

day test of the generator, for example, the pressure was substantially constant except for a slight momentary increase experienced whenever a fresh supply of acid dropped upon the solid substance.

Summary

The apparatus described in the preceding pages possesses the following advantages:

(1) It is capable of furnishing a moderately rapid current of gas at substantially constant pressure.

(2) The spent acid is automatically discharged (by means of the accessory device shown in the figure) without changing the pressure in the apparatus.

(3) A new charge of acid may be introduced at any time without interrupting the generation of gas, by simply filling the bottle D and setting it into position.

(4) A new charge of solid may be introduced without removing the acid in B and C, provided the bottle D is temporarily removed, and a glass rod tipped with a short piece of tubing is pressed into the tube *m*.

(5) No surface of acid or of spent solution is directly exposed to the air, and consequently no fumes are given off.

(6) The acid can not be forced back by the generation of an excess of gas so as to overflow from the apparatus.

(7) In proportion to the desk space it occupies, it has an unusually large available capacity for both acid and solid.

CORNELL UNIVERSITY,

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A CONSTANT PRESSURE GAS GENERATOR FOR USE OVER A WIDE RANGE OF PRESSURE.

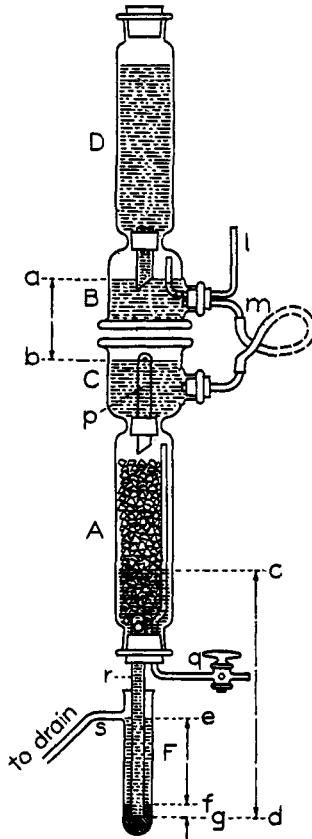
BY A. W. BROWNE AND M. J. BROWN.

In the preceding article a portable modification of the Browne-Mehling gas generator¹ has been described. Entirely similar in principle to this device is the apparatus described in the following paragraphs. This apparatus has been employed by the authors for the generation of gases at approximately constant pressures of from 5 mm. to 270 mm. of mercury. In order to avoid unnecessary repetition and to emphasize the similarity in principle existing between this and the other generators devised in this laboratory, the accompanying sketch is lettered similarly part for part with the sketches in the articles to which reference has already been made. The apparatus consists essentially of two Fresenius calcium chloride towers placed base to base and connected by means of a long rubber tube. By raising the tower BD any desired pressure may be obtained and the pressure will in any case be approximately constant,

¹ This Journal, 28, 838-845 (1906).

owing to the fact that the acid in B cannot fall below the level *a* so long as acid remains in the reservoir D.

When the stop-cock *q* is opened, acid flows from B through *m* into C and thence through *p* into A, where it comes into contact with the solid substance. When *q* is closed the influx of acid is quickly checked, and any excess of gas that may be generated forces the acid in C back through *m* into B. When the acid in C has been completely displaced, any additional gas that may be generated will bubble up through the acid in B



finally escaping through the tube *l*. When the apparatus is employed for the generation of gas at high pressures the production of a large excess of gas should be carefully avoided, since displacement of the acid in the tube *m* relieves the pressure in the apparatus, with the result that large volumes of gas are blown upward through the acid in B. Under these conditions acid is sometimes blown out through the tube *l*. To avoid the generation of a large excess of gas the following precautions should be observed. (1) The lower end of the rubber tube *m* should be

closed by means of a screw clamp until the entire apparatus has been set into final position. It is particularly important that the tube r be immersed to a sufficient depth in the mercury contained in F. It is usually advisable to immerse r at first to a greater depth than is absolutely necessary, and subsequently, after the apparatus has been working for a time, very carefully to lower F until the level c of the spent solution is brought to a point just beneath the rubber stopper. (2) The stopcock q should never be opened so suddenly as to permit large quantities of acid to enter A, and should never be closed suddenly after the apparatus has been furnishing a rapid current of gas for any considerable length of time. The use of a short piece of capillary tubing connected with the delivery tube of the generator greatly diminishes the danger arising from neglect of these precautions. (3) The aperture in p should not be too large. In general the diameter should be about 1.0 mm. (4) The acid employed should be no stronger than 6 N. In the special tests made by the authors, acid of this strength has been employed with satisfactory results. As a rule, however, it is safer to use a more dilute acid especially in the generation of carbon dioxide (from calcium carbonate and hydrochloric acid).

The spent solution passes from A through the tube r into F escaping automatically from the apparatus through the side-arm s . The upper level c of the spent solution may be shifted at will by raising or lowering F. The depth to which the tube r is submerged in the mercury must obviously vary directly with the pressure under which the apparatus is working. At whatever pressure the gas may be generated, the spent solution is automatically discharged without changing the pressure in the apparatus.

In addition to the test of ordinary usage (generation of carbon dioxide, hydrogen sulphide and hydrogen), the generator has been subjected to special tests covering a range of pressures from 5 mm. to 270 mm. of mercury. In each test a slow current of gas was permitted to bubble through a column of mercury of appropriate height for one-half hour or more without interruption. The pressure in every case was remarkably constant except for a slight momentary increase whenever acid fell upon the solid. This occasional increase in pressure may be minimized by the use of more dilute acids.

To refill the reservoir D the rubber tube m should be closed by means of a screw clamp, and the end of the tube l should be closed by means of a short piece of rubber tubing provided with a glass plug. The uppermost rubber stopper is then removed to permit the introduction of the new acid.

In the selection of calcium chloride towers for this apparatus care should be taken that the side tubulus on one of the towers should be

close to the base ; on the other tower it should be near the constriction. The inner diameter of the constriction should in each case be smaller than the inner diameter of the neck in order to permit the introduction of the rubber stoppers and glass tubes. In setting up the apparatus for ordinary use an iron ring-stand with three clamps holding the apparatus at D, A and F, respectively, may be employed.

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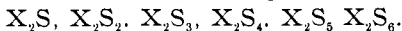
THE SELENIDES OF SODIUM.

BY C. H. MATHEWSON.

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The existence of selenides of the general formula Na_2Se_x has long been known but no systematic attempt to prepare and study the series by crystallization from solutions corresponding in composition to various possible formulas or by physical chemical methods has been undertaken. Uelsmann¹ in 1860 observed that selenium and sodium combine very readily at moderately low temperatures, with evolution of heat and light. He prepared a compound which he assumed to be Na_2Se by passing hydrogen selenide into strong sodium hydroxide solutions. No analysis was given to support this conclusion. Hugot² prepared the monoselenide by action of sodammonium in excess on selenium and described it as a white amorphous substance soluble in water free from air producing a colorless solution. Air causes the immediate separation of red selenium. Fabre³ obtained several crystalline monoselenides by treating sodium hydroxide solutions with hydrogen selenide. Ignition in nitrogen expels water of crystallization without further decomposition. Jackson⁴ reduced sodium selenide with carbon, a method used by Wohler and Dean⁵ for preparing the potassium compound. The resulting selenide gave a dibenzyl diselenide when treated with benzylchloride which characterized the alkali selenide as Na_2Se_2 and not Na_2Se . Ratlike⁶ explained this formation of diselenide by the unavoidable presence of water in the carbon used for reduction, with consequent oxidation of the monoselenide. Sodium tetraselenide, Na_2Se_4 , was prepared by Hugot⁷ by the action of sodammonium on an excess of selenium.

Alkali sulphides of the following six types are known :—



Rigid experimental proof of the existence of this unbroken series of sul-

¹ Ann. Chem. Pharm., 116, 122 (1860).

² Compt. rend., 129, 299 (1899).

³ Ann. chim. phys., (6), 10, 500 (1887).

⁴ Ber., 7, 1277 (1874).

⁵ Ann. Chem. Pharm., 97, 5 (1856).

⁶ Ann., 152, 181 (1869).

⁷ loc. cit., page 1.