XLVIII.—*Gas Analysis under Greatly Diminished Pressure.*

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BUNSEN'S method of gas analysis is so simple and accurate, that it seems scarcely possible to improve it. In the analysis of gases rich in hydrocarbons, however, such as have now frequently to be made in the laboratory, the atmospheric air, which has to be added to moderate the violence of the explosion, causes some inconvenience, and, moreover, is liable to affect the accuracy of the results, since it is difficult to hit the point at which all the combustible gas shall be completely burned without oxidising any of the nitrogen.

It is well known that the energy of combustion of explosive gaseous mixtures can be greatly moderated by diminishing the pressure, so much so indeed, that they may even become incapable of being ignited. Davy has shown (*Phil. Trans.*, 1817) that when the pressure of the oxyhydrogen mixture is reduced to $\frac{1}{15}$ th, it no longer explodes. The application of this principle for the purposes of gas analysis has indeed been attempted of late years, but has not been generally adopted, on account of the complicated nature of the apparatus.

In 1869 McLeod (this Journal, **22**, 320) described a gas analysis apparatus in which the violence of explosion of the gaseous mixture was moderated by diminishing the pressure. In 1879 T. W. Thomas (this Journal, 1879, *Trans.*, **35**, 213) determined the pressure for a number of combustible gaseous mixtures at which the explosion was harmless, and observed that the rarefaction produced by diminution of pressure was more effective in weakening the force of explosion than dilution with an indifferent gas; a result fully confirmed by our own observations. In the paper referred to, the author only gives a few analyses of methane, but had analysed other gases with satisfactory results.

The ease with which any pressure between 0 mm. and the ordinary atmospheric pressure may be obtained by Schoop's apparatus (*Inaug. Diss.*, Tübingen, 1880; *Ann. Phys. Chem.*, 1881, **12**, 550), induced us to apply it to gas analysis by explosion under diminished pressure, in place of the usual method of diluting it with an indifferent gas. The method proved to be not only easy to carry out and fairly accurate, but is safe and rapid.

The apparatus employed is a simplified modification of that described by Schoop (*loc. cit.*). Instead of the tube for vapour-density determinations, a eudiometer E, Fig. 1, is fixed in the mercury trough, and instead of the tube DE of the original drawing, there is a

barometer tube B, which is joined at the upper end to a capillary tube bent parallel to the barometer tube, and reaching nearly to the bottom of the trough.* The barometer B of Schoop's apparatus is suppressed. The barometer tube B is screwed by means of an iron nipple into the cast-iron bottom of the mercury trough W, and the eudiometer tube E, which is about 400 mm. long, is fastened in a similar manner by a turned iron plug. The arrangement of the iron plug, which is held fast by a bayonet-joint, is given in Fig. 2, and is fully described in Schoop's memoir. The tubes B and E, when in place, communicate by means of a horizontal perforation in the bed of the trough, into which the glass tube *g* is cemented; this is bent downwards at right angles, and passing through a perforation in the table T, reaches nearly to the floor. The lower end of the tube *g* is connected by means of a strongly covered caoutchouc tube with the mercury reservoir Q, which is placed on a wooden traveller, capable of moving vertically on the upright L. The reservoir can be raised or lowered at pleasure by means of a cord passing over the pulley L. The barometer tube is divided into millimetres and screws firmly into the base of the trough, the screw being lubricated so as to make it fit perfectly air-tight.

If, as is usually the case, moist gases have to be analysed, a few drops of water should be introduced into the barometer, either before it is screwed into its place or afterwards. In the latter case, the eudiometer tube E must be removed and the mercury reservoir Q lowered until the mercury has run out of the trough so far as to leave the end of the capillary tube uncovered. A small vessel of water, such as a crucible, is then placed under the capillary tube, so that the end of it may dip into the water, and the eudiometer E filled with mercury is again put in its place. The reservoir is now raised to expel some of the air, and then lowered so as to suck in part of the water, which is carried down by the current of air through the "Bunte's tube" *s*, which is sealed in the barometer tube about 10 cm. from the bottom. When the reservoir is again raised, a part of the water is retained here, whilst the excess is driven out with the air through the capillary tube. By repeatedly raising and lowering Q, the air may be entirely driven out of B. In this way, the sides of the tube are wetted sufficiently to render correction for the vapour-tension of water unnecessary.

The eudiometer, after it has been moistened with a drop of water, is filled with mercury in the usual manner as described by Bunsen. When it is fixed in its place, the pressure is gradually diminished, so as to detach any gas-bubbles adhering to the glass, and they are

* Similar to that employed by W. Hempel, "Neue Methoden zur Analyse der Gase," Braunschweig, 1880, p. 92, &c.

then driven to the top of the tube by again raising Q; if any air-bubbles are then visible near the wires of the eudiometer, Q is lowered so as to bring the mercury in the reservoir on a level with that in the trough, and they are removed by taking out the eudiometer and inverting it in the usual way.

EXPLOSIVENESS OF GASEOUS MIXTURES UNDER DIMINISHED PRESSURE.

It seemed advisable, first of all, to determine at what pressure explosive gaseous mixtures could be fired without injury to the apparatus. For passing the spark, a small Rühmkorff's coil worked with six Bunsen dichromate cells was used, or sometimes a smaller apparatus such as is sold commercially for igniting gas-flames (Clarke's Patent, Nos. 2229 and 245). The latter contains a dichromate cell, which is put in action by pressing a button, and can readily be adapted for firing the eudiometer by replacing the connectors by two flat brass springs. The eudiometer tube is placed between the two springs, and these are raised until they touch the loops of the platinum wires. On pressing the button, the spark passes. This only requires the use of *one* hand, and in conjunction with its portability, makes the apparatus very convenient. In this paper Rk. signifies the spark from the Rühmkorff, F. that from Clarke's machine.

Various hydrocarbons were mixed with somewhat more than the quantity of oxygen necessary for complete combustion, and the mixture tested as to its explosibility under greatly diminished pressure, which was gradually increased until the limit at which explosion took place was determined approximately. The numbers corresponding with the pressure at which explosion takes place are somewhat variable, as the size of the spark was not always the same. All the experiments were made with moist gases, that is, the eudiometer tube was wetted.*

1. *Methane*, CH₄.

The gas was prepared by heating a mixture of sodium acetate with soda-lime.

* In Thomas's memoir (*loc. cit.*), limits are given at which the explosion of mixtures of hydrogen and of some hydrocarbons with oxygen can take place without endangering the eudiometer tube. Thomas gives us convenient pressures:—

H ₂ + O.....	200 mm. pressure.
CH ₄ + 2·5O ₂	170 " "
C ₂ H ₆ + 4O ₂	120 " "
C ₂ H ₄ + 3·5O ₂	130 " "
Heavy hydrocarbons.	130 " "

He found the lowest limit for the explosion of CH₄ + 2O₂ to be 130 mm. pressure, whilst we have noticed explosion at 116·6 mm. Here the size of the spark, as might be imagined, greatly affects the result.

For complete combustion methane requires twice its volume of oxygen, as shown by the equation—

The mixture contained 1 CH_4 to 2.297 oxygen.

Experiment.	Pressure in mm.	
I.	$\left\{ \begin{array}{l} 48.0 \\ 63.0 \\ 82.7 \\ 106.1 \end{array} \right\}$	Rk. no action.
	130.7	Rk. explosion.
II.	119.2	Ditto.
III.	114.4	Rk. no action.
„	122.0	„ explosion.
IV.	117.0	Ditto.
V.	116.6	Rk. explosion after several sparks.
VI.	140.0	F. explosion.
VII.	130.0	Ditto after several sparks.

For analysis, therefore, a pressure of 140 mm. should be used, as ignition will then take place even with a small spark.

2. Propane, C_3H_8 .

The gas was prepared from propyl iodide and aluminium chloride according to Köhnlein's method (*Ber.*, **16**, 560).

Propane requires five times its volume of oxygen for combustion:—

The mixture contained 5.645 volumes of oxygen to 1 of propane.

Experiment.	Pressure in mm.	
I.	$\left\{ \begin{array}{l} 41.4 \\ 56.8 \end{array} \right\}$	F., Rk. no action.
„		
	83.0	F. explosion.
II.	66.4	„ no action; Rk. explosion after several sparks.
III.	71.7	F. ditto.

With propane, explosion takes place quietly at a pressure of about 80 mm.

3. Ethylene, C_2H_4 .

The gas was prepared by heating a mixture of alcohol with con-

centrated sulphuric acid. It requires three times its volume of oxygen :—

The mixture contained 3·539 volumes of oxygen to 1 of ethylene.

Experiment.	Pressure in mm.	
I.	42·1	F. no explosion.
„	71·2	A moderate explosion.
II.	$\left\{ \begin{array}{l} 41·7 \\ 50·7 \end{array} \right\}$	F. no action.
„	63·2	„ explosion after several sparks.
III.	35·6	Rk. immediate explosion.

When a feeble spark is used, ethylene requires a pressure of 70—80 mm. to insure explosion.

4. *Propylene*, C_3H_6 .

The gas was prepared from thymol and phosphoric anhydride. It requires 4·5 times its volume of oxygen for complete combustion :—

The mixture contained 4·747 volumes of oxygen to 1 of propylene.

Experiment.	Pressure in mm.	
I.	$\left\{ \begin{array}{l} 31·6 \\ 37·6 \\ 50·3 \end{array} \right\}$	F., Rk. no action.
„	89·3	F. explosion.
II.	53·7	F., Rk. no action.
„	64·5	F. explosion after several sparks.
III.	63·2	Ditto ditto.

A pressure of about 80 mm. is required.

5. *Acetylene*, C_2H_2 .

The gas was separated from its copper compound by hydrochloric acid. It requires 2·5 times its volume of oxygen for combustion :—

The mixture contained 3·224 volumes of oxygen to 1 of acetylene.

Experiment.	Pressure in mm.	
I.	73·7	F. vigorous explosion.
II.	$\left\{ \begin{array}{l} 21·3 \\ 23·2 \end{array} \right\}$	F., Rk. no action.

Experiment.	Pressure in mm.	
II.	32.4	F. moderate explosion.
III.	40.0	„ explosion.
„	28.2	F., Rk. no action.
„	32.7	F. good explosion.

A mixture of acetylene and oxygen, therefore, can be exploded without any danger under a pressure of 40—50 mm., whilst in Bunsen's eudiometer, even when a large proportion of nitrogen is present, the tube is often shattered (comp. E. v. Meyer, *J. pr. Chem.*, 1874, 10, 323).

6. Carbonic Oxide, CO.

The gas was prepared from magnesium formate and sulphuric acid. It requires half its volume of oxygen for complete combustion:—

The mixture contained 0.528 volume of oxygen to 1 of carbonic oxide.

Experiment.	Pressure in mm.	
I.	$\left\{ \begin{array}{l} 46.2 \\ 58.5 \\ 73.8 \\ 103.7 \\ 136.0 \\ 192.6 \end{array} \right\}$	F., Rk. no action.
„	243.5	Good explosion.
II.	219.0	F. ditto.

A pressure of about 230 mm. should be used with a mixture of carbonic oxide with oxygen.

7. Hydrogen, H₂.

The mixture of oxygen with hydrogen was obtained by the electrolysis of water.

Experiment.	Pressure in mm.	
I.	175.9	F. moderate explosion.
II.	143.0	„ feeble „
III.	$\left\{ \begin{array}{l} 54.0 \\ 60.0 \\ 72.7 \\ 85.0 \\ 101.0 \\ 115.0 \\ 124.2 \end{array} \right\}$	F. no action.

Experiment.	Pressure in mm.	
III.	127·2	F. explosion after several sparks.
IV.	123·2	F. no action.
„	126·7	„ explosion after several sparks.
V.	125·0	Ditto ditto.
VI.	102·9	Rk. immediate explosion.
VII.	49·2	„ no action.
„	70·5	Kk. In this case, there was

no action until several sparks had been passed, and even then there was no emission of light, and only part of the gas was burned; the remainder disappearing when the pressure was again increased to 72·2 mm. and the spark passed once more.

This observation was confirmed by two similar experiments.

Experiment.	Pressure in mm.	
VIII.	64·2	Rk. no action.
„	67·8	„ partial explosion as in VII.
„	72·1	„ the rest of the gas disappeared.
IX.	70·3	Rk. partial explosion.
„	72·9	„ the action completed.

On reading the volumes and pressures, and reducing them to 0° and 1000 mm., the following results were obtained :—

Experiment.	Burnt at first.	Residue burning when the pressure was increased.
VII.	73·16 per cent.	26·84 per cent.
VIII.	71·63 „	28·37 „
IX.	77·41 „	22·59 „

It would seem, therefore, that at a pressure of about 70 mm., but three-fourths of the gas is burnt, and the remainder only on increasing the pressure until it is the same as it was before the first explosion. This abnormal result is caused by the very high conductivity of hydrogen for heat, which cools the diluted gas so quickly, in spite of the high temperature produced by the combustion of the mixture, that at a distance from the source of heat the temperature sinks below that necessary to produce explosion. This is quite in accordance with the fact that when the explosion was effected by the small spark F, it was complete. The pressure in this case being more than 50 mm. greater, the gas was so dense that when ignition had once taken place the conductivity of the hydrogen was no longer able to extinguish it.

According to Bunsen (*Gasometrische Methoden*, 2nd Aufl., p. 338), the oxyhydrogen mixture no longer explodes if it is mixed with oxygen so that the percentage of the former is less than 9.66 (at 717 mm. pressure). This limit corresponds with a partial pressure of 70 mm. for the oxyhydrogen mixture, and, consequently, agrees with that found in our experiments. That the combustion in Bunsen's experiment was *complete*, whilst in ours it was only *partial*, shows that the expansion of a gas produced by diminishing the pressure is more effective in moderating the violence of explosion than when it is produced by diluting it with oxygen. As already noticed, Thomas had also made the same observation.

The combustion of the hydrocarbons and of carbonic oxide in presence of excess of oxygen was always complete, as after removal of carbonic anhydride by soda solution, the residual gas showed no diminution of volume on passing the spark, even when strongly compressed, and consisted merely of the excess of oxygen.

In these experiments, the gases burned under the following pressures:—

					Pressure in mm.
1 vol. methane with	about	2 vols. oxygen..			116.6 Rk.
"	"	2	"	..	130.0 F.
1 vol. propane	"	5	"	..	66.4 Rk.
"	"	5	"	..	71.7 F.
1 vol. ethane	"	3	"	..	63.2 "
" propylene	"	4.5	"	..	63.2 "
" acetylene	"	2.5	"	..	32.4 "
" carbonic oxide	"	0.5	"	..	219.0 "
" hydrogen	"	0.5	"	..	125.0 "
"	"	0.5	"	..	102.9 Rk.
"	"	0.5	"	..	67.8—70.5 Rk. (only partially).

The order in which mixtures of these gases with the proper quantity of oxygen cease to ignite under diminished pressure is as follows:—First of all carbonic oxide, then methane and hydrogen, whilst propane, ethylene, and propylene are nearly equal, and acetylene comes last, and requires to be expanded to nearly double the extent of those immediately preceding it. The abnormal behaviour of oxyhydrogen mixture when greatly rarefied and with a strong spark has been already noticed.

ANALYSES.

When the limit of expansion at which the above gaseous mixtures could be safely exploded had been determined, a number of analyses were made of mixtures for which these furnished the material. Their

composition was only known incidentally, and they were determined both by the new and also by the old method (dilution with atmospheric air). The manner of carrying out these analyses is very simple. After the eudiometer has been completely filled with mercury in the usual manner, the gas to be analysed is introduced, so that the total volume of gas at the ordinary atmospheric pressure and after the addition of the necessary quantity of oxygen is only about one-tenth the capacity of the eudiometer. For example, in the apparatus employed, the width of the tube is 18 mm. and its area, therefore, 25 square cm., and a length of 400 mm. corresponds with 100 c.c.; about 10 c.c. of the explosive mixture is taken. With gases which do not require a very great diminution of the pressure, this limit may be proportionally exceeded.

In order to facilitate the measurement of these small volumes of gas, a small measuring vessel of about 2 c.c. is used for the air calibration of the eudiometer (Bunsen, *loc. cit.*, p. 74), and for analysis 1 vol. of the denser and 2 to 3 vols. of the lighter gases are taken.

As the amount of gas has to be determined from its volume and pressure, the measurements can be most accurately made if both the pressure and volume are represented by the same number of millimetres, as any inaccuracy in reading causes the error in the final result to be greater the smaller the absolute measurement, whether of pressure or volume. For example, if the possible error in the measurement of the pressure and volume is 0.1 mm. in 10 vols. measured at 500 mm. pressure, or in 500 vols. at 10 mm., it would be $\frac{0.1}{10} + \frac{0.1}{500} = 0.0102$, or about 1 per cent., whilst if the same quantity of gas were measured at 70 vols. under a pressure of 71.43 mm., the error would be only $\frac{0.1}{70} + \frac{0.1}{71.43} = 0.0027$, or about a quarter per cent. In order

to obtain this favourable result, it is merely necessary to place the reservoir Q at such a height that the surface of the mercury in B is nearly level with the upper closed end of the eudiometer E. The readings may be taken after the lapse of 15 to 20 minutes, as, with the small quantities of rarefied gas used, equilibrium is very soon established. The level of the mercury in the eudiometer and the corresponding number on the scale of the barometer are read first. If the axis of the cathetometer is accurately vertical, so that the telescope moves in a horizontal plane, the readings may be taken directly, but it is easier and sufficiently accurate if the distance between E and B is made so small that the scales of both are in the field at the same time. The graduations are illuminated by a white paper screen on E (Fig. 1, p. 582); by this means it is easy to read to 0.1 mm. The

height of the mercury surface in B and the temperature indicated by the thermometer t are read in the usual way.

The pressure is now diminished to the necessary extent, and the spark passed. If there is no explosion, Q is raised and the spark passed again. Explosion always takes place with a bright light, and so quietly that in spite of the small pressure-column of mercury, there is only a slight oscillation in E, and gas-bubbles are never forced down to the bottom of E. The sides of the eudiometer tube are washed by alternately lowering and raising Q, and the reading is taken after the pressure and volume of the residual gas have again been made as nearly equal as possible.

Soda solution of 7 per cent. NaHO, as recommended by Bunsen, is employed for absorbing the carbonic anhydride. The requisite quantity of it should be boiled in an Erlenmeyer's flask for about ten minutes to expel the absorbed air, and then introduced warm into the eudiometer. This is done by a pipette in the usual way after Q has been lowered so that the level of the mercury in the reservoir and trough is the same, and E has been disconnected. When the eudiometer is again in place, the pressure is increased so that the soda solution as nearly as possible reaches the spark-wires without actually wetting them. If this occurs, a slight error is caused by some of the liquid being retained between the wires and glass by capillary attraction, thus causing the volume of the gas to appear larger than it is. Correction for this minute error may be made, if the volume of the solution is read before increasing the pressure. With the small volume of gas, absorption of the carbonic anhydride proceeds very quickly, and may be considered as complete after the lapse of half an hour. The pressure and volume are then equalised as before, and a quarter of an hour later the readings are taken—of course observing the level of the soda solution also.

In calculating the analysis, the volumes corresponding with the divisions on the eudiometer are found from the calibration table, and a correction made for the meniscus. The pressure of the gas is the difference between the mercury level in B and E. A correction for the tension of water-vapour is not needed, as the barometer tube is wet. The only correction necessary is that required to reduce the pressure of the mercury as read on the glass scale to 0° , and this is very small, as the length is but short. In the absorption of the carbonic anhydride, the height of a column of mercury corresponding with the soda solution has to be deducted from the pressure, and the difference between the vapour-tension of soda solution and that of pure water to be added (Bunsen, *loc. cit.*, pp. 357 and 360).

We now give the analytical results exactly as recorded. It is however to be noted that the gases analysed were not quite pure, although

nearly so; any discrepancies in the analytical results, therefore, are not necessarily due to the methods employed.

For comparison, analyses of the same gaseous mixtures were made in Bunsen's eudiometer as well as in the apparatus described. As an example of the mode of working full details of the first analyses are given.

1. METHANE AND OXYGEN.

In these experiments p is the pressure in metres, b is the volume of combustible gas—

$$\begin{array}{ll} c, \text{ the contraction} & = 2b, \\ d, \text{ the carbonic anhydride} & = 1b. \end{array}$$

Experiment I.

α . After introduction of the gaseous mixture—

Vol. read	179.0	Barometer level..	0.5930 m.
Vol. cor.	183.97	Level in E.	0.3975 „
Temp. $t = 21.8^\circ$			
		$p =$	0.1955
		$p \text{ cor.} =$	0.19477

The pressure was diminished to 140 mm. and the spark passed.

β . After explosion—

Vol. read	110.5	Barometer level..	0.5237
Vol. cor.	116.38	Level in E.	0.4030
$t = 21.9^\circ$			
		$p =$	0.1207
		$p \text{ cor.} =$	0.12025

Boiled solution of soda (7 per cent. NaHO) was introduced into the eudiometer.

γ . After absorption of the carbonic anhydride—

Mercury in E.	48.0	Barometer level . . .	0.4615
Vol. read	43.0	Level in E.	0.3974
Vol. cor.	48.69		
Soda solution.	5.0	$p =$	0.0641
		$p \text{ cor.} =$	0.06475

This calculated to 0° and 1000 mm. pressure gives—

Gas	33.184	Methane.
Difference <i>c</i> ...	20.233	$b = \frac{1}{2}c = 10.117$ or 30.49 per cent.
After explosion	12.951	
Difference <i>d</i> ...	10.033	$b = 1d = 10.033$ or 30.23 per cent.
After absorption		Difference 0.084
of CO ₂	2.918	

Experiment II.

	Cor. vol.	Cor. pressure.	<i>t.</i>
Gas	147.3	0.16258	21.8°
After explosion	93.1	0.10053	21.8°
After absorption of CO ₂ ..	40.9	0.05232	21.6°
Soda solution = 4.8.			

This calculated to 0° and 1000 mm. pressure gives—

Gas	22.178	Methane.
Difference <i>c</i>	13.510	$b = \frac{1}{2}c = 6.755$ or 30.46 per cent.
After explosion.	8.668	
Difference <i>d</i> ..	6.685	$b = 1d = 6.685$ or 30.14 per cent.
After absorption		Difference 0.070
of CO ₂	1.983	

2. PROPANE AND OXYGEN.

In these experiments, *b* is the volume of combustible gas—

c, the contraction = $3b$,

d, the carbonic anhydride = $3b$.

Experiment I.

	Cor. vol.	Cor. pressure.	<i>t.</i>
Gas	149.3	0.15076	13.4°
After explosion	112.05	0.11125	13.5°
After absorption of CO ₂ ..	48.1	0.04476	13.3°
Soda solution = 4.8.			

This calculated to 0° and 1000 mm. pressure gives—

Gas	21.460	Propane.
Difference <i>c</i>	9.582	$b = \frac{1}{3}c = 3.194$ or 14.88 per cent.
After explosion.	11.878	
Difference <i>d</i>	9.825	$b = \frac{1}{3}c = 3.275$ or 15.26 per cent.
After absorption		Difference 0.081
of CO ₂	2.053	

Experiment II.

	Cor. vol.	Cor. pressure.	<i>t.</i>
Gas	144.42	0.13622	12.2°
After explosion	101.07	0.10767	12.2°
After absorption of CO ₂ ..	36.70	0.05206	12.4°
Soda solution = 4.0.			

This calculated to 0° and 1000 mm. pressure gives—

Gas	18.832	Propane.	
Difference <i>c</i> ...	8.415	$b = \frac{1}{3}c = 2.805$ or 14.90 per cent.	
After explosion.	10.417		
Difference <i>d</i> ..	8.589	$b = \frac{1}{3}d = 2.863$ or 15.20 per cent.	
After absorption		Difference 0.058	
of CO ₂	1.828		

Experiment III.

	Cor. vol.	Cor. pressure.	<i>t.</i>
Gas	137.45	0.14907	12.8°
After explosion	105.33	0.10707	12.4°
After absorption of CO ₂ ..	36.70	0.05402	12.0°
Soda solution = 6.0.			

This calculated to 0° and 1000 mm. pressure gives—

Gas	19.574	Propane.	
Difference <i>c</i> ..	8.786	$b = \frac{1}{3}c = 2.929$ or 14.96 per cent.	
After explosion.	10.788		
Difference <i>d</i> ...	8.880	$b = \frac{1}{3}d = 2.960$ or 15.12 per cent.	
After absorption		Difference 0.031	
of CO ₂	1.908		

Experiment IV (in Bunsen's Eudiometer).

In consequence of an accident, the mixture employed in the first three experiments could not be used for this, but in order to prove the purity of the propane a fresh mixture of propane and oxygen was prepared and analysed—

	Cor. vol.	Cor. pressure.	<i>t.</i>
Propane and O	187.27	0.31542	11.8°
After adding air.....	419.53	0.55060	11.2°
After explosion	382.66	0.51043	11.8°
After absorption of CO ₂ .	337.72	0.47510	11.5°
Soda solution 7.6.			

This calculated to 0° and 1000 mm. pressure gives—

Gas	56·624	
Gas and air....	221·900	Propane.
Difference <i>c</i>	34·66	$b = \frac{1}{3}c = 11·55$ or 20·4 per cent.
After explosion.	187·24	
Difference <i>d</i> ...	33·81	$b = \frac{1}{3}d = 11·27$ or 19·90 per cent.
After absorption		Difference 0·28
of CO ₂	153·43	

3. ETHYLENE AND OXYGEN.

In these experiments, *b* is the volume of combustible gas—

c, the contraction = 2*b*,

d, the carbonic anhydride = 2*b*.

The explosion was effected at about 100 mm. pressure.

Experiment I.

	Cor. vol.	Cor. pressure.	<i>t</i> .
Gas	66·06	0·41874	9·2°
After explosion	125·27	0·12545	9·0°
After absorption of CO ₂ ..	69·03	0·04646	8·6°
Soda solution 3·8.			

This calculated to 0° and 1000 mm. pressure gives—

Gas	26·761	Ethylene.
Difference <i>c</i>	11·547	$b = \frac{1}{2}c = 5·774$ or 21·58 per cent.
After explosion.	15·214	
Difference <i>d</i> ...	12·105	$b = \frac{1}{2}d = 6·053$ or 22·62 per cent.
After absorption		Difference 0·279
of CO ₂	3·109	

Experiment II (in Bunsen's Eudiometer).

	Cor. vol.	Cor. pressure.	<i>t</i> .
Gas	303·9	0·28106	11·5°
Same with air	642·9	0·61905	11·3°
After explosion	612·6	0·58610	11·4°
After absorption of CO ₂ ..	579·4	0·55321	11·7°

This calculated to 0° and 1000 mm. pressure gives—

Gas	82.418	
Gas and air....	381.96	Ethylene.
Difference <i>c</i>	36.49	$b = \frac{1}{2}c = 18.25$ or 22.14 per cent.
After explosion.	345.47	
Difference <i>d</i>	35.90	$b = \frac{1}{2}d = 17.95$ or 21.78 per cent.
After absorption		Difference 0.30
of CO ₂	309.57	

4. PROPYLENE AND OXYGEN.

In these experiments, *b* is the volume of combustible gas—
c, the contraction = $2.5b$,
d, the carbonic anhydride = $3b$.

The explosion took place under a pressure of 60 mm.

Experiment I.

	Cor. vol.	Cor. pressure.	<i>t</i> .
Gas	133.79	0.13039	9.8°
After explosion	101.95	0.10023	10.0°
After absorption of CO ₂ ..	39.80	0.03165	10.2°
Soda solution = 4.1.			

This calculated to 0° and 1000 mm. pressure gives—

Gas	16.833	Propylene.
Difference <i>c</i>	6.975	$b = \frac{2}{3}c = 2.790$ or 16.57 per cent.
After explosion.	9.858	
Difference <i>d</i> ...	8.644	$b = \frac{1}{3}d = 2.881$ or 17.12 per cent.
After absorption		Difference 0.091
of CO ₂	1.214	

Experiment II.

	Cor. vol.	Cor. pressure.	<i>t</i> .
Gas	131.42	0.13256	10.8°
After explosion	98.14	0.09852	10.7°
After absorption of CO ₂ ..	26.28	0.02345	10.5°
Soda solution = 6.4.			

This calculated to 0° and 1000 mm. pressure gives—

Gas	16.759	Propylene.
Difference c ...	7.455	$b = \frac{2}{3}c = 2.982$ or 17.79 per cent.
After explosion.	9.304	
Difference d ...	8.711	$b = \frac{1}{3}d = 2.904$ or 17.33 per cent.
After absorption		Difference 0.078
of CO_2	0.593*	

Experiment III (in Bunsen's Eudiometer).

	Cor. vol.	Cor. pressure.	t .
Gas	277.29	0.23768	10.2°
Same with air.....	576.70	0.54442	9.8°
After explosion	552.91	0.51596	10.8°
After absorption of CO_2 ..	516.59	0.48671	11.8°
Soda solution = 6.2.			

This calculated to 0° and 1000 mm. pressure gives—

Gas	63.534	
Gas and air....	303.100	Propylene.
Difference c ...	28.66	$b = \frac{2}{3}c = 11.46$ or 18.04 per cent.
After explosion.	274.44	
Difference d ...	33.42	$b = \frac{1}{3}d = 11.14$ or 17.54 per cent.
Same after ab-		Difference 0.32
sorption of CO_2	241.02	

5. ACETYLENE AND OXYGEN.

In these experiments, b is the volume of combustible gas—

c , the contraction = $1.5b$,

d , the carbonic anhydride = $2.0b$.

The explosion took place under a pressure of 50 mm.

Experiment I.

	Cor. vol.	Cor. pressure.	t .
Gas	122.29	0.12770	8.8°
After explosion	104.52	0.09705	8.7°
After absorption of CO_2 ..	49.50	0.05479	8.5°
Soda solution = 3.9.			

* This number is about 0.6 too small, as may be seen by comparison with Experiment I. That a larger volume of oxygen was used is due to the fact that it went to oxidise a small quantity of mercury adhering to the wires of the eudiometer. If this 0.6 be subtracted from the contraction c , this becomes 6.855, and the propylene 2.742 or 16.36 per cent.

This calculated to 0° and 1000 mm. pressure gives—

Gas	15·129	Acetylene.
Difference <i>c</i> ...	5·298	$b = \frac{2}{3}c = 3·532$ or 23·35 per cent.
After explosion.	9·831	
Difference <i>d</i> ...	7·201	$b = \frac{1}{2}d = 3·601$ or 23·80 per cent.
After absorption		Difference 0·069
of CO ₂	2·630	

Experiment II.

	Cor. vol.	Cor. pressure.	<i>t.</i>
Gas	124·57	0·11502	8·7°
After explosion	104·14	0·08956	8·7°
After absorption of CO ₂ ..	52·60	0·04678	8·9°
Soda solution = 3·7.			

This calculated to 0° and 1000 mm. pressure gives—

Gas	13·886	Acetylene.
Difference <i>c</i> ...	4·847	$b = \frac{2}{3}c = 3·231$ or 23·27 per cent.
After explosion.	9·039	
Difference <i>d</i> ..	6·656	$b = \frac{1}{2}d = 3·328$ or 23·97 per cent.
After absorption		Difference 0·097
of CO ₂	2·383	

Experiment III (in Bunsen's Eudiometer).

	Cor. vol.	Cor. pressure.	<i>t.</i>
Gas	248·9	0·21432	9·1°
Same with air.....	554·12	0·52264	9·4°
After explosion	537·0	0·50500	9·2°
After absorption of CO ₂ ..	510·26	0·48112	9·4°
Soda solution = 6·5.			

This calculated to 0° and 1000 mm. pressure gives—

Gas	51·625	
Gas and air....	279·973	Acetylene.
Difference <i>c</i> ...	17·620	$b = \frac{2}{3}c = 11·747$ or 22·75 per cent.
After explosion.	262·353	
Difference <i>d</i> ...	25·022	$b = \frac{1}{2}d = 12·511$ or 24·23 per cent.
After absorption		Difference 0·764
of CO ₂	237·331	

In conclusion, we give the analyses of some of the gases carried out in the manner described.

Analyses of Methane.

Analysis I.	Cor. vol.	Cor. pressure.	<i>t.</i>
Oxygen	187·84	0·20114	22·3°
After adding methane ..	209·65	0·22086	22·3°
After explosion	167·53	0·17363	22·3°
After absorption of CO ₂ ..	134·81	0·15461	22·3°
Soda solution = 4·9.			

Explosion took place under a pressure of 160 mm. Calculated to 0° and 1000 mm. pressure it gives—

Oxygen	34·931		Methane.
Difference <i>b</i> ...	7·879	<i>b</i> =	7·879
After adding methane	42·810		
Difference <i>c</i> ...	15·917	<i>b</i> = $\frac{1}{2}c$ =	7·959
After explosion.	26·893		
Difference <i>d</i> ...	7·623	<i>b</i> = <i>ld</i> =	7·623
After absorption of CO ₂	19·270	Difference	0·336

Analysis II.	Cor. vol.	Cor. pressure.	<i>t.</i>
Oxygen	162·81	0·17440	22·0°
After adding methane ..	191·22	0·20895	22·1°
After explosion	122·79	0·13828	21·8°
After absorption of CO ₂ ..	69·47	0·08286	21·7°
Soda solution = 5·6.			

This calculated to 0° and 1000 mm. pressure gives—

Oxygen	26·278		Methane.
Difference <i>b</i> ...	10·687	<i>b</i> =	10·687
After adding methane	36·965		
Difference <i>c</i> ...	21·240	<i>b</i> = $\frac{1}{2}c$ =	10·620
After explosion.	15·725		
Difference <i>d</i> ...	10·391	<i>b</i> = <i>ld</i> =	10·391
After absorption of CO ₂	5·334	Difference	0·229

Analysis of Propane.

	Cor. vol.	Cor. pressure.	<i>t.</i>
Oxygen	185·36	0·21010	19·4°
After adding propane ...	210·9	0·21838	19·2°
After explosion	150·8	0·16068	18·9°
After absorption of CO ₂ ..	41·4	0·04930	18·8°

This calculated to 0° and 1000 mm. pressure gives—

Oxygen.....	36·362		Propane.
Difference <i>b</i>	6·669	$b =$	6·669
After adding			
propane.....	43·031		
Difference <i>c</i>	20·369	$b = \frac{1}{3}c =$	6·790
After explosion.	22·662		
Difference <i>d</i>	20·752	$b = \frac{1}{3}d =$	6·917
After absorption		Difference	0·127
of CO ₂	1·910		

Analysis of Acetylene.

	Cor. vol.	Cor. pressure.	<i>t.</i>
Oxygen	126·46	0·12750	18·0°
After adding acetylene..	136·78	0·14665	18·0°
After explosion	113·82	0·12491	18·0°
After absorption of CO ₂ ..	67·54	0·08857	18·4°

This calculated to 0° and 1000 mm. pressure gives—

Oxygen.....	15·127		
Difference <i>b</i>	3·692	$b =$	3·692
After adding			
acetylene....	18·819		
Difference <i>c</i>	5·480	$b = \frac{2}{3}c =$	3·653
After explosion.	13·339		
Difference <i>d</i> ...	7·734	$b = \frac{1}{2}d =$	3·867
After absorption		Difference	0·214
of CO ₂	5·605		

TABLE OF ANALYTICAL RESULTS.

I. *Mixture of Gases with Oxygen.*

B signifies that the analysis was made in a Bunsen's eudiometer; α gives the percentage calculated from the contraction, β that from the carbonic anhydride formed, and γ the differences between these two.

	α .	β .	γ .
Methane—			
Experiment I	30.49	30.23	— 0.26
„ II	30.46	30.14	— 0.32
Propane—			
Experiment I	14.88	15.25	+ 0.38
„ II	14.90	15.20	+ 0.30
„ III	14.96	15.12	+ 0.16
„ IV (B)	[20.40	19.90	— 0.50]
Ethylene—			
Experiment I	21.58	22.62	+ 1.04
„ II (B)	22.14	21.78	— 0.36
Propylene—			
Experiment I	16.57	17.12	+ 0.55
„ II	17.79	17.33	— 0.46
„ III (B)	18.04	17.54	— 0.50
Acetylene—			
Experiment I	23.35	23.80	+ 0.45
„ II	23.27	23.97	+ 0.70
„ III (B)	22.75	24.23	+ 1.48

II. Combustible Gas Measured by Itself.

The measurements are corrected to 0° and 1000 mm. A is the volume taken; α that calculated from the contraction, β that from the carbonic anhydride formed, and γ the difference.

	A.	α .	β .	γ .
Methane—				
Analysis I.....	7.879	7.959	7.623	0.336
„ II.....	10.687	10.620	10.391	0.229
Propane	6.669	6.790	6.917	0.127
Acetylene.....	3.692	3.653	3.867	0.214

A comparison of the results given in these tables shows that the diminished pressure method gives results quite as favourable as those obtained by dilution with nitrogen or atmospheric air, moreover, it has the advantages of being more rapid and of avoiding the inconvenience arising from either too violent or incomplete explosion, which may occur when nitrogen is used.

Our apparatus requires very careful work on the part of the maker

so that the iron plug may fit perfectly air-tight into the base of the trough. After some preliminary trials, however, it was found that this delicate and somewhat costly contrivance could be replaced by a simpler one; the modified apparatus is represented in Fig. 3 (p. 582). In this both the endiometer and the barometer are connected with the glass tube *g*, by good vulcanised india-rubber corks, the broad ends of which are let into the bottom of the trough, and if necessary are cemented to it. In this way a perfectly tight joint is formed under the mercury. The tube *g* should be somewhat longer than the barometric column, so that there may be no danger of air entering where it is connected with the covered tube at its lower end. If this should happen, it can only enter the barometer tube, from which it may readily be removed by raising *Q*. In this method of fastening the tubes, it is necessary to support them, which may be most conveniently effected by using a stand similar to that employed with Bunsen's trough. If the reservoir is globular, the table and supports need not be so high, or the reservoir may be used with a detached support (W. Hempel, *loc. cit.*, p. 93, Fig. 14).

We intend to improve and extend this method as far as possible. The saving of time is a great advantage, as an analysis can be completed in three to four hours, and the difficulty arising, even in skilled hands, from too violent or incomplete combustion when air is used is avoided. Moreover, the manipulation of the apparatus is simple, and the results obtained even with small quantities of gas are sufficiently accurate.