TABLE VIII (*Concluded*)

E. Thickness of silver, 0.205 mm.; pressure of oxygen, 760 mm.

Temp., °C	420	460	500	550	600	640
Rate[a] calc	7.8	22.9	39	97	229	442
Rate[a] obs	7.0	19.0	43	99	239	495

F. Thickness of silver, 0.0787 mm.; pressure of oxygen, 760 mm.

Temp., °C	400	425	450	475	500	...
Rate[a] calc	13.3	22.7	37.8	62	101	...
Rate[a] obs	10.5	22.5	39.5	64	98	...

[a] Rate of diffusion: cc. per sq. meter per hour.

Summary

1. An apparatus has been described for the investigation of the rate of diffusion of oxygen through silver.

2. The rate of diffusion of oxygen through silver has been measured at temperatures varying between 400° and 630°, at oxygen pressures of 159 mm. 392 mm. and 760 mm., and for thicknesses of silver of 0.0787 mm., 0.135 mm. 0.205 mm. and 0.248 mm.

3. The relation between the rate of diffusion and the gas pressure, temperature and thickness of silver has been deduced from the curves obtained, and it has been found that the rate of diffusion varies as the 14.62 power of the absolute temperature, as the square root of the pressure and inversely as the thickness of silver.

4. An equation has been derived from which the rate of diffusion of oxygen through silver can be calculated for any pressure, temperature and thickness of silver. This equation is in the form $X = \frac{1.71}{10^{43}}\sqrt{\frac{p}{h}}\,T^{14.62}$ where X is the rate of diffusion in cc. per sq. meter per hour, p the pressure of the oxygen in millimeters of mercury, h the thickness of the silver in millimeters, and T is the absolute temperature.

MONTREAL, CANADA

[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

A METHOD FOR THE DETERMINATION OF CALCIUM CARBIDE[1]

BY J. Y. YEE AND H. J. KRASE

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In connection with an investigation on the thermal decomposition of calcium cyanamide and of calcium carbide, an accurate method for the determination of the latter was necessary. The commonly used methods involve the measurement of the total gas liberated when the carbide is treated with water, the gas volume being dependent on such variables as

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[1] The method described in this paper has also been successfully used in this Laboratory for the analysis of sodium carbide.

the vapor pressure of the liquid over which the measurement is made, the solubility of acetylene in the liquid, as well as changes of temperature and pressure. Even with special refinements in apparatus and technique,[2] this method gives variable results.

In view of the excellent results obtained by Ross and Trumbull[3] on the analysis of gas mixtures containing acetylene and ethylene, with their modification of the method of Chavastelon, it was decided to determine the applicability of this same method to the determination of calcium carbide.

Chavastelon's method involves the absorption of acetylene in neutral or ammoniacal silver nitrate. With the neutral solution and an excess of silver nitrate, the reaction is quantitative according to the equation

$$C_2H_2 + 3AgNO_3 \doteq C_2Ag_2AgNO_3 + 2HNO_3 \qquad (1)$$

With ammoniacal silver nitrate the reaction is also quantitative,

$$C_2H_2 + 2AgNO_3 + 2NH_4OH = Ag_2C_2 + 2NH_4NO_3 + 2H_2O \qquad (2)$$

In the first reaction, the liberated nitric acid can be directly titrated, while the application of the second reaction makes necessary a determination of the excess of silver nitrate.

We found that both of these methods could be adapted to our work. In the determination of carbides containing no nitrides, neutral silver nitrate was employed and the acid titrated (Equation 1), since it is the most rapid method. With carbides containing nitrides, however, Reaction 2 was employed.

Apparatus and Method

The apparatus used for the determination of carbide is shown in Fig. 1.

Acetylene gas is generated by dropping an aqueous solution from the funnel J onto the carbide sample contained in G which has a capacity of 40 to 50 cc. The gas passes up through the condenser M by way of the tube F into a previously evacuated flask A of 1 liter capacity containing the silver nitrate solution. When sufficient solution has been added to the carbide sample in G, Stopcock I is turned through 180° and a slow stream of air drawn through a solution of silver nitrate contained in the bubbler K. At the same time, the liquid in G is heated to boiling by means of a glycerol bath and in this way the last traces of acetylene are expelled from the solution. This gas is swept by the air current into the flask A, where it is absorbed by the silver solution.

To prevent dust from being carried over into the silver solution, a small wad of glass wool is inserted in the tube at the point F. Another precaution necessary is that a glass apron C be attached to the tube entering the absorption flask to prevent the solution from coming into contact with the rubber stopper during the shaking.

The solution used in J is either a saturated sodium chloride or lead nitrate solution, the latter being used if sulfides are present in the car-

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[2] Berl and Jurissen, *Z. angew. Chem.*, **23**, 248 (1910).

[3] Ross and Trumbull, THIS JOURNAL, **41**, 1180 (1919).

bide. Attempts were made to develop a method applicable to carbides containing phosphides, but without success.

The length of time of boiling required to expel all of the acetylene was determined by making quantitative tests for acetylene in the gas coming from the decomposition flask. It was found that at least half an hour was necessary to expel all of the acetylene.

The length of time required to absorb all of the acetylene from the gas in the absorption flask was determined by another series of experiments. It was found that at least one hour was necessary to insure complete absorption.

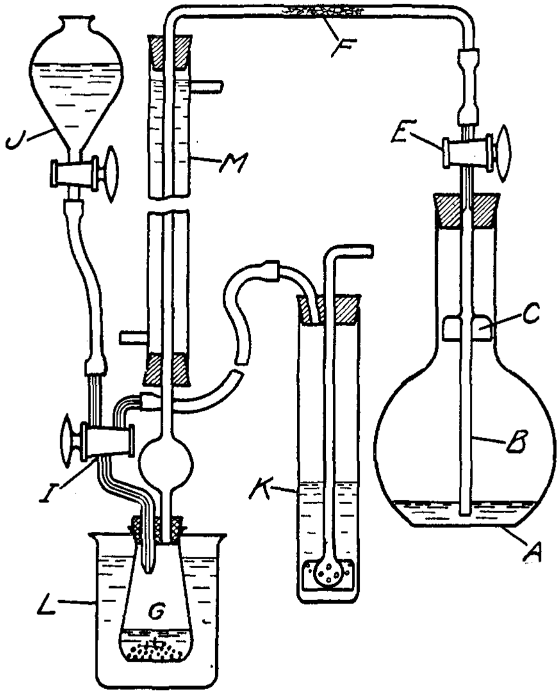

Fig. 1.

To prevent decomposition of the carbide by atmospheric moisture, the transference of the sample to the weighing bottle was carried out within a large desiccator containing phosphorus pentoxide. This desiccator was provided with a Bakelite cover which contained handholes and a window. Long surgeon's gloves were clamped with rings in the handholes. In this way many operations with carbide, such as pulverizing in a mortar, screening and mixing can be carried out without appreciable decomposition of the substance.

The determination of the carbide is carried out in the following manner.

The absorption flask, containing 50 cc. of 0.5 *N* silver nitrate solution, is tilted while the inlet tube B is put in place and the flask evacuated. The flask is then connected with tube F. Stopcock I is closed and the weighing bottle containing the sample (about 0.2 g. in the case of 80% calcium carbide) quickly put in place. After the stopcock E has been opened, the 3-way stopcock I is slowly turned so as to allow the saturated salt solution in the dropping funnel J to run into the decomposition flask, drop by drop. Care should be taken not to place the main body of the sample directly under this inlet. After the sample is practically all decomposed, 10 cc. more of solution is added and the whole is slowly brought to boiling by means of the glycerol bath L. Then Stopcock I is turned through 180° in order to permit a very slow current of air to be drawn through the silver nitrate Bubbler K. When the residue has been boiled for 30 minutes, I is opened to admit air rapidly to replace the gas in the decomposition flask and in the condenser tube. When the air has ceased flowing, E is closed and the absorption flask placed on a reciprocating shaker and agitated vigorously for an hour. The inlet tube B is then removed and washed into the flask. The nitric acid in the flask is titrated by adding a slight excess of standard 0.1 *N* sodium hydroxide solution, as shown by the presence of the brown oxide of silver. To precipitate the excess of silver in the solution 25 cc. of *N* sodium chloride solution is added, after which the excess of alkali is titrated with standard 0.1 *N* hydrochloric acid, using methyl red as indicator. The percentage of calcium carbide is then calculated from the sodium hydroxide used.

If ammoniacal silver nitrate (0.1 *N*) has been used, the procedure is carried out in the same way with the exception that the precipitated silver carbide is filtered and washed free from soluble silver. This can be done conveniently by using suction and a platinum filter cone. The filtrate is made slightly acid with nitric acid and the silver determined by titrating with 0.1 *N* potassium thiocyanate solution using ferric ammonium sulfate as an indicator.

Accuracy of the Method

The results of these two methods on the same sample of carbide are shown in Table I.

TABLE I

COMPARISON OF METHODS OF ANALYSIS. PERCENTAGE OF CaC_2 IN SAMPLE

Acid titration.....	70.60	70.55	70.58	70.62	70.55	70.60	70.52	av. 70.57
Excess of $AgNO_3$..	70.50	70.60	70.50	70.45	70.55	70.60	70.64	av. 70.55

Since no 100% calcium carbide was available for an absolute test of the method, a sample of carbide made in this Laboratory from pure materials was analyzed by this method and also by the usual combustion method for total carbon. The sample contained besides carbide some uncombined carbon and calcium oxide. The uncombined carbon was determined by treating the sample with dil. nitric acid, filtering off the carbon and weighing. The difference between the uncombined carbon and total carbon, obtained by combustion, represents carbon combined as carbide. These values are recorded in the last column of Table II.

Table II

Analyses of Samples

CaC_2 %	C as CaC_2 %	Total C minus uncombined C %
72.08	27.01	27.02
66.47	24.91	24.97

It will be seen that the agreement obtained for carbide carbon by the two methods is satisfactory.

Summary

An accurate method has been developed for the determination of carbides that yield acetylene when treated with water. Traces of sulfides do not interfere when proper precautions are taken. Phosphides, however, should be absent.

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[Contribution from the Chemical Laboratory of the University of California]

A SIMPLE PRESSURE-MEASURING DEVICE FOR USE WITH CORROSIVE GASES

By David F. Smith[1] and Nelson W. Taylor

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Perhaps the simplest and most satisfactory glass pressure-measuring device heretofore described is that of Daniels and Bright[2] or the later modification described by Karrer, Johnston and Wulf.[3] Our experience in the use of these devices has brought out several inherent disadvantages in them, however. In the first type it is difficult to make the diaphragm thin enough to be sensitive and at the same time thick enough to avoid breakage in use or distortion in the process of burning in the platinum. The platinizing process is itself very troublesome. Many otherwise good pieces are spoiled by faulty platinizing. The adjusting of the contact points is troublesome and often results in damage to the diaphragm; and eventually the diaphragm becomes useless on account of the wearing off, burning by the current, or smutting of the platinum at the contacts. Moreover, the whole process of setting up the pieces must be gone through in order to determine whether the diaphragm is suitable.

[1] National Research Fellow in Chemistry.

[2] Daniels and Bright, This Journal, **42,** 1131 (1920).

[3] Karrer, Johnston and Wulf, *J. Ind. Eng. Chem.*, **14,** 1015 (1922).