LXXXVIII. NOTE ON THE CALIBRATION OF BARCROFT MANOMETERS[1].

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THE extensive use of manometric methods in studying processes involving gas exchanges, carried out largely with the type of manometer employed by Warburg, makes a simple method of calibrating the apparatus desirable. The method proposed by Warburg [1923] is accurate only to a few per cent. Recourse may be had to the accurate but tedious method of determining capacity by weighing the vessels (bound to the manometer) filled with mercury, several weighings and some dismantling of the apparatus being necessary.

The method proposed by Warburg can however be rendered more accurate by a more exact consideration of the conditions. The discussion by Rona and Nicolai [1926] is incomplete.

Details of the apparatus are given by Warburg [1923, 1926]. It is sufficient here to emphasise that the manometer in question is not a differential manometer, but a constant volume manometer, the level of the manometric liquid being adjustable by means of a reservoir.

It is desired to determine the capacity V of the vessel bound to the manometer, including that of the capillary down to a level M on the manometer, it being intended always to keep the level at M when the manometer is in use. The vessel, containing a cc. of water, is bound to the manometer, and is then allowed to reach equilibrium in a thermostat at $\theta°$ K. (say, 37·5° C.) by allowing the manometer to swing to and fro for 15–20 minutes.

The level of the manometric liquid (Brodie's fluid, of which 10,000 mm. equal one atmosphere) is allowed to become steady at a suitable mark below M (on that arm of the U-tube attached to the vessel). The barometric pressure $p_{bar.}$ and the room temperature T (° K.) are observed. The difference h_1 between the pressures inside and outside the vessel is measured (in mm.). As slight changes in temperature and barometric pressure take place during the measurements, these are allowed for by having in the thermostat a similar vessel bound to its manometer, in which no changes of volume are made, and subtracting from h_1 and subsequent readings the changes in manometric readings shown by this "control" vessel. We understand values of h_1 (h_1 being a mean of several readings) and subsequent readings to have been corrected in this way.

When h_1 has been obtained, the manometric liquid is forced up to the level M, and after 10–15 minutes' shaking the difference between pressures inside and outside is again measured (h_2), several readings being made.

The same operations are repeated after the volume of water in the vessel has been increased to a'. (The volumes a and a' should be chosen so that $V - a'$ is about one-half of $V - a$.) Measurements of h_1' and h_2' are made, with the same levels on the arm bound to the manometer as before. The room temperature T' is measured. (Any change in barometric pressure is taken account of by the change in the reading of the "control" vessel, which is left in the thermostat.)

We can now calculate the value of V.

Let the initial volume be $V - a + x$, the air pressure in the vessel being p_1. x is a quantity representing the air contained in the manometer capillary between the level M and the initial level.

Then
$$p_1 = p_{\text{bar.}} + h_1 - p_{\text{H}_2\text{O}},$$
where $p_{\text{H}_2\text{O}}$ is the vapour pressure of water at the temperature $\theta°$ K. The volume of the air in the vessel is now decreased to $(V - a)$. Then p_1 increases to p_2, and
$$p_2 - p_1 = h_2 - h_1 = h.$$

From gas theory,
$$h = p_1 \frac{x}{V - a}.$$

Allowance must however be made for the influence of the change in pressure on the solubility of air in the water contained in the vessel.

Let α be the Bunsen coefficient for air. (At $37.5°$ C. α for nitrogen is 0.0135 and for oxygen 0.0242, hence for air α is 0.0156.)

It can be shown that the corrected formula is
$$h = \frac{p_1 x}{V - a\left(1 - \alpha\dfrac{\theta}{273}\right)}.$$

Similarly
$$h' = \frac{p_1' x'}{V - a'\left(1 - \alpha\dfrac{\theta}{273}\right)}.$$

Now x and x' represent the same volume and therefore when allowance is made for any change in room temperature:
$$x/x' = T'/T.$$

Combining the above three equations, we find:
$$V = \frac{\left(1 - \alpha\dfrac{\theta}{273}\right)\left(\dfrac{Tha}{p_1} - \dfrac{T'h'a'}{p_1'}\right)}{\dfrac{Th}{p_1} - \dfrac{T'h'}{p_1'}}.$$

A further correction should be made for the expansion of water (a and a' terms) from room temperature to $\theta°$ K. Assuming room temperature to be $15°$ C.

for this purpose, the expansion to $37 \cdot 5°$ C. is from 1 to $1 \cdot 0060$, and when the thermostat temperature is $37 \cdot 5°$ C., we have

$$V = \frac{0 \cdot 988 \left(\dfrac{Tha}{p_1} - \dfrac{T'h'a'}{p_1'} \right)}{\dfrac{Th}{p_1} - \dfrac{T'h'}{p_1'}}.$$

An illustrative set of values are given below:

$$\begin{array}{ll}
a, a'. & 2 \cdot 50,\ 8 \cdot 01. \\
h_1, h_1'. & +5,\ -9. \\
h, h'. & 71 \cdot 9,\ 139 \cdot 7. \\
T, T'. & 289 \cdot 8,\ 290 \cdot 2. \\
p_{\text{bar.}} & 755/0 \cdot 076. \\
p_{H_2O}. & 48 \cdot 4/0 \cdot 076. \\
p_1, p_1'. & \cdot 707 \cdot 0/0 \cdot 076,\ 705 \cdot 9/0 \cdot 076.
\end{array}$$

Hence it was found that $V = 13 \cdot 58$ cc.

A comparison was made of the values obtained by this method and by the method of weighing. The results on four different manometers and vessels, given below, show that the manometric method is accurate to about 1 %.

V (manometrically)	V (weighing)	Difference %
13·67	13·54	+1·0
13·66	13·68	−0·1
13·10	13·21	−0·9
13·74	13·91	−1·2

It should be noted that for accurate results h' should be as large as possible.

SUMMARY.

A revised and simple method, accurate to about 1 %, of calibrating the Barcroft constant-volume manometer is described.

REFERENCES.

Rona and Nicolai (1926). *Biochem. Z.* **172**, 82.
Warburg (1923). *Biochem. Z.* **142**, 325.
—— (1926). Über den Stoffwechsel der Tumoren (Berlin), 1–7.