[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

VAPOR PRESSURES OF ORGANIC CRYSTALS BY AN EFFUSION METHOD

BY THOMAS H. SWAN AND EDWARD MACK, JR.

RECEIVED APRIL 10, 1925 PUBLISHED AUGUST 5, 1925

The authors are interested in obtaining vapor-pressure data for certain volatile organic crystals at several temperatures with sufficient accuracy to justify calculation of the heats of vaporization by the Clapeyron-Clausius equation. Numerous methods for determining small vapor pressures have been described in the recent literature. Among them may be mentioned the quartz fiber suggested by Langmuir,[1] employed by Haber and Kerschbaum,[2] and later modified by Coolidge;[3] the ionization gage;[4] an improved optical-lever manometer;[5] the Knudsen gage;[6] several special forms of Walker's dynamic method;[7] the hot wire manometer;[8] and others. It has seemed to the present authors that the method based on the work of Knudsen[9] on the effusion of gases and vapors through small holes of known area, offers as convenient and as reliable a means as any of the other methods just mentioned, for the determination of small vapor pressures.

The Knudsen method, in addition to its first employment by Knudsen himself in the determination of the vapor pressure of mercury, has been used with notable success by Egerton[10] for the vapor pressures of mercury, cadmium and zinc and also of lead; and in a slightly modified form by Langmuir,[11] and by Langmuir and Mackay[12] for the vapor pressure of electrically-heated metal filaments; by Pilling[13] for the vapor pressure of calcium. Our apparatus is very much like that of Egerton although in some features it resembles that of Pilling.

---

[1] Langmuir, THIS JOURNAL, **35**, 107 (1913).

[2] Haber and Kerschbaum, *Z. Elektrochem.*, **20**, 296 (1914).

[3] Coolidge, THIS JOURNAL, **45**, 1617 (1923).

[4] Buckley, *Proc. Nat. Acad. Sci.*, **2**, 683 (1916). Found and Dushman, *Phys. Rev.*, **17**, 7 (1921).

[5] Carver, THIS JOURNAL, **45**, 59 (1923).

[6] Knudsen, *Ann. Physik*, **32**, 809 (1910). Woodrow, *Phys. Rev.*, **4**, 49 (1914). Shrader and Sherwood, *ibid.*, **12**, 70 (1918).

[7] Barker, *Z. physik. Chem.*, **71**, 235 (1910). Baxter, Hickey and Holmes, THIS JOURNAL, **29**, 127 (1907). Von Wartenberg, *Z. Elektrochem.*, **19**, 482 (1913).

[8] Pirani, *Verh. Deut. Phys. Ges.*, **4**, 686 (1906). Hale, *Trans. Am. Electrochem. Soc.*, **20**, 243 (1911).

[9] Knudsen, (a) *Ann. Physik*, **28**, 999 (1909); (b) **29**, 179 (1909).

[10] Egerton, *Phil. Mag.*, **33**, 33 (1917); *Proc. Roy. Soc.*, **103A**, 469 (1923).

[11] Langmuir, *Phys. Rev.*, **2**, 239 (1913).

[12] Langmuir and Mackay, *ibid.*, **4**, 377 (1914).

[13] Pilling, *ibid.*, **18**, 362 (1921)

Experimental Part

Fig. 1 shows the apparatus.

The volatile substance is placed in a thin layer on the bottom of the hollow brass box H, which is shaped like a pill box. It is provided with a lid which screws on hermetically. In the center of the lid is a hole about 1 cm. in diameter, which has been completely covered by soldering over it a piece of very thin copper foil, and in the center of this foil a small circular hole has been made with a needle. It is through this small hole that the volatile substance effuses into the evacuated space above. The area of the hole was measured, after the ragged edges had been removed with fine emery paper, by a photomicrographic method, and also by direct observation with a calibrated microscope eye-piece scale. The box H can be removed from the rest of the apparatus and weighed on a balance, to find the weight of volatile material lost by effusion.

The hollow, cylindrical, brass block B, which holds the box H, is sealed with de Khotinsky cement to the open end of the glass form F, as indicated in the figure. This glass form, in which the vacuum is maintained, is connected through the trap T (cooled with solid carbon dioxide and acetone) with a McLeod gage and with an evacuation system consisting of a Langmuir pump, backed by a Stimson diffusion pump which, in turn, is backed by a large oil pump, motor-driven. The volume of the entire apparatus is about 3 liters, and the three pumps reduce the pressure to 0.0001 mm. in about two minutes and then rapidly to 0.00001 mm. The trap T is to prevent the entrance of mercury vapor from the pumps into the chamber F, and also to stop the organic vapors which come from chamber F, and keep them from contaminating the pumps.

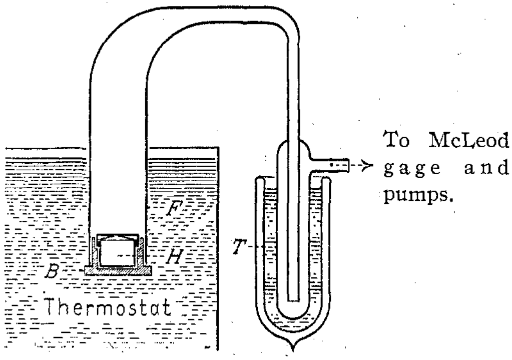

Fig. 1.

Before starting the vacuum, the box H and block **B** are mounted and sealed in position and allowed to stand for an hour in a thermostat to come to the experimental temperature, which is measured on a Bureau of Standards thermometer, and is kept constant within 0.01°.

The vapor pressure is calculated from the equation[9a]

$$p_1 - p_2 = \frac{G}{t} \times \frac{w_1 + w_2}{\sqrt{\rho}} \qquad (1)$$

where p_1 is the pressure of the saturated vapor inside the box H, p_2 the pressure in the vacuum above the effusion hole, G the grams lost by effusion, t the time in seconds, w_1 the resistance of the hole, w_2 the resistance of the tube F (Fig. 1), and ρ the density of the vapor at the temperature of the experiment and at a pressure of 1 dyne per sq. cm.; $w_1 = \sqrt{2\pi}/A$, where A is the area of the effusion hole; w_2 in the present experiments is negligibly small because of the relatively very large cross-sectional area of tube F (21.24 sq. cm.), as compared to the area of the effusion holes which we have used $(6.66 \pm 0.03) \times 10^{-3}$, $(3.02 \pm 0.02) \times 10^{-3}$ and $(6.390 \pm 0.001) \times 10^{-4}$ sq. cm. In Equation 1, p_2 is so small compared to p_1 that it may be neglected. The equation reduces then to the familiar Langmuir equation

$$p = \frac{g}{A\,.\,t} \Big/ \sqrt{\frac{M}{2\pi RT}} \qquad (2)$$

where p is the pressure (in dynes per sq. cm.) of the vapor in the box H, in equilibrium with the surface of the crystals, g the grams lost by effusion, A the area of the hole; t the time in seconds for loss of g grams; M the molecular weight of the substance; R the universal gas constant (in ergs), and T the absolute temperature.

This equation is strictly applicable only when the walls of the evacuated chamber F are very remote from the effusion hole, or when the walls are cooled so that vapor molecules that strike them condense and do not evaporate again. We have not cooled the walls at all, as did Egerton, but we have made the area of the effusion hole so small in comparison with the cross-sectional area of the chamber F as stated above, that very little reflection of molecules back into the effusion hole occurs. We have thought it advisable not to attempt cooling the walls of F, not only for the sake of avoiding the very troublesome experimental difficulty of doing so, but also for fear of affecting the temperature of the organic crystals in the box H. Even in the case of the largest hole, which presented therefore the most unfavorable situation, the error due to reflection is considerably less than 1%.

Probable Error of the Determination.—The main source of error lies in an *uncertainty about the temperature of the surface* of the crystalline substance which is evaporating. Since the thermal conductivity of organic solids is small it is possible that as the volatile substance evaporates, its surface temperature drops below that of the thermostat. This difficulty has been overcome by choosing a hole of such size for each separate substance as to make the rate of evaporation so small that the heat intake is sufficiently rapid to maintain constant surface temperature. It would be difficult to measure accurately the surface temperature. The assurance that we have of its constancy is the consistency of the results which we obtain when layers of different depths of substance are loaded into the box.

Since the actual time during which effusion occurs was always at least two, and generally three or four hours, the error introduced at the beginning of the determination by the time required to attain a good vacuum, was less than 1%. The area of the holes was measured with an error much less than 1%. The weight of substance lost by effusion was found, within 0.1 mg., on a good chemical balance with calibrated weights, and the error of weighing was generally much less than 1%. It seems, therefore, that the error of the determination should seldom be much larger than 1 or 2%.

A careful record of the pressure in the apparatus, as measured on the McLeod gage, was made at regular intervals during each determination.

With very slightly volatile substances it is important to maintain a very low pressure to insure that p_2 in Equation 1 is really negligible in comparison with p_1. In such cases we have found it necessary to "out-gas" the glass form F for several hours before starting the experiment. Volatile materials in the de Khotinsky cement apparently caused no trouble.

The samples of organic crystals for use in the determinations were prepared from materials of already tested purity by repeated recrystallization until they showed sharp melting points.

Table I

Vapor Pressures in Millimeters

	10° ± 0.01°	20° ± 0.01°	30° ± 0.01°
Naphthalene (highly purified)	(4)[a] 0.0174 ±0.0002	(5) 0.0648 ±0.0005	(3) 0.177 ±0.001
Naphthalene (purified by Barker's method)	....	....	(2) .163 ± .0003
p-Chloro-aniline	(2) .00385 ± .00002	(3) .0155 ± .0002	(3) .0487 ± .0007
p-Chloronitrobenzene	(3) .00382 ± .00004	(3) .0128 ± .0002	(2) .0395 ± .0002
	20° ± 0.01	30° ± 0.01	40° ± 0.01
p-Bromonitrobenzene	(1) 0.00097	(2) 0.00272 ±0.00002	(2) 0.00986 ±0.00007

[a] The values in parentheses show the number of determinations made of which the average is given in the table.

Discussion

In Table I, the naphthalene purified in the manner described by Barker[7] gave a vapor pressure at 30° of 0.163 mm. Barker himself found by a dynamic method 0.164 mm. However, when we purified the naphthalene to a high degree by repeated precipitation from an alcoholic solution at about 75° by the addition of water and then by repeated sublimation, the vapor pressure rose to 0.177 mm. It is interesting to compare the results that we have obtained for naphthalene at 10°, 20° and 30° with those of Allen,[14] Barker[7] and Daly.[15] Such a graphical comparison is made in Fig. 2. We are inclined to believe that the differences

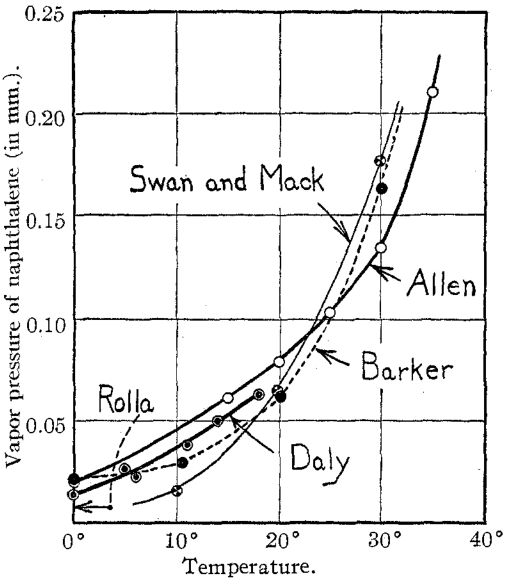

Fig. 2.

---

[14] Allen, *J. Chem. Soc.*, **77**, 412 (1900).

[15] In a paper by Mary R. Andrews, *J. Phys. Chem.*, **27**, 271 (1923), is given a table of vapor-pressure data obtained by Mary Daly with an ionization gage.

among the various results are due as much to different degrees of purity of the samples with which the determinations were made, as to the methods of determination. Phenol seems to be a persistent impurity in naphthalene and, of course, other impurities may also be present.

We should perhaps call attention to the fact that the vapor pressures given in Table I are for crystals that have been melted and then solidified. This is what happens when the box H and block B are sealed into the apparatus with de Khotinsky cement. There should be, however, no appreciable difference between the vapor pressure of such a solidified mass and that of the unmelted crystals if the substance is pure. We have tested this for naphthalene. We were able to seal the cement with the end of a small hot file without melting the naphthalene crystals (m. p., 80.5°). The vapor pressure of large crystals was found to be 0.180 ± 0.002, of small crystals 0.177 ± 0.001 and of the solidified melt 0.176 ± 0.004 mm.; all of which are the same within the experimental error.

In Table II are given empirical equations for the vapor-pressure curves, and the heats of vaporization obtained by differentiating the empirical expressions and substituting in the Clapeyron-Clausius equation.

TABLE II

HEATS OF VAPORIZATION

		Molar heat at 20° cal.	Latent heat at 20° cal.
Naphthalene	$\log p(\text{mm.}) = -29{,}820/T - 200.682 \log T + 595.642$	19,600	153 ±1.5
p-Chloro-aniline	$\log p(\text{mm.}) = -22{,}332/T - 138.475 \log T + 416.007$	21,600	169.5 ±2
p-Chloronitrobenzene	$\log p(\text{mm.}) = -4339.2/T + 12.918$	19,900	126.5 ±1.5
p-Bromonitrobenzene	$\log p(\text{mm.}) = 35{,}611/T + 305.935 \log T - 879.254$	21,200 (at 30°)	105 ±1 (at 30°)

The authors desire to express their indebtedness to Professor H. G. Heil, of the Physics Department, Ohio State University, for assistance in the design and construction of the vacuum system.

Summary

1. The application of a modified Knudsen method to the determination of the vapor pressure of organic crystals is described.

2. Vapor-pressure data at three temperatures are presented for naphthalene, *p*-chloro-aniline, *p*-chloronitrobenzene and *p*-bromonitrobenzene and a graphical comparison of the vapor-pressure data of several investigators for naphthalene is given.

3. The latent and molar heats of vaporization for the four substances just mentioned are calculated.

COLUMBUS, OHIO