

### XIII. *On a Slight Modification of Hofmann's Vapour-density Apparatus.*

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1. IN a recent communication (*Deut. Chem. Ges. Ber.*, ix, 1304) Hofmann has described a method for determining vapour-densities whereby the employment of a graduated barometer-tube is no longer rendered necessary. In working with aniline vapour, or that of some other liquid of high boiling point, a graduated tube is very liable to crack: hence the importance of any device which will do away with the employment of such tubes.

Hofmann's modification of his original process consists in supporting the barometer-tube and mantle on a plate of caoutchouc sunk beneath the mercury in a cistern, the caoutchouc having a groove cut in it whereby communication is ensured between the mercury in the barometer-tube and that in the cistern. The caoutchouc plate rests upon a circular sheet of thin iron, to which a handle is attached, passing above the level of the mercury in the cistern. When the level of the mercury in the barometer-tube has become constant—that is, when the whole of the liquid under examination has been converted into vapour—communication between the mercury in the barometer-tube and that in the cistern is cut off by pushing (by means of the projecting handle) the caoutchouc plate into a position such that the end of the groove is no longer covered by the barometer-tube. When the apparatus has cooled the level of the mercury is read off, and marked by means of a piece of gummed paper; the tubes are removed from their places, and the barometer-tube is filled to the mark with mercury, which is then weighed.

Hofmann has also shown, in the communication referred to, how a very small quantity of liquid may be caused to maintain the temperature of the apparatus at a constant point for an indefinite period; but it is with the first-described modification that we have here to do.

2. In the course of an investigation upon essential oil of sage, with which we are at present engaged, it became necessary for us to make several determinations of vapour-densities; these we endeavoured to perform by the use of Hofmann's modified apparatus. It occurred to us that the use of a movable caoutchouc plate was not a necessity; that, given a communication between the mercury in the cistern and that in the barometer-tube, and given a method of determining the exact height of the column of mercury in the latter at the time when the level of that liquid had become constant, it was possible, at any

time after cooling, to redetermine, and therefore to mark the spot at which the level of the mercury formerly stood. If this could be done it was of course possible to determine the capacity of that portion of the tube occupied by the hot vapour.

3. We think we have succeeded in doing away with the use of a movable caoutchouc plate, and in still retaining the great advantages of the non-graduated tube.

The barometer-tube, not necessarily of uniform bore, is supported upon a circular plate of native unvulcanised india-rubber, about 60 to 70 mm. in diameter, and 5 mm. in thickness; through this plate two holes are bored; the plate is placed upon another similar plate of cork in which two grooves are cut; each hole in the plate is immediately over the inner end of one of these grooves. A piece of glass tubing is bent so as to pass along one of the grooves in the cork, and then upwards through one of the holes in the india-rubber plate, and to project about 10 mm. above the surface of the mercury in the cistern, when the cork and india-rubber are pressed firmly upon the bottom of the cistern itself. This tube passes in the other direction over the edge of the cistern, and communicates with the condensing apparatus. A small piece of glass tubing passes through the second hole in the india-rubber plate and along the groove in the cork beneath; the upper extremity of this tube projects about 2 mm. above the surface of the caoutchouc; when the cistern is filled with mercury this tube is entirely beneath the surface of that metal. The object of the second tube is to ensure free communication between the mercury in the barometer-tube and that in the cistern; we found that the pressure of the barometer-tube upon the india-rubber plate tended to squeeze together the sides of the hole in the latter, and so to prevent free egress of mercury. When the apparatus is set up, the lower extremity of the barometer-tube must entirely cover the orifice of this tube. The outer mantle of course covers the barometer-tube and the tube communicating with the condenser. The mantle tube which we employ is of approximately uniform bore, and is not drawn out at the upper end, but is there closed by a good cork, through which passes the tube from the cistern in which the liquid—water, aniline, &c.—is boiled. In working with aniline we employ a tube of block tin as a means of communication between the cistern for liquid and the upper extremity of the mantle tube. This tin tube is unacted upon by boiling aniline, and by reason of the flexibility of the material composing it, freedom of motion is allowed while fixing the corks of the cistern and of the mantle tube firmly in their places. We generally cover the tin tube with felt or other non-conducting material.

4. When the level of the mercury in the barometer-tube has ceased to fall, we bring a pendulum cathetometer alongside of the apparatus,

adjust the pointer to the level of the mercury in the cistern, and the movable side-piece to the lower level of the meniscus in the tube; we then read off the height of the column of mercury in the barometer-tube, noting at the same time the height of the barometer and the temperature of the air. The apparatus is now allowed to cool to such a temperature as shall allow of easily grasping the outer tube. When this point is reached, the outer tube is cautiously removed, the barometer-tube being held in its place by an assistant; the latter tube is clamped securely, and by looking through the cathetometer the exact former level of the mercury is marked by means of a piece of gummed paper. The clamp is now removed, the barometer-tube is emptied, and dried mercury is poured in from a weighed vessel until the upper level of the meniscus is very slightly above the mark in the tube; from the result of a second weighing of the vessel the amount of mercury so poured in is determined.

5. After removing the mantle tube the small quantity of condensed aniline which has gathered on the surface of the mercury between the outer and inner tubes, flows over the mercury in the cistern, and it becomes difficult to recover the whole of it. We therefore pour mercury down a long tube from the top of the mantle, before removing the latter, until the whole of the aniline flows out through the condenser into the flask containing the main portion.

6. We do not pretend that this method enables determinations of vapour-density to be taken with anything approaching to absolute accuracy, nevertheless we think that for general purposes the method gives very fair results, and it can certainly be quickly and easily carried out. We venture to think that a fair degree of accuracy is all that is generally required in the determination of vapour-densities, and that any method for rendering the attainment of such a degree of accuracy more easy, and thence for bringing these determinations, which really give so much knowledge, into more general use, is not to be altogether despised.

7. As examples of the working of the method we subjoin the following determinations:—

H = barometer reading.

h = „ „ corrected for

$$\text{temperature} \dots\dots\dots = \frac{H}{1 + (0.00018 \times t)}.$$

t = temperature of air.

v = volume of vapour in c.c. in

$$\text{barometer tube} \dots\dots\dots = \text{Hg} \div \frac{13.6}{1 + (0.00018 \times t)}.$$

Hg = weight of mercury in grams required to fill barometer-tube to mark.

$t'$  = temperature of mercury at moment of weighing.

$h'$  = corrected height of column of

mercury in barometer-tube .. =  $\frac{K + ts}{1 + (0.00018 \times t^\circ)}$ .

$K$  = reading by cathetometer.

$ts$  = tension of mercury vapour at  $t^\circ$ .

$t^\circ$  = temperature of vapour (determined generally by actual experiment).

$Hy$  = weight of volume of hydrogen equal to that of vapour, under similar conditions =  $\frac{v \times 0.00008936 \times 273 \times (h - h')}{760 \times (273 + t^\circ)}$ .

$W$  = weight of liquid.

*Isoheptane.* B. P. =  $89^\circ$ — $91^\circ$ .

$C_7H_{16}$ .

$H$  = 758 mm.

$h$  = 755.6 mm.

$t$  =  $17^\circ$ .

$v$  = 75.21 c.c.

$Hg$  = 1018.4 gram.

$t'$  =  $20^\circ$ .

$h'$  = 552 mm.

$K$  = 562 mm.

$ts$  = neglected as very small.

$t^\circ$  =  $100^\circ$ .

$Hy$  = 0.0013 gram.

$W$  = 0.0628 gram.

$\frac{M}{2}$  calculated = 50.

$\frac{M}{2}$  experimental = 48.3.

*Terpene from Sage Oil.* B. P. =  $157^\circ$ — $160^\circ$ .

$C_{10}H_{16}$ .

$H$  = 755 mm.

$h$  = 752.7 mm.

$t$  =  $17^\circ$ .

$v$  = 73.28 c.c.

$Hg$  = 992.15 grams.

$t'$  =  $22^\circ$ .

$h'$  = 554.5 mm.

$K$  = 561 mm.

$ts$  = 12 mm.

$t^\circ$  =  $185^\circ$ .

$Hy$  = 0.00101 gram.

$$W = 0.0682 \text{ gram.}$$

$$\frac{M}{2} \text{ calculated} = 68.$$

$$\frac{M}{2} \text{ experimental} = 67.5.$$

We take this opportunity of offering our best thanks to Mr. A. Barron for the aid which he has afforded us, and for the suggestions which he has made to us while carrying out the experiments, the results of which are detailed in the present note.

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