XXV.—*The Influence of Hydrogen and of Water Vapour on the Ignition of Carbon Monoxide.*

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Introduction.

THE experimental work now recorded was commenced some years ago at the University of Leeds by Mr. H. Whitaker, and the point at issue seemed to be determined satisfactorily by 1923. Subsequently, however, further verification was deemed desirable before publication. Professor H. B. Baker advised the continuation of the work and, thanks to his kindness and to the generosity of the Worshipful Company of Salters in providing assistance, the experiments were resumed after a long interval by Miss Holmes. The greater part of the designing of the apparatus and the whole of the actual execution of the work fell to Mr. Whitaker and Miss Holmes, and in the second stage we have had the great advantage of being able always to count upon Professor Baker for advice.

The experiments arose from some rather speculative deductions (which I no longer entertain) from the Lewis–Langmuir cubical atom conceptions soon after they appeared. In attempting to apply them to the standing problem of the combustion of carbon monoxide, I found they appeared to give a plausible explanation of a striking observation made shortly before by Bone and Haward

(*Proc. Roy. Soc.*, 1921, *A*, **100**, 67). In their experimental study of gaseous combustion at high pressures, they had obtained results which showed a " peculiar influence of hydrogen in accelerating the rise of pressure in the explosion of hydrogen–carbon monoxide mixtures at high pressures, an effect which can be shown to be altogether disproportionate to the volumetric amount of it present." They add : " Our experiments seem to point to hydrogen being even more potent than its equivalent of steam as a promoter of the combustion of carbonic oxide (though this is a matter needing further investigation)." It appeared desirable to try to measure the relative catalytic influence of hydrogen and water vapour on the initial ignitability of a carbon monoxide–oxygen mixture in a eudiometer at or near atmospheric pressure.

Since 1921, the relative catalytic influence of water and steam on the combustion of carbon monoxide has acquired greater interest and has been the subject of much investigation. Professor Bone and his collaborators have followed up the original experiments and made many new ones of an exact quantitative character bearing on the subject during their researches on the combustion of gases at high pressure. Bone, Newitt, and Townend (J., 1923, **123**, 2008) obtained definite evidence that the substitution of hydrogen for a small part of the carbon monoxide had a specific accelerating effect on the rising pressure curve much greater than that produced by an addition of water vapour. Later, the same authors (*Proc. Roy. Soc.*, 1928, *A*, **120**, 546) and Bone, Townend, and Smith (*ibid.*, p. 563) recorded further experiments on the relative influence of hydrogen and steam on the carbon monoxide combustion. These cannot be summarised without quoting numerical values, but they confirm and amplify Bone's earlier conclusions in reference to the relative influence of hydrogen and water vapour as catalysts. An important matter in the last-named paper is the reference to " the sensitiveness as regards explosion time of theoretical carbon monoxide–air explosions to slight changes in hygroscopic conditions at high initial pressures, even though the moisture actually present in the system be less than 0·04 per cent."

Other relevant observations are those of Dixon and Walls (J., 1923, **123**, 1025), who found that the carbon monoxide–oxygen mixture with 5·5% of water vapour had a maximum rate of explosion of 1738 m./sec., whereas with 5·5% of hydrogen the rate was 1782 m./sec.

Payman and Wheeler (*ibid.*, p. 1251) concluded that " whereas a trace of water vapour is more effective in enabling propagation of flame to take place in dried mixtures of carbon monoxide and air, twice as much of it is required to give to that propagation its complete freedom." They found that the amounts necessary for this were 6% of water and 3% of hydrogen.

Fenning (*Phil. Trans.*, 1926, *A*, **225**, 331), in a study of carbon monoxide–air explosions in a closed vessel, found that with hydrogen less time was taken to reach maximum pressure than with water vapour.*

An excellent account of investigations relating to the combustion of carbon monoxide, beginning with Dixon's primary discovery of the influence of water, is given by Bone and Townend ("Flame and Combustion in Gases," Longmans, 1927).

(A. S.)

The present experiments aimed at a direct comparison of the efficiency of hydrogen and water vapour in facilitating the ignition of a mixture of carbon monoxide and oxygen by passing a spark through two eudiometers in series, one containing, beside the carbon monoxide and requisite oxygen, a known amount of hydrogen, and the other an equimolecular amount of water vapour.

Preparation and Purification of Gases.—The carbon monoxide was prepared in an apparatus similar to that used by Waran (*Phil. Mag.*, 1921, **42**, 246) by adding redistilled formic acid to pure sulphuric acid. The gas was passed through (1) potassium hydroxide solution to remove any carbon dioxide, (2) sulphuric acid to catch any alkaline spray and act as a preliminary drying agent, (3) phosphoric oxide tubes for final drying, and (4) a tube cooled by liquid air.

The oxygen, prepared by heating potassium permanganate, passed through (1) a tube containing solid potassium hydroxide and glass wool, (2) phosphoric oxide tubes, and (3) a liquid-air tube.

The hydrogen was prepared by electrolysis (see Baker, J., 1902, **81**, 7, 400) between platinum electrodes, of baryta, recrystallised three or four times, dissolved in conductivity water. It was passed through (1) an electrically heated tube containing copper gauze, which had previously been heated to redness first in a current of dry air and finally in a current of dry hydrogen, to remove any oxygen which might have diffused into the hydrogen during electrolysis; (2) a liquid-air tube; (3) a calcium chloride tube for preliminary drying; and (4) phosphoric oxide for final drying.

Water Vapour.—To obtain an admixture of water vapour in desired proportion with the combustible gases, dilute sulphuric

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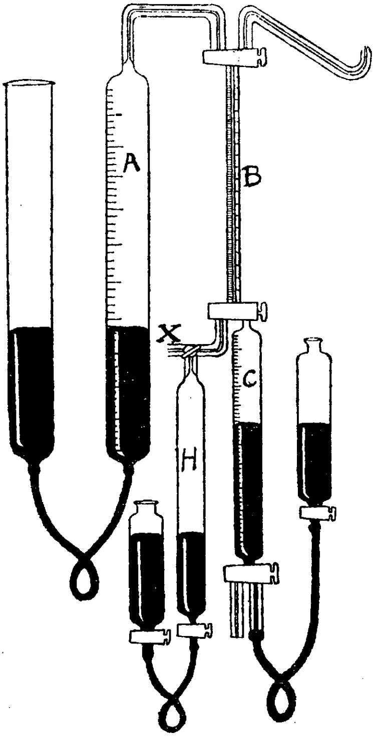
* The paper just published by Garner and Roffey (J., 1929, 1123) on "The Effect of the Addition of Hydrogen and Water on the Radiation emitted from the Carbon Monoxide Flame" is of great interest in relation to our own experiments.

acid was used, 1 c.c. of the liquid being passed into the eudiometer by means of a bent pipette, and the temperature at which the tube must be kept to maintain the required vapour pressure was calculated. The vapour-pressure values used were taken from Regnault's tables; although doubt has been thrown upon his values at such high concentrations, it is believed that they are not so inaccurate as to invalidate the conclusions drawn from these experiments. Careful tests showed no measurable evolution of gas from the contact of the diluted acid with mercury under all the conditions of the experiments.

FIG. 1.



Phosphoric Oxide.—The phosphoric oxide used was prepared by redistillation in a current of oxygen, and was shown to be of a high degree of purity. For some of the earlier experiments, highly purified material kindly supplied by Sir Richard Threlfall, F.R.S., was used.

Ignition Arrangements. — The gas mixture was subjected to a spark from the secondary of an induction coil run at a constant voltage.

Gas Storage and Dilution Apparatus.—The gases were collected and mixed in the proportion of 2 vols. of carbon monoxide to 1 vol. of oxygen in the apparatus shown in Fig. 1. This consisted of three graduated tubes of approximate capacities (A) 150 c.c., (B) 2 c.c., (C) 12 c.c., and a fourth tube (H) of approximately 100 c.c. capacity. The apparatus was cleaned with chromic acid mixture, washed with distilled water, steamed out for some hours, and dried by the passage of hot dry air, the apparatus itself being heated wherever possible.

After calibration of the graduated tubes, the apparatus was dried finally and filled with freshly distilled mercury. The carbon monoxide and oxygen were mixed in the required proportion in the large tube A by connecting the apparatus at X successively to the two generating apparatus. From this mixture the required volume for an experiment was withdrawn into the graduated tube C, where it was exactly measured, before being passed through B and the delivery tube into the eudiometer.

As accurately known, very small volumes of hydrogen were required in the experiments, this gas was first mixed in measured proportion with a large volume of carbon monoxide–oxygen mixture and then added in small quantities to the main bulk of the two gases used in an experiment. This was carried out by filling the narrow-bore tube B with pure hydrogen and passing any desired volume of it into the carbon monoxide–oxygen mixture in A. After allowing time for complete admixture, the diluted hydrogen was passed into H for storage.

Explosion Tubes.—The experiments were carried out in glass eudiometers of approximately 1·5 cm. internal diameter with platinum wire electrodes. The gap between the electrodes was fixed and measured under a travelling microscope.

The eudiometers were cleaned as previously described, and carefully dried by the passage of purified, dry air while the ends were heated strongly.

To remove occluded gas in the electrodes, sparks were passed across them for some hours while a current of pure, dry oxygen was passed through the eudiometers. They were then filled with freshly distilled mercury, which was immediately replaced by a known volume of the gas mixture from the storage apparatus.

As the eudiometers had to be water-jacketed during an experiment, it was necessary to insulate the junctions of the electrodes with the leads. This was done in the earlier experiments by fitting vertical glass tubes with their ends bent suitably to cover the projecting loops of the electrodes, the junction being held and covered by a ring of rubber tube. These vertical tubes were filled with mercury and the leads dipped into their open ends. In the later experiments, the projecting ends of the electrodes were protected with enamel beads to which rubber tubes were attached as shown in Fig. 2. By attachment of a second limb of tubing, as a levelling tube, to the mouth of the eudiometer, and adjustment of the mercury column in it, atmospheric pressure was secured in the gas mixture. The ends of the levelling tubes were closed with rubber caps during the sparking to prevent scattering of the mercury.

Temperature Control.—The arrangements for temperature control are shown in Fig. 3. The eudiometers were fixed in inverted bell-jars which served as water-jackets, and water flowed into these continuously from a thermostat reservoir.

Procedure.—In each experiment one eudiometer, containing only carbon monoxide and oxygen in combining proportion and phosphoric oxide, was used as a control. Immediately upon charging the first eudiometer a second was taken, and to it was added the gas mixture containing a known small quantity of hydrogen. A small stick of compressed phosphoric oxide was passed up this tube and floated on the mercury surface. (The volume of the stick was about 1 c.c., and the entangled air not more than 0·1% of the total volume of gas in the eudiometer.) In a third eudiometer containing the carbon monoxide–oxygen mixture, 1 c.c. of suitably diluted sulphuric acid was brought on to the mercury surface by means of a bent pipette. The eudiometers so arranged were allowed to stand for at least 10 days, and if a spark then failed to fire the mixture in the control eudiometer, the experiment was proceeded with. The water-jackets of the two other eudiometers were connected with the thermostat reservoir and kept at a temperature sufficient to give in the third eudiometer a concentration of water vapour molecularly equal to that of the hydrogen in the second eudiometer. After 3 days had been allowed for the attainment of liquid–vapour equilibrium, the electrodes of the two eudiometers were connected in series to the coil and a single spark was passed. If this failed to produce ignition in either tube, sparking was continued for some seconds.

FIG. 2.

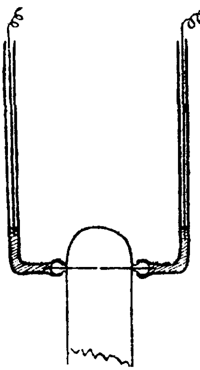
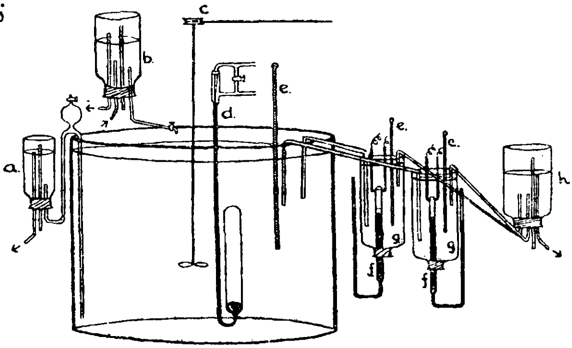


FIG. 3.



a.	*Water leveller.*	e, e, e.	*Thermometers.*
b.	*Water inlet.*	f, f.	*Eudiometers.*
c.	*Stirrer.*	g, g.	*Inverted bell-jars.*
d.	*Thermal regulator.*	h.	*Bell-jar water leveller.*

Results.

The results of the first two series of experiments are in Tables I and II, those in Table I, which were made at Leeds, being merely preliminary. It was, of course, sought in each experiment to have equal volumes of the carbon monoxide–oxygen mixture for trial with equal hydrogen and water additions. The exact measurements of these volumes with hydrogen and water vapour respectively in each experiment show such a close approach to equality that, to avoid complicating the table, a mean figure is used.

TABLE I.

	Volume of gas, c.c.	Hydrogen, %.	Conc. and temp. of H_2SO_4 soltn. required to give volumes of water vapour equivalent to hydrogen.	Time of drying, days.	Behaviour on sparking.	
					Water mixture.	Hydrogen mixture.
1.	10·04	3·4	0·0%; 22·2°	13	Instant flash	Instant flash
2.	10·09	0·48	60%; 20·2	23	Instant flash	Instant flash
3.	9·26	0·044	84·5%; 34·5	16	Flame travelled slowly	Blue flash
4.	9·89	0·037	84·5%; 30·7	14	No ignition	Flash
5.	12·64	0·037	84·5%; 28·0	15	No ignition	Flash
6.	9·96	0·042	84·5%; 29·4	18	No ignition	Blue flash

TABLE II.

1.	7·45	0·049	82·4%; 25·8°	38	No ignition	Ignition
2.	8·70	0·049	81·7%; 25·0	24½	,,	,,
3.	6·65	0·048	81·7%; 23·75	20	,,	,,
4.	7·43	0·047	82·4%; 24·9	126	,,	,,
5.	8·10	0·045	80·5%; 36·2	126	,,	,,
6.	7·25	0·045	80·5%; 26·0	105	,,	,,
7.	4·80	0·057	80·5%; 30·0	15	,,	,,
8.	5·50	0·058	80·5%; 30·2	10	,,	,,
9.	7·45	0·032	81·7%; 20·0	23	,,	No ignition

Table I indicates that below approximately 0·04% of catalyst there is a difference in the effects of hydrogen and water vapour. From Table II, it is seen that with proportions of both hydrogen and water vapour throughout the range of about 0·03 to 0·06% the hydrogen alone conferred ignitability, except in Expt. 9, where there was no ignition in either tube. This value is slightly higher than that found in the preliminary experiments. The difference may well be due to the different sparking conditions, for a different sparking coil was used. Also, in the earlier experiments (Table I) the pressure was only approximately atmospheric and varied slightly in the two tubes.

Minimum Proportions of Hydrogen and Water Vapour required to permit Spark Ignition.—It will be seen in Expt. 9 of Table II that, when the concentration of hydrogen had been reduced to 0·032%, the mixture no longer ignited. This observation was verified, and an attempt was made to ascertain the limit more closely by beginning with a mixture containing approximately 0·02% of hydrogen and adding further small quantities of hydrogen.

Table III gives the results, from which it appears that the 0·032% of Expt. 9 was in fact about the limiting concentration.

TABLE III.

Volume, c.c.	Hydrogen, %. No ignition.	Hydrogen, %. Ignition.	Temp.	Press., mm.	Time of drying.
7·2	0·023	0·033	18°	760	18 days
7·2	0·021	0·041	18	760	18 ,,
9·4	0·032	0·049	25	762	23 ,,
7·3	0·018	0·032	17	760	19 ,,
4·63	0·018	0·038	19	768	3 months

An attempt was also made to discover the limiting concentration of water vapour that determined ignitability. This was done by a step-wise elevation of the temperature of a submerged eudiometer containing the gas mixture and diluted sulphuric acid. The results given in Table IV show that the limiting concentration is approximately 0·12% of water vapour.

TABLE IV.

Volume of gas, c.c.	Conc. of H_2SO_4, %.	Time, days.	Press., mm.	Temp. between which ignition occurred.	Equivalent percentage of water vapour.
6·3	80·5	110	765	34—39·6°	0·12—0·14
4·8	80·5	103	768	32—36	0·10—0·13
4·9	80·5	100	768	32—36	0·10—0·13
7·45	82·4	143	775	36—42	0·07—0·12

In the experiments described in the foregoing pages, the drying of the gas mixtures used was not carried to an extreme degree. It has been shown by Baker (J., 1902, **81**, 7, 400) that considerably more thorough drying is necessary to prevent the combination of hydrogen and oxygen than that of carbon monoxide and oxygen. It seemed desirable, therefore, to find whether the catalysing influence of hydrogen on the combination of carbon monoxide and oxygen would be affected by a more thorough drying of the gas mixture. Experiments were accordingly carried out in the same way as those already described, but with considerably more intense and prolonged drying of the apparatus, as rapid filling as possible, and more protracted exposure of the gases to phosphoric oxide. The results are in Table V.

TABLE V.

	Volume of gas, c.c.	% Volume of hydrogen.	Time of drying.	Result of first sparking.	Sparking on addition of undried air.
1.	4·5	0·043	12 weeks	No ignition	Ignition
2.	4·2	0·040	19 ,,	No ignition	Ignition
3.	4·2	0·042	20 ,,	No ignition	Ignition

Since in all cases the admission of a small bubble of undried air to these mixtures made them ignitable by the spark, it appears from these experiments that the catalytic action of hydrogen is conditioned by the presence of a minimal quantity of water vapour.

Variation of Electrodes.—With a view to find whether a change in the material of the electrodes would reveal anything of interest, eudiometers were made with electrodes of copper, nickel, silver, and gold. After the usual experimental procedure, it was found in all cases that the results were the same as those obtained by the use of the eudiometers with platinum electrodes. In these experiments, the difficulty of sealing metals directly into glass was overcome by the use of seals of "red platinum" (copper deposited electrolytically on a nickel alloy).

General Observations on the Results.—It is, of course, to be understood that the significance of the numerical results recorded in this paper may be considerably restricted by the particular conditions of the experiments. Slight variation in procedure and especially in the conditions of spark ignition may be suspected to have far-reaching effects. Experiments now in progress have shown that the effective proportion of the catalyst gases varies considerably with the length of the spark gap and the character of the discharge. But, working within the conditions described, precautions have been taken to interchange the eudiometers used respectively for the hydrogen and the water vapour additions, and to change the material of the electrodes.

Summary.

A comparison has been made of the relative influence of hydrogen and water vapour on the ignitability of a mixture of carbon monoxide and oxygen by the spark discharge. To the purified gases, mixed in combining proportions and contained in two eudiometers, hydrogen and water vapour were added in equivalent proportion, and after time had been allowed for admixture a spark was passed simultaneously in series through each mixture.

It appeared in the first instance, when the drying of the carbon monoxide–oxygen mixture had not been greatly prolonged, that hydrogen was more effective than water vapour in conferring ignitability. Through a range of concentrations varying from approximately 0·03 to 0·06%, hydrogen was effective, whilst water vapour was not. An estimation of the minimum quantities necessary gave 0·03% for hydrogen and 0·12% for water vapour. These figures are not to be taken as absolute values, for they are affected by the particular conditions of the experiments.

In later experiments with more intensive drying of the com-

bustible mixture, it was found that the activity of the hydrogen was altogether inhibited. In other words, the superior catalytic effectiveness of hydrogen just described was in its turn conditioned by the presence of a minimal quantity of water vapour. It may equally well be said, alternatively, that in the presence of hydrogen a minimal quantity of water sufficed to confer ignitability.

These results are in harmony with our earlier observations and with those of other workers.

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