NASA MEMO 12-23-58E

N-25
394629

NASA MEMO 12-23-58E

NASA

MEMORANDUM

A STUDY OF OXIDATION OF HYDROGEN BASED ON FLASHBACK OF HYDROGEN-OXYGEN-NITROGEN BURNER FLAMES

By Burton D. Fine

Lewis Research Center
Cleveland, Ohio

NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION
WASHINGTON
January 1959

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MEMORANDUM 12-23-58E

A STUDY OF OXIDATION OF HYDROGEN BASED ON FLASHBACK OF HYDROGEN-OXYGEN-NITROGEN BURNER FLAMES

By Burton D. Fine

SUMMARY

The flashback of hydrogen-oxygen-nitrogen flames was studied as a function of pressure, burner diameter, equivalence ratio, and oxidant strength. The results were treated on the assumption that the product of the critical boundary velocity gradient for flashback and the initial concentration of that reactant which is not in excess is proportional to a mean reaction rate associated with the flame zone. It was further assumed that this reaction rate can be expressed in terms of initial concentrations and flame temperature.

Measurements at constant flame temperature yield orders of reaction with respect to hydrogen and oxygen. These do not vary with flame temperature. Measurements in which pressure is varied for several values of oxidant strength at constant equivalence ratio yield a total order of reaction and a function describing the dependence of the mean reaction rate on flame temperature. The total reaction order is independent of flame temperature and equal to the sum of the orders for hydrogen and oxygen. The dependence of the reaction rate on flame temperature cannot be described by a constant activation energy. The activation energy obtained apparently increases with flame temperature. Flashback results can be described by a single rate constant which is independent of equivalence ratio. Values were estimated for this rate constant as a function of flame temperature.

INTRODUCTION

The thermal concept of flame propagation predicts that the critical boundary velocity gradient for flashback should be related to the mean reaction time within the flame and should be independent of transport processes occurring through the flame zone (refs. 1 to 3). Previous studies have indicated that the exponent describing the dependence of the critical gradient on pressure is closely related to an over-all reaction

E-107

order within the flame (refs. 3 and 4). However, if one assumes that the dependence on flame temperature of the mean flame reaction rate can be described by an activation energy given in the Arrhenius form, the overall reaction order shows considerable variation with change of diluent or oxidant strength for a single fuel, or on substitution among chemically similar fuels (ref. 5).

The present study is an attempt to evaluate, through suitable flashback measurements, the various parameters in the rate expression for the hydrogen-oxygen-nitrogen flame as a function of flame temperature. In this way one might investigate, in detail, the apparent change of overall reaction order with flame temperature. The hydrogen-oxygen-nitrogen flame was chosen for several reasons. First, the flame reaction is probably the simplest among active flames involving fuel and oxygen. Second, the fact that all constituents are diatomic (and thus have similar heat capacities) makes possible many changes in proportion of constituents of the initial mixture without significant change in flame temperature. Third, flashback could be obtained over a range of pressures and burner diameters compatible with existing apparatus.

THEORETICAL BACKGROUND

The Semenov equation expresses the burning velocity as a function of rates of heat and mass transport and average rates of heat release occurring within a flame. The derivation of this equation and the assumptions involved are presented in reference 6. According to reference 7, the Semenov equation may be approximated, under certain conditions, as

$$U_b^2 = \frac{2\alpha_b\bar{\omega}_b}{a_o}\frac{\rho_b}{\rho_o} \tag{1}$$

(All symbols are defined in the appendix.) Here α_b is the thermal diffusivity associated with the flame zone, defined as $\lambda_b/c_{p,b}\rho_b$. The quantity $\bar{\omega}_b$ is a mean flame reaction rate defined as $\int_{T_o}^{T_b} \omega_b \, dT/(T_b - T_o)$. The quantity a_o may be defined by considering equation (20) of reference 6, which relates the highest temperature attained in the flame zone T_b to the amount of heat Q released by the chemical reaction. The equation is given as

$$a_oQ = \rho_o c_{p,o}(T_b - T_o) \tag{2}$$

Here Q is in molar units, but $c_{p,o}$ is the specific heat per unit mass, assumed to be constant. Thus, if T_o is constant and T_b is a maximum for nearly stoichiometric proportions of initial constituents, a_o is roughly equal to fuel concentration for lean flames and oxygen concentration for rich flames. For stoichiometric flames a_o may refer to either fuel or oxygen, provided that Q is expressed in the proper units. The proportionality between a_oQ and $T_b - T_o$ further requires that the extent of dissociation at temperatures near T_b is not too large.

The thermal quenching equation of reference 8 has the form

$$d_q^2 = \frac{FG\alpha_q a_o(\rho_q/\rho_o)}{\overline{\omega}_q} \tag{3}$$

Here the subscript q generally denotes conditions in a nearly quenched flame, and a_o has the same meaning as before. Since $\overline{\omega}_b/\overline{\omega}_q$ is very nearly constant for similar flames (ref. 7), equations (1) and (3) may be combined and simplified to give

$$\frac{U_b}{d_q} \propto \frac{\overline{\omega}_b}{a_o} \tag{4}$$

The critical boundary velocity gradient for flashback g_f is generally proportional to U_b/d_q (refs. 2 and 3). Thus, equation (4) may be written as

$$g_f a_o \propto \overline{\omega}_b \tag{5}$$

One may assume that the mean reaction rate for a hydrogen-oxygen flame reaction may be expressed in terms of a general mass-action law

$$\overline{\omega}_b = k^o a_{H_2}^m a_{O_2}^n a_x^l F(T_b) \tag{6}$$

where l, m, and n are constants. The quantity $F(T_b)$ is a function of flame temperature alone. It is apparent that equation (6) may refer to the rate of disappearance of either hydrogen or oxygen or to the rate of formation of water. At constant flame temperature equations (5) and (6) may be combined to give

$$g_f \propto a_{H_2}^{m-1} a_{O_2}^n a_x^l \tag{7}$$

for lean flames and

$$g_f \propto a_{H_2}^{m} a_{O_2}^{n-1} a_x^{l} \qquad (8)$$

for rich flames. For stoichiometric flames, either equation would apply. This result follows from the definition of a_o as the concentration in the initial mixture of the reactant which is not in excess. It also assumes that concentrations in the initial mixture can be used to describe a reaction taking place within the flame zone at flame temperature. That is, it does not account for changes in concentration due to heating or depletion of reactants caused by reaction in the flame zone. (To avoid the use of double subscripts, it is noted here that all concentrations in equations (5) and (6) and in all subsequent discussion refer to initial concentrations, unless otherwise noted.) The effect of heating may be incorporated into $F(T_b)$, but not the effect of reactant depletion. Expressions for correcting initial concentrations as a function of flame temperature and equivalence ratio are developed in reference 6. However, from results of calculations of burning velocity as a function of equivalence ratio presented in reference 9, it appears that the correction suggested in reference 6 will often overcompensate for depletion. The procedure followed here is to evaluate parameters appearing in the rate expression in terms of initial concentrations. Before conclusions are drawn based on these values, however, the effect of correcting initial concentrations for depletion is examined.

The form of equations (6) to (8) suggests the following methods based on flashback by which the various unknown parameters might be evaluated:

(1) At equivalence ratios less than unity, one might replace nitrogen by oxygen in various proportions at a constant concentration of hydrogen. This substitution should maintain nearly constant flame temperature. At constant pressure, then, $g_f \propto a_{O_2}^{n}$, provided that $l = 0$, that is, that the reaction rate does not depend on the concentration of inert gas. In that case, a plot of $\log g_f$ against $\log a_{O_2}$ should have a slope equal to n.

(2) At equivalence ratios greater than unity, one might replace nitrogen by hydrogen in various proportions at a constant concentration of oxygen. This substitution should also maintain flame temperature nearly constant and, at constant pressure, should permit determination of the order with respect to hydrogen, again provided that $l = 0$.

(3) The over-all reaction order r is defined as

$$r = l + m + n \qquad (9)$$

The relation between r and g_f may be shown by expressing equation (7) in terms of equivalence ratio as follows:

$$g_f \propto (2\varphi)^{-n} a_{H_2}^{n+m-1} a_x^{l} F(T_b) \tag{10}$$

This equation applies for lean or stoichiometric flames. If g_f is varied at constant pressure and equivalence ratio, equation (10) may be written

$$g_f \propto a_{H_2}^{r-1} a_x^{l} F(T_b) \tag{11}$$

If the reaction rate depends only on hydrogen and oxygen, $l = 0$ and equation (11) becomes

$$g_f \propto a_{H_2}^{r-1} F(T_b) \tag{12}$$

If a form for $F(T_b)$ is assumed, for example, the Arrhenius form with an assumed activation energy, equation (12) can be used to determine r in terms of the pressure exponent on g_f and known properties of the initial mixture. However, if a form cannot be assumed for $F(T_b)$, then equation (12) contains two unknowns, r and $F(T_b)$. In order to evaluate these two quantities, two independent flashback measurements are necessary. One suitable measurement would be the variation of g_f with pressure for a single initial mixture. Another measurement would be the variation of g_f at constant pressure and equivalence ratio with increasing proportion of oxygen in the oxidant mixture. By performing both measurements over a range of flame temperature, one could examine any change in r with T_b. Furthermore, comparison of r values so obtained with values obtained independently for m and n would serve as a check on the assumption that $l = 0$.

APPARATUS AND PROCEDURE

The low-pressure combustion chamber and the system for metering and mixing gases are described elsewhere (ref. 5). The main burner was a tube about 125 centimeters long which had a diameter of 1.89 centimeters. It was water-cooled near the lip. Burner diameter was varied by using inserts with inside diameters of 0.928, 1.016, and 1.459 centimeters. For flashback measurements a stable flame was established first. Then pressure was increased slowly at constant mass flow until the flame flashed back. Wherever it was possible, flashback was obtained with normal laminar flames. However, where the initial mixture contained 29.6 percent hydrogen at equivalence ratios less than 1, flames were unsteady and polyhedral, and flashback was obtained under turbulent conditions.

Tank hydrogen (98 to 99 percent H_2) was used as fuel. Oxidant mixtures having various nitrogen-oxygen ratios were generally prepared by metering the flow of tank nitrogen and oxygen separately and allowing the two gases to mix. Two oxidant mixtures (one 35 percent oxygen and 65 percent nitrogen, the other 50 percent oxygen and 50 percent nitrogen) were specially prepared and available in tanks. All materials were used without further purification.

TREATMENT OF DATA

Reduction of Data

For laminar flames g_f was computed from

$$g_f = 8\overline{U}_f/d \tag{13}$$

(ref. 10). For turbulent flames the expression

$$g_f = 0.023 \frac{\overline{U}_f}{d} Re_f^{0.8} \tag{14}$$

was used (ref. 10) where Reynolds number of flashback is defined as

$$Re_f = \overline{U}_f d\rho/\mu \tag{15}$$

The density was computed on the assumption that the gases were ideal. The viscosity was estimated from plots of viscosity as a function of composition (ref. 11) for hydrogen-nitrogen and hydrogen-oxygen mixtures.

Effect of Burner Diameter

If g_f is to serve as a measure of a time associated with the flame reaction, it must be independent of burner diameter. In the present experiments, this condition held for all burners used, provided the oxidant strength ψ was less than 0.5. For $\psi \geq 0.5$, however, critical flashback gradients for the two smallest burners (1.016 and 0.928 cm in diam.) were considerably smaller than those obtained with the two largest burners. This effect did not depend on the material of which the burner was made or the mechanical condition of the burner lip.

A review of past flashback experiments performed with the present experimental arrangement shows that this deviation follows a trend previously observed. Thus, for flames having burning velocities in the range 200 to 300 centimeters per second (hydrogen-air and propane-oxygen-nitrogen mixtures with $\psi = 0.5$) burners 1.89 to 0.55 centimeter in diameter gave consistent flashback gradients; a burner 0.3 centimeter in diameter caused flashback at much lower values of g_f. For flames having burning velocities of about 400 centimeters per second (propane-oxygen and ethylene-oxygen-nitrogen mixtures with $\psi = 0.5$), a burner 0.55 centimeter in diameter tended to deviate to lower values of g_f. Thus, the present deviation by a 1-centimeter burner seems to be associated with burning velocities of about 600 centimeters per second or larger.

The cause of this decrease in g_f is not presently known. The deviation is favored by high burning velocities and small diameters; it is probably peculiar to the present apparatus, since such an effect has not been previously reported. The procedure followed here is to ignore those results obtained in 1-centimeter burners which show deviation toward small g_f values.

Other slight deviations, associated with low Reynolds numbers, are shown as dotted lines in figure 1(a). These had been observed previously (ref. 3) and attributed to partial quenching of the flame by the cooled wall.

RESULTS AND DISCUSSION

General Description of Results

Critical boundary velocity gradients for flashback are shown as functions of pressure within the combustion chamber in figures 1 and 2. Results are shown for various values of burner diameter and initial composition. Since the initial gas mixtures contain three components in generally varying proportions, two quantities must be specified to define the composition. Those chosen are the equivalence ratio

$$\varphi = \frac{X_{H_2}}{X_{O_2}} \Bigg/ \left(\frac{X_{H_2}}{X_{O_2}}\right)_{\text{stoich}} \tag{16}$$

and the oxidant strength

$$\psi = \frac{X_{O_2}}{X_{O_2} + X_{N_2}} \tag{17}$$

Values of g_f for stoichiometric hydrogen-air flames shown as dashed lines in figures 1(c), 1(d), and 2 are based on previously reported measurements, which were obtained near an equivalence ratio of 1 (ref. 4).

Thus, the dashed lines represent an interpolation between $\varphi = 0.95$ and $\varphi = 1.10$ for laminar flames and $\varphi = 0.95$ and $\varphi = 1.20$ for turbulent flames (ref. 12).

All flame temperatures discussed are calculated equilibrium temperatures obtained by the method of reference 13. They are based on a single set of thermochemical data and are therefore consistent among themselves. In general, slopes with respect to pressure have been estimated by eye. If least-square methods were used, certain points would have had to be arbitrarily weighted and others disregarded, particularly at low Reynolds numbers, where quenching may have affected the data, and at high Reynolds numbers, where instability in the flow may have affected the results. Accordingly, the second decimal place in the pressure slopes probably has little physical significance. However, it was retained through subsequent calculations.

Results at Constant Flame Temperature

Results near 2580° K. - As discussed in the section THEORETICAL BACKGROUND, the individual contributions of fuel and oxygen to the overall order of reaction can be determined from the change in the critical flashback gradient with change in the fuel or oxygen concentration in the original mixture at constant pressure and flame temperature. The approach outlined in that section has been applied in the following way. A stoichiometric flame having an oxidant strength of 0.35 and a calculated flame temperature of about 2560° K at a pressure of 15 centimeters of mercury was chosen as an experimentally convenient reference. The change of g_f with pressure for this flame was determined. Then, similar measurements were made on mixtures obtained from the reference mixture by replacing nitrogen by oxygen at constant hydrogen concentration. All such lean mixtures have flame temperatures equal to about 2560° K at a pressure of 15 centimeters of mercury. One may also replace nitrogen by hydrogen at constant oxygen concentration. If the reference stoichiometric flame is again taken to be that for which $\psi = 0.35$, all rich mixtures obtained by such substitution will have flame temperatures calculated to be about 2620° K at 15 centimeters of mercury. Thus, values for the order with respect to fuel and oxygen determined in this way refer to flame temperatures which differ by about 60° K.

Flashback results for flames at these temperatures are shown in figures 1(a) and (b). The variation in flame temperature with pressure over the range of pressures for which data were obtained is less than the difference between calculated temperatures on the lean and rich sides and need not be considered. On the lean side (fig. 1(a)) the concentration of hydrogen is kept constant at 41.0 percent. On the rich side (fig. 1(b)), an oxygen concentration of 20.5 percent is maintained. Since $d \ln g_f / d \ln P$ is constant, within experimental uncertainty, for lean, stoichiometric, and rich flames, the temperature difference of 60° K between the lean and rich side is not significant. The fact that $d \ln g_f / d \ln P$ is constant permits cross plots of g_f against fuel concentration for lean flames at constant pressure with reasonable assurance that results so obtained will be independent of pressure. Such cross plots are shown on the right in figures 1(a) and (b). It is seen that $\log g_f$ is linear in $\log X_{O_2}$ or $\log X_{H_2}$.

The fact that $(\partial \log g_f / \partial \log a_{O_2})_{a_{H_2}}$ is constant indicates that the dependence of the reaction rate on the concentration of inert gas is zero. By logarithmic differentiation of equation (7) at constant hydrogen concentration, one obtains

$$\left(\frac{\partial \log g_f}{\partial \log a_{O_2}}\right)_{a_{H_2}} = n + l\left(\frac{\partial \log a_x}{\partial \log a_{O_2}}\right)_{a_{H_2}} \tag{18}$$

The value of $(\partial \log a_x / \partial \log a_{O_2})_{a_{H_2}}$ is sufficiently large and sufficiently variable that l must be very close to zero for the exponential dependence of g_f on oxygen concentration to appear constant. A similar argument, based on equation (8), applies for the apparent constancy of m. The results of the cross plots at constant pressure give $n = 0.92$ at pressures of 15 and 11 centimeters of mercury and $m = 1.37$ at 13 centimeters of mercury. The calculations are summarized in table I. The sum of m and n is about 2.29, which agrees rather well with values for the over-all reaction order for the hydrogen-air flame obtained from measurements of flashback, burning velocity, and quenching distance (refs. 4 and 14).

Results near 2300° K. - It is of interest to repeat the measurements described in the preceding section under conditions yielding significantly different values of flame temperature. This should give some information regarding the behavior of individual and over-all reaction orders with changes in flame temperature. It was not feasible to work at flame temperatures much above 2600° K; therefore, measurements were made at lower flame temperatures. The stoichiometric hydrogen-air flame, having a calculated temperature of 2348° K at a pressure of 1 atmosphere, was chosen as a reference. Results are shown in figures 1(c) and (d) and summarized in table I.

For rich flames flashback followed a normal course. A cross plot of $\log g_f$ against $\log a_{H_2}$ at 14.8 percent oxygen and $P = 19$ centimeters of mercury gave $m = 1.39$, a result in excellent agreement with that obtained near 2580° K. On the lean side, however, flames of 29.6 percent hydrogen were polyhedral in shape and unsteady and displayed a regular spinning motion. The relation between g_f and P observed for such flames was complicated and clearly unrelated to the flame reaction. Therefore, the attempt was made to obtain values of m and n on the lean side for mixtures containing 29.6 percent hydrogen by observing the flashback of turbulent flames. Previous studies on the flashback of turbulent flames had indicated that critical boundary velocity gradients for laminar and turbulent flashback differ by a factor that is independent of pressure and nearly the same for all systems studied (refs. 3 and 12). Thus, one should obtain the same values of m, n, and l regardless of whether measurements are based on laminar or turbulent flashback. Furthermore, since turbulent flashback seems to be controlled by processes taking place in a nearly laminar portion of the turbulent boundary layer, results obtained from turbulent flashback should apply at the temperature of the corresponding laminar flame, even though the space-average temperature of the turbulent flame might be somewhat lower.

Accordingly, results are shown in figure 1(d) for air (interpolated for $\varphi = 1$ from the data of ref. 12) and for mixtures with $\psi = 0.35$ and 0.50. Calculated flame temperatures for this series of lean flames were nearly constant, but the value for lean flames was about 60° K lower than that for the reference stoichiometric flame (see table I). However, as shown on the right side of figure 1(d), all three points fall on the same straight line. The slope has a value of about 0.92, in agreement with the value for n found at the higher flame temperature.

Comparison of results based on initial and effective concentrations. - According to the Semenov theory, the concentrations which affect the flame reaction rate are effective concentrations in the flame zone. Expressions for these effective concentrations are given in reference 9. However, in figure 1, flashback gradients are plotted as functions of initial concentrations. It is important, then, to see how the results would look in terms of concentrations corrected by the expressions given in reference 9. For a hydrogen-oxygen-inert gas flame the relation between a_{O_2} and $a^*_{O_2}$ can be expressed approximately as

$$a^*_{O_2} = \left(\frac{T_o}{T_b}\right)\left[a_{O_2} + \left(\frac{a_{O_2}}{a_{H_2}}\right)_{stoich}(\delta - 1)a_{H_2}\right] \tag{19}$$

for $\varphi < 1$. An equation symmetrical in a_{O_2} and a_{H_2} would apply for $\varphi > 1$. The quantity δ is a constant whose order of magnitude is given by $(RT_b^2/E_{act})/(T_b - T_o)$. According to reference 6, the value of this quantity should not exceed 0.1 for the assumptions in the theory to be justified. Therefore, it will be assumed that $\delta = 0.1$, even though the value of E_{act} which follows from this assumption, about 50 kilocalories, is rather large compared with other values of E_{act} estimated from flame properties. If one defines an effective mole fraction as $X^* = a^* (RT_b/P)$, one may use equation (1) to relate initial and effective mole fractions at constant pressure and flame temperature. For lean flames, one obtains

$$X_{O_2}^* = X_{O_2} - 0.45\ X_{H_2} \qquad (20)$$

and for rich flames

$$X_{H_2}^* = X_{H_2} - 1.80\ X_{O_2} \qquad (21)$$

One may evaluate $X_{O_2}^*$ and $X_{H_2}^*$ from data given in table I.

Figure 3 shows plots of $\log g_f$ against $\log X_{O_2}^*$ and $\log H_2^*$ under the same conditions as in figures 1(a) and (b). Results in terms of X^* are considerably more complex than in terms of X. Both m and n are considerably less than 1 and are strongly dependent on X^*. Consequently, no simple relation exists among m, n, and r. There is no prior reason for rejecting results in terms of X^* in favor of those in terms of X. However, if one accepts results in terms of X^* as valid, one cannot use them to develop a conventional mass-action expression. In order to develop such an expression from flashback data, one must assume that the expressions for effective concentrations given in reference 9 overcorrect for depletion of reactants and that initial concentrations are a more satisfactory approximation to true effective concentrations.

Results at Constant Equivalence Ratio

Figure 2 shows g_f plotted against chamber pressure at a constant equivalence ratio of 1 for varying values of oxidant strength. The slopes of the lines increase slightly but significantly with increasing ψ. This increase is of the same order of magnitude as that previously observed for hydrocarbon-oxygen-inert gas flames (ref. 3). One may relate the slopes to the reaction order r by differentiating equation (12) logarithmically with respect to pressure at constant ϕ and ψ:

$$\frac{d \ln g_f}{d \ln P} = r - 1 + \frac{\partial \ln F(T_b)}{\partial \ln T_b} \frac{d \ln T_b}{d \ln P} \qquad (22)$$

As a first approximation on $F(T_b)$ one may assume that the dependence of the rate of the flame reaction on flame temperature is a simple exponential function which can be described by a constant activation energy. For this model, which is discussed in references 3, 4, and 14, one may write equation (22) in the form

$$\frac{d \ln g_f}{d \ln P} = r' - 1 - \frac{E_{act}}{2R}\left(\frac{1}{T_b} + \frac{1}{T_q}\right)\frac{d \ln T_b}{d \ln P} \tag{23}$$

and evaluate an approximate reaction order r'. For consistency with previous applications of equation (23), an activation energy of 23 kilocalories per mole was assumed for the hydrogen-oxygen flame reaction. The flame temperature was related to T_q, the temperature of a nearly quenched flame, by

$$T_q = 0.8\ T_b + 0.2\ T_o \tag{24}$$

(ref. 7). Values of $d \ln T_b/d \ln P$ are based on flame temperatures calculated at pressures of 1 and 0.1 atmosphere.

Values of r' based on equation (23) are shown in table II. It can be seen that the apparent reaction order increases with flame temperature and that the value of r' for $\psi = 0.35$ is significantly greater than the value of the over-all order previously determined as the sum of orders for hydrogen and oxygen. These two factors suggest that the assumption of a simple exponential dependence of the flame reaction rate on flame temperature is inadequate, at least for the hydrogen-oxygen flame reaction.

However, if $F(T_b)$ is treated as an unknown function, the data plotted in figure 2 can be used along with values of the approximate reaction order r' to determine the form of $F(T_b)$ and evaluate its dependence on flame temperature. With this information, equation (22) can be used to compute a better approximation to the over-all reaction order at various flame temperatures. The procedure is outlined in the section THEORETICAL BACKGROUND and is based on the fact that, as shown by equation (12), $g_f/a_{H_2}^{r-1}$ is a function of flame temperature alone if equivalence ratio is held constant. A plot of log $(g_f/X_{H_2}^{r'-1})$ against $1/T_b$ is shown in figure 4 for a constant pressure of 15 centimeters of mercury and a constant equivalence ratio of 1. This quantity should be proportional to $F(T_b)$. The plot shows considerable curvature, which supports the previous suggestion that the dependence of the reaction rate on flame temperature could not be described by a constant activation energy, at least for the present flame system. One may obtain approximate values of $\partial \ln F(T_b)/\partial(1/T_b)$ for various values of T_b from the slopes of tangents drawn to the dotted curve in figure 4. The actual slopes must be multiplied by $-0.434/T_b$ to give $\partial \ln F(T_b)/\partial \ln T_b$. These values may be used in equation (22) to recompute a set of better approximations to r. The results of this calculation are shown in the first column on the right in table II. The values obtained scatter between 2.15 and 2.34; they show no significant trend with flame temperature, in contrast with the set of r' values. Of course, the accuracy of this calculation is not very high, since it depends on evaluations of derivatives from a curve which is itself not especially well defined by experimental data. However, the results suggest that, within the relatively large experimental error, the reaction order has a value of about 2.2 or 2.3 independent of flame temperature. This agrees well with the value of about 2.3 obtained from the determination of individual orders at constant flame temperature. One may use this value in equation (12) and compute a second approximation to $F(T_b)$. This is shown as the solid line in figure 4. The two sets of data points define curves which are similar in shape and position. Specifically, the curvature in the plot of $\log F(T_b)$ against $1/T_b$ is not sensitive to assumptions made regarding the reaction order.

It should be noted that results for hydrogen-argon-"air" flames (ref. 3) shown in table II and plotted in figure 4 are in satisfactory agreement with values for corresponding hydrogen-oxygen-nitrogen flames. This is a further indication that the nature of the diluent does not affect the course of the hydrogen oxidation at these temperatures.

Comparison of Results for Lean and Rich Flashback at Constant Flame Temperature

For the several curves plotted in figures 1(a) and (b), both oxygen concentration and equivalence ratio are varied. Therefore, the data plotted in these figures may be further cross-plotted as a function of equivalence ratio at constant pressure. Such a cross plot is shown in figure 5 for a pressure of 13 centimeters of mercury. The curve consists of a lean and a rich branch and has a minimum at an equivalence ratio of 1. The lean branch corresponds to a flame temperature of about 2540° K, whereas the rich branch represents a temperature of about 2620° K. The curve as a whole is not significantly different from that which would be obtained for a single flame temperature of about 2580° K. Thus, it is analogous to plots of mass burning velocity against equivalence ratio at constant flame temperature that are presented in references 15 and 16. The fact that the curve in figure 5 goes through a minimum at an equivalence ratio of 1 reflects the fact that the concentration product portion of the rate expression in terms of initial concentrations goes through a minimum for a stoichiometric initial mixture.

Figure 5 shows that g_f is a double-valued function of equivalence ratio. If g_f measures a reaction time, then one should be able to describe lean and rich branches by the constants $\varkappa_l$ and $\varkappa_r$, respectively, which are related to the specific rate constant for the reaction between hydrogen and oxygen. On the lean side one may assume a relation of the form

$$g_f a_{H_2} = \varkappa_l a_{H_2}^m a_{O_2}^n \tag{25}$$

and on the rich side

$$g_f a_{O_2} = \varkappa_r a_{H_2}^m a_{O_2}^n \tag{26}$$

The constants $\varkappa_l$ and $\varkappa_r$ are most easily computed from equations (25) and (26) by use of the cross plots shown on the right in figures 1(a) and (b). Thus, in terms of mole fractions equation (25) may be solved for $\varkappa_l$ to give

$$\varkappa_l = \frac{g_f}{X_{H_2}^{m-1} X_{O_2}^n}\left(\frac{RT_o}{P}\right)^{m+n-1} \tag{27}$$

and equation (26) becomes

$$\varkappa_r = \frac{g_f}{X_{H_2}^m X_{O_2}^{n-1}}\left(\frac{RT_o}{P}\right)^{m+n-1} \tag{28}$$

Using any convenient sets of g_f values from figures 1(a) and (b), one obtains $\varkappa_l = 9.1\times10^6$ and $\varkappa_r = 4.3\times10^6$. Thus $\varkappa_l$ is about twice as great as $\varkappa_r$. From the data of figures 1(a) and (b) it is easily seen that the product $a_{H_2}^m a_{O_2}^n$ for a given value of g_f on the lean side equals $a_{H_2}^m a_{O_2}^n$ for the same value of g_f, on the rich side at constant pressure and flame temperature. Thus, the observation that $\varkappa_l/\varkappa_r$ is about 2 is consistent with the fact that the steady rate of consumption of hydrogen, which is proportional to $g_f a_{H_2}$, is twice the rate of consumption of oxygen, which is proportional to $g_f a_{O_2}$.

Calculation of Specific Rate Constant for Hydrogen-Nitrogen-Oxygen Flame Reaction

One may define a rate constant by the expression

$$k(T) = \varkappa/\beta \tag{29}$$

where β is a constant. The variation of k with T should be represented by the best approximation to $F(T_b)$ given in figure 4. It is apparent that in order to evaluate $k(T)$ one must know β or must be able to calculate β from a known value of $-da_{H_2}/dt$, the average rate of consumption of hydrogen in the flame. A calculation of $-da_{H_2}/dt$ is made in reference 7 for a stoichiometric hydrogen-air flame at a pressure of 1 atmosphere. This calculation, based on burning velocity and quenching distance, gave a value of 169 moles per liter per second. The value of g_f for a stoichiometric hydrogen-air flame is known to be about 8500 second^{-1} at 1 atmosphere (refs. 4 and 10). Therefore, one may use the relation

$$g_f a_{H_2} = -\beta \frac{da_{H_2}}{dt} \tag{30}$$

to evaluate β. A value of 0.60 is obtained. Since β is a constant independent of temperature and pressure, one may use it in equation (29) along with the value for $\varkappa_l$ determined in the previous section to obtain the result $k(2580) = 1.46\times10^{7}\ (\text{moles}^{1.3})(\text{liters}^{-1.3})(\text{sec}^{-1})$. If the dependence of the reaction rate on flame temperature is given by the best approximation to the quantity proportional to $F(T_b)$ shown in figure 4, then one should be able to write

$$k(T) = k^{o}F(T_b) \tag{31}$$

If one solves equation (31) for k^{o} in terms of $k(2580)$ and $F(2580)$ one obtains $k^{o} = 1.55\times10^{3}$. One may then plot $k(T)$ as a function of T_b. Such a plot is shown as a solid line in figure 6.

It is possible to obtain values of k over a range of flame temperature by a different method. First, one may evaluate k for a stoichiometric hydrogen-air flame by

$$\frac{-da_{H_2}}{dt} = k(2348)a_{H_2}^{1.38}a_{O_2}^{0.92} \tag{32}$$

This gives $k(2348) = 0.66\times10^{7}$. One may then extrapolate each of the curves in figure 2 to a pressure of 1 atmosphere and estimate values of $-da_{H_2}/dt$ by assuming a relation of the form

$$\frac{\left[g_f(1\ \text{atm})a_{H_2}\right]_2}{\left[g_f(1\ \text{atm})a_{H_2}\right]_1} = \frac{(da_{H_2}/dt)_{2,1\ \text{atm}}}{(da_{H_2}/dt)_{1,1\ \text{atm}}} \tag{33}$$

where the subscripts denote any two values of oxidant strength. Insertion of resulting values of $-da_{H_2}/dt$ into equation (32) gives k as a function of T_b. These results are shown as the dotted curve in figure 6.

The agreement between the two curves is satisfactory, considering the many possibilities for systematic error involved in their determination. It is difficult to decide which of the two is preferable. The dotted curve involves several long extrapolations of low-pressure data up to 1 atmosphere. The solid curve assumes that β is independent of flame temperature, an assumption which cannot be checked by use of existing data.

SUMMARY OF RESULTS

The flashback of hydrogen-oxygen-nitrogen flames has been measured at reduced pressures as a function of burner diameter, pressure, equivalence ratio, and oxidant strength. On the basis of a treatment which assumed the critical boundary velocity gradient for flashback to be a measure of a mean flame reaction time, the following conclusions were drawn:

1. The order of the flame reaction with respect to hydrogen is about 1.4, independent of flame temperature.

2. The order of the flame reaction with respect to oxygen is about 0.9, independent of flame temperature.

3. The total order of reaction is independent of flame temperature and equal to the sum of the orders with respect to hydrogen and oxygen.

4. The variation of flame reaction rate with flame temperature cannot be described by a constant activation energy.

5. From relations among flashback, burning velocity, and quenching distance, a specific rate constant for the flame reaction can be estimated as a function of flame temperature.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, October 1, 1958

APPENDIX - SYMBOLS

a	concentration, moles/liter
c_p	specific heat, cal/(g)($^{\circ}$K)
d	burner diameter, quenching distance, cm
E_{act}	activation energy, kcal/mole
F	dimensionless coefficient, $(T_q - T_o)/(T_b - T_o)$
G	dimensionless geometric factor
g	critical boundary velocity gradient, sec^{-1}
k	specific rate constant, (moles$^{-1.3}$)(liters$^{-1.3}$)(sec^{-1})
l	exponential dependence of reaction rate on concentration of inert constituents, dimensionless
m	exponential dependence of reaction rate on hydrogen concentration, dimensionless
n	exponential dependence of reaction rate on oxygen concentration, dimensionless
P	pressure, atm or cm Hg
Q	heat of reaction, cal/mole
R	gas constant, cal/(mole)($^{\circ}$K) or (liters)(atm)/$^{\circ}$K
Re	Reynolds number, dimensionless
r	total reaction order, dimensionless
T	temperature, $^{\circ}$K
t	time, sec
$\bar{U}$	mean stream velocity, cm/sec
U_b	burning velocity, cm/sec
X	mole fraction
α	thermal diffusivity, cm^2/sec
β	dimensionless coefficient

δ	dimensionless additive term
$\varkappa$	rate constant in terms of flashback
λ	thermal conductivity, cal/(sec)(cm)(^{o}K)
μ	viscosity, poises
ρ	density, g/cm^3
φ	equivalence ratio, dimensionless
ψ	oxidant strength, dimensionless
ω	reaction rate, moles/(liter)(sec)

Subscripts:

b	normal flame
f	flashback
H_2	hydrogen
N_2	nitrogen
O_2	oxygen
o	initial conditions
q	quenched flame
r,l	rich and lean equivalence ratios
x	chemically inert constituents of original mixture

Superscripts:

$-$	mean value
o	independent of temperature
'	first approximation
*	corrected for depletion of reactants

REFERENCES

1. Wohl, Kurt, Kapp, Numer M., and Gazley, Carl: The Stability of Open Flames. Third Symposium on Combustion and Flame and Explosion Phenomena, The Williams & Wilkins Co., 1949, pp. 3-21.

2. Berlad, A. L., and Potter, A. E.: Relation of Boundary Velocity Gradient and Flash-Back to Burning Velocity and Quenching Distance. Combustion and Flame, vol. 1, no. 1, Mar. 1957, pp. 127-128.

3. Fine, Burton: Stability Limits and Burning Velocities for Some Laminar and Turbulent Propane and Hydrogen Flames at Reduced Pressure. NACA TN 4031, 1957.

4. Fine, Burton: Stability Limits and Burning Velocities of Laminar Hydrogen-Air Flames at Reduced Pressures. NACA TN 3833, 1956.

5. Fine, Burton: The Flashback of Laminar and Turbulent Burner Flames at Reduced Pressure. Combustion and Flame, vol. 2, no. 3, Sept. 1958, pp. 253-266.

6. Semenov, N. N.: Thermal Theory of Combustion and Explosion. III - Theory of Normal Flame Propagation. NACA TM 1026, 1942.

7. Potter, A. E., Jr., and Berlad, A. L.: A Relation Between Burning Velocity and Quenching Distance. NACA TN 3882, 1956.

8. Potter, A. E., Jr., and Berlad, A. L.: A Thermal Equation for Flame Quenching. NACA Rep. 1264, 1956. (Supersedes NACA TN 3398.)

9. Dugger, Gordon L., and Simon, Dorothy M.: Prediction of Flame Velocities of Hydrocarbon Flames. Fourth Symposium (International) on Combustion, The Williams & Wilkins Co., 1953, pp. 336-345.

10. Lewis, Bernard, and von Elbe, Guenther: Combustion, Flames and Explosions of Gases. Academic Press, Inc., 1951, p. 279.

11. Rubin, F. L.: Finding the Properties of Hydrogen Mixtures. Petroleum Refiner, vol. 35, no. 3, 1956, pp. 140-149.

12. Fine, Burton: Further Experiments on the Stability of Laminar and Turbulent Flames at Reduced Pressures. NACA TN 3977, 1957.

13. Huff, Vearl N., Gordon, Sanford, and Morrell, Virginia E.: General Method and Thermodynamic Tables for Computations of Equilibrium Composition and Temperature of Chemical Reactions. NACA Rep. 1037, 1951. (Supersedes NACA TN's 2113 and 2161.)

14. Potter, A. E., Jr., and Berlad, A. L.: The Effect of Fuel Type and Pressure on Flame Quenching. Sixth Symposium (International) on Combustion, Reinhold Pub. Corp., 1957, pp. 27-36.

15. Botha, J. P., and Spalding, D. B.: The Laminar Flame Speed of Propane Air Mixtures with Heat Extraction from the Flame. Proc. Roy. Soc. (London), ser. A, vol. 195, no. 1160, Aug. 6, 1954, pp. 71-95.

16. Heimel, Sheldon: Effect of Initial Mixture Temperature on Burning Velocity of Hydrogen-Air Mixtures with Preheating and Simulated Preburning. NACA TN 4156, 1957.

TABLE I. - INDIVIDUAL REACTION ORDERS

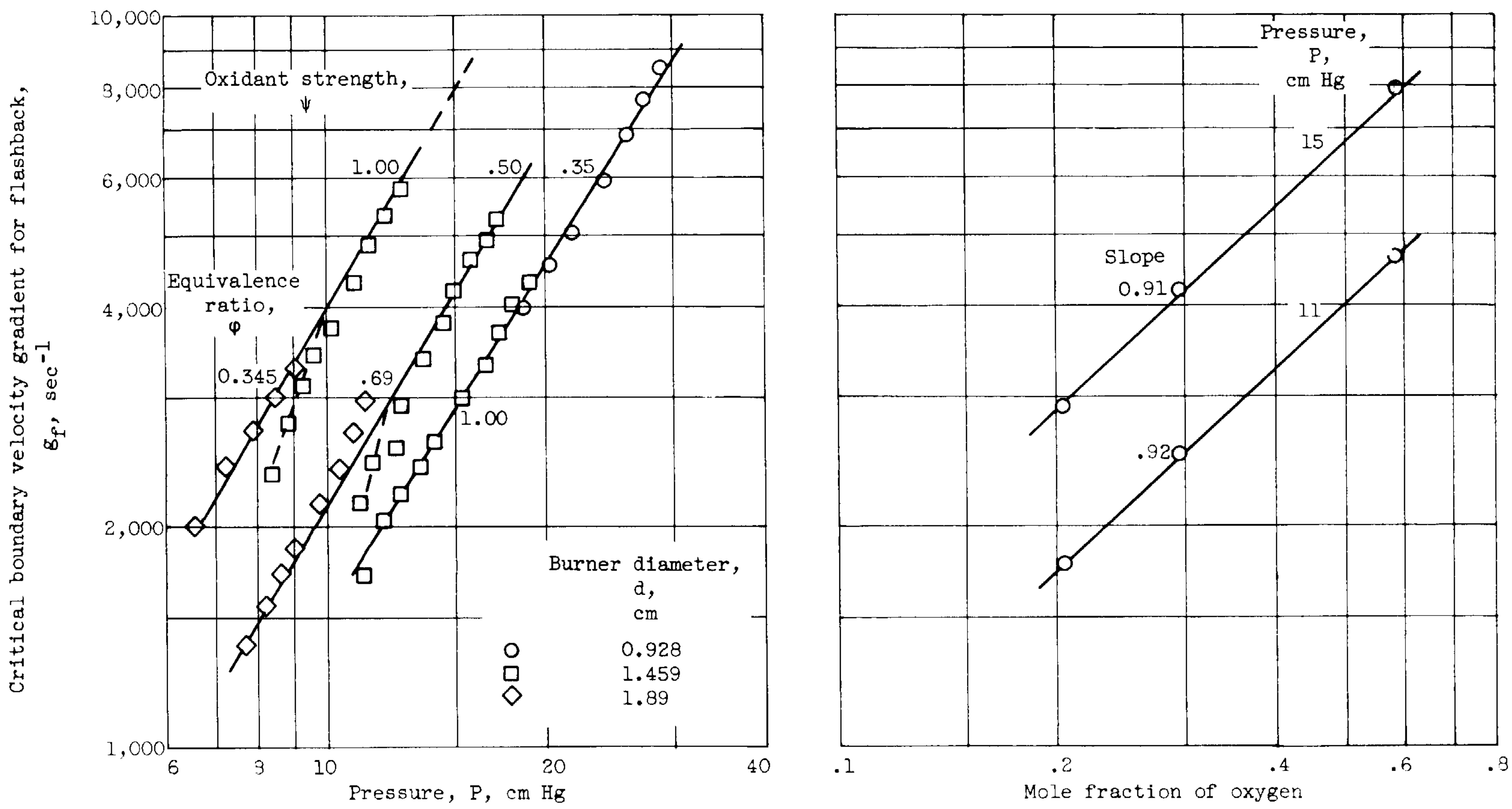
Temperature, T, °K	Equivalence ratio, φ	Oxidant strength, ψ	Pressure, P, cm Hg	Critical boundary velocity gradient for flashback, g_f, sec^{-1}	Dependence of reaction rate on hydrogen concentration, m	Dependence of reaction rate on oxygen concentration, n	Hydrogen concentration, percent	Oxygen concentration, percent
2300 2290 2270	1.00 .60 .40	0.21 .35 .50	25 ↓	[a]6,000 [a]9,000 [a]13,300		0.92 ↓	29.6 ↓	14.8 24.6 35.5
2300 2360 ↓	1.00 1.20 1.40 1.60	0.21 .229 .250 .281	19 ↓	1,570 2,100 2,590 2,995	1.37 ↓		29.6 36.5 41.8 47.5	14.8 ↓
2560 2560 2510	1.00 .69 .345	0.35 .50 1.00	15 ↓	2,900 4,200 8,000		0.92 ↓	41.0 ↓	20.5 29.5 59
2560 2620 ↓	1.00 1.22 1.44 1.59	0.35 .40 .493 .585	13 ↓	2,250 3,130 3,900 4,750	1.39 ↓		41.0 50.0 58.5 65.0	20.5 ↓

[a] Turbulent flames.

TABLE II. - DETERMINATION OF OVER-ALL REACTION ORDER FROM FLASHBACK OF STOICHIOMETRIC HYDROGEN-OXYGEN-NITROGEN FLAMES

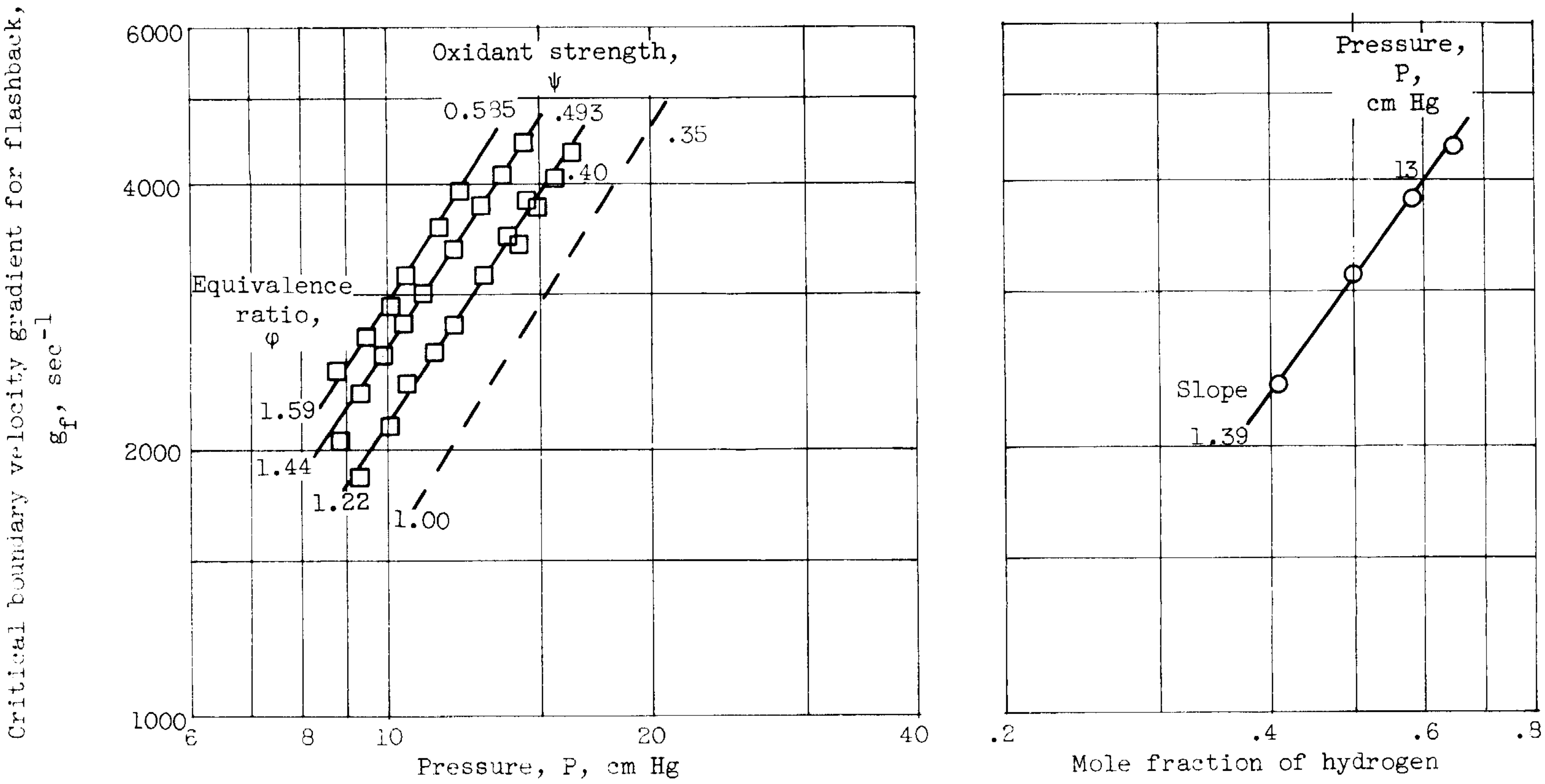
Oxidant strength, ψ	Mole fraction of hydrogen, X_{H_2}	Flame temperature, T_b, °K, 1 atm	$\frac{d \ln T_b}{d \ln P}$	$\frac{d \ln g_f}{d \ln P}$	Total reaction order	
					r'	r
0.21	0.296	2348	0.017	1.33	2.25	2.26
[a].21	[a].296	[a]2590	[a].027	[a]1.51	[a]2.38	[a]2.31
.28	.365	2570	.025	1.54	2.41	2.34
.35	.411	2683	.030	1.55	2.41	2.17
.50	.500	2834	.034	1.72	2.57	2.15
.70	.583	2936	.040	1.79	2.62	2.16

[a] Nitrogen in air replaced by argon or helium.



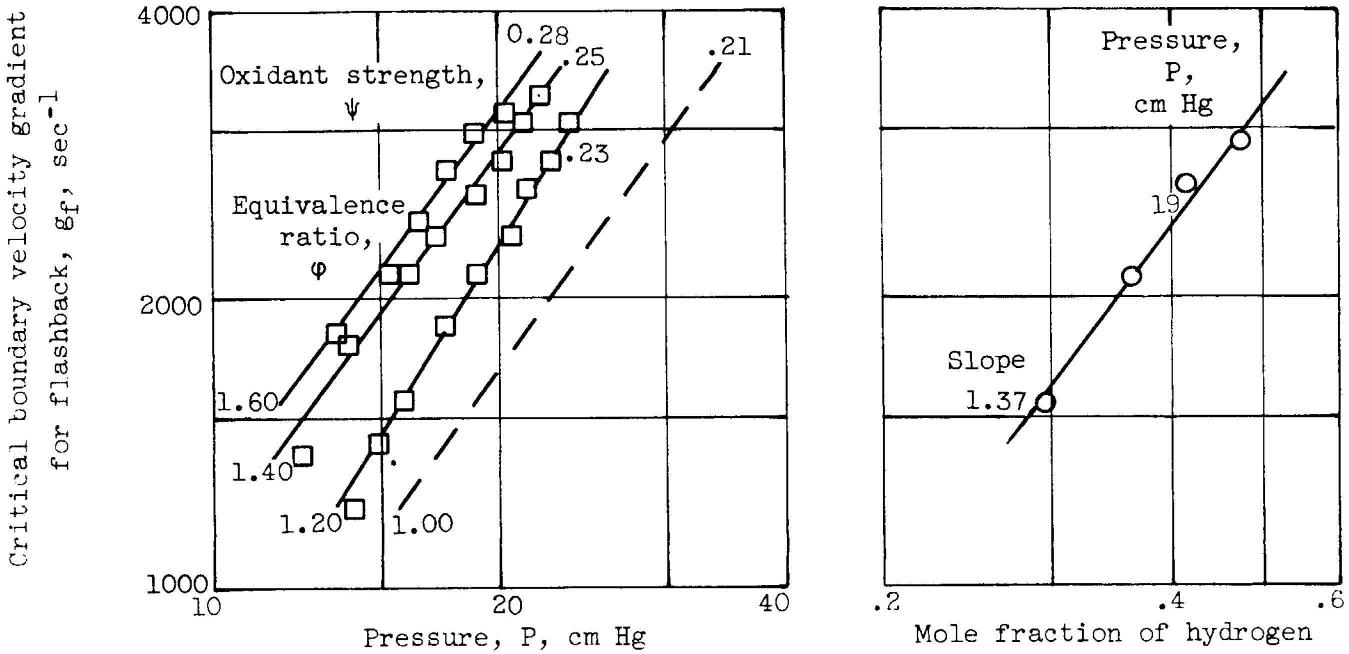
(a) Mole fraction of hydrogen, 0.41; flame temperature, 2560° K.

Figure 1. - Flashback of hydrogen-oxygen-nitrogen flames at constant flame temperature.



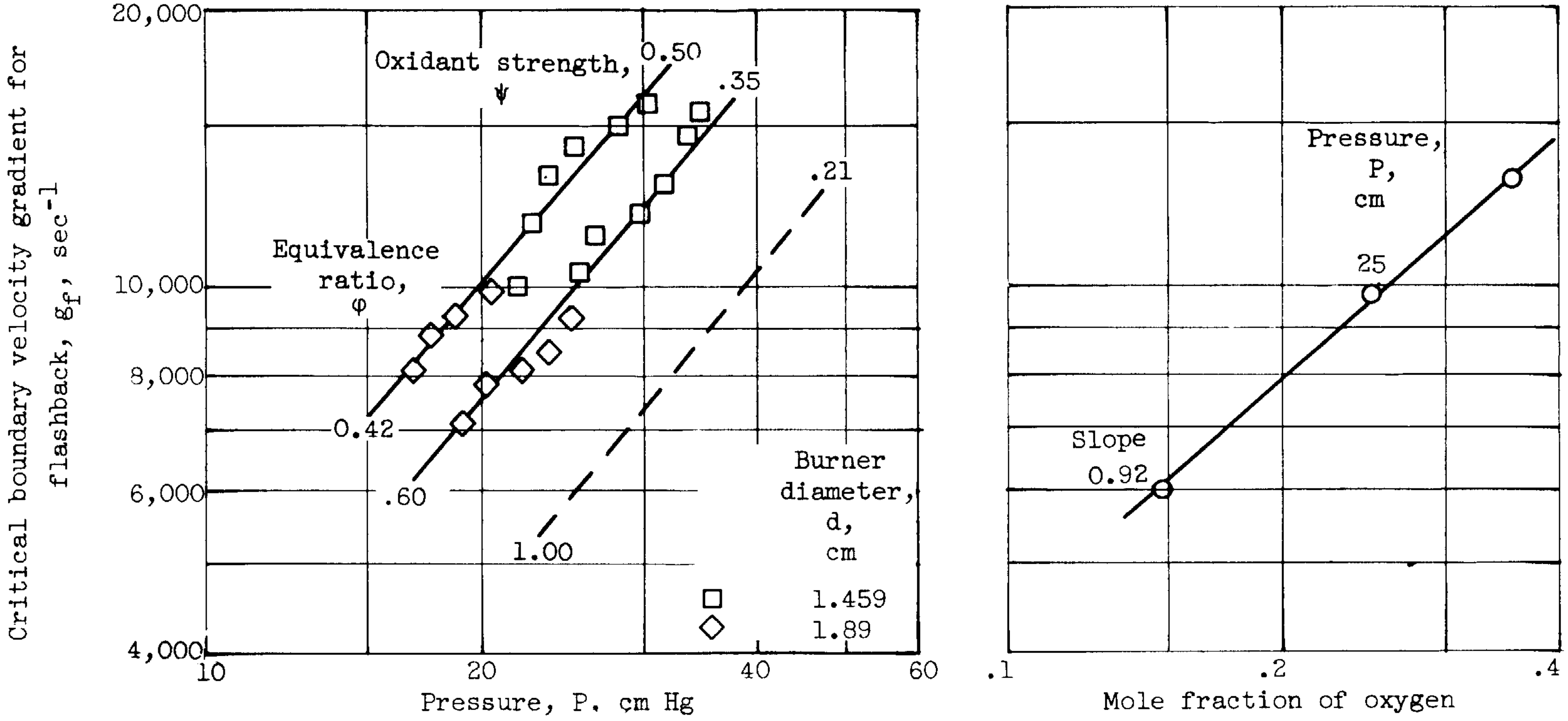
(b) Mole fraction of oxygen, 0.205; flame temperature, 2620° K; burner diameter, 1.459 centimeters.

Figure 1. - Continued. Flashback of hydrogen-oxygen-nitrogen flames at constant flame temperature.



(c) Mole fraction of oxygen, 0.148; flame temperature, 2300° K; burner diameter, 1.459 centimeters.

Figure 1. - Continued. Flashback of hydrogen-oxygen-nitrogen flames at constant flame temperature.



(d) Turbulent flames; mole fraction of hydrogen, 0.296; flame temperature, 2300° K.

Figure 1. - Concluded. Flashback of hydrogen-oxygen-nitrogen flames at constant flame temperature.

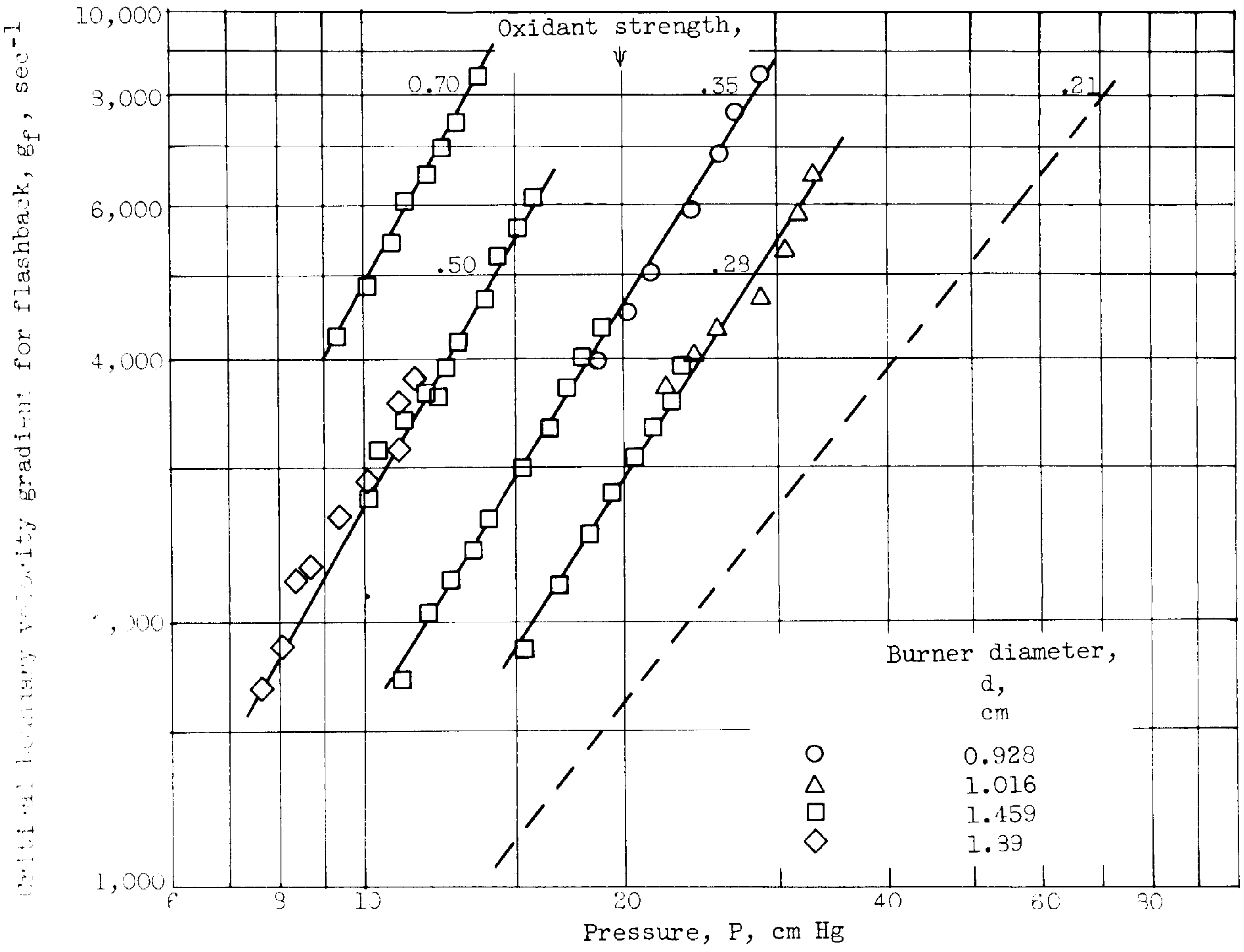


Figure 2. - Flashback of stoichiometric hydrogen-oxygen-nitrogen flames.

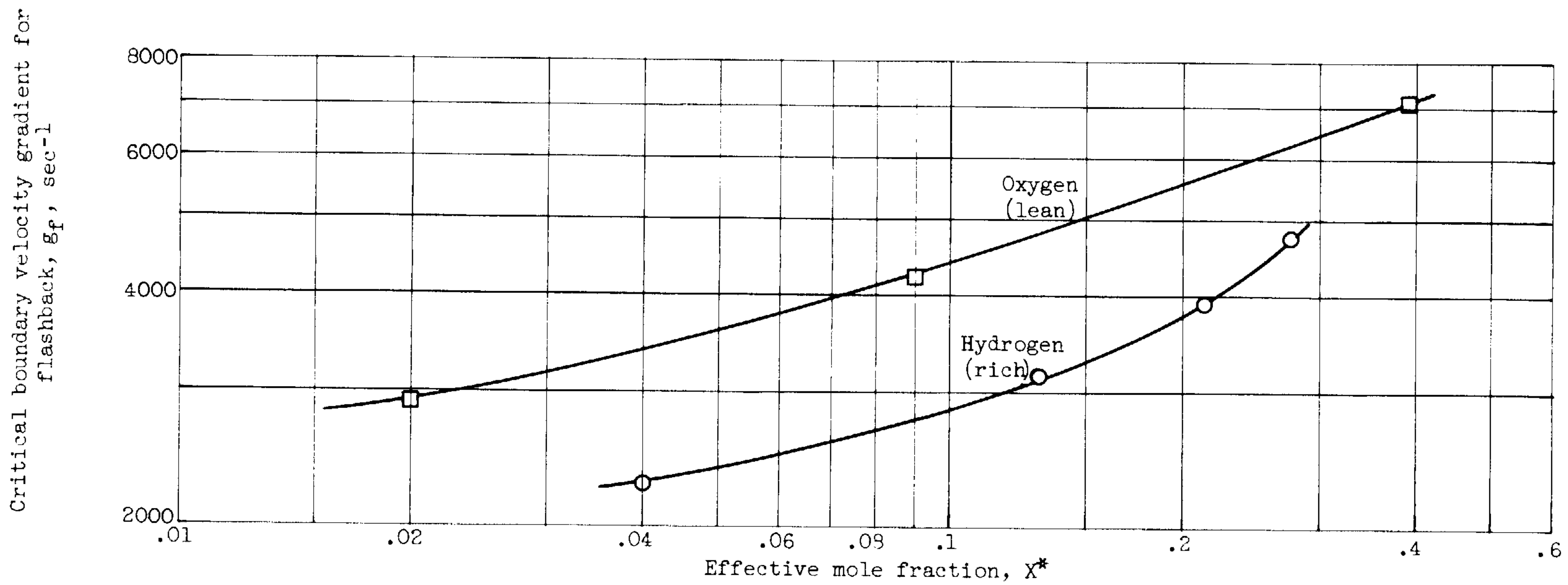


Figure 3. - Dependence of critical boundary velocity gradient for flashback on effective concentrations calculated by Semenov equation. Flame temperature, 2580° K.

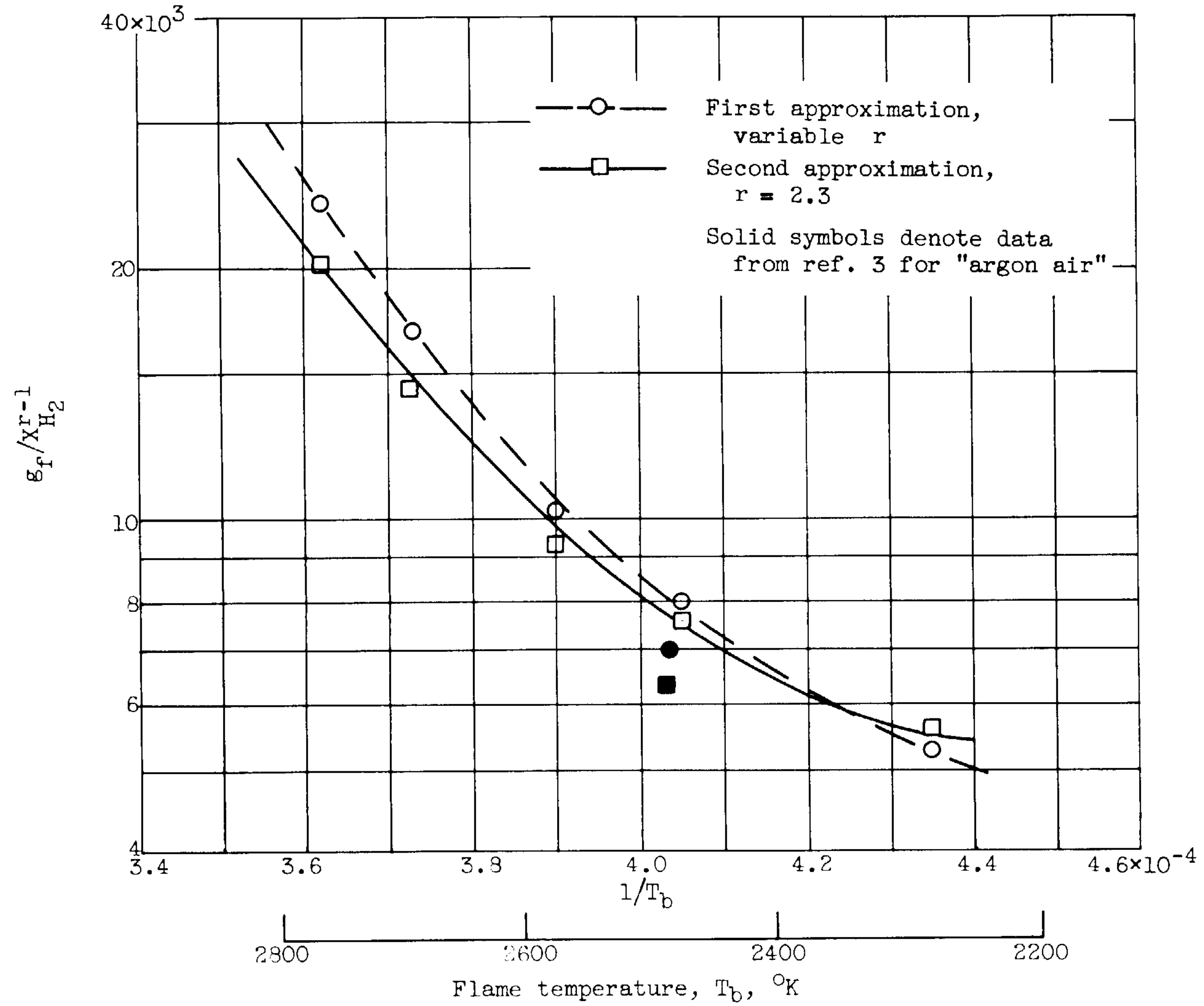


Figure 4. - Dependence of $g_f/X_{H_2}^{r-1}$ on flame temperature. Equivalence ratio, 1.0; pressure, 15 centimeters of mercury.

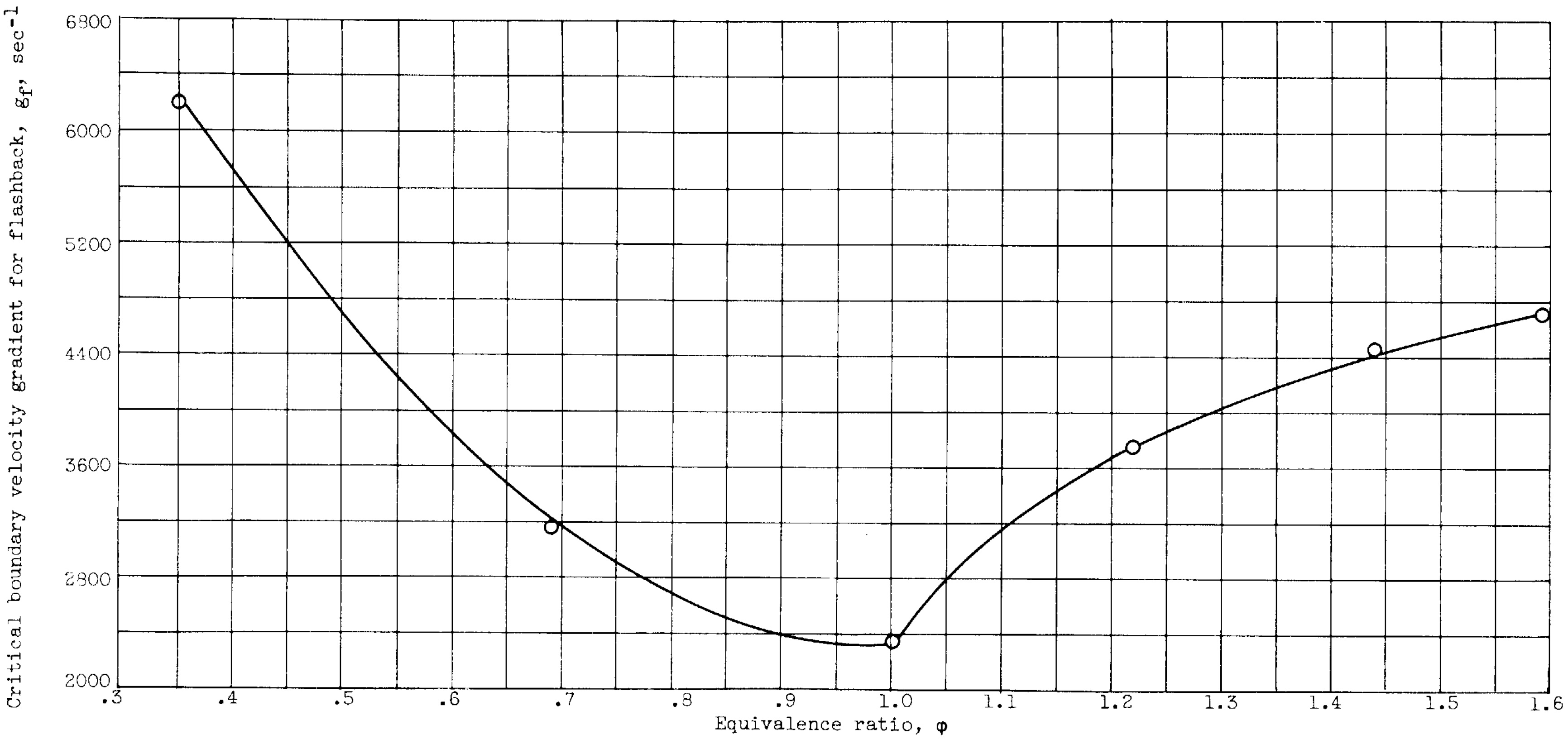


Figure 5. - Dependence of critical boundary velocity gradient for flashback on equivalence ratio at constant temperature and pressure. Flame temperature, 2580° K; pressure, 13 centimeters of mercury.

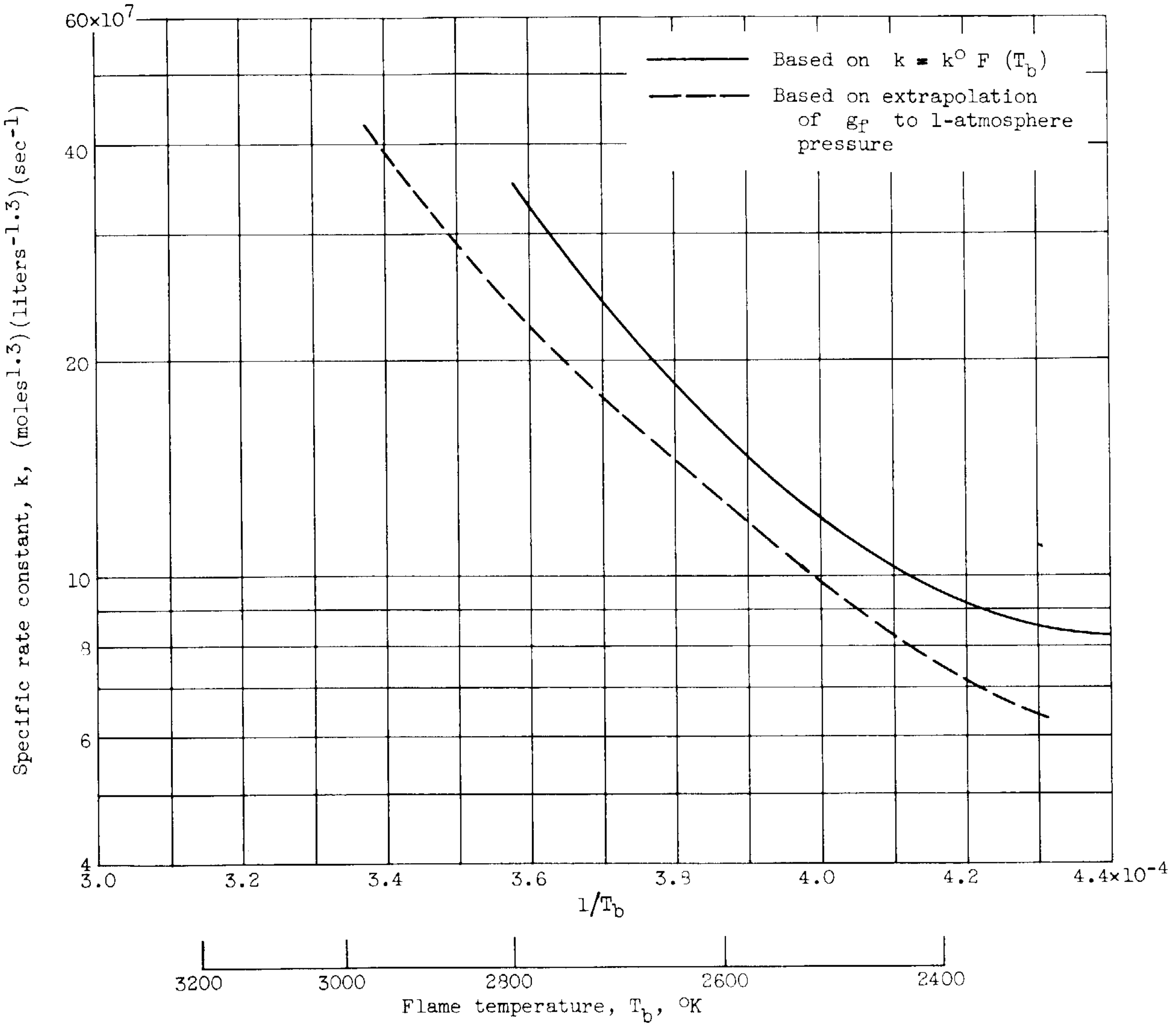


Figure 6. - Dependence of specific rate constant on flame temperature.

NASA - Langley Field, Va.

NASA MEMO 12-23-58E
National Aeronautics and Space Administration.
A STUDY OF OXIDATION OF HYDROGEN BASED ON FLASHBACK OF HYDROGEN-OXYGEN-NITROGEN BURNER FLAMES. Burton D. Fine. January 1959. 31p. diagrs., tabs.
(NASA MEMORANDUM 12-23-58E)

The flashback of hydrogen-oxygen-nitrogen flames was measured at reduced pressures as a function of burner diameter, pressure, and mixture composition. On the assumption that the critical boundary velocity gradient for flashback is a measure of the mean reaction time within a flame, the data were used to evaluate parameters in the rate expression for the flame reaction. The reaction order with respect to oxygen was about 0.9 and that for hydrogen was about 1.4, independent of flame temperature. The dependence of the specific rate constant, for which values were estimated, on flame temperature could not be described by a constant activation energy.

Copies obtainable from NASA, Washington

1. Combustion, Laminar-Flow (3.5.1.1)
2. Combustion, Turbulent-Flow (3.5.1.2)
I. Fine, Burton D.
II. NASA MEMO 12-23-58E

NASA

NASA MEMO 12-23-58E
National Aeronautics and Space Administration.
A STUDY OF OXIDATION OF HYDROGEN BASED ON FLASHBACK OF HYDROGEN-OXYGEN-NITROGEN BURNER FLAMES. Burton D. Fine. January 1959. 31p. diagrs., tabs.
(NASA MEMORANDUM 12-23-58E)

The flashback of hydrogen-oxygen-nitrogen flames was measured at reduced pressures as a function of burner diameter, pressure, and mixture composition. On the assumption that the critical boundary velocity gradient for flashback is a measure of the mean reaction time within a flame, the data were used to evaluate parameters in the rate expression for the flame reaction. The reaction order with respect to oxygen was about 0.9 and that for hydrogen was about 1.4, independent of flame temperature. The dependence of the specific rate constant, for which values were estimated, on flame temperature could not be described by a constant activation energy.

Copies obtainable from NASA, Washington

1. Combustion, Laminar-Flow (3.5.1.1)
2. Combustion, Turbulent-Flow (3.5.1.2)
I. Fine, Burton D.
II. NASA MEMO 12-23-58E

NASA

NASA MEMO 12-23-58E
National Aeronautics and Space Administration.
A STUDY OF OXIDATION OF HYDROGEN BASED ON FLASHBACK OF HYDROGEN-OXYGEN-NITROGEN BURNER FLAMES. Burton D. Fine. January 1959. 31p. diagrs., tabs.
(NASA MEMORANDUM 12-23-58E)

The flashback of hydrogen-oxygen-nitrogen flames was measured at reduced pressures as a function of burner diameter, pressure, and mixture composition. On the assumption that the critical boundary velocity gradient for flashback is a measure of the mean reaction time within a flame, the data were used to evaluate parameters in the rate expression for the flame reaction. The reaction order with respect to oxygen was about 0.9 and that for hydrogen was about 1.4, independent of flame temperature. The dependence of the specific rate constant, for which values were estimated, on flame temperature could not be described by a constant activation energy.

Copies obtainable from NASA, Washington

1. Combustion, Laminar-Flow (3.5.1.1)
2. Combustion, Turbulent-Flow (3.5.1.2)
I. Fine, Burton D.
II. NASA MEMO 12-23-58E

NASA

NASA MEMO 12-23-58E
National Aeronautics and Space Administration.
A STUDY OF OXIDATION OF HYDROGEN BASED ON FLASHBACK OF HYDROGEN-OXYGEN-NITROGEN BURNER FLAMES. Burton D. Fine. January 1959. 31p. diagrs., tabs.
(NASA MEMORANDUM 12-23-58E)

The flashback of hydrogen-oxygen-nitrogen flames was measured at reduced pressures as a function of burner diameter, pressure, and mixture composition. On the assumption that the critical boundary velocity gradient for flashback is a measure of the mean reaction time within a flame, the data were used to evaluate parameters in the rate expression for the flame reaction. The reaction order with respect to oxygen was about 0.9 and that for hydrogen was about 1.4, independent of flame temperature. The dependence of the specific rate constant, for which values were estimated, on flame temperature could not be described by a constant activation energy.

Copies obtainable from NASA, Washington

1. Combustion, Laminar-Flow (3.5.1.1)
2. Combustion, Turbulent-Flow (3.5.1.2)
I. Fine, Burton D.
II. NASA MEMO 12-23-58E

NASA