## 87. *Some Properties of Arced Gases.*

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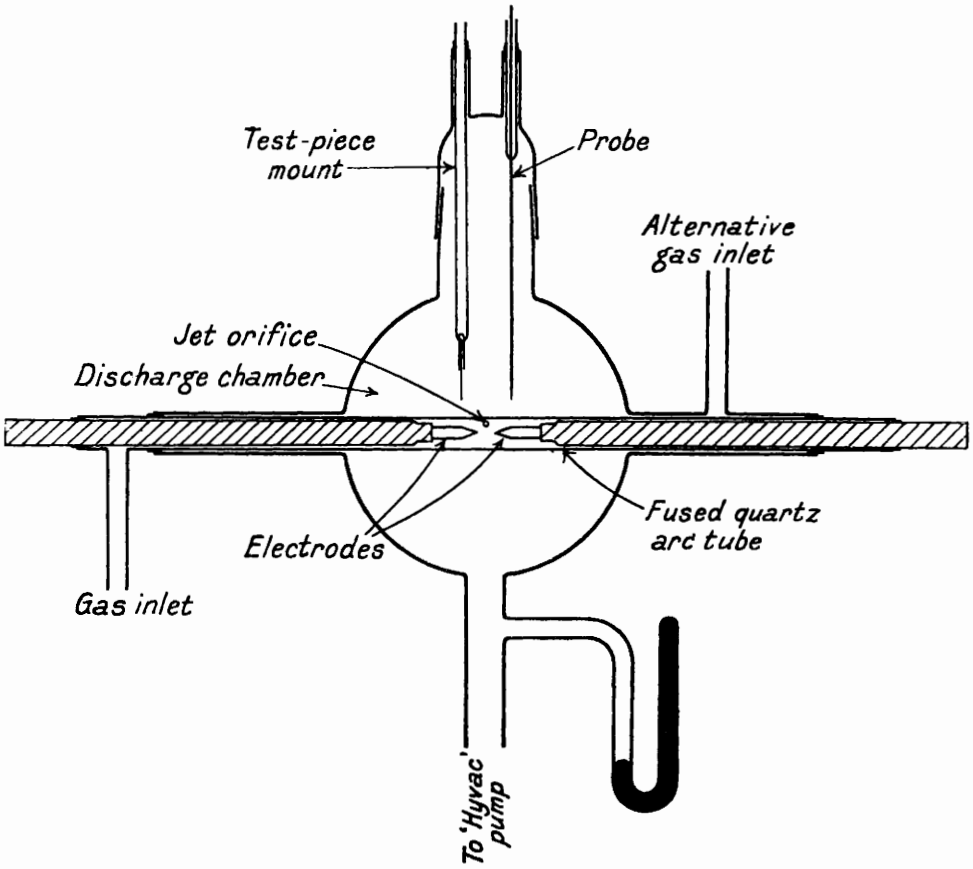
It has previously been shown (*Proc. Roy. Soc.*, 1926, **111**, *A*, 257) that combustion of a gaseous mixture can be confined to the cathode zone of a high-tension discharge by a suitable choice of pressure, current, and gap width, and that its rate is directly proportional to the current. Metal atoms, proportional in number to the current, can be introduced into the cathodic reaction zone by the use of a freely sputtering metal as cathode (*ibid.*, 1930, **129**, *A*, 314). It was further found that the presence of metal atoms (*ibid.*, 1929, **124**, *A*, 303), steam (*ibid.*, 1929, **125**, *A*, 532), or hydrogen (*ibid.*, 1930, **129**, *A*, 656, 672) greatly accelerated the rate of cathodic combustion of dry carbon monoxide–oxygen mixtures; for example, although at a non-sputtering cathode the rates of combustion of dry mixtures of these gases never exceeded 0·05 c.c./min./mA., yet at a freely sputtering cathode or in the presence of steam or hydrogen, rates as high as 0·36, 0·45, and 0·67 respectively were recorded. These facts, in conjunction with the results of analyses of the intermediate combustion products, showed clearly that such promoters profoundly affected the nature of the reaction mechanism whereby dry carbon monoxide–oxygen mixtures burn cathodically. In view of the relatively high levels of excitation of each gas shown to have been attained in the cathode zone (*ibid.*, p. 314), the remarkable resistance of the monoxide to combustion in the absence of a promoter suggested that under the conditions of these experiments the two gases were most reluctant to combine directly. Moreover, it was shown experimentally that much of the relatively small amount of combustion observed in the case of the dry gaseous mixtures was due to the prior cathodic auto-oxidation of carbon monoxide, whereby the dioxide and carbon were formed, the latter being subsequently burnt by oxygen.

Whereas metal atoms thus promoted the cathodic combustion of dry carbon monoxide, their presence reduced the rate of cathodic combustion of hydrogen–oxygen mixtures, particularly in the presence of excess hydrogen (*ibid.*, 1931, **133**, *A*, 173). Finally, although carbon monoxide disappeared more rapidly than hydrogen in mixtures of these two gases with oxygen undergoing cathodic combustion, it was found that the rate of such combustion was wholly characteristic of the cathodic combustion of hydrogen (*ibid.*, 1930, **129**, *A*, 672). These facts led to the view that, as with carbon monoxide and oxygen, the direct union between hydrogen and oxygen could only be induced with difficulty, but that in the presence of steam combustion was in effect promoted in both cases by hydroxyl.

FIG. 1.




This investigation was therefore carried out with the object of subjecting the above and other views to further experimental test. The properties of streams of gases excited by previous passage through a high-tension arc were examined, and their mutual interactions studied in relevant cases.

## EXPERIMENTAL.

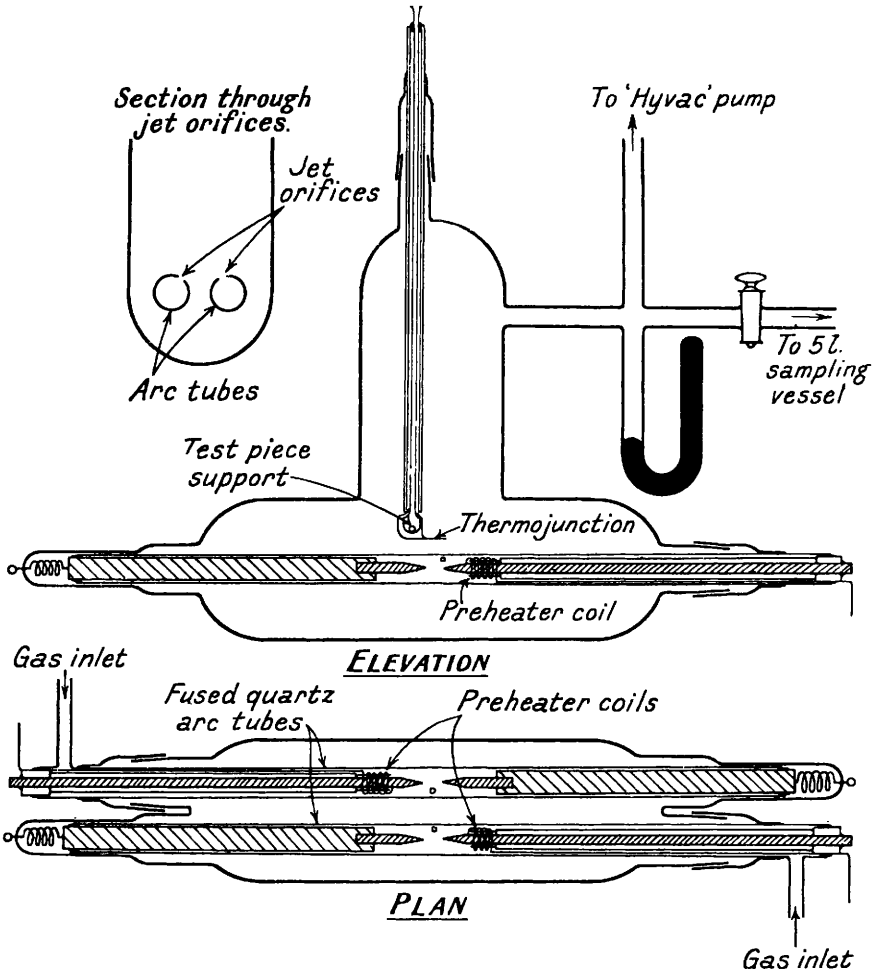
Several forms of apparatus were employed which enabled one or more jets of previously arced gases to be discharged into a partially evacuated vessel. It will suffice to describe briefly the two final forms employed, the one serving for the production of single jets, the other for double jets of gases.

*The Single-jet Apparatus.*—Fig. 1. This apparatus enabled a stream of gas to be drawn

through a high-tension arc prior to discharge into an 18-cm. diameter Pyrex vessel, through an orifice, 0·2 mm. in diameter, blown into a quartz arc tube. The diagram (Fig. 1) is self-explanatory.

*The Double-jet Apparatus.*—Fig. 2. This apparatus was similar in principle. Platinum pre-heating coils enabled the temperature of the arced gas streams to be raised from about 35° to 600°. The streams could be caused to impinge on each other at varying distances from the orifices by rotational adjustment of the arc tubes. The test piece support carried a platinum–platinum-rhodium thermo-junction for measuring the temperature of the gas streams. Other

FIG. 2.




services were essentially as in the case of the first apparatus, except that provision was made for the withdrawal of samples into a 5-litre vessel for subsequent analysis.

*Results with Single Jets.*—The gas was streamed through the arc (6 mA., between 600 and 800 V.) under pressures between 1 mm. and 150 mm. and discharged through the jet orifice into the discharge vessel, which was evacuated at a rate enabling any desired pressure to be maintained therein. With oxygen streaming through the arc into the discharge vessel containing oxygen at about 85 mm. pressure or less, the pressure fall in the orifice being about 15 mm., a well-defined and luminous beam was obtained. The appearance and properties of the arced gas streams produced in the single-jet apparatus are summarised as follows:

| Arced gas. | Discharge vessel pressure range, mm. | Colour of after-glow. | Length of after-glow. | Chemical properties of arced gas stream. |
|---|---|---|---|---|
| $H_2$ dry | 5—150 | Nil | Nil | No reduction of CuO |
| $H_2 + 1\%H_2O$ | | Nil | Nil | CuO rapidly reduced |
| $O_2$ dry | 50—95 | Greenish | From 2 mm. to impinging on vessel wall | Gave characteristic $O_3$ tests: positive reaction with tetramethyl base; solid $O_3$ (highly explosive) frozen out on liquid-air cooled tube in contact with glow |
| $O_2 + 1\%H_2O + 1\%H_2$ | | Nil | Nil | No $O_3$, but traces of $H_2O_2$ [$Ti(SO_4)_2$ test] |
| $O_2 + 1\%CO$ | | Bright lavender | 2—30 mm. | |
| ($O_2$ could be discharged into either moist or dry unarced $H_2$ or CO without appreciably affecting the appearance of the beam.) | | | | |
| $N_2$ dry | 50—95 | Yellowish | 5—50 mm. | |
| $N_2 + 1\%H_2O + 1\%H_2$ | | Nil | Nil | |
| ($N_2$ could be discharged either into unarced moist $N_2$ or into $H_2$ without appreciably affecting the appearance of the beam.) | | | | |
| $N_2 + 1\%CO$ | | As with $N_2$, *i.e.*, glow unaffected. | | |
| CO dry | 30—80 | Light blue, 5-mm. tongue issuing from jet orifice: beam otherwise apple-green | 15—50 mm. | Rapidly reduced cathodically sputtered $PtO_2$ films, which are otherwise only slowly reduced by unarced CO |
| $CO + 1\%H_2O$ | | Nil | Nil | |
| $CH_4$ | 30—80 | Nil | Nil | Slight C deposition on electrodes |
| $CO_2$ | 30—80 | Nil | Nil | Slowly reduced $PtO_2$, and gave $O_3$ reactions. |

The above gases all gave rise to extensive cone-shaped glows when the discharge chamber pressures were below 2—4 mm. Below 2 mm. the glows could be made to fill the entire discharge chamber.

*Results with Mixed Jets.*

| Gas streams. | Analysis of products. | Remarks. |
|---|---|---|
| Dry arced $O_2$ alone | 0·02%$CO_2$ (Baryta blank) | |
| Dry arced CO alone | 0·11%$CO_2$ | Auto-oxidation |
| Dry arced CO and arced $O_2$ mixed | 0·12—0·02 = 0·10% $CO_2$ | Allowing for auto-oxidation, no direct union between CO and $O_2$ |
| Dry arced CO alone | 0·057% $CO_2$ | Auto-oxidation reduced owing to carbon accumulated on electrodes |
| Arced ($O_2$ + 2% $H_2O$) | 0·035% $CO_2$ (Baryta blank) | |
| Dry arced CO mixed with unarced ($O_2$ + 2% $H_2O$) | *a.* 0·069 less blanks = 0·034% $CO_2$<br>*b.* 0·045 ,, ,, = 0·012 ,, | Auto-oxidation only, but no combustion direct |
| Dry arced CO mixed with arced ($O_2$ + 2% $H_2O$) | *a.* 0·190 less blanks = 0·098% $CO_2$<br>*b.* 0·140 ,, ,, = 0·048% ,, | Slight interaction between CO and products of arced steam |

While the after-glows of neither carbon monoxide nor oxygen were affected when run into atmospheres of unarced oxygen or monoxide respectively, the colour of the monoxide jet changed abruptly from apple-green to bright lavender on coming into contact with the arced oxygen stream.

| Gas streams. | Analysis of products. | Remarks. |
|---|---|---|
| Dry arced $H_2$ mixed with dry arced $O_2$ | *a*. 0·22% $H_2O$<br>*b*. 0·28 ,, | Appreciable combustion |
| Dry arced $H_2$ mixed with dry unarced $O_2$ | *a*. 0·00 ,,<br>*b*. 0·01 ,, | No combustion |
| Dry unarced $H_2$ mixed with dry arced $O_2$ | *a*. 0·06 ,,<br>*b*. 0·066 ,, | Slight combustion |
| 3 vols. arced moist $H_2$ (16·8% $H_2O$) + 4 vols. arced moist $O_2$ (16·8% $H_2O$) | 7·0 ,, | Much steam decomposed |
| 3 vols. arced moist $O_2$ (16·8% $H_2O$) + 1 vol. arced moist $H_2$ (16·8% $H_2O$) | 11·5 ,, | Less steam decomposed |

Experiments were then carried out in order to determine the effects of previous arcing upon the ignition temperatures of the mixed streams, first for homogeneous ignition at the junction of the preheated arced streams, and second for ignition on the surface of an internally-heated fused quartz tube (not shown in Fig. 2) which could be brought into the zone of the mixed gases by rotation of a supporting arm passing through a ground-glass joint. With unarced impinging streams of hydrogen and oxygen delivering into a discharge-chamber pressure of 90 mm. of hydrogen plus oxygen, homogeneous ignition occurred when either the hydrogen stream was heated to 590°, or the oxygen stream to 580°, the other stream in each case being cool ($< 35°$). Preheating of both streams enabled the ignition temperature to be slightly reduced. Thus, ignition took place with hydrogen at 570° mixing with oxygen at 560°. These results were wholly unaffected by previous arcing of either the one or both gas streams, or by the presence of steam up to about 10% and possibly more.

The least temperature of the outside surface of the silica tube necessary to effect heterogeneous ignition was found to be practically unaffected by either (i) water contents of gases up to 10% and possibly more, (ii) previous arcing of either or both gases, (iii) preheating of either or both gases, arced or otherwise, up to stream temperatures within 20° below the ignition temperature. The discharge-chamber pressure was, as before, maintained at 90 mm. of hydrogen plus oxygen.

Thus, in no case was the ignition temperature affected by previous arcing or otherwise of the gas streams, and in this respect it was immaterial whether ignition occurred under homogeneous or heterogeneous conditions.

## Discussion.

A spectrographic study (*Proc. Roy. Soc.*, 1930, **129**, *A*, 314) has shown that within the cathode zone dry oxygen, but not dry hydrogen, is atomised, whereas moist hydrogen or steam decomposes in the main to hydrogen atoms and hydroxyl. These three products have different lives. The well-known properties of the hydrogen atom are such that it can be expected to survive in the arced streams; that it does so in quantity has, indeed, been proved by the rapid reduction of copper oxide obtained in our experiments. The life of hydroxyl is so brief (Bonhoeffer and Pearson, *Z. physikal. Chem.*, 1931, **14**, *B*, 1) that, under the conditions of our experiments, it could never have survived passage through the jet orifice. There is some doubt as to the longevity of oxygen atoms as such, though experiments recently carried out in this laboratory (of which an account will shortly be published) support the view that these, like hydroxyl, are short-lived. However this may be, the arced oxygen streams contained ozone in abundance. Strutt's results (*Proc. Physical Soc.*, 1910, **23**, 66; 1912, **24**, 1) suggest that the after-glow in arced oxygen streams is due to ozone decomposing to molecular oxygen. Finally, the after-glows observed in several arced gas streams testify to the existence therein of molecules in metastable states of relatively high levels of excitation. Nevertheless, previous arcing was found to be without effect upon the ignition temperatures observed in mixed hydrogen and oxygen streams. In view of these facts, and of the crucial nature of the experiments whereby they have been brought to light, it is difficult to resist the conclusion that, whatever rôle atomic hydrogen as such may play in the homogeneous combustion of hydrogen by oxygen, it certainly does not act therein as a promoter. This conclusion conflicts with the well-known views of the mechanism of the combustion put forward by Haber and his collaborators (*Z. physikal. Chem.*, 1928, **137**, *A*, 263; 1932, **16**, *B*, 443) and by Taylor (*Trans. Faraday Soc.*, 1932, **28**, 569) and others, according to which atomic hydrogen is an essential and all-important active member in their postulated reaction chains.

The results obtained on mixing arced dry streams of carbon monoxide and oxygen, both exhibiting strong after-glows which changed colour in a remarkable manner on mixing, are in agreement with the facts relating to the cathodic combustion of such mixtures; they show that, within the pressure range covered in these experiments, the monoxide is most reluctant to combine with oxygen directly, *i.e.*, without the intervention of steam or metal atoms.

The resistance to combustion offered by dry hydrogen and oxygen is less than that observed in the case of carbon monoxide. Even so, no interaction occurred when the hydrogen stream alone was arced, and only traces of combustion could be detected when arced oxygen was mixed with unarced hydrogen; it is, indeed, well known that hydrogen and ozone interact at room temperature, though only very slowly, to form water.

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