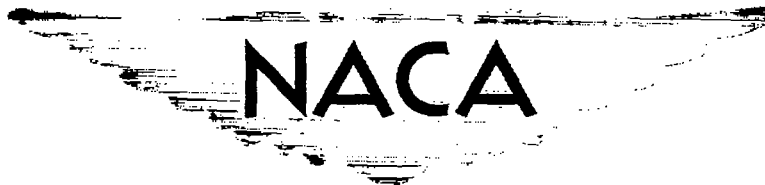


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RESEARCH MEMORANDUM

EFFECT OF WATER ON CARBON MONOXIDE - OXYGEN
FLAME VELOCITY

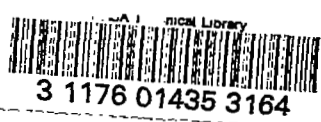
By Glen E. McDonald

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS

WASHINGTON
February 5, 1954

Lewis Flight Propulsion Laboratory
Langley Field, Virginia



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RESEARCH MEMORANDUM

EFFECT OF WATER ON CARBON MONOXIDE - OXYGEN FLAME VELOCITY

By Glen E. McDonald

SUMMARY

The flame velocities were measured of 20 percent oxygen and 80 percent carbon monoxide mixtures containing either light water or heavy water. The flame velocity increased from 34.5 centimeters per second with no added water to about 104 centimeters per second for a 1.8 percent addition of light water and to 84 centimeters per second for an equal addition of heavy water. The addition of light water caused greater increases in flame velocity with equilibrium hydrogen-atom concentration than would be predicted by the Tanford and Pease square-root relation. The ratio of the flame velocity of a mixture containing light water to that of a mixture containing heavy water was found to be 1.4. This value is the same as the ratio of the reaction rate of hydrogen and oxygen to that of deuterium and oxygen. A ratio of reaction rates of 1.4 would also be required for the square-root law to give the observed ratio of flame-velocity changes.

INTRODUCTION

The flame-velocity theory of Tanford and Pease (ref. 1), which relates flame velocity to the diffusion of free radicals from the flame zone, has led to considerable interest in flames of various hydrogen-atom concentrations. Although this flame-velocity theory of Tanford and Pease was originally developed for carbon monoxide, it was later extended to hydrocarbon fuels. In other investigations, the flame velocities of hydrocarbons have been correlated with those changes in hydrogen-atom concentration which are produced by changes in initial temperature (ref. 2), hydrocarbon structure (ref. 3), and fuel concentration (ref. 4). However, it is an advantage to use carbon monoxide flames to determine the effect of hydrogen atoms on flame velocity, because the radical concentration can be easily changed by the addition of small amounts of water, without producing excessive changes in flame temperature or fuel concentration.

In this research conducted at the NACA Lewis laboratory, the effect on flame velocity of adding various amounts of water to a carbon monoxide - oxygen mixture was studied. The water produced changes in the

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calculated equilibrium concentration of hydrogen atoms without producing significant changes in the thermal properties of the mixture. The changes in flame velocity produced by the addition of water are correlated with the thermal equilibrium concentrations of hydrogen atoms which exist in the flames.

In addition, the effect of isotopes on flame velocity was studied by adding either heavy or light water to a carbon monoxide flame. The light water contains hydrogen and the heavy water contains deuterium. In general, reaction rates involving molecules which contain hydrogen differ from the reaction rates involving molecules which contain the isotope deuterium. Flame velocities were measured by the Bunsen burner method using shadow photography for carbon monoxide - oxygen mixtures which contained 80 percent carbon monoxide, 20 percent oxygen, and up to 1.8 percent either heavy or light water. The measured differences in the flame velocities of the "isotopic flames" are compared with changes in the reaction characteristics which resulted from the substitution of the isotopes.

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EXPERIMENTAL DETAILS

Apparatus. - The apparatus is diagrammatically illustrated in figure 1. The experimental procedure was as follows: Mixtures of gases were prepared by admitting the desired partial pressures of water vapor stored in F, carbon monoxide stored in D, and tank oxygen into an evacuated cylinder G. Mixing was accomplished with a small stirrer which entered through the wall of the cylinder. The pressure of the water vapor was measured with an oil manometer. For a determination of flame velocity, the gases were moved by mercury displacement through a flowmeter H and burned in a Bunsen cone above a burner 35 centimeters long and 0.7 centimeter in diameter. The flame was photographed in a parallel-beam shadowgraph system with a zirconium arc as a light source.

Materials. - The carbon monoxide used in these experiments was prepared by the sulfuric acid dehydration of 98- to 100-percent formic acid. The apparatus in which the carbon monoxide was generated and collected was evacuated before use, and the sulfuric acid was degassed. Before collection, the generated carbon monoxide was passed through a trap at -78°C to remove traces of sulfuric acid, formic acid, and water vapor. The light and the heavy water were degassed and stored under vacuum. The heavy water, which was obtained from the Stuart Oxygen Company, had a purity of 99.8 percent.

Drying procedure. - The carbon monoxide and oxygen were dried before mixing by passage through anhydrous magnesium perchlorate. The flow system up to the lip of the burner was evacuated in a high vacuum system to remove absorbed water.

Flame-velocity measurement. - The flame velocity was calculated from a planometer measurement of the area of the photograph of the flame and the volumetric rate of mixture flow. The surface area of the combustion zone S was calculated from the approximate relation:

$$S = \pi Al/h$$

where

A area, measured with the planometer, of projection of combustion cone

l slant height of cone

h height of combustion cone

The flame-surface areas were held nearly constant, and the flow rate was varied to minimize differences which might arise from the choice of a flame surface and the method of calculating flame velocity. An average value of l/h was used in the calculations. This procedure improves the precision in the relative values of flame velocity, although the absolute flame velocities may differ slightly from those calculated in another manner. In most cases, two determinations were made of the flame velocity of each mixture.

EXPERIMENTAL RESULTS

The flame velocities of the carbon monoxide - oxygen mixtures are plotted against the percentage of added water in figure 2 and are listed in table I. The flame velocities are for dry carbon monoxide and for various additions of light and heavy water from zero to 1.8 percent. The experimental flame-velocity values, shown in figure 2, increase from 34.5 centimeters per second with no added water to about 104 centimeters per second for a 1.8 percent addition of light water and to about 84 centimeters per second for an equal addition of heavy water.

DISCUSSION

When water is added to the carbon monoxide flame, the calculated equilibrium flame temperature decreases progressively, while the calculated equilibrium hydrogen-atom concentration increases progressively. The equilibrium flame temperatures and the thermal equilibrium hydrogen-atom concentrations for the additions of light water which were used in these experiments are presented in table II. The temperatures and the atom concentrations were calculated by the method of reference 5.

Since addition of water to a carbon monoxide - oxygen flame produces a decrease in the temperature of the flame, it is evident that the concurrent increase in flame velocity is not of thermal origin. The higher flame velocity is the result of the substitution of a more rapid chemical reaction for the slower reaction which occurs in the dry carbon monoxide flame. Tanford and Pease (ref. 1) postulated that the faster reaction which occurs when water is added is a result of the formation of hydrogen atoms in the flame zone which diffuse into the unburned gas where they initiate the flame reactions. These authors related flame velocity to the thermal equilibrium concentration of hydrogen atoms in the combustion zone. The variation found in the present investigation is shown in figure 3. Tanford and Pease predicted that the relation between the flame velocity and the hydrogen-atom concentration would have the form

$$U_f = C_1 + (kDp_H)^{0.5} \quad (1)$$

where

U_f flame velocity, cm/sec

C_1 constant

k reaction rate constant

D diffusion coefficient

p_H partial pressure of hydrogen atoms

They suggested that the constant C_1 be considered the flame velocity of a dry carbon monoxide flame where $p_H = 0$. Since k and D are not changed by the addition of water,

$$\Delta U_f = U_f - U_f^0 = C_2 (p_H)^{0.5} \quad (2)$$

where

U_f^0 flame velocity of mixture of dry carbon monoxide and oxygen

C_2 constant

The straight line obtained in a log-log plot of $U_f - U_f^0$ against p_H is shown in figure 4. Instead of the predicted slope of 0.5, however, a slope of 1.26 is found; the resulting equation

$$\Delta U_f = U_f - U_f^0 = C_3(P_H)^{1.26} \quad (3)$$

indicates a much greater dependence of flame velocity on hydrogen-atom concentration than is predicted by Tanford and Pease.

In order to investigate further the reactions which might control the flame propagation, the light water was replaced by heavy water in a series of flame-velocity measurements. When the heavy water is added to a carbon monoxide flame, the velocity is increased by an amount different from that produced by the addition of light water (see fig. 2). Only small thermal differences result from the isotopic substitution.

The over-all thermal conductivity of the preflame gases is not changed a significant amount by the addition of heavy water in place of light water, because the total conductivity is proportional only to the sum of the products of conductivity and mole fraction of each component, that is,

$$K \propto K_1 \frac{n_1}{n} + K_2 \frac{n_2}{n}$$

The change in conductivity K of the isotopic water is inversely proportional to the square root of the ratio of the masses

$$K_1/K \propto \sqrt{m/m_1} = \sqrt{20/18} = 1.05$$

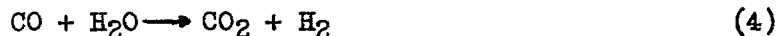
Therefore, no significant change is made in the thermal conductivity of the preflame gases by the isotopic substitution.

In the flame itself, the isotopic substitution produces isotopic radicals which have a larger percentage difference in mass than the isotopic waters in the preflame gas. However, the two groups which have the greatest difference in thermal conductivity - the isotopic hydrogen atoms and the isotopic hydrogen molecules - have a combined equilibrium concentration of less than 0.5 percent. Consequently, the thermal conductivity of the flame gases is not changed significantly.

The flame temperature is changed by the isotopic substitution; but, since the amount of water added to the flame is less than 2 percent, the flame temperature is about 1° K lower for the heavy-water flame.

Since there is no difference between the isotopic flames in the amount of thermal energy transferred from the flame to the preflame gas, any difference in flame velocity must be due to the differences between the rates of chemical reaction in the two flames. One may then look for chemical reactions which will show the proper isotopic effect.

The steps in the direct oxidation of carbon monoxide in the presence of water vapor have been reported (ref. 6). They suggest that the primary reaction

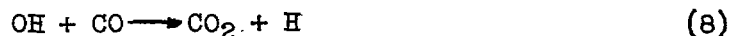
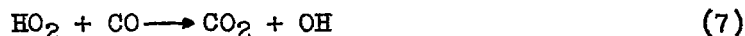


may take place on the surface at low temperatures and in the gas phase in flames.

The hydrogen which is formed, in turn, sets up reaction chains which have an estimated length of 10^6 . The initiation reaction for the chain propagation is the oxidation of the hydrogen



which is followed by reactions of the type



In a study of the inhibition of the chain propagation reactions (6, 7, and 8), it was found that the carbon monoxide reaction in the presence of water involves the same intermediate products as the hydrogen-oxygen reaction (ref. 6). Therefore, it may be expected that the relative effects of light and heavy water on the over-all carbon monoxide - oxygen reaction might be the same as the relative effect of substituting deuterium for hydrogen in the hydrogen-oxygen reaction. It has been determined (ref. 7) that the hydrogen-oxygen and deuterium-oxygen slow oxidations have velocities in the ratio of approximately 1.4. The ratio of the increase in flame velocity resulting from adding light rather than heavy water to the carbon monoxide flame also has a value of 1.4 (table I or fig. 2). The difference between the light and the heavy water is approximately the same as is observed between the hydrogen-oxygen and deuterium-oxygen reactions.

The flame-velocity ratio $U_f(\text{H}_2\text{O})/U_f(\text{D}_2\text{O})$ can thus be taken to be governed only by the ratio of the reaction rates of the isotopes H_2 and D_2 , and the controlling reaction in moist carbon monoxide - oxygen flames can be taken to be the molecular reaction $\text{H}_2 + \text{O}_2$, which is independent of diffusion. Thus, the ratio of the flame velocities is determined by the direct ratio of the reaction rates of the rate controlling steps in the two isotopic reactions. It should be pointed

out, however, that most current theoretical treatments relate flame velocity to the square root of the reaction rate (ref. 9).

Tanford and Pease concentrated on a different set of controlling reactions and placed the emphasis on the hydrogen-atom concentration being controlled by diffusion. For this isotopic substitution, the changes which would affect the flame velocity are the concentration, the diffusion coefficient, and the specific reaction rate of the isotopic atoms. The ratio of the change in flame velocity produced by adding light and heavy water is given by

$$(\Delta U_F)_{H_2O} : (\Delta U_F)_{D_2O} = (k_{DPH})_{H_2O}^{0.5} : (k_{DPD})_{D_2O}^{0.5} \quad (9)$$

If D_2O is substituted for H_2O in amounts less than 2 percent, the equilibrium deuterium-atom concentration is approximately equal to the equilibrium hydrogen-atom concentration (ref. 8) so that it can be assumed that

$$p_H/p_D = 1 \quad (10)$$

The diffusion coefficient of the hydrogen isotope depends on the square root of masses so the ratio is given by

$$D_H/D_D = 1.4 \quad (11)$$

The effect of the isotopic substitution on the reaction rates is more difficult to assess. First, it is not certain with what species the hydrogen atom reacts, although Tanford and Pease have intimated that the reaction is with the fuel molecule. Second, there has been no direct measurement of the relative rates of reaction of the isotopic-hydrogen atoms. Third, while a possible ratio of reaction rates might be calculated, the effective temperature at which the reaction occurs is uncertain.

If the known ratios of diffusion coefficients and atom concentration which are produced by the isotopes (eqs. (10) and (11)) are substituted into equation (9) then the ratio of the specific-reaction-rate constant required will have to be 1.4 to give the experimental ratio

$$(\Delta U_F)_{H_2O} / (\Delta U_F)_{D_2O} = 1.4$$

However, since the relative reaction rates of the isotopic-hydrogen atoms have not been measured and cannot be unambiguously calculated, it is not known whether the isotopic-reaction rates have the ratio of 1.4. Therefore, it is not known whether the ratio of the velocities at the isotopic flames have the value which would be predicted by the theory of Tanford and Pease.

CONCLUDING REMARKS

It appears that the effect of substituting heavy water for light water on the velocity of the moist carbon monoxide - oxygen flame is consistent with the changes observed in the hydrogen-oxygen and deuterium-oxygen reactions when a direct proportionality between flame velocity and reaction rate is assumed, and it may be consistent with the Tanford and Pease equation if the ratio of rate constants $k_H/k_D = 1.4$.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, November 30, 1953

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TABLE I. - FLAME SPEED OF CARBON MONOXIDE - OXYGEN MIXTURES

Added water, percent	Flame velocity, cm/sec		
	Dry	H ₂ O added	D ₂ O added
0.0	35.2	35.2	----
		35.2	----
0	34.0	34.0	----
		34.0	----
.12	----	43.1	42.8
			43.4
.31	----	54.0	54.6
			53.5
.50	----	63.2	63.2
			63.2
.50	----	64.0	64.2
			63.8
1.03	----	84.3	68.4
			68.7
			68.1
1.66	----	----	82.4
			82.5
			82.2
1.66	----	----	81.1
			81.4
			80.8
1.78	----	104.7	

TABLE II. - TEMPERATURE OF CARBON MONOXIDE - OXYGEN FLAMES

[80.1 Percent CO, 19.5 percent O₂, and
0.4 percent N₂.]

Added light water, percent	Equilibrium flame temperature, °K	Hydrogen- atom concentration, atm
0.0	2876	0
.125	2870	.00085
.31	2865	.00165
.5	2861	.00225
1.03	2850	.0034
1.78	2837	.0045

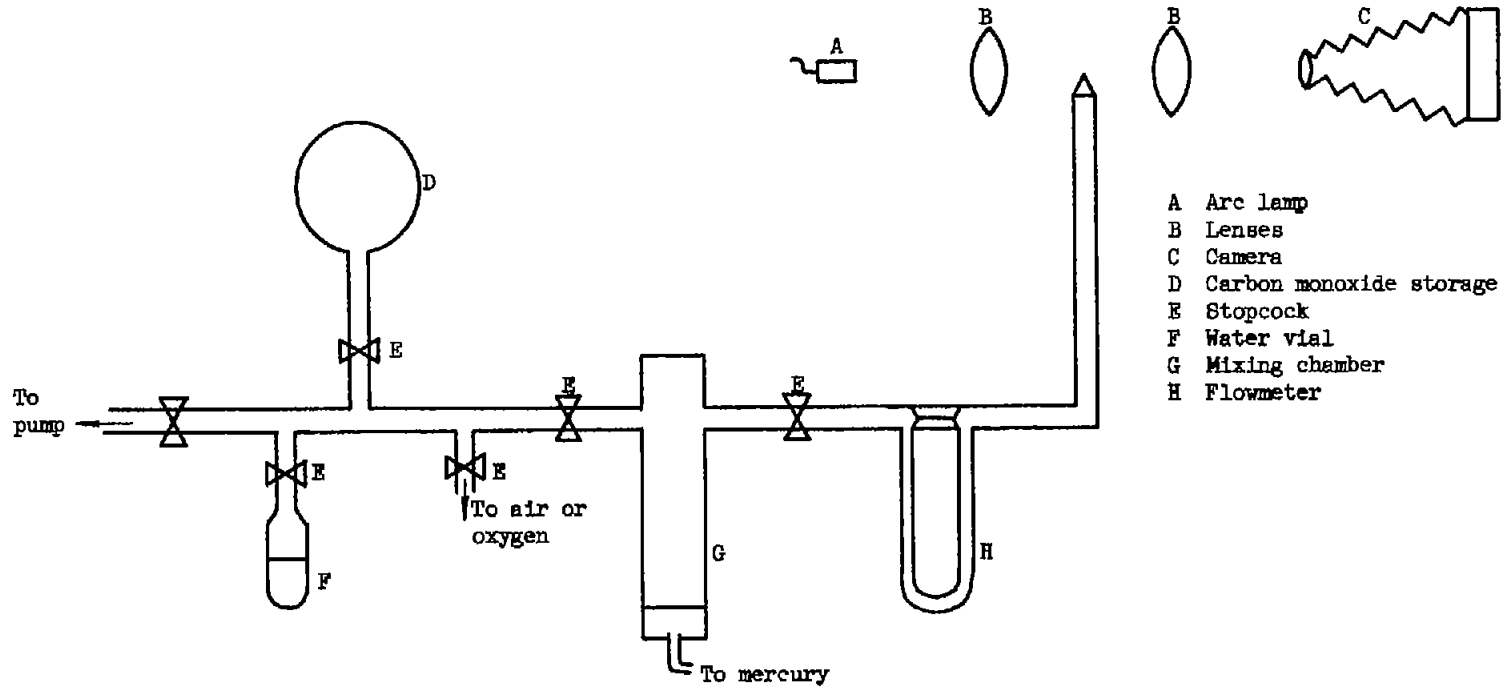


Figure 1. - Diagrammatic sketch of apparatus.

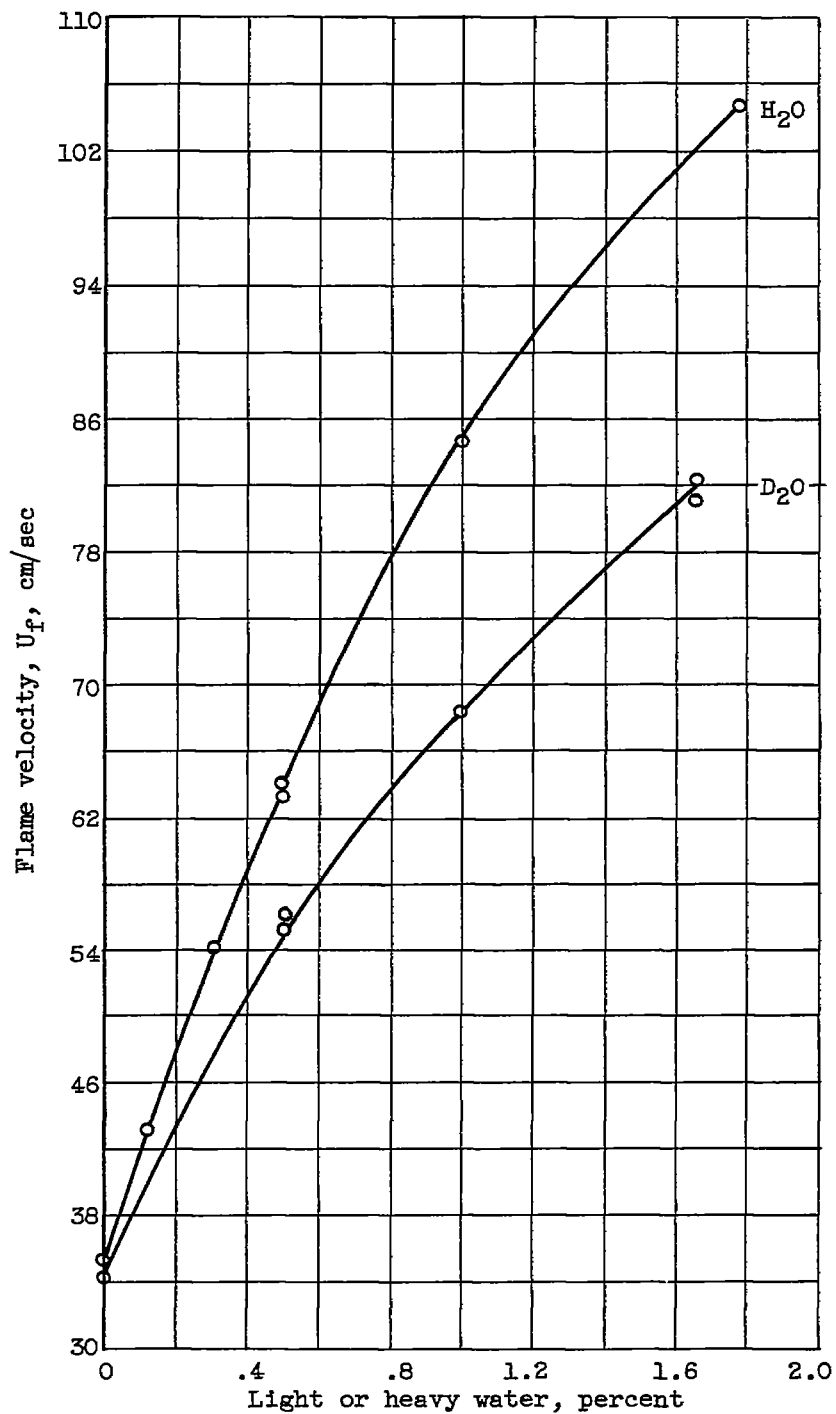


Figure 2. - Variation of flame velocity of mixtures carbon monoxide and oxygen with additions of light or heavy water.

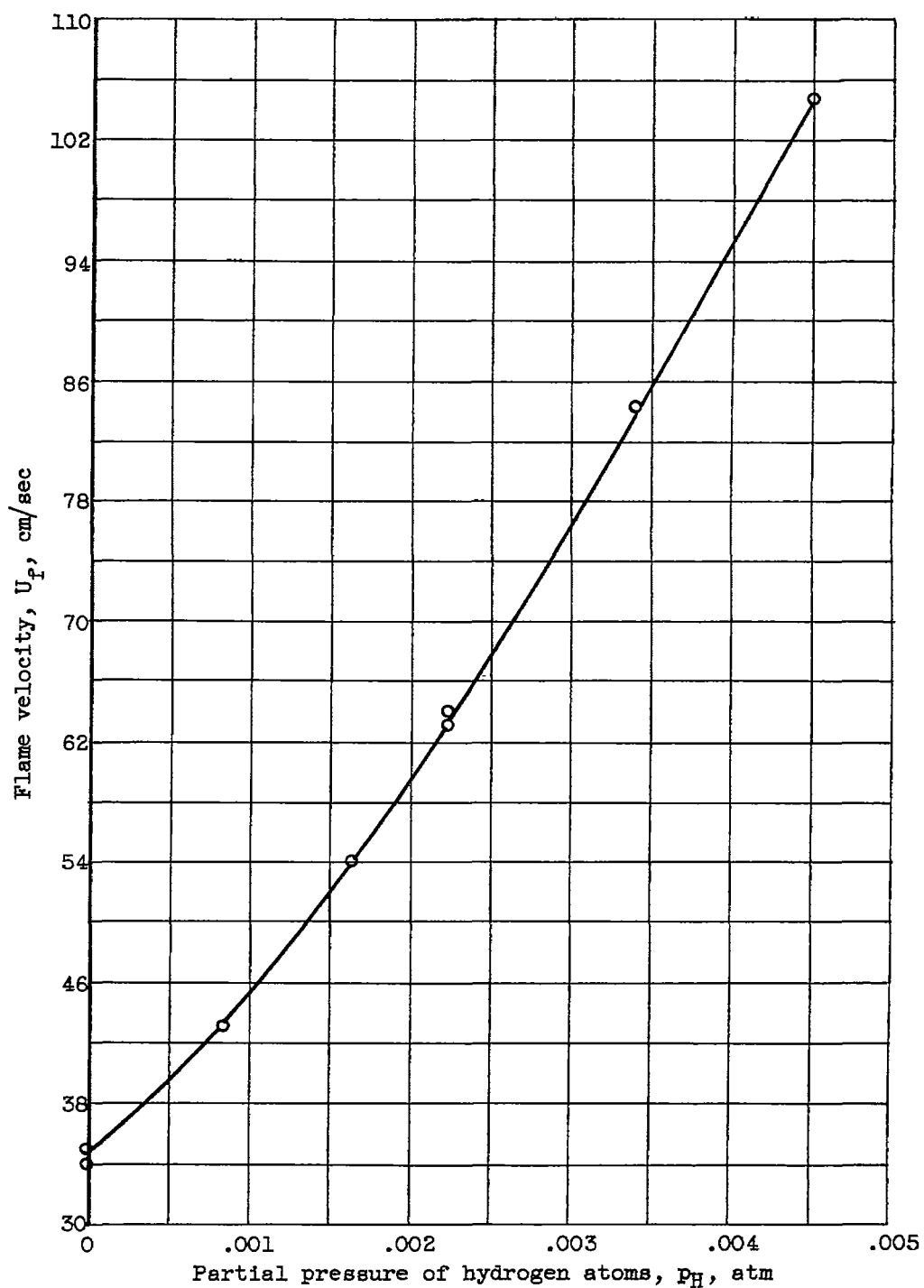


Figure 3. - Variation of flame velocity of mixtures of carbon monoxide, oxygen, and water with hydrogen-atom concentration.

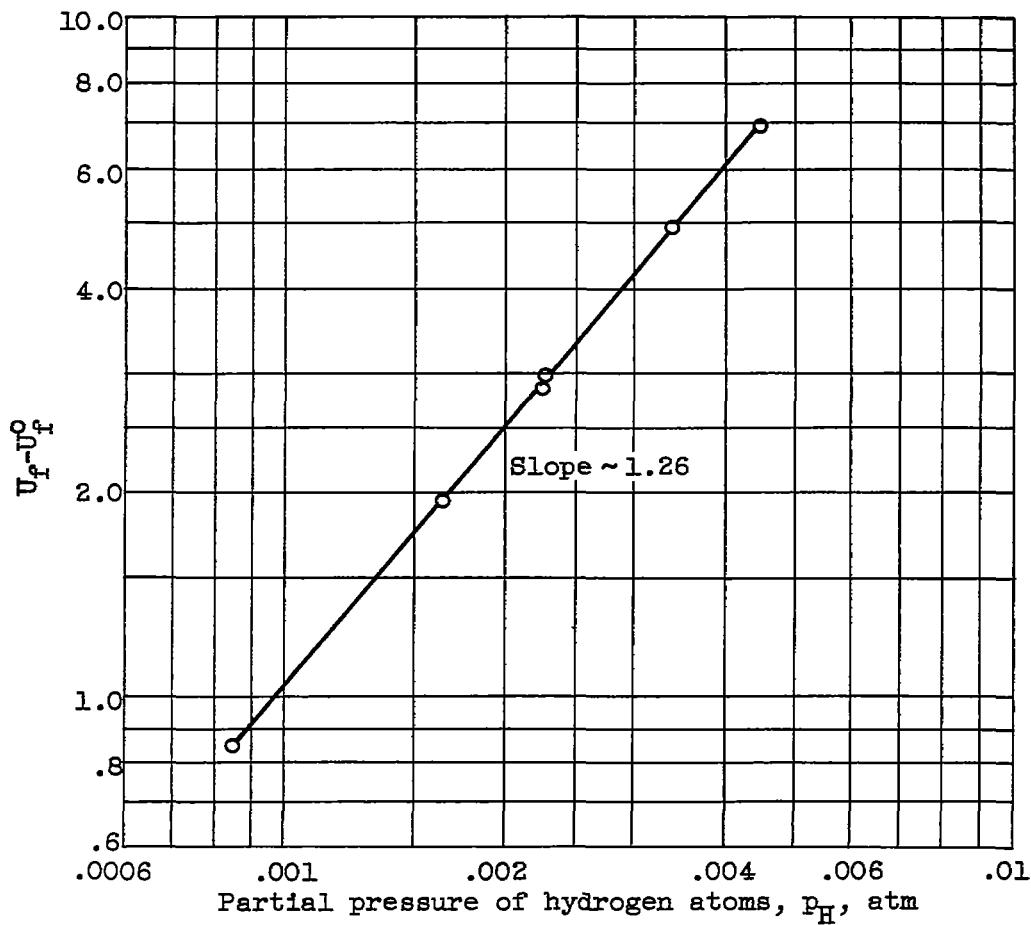


Figure 4. - Variation of flame-speed augmentation ($U_f - U_f^0$ where $U_f^0 = 34.6$) with hydrogen-atom concentration.

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