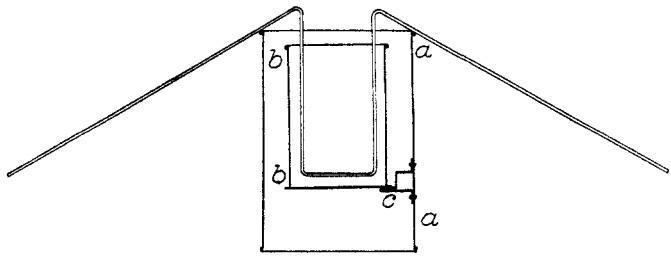
ON THE DETERMINATION OF HYDROGEN IN GAS MIXTURES.

By Francis C. Phillips.

Received March 11, 1901.

THE strongly exothermic character of the reaction involved in the combustion of hydrogen renders it possible to determine this gas by oxidation over palladium asbestos without the application of external heat. As the moisture produced in the reaction is liable to condense and cause the palladium to become wet, it is usual to apply heat in order to prevent this condensation and to insure the completeness of the reaction. For this purpose Winkler[1] recommends the use of a gas flame placed directly below the palladium asbestos tube. In heating over a flame the obvious danger occurs of burning hydrocarbons along with the hydrogen. The use of hot water as a source of heat presents the advantage that the temperature of the palladium is prevented from rising much above 100° C., provided that the rate of passage of the gas through the palladium asbestos tube is slow. Still it is somewhat difficult by any existing device to preserve a constant and definite temperature. The form of apparatus described below has proved convenient for maintaining the palladium asbestos at the temperature of boiling water for a period of time sufficient for the performance of a series of hydrogen determinations.

In the drawing, which represents the apparatus in section, *a a*



is a brass cylinder 30 cm. long and 18 cm. wide. It is open at both ends, the rims being strengthened by wires. *b b* is a cup-shaped vessel 18 cc. deep and 12 cc. wide. When in use this inner vessel rests upon three supports which are riveted to the

[1] Winkler and Lunge: "Handbuch of Technical Gas Analysis," 1885, p. 79.

inner surface of the cylinder *a a*. One of these supports is shown at *c*. The space between the cup and the cylinder is nearly 3 cm. wide. The cup is silvered on the outside and the cylinder is silvered on both sides. Any of the mixtures which are sold for giving a silver coating to brass will serve for the purpose.[1] The palladium asbestos is introduced into the middle of a glass tube 70 cm. long and about 3 mm. in internal diameter. The tube is then bent into the form shown in the sketch and the U-shaped part placed in the brass cup, which is then filled with water. A small flame is kept burning under the cup and the water maintained at a temperature approaching the boiling-point. The glass tube containing the palladium asbestos is connected at one end with a gas burette and at the other end with a Hempel pipette. The gas in which the hydrogen is to be determined, together with the necessary volume of air having been introduced into the burette, and the water-levels being carefully adjusted, the gas is caused to flow slowly through the palladium asbestos tube into the pipette, and back again to the burette, the volume of the hydrogen being ascertained in the usual manner. The polished silver surfaces prevent radiation to such an extent that the accuracy of the gas measurements is not affected by the close proximity of the measuring apparatus to the source of heat.

The palladium asbestos is prepared by moistening long-fibered asbestos with palladium chloride solution and igniting over a Bunsen burner flame, the process being repeated until the asbestos receives a sufficient quantity of the reduced metal (about 6 per cent. of the weight of the original asbestos has been found to be a convenient proportion). The deposition of the palladium occurs mainly on the surface of the bundle of asbestos fibers. It is well, therefore, in order to distribute the reduced metal as evenly as possible throughout the mass of the asbestos, to roll the fibers under a glass rod on a glass plate once or twice during the process of alternately impregnating with palladium chloride and igniting. Minute crusts of palladium accumulated upon the surface of the asbestos are liable to glow intensely, even when the

[1] A silvering mixture may be prepared according to the following formula: Dissolve 8 grams of silver nitrate, 10 grams of potassium cyanide, and 0.5 gram of potassium tartrate in 100 cc. of water. Add sufficient French chalk to make a thin paste. This mixture, applied with friction by help of a piece of Canton flannel, will produce a highly lustrous silver surface upon brass or copper.

tube is immersed in water, during the passage of a gas containing hydrogen and oxygen, and by so doing cause a partial combustion of any hydrocarbons that may be present. It is important, therefore, that the palladium should be distributed as uniformly as possible throughout the asbestos. As a result of the ignition, after impregnation with palladium chloride solution, the asbestos becomes somewhat more rigid and the bundle of fibers may be readily pushed, by help of a copper wire, far into the narrow glass tube.

[CONTRIBUTION FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

ON THE SEPARATION OF TUNGSTIC AND SILICIC ACIDS.

BY H. L. WELLS AND F. J. METZGER.

Received April 15, 1901.

IN a recent number of a German periodical[1] appears an article by Otto Herting, of Philadelphia, in which the assertion is made that the method given in the text-books for expelling silica from tungstic acid by means of hydrofluoric acid is incorrect. This statement is made on the ground of alleged numerous quantitative experiments with mixtures of pure tungstic acid and pure ignited silicic acid, but no details in regard to the results are given. Herting believes that upon ignition, silicic and tungstic acids form a silicotungstic acid which is volatile when treated with hydrofluoric acid, and finally says that he should be pleased if, by means of his article, he should bring about the more careful study of the "action of hydrofluoric acid upon tungstic acid in the presence of silicic acid."

Since Herting's statement throws doubt upon a method that is generally used, we have undertaken an examination of the matter. For this purpose, we dissolved some of Kahlbaum's tungstic acid in ammonia, precipitated with nitric acid, washed with water by decantation, digested repeatedly with sulphuric acid of sp. gr. 1.378 to separate any molybdic acid that might possibly be present,[2] washed the residue and ignited it. The tungstic acid thus prepared was used for the experiments that follow.

A weighed quantity of tungstic acid in a platinum crucible

[1] *Ztschr. angew Chem.*, 1901, 165.

[2] See Ruegenberger and Smith : This Journal, **22**, 772.