compound G was determined by two procedures: 1) from a change in the elongation of a quartz spiral with a suspended effusion cell; 2) by weighing the cell on an analytical balance before and after the experiment.

FIG. 1

a Detail of the Effusion Cell, b Apparatus for Measuring Vapour Pressures by the Effusion Method (Details given in the textual part)

Procedure *J*: A cylindrical effusion cell (Fig. 1*a*) made of duraluminium, weight 0.6 g, height $L = 10$ mm, $2R = 10$ mm in diameter was filled with a layer of the measured compound, 2–3 mm thick. The cell was closed with a lid 1 having a circular depression 2 for a gold foil, thickness $l = 0.03$, into which an orifice was bored having diameters $2r = 0.64, 0.70, 0.74, 0.87, 1.05, 1.23$ mm, or with a lid having a conical orifice with an apex angle of 120° and the smaller diameter $2r = 0.93$ or 1.055 mm. The foil and the lid were glued with nitrocellulose lacquer. The orifice diameters were determined on a two-dimensional Zeiss-Jena reading microscope having an average reading error in four different directions ± 0.04 mm in the range $20\text{--}60^\circ\text{C}$. The orifice size in the individual experiments was chosen so that conditions *a*) to *f*) for the validity of Eq. (1) were satisfied simultaneously, the experiments (at a minimum change of 10 mm in the spiral length) lasted not longer than 24 h, and the thermostating of the sample was not made impossible by too fast evaporation.

The cell 3 (Fig. 1*b*) was suspended on the quartz spiral 5 (maximum load 1 g, sensitivity 2.5 mg/mm) via a branch for the freezing trap 4. The spiral was placed in a glass tube 6 with the connection 7 for vacuum line (10^{-5} to 10^{-6} Torr) and Penning's gauge 8. A device for raising and lowering of the spiral was attached to the upper end of the tube through a ground joint. The device consisted of a pulley 9 rotating around vertical axis and controlled from the outside by a magnet 10. A siron filament 11 bound to the spiral was wound on the pulley. In this fashion, the cell could be inserted into the hole 12 in the block 13 (AKV steel) at the bottom of the tube during the experiment and removed from the block while weighing. The block provided heat transfer from the water thermostat by which the temperature was adjusted and maintained during the experiment (range of temperatures attained was $10\text{--}50^\circ\text{C}$, accuracy $\pm 0.02^\circ\text{C}$, only for 10°C the stability was $\pm 0.05^\circ\text{C}$). One part of the tube with the quartz spiral was thermostated to $30.0 \pm 0.2^\circ\text{C}$ with an air thermostat. The spiral was calibrated at this temperature. The spiral elongation was read by means of a cathetometer produced by Griffin and George (Great Britain) with an accuracy of ± 0.02 mm. The effusing compound condensed in the freezing trap which

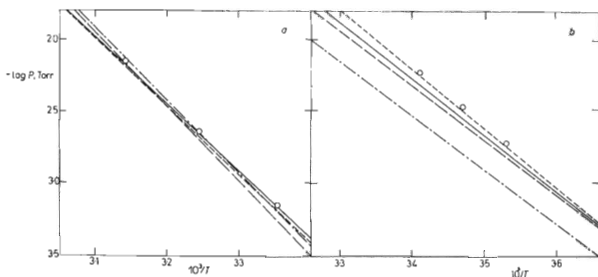


FIG. 2

Temperature Dependence of the Vapour Pressure P (Torr)

a Benzophenone: \circ our results, --- ref.¹⁸, - · - · - ref.¹⁹, ——— ref.²⁰, - - - - ref.²¹.
b Diphenyl: \circ our measurements; - · - · - ref.²², - - - - ref.²³, - - - - ref.²⁴ (effusion method); ——— ref.²⁵ (Langmuir's viscosity gauge).

was automatically completed to the mark by liquid nitrogen from a spare Dewar flask (25 l). The freezing trap was placed at such a minimum distance from the cell that it still did not affect its thermostating.

Prior to each measurement the spiral with the cell was raised, the system was separated from the vacuum line and the pressure was raised to 60 Torr by admitting the air. The evaporation rate was thus reduced to a negligible value. After eight minutes needed for stabilizing the position of the spiral its elongation was read off; by lowering the spiral the cell was again placed in the block. The time that elapsed between connecting the tube with the vacuum line and the subsequent admission of the air was regarded as the effusion time between two weighings.

Procedure 2: The thermostating of the cell resting by its own weight on the bottom of the metal block is much more reliable than that of a cell freely suspended in vacuo. It need not of course be sufficient at any effusion rate. Therefore, control tests were made for higher rates by a procedure which, although being slower and less convenient, allowed nevertheless a better heat transfer to be achieved. A good agreement between the results obtained by procedures 1 and 2 was considered to be the proof of the fact that the orifice of a given size (and smaller orifices) is satisfactory from the thermostating point of view for a given vapour pressure (and lower pressures). The cell made of duraluminium, 7 g in weight, $L = 15$ mm high and $2R = 15$ mm in diameter, could be screwed into the block. The initial and final weights of the cell were determined with an analytical balance. The experiments had to last longer than when weighing on a spiral (2 to 4 days) with respect to the undefinability of their origin (evacuation of the system) and a higher total weight of the cell.

Application range. The apparatus described here is suited for measuring pressures from 10^{-3} to 10^{-4} – 10^{-5} Torr. The lower limit of measurable pressures is a function of the available vacuum, the upper is connected with the critical Knudsen's number. The limitation concerning higher pressures is more difficult to adjust. Although the magnitude of Knudsen's number is raised by using smaller orifices, the portion of surface diffusion is also raised at the same time.

RESULTS

Benzophenone. Benzophenone was used to check the operation of the apparatus. Table I summarizes averaged experimental results obtained by both procedures with orifices of different sizes. Vapour pressures were evaluated according to Eq. (1) to (4). The transmission coefficients W_1 and W_2 were calculated after De Marcus³,

TABLE I
Vapour Pressure of Benzophenone

T, K	$P_K \cdot 10^3$ Eq. (1)	$P_C \cdot 10^3$ Eq. (2)	$P_M \cdot 10^3$, Eq. (4)		$P_s \cdot 10^3$ Eq. (3)
			$\alpha = 0.5$	$\alpha = 1$	
298.11	0.689	0.716	0.723	0.717	0.713 ± 0.003
308.21	2.24	2.33	2.32	2.33	2.29 ± 0.01
318.01	7.21	7.39	7.49	7.45	6.95 ± 0.01

the ratio f varied from $5 \cdot 10^{-3}$ to $1 \cdot 5 \cdot 10^{-2}$ for procedure 1 and from $3 \cdot 10^{-3}$ to $7 \cdot 10^{-3}$ for procedure 2. It can be seen from the Table that the recoils from the walls of the orifice are reflected in the magnitude of the calculated pressure ($P_K \neq P_C$), Motzfeld's coefficient almost equals unity for cells and orifices used ($P_C \approx P_M$), P_M does not virtually vary within a broad range of α (from 0.5 to 1), so that it is not necessary to know the actual value of α in this case.

The least scatter about the average was found for the P_s values which also did not exhibit any systematic dependence on the orifice size. This is why the average P_s values were used in Fig. 2a and for calculating the constants of the Clausius-Clapeyron equation. It can be seen from Fig. 2a that the agreement with the results obtained by other authors¹⁸⁻²¹ is good. Our results lie rather near the higher values of the literature data. An explanation can be sought in that in contrast with the majority of other authors, we devoted our attention to the thermostating of the sample.

The results obtained here can be adequately expressed by the Clausius-Clapeyron equation in the form

$$\log P = -4698/T + 12.611, \quad 298 \text{ K} < T < 318 \text{ K}, \quad (5)$$

where P is pressure in torrs. The slope was obtained by the gravity centres method with an equivalent participation of experimental points at three different temperatures. The intercept on the $\log P$ axis was calculated as an arithmetic mean from intercepts satisfying the individual pairs of the measured values of P_s , T . The equation gives the heat of sublimation $\Delta H = 89.96 \text{ kJ/mol}$ which fits in well with the

TABLE II

Vapour Tension of Compounds Investigated, P_s Calculated from Eq. (3), Constants of the Dependence $\log P_s = -A/T + B$ and Heat of Evaporation or Sublimation ΔH for Compounds Investigated

Compound	T K	$P_s \cdot 10^3$ Torr	A	B	ΔH kJ/mol
DFB	288.11	0.52 ± 0.02	3 841	10.046	73.55
	298.18	1.44 ± 0.01			
	303.18	2.40 ± 0.02			
mDT	288.12	1.10 ± 0.02	3 754	10.085	71.88
	298.10	3.26 ± 0.03			
	308.30	7.99 ± 0.07			
DF	283.31	1.88 ± 0.03	3 926	11.145	75.18
	288.18	3.35 ± 0.01			
	293.18	5.63 ± 0.02			
oDT	283.68	5.55 ± 0.06	3 428	19.829	65.65
	288.16	8.54 ± 0.03			

literature data, namely: 89.11 kJ/mol (ref.¹⁸), 95.09 kJ/mol (ref.¹⁹), 96.10 kJ/mol (ref.²⁰), 91.24 kJ/mol (ref.²¹).

Aromatic hydrocarbons. Table II summarizes the results of vapour pressure measurements of 1,3-diphenylbutane (DPB), 3,3'-ditolyl (mDT), diphenyl (DP), 2,2'-ditolyl (oDT) and the quantities derived therefrom. The measurements were carried out with orifices of various sizes by using procedures 1 and 2. The pressures, A and B constants of the Clausius-Clapeyron equation, and the heats of evaporation or sublimation ΔH were determined as in the case of benzophenone. The vapour pressure of the three first compounds was determined at three temperatures, the vapour pressure of oDT was determined at two temperatures for which condition *b*) was fulfilled. Only for DP literature data were found with which our measurements could be compared (Fig. 2*b*). The fact that our vapour pressures lie rather near the higher values of the literature data can be assigned to the control of the sample temperature, similarly to benzophenone. Our value of the heat of evaporation of diphenyl also coincides with the literature data obtained: 72.74 kJ/mol (ref.²²), 81.61 kJ/mol (ref.²³), 75.02 kJ/mol (ref.²⁴), 75.81 kJ/mol (ref.²⁵).

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