XLVII.—*On a Simple Method of Determining Vapour-densities in the Barometric Vacuum.*

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IN spite of the great degree of simplicity to which the determination of vapour-densities has recently been brought by Meyer and others, there still remain many cases, *e.g.*, those of easily decomposable substances of high boiling point, and substances attacked by oxygen, in which the older method of Hofmann would be preferable. It has been shown, too, that to volatilise most liquids in a vacuum a temperature of 100° is sufficient; and as this temperature is rapidly attained and easily kept constant for any length of time, this fact is strongly in favour of Hofmann's method.

In the following modifications of Hofmann's apparatus, two new devices are introduced. Firstly, by varying the external pressure or otherwise, the vapour is made to occupy a known volume; and, secondly, its pressure is directly determined by a single observation, which is independent of the atmospheric pressure. The calculations are thus enormously simplified, and no room is left for errors of observation.

The simplest form of our apparatus, which we have adopted after many experiments, consists of an experimental cylinder and a steam-jacket. The first is composed of a glass cylinder 34 cm. long and 3.3 cm. in internal diameter, closed at one end, and at the other fused on to a stout glass tube 8 mm. in internal diameter, and about 83 cm. in length. 5 cm. below the junction a second tube of nearly the same diameter is fused into the latter at right angles. This tube, which serves as a barometer, is then bent upwards so as to be parallel and close to the cylinder, and is sealed off about 1 cm. below its upper end. The lower end of the long stem is provided with a well-fitting india-rubber cork, through the centre of which passes a short glass tube of narrow bore provided with an air-tight stop-cock. This tube may also with advantage be fused into the

long stem a little above its end, in which case the stem is closed with a plain india-rubber cork.

About 1 cm. below its junction with the cylinder a fine line is etched on the stem, and from a point on exactly the same level the barometer is graduated upwards in millimeters, the graduation being continued for a few millimeters below the zero point. If a cathetometer is available this graduation is unnecessary.

The steam-jacket consists of a glass cylinder sufficiently wide and long to pass easily over, and completely envelop, the cylinder and barometer. The upper end of this may be closed with a perforated cork, carrying a tube to admit the heating vapour. The lower end is closed with a doubly perforated cork (preferably of india-rubber). Through one hole passes the stem of the cylinder; the other is filled by a tube which serves to carry off the heating vapour. When in use the lower cork rests on the ring of a retort stand, which thus supports the whole apparatus.

The volume of the cylinder down to the line on the stem is once for all accurately determined, and the weight of hydrogen (or air) which it could contain at 100° and 10 mm. pressure of *mercury at 100°* calculated, due allowance being made for the expansion of the glass. This weight may be called the *constant* of the apparatus. It will be convenient to calculate its value for several half-degrees above and below 100° . Should other heating vapours than steam be used, the value of the constant should be determined for 100° absolute temperature, and 10 mm. pressure of mercury at 0° .

The depression of mercury in the barometer below that in the stem due to capillarity, may be either calculated or experimentally determined. The correction for this may be made to include any error in fixing the zero point of the scale.

To make an experiment, the cylinder, barometer, and stem are first completely filled with mercury, air bubbles being removed as far as possible. The substance, sealed up in a small bulb which it almost fills, is then placed on the surface of the mercury at the mouth of the stem, and pressed down by the india-rubber cork, which is then screwed firmly home, the stop-cock being in the meantime open. The stop-cock is then closed, the cylinder held vertically, and mercury allowed to flow out through the tap until communication is established between the cylinder and barometer, by which means any traces of air are uniformly distributed.

By now immersing the beak of the tap in some mercury and inclining the apparatus, the metal may be caused to rise again until it occupies the lower sixth of the cylinder. If this be done gradually there is no risk of air entering from the joint of the stop-cock or cork. The stop-cock is now closed, the apparatus and cork placed on the

ring of the retort stand, the steam-jacket adjusted, and the heating vapour passed through it. The bulb having burst, and a uniform temperature having been obtained, the barometer is held in a strictly vertical position, and mercury again allowed to escape until its level sinks exactly to the mark on the stem. The height of the column in the barometer tube, corrected if necessary for capillarity, now gives the pressure of the vapour; and by dividing the weight of the substance by the constant multiplied by the pressure expressed in centimeters of mercury, we at once get the density of the vapour referred to hydrogen or air. When a heating vapour other than steam is used the method of calculation is obvious. The manipulation of this apparatus is exceedingly simple: and as a comparatively small quantity of mercury is rendered impure at each experiment, a number of determinations may be made in a comparatively short time.

The only source of error lies in the change in volume, and therefore in pressure, of the small quantity of air in the barometer, owing to the rise of the mercury. This, however, is scarcely perceptible, and might be rendered absolutely inappreciable by expanding the upper end of the barometer tube into a bulb.

Another form of apparatus which has certain advantages, though by no means so easily manipulated as the above, comprises, in addition to the parts already described, a mercury trough made of dense wood. This has a circular bowl about 10 cm. in diameter and 7 cm. deep, prolonged below into a tube about 25 mm. in diameter and 50 cm. deep. The india-rubber cork and stop-cock of the stem are dispensed with. To make an experiment the trough, resting on the ground, is partly filled with mercury. The cylinder is also filled as before, the mouth of the stem closed by the finger, inverted in the mercury in the trough, and supported in a vertical position by the cork of the steam-jacket which rests on the ring of a weighted retort-stand placed at the edge of a table. The weighed bulb having been introduced, communication between the cylinder and barometer is made by raising the experimental tube. The latter is then lowered until the cylinder is half-full of mercury, the jacket adjusted, and vapour injected. The mercury having been thoroughly heated and the liquid vaporised, the cylinder is raised until the vapour occupies the proper volume, the rest of the operation being conducted as before. It would of course be easy to construct a support, more or less elaborate, to suit the fancy of the operator, which would serve the same purpose as the retort-stand.

In addition to the advantages already mentioned, these methods have another which may be of considerable importance. Brühl (*Ber.*, 12, 197) has shown that at temperatures above 180° the tension of mercury vapour becomes so considerable as to render the results obtained by Hofmann's method exceedingly inaccurate. Although we

have not as yet used our apparatus at high temperatures, this objection would obviously not apply to it, since the mercury in the cylinder and that in the barometer would be equally depressed.

How far these devices may be of use in facilitating the measurement of vapour-tensions, we intend to make the subject of special experiment.

The following are some of the results obtained by means of this apparatus:—

Temperature in all cases 100°C .

Cylinder A. Capacity = 282.3 c.c. Capillarity = 2.5 mm. Constant = 0.0024512.

Body.	Weight in grams.	Pressure in c.m.	Vapour- density (found).	Vapour- density (calculated).	Vapour-density (other observers).
Benzene	0.122	12.35	40.3	39.0	40.2
Pyrrrol	0.0883	10.7	33.7	33.5	34.7
Water	0.046	20.65	9.1	9.0	9.0
Amyl iodide ...	0.1974	7.7	104.6	99.0	96.5
Amyl alcohol ..	0.083	7.6	44.5	44.0	45.5

Cylinder B. Capacity = 313.4 c.c. Capillarity = 1 mm. Constant = 0.002654.

Amyl iodide ...	0.1509	5.63	101.0	99.0	96.5
Water	0.046	19.0	9.1	9.0	9.0
Butyric ether ..	0.0771	4.9	59.3	58.0	58.4

The numbers in the last column are taken from *Watts's Dictionary*; the numbers there given being referred to air as unity, have been multiplied by 14.45.

The column headed "pressure" gives the observed pressure plus the capillarity.