

characteristic of the curve, *i. e.*, the acid radical is the basis of the structure of the molecule, and the bases in combination with it, do not alter the general molecular architecture.

When more complete data have been obtained some interesting developments in this direction may be expected.

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THE DETERMINATION OF METHANE AND HYDROGEN BY EXPLOSION.¹

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IN making an analysis of illuminating gas by Hempel's method it was noticed that the determination of the constituents by explosion was by no means as accurate as that made by absorption. This had been observed by Hinman³ and is probably due (1) to the fact that an aliquot part of the residue (after all absorptions had been made) containing the methane and hydrogen is used, necessitating the multiplication of errors by a factor as large as four or five, and (2) to the possible absorption of the carbon dioxide formed by the water in the burette. To obviate these difficulties, it was determined to use all the gas left after the absorptions had been made, mercury as the confining liquid and to explode with pure oxygen rather than with air. Instead of using the gas left after the actual absorptions, which would be of unknown composition and troublesome to obtain, an artificial mixture, made from methane, hydrogen and nitrogen, approximating closely to the composition of the residue, was employed.

Preparation of the Gaseous Mixtures.—The hydrogen was prepared by the electrolysis of water; it was then shaken up with potassium pyrogallate to remove the slight quantity of oxygen with which it was mixed, and upon analysis was found to contain four and two tenths per cent. of nitrogen. In making an analysis of hydrogen, we would lay especial emphasis upon the necessity of having the ratio of explosive mixture to inert gases as great as 1:6 as Hempel⁴ recommends, in order not to burn the nitrogen.

¹ Prepared for the Springfield Meeting, August 28, 1895.

² The work described in this paper formed the basis of a thesis presented by Mr. Hunt to the Faculty of the Massachusetts Institute of Technology for the Degree of Bachelor of Science.

³ Massachusetts Senate Document No. 16, 1892. Inspection of Gas and Gas Meters, p. 12.

⁴ Hempel, "Gasanalytische Methoden" p. 132

This is considerably larger than that which Bunsen¹ recommended, which may vary between the limits twenty-six and sixty-four of combustible gas to 100 of incombustible. Unless the larger ratio be adopted the determination of hydrogen may come two and a half per cent. high, as is shown by the following table :

TABLE I. DETERMINATION OF THE PURITY OF THE HYDROGEN.

Hydrogen taken cc.	Air used cc.	Ratio.	Per cent. hydrogen.
20.5	185.0	1 : 5.7	95.8
20.5	185.0	1 : 5.7	95.8
50.0	115.0	1 : 1.2	98.3
50.0	115.0	1 : 1.2	98.0

The nitrogen probably burns to N_2O_4 , as the characteristic dark red fumes of this gas were frequently seen in the pipette. By the Griess test with α -naphthylamine we were able to prove the presence of quite a quantity of nitrites in several cases.

In making the analyses of hydrogen by the first method it was necessary to connect and disconnect the burette three times in each case ; the error which might be introduced was determined with the following results :

TABLE II. SHOWING THE ERRORS IN MANIPULATION IN CONNECTING THE BURETTE AND PIPETTE.

Buretfuls.	Air put in cc.	Air taken out cc.	Errors cc.	Remarks.
3	210.3	207.4	-2.9	No connections wired.
3	216.0	216.6	+0.6	
3	210.2	208.7	-1.5	
3	213.3	213.8	+0.5	All connections wired but one.
1	97.6	97.2	-0.4	
1	97.2	96.8	-0.4	All connections wired.
3	237.5	237.3	-0.2	

The oxygen was obtained in a similar manner to the hydrogen and contained one and six-tenths per cent. hydrogen and one and four-tenths per cent. nitrogen. The nitrogen in both these gases probably came from the distilled water electrolyzed, which was not freshly boiled before use.

The nitrogen employed was prepared by removing the oxygen from the air by means of phosphorus, allowing the gas to stand in the light twenty-four hours to decompose any ozone, and subsequent treatment with a small quantity of alkaline pyrogallate.

¹ Bunsen, "Gasometrische Methoden" (1877) p. 73.

An attempt was made to prepare the methane by the usual method of heating sodium acetate with sodium hydroxide and quicklime; the gas was found to be so largely contaminated with hydrogen,—as high as ten per cent. being found—as to be unfit for our purpose. This result is directly at variance with the statement of Freyer and Meyer¹ who say that this process “furnishes a very approximately pure gas.”

Nor did the method of Gladstone and Tribe,² the reaction of a zinc-copper couple upon methyl iodide, at first yield any better results, owing possibly to the water in the alcohol used. To obviate this and also prevent the possible formation of ethane, anhydrous methyl alcohol was substituted for the ordinary alcohol usually employed. The air in the apparatus was displaced by carbon dioxide and the methane collected, treated with potassium hydroxide to absorb this impurity. An analysis of the gas thus made, by explosion with oxygen and also with air—care being taken to avoid burning any nitrogen—showed the methane to be chemically pure.

The gases thus prepared and also the mixtures made from them, were stored in bottles provided with doubly-perforated rubber stoppers carrying a tube for the introduction of water and a tube for the egress of the gas. To render these absolutely tight, the stoppers were fastened in by fitting a brass plate to cover the top of the stopper, and by means of brass bolts and nuts passing through wire loops around the neck of the bottle, pressing the stopper firmly into the neck of the bottle. Joints of this kind are sufficiently tight to withstand a pressure of hydrogen.³ To reduce the possibility of the transfusion of the gases to a minimum, a slight outward pressure was maintained in each bottle and it was inverted in a pan of water. The separate gases were kept in this way for about two months, freshly distilled water being used to displace the quantities requisite for the various mixtures. These mixtures made from them stood in no case over two days, before being completely used up, so that the amounts of methane and hydrogen dissolved by the distilled water, used to displace the various volumes taken, were negligi-

¹ *Ztschr. phys. Chem.*, **11**, 28.

² *J. Chem. Soc.*, **45**, 154.

³ Gill: *J. Anal. Appl. Chem.*, **6**, 601.

ble ; the coefficients of absorption of the various gases not being widely different the ratio of the gases would remain the same within the errors of the analysis.

The gases were mixed by displacing the water from a liter bottle with the proper amounts of methane, hydrogen and nitrogen—measured by a burette—care being taken to leave some of the water to act as a stirrer, and then thoroughly shaking the bottle. By connecting this with a bottle of distilled water by means of a siphon, the requisite quantity of gas for an experiment could be displaced into the burette.

Method of Procedure.—Fifty cubic centimeters—this being about the usual residue from Boston gas after all the absorbable constituents had been removed—were measured out, mixed with about sixty cc. of oxygen and burned in an explosion pipette devised by one of us.¹ This combustion took place in different ways, at first as one explosion, and later by two explosions, with the idea of diminishing the error due to the possible combustion of nitrogen. In using the latter method it was found necessary to make the ratio of the explosive mixture to inert gases, nearly 1 : 2 in order that any explosion might take place ; with some mixtures not strong enough to explode, if care be not taken to pass the spark but a short time, the fine platinum wire becomes heated and finally glows, similar to the platinum sponge in the Döbereiner lamp, producing a very slow combustion, causing annoyance and delay in the analysis. A rough experiment may very well be made at first, to determine the composition of the gas under investigation and then suitable quantities of oxygen added for the first and second explosion.

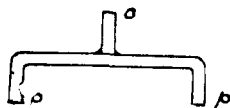
The residue in the explosion pipette was, in every case, transferred to an ordinary Hempel burette for measurement, mercury, instead of water, being the confining liquid ; the gas was passed into potassium hydroxide and then into pyrogallate for the determination of carbon dioxide and oxygen. It is almost impossible to avoid sucking back some of the absorbents into the burette, which being strongly alkaline, would vitiate the next analysis by absorbing carbon dioxide ; to obviate this difficulty the instrument was washed out with dilute acetic acid² and then with

¹ Gill : *J. Am. Chem. Soc.*, 17, 771.

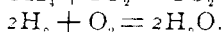
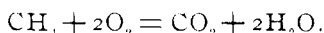
² If hydrochloric acid be used it forms a precipitate of mercurous chloride upon the walls of the pipette, coming from the mercurous salts produced by the action of the oxides of nitrogen upon the mercury.

water, almost filled with mercury allowed to stand about half an hour, the water which collected at the top displaced and then used for the next determination.

Instead of using the ordinary doubly bent connecting tube, this was varied by the introduction of a T joint, which is found especially convenient in adding successive portions of oxygen. The burette being connected at b, the pipette at p, and the oxygen at o, one can add the oxygen without disconnecting the burette each time. By connecting in a short tube at o, and filling it with mercury, the capillaries can be filled with mercury, an important point in preventing the rubber connectors from being burst by the force of the explosion. All connections should be carefully wired. By the use of two sets of apparatus two analyses may be executed at one time, in one an absorption be taking place, in another an explosion, etc. Six analyses in three hours were frequently made.



Calculation of Results.—The calculation of the results of the explosion was made according to the directions of Hempel,¹ that is in accordance with the reactions :



The volume of carbon dioxide obtained represents the methane present, and twice this volume subtracted from the total contraction, gives the contraction due to hydrogen; this latter being multiplied by two-thirds, gives the amount of hydrogen present. Table III shows the results obtained.

TABLE III.—ANALYSIS OF A MIXTURE OF METHANE, HYDROGEN AND NITROGEN BY ONE EXPLOSION WITH OXYGEN.

Mixture cc.	Oxygen per cent.	Methane per cent.	Hydrogen per cent.	Nitrogen per cent.
49.8	65.2	34.7	54.8	10.5
51.9	65.0	35.3	54.1	10.6
49.7	65.6	35.1	53.9	11.0
50.1	61.3	34.5	55.0	10.5
51.5	61.8	35.0	53.6	11.4
59.4	72.8	34.4	55.0	10.6
49.4	56.2	34.3	55.0	10.7
49.2	56.0	34.0	54.9	11.1
49.2	58.3	33.4	55.0	11.6
49.9	55.6	34.8	54.9	10.3
	Average	34.5	54.7	10.8
	Theory	34.7	53.5	11.8

¹ *Loc. cit.*, 217.

The results obtained in the estimation of the methane are quite satisfactory and are probably within the limits of error of the apparatus. The hydrogen is high, due to the fact that the methane is low, and possibly also to the burning of the nitrogen.

In order to diminish the error from the latter source, a new mixture was made, and analyzed by exploding twice successively with oxygen, care being taken to add as little oxygen for the first explosion as would make the mixture combustible. Table IV shows the results obtained.

TABLE IV.—ANALYSIS OF A MIXTURE OF METHANE, HYDROGEN AND NITROGEN BY TWO EXPLOSIONS WITH OXYGEN.

Mixture cc.	Oxygen used		Methane per cent.	Hydrogen per cent.	Nitrogen per cent.
	first time,	second time.			
51.2	40.0	40.9	32.6	46.6	20.8
51.1	41.0	39.9	32.0	46.5	21.5
56.7	40.0	50.3	32.1	46.7	21.2
48.5	31.0	45.7	32.2	47.5	20.3
50.3	31.0	49.8	32.4	48.0	19.6
50.9	32.0	51.1	32.3	47.6	20.1
53.4	35.0	45.6	31.7	48.1	20.2
50.9	30.0	52.9	32.1	48.1	19.8
49.3	29.0	47.7	32.2	47.9	19.9
50.7	31.0	49.6	32.3	48.5	19.2
		Average	32.2	47.55	20.25
		Theory	32.2	47.7	20.1

The results are very satisfactory and if we compare them with those of the preceding table (III), we see that the average is more nearly correct than that of the former, and the deviations from the mean much less. The first three present the greatest variation in regard to hydrogen, it being one per cent. too low, these two had the greatest proportional amount of oxygen in the first explosion which is anomalous.

In order to obtain an idea of what takes place during the first explosion, several were performed and the per cents. of methane and hydrogen which burned determined.

TABLE V.—SHOWING THE AMOUNT OF METHANE AND HYDROGEN BURNED WHEN AN INSUFFICIENT QUANTITY OF OXYGEN IS PRESENT.

mixture cc.	oxygen cc.	Methane			Hydrogen		
		present cc.	burned cc.	burned per cent.	present cc.	burned cc.	burned per cent.
53.0	29.2	17.1	4.0	23.4	25.0	12.5	50.0
53.4	29.1	17.2	4.3	25.0	25.2	11.7	46.3
55.0	33.6	17.7	4.9	27.7	26.0	16.7	64.3
57.4	35.2	18.5	5.2	28.1	27.1	17.0	63.8

About sixty per cent. of the hydrogen burned and, contrary to the usual opinion, twenty-five per cent. of the methane and only about fifty per cent. of the oxygen.

By way of comparison with the usual method, a series of analyses of the same mixture was carried through, employing a smaller quantity and exploding with air; the mercury explosion pipette was used as before and the residue after explosion measured in a burette using water, as is customary, instead of mercury as the confining liquid.

TABLE VI.—ANALYSIS OF A MIXTURE OF METHANE, HYDROGEN AND NITROGEN BY EXPLODING WITH AIR.

Mixture cc.	Air cc.	Methane per cent.	Hydrogen per cent.	Nitrogen per cent.
17.8	79.8	29.8	45.3	24.9
15.3	82.2	31.4	49.3	19.3
16.3	81.4	33.7	42.5	23.9
15.9	82.4	31.4	38.6	30.0
16.1	78.2	39.1	30.4	30.5
16.8	80.5	33.3	42.3	24.4
16.1	82.0	30.4	44.1	25.5
16.2	81.2	36.4	33.4	30.2
15.8 ¹	79.5	31.6	40.0	28.4
15.1	82.5	33.8	38.0	28.2
16.2	82.6	31.2	42.9	25.9
14.8	83.8	34.4	38.4	27.2
15.9	84.3	33.9	37.7	28.6
	Average	33.1	42.2	26.7
	Theory	32.2	47.7	20.1
	Deviation	+0.9	-7.5	+6.6

These figures substantiate those of Hinman,² the results for methane and nitrogen being high and those for hydrogen low, the variations between the different analyses are even more marked. It is to be noticed that, contrary to expectation, the results upon the methane are high, indicating perhaps that the water in the burette is without appreciable solvent action upon the carbon dioxide formed. The discrepancy in the estimation of hydrogen is explained by the increase in the percentage of methane, any increment here being first doubled and subtracted from the "total contraction," and then approximately doubled in making the calculation, lowering as a consequence the hydro-

¹ These last five were measured after explosion with the mercury burette.

² *Loc. cit.*

gen by about four per cent., leaving three and five-tenths per cent. to be accounted for.

Almost the only supposition to account for this phenomenon is the somewhat anomalous one, that under these conditions the hydrogen is not completely burned.

In order to determine the effect of certain errors, such as the reading of the burette—graduated in fifths of a cubic centimeter—and any mistakes made in transferring the gases, the following assumptions were made (Table VII), and the deviations these might produce were calculated by the method of least squares, with the results showed in Table VIII.

TABLE VII.—SHOWING THE VOLUME OF GASES TAKEN AND THE ERRORS ASSUMED IN THEIR MEASUREMENT AND MANIPULATION.

	Oxygen method.		Air method.	
	cc.	error.	cc.	error.
Gaseous mixture taken.....	50.	0.15	15.	0.15
Oxygen (or air) used	60.	0.15	85.	0.15
Residue after explosion.....	33.	0.25	21.	0.25
Carbon dioxide formed.....	16.	0.25	5.	0.25

TABLE VIII.—SHOWING THE DEVIATIONS TO BE EXPECTED IN THE DETERMINATIONS OF THE VARIOUS GASES UPON THE ASSUMPTIONS IN TABLE VII.

	Oxygen method. per cent.	Air method. per cent.
Methane.....	0.51	1.64
Hydrogen	0.82	2.40
Nitrogen (by difference)	1.70	4.30

The results of this investigation may be summarized as follows:

- (1) The method of preparation of methane by heating sodium acetate, hydroxide and lime together does not yield a pure gas.
- (2) The method of determination of methane and hydrogen by one explosion yields results accurate to less than five-tenths per cent. of the methane and three-tenths per cent. of the hydrogen.
- (3) The method by two explosions yields results with in two-tenths per cent. of methane and three-tenths per cent. of the hydrogen.
- (4) When a mixture of hydrogen and methane is exploded with a quantity of oxygen insufficient for both, but more than sufficient for either, about sixty per cent. of the hydrogen and

twenty-five per cent. of the methane and fifty per cent. of the oxygen are consumed.

(5) The method of determination of the gases by one explosion with air gives results not within nine-tenths per cent. of the methane and seven and five-tenths per cent. of the hydrogen.

In concluding this article we would express our indebtedness to Mr. R. B. Price for preliminary work which served as the foundation of this thesis.

NEW BOOKS.

A MANUAL OF QUALITATIVE CHEMICAL ANALYSIS. BY E. P. HARRIS, PH.D., LL.D., Professor of Chemistry in Amherst College. New edition. Thoroughly revised and corrected. Amherst, Mass.: Carpenter & Morehouse. 1895. pp. 308. Price \$1.50.

The author of this book is a veteran teacher, and this new edition is the result of the experience of his laboratory teaching for over a third of a century. The book is divided as follows:

Part I. Examination of solutions: Sec. I, Bases; Sec. II, Acids.

Part II. Examinations of solids.

Part III. Qualitative separations: Sec. I, Bases; Sec. II, Acids.

Supplement: Reaction of rare elements; Use of the spectroscope in analysis.

Appendix: Preparation of reagents; Table of solubility; Index.

Part first gives the reactions of each of the metals and acids, and is interleaved that the student may write out the reaction-equations on the blank pages. This is intended to be used in connection with unknown solutions containing a single base and acid.

Part second is a guide to the systematic examination of solids according to the plan which was first introduced by the author and has since been very generally adopted. This is perhaps the most valuable part of the book.

Part third takes up the separations of metals systematically, using the methods which have proved most satisfactory in the Amherst laboratory. Alternate methods are in a number of instances given, but generally only a single method; the idea is to avoid confusing the student with a number of different ways of working, the relative merits of which he is incapable of estimating. This part is very complete, covering practically all cases