45

EXPERIMENT INCORPORATED

CARBON DISULFIDE FLAMES
INFLUENCE OF MOISTURE

TM-642

RICHMOND 2, VIRGINIA

28

EXP 1-2

CF No. 2264
1 May 1954

CARBON DISULFIDE FLAMES
INFLUENCE OF MOISTURE

TM-642

G. J. Gibbs, I. R. King, and H. F. Calcote

EXPERIMENT INCORPORATED
Richmond 2, Virginia

Submitted to the Department of the Navy - Bureau of Ordnance as partial fulfillment of requirements under contract NOrd 9756.

CONTENTS

TABLES

FIGURES

SUMMARY

The burning velocity of carbon disulfide - air flames increases exponentially as the concentration of water is reduced so that on a Bunsen burner for very dry mixtures flash back was inescapable. Flame propagation in a 1.5-inch closed tube increased from 550 for a water-saturated to 1150 cm/sec for a very dry mixture. The minimum spark-ignition energy and quenching distance also were markedly affected by the moisture content.

Both a diffusional transfer and a thermal transfer theory are marginal in explaining the results. However, it appears more reasonable that hydrogen atoms or hydrogen-containing species from water inhibit the reaction chain. More refined work is required.

INTRODUCTION

In a recent paper (1) it was found that carbon disulfide deviated from other fuels in a correlation involving the burning velocity and lean-limit flame temperature. A similar lack of consistency has also been observed when correlations of ramjet-burner efficiencies are made with combustion properties. These deviations might be explained by assuming that normally the significant transport property is diffusion of hydrogen atoms or similar species, but in the case of carbon disulfide the transport property is thermal diffusion. Carbon disulfide is of further interest because it is one of the few fuels which does not contain hydrogen or light radicals capable of rapid diffusion. In hydrogen-containing mixtures diffusion ahead of the flame front can be of significance only when the diffusing species can effectively react there. These considerations have inspired the study of the effect of water vapor on the combustion characteristics of carbon disulfide flames.

Measurements have been made of burning velocity on a Bunsen burner, flame propagation in a 1.5-inch tube, and the minimum spark-ignition energy and quenching distance. The experimental equipment has been previously described (2, 3).

BURNING VELOCITY

The burning velocities as a function of equivalence ratio (stoichiometric air-fuel ratio divided by the actual air-fuel ratio) for flames containing varying quantities of water vapor are presented in Figure 1. These measurements were made by the usual Bunsen-burner technique employed in this laboratory at atmospheric pressure and 25°C (3).

The burner exhausted into a closed chamber employed for subatmospheric burner studies so that the secondary air could be controlled. Decreasing the quantity of water vapor was observed to increase the burning velocity. The third curve from the bottom was obtained by passing the air through a potassium hydroxide tower and then through a trap containing solid carbon dioxide. In an attempt to obtain extremely dry air with very little hydrogen a synthetic air mixture was employed. This contained 20.6% oxygen, 79.4% nitrogen, and approximately 0.0008% hydrogen, which compared favorably with normal atmospheric air containing 20.99% oxygen, 78.03% nitrogen, 0.01% hydrogen, 0.94% argon, etc. When this synthetic air mixture was employed, it sometimes became impossible to stabilize the flame. On several occasions a run was in progress when the flame began to flash back violently. Attempts were made to stabilize the flame by varying the flow rate from 100 to 200 cc/sec (burner diameter equals 0.784 cm) and the equivalence ratio from 0.9 to 1.1 with no success. The flow velocity for the reported curve was 120 cc/sec. The flame was finally stabilized by connecting a T-tube in the air line to a small water reservoir. When the valve to this was open for about 15 seconds, the system became slightly contaminated with water vapor, and the flame could be stabilized atop the burner. After a period of approximately three minutes, violent flash back occurred again. This was reproducible and indicated an extremely high burning velocity for very dry mixtures.

The burning velocity for stoichiometric mixtures is plotted in Figure 2 against the estimated mole-percent water in the air. The number of experiments is given in the circle, and the variation in results is indicated by the vertical line. The burning velocity increases exponentially with decreasing concentrations of water.

The carbon disulfide used in these experiments was Baker and Adams's reagent grade; the air was normal laboratory compressed air except for

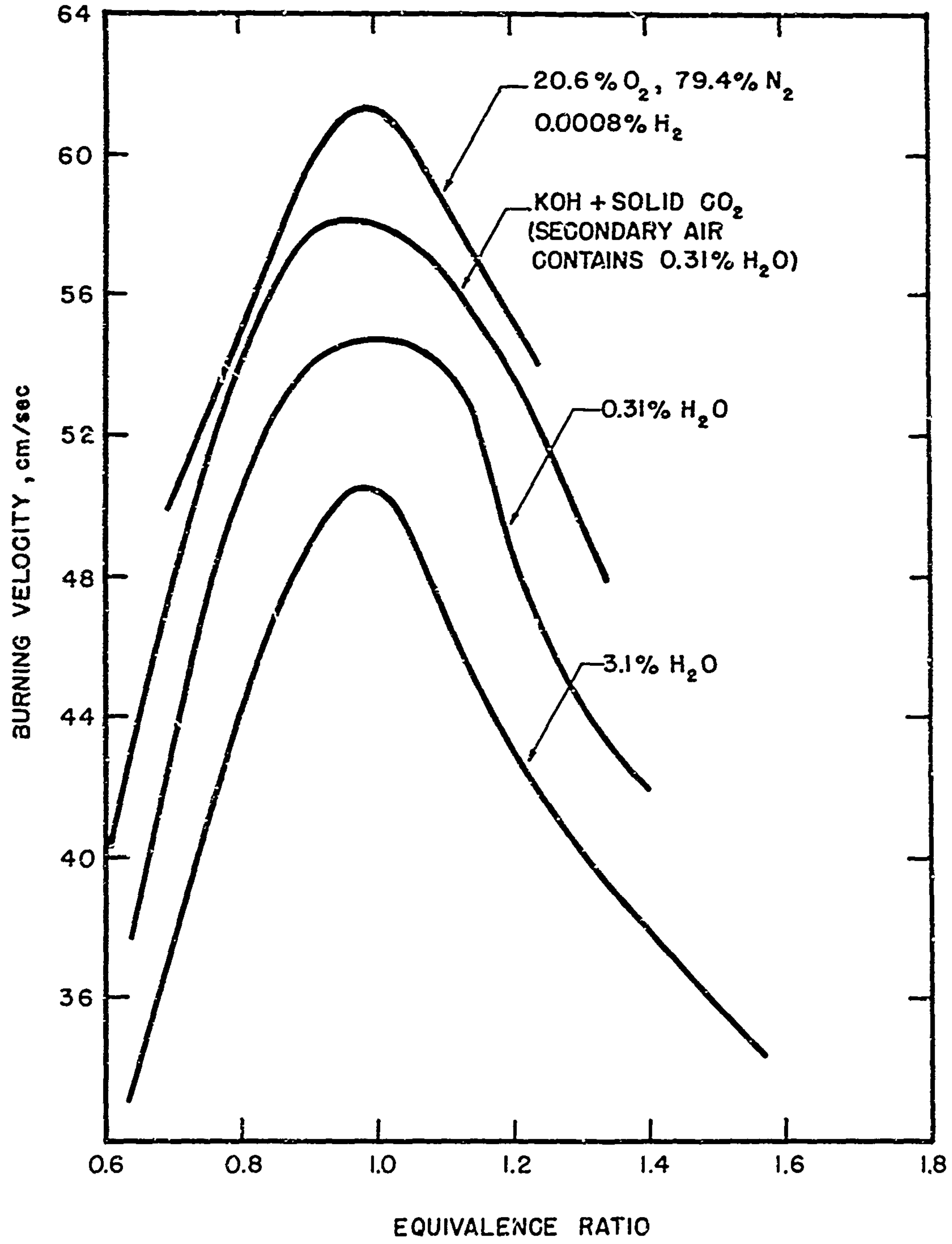

FIGURE I. BURNING VELOCITY OF CARBON DISULFIDE-AIR MIXTURES

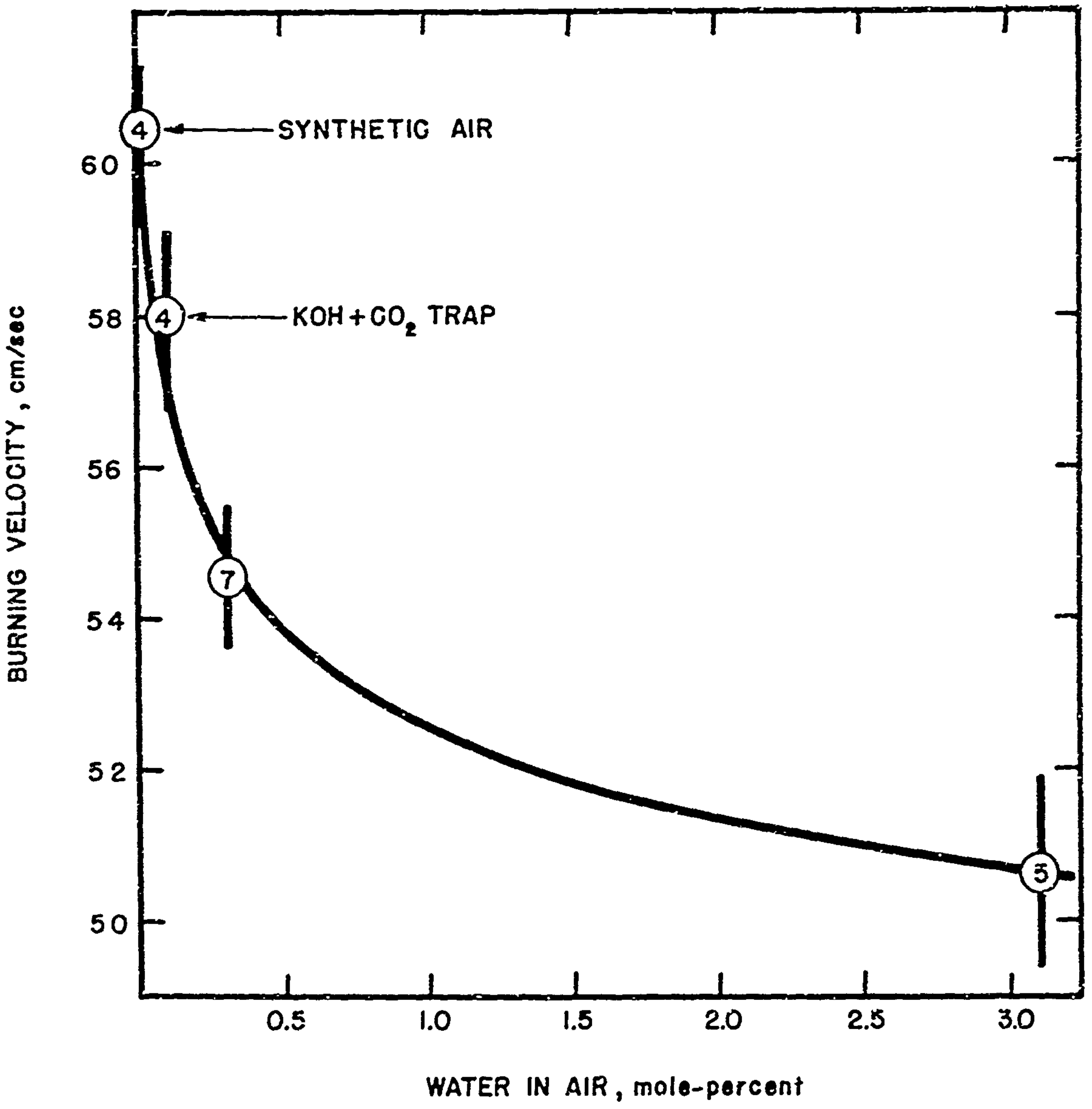

FIGURE 2. EFFECT OF WATER VAPOR ON THE BURNING VELOCITY OF CARBON DISULFIDE-AIR MIXTURES

$\phi = 1.0$ P = 1.0 ATM

the synthetic mixture (20.6% oxygen, 79.4% nitrogen, 0.0008% hydrogen) which was prepared by the Matheson Company from extra dry oxygen 99.6% pure and prepurified nitrogen 99.9% pure.

FLAME PROPAGATION IN A TUBE

Because of the difficulty of obtaining really dry mixtures in a Bunsen-burner flow system without considerable effort, some somewhat crude experiments were carried out in a Pyrex tube in which the rate of flame propagation was photographed. The experimental arrangement involved six 1.5-inch i.d. by 48-inch long Pyrex glass tubes with Teflon-coated rubber stoppers in each end. One stopper was equipped with copper electrodes for the purpose of igniting the gaseous mixture. The other end was equipped with a 3/8-inch Pyrex tube and stopcock for loading and evacuating the tube. The mixtures were made up by partial pressures. A Moore Products differential-pressure transmitter in conjunction with a mercury manometer was used to measure the water and carbon disulfide vapor pressures as well as the total pressure. An attempt was made to dry the tubes by heating them during evacuation overnight. Moving pictures were taken of the propagating flame at 64 frames per sec. The tube was marked with a scale so that flame velocities could be determined from the motion pictures. The time scale was obtained with a pendulum having a one-second period. The data obtained by this procedure were not very accurate but still indicated a strong influence of water (Figure 3). The addition of 2.6 mole-percent water decreased the flame velocity from 1150 to 550 cm/sec. The number of experiments averaged is given in the circles, and the standard deviation from the mean is indicated by the length of the lines extending from the points.

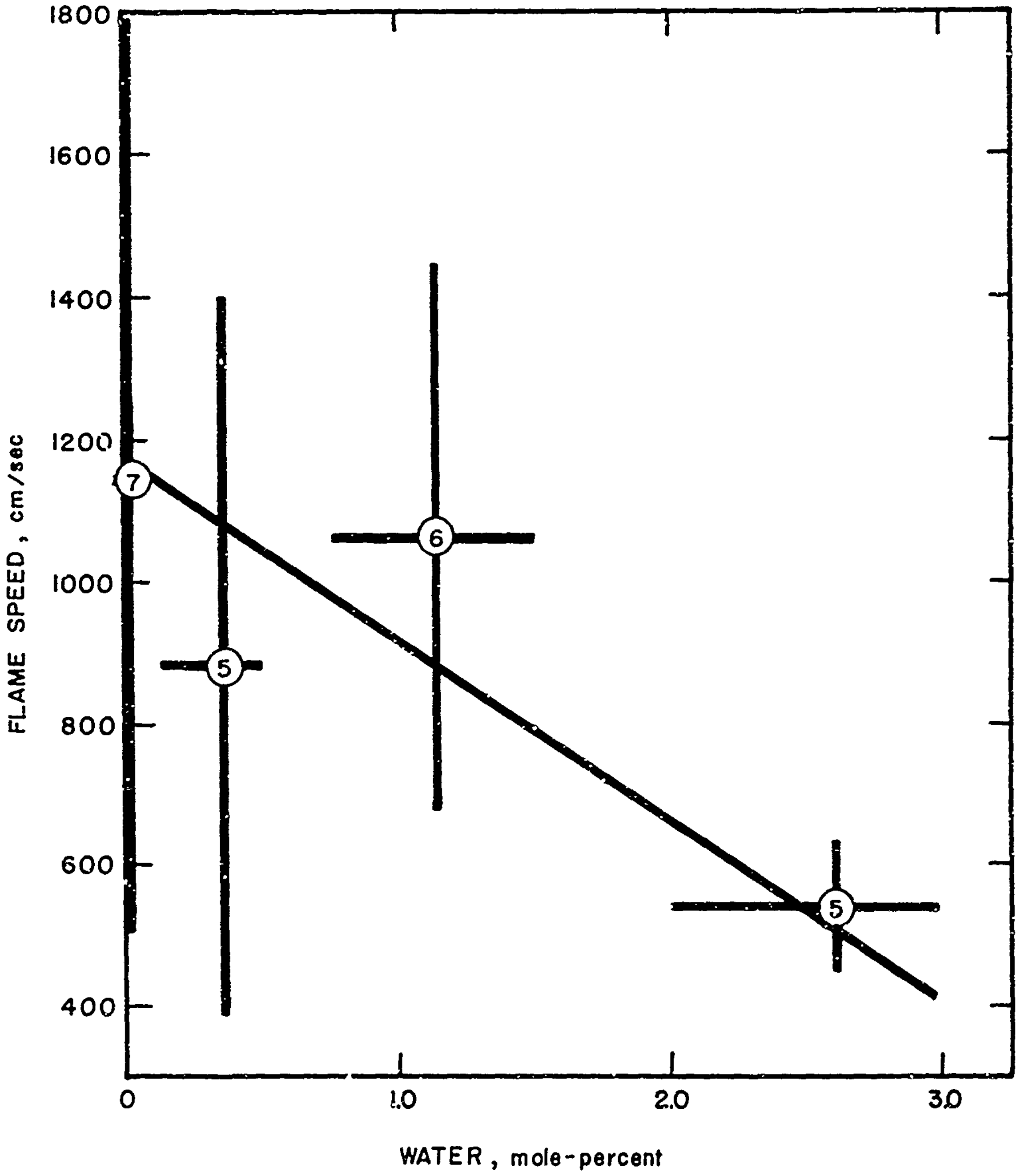

FIGURE 3. EFFECT OF WATER VAPOR ON THE FLAME SPEED OF CARBON DISULFIDE-AIR MIXTURES

$\phi = 1.0$ $P = 1.0$ ATM

MINIMUM SPARK-IGNITION ENERGY AND QUENCHING DISTANCE

The minimum spark-ignition energies and quenching distances were obtained by our usual procedures (2). For the ignition-energy determinations the electrodes were 1/8-inch stainless-steel rods with the tips rounded and a stainless-steel flange 0.5 inch in diameter set back 0.01 inch from the tip of the cathode. The energy of the spark was assumed to be equal to the energy stored on the condenser. The quenching distances were obtained with one-inch glass flanges mounted flush with the tip of the electrodes.

The results are reported in Figure 4 and Table I. Measurements were made at 0.5 atmospheres because of the small value of the minimum spark-ignition energy for carbon disulfide at one atmosphere. Although the effect of water is definite, it does not appear as great as on the burning velocity. The use of "synthetic air" (Table I) did not produce the same result as expected from burning velocity, i.e., an extremely low ignition energy.

Incidental to this study some data on the effect of composition, pressure, and temperature were obtained, and these are presented in Table II and Figures 5 and 6.

In determining the temperature effect on the minimum spark-ignition energy of carbon disulfide - air mixtures, it was observed that stoichiometric mixtures ignited spontaneously at temperatures above 150°C. Figure 7 shows the results of some preliminary measurements of the autoignition temperature of such mixtures. In these determinations, the mixture at room temperature was introduced rapidly into the heated bomb through a toggle valve. The time of introduction was approximately 0.5 second. The time delay for ignition was measured from the instant the toggle valve was opened until ignition took place. Initial pressure, bomb temperature, and time for ignition were measured.

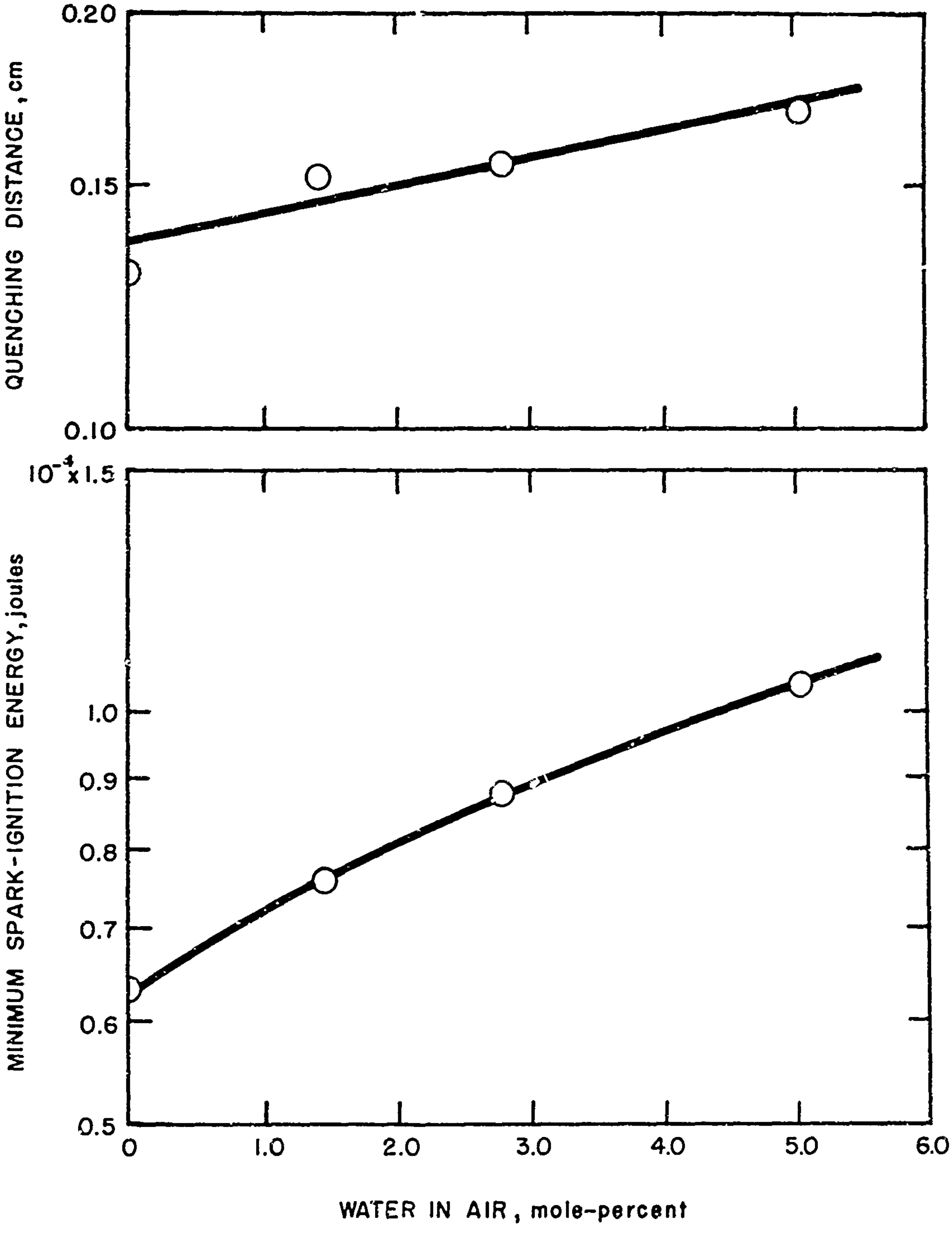

FIGURE 4. EFFECT OF WATER VAPOR ON THE MINIMUM SPARK-IGNITION ENERGY AND QUENCHING DISTANCE OF STOICHIOMETRIC CARBON DISULFIDE-AIR MIXTURES AT 0.5 ATMOSPHERES

TABLE I

MINIMUM SPARK-IGNITION ENERGIES AND QUENCHING DISTANCES FOR CARBON DISULFIDE - AIR MIXTURES CONTAINING WATER

Equivalence Ratio, 1.0 Pressure, 0.5 atm

H_2O in Air, mole-percent	Temperature, °C	Minimum Spark-Ignition Energy, joules	Quenching Distance, mm
0[a]	28	0.63×10^{-4}	1.3
1.43	25	0.76	1.52
2.80	25	0.87	1.56
5.05	25	1.05	1.70
0[b]	21	0.84	1.50
1.43[b]	21	1.02	-
2.80[b]	21	1.25	-

---

[a] CS_2 dried by solid carbon dioxide. Laboratory air dried by liquid nitrogen.

[b] Synthetic air 79.4% N_2, 20.6% O_2, and 0.0008% H_2.

TABLE II

MINIMUM SPARK-IGNITION ENERGIES AND QUENCHING DISTANCES FOR CARBON DISULFIDE - AIR MIXTURES

Air Dried by Activated Alumina

Equivalence Ratio	Temperature, °C	Pressure, atm	Minimum Spark-ignition Energy, joules	Quenching Distance, mm
0.35	25	0.50	$\sim 30 \times 10^{-4}$	-
0.50	30	0.50	3.3	2.75
0.50	30	1.0	1.9	1.90
0.50	100	0.50	2.1	2.15
0.50	100	1.0	0.72	1.55
0.70	30	0.50	1.45	1.80
0.70	30	1.0	0.78	1.10
0.70	100	0.50	0.94	1.65
0.70	100	1.0	0.3	0.95
0.80	25	1.0	0.49	-
1.00	25	0.20	4.8	3.3
1.00	25	0.25	2.8	2.6
1.00	25	0.35	1.3	1.85
1.00	30	0.50	0.68	1.30
1.00	25	1.0	0.39	0.75
1.00	25	1.5	-	0.58
1.00	25	2.0	-	0.50
1.00	-20	0.5	1.51	-
1.00	0	0.5	0.85	-
1.00	100	0.50	0.49	1.15
1.00	130	0.50	0.42	-
1.00	150	0.50	0.38	-
1.6	27	0.50	0.32	1.20
1.6	100	0.50	0.225	0.80
2.4	28	0.50	0.30	1.50
3.0	28	0.25	1.6	2.90
3.0	28	0.50	0.38	1.80
3.5	25	0.50	0.48	-
4.0	25	0.50	0.68	-

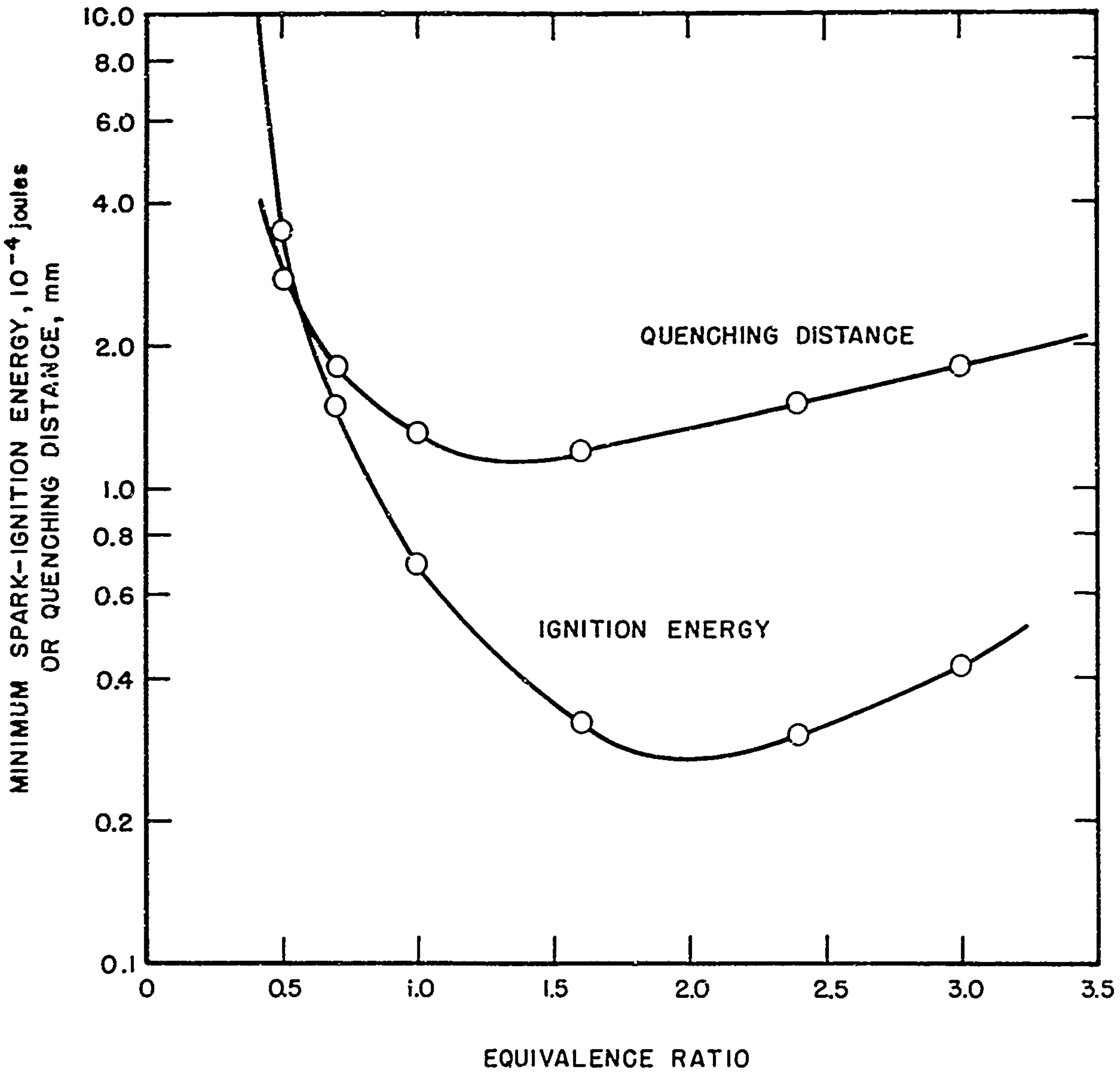

FIGURE 5. EFFECT OF COMPOSITION ON THE MINIMUM SPARK-IGNITION ENERGY AND QUENCHING DISTANCE OF CARBON DISULFIDE - AIR MIXTURES

T = 25°C P = 0.5 ATM

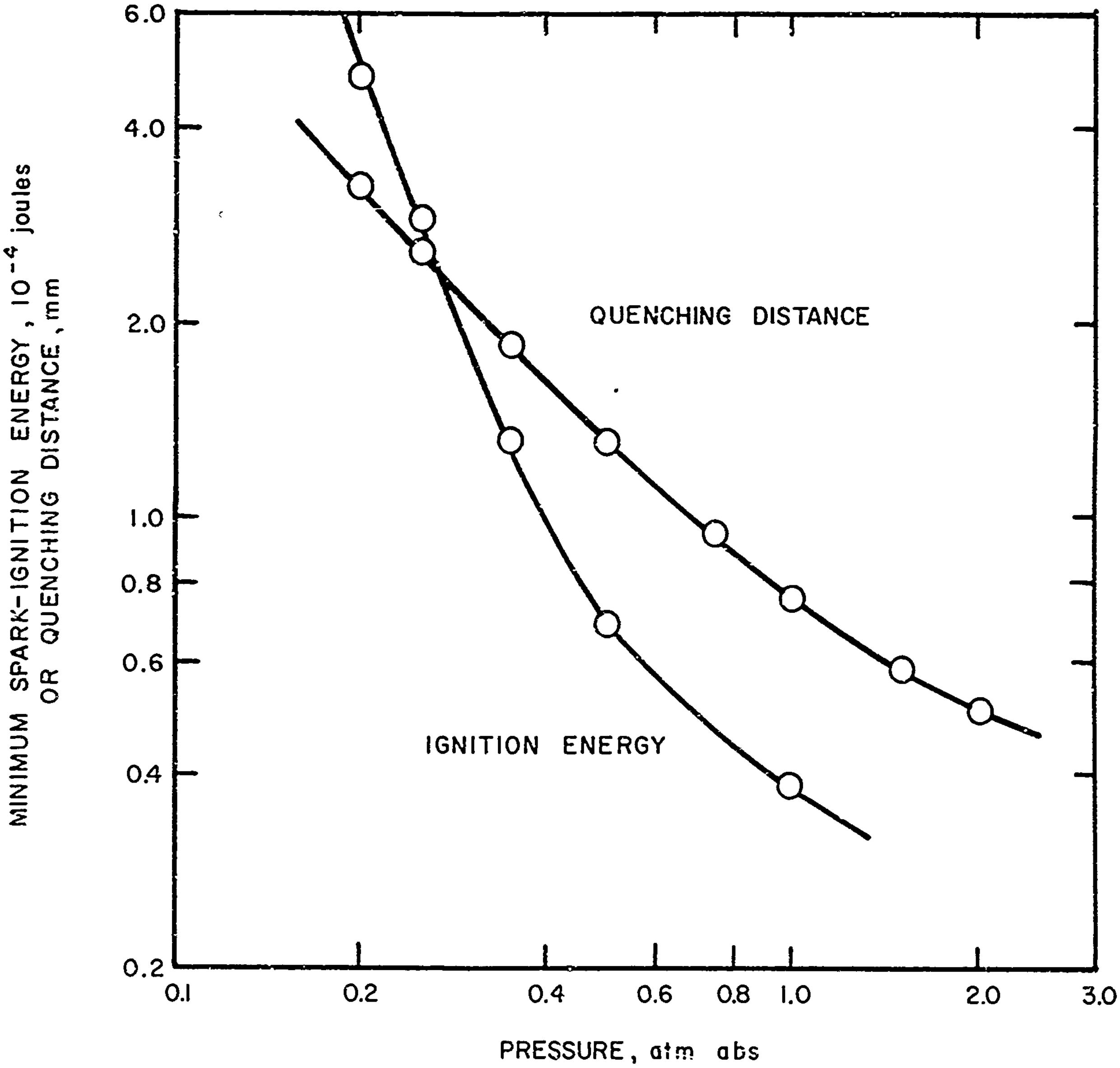

FIGURE 6. EFFECT OF PRESSURE ON THE MINIMUM SPARK-IGNITION ENERGY AND QUENCHING DISTANCE OF STOICHIOMETRIC CARBON DISULFIDE-AIR MIXTURES

AIR DRIED WITH ACTIVATED ALUMINA

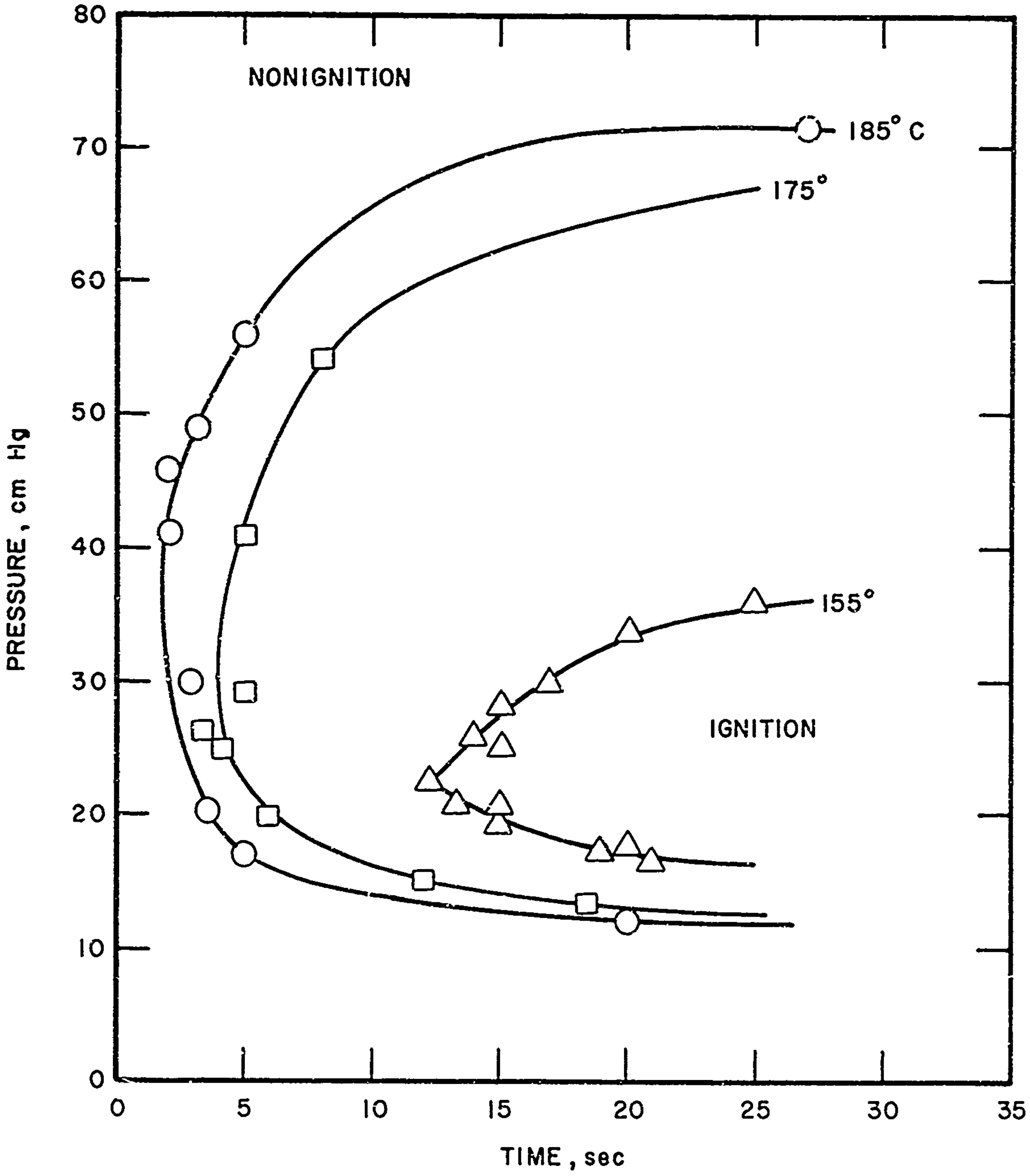

FIGURE 7. AUTOIGNITION OF STOICHIOMETRIC CARBON DISULFIDE-AIR MIXTURES

ADIABATIC FLAME TEMPERATURE

The adiabatic flame temperature and equilibrium product composition were calculated and are reported in Table III and IV and Figures 8, 9, and 10. The addition of 3.1 mole-percent water reduced the flame temperature at stoichiometric conditions from 2265°K to 2210°K, i.e., 55° or only 2.4 percent.

DISCUSSION

Hydrogen-containing species cannot play a role in the dry flames because no hydrogen is present in the reactant mixture. If diffusion is to be important in transport some heavy species such as oxygen atoms must be involved. The next highest diffusion coefficient would be expected for sulfur atoms, which are present in extremely small concentrations. It is well to note here that the initial argument for diffusion as playing a role in flame propagation was that the concentration of hydrogen atoms ahead of the flame front due to diffusion exceeded the local thermal equilibrium concentration due to heat transfer ahead of the flame (4). "It is shown that the temperature falls rapidly as the distance from the flame front increases, and that the local thermal equilibrium concentration of hydrogen atoms, being a negative exponential of that temperature, falls more rapidly still. On the other hand, the local nonequilibrium concentration of hydrogen atoms, which is caused by diffusion from the flame front into unburnt gas, falls only slowly with distance. It is thus concluded that diffusion plays a more important role than heat." The original work of Tanford and Pease (4, 5) is frequently the basis of discussions in which diffusion is considered as the rate-limiting step. This seems unrealistic when the argument for considering diffusion is that it is a fast process. The concentration of oxygen atoms and sulfur atoms are sufficiently greater in the dry mixture (Table V) to explain reasonably the effect of water by their diffusion ahead of the flame. However, before this can be accepted as the explanation, it must be demonstrated: (a) that their concentration ahead of the flame front by diffusion exceeds that due to local thermal effects and (b) that the particular radical in question can play a significant role in the reaction.

TABLE III

ADIABATIC FLAME TEMPERATURE AND PRODUCT DISTRIBUTION IN CARBON DISULFIDE - AIR FLAMES AS FUNCTIONS OF EQUIVALENCE RATIO

Equivalence Ratio	0.6	0.8	0.9	1.0	1.1	1.2	1.6	2.0	4.0	∞
Flame Temperature, °K	1625	1985	2150	2265	2215	2180	2070	2000	1630	713

Concentration of Products, mole-fractions

C (gr.)	-	-	-	-	-	-	-	-	-	.349
CO_2	.0402	.0557	.0611	.0603	.0377	.0347	.0402	.0483	.0805	-
SO_2	.0840	.112	.126	.139	.147	.144	.121	.0989	.0112	-
S_2	-	-	2.4×10^{-9}	9.25×10^{-7}	.00252	.00790	.0407	.0732	.201	.0482
N_2	.790	.788	.787	.785	.774	.764	.731	.701	.582	-
CO	-	.00033	.00189	.00938	.0377	.0466	.0635	.0758	.126	-
SO	-	.00001	.00006	.00050	.00337	.00322	.00298	.00238	.00012	-
S	-	-	3.50×10^{-7}	1.253×10^{-5}	.00054	.00075	.00086	.00070	.00005	.602
O_2	.0840	.0404	.0198	.00380	.00005	.00002	-	-	-	-
O	-	.00013	.00030	.00027	.00002	.00001	4.254×10^{-10}	-	-	-
NO	-	.00339	.00361	.00204	.00020	.00011	-	-	-	-

TABLE IV

ADIABATIC FLAME TEMPERATURE AND PRODUCT DISTRIBUTION IN CARBON DISULFIDE - AIR FLAMES WITH 3.1 MOLE-PERCENT WATER IN AIR AS FUNCTIONS OF EQUIVALENCE RATIO

Equivalence Ratio	0.6	1.0	1.2	2.0
Flame Temperature, °K	1585	2210	2140[a]	1940
	Concentration of Products, mole-fractions			
CO_2	.0407	.0603	.0384	.0517
SO_2	.0814	.135	.140	.0973
S_2	2.26×10^{-36}	4.81×10^{-7}	.00734	.0711
N_2	.765	.761	.740	.681
CO	-	.00723	.0406	.0691
SO	-	.00033	.00272	.00173
S	1.93×10^{-18}	6.92×10^{-6}	.00052	.00047
O_2	.0814	.00308	-	-
O	-	.00017	-	-
NO	-	.00161	-	-
H_2	-	.00066	.00515	.09640
OH	.000025	.00086	.00014	-
H	-	.00015	.00026	-
H_2O	.0310	.02967	.0247	.0211

---

[a] This temperature has been approximated and the product distribution given is for T = 2125°K.

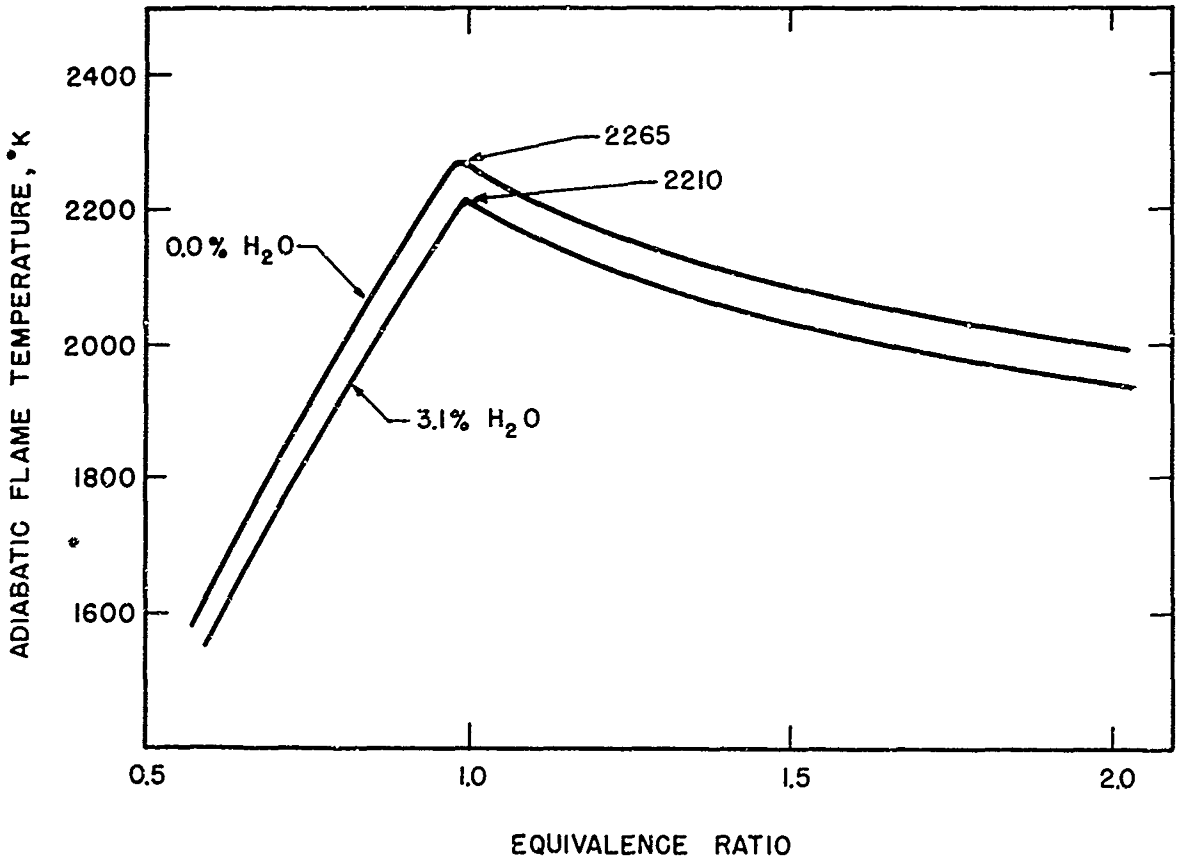

FIGURE 8. THE ADIABATIC FLAME TEMPERATURE OF CARBON DISULFIDE-AIR FLAMES

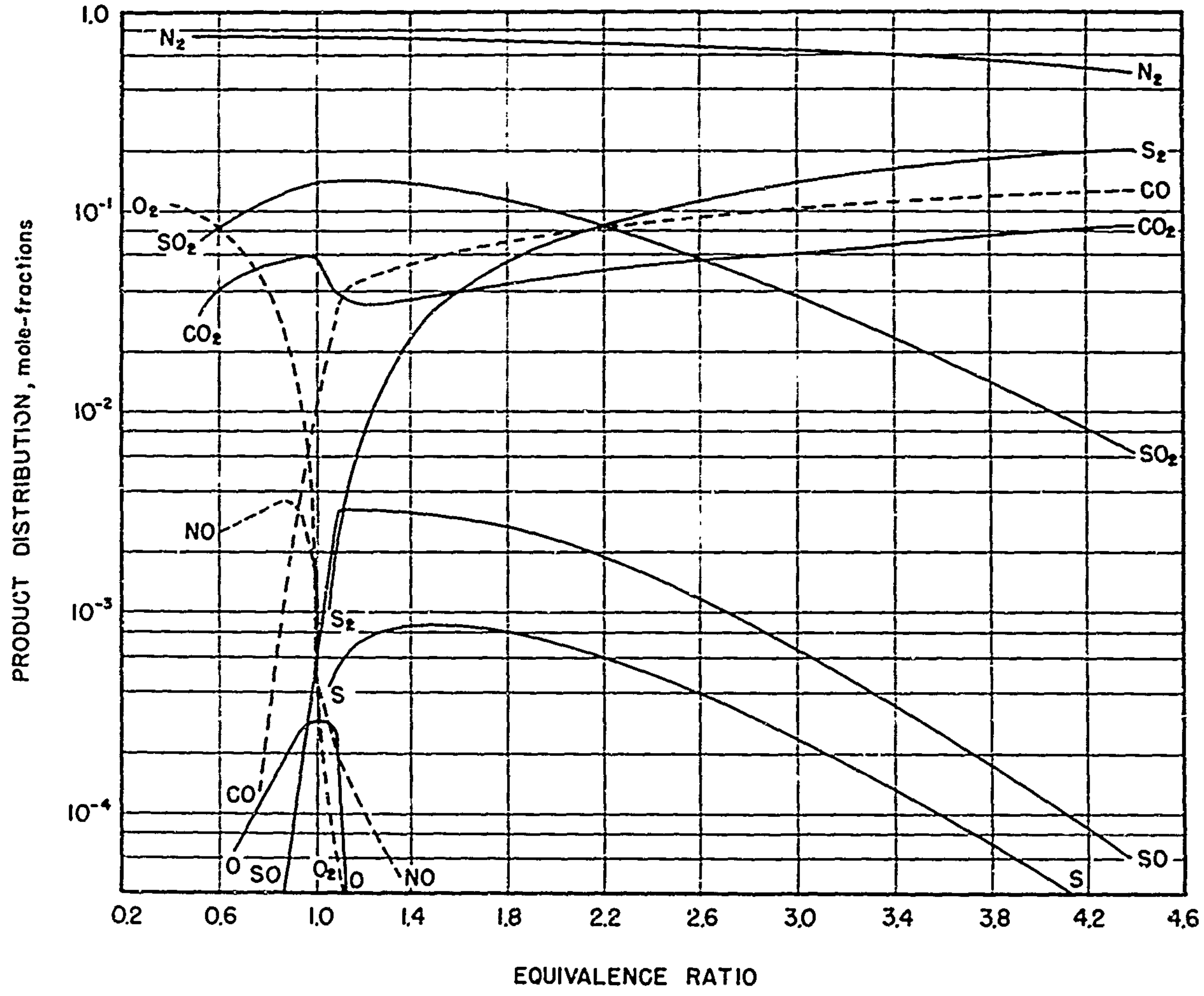

FIGURE 9. PRODUCT DISTRIBUTION IN CARBON DISULFIDE-AIR FLAMES AS A FUNCTION OF EQUIVALENCE RATIO

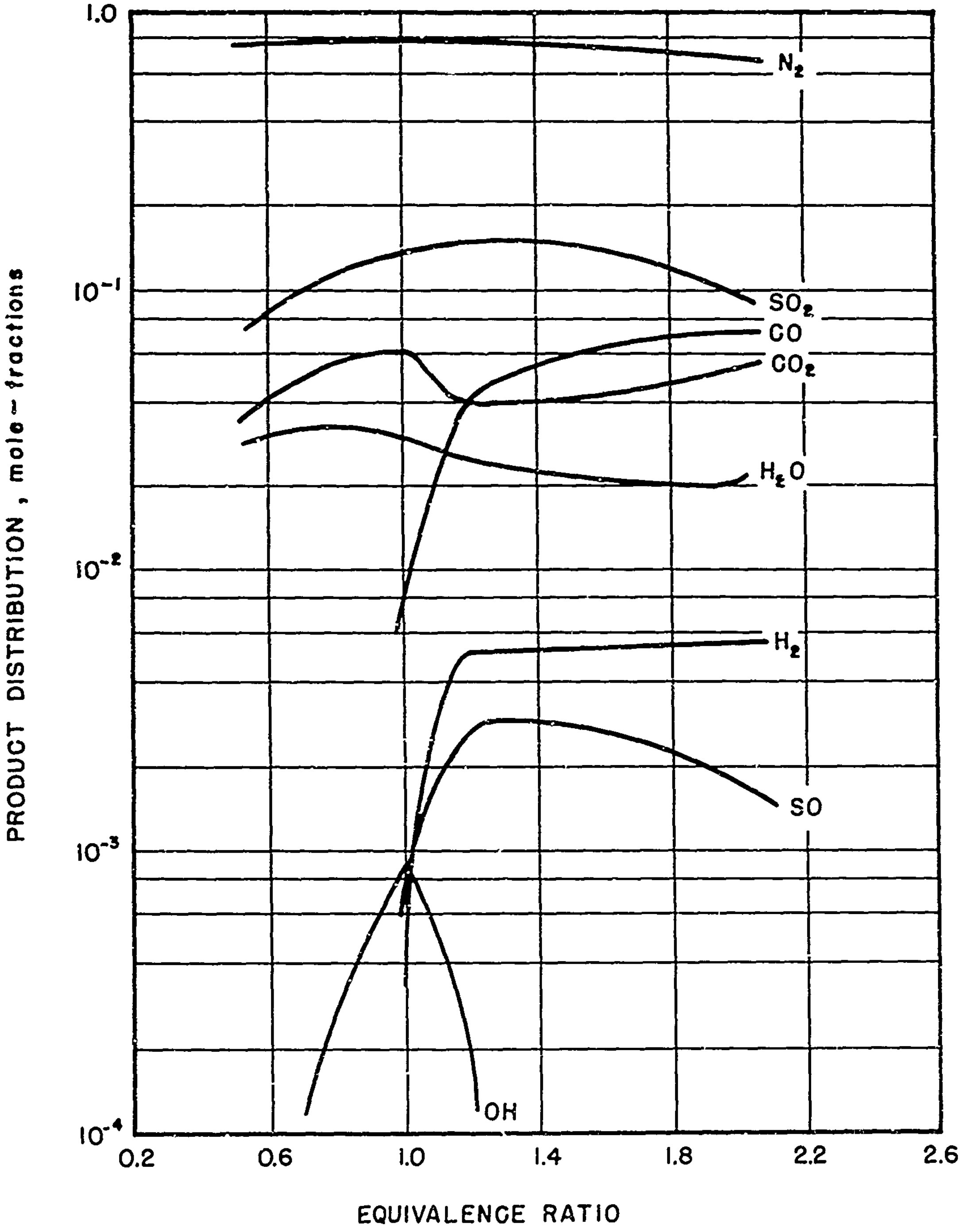

FIGURE 10. PRODUCT DISTRIBUTION IN CARBON DISULFIDE - AIR FLAMES WITH 3.1 MOLE-PERCENT WATER IN AIR AS A FUNCTION OF EQUIVALENCE RATIO

TABLE V

EFFECT OF WATER ON THE PRODUCT COMPOSITION OF A STOICHIOMETRIC CARBON DISULFIDE - AIR FLAME

Species	Ratio of Concentration in Dry Flame to Flame Containing 3.1 mole-percent H_2O	Concentration in Dry Flame, mole-fraction
S_2	1.92	9.3×10^{-7}
S	1.81	1.3×10^{-5}
O	1.59	2.7×10^{-4}
SO	1.51	5.0×10^{-4}
CO	1.30	9.4×10^{-3}
NO	1.26	2.0×10^{-3}
O_2	1.23	3.8×10^{-3}
SO_2	1.03	1.4×10^{-1}
CO_2	1.00	6.0×10^{-2}

The possibility that the effect of water is simply a thermal effect, i.e., a change in the temperature at which the reactions occur in the flame, can be considered by employing the Zeldovich, Frank-Kamentetsky, Senenov equation for a bimolecular reaction (6). When it is desired to determine the effect of temperature only, this equation can be reduced to give the ratio of burning velocity in a dry mixture, S_b (dry) to that in a wet mixture, S_b (wet):

$$\frac{S_b^2\ (\text{dry})}{S_b^2\ (\text{wet})} = \frac{T_b^4 \left[\dfrac{e^{-E/RT_b}}{(T_b - T_0)^3}\right]_{\text{dry}}}{T_b^4 \left[\dfrac{e^{-E/RT_b}}{(T_b - T_0)^3}\right]_{\text{wet}}}$$

where T_0 = temperature of unburned gas = 298°K

T_b = temperature of burned gas = 2265°K (dry) and 2210°K (wet)

E = activation energy

and "wet" indicates 3.1 mole-percent water.

If we employ an activation energy of 16 kcal/mole (1), this ratio is 1.12; and if an activation energy of 27.2 kcal/mole (7) is employed, the ratio is 1.18. The experimental ratio is greater than 60.0/50.5 = 1.19. A thermal explanation may thus be reasonable. At least it cannot be ruled out by this analysis.

The very rapid burning rates as indicated by flash back, when it was impossible to stabilize the flame, are not easily explained. They might conceivably have arisen because of a very rapid branching chain in dry carbon disulfide - air, which, in a wet mixture is inhibited by the presence of water or the products of its decomposition.

It was hoped that these rather preliminary experiments would show sufficient divergence from theory that their explanation would be apparent. This evidently is not the situation and considerably more refined experiments and analysis would be desirable.

REFERENCES

(1) J. B. Fenn and H. F. Calcote, Fourth Symposium (International) on Combustion, p. 231. Baltimore, The Williams and Wilkins Co., 1953.

(2) H. F. Calcote, C. A. Gregory, Jr., C. M. Barnett, and R. B. Gilmer, Ind. Eng. Chem., 44, 2656 (1952).

(3) H. F. Calcote and G. J. Gibbs, "Burning Velocity - Effect of Mulecular Structure," Experiment Incorporated TM-641, CF No. 2263, 1 July 1953.

(4) C. Tanford, J. Chem. Phys., 15, 433 (1947).

(5) C. Tanford and R. N. Pease, J. Chem. Phys., 15, 431, 861 (1947).

(6) N. Semenov, Uspekhi Fiz. Naut, 24, 433 (1940), translated by N.A.C.A. Tech. Mem. 1026; Ya. B. Zeldovich and N. Semenov, Zhur. Exptl. i Teoret. Fiz., 10, 1116 (1940), translated by N.A.C.A. Tech. Mem. 1084.

(7) B. P. Mullins, Fuel, 32, 481 (1953).