369. *The Water-gas Reaction in Low-pressure Explosions.*

By B. W. BRADFORD.

EQUILIBRIUM is attained in the reaction $CO_2 + H_2 \rightleftharpoons CO + H_2O$ without change in the total number of molecules; hence, by the usual interpretation of the law of mass action, the expression $K_p = p_{CO} \cdot p_{H_2O}/p_{CO_2} \cdot p_{H_2}$ should be constant and independent of the total pressure at which equilibrium is established. In one of the earliest investigations of the reaction, Dixon (*Phil. Trans.*, 1884, **175**, *A*, 618) found that the value of K_p derived from the composition of the cooled explosion products of CO–O_2–H_2 mixtures varied with the initial pressure of the gaseous mixture in certain conditions. Dixon, apparently, made no further study of this variation, and the possibility of a genuine pressure effect has been scarcely considered by later workers (compare Haber, *Z. physikal. Chem.*, 1904, **44**, 513; 1904, **48**, 735; Haber and Richardt, *Z. anorg. Chem.*, 1904, **38**, 5). It has, however, recently been shown by Finch and Patrick (*Proc. Roy. Soc.*, 1930, **129**, *A*, 672) that the homogeneous cathodic combustion of CO–O_2–H_2 mixtures at either sputtering or non-sputtering electrodes occurs in such a way that carbonic oxide is burnt preferentially, and that this preferential combustion becomes more pronounced with decreasing pressure. It was suggested to the author by Professor Finch that a similar effect should operate in gaseous explosions, and the following investigation was undertaken with the object of testing this view.

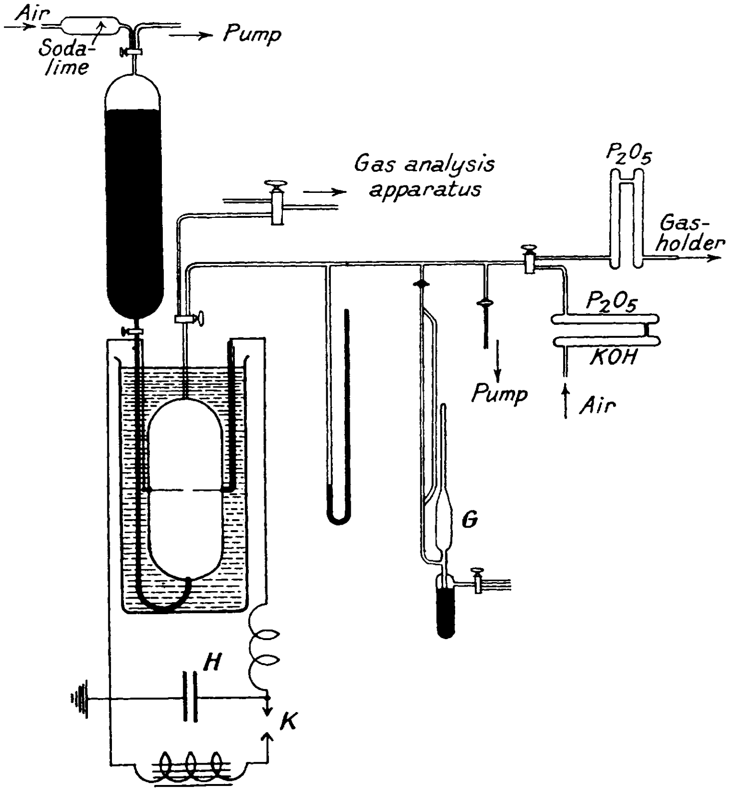
EXPERIMENTAL.

Dry gaseous mixtures of carbonic oxide and hydrogen in varying proportions, with insufficient oxygen for complete combustion, were ignited in a glass explosion vessel which was maintained at such a temperature that no wall-condensation occurred. The products of combustion were compressed by means of mercury and transferred for analysis to a modified Bone–Newitt apparatus in direct connection with the explosion bulb. The range of initial pressures employed was from 300 to 8·5 mm.; a special igniting circuit, described below, was necessary in order to initiate explosion at the lower pressures.

Apparatus.—Fig. 1 is self-explanatory of the apparatus employed. Two explosion vessels were used for different series of experiments, the smaller (volume 100 c.c.) for explosions at initial pressures above 100 mm., and the larger (volume 800 c.c.) for initial pressures below 100 mm. Both vessels were fitted with stout platinum-wire electrodes separated by a central 3-mm. spark gap. Initial explosion pressures above or below 25 mm. were measured on a closed-limb manometer or a McLeod gauge, respectively. After compression of the products of an explosion and transference to the gas-analysis apparatus, mercury was displaced from the explosion vessel by admitting dry air to it, and simultaneously evacuating the mercury reservoir. The explosion vessel was completely immersed in a water-bath maintained at a uniform temperature of 70° throughout the experiments. It was established in a preliminary investigation that no disturbance of the equilibrium by condensation occurred at this temperature.

Ignition Circuit.—The mixtures were ignited by high-frequency sparks, produced by the discharge of a bank of condensers (represented in Fig. 1 by the capacity *H*). The condensers were charged by an induction coil through the auxiliary gap *K*. In order to minimise loss of electrical energy, the connections between the condensers and the explosion vessel spark gap were made with 0·5-cm. diameter Litzendraht, and a 10μH inductance was included in the discharge circuit with the object of reducing the frequency and increasing the igniting power of the discharges (cf. Finch and Thompson, *Proc. Roy. Soc.*, 1931, **134**, *A*, 343). The wide explosion vessel spark gap (3 mm.) allowed the building-up of a sufficiently high breakdown potential, and hence a sufficient discharge of electrical energy, at the lowest gas pressures employed.

Fig. 1.



At initial pressures greater than 100 mm., the capacity of the explosion vessel leads was sufficient to ensure ignition. The additional capacity necessary at lower pressures increased from 0·0025μF at 50 mm. to 15μF at 10 mm. The validity of Paschen's law over this range of pressures being assumed, the quantity of energy dissipated in the latter case was approximately 250 times that in the former. It has been shown by Bone, Frazer, and Witt (*Proc. Roy. Soc.*, 1927, **114**, *A*, 442) that the amount of spark energy dissipated during the ignition of a gaseous mixture has a marked effect on the characteristics of the subsequent explosion. Tests were therefore made to eliminate the possibility of irregularities due to this cause. It was found that precisely the same results were obtained with a $2CO + O_2 + 2H_2$ mixture whether exploded at 150 mm. by the discharge of 0·0025, 1, or 5μF, and with a $3CO + O_2 + H_2$ mixture at 25 mm. and capacities of 5 or 15μF.

Preparation and Analysis of Gases.—Carbonic oxide, oxygen, and hydrogen were prepared in the manner previously outlined (*Proc. Roy. Soc.*, 1929, **124**, *A*, 306); argon was purified by circulation for some hours over a mixture of red-hot lime and magnesium. Precautions were taken to exclude nitrogen from the gaseous mixture, in view of the possibility of its undergoing oxidation in the explosions: the amount of this gas never exceeded 0·2% and was usually less than 0·1%. Redistilled phosphoric oxide was used in all drying trains. The explosive mixtures were stored in a steel gas-holder over mercury; in order to ensure constancy of composition, several analyses of the original mixture were made during each series of explosions.

The explosion products of certain mixtures at low initial pressures contained appreciable amounts of unburnt oxygen, which was determined by absorption in alkaline sodium hydrosulphite (hyposulphite) or potassium pyrogallate solution; in such cases corrections for solution of carbonic oxide and hydrogen were applied when insufficient of the combustion products remained for independent determination of these two gases.

The equilibrium constant K_p was calculated from the expression:

$$K_p = A[(x + A)\frac{c}{a} - C]/Cx$$

where the percentage compositions of the initial and final gaseous mixtures are as follows:

	CO_2.	CO.	H_2.
Original mixture	—	a	c
Cooled products	x	A	C

When appreciable amounts of unburnt oxygen remained in the explosion products, the percentages of carbonic oxide and hydrogen were corrected accordingly, on the assumption that a volume of the initial mixture proportional to the unburnt oxygen took no part in the explosion. The corrections were, in any case, small.

Results.

Series 1 (Range of initial pressures: 300—50 mm.). The following table shows, for three different mixtures, the initial compositions, and the values of K_p obtained at a series of initial pressures.

	Composition, %.				K_p for initial pressure (mm.).				
Mixture.	O_2.	CO.	H_2.	N_2.	300.	200.	150.	100.	50.
A	19·5	36·7	43·7	0·1	3·89	3·83	3·76	3·65	3·15
B	25·1	24·9	49·9	0·1	4·16	4·10	—	3·89	—
C	20·6	49·3	29·9	0·2	3·41	3·36	—	3·29	—

These results made it clear that in every case K_p decreased slightly but definitely as the initial explosion pressure was diminished from 300 to 100 mm., and indicated that the rate of decrease of K_p became considerably greater at initial pressures lower than 100 mm.

Series 2 (Initial pressures below 100 mm.). The experiments were continued at lower initial pressures in the larger explosion vessel. The compositions of the gaseous mixtures used were as follows:

	Composition, %.					Composition, %.			
Mixture.	O_2.	CO.	H_2.	N_2.	Mixture.	O_2.	CO.	H_2.	N_2.
D	20·0	40·0	40·0	0·0	G	9·8	50·8	39·4	0·0
E	24·3	25·5	50·1	0·1	H	14·5	73·9	11·5	0·1
F	23·3	51·9	24·8	0·0	K	18·7	41·7	39·6	0·0

Explosions were carried out with each of these mixtures at initial pressures down to the lowest at which ignition could be effected. The following analytical results for the series of explosions with mixture K will suffice to indicate the progressive alteration which occurred in the composition of the explosion products. Tests were frequently applied for methane and other hydrocarbons, always with negative results.

	Initial explosion pressure (mm.).				
Composition of cooled products.	50.	34.	20.	16.	13.
CO_2	26·1	26·0	26·9	27·4	27·8
CO	47·9	46·8	45·2	43·8	43·0
H_2	25·8	26·8	27·7	28·2	28·8
O_2	0·1	0·2	0·2	0·3	0·4
$N_2 < 0·2\%$					
K_p	3·17	2·83	2·45	2·22	2·06

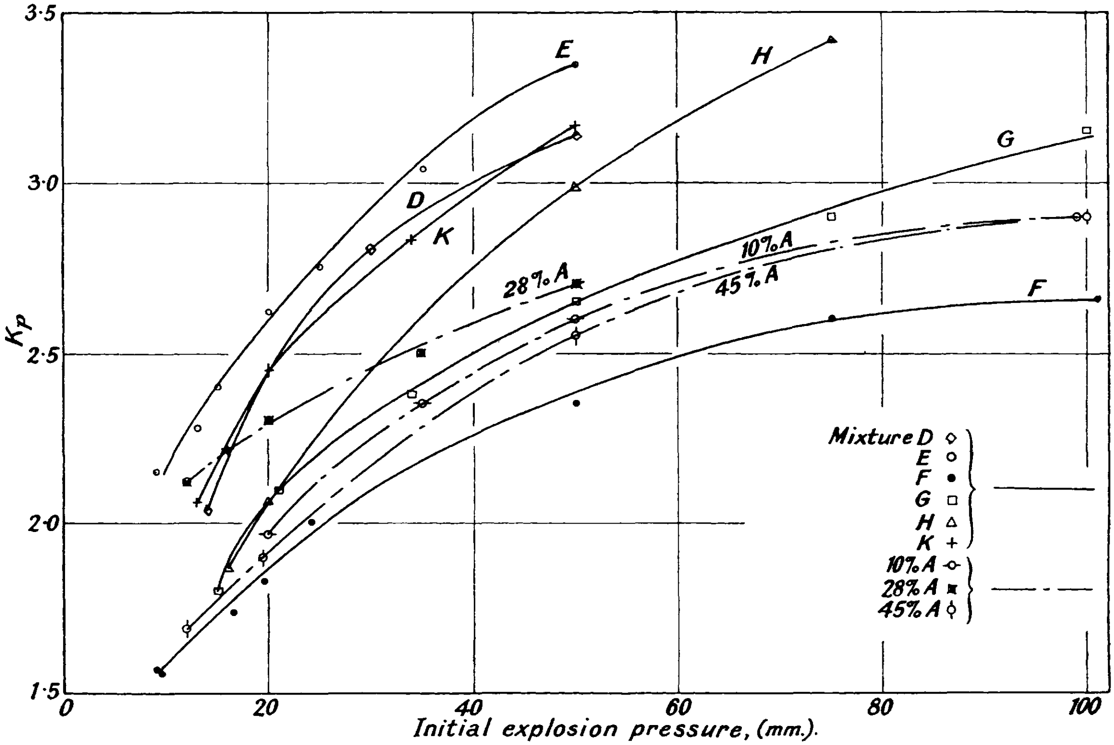
It is unnecessary to give similarly detailed figures for all the mixtures examined. The experimental results are summarised in Fig. 2.

Series 3 (Argon-diluted mixtures). Finally, mixture K was divided into three equal parts and diluted with 45, 28, and 10% of argon respectively. The compositions of the three mixtures thus prepared were as follows :

	Composition, %.			
Mixture.	O_2.	CO.	H_2.	A.
1	10·2	22·7	21·5	45·6
2	13·4	30·0	28·5	28·1
3	16·8	37·4	35·5	10·3

The values of K_p given by these mixtures are plotted in Fig. 2.

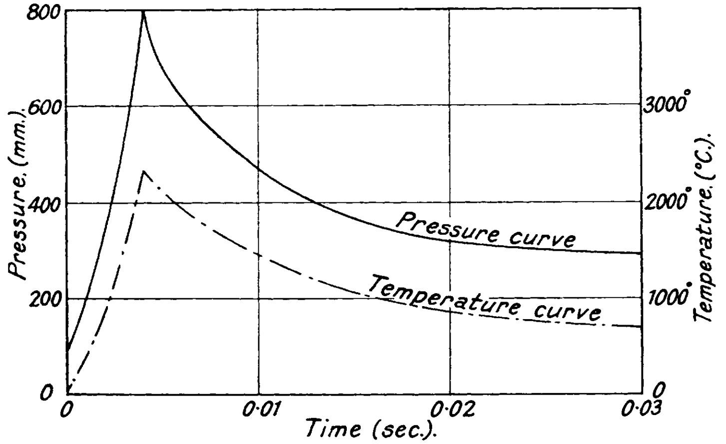
FIG. 2.



Pressure Changes during Explosion.—In order to gain further insight into the mechanism of the explosive reaction, pressure–time records of several explosions were taken. For this purpose mixtures were exploded in an electrically heated, 750-c.c. cylindrical glass vessel, on a short side-tube of which a 1/64" stainless-steel diaphragm was clamped. Motion of the diaphragm was communicated to the centre of a stiff strip of spring steel rigidly held at both ends and carrying a concave mirror. A condensed beam of light from a tungsten point lamp was reflected and focused by the mirror on to a strip of negative paper stretched round a rotating drum, the peripheral speed of which could be determined with accuracy. The explosions were somewhat violent and necessitated control of the diaphragm by a strong retaining spring, in order to eliminate natural oscillations of the moving parts. The consequent restriction of sensitiveness did not allow satisfactory records to be obtained at initial pressures much below 100 mm.

A typical record of an explosion at an initial pressure of 100 mm. is shown in Fig. 3. The curve of corresponding temperatures is plotted in the same figure. Approximate corrections based upon the experiments of Bjerrum (*Z. physikal. Chem.*, 1912, **79**, 513) have been applied for cooling loss and dissociation. The characteristic feature of the explosion record is the exceedingly high rate of cooling, which is considerably greater than any recorded for explosions of similar mixtures at or above atmospheric pressure. It has been shown by Bone, Newitt, and Townend (" Gaseous Combustion at High Pressures," 1929, p. 296) that, in explosions of hydrocarbon–oxygen mixtures initially at or above atmospheric pressure, the value of the water-gas equilibrium constant, K_p, calculated from the composition of the cooled products may be taken as a measure of the rate of cooling of the gaseous medium from its maximum temperature. With *increasing* pressure and consequently decreasing rate of cooling, the value of K_p decreased, thus corresponding to a lower temperature at which the position of equilibrium ceased to change during cooling. In the present experiments K_p decreased with *decreasing* initial pressure, and therefore, since there is no evidence for the assumption that the rate of cooling ceased to increase in explosions at initial pressures lower than 100 mm., it is clear that a similar explanation cannot apply to the present case. Any changes in K_p resulting from changes in the rate of cooling must have tended to diminish the fall of K_p with decreasing pressure. Consideration of the displacements in the value of K_p brought about by variations in the mixture composition or by dilution with argon shows that such displacements cannot be ascribed to the differences in rates of cooling of mixtures containing different proportions of hydrogen (compare the results for mixtures G, K, and H).

FIG. 3.



Moreover, there is no reason to suppose that the values of K_p calculated from the composition of the cooled explosion products represent other than equilibrium conditions. The maximum temperature attained in the explosions was considerably higher than 2000° C., and it has been shown by Haber (*loc. cit.*) that equilibrium is attained in the water-gas reaction taking place in flames at atmospheric pressures at temperatures above 1200°. It will be seen from Fig. 3 that in the present experiments the explosion temperature was higher than this for a period of 0·014 sec. after the attainment of maximum pressure. In the light of these considerations, it may be assumed that the values of K_p derived above correspond to states of equilibrium at pressures in each case rather less than the maximum attained in the explosion, and at temperatures which probably did not vary greatly throughout the experiments.

The Relation of K_p *and Pressure.*—The data connecting K_p and the initial explosion pressures, p, give straight-line graphs when substituted in the equation $\log K_p = \alpha \log p + B$. Hence the K_p–p curves are of the form $K_p = \beta p^{\alpha}$ where $\log \beta = B$ and α and β are constants for a series of experiments with a mixture of given composition.

There is no means of determining the relation between the initial pressures, p, of the explosion and the corresponding pressures, P, at which the position of equilibrium ceased to change with falling temperature. If the reasonable assumption be made, however, that the two pressures were proportional throughout each series of experiments, then, substituting P/k for p, we have $K_p = bP^{\alpha}$, where $b = \beta/k^{\alpha}$.

The values of the parameters for the various mixtures are tabulated in the following :

Mixture.	Partial pressure of H_2O, %.	Explosion products.					
		H_2/CO.	H_2O/H_2.	a.	B.	β.	b.
D	30·5	0·60	1·50	0·339	−0·066	0·859	0·528
E	50·3	1·0	3·15	0·264	+0·080	1·202	0·834
F	24·3	0·30	3·05	0·264	−0·078	0·836	0·575
G	14·0	0·65	0·40	0·390	−0·198	0·634	0·344
H	7·2	0·10	1·25	0·325	−0·107	0·782	0·480
K	29·1	0·60	1·45	0·347	−0·073	0·845	0·509
45% A	17·6		1·45	0·302	−0·097	0·800	0·500
28% A	21·8		1·90	0·186	+0·118	1·312	0·993
10% A	24·3		1·30	0·290	−0·085	0·822	0·535

DISCUSSION.

The law of mass action requires that the position of equilibrium in the reaction $CO_2 + H_2 \rightleftharpoons CO + H_2O$ shall be independent of pressure, and that the value of K_p shall be constant for mixtures of the reactants in different proportions. It has been shown in the foregoing, however, that neither of these criteria is satisfied when the reaction takes place at pressures lower than about 500 mm. It is therefore clear that the above equation is not an accurate representation of the chemical reactions which occur in the exchange of equilibrium. From other considerations it appears highly probable that the two reactions thus represented take place homogeneously with considerable difficulty, if at all. For instance, Haber (*loc. cit.*) failed to attain equilibrium in flames at temperatures below 1200°, and the lowest value of K_p recorded by Bone, Newitt, and Townend (*op. cit.*, p. 284) corresponds to a minimum reaction temperature of 1100°. The following table, compiled from the investigations of Hinshelwood and his collaborators (*Proc. Roy. Soc.*, 1928, **118**, *A*, 170; 1932, **138**, *A*, 297), gives the approximate temperatures at which measurable rates of reaction are first attained in comparable conditions in a series of combustible gaseous mixtures heated in silica bulbs at pressures of several hundred mm. :

$2H_2 + O_2$	500°	$2CO + O_2$ (dry)	700°
$2CO + O_2$ (moist)	600°	$CO + H_2O$	800°

In each case, wall reactions were responsible for a considerable part of the total rate. Hence, there is strong evidence for supposing that the homogeneous reaction $CO + H_2O \longrightarrow CO_2 + H_2$ occurs with even less ease than the notoriously insensitive dry oxidation of carbonic oxide. Moreover, since the water-gas equilibrium constant is of the order of unity, it follows that the reverse reaction $CO_2 + H_2 \longrightarrow CO + H_2O$ must occur with approximately equal difficulty.

Evidence from several quarters indicates that a not improbable mechanism for the oxidation of both carbonic oxide and hydrogen in flames involves the operation of OH radicals (Bonhoeffer and Haber, *Z. physikal. Chem.*, 1928, **137**, *A*, 263; Finch and Patrick, *Proc. Roy. Soc.*, 1930, **129**, *A*, 768; Finch and Mahler, *ibid.*, 1931, **132**, *A*, 178). The presence of OH radicals in steam and in mixtures of steam with oxygen and hydrogen at temperatures above 1250° has been established by Bonhoeffer and Harteck (*Z. physikal. Chem.*, 1928, **139**, *A*, 75), and in flames of hydrogen, moist carbonic oxide, and water-gas by Weston (*Proc. Roy. Soc.*, 1925, **109**, *A*, 177, 523).

In the present case, maintenance of equilibrium may be considered to involve the two opposing oxidations and reductions $CO + OH \rightleftharpoons CO_2 + H$ and $H_2 + OH \rightleftharpoons H_2O + H$. After the initial processes of oxidation in the flame are completed, the supply of OH must be chiefly maintained by the dissociation of water: $H_2O \rightleftharpoons H + OH$ (where $\rightleftharpoons$ indicates a process requiring the intervention of a third body). The reactions $H_2O \rightleftharpoons H_2 + O$ and $CO_2 \rightleftharpoons CO + O$ do not appear to be excluded: several considerations indicate, however, that the opposing oxidations of carbonic oxide and hydrogen by atomic oxygen are likely to be negligible by comparison with other processes occurring in the flame.

It is clear that no completely reversible reaction mechanism such as the following:

$$CO + OH \rightleftharpoons CO_2 + H;\ H_2 + OH \rightleftharpoons H_2O + H;\ 2H_2O \rightleftharpoons 2OH + 2H$$

is thermodynamically capable of explaining isothermal change of K_p with pressure, although the equilibrium constant of the last equation is not independent of pressure. At least one of these reactions must be, in some sense, irreversible.

From a statistical point of view the equilibrium constant may be regarded as representing the ratio of two reaction velocity constants:

$$K_p = v'(CO_2 + H_2 \longrightarrow)/v''(CO + H_2 \longrightarrow)$$

There are grounds for supposing that these two reaction velocities are differently affected by pressure change (compare Finch and Mahler; Finch and Patrick, *locc. cit.*) and that changes in K_p are governed by the corresponding relative changes in the rates of the two opposed reactions $CO + OH \rightleftharpoons CO_2 + H$ in a manner which may be expressed by writing

$K_p = [m + f'(\bar{H})]/[n + f''(\overline{OH})]$, where m and n are constants and f', f'' are unknown functions.

We may now attempt to correlate the experimental results with the suggested mechanism outlined above.

(1) The variation of K_p with pressure was expressed by $K_p = bP^a$. Decrease of pressure, which favours the oxidation of carbon monoxide at the expense of hydrogen, must also favour dissociation of water. The concentrations of H and OH depend upon the equilibria $H_2O \rightleftharpoons H + OH$ and $H_2 \rightleftharpoons 2H$, and both increase with decreasing pressure (compare Bonhoeffer and Reichardt, *Z. physikal. Chem.*, 1928, **139**, *A*, 75). Hence it must be concluded that the variation of K_p with pressure is chiefly governed by changes in the OH concentration. The accelerating effect of diminished pressure upon the oxidation of CO is strong evidence against the supposition that oxidation is effected by condensed oxygen carriers such as H_2O_2 or HO_2.

(2) Comparing undiluted mixtures of different compositions and excepting F and H, in which the ratio of carbon monoxide to hydrogen was unusually high: (i) the parameter b is proportional to the percentage partial pressure of water in the explosion products (see table, p. 1561). Since the relative partial pressure of OH must depend upon that of water, this fact further supports the view that the equilibrium is governed by the rate of the reaction $CO + OH \longrightarrow CO_2 + H$. (ii) The parameters a and b are inversely proportional; hence an opposing effect is brought into play when the relative partial pressure of water is increased. This may be due to atomic hydrogen either suppressing the dissociation of water or increasing the relative rate of the reverse reaction $CO_2 + H \longrightarrow CO + OH$.

(3) The proportionalities of b to the water-vapour partial pressure, and of a to b both break down for the series of experiments with the high CO/H_2 ratio mixtures F and H and for the argon-diluted mixtures. It is clear, therefore, that other than purely diluent effects must operate, possibly deactivation, primarily of excited CO_2, and secondarily of excited CO molecules.

To summarise, it has been shown that the observed variations in the position of the water-gas equilibrium at low pressures may be accounted for by supposing that oxidation and reduction of the reactants take place, not directly, but through the intermediary of OH radicals and atomic hydrogen, the equilibrium being chiefly determined by the rate of the reaction $CO + OH \longrightarrow CO_2 + H$, which is itself governed by the concentration of the OH radicals produced by dissociation of water. The present investigation arose from the observation of Finch and Patrick previously cited that in cathodic combustion the preferential oxidation of carbon monoxide in $CO–O_2–H_2$ mixtures increased with decreasing pressure. The view was expressed by those authors that "there is no fundamental difference between cathodic combustion and combustion in flames in general" (*loc. cit.*, p. 685) and the foregoing results confirm this opinion.

It has been shown by Finch, Bradford, and Greenshields (*Proc. Roy. Soc.*, in the press) that the value of K_p in the cathodic water-gas equilibrium falls as the gaseous pressure is diminished from 90 to 65 mm., and thereafter rises. The pressure at which equilibrium was established in the majority of the present experiments was probably from six to eight times the initial pressure, and it was not therefore found possible to reproduce the conditions in which the cathodic equilibrium constant passed through a minimum value. Variation of initial composition had no effect on the cathodic equilibrium: the divergence between this result and the variation which was found to occur in the explosive combustion is attributable to differing degrees or rates of activation in the two cases.

IMPERIAL COLLEGE, LONDON, S.W. 7.

[*Received, October* 14*th*, 1933.]