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A MANOMETRIC GAS ANALYSIS APPARATUS

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ABSTRACT

The apparatus here described is designed for the analysis of gas mixtures under the following conditions:

(1) When the volume of the sample is small—about 5 to 0.5 ml—and a reasonably accurate analysis is desired.

(2) When the volume of the sample is of the order of magnitude of 0.2 to 0.1 ml, and an approximate microanalysis is desired.

(3) When the gases to be analyzed are dissolved in some liquid from which they must be liberated prior to analysis, as in the analysis of blood gases.

The apparatus is adapted for use with the admirable procedures of Van Slyke. The present design eliminates the two principal errors inherent in the Van Slyke apparatus, as well as the mechanical shaking, which some have found to be an objectionable feature. By extending the apparatus here described, analysis by combustion may be performed, and greater operating conveniences achieved if desired.

CONTENTS

I. INTRODUCTION

In the field of gas analysis which lies between the strictly micromethods and the usual macromethods, and which includes the analysis of gases dissolved in liquids such as blood, the work of Van Slyke is outstanding. The Van Slyke methods have been described so comprehensively that the text[1] can be recommended as a standard reference on this particular type of gas analysis.

In 1934, several errors inherent in the Van Slyke apparatus were discussed and experimentally demonstrated.[2] At that time, a modification of the Van Slyke apparatus and procedure was suggested as follows:

"The Van Slyke apparatus may be modified by placing two parallel chambers in the water jacket, one to function as an extraction and reaction chamber, the other as a fixed volume burette.

"This procedure would possess several additional advantages. It would always be possible to avoid redissolving some portion of an

[1] John P. Peters and Donald D. Van Slyke, Quantitative Clinical Chemistry, Vol. 2 (The Williams and Wilkins Co., Baltimore, Md., 1932).

[2] Martin Shepherd, *Significant vapor pressure considerations of the Van Slyke manometric methods of gas analysis*, BS J. Research 12, 551 (1934) RP680.

extracted gas sample, for which the correction is troublesome and not always satisfactory. This could be achieved by transferring the liberated gas from the extraction chamber to the burette under the pressure at which extraction occurred. Each reagent could be freed from gas in the apparatus before bringing the gas mixture into the reaction chamber. Physical solution of components of the gas mixture in the reagent employed could be reduced for macroanalyses and almost avoided for microanalyses. The various fractions of the gas mixture would always be accurately measured under the same condition of humidity. The measurement of gas volumes (or pressures) would always be made by adjusting a clean mercury meniscus to a reference mark, thus avoiding obscure solution menisci. Solutions from which gas samples were extracted, as well as reagents subsequently employed, could be expelled from the extraction chamber at each step of the analysis. This technique would permit straightforward, clean reactions with no interference, either chemical or physical, from accumulating mixtures of various liquids that have already served their purpose in the analysis. Reagents of any desired strength could be employed. There would be no hydrostatic pressure to correct for, and the *c correction*, as well as all others applied by Van Slyke, would merely resolve into a simple correction for the change of pressure of the gas and saturated water vapor with any change of temperature which might occur during the analysis."

Shortly thereafter an apparatus which realized all of the advantages mentioned above was constructed. The use of this apparatus in our laboratory has been limited during the past 6 years, and other projects have prevented its further development along lines suggested in what follows. Its possibilities, accordingly, have not been thoroughly explored, but enough experimental work has been done to indicate its value and warrant describing it in its present form.

II. DESCRIPTION OF APPARATUS AND PROCEDURES

The construction of the apparatus is illustrated in the drawing (fig. 1) and photograph (fig. 2). The essential feature is the inclusion of an extraction and reaction chamber, *R*, which is separate from the constant-volume burette, *B*. The Van Slyke apparatus has only a vessel corresponding to *B*.

For those not familiar with this type of apparatus, a very brief outline of the general procedure to be used with the Van Slyke and the new apparatus will serve to clear the picture and to point out the reasons for the new deisgn.

With the Van Slyke unit, the procedure is as follows: Blood to be outgassed (or a sample of free gas) is introduced over mercury into the single vessel corresponding to *B*. The mercury is then dropped to a level corresponding to the 50 ml mark of figure 1, and the evolved gas is collected in the partial Torricellian vacuum above. The gas is then measured by raising the mercury back to a level corresponding to the 2 ml or 0.5 ml mark and noting the pressure on the attached manometer. Some gas will redissolve in any liquid present during this procedure. Next, the reagents are admitted, one at a time, to absorb various constituents of the freed gas. With the addition of each reagent, a correction for hydrostatic head must be made. Furthermore, a correction for the lowering of vapor pressure is necessary each time; and, as this is prescribed by Van Slyke, a change in temperature may introduce further error in this correction.[3] In addition, the accumulating reagents (which must be selected with reference to their chemical behavior with each other as well as with the gases) cause increasingly greater errors of physical solubility, which must be accounted for. Sometimes these reagents make difficult the adjustment of the confining meniscus.

This procedure should be compared with the general one used with the new apparatus. Here, if a sample of blood or liquid containing dissolved gases is to be examined, it is introduced into *R* and there outgassed. The *gas* only is then transferred, at the lowest pressure existing during outgassing, to the clean burette, *B*, and there, isolated from the liquid, it is measured while saturated with respect to water vapor only. The blood or other substance is then expelled from *R*, the first analytical reagent is introduced and outgassed directly in *R*, the gas liberated from this reagent is discarded, and then the gas in *B* is transferred to *R* for the reaction. After the absorption, the residual gas is transferred back to *B* at the lowest pressure existing during absorption, and again measured while saturated with respect to water vapor only. The two volumes so measured compare directly with respect to saturation. No gas has been absorbed by the original liquid, or by the reagent. Furthermore, no gas has been given off from the reagent during the actual absorption.

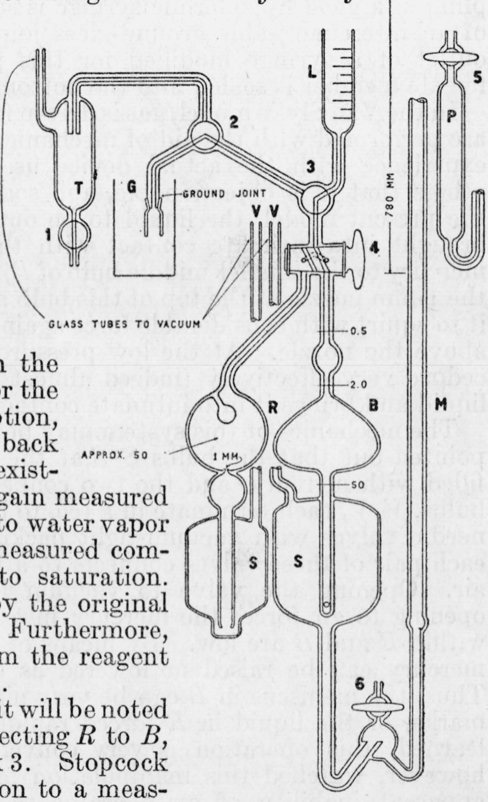

FIGURE 1.—*Assembly drawing of manometric gas analysis apparatus.*

Referring again to figure 1, it will be noted that stopcock 4 permits connecting *R* to *B*, and either *R* or *B* to stopcock 3. Stopcock 3, in turn, provides connection to a measuring tube *L* (a feature of the Van Slyke design which has been retained) or to stopcock 2. Finally, stopcock 2 offers connection to a trap used to collect and discard liquids from *R*, and to a small bell, *G*, which may be used to collect small samples of gas for analysis when this bell is immersed in mercury.

With this arrangement, liquids to be outgassed are measured in *L* and transferred therefrom to *R*, the various reagents are introduced by the same route, exactly as prescribed by Van Slyke, a procedure which is objectionable because of the difficulty of maintaining the lubricant of stockcock 4 in good condition under this treatment. For this reason, a later modification, not shown in figure 1, has been added.

[3] See footnote 2 for complete discussion of this "c correction."

This is a capillary delivery tube leading from a reservoir (located next to T) directly into the middle bulb of *R* by means of a ring seal. The reservoir is provided with a vacuum connection at the top, and the reagent, in considerable quantity, can be outgassed in this reservoir. This eliminates one step in the analysis, and provides a reserve supply of gas-free reagent. As many of these reservoirs as there are required reagents, connected by a suitable manifold for delivery of liquids from the bottom and another for evacuation from the top, would prove a great convenience. This arrangement also prevents fouling of the lubricant of stopcock 4, which *must never leak*.

In the introduction of blood or other liquids for outgassing, sampling in a good hypodermic syringe is suggested. The male member of an interchangeable ground-glass joint should be attached to the outlet of a syringe modified for this purpose. The corresponding female member is sealed into the bottom of the tube, *L*.

In the Van Slyke model, gas is driven from solution and the reactions are performed with the aid of mechanical shaking. We have had no experience with the actual device used, but we understand from others that it is objectionable, and sometimes causes breakage. In the present model, the liquid to be outgassed, or the reagent to be brought into intimate contact with the gases, is transferred over mercury to the smaller middle bulb of *R*, and then forced back through the 1-mm nozzle at the top of this bulb at rates great enough to cause it to squirt with considerable force against the spherical baffle directly above the nozzle. At the low pressures existing within *R*, this procedure very effectively (indeed almost spectacularly) breaks up the liquid and brings it into intimate contact with all of the space in *R*.

The mechanics of this system may be readily understood when it is pointed out that the bulbs *S–S* at the bottom of both *R* and *B* are filled with mercury, and the two connections from the tops of these bulbs, *V–V*, each terminate in a tee, to both arms of which are affixed needle valves with vacuum-tight packings (Stimson type). One of each pair of these valves connects to a vacuum line, the other to the air. Opening the valve to vacuum lowers the mercury in *S–S;* opening to air forces the mercury into *R* and *B*, since the pressures within *R* and *B* are low. By means of the needle valves for control, mercury can be raised or lowered as slowly or rapidly as desired. Thus, the meniscus in *B* can be very nicely adjusted to the reference marks, or the liquid in *R* forced rapidly through the nozzle. Once learned, this operation is very conveniently performed. We have, however, watched this manipulation fail repeatedly because of the apparent inability of an operator to acquire the necessary skill. Therefore, the following modification is suggested for those who may prefer it. The lower ends of *S–S* may be terminated in tubes to which control stopcocks [4] are sealed. To these cocks, ordinary leveling bulbs may be connected by means of rubber nitrometer tubing. Ring supports for these bulbs, at the levels of stopcocks 3 and 6, will permit adjustment of the mercury levels so that the necessary operations can be performed. The leveling bulbs need not be held in the hand, but instead, the flow of mercury can be regulated by the control cocks with the bulbs in one of the two fixed positions. Traps should be interposed between the leveling bulbs and the two vessels *R* and *B*, so that no air can be carried into the apparatus.

[4] Martin Shepherd, *A simple control stopcock for gas analysis apparatus*, BS J. Research 4,23 (1930) RP130

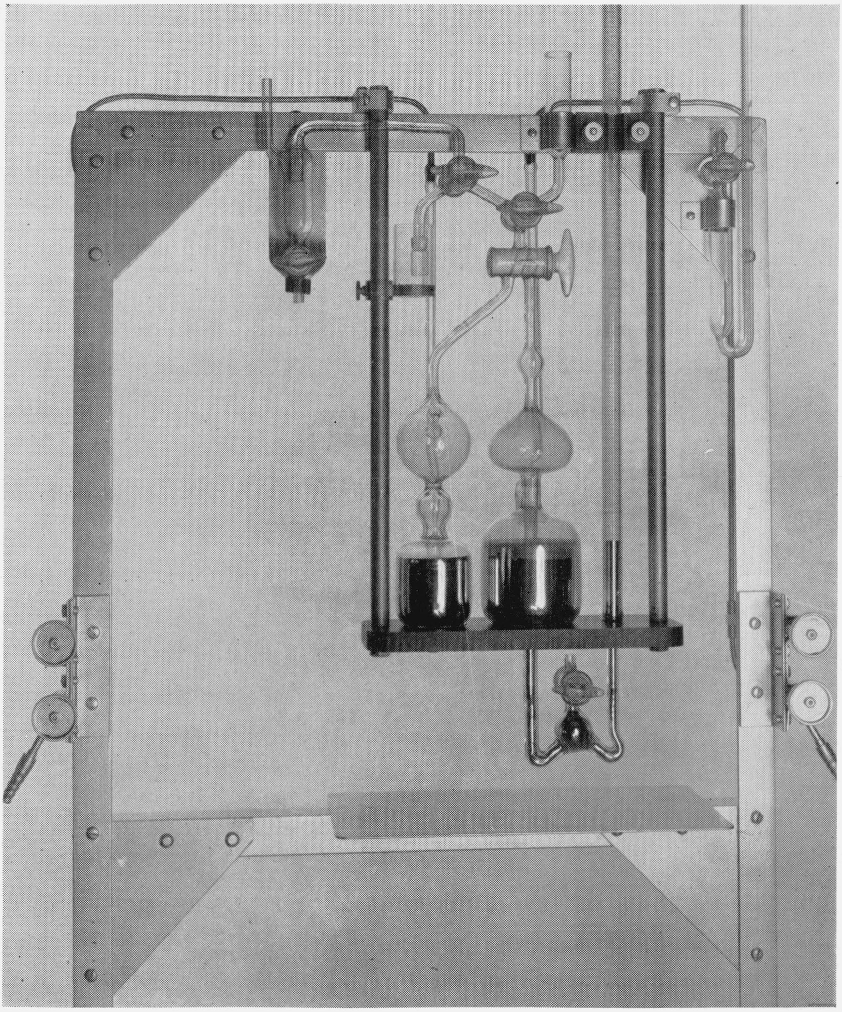

FIGURE 2.—*Manometric apparatus.*

The burette, *B*, is calibrated as shown (fig. 1). For approximate microanalysis, lesser volumes should be included in this calibration. Blackened copper collars are affixed to the stems at the etched lines, since the adjustment of a mercury meniscus to the lower edge of such a collar, in the manner in which a barometer is read, can be made with greater reproducibility than adjustment to an etched mark.[5]

The manometer, *M*, registers the pressures obtained within *B*. This may be provided with a sliding scale with stops at the three positions corresponding to the levels of the three reference marks on *B;* or the scale may be engraved on the tube of *M*, and the three readings of this fixed scale, which correspond to the reference marks on *B*, can be determined with a suitable telescope. The stopcock affixed to the top of the Van Slyke manometer has been eliminated in favor of the considerably more certain arrangement shown (fig. 2). This is a standard form in which the vacuum is obtained by forcing mercury around the capillary at the top of *M* and down into the reservoir, *P*. Vacuum applied at stopcock 5, and pressure through stopcocks 2 and 4 to B, will fill the manometer. Opening cock 5 to the air will complete the operation. The lower entrance to *M* is guarded by trap 6, from which accumulated gas may be removed via the stopcock there placed.

The whole unit, up to the level of stopcock 4, is immersed in a water jacket. A good grade of museum jar is well suited for this purpose. The method of mounting is shown in the photograph. The jar rests upon the metal shelf shown below the trap at stockcock 6. The needle valves for control of mercury flow are conveniently placed to the right and left on the supporting frame.

After the discussion which has preceded, no detailed schedule of operation is necessary. For the actual technique and procedures involved, the remarkably complete account of Van Slyke should be consulted, and modified only as indicated in the following section.

III. PRECAUTIONS IN OPERATING THE APPARATUS

Three characteristics of the new apparatus should be mentioned in order to avoid trouble during the initial stages of manipulation.

It must be remembered that, while the pressures in *R* and *B* during an analysis are low, they are nevertheless above atmospheric. It is therefore possible, by injudicious and too abrupt manipulation of the controlling needle valves, to reduce the pressures above the mercury in the reservoirs *S–S* to a point where gas and liquid in *R*, or gas in *B*, will be drawn down the tubes and around the mercury seals into *S–S*. This is easily enough avoided, and a little experience will suffice to eliminate the danger.

Sometimes the spherical baffle in *R* does not prevent the formation of slugs of liquid in the capillary connecting this bulb to stopcock 4. If these form, they must be removed before transferring gas from *R* to *B*—otherwise the whole object of the new design will be defeated. These slugs of liquid can be removed by adjusting the level of liquid in *R* to the lowest point, and then slowly admitting mercury from *L* through 3 and 4 to *R*.

Once in a while, if the mercury and liquid above it have been too abruptly lowered in *R*, a bubble of vapor forms beneath the nozzle

[5] E. R. Weaver and Martin Shepherd, *A burette for the accurate measurement of gas volumes without gas onnection to a compensator*, Sci. Pap. BS **22**, 375 (1927) S599.

and prevents drainage of some of the liquid (not mercury) into the small middle reservoir. The only remedy for this difficulty is to force the mercury back through the nozzle and repeat the operation of lowering the liquid, using a more gentle approach. This difficulty has been experienced occasionally with a 1-mm nozzle, but not with a 2-mm nozzle. The larger nozzle does not produce the fine spray and complete breaking up of the liquid that was obtained with the smaller one. The optimum size has not been determined, but the smaller of the two sizes tried seems preferable.

In addition to the above precautions, the prospective user should have in mind the general volumetric limitations of an apparatus of this type. In this particular model, when gas is transferred from *R* to *B*, it should be remembered that liquid from *R* must not enter *B*. This means that the reagent in *R* must be raised only to a point level with the entrance of the V-bore of cock 4. The bore of this cock then contains some of the gas that should be measured in the fixed volume burette, *B*. A slight error is thereby introduced. This may be calculated for the worst cases:

(1) the volume of the bore is 0.05 ml. (It could be made smaller.)

(2) The pressure of a gas in *B* adjusted to any reference mark rarely exceeds 600 mm.

(3) The percentage errors will be highest when small volumes are measured. Therefore, assume 0.5 ml of gas at 600-mm pressure. When this gas is transferred between *R* and *B*, the pressure existing in the V-bore of cock 4, which is the pressure of the gas trapped therein, is 6 mm. Its volume at 600 mm would therefore be 0.0005 ml. This is 0.1 percent of the total gas volume.

(4) Since, with each measurement of a volume, the amount of gas trapped is decreased in proportion to the amount absorbed, the resulting error in comparing any two constituents is <0.1 percent of the mixture, and the overall error from this source, if all constituents were removed, would be 0.1 percent.

This feature of design is therefore not objectionable. Much more serious is the fact that the amount of water above and below the mercury in *B* may vary. In practice a film of water should be kept upon the walls of *B*, but water must not obscure the mercury meniscus. If water collects above the mercury, the "fixed" volume will have changed; and the amount of this change may be expected to shift slightly but significantly during the analysis. This difficulty is somewhat more aggravated in the Van Slyke model, but is sufficiently troublesome in the present one to prevent the use of the apparatus for accurate work with very small volumes. The same thing is true for most micro gas analysis apparatus. If high accuracy is required, one must use considerably more complicated apparatus, and procedures, involving the transfer of gases by condensation or freezing to negligible vapor pressures, or by mercury displacement pumps, and the measurement of gas in the dry state.

WASHINGTON, November 14, 1940.