paratus used above in the case of combustions. The first soda-lime ⊔-tube lost one and eight-tenths milligrams, while the second containing also calcium chloride gained one and six-tenths milligrams, which shows that no carbon dioxide was driven out of the spent soda-lime. A large amount of water was, however, given off, indicating that the white seemingly dry carbonate had really absorbed considerable water hygroscopically. The whitening in a tube is not, therefore, due to drying out. Experiment has also shown that moistening white, spent soda-lime does not increase its absorbent power for carbon dioxide.

Soda-lime prepared as outlined above is recommended as a general reagent for freeing gases from carbon dioxide, such as normal air in determining gas densities. As a reagent for the quantitative determination of carbon dioxide, both in elementary organic analysis and in air analyses, it has given excellent satisfaction. The air analyses were made in connection with the respiration calorimeter above referred to. It appears to be an excellent general substitute for potassium hydroxide solution in all cases where the solid form of reagent is not proscribed.

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THE DETERMINATION OF CARBON MONOXIDE, METHANE, AND HYDROGEN BY COMBUSTION.

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IN the development of technical gas analysis the researches of Winkler, Hempel, Lunge, and others have given us many methods which are both rapid and exact and which yield results quite as satisfactory as those obtained by the classical methods of Bunsen. But for the determination of hydrogen and methane modern methods have been found to be far from satisfactory. The combustion of hydrogen and hydrocarbons by means of copper oxide is no longer used because of its inconvenience. The combustion of hydrogen by means of palladium asbestos is open to the error which may result from the partial burning of the methane present. The fractional combustion of hydrogen by palladium sponge and the absorption of hydrogen by palladium

black are exact, but the palladium needs to be frequently removed from the tube and heated, to render it again active. The last three of these methods, moreover, leave the methane still to be determined, a detail which so prolongs the analysis as to exclude the methods from general adoption.

It was but natural that gas analysts should prefer to use some method by which both hydrogen and methane could be simultaneously determined, and the procedure which is now most frequently employed is the Hempel explosion method or some modification of it. In speed and convenience of manipulation this method leaves little to be desired. Unfortunately, however, the results are neither constant nor accurate, first because of the smallness of the gas volume which is exploded, any error being thus multiplied about eightfold, and second because of the danger of the formation of oxides of nitrogen. This last difficulty is largely avoided if the determination is carried out as Hempel directs, but in the employment of an explosion pipette in which the gases are confined between two glass stop-cocks, there is no way of judging of the violence of the explosion. This is a point of considerable importance, for if the explosion is too violent the formation of oxides of nitrogen is probable, while if too weak the combustion is liable to be incomplete. If the explosion is made with oxygen instead of air the danger of formation of oxides of nitrogen from the nitrogen originally present in the gas mixture is increased[1] and the violence of the explosion becomes so great that Gill, who recommends this procedure, divides the explosion into two parts, using half of the required oxygen in each.

It seemed necessary, therefore, in seeking to improve the procedure for the determination of hydrogen and methane, to devise some method which would permit of the use of large volumes of gas and would so diminish the violence of the union of oxygen and the combustible gases as to reduce to a minimum the possibility of injury to the operator, and the probability of the formation of oxides of nitrogen. It was apparent that to attain these ends it would be necessary to abandon the method of explosion and to replace it by some form of slow combustion. The gris-

[1] See the researches of Bunsen and Hempel upon this point.

oumeter devised by Winkler seemed to be an apparatus which might be adapted to this purpose provided that it were found possible to attain complete combustion without mixing the combustible gases and the oxygen *before*[1] their introduction into the grisoumeter. This proved to be feasible.

The determination of carbon monoxide by absorption with cuprous chloride offers many difficulties. The absorbent is somewhat difficult to prepare and keep, and the absorption can be completed in a reasonable time only by using two solutions of cuprous chloride and bringing the gas and the reagent into intimate contact by vigorous shaking.[2] Vignon[3] and later Noyes and Shepard[4] have avoided this absorption of carbon monoxide by exploding the gas simultaneously with the hydrogen and methane and then determining the contraction, the volume of carbon dioxide formed, and the oxygen consumed in the explosion. As will be seen below this procedure can also be carried out with satisfactory results by means of the combustion method which is here described.

The apparatus used for the combustion of the various gases is quite similar to the "grisoumeter" described by Winkler[5] and was made from a Hempel simple gas pipette for solid and liquid reagents[6] by cutting off the upper bulb and attaching in its place, by means of a rubber tube, a level bulb like that used by Hempel in his explosion pipette.[7] Through the opening of the single-hole rubber stopper a there passes a glass tube b which is open at both ends and contains an iron wire c three mm. in diameter. Another iron wire m of about one and five-tenths mm. diameter is pushed through the stopper and is then wound several times around the glass tube and cut off at the same height as the larger wire. This arrangement of the conducting wires is preferable to that suggested by Winkler, since the relative positions of the wires remain unchanged when the stopper

[1] Mixing the oxygen and combustible gases before passing them into the grisoumeter was not attempted, for the combustion has been known to pass back through the capillary and explode the main mixture with most deplorable results.

[2] See Dennis and Edgar : This Journal, 19, 859.

[3] *Bull. Soc. Chim.*, *1897*, p. 832.

[4] This JOURNAL, 20, 343.

[5] *Ztschr. anal. Chem.*, 28, 288 ; Hempel : Methods of Gas Analysis, p. 236.

[6] Hempel : Methods of Gas Analysis, p. 35, Fig. 21, *b*.

[7] *Ibid.*, p. 103, Fig. 44.

is pushed into place and, as will be seen later, the use of a cement of any sort is avoided. The upper ends of the iron wires are connected by a platinum spiral d, contact between the platinum and iron being effected by simply wrapping the platinum wire several times around the iron wires. The platinum wire is one-fourth mm. in diameter and the coil into which it is bent is about two mm. in diameter and contains from twenty to thirty turns. After the spiral has been attached to the iron wires it is bent into the form of a horizontal S. Below the rub-
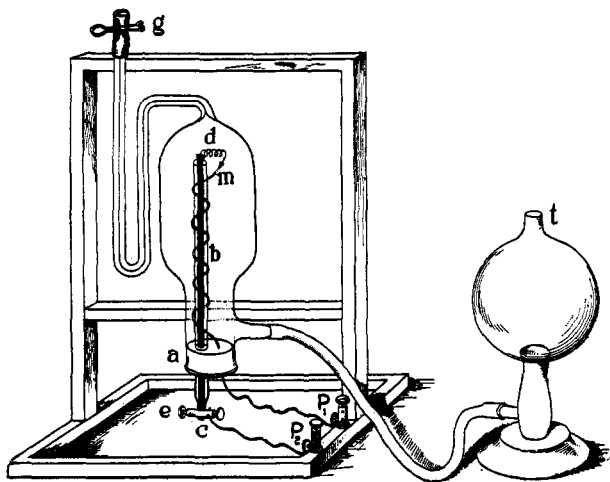

Fig. 1.

ber stopper the smaller iron wire is fastened directly to the double binding-post P. The opening between the large iron wire and the tube through which it passes is closed air-tight by means of a piece of small rubber tubing carefully wired in place. The lower end of the iron wire is connected, by means of a binding-screw e and a piece of suitable wire, to the second binding-post P_2. Both binding-posts P_1 and P_2 should be insulated from the iron stand.

After the rubber stopper carrying the spiral has been inserted in place and the iron wires have been connected with the binding-posts, the pipette and capillary are filled with mercury by raising the level-bulb, the pinch-cock g on the rubber tube on the capillary is closed, and suction is applied to the tube t of

the level-bulb by means of a water suction-pump. The air contained in the glass tube b is thus removed and the tube remains completely filled with mercury.

The gas volumes were measured in a simple Hempel burette[1] provided with a water-jacket (see Fig. 2). Mercury was used as the confining liquid and a drop of water was introduced into the
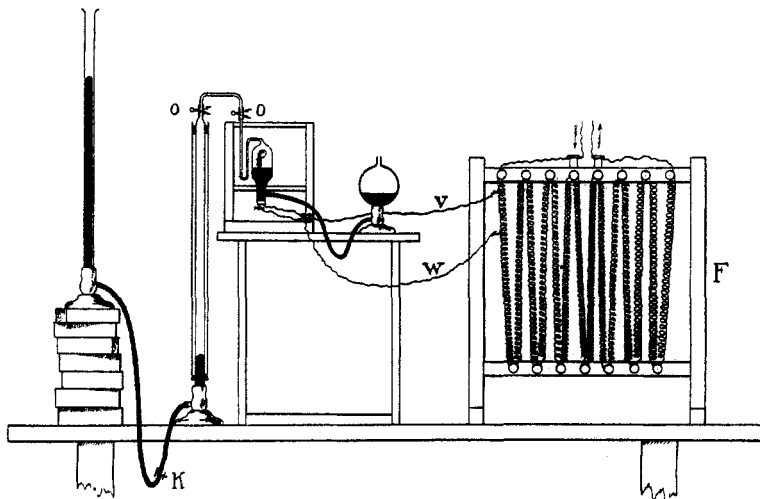

Fig. 2.

burette to insure the complete saturation of the gases with moisture.

The method of procedure which was finally adopted for the combustion of the gases is as follows :

The combustion pipette is first completely filled with mercury by raising the level-bulb, and a measured quantity of the gas to be burned is then introduced. A quantity of oxygen more than sufficient to completely burn the gas is drawn into the gas burette and its volume noted. The burette is then connected with the pipette by the usual bent capillary tube (see Fig. 2) and the level-bulb of the pipette and the level-tube of the burette are placed at such heights that the gases in both pipette and burette are approximately under atmospheric pressure. A screw pinch-cock k which has previously been placed upon the rubber tube joining the burette with its level-tube is now tightly screwed down so as to prevent, for the present, any movement of the mer-

[1] Hempel : Methods of Gas Analysis, p 22. Fig. 17.

cury in the burette. The level-tube is now placed at such a height that when the screw pinch-cock k is opened the mercury will rise to the top of the burette but will not pass over into the pipette. The pinch-cocks o,o on the connections between the burette and pipette are now opened and the electric current, which should be just strong enough to maintain the spiral at a red heat, is turned on. Any electrical apparatus furnishing a current of sufficient strength to heat the platinum spiral to redness may, of course, be employed. If the current from a dynamo or storage battery is at the operator's disposal, the arrangement shown in Fig. 2. can be recommended as being both simple and convenient. The current is passed through the resistance frame F. (We have used a small frame carrying German silver wire about one and five-tenths mm. in diameter.) The terminals on the combustion pipette are connected with the frame by means of the flexible wires V and W, the ends of these wires being simply hooked into the coiled wire of the frame. The current passing through the platinum spiral can then be varied at will by simply hooking the end of W into the resistance coil at a greater or less distance from V.

When the spiral has been brought to the proper temperature the screw pinch-cock k is carefully opened and a slow and steady current of oxygen is passed over into the pipette. From ten to twenty cc. of oxygen per minute may be introduced, but the amount is, of course, somewhat dependent upon the length and temperature of the spiral. The combustion takes place quietly without the appearance of a flame and if the operation is properly conducted there is no possibility of an explosion since the combustible gas and the oxygen are in separate vessels and are made to combine as fast as they mix. Nevertheless a screen of heavy glass is always placed between the pipette and the operator to insure protection for the face in case of possible accident.[1] After the oxygen has been passed into the pipette, the spiral is kept at a red heat for about one minute to insure complete combustion of the gas. When, however, hydrogen alone is being burned, the combustion is complete almost as soon as sufficient oxygen has been introduced. When the combustion is finished

[1] This precaution is invariably taken in this laboratory in all combustion or explosion analyses of gas mixtures.

the residual gas is passed back into the burette and measured.

The volume of gas which may be taken for the combustion is limited only by the capacity of the measuring burette, but for convenience in handling neither the combustible gas, the oxygen required, nor the residue after combustion is allowed to exceed 100 cc. The volume of gas in the pipette at any time during the combustion should be sufficient to prevent the mercury from rising and covering the spiral, or short-circuiting the current. This would take place if pure hydrogen were burned by adding pure oxygen, but the difficulty in this case is avoided by introducing into the 100 cc. of hydrogen about 95 cc. of a mixture of equal parts of oxygen and air.

In the following tables are given the results obtained with this apparatus in the determination of hydrogen and carbon monoxide and in the analysis of the residue of illuminating gas both before and after the removal by absorption of carbon monoxide. No corrections were made for the slight changes in temperature and barometric pressure which may have taken place during the progress of any one determination.

HYDROGEN.

The hydrogen was made by allowing hydrochloric acid to act upon zinc[1], the vapors of the acid being removed by shaking the gas with a strong solution of potassium hydroxide.

	I. cc.	II. cc.	III. cc.	IV. cc.	V. cc.	VI. cc.	VII. cc.	VIII. cc.	IX.[2] cc.	X.[2] cc.
Hydrogen taken..	99.6	100.0	98.6	99.8	99.4	95.35	97.5	51.15	35.0	34.75
Oxygen and air added	99.6	99.95	99.9	100.0	99.1	96.6	99.75	48.95	100.0	100.0
Total	199.2	199.95	198.5	199.8	198.5	191.95	197.25	100.10	135.0	134.75
Residue after combustion	50.0	50.1	50.8	50.55	49.7	49.1	51.2	23.4	82.65	82.75
Contraction	149.2	149.85	147.7	149.25	148.8	142.85	146.05	76.7	52.35	52.00
Equivalent to hydrogen	99.47	99.9	98.47	99.5	99.3	95.23	97.37	51.13	34.9	34.67
	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
Hydrogen found .	**99.9**	**99.9**	**99.9**	**99.7**	**99.9**	**99.9**	**99.9**	**100.0**	**99.7**	**99.8**

CARBON MONOXIDE.

This was prepared by heating together oxalic and sulphuric

1 Cf. Cooke and Richards : *Am. Chem. J.*, (*1888*), 10, 100.

2 In IX and X air alone was added, and smaller amounts of hydrogen were taken. The results are fairly good but are not as satisfactory as those obtained with oxygen and air.

acids and removing the carbon dioxide with potassium hydroxide. Duplicate volumetric analyses by absorption with cuprous chloride showed the gas to be 99.7 per cent. pure.

The oxygen which was used in these and the other combustions was made from potassium chlorate and manganese dioxide and was purified by being shaken with a solution of potassium hydroxide. Absorption by alkaline pyrogallol showed it to be very nearly pure, 99.9 per cent.

Two volumes of carbon monoxide unite with one volume of oxygen to form two volumes of carbon dioxide. Hence the volume of the carbon monoxide taken is equal either to the volume of carbon dioxide which is formed, or to twice the contraction resulting from the combustion. In the following tabulation of results the percentages of carbon monoxide obtained in both ways are given. There are also added the percentage results calculated on the assumption that the gas contained only 99.7 per cent. of carbon monoxide as indicated by the absorption with cuprous chloride.

	I. cc.	II. cc.	III. cc.	IV. cc.	V. cc.	VI. cc.	VII. cc.	VIII. cc.
Carbon monoxide taken	73.1	60.7	82.1	80.95	78.1	77.95	83.05	79.0
Oxygen taken...................	50.7	49.65	52.2	49.8	50.55	50.8	52.4	50.4
Total	123.8	110.35	134.3	130.75	128.65	128.75	135.45	129.4
Residue after combustion	87.4	80.1	93.3	90.4	89.65	89.8	93.95	89.95
Contraction	36.4	30.25	41.0	40.35	39.0	38.95	41.50	39.45
Residue after absorbing CO$_2$ in KOH pipette	14.5	19.5	11.5	9.6	11.7	12.05	11.05	11.25
Carbon dioxide	72.9	60.6	81.8	80.8	77.95	77.75	82.90	78.70
	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.	Per ct.
CO, calculated from contraction	99.6	99.7	99.9	99.7	99.9	99.9	99.9	99.9
CO, calculated from CO$_2$ formed	99.7	99.8	99.6	99.8	99.8	99.7	99.8	99.6
CO, from contraction, assuming gas to be 99.7 per cent. pure ..	99.9	100.0	100.2	100.0	100.2	100.2	100.2	100.2
CO, from CO$_2$, assuming gas to be 99.7 per cent. pure	100.0	100.1	99.9	100.1	100.1	100.0	100.1	99.9

METHANE.

Methane was first prepared from zinc dust and chloroform in aqueous alcohol, as proposed by Sabanejeff[1] and recommended by Phillips.[2] The product was, however, very unsatisfactory as

1 *Ber. d. chem. Ges.*, 9, 1810.
2 *Am. Chem. J.*, 16, 172.

it contained not only vapors of alcohol and chloroform but also a considerable amount of hydrogen. Methane was then made from sodium acetate and soda-lime and the hydrogen which is simultaneously formed was removed by passing the gas over palladium black. Four determinations, by this method, of the hydrogen present gave the following results :

	I. cc.	II. cc.	III. cc.	IV. cc.
Gas taken	99.2	100.0	99.55	99.2
Residue after passage over palladium black	92.75	93.5	93.0	92.8
Hydrogen	6.45	6.5	6.55	6.4
	Per cent.	Per cent.	Per cent.	Per ct.
Hydrogen	6.5	6.5	6.6	6.5

It was to be expected that the residue from the hydrogen determinations would be pure methane, but when 40.75 cc. of this gas was burned with oxygen in the combustion pipette the contraction amounted to 81.65 cc. and 42.5 cc. of carbon dioxide was formed, thus plainly indicating the presence of a gas or vapor with more than one carbon atom in the molecule. The gas was therefore not of sufficient purity to give trustworthy data concerning the accuracy of the combustion method when used for methane alone, and unfortunately there was not sufficient time at our disposal to permit of further experiments upon the preparation of pure methane. In order, however, to obtain, in an indirect way at least, some idea as to the accuracy of the method in the determination of methane, a series of combustions was made of the residue from illuminating gas after the removal of the absorbable gases.

SIMULTANEOUS COMBUSTION AND DETERMINATION OF HYDROGEN AND METHANE.

Illuminating gas was passed into fuming sulphuric acid to remove hydrocarbon vapors and heavy hydrocarbons, then shaken with alkaline pyrogallol to remove oxygen, carbon dioxide, and the fumes of the sulphuric acid, and finally shaken first with old and then with fresh cuprous chloride to remove carbon monoxide. Measured portions of the residue which now contained hydrogen, methane, and nitrogen were then introduced into the combustion pipette and burned with oxygen in the manner described above.

	I. cc.	II. cc.	III. cc.	IV. cc.	V. cc.
Gas residue taken	61.4	64.5	67.0	64.0	65.7
Oxygen taken	98.5	96.55	98.55	97.6	100.0
Total	159.9	161.05	165.55	161.6	165.7
Residue after combustion	58.8	54.95	55.3	56.3	57.6
Contraction	101.1	106.1	110.25	105.3	108.1
Residue after absorbing CO_2 in KOH pipette	34.3	29.15	28.6	30.7	31.4
Carbon dioxide found	24.5	25.80	26.7	25.6	26.2
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Hydrogen	56.4	56.3	56.6	56.4	56.5
Methane	39.9	40.0	39.9	40.0	39.9
Nitrogen (diff.)	3.7	3.7	3.5	3.6	3.6

To obtain an idea of the relative accuracy and constancy in the results by the combustion and explosion methods in the hands of the same operator, two analyses of the same gas residue were carefully made with the Hempel explosion pipette, mercury being used here also as the confining liquid.

	I. cc.	II. cc.
Gas residue taken	12.0	12.35
Air added	83.2	83.45
Total	95.2	95.8
Residue after explosion	75.3	75.25
Contraction	19.9	20.55
Residue after absorbing CO_2 in KOH pipette	70.35	70.2
Carbon dioxide found	4.95	5.05
	Per cent.	Per cent.
Hydrogen	55.3	56.4
Methane	41.3	40.9
Nitrogen (diff.)	3.4	2.7

SIMULTANEOUS COMBUSTION AND DETERMINATION OF CAR-
BON MONOXIDE, HYDROGEN, AND METHANE.

A mixture of these gases together with nitrogen was obtained by extracting from illuminating gas by means of the usual absorbents, only the hydrocarbon vapors, heavy hydrocarbons, oxygen, and carbon dioxide. A measured volume of the residue was transferred to the combustion pipette and burned with oxygen. The residual gas was then passed back into the burette, measured to ascertain the contraction, and then passed into the caustic potash pipette to absorb the carbon dioxide and again drawn

back and measured.   In the meantime a known volume of hydrogen had been brought into the combustion pipette.   This was then connected with the burette which now contained nitrogen and the unconsumed oxygen, the current was turned on, and the oxygen was passed over into the hydrogen.   From the resulting contraction the excess of oxygen was ascertained and the difference between this and the oxygen first taken gives the amount of oxygen consumed in the combustion of the carbon monoxide, hydrogen, and methane.

Having thus ascertained the contraction resulting from the combustion, the volume of carbon dioxide formed, and the amount of oxygen consumed, we have all the data necessary for the calculation of the amounts of carbon monoxide, hydrogen, methane, and nitrogen existing in the original mixture.   The reactions which take place in the combustion and the volume changes due to these reactions are the following :[1]
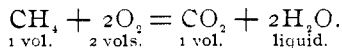
$$\underset{\text{2 vols.}}{2CO} + \underset{\text{1 vol.}}{O_2} = \underset{\text{2 vols.}}{2CO_2}.$$
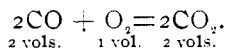
Contraction in burning 2 vols. $CO = 1$ vol.
Hence contraction for 1 vol. $CO = \frac{1}{2}$ vol.

$$\underset{\text{2 vols.}}{2H_2} + \underset{\text{1 vol.}}{O_2} = \underset{\text{liquid.}}{2H_2O}.$$
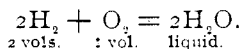
Contraction in burning 2 vols. $H = 3$ vols.
Hence contraction for 1 vol. $H = 1.5$ vols.

$$\underset{\text{1 vol.}}{CH_4} + \underset{\text{2 vols.}}{2O_2} = \underset{\text{1 vol.}}{CO_2} + \underset{\text{liquid.}}{2H_2O}.$$

Contraction in burning 1 vol. $CH_4 = 2$ vols.

From the above equations we have
Contraction $= \frac{1}{2} CO + \frac{3}{2} H + 2CH_4$.
Carbon dioxide formed $= CO + CH_4$.
Oxygen consumed $= \frac{1}{2}CO + \frac{1}{2}H + 2CH_4$.

From these last three equations a variety of formulas for the calculation of the various components of the original mixture may be derived.   Noyes and Shepard give

(1) $H =$ Contraction minus oxygen consumed.
(2) $CO = \frac{2}{3}(2CO_2 + \frac{1}{2}H$—oxygen consumed).
(3) $CH_4 = CO_2$—CO.

[1] Cf. Vignon : *Bull. Soc. Chim.. 1897,* p. 852.

(4) $N =$ Original volume $- (H + CO + CH_4)$.

Instead of (2) and (3) we may also use

$$CO = CO_2 - CH_4.$$
$$CH_4 = \frac{2 \text{ Contraction } - CO_2 - 3H}{3}.$$

If no nitrogen is present in the original mixture the following equations of Vignon may be employed, V representing the volume of the gas mixture taken for the combustion.

$$H = V - CO_2.$$
$$CO = \tfrac{1}{3}CO_2 + V - \tfrac{2}{3} \text{ contraction}.$$
$$CH_4 = \tfrac{2}{3}CO_2 + \tfrac{2}{3} \text{ contraction} - V.$$

|	I. cc.	II. cc.	III. cc.	IV. cc.
Volume of gas residue taken	83.45	85.05	83.05	86.95
Oxygen added	97.65	96.25	97.90	99.95
Total	181.10	181.30	180.95	186.90
Volume after combustion	49.3	46.95	49.75	49.5
Contraction resulting from combustion	131.8	134.35	131.20	137.4
Volume after absorption of carbon dioxide	13.05	10.15	13.75	12.0
Volume of carbon dioxide formed in the combustion	36.25	36.80	36.0	37.5
Hydrogen taken for determination of excess of oxygen	50.65	40.8	41.35	40.9
The preceding $+$ volume remaining after absorption CO_2	63.70	50.95	55.10	52.9
Volume after combustion	32.15	28.3	21.2	24.75
Contraction resulting from this combustion	31.55	22.65	33.9	28.15
Oxygen in excess ($\frac{1}{3}$ preceding contraction)	10.52	7.55	11.3	9.38
Oxygen consumed in combustion of CO, H, and CH_4	87.13	88.70	86.6	90.57

From the above experimental results the calculated percentages of the various gases are as follows :

	I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.
Carbon monoxide	6.2	6.1	6.2	6.0
Hydrogen	53.5	53.7	53.7	53.9
Methane	37.3	37.2	37.2	37.1
Nitrogen (difference)	3.0	3.0	2.9	3.0

In carrying on the various combustions by which the above results were obtained, it was observed that a much stronger current is required to maintain the spiral at a red heat in an atmosphere of gases of low molecular weight than is needed with heav-

ier gases, this being probably due to the different thermal capacities of the various gases and to the varying velocities of the different gas molecules. This phenomenon is especially marked in the combustion of hydrogen, for with this gas it is necessary to markedly decrease the strength of the current as the combustion proceeds, since otherwise a current which will heat the spiral only to redness in the atmosphere of hydrogen at the beginning, is liable to melt the platinum wire in the mixture of nitrogen and oxygen which remains after the combustion is completed.

An interesting reaction which was observed during the progress of the work is that a mixture of methane and water vapor when heated by the spiral reacts as follows :

$$CH_4 + H_2O = CO + 3H_2.[1]$$
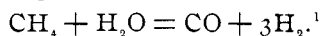
According to this equation one volume of methane should yield four volumes of the mixture of carbon monoxide and hydrogen. On actual experiment it was found that 24.1 cc. of impure methane expanded to 74.5 cc. from which cuprous chloride absorbed 16.5 cc. This 16.5 cc. of carbon monoxide shows that an equal volume of methane was present in the original gas, and according to the above equation the 16.5 cc. of methane on being heated in the presence of the water vapor, should show an increase in volume of 49.5 cc. The expansion observed was 50.4 cc., a result which is sufficiently close to sustain the above reaction. That the observed expansion does not agree more nearly with the calculated increase in volume is doubtless due to the fact that at high temperatures carbon monoxide reacts with water vapor, forming carbon dioxide and hydrogen.[2] We confirmed the accuracy of this statement by introducing into the combustion pipette 79.75 cc. of pure, moist carbon monoxide, and heating the spiral for five minutes. The volume was thereby increased to 82.75 cc. from which 3.05 cc. of carbon dioxide were absorbed by potassium hydroxide.

CORNELL UNIVERSITY, July, 1898.

[1] Several years ago Coquillion observed that the same reaction takes place in the presence of a red-hot palladium spiral.—*Compt. rend.*, **86**, 1198.

[2] Cf. Dixon : *J. Chem. Soc.*, **49**, 99, 100.