tion, and, for comparison, Curve III gives the degrees of dissociation as measured by conductivity methods.[1]

NOTE.—In a private communication Professor Loomis informs me that a statement in regard to his work in one of my articles (THIS JOURNAL, 39, 2604 (1917)) is rather ambiguous: "The remark might be interpreted to intimate that I have claimed equal thermodynamic degrees of dissociation for KCl and HCl solutions at all concentrations. As a matter of fact my articles have dealt only with decinormal concentrations, and in my latest article I have suggested a possibility that my results may be accounted for by a slightly lower degree of dissociation for 0.1 *N* KCl than for 0.1 *N* HCl."

BERKELEY, CAL.

[CONTRIBUTION FROM CHEMICAL LABORATORY, EDGEWOOD ARSENAL.]

A MODIFIED METHOD FOR THE ANALYSIS OF MIXTURES OF ETHYLENE AND ACETYLENE.[2]

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In the course of an investigation on the preparation of ethylene from acetylene, mixtures of these two gases were recovered in association with variable quantities of other gases as ethane and hydrogen. It thus became necessary in carrying on the work to make accurate analyses of gas samples containing ethylene in the presence of acetylene and other hydrocarbons in order to determine the effect on the production of ethylene of any special change in the conditions of the experiment.

In the preliminary work use was made of the Tucker and Moody[3] method for determining ethylene in the presence of acetylene. This method involves the use of an ammoniacal silver nitrate solution which is claimed to remove the acetylene completely but only a relatively small amount of ethylene. It was found, however, that the quantity of ethylene absorbed varied with the time that the mixture was shaken with the silver nitrate solution, and that the results obtained varied continuously with the time taken in making an analysis. This was demonstrated by shaking samples of 80% ethylene, known to be free from acetylene, with the silver nitrate solution for 5-minute periods, and reading the residual volume of gas after each period. The results are given in Table I.

In a number of tests made with known mixtures of ethylene and acetylene, note was made of the relative proportion of each absorbed when the mixture of gas was shaken with the silver nitrate solution for different lengths of time. It was thought that tolerably good results might possibly be obtained in the analysis of unknown mixtures if the gas were shaken in the silver nitrate pipet for the same length of time as that which gave best results with the known mixtures. This might possibly prove true

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[1] Noyes and Falk, THIS JOURNAL, 34, 475 (1912).

[2] Published by permission of the Director of the Chemical Warfare Service.

[3] THIS JOURNAL, 23, 671 (1901); Dennis', *Gas Analysis*, p. 248.

in case the mixtures remained approximately of the same composition, and the strength of the silver nitrate solution remained constant. As these factors changed, however, the accuracy of the method was found to range between such wide limits as to make its use unsuited for the accurate analysis of ethylene-acetylene mixtures, particularly when the mixtures contained relatively small amounts of one or the other of these constituents.

TABLE I.—ABSORPTION OF ETHYLENE IN AMMONIACAL 2% SILVER NITRATE SOLUTION.

Time of shaking. Min.	Volume of residual gas. Sample No. 1. Cc.	Sample No. 2. Cc.
0	99.2	100.0
5	93.8	95.0
10	90.6	92.8
15	88.6	90.4
20	86.4	88.0
25	83.6	85.6
30	82.2	83.0
35	80.0	81.0
40	78.6	78.6
45	76.4	76.4
50	75.0	74.6
55	72.2	72.0
60	70.4	70.0

A method for determining acetylene gravimetrically has been suggested by Hempel, which consists in absorbing the gas in ammoniacal cuprous chloride solution with which the acetylene reacts to form a precipitate of copper acetylide. From the weight of copper in the precipitate, which may be determined by any one of several methods, the percentage of acetylene in the sample is then calculated.[1] This method is claimed to give accurate results, but was found to be unsuitable for our work on account of the time taken in making an analysis.[2]

Experiments were then undertaken to determine the limits of accuracy of a volumetric method outlined by Chavastelon[3] for the determination of acetylene in gaseous mixtures. It is known that when an excess of acetylene is passed into an ammoniacal solution of silver nitrate a precipitate is formed of the composition C_2Ag_2.[4] When the solution is neutral, however, and the silver nitrate is in excess, the precipitate then has the composition $C_2Ag_2.AgNO_3$,[3] and a definite proportion of nitric acid is set free in the reaction as represented by the equation

$$C_2H_2 + 3AgNO_3 = C_2Ag_2.AgNO_3 + 2HNO_3.$$

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[1] J. Scheiber, *Z. anal. Chem.*, **48**, 529 (1908).

[2] S. A. Tucker and H. R. Moody, THIS JOURNAL, **23**, 672 (1901).

[3] *Compt. rend.*, **125**, 245 (1897).

[4] E. H. Keiser, *Am. Chem. J.*, **14**, 286 (1892); R. Chavastelon, *Compt. rend.*, **124**, 1364 (1897); G. Arth, *Ibid.*, **124**, 1534 (1897).

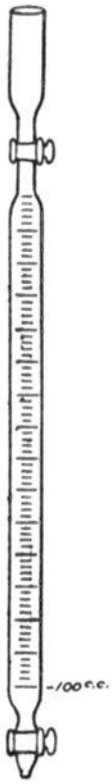

Fig. 1.

This reaction has accordingly been suggested by Chavastelon as the basis of a method for determining acetylene by simply titrating the acidity of the solution recovered when a known volume of gas, free from acid constituents, was absorbed in a solution of silver nitrate. The gas holder devised by Raoult,[1] and represented in Fig. 1, was recommended as the most suitable for use in this determination. When the volume of the sample was sufficiently great the holder was filled by displacement of the air with the sample. With a smaller sample it was suggested that this might be collected directly in the holder over mercury, or by passing it into the holder after the latter had been evacuated. An excess of 10% silver nitrate solution was then placed in the funnel of the gas holder and introduced into the holder where it was shaken until absorption of the gas was complete. The acidity of the resulting solution was then determined by titration and it was held that from the data thus obtained and knowing the volume, temperature and pressure of the gas sample taken, the percentage of acetylene present could then be readily calculated. No further details were given for carrying out the analysis or for making the calculations, and no results of analysis were listed to show the limits of accuracy of the method.

Development of the Method.

When undertaking analyses of gas samples by the method as thus outlined, use was made of the gas holder represented in Fig. 2. Each holder had a capacity of about 45 cc., and was provided with a water jacket to prevent the inclosed gas from undergoing the sudden changes in temperature which were found to occur when no jacket was used.

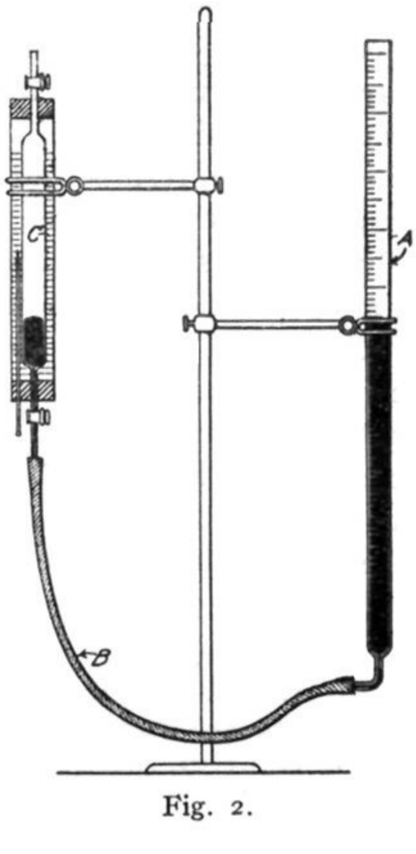

Fig. 2.

Since acetylene is soluble in water to the extent of 1.1 volume per volume of water at ordinary temperature, and since the use of water requires that a factor be applied to correct for the pressure of water vapor, it was decided to avoid both complications by collecting the samples over mercury. This was contained in the graduated tube A, Fig. 2, which was connected with the gas holder C by means of the rubber tube B. The holder was filled with mercury by opening the stopcocks and lowering it to the proper level. A sample of gas was collected by displacing the mercury into the graduated tube again,

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[1] *Compt. rend.*, **82,** 844 (1876).

and closing the lower stopcock. The upper stopcock was not closed until the gas was passed into the holder under slightly increased pressure. The holder was then removed from its connection with the graduated tube and allowed to stand until the gas had reached temperature equilibrium. One of the stopcocks was then opened for an instant to bring the gas to normal pressure. C was finally connected to the lower end of a two-foot column of a 5% silver nitrate solution and an excess of the solution then added and shaken up with the gas in the holder until absorption was complete. In the preliminary experiments a 10% solution was used as suggested by Chavastelon, but the less concentrated solution proved the more satisfactory. The solution containing the precipitated silver acetylide was finally transferred to a beaker and titrated with standard sodium hydroxide solution, using phenolphthalein as indicator. It was found, however, that the end-point of the titration when carried out in the way described was too indefinite to give satisfactory results, since the brown color of silver oxide masked the end-point. Attempts were then made to overcome this difficulty by eliminating the excess of silver ion by precipitation with sodium chloride solution. When this was added before the alkali the result was still unsatisfactory, presumably because it effected a reversal of the reaction between the acetylene and the silver nitrate. It was found, however, that when the standard alkali was first added in excess, and the silver then precipitated with sodium chloride, the excess of alkali could be titrated to a very sharp end-point with standard hydrochloric acid solution. When making a titration with this modification, the standard alkali was added until the brown color of silver oxide appeared; the excess of silver in solution was precipitated with about 5 cc. of neutral 20% sodium chloride solution, and the original acidity of the solution then determined by titrating the excess of alkali with standard acid as already explained.

When the volume of gas available for analysis was less than the capacity of the gas holder, the amount collected was measured by noting the rise of mercury in the graduated tube after the surface of the mercury in each vessel was brought to the same level. The upper stopcock was then closed, and the gas holder raised until all the mercury had passed through the lower stopcock. The latter was then closed, and the analysis completed in the usual way.

The following method was used in calculating the results:

Let V_g = volume of gas holder.
T = absolute temperature, 273°.
T_0 = temperature of gas sample when collected.
P = standard pressure, 760 mm.
P_0 = barometric pressure at the time the sample was collected.

Then the volume of the sample collected in the gas holder when reduced to standard conditions,

$$V = V_g \times P_0/P \times T/T_0 = V_g \times P_0/T_0 \times 0.3592.$$

Since acetylene reacts with silver nitrate to give two molecules of nitric acid per molecule of gas taken, it follows that 1 cc. of acetylene reduced to standard conditions is equivalent to 0.893 cc. of 0.1 N sodium hydroxide solution; or 1 cc. of 0.1 N sodium hydroxide solution is equivalent to 1.120 cc. of acetylene. The number of cc. of 0.1 N sodium hydroxide solution required in the titration of any sample multiplied by the factor 1.12 thus gives directly the volume which the acetylene in the sample would occupy under standard conditions, and this volume expressed in terms of the total volume of the sample taken gives directly the percentage of acetylene in the sample. By thus calculating once for all the volume of acetylene under standard conditions to which 1 cc. of the standard alkali is equivalent the necessary calculation for subsequent analyses becomes very much simplified.[1]

To test the accuracy of the method as thus developed analyses were made of the gas from an acetylene cylinder and the results compared with those obtained by absorption in fuming sulfuric acid. The acetone in the acetylene coming from the cylinder was removed by passing the gas through a suitable column of water, and the moisture then removed by means of anhydrous calcium chloride. With the volumetric method, using phenolphthalein as indicator, the results were found to vary in the case of 6 analyses from 97.8% to 100.8% of acetylene with a mean of 98.2%. Analysis of the same gas by the method of absorbing in fuming sulfuric acid gave a mean value of 96.3%. The results obtained by the volumetric method thus not only did not agree very closely among themselves but were over 2% greater on an average than the mean value found by the absorption method.

In order to determine the cause of this disagreement in the results, a number of blank titrations were run using the same proportion of the reagents, acetylene alone being omitted, as were taken for the analysis of the gas from the acetylene cylinder. It was found that the reagents exhibited a decided acidity towards phenolphthalein, and that the extent of the acidity varied with the amount of standard sodium hydroxide solution used in the titration. This is shown by the results given in Table II. In each of the experiments there were used 40 cc. of a 5% silver nitrate solution and 5 cc. of a 20% sodium chloride solution with water to make 150 cc.

In the analysis of the acetylene samples already referred to, 40 cc. of the standard alkali was added to the solution containing the silver acetylide precipitate, and the excess of alkali then titrated back with the standard

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[1] In the analysis of acetylene that is stored or collected over water, the value of the vapor pressure of the water at the temperature of the experiment must be subtracted from the barometric pressure. With this correction the remainder of the calculation is then completed in the usual way.

acid. For the analysis in question between 2 and 3 cc. of acid was required. In order to determine the blank that might most closely correspond to these conditions, about 36 cc. of the standard acid was added to the acetylene-free silver nitrate solution, followed by 40 cc. of standard alkali. The solution was then titrated with standard acid again to neutrality as indicated by phenolphthalein. Under these conditions the apparent acidity of the reagents amounted to 0.65 cc. of the 0.1 *N* hydrochloric acid. It was found, however, that when methyl orange was used as the indicator in titrations carried out in the same way the reagents then showed exact neutrality.

TABLE II.—VARIATION IN THE APPARENT ACIDITY OF THE REAGENTS USED IN ACETYLENE ANALYSIS WITH THE AMOUNT OF STANDARD ALKALI USED IN THE TITRATION.

Expt. No.	0.1 *N* NaOH added. Cc.	0.1 *N* HCl required. Cc.	Apparent acidity of the reagents in cc. of 0.1 *N* HCl.
1	2.00	1.82	0.18
2	5.00	4.80	0.20
3	6.00	5.77	0.23
4	10.00	9.62	0.38
5	40.00	39.05	0.95

An analysis was now made of the acetylene from the same cylinder as before, using first methyl orange as indicator, following which a little more standard alkali was added and the titration with acid repeated with use of phenolphthalein. It was found that when the correction of 0.65 cc. was added to the 0.1 *N* hydrochloric acid titration obtained with phenolphthalein the results as calculated from the values found with this indicator were then in exact agreement with those obtained directly with methyl orange. On applying the same correction in a recalculation of the results already reported for the analysis of the gas from an acetylene cylinder it was found that the mean value for the acetylene in the gas analyzed now amounted to 96.7%, instead of 98.2%, which is in quite close agreement with the value 96.3% found by the absorption method.

It is apparent from the results given in Table II, however, that in the analysis of a gas containing a lower percentage of acetylene a different blank correction would have to be applied when using phenolphthalein. This indicator was accordingly discarded in all subsequent analyses in favor of methyl orange. With the latter indicator the end-point is not quite as sharp as with phenolphthalein but the accuracy of any titration may be readily checked by adding successive portions of the standard alkali and then titrating to neutrality as before with the standard acid.

A number of analyses were now undertaken to ascertain the accuracy of the method in the analysis of mixtures of ethylene and acetylene. Pure ethylene does not give any precipitate with silver nitrate solution, but it was noticed that when samples of this gas were collected in the gas holder over mercury a slight precipitate sometimes occurred with development of a corresponding acid reaction. This was traced to the presence of small droplets of mercury which adhered to the interior walls of the gas holder and which then reacting with the silver nitrate used in the analysis, gave rise to an acid reaction through hydrolysis of the mercury salt formed. With a perfectly clean gas holder any quantity of mercury adhering to the gas holder was too small to have any effect on the analysis, but it was found that any appreciable amount of mercury in the solution to be titrated produced a wide variation in the results.

In order to obviate the danger from contamination with mercury a new apparatus was devised to replace that represented in Fig. 2. This is shown in Fig. 3. B is an ordinary gas buret in which the sample to be analyzed is collected over mercury. The gas bulb D has a capacity of

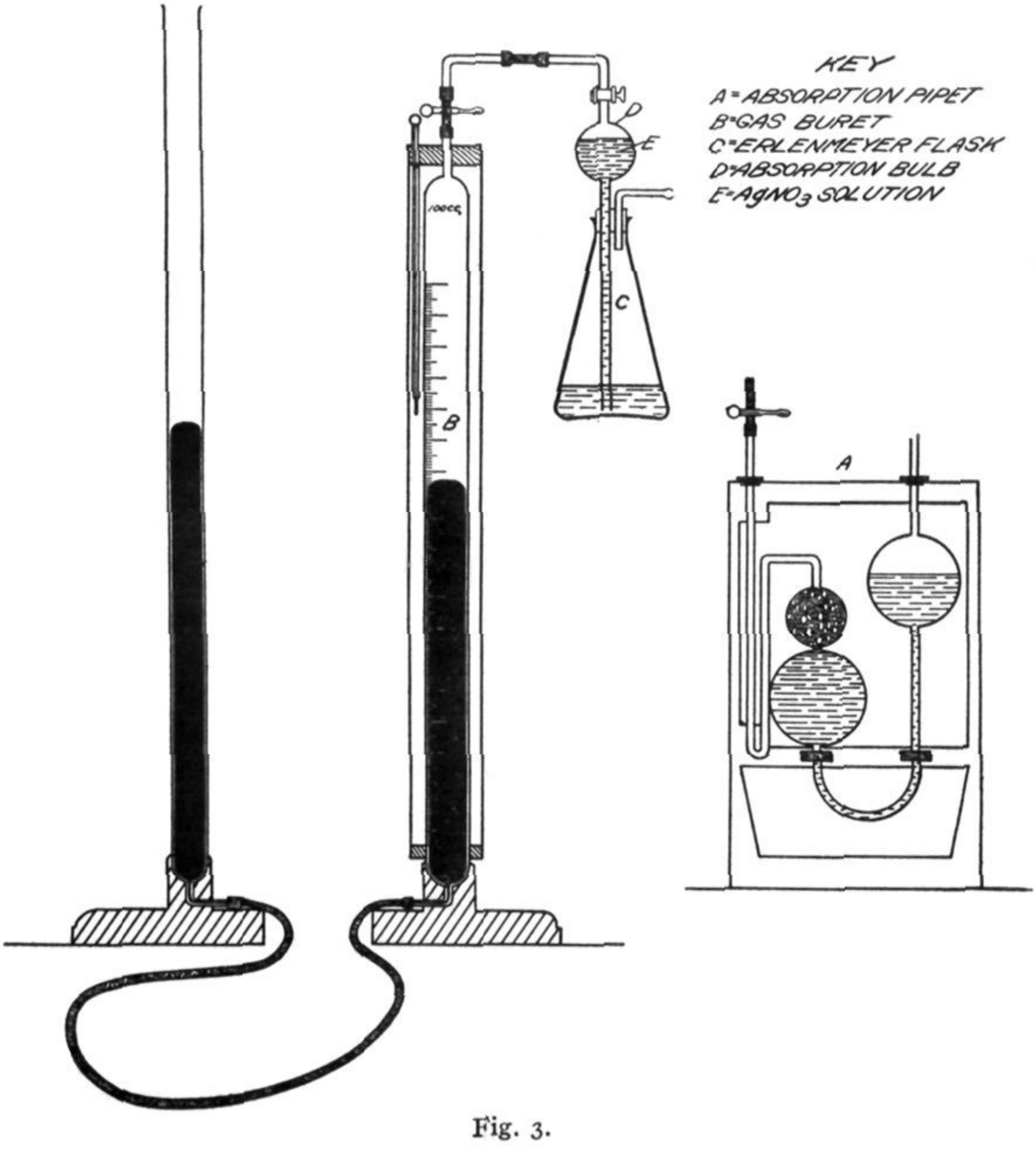

Fig. 3.

about 55 cc. In the Erlenmeyer flask C is placed about 90 cc. of a 2.5% silver nitrate solution. This is then sucked up into the glass bulb and the stopcock at the top closed. Connection is then made with the gas buret as indicated, and about 45 cc. or less of the sample to be analyzed is passed into the bulb over the silver nitrate solution. The stopcock of the glass bulb is then closed, and the latter with its connecting flask disconnected from the buret and shaken until absorption of the gas is complete, or until there is no further rise of the solution into the bulb. The stopcock is then opened, allowing the solution and precipitated silver acetylide to run into the flask. To this is added the rinsings from the bulb, and the titration then made directly in the flask in the usual way.

By use of this procedure for absorbing the gas the occasion for drying a portion of the apparatus before making an analysis, as in the case when a gas holder is used, is avoided, and a further advantage is to be found in the fact that any leak in the apparatus is always inwards so that no loss of the sample takes place.

When testing the accuracy of the method as thus modified in the analysis of ethylene-acetylene mixtures, special precautions were taken to prepare the separate gases free from all other hydrocarbons. The acetylene used was prepared by passing the gas from an acetylene cylinder through water and chromic acid solution, then over solid sodium hydroxide and phosphorus pentoxide and finally through a tube dipped in liquid air. The solid acetylene thus obtained was then allowed to evaporate and the middle portion collected over a 20% sodium chloride solution through which acetylene had abeen allowed to bubble for a time to expel dissolved air. The gas thus collected gave 99.7% absorption in fuming sulfuric acid.

Ethylene of corresponding purity was prepared by dropping ethylene dibromide into an alcoholic solution containing a zinc-copper couple. Known mixtures of the two gases were then made up and analyzed first for acetylene by the volumetric method and then for total ethylene and acetylene by absorption in the fuming sulfuric acid pipet A, Fig. 3. The ethylene percentage was obtained by difference. The results are given in Table III.

TABLE III.—ANALYSIS OF MIXTURES OF ETHYLENE AND ACETYLENE.

Analysis No.	% taken.			% found.		
	Acetylene.	Ethylene.	Total.	Total.	Acetylene.	Ethylene.
1	99.7	0.0	99.7	99.7	99.3	0.0
2	49.9	42.7	92.6	92.3	49.7	42.6
3	28.3	60.4	88.7	87.7	28.0	59.7
4	28.1	60.5	88.6	88.9	28.3	60.6
5	11.8	74.3	86.1	86.1	11.6	74.5
6	10.5	75.6	86.1	86.1	10.3	75.8

In Table IV are given some results which show the agreement to be expected in successive analyses of the same gas by the volumetric method.

The gas to be analyzed was obtained from an acetylene cylinder and purified by passing successively through water, dry calcium chloride, chromic acid deposited on pumice, dry calcium chloride again and finally over sticks of solid potassium hydroxide. Analysis of this gas by the absorption method gave a mean value of 98.1%.

TABLE IV.—SUCCESSIVE ANALYSIS OF SAMPLES OF ACETYLENE FROM THE SAME SOURCE BY THE VOLUMETRIC METHOD.

Analysis No.	Sample taken.	Barometric pressure.	Temperature.	Acetylene found.
1	46.9	761.8	22.0	97.9
2	45.5	761.8	22.0	98.0
3	46.6	761.8	22.1	98.3
4	44.8	765.4	22.1	98.1
			Mean =	98.1

The values given in Table IV show that with careful analysis very closely agreeing results may be obtained by the volumetric method, and that in the analysis of acetylene free from other absorbable hydrocarbons results are obtained which agree very closely with those given by absorption in fuming sulfuric acid.

When acetylene is prepared from ethylene dibromide by treatment with alcoholic potash there is always present a greater or less proportion of vinyl bromide, depending on the temperature and column of alkali through which the evolved gas is passed. In one sample collected this amounted to as much as 60% of the gas while the content of acetylene amounted to only 39%. Vinyl bromide undergoes rapid and complete absorption in fuming sulfuric acid and in neutral or ammoniacal silver nitrate. No distinction could therefore be made between acetylene and vinyl bromide by the Tucker and Moody method for determining acetylene. Vinyl bromide, however, does not give rise to any acidity in silver nitrate solution, and accurate results may therefore be obtained by the volumetric method in the analysis of acetylene mixtures containing this gas or any other hydrocarbon having a single or double bond.

Summary.

An account is given of a modification of the method of Chavastelon for the determination of acetylene in the presence of ethylene, or other single or double bond hydrocarbons, which is based on the volumetric determination of the nitric acid set free when acetylene is precipitated with excess of silver nitrate solution. When making an analysis according to this method, the sample is collected in an ordinary water-jacketed gas buret under observed conditions of temperature and pressure, and passed into an apparatus of simple design containing an excess of silver nitrate with which the gas is shaken until absorption is complete. Standard alkali solution is then added directly to the solution containing the precipitated silver acetylide until the brown color of silver oxide appears;

the excess of silver is then precipitated with neutral 20% sodium chloride solution, and the excess of free alkali in solution finally determined by titration with standard hydrochloric acid solution using methyl orange as indicator. Having calculated once for all the volume of acetylene under standard conditions of temperature and pressure to which 1 cc. of the standard alkali is equivalent, the acetylene in any sample analyzed follows directly from the volume of standard alkali required for the titration, and this volume of acetylene expressed in terms of the volume of the sample taken, when also reduced to standard conditions of temperature and pressure, gives the percentage of acetylene in the sample.

The method as described is rapid, accurate and simple of manipulation, and has the added advantage of giving accurate results for acetylene in mixtures of ethylene or of a gas of such similar properties as vinyl bromide which is readily absorbed in bromine, fuming sulfuric acid and in neutral or ammoniacal silver nitrate.

EDGEWOOD, MD.

NOTE.

The Use of Coal as a Substitute for Talcum to Induce Rapid Boiling.—While we were attempting to improve the method for the determination of small amounts of iodine, some substitute for talcum was sought which would cause a rapid boiling of the solution. The usual laboratory agents, such as pumice stone, powdered brick, broken glass, glass beads, granite, etc., were tried and found to be unsuitable. The theoretically ideal agent would have to be insoluble in acid and alkali and not acted on by reduction or oxidation.

Carbon in its various forms answers the theoretical requirements. It was found, however, that the various forms of carbon differ greatly in their power to cause rapid boiling of a solution. While powdered charcoal or coke has slight power in this respect, anthracite coal is without exception the very best substance to bring about the rapid boiling of a solution. The formation of bubbles does not take place on the sharp edges and corners alone, but over the hard, smooth surfaces of the coal minute bubbles form with great rapidity, and under some conditions a piece of coal 2 cm. cube can be raised from the bottom of the flask by the rapid formation of bubbles on its surface. It acts in a similar manner in the acidification of a carbonate or sulfite solution. The bubbles of sulfur or carbon dioxide are liberated on the surface of the coal. Coal is equally successful in preventing bumping in Kjeldahl flasks and in the distillation of organic liquids. If the coal is kept under water indefinitely it becomes less active, but heating in an oven will restore its activity, Another great advantage of coal is the fact that it is easily cut with a dental drill and a small glass hook can be inserted in the coal. After