cut out and then the instruments showed 175 amperes, and 90 volts. A few moments after this the reading was 125 amperes, and 100 volts or 12,500 watts.

The only difficulty in using this type is to prevent the extinction of the arcs, but that trouble is far from insurmountable. The dimensions given for the furnace are suitable for currents up to 300 amperes, at 70 volts. For work requiring more power than this it is necessary to increase the size throughout and use electrodes of 2-inch diameter.

If the luting has been carefully done the furnace will be sufficiently gas-tight to permit a fusion to be carried on in an atmosphere of any desired gas, the gas being introduced through an annular electrode. This furnace is adapted to almost all kinds of fusion processes, and has been used in the greatest variety of work.

[CONTRIBUTION FROM THE LABORATORY OF ANALYTICAL AND APPLIED CHEMISTRY, UNIVERSITY OF MICHIGAN.]

THE OXIDATION OF NITROGEN AS A SOURCE OF ERROR IN THE ESTIMATION OF HYDROGEN AND METHANE.

BY ALFRED H. WHITE.

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THE author had occasion some time ago to estimate accurately a small amount of methane mixed with a large amount of hydrogen. A sample mixed with air was exploded in a Hempel pipette with due precautions to insure accuracy, the measurements being made in the author's burette for exact gas analysis previously described in this Journal.[1] Though great care was taken in the work, the results were so discrepant as to be entirely useless for the purpose. The results of a series of five experiments follow, arranged in the order of explosive ratios.

TABLE I.—EXPLOSION OF HYDROGEN AND A SMALL AMOUNT OF METHANE.

		After explosion.				
Gas sample. cc.	Air. cc.	Contraction. cc.	CO_2. cc.	Hydrogen. Per cent.	Methane. Per cent.	Explosive ratio.
12.87	103.24	16.97	0.05	87.64	0.39	5.77
13.79	86.89	18.39	0.04	88.51	0.29	5.08
13.17	84.18	17.56	0.06	88.27	0.45	4.54
14.77	87.23	19.66	0.09	87.92	0.62	4.20
18.38	87.03	24.48	0.16	87.62	0.87	3.30

The increasing amounts of carbon dioxide can not be laid to

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[1] This Journal, **22**, 343.

diffusion through the potassium hydroxide used, for the pipette carried enough mercury in the bottom to form a trap, nor to solution of gas by the potassium hydroxide, for the pipette had been carefully saturated by a blank experiment, nor to leak in connections because in each case after removing the carbon dioxide by potassium hydroxide, and reading the volume, the gas was passed back into the same potassium hydroxide pipette, allowed to stand and again drawn back into the burette and the volume read. In only one case, the third given, did the variation in volume after such second treatment with potassium hydroxide amount to as much as 0.02 cc. In two other cases, the variation was 0.01 cc. and in the other two there was no change in volume. Leaving out of account the first of the series where it is probable the great dilution caused incomplete combustion, the other four results show increasing methane and decreasing hydrogen as the explosive ratio (ratio of the inert to the exploding gas) grows smaller. The decrease in the percentage of hydrogen results from the method of calculation, all the contraction over potassium hydroxide being considered as carbon dioxide, and calculated to methane. The increase in the apparent carbon dioxide points strongly to the formation of oxides of nitrogen. That these are formed and may cause error in explosion analyses was shown long ago by Bunsen, who experimentally determined certain limits within which there was no appreciable error. The explosive ratio for pure hydrogen, according to Bunsen, might safely vary from 3.81 to 1.55. He did not determine whether any gases absorbable in potassium hydroxide were formed in the explosion. The results above cited have, with one exception, higher explosive ratios than his highest, and yet there is apparently considerable formation of an oxide of nitrogen which is absorbed by potassium hydroxide.

Bunsen's results have been seemingly everywhere accepted without question. Hempel, in the 1900 edition of his "Gasometrische Methoden," quotes Bunsen's results[1] with the comment that "by keeping to the Bunsen norm the worst that may happen is that the mixture is not explosive. The combustion of nitrogen will certainly be avoided."

The marked disagreement of the results given by Bunsen and those of Table I made it desirable to make a series of experiments

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[1] Hempel: "Gasometrische Methoden," 3te Auflage, p. 113.

on pure hydrogen. The hydrogen was generated by the action of potassium hydroxide on aluminum in order to obtain it free from the small amounts of hydrocarbons usually present in gas obtained by the action of an acid on a metal. The results are given in Table II.

TABLE II.—EXPLOSION OF PURE HYDROGEN.

						Bunsen's results recalculated.	
Sample hydrogen. cc.	Air. cc.	Contraction after explosion.	Hydrogen. Per cent.	Contraction over potassium hydroxide.	Explosive ratio.	Explosive ratio.	Hydrogen. Per cent.
11.35	84.80	16.90	99.26	0.00	4.64	3.81	99.92
12.11	85.57	18.08	99.53	0.00	4.37	2.90	99.56
14.19	84.27	21.27	99.92	0.00	3.62	2.29	99.84
16.77	85.77	25.13	99.90	0.01	3.06	1.95	100.04
16.54	82.64	24.76	99.80	0.01	3.00	1.55	100.15
18.19	83.22	27.29	100.01	0.01	2.71	1.25	100.72
21.10	83.28	31.74	100.28	0.00	2.29	1.04	103.14
27.04	83.86	40.80	100.59	0.11	1.73	0.37	105.06

Bunsen's results recalculated to permit direct comparison are appended. Bunsen held that the explosive ratio might vary from 3.81 to 1.55 without causing appreciable error, though the smaller ratio gives erroneous results according to his own figures.

These figures for the explosion of pure hydrogen in Table II do not show as great variations with change of explosive ratio as do the results in Table I of explosion of a gas carrying a small amount of methane mixed with a large amount of hydrogen. To determine if the methane caused the difference, a series of explosions of methane and air were made. The methane was made from methyl iodide and the zinc copper couple, and both gas and air were freed from carbon dioxide before use. Table III gives the results of this series.

TABLE III.—EXPLOSION OF METHANE.

Sample methane. cc.	Air. cc.	Contraction after explosion.	Carbon dioxide cc.	Methane. Per cent.	Hydrogen. Per cent.	Explosive ratio.	Ratio $\frac{\text{contraction}}{\text{sample}}$.
7.05	92.07	13.09	6.53	92.62	0.28	4.05	1.85
8.93	104.17	16.66	8.31	93.28	0.14	3.53	1.86
9.07	98.35	17.10	8.54	94.15	0.14	3.19	1.88
10.20	98.22	19.27	9.63	94.41	0.06	2.61	1.89

In these experiments the explosive ratios all lie within Bunsen's limits for methane of 4–2.7; still there is a variation of 1.6 per cent. in the apparent percentage of methane as calculated by the usual methods and a corresponding variation in the amount of hydrogen. The precautions mentioned before were taken to prevent error from diffusion or solution in the potassium hydroxide pipette. In all these experiments the gases had been diluted with air and the preponderating inert gas was nitrogen. Several experiments were made with mixtures of hydrogen and methane to determine whether any more trustworthy results might be obtained, using oxygen alone in excess. The oxygen gas used was 96.5 per cent. pure. The results showed that the errors when using oxygen thus were rather greater than when using air in similar amount. In several cases, both when using oxygen and air, Griess' reagent for nitrites (naphthylamine hydrochloride and sulphanilic acid) was introduced into the pipette before explosion, with the result that a deep red color was always formed after explosion, proving the formation of nitrous acid.

The explanation of the discrepancies between the author's work and Bunsen's is probably to be sought for in the different forms of apparatus employed. Bunsen used a narrow eudiometer in which the propagation of the explosion and liberation of heat would be slower and the absorption of heat by the glass walls more rapid than in the nearly spherical Hempel pipette; hence the temperature of combustion would be less in Bunsen's work and there would be a smaller amount of oxides of nitrogen formed. In Bunsen's eudiometer also explosion took place under diminished pressure, while in the Hempel apparatus a considerable plus pressure was generated in the explosion. It follows that when working with the Hempel apparatus a greater amount of inert gas than Bunsen found necessary should be present. Apparently the most nearly correct results are obtained in the case of hydrogen when the ratio of the non-explosive to the explosive gases follows Bunsen's higher figure; *i. e.*, when the explosive ratio varies from 4 to 3. In no case will absolutely correct results be obtained, as probably in all cases of explosion under these conditions nitrogen is oxidized to some extent. In the case of methane the higher temperature of combustion causes greater errors and here also the higher explosive ratio given by Bunsen should be adhered to.

The method of Dennis and Hopkins,[1] in which the gas in contact with a glowing platinum spiral burns quietly in a current of

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[1] This Journal, 21, 398.

oxygen and air, allows the use of a larger sample. It is moreover indorsed by Hempel in the following words:[1] "The advantage gained is that in the beginning, where the combustion might become too intense, there is always an excess of combustible gas, so that on the one hand no explosion can take place, and on the other none of the nitrogen can burn, as the combustion takes place at the beginning with an insufficient amount of oxygen, and towards the end when the combustion becomes complete, such high temperatures as are necessary for the combustion of nitrogen are not reached at all."

Some preliminary experiments having shown that it was by no means so certain that nitrogen might not burn under these conditions, tests were made on air with Griess' reagent for nitrites in the pipette, when it was found that a test for nitrites quickly developed after heating the wire. Table IV shows quantitatively the effect on the volume of air when the spiral is heated to redness. The air was freed from carbon dioxide and the samples were as nearly as might be 80 cc. each. While it was not possible to measure accurately the temperature of the wire, a comparison could be obtained by measuring the current heating it. A current of 4 amperes heated the wire to barely visible redness in the daylight and 5.35 amperes heated it to a white heat. The time was in each case two minutes.

TABLE IV.—EFFECT OF HEATING PLATINUM SPIRAL IN AIR.

Sample air. cc.	Current amperes.	Contraction after heating. cc.	Contraction after potassium hydroxide. cc.	Total contraction. cc.
80.90	4.0	0.01	0.00	0.01
82.51	4.55	0.04	0.02	0.06
80.99	4.6	0.03	0.03	0.06
81.22	4.65	0.04	0.01	0.05
81.70	4.8	0.04	0.10	0.14
81.88	5.0	0.11	0.10	0.21
83.10	5.1	0.08	0.17	0.25
80.49	5.3	0.06	0.18	0.24
80.67	5.35	0.12	0.18	0.30

It will be observed that the sum of the contraction after heating and after potassium hydroxide given in the last column increases quite regularly with increase in temperature, but that there is considerable irregularity in the ratios between the contraction after heating and the contraction after potassium hydroxide. It

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[1] "Gasometrische Methoden," 3te Aufl., p. 123-124.

may be that the more or less complete condensation of the nitric acid formed, depending upon time, contact, and the amoünt of water present, is sufficient to account for it.

To afford a direct comparison between the explosion and combustion method, hydrogen generated from aluminum and caustic potash was stored in a gas-holder containing mercury and a little dilute caustic potash. The hydrogen was supposed to be pure but evidently contained a little air. The oxygen used was about 97 per cent. pure.

TABLE V.—COMPARISON OF EXPLOSION AND COMBUSTION METHODS ON HYDROGEN.

Sample hydrogen. cc.	Air. cc.		Contraction after explosion. cc.	Contraction over potassium hydroxide. cc.	Hydrogen. Per cent.	Explosive ratio.
Explosions with Air.						
15.32	85.34		22.71	0.04	98.82	3.43
18.15	82.39		26.93	0.06	98.91	2.73
Explosions with Oxygen.						
	Oxygen.					
14.82	93.51		22.04	0.02	99.14	3.91
16.48	82.18		24.51	0.02	99.15	3.02
20.58	80.09		30.60	0.03	99.12	2.29
Combustions by the Dennis and Hopkins Method.						
	Oxygen.	Air.				Oxygen in excess.
91.29	51.65	54.55	136.72	0.04	99.84	13.72
58.48	53.39	50.14	87.43	0.10	99.66	40.89
89.31	40.77	50.21	133.57	0.07	99.70	3.73

The results of the explosions with oxygen are slightly higher than those with air, show very little contraction over potassium hydroxide, and remarkably little variation with change in explosive ratio. The results with the Dennis and Hopkins method are about 0.6 per cent. higher than those obtained by explosion with oxygen. The variations in the individual results by this method may easily be accounted for by the intentional variation in the proportions of nitrogen and oxygen used, and the unavoidable differences in temperature of spiral and time of heating.

The question naturally arises, which of these methods is more reliable. That none of them are entirely correct is certain, for if nitrogen of the air is oxidized to an appreciable extent by a platinum spiral heated to dull redness, oxides of nitrogen must be formed in all combustions. This has been shown by Ilosvay[1] for

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[1] *Bull. Soc. Chim.*, 11, 737 (1889).

flames, even when the temperature of combustion was much reduced by dilution of the gas with carbon dioxide. The same author also found a slight formation of nitrous acid in the case of air burning in an atmosphere of illuminating gas, where a reducing atmosphere would always be present.

SUMMARY.

Oxides of nitrogen are always formed in explosion analysis in amount increasing with the violence of the explosion. The dilution recommended by Bunsen, when exploding in eudiometer tubes under reduced pressure, is not sufficient when working with the Hempel explosion pipette. If the explosive ratio is kept between four and three, the error is negligible in the technical analysis of gases almost entirely hydrogen. The presence of small amounts of methane increases the error and if large amounts of methane are present, the error may easily amount to a per cent. or more. The explosive ratio should be kept between four and three as in the case of hydrogen. The method of Dennis and Hopkins tends to give high results, and the errors may easily become of importance if care is not taken to avoid heating the spiral too hot and too long. Neither the explosion method nor any method involving active combustion can give strictly accurate results.

ANN ARBOR, MICHIGAN,
June, 1901.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE.]

NOTE ON SOME MODIFIED FORMS OF PHYSICO-CHEMICAL MEASURING APPARATUS.

BY ALLERTON S. CUSHMAN.

Received May 21, 1901.

a. A CONVENIENT ARRANGEMENT OF THE KOHLRAUSCH-OSTWALD CONDUCTIVITY CELL.

IN working with the usual form of Kohlrausch-Ostwald conductivity cell the writer has experienced some difficulty in arranging the electrodes so that they may be easily adjusted at any required distance one from the other, while on the other hand, when once set to a position the constant for the cell may be depended upon. The growth of physico-chemical methods of investigation has been so sudden that the manufacturers of instruments of precision have not kept pace with the requirements of