# LIX.—*The Combustion of Carbon Disulphide.*

### By HAROLD BAILY DIXON and EDWARD JOHN RUSSELL.

THE first chemists to examine the combustion of carbon disulphide with any degree of accuracy seem to have been Berzelius and Marcet (*Phil. Trans.*, 1813, p. 171). They mixed oxygen with excess of carbon disulphide in a eudiometer and passed a spark; after the explosion they noticed a few drops of liquid which had condensed on the side of the tube. Water was admitted to dissolve the sulphur dioxide, and on shaking the remainder of the gas with lime water, part was absorbed, and a precipitate of calcium carbonate formed. The residue was mixed with oxygen and sparked, and then gave a precipitate with lime water showing that it had been carbon monoxide.

In 1861 (*Quart. Journ. Chem. Soc.*, **13**, 248), Playfair showed that the vapour of dry carbon disulphide was not decomposed by passing over red-hot pumice or charcoal.

In 1862 (*Chem. News*, **6**, 3), Frankland determined its ignition point, which he stated to be 300° F., but he does not seem to have investigated the products of combustion.

Bunsen gives no method for estimating carbon disulphide vapour in his book on Gas Analysis, but in later text-books a method is given based on the assumption that when exploded with air or oxygen one volume of the vapour gives two volumes of sulphur dioxide and one of carbon dioxide. We cannot, however, find who was the originator of this method, nor indeed can we find any literature bearing on the subject until quite recent years.

In 1888 (*Phil. Trans.*, **179**, 582), Brereton Baker showed that carefully dried and purified carbon disulphide explodes with oxygen just as readily as when moist.

In 1890 (Trans., **57**, 625), Pedler exploded mixtures of carbon disulphide, air, and oxygen, and showed that, owing to the great amount of heat evolved, nitrogen was oxidised and the contraction observed was more than that calculated. The nitrogen oxides thus formed combine in presence of steam with some of the sulphur dioxide, and the quantity of this gas is therefore always less than it should be.

In 1890 (*Brit. Assoc. Report*, 776), G. S. Turpin showed that carbon disulphide underwent a "slow combustion" when heated with air or oxygen, and that a reddish-brown solid was formed by the burning of a portion of the sulphur, a lower sulphide of carbon being left.

In 1894 (Trans., **65**, 616), Brereton Baker, following up his earlier experiments, stated that carbon disulphide vapour decomposes between 200° and 218°, whilst ignition does not take place below 260°. He concludes that combustion must be preceded by decomposition into carbon and sulphur, and suggests as a possible explanation of the combustion of pure carbon disulphide that, in this nascent state, carbon and sulphur may combine with oxygen, whether dry or not.

During the past few years, different methods have been studied in this laboratory for investigating the manner in which carbon compounds burn, and it appeared of interest to apply these methods to the study of the combustion of carbon disulphide. Unfortunately, the mode of combustion appears to be a complicated one, and no simple interpretation of the results presents itself.

### *Purification of the Carbon Disulphide.*

The best commercial carbon disulphide was allowed to stand some hours with bromine in the cold, the bromine was then removed by potash, and the carbon disulphide shaken for an hour with alkaline permanganate. After washing well with water, it was dried over calcium chloride and distilled, the first portion only being collected. Care was always taken to avoid unnecessary exposure to light. The substance thus obtained boiled very constantly at 46·8° under 772 mm. pressure.

### *Influence of Moisture on the Burning of Carbon Disulphide.*

As already stated, Brereton Baker found that dryness does not affect the burning of carbon disulphide, and our experiments confirm this result.

Using the purest carbon disulphide we were able to prepare, we made mixtures with oxygen and nitrous oxide in varying proportions, and allowed them to dry over phosphorus pentoxide for periods varying from a fortnight to eighteen months. In every case, there was an explosion on passing a spark, and combustion was complete.

When dried mixtures of carbon disulphide and carbon monoxide with excess of oxygen were sparked, it was always found that the carbon monoxide was largely unburnt whilst the carbon disulphide burnt completely. The union of the carbon disulphide and oxygen thus occurs when the gases have been brought to a state of dryness in which carbon monoxide and oxygen are incapable of combining.

Further evidence was obtained by a comparison of the rates of explosion of wet and of dry mixtures. If moisture is necessary for combustion, the velocity of explosion in a mixture of moist gases should be greater than that in a mixture of dry gases. We found it to be less.

| Mixture. | Rate of explosion of *dried* gases. | Rate of explosion of gases saturated with water vapour at 15°. |
|---|---|---|
| $CS_2+3O_2$ | 1802 metres per sec. | 1755 metres per sec. |
| $CS_2+5O_2$ | 1732 ,, | 1672 ,, |

In no experiments have we been able to find any indication that pure carbon disulphide will not burn.

### *Temperature of Ignition of Carbon Disulphide.*

The ignition point of carbon disulphide has been estimated at rather widely divergent temperatures. Whilst Berzelius placed it at "just above the boiling point of quicksilver," Frankland gave the ignition temperature as 300° F., or 149° C. Böttger fired carbon disulphide by molten tin at 228° C.; Brereton Baker gives the ignition point of carbon disulphide mixed with oxygen as 258—260°. Turpin states that when carbon disulphide is mixed with 10 times its volume of oxygen, the slow combustion develops into ignition at 160°; and when mixed with 10 times its volume of air it ignites at 290°.

We have endeavoured to determine the ignition point of carbon disulphide vapour and air by allowing the vapour to come into contact with a round glass flask filled with heated oil.

In the first experiments, the flask was heated by allowing a current of heated oil to circulate through the flask in which a thermometer was immersed; in the later experiments, the flask was heated externally by a flame, and the temperature allowed to fall 20—30° before the vapour was brought in contact with the glass. The liquid was contained in a porcelain basin, which was brought directly under the flask so that the surface of the liquid was about 2 inches from the bottom of the flask.

At temperatures above 260°, the vapour lit immediately or within a second or two. Below 260°, a retardation in the ignition was observed, an interval of 8—10 seconds occurring before the vapour burst into flame. When the carbon disulphide inflamed, the basin was removed and another substituted in its place.

*First Series.*—In one experiment, the vapour fired at 239°, in another at 240°; in two experiments, no ignition occurred at 239°. It was noticed that the inflammation began near the top of the flask.

| Ignition points. | Ignition points. | Ignition points. |
|---|---|---|
| 257° | 254° | 248° |
| 246 | 251 | 245 |
| 239 | 247 | 240 |
| | 239 *no ignition* | 239 *no ignition* |

*Second Series, with a different Flask.*—The oil in the flask was allowed to cool to 240°, and then the disulphide was brought beneath it. The temperature fell slowly to 236°, when the vapour inflamed. In other experiments :—

| | | | |
|---|---|---|---|
| Started at | 238° | vapour lit at | 237° |
| ,, | 240 | ,, | 238 |
| ,, | 238 | ,, | 235 |
| ,, | 238 | ,, | 232 |

On repeating these experiments in the dark, it was observed that the vapour entered into a gentle phosphorescent combustion before inflammation, the lambent phosphorescence beginning near the top of the flask where the vapour had been longest in contact with the heated surface.

When the flasks were heated at 230°, the vapour glowed, but in no case ignited. A small pencil of light was focussed on to the thermometer from a lantern, the rest of the apparatus being in the dark. Starting at 230°, the vapour glowed vigorously for some time and the phosphorescence was visible until the temperature had fallen to 195°. When oxygen is mixed with the air and disulphide vapour, the phosphorescent flame becomes brighter, and the ignition point falls. We have ignited a mixture of oxygen and carbon disulphide below 180°. When a stream of air and oxygen is passed over carbon disulphide and the mixture flows through a glass tube heated at 200°, the "glow" can be maintained for any length of time ; sulphur dioxide is formed and a reddish-brown volatile substance condenses.

Carbon disulphide, owing to this 'silent combustion,' does not exhibit a sharply-fixed temperature of ignition. It must be ranked with carbon monoxide, which, according to the experiments of Victor Meyer and Münch (*Ber.*, 1893, **26**, 2429), undergoes a silent combustion with oxygen, and therefore shows wide limits for the observed temperatures of explosion. It differs from the hydrocarbons, which, according to the same experimenters, do not exhibit quiet combination but have sharply defined temperatures of explosion.

## *Temperature at which Carbon Disulphide decomposes.*

Whilst Playfair states that dry carbon disulphide is not decomposed by passing over red-hot pumice or charcoal, Brereton Baker, on the other hand, found that carbon was deposited when excess of carbon disulphide was exploded with oxygen, and that carbon disulphide vapour was decomposed in glass tubes at 216—218°. According to Brereton Baker's experiments, carbon disulphide decomposes below its ignition point.

We have repeated Playfair's experiment in the following way: Purified carbon disulphide was distilled through a long combustion tube packed with pieces of freshly broken porcelain surrounding a nitrogen thermometer. The glass tube was placed inside a porcelain tube, and the whole was heated until the thermometer stood at 400°. The vapour was then slowly passed through the heated tube in a current of nitrogen, and then through a flask surrounded by a freezing mixture. The condensed liquid was exceedingly clear and colourless. On examining the white porcelain after 40 c.c. of the liquid had been distilled, no trace of any deposit of carbon could be detected.

On the other hand, when a small glass bulb filled with carbon disulphide was sealed up in a glass tube containing nitrogen, and the whole kept at 230° in an air-bath, the tube gradually became coated with a very thin, yellow deposit, similar in appearance to that produced by the prolonged action of sunlight on the vapour in a glass tube. The deposit only became visible after many hours heating.

We have often exploded excess of carbon disulphide vapour with oxygen in glass and in lead tubes, but except when a detonator of fulminate was used to fire the mixture, we have not detected any deposit of carbon in the tubes. When, however, the gases are exploded over mercury, a black deposit is often formed which we at first mistook for carbon, but it turned out to be finely divided mercury sulphide, containing free sulphur and unburnt carbon disulphide. The black deposit is volatile, dissolves in aqua regia, and the solution gives the reaction of mercuric salts. Our experiments, therefore, do not confirm the view that carbon disulphide, when exploded with oxygen, decomposes into its elements.

### *Decomposition of Carbon Disulphide by Light.*

Some carbon disulphide was sealed up in a tube with nitrogen, and exposed during a whole summer to the action of sunlight. The interior of the tube soon became coated with a thin, dark brown film which seemed to protect the liquid from further action; at any rate, even at the end of three months, decomposition was very incomplete.

Electric light decomposes carbon disulphide, but only very slowly. Mr. Hans Renold kindly allowed us to place tubes containing carbon disulphide inside the globe of a powerful arc light in use on his premises. In one tube, oxygen was present; in another, nitrogen. After 100 hours exposure, the tubes were covered with a very faint film which could only just be seen; the liquid in the oxygen tube was unchanged in colour, that in the nitrogen tube had turned yellowish. On evaporation, both liquids yielded brown, uninviting-looking, gummy masses, which were examined under a polarising microscope.

Part of the substance showed interference colours, which were extinguished four times in a rotation of 360° ; this suggested a crystalline structure, but no definite forms could be made out. The greater part of the substance, however, showed no interference colours, and so was not crystalline. The deposit would seem to consist of a gummy substance, together with some free sulphur. We have not further examined it.

### *Rate of Explosion of Carbon Disulphide.*

The rates of explosion for different mixtures were measured by means of the apparatus described in the Bakerian Lecture for 1893 (*Phil. Trans.*, **184**, 97), and, in metres per second, were as follows :

| $CS_2 + O_2$. | $CS_2 + 1\frac{1}{2}O_2$. | $CS_2 + 2O_2$. | $CS_2 + 3O_2$. | $CS_2 + 4O_2$. | $CS_2 + 5O_2$. | $CS_2 + 6O_2$. |
|---|---|---|---|---|---|---|
| 1584 | 1685 | 1752 | 1791 | 1754 | 1710 | 1622 |
| 1601 | 1719 | 1756 | 1810 | 1751 | 1740 | 1657 |
|  |  | 1747 | 1802 |  | 1747 |  |
| Mean 1592 | 1702 | 1751 | 1802 | 1753 | 1732 | 1640 |

It will be noticed that the maximum velocity is obtained when sufficient oxygen is used to burn the carbon to carbon dioxide and the sulphur to sulphur dioxide.

Mixtures of carbon disulphide and nitric oxide will not detonate with a spark. Le Chatelier states that the mixture $CS_2 + 6NO$ requires a ball of gun cotton with potassium chlorate to detonate it.

Mixtures containing more than two volumes of carbon disulphide vapour to one of oxygen will not ignite on sparking. If more oxygen is added, a flame can be started, but it dies out after travelling a short distance, and a true explosion-wave does not appear to be set up. We have tried to set up the wave by all of the methods previously found successful in such cases, namely, by starting the explosion with

(1) Fulminate fired in a bomb ;

(2) A mixture of hydrogen and oxygen ;

(3) A mixture of carbon disulphide with excess of oxygen ;

we found the explosion travelled at rates varying from 800 to 1430 metres per second. By photographing the flash, we found it to possess none of the characteristics of an explosion-wave ; the flame varied in intensity and velocity, and usually died out before reaching the end of the tube.

The richest mixture that will detonate in a lead tube of 1/2 inch diameter contains 1 volume of oxygen to 1½ volumes of carbon disulphide vapour.

With the assistance of Messrs. Jones and Bower, of this College, we took photographs of the explosion flame of carbon disulphide on a rapidly rotating film, according to the method described by Dixon Strange, and Graham (Trans., 1896, **69**, 759), who were able to obtain information as to the mode of combustion of cyanogen by comparing the length of the columns of ignited gases when cyanogen was fired in a long tube with different proportions of oxygen. Our photographs show that the luminous column is much the same length, whether the disulphide is exploded with its own volume or with 5 volumes of oxygen, and so the method does not throw any light on the way in which carbon disulphide burns.

As seen by the eye, the flash has a very bright violet colour.

### *Method of making the Mixtures used in these Experiments.*

Oxygen was saturated with carbon disulphide by being bubbled slowly through the liquid contained in a glass worm and flask. These were kept at the same constant temperature by immersion in a large water-bath of bright tin, this temperature being indicated by a delicate thermometer inserted in the flask. Since the temperature could be maintained within 0·1°, any desired mixture could be obtained by aid of the table of vapour pressures of carbon disulphide given by Ramsay and Young (Trans., 1885, **47**, 653). We append some analyses of the mixtures obtained by this method.

| Temp. of bath. | Barometer. | Partial pressure of $CS_2$. | Ratio $\frac{O_2}{CS_2}$ | |
|---|---|---|---|---|
| | | | Calcd. from vapour pressure. | Found by analysis. |
| 0·3—0·5° | 761 mm. | 130·3 mm. | 4·81 | 4·71 |
| 2·8° | 760 ,, | 145·2 ,, | 4·38 | 4·45 |
| 4·7—4·9° | 763 ,, | 158·6 ,, | 3·81 | 4·07 |
| 11·9—12° | 765 ,, | 215 ,, | 2·56 | 2·58 |
| 17—17·1° | 766 ,, | 264·6 ,, | 1·89 | 1·86 |

The mixtures were analysed by absorbing the carbon disulphide with alcoholic potash.* In the first three cases, the gas analysis apparatus

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* Carbon disulphide is only slightly absorbed by aqueous potash, but it is rapidly absorbed by a solution containing 1 part by weight of potash dissolved in 2 parts of water with a volume of pure alcohol added equal to that of the solution.

was employed; in the others, the gas was passed through alcoholic potash contained in Geissler's bulbs, and then collected over water. The increase in weight of the bulbs gave the amount of carbon disulphide present, whilst the volume of oxygen was obtained from the weight of water it displaced.

### *Explosion of Carbon Disulphide with a quantity of Oxygen insufficient for complete Combustion.*

It has been repeatedly shown that when ethylene is exploded with its own volume of oxygen, the oxygen goes entirely to the carbon and none of it to the hydrogen. The end products are given by the equation,

$$C_2H_4 + O_2 = 2CO + 2H_2.$$

In the case of carbon disulphide, however, we have never obtained products corresponding to the equation,

$$2CS_2 + O_2 = 2CO + 2S_2;$$

the reaction is much more complicated, sulphur dioxide, carbon dioxide, carbon monoxide, and carbonyl sulphide are formed, and much carbon disulphide remains unburnt. When the oxygen was not fairly dry, hydrogen sulphide was also formed; sulphur was deposited, but no carbon.

The mixtures exploded, and the gases obtained are given in the following table:

| Original gas. | $SO_2$. | $CO_2$. | $COS + CS_2$. | CO. |
|---|---|---|---|---|
| $CS_2 + 2O_2$ | 51·4 | 37·6 | 2·7 | 6·2 |
| $CS_2 + 1\frac{1}{2}O_2$ | 39·9 | 38·7 | 5·2 | 12·9 |
| $CS_2 + O_2$ | 25·4 | 38·7 | 6·2 | 26·1 |
| $100CS_2 + 55O_2$ | 4·4 | 21·0 | 19·8 | 56 |

We have been able to trace no simple relationship between the products of combustion and the original gases.

The method of analysis consisted in absorbing the sulphur dioxide by means of a manganese dioxide bullet, then removing carbon dioxide with a moist stick of potash (which only acts very slowly on carbonyl sulphide), and afterwards allowing the residue to stand over dilute potash to remove carbonyl sulphide. The carbon monoxide was estimated as usual by means of acid cuprous chloride. So long as carbon disulphide was not present in large quantity, the method is fairly good, but the figures are to be taken as approximate only, especially in the last case. Unfortunately, an explosion method is not available for the analysis of this mixture, as two of the equations come out to be the same, so that there are more unknown quantities than equations.

In mixtures rich in carbon disulphide (for example, $100\ CS_2 + 55O_2$), something like 20 per cent. of the disulphide escapes combustion, and is deposited as a dew on the sides of the tube after cooling. Its identity was established in the following manner: The mixture, $CS_2 + \frac{1}{2}O_2$, was passed into a glass tube provided with a Geissler tap at one end and an ordinary tap, into which platinum wires had been fused, at the other. The tube was fixed in an air-bath with a glass top, the temperature of which was kept considerably higher than 38°, at which carbon disulphide condenses from this mixture; the excess of the mixture escaped through one limb of the Geissler tap. Before firing, the tube was carefully examined through the top of the bath to see if any liquid had deposited, but none was ever seen. A spark was then passed, and a pale blue flame travelled right down the tube. After allowing the dense fumes of sulphur to settle, a stream of dry carbon dioxide was slowly passed through the tube, and the products driven out through the second limb of the Geissler tap, where they were collected in a Meyer's stoppered phial cooled by solid carbon dioxide.

A small quantity of liquid was obtained, which had the following properties:

(1) Highly refractive.
(2) Very volatile and inflammable.
(3) Gave red crystals with triethylphosphine.
(4) In a determination of the sulphur by Carius' method,

0·0234 gave 0·1402 $BaSO_4$. S = 82·2. $CS_2$ requires S = 84·2 per cent.

The liquid therefore was carbon disulphide.

Incidentally, we have examined the sulphur deposited in these explosions. It was isolated in two ways: (1) by cutting open the eudiometers in which the mixtures had been fired; (2) by firing the mixtures in long glass eudiometers, open at one end and having a long glass rod placed inside, on which the sulphur was very largely deposited. The latter method was very convenient, as the rod never broke, even though the eudiometer was shattered.

The sulphur was very sticky to the touch, and almost white. Under the microscope, it was seen to consist of minute globules, and when scratched with a pin it behaved like a very thick liquid, and strands of gummy matter were seen to follow the pin. If not exposed to air, the drops remain liquid for 10 or more days; exposure to the air of the laboratory, however, slowly caused them to solidify, and the solid showed distinct signs of crystallisation under the microscope. Berthelot (*Compt. rend.*, 1857, **44**, 378) states that sulphur deposited during the incomplete combustion of carbon disulphide is insoluble in carbon disulphide; we find, however, that much of it, though not all, is soluble, and that when the solvent is evaporated a gummy mass remains behind, which in a few hours becomes solid; this change takes place immediately on touching with ordinary sulphur.*

We have already stated that we were never able to observe any deposit of carbon in our explosions; we investigated this point somewhat fully, as it constitutes one of the differences between the combustion of carbon disulphide and that of other carbon compounds.

Mixtures of carbon disulphide with from 1/2 to 5 volumes of oxygen have been fired; some were dry, others saturated with moisture at 15°; the initial pressure was varied from 250 to 1200 mm., and the tubes were sometimes short, so that the explosion-wave was not set up, and sometimes long, so that it was. Finding that some quantity of carbon disulphide remained unburnt in the explosion of mixtures containing 1/2 to 1 volume of oxygen to 1 volume of carbon disulphide, a series of experiments were made in which these mixtures were fired with mercury fulminate in a steel bomb attached to a long explosion tube. On cutting the tube into small pieces and examining the deposit, we found that for a distance of some feet it consisted of carbon and sulphur, but beyond that, to the end of the tube, it consisted of sulphur only. When carbon disulphide vapour alone is exposed to the shock of a fulminate explosion, it is decomposed into carbon and sulphur, but the decomposition dies out at a distance of a few feet from the fulminate (Dixon and Harker, *Manchester Memoirs*, 1892; Trans., 1896, **69**, 790). The deposit of carbon in our tube would appear, therefore, to be due to the decomposition of the carbon disulphide started by the fulminate; the absence of any deposit of carbon beyond the first few feet shows that the relatively less violent explosion produced by the carbon disulphide and oxygen is not sufficient to decompose the excess of carbon disulphide into its elements.

### *Explosion of Carbon Disulphide with Excess of Oxygen.*

When exploded in a short tube, the products found are carbon dioxide, sulphur dioxide, and sulphur trioxide, and sulphur is frequently deposited. In the explosion-wave, carbon monoxide, carbonyl sulphide, and carbon disulphide are also found. The equation:

$$CS_2 + 3O_2 = 2SO_2 + CO_2$$

never represents the change that takes place on explosion; the volume of sulphur dioxide is always less than twice that of carbon dioxide, sometimes considerably less. If only small quantities of

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*Possibly some subsulphide of carbon may be formed in the incomplete combustion of carbon disulphide.

nitrogen are present, some of it is invariably oxidised. A series of experiments were done to find the amount of carbon monoxide produced, and the extent to which the nitrogen was oxidised :—

| Ratio of $CS_2$ to $O_2$ in original mixture. | Percentage of $N_2$ in original mixture. | Percentage of CO in explosion products. | Percentage of $N_2$ in explosion products. |
|---|---|---|---|
| 1 : 3·12 | 1·46 | 0·56<br>0·56 | 0·84<br>0·84 |
| 1 : 3·50 | 1·56 | 0·56 | 0·18 |
| 1 : 4·09 | 0·63 | 0·48 | 0·13 |
| 1 : 4·71 | 1·25 | 0·92<br>1·05 | 0·62 |
| 1 : 3·60 | 16·85 | 1·04<br>1·35 | 19·77<br>19·94 |

In each case (except the last), the percentage of nitrogen comes out less after explosion than before, whereas, owing to the contraction after explosion, it should be greater. In the last case, there is practically no disappearance of nitrogen ; 100 volumes of the original gas yield 83·41 volumes after explosion, so that the 16·85 per cent. of nitrogen should become 19·89.

These explosions were done in a coil of lead pipe 18 feet long and 1/2 inch in diameter, heated at 100° in a water-bath. The glass firing piece could not be fastened into the metal tube by Faraday's cement, since this is acted on by carbon disulphide; we therefore fastened it in with plaster of Paris, and soaked the joint with syrupy sodium silicate. We found that joints so made remained quite tight. As a lubricant for the taps, we used finely sifted plumbago, since the ordinary lubricants (tallow, &c.) absorb carbon disulphide.

In order to confirm the presence of carbon disulphide in the gases, mixtures containing 3 to 6 volumes of oxygen to one of carbon disulphide were exploded in a long lead tube heated at 100°, which could be opened at a point 5 feet from the end. By collecting the gases here, all danger of the carbon disulphide found being simply some which might have stuck to the tap was avoided. A slow stream of carbon dioxide displaced the products from the tube, and these were sent first through a flask containing lead acetate dissolved in excess of potash, and then into a flask containing triethylphosphine. A black precipitate was always obtained in the first flask, indicating carbonyl sulphide, and a red precipitate in the second, showing carbon disulphide.*

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* It is necessary to remove sulphur dioxide before passing into triethylphosphine, as sulphur dioxide considerably impairs the delicacy of the reaction. Hydrogen sulphide (the only other gas which would give the black precipitate) was always tested for, but found to be absent.

From a long tube, some 10 c.c. of carbon monoxide were isolated from the products of explosion of a mixture of $CS_2 + 6O_2$, by allowing the products, displaced as above, to stand over potash and subsequently removing oxygen.

We find then that, even using twice as much oxygen as is theoretically necessary for complete combustion, there always remain over, *in the combustion that takes place in the explosion-wave,* carbon monoxide, carbonyl sulphide, and carbon disulphide.

### *Combustion in the Smithells' Separator.*

It is quite easy to separate the carbon disulphide flame into two cones, the most convenient method being to send air dried by passing through strong sulphuric acid in towers filled with broken glass, into a glass flask of 100 c.c. capacity containing carbon disulphide and glass wool, the jet of air being allowed to play on the surface of the wool. The flask is surrounded by warm water, and the mixture of air and carbon disulphide vapour passes into the separator and burns with a flame which easily divides into two cones.

The outer cone is pale blue, and shows a bright, continuous spectrum. A piece of cold porcelain placed in the flame gives a deposit of sulphur, and sulphur is deposited in the space between the flames. No carbon is deposited. The inner cone is a greenish-grey, it shows a bright, continuous spectrum. Analysis of the interconal gases gave some very remarkable results. It was found that there was always some unchanged carbon disulphide, but only very small quantities of carbon dioxide and carbonyl sulphide. The products consist almost entirely of equal volumes of sulphur dioxide and carbon monoxide. One hundred volumes of interconal gases contain :—

| $SO_2$. | $CO_2 + COS + CS_2$. | CO. | $N_2$. |
|---|---|---|---|
| 10·32 | 1·96 | 9·58 | 78·14 |
| 11·30 | 0·74 | 10·32 | 77·64 |
| 11·3 | 2·5 | 11·7 | 74·5 |

These experiments were done at different times and in different pieces of apparatus. It is thus evident that the conditions attending a steady flame in the separator are fairly constant.

Attempts to increase the amount of carbon disulphide were unsuccessful, as also were attempts to increase that of air. In the latter case, the flame always struck back. Samples could occasionally be taken, however, before the striking back occurred, and an analysis of such a sample showed that 100 volumes of interconal gases contained :—

| $SO_2$. | $CO_2 + COS + CS_2$. | CO. | $N_2$. |
|---|---|---|---|
| 16·2 | 2·5 | 9·1 | 72·2 |

The increased oxygen simply results in an increase in the amount of sulphur dioxide.

## CONCLUSIONS.

1. We have not been able to obtain any evidence which would lead us to suppose that pure carbon disulphide will not explode when mixed with oxygen and sparked.

2. Before igniting in the air, carbon disulphide undergoes a phosphorescent combustion. The change from this to actual ignition is not sharp, and hence carbon disulphide cannot be said to have any definite ignition point. The discrepancies between the recorded determinations can thus be accounted for. In the phosphorescent combustion part of the sulphur appears to burn, leaving a sub-sulphide of carbon.

3. Carbon disulphide is comparatively stable when heated. At 230°, prolonged heating is necessary before the slightest decomposition is noticeable, and no change can be observed on passing it through a tube kept at 400°. It does not split up into carbon and sulphur, either when passed through a steady flame as in the Smithells' separator, or at the high temperature of the explosion-wave. Even when this decomposition is started by means of mercury fulminate, it soon dies out.

4. Our experiments do not confirm the view that the combustion of carbon disulphide is preceded by a decomposition into its elements.

5. Carbon disulphide is slowly decomposed by exposure to electric light.

6. The reaction that takes place when carbon disulphide is exploded with oxygen can in none of the cases observed by us be expressed by any simple equation.

(*a*) When excess of oxygen is used, the products are carbon dioxide, sulphur dioxide, sulphur trioxide, sometimes free sulphur; and in the explosion-wave, carbon monoxide, carbonyl sulphide, and unchanged carbon disulphide.

(*b*) With an insufficient quantity of oxygen, the products are carbon dioxide, sulphur dioxide, carbon monoxide, carbonyl sulphide, and carbon disulphide. When the amount of oxygen is successively diminished, the quantity of sulphur dioxide falls off, and that of the carbon monoxide, carbonyl sulphide, and unchanged carbon disulphide increases.

(*c*) Even with small amounts of oxygen, there is always a division of the oxygen between the carbon and sulphur. Using a mixture, $CS_2 + \frac{1}{2}O_2$, only a portion of the carbon disulphide takes part in the reaction.

7. The mixture richest in carbon disulphide that can be made to

detonate (that is, to give the "explosion-wave") by any of the methods tried by us contains 1 volume of oxygen to 1½ volumes of carbon disulphide vapour. In the other direction, the limit is not so quickly reached, and mixtures containing 6 or 7 volumes of oxygen to 1 volume of carbon disulphide vapour still detonate.

8. Where burnt in the Smithells' separator, the phenomena are altogether different from those observed in the explosions. The interconal gases consist of nearly equal volumes of sulphur dioxide and carbon monoxide, together with sulphur vapour and some unchanged carbon disulphide, and small quantities of carbonyl sulphide and carbon dioxide.

9. The combustion of carbon disulphide differs from that of other carbon compounds investigated in the following respects :—

(*a*) Carbon is not deposited.

(*b*) The explosion-wave is not propagated through the mixture $2CS_2 + O_2$, and we could never realise the equation,

$$2CS_2 + O_2 = 2CO + 2S_2,$$

analogous to the well-established equation,

$$C_2H_4 + O_2 = 2CO + 2H_2,$$

(*c*) The maximum velocity of explosion is attained with the mixture, $CS_2 + 3O_2$, that is, when sufficient oxygen is present to burn the carbon to carbon dioxide and the sulphur to sulphur dioxide.

THE OWENS COLLEGE,
MANCHESTER.