Nomograms for Manometer Constants

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By the use of the nomograms described below, the constants of Warburg (constant-volume) and Barcroft (differential) manometers can be obtained in a small fraction of the time required for calculation by the usual methods.

I. THE WARBURG MANOMETER

The constant of the Warburg manometer is given by the expression

$$k = \frac{\frac{273}{T} v_g + v_F \alpha}{P_0}, \quad (1)$$

where T is the absolute temperature, v_g and v_F are the volumes (in $\mu\text{l.}$) of the gas and liquid phases in the vessel, α is the solubility (Bunsen coefficient) of the particular gas being measured, and P_0 is the number of mm. of manometric fluid equivalent to 760 mm. Hg.

In practice it is more convenient to express v_g and v_F in ml. instead of $\mu\text{l.}$; this may be done without changing the value of k if P_0 is expressed in m. instead of mm. When Brodie solution is used the value of P_0 may then be taken as 10.

A nomogram to take account of all the variables in the above expression would be somewhat complex, but in practice P_0 is constant, and if T is also taken as constant, α for a particular gas is also constant and the expression is then represented by a very simple form of nomogram. This will apply to only one particular temperature, but most experimental work is carried out at a constant temperature, and as scales for two or more temperatures may be drawn on the same nomogram, most requirements will be met.

v_g is obtained by subtracting v_F from the total volume V of the vessel, which is usually marked on the instrument, and it is convenient to make the nomogram perform the subtraction automatically. Substituting $v_g = V - v_F$ in equation (1), we get

$$k = \frac{273}{TP_0} V - \left(\frac{273}{TP_0} - \frac{\alpha}{P_0} \right) v_F. \quad (2)*$$

* After this paper was sent to press, my attention was drawn to a note by MacLeod & Summerson (1940) in which equation (2) is given and is made the basis of a graphical method (not a nomogram) for determining Warburg manometer constants. In this method a separate graph is drawn for each manometer vessel, by plotting the values of k against the corresponding values of v_F . The value of k for

For O_2 at 37° , $\alpha = 0.024$ and we have therefore

$$k = 0.0881V - 0.0857v_F. \quad (3)$$

For CO_2 at 37° ,

$$k = 0.0881V - 0.033v_F. \quad (4)$$

The theory of nomograms corresponding to expressions of this type is given by Allcock & Jones (1941, p. 42). The nomogram consists of three parallel straight lines carrying scales of V , v_F and k . It is used by placing a straight-edge so that it passes through the correct values of V and v_F ; the edge then cuts the k scale at the required value of k . Fig. 1 shows the nomogram for Warburg manometer constants, with scales for both O_2 and CO_2 constants at two different temperatures. By its use the values of the constants may be obtained in a few seconds.

A strip of celluloid or other transparent material, with a straight line scribed on its under surface, will be found preferable to the edge of a ruler, since it does not obscure any part of the scales.

The nomogram may be constructed by making use of the mathematical theory given by Allcock & Jones, but it is simpler and, if care is taken, equally accurate, to use the following graphical method. A straight line is drawn near the left-hand side of the paper and marked off with a uniform scale of V values, in any convenient scale units so that the scale covers the range of values likely to be encountered. At any convenient distance another straight line is drawn parallel to the first and marked off with a scale of v_F in any convenient units, but running downwards. Two values of k , fairly well

Table 1. *Corresponding values of k , v_F and V*

k	v_F	V
2.0	1	23.68
2.0	3	25.63
1.5	2	18.97
1.5	4	20.92

separated, are then chosen arbitrarily; for each value of k two convenient values of v_F are selected, and the corresponding values of V are calculated (e.g. from equation (3)), as in Table 1. Four pencil

any value of v_F can then be read off from the appropriate graph. It is necessary to draw a separate graph for each manometer, for O_2 and CO_2 , and for each temperature. The labour, however, is lightened by the fact that the graphs are straight lines and (for a given gas and temperature) parallel to one another, so that parallel rulers may be used. The nomogram seems to be a more convenient method.

lines are then drawn to join the corresponding pairs of V and v_F values and a straight line for the k scale is drawn through the two points of intersection.

the scale to the ends of the line. This is done most easily by the usual method of drawing a pencil line at any convenient angle to pass through one of the

Fig. 1. Warburg manometer constants.

This should be found to be accurately parallel to the other two scales. The scale of k values is then set off along this line by dividing the distance between the two points of intersection into the correct number of equal parts, in this case 5, and continuing

points of intersection, marking it off in inches or other convenient units, drawing a line from the fifth mark to the other point of intersection, and drawing parallel lines from the other marks to cut the k scale. This will divide the k scale into intervals of 0.1.

Each interval may conveniently be divided into 10 parts to give the 0.01 graduations as follows. A pencil of 11 equally spaced lines diverging from a point is drawn on a separate piece of paper, and is cut off with scissors at right angles to the centre line at a point where the total width of the pencil is equal to the distance between the 0.1 graduations of the k scale. If the cut edge is then placed in contact with the k scale, the 0.01 graduations may easily be inserted accurately. The same pencil of lines may be used for several different scales, if they are taken in the proper order, by cutting off the appropriate portions successively. As pointed out by Allcock & Jones (1941), this device may frequently be used for non-uniform scales by making the cut at an appropriate angle.

If desired, a check on the accuracy of the construction of the nomogram may be made, using the mathematical theory as follows. If the distance between the V and v_F scales is 18 cm., if 1 unit of V occupies 2 cm. on the scale and 1 unit of v_F occupies 5 cm., and if the nomogram represents equation (3), the k scale will be situated at a distance of $18 \left(1 + \frac{5 \cdot 0.0881}{2 \cdot 0.0857}\right)$ cm. or 5.04 cm. from the V scale, and 1 unit on the k scale (i.e. 10 of the 0.1 intervals) will occupy $\frac{2 \times 5}{2 \times 0.0857 + 5 \times 0.0881}$ or 16.35 cm.

In some laboratories the vertical type of manometer has been abandoned in favour of a type of Warburg manometer in which the U-tube and scale are tilted backwards at an angle θ with the vertical, as in the Barcroft manometer, for convenience in reading and handling. The constant is then given by the expression

$$k = \cos \theta \frac{\frac{273}{T} v_g + v_F \alpha}{P_0} \quad (5)$$

The same nomogram applies, except that the values shown on the k scale must all be $\cos \theta$ times those shown in Fig. 1.

II. THE BARCROFT MANOMETER

The case of the Barcroft (differential) manometer is more complicated, but the saving of time by using the nomogram method is even more marked. By this method it is easily possible to calculate a constant within 30 sec.

The constant for this manometer is given by the expression (Dixon, 1943, p. 27)

$$k = \left(\cos \theta + \frac{AP_0}{2v'_g} \right) \left(\frac{\frac{273}{T} v_g + v_F \alpha}{P_0} + \frac{A}{2} \frac{273}{T} \right), \quad (6)$$

where A is the cross-section of the U-tube in sq.mm., v'_g is the volume of the gas phase in the left-hand (control) vessel, and the other symbols have the same meanings as in the previous section.

A single nomogram to represent the whole of this expression would be inconveniently complicated,

and it is preferable to use two separate nomograms to obtain the two expressions in brackets, afterwards multiplying them together. Calling the expression in the first brackets C , and that in the second brackets D , we have

$$k = CD. \quad (7)$$

C is identical with the 'correction factor C ' (Dixon, 1937), used in the measurement of CO_2 retention, and the nomogram is also useful for its determination.

It appears that equation (6) involves seven independent variables, but as before several of these may be taken as constant. θ remains fixed for a given installation, P_0 and T may again be considered as constants and α is then fixed for a given gas. We are left with the two variables A and v'_g determining C , and with the three variables A , v_F and v_g (or V) determining D .

If θ is 15° and P_0 (for kerosene) is 13.1 m., we have

$$C = 0.966 + 6.55 \frac{A}{v'_g}. \quad (8)$$

The corresponding nomogram consists of two parallel scales for A and v'_g and a non-uniform C scale which is not parallel to the others, but passes through their respective zeros. It is shown in Fig. 2a. It is readily constructed by the graphical method of the previous section, using two pairs of intersecting lines, drawn between corresponding values calculated from equation (8), to fix the position of the C scale. Any convenient positions and units may be chosen for the A and v'_g scales, provided that they are parallel, cover the required range of values, and run in opposite directions. As the C scale is non-uniform, it is most easily graduated by drawing lines corresponding to a number of selected values of C between A and v'_g values obtained from equation (8). The scale is a very open one, with few graduations, and gives a much greater degree of accuracy than is needed.

In the nomogram for D it is convenient to make the calculation of v_g automatic by substituting $v_g = V - v_F$, as in the previous section. This gives

$$D = \frac{273}{TP_0} V + \frac{273}{2T} A - \left(\frac{273}{TP_0} - \frac{\alpha}{P_0} \right) v_F. \quad (9)$$

For $T = 37^\circ$ and for O_2 , taking the same value for P_0 ,

$$D = 0.0672V + 0.440A - 0.0654v_F, \quad (10)$$

and for CO_2

$$D = 0.0672V + 0.440A - 0.0252v_F. \quad (11)$$

As these expressions for D contain three independent variables, instead of two as in the previous cases, a single alinement nomogram cannot be used. Two alternative types of nomogram are available, namely a 'set-square' nomogram, as shown in Fig. 2b, or a double-alinement nomogram, as shown

in Fig. 2c. The writer prefers the set-square type, but both have their advantages, and as some have expressed a preference for the second type, both are given here.

To use the nomogram in Fig. 2b, a 90° set-square (the corner of a sheet of paper is usually sufficiently accurate) is placed so that one edge passes through V and A and the other edge passes through v_f . The

against it, so as to form a T-square. This is the case, for example, for all values of v_f when $V=34$ and $A=0.8$.

The best way of using this nomogram is to have a sheet of celluloid or thin perspex with its under surface scribed with two straight lines meeting accurately at 90° so as to form a T. With this, no difficulties will arise, and no part of the scales will

Fig. 2a. Barcroft manometer constants. I.

value of D is then indicated by the point at which the second edge passes through the D scale. The square may be placed on the nomogram in any position, provided only that one side passes through V and A and the other through v_f and D . With a few combinations of values (such that the corner of the square lies between the V and A scales or between the v_f and D scales) it will be found that this can only be done if one or other of the sides of the square is prolonged by placing a straight-edge

be obscured as with a set-square or sheet of paper. In reading the intermediate divisions of the D scale, it is necessary to bear in mind that this scale runs from right to left.

The construction is as follows. A straight line is drawn in any convenient position near the left-hand side of the paper and is marked with a uniform scale of V values, using any convenient units. A line for the A scale is drawn parallel to the V scale at a convenient distance from it. The positioning of the

A scale along this line is arbitrary, but should be chosen so that the centre of the useful range of A values comes fairly near the centre of the V scale. The actual units of the A scale, however, cannot be

(or 10 divisions of 0.1) must occupy $2 \times \frac{0.440}{0.0672}$ or 13.1 cm. The A scale must run in a downward direction.

Fig. 2b. Barcroft manometer constants. II.

arbitrarily chosen, but are fixed by the units chosen for the V scale. If the nomogram is to represent either equation (10) or equation (11), and 1 unit on the V scale occupies 2 cm., 1 unit on the A scale

A line for the D scale is drawn in any convenient position accurately at right angles to the V and A scales, and a line for the v_F scale is drawn at a convenient distance away from the D line and parallel

to it. The placing of the v_F scale along this line is arbitrary, but controls that of the D scale, and it should be chosen so that the range of D values most

nomogram is for equation (10), 1 v_F unit must occupy $2 \times \frac{0.0654}{0.0672} \times \frac{1.5}{3.0}$ or 0.973 cm. For CO_2 (equa-

Fig. 2c. Barcroft manometer constants. II (alternative form).

likely to be required lies within the boundaries of the nomogram. The v_F scale units depend on the distances between the two pairs of scales, the constants of the equation, and the units chosen for the V scale. If the distance between the V and A scales is 3 cm. and that between the v_F and D scales is 1.5 cm., and if 1 V unit occupies 2 cm. and the

tion (11)), 1 v_F unit must occupy $2 \times \frac{0.0252}{0.0672} \times \frac{1.5}{3.0}$ or 0.375 cm. The zeros of the v_F scales for O_2 and CO_2 must be placed to coincide if the same D scale is to apply to both. One unit on the D scale (or 10 divisions of 0.1) will occupy $2 \times \frac{1}{0.0672} \times \frac{1.5}{3.0}$ or 14.88 cm.,

and one setting of the square with known values of the variables, calculated from equation (10) or (11), is sufficient to fix its position. All the scales are

edge is then placed so as to pass through this mark and v_p , and the value of D read off at the point at which it intersects the appropriate D scale.

Fig. 2d. Barcroft manometer constants. III.

uniform, and they may be divided by the methods given in section I.

The double alinement nomogram for D (Fig. 2c) is used as follows. A straight-edge is placed so as to pass through A and V , a mark is made at the point where it cuts the reference line B , the straight-

This nomogram is really a combination of two nomograms, each of the type shown in Fig. 1. B is actually the sum of the first two terms in equation (10) and it is determined from the V and A scales. The second setting gives the sum of B and the last term of the equation for D . It is unnecessary to

provide the B line with scale divisions, as it is used merely as an intermediate reference line.

The construction is carried out in two stages exactly according to the principles given in section I. The positions and units of the V , A and v_p scales may be chosen arbitrarily. The position and units of the V and A scales fix the position of the B line, which may be determined either graphically or by calculation as described earlier. The B and v_p scales then fix the D scales according to the same principles. All the scales are uniform and parallel.

In practice, this type is not so rapid in use as the set-square type and it requires more care and accuracy in setting. It is also slightly more confusing and there is some slight danger of taking the scales in the wrong order. Another disadvantage is that it is necessary to mark the nomogram and wear will be caused by erasure of the marks. If the marks are not erased each time, there is some danger of using a previous mark by mistake. On the other hand, its operation is somewhat easier to understand, and it has the advantage that the values for both the O_2 and CO_2 constants of a manometer can be read off at one setting. The accuracy of both types is all that can be desired, being of the order of 0.1%.

To obtain the constant, the values of C and D obtained from their respective nomograms are multiplied together. This may be done with a slide rule, or if desired by a separate nomogram, as shown in Fig. 2*d*. This is an ordinary single-alinement nomogram, except that all three scales are logarithmic. This is most easily constructed by drawing two uniform and parallel scales of $\log C$ and $\log D$, covering the required ranges of C and D , but with the figures only temporarily inserted in pencil. After completing the nomogram with the scale of $\log k$, the actual values of C , D and k are inserted at the correct points to coincide with their logarithms, using a table of logarithms, and the pencil figures erased. Alternatively, the scales may be graduated by projection from a standard logarithmic scale, e.g. a slide rule. This nomogram should be made of reasonably large size, if the accuracy is to be comparable with that already obtained.

The nomogram for C is independent of temperature, but D changes with the temperature. As in the case of the Warburg manometer, scales for more than one temperature may be drawn on the nomogram for D . The double-alinement type (Fig. 2*c*) is

less suitable for this than the set-square type, owing to the confusing effect of the larger number of parallel scales. In the set-square type, since the effect of temperature on the coefficients of the V and A terms is the same, as shown by equation (9), the same V and A scales can be used for both temperatures. The same D scale may also be used if a separate v_p scale is drawn for each temperature at suitably adjusted distances from the D scale. But as the v_p lines for the different temperatures lie very close together it is difficult to avoid overlapping, and it is preferable to draw a separate D scale and associated v_p scale for each temperature. As the placing of these scales is quite arbitrary, provided only that they are at right angles to the V and A scales and that the D and v_p scales retain their relative position, the pair of scales for the second temperature may be placed at any convenient position on the diagram, e.g. near the top, so that there is no risk of confusion between the scales for different temperatures.

It may be pointed out that for O_2 D varies inversely as T ; this is not accurately the case for CO_2 , owing to the large effect of temperature on its solubility.

III. OTHER MANOMETERS

Practically all the types of manometers now in use are covered by one or other of the nomograms given here. Equation (1) gives the constants of the constant-volume differential manometers of Dickens & Greville and of Summerson, as well as those of the Heatley micro-respirometer and Needham's Cartesian diver micro-respirometer. The nomogram of Fig. 1 can therefore be used for all these cases. Equation (6) applies also to the Dixon-Keilin manometer, and the nomograms of Fig. 2 are applicable. It must be noted, however, that the use of other manometric fluids generally requires a change in the scales. This is especially the case if one of the heavy liquids is used, as in the original Dixon-Keilin method.

SUMMARY

Nomograms are given by which the constants of Warburg (constant-volume) and Barcroft (differential) manometers may be determined accurately in a small fraction of the time required for calculation by other methods. Directions are given for their construction.

The nomograms in this paper are being published in booklet form by the Cambridge University Press, Bentley House, 200 Euston Road, London, N.W. 1., price sixpence.

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