No	As usual. Carbon. Per cent.	Left-hand shade ignored. Carbon. Per cent.	Combustion. Carbon. Per cent.
A4.....	0.96 0.99 0.99	0.89	0.88
A6.....	0.955 0.965	0.85	0.85 0.85

LABORATORY OF HENRY DISSTON AND SON'S STEEL WORKS,
PHILADELPHIA, PA.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL AND APPLIED CHEMISTRY, UNIVERSITY OF MICHIGAN.]

A BURETTE FOR ACCURATE GAS ANALYSIS.

BY ALFRED H. WHITE.

Received April 27, 1900.

EVERYONE who has attempted to make accurate analyses of gases with the usual Hempel apparatus for technical gas analysis, knows there are many unavoidable sources of error, slight in themselves, but enough to make an exasperatingly large total at the end of a long analysis. The apparatus to be described was devised in the effort to eliminate some of these sources of inaccuracy. It is a modification of the Hempel burette with Petterson correction tube, the alterations being in the design of stop-cock and the position and form of the manometer, besides a change in the shape of the graduated tube to permit a more accurate reading of the gas volume. It has been used in its present form for the past year in this laboratory, and has been found to fulfil its purpose.

Some of the errors incident to analyses as usually conducted may be avoided by well-known precautions. If mercury instead of water is used as the liquid in the burette, errors due to solubility of the gas in the burette liquid and errors in reading due to water adhering to the walls of the burette, vanish. Errors due to solubility of gas in the reagent of the absorption pipette may be minimized by the use of a small quantity of the reagent in a pipette otherwise filled with mercury and may be greatly lessened when using an ordinary pipette by saturating the absorbing liquid with gas like that to be analyzed. Errors due to diffusion of gas through the liquid in the pipette are much more important than is usually believed, but may be obviated for most reagents by the use of a few cubic centimeters of mercury, forming a trap at the bottom of the pipette. The errors which this paper aims to discuss and in part to remedy are those due to: Change in temperature and barometric pressure during an analysis; inclusion of air or leakage of gas while making connection with pipettes; and inaccuracy in reading gas volume.

Gas burettes in which the gas volume is unaffected by change of temperature and pressure have been devised and are well known. The Petterson correction tube as modified by Hempel, Drehschmidt, and others, consists of a glass tube of about the same dimensions as the burette, sealed at its lower end and with its upper end connected to one arm of a manometer whose other arm connects through a three-way stop-cock with the gas burette. This correction tube is enclosed in the same water-jacket as the burette, and hence the gas volume in it is affected by changes of temperature to just the same extent as the gas in the burette. When the liquid stands at the same height in both arms of the manometer, the pressure in the burette is the same as in the correction tube and therefore a constant, as the correction tube is sealed at its lower end. If the gas volume is read under these conditions it will be independent of changes in external temperature and pressure. There are several objections to the Hempel form of apparatus. The two rubber connections of the manometer may allow leakage of gas and consequent change in the supposedly constant pressure of the correction tube. Second, in drawing the gas out of the manometer into the burette there is a pronounced tendency on the part of the column of liquid to break when it starts down hill, especially at the rubber connection, with the result that some of it becomes carried into the burette with consequent change in the pressure indicated by the manometer. Figures 1 and 2 show the arrangement designed to overcome this difficulty. There is but one rubber connection in the manometer, and that is placed so that only mercury and never gas is brought in contact with it, thus rendering a leak with consequent change in pressure of the correction tube impossible. Communication with the manometer is established by turning stop-cock to position in Fig. 4. By placing the manometer below the stop-cock the further advantage is gained that in drawing the gas out of the manometer the mercury travels but a short distance and up hill only, meets with no bends

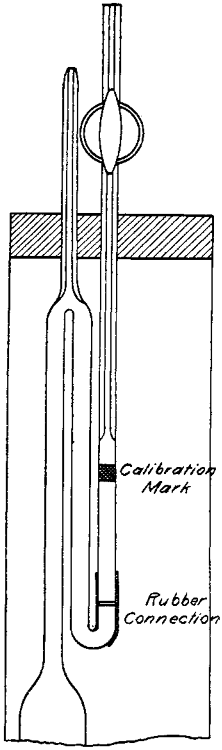

Fig. 1.

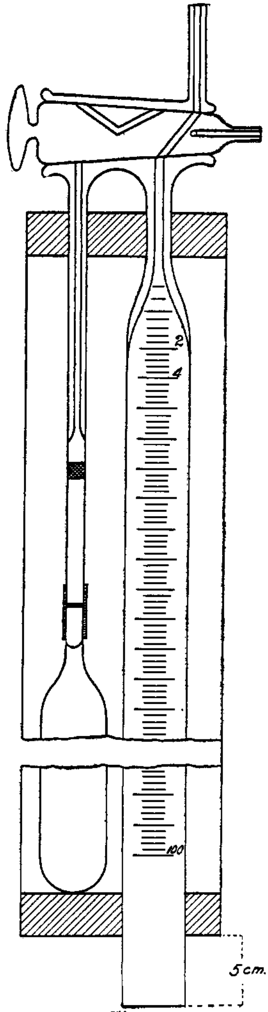

Fig. 2.

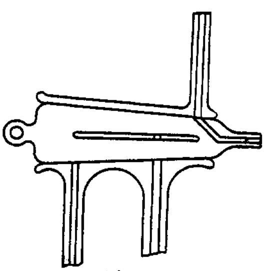
Fig. 3.

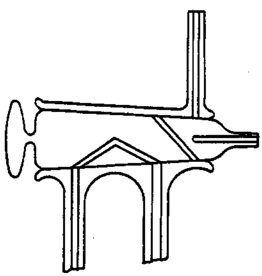
Fig. 4.

or inequalities in the tubing, and so may be drawn with great exactness to the stop-cock, drawing out all the gas without losing any of the mercury. The apparatus is all enclosed in the water-jacket and therefore all the same temperature, and is less cumbrous and apt to get broken than in other forms. The capillary tube projecting into the air behind the stop-cock as shown in Fig. 1 is to be sealed, under observed barometric pressure if desired, when the apparatus is first set up. The gas volume may be read when the mercury is at the same height in the two arms of the manometer and may then be reduced to standard conditions if desired. When this is not required, it is much more accurate to bring the mercury to a mark etched on the glass, or better tangent to the lower edge of a black metallic collar cemented around the manometer tube. In this case the gas will not be under the same pressure as that in the correction tube, but the variation will be a constant one and will cause no error. The connection between the burette and pipette is, as usual, made by a bent capillary tube and two rubber connections. Rubber connections, if properly made, introduce no appreciable error, but, because of their tendency to leak, form a serious menace to accuracy. Unfortunately no way has been found to dispense with them, and they are accepted by the author as a necessary evil. There is, however, an inherent source of error in the usual method of making the connection which the burette here presented completely obviates. With the apparatus ordinarily used, some of the gas under analysis will escape, or some unmeasured volume of air will be admitted to it whenever a connection is made. Perhaps usually both happen. The capillary tip of the burette, the connecting capillary, and the capillary tip of the absorption pipette, have a combined volume of about 0.5 cc. Although by various manipulative devices it is possible to restrict the error thus introduced from any individual operation to a fraction of this volume, it amounts in the course of a long analysis to a serious total. In the burette here presented it is completely eliminated.

By referring to Fig. 3, the stop-cock is shown turned in such a way that there is a clear passage from the capillary exit tube of the burette through the stop-cock to the outer air again. With the stop-cock in this position the pipette is to be connected in the customary way to the burette but without any of the usual precautions to prevent inclusion of air. The liquid in the pipette is now blown up and through the capillary till it reaches the stop-cock. The capillary tube is thus completely filled with liquid. By turning the stop-cock to the position shown in Fig. 2 communication is established between the burette and pipette, and the gas may be passed over and absorbed as usual. After the absorption it is drawn over till the pipette-liquid just reaches the stop-cock, which is then turned back to the position in Fig. 3, allowing the liquid in the capillary of its own accord to siphon back into the pipette. The capillary is then to be rinsed out with a wash-bottle. In this way all the gas is each time drawn back into the burette for measurement. There is no gas lost in the capillary connecting tube, and no air is introduced, if the rubber connections have been properly made.

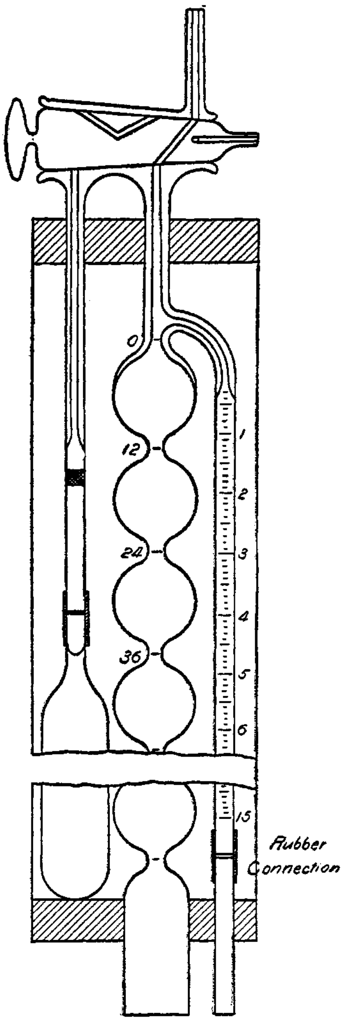

Fig. 5.

The gas volume in an ordinary gas burette may read with great accuracy with the assistance of a telescope, or some similar help, but it was desired to render such an adjunct unnecessary. The suggestion was taken from one of Bleier's[1] sketches. Fig. 5 shows schematically a gas burette with stop-cock and manometer as already described. The main body of the burette contains twelve bulbs, each of a capacity approximating 12 cc. A line is etched on each constriction and the capacity of the

[1] C. Bleier, "Ueber gasometrische Apparate." *Ber. d. chem. Ges.*, **31**, I, 238.

bulb between these marks is determined. Starting from the capillary above the top bulb a side arm springs, terminating in a small burette with total capacity of 15 cc. and graduated in 0.1 cc. Both these burette tubes connect at the bottom by means of heavy rubber tubes and a Y with a stop-cock on each arm, to a common leveling bottle. A screw clamp on each rubber tube serves for the exact adjustment of the mercury. To measure a gas, the stop-cock is placed in position in Fig. 3 and the mercury in the bulbed tube brought to the mark in one of the constricted portions by opening the proper stop-cock on the Y and raising or lowering the leveling bottle. When adjusted, the mercury is held in its proper position by closing the stop-cock on the Y. The stop-cock leading to the small burette tube is then opened and the gas brought to approximately atmospheric pressure by proper change in the mercury level. The three-way stop-cock at the top of the burette tube being now turned to position in Fig. 4, the burette is brought into connection with the manometer, which is properly set by further changing the level of the mercury in the small burette. The final adjustment in both burettes is made by the screw clamps on the rubber tubes. The volume of the gas will be read as x cc. in the bulbs $+ y$ cc. in side burette $+ z$ cc. in manometer. As there are these three readings to be made it is necessary that each be very accurate. Let us see how accurately this may be done. First, the mercury in the bulbed tube is to be brought to a specified mark in a tube of about 5 mm. internal diameter. By means of the screw clamp this may be done with such accuracy that the error is negligible. Second, the volume of gas in the side tube must be read. Each 0.1 cc. in this tube occupies a space of a little over 2.5 mm. and it is possible to interpolate 0.01 cc. with the eye with an error of less than 0.02 cc. Third, the mercury in the manometer must be brought to a definite mark with such exactness that the barometric pressure, under which the gas volume is read, shall be almost identical each time. A difference of 1 mm. of mercury pressure changes the gas volume 0.13 per cent., which on a volume of 100 cc. equals 0.13 cc., an error far too large. It was found impracticable to attain the required accuracy when it was attempted to bring the mercury to a mark etched on the glass. The best device was found to be a band of thin, blackened copper, wrapped around the tube and cemented to the glass. It is possible to bring the mercury tangent to the lower surface of this with great exactness. In working with this burette the author is accustomed to make all readings in duplicate, readjusting at all points each time, and to repeat if the two differ from each other by more than 0.01 cc. Duplicates usually agree within this limit. The greatest difficulty found in manipulation is to draw the liquid from the pipette over exactly to the burette stop-cock and stop it there. If it gets into the burette, a bubble lodging in one of the capillary tubes frequently damps the sensitiveness of the manometer. If this happens the bubble may be shot out of its lodging place by compressing the rubber tube above the screw clamp. Such a bubble may also be carried into the manometer, where it will obscure the surface of the meniscus. To remedy this it is well to keep 2 or 3 mm. of water on the surface of the mercury in the manometer. This allows a perfectly sharp reading of the mercury meniscus below the water-level. The manometer should respond to a very slight movement of the screw clamp.

The advantages of this burette may be summarized as follows: It is a compact burette which, without reading-telescope or other accessories, allows the volume to be read with an error of less than 0.02 cc., compensates automatically for changes of temperature and pressure, and avoids completely all errors due to inclusion of air or loss of gas in making connections with the absorption pipettes. The disadvantages so far developed are chiefly those inherent in all forms of apparatus which possess a stop-cock and rubber connections. Both may leak: but on the other hand both may be kept so tight for limited periods of time as to introduce no measurable error.

Accurate apparatus is essential for accurate work and the author feels it but a just acknowledgment to thank Messrs. Greiner and Friedrichs for the care and skill with which they manufactured the burettes from his sketches.

ANN ARBOR, MICHIGAN,
April, 1900.