A COMPREHENSIVE BOYLE'S LAW APPARATUS.

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IT is often desirable in the laboratory to attack an experimental problem in two or more ways. The most direct and obvious method has the advantage of logical simplicity and, frequently, ease of manipulation, while an indirect means that tests some consequence is, in many cases, far more accurate and instructive.

The piece of apparatus and its manipulations described below enable one to study the relation between the pressure and volume of a gas, at constant temperature, in several different ways. One of these is the usual direct and simple, but unreliable, method that assumes the bore of a tube to be perfectly constant, while certain of the others are less obvious, but instructive, free from assumptions and very accurate.

Referring to the figure, V is a tube of about one centimeter diameter, and seventy to eighty centimeters long, closed at each end with a two-way stopcock. One of the openings at the lower stopcock connects with a tube S that descends in line with V some seventy-five centimeters, where it turns back parallel to itself and rises vertically to any desired height, say for laboratory work from one to two meters above the upper stopcock A . To avoid errors due to capillary action the diameter of this branch should be the same as that of V . A third cock C is placed at the bend and arranged to empty simultaneously both sides of the tube.

CROSS-SECTION OF V CONSTANT.

If the cross-section of V is constant then the volumes of different portions of it are to each other as their respective lengths, and the manipulation is as follows: Close C , turn B till E and V are in communication and leave A open to F or G . Then fill T with clean mercury till it rises to any desired height in V . Next close A and measure the length of V that is still empty. If now the

object is to test the relation for pressures greater than one atmosphere, add more mercury to *T* and at convenient intervals note the lengths of the unfilled portions of *V* and the corresponding differences in level of the mercury in *V* and *T*. If, however, pressures less than one atmosphere are to be studied, then run some of the mercury out at *C* and as before measure the corresponding lengths of *V* and differences in level of the mercury in the two tubes. This difference is always to be taken as positive or negative according as the mercury stands highest in *T* or in *V*. Of course it is seen at once that as the pressure increases the volume decreases, and the law is easily discovered. Let *a* be the height of the barometer, that is, the length of mercury column that would have to be added to *T*, if it was in a vacuum, to produce the same pressure as actually obtains there, at the time of the experiment, due to the atmosphere above it. Also let *l_i*, *l_k* and *h_i*, *h_k* be any two corresponding lengths of *V* and differences in level of mercury in *V* and *T*, then it will be found that approximately

$$l_i : l_k = a + h_k : a + h_i.$$

But $a + h_k : a + h_i = p_k : p_i$ where *p* is the actual pressure on the gas in *V*, and if the cross-section of *V* is constant $l_i : l_k = v_i : v_k$ where *v_i* and *v_k* are the corresponding volumes. Therefore $v_i : v_k = p_k : p_i$ or $p_v = \text{a constant}$.

If a good barometer is not at hand a slightly different method may be adopted, that is Boyle's law, $p_v = \text{a constant}$ (very nearly as we know, at ordinary temperatures and pressures) may be assumed and the assumption experimentally tested by finding the barometric pressure *a* from the proportion $p_i : p_k = v_k : v_i$, or $a + h_i : a + h_k = l_k : l_i$ which gives

Fig. 1.

$$a = \frac{h_i l_i - h_k l_k}{l_k - l_i},$$

and the proof of the law consists in showing that a , as thus found, is, during the experiment, approximately a constant for different values of h and l .

Both the above slightly different methods are unsatisfactory, because they involve the assumption that the bore of V is uniform, which is never exactly true and often far from it, so that in the end the experiment is rather a qualitative calibration of the tube than a proof of Boyle's law.

ACCURATE RATIOS OF VOLUMES.

An exceedingly exact method that involves no assumptions is — open A to F or G and run mercury from T to V till it finally passes into or through A , then close B and turn A till it communicates with the other and still empty opening, and finally turn B sufficiently to allow the mercury that fills V to run out D where it is caught in any convenient vessel and weighed. For pressures greater than one atmosphere close A and again run mercury through B into V , this time compressing the gas, and when it has come to rest close B and measure the difference in level of the mercury in V and T , then open A and B in the order named, collect and weigh the mercury as before. Repeat for as many different pressures as desired.

Let a = height of the barometer,

W = weight of mercury to fill V ,

w = weight of mercury run in to compress the gas,

h = difference in levels of the mercury,

V = entire volume of tube V ,

v = volume of compressed gas.

The observations will show that $W : W - w = a + h : a$. But $W : W - w = V : v$. Therefore $V : v = a + h : a$ and pv = a constant. Or the law may be assumed, giving at once

$$V : v = a + h : a = W : W - w,$$

from which

$$a = \frac{h(W - w)}{w} = \frac{h'(W - w')}{w'} = \text{etc.},$$

and the proof of the law is the constant value of a as thus determined.

This form of the experiment is identical with that given by me in the *PHYSICAL REVIEW* for February, 1900, and is repeated here only for the sake of completeness.

For pressures below one atmosphere leave A open and let the mercury into V till it rises to any common level as J , then collect this and weigh it; again fill to the same level at atmospheric pressure, close A and open C till some lower pressure is obtained, close B , take the difference in level of the mercury in V and T , open A and B in the order named and weigh the mercury that runs out. Repeat for other pressures.

The results give $W - w : W - w_1 = v : v_1 = a - h_1 : a$ from which as before, $pv = a$ constant.

Or, assuming the law,

$$a = \frac{h_1(W - w_1)}{w - w_1} = \frac{h_2(W - w_2)}{w - w_2} = \text{etc.},$$

and, as for higher pressures, the law is established through the constant value found for a .

ARBITRARY FIXED DIFFERENCES IN VOLUME.

Put V in permanent communication with T and by the aid of A and C , but finally with A closed, bring the mercury to any known point in V , to H say, then note the difference in level, now add more mercury to T till it rises to some other point as I (to get the exact place it may be convenient to go above it and finish with C), again take the difference in level, and similarly find at least a third point J . Repeat the whole process with a different amount of gas in V , which is easily obtained by the proper use of the cocks A and C . The mercury must be brought under the resulting new pressures to the same places H, I, J in V as before and the corresponding levels taken.

Let the differences in level for one set of observations be h_H, h_I, h_J , and for another, with a different quantity of gas in V , let the corresponding differences in level be h'_H, h'_I and h'_J .

On comparing these values it will be found that within narrow limits $h_I - h_H : h_J - h_H = h'_I - h'_H : h'_J - h'_H$. That is, whatever

the pressure to begin with, increasing it any number fold decreases the volume to about the same fraction of itself. In other words the relation, whatever it is, between any given pressure and volume is approximately the same for the other pressures and volumes; and to find it for any one it is sufficient to weigh the amounts of mercury necessary to fill V up to the respective heights H , I and J . Let these weights be W_H , W_I and W_J and let the corresponding but unknown pressures be p , np , mp . In this case the differences in level of the mercury columns are to each other as $n - 1 : m - 1$, while the volumes of compressed gas of course are v , v/n , v/m , and the decrements in volume are to each other as $(n - 1)/n : (m - 1)/m$, or as $W_I - W_H : W_J - W_H$. Therefore the final part of the proof that $p v$ is a constant consists in showing that, when the ratio of the changes in pressure is c/d , that of the corresponding differences of mercury in V is $(cd + c)/(cd + d)$.

CALIBRATION.

It is quite practicable for the average beginner to make a partial calibration by means of which accurate results may be obtained. This method is to take the weights of the mercury necessary to fill V to any two levels as H and I , and entirely full. Let V_H and V_I be the volumes of the tube above H and I , and let M_H and M_I be the weights of mercury required to fill these volumes. Let h_H and h_I be the differences in the level of the mercury when it stands at H and I , then the proof of the law consists in showing that for various initial pressures of gas in V , $a + h_H : a + h_I = M_I : M_H$. Or, by assuming the law, in showing that $\frac{h_I M_I - h_H M_H}{M_H - M_I} = \text{a constant}$ (the height of the barometer) whatever the amount of gas and pressure on it in V .

Of course instead of any of the above methods one might first carefully calibrate V through its entire length, and then proceed according to a method too obvious to justify description. But, on account of the time and skill required, this form of the experiment is scarcely adapted to the general laboratory.

SUGGESTIONS.

A few practical hints, born of experience, may not be out of place.

The stopcocks should be kept tight with a suitable stiff lubricant — paraffin with a little vaseline works well. It is advisable to introduce the mercury into T by means of a small funnel or thistle top K whose stem is drawn down to a fine opening. In this way dirt and dust are kept out and only clean mercury admitted.

The differences in level may be read with cathetometers or otherwise as one may desire. For general work a fixed scale back of the instrument is convenient, by means of which the levels can easily be gotten with the aid of paper strips held around the tubes. The levels H, I, J should be arbitrarily chosen points on the scale, or better, temporarily fixed marks on the tube.

If it is desired to have the air in V dry, it may be accomplished by connecting F and G to a suitable drying tube, and of course the whole may be surrounded, though there is but little necessity for it, with a constant temperature jacket. Finally, if the length of T justifies it, high pressures may be obtained in V by means of a compression pump attached to F or G , though the same result may more easily be gotten by adapting the volume of S to the height of T . That is, if the length of T is na , when a is the height of the barometer, the instrument may be worked to its limit without the aid of a pump by having the volume of S roughly $n/2$ times that of V , and therefore, for most laboratory practice, it is sufficient to have these two volumes approximately equal to each other, since this would provide for working with large volumes of gas, when of course changes of volume are most marked, at pressures ranging from zero to three or four atmospheres.

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