LABORATORY AND PLANT

PREPARATION AND TESTING OF HYDROGEN OF HIGH PURITY

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In the course of a study of the properties of pure gases, the preparation of pure hydrogen by several different methods was undertaken. W. A. Noyes has already shown¹ in his work on the atomic weight of hydrogen, that hydrogen of exceptional purity could be prepared by the electrolysis of a solution of barium hydroxide. His work leaves little further to be said regarding the purity of hydrogen, which can be produced in that manner if the proper precautions are adopted. Where the highest purity is not essential, other methods may offer certain advantages. Chief of these is the greater speed with which hydrogen can be generated by such means as the reaction between zinc and acid or of hydron (sodium-lead alloy) and water. For example, the maximum rate of generation from a small electrolytic cell taking 10 amp. is about 4.4 l. per hr., whereas 10 to 20 times that rate can be easily attained with a small-sized Kipp generator for relatively short periods of time.

The Kipp generator, however, has two disadvantages where purity of the product is the first requisite. The residual air must be swept out (which consumes time and material), and the acid is in contact with air in the upper reservoir; this air dissolving in the acid may slowly diffuse into and contaminate the hydrogen. To obviate these difficulties, the generator shown in Fig. 1 was designed by the author in coöperation with Mr. E. R. Weaver.

The operation of the generator is apparent from the figure. The chief advantages claimed for this generator are:

- 1—The sweeping-out period of generation is eliminated.
- 2—An atmosphere of pure hydrogen is maintained in all parts of the apparatus at all times.
- 3—Pure hydrogen can be obtained from the generator at any time—immediately after filling or after standing for long periods.
- 4—Fresh acid can be introduced without admitting air.

The manipulation by which this is accomplished is as follows: Before filling the apparatus it is first evacuated through *a*. The residual pressure in the generator is indicated by the height of the mercury in the tube *d* which serves as a manometer and also as a blow-off. Any leak can thus be detected by the indications of this manometer. If the generator contains any liquid, the pressure cannot, of course, be reduced below its vapor pressure. Continued pumping will, however, sweep out the generator with a stream of water vapor. The acid to be introduced (sulfuric, 1 : 8) is contained in and nearly fills the flask *f* which is connected to the generator by a delivery tube as shown. Several pieces of zinc are introduced into the flask, in order to sweep all the air out of the acid and saturate it with hydrogen. When this has been accomplished, the vent *e* is closed until the pressure

increases sufficiently in *f*, from the generation of hydrogen, to force the acid through the delivery tube and out the end of the Geissler stopcock; all air is thus removed from the connections. On turning the cock to connect with the generator, the acid will then run into the evacuated generator. Before the acid has reached the level of the zinc, the hydrogen dissolved in it can be removed by pumping in order to further ensure complete absence of air. The proper amount of acid is then allowed to enter and hydrogen generated until it bubbles out through *d*, which shows that the generator is under pressure. The rate of generation is regulated by the cock *c*.

FIG. 1—GENERATOR OF EDWARDS AND WEAVER FOR PURE GASES

The generator illustrated was made from two large calcium chloride towers with glass stoppers. The stopcock at *b* entered through a rubber stopper which was always under liquid. All parts are rigidly mounted on a stand to prevent breakage of the glass connections. The size, shape and arrangement of parts can of course, be modified as occasion demands.

PURITY OF HYDROGEN FROM ZINC AND ACID

Although the purity of the gas may vary with the purity of the materials employed, the present tests are of interest as showing the possibilities of the method. The zinc used was a very pure sample from an English source; the acid was J. T. Baker's "C. P." sulfuric acid. The possibility of the hydrogen containing the following impurities should be considered: Oxygen and nitrogen, sulfur dioxide, hydrogen sulfide, acetylene, methane or other hydrocarbons, carbon monoxide, carbon dioxide, arsine, phosphine, stibine, and water vapor.

¹ Bureau of Standards, *Bulletin* 4 (1908), 345.

Of these impurities, oxygen and nitrogen which might come from air leaks, had to be rigidly excluded because there is no satisfactory method of removing traces of nitrogen. Sulfur dioxide, hydrogen sulfide, and carbon dioxide were removed by passing the gas over solid potassium hydroxide. The gas was thoroughly dried by passing through three tubes of sublimed phosphorus pentoxide. All connections were glass to glass sealed with de Khotinsky cement where necessary. The following tests for impurities were applied to the gas.

REFRACTIVITY—The refractivity of a sample of hydrogen is a delicate criterion of its purity because all gases which are likely to be present have much higher refractive indices than hydrogen; helium and neon are the only gases having lower refractive indices. The gas interferometer,¹ which measures the difference in refractivity of two samples of gas, may thus be used for detecting impurities in hydrogen. The interferometer was calibrated by the method of Edwards.² For the standard of comparison, hydrogen was generated by electrolysis of barium hydroxide in an all-glass electrolytic cell³ and purified by passage over hot platinized quartz, solid potassium hydroxide, and sublimed phosphorus pentoxide. Every precaution was taken to secure the requisite purity of the materials and to exclude leaks in the apparatus. The hydrogen so generated was considered to have considerably less than 1 part in 10,000 of impurity present.

When compared with this gas in the interferometer, the hydrogen from zinc showed a total impurity, calculated as air, of less than 0.01 per cent. The interferometer was of such sensitivity that 0.005 per cent air in hydrogen could be detected. If gases other than air were present, the actual percentage would be still lower because their higher refractive index gives a greater sensitivity in the reading of the interferometer.

TESTS FOR CARBON COMPOUNDS—To test for carbon compounds, the hydrogen was burned with carbon-free air in a hard glass tube filled with copper oxide. The residual air was then passed through a solution of barium hydroxide contained in the spiral wash bottle⁴ of Weaver and Edwards. The precipitated barium carbonate was filtered off and washed free from barium hydroxide without removing it from the wash bottle or allowing it to come into contact with air containing carbon dioxide. The small precipitate of barium carbonate which was formed yielded 4.4 mg. of barium sulfate, equivalent to 0.83 mg. of carbon dioxide. If this came from the oxidation of acetylene it would have corresponded to 8 p. p. m. by volume in the 25 l. of hydrogen from which it came.

Acetylene was determined directly in the gas by the colorimetric method of Weaver⁵ using an absorbing solution of cuprous chloride containing gelatin, hy-

droxylamine hydrochloride, alcohol, and ammonia in the proportions recommended in the article cited. The limit of visibility was about 0.02 mg. of acetylene. Only the faintest coloration was secured which indicated not more than 1 or 2 p. p. m. of acetylene. The remainder of the carbon found in the previous test may have come from traces of carbon monoxide, methane, or other hydrocarbons.

Hydrogen generated from a sample of hydrone contained 4 p. p. m. of acetylene as determined in the same manner.

TESTS FOR ARSINE AND STIBINE—Arsine and stibine were absent as indicated by the lack of any deposit on the passage of the gas through a heated tube. Arsenic and antimony were not detected in the chemical analysis of the zinc.

All of these results confirm the conclusions arrived at from the indications of the interferometer, namely, that hydrogen containing not more than 1 part in 10,000 of impurity can be prepared from zinc with the generator described.

It was of interest to determine the purity of gas obtained from an ordinary Kipp. The gas was compared with the hydrogen from the generator shown in Fig. 1, by means of the interferometer. The gas from the Kipp was purified by passage through soda lime and anhydrous, granular calcium chloride. There was a short piece of rubber tubing leading to the drying tower and three rubber stoppers in the line. No leaks were detected in the system upon evacuation. The purity of the hydrogen and the amount generated by the Kipp were determined every 5 min. The results are shown in Table I.

TABLE I—COMPARISON OF PURITY AND YIELD OF HYDROGEN FROM KIPP GENERATOR

Time from Start of Generation Min.	Purity of Hydrogen Per cent	Total Volume of Gas Generated Liters	Calculated Volume of Gas Required to Reach Indicated Purity Liters
17	83.86	3.96	4.00
22	93.59	6.02	6.03
27	97.86	8.50	8.45
32	99.51	11.58	11.70
37	99.92	15.00	15.69
42	99.97	18.35	17.84
57	99.974	28.4	18.17
77	99.973	41.7	18.17
112	99.976	74.3	18.3

The results given in Column 4 of the table were calculated from the following equation:¹

$$\frac{\text{Total Gas Evolved}}{\text{Total Gas Space}} = \log_e \left(\frac{1}{1 - \frac{a}{100}} \right)$$

In this equation a is the purity of the hydrogen expressed as a percentage. The gas space in the case of the generator tested was 2.2 l. It is assumed in this equation that there is perfect mixing at all times of the hydrogen with the air in the generator. The agreement between the experimental and the calculated values is quite satisfactory and shows that the equation can be used in calculating the sweeping-out period for any similar generator when gas of any required purity is desired.

¹ Weaver, "Generation of Hydrogen from Ferrosilicon," 4th Annual Report Nat. Adv. Comm. for Aeronautics, 1918.

¹ For a description of the gas interferometer, see L. H. Adams, *J. Am. Chem. Soc.*, **37** (1915), 1181.

² *Ibid.*, **39** (1917), 2382.

³ Similar in design to that of Weber, Bureau of Standards, *Bulletin* **9** (1913), 135.

⁴ *THIS JOURNAL*, **7** (1915), 534.

⁵ *J. Am. Chem. Soc.*, **38** (1916), 352.

Hydrogen of approximately the same purity (99.97 per cent hydrogen) was prepared in the same Kipp from J. T. Baker's "C. P." zinc said to contain a trace of arsenic and antimony.

SUMMARY

A generator is described with which hydrogen containing not more than 1 part in 10,000 of impurities can be prepared from zinc and acid. Methods of testing for contaminating gases are described. The relation between the volume of gas generated and purity of the product is given by an equation which was verified experimentally.

BUREAU OF STANDARDS
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AN APPARATUS FOR RAPID GASTRIC ANALYSIS TOGETHER WITH A METHOD FOR THE PRESERVATION OF STARCH SOLUTION

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Considerable of the success accomplished along the line of gastric investigation conducted at the Jefferson Medical College recently is due to an apparatus designed by one of the members of the research staff, the author of this contribution. With the aid of this apparatus the manipulation of different solutions used in the several analyses has been shortened. The apparatus demonstrates its real value not in the handling of one case for analysis but rather when three or more are to be run.

FIG. 1

a—Alkali Burette	d—Syphon Device (Starch)
b—Thiosulfate Burette	e—Formation Reservoir
c—Automatic Pipette	f—Starch Solution

In gastric analysis as conducted in this laboratory the following determinations are considered of most importance:

- 1—Total Acidity: Titration with $N/100$ potassium hydroxide.
- 2—Free Acidity (Sahli Method): Titration with $N/100$ sodium thiosulfate, finishing with starch solution.
- 3—Formol Titration or Amino Acid Nitrogen Complex: Addition of neutral formalin and titrating with $N/100$ potassium hydroxide.

The apparatus is designed to meet the requirements for these three determinations.

APPARATUS

To set up the apparatus the following material is necessary:

- 1—Double burette stand.
- 2—Two certified burettes, 30 cc. capacity, graduated to 0.05 cc.
- 3—Capillary glass tubing, 1 to 2 mm. inner diameter.
- 4—Four glass T tubes: Three, inner diameter 3 mm. One, inner diameter 4 mm.
- 5—Red rubber tubing, inner diameters of 1 to 2 mm. and also 4 mm.
- 6—Pinchcocks, three plain and one special two-way cock.
- 7—Adhesive tape.

Fig. 1 shows the apparatus as completed and in running order in the laboratory. The burette on the right is connected

to the alkali reservoir, that on the left to the thiosulfate. At the top of the burettes is placed an arrangement which is shown in detail in Fig. 2. Near the base of the burette stand two devices will be observed. The one on the right leading to the tip of the alkali burette is an automatic pipette used in the formol titration, and is shown in detail in Fig. 3. The attachment on the left leading to the tip of the thiosulfate burette is an ordinary gravity device for the rapid addition of starch solution.

FIG. 2

Fig. 2 illustrates the overhead arrangement whereby the burette can be filled by suction and when the same is released any excess solution drawn over is immediately withdrawn back into the reservoir, leaving the burette reading 0.00 cc.

Fig. 3 shows the automatic pipette which, as soon as its charge is delivered, automatically fills up to approximately its former level and is again ready to be discharged. The principle upon which this device depends is a two-way pinchcock as illustrated at A, Fig. 3. This type pinchcock was designed by another author and reported some time since.

Very little has been said in regard to the assembling of material for the several devices as it has been taken for granted that the figures are self-explanatory. Perhaps but one thing needs an explanation and that is the purpose of the adhesive tape. It will be observed in Fig. 1 that the automatic pipette *c* and the starch