The existence of the water-gas equilibrium constant, and a carbon monoxide-hydrogen ratio in the exhaust gases of an internal combustion engine has been the subject of much controversy in recent years. The prevailing differences of opinion among investigators has led to this research.

The object of this thesis was to study the effect upon the water-gas equilibrium constant and upon the carbon monoxide-hydrogen ratio when carbon dioxide, or water was added to the air-fuel mixture entering an internal combustion engine.

Exhaust gas samples were obtained from a Model A Ford engine in which was burned the air-fuel mixture and added constituent—either carbon dioxide or water. These samples were tested in the Engelhard Gasalyzer, Precision Fisher Gas Analyzer, and the Hayes' Gas Analyzer. From exhaust gas analyses the water-gas equilibrium constant and the carbon monoxide-hydrogen ratio were calculated.

The conclusions reached were:

1. When either water or carbon dioxide was added to the air-fuel mixture, the water-gas equilibrium constant did not remain a constant as it should have done if the water-gas reaction does reach equilibrium conditions.
2. The ratio of carbon monoxide to hydrogen does not remain constant, but does bear a definite relationship to the calculated water-gas equilibrium constant under conditions tested.

3. The ratio of water to carbon dioxide remained more nearly constant than any other relationship.

4. The equilibrium constant as calculated from exhaust gas analyses in this research did not show any indication of being in a true equilibrium state when correlated with the temperatures corresponding to a true equilibrium constant of the same value.
WATER-GAS REACTION AND EQUILIBRIUM CONSTANT IN AN INTERNAL COMBUSTION ENGINE

by

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Chairman of College Graduate Council.
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INTRODUCTION

Object of Investigation

In the past few years, a great deal of discussion has been devoted to the significance of the exhaust gas analysis and its relationship to the combustion of the motor fuels. If definite correlations could be established between combustion and exhaust gas analyses, the effect of various manifold, valve, and head designs could be studied more readily. An effort has been made, in view of this fact, to ascertain if there exist definite relationships between the various constituents, and to determine the controlling factor or factors.

In view of the various opinions regarding the water-gas equilibrium constant and the carbon monoxide-hydrogen ratio, the subject for this thesis was chosen to further the study of the effect upon the foregoing relationships of bleeding into the air-fuel mixture of an automotive engine various quantities of carbon dioxide and water.
Review of Previous Investigations

In the following paragraphs are presented the opinions of several previous investigators of this subject.

C. C. Minter (11) has claimed that the water-gas equilibrium exists and is actually at equilibrium conditions before exhaust occurs. He also claims that the water-gas equilibrium is the controlling factor in the relationship between carbon monoxide and hydrogen. J. J. Morgan and C. Stolzenbach (13) burned many kinds of fuels in a furnace and analyzed the combustion products for carbon monoxide and hydrogen. They found that the ratio by volume of carbon monoxide to hydrogen for all fuels was a constant of approximately 2.9. They specified, however, that the hydrogen percentage must not exceed three per cent by volume in the combustion products. They also concluded that the water-gas equilibrium governed this ratio, but disputed the claims of others that hydrogen burned 2.86 times as fast as carbon monoxide. W. G. Lovell, J. D. Coleman, and T. A. Boyd (10), in an effort to gain more intimate knowledge of combustion through the medium of exhaust analysis, claimed the existence of the water-gas equilibrium in a single cylinder engine and in other multi-cylinder analyses. They maintained that hydrogen burns 2.35 times as fast as carbon monoxide and
their curve, plotted from the reciprocals of the volumes of hydrogen and carbon monoxide, was a straight line.

The work of R. T. Haslam (8) shows that the ratio of carbon monoxide to hydrogen equals 2.86 only in case the velocities of both reactions change with temperature to about the same extent. In Haslam's discussions, he referred to Falk (8), who has shown that these velocities change at about the same rate up to 900°C. A recent article by G. W. Gleeson and W. H. Paul (3) substantiated C. C. Minter and Morgan and Stolzenbach in representing the data for low ranges of hydrogen (0 to 2%) and carbon monoxide (0 to 5%). They claimed that for higher percentages of hydrogen and carbon monoxide a curve plotted from the reciprocals by volume of hydrogen and carbon monoxide becomes almost lineal. They noted that the water-gas equilibrium constant was essentially constant for percentages of hydrogen as high as 2.5. Beyond this limit the value of the constant decreased. They concluded that the water-gas equilibrium is not established since it could not go below 3.4 if the 1500°C freezing temperature holds as Haber (3) has suggested.

In a publication by S. H. Graf, G. W. Gleeson, and W. H. Paul (5), a discussion of the equilibrium showed that values of the water-gas equilibrium constant for 160
average analyses varied from 2.50 to 7.00. The values showed only a very general trend toward higher values of water-gas equilibrium constant for higher air-fuel ratios. They show that the water-gas equilibrium constant increased to a maximum at an air-fuel ratio of approximately 13.4 and then decreased.

Fundamental Concepts Involved in Study

The combustion of fuels involves the study of chemical laws and their application to the combustion reactions. In dealing with the combustion of gasoline which consists of carbon and hydrogen there are eight reactions which may take place. They are:

(1) \( 2H_2 + O_2 = 2H_2O \)
(2) \( C + O_2 = \text{CO}_2 \)
(3) \( 2C + O_2 = 2 \text{CO} \)
(4) \( C + \text{CO}_2 = 2 \text{CO} \)
(5) \( 2\text{CO} + O_2 = 2 \text{CO}_2 \)
(6) \( C + \text{H}_2\text{O} = \text{CO} + \text{H}_2 \)
(7) \( C + 2\text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2 \)
(8) \( \text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O} \)

Equation (8) is called the water-gas reaction and is the reaction around which much of the following discussion will be centered. The water-gas reaction is a reversible reaction, that is, it is capable of reacting from left to
right and from right to left depending upon the concentrations of the constituents. The direction of reaction is governed by the law of mass action. The law of mass action states that the product of the active masses of the products divided by the product of the active masses of the reactants equals a constant. Applying the law of mass action to the water-gas reaction gives what is termed the water-gas equilibrium constant ($K_{wg}$)

$$K_{wg} = \frac{a_{CO} \times a_{H_2O}}{a_{CO_2} \times a_{H_2}}$$

Where "a" equals the activity of the constituent.

The water-gas equilibrium constant is also a function of the equilibrium constants of the following two equations.

(9) $2CO + O_2 = 2CO_2$

(10) $2H_2 + O_2 = 2H_2O$

Equation (9) and (10) represents according to the hydroxylation theory the main reaction which eventually occurs when a hydrocarbon is burned at high temperatures. It can be shown that the ratio of the equilibrium constants for these two equations is equal to the water-gas equilibrium constant.

(11) Equilibrium Constant $k_{CO} = \frac{2^{(a_{CO}) \times (a_{O_2})}}{(a_{CO_2})^2}$
(12) Equilibrium Constant \( k_H = \frac{(a_{H_2})^2 \times (a_{O_2})}{(a_{H_2O})^2} \)

Equating the two equations and solving for \( \sqrt{\frac{k_{CO}}{k_H}} \)

\[
\sqrt{\frac{k_{CO}}{k_H}} = \frac{(a_{CO}) \times (a_{H_2O})}{(a_{CO_2}) \times (a_{H_2})}
\]

From the similarity of physical characteristics of the two reactions (9) and (10) various relationships have been suggested between carbon monoxide and hydrogen. If it is assumed that the velocity of reaction, that is the time rate of change of concentration, is the same, the ratio of carbon monoxide to hydrogen is equal to a constant.

(13) Velocity of reaction for equation (9)

\[
-\frac{d(CO)}{dt} = c_1 (CO)^2 \times (O_2)
\]

(14) Velocity of reaction for equation (10)

\[
-\frac{d(H_2)}{dt} = c_2 (H_2)^2 \times (O_2)
\]

Since the velocity of reaction of the two are assumed equal:

\[
\frac{CO}{H_2} = \frac{c_1}{c_2} = \text{Constant}
\]
If, however, the temperature coefficient of the reaction velocity, that is the rate of change in velocity of reaction due to temperature, is the same, then the time and oxygen concentration factors may be eliminated by dividing equation (13) by equation (14)

\[
\frac{d(CO)}{d(H_2)} = \frac{c_1 (CO)^2}{c_2 (H_2)^2}
\]

Upon separating variables and integrating between finite limits the following relationship would exist.

\[
(15) \frac{1}{CO} = \frac{c_1}{c_2 H_2} + C
\]

With the aid of these fundamental facts the following discussion should be more easily followed.
STUDY OF CONDITIONS IN AN INTERNAL COMBUSTION ENGINE
Conditions Affecting Equilibrium

According to the law of mass action, the water-gas reaction establishes an equilibrium constant. However, there are specific conditions which influence the value of the constant such as, temperature, pressure, sufficient time for equilibrium to become established, and the use of active masses or fugacities instead of concentrations or partial pressures. No other substances can be present which might form complex compounds or react in any way or interfere with the reactants or products of the reaction.

The question now arises, 'Are these requirements fulfilled in the combustion process within an automobile engine?'. First consider the temperature. During the combustion stroke which occupies a time interval of about 0.02 of a second at 1,500 revolutions per minute, the temperature change is in the neighborhood of 3000°F. At this rapid rate of temperature change, the water-gas reaction would have to adjust itself instantly if an equilibrium is to be established. R. T. Haslam (7) claims that the water-gas reaction is practically instantaneous above 2700°F (1492°C) but relatively slow
below 1650°F (900°C). G. A. Goodenough and G. T. Felbeck (4) showed by formulae that there is a difference in the effect of temperature upon the equilibrium constant at temperatures above and below 2900°F (1593°C). From these discussions one might doubt the consistency of an equilibrium constant due to the rapid change in temperature, even if the reaction were instantaneous. If the water-gas reaction controlled the combustion, it would be impossible, using the products of combustion to predict conditions other than those at the freezing temperature or for the temperature corresponding to the equilibrium constant.

According to the principle of Le Chatelier, pressure should not affect the water-gas reaction with respect to the amount of constituents present, because an equal number of molecules are present on both sides of the equation. However, a recent investigation by B. W. Bradford (1) has shown that at low pressure explosions (below 500 mm. Hg) the water-gas equilibrium constant decreases with a decrease in pressure. It has also been suggested by C. C. Winter (11) that high pressures attained in an engine would greatly promote the establishment of equilibrium conditions. However, the pressure at the time of sampling is but slightly greater
than atmospheric pressure and should not have much ef-
flect upon the attainment of an equilibrium constant.

Very little seems to be known about the absolute
time necessary for the water-gas reaction to come to
equilibrium. The time element depends upon so many
factors that there seems scant possibility for the
same conditions to be present repeatedly. A few of the
factors that might be mentioned are: temperature, pres-
sure, catalysts, distance of the concentrations from
the equilibrium conditions, and the speed of the in-
dividual or complex reactions which are part of the
main reaction.

The use of the activities or fugacities is nec-
essary if a consistent equilibrium constant is to be
obtained. However, in this work mol fractions or
partial pressures are used—which means that a small
error is being incurred.

The presence of other gases may, or may not, af-
flect the water-gas reaction. If other gases do, the
effect would be approximately the same, since the a-
mount of other gases present varies but little. The
presence of varying quantities of methane would undoubt-
edly affect the amount of carbon and hydrogen in the
form of gases present in the water-gas reaction.

The conditions which may favor the establishment of the water-gas equilibrium in an automotive engine are those of high temperatures and perhaps high pressures. The conditions which may impair the equilibrium are rapidly changing temperatures and presence of other gases. The use of mol fractions instead of fugacities in calculating the equilibrium constant is a small error.

Possible Changes due to Addition of Water and Carbon Dioxide

Assuming the water-gas equilibrium does hold and is frozen at or prior to the time of sampling, it might be of interest to study what changes might be expected with the addition of water.

\[ K_{wg} = \frac{CO \times H_2O}{CO_2 \times H_2} \]

If the amount of fuel and air admitted were kept constant and water added, the water concentration in the combustion products should increase. Due to the dissociation of water, which is 0.02 per cent at 2730°F (1500°C), the hydrogen content may increase. Then, in order to maintain an equilibrium constant the carbon dioxide content must increase and the carbon monoxide concentration decrease. If the suggested carbon monoxide-hydrogen ratio (13) existed, the carbon monoxide concen-
tration should increase in accordance with the increase in hydrogen and the carbon dioxide content would have to increase sufficiently more to mathematically equal the equilibrium constant.

Next, consider the effect of adding carbon dioxide. Again assuming the same air-fuel ratio to exist, the water and carbon monoxide concentrations should increase and the hydrogen concentration should decrease. The dissociation of carbon dioxide is 0.048 per cent at 2730°F (1500°C) or 2.4 times as much as water. This suggests higher carbon monoxide concentrations and more hydrogen burned to water in the combustion products. The change which seems most likely to occur is higher water and carbon monoxide concentrations and lower hydrogen concentrations.
APPARATUS AND PROCEDURE
APPARATUS AND PROCEDURE

The present diversity of opinion which prevails upon the subject of the water-gas equilibrium indicates that a brief description of the apparatus used, and the procedure followed, might prove of value to future investigators, and substantiate the authenticity of the results obtained.

General Assemblage

The general assemblage was a Model A Ford engine equipped with a Stromberg carburetor and directly connected to a fan dynamometer. The fuel was siphoned into the carburetor from a large beaker on a balance beam scale. The added products were drawn into the intake manifold about four inches above the carburetor flange. Thermometers were placed in the cooling water inlet and outlet connections. The oil temperature was taken through the oil gage opening. The fan dynamometer was constructed according to the specifications given in Mark's Mechanical Engineers' Handbook.

Apparatus Used in Analyzing Exhaust Gases

The exhaust gas analyses were made on a Precision Fisher Gas Analyzer, Hayes Gas Analyzer, and Engelhard
Gasalyzer. The air-fuel ratio was set by an Engelhard Air-Fuel Meter. The carbon dioxide, carbon monoxide, and oxygen contents were determined on both the Precision Fisher Gas Analyzer and the Hayes Gas Analyzer. The hydrogen content was determined by the Engelhard Gasalyzer, and several checks were made on the Precision Fisher Gas Analyzer.

**Theory and Calibration of Engelhard Gasalyzer**

The operation of the Engelhard Gasalyzer depends upon the thermal conductivity of the gases. All the diatomic gases, except hydrogen and helium, have approximately equal thermal conductivities. The thermal conductivity of hydrogen is approximately ten times that of carbon dioxide and about six times that of air. The Engelhard Gasalyzer was calibrated by mixing known quantities of air and hydrogen and recording the needle deflection which each mixture brought about. The plotted points lay on a straight line with very few points off the curve. Those points which did miss the curve were very close and probably due to errors in measuring the individual gases mixed. In determining the hydrogen concentration of the exhaust products, the gases were passed from the sampling bottles through a potassium hydroxide bubbling tower. From the bubbling tower the gases were
dried and allowed to flow through the Engelhard Gasalyzer. The hydrogen percentage was taken from the calibration curve. It was deemed best to remove the carbon dioxide, because the carbon dioxide content varies considerably for different air-fuel ratios, and its thermal conductivity is much lower than that of air.

**Sampling of the Exhaust Gases**

The gas samples were drawn into bottles as shown in illustration (2). A series of five two-liter bottles was connected to a glass header which distributed the confining liquid received from a reservoir bottle. The reservoir bottle was connected by a rubber hose which allowed raising or lowering of the bottle to transfer the liquid by gravity. The confining liquid was a solution of 20 per cent sodium sulphate by weight and sufficient sulphuric acid, about two per cent, to acidify. The acidity was shown by a small amount of added methyl orange indicator. The gas was conveyed through a rubber hose to the top of the bottles. Pinch cocks were used to control the flow of exhaust gas samples and confining liquid. Care was taken to insure a small pressure on the gas sample at all times to avoid dilution with air. A composite gas sample from the four cylinders was taken
16 inches from the last cylinder

**Measurement of Fuel Consumption**

The rate of fuel consumption was determined by observing the time required for the combustion of one pound of gasoline. The fuel was weighed by a beam balance scale. The timing was accomplished electrically. The electrical timing device depended upon the falling of the balance arm to which was attached a brass rod. The brass rod closed an electric circuit by dipping into a beaker of mercury. Upon completing the electrical circuit the current passed through a coil which produced an electro-magnetic attraction which caused a lever to stop or start—as the case may be—a stop watch.

**General Conditions Maintained**

The load was approximately twenty horsepower at 1200 revolutions per minute. The speed was taken with a Biddle tachometer. The outlet cooling water temperature was kept within five degrees of 175°F. The engine was allowed to run until the oil temperature had reached approximately 200°F before data were taken. No adjustments were made on valve or ignition timing throughout the test. A previous test on this engine showed that the distribution of fuel was very good. A check was made with an
Engelhard Air-Fuel meter and it attested to equal distribution to all cylinders.

**Procedure Followed in Adding Water**

Illustration 1 shows the set-up used when water was being added. The water was allowed to flow from the reservoir (a) into the burette. The amount of water added was adjusted by valve (d). This adjustment determined the setting of valve (b) for a constant head in the burette. The rate of flow was determined volumetrically. The time required for the passing of thirty cubic centimeters when no water was entering the burette was recorded four times during the run. The average time was used in making calculations. Runs were made at constant speed (1200 R.P.M.) and at constant throttle setting. These runs were made without readjusting the needle valve setting on the carburetor. Data was secured for various air-fuel mixtures on the rich side of the theoretical mixture to avoid the presence of large oxygen contents. The maximum water rate was determined by a marked decrease in speed. The water-fuel ratio varied from zero to one.
Illustration 1

Illustration 2
**Procedure Followed in Adding Carbon Dioxide**

Illustration 2 shows the instruments and general arrangement used in adding carbon dioxide. The carbon dioxide was allowed to expand to a pressure of 1 inch of water above atmospheric pressure through the valve (a) into the tank (b). From the tank, the gas passed through the wet test meter and thence into the intake manifold. The rate of flow was controlled by valve (c). The pressure on the meter was obtained by a U-tube manometer. The temperature of the carbon dioxide was taken as the gas entered the wet test meter. As in the case of adding water, the maximum amount added was governed by a marked decrease in the speed of the engine. The engine was first run without adding carbon dioxide, in order that a sample of the exhaust gases might be taken. Carbon dioxide was then added in increasing amounts. A sample was taken for each different rate of flow of carbon dioxide. After three different amounts of carbon dioxide had been added, the engine was again run on straight gasoline to check the air-fuel ratio. Then the procedure was repeated with the engine again operating at constant throttle setting at a speed of 1200 revolutions per minute without added gas. The gas samples were completely analyzed on the Precision Fisher Gas Analyzer and checks made on the Hayes and Engelhard Gasalyzer.
Even though it was more laborious, this procedure was found necessary to determine how much methane was present. The check analyses verified the recorded values within 2.5 per cent.

Difficulties Encountered

As in the case of almost all experimental undertakings, several difficulties had to be surmounted before satisfactory results could be recorded.

One of these difficulties arose when an unreasonably high percentage of hydrogen was found in the exhaust gas samples. It was noticed that bubbles seemed to appear when samples were taken from the sampling bottles. The bubbles seemed to come from above the inlet pinch cock. When the pinch cock was opened to let in the confining liquid, several bubbles were entrained. After careful study, it was discovered that these bubbles were hydrogen which had been liberated from the reaction of sulphuric acid upon the iron pipe header. This reaction had not caused like difficulty previously because water had hitherto been used as the confining liquid. The trouble was overcome by replacing the iron pipe header with a glass header.

From this experience, it is to be inferred that any metal above hydrogen in the activity series should
not be used to inclose a confining liquid containing any strong acid.

A second difficulty was met when the first few runs showed an exceedingly high oxygen content, even on very rich mixtures. Here the trouble lay in a leaky exhaust gasket. The air was leaking in around the exhaust pipe—perhaps due to the aspirating effect of the flowing gases.

Pressure fluctuations from the intake manifold were smoothed out by placing a section of a rubber inner tube between the manifold and the wet test meter. The rubber inner tube was fitted with two wooden blocks at either end, and with a coil of wire to prevent the tube’s collapsing.

Another problem which was not completely solved was that of maintaining a constant air-fuel ratio. At first, an attempt was made to hold a constant speed for any one series of runs. Thus, when the water was added and the speed dropped, the throttle was opened. Due to the inability of the carburetor to maintain a constant air-fuel ratio at various throttle settings, the air-fuel ratio changed and the results were no longer on a comparable basis. The only alternative was a constant throttle setting. Although the speed decreased approx-
imately 4\%, the air-fuel mixture seemed to remain more nearly constant. The constant throttle setting also showed the effect upon the speed of adding the various products. The speed in turn, was directly proportional to an exponential function of the power output according to the calibration curve for the fan dynamometer.
DISCUSSION OF PREPARING RESULTS
**DISCUSSION OF PREPARING RESULTS**

**Fundamental Symbols and Assumptions**

The calculations involved in this paper were based on complete analysis, and they adhere to the following symbolic notations and assumptions:

The symbols $CO_2$, $CO$, $O_2$, $H_2$, $CH_4$, and $N_2$ are, respectively, the percentages by volume of carbon dioxide, carbon monoxide, oxygen, hydrogen, methane, and nitrogen in the dry exhaust gases. The term mol is defined as a quantity equal to the molecular weight of the particular substance expressed in pounds. That is, 44 pounds of carbon dioxide is one mol of carbon dioxide. The expression $A/F$ represents the ratio of air to fuel by weight.

The air was assumed to contain 21 per cent by volume of oxygen, and 79 per cent by volume of nitrogen. The nitrogen content of the exhaust gas sample was assumed to be the difference between one-hundred and the sum of the other five previously mentioned gases. The moisture in the air was calculated and found to be approximately five hundredths of a mol per hundred mols of exhaust gas. This value was small, compared with the total amount of water formed, and, therefore, neglected in the calculations.
Methods of Calculations

The easiest, and probably the most understandable, method of describing the calculations involved is to discuss each case separately. The sheet of tabulated results has each column lettered. The following paragraphs will show how the values in each column were calculated.

Results for the Addition of Water

Columns B, C, D, H, J, K, and S were experimental values.

Column E is the total amount of carbon present in the exhaust gas.

\[ E = B + C \]

Column F is the per cent of carbon burned to CO₂ and CO, and its values were obtained from Fig. 14 in reference (5).

Column G was determined by the method described in reference (5). This method of determining methane is probably not exact, but is a very close approximation as shown by experimental and calculated results in the aforementioned reference.

\[ \text{Column } G = \frac{E \times 100}{F} \]

Column I = 100 - (B + C + D + G + H).
Column L is the ratio of water added to fuel consumed by weight

\[ \text{Column } L = \frac{K}{J} \]

Column M is the pounds of fuel burned to produce 100 mols of exhaust gases. This figure was obtained by determining how much fuel would have to be burned to produce an amount equivalent to the carbon present in exhaust gases. The percentage of carbon in the fuel was calculated from several complete analyses without the addition of water. The fuel was found to contain 84.6 per cent carbon and 15.4 per cent hydrogen.

\[ \text{Column } M = \frac{B + C + G}{0.846} \]

Column N is the amount in mols of hydrogen burned from the fuel per 100 mols of exhaust gases.

\[ \text{Column } N = \frac{M \times 0.154}{2} \]

Column O is based on a hydrogen balance and the assumption that added water does not dissociate. Such an assumption was not entirely justified, but it served as a basis upon which to calculate the total amount of water. This assumption did not affect the final calculated value of the water concentration.

\[ \text{Column } O = N - H - 2(G) \]

Column P is the mols of water added per 100 mols of
exhaust gases.

\[ \text{Column } P = \frac{L \times M}{18} \]

Column \( Q = O + P \)

Column \( R = \frac{C \times Q}{B \times H} \)

Results for the Addition of Carbon Dioxide

Column A, B, C, D, E, H, I, and R were experimental data.

Column \( E = 100 - (A + B + C + D + E) \)

Column G is the sum of the carbon present in 100 mols of exhaust gas.

Column \( G = A + B + D \)

Column J -- The weight of \( \text{CO}_2 \) per minute was determined by the general gas law -- \( PV = \text{WRT} \). The accuracy required did not warrant the use of the more accurate Van de Waal's equations.

\[ \text{Column } J = \frac{\text{Pressure} \times \text{I}}{35.1 \times \text{Abs. Temperature}} \]

Column \( K = \frac{H}{J} \)

Column L is the total number of pounds of carbon added by carbon dioxide and fuel per pound of fuel. The fuel was found to contain 84 per cent carbon. This value is 0.6 of a per cent less than in the case where water was
added, a difference which was due to a change in the brand of fuel used.

\[
\text{Column L} = \frac{12 \text{ mol CO}_2 \times K + 0.84}{\frac{44 \text{ # CO}_2}{\text{mol CO}_2}} \text{ # fuel}
\]

\[
\text{Column M} = \frac{L}{12} \frac{\text{#C}}{\text{mol C}}
\]

\[
\text{Column N} = \frac{G}{M}
\]

\[
\text{Column O} = \frac{0.16 \text{ mol H}_2 \times N}{2} \frac{\text{# fuel}}{}
\]

\[
\text{Column P} = 0 - \left[ E + 2(D) \right]
\]

\[
\text{Column Q} = \frac{B \times P}{A \times E}
\]
PRESENTATION OF DATA AND CURVES
Explanation of Curves When Water was Added

The calculated results from data sheet No. 1 have served as a basis for Figures 1 and 2.

Figure 1 shows the effect of adding water to the air-fuel mixture upon the water-gas equilibrium constant. There was a decided decrease in the water-gas equilibrium constant as the water-fuel ratio was increased. The equilibrium constant value checked very closely those values found in other references for the same air-fuel ratio when no water was added. However, with the addition of water to the same air-fuel mixture, the equilibrium constant dropped as low as 0.97. For the air-fuel ratio of approximately 13.4 the equilibrium constant at first decreased very rapidly and then changed much more slowly. The 11.5 air-fuel mixture at constant throttle setting did not show such a marked deviation from the initial equilibrium constant. Interesting phenomena are the shapes of the two curves, one for constant throttle setting and one for constant speed. The air-fuel mixtures were approximately equal; but in the case of constant speed the equilibrium constant followed the curve for constant throttle setting up to a water-fuel
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<th>P</th>
<th>CH₄</th>
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Data Sheet No 1
# TABULATED RESULTS

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Data Sheet No.2
EFFECT OF ADDING WATER ON THE WATER-GAS EQUILIBRIUM CONSTANT

Fig. 1

RATIO OF WATER TO FUEL IN POUNDS

EFFECT OF ADDING WATER ON THE CARBON MONOXIDE AND HYDROGEN CONTENT

Fig. 2

RATIO OF WATER TO FUEL IN POUNDS
ratio of 0.2, then the equilibrium constant dropped at an increasing rate as this ratio increased.

Figure 2 shows the effect of adding water upon the volume concentrations of carbon monoxide and hydrogen. In all three curves the carbon monoxide concentration apparently decreased in a straight line relationship, while the hydrogen concentration increased to a maximum and then very slowly decreased. The hydrogen curve for constant speed setting was not included because of great variations, which were probably due to the change in throttle settings. The carbon dioxide content did not change appreciably. If there was any change, it was a slight increase in the carbon dioxide content.

**Explanation of Curves When Carbon Dioxide was Added**

The changes in the water-gas equilibrium constant resulting from the addition of carbon dioxide into the air-fuel mixture, are depicted in Figure 3. This curve was plotted from data obtained at very nearly the same air-fuel ratio, thus, an average curve was drawn through the points. The upper points represent a slightly greater air-fuel ratio than the lower points. The curve shows a gradually increasing rate of increase in the value of the equilibrium constant until a maximum was reached. The
apparent decrease in the constant may be due to the marked decrease in speed, which may have changed the air-fuel ratio. The addition of carbon dioxide increased the equilibrium constant as much as 100 per cent at an air-fuel ratio of approximately 12.

Figure 4 shows the average curves representing the data for the three gases, carbon dioxide, carbon monoxide, and hydrogen. The air-fuel ratio was not exactly the same in the two runs but was similar enough to consider them as checking data. The carbon dioxide content was increased 50 per cent when the largest amount of carbon dioxide was added. The carbon monoxide and the hydrogen concentrations decreased about 20 per cent and 70 per cent respectively.
EFFECT OF ADDING CARBON DIOXIDE
On The
WATER-GAS EQUILIBRIUM
CONSTANT

Fig. 3

Ratio of Carbon Dioxide to Fuel in Pounds

EFFECT OF ADDING CARBON DIOXIDE
On The
GASES IN THE WATER-GAS REACTION

Fig. 4

- Carbon Dioxide
- Carbon Monoxide
- Hydrogen

Percentage by Volume of Gas

Ratio of Carbon Dioxide to Fuel in Pounds
**Explanation of Combined Data**

Figure 5 represents graphically the relationships of the water-gas equilibrium constant to the two ratios carbon monoxide-hydrogen and water-carbon dioxide, and includes the results of the addition of carbon dioxide and of water. The water-carbon dioxide ratio decreased comparatively little with values of the equilibrium constant ranging from 1 to 6.6. However, the carbon monoxide-hydrogen ratio increased almost directly as the equilibrium constant increased. For an additive change of 5.6 in the equilibrium constant, the carbon monoxide-hydrogen ratio increased from 0.3 to 6.0. It is quite evident that this ratio was not a constant when one of the water-gas reaction products or reactants was added to the air-fuel mixture. When the engine was operated on gasoline alone, the carbon monoxide-hydrogen ratio was found to be about 2.5. This value checks that found by other investigators very closely.

The variations in the carbon monoxide ratio when either carbon dioxide or water was added are depicted in Figure 6. The curves are drawn from data secured for approximately the same air-fuel ratio. The addition of carbon dioxide to the air-fuel mixture greatly increased the carbon monoxide-hydrogen ratio in the exhaust gases.
as the carbon dioxide-fuel ratio was made greater; whereas, when water was added the reverse effect was obtained, that is, a decrease in the carbon monoxide-hydrogen ratio was found to exist. The decrease due to the addition of water was not as pronounced as was the increase when carbon dioxide was added. This situation was perhaps due to the difference in the dissociation of the two added products, carbon dioxide dissociating more readily than water.
GENERAL DISCUSSION
GENERAL DISCUSSION

Water-Gas Equilibrium Constant

There are several approaches which may be used in attacking the problem of the existence of the water-gas equilibrium conditions. The method used was that of adding carbon dioxide or water, two of the constituents involved in the water-gas reaction, to the air fuel mixture. The addition of one of these constituents should not affect the equilibrium constant if the water-gas equilibrium constant existed; the only effect would be that of changing the concentrations of the other constituents as mentioned in the forepart of this paper. However, the data and curves presented show definitely that the water-gas equilibrium did not remain constant when either of these products, carbon dioxide or water, was added. The results show that there was apparently a definite tendency or an equilibrium to be established but something was impairing the reaching of the equilibrium state. In order to more specifically convey the above meaning, each case will be separately analyzed.

On page 11 the possible changes which might be expected when water is added were explained under the assumption that the water-gas equilibrium constant existed and was frozen at or prior to the time of sampling. The
anticipated changes did occur but not sufficiently to maintain an equilibrium constant. The carbon dioxide, which should have increased in proportion to the decrease in carbon monoxide, did not change appreciably. This is accounted for by the fact that less fuel was required per 100 mols of exhaust gas, thus more carbon was burned to carbon dioxide and less to carbon monoxide. The water formed from the combustion of the fuel decreased, but the total water concentration was increased almost as much as the amount of water added. The addition of water which is known to be a good anti-knock agent, showed lower equilibrium constants in accordance with the findings of W. G. Lovell, J. D. Coleman, and T. A. Boyd (10) who found the existence of lower equilibrium constants as fuels having less tendency to knock were used.

In the case of adding carbon dioxide to the air-fuel mixture the general expected changes occurred in the decreasing of the hydrogen concentrations and a corresponding increasing in the water concentration. However, the carbon monoxide content decreased instead of increased as might have been expected. Since the carbon monoxide did decrease, it is quite evident that according to the water-gas equilibrium constant equation the equilibrium constant value could not exist. The fact
that the equilibrium constant increased over that value obtained when no carbon dioxide was added is explained by the great decrease in hydrogen and the large increase in water concentration. Figure 5 shows that the ratio of water to carbon dioxide was more nearly constant than the carbon monoxide-hydrogen ratio.

**Carbon Monoxide-Hydrogen Ratio**

The contentions of previous investigators (11 and 13) that the carbon monoxide-hydrogen ratio is a constant was not found to be the case according to the results obtained in this experimental work. The mentioned ratio decreased when water was added and increased when carbon dioxide was added. The change in the ratio did not follow the same order of equation in both cases, but definitely showed the same trend of change in each case. There does seem to be a direct relationship between the calculated equilibrium constant and the carbon monoxide-hydrogen ratio as shown in figure 5. The relationship of the carbon monoxide-hydrogen ratio to the equilibrium constant approximated a lineal curve between a ratio of 1 to 4; above or below those limits the relationship apparently followed a convex curve. Since the deviations from the lineal curve occurred at high ratios of added products to fuel, the change in the curve may be due to a
change in the air-fuel mixture.

The results seem to support the view that the water-gas equilibrium constant controls the carbon monoxide-hydrogen ratio, or vice versa; but the calculated equilibrium constant from the exhaust gases does not seem to have any definite significance to temperatures corresponding to a true equilibrium constant. This is shown by the fact that for the range of equilibrium constants calculated the corresponding temperatures for a true equilibrium constant ranges from $800^\circ$C for the lowest constant value to $2200^\circ$C for the highest constant value. Such a temperature differential could not possibly have existed at the time of sampling the gases.
CONCLUSIONS

The conclusions which might logically be drawn from this experimental research are enumerated as follows:

1. When either water or carbon dioxide was added to the air-fuel mixture, the water-gas equilibrium constant did not remain a constant as it should have done if the water-gas reaction does reach equilibrium conditions.

2. The ratio of carbon monoxide to hydrogen does not remain constant, but does bear a definite relationship to the calculated water-gas equilibrium constant under conditions tested.

3. The ratio of water to carbon dioxide remained more nearly constant than any other relationship.

4. The equilibrium constant as calculated from exhaust gas analyses in this research did not show any indication of being in a true equilibrium state when correlated with the temperatures corresponding to a true equilibrium constant of the same value.
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