A MODIFIED HYDROGEN SULPHIDE GENERATOR.

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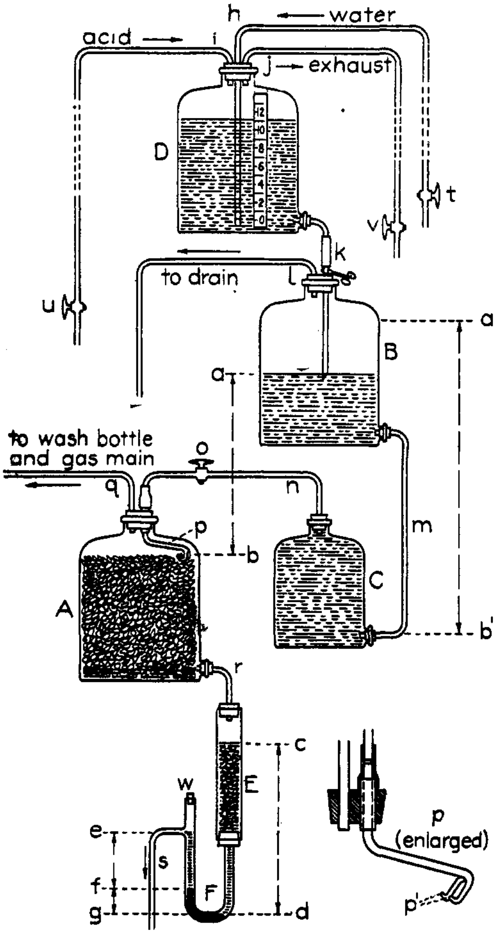
In 1892 Ostwald[1] described a gas generator of a type that has since been employed in more or less modified form by many teachers of analytical chemistry. For several years an apparatus of this sort has been put to a practical test in this laboratory, with the result that it has for our purposes proved unsatisfactory in at least four particulars. In the first place, the gas is not evolved at uniform pressure. The level of the acid in the uppermost bottle often undergoes appreciable change due to the alternate generation and utilization of an excess of gas. Aside from this oscillatory change in pressure there is also a continuous diminution in pressure, owing to the gradual consumption of the acid. Second, the progressive accumulation of spent acid in the lowest bottle materially diminishes the active surface of the ferrous sulphide. Third, the constant dropping of the acid upon one spot tends toward the formation of a cylindrical channel through the solid, with the result that the fresh acid has but little opportunity to act upon the solid before mixing with the spent acid below. And fourth, the apparatus requires entirely too much attention. This was found to be the case even when bottles capable of holding 25 kg. of ferrous sulphide and 14 liters of acid, respectively, were employed. It must be admitted, however, that the test to which the apparatus has been subjected was a rather severe one. Other well-known forms of apparatus have been subjected to the same practical test in this laboratory through a period of years, with equally unsatisfactory results. The elementary classes in analytical chemistry to be supplied in this laboratory with hydrogen sulphide contain from 175 to 275 students, of whom from 50 to 125 work in the laboratory at the same time, and the great majority of whom work in the laboratory at least nine hours per week. In order conveniently to supply classes of this size with an adequate amount of hydrogen sulphide it is essential that the generator should be capable of producing the necessary amount of gas under constant pressure, of regulating automatically the supply of fresh acid, and of effecting automatically the removal of the waste solution after the acid has been thoroughly neutralized.

[1] Z. anal. Chem. 31, 183 (1892); Grundlinien der Anorg. Ch. p. 282, (1904).

In attempting to modify the Ostwald apparatus so as to adapt it to the requirements of this laboratory, the authors have made free use of many suggestions contained in the literature of gas generators. Especial indebtedness to the excellent treatises of Küster,[1] Richards,[2] Bradley[3] and Parsons[4] must be acknowledged.

The apparatus finally adopted and tested during the past year is shown in the accompanying sketch. The tubulated bottles



[1] J. pr. Chem. [2] 48, 595 (1893); Chem. Ztg. 29, 158 (1905).

[2] Am. Ch. J. 20, 189 (1898).

[3] Ibid. 21, 370 (1899).

[4] This Journal, 25, 231 (1903).

A, B and C correspond with the main parts of the apparatus of Ostwald, Küster and Bradley. A and B each have a capacity of about 14 liters, while C is considerably smaller. Hydrochloric acid (prepared by diluting the concentrated commercial acid with an equal volume of water[1]) flows from B through m into C and then through n, o and p into the ferrous sulphide bottle A. The evolved gas passes through q into a wash-bottle containing water, and thence through a lead pipe to the hoods, where it may be obtained as needed by the students through 52 separate outlets. For the sake of economy, a device somewhat similar to that used by Parsons has been adopted, the flow of gas through the outlets being restricted to from 2 to 5 bubbles per second. Still further economy has been gained by insisting that precipitation shall be effected, whenever feasible, in closed flasks, somewhat after the manner suggested by Graebe.[2] The hoods and the generator itself are located in a separate room thoroughly ventilated by means of a fan operated by an electric motor. Leakage from the apparatus itself has been prevented by previously soaking all rubber stoppers and tubes in molten paraffin before wiring them in place.

The difficulties experienced with the Ostwald apparatus have been overcome as follows: In the first place, the oscillatory changes in pressure have been entirely obviated by causing the acid to fall upon the solid through two openings of small diameter. When the apparatus is furnishing but a small amount of hydrogen sulphide (as is the case for example when gas is being drawn from not more than 10 to 12 outlets at once), the acid slowly oozes from the two tips marked p′, flows down the outside of the tubes, and finally drops from the two elbows (see enlarged sketch of p) upon the solid below. When the apparatus is suddenly compelled to furnish comparatively large amounts of gas, however (as is very often the case when, at the beginning of a period, gas is being drawn simultaneously from every outlet), the acid is automatically thrown out through the tips for a few seconds in two diverging streams. Thus a large surface of the solid is almost instantaneously moistened with the acid, and gas is at once evolved in considerable quantity. As soon as pressure equilibrium is restored, the supply of acid is automatically cut down to a speed depending upon the rate of consumption of the gas

[1] Sartorius: Chem. Centr. 1904, I, 246.

[2] Ber. 31, 2981 (1898).

by the students. Even if all outlets are suddenly closed at this time there is no appreciable excess of gas evolved. In fact, during the normal running of the apparatus, an excess of gas sufficient to force its way over into C or even up into p for any considerable distance is never evolved. It is obvious that the nicety of this automatic adjustment of the supply of acid must depend upon the promptness with which the acid and the solid react. After A has been freshly filled with ferrous sulphide the reaction takes place rather slowly, however, even though the solid has just been broken up, and may have many perfectly fresh surfaces. For one or two days after the semi-annual filling has been accomplished, the apparatus does not work at quite its normal efficiency, unless the precaution has been previously taken of permitting the ferrous sulphide to stand for a time in a solution of ferrous chloride, before subjecting it to the action of the hydrochloric acid.

The gradual diminution in pressure noticed with the Ostwald apparatus, and due to the consumption of the acid, has been prevented by using the tubulated, 14-liter bottle D. When all of the stop-cocks t, u and v on the glass tubes h, i and j are closed, the acid in D will flow out through the tube k only so fast as is necessary to keep the acid in B at the level a. Devices entirely similar in principle have of course long been used in other fields of work, and have been employed by Breyer,[1] Kalecsinszky[2] and Parsons for the maintenance of constant pressure in gas generators. In order to prevent the trapping of air bubbles it is important that the upper part of the tube k should not be exactly horizontal, but should slope downward at every point. The inside diameter of k should not be less than 1.5 cc. The tube l serves the purpose of carrying off fumes that may gather in B. It is open at the end, as atmospheric pressure should prevail in B. In our earlier experiments D was filled by pouring in water and acid by hand, after slipping a spring clamp over the short piece of rubber tubing at k, and was then tightly closed at the top by means of an unperforated rubber stopper. It was found possible to accomplish this rather disagreeable task much more rapidly and conveniently by means of an ordinary laboratory suction-pump. The glass tube h reaches to the bottom of a cylinder capable of holding about 6.5 liters of water, and placed con-

[1] Z. anal. Chem. 28, 438 (1889).

[2] Ibid. 31, 544 (1892).

veniently beneath a water tap. The glass tube i leads to the bottom of a carboy of concentrated commercial hydrochloric acid, while j communicates with a strong suction-pump. In order to fill D the suction-pump is turned on, the stop-cocks t and v are opened, and u is closed. After about 6.5 liters of water have been drawn in, t is closed, and u opened until the same quantity of acid has been introduced, when u is again closed. To insure thorough mixing of the acid and water t is now opened for a moment to permit air to bubble in through h, and is then closed, after which the spring clamp is slipped off from the rubber tube at k. One filling usually suffices to keep the apparatus running at constant pressure for at least one week, even when the class numbers about 275 students. When the class is smaller the supply lasts proportionally longer.

The second difficulty with the Ostwald apparatus was eliminated by effecting the continuous removal of the thoroughly neutralized spent acid. By the force of gravity the spent acid flows down through r, the inside diameter of which should be not less than 1.5 cc. in order to prevent the tube from acting as a siphon, or from being clogged with sediment. Care should be taken, moreover, not to have the upper portion of this tube exactly horizontal, but to have it slope downward at every point, in order to prevent trapping of gas bubbles. After passing through r, the spent acid enters E, a glass tube with an internal diameter of about 5 cm. This tube is filled with pieces of ferrous sulphide which serves the double purpose of thoroughly completing the neutralization of the acid, and of indicating in a general way the extent to which neutralization has been accomplished in A. Only very rarely may effervescence be seen to take place in E as the spent acid falls upon the solid. If, however, the level of the solid in A has been permitted to fall too low, or if for any reason the acid is cutting a channel through the solid in A, then a more or less brisk effervescence in E will call attention to the fact. From E the thoroughly neutralized acid flows by gravity into the U-tube F, which should have an inside diameter of not less than 2 cm. The right-hand end of this tube is sealed off, but is provided with two lateral openings each with a diameter of about 1 cm. This arrangement prevents clogging of the tube with small pieces of ferrous sulphide. The left arm of F is furnished with a side tube, s, through which the spent acid is finally carried to the drain. The lower part of F is filled with mercury. This obviates the necessity of prolonging the left arm of F to a considerable elevation, and very effectively prevents the clogging of F with the fine material that gradually settles to the bottom, especially when the stop-cock o is closed and the apparatus allowed to remain inactive for some time. The apparatus has been permitted to rest in this condition for a number of weeks, and yet has not in any case shown the slightest sign of clogging when once more set in operation. The side tube s must enter F at a distance above the mercury sufficient to prevent loss of mercury globules thrown up by the occasional rapid bubbling of spent acid past the mercury. The amount of mercury to be used in F must obviously be governed by the following facts: The sum of the pressures represented by the vertical lines f g and e f must be greater than the pressure represented by a b, the normal pressure of the apparatus, in order to prevent loss of gas through F. It may also be made greater than the pressure represented by a′b′ the maximum pressure theoretically obtainable in the apparatus in case an excess of gas sufficiently great to force all acid in C back into B should be generated. As a matter of fact, however, this condition is never even approximately realized in practice. Experiment has shown that even when a partial vacuum has been purposely established in A and E, the sudden opening of o does not admit sufficient acid to generate an excess of more than from 100 to 200 cc. of gas. The sum of the pressures represented by e f and f g must, moreover, be less than the sum of the pressures represented by a b and c d, in order that the spent acid may flow out. The level c of the spent acid may be changed at will, without varying the pressure in A, by changing the amount of mercury in F. This is readily accomplished by means of a pipette introduced through the aperture w, which is ordinarily closed by means of a rubber stopper. By increasing the amount of mercury in F the level c may be raised until it reaches any desired point within A. If it should be desired to simplify the overflow apparatus, E could be dispensed with entirely, and a single tube could be used to replace r and F. In this case it would be advisable to introduce a sufficient quantity of mercury to raise the level c to a point about one-fourth of the distance from the bottom to the top of A. In our experience it has been found almost impossible to effect complete neutralization of the acid without permitting it to remain in contact with the solid for some little time.

The third difficulty enumerated in the opening paragraphs was overcome with the aid of the double dropper, p, to which reference has already been made. The use of this device has greatly lessened the tendency toward the formation of channels in the solid. If the apparatus is but rarely required to supply large amounts of gas, however, the acid always slowly drops from the two elbows, and may in time produce channels, particularly if the pieces of ferrous sulphide are small. Trouble from this source may be quickly remedied by grasping the tube p at the point where it emerges from A beneath the rubber tubing, and twisting it around through an angle of about 90°. This operation is rendered very simple by the fact that p does not actually touch the rubber stopper through which it passes, but is encased in a short close-fitting piece of glass tubing as shown in the enlarged sketch. In our work it has been found sufficient to twist p two or three times during the course of the term's work.

The extent to which the fourth difficulty has been overcome may be inferred from the following statements: One filling of the ferrous sulphide bottle usually suffices for an entire term's work. The only daily task of the attendant consists in opening the stop-cock o at the beginning, and closing it at the end of a laboratory period. Even this precaution is not necessary, except to prevent leakage of gas through outlets inadvertently left open by the students. The acid bottle D is filled at intervals of from one to two weeks, as stated above. This operation is accomplished semi-automatically, involves no handling of acid, and requires but a few minutes of time. Moreover, no fumes, either of hydrochloric acid or of hydrogen sulphide, are permitted to escape into the room. To supply a class of 180 students during one term's work, the consumption of one carboy (50 liters) of commercial hydrochloric acid and about 23 kg. of ferrous sulphide was found to be necessary.

SUMMARY.

By modifying the Ostwald gas generator in the manner indicated in the preceding pages an apparatus possessing the following advantages may be constructed.

(1) It readily furnishes hydrogen sulphide in quantities sufficient to supply a class numbering 275 students, provided that the gas is made to bubble through the 52 outlets at a rate of from

2 to 5 bubbles per second, and provided that precipitation is usually effected in closed flasks.

(2) The gas is evolved at uniform pressure whatever may be the rate of its consumption, provided only that this rate does not exceed the maximum rate of generation of which the apparatus is capable.

(3) One charge of ferrous sulphide usually suffices for a term's work. The removal of a single rubber stopper permits the introduction of a new charge.

(4) One charge of acid (1 : 1 hydrochloric) suffices for a period of from one to two weeks. The charge may be renewed at any time without manual labor, by the simple manipulation of a few stop-cocks.

(5) No fumes, either of hydrogen sulphide or of hydrochloric acid, can escape into the air at any time except to some extent during the semi-annual renewal of the charge of ferrous sulphide.

(6) The spent acid is automatically discharged without changing the pressure in the apparatus, and not until it has stood in contact with ferrous sulphide for a sufficient length of time to insure its complete neutralization.

(7) The stop-cock o may be discarded entirely if this is desirable. The actual working parts of the apparatus will then be devoid of stop-cocks, as t, u, v and the pinch-cock at k are used solely for the purpose of filling D.

(8) Since the apparatus is made of glass parts, its condition at any time may be seen at a glance.

(9) The apparatus may be set up without difficulty by any one who has had a little experience in amateur glassblowing. The tubulated bottles are ordinarily carried in stock by manufacturers of laboratory apparatus.

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