228. *Flame Phenomena of Carbon Monoxide.*

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SINCE the researches of Dixon (*Phil. Trans.*, 1884, **175**, *A*, 617) much work has been published on the effect of hydrogen and water vapour on the combustion of carbon monoxide (for recent work and earlier references, see Bawn and Garner, J., 1932, 129; Finch, *Proc. Roy. Soc.*, 1931, **134**, *A*, 343; Hinshelwood, Thompson, and Hadman, *ibid.*, 1932, **138**, *A*, 297; Bone, Weston, and Winton, *ibid.*, 1929, **123**, *A*, 285). Most of the experiments have been carried out in closed vessels. The present communication describes observations on the formation of ozone and hydrogen peroxide in the open flame burning at a jet in oxygen. The influence of hydrogen, and of certain metals and salts, on the luminescence in the flame is also dealt with.

In order to obtain large volumes of dry gases, such as are necessary in studying the open flame of carbon monoxide in oxygen, the drying agent used must have a low ultimate vapour pressure of water, and must absorb the water molecules colliding with it as quickly as possible. Phosphoric anhydride is not very suitable, since its most active points are used up first of all, leaving a drying agent of uncertain vapour pressure and increasing sluggishness. It was therefore decided to use U-tubes, packed with glass-wool to give a large surface, and immersed in liquid oxygen. The vapour pressure of any ice formed is less than 10^{-19} mm., so that the gas issuing from the tubes is very dry indeed. The driers are sealed to the combustion apparatus without the intervention of taps or greased joints, and experiments showed that water absorbed in the walls of the combustion apparatus was so rapidly removed by the stream of dry gases, that in 5—30 minutes further evolution of water from layers deep below the surface of the vessel was too slow to be detectable. The convenience and certainty of action of these driers made the detection of a mol. fraction of 10^{-7} of hydrogen in the gases a relatively simple matter.

EXPERIMENTAL.

Description of Apparatus.—The main details are shown in Fig. 1. The Pyrex combustion chamber *P*, of diameter 3 cm., is closed at the bottom by immersion in a trough of mercury, previously dried by warming. Separate experiments showed that mercury had a negligible effect on the carbon monoxide flame at the concentrations carried by the oxygen stream. Intensively dried oxygen enters at the two diametrically opposed inlets about 2 cm. above the mercury surface. The monoxide burns at the silica jet *Q*, the top of which can be heated by passing an electric current through a platinum wire, wound in close contact with the jet, and encased in silica to avoid introduction of platinum vapour into the flame. With this arrangement, the mixture of monoxide and oxygen came into contact with the coil, whilst it was heated to 1200° or more.

The jet is held in the tightly-fitting Pyrex holder *J*, which is sealed to the drier *D*, all paths being kept as short as possible to accelerate self-drying. The drier *D* is tightly packed with about 10 g. of glass-wool, giving a total surface of 10^4 sq. cm., and is kept immersed well below the surface of liquid oxygen. It could be freed from ice, when necessary, by heating in a current of air. Experiments showed that even with carbon monoxide from a water-sealed reservoir intensely dry gas issued from *D*, but to avoid the accumulation of ice both oxygen and carbon monoxide were roughly dried over phosphoric oxide before passage through the U-tubes. Although various workers have dried gases with liquid air (*e.g.*, Girvan, P., 1903, **19**, 236), it is essential to provide a large cold surface for the intensive drying of streams of gas.

Various salts could be placed in the platinum cup *R*, mounted concentrically with the jet *Q*, and were volatilised into the flame by heating the cup with alternating current. All platinum parts were glowed in oxygen before use to remove traces of dissolved hydrogen. Small cylinders of metal foil were inserted into the top of the jet when the influence of various metals on the flame was being studied.

The oxygen and hydrogen used were obtained from cylinders supplied by the British Oxygen Company, and the carbon monoxide was prepared by the interaction between pure formic and sulphuric acids, and was stored in water-sealed reservoirs, and passed over solid potassium hydroxide before use.

All impurities except the permanent gases are effectively removed in the driers. The oxygen contained 1—2% of nitrogen, and direct weighing of the water collected from the combustion of 10 litres of dried gases showed that the monoxide and oxygen definitely contained less than a mol. fraction 2×10^{-4} of hydrogen. The concordant results obtained when the amount of hydrogen added to the carbon monoxide was less than 10^{-6} show that the actual impurity of hydrogen was much less than the smallest amount that could be detected by direct weighing. Rate of flow of the gases was measured by the pressure difference at the ends of calibrated capillaries, using vacuum-pump oil (vapour pressure 10^{-7} cm.) as manometer liquid. The combustion products issuing at the top of the chamber could be passed over test papers, and their composition determined to 0·3% in a simple gas analysis apparatus. The flow of intensely dried gases (about 5 c.c./sec.) was found to prevent back diffusion of moisture without further precautions.

Experiments with the Carbon Monoxide Flame.—(a) *The self-drying flame.* In performing an experiment, the carbon monoxide flame is lit in air and inserted in the chamber, which is surrounded by an air jacket (not shown) to avoid draughts from irregular cooling of the walls. The chamber is gradually immersed in mercury by raising the trough, care being taken to avoid sudden changes of pressure, which tend to put out the flame. When the chamber is closed, the flame is at first quite small, and the region of luminous combustion begins inside the edge of the jet, showing that some oxygen diffuses in. As the water evaporating from the walls lessens, the flame begins to lengthen, even though the gas flow is kept constant. The bottom of the flame likewise rises, showing that the velocity of combustion at any given concentration of oxygen (which is unaltered by the presence of water) decreases. As self-drying proceeds, the bottom of the flame rises to 1 mm. or more above the jet, being separated from it by a dark space. Experiments described in the next section show that by adding suitable amounts of hydrogen to the monoxide every phase of the self-drying flame can be stabilised. In the absence of added hydrogen, self-drying proceeds, and the black space enlarges so much round the edge of the jet that the flame goes out. This stage corresponds with a mol. fraction of hydrogen of about $10^{-4\cdot5}$ and analysis of the combustion products just before this point shows that about 4% of the monoxide escapes unburnt, compared with less than 0·5% from the wet flame.

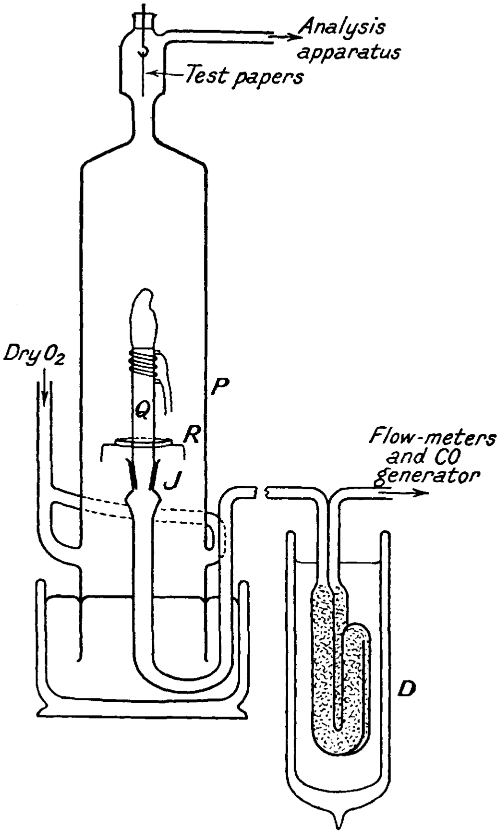
Since the flame enlarges on drying, the heat of combustion is dissipated over a larger volume of gases. In order to test whether the extinction of the flame was not due to this, the jet was heated to about 1000°, by passing a current through the wire before the black space got too large. This causes the flame to shrink back into the jet; as the additional water supplied from the silica diminishes, however, the flame once more enlarges. It now passes through a phase of oscillation on the jet, as if the supply of molecules maintaining the flame no longer proceeds uniformly from all parts of the jet, leading to irregular impulses on the flame. In one case, a region of the jet particularly active in maintaining the flame was found to be abnormally devitrified after the experiment, emphasising the connexion between the nature of the jet and its ability to start fresh reaction chains. As self-drying proceeds at the heated jet, the dancing of the flame becomes more pronounced, and finally the flame goes out.

If the temperature of the jet is raised at this point, a blue glow surrounds the silica sleeve, and increases in size with rising temperature, till the unburnt gas above the jet kindles. A large soft flame travels up the chamber, and once the monoxide is kindled, the flame persists for some time even if the temperature be again lowered. Examination of this process through a small direct-vision spectroscope showed that kindling at higher temperatures is associated with the reappearance of the sodium line, which soon again fades. The flame gradually lengthens and goes out.

Under the conditions of the experiment, the stability of carbon monoxide burning in oxygen is definitely dependent on the supply of water or other molecules, even with the jet at 1400°. At still higher temperatures, a permanent flame may be possible, but the heated platinum will not stand the prolonged experiment necessary to make sure that the flame is not changing on further self-drying. Tests with helium showed that it did not maintain a dry monoxide flame, so that the effect is not due to high thermal conductivity of the impurity.

(b) *Carbon monoxide flame with added hydrogen.* Although the effect of progressive removal of water on the monoxide flame is easily demonstrated in the above experiments, a quantitative study of the effect of minute amounts of water is hampered by the slow establishment of equilibrium with the walls, at any particular concentration. This objection does not apply to minute amounts of hydrogen, the effect of which is probably not very different from that of water, owing to the establishment of the water-gas equilibrium (cf. Passauer, *Z. physikal. Chem.*, 1932, **161**, 299). Separate tests with intensely dry hydrogen in oxygen showed that sufficient water molecules were always formed on the hot silica walls to promote the combustion of dry hydrogen in the gas (contrast Smithells, Whitaker, and Holmes, J., 1930, 185, who sparked the dry gases).

FIG. 1.



A small amount of hydrogen was thoroughly mixed with carbon monoxide in a calibrated gas holder, and the mixture was passed through the driers and burnt at the jet, which was heated with a constant current. The flow of oxygen being kept constant, the height of the flame cap above the jet was measured at various rates of flow of a given mixture. Measurements consistent to 1 mm. were obtained by observing the flame in a darkened room, and raising the telescope of the cathetometer till the luminescence at the tip of the pale blue flame was just visible above the cross line. The dancing of the flame at low hydrogen content facilitates the observation of faint luminescence, since the image falls on fresh patches of the retina. Measurements were not recorded till the flame had reached constant height, showing that this depended on hydrogen content, and not on adventitious moisture. In some cases, preliminary self-drying with pure carbon monoxide was used, to economise the mixture, and a change over was made when self-drying was nearly complete. After each run, the gas remaining in the gasometer was diluted with fresh monoxide, and thoroughly mixed, so that the molar fraction of hydrogen was finally reduced to 10^{-8} or less.

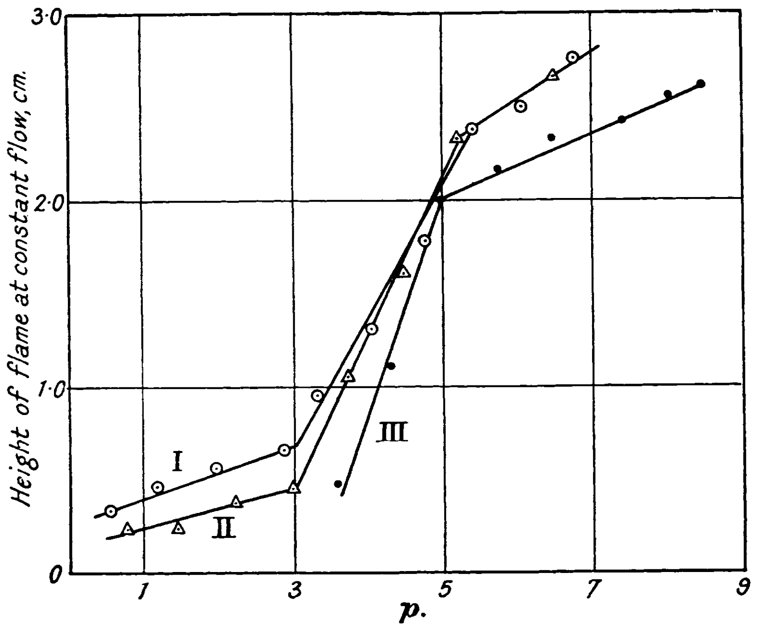
When all other conditions are kept constant, the height of the flame is approximately proportional to the flow of carbon monoxide. Increase of the oxygen flow, and heating of the jet, gives a flame which is smaller, and stable at lower ultimate concentrations of hydrogen. This suggests that carbon dioxide interferes with the combustion (cf. Bawn and Garner, *loc. cit.*). Fig. 2 gives a plot of the height of the flame, for a single rate of flow of monoxide (1·15 c.c./sec.), against p, where the molar fraction of hydrogen is 10^{-p}. Curve I refers to a jet of diameter 0·46 cm., an oxygen flow of 2·8 c.c./sec., and an expenditure of 18 watts in heating the jet; curve II to a jet of diameter 0·65 cm., oxygen flow 2·6 c.c./sec.; curve III, obtained with a jet similar to I, is incomplete, but is included to show the limits at which the influence of hydrogen can still be detected. Observations at each p_{H_2} were made at various rates of flow of carbon monoxide, and the height at 1·15 c.c./sec. obtained from the straight line drawn through the results, in order to obtain increased accuracy.

Inspection of Fig. 2 shows that as the molar fraction of hydrogen decreases between 10^{-1} and 10^{-3}, and from 10^{-5} onwards, the height of flame gradually increases. Between a p_{H_2} of 3 and 5 a critical region is traversed in which the height of the flame increases five-fold. This phenomenon probably corresponds with the region observed by Garner and co-workers (*loc. cit.*) in the radiation from carbon monoxide flames travelling down closed tubes, though the limits with the open flame are extended to somewhat higher and lower values of p. Observations of the flame in the middle of this region show an inner region of bright luminescence merging into a very pale outer one of greater height, the height of the outer region being recorded on the graph, since the inner cannot be easily measured. As the molar fraction of hydrogen decreases to 10^{-5}, the outer mantle gets brighter, and beyond this concentration the two regions are indistinguishable again. This provides visual evidence of two types of monoxide combustion, with the change over in this critical region, as was also postulated by Garner.

We may accept as a provisional hypothesis that in the absence of hydrogen excited carbon dioxide molecules produced in combustion lose their energy either by radiation or by collisions incapable of continuing a reaction chain, but that a sufficient concentration of hydrogen facilitates the continuation of a given type of chain. Since the collision interval is of the order 10^{-10} sec., and the excited carbon dioxide must collide with hydrogen before losing its energy, if the chain is to continue, a critical change in the combustion process where less than 1 collision in 10^3 is with hydrogen indicates that the life of the excited dioxide is of the order 10^{-7} sec.

FIG. 2.

Molar fraction of $H_2 = 10^{-p}$.



Further evidence is being obtained on the cause of the second break in the curves, at a molar fraction 10^{-5} of hydrogen. It is remarkable that in this region the height of flame is the same for the same flow of carbon monoxide; in spite of the linear velocity through jet I being double that through jet II, of larger cross section. It is clear, however, that, with the apparatus described, concentrations of hydrogen of 10^{-7} can be detected and estimated in carbon monoxide. By mixing in 1% of an inert gas whose hydrogen content is to be estimated, measurements are still possible if the initial concentration is above 10^{-5}, with the further advantage that non-permanent gases, *e.g.*, hydrocarbons, are frozen out in the driers. This would appear to be the most sensitive means of estimating small concentrations of hydrogen yet available.

Analysis of the gases issuing at the top of the chamber showed that the proportion of carbon monoxide escaping unburnt gradually increased to about 4% as the hydrogen content decreased.

(c) *Formation of ozone and hydrogen peroxide in the flame.* The formation of these two products in flames of hydrogen and methane has been recently studied by Riesenfeld and co-workers (*Z. physikal. Chem.*, 1924, **110**, 801; 1928, **139**, *A*, 169), and in the moist carbon monoxide flame by von Wartenberg and Sieg (*Ber.*, 1920, **53**, 2192). In all cases the ozone is said to be formed *via* hydrogen peroxide. This does not seem to agree with the experiments on the monoxide flame with varying moisture content, described below.

In order to test whether the ozone was formed by the photochemical action of the radiation from the flame on the surrounding oxygen, a slow stream of oxygen was passed through an outer jacket fitting round a silica combustion chamber, with the monoxide flame inside. Filter-papers soaked in tetra-base (tetramethyldiaminodiphenylmethane) or in alcoholic benzidine solution (cf. Mellor, " Treatise of Inorganic Chemistry," Vol. I, 1922) gave definite tests for ozone in less than 2 minutes in the combustion products, and no test in 3 hours in the outer stream of oxygen. Ozone is therefore formed from activated molecules in the combustion products and not photochemically.

The rate of colouring of the test papers increases as the gases get drier, and oxides of nitrogen are also formed, from the nitrogen in the oxygen. The following table gives the order of magnitude of total oxidising products collected over acidified potassium iodide, from the combustion of 1 litre of carbon monoxide and 3 litres of oxygen, supplied at a constant rate of flow (about 1 c.c. and 3 c.c./sec.).

V. p. of H_2O, mm.	*ca.* 0·01 *	*ca.* 0·1	1·6	7·5	12·8
Height of flame, cm............	1·0	0·48	0·45	0·37	0·35
Equiv. iodine $\times 10^6$	14·7	6·5	5·7	5·7	3·0

* Flame unstable.

In spite of experimental difficulties in collecting all the products, particularly from the drier and more unstable flames, these figures show that more oxidising products can be isolated from the drier flames. Since these expose a larger surface to the surrounding oxygen, they give a greater chance of escape to activated products. The concentration of water molecules in the gases dried over phosphoric oxide, which corresponds with less than 2×10^{-5} mol. of water in the 4 litres of gas used, and their duration in the flame would seem to be insufficient to account for the formation of 10^{-5} g.-equiv. of oxidising products. The amount formed round the flame is certainly greater than this, since both hydrogen peroxide and ozone would begin to decompose before reaching the collecting vessel, and since the qualitative tests show that the amount of ozone is greater for the drier flames, there seems little doubt that ozone is formed by the escape of oxygen atoms or activated molecules into the surrounding oxygen, and not *via* hydrogen peroxide.

Similar remarks apply to the oxides of nitrogen also present. Attempts to stabilise the self-drying flame by using ozonised oxygen were unsuccessful, so that the occurrence of ozone as an essential step in initiating the combustion process is unlikely.

(d) *Effect of salts on the flame.* The flash of sodium luminescence mentioned in section (a) led to attempts to kindle the flame, after it had gone out through self-drying, by volatilising various salts previously melted in the cup *R*, and dried by warming in intensively dry oxygen. These were all unsuccessful, possibly because the salt molecules reunite to small crystals before reaching the combustible mixture. If salts are volatilised into carbon monoxide flames already burning, no great effect is visible unless the concentration of hydrogen is below the critical value 10^{-3}, whereat a striking change is observed. The phenomena are most easily demonstrated for cæsium chloride, on account of its volatility, and are shown in varying degree by the chlorides of sodium, potassium, and rubidium; the effects of iodine and of the iodides of potassium, silver, and mercury on the flame were inconclusive, and cæsium nitrate seemed to hinder the combustion of carbon monoxide, possibly on account of the nitrogen peroxide liberated.

With cæsium chloride a characteristic experiment was as follows: the flame of pure carbon monoxide burning at a heated jet was inserted in the chamber, and gradually enlarged as self-drying proceeded. When the height had reached 1·8 cm., a current was passed through the platinum cup containing the chloride, which had previously been melted and partly volatilised to drive off water. The flame immediately became brilliantly coloured, and shrank to 0·35 cm. When the current was turned off, the flame rapidly enlarged, and shrank again when more chloride was volatilised.

Small pressure changes easily extinguish the small dry flames with cæsium chloride, whereas if the shrinkage observed were due to water in the salt, the flames would be much more stable. Special tests showed that this chloride has little effect on the height, stability, or percentage combustion in the moist monoxide flame. Furthermore, if the decrease in size in presence of these salts were due to water, the proportion of unburnt monoxide would not exceed 1%. In a characteristic case, it changed from 13% in the large ill-defined flame to 12% in the small flame with cæsium chloride. The effect observed is therefore due to the alkali halide, and not to water expelled from the heated salt.

Observation of the flames in the presence of each of the alkali halides shows that the blue continuous spectrum decreases in intensity, and that a large number of lines are excited. This indicates high excitation and probably ionisation of the alkali metal, which seems to play a rôle similar to that of hydrogen (or water ?) in deactivating excited combustion products before these lose their energy by luminescence, or as translational energy. Since the proportion of unburnt monoxide does not greatly change in the presence of cæsium, the excited alkali atoms are less efficient in handing on energy to new molecules of reactant.

There is no doubt that the decrease in height and blurred appearance of the flame in presence of hydrogen or alkali halides is in part due to the scavenging of excited combustion products by these substances. Excited atoms emitting the blue cæsium lines were, however, observed as much as 4 cm. above the flame tip, so that the luminescence phenomena are more complicated than the above explanation suggests.

(e) *Effect of platinum vapour on the flame.* Attempts were made to introduce the vapours of platinum, palladium, gold, nickel, copper, silver, and iron into the flame, by inserting a small cylinder of the appropriate foil into the heated silica jet. In the absence of hydrogen, definite maintenance of luminous flame was observed for platinum only. A possible reason for this is that for this metal intense heterogeneous combustion raises the foil to a white heat, thus leading to sufficient evaporation of metal atoms. This does not take place with the other metals used.

With platinum, a thin blue flame was observed even when self-drying was complete, and all dissolved hydrogen had been removed by prolonged glowing of the metal. Analysis showed 11·9% of unburnt carbon monoxide in a characteristic case. Increasing the temperature of the jet leads to a larger flame at the same rate of flow of monoxide, unlike the effect on flames maintained by hydrogen. This is probably due to the greater volatilisation of platinum at higher temperatures. Increasing the rate of carbon monoxide leads to an enlarged flame, which periodically leaves the jet and travels up the chamber; a tiny flame then reappears at the platinum and rapidly grows again. A black deposit of platinum oxide gradually collects at the top of the chamber.

The blue luminescence of flame obtained in the presence of platinum differs from that in the presence of hydrogen, in that it is completely extinguished by traces of cæsium chloride, and rekindles spontaneously when the chloride in the cup is allowed to cool. Traces of this chloride raise the proportion of unburnt monoxide from 11·9 to 31·6% in a characteristic case.

SUMMARY.

A method is described for obtaining large volumes of pure gases in a very dry state, and the phenomena observed with the self-drying flame of carbon monoxide in oxygen are discussed. From the variation in the height of flame with hydrogen content, the luminescence is shown to depend in a marked way on the molar fraction of hydrogen, when this falls below 10^{-3}. A method of estimating concentrations of hydrogen in other gases, down to a molar fraction of 10^{-7}, is also suggested.

Evidence is provided to show that the ozone and oxides of nitrogen appearing in the combustion products of carbon monoxide are formed neither by photosynthesis nor from the decomposition of hydrogen peroxide.

The effect of alkali-metal halides and platinum vapour on the luminescent combustion of carbon monoxide is shown to differ in several respects from that of hydrogen.

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