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## FOREWORD

This report was prepared by the Explosives Research Laboratory of the U. S. Bureau of Mines under USAF Contract No. DO (33-616) 60-5, Amendment 1 (60-688). The contract was initiated under Project No. 3048 "Aviation Fuels", Task No. 30195 "High Temperature Hydrocarbon Fuels". It was administered under the direction of the Materials Central, Directorate of Advanced Systems Technology, Wright Air Development Division, with Mr. Bobby McConnell acting as project engineer.

This report covers the work performed during the period 1 November 1959 to 31 October 1960.

Dr. Robert W. Van Dolah was the administrator for the U. S. Bureau of Mines and Dr. M. G. Zabetakis, Messrs. J. M. Kuchta, A. Bartkowiak, I. Spolan, A. Smith and R. E. Kennedy, and Misses A. C. Imhof and P. M. Gussey actively participated on this project at the U. S. Bureau of Mines Research Center, Bruceton, Pennsylvania.

WADD TR 61-89

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## ABSTRACT

Data are presented on the flammability and auto-ignition temperature characteristics of JP-6, JP-150 and HTF-59-24 fuels. Flammability limits of the vapors of these fuels were determined in air at elevated temperatures and at atmospheric pressure. Auto-ignition temperatures and corresponding ignition delay times were obtained under static and dynamic conditions as a function of the pressure and the oxygen concentration of the ambient medium; the effect of fuel volume on auto-ignition was also determined in some static tests. In addition, the auto-ignition of JP-6 fuel vapor-oxygen-nitrogen mixtures was studied in various vessels which were heated uniformly and non-uniformly; critical heat flow requirements for auto-ignition were found for spherical and cylindrical copper vessels and a spherical stainless steel vessel.

## PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



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## I. INTRODUCTION

In general, the hydrocarbon fuels used in aircraft are relatively stable even at elevated temperatures. However, mixtures of their vapors with air or other oxidants may be unstable under the same conditions; these mixtures may even ignite and propagate flame when brought in contact with a heated surface or exposed to an electrical discharge. Such flame propagation occurs only between the limits of flammability of the fuel vapor-air system under consideration. Further, auto-ignition will not occur unless the surface temperature has exceeded a critical value which is governed in part by the nature of the surface and the length of time that the mixture contacts it; in the case of an electrical discharge, the energy requirements for ignition are governed in part by the duration of the discharge and the nature of the electrodes between which the discharge occurs. Since aircraft fuels may be exposed to a heated surface or other ignition sources, the flammability and auto-ignition temperature characteristics of their vapors should be determined.

In practice, an aircraft fuel may be subjected to varied conditions of temperature and pressure. During flight operations, the temperatures of aircraft components may increase and thus increase the hazards associated with auto-ignition of fuel vapor, particularly where these components are in contact with the vapor for some interval of time (fuel residence time). The variation of the auto-ignition temperature of a fuel vapor-oxidant mixture with fuel residence time is useful in predicting the auto-ignition behavior of that mixture over a particular range of operating conditions. Since pressure (altitude) is also a variable in flight operations, one should know the effect of pressure on the auto-ignition temperature and the limits of flammability of the fuel vapor-oxidant system present. Furthermore, the rate of heating and distribution of heat in vessels containing fuel may be of considerable importance. For example, the rate of heating of fuel cells or fuel compartments of present aircraft and missiles traveling at supersonic speed can be very great and may present a serious explosion hazard. This hazard can be evaluated if the flammability and auto-ignition characteristics of the fuel are known for the various conditions cited above.

The present investigation concerns the fire and explosion hazards associated with the use of several aircraft fuels and is a continuation of the program of research on the flammability characteristics of aircraft fuels and hydraulic fluids begun at the Bureau of Mines in 1950. A summary of the work performed during the period from 1 November 1959 to 31 October 1960 is presented in this report and is grouped under two separate parts:

- A. High Temperature Hydrocarbon Fuel Studies
- B. Hazards of Aerodynamic Heating of Fuel Cells

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Manuscript released by authors November 1960 for publication as a WADD Technical Report.

## II. EXPERIMENTAL APPARATUS AND PROCEDURES

### A. High Temperature Hydrocarbon Fuel (HTF) Studies

The fuels investigated in these studies included JP-6, JP-150 and HTF-59-24. These fuels consisted primarily of saturated hydrocarbons; HTF-59-24 and JP-150 contained about 6.2 and 3.2 volume percent unsaturated compounds, respectively. Physical properties of each of these fuels are listed in Table 1.

In the first part of this investigation, tests were conducted with each of the fuels to determine flash and fire points, flammability limits and auto-ignition temperatures; some of the test data reported here for JP-6 jet fuel are from previous work (Ref. 1). All flash and fire point data were obtained in the Cleveland Open Cup Tester (ASTM D92-56) and/or the Tag Closed Cup Tester (ASTM D56-56) (Ref. 2). The remaining data were obtained by use of the experimental procedures described in the following paragraphs.

#### 1. Limits of Flammability

A limit of flammability is obtained for a mixture of gases by determining the critical composition that lies in the transition region between flammable and nonflammable mixture compositions. For most gas mixtures, there exists a combustible-lean (lower) limit and a combustible-rich (upper) limit of flammability; mixture compositions that lie within these limits will propagate a flame if ignited. An increase in temperature, pressure or oxygen concentration of the system to be tested will generally widen these limits, i.e., increase the range of flammable compositions. The flammability limits of the fuels (vapors) tested here were determined in air at atmospheric pressure in the Bureau of Mines F-11 apparatus (Ref. 3) equipped with a spark ignition source. Flame propagation is observed here in a cylindrical explosion tube, 2 inches I.D. and 48 inches long. All the tests with JP-150 and HTF-59-24 were conducted at 302°F. and those with JP-6 at 212°F. (lower limit) and 302°F. (upper limit). Elevated temperatures were employed because of the low vapor pressures of these fuels.

#### 2. Auto-ignition Temperatures under Static Conditions

The minimum auto-ignition temperature (M.A.I.T.) and corresponding ignition delay of each fuel were determined in air and in oxygen at atmospheric pressure and in air at both reduced and elevated pressures; all tests were conducted under quiescent conditions. Low pressure tests (1/4, 1/2 and 1 atmosphere) were conducted in the Bureau of Mines I-8 apparatus (Ref. 4) equipped with a 200 cc. pyrex vessel (erlenmeyer flask) and the high pressure tests (2 and 5 atmospheres) in a similar apparatus equipped with a cylindrical 40 cc. stainless steel vessel. The fuel volume and system temperature were varied and ignition was detected by noting the presence of flame at low pressures and by measurement of a pressure rise at elevated pressures. Ignition delay was measured as the total time delay that occurred prior to ignition



following the injection of the liquid fuel into the test vessel. By varying the system temperature, auto-ignition of the fuel was examined for a range of ignition delay times. Delay times of one second or greater may be measured with the I-8 apparatus; shorter delay times are obtained with a flow apparatus.

The effect of fuel volume on the auto-ignition temperature was studied with JP-6 in pyrex erlenmeyer flasks with volumes of 85 and 206 cc. The fuel volume was varied between 0.0024 and 0.02 cc. in the smaller vessel and between 0.0046 and 0.05 cc. in the larger one.

### 3. Auto-ignition Temperatures under Dynamic Conditions

Dynamic flow conditions were employed to determine auto-ignition temperatures corresponding to short fuel residence times (ignition delays of less than one second). The tests were conducted in the Bureau of Mines I-28M flow apparatus (Ref. 1) equipped with an Inconel combustion tube, 2 inches I.D. and 48 inches long. In these tests, liquid fuel was injected into a heated air stream at various air flow rates, temperatures, and pressures, and auto-ignition was observed over a range of fuel residence times extending from about 20 to 300 milliseconds. The residence time required for the fuel to ignite at the nozzle exit plane is defined as the ignition delay and is calculated from the flow conditions for each test.

Tests were conducted with JP-150 and HTF-59-24 fuels in air at combustion chamber pressures of 2, 3, 4 and 5 atmospheres. In addition, the effect of nitrogen dilution on the auto-ignition of JP-6 fuel was determined at 2 atmospheres pressure using nitrogen-air mixtures containing 79 to 88 percent by volume of total nitrogen. In practice, a great number of tests was required to obtain each set of auto-ignition temperatures and corresponding ignition delay values under the varied experimental conditions employed here. Only the average values from these tests are presented in this report.

### B. Hazards of Aerodynamic Heating of Fuel Cells

In previous work (Ref. 1) a study was undertaken of the hazards associated with the heating of fuel cells with spherical copper vessels of light (thin) walls and cylindrical copper vessels of heavy walls. These vessels or fuel cells contained small quantities of HTF-27 (monoisopropylbicyclohexyl) fuel vapor and air which were subjected to uniform and nonuniform heating conditions. In the present work, JP-6 jet fuel was used and the tests were conducted at atmospheric pressure with both copper and stainless steel spherical vessels and with a cylindrical copper vessel, all of thin-wall construction (see Figures 1 and 2). As in the previous studies, the fuel cells were heated both uniformly and nonuniformly at various rates. The initial oxygen concentration in the fuel cell was also varied in these tests. The test procedures employed for obtaining data under the two types of heating conditions are described below.

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## 1. Uniform Heating Conditions

The uniform heating experiments were conducted by immersing the vessels and their contents (JP-6 fuel vapor and air) in a preheated furnace that was maintained at a constant temperature. The furnace was completely insulated with asbestos to minimize heat losses and to insure uniform heating of the vessels. Only 0.5 cc. of fuel was used here to simulate a nearly "empty" fuel tank condition. During a test, gas mixture temperatures were measured with Pt-Pt+10% Rh thermocouples (24-gage) and vessel wall and furnace air temperatures with chromel-alumel thermocouples (22- or 28-gage). Initially, the measurements were made at various points in the gas mixture and on the vessel walls. Since each of these sets of temperatures did not vary greatly with position, only those for the central gas mixture and bottom wall were subsequently employed. The temperatures were recorded continuously on a multi-channel high-speed temperature recorder from which rates of temperature rise and temperatures at the time of ignition could be obtained. Ignition of the mixtures was evidenced here by a sudden rise in gas temperature.

In the above experiments, the critical heating rate for the auto-ignition of the combustible mixture was obtained by varying the furnace air temperature. For the spherical vessels, the tests were conducted at furnace air temperatures between 380° and 700°F. and, for the cylindrical vessel, between 560° and 850°F.

## 2. Non-uniform Heating Conditions

In the non-uniform heating experiments, the cylindrical vessel was heated by applying a flame from a ribbon-type natural gas burner to the bottom surface of the cylinder along its entire length (see Figure 2). The area of the heated surface directly in the path of the burner flame represented about 4 percent of the total circumferential area of the cylinder; a flame of about 0.4-inch width was applied to the cylinder whose circumference was 9.7 inches. With spherical vessels, the flame from a Meker-type burner was applied to the bottom surface as illustrated in Figure 1; here, the area of the heated surface was slightly greater than 4 percent of the total surface area. As in the uniform heating tests, measurements of the bottom wall (in the zone of applied heat) and central gas mixture temperatures were relied upon to indicate the rate of heating and the extent of reaction of the combustible mixture. In addition, a partially shielded Pt-Pt+10% Rh thermocouple was employed to determine the temperature in the burner zone about 1/4-inch from the bottom wall of the vessel. The latter were not comparable to true flame temperatures and were used primarily to indicate the intensity of the heating for each test. Under the non-uniform heating condition, the spheres and cylinder were not insulated. Heating rates were varied by adjusting the burner gas flow.

Some experiments were conducted with 0.2 cc. JP-6 fuel but, for the most part, 0.5 cc. was used. Tests were performed with this fuel and air in the cylindrical and spherical vessels. In addition, tests were conducted in the cylindrical vessel with various JP-6 fuel vapor-oxygen-nitrogen mixtures. Oxygen-nitrogen mixtures containing 2 to 100 volume percent oxygen were used; the 21 percent oxygen-containing mixture was formed with air.

## III. RESULTS AND DISCUSSION

### A. High Temperature Hydrocarbon Fuel Studies

#### 1. Limits of Flammability

The limit-of-flammability data obtained for each of the fuels considered here are given in Table 2(A). Note that although the lower limits of flammability for JP-6 (46 mg./l.) and JP-150 (43 mg./l.) are different, these data were not obtained at the same test temperature. If the same temperature had been used for both fuels, their limits would be in closer agreement; a value of about 44 mg./l. would be expected for JP-6 at the test temperature (302°F.) used to obtain the JP-150 data. However, the temperature effect alone cannot account for the lower limit obtained with HTF-59-24 (40 mg./l.). For many saturated hydrocarbons, a lower limit value of about 45-50 mg./l. can be expected (Ref. 3), and moderate changes in chemical composition are relatively unimportant. Accordingly, the HTF-59-24 fuel must differ significantly from JP-6 in chemical structure. Table 1 shows that HTF-59-24 contains 4.1 percent aromatics and 2.1 percent olefins. The presence of these unsaturates may account for the lower limit values obtained for this fuel and JP-6. The upper limits of flammability of these fuels were consistent with the lower limits in that the greatest range of flammable vapor concentrations was obtained with HTF-59-24. Here again, differences in chemical composition were significant in range of compositions over which flame propagation was obtained with these fuels.

#### 2. Variation of Auto-ignition Temperature with Ignition Delay-Static Conditions

Table 2(B) summarizes the minimum auto-ignition temperature (M.A.I.T.) data obtained for JP-6, JP-150 and HTF-59-24 fuels in quiescent atmospheres of air and oxygen at various pressures. The M.A.I.T.'s of the fuels were similar in air at atmospheric pressure and were not affected greatly by increasing the oxygen content from 21 to 100 volume percent. In previous work (Ref. 1), the effect of initial oxygen concentration on the spontaneous ignition of several high temperature hydrocarbon fuels was very pronounced if the fuel was an unsaturated hydrocarbon (e.g., monoisopropylbiphenyl, tetralin, and methylcyclopentadiene). These unsaturates would be expected to have a relatively high knock resistance, which is associated with resistance to oxidation, so that their M.A.I.T. values should vary greatly with oxygen concentration if oxidation reactions are controlling. The fuels of the present work, JP-6, HTF-59-24 and JP-150, are apparently much more readily oxidized than the unsaturated compounds mentioned here. Accordingly, the M.A.I.T.'s of the present fuels in air (1 atmosphere) should not vary greatly with a moderate increase in pressure; greater variations should be expected with a corresponding decrease in pressure. The results in Table 2(B) at 2 and 5 atmospheres and those at 1/4 and 1/2 atmosphere display such behavior. Little difference in M.A.I.T. values is observed between 1 and 5 atmospheres, but the values at 1/2 atmosphere are at least double those found at 1 atmosphere; below 1/2 atmosphere, the effect of pressure is less pronounced.

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If auto-ignition of the test fuels under static conditions is controlled by a chemical process, such as oxidation, the temperature dependence or temperature coefficient of the process should be relatively great. We can determine the magnitude of the temperature coefficient for at least the over-all process in our experiments by obtaining the relationship between auto-ignition temperatures and the corresponding ignition delays. An indication of this dependence is illustrated in Figure 3 where the logarithm of ignition delay ( $\tau$ ) is plotted versus the reciprocal of the auto-ignition temperature ( $1/T$ ). Each curve was reproduced from an individual graph on which average slopes had been drawn to represent the experimental data for each fuel. If we assume that the measured ignition delays are related to the time required for the precursory chemical reactions and active species to effect ignition, we can represent the data in a form similar to that used in the Arrhenius rate law,

$$\ln \tau = A/T + \ln k \quad (1)$$

where  $T$  is the auto-ignition temperature ( $^{\circ}R$ ),  $\tau$  is the ignition delay in milliseconds and  $k$  is a constant;  $A$  may be related to the activation energy  $E$  (cal./mole), of the controlling process and is equivalent to  $E/R$ , where  $R$  is the molar gas constant (cal./degree-mole).

The 1 atmosphere pressure data in Figure 3 show that auto-ignition of each fuel is most temperature sensitive over the range of low temperatures ( $<550^{\circ}F.$ ) employed in these tests. Apparent activation energies between 34 and 40 kcal/mole appear to represent the data obtained for all the fuels in this low temperature range. These values indicate that chemical processes, such as oxidation, should be most important here. However, at higher temperatures ( $>550^{\circ}F.$ ), the calculated values lie between 11 and 17 kcal/mole and are not indicative of common hydrocarbon oxidation processes. The data at 1/2 atmosphere pressure display greater temperature dependence than those obtained at 1 atmosphere pressure over the same range of ignition delay times, i.e., 1 to 6 seconds. In the auto-ignition of these fuels, the rates at which complex active species form and react are relatively low at temperatures close to the M.A.I.T. of the fuel in question. Thus, the fraction of ignition delay time due to chemical processes can be great compared to that which may be attributed to evaporation, mixing, etc. In this event, the temperature coefficient of the process would be expected to be greatest near the M.A.I.T. of the fuel. This explanation is suggested to account for the change in auto-ignition temperature dependency observed below and above  $550^{\circ}F.$  in the tests at atmospheric pressure. Admittedly, the chemical reactions themselves can also change with temperature and account for the above behavior.

Generally, fuel-air ratio is not considered as important in auto-ignition as in flame propagation. This stems from findings which show that the M.A.I.T. values of many fuels are not very sensitive to changes of fuel concentration, whereas their flame temperatures vary considerably with concentration changes. Figure 4 illustrates the effect of fuel-vessel volume ratio, or fuel concentration, on the auto-ignition temperature of JP-6 in air for two vessel volumes (85 cc. and 206 cc.). For each vessel, fuel concentration was relatively unimportant at the temperatures approximating the M.A.I.T. of JP-6 ( $449^{\circ}F.$  in a 206 cc. vessel). However, at higher temperatures, the effect of fuel concentration is quite pronounced. Also in Figure 4 the curves show that little variation of auto-ignition temperatures is obtained with the two vessel sizes

when the data are compared on the basis of the fuel-vessel volume ratio or, essentially, the equivalence ratio of the fuel vapor-air mixture present. Apparently, wall effects are not appreciably different for the two vessels (85 cc. and 206 cc.) used here, but such effects would be expected to become more evident as the vessel volume is decreased below 85 cc.

### 3. Variation of Auto-Ignition Temperature with Ignition Delay-Dynamic Conditions

Table 3 summarizes the auto-ignition temperature (A.I.T.) data obtained for JP-150 and HTF-59-24 fuels in heated air streams at 2, 3, 4 and 5 atmospheres pressure. Generally, the auto-ignition temperatures for HTF-59-24 were higher than those for JP-150 at comparable flow conditions. The effect of pressure was most evident at high flow rates (short fuel residence times); auto-ignition temperatures at a fuel residence time or ignition delay of about 30 milliseconds were decreased by about 450°F. when the pressure was increased from 2 to 4 atmospheres. All of these data are also plotted in Figures 5 and 6 in the same form as is used for the static A.I.T. results. If equation (1) is assumed to be also applicable here, the following empirical expressions approximate the temperature coefficient of the auto-ignition of these fuels at 2 atmospheres pressure and at temperatures (T) between 1210° and 1760°R (750° and 1300°F.).

$$\begin{array}{ll} \text{JP-150} & \ln \tau = 5100/RT + \ln 2.31 \quad (2) \\ \text{HTF-59-24} & \ln \tau = 5800/RT + \ln 1.68 \quad (3) \end{array}$$

The apparent activation energies indicated by the above expressions cannot be considered representative of chemical processes that would be expected in hydrocarbon autoignition. Even at 5 atmospheres pressure, the temperature dependence of ignition delay did not differ much from that at one atmosphere. Mass transfer processes, such as evaporation and diffusion, would be expected to display the small temperature dependence found in these tests. Thus, the auto-ignition of JP-150 and HTF-59-24 appears to be controlled by physical processes under the flow conditions listed in Table 3. Similar results were obtained previously with JP-6 and several other HTF fuels (Ref. 1). Over-all, the auto-ignition of the fuels investigated in this and the previous work is considerably less temperature dependent under dynamic than under static conditions, although the previously reported data indicated that the temperature coefficients may be similar at temperatures below about 700°F. The static test data should be extended to temperatures comparable to those employed in the dynamic tests. Auto-ignition temperature data for the fuels of this work could then be compared over the same range of ignition delay times under quiescent and turbulent flow conditions.

Results of the inerting tests with JP-6-air-nitrogen mixtures are shown in Figure 7 where ignition delay time is plotted as a function of auto-ignition temperature and initial oxygen content. Higher temperatures were required for ignition as the oxygen content was decreased from 21 to 11.5 volume percent. On the basis of the static data for JP-6 at reduced pressures, auto-ignition temperatures would be expected to increase appreciably with a decrease in



oxygen concentration. The data shown in Figure 7 were not consistent over the entire range of ignition delay times and temperatures; actually, the curves tend to merge at short delay times where oxygen concentration was found to exert little influence on the auto-ignition of the JP-6 fuel. Thus, the physical or chemical processes controlling the ignitions appear to be changing over the range of temperatures and ignition delay times investigated here. Ignitions in these tests were more difficult to discern than those with air. This difficulty may be partly attributed to the variable and unknown quantity of moisture present in the air supply system.

## B. Hazards of Aerodynamic Heating of Fuel Cells

### 1. Auto-Ignition in Various Fuel Cells Subjected to Uniform and Nonuniform Heating Conditions

A series of temperature-time records was obtained in determining the critical heating conditions for the auto-ignition of various JP-6 fuel vapor-oxygen-nitrogen mixtures in cylindrical and spherical vessels. Average rates of temperature rise were calculated from these records after a heating time of 1/2 minute and were selected to represent the initial heating rates; at this time, the initial heating rates were relatively constant in most of the wall and central gas mixture temperature records. In early tests, the initial rates at other transient conditions were selected but were not found to be as applicable in some of the later tests. The data representing critical heating conditions were averaged from the records which defined the ignition and non-ignition rates; these data are summarized in Table 4 and shown graphically in Figures 8-11.

With uniform heating conditions, the heat requirements for the auto-ignition of JP-6 fuel vapor-air mixtures appeared to be greater in vessels of stainless steel than in those of copper. A vessel wall heating rate of 91°F./min. was required for ignition in the steel sphere as compared to 66°F./min. in the copper one (see Table 4A). These results can be explained on the basis that the thermal conductivity of stainless steel is much less than that of copper. The results for the copper sphere were not much different from those obtained with the copper cylinder and indicated that vessel geometry was not important in these tests. Wall effects could be expected to be a factor here if the surface area to volume ratio of the cylinder used was increased sufficiently.

Figure 8 shows the critical temperature-time curves for auto-ignition obtained in the uniform heating tests. The central gas mixture temperature curve for the copper sphere is not shown because of questionable records. The greatest difference between central gas mixture and vessel wall temperatures was observed with the stainless steel sphere during the early stages of heating (<3 minutes). Thereafter, the difference between these temperatures was relatively constant (125°F.) for the steel sphere and the copper cylinder. The central gas mixture temperatures at ignition were less than the M.A.I.T. of this fuel (449°F.) determined in air with the I-8 apparatus. Accordingly, the ignitions in these tests probably occurred close to the walls of the vessels.

In the non-uniform heating tests, the heating rates necessary for ignition varied considerably with the vessels employed, (see Table 4B). The critical wall heating rate for the steel sphere (470°F./min.) was more than twice that for the copper sphere (213°F./min.). Here, the effect of the different thermal conductivities of steel and copper is most evident; note that the rates of gas mixture temperature rise were nearly the same for both spheres although their wall heating rates varied greatly. Of the two copper vessels, the cylinder required the lowest wall heating rate (82°F./min.) for ignition. Although this behavior can be attributed in part to geometric effects, the types of non-uniform heating employed here were probably more important factors. Whereas the flame was applied to a circular area on the sphere, in the case of the cylinder the flame was spread over a long rectangular area; furthermore, the temperature of the latter flame was generally about 200-300°F. less than that used to heat the sphere over the range of experimental conditions.

The critical temperature-time curves for auto-ignition under the non-uniform heating conditions are shown in Figure 9 and illustrate the varied results obtained with the three different vessels. The central gas mixture temperature curve for the steel sphere is not included because of the great lag between this temperature and that of the vessel wall. The data for the copper sphere also displayed this behavior but to a much smaller extent than encountered above; note also that ignition occurred in 4.3 minutes with this sphere and in 1.4 minutes with the steel sphere. A comparison of the wall heating rates for uniform and non-uniform heating shows that the results obtained with the copper cylinder did not vary greatly. However, the rates for the copper and stainless steel spheres were much greater under the non-uniform heating condition.

Table 4C summarizes the data obtained on the effect of initial oxygen concentration in the non-uniform heating tests with the copper cylinder. The critical rates of temperature rise for ignition in these tests are shown in Figure 10 (central gas mixture temperature) and Figure 11 (vessel wall temperature). It was found that both the central gas mixture and wall heating rates necessary for ignition increased when the initial oxygen content was varied from 100% to 4%. Nearly all of the wall heating rates were at least 2-1/2 times greater than those of the gas mixture heating rates. Generally, wall temperatures at ignition increased with decreasing oxygen concentration and were more consistent with the M.A.I.T. values (Table 2) than were gas mixture temperatures.

With 2% oxygen, ignitions were not obtained with a wall heating rate of 160°F./min. It is not known whether ignitions would occur with mixtures of this oxygen content at higher heating rates or temperatures.

## 2. Heat Flow Requirements for Auto-Ignition

Since the heat requirements for auto-ignition are of interest, rates of radial heat flow were calculated for the various experimental conditions given

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in Table 4. Only the wall area in the zone of applied heat was considered in each case. Accordingly, the total mean surface areas of the vessels were used in computing the uniform heating data. In the case of non-uniform heating, the heated zones represented about 4 percent of the total curved surface areas of the spheres and cylinder; these areas could be assumed to have a uniform wall temperature during the tests without serious error. All of the calculations were made for the critical transient conditions (for ignition) that prevailed after 1/2 minute of heating. At about this time, the wall heating rates were most nearly constant for all of the tests considered here. The local rates of heat flow ( $dQ/dt$ ) through the heated walls of the vessels were calculated by the use of the following equation,

$$dQ/dt = \rho_w c_w \Delta r_w dT_w/dt \quad (4)$$

where  $\underline{w}$  refers to the vessel wall,  $\Delta r_w$  to wall thickness, and the other symbols have their usual meaning.

In equation (4), the local heat flow rates are expressed in Btu/ft.<sup>2</sup>-min. and are converted to total rates by multiplying by the areas involved. The most accurate rates are those obtained for uniformly heated vessels, since the heat losses from the vessel walls to the insulated furnace walls were minimized. However, for non-uniform heating, the rates should be considered as net values applicable only to the specified zone of heating; the fraction of the total heat entering the vessel was diminished by that amount lost from lateral conduction to the unheated walls and radiation from these walls. Results of these calculations are given in Table 4.

Since temperature is very important in the auto-ignition of fuel vapors, the local heat flow (Btu/ft.<sup>2</sup>-min.) should be more significant than the total heat flow (Btu/min.). Therefore, only the former rates are discussed here. These values were generally consistent with the trends indicated by the wall heating rates. For uniform heating conditions, the heat flow requirements for the auto-ignition of JP-6 fuel vapor-air mixtures were greatest with the stainless steel sphere (13.1 Btu/ft.<sup>2</sup>-min.) and varied only slightly with the copper sphere (11.4 Btu/ft.<sup>2</sup>-min.) and cylinder (11.8 Btu/ft.<sup>2</sup>-min.). Similarly, the greatest heat flow rate was required with the steel sphere (77.2 Btu/ft.<sup>2</sup>-min.) under non-uniform heating conditions, and the rates for all the vessels were considerably greater than those obtained under the previous heating condition. The consistency of these heat flow rates with corresponding wall heating rates can be attributed primarily to the small variation between the specific heat ( $c_w$ ) of copper and stainless steel.

Critical heat flow rates for ignition are also given in Table 4 for the tests with non-uniformly heated vessels that contained various JP-6 fuel vapor-oxygen-nitrogen mixtures. With 100 percent oxygen, the required heat flow rate was 15.2 Btu/ft.<sup>2</sup>-min. With 2 percent oxygen, a heat flow rate of 32.2 Btu/ft.<sup>2</sup>-min. was not sufficient to produce ignition under the test conditions used here. It is interesting to compare the heat flow requirements



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for ignition with the wall and central gas mixture temperatures at ignition in these tests. Whereas the critical rates of heat flow increased considerably as the oxygen content was varied from 4 percent to 100 percent, the above temperatures also increased but to a lesser extent. Therefore, temperature was more important than rate of heat flow in the latter experiments.

In actual free-flight tests with rocket-propelled models (Ref. 5), NASA obtained aerodynamic heat transfer data relative to the nose sections (conical and parabolic) of these models at free-stream Mach numbers ( $M_0$ ) between 1 and 5. Temperature measurements were made in wall sections constructed of Inconel skin approximately 0.03-inch thick, which was the wall thickness of the stainless steel vessel employed in our work. Results of one of the above tests showed wall heating rates of at least 125°F./sec. were obtained during the early stages of flight ( $M_0 < 3$ ) and as high as 285°F./sec. during the final period ( $M_0 > 3$ ). For a stainless steel wall, comparable rates would be expected since the thermal conductivity of both metals is nearly the same. The above heating rates are considerably higher than any of the values required for ignition in the present work. For example, a wall heating rate of 470°F./min. (7.8°F./sec.) was required with the steel sphere under non-uniform heating (Table 4B); in obtaining this value we conducted additional tests at wall heating rates as high as 2400°F./min. (40°F./sec.) and ignition resulted most readily. Also in the flight tests, the wall temperatures were as high as about 900°F. Since such high heating rates and temperatures are possible, it is apparent that the hazards of aerodynamic heating of fuel cells under expected flight conditions pose a serious problem. Efforts to eliminate or minimize the hazards must be directed to reducing the heat transfer rate through the walls by use of insulated walls, or to eliminate the formation of explosive fuel vapor-oxidant mixtures by blanketing the fuel with an inert gas or by removing the oxygen from the vapor space.

## IV. SUMMARY AND CONCLUSIONS

The flammability and auto-ignition characteristics of JP-6, JP-150 and HTF-59-24 fuels were investigated under various experimental conditions. Limits of flammability of these fuels were determined in air at elevated temperatures and atmospheric pressure. Auto-ignition temperatures and corresponding ignition delay times were obtained under static and dynamic conditions as a function of pressure and oxygen concentration of the ambient medium; the effect of fuel volume was also considered in some of these tests. In addition, the auto-ignition of JP-6 fuel vapor-oxygen-nitrogen mixtures was studied in various vessels which were subjected to uniform and non-uniform heating conditions. The main results and conclusions from this work are summarized below:

(1) Flammable mixtures are formed at 302°F. in air with JP-150 fuel vapor concentrations between 43 and 321 mg./S.T.P. liter of air and with HTF-59-24 concentrations between 40 and 352 mg./S.T.P. liter of air. The flammability data for JP-150 are consistent with those obtained for JP-6 and other hydrocarbon fuels.

(2) The minimum auto-ignition temperatures of JP-6, JP-150 and HTF-59-24 under static conditions are 449°, 475°, and 471°F., respectively, in air at atmospheric pressure. These values were not affected appreciably by increasing the pressure to 5 atmospheres or the oxygen content of the ambient medium to 100 percent. However a reduction in pressure to 1/4 atmosphere more than doubled the above values obtained in air at atmospheric pressure. Auto-ignition under these conditions (temperatures below 550°F. and at 1 atmosphere pressure) appears to depend on chemically controlled processes.

(3) Auto-ignition temperatures of JP-150 and HTF-59-24 in air are decreased with increasing pressure under flow conditions at 2-5 atmospheres. The variation of auto-ignition temperature with ignition delay was not great, and the data indicate that physical processes are exerting the greatest influence on the auto-ignition of these fuels under the flow conditions used, especially at 2 atmospheres pressure. With JP-6 as the fuel, the auto-ignition temperatures increased as the initial oxygen content of the air stream was decreased; temperature appeared to be more important than oxygen concentration in the region of short ignition delay times investigated here.

(4) Heat flow requirements for the auto-ignition of JP-6 fuel vapor-oxygen-nitrogen mixtures are greater in stainless steel than in copper vessels, especially under non-uniform heating conditions. Little difference can be expected between such data for copper spheres and cylinders under uniform heating conditions. A decrease in initial oxygen content (from 100% to 4%) of the combustible mixture increased the heat flow requirements for a copper cylinder heated non-uniformly; ignitions did not occur with mixtures containing only 2 percent oxygen in this cylinder when subjected to a heating rate of 160°F./min. and a local heat flow rate of about 32 Btu/ft.<sup>2</sup>-min.

## V. RECOMMENDATIONS FOR FUTURE WORK

Auto-ignition temperature studies in quiescent atmospheres should be extended with the fuels of interest to temperatures comparable to those that were employed here under dynamic test conditions. Vapor phase injection (with mixed and unmixed fuel and oxidant) should be included in such work. In addition, the vaporization rates of the fuels are needed over a range of temperatures extending from the boiling point to the auto-ignition temperature of the fuel. Data from the above studies would help in predicting the auto-ignition temperature characteristics of the fuels over an extended range of temperature and mixing conditions.

The hazards associated with the heating of fuel cells containing small amounts of combustible fuel vapor should be investigated under simulated aerodynamic heating conditions. Efforts should also be directed to a study of fuel cell configurations and materials that would have the desired heat transfer properties for preventing ignition of most aircraft fuels under certain specified heating conditions.

Limits of flammability, auto-ignition temperatures, flash points, and fire points should be determined for any new fuels, hydraulic fluids and oils.

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## APPENDIX I - TABLES

TABLE 1. - Physical Properties of Three Hydrocarbon Type Fuels.

	<u>JP-6</u>	<u>JP-150</u>	<u>HTF-59-24</u>
Density, gm./cc., 70°F.	0.782	0.693	0.860
Boiling Pt., °F.	370	160-315	379-477
Freezing Pt., °F.	--	<-76	<-76
Viscosity, c.s., 100°F.	1.17	0.65	2.88
Surface Tension, dynes/cm., 80°F.	24.5	20.1	24.1
Refractive Index, 68°F.	1.4383	1.4016	1.4671
Heat of Combustion, BTU/lb.	18,620	19,070	18,450
Aromatics, Vol. %	--	1.6	4.1
Olefins, Vol. %	--	1.6	2.1
Sulfur, Total %	--	0.002	0.001
Existent Gum, mg./1.00 ml.	--	1	0.8
Smoke Point, mm.	--	50+	16
Flash Pt., °F.			
Cleveland Open Cup	100	36	205
Tag Closed Cup	97	21	168
Fire Pt., °F.			
Cleveland Open Cup	110	38	210

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TABLE 2. - Limits of Flammability and Minimum Auto-Ignition Temperatures of Three Fuels in Air and/or Oxygen Atmospheres.

A. Limits of flammability in air at atmospheric pressure.

	T	JP-6	JP-150	HTF-59-24
Lower limit, mg./S.T.P.liter of air, 302°F.:	46(212°F.)	43	40	40
Upper limit, mg./S.T.P.liter of air, 302°F.:	290	321	352	352

B. Minimum Auto-Ignition Temperatures (M.A.I.T.) and Corresponding Ignition Delays ( $\tau$ ) Under Static Conditions in Air and Oxygen at Various Pressures.<sup>1/</sup>

Ambient Atmospheres	Ambient Pressure (atms.)	JP-6		JP-150		HTF-59-24	
		M.A.I.T. (°F.)	$\tau$ (sec.)	M.A.I.T. (°F.)	$\tau$ (sec.)	M.A.I.T. (°F.)	$\tau$ (sec.)
Air	1/4	1134	4	--	--	1137	1.8
"	1/2	924	8	1054	6	950	5
"	1	449	145	475	53	471	81
"	2	444	168	468	60	--	--
"	5	435	272	450	67	457	116
Oxygen	1	435	221	453	58	464	114

- <sup>1/</sup> I-8 apparatus with pyrex vessel used in tests at 1/4-1 atmosphere pressure (206 cc. erlenmeyer).  
 I-33 apparatus with stainless steel vessel used in tests at 2 and 5 atmospheres pressure (400 cc. cylinder).

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TABLE 3. - Summary of Auto-Ignition Temperature (A.I.T.) and Ignition Delay ( $\tau$ ) Data<sup>1/</sup> for JP-150 and HTF-59-24 Fuels in Air at Various Pressures Under Dynamic Test Conditions. (I-28M Apparatus with Combustion Tube Length of 4 Feet and I.D. of 2.0 Inches).

JP-150				HTF-59-24			
Q(NPT) ft. <sup>3</sup> /sec.	V ft./sec.	A.I.T. °F.	$\tau$ millisec.	Q(NPT) ft. <sup>3</sup> /sec.	V ft./sec.	A.I.T. °F.	$\tau$ millisec.
<u>2 atmospheres</u>							
2.165	168	1278	29	2.180	167	1280	29.5
1.460	106	1192	46	1.465	108	1200	45
0.930	52	790	94.5	0.935	55.5	880	88
0.470	22	605	221	0.470	24	685	205
<u>3 atmospheres</u>							
3.815	154	1918	32	3.560	168	1150	29
2.580	94.5	790	52	2.450	98	895	50
1.580	54	700	91	1.560	55.5	805	88
0.775	24	596	205	0.470	23.5	615	210
<u>4 atmospheres</u>							
5.700	160	822	30.5	5.250	162	935	30.5
3.565	95	738	51.5	3.600	100	810	49
2.235	55	664	89	2.085	54.5	715	90
1.085	25	590	195	1.080	25.5	605	192
<u>5 atmospheres</u>							
5.000	104	710	47	4.730	100	740	49
2.755	53.5	642	92	2.895	57.5	665	85
1.490	27.5	584	180	1.390	25.5	575	193

<sup>1/</sup> Average values.

TABLE 4. - Summary of Data for Auto-Ignition of Various JP-6 Fuel Vapor-Oxygen-Nitrogen Mixtures in Cylindrical and Spherical Vessels Under Uniform and Non-Uniform Critical Heating Conditions (0.5 cc. Fuel).

Vessel	Oxygen Content %	Initial Heating Conditions <sup>1/</sup>			Temperatures at Ignition		
		$dTg/dt^2/$ °F./min.	$dTw/dt^2/$ °F./min.	$dQ/dt^3/$ Btu/ft. <sup>2</sup> -min.	t min.	Tg °F.	Tw °F.
<u>A. Uniform Heating Conditions</u>							
Copper Cylinder	21	38	59	5.43	11.78	12.4	420
Copper Sphere	21	(35)	66	3.89	11.38	9.7	<425
St. Steel Sphere	21	49	91	4.51	13.10	10.8	351
<u>B. Non-Uniform Heating Conditions</u>							
Copper Cylinder	21	33	82	0.237	16.44	13.9	417
Copper Sphere	21	73	213	0.536	37.20	4.3	398
St. Steel Sphere	21	(68)	470	1.112	77.22	1.4	<410
<u>C. Non-Uniform Heating Conditions</u>							
Copper Cylinder	100	31	76	0.220	15.21	14.7	405
"	21	33	82	0.237	16.44	13.9	417
"	10	35	107	0.310	21.48	11.4	408
"	5	43	113	0.328	22.71	10.3	415
"	4	56	131	0.381	26.38	8	427 <sup>4/</sup>
"	2	60	160	0.465	32.22	15	571 <sup>4/</sup>

<sup>1/</sup> Average data after 1/2 minute of heating.

<sup>2/</sup> Rates of temperature rise for central gas mixture (Tg) and vessel wall (Tw).

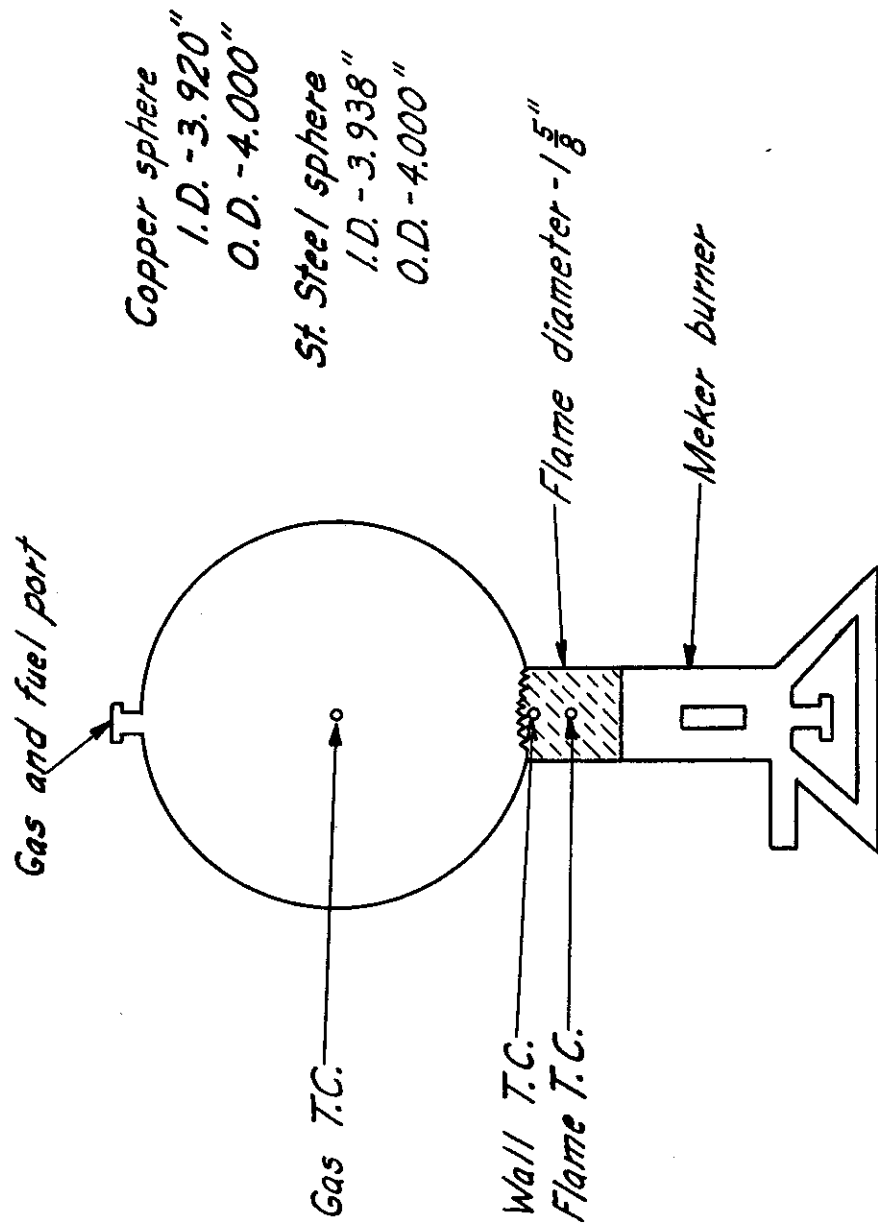
<sup>3/</sup> Rates of heat flow through vessel wall.

Uniform heating rates apply to total surface area of vessel.

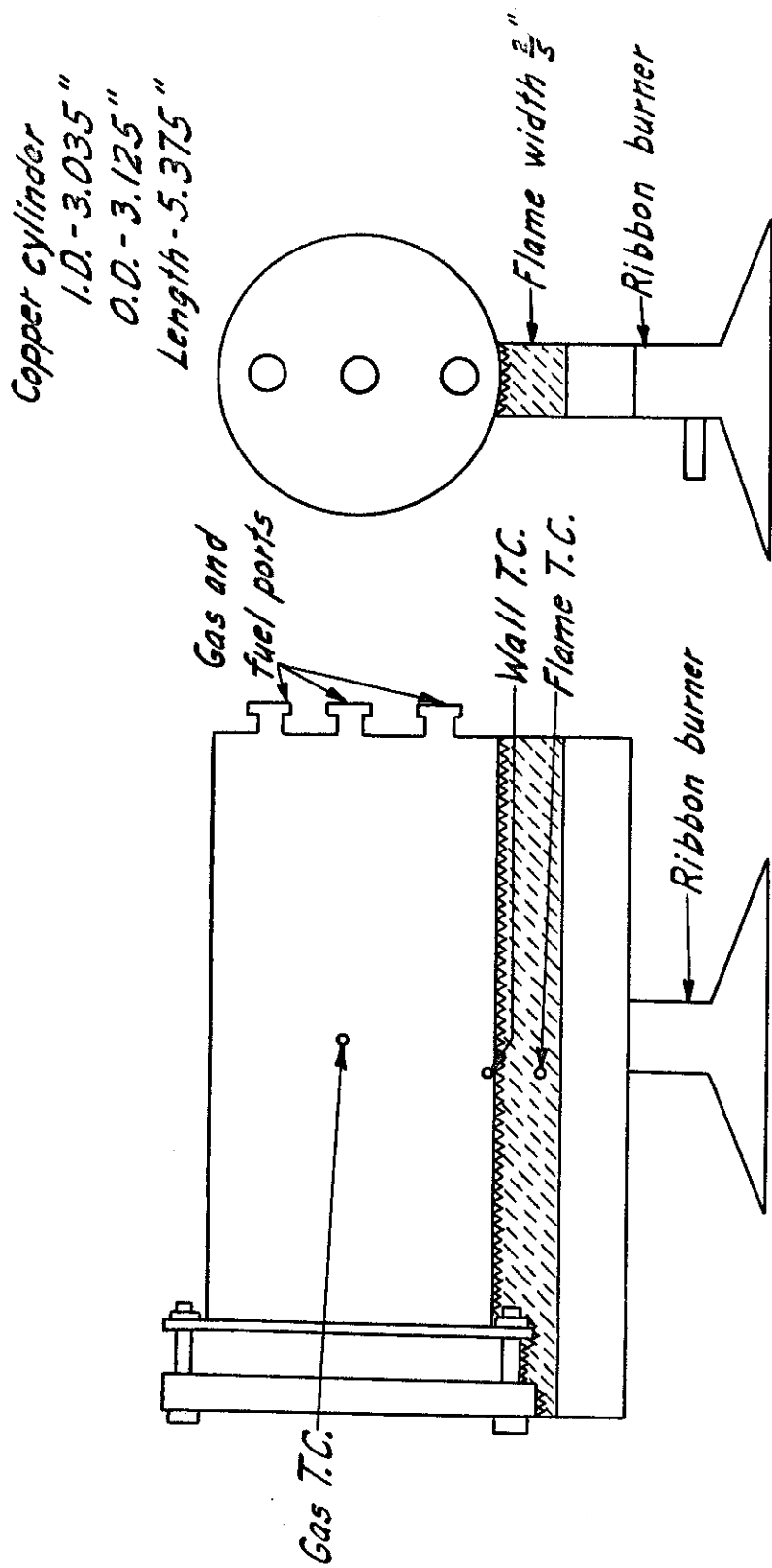
Non-uniform heating rates apply to about 4 percent of circumferential area of vessels.

<sup>4/</sup> No ignition obtained.





*Figure 1.- Nonuniform heating arrangement with spherical vessels.*



*Figure 2.- Nonuniform heating arrangement with cylindrical vessel.*

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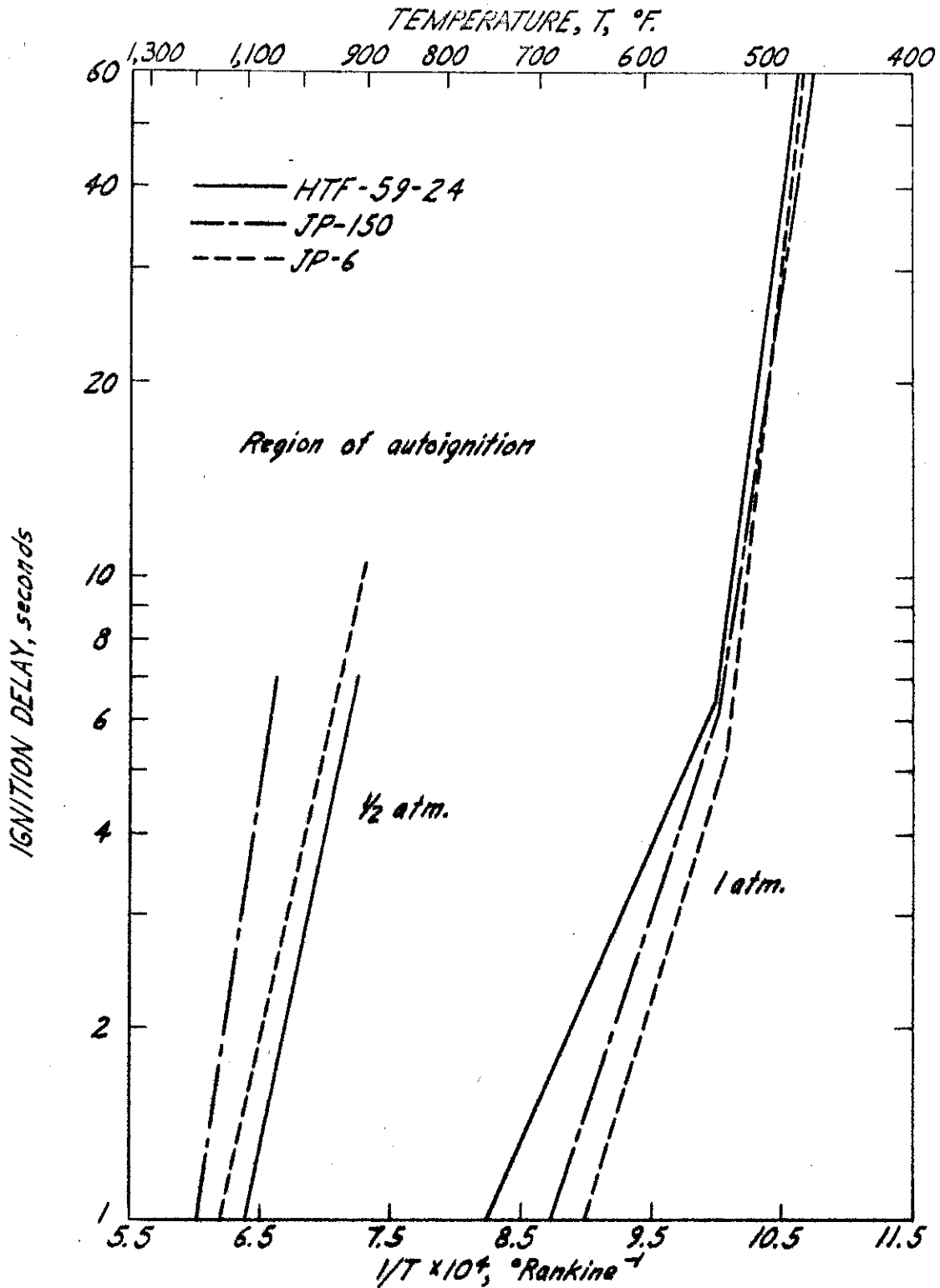


Figure 3.- Summary of autoignition temperatures and corresponding ignition delays for HTF-59-24, JP-150 and JP-6 fuels in air under static test conditions (I-8 apparatus).

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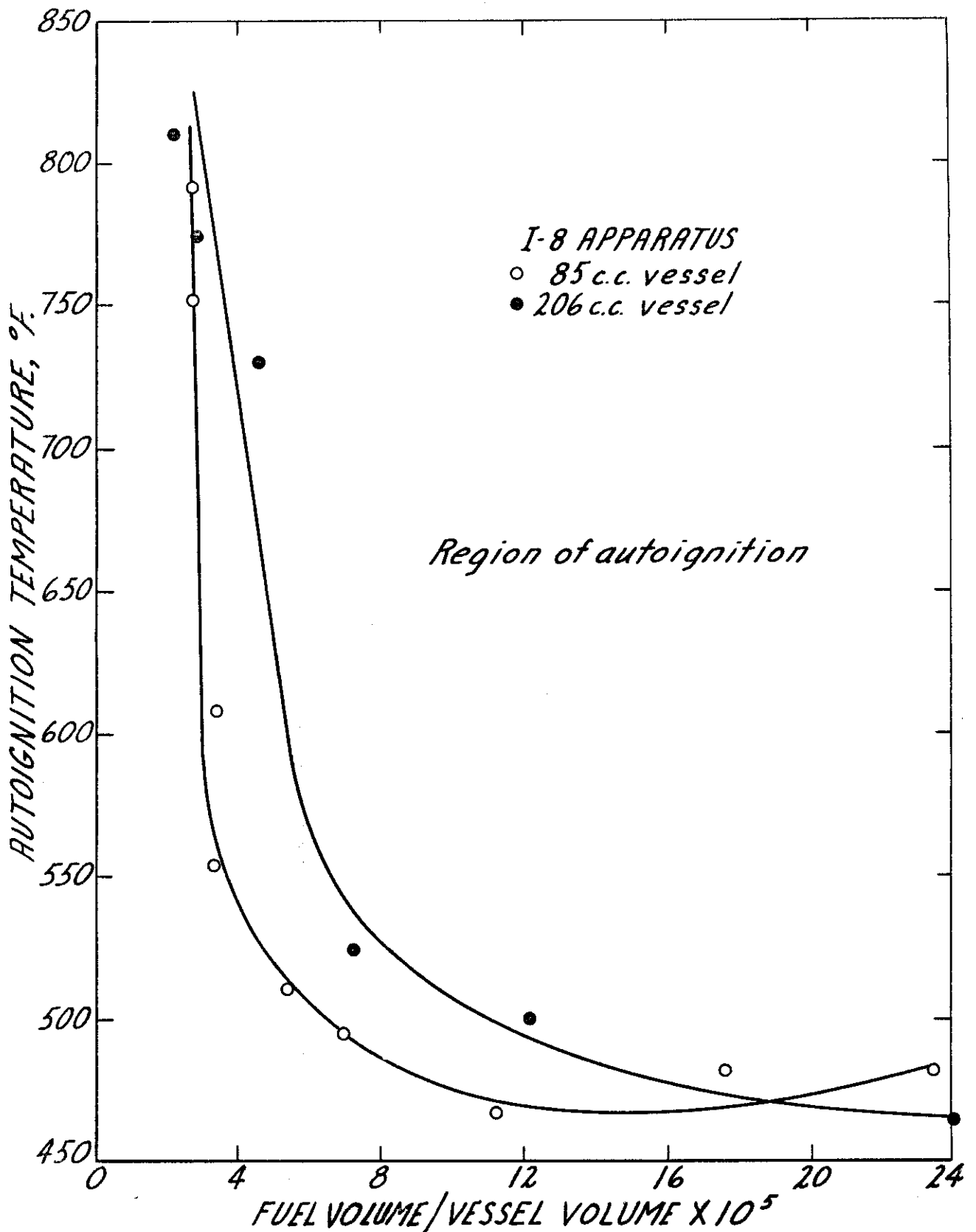


Figure 4.- Variation of autoignition temperature of JP-6 in air with ratio of fuel volume to vessel volume.

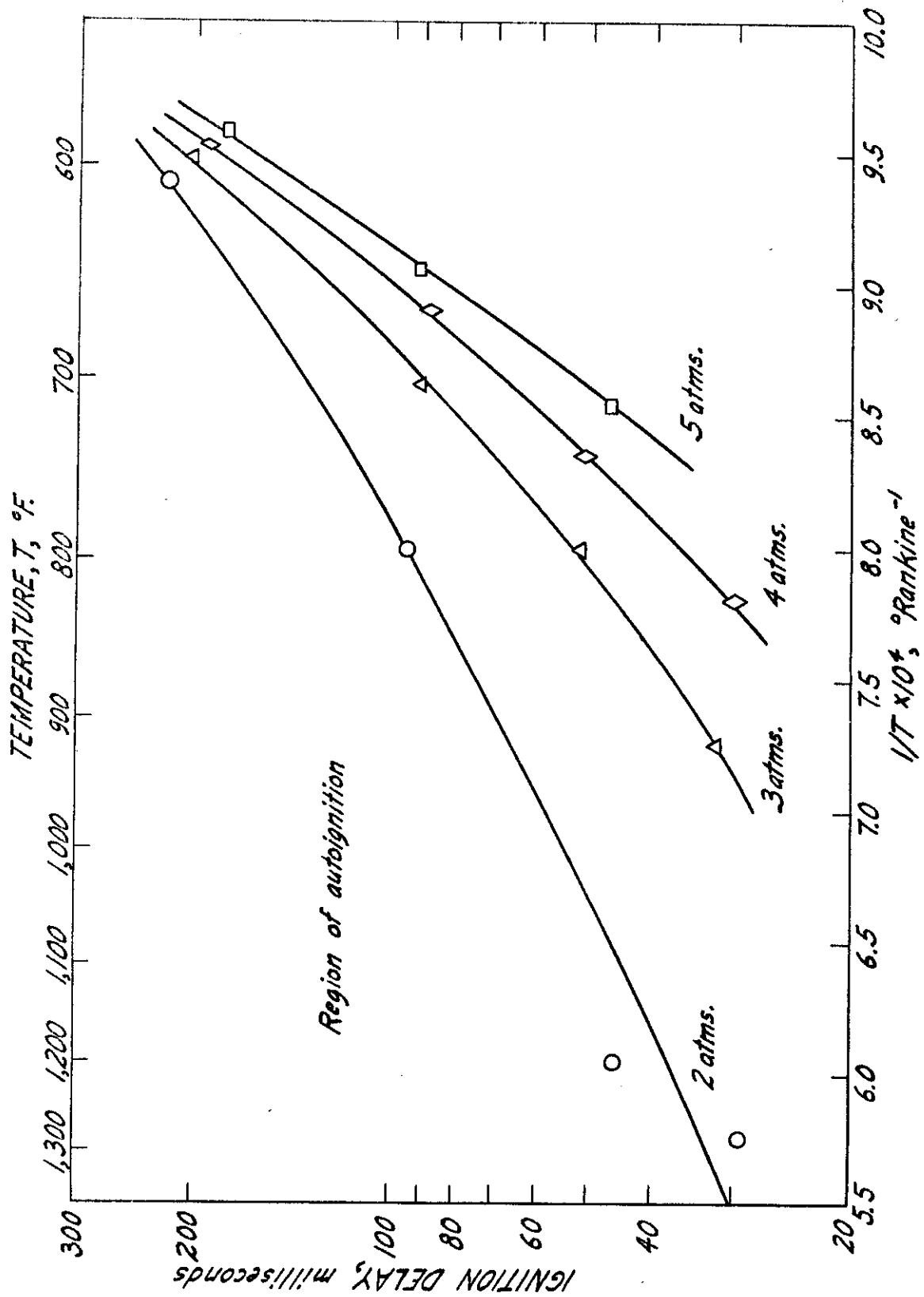


Figure 5. - Autoignition temperatures and corresponding ignition delays for JP-150 fuel in air at various pressures under dynamic test conditions (I-28M apparatus).

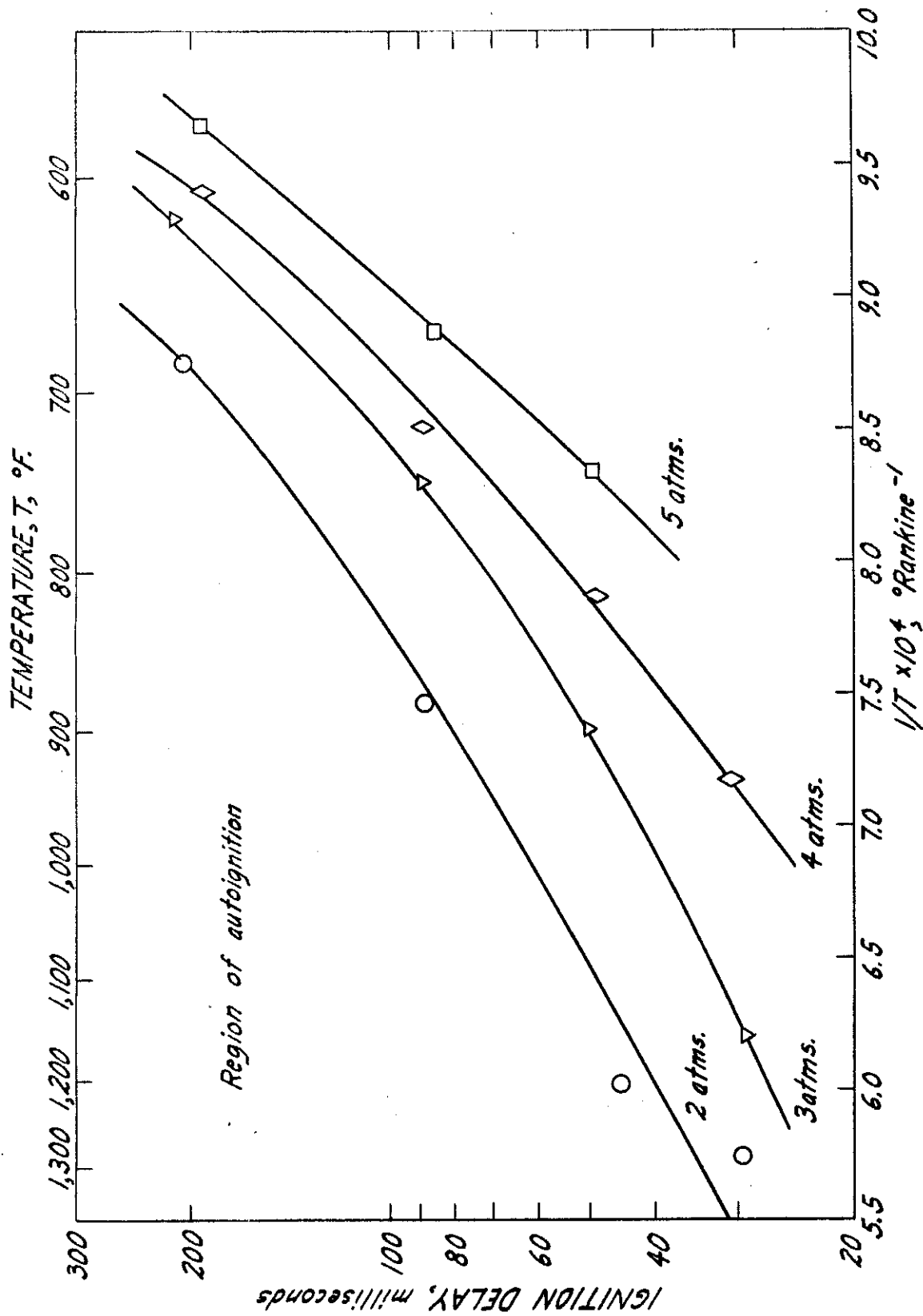


Figure 6.- Autoignition temperatures and corresponding ignition delays for HTF-59-24 fuel in air at various pressures under dynamic test conditions (I-28M apparatus).

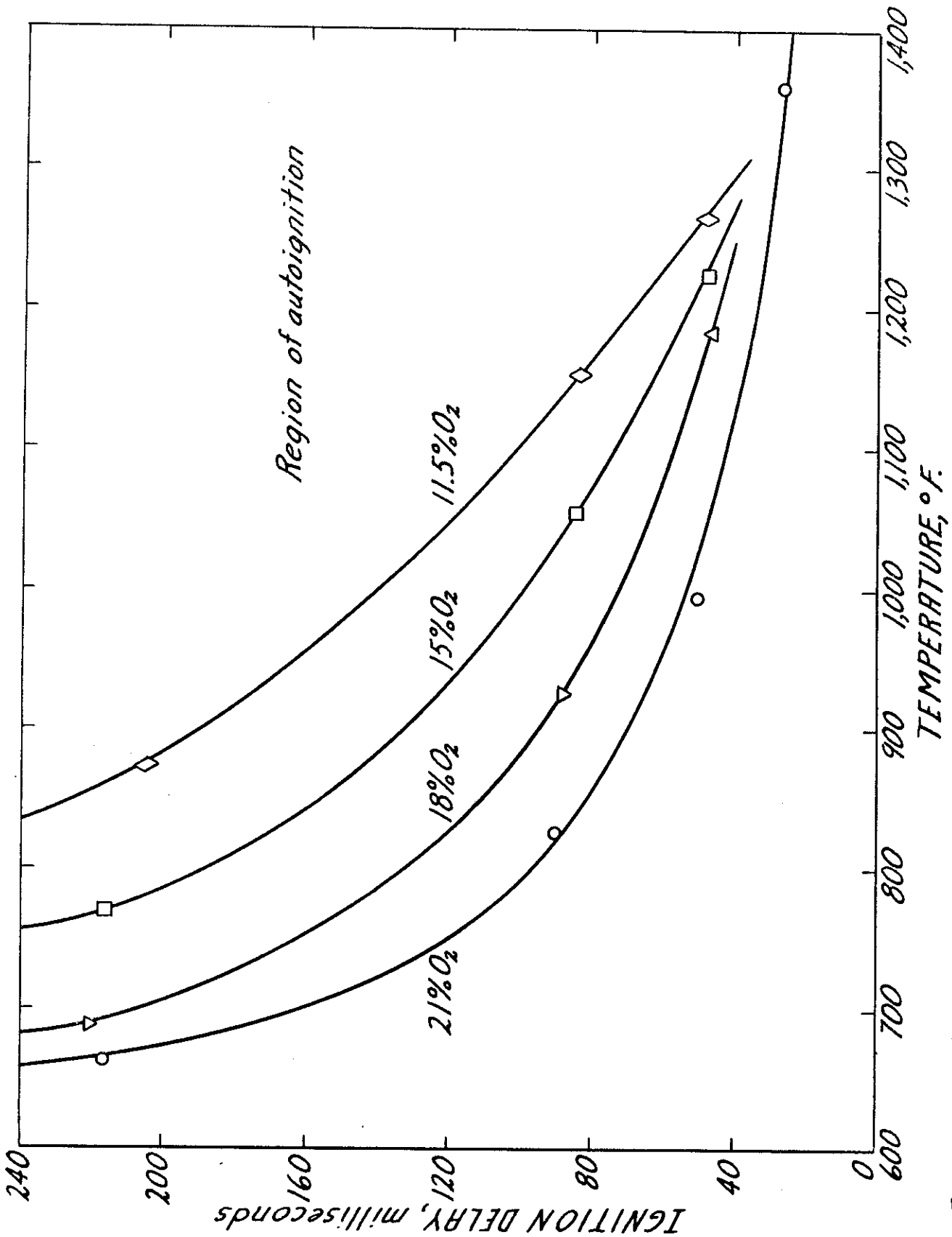


Figure 7.- Autoignition temperatures and corresponding ignition delays for JP-6 fuel in various nitrogen-air mixtures at 2 atmospheres pressure under dynamic test conditions (I-28M apparatus).

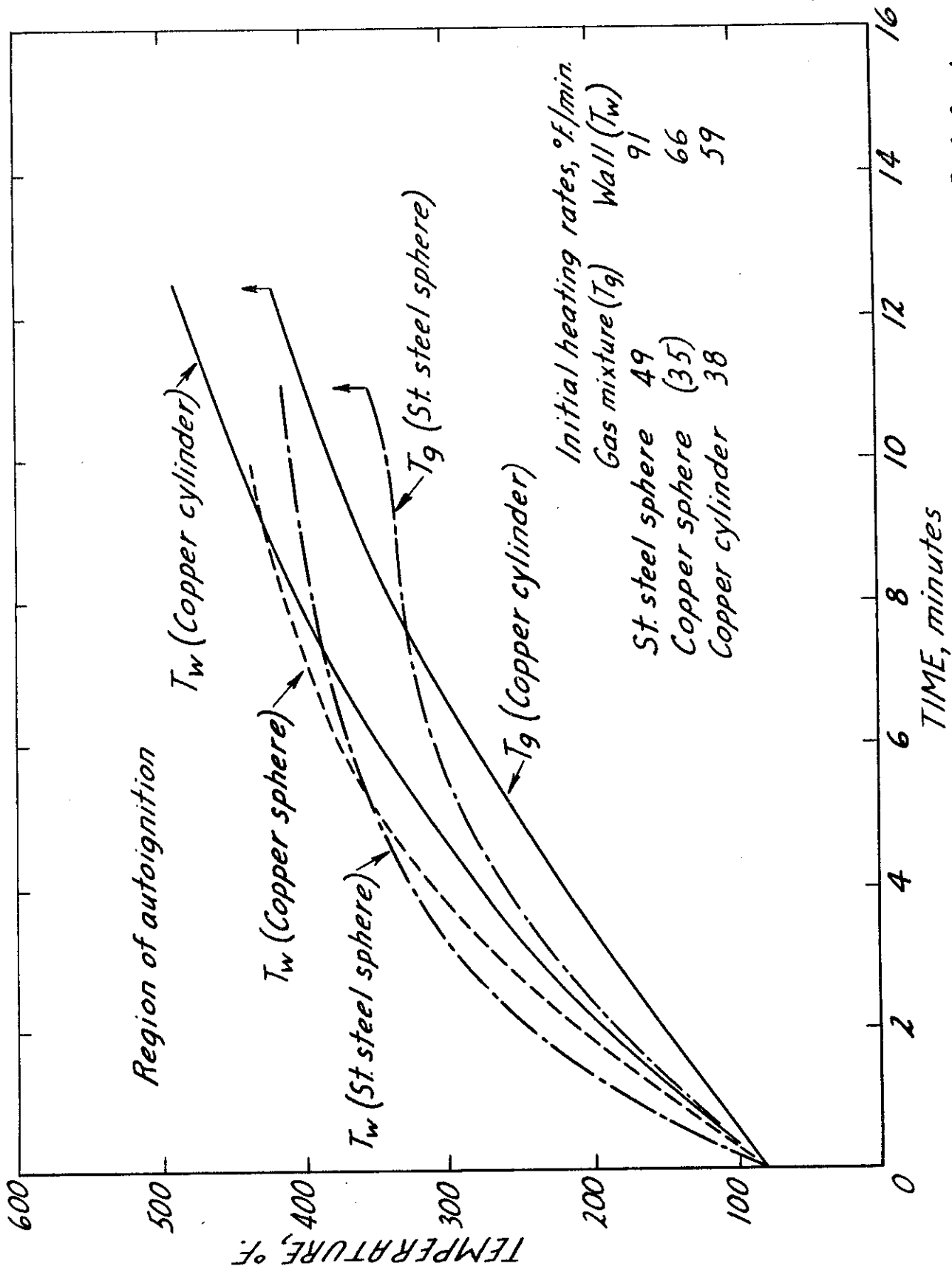


Figure 8. - Critical temperature-time curves for autoignition of JP-6 fuel vapor-air mixtures in cylindrical and spherical vessels (Uniform heating).



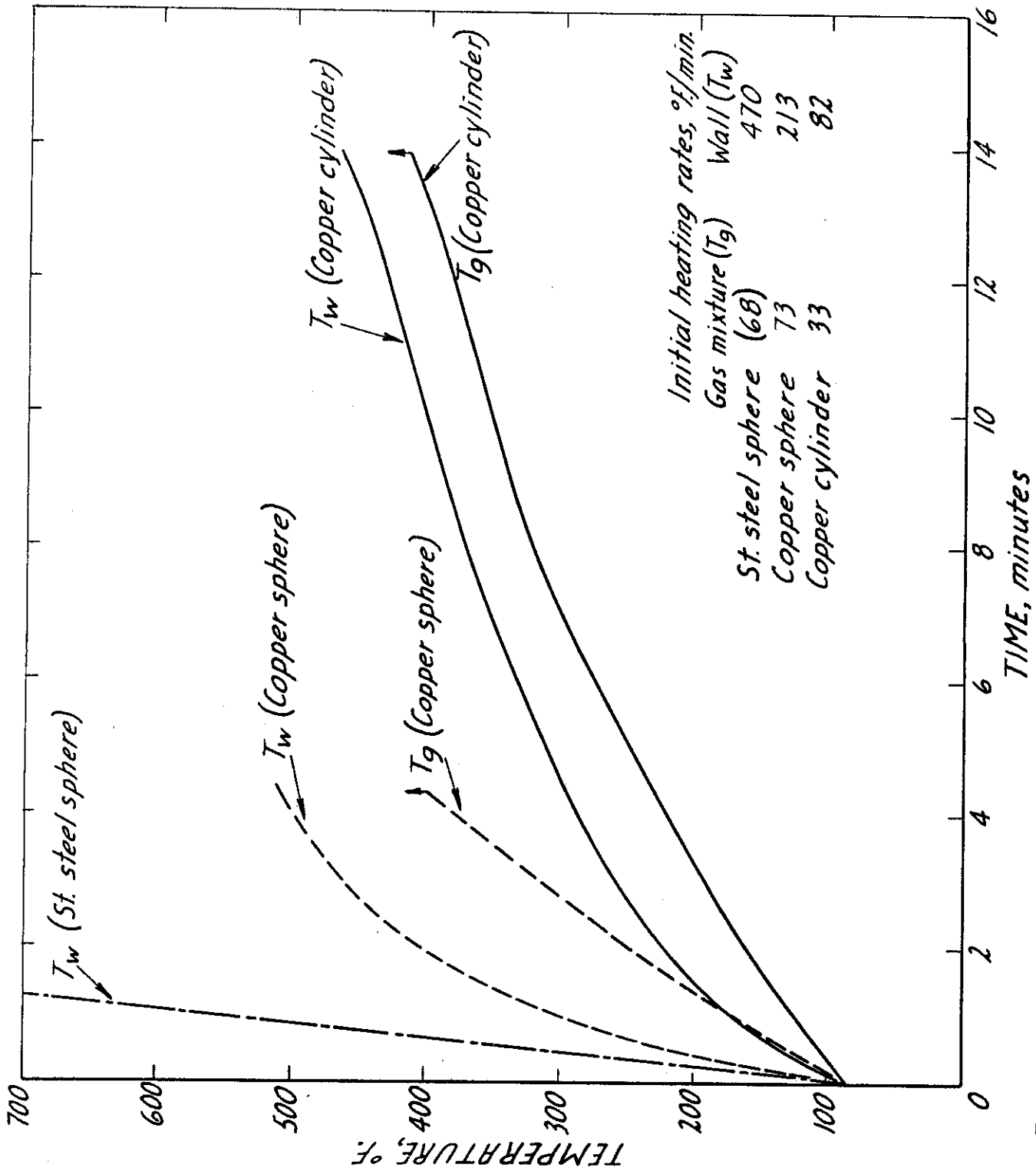


Figure 9.-Critical temperature-time curves for autoignition of JP-6 fuel vapor-air mixtures in cylindrical and spherical vessels (Nonuniform heating).

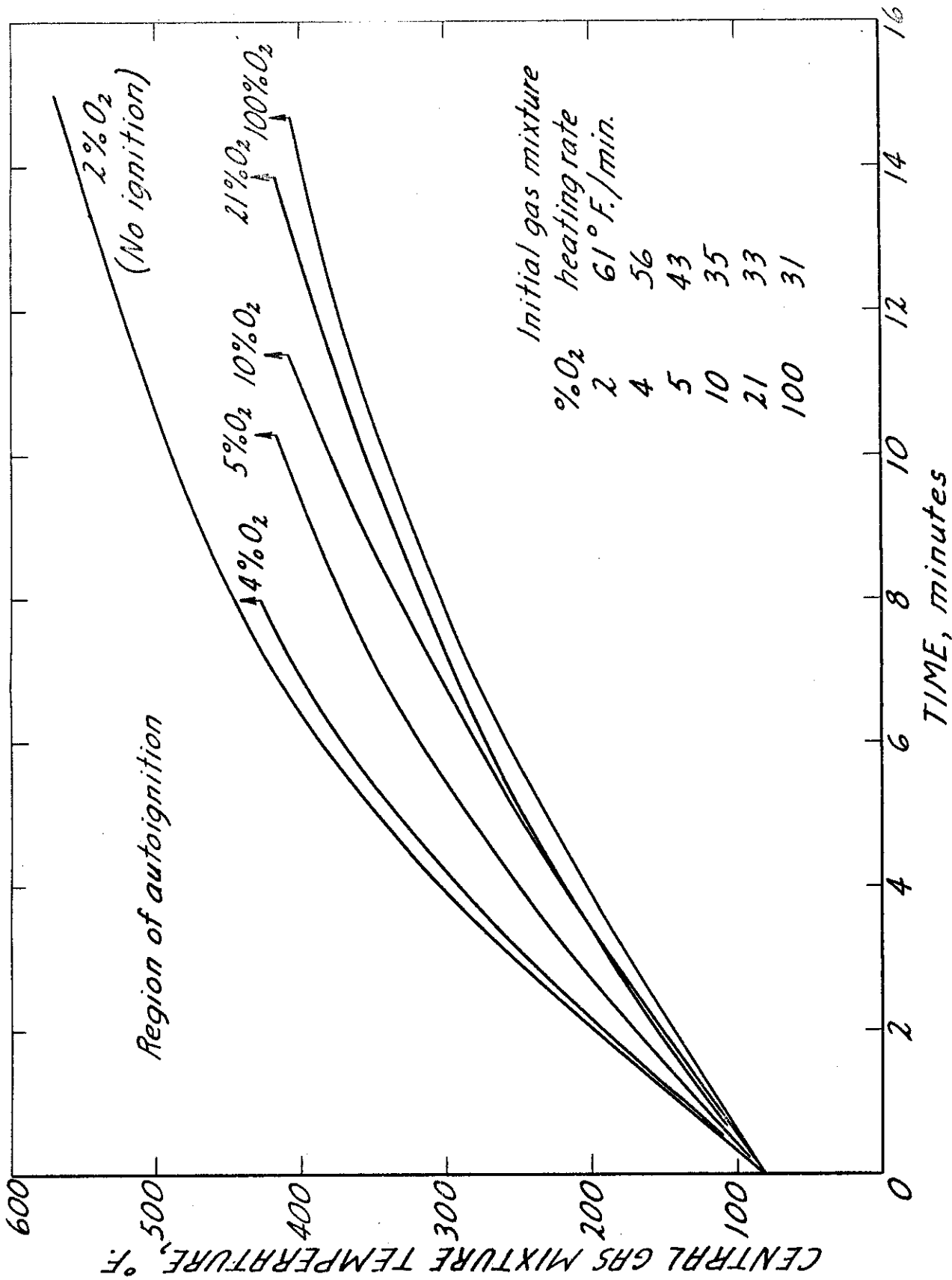


Figure 10. - Critical gas mixture temperature-time curves for autoignition of various JP-6 fuel vapor-oxygen-nitrogen mixtures in a cylindrical vessel (Nonuniform heating).

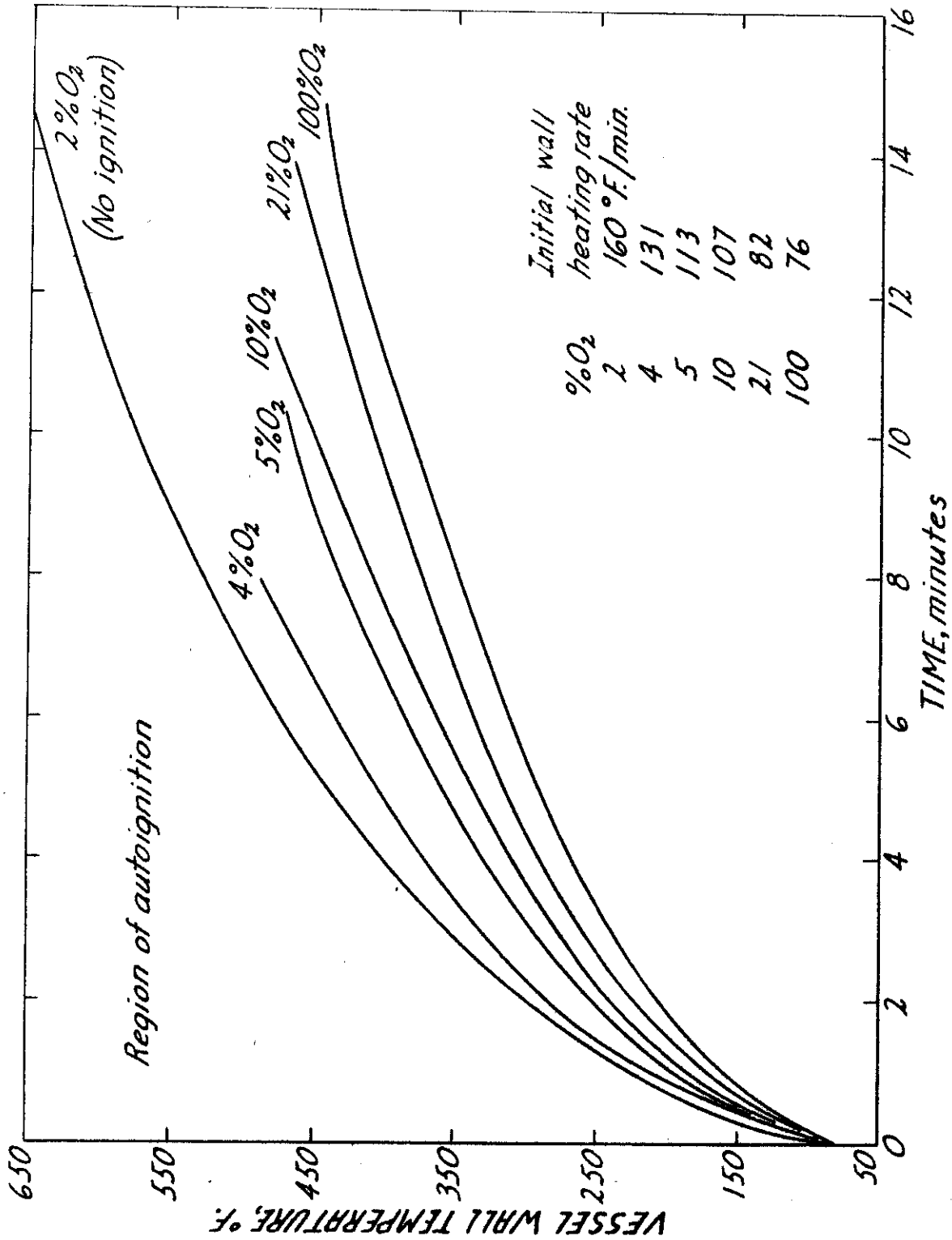


Figure 11. - Critical wall temperature-time curves for autoignition of various JP-6 fuel vapor-oxygen-nitrogen mixtures in a cylindrical vessel (Nonuniform heating).