

A STUDY OF CERTAIN FUELS FOR USE IN JET-PROPULSION EQUIPMENT

Thesis by
Eldred W. Hough

In Partial Fulfillment
of the
Requirements for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California
1943

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INTRODUCTION

The work presented here is a part of that accomplished during the last two years in the California Institute of Technology Department of Chemical Engineering in connection with the development of jet-propulsion equipment by the Guggenheim Aeronautical Laboratory of the Institute for the use of the United States Army Air Corps.

The primary object has been to collect fundamental data regarding the behavior of fuels which would aid in the design and use of jet-propulsion equipment. Wherever possible, calculation of the behavior has been made for comparison with experiment with a view to eliminating the necessity for future similar experiment.

The thesis consists of descriptions of methods and apparatus used, tabulation of results, calculated results when such calculations were possible, and conclusions regarding the behavior of the fuels in contact. This information is used at present primarily in the design of the jet-propulsive unit itself, i.e., injector, reaction chamber, and nozzle.

The appendices contain information concerning the properties of individual fuels. These data are used in consideration of storage, expulsion of fuels from storage, and the transfer of heat from the jet unit to the incoming fuels.

PART I. THE REACTION OF NITRIC ACID AND GASOLINE

A. The Reaction at Atmospheric Pressure, Utilizing Premixing.

Purpose: In this work it was desired to ascertain, by visual observation of the reaction between the two fuels, first, the effect of mixing the reactants, and, second, the effect of mixture ratio.*

Apparatus: Figure 1 constitutes a schematic drawing of the apparatus used. The acid was stored in the glass flask A and flowed to the apparatus through the resistance B. The pressure drop across the resistance was indicated by the difference in level of the acid in the arms of the manometer C, the top of which was connected to the top of the storage flask by means of the tube D. The gasoline was stored in a similar flask E and admitted to the apparatus through the resistance F. Two mercury-in-glass manometers G and H were provided to measure the pressure in the gas space above the fuels. The gas volumes above the two fuels were not connected in later measurements. Provision was made to add resistance to the respective fuel circuits by inserting glass rods J and K into the glass tubing just below the storage tanks for the purpose of varying the relative rates of flow of the two liquids. The absolute rate of flow was varied by varying the pressure on the fuels in the storage vessels, using the regulator L connected between the fuel system and a nitrogen tank.

Figure 2 illustrates the details of the premixing injector.

Gasoline entered through the tube M and was forced upward, along with the acid which entered in the tube Q, through the small annular space between the outside of a glass rod N and the inside of a glass tube P and into the

* Mixture ratio was taken as the number of pounds per second of acid used per pound per second of gasoline.

nozzle R. The two fluids were mechanically mixed by rotation of the rod N, the lower end of which was immersed in mercury and connected by means of a short piece of rubber tubing to a steel shaft T, which was connected to an external pulley through a packing gland. Since the clearance between N and P was quite small, about 0.01 inch, and the rod P could be driven at speeds up to 500 revolutions per minute by a small electric motor, it is certain that the two nearly immiscible fluids were well mixed mechanically. Cooling of the mixing chamber was provided by the water jacket S.

The nozzle R of Figure 2 was placed through a rubber closure into the bottom of a steel tube V of Figure 1 which was provided with three small observation ports and was exhausted to the atmosphere by means of a suction fan. Water was circulated on the inside surfaces of the tube to remove unreacted fuels and to prevent excessive corrosion from the presence of free nitric acid.

Procedure: The mixture ratio was adjusted, the flow started, and the reaction then initiated by means of an oxygen-gas flame inserted through an observation port. The mixture ratio was adjustable during a run as was the mixing, the latter by varying the motor speed.

Results: Two different grades of nitric acid were tried: technical and red fuming. The first exhibited a specific weight of 83.528 pounds per cubic foot at 77° F, which corresponds to 0.465 per cent water according to reference (1). The specific weight of the second was 98.65 pounds per cubic foot at 77° F, which corresponds to 0.19 weight fraction nitrogen dioxide if no water is present, according to Klemenc and Rupp (2). One grade of gasoline was used, namely, summer-grade unleaded automotive fuel

(sample 210) purchased from the Texas Company. This fuel had a specific weight of 46.269 pounds per cubic foot at 80° F and a carbon-hydrogen ratio which can be expressed by the formula $C_8H_{16.18}$. Both samples of nitric acid behaved in much the same manner. The mixture ratio was varied between the limits of 4 to 1 and 10 to 1, and the flow rates were about 1.8×10^{-3} pounds per second of total reactants, which, with the glass rod P of Figure 2 turning at 500 revolutions per minute, gave a well-dispersed emulsion in the tip. The dispersed mixture was ignited by means of a small oxygen-gas flame mounted to come in contact with the fluid in the immediate vicinity of the tip of the capillary nozzle R shown in Figure 2. The reaction, at atmospheric pressure, did not occur at any time in the immediate vicinity of the tip. In the region above the tip the more intense burning was on the surface of the droplets, which burned more rapidly as their size decreased upon falling through the surrounding blue flame of the gasoline reacting with the air.

This behavior indicates that the reaction is of the gas-phase type* at atmospheric pressure since, even with good liquid-liquid dispersion, rapid rates of reaction do not occur. In the case of full-scale equipment utilized by other parts of this project (3), the probable reason for the more violent reaction experienced, if the reaction is of the gas-phase type at higher pressures, is the increased rate of heat transfer to the droplets of liquid from the gas, which is known to be approximately proportional to

* In this dissertation, "gas phase", referring to the reaction between two liquids at a given pressure, will be used to indicate that a large amount of heat transfer into the reactants, presumably enough to cause their vaporization, is a much more important factor in obtaining energy from the reaction than is mixing. "Liquid phase" will be used to denote the opposite type of reaction; that is, the reaction between two liquids at a given pressure is of the liquid-phase type if the intimacy of contact of the liquids, referring specifically to interfacial area per unit of total volume, is of more importance in obtaining energy from the reaction than is heat transfer into the liquids.

the pressure (4) for constant-temperature difference between the gas and the droplets.

B. The Reaction of the Preheated Fuels at Atmospheric Pressure.

Purpose: The experiment described previously, which indicates that the reaction between nitric acid and gasoline does not occur to an appreciable extent in the liquid phase at atmospheric pressure, suggests the investigation of the reaction with preheating. This was done, with the object of determining the minimum preheating temperatures of the fuels necessary to give reasonably rapid reaction in the cases of several grades of nitric acid, and of ascertaining the nature of the products of reaction as a function of mixture ratio in the case of the red fuming type of acid if the preheating temperatures were held constant at these minimum values.

Apparatus: The equipment used for the study of the gas-phase reaction is shown in Figures 3 and 4 and is shown in schematic representation in Figure 5. The flow of the two fluids from the storage flasks was controlled and measured in the same manner as for the liquid-phase apparatus. The nitric acid was introduced into a primary preheating section A in Figure 5 of large cross-section compared to the line before it. Thus the acid vapors were permitted to escape without disturbing the flow of the liquid. The vaporized and partially decomposed acid was then introduced into a preheating section B, which raised the temperature of this material to the desired value. A thermocouple in the well E was provided to measure the temperature of the preheated oxidizing agent before it entered the reaction chamber G. The preheaters A and B were constructed of pyrex glass tubing, with resistance wire wound on the glass, and were operable up to 750° F. There was sufficient heat capacity to avoid appreciable variations in outlet temperature due to

minor variations in flow rate. The gasoline was preheated in a similar fashion, but in a single preheating chamber C, and its temperature was observed by a thermocouple in the well F.

The reaction was initiated by means of a spark plug located at K, and the products were removed through a trap H by a suction fan attached to J. The pressure existing within the chamber could be ascertained by a water-in-glass manometer L. Product samples for analysis were drawn off through a heated filter M, through a condenser N at 60° F, and then through a trap O, a condenser P, and a second trap Q, all at 32° F. From the trap Q, the gas flowed into the storage reservoir R, which had been evacuated previously through the line S. The pressures existing in the different parts of the system were ascertained by two mercury-in-glass manometers T. Samples of gas were withdrawn for analysis through the stopcock U. The water condensing in the traps O and Q was measured gravimetrically, and the acid present was titrated. These data together with the total quantity and analysis of the gas collected in R permitted the evaluation of the water content of the products of reaction. The container R was filled at the rate of about 1 cubic foot per hour, maintaining the vapor pressure of water in the container essentially the same as that in the second trap, about 2 millimeters of mercury, which made the quantity of water in R negligible compared to the quantity in the traps O and Q.

The Orsat gas-analysis apparatus used in these investigations consisted of a manifold with various absorption pipettes connected through stopcocks and of a constant-volume burette connected directly to the manifold. A mercury-in-glass manometer measured pressure in the burette relative to the atmosphere. Constant temperature in the measuring burette was maintained by means of a

water jacket. The sample of gas to be analyzed was passed successively through solutions of sulfuric and nitric acids, potassium hydroxide, potassium pyrogallate, and cuprous chloride to determine, respectively, the relative quantities of oxides of nitrogen, carbon dioxide, oxygen, and carbon monoxide. In one case (0.159 weight fraction gasoline) the relative quantities of nitric oxide and nitrogen dioxide were measured by selective absorption in concentrated sulfuric acid and in concentrated sulfuric acid with concentrated nitric acid. From the determination of the total nitrogen and the trivalent nitrogen in the first solution, and of the trivalent nitrogen in the second solution, the oxides of nitrogen could be calculated. The total nitrogen was determined by nitrometer, while the trivalent nitrogen was determined by titration with potassium permanganate. It was not possible to determine hydrogen or hydrocarbons with this apparatus.

An improved Orsat apparatus was constructed for later measurements. An absolute-pressure manometer and a calibrated burette in a constant-temperature air bath are used for measurement of the quantity of gas. A copper oxide combustion tube and a platinum wire combustion pipette have been added for the determination of carbon monoxide and hydrogen, and of hydrocarbons, respectively. This apparatus is shown in the photograph, Figure 6. The air bath containing the measuring burette is shown at the right of the apparatus, and the electronic circuits associated with the absolute-pressure manometer and the air bath are in the box near the center of the apparatus. The absolute-pressure manometer is above the measuring burette.

Procedure: The vaporizing and preheating tubes A, B, and C were brought to the desired temperatures. Then a small stream of air was introduced into the reaction chamber through a stopcock (not shown) between the manometer L and the reaction chamber G. The spark K was started. When gasoline was admitted to the chamber G through the tube C, a gasoline-air reaction resulted. Acid was admitted through A and B, and the air was stopped as soon as the gasoline-acid reaction started. The suction fan was adjusted so that the reaction chamber was at a pressure of a few inches of water above the atmospheric pressure. Then a sample of gas was drawn through the condenser and trap sequence N O P Q into the evacuated glass bottle R. The time involved in starting the reaction was about 10 minutes, after which time the lower part of the steel reaction vessel maintained a steady temperature of about 1300° F. The withdrawal of the sample required another 20 minutes. During all this time the reaction proceeded smoothly, and no difficulty was experienced with respect to either instability or explosion.

Results: Three different samples of nitric acid of different specific weights were tried with the same sample of gasoline previously described in order to establish optimum preheating temperatures.

The first sample of nitric acid, No. 213, was of the c.p. red fuming variety, and exhibited a specific weight of 97.965 pounds per cubic foot at 80° F, corresponding to 0.170 weight fraction nitrogen dioxide. This reacted with the gasoline described in the liquid-liquid experiment (sample 210) to give the hottest flame, using the minimum preheating temperature of 490° F for the acid and 490° F for the gasoline, at weight fraction of 0.875 red fuming acid in the fuel. As a matter of interest simple equations were computed for this particular sample of acid, the composition of which is derivable

from the density if no water is present (2), and for this gasoline, assuming a molecule that would give the correct carbon-hydrogen ratio. If all the products are assumed to be carbon dioxide, water, and nitrogen, the simple reaction indicates 0.8417 weight fraction red fuming nitric acid in the reactants. Taking the products to be carbon dioxide, water, and nitric oxide, the equation corresponds to a weight fraction of red fuming nitric acid of 0.9014 in the fuel. It is realized that the products assumed here are quite different from the true ones, but this type of calculation seems to have definite value in estimating the mixture ratio to be tried first when experimenting with or making more exact calculation for an unknown fuel. In this case the experimental value of weight fraction nitric acid which gives the best reaction with the lowest preheating temperature lies between the two calculated values.

The second sample of nitric acid tried, No. 214, was of the commercial fuming variety and was found to have a specific weight of 92.081 pounds per cubic foot at 77° F, which corresponds to 0.156 weight fraction water in the acid. With sample 210 of gasoline the optimum preheating temperatures were found to be 530° F for the acid and 460° F for the gasoline, the corresponding weight fraction of white fuming acid in the fuels being 0.815. However, a somewhat more intense reaction was obtained at a weight fraction of 0.844 fuming acid in the fuels, the acid being preheated to 700° F. This reaction was not so intense as that of the red fuming acid.

Simplified equations give 0.9650 weight fraction fuming nitric acid in the reactants if the products are assumed to be carbon dioxide, water, and nitrogen, and 0.9129 weight fraction acid in the case of carbon dioxide, water, and nitric oxide.

The third sample of nitric acid, No. 209, possessed a specific weight of 83.528 pounds per cubic foot at 80° F, which corresponded to 0.465 weight fraction water in the acid. It was not possible to sustain a reaction of this material and sample 210 of gasoline, even though both reactants were preheated to 750° F.

This behavior bears out that predicted by the other two samples of acid. The very deleterious effect of water is probably due to the large amount of energy required for its dissociation (5). The results of these essentially qualitative experiments are presented in Table I.

The products of reaction of the sample of commercial red fuming nitric acid, No. 217, of specific weight 98.459 pounds per cubic foot at 80° F, which corresponds to 0.1905 weight fraction nitrogen dioxide if no water is present, and of the sample 210 of gasoline used earlier were determined as a function of mixture ratio at the optimum preheating temperature of 480° F for both reactants. The actual rate of flow, in the case of 0.159 weight fraction gasoline, was 3.48×10^{-4} pounds per second and 0.66×10^{-4} pounds per second for the nitric acid and gasoline, respectively. The uncertainties in these rates are about 0.033×10^{-4} pounds per second.

The composition of the products for three different weight fractions of gasoline in the mixture is indicated in Table II. The amount of carbon monoxide in the products varies markedly with mixture ratio, being less than 0.01 mole per cent at 0.120 and 0.159 weight fractions of gasoline but increasing to 17.30 mole per cent at 0.266 weight fraction gasoline. Also the quantity of oxides of nitrogen present at this pressure is quite small in the case of 0.266 weight fraction gasoline, but is larger for the mixtures more rich in acid. Carbon dioxide is higher in the case of the lower weight fractions of gasoline. No free oxygen was found in any case.

It is possible to estimate the amount of free carbon produced in the reaction from material balance. As a matter of interest this has been done, and the results expressed in Table III. By material balance, the relative amounts of hydrogen and nitrogen in the gas inert to the early Orsat analysis apparatus described above were estimated. It is seen that the carbon and hydrogen increase if the weight fraction of gasoline in the reactant mixture is increased.

The enthalpy change of reaction assuming reactants and products at 64° F has been calculated from the data of the Bichowsky and Rossini (5) relating to the molal enthalpies of the components, and is shown in Table III. It is seen that the energy obtained, per pound of reactants, does not vary greatly as the mixture ratio is varied. This is to be expected since the enthalpy change for formation from elements in the molecular state of nitric acid, water, and carbon dioxide is high compared to carbon monoxide, hydrogen, and gasoline. Increasing the amount of acid, which is the oxidizer, gives more carbon dioxide and water which have high enthalpies of formation, but more energy is also required to decompose the additional nitric acid, resulting in a very small overall effect of mixture ratio upon energy released.

The adiabatic temperature of the reaction has been calculated using the relation which assumes a thermally perfect^a but calorically imperfect^b gas:

^a A thermally perfect gas obeys the equation of state $p v = b T$, where p is the total pressure, v is the specific volume, T the absolute temperature of the gas, and b a constant.

^b A calorically perfect gas is defined as a thermally perfect gas with constant specific heat under constant pressure or constant volume.

$$-\Delta H = \sum_h m_h \int_{t_0}^{t_c} C_{Ph} dt$$

where ΔH = enthalpy change per pound of reactants for both reactants and products at a temperature t_0 °F

t_c = chamber or reaction temperature in °F

t_0 = temperature of reactants in °F

m_h = weight fraction of component h present in products

C_{Ph} = heat capacity of product h in Btu/lb/°F

The values of enthalpy have been calculated, from spectroscopic transition probability and energy level values of heat capacity available in the literature, by the Department of Chemical Engineering (6). These temperatures are recorded in Table III.

The expressions for the equilibrium constants for several reactions between the products have been computed on the basis of analytical results and compared with the equilibrium constants given by Lewis and von Elbe (7) evaluated at the adiabatic reaction temperature. In general, considerably more oxides of nitrogen and carbon are present than equilibrium values indicate. This may mean that equilibrium is not attained in the reaction, or that the equilibrium shifts during the sampling process, or both.

The nitrogen dioxide found was considered to be all decomposed to nitric oxide and oxygen at the reaction temperature for the purposes of calculation of experimental expressions. The symbol (h) will be used to denote the fugacity in atmospheres of the component h. The fugacities of the gases present were computed on perfect gas assumptions.

In the case of 0.266 weight fraction gasoline of Table II, the experimental value of the expression for the water-gas reaction, $(\text{CO})(\text{H}_2\text{O})/(\text{CO}_2)(\text{H}_2)$, is 8.78, compared to 5.75 for the equilibrium constant at 3780° F. This is good agreement. The computed value of $(\text{CO})^2/(\text{CO}_2)(\text{C})$ is probably of the order of 10, while the equilibrium constant has a value of 191,000. This is possibly satisfactory, because no actual determination was made of the carbon. The oxygen, computed from the equilibrium value of the $(\text{CO})(\text{O}_2)^{\frac{1}{2}}/(\text{CO}_2)$ expression, 0.0166, comes out to be 0.000132 mole fraction, which checks because no oxygen was detected. The oxygen can also be computed from the equilibrium constant $(\text{H}_2)(\text{O}_2)^{\frac{1}{2}}/(\text{H}_2\text{O})$ which has a value of 0.0030. The oxygen computed on this basis is 0.00033 mole fraction. However, the check with respect to the nitric oxide, which can be computed from the equilibrium constant $\text{NO}/(\text{O}_2)^{\frac{1}{2}}(\text{N}_2)^{\frac{1}{2}}$ whose value is 0.046, and from the average of the two above indirect values for oxygen, 0.00023 mole fraction, is not satisfactory. The calculated value of nitric oxide comes out to be 0.000377 mole fraction, while the measured value is 0.0545 mole fraction.

The water-gas reaction does not enter into the check for the two mixtures with more oxidizer, since no hydrogen or carbon monoxide was found.

In the instance of 0.159 weight fraction gasoline, some oxygen is present if the nitrogen dioxide is considered decomposed. Using this amount to calculate the value of $(\text{NO})/(\text{O}_2)^{\frac{1}{2}}(\text{N}_2)^{\frac{1}{2}}$ gives 3.30, which is much larger than the 0.066 indicated for equilibrium. Again there is too much nitric oxide present. The experimental and equilibrium values of $(\text{CO})^2/(\text{CO}_2)(\text{C})$ are, respectively, indeterminate, because carbon monoxide was not detected and carbon was not measured, and 300,000, which is possibly satisfactory. By the expression $(\text{CO}_2)/(\text{O}_2)^{\frac{1}{2}}(\text{CO})$, which has a value at equilibrium of 0.050, and the above-mentioned value for oxygen, it is possible to calculate the

value of carbon monoxide if equilibrium is obtained. This comes out to be 0.0806 mole fraction and actually none is observed. Similarly it is possible to calculate the value for the hydrogen present from the equilibrium constant $(\text{H}_2\text{O})/(\text{O}_2)^{\frac{1}{2}}(\text{H}_2)$, which has a value of 0.0087. The calculated value for hydrogen is 0.00237 mole fraction, against none observable by attempting to burn the gas inert to the Orsat analysis. This is considered to be only qualitative evidence that this equilibrium is not satisfied.

For the 0.120 weight fraction gasoline point, there is again too much nitric oxide found experimentally. The value of $(\text{NO})/(\text{O}_2)^{\frac{1}{2}}(\text{N}_2)^{\frac{1}{2}}$ computed from the analysis, evaluating the oxygen from the decomposition of the nitrogen dioxide as before, is 1.51. The equilibrium value is 0.060. The values of $(\text{CO})(\text{O}_2)^{\frac{1}{2}}/\text{CO}_2$, $(\text{H}_2)(\text{O}_2)^{\frac{1}{2}}/(\text{H}_2\text{O})$, and $(\text{CO})^2/(\text{CO}_2)(\text{C})$ are calculated to be, respectively, 0, 0, and indeterminate, and the equilibrium values are 0.039, 0.0068, and 300,000, respectively. These are considered to be in satisfactory agreement.

C. A Study of the Reaction from Full-scale Jet-propulsion Equipment.

Purpose: Since equilibrium does not obtain in the reaction at atmospheric pressure, it was desirable to investigate the reaction at higher pressure, considering the possibility of calculating performance if equilibrium were actually established.

The values of temperatures obtained from a gas analysis are of practical importance in design consideration, and in addition it would be possible to check the efficiency of the unit.

Apparatus: The jet unit used was similar to that described in a report (3) of another section of this project, and in fact was designed, built, and operated by that section.

The chamber was 3 inches in diameter by 1 foot in length, inside dimensions. The jet diameter was 0.75 inch at the throat and 1.5 inch at the lip. A short sample tube with valve attached was inserted in a drilled hole leading into the jet which made an angle of 60 degrees to the direction of flow. The location of the inside end of the hole in the copper jet wall was halfway between the throat and lip. This tube connected to a container approximately 0.67 cubic foot in capacity through two ice-cooled traps in series, all of which could be evacuated. The injector consisted of 36 holes 0.031 inch in diameter through which red fuming nitric acid entered, and of 18 holes 0.025 inch in diameter through which gasoline was injected. The fuel injector holes were arranged on a circle about 2 inches in diameter, while half of the acid holes were on a circle about 0.25 inch less in diameter and half on a circle about 0.25 inch more in diameter, so that each stream of gasoline was impinged from two sides by streams of acid.

Procedure: The sampling system was evacuated up to the valve near the jet. To insure the sample's being representative of the steady-state reaction the sample was taken during a 16-second time interval which omitted 3.5 seconds at the beginning and 3.5 seconds at the end of the run. The nitric acid used was of the commercial red fuming variety similar to sample 217 described earlier, and the gasoline was of the aviation type, 100 octane, leaded.

Results: The first part of Table IV contains the results of the gas analysis. It is obvious that some air entered the sampling apparatus, because the presence of hydrogen is not compatible with that of oxygen. The water-gas equilibrium is well satisfied here. The value of $(CO)(H_2O)/(CO_2)(H_2)$ from the gas analysis is 4.29, while that of equilibrium at this temperature is 5.9.

This indicates that the results are probably fairly reliable from the standpoint of calculation of performance, because a large part of the enthalpy change of the reaction is determined by this equilibrium. There is definitely nitric oxide in excess, since using the value for the oxygen due to nitrogen dioxide and nitrogen tetroxide considered decomposed, plus that found in the free state at room temperature, a value probably larger than actual, gives a value for $(NO)/(O_2)^{\frac{1}{2}}(N_2)^{\frac{1}{2}}$ of 1.592 compared to 0.051 for equilibrium. Certainly too much nitric oxide is present. The experimental values of $(O_2)^{\frac{1}{2}}(CO)/(CO_2)$ and $(H_2)(O_2)^{\frac{1}{2}}/(H_2O)$ are both of about an order of magnitude larger than the equilibrium values, perhaps because of the presence of air in the sample.

Unfortunately the experimentally measured values of thrust, flow of reactants, and chamber pressure are not available because of failure of the recording apparatus. However, the values calculated from the gas analysis agree fairly well with other similar runs. The main sources of error in the gas analysis are (i) the reaction of the oxides of nitrogen with the mercury used as a confining fluid in the Orsat apparatus, (ii) the solubility of the carbon dioxide in the sulfuric acid used as an absorbent for the oxides of nitrogen, which was corrected for but may cause the determination of carbon dioxide to be in error by as much as 0.05 mole fraction according to the data of Markham and Kobe (8), and (iii) the presence of hydrocarbons in the gas inert to the solutions used and to copper oxide at 482° F, which is probably small because this gas would not burn in air.

It is possible to test the consistency of the gas analysis by a relation between exhaust temperature, the angle between the direction of

flow and the direction of observable discontinuities in the jet discharge, the exhaust velocity, the average molecular weight, and the ratio of isobaric to isochoric heat capacity. The relation whose development is indicated elsewhere (9) is

$$T_e = \frac{U^2 \sin^2 \alpha M}{\gamma Rg}$$

- where
- T_e = exhaust temperature °R
 - U = exhaust velocity, feet per second
 - α = angle between direction of flow and observable disturbances in the stream
 - M = average molecular weight
 - γ = ratio of isobaric to isochoric heat capacity of the gas
 - R = gas constant in foot pounds per °F per pound mole
 - g = acceleration due to gravity in feet per second per second

Using the values obtained from the gas analysis $U = 6014$, $M = 26.04$, $\gamma = 1.20$, and a value of α obtained from a photograph of a similar run, $\alpha = 24^\circ$, the exhaust temperature is found to be 2145° F, with an uncertainty of about 300° F, due mostly to the uncertainty of 1.5 degrees in measuring α . This is in agreement with the value of 2175° F of Table IV.

It is to be regretted that these measurements could not be repeated and made more satisfactory from the standpoint of correlating the measured large-scale data to the gas analysis, and also from the standpoint of eliminating air from the sample. At this time the problem of ignition and of stability of operation was more pressing than the analysis of the efficiency of the operation of the jet unit.

D. The Initiation of the Reaction.

Purpose: The previous investigation indicated that the reaction between nitric acid and gasoline at atmospheric pressure is of the gas-phase type. This implies then that at higher pressures the reactants should be introduced separately into the chamber in the gas phase to eliminate irregularities that might occur in their vaporization if the energy for this process were supplied by the conduction and radiation from the hot gases of the reaction. However, objections to this procedure were raised by other sections of this project on the grounds that application of such a jet unit would be too complicated for practical use.

An appreciable part of the difficulty connected with a unit that does not use preheating arises in starting the reaction. This process necessarily takes place near atmospheric pressure which is the pressure of poorest heat transfer from the gas to the liquid. Hence it was decided to study the initiation of the reaction of the dispersed reactants with various mixture ratios and different degrees of dispersion, using different ignition devices.

Apparatus: The schematic diagram of the flow of the reactants is shown in Figure 7. The acid was stored in a welded stainless-steel tank A and was maintained at a pressure of 20 pounds per square inch on the inlet side of a calibrated chemical proportioning pump K, by means of air pressure. The pump is of stainless-steel construction with 0.375-inch bore, a stroke continuously adjustable from zero to 1.5 inches, and a speed of 59 cycles per minute. The discharge from the pump K entered a pressure vessel B, supported on a balance C. The null point was indicated by electric contacts at D, which actuated small neon lamps through electronic circuits at E and F, and

was accurate to about 0.001 pound (0.5 gram). Nitrogen was introduced into the upper part of the vessel B from a supply tank G, and the pressure on the system was indicated by a gauge I. This chamber, in addition to indicating steady-state conditions of flow through the system, served to smooth the pulsating flow from the proportioning pump. An analogous system, designated by primed letters, was provided for the gasoline. The two pumps were linked mechanically.

Figure 8 shows this apparatus with the proportioning pump in the right foreground, the controls in the left center, the balances with pressure vessels suspended below in the right center, and storage tanks at the far right.

After leaving the vessel B of Figure 7, the oxidant was passed through a heat exchange coil J. The coil, whose surface area in contact with agitated oil was 1.2 square feet, was quite large for the flow which was less than 0.01 pound per second. A similar heat exchanger J' was provided for the gasoline. The components of the heat exchanger are shown photographically in Figure 9. A cross-sectional diagram constitutes Figure 10. The fluid entered the device through the tubing A at the fitting E and passed downward through a tubing in contact with heated oil which was circulated by the impeller F. A valve B controlled the discharge of the fluid. The oil bath was heated electrically by chromel ribbon heaters wound on the outer wall of steel tubing. The impeller was driven through a water-cooled packing gland G. A similar heat exchanger J' of Figure 7 was provided for the gasoline. Platinum gaskets were used to seal the tubing to fitting joints where nitric acid was involved, while copper gaskets were used in the case of the gasoline. Provision was made to control temperature

automatically by a thermoregulator J.

As shown in Figure 7, the outlet of the heat exchangers connected directly to the reaction chamber through electrically heated lines. The products of reaction were removed by an exhaust fan after being washed with a water spray in the scrubber unit S.

The arrangement of one reaction chamber is shown in Figure 11, and a view of the component parts is shown in Figure 12. Referring to Figure 11, the reactants were introduced through small opposed nozzles B and C into the chamber A. The diameters of the different nozzles used varied from 0.0041 inch to 0.0168 inch. A fritted-glass filter of opening approximately 0.0015 inch was used before each nozzle less than 0.010 inch in diameter. A pyrex window which also acted as a blow-out plug was provided in the fitting D. A pressure release valve H which could be loaded by the spring K and adjusted by a hand wheel L permitted the products of reaction to escape through the chamber M to the exhaust port J. A stream of water was maintained in M to remove any unreacted material, and a thermocouple was placed in J to detect ignition in the chamber. The chamber, which was of copper, was water cooled near the valve seat at the annular space N, and the valve H was also cooled by water circulating in the interior. Ignition devices were introduced through the fitting F. Fittings F and D were interchangeable. A slightly different chamber was constructed from stainless steel to avoid ionic corrosion from unreacted oxidant. The nozzles which injected the reactants were located at an angle of 90 degrees to each other, and a separate pyrex window and blow-out plug were provided. Provision was made to heat the chamber electrically. Ignition devices were introduced into the chamber through a fitting at the top. This fitting was later

altered to accommodate a sample line for the study of the products of reaction of nitric acid and aniline. The chamber with this revised fitting will be shown later (Figures 16 and 17).

The ignition devices used are shown in Figure 13. The fittings a and b utilize an electric spark, while the active element in c is a hot wire. The electric insulation of the fitting a was maintained in the presence of dispersed nitric acid by a continuous stream of oil introduced at C into the space B. The approximate energy of the spark was measured by a wattmeter in the primary of the spark transformer, and the resistance of the unit was ascertained by a milliammeter placed in series with the secondary. An improved form of this spark fitting is shown in Figure 13b. The effective dynamic oil surface was vertical, on the surface of the porous plug F, so that a smaller flow of oil was required to maintain the insulation of the plug. In the case of the hot-wire fitting c no special insulation was necessary because low potential was used. The current in and voltage drop across the hot-wire element were measured at the temperature used in ignition attempts and at the ice point with a smaller current. This made possible a computation of an average temperature of the element and of the power dissipated per unit surface.

All temperature measurements were made by copper-constantan thermocouples. The potentials were measured on a potentiometer. The thermocouples were calibrated against a strain-free platinum resistance thermometer which had been calibrated at the National Bureau of Standards. Final temperature measurements are probably within 0.5° F of the international platinum scale.

Pressure measurements were with Bourdon-tube gauges and were probably uncertain by less than 5 per cent. This large value is acceptable for the present experiment because the ignition is experimentally found to be fairly insensitive to pressures in various parts of the system.

The rate of flow of the reactants was ascertained from direct calibration of the pumps at various pressures and stroke lengths. The uncertainty was probably about 3 per cent, except for a short period when, because of corrosion of the pump valves, the uncertainty was much larger, possibly 10 per cent.

Procedure: The heat exchangers, lines, and chamber were brought to the desired temperature. Then pressure was built up in the chambers B and B'. In general a few seconds before the flow was started the ignition device was turned on by opening the valves between the heat exchangers and the reaction chamber. For short periods of flow it was found more accurate to calibrate the discharge characteristics of the nozzles in order to ascertain the rate of flow of the reactants. The inside of the chamber was observed continuously through the observation port with a telescope and mirror arrangement to ascertain if reaction occurred or, in case no reaction occurred, if the injection nozzles were aligned. If the reaction did not occur, the flow of reactants was terminated after 10 seconds, the equipment flushed with nitrogen, and the process repeated. After each series of trials the whole apparatus was dismantled and cleaned to avoid ionic corrosion.

Results: The influence of temperature, mixture ratio, and dispersion was investigated along with the power input and, in the case of the hot wire, the surface density of power.

The gasoline used was of the unleaded aviation type, 89.5 octane, which had a specific weight of 44.261 pounds per cubic foot at 77° F, and was refined by the Shell Oil Company. The color was water white, and there was no noticeable gum formation from the fuel.

The acid used was of the commercial red fuming variety, with specific weight between 97.350 and 98.624 pounds per cubic foot at 77° F. If it is assumed that no water is present, these values correspond to 0.137 and 0.190 weight fraction nitrogen dioxide, respectively.

The results may be divided into two parts, (i) opposed injection nozzles using the copper chamber and (ii) injection nozzles intersecting at 90 degrees using the stainless-steel chamber.

In the case of the opposed jets, spark ignition of about 15 watts power was tried first, at atmospheric pressure, with injectors in the range from 0.0063 to 0.014 inch in diameter, and injection pressure 75 to 100 pounds per square inch above chamber pressure. Ten attempts at ignition with no air present gave no ignitions. Seventeen trials with air introduced at the start gave seven successful ignitions, which reacted smoothly after starting. These results are summarized in Table V. It is believed that the resistance of dispersed nitric acid and gasoline is so low that effective development of energy between the electrodes of the spark to ignite the mixture is prevented since, when the reactants were introduced, the spark would gradually lose its intensity. However, it was by no means due to a failure of the insulation of the ignition fitting itself, because the discharge would recover to its original intensity when the flow of the reactants was stopped. This could be repeated a large number of times.

It was possible to start the reaction with fair certainty by introducing oxygen at the beginning. The first reaction was gasoline-oxygen, initiated by the spark, which was of sufficient intensity to start the gasoline-acid flame when the acid was introduced.

Opposed injection jets with hot-wire ignition were investigated. In general for average wire temperature greater than 1400° F, corresponding to a surface dissipation of energy of 390 watts per square inch, the ignition was satisfactory for mixture ratios of acid-gasoline lying between 4.5 and 9.2 if the wire was located so as to come in contact with a portion of the reactants which are roughly in this range of mixture ratio. In this apparatus, the lower limit of hot-wire surface was about 0.05 square inch, smaller surface areas giving pressure surges because the probability of vaporizing enough reactants to start the reaction in a time before there is a large accumulation of reactants in the chamber decreases with the amount of hot-wire surface. These results are indicated in Table VI.

In general, oxygen or air was not necessary to start the reaction in this case. Nor was preheating essential. These facts indicate that the reaction, under the conditions of ignition in jet-propulsion equipment, is in the gas phase, since the hot wire, which gives successful ignition, tends to vaporize a large quantity of the reactants, while the spark treats more violently a smaller quantity.

The ignition characteristics of the chamber in the jets intersecting at 90 degrees were ascertained. Careful alignment with water at the pressure of the reactants, as well as subsequent visual observation, insured that the intersection of the jets of reactants involved at least 75 per cent of the

cross-sectional area of each jet. A simple model, assuming that the two reactants mix and have identical velocities afterward, indicates that 64 per cent of the original kinetic energy of the jets is used in the mixing process in the case of opposed jets but that this figure is reduced to 28 per cent in case of the 90-degree intersection, if the mixture ratio in pounds of acid to pounds of gasoline is taken as 4 to 1. The time required for the dispersed reactants to traverse a given distance is only 30 per cent less in the case of jets intersecting at 90 degrees. One would expect then that the ignition characteristics with the apparatus under consideration might be markedly different, because of poorer dispersion.

This difference was verified experimentally. In no case was ignition satisfactory with the hot wire, which the previous experiments indicate is better than the spark. In one case, however, air was introduced and the reaction proceeded. In one other case when the reactants and chamber were preheated to 200° F, the reaction proceeded but was unstable. A large variety of geometric configurations of the hot wire were tried, and during the whole time the reactant jets were of velocity of the order of 100 feet per second. Table VII summarizes these results.

E. Summary of the Nitric Acid and Gasoline Reaction.

All of the evidence collected indicates that the reaction of nitric acid and gasoline as utilized in the various pieces of apparatus described is of the gas-phase type.

On this hypothesis ignition is difficult because, starting at atmospheric pressure, heat transfer to the droplets of the reactants is probably at least one order of magnitude smaller than during the operation

of the unit, if heat transfer is considered proportional to the pressure, for a given temperature.

In large-scale practice when preheating is not employed, the reaction has been found to be inherently unstable. This indicates a time delay between the introduction of the fuels into the chamber and their reaction.

Mechanisms for two types of oscillations can be seen. The first is the simple mechanical oscillation. A small rise in chamber pressure will result in a drop of pressure across the injection orifices, which will slow down the rate of injection of the reactants and cause the chamber pressure to drop. The lower chamber pressure will result in a larger pressure drop across the injection orifices, which will give a surge of reactants resulting in a higher chamber pressure, and so on. The absolute pressure in the chamber needed to stop the reacting process completely in this case is the injection pressure, which in practice is about 200 pounds per square inch above the normal chamber pressure of 300 pounds per square inch absolute. The period of the oscillations would depend on the length of the fuel lines, but the observed period of 0.2 to 0.1 second, approximately, is not an unreasonable value to expect for this sort of oscillation. More detailed consideration has been given to this problem by another section of this project. The question of whether or not this instability enters in could be decided by using a very high injection pressure with a large amount of resistance in the reactant lines. This has not been done on a large scale.

The second type of instability that may enter probably has a very high frequency, of the order of 3×10^2 or higher. It may be possible that this oscillation couples with the first type to give the observed frequency.

The reason advanced for this possible instability is that, assuming vaporization to be essential for a reasonably complete reaction, an increase in pressure of only 135 pounds per square inch can completely reverse the evaporation from the nitric acid in the droplets, if it occurs before the temperature of the droplet has changed appreciably. This value is estimated from the values of the bubble points for red and white fuming nitric acids given in Appendix B. At 300 pounds per square inch absolute, it is estimated that the dew-point temperature of nitric acid containing 0.15 weight fraction nitrogen dioxide is 289° F. At this temperature the bubble-point pressure is estimated to be 435 pounds per square inch absolute. The increased pressure required to stop the evaporation is very much less than this for acid that contains less nitrogen dioxide. Also it is probable that the difference between bubble and dew points for gasoline at a given temperature is larger than for the red fuming acid. For one sample investigated by Bahlke and Kay (10), at the temperature of 560° F, corresponding to a dew point of 300 pounds per square inch, the bubble-point pressure is 510 pounds per square inch. If such an interruption of evaporation occurred it would have to occur in a fairly short time before the temperature of the drop increased markedly. An estimation of this possibility can be had. Consider that the injection velocity is about 100 feet per second and that the drop probably travels one-third of the chamber length of 1 foot before evaporation. This would

indicate that the pressure increase would have to take place in less than 3×10^{-3} seconds, or with a frequency of at least 3×10^2 per second. The velocity of sound in the chamber is about 3140 feet per second for the example of full-scale equipment given earlier. Thus a pressure wave could be transmitted to any part of the chamber in 3×10^{-4} seconds. After the slowing down of evaporation due to a slight increase in pressure, the pressure would drop because the reaction had been slowed, the temperature of the acid droplets in the hot chamber would rise somewhat, and finally a flush of gas would occur, resulting in a larger mass of reacting material and therefore a rise in pressure. Thus oscillation could be set up. It is possible that supersaturation of the droplets could aggravate the situation. The process is possible if these assumptions are true.

No pulses of this frequency have been measured. However, it would be recommended that an attempt be made to observe them if further work is to be done on the use of this reaction without preheating.

The indicated procedure to cure either type of instability is to preheat the reactants. If the first type is predominant, preheating will decrease the time required for the reaction after the reactants enter the chamber. If the second type is important, preheating will eliminate altogether uncertainties in the process of vaporization.

In the case of the aniline-acid reaction discussed in the second part of this dissertation, the second type of instability presumably does not enter, because it would take extremely large pressures to affect a reaction of the liquid-phase type, even assuming that pressure influences it adversely.

It can also be concluded that gas analysis is of definite value in

estimating temperature and performance of the jet unit.

PART II. THE REACTION OF NITRIC ACID AND ANILINE

It was found by others (11) of this project that the reaction of nitric acid and aniline was well behaved and stable on the large scale. The limitations were efficiency of the weight ratio used (1.5 to 1) and the high freezing point of aniline (21.02° F). It was desired to study the reaction to ascertain if improvements could be made.

A. Crucible Tests with Nitric Acid and Aniline.

Purpose: In order to get the feel of the reaction and to ascertain the effect of additive agents in the aniline for freezing point lowering upon the spontaneity, it was decided to investigate the reaction of the reactants mixed relatively slowly in a small crucible.

Apparatus and Procedure: A porcelain crucible approximately 1 inch in diameter, 1 inch deep, and 0.03 inch thick, insulated from its surroundings by an air jacket, was used. The total amount of reactants used was about 0.001 pound (0.4 gram). Doubling this amount did not appreciably affect the time required for reaction. A chromel-alumel thermocouple using wire 0.010 inch in diameter was placed in the bottom of the vessel.

One reactant, usually the aniline, because the acid had a corrosive effect on the thermocouple, was placed in the crucible, having been measured volumetrically from a micropipette. Then the other reactant was introduced in as short an interval as possible from another pipette kept at the same temperature as the crucible. The temperature of the reactants was observed on a critically damped galvanometer of a period of 0.5 second connected to a potentiometer. In general the temperature of the reactants would rise at a

fairly slow rate, of the order of 100° F per second, to about 370° F, after which temperature flame was observed and the rate of increase of temperature was too rapid to be followed with the apparatus used. The time interval beginning with the introduction of the second reactant and ending at the ignition was measured.

Results: It is emphasized that these experiments do not exhibit the reaction under the same conditions as it occurs in jet-propulsion equipment. The time required for complete mixing is at least two orders of magnitude larger in the present experiment, and the heat losses are greater. The former, however, is of much greater importance, as is borne out by the rate experiment.

The acid used had a specific weight of 97.781 pounds per cubic foot at 77° F, corresponding to 0.155 weight fraction nitrogen dioxide if no water is present. The aniline used was of c.p. grade with a boiling range of 361.4° to 366.8° F and with less than 0.0004 per cent non-volatile material present.

Figure I* shows the time delay associated with the ignition of nitric acid and aniline at 77° F as a function of mixture ratio. Each point is an average of 5 to 10 experimental points, some of which may differ from the average by as much as 50 per cent of the average value. This difference is probable due to the fact that much of the mixing was from convection from the heat generated in the reaction. A minimum average time delay is obtained in the vicinity of 3 or 4 weight ratio of acid to aniline. Later equilibrium calculations and experiment on a large scale have indicated a maximum of

* Figures indicated by roman numerals refer to data. Figures referred to by arabic numerals contain descriptions of apparatus.

reaction temperature in this region, but it is clear that such conclusions cannot be extended to large scale from the present experiment.

Appendix A contains data relating to the efficient freezing point lowering substances for aniline, acetone, and methanol. Having ascertained the crucible test behaviors of a mixture (acid and aniline) whose behavior in jet-propulsive apparatus was known, it was desirable to try crucible tests on unknown mixtures, such as acid and aniline containing acetone or methanol.

This was done, and the results are shown in Figures II and III for acetone and methanol, respectively. Compositions corresponding to points enclosed by the broken lines are within the region judged to be satisfactory with respect to time of ignition, compared to the nitric acid-aniline reaction. It is seen that in this experiment it is possible to add to the aniline up to about 0.25 weight fraction acetone without impairing ignition. This figure is lower for methanol, perhaps 0.15 weight fraction. Lowered temperatures did not greatly influence results.

The conclusion is that, until data from actual large-scale runs are available, acetone is to be used instead of methanol because it has a less deleterious effect on the reaction in the crucible than has methanol.

B. Rate of Reaction Experiment.

Purpose: It was hoped to design an apparatus that would give the time-temperature history of the reaction of nitric acid and aniline. It was proposed to force the reacting materials at a known rapid rate through a tubing and to measure the temperature at different points of the path. The reaction proved to be rapid enough to render the obtaining of such data

impractical. However, useful information was obtained from the experiment.

Apparatus: The system used to supply the reactants at a known rate, pressure, and temperature was exactly that described earlier and shown in Figures 7 and 8. The rate apparatus itself is shown in Figures 14 and 15. Referring to Figure 14, the red fuming nitric acid entered through the fitting A, passed through the check valve B, the nozzle N, and into the chamber C. Aniline was forced into C through a similar fitting A'.

The reacting mixture passed downward through a tube D, on which thermocouples were located at predetermined distances. A loose-fitting stainless-steel cylinder P occupied most of the space above the two horizontal holes leading into C. A shear disc S was provided to permit the plug P to be blown out if high pressures were encountered. All parts were of stainless steel with the exception of the gaskets and the shear disc, which were of lead.

Procedure: In actual operation, a liquid such as kerosene, that does not react spontaneously with nitric acid and is relatively insoluble in aniline, was introduced into a part of aniline line next to the apparatus. This enabled the flow to be started and adjusted before the nitric acid and aniline came into contact. A mixture ratio of 7, much leaner than the optimum, which lies between 3 and 4, indicated by crucible tests and equilibrium calculations, was chosen for the first trial. The acid used contained about 0.15 weight fraction nitrogen dioxide. The thermocouple immediately below the chamber was observed continuously, and provision was made to read the other six in rapid succession.

Results: The consequence of this experiment was a rupture of the shear disc S of Figure 14 and of the tubing D, just below the fitting. The time required for the reactants to pass through the chamber C and the 2.5 inches of narrow tubing to the point D was 0.037 second. The temperature of a point on the tubing located 6 inches below D did not change as much as 5° F during the operation. Thus the time required for fairly complete reaction was probably about 0.03 second. When compared to the previous experiment, this shows that the time required for ignition of this reaction depends primarily on the mixing of the reactants and not on the conditions of heat transfer to the surroundings.

In the present experiment, the heat transfer from the reactants to the surroundings was very good, the reactants being in a small cavity, 0.0084 cubic inch in volume (average linear dimension about 0.2 inch), in a large steel block at room temperature. The time for fairly complete mixing was also very short, probably of the order of 10^{-2} seconds, the velocity of the fluid in the nozzle tip N being about 50 feet per second, in the chamber C about 2 feet per second, and in the fitting and tubing after the chamber about 20 feet per second.

The crucible experiment described previously gave reaction times of the order of 3 seconds, with the heat transfer to the surroundings per unit volume of reactant lower by at least a factor of 3, but with mixing time of the order of 1 second.

Thus it can be concluded that mixing and not heat transfer plays the main role in time required for ignition, for mixing times of the order of greater than or equal to 10^{-2} seconds, and that the reaction is therefore of the liquid-phase type.

C. The Analysis of the Products of Reaction of Nitric Acid and Aniline.

Purpose: It was desired to ascertain experimentally the products of the reaction of nitric acid and aniline in order to evaluate efficiency and reaction temperature and to check the values calculated assuming equilibrium to see if equilibrium actually obtained.

Apparatus: The system used to supply the reactants is the same as that used earlier. The reaction chamber, the same as that used in the nitric acid and gasoline ignition experiments with injection jets intersecting at 90 degrees, is shown in Figures 16 and 17. A slight modification was made in the valve seat to permit the eroded parts to be renewed when necessary. Molybdenum or copper inserts were used.

The sampling apparatus was similar to that used earlier and will not be described here. The Orsat gas-analysis apparatus was the same as described earlier, but since no nitrogen dioxide was found in the products of any reaction studied, a more exact gas analysis procedure was possible. Solutions used were potassium hydroxide for carbon dioxide, ferrous sulfate for nitric oxide, alkaline pyrogallol for oxygen, fuming sulfuric acid for unsaturated hydrocarbons, followed by copper oxide at 500° F for water and carbon monoxide, and a combustion pipette for hydrocarbons. The water present was ascertained gravimetrically from ice-cooled traps in the sampling apparatus, but the final values shown in the tables are estimated from material balance. In one instance the carbonaceous residue in the sample line and traps was analyzed and measured. The value for the weight fraction nitrogen dioxide present in the nitric acid computed from specific weight measurement may be a few per cent difference too low, because of the presence of water probably in amount of not more than 3 per cent. This was not known at the time the measurements were made.

Procedure: The reactants were forced into the chamber where the reaction started spontaneously. The regulating valve was adjusted to yield the desired pressure, and after allowing about 10 seconds for steady-state conditions, the sample was withdrawn over a period of about 50 seconds.

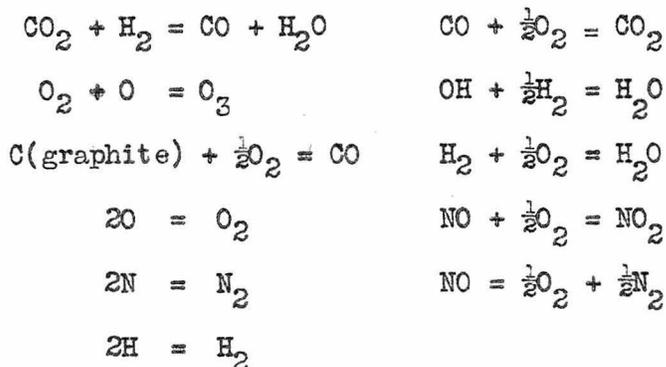
Results: Four runs were made with nitric acid and aniline at various pressures from 14.7 to 515 pounds per square inch. The results are shown in Table VIII. The results of equilibrium calculations (12) are shown in Table IX. It is seen that agreement of the various components is fairly good in the case of pressures of 315 pounds per square inch or higher. For lower pressures it is seen that the equilibrium between nitric oxide, nitrogen, and oxygen is not satisfied, as was found for the atmospheric pressure reaction of acid and gasoline. As a matter of interest, the calculated reaction temperatures are plotted in Figure IV with the reaction temperature calculated for the two runs of 315 and 615 pounds per square inch of pressure. Specific impulse, assuming isentropic expansion to atmospheric pressure, is also indicated.

The theoretical highest adiabatic reaction temperature is about 5100° F, which occurs at about a weight ratio of 3 to 1 of acid to aniline. Experiments carried out by other sections of this project with large-scale apparatus indicate a maximum between 3 and 4. The effect of pressure on temperature is small, being not larger than 0.4° F per pound per square inch. The result of the calculated composition is shown in Figure V. At the weight ratio of 3, the principal products are water, carbon monoxide, nitrogen, and carbon dioxide, with some hydrogen and traces of hydroxyl, atomic hydrogen, oxygen, nitric oxide, and atomic oxygen. It is expected that mixture ratios greater than 3 would give very corrosive products because of the presence of

molecular and atomic oxygen. In general, on the rich side of the mixture ratio 3, where there is a scarcity of oxidizer, the water-gas equilibrium determines to a large degree how much energy will be released by the reaction. On the lean side of the mixture ratio 3, the reaction between carbon monoxide, oxygen, and carbon dioxide is most important.

The calculations which lead to the compositions tabulated assume the following:

1. Equilibrium is actually attained.
2. The fugacity of the gaseous component h in the products is the total pressure times the mole fraction of h present.
3. The gas obeys the equation of state for a perfect gas; that is, the gas is thermally perfect.
4. The heat capacities of the monatomic gases are taken as half the values for the corresponding diatomic gases.
5. The reactions considered are:



6. The laws of perfect solutions apply to the nitric acid-nitrogen dioxide system used as an oxidizer.

The starting point used in the calculation of an equilibrium composition and temperature for a given composition of reactants was the assumption of a reaction temperature. A set of simultaneous equations involving (i) the equilibrium constants evaluated at the assumed temperature, (ii) the material balances of the reactions considered, and (iii) the given

chamber pressure was solved to give an actual possible composition of the products. This composition was the true one if the relation between enthalpy change, weight fractions and specific heats of the products, and assumed reaction temperature stated in Part I-B was satisfied. If this relation was not satisfied, another temperature was assumed, and the true result arrived at by trial and error. The exhaust velocity the gas would have in a jet unit was computed from the overall energy balance, assuming isentropic expansion for a calorically perfect gas to atmospheric pressure. Specific thrust was computed from Newton's second law.

These computations were carried out by other members of the Department of Chemical Engineering.

Similar experimental data with acetone in the aniline for the purpose of freezing point lowering of aniline are shown in Table X. No difficulty was experienced in the ignition or stability of the reaction at any time, using approximately 0.2 weight fraction acetone in the aniline. Calculated data for this reaction are presented in Table XI, and comparison is made between calculated and experimentally evaluated temperatures in Figure VI. Again it is seen that the agreement is good for pressures above 300 pounds per square inch.

Orthotoluidine, whose freezing point is lower than that of aniline, both of which are discussed Appendix A, was tried next. It operated satisfactorily in every respect in this apparatus. The experimental data are in Table XII, the calculated in Table XIII, and the comparisons between experiment and calculations in Figure VII. Orthotoluidine and aniline form their lowest eutectic of -26° F at 0.81 orthotoluidine in aniline. This is completely discussed in Appendix A. Accordingly this mixture was tried with red fuming

nitric acid. The experimental results and calculated values are in Tables XIV and XV, respectively. The comparison is in Figure VIII. Orthotoluidine is more desirable than acetone as a freezing point lowering agent because orthotoluidine has a very low vapor pressure and hence a negligible inflammability hazard with air.

D. Summary.

The conclusions to be drawn are as follows:

The aniline-red fuming nitric acid reaction is of the liquid-phase type for the mixing times investigated, since the rapidity of the reaction depends on the mixing in the liquid phase. That is, mixing is of controlling importance, rather than heat loss, in the time required for ignition, insofar as mixing times of the order greater than 10^{-2} seconds are concerned.

The reaction can be predicted with accuracy satisfactory for present engineering purposes by means of equilibrium calculations, provided that sufficiently high pressures are used.

Other fuels that operate satisfactorily with red fuming nitric acid at ordinary temperatures are aniline containing up to 0.2, probably up to 0.3, weight fraction acetone, orthotoluidine, and a mixture of 0.19 weight fraction aniline in orthotoluidine.

ACKNOWLEDGMENTS

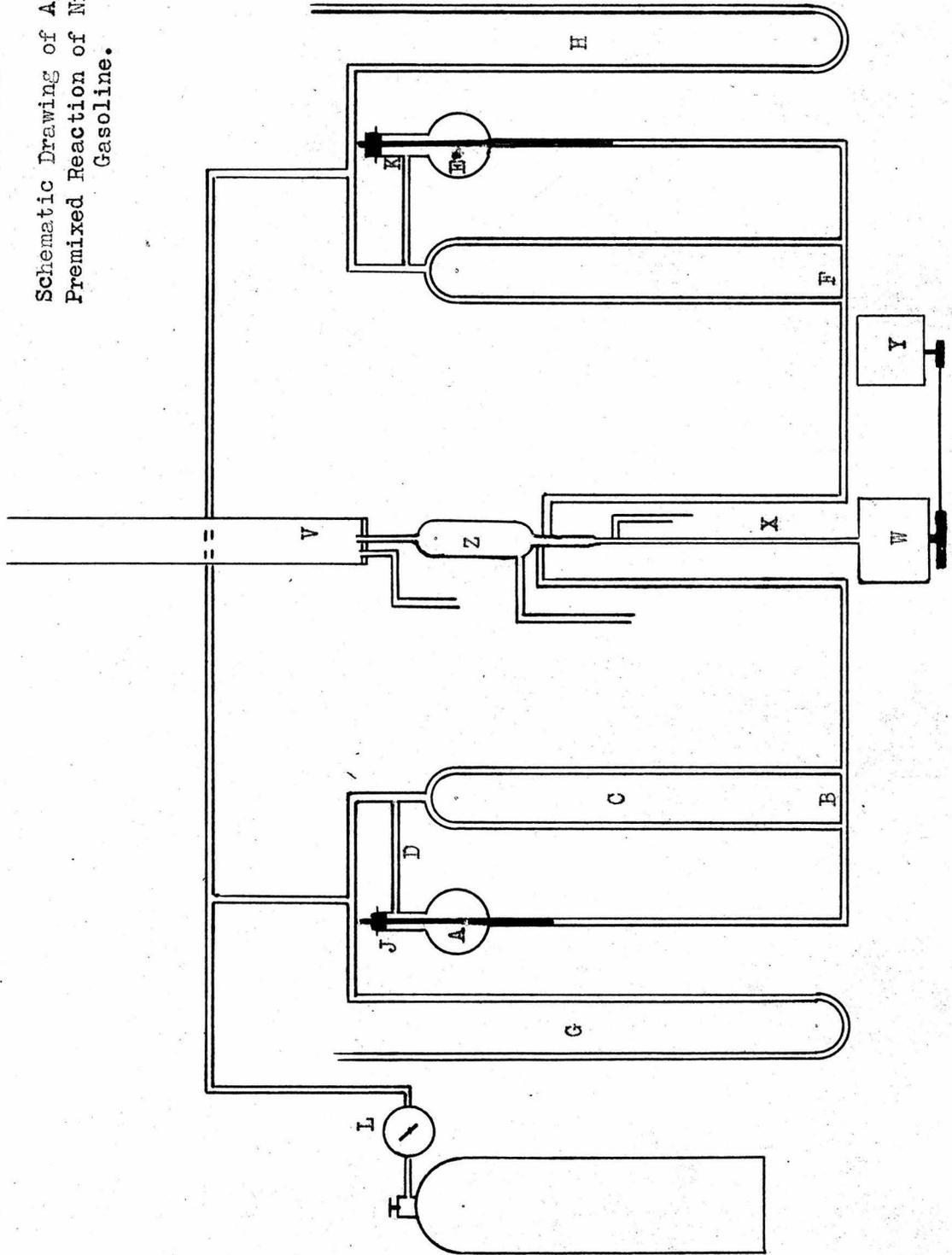
Sincere appreciation is expressed to Professor W. N. Lacey and Professor B. H. Sage of the Department of Chemical Engineering, and to Professor T. von Karman, Professor C. B. Millikan, and Doctor F. J. Malina of the Guggenheim Aeronautical Laboratory for suggesting these problems. The assistance of certain members of the Department of Chemical Engineering was invaluable. Acknowledgment is made to Mr. J. M. Green for assistance with the experiments and for development of certain analytical techniques, and to Mr. R. N. Wimpers for calculation of the equilibrium compositions. The copper reaction chamber and rate of reaction apparatus were designed in part by Mr. Glen W. Miller. The cooperation of certain personnel of other sections of the project, including Doctor M. Summerfield, was the essence of one experiment and helped immeasurably in others.

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FIGURE 1

Schematic Drawing of Apparatus for the
Premixed Reaction of Nitric Acid and
Gasoline.



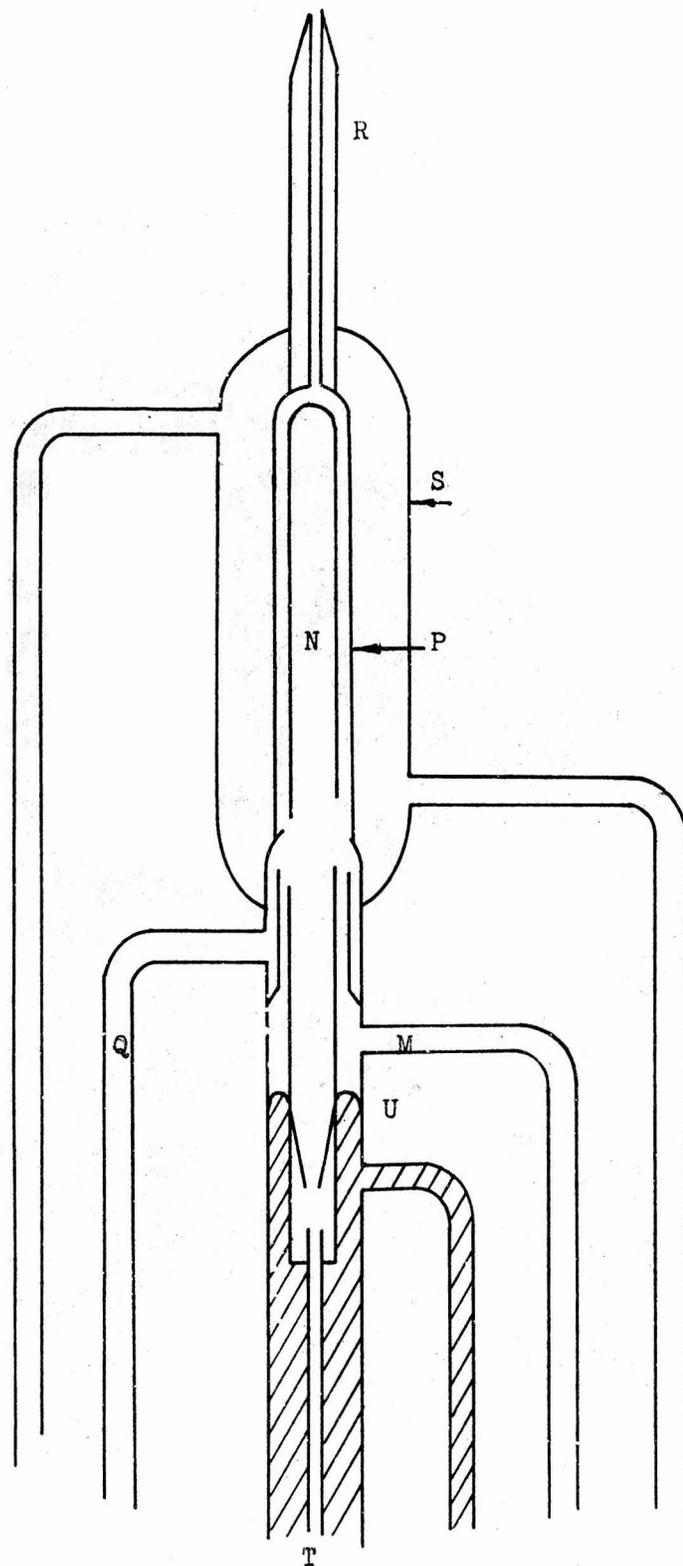


Figure 2

Details of Mixing Chamber for
Liquid-Phase Reaction Equipment

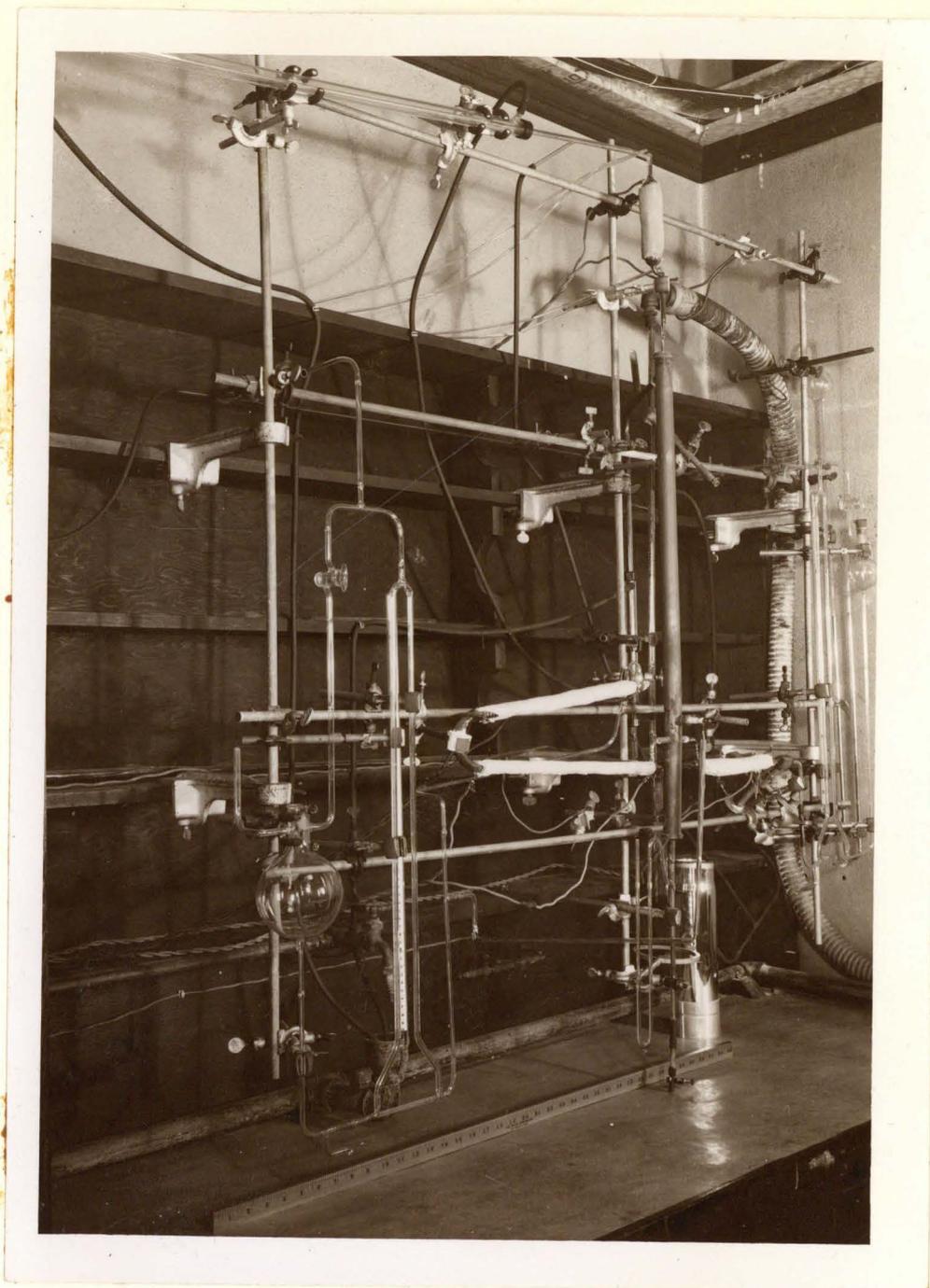


Figure 3. Gas-phase Reaction Apparatus for Nitric Acid and Gasoline.

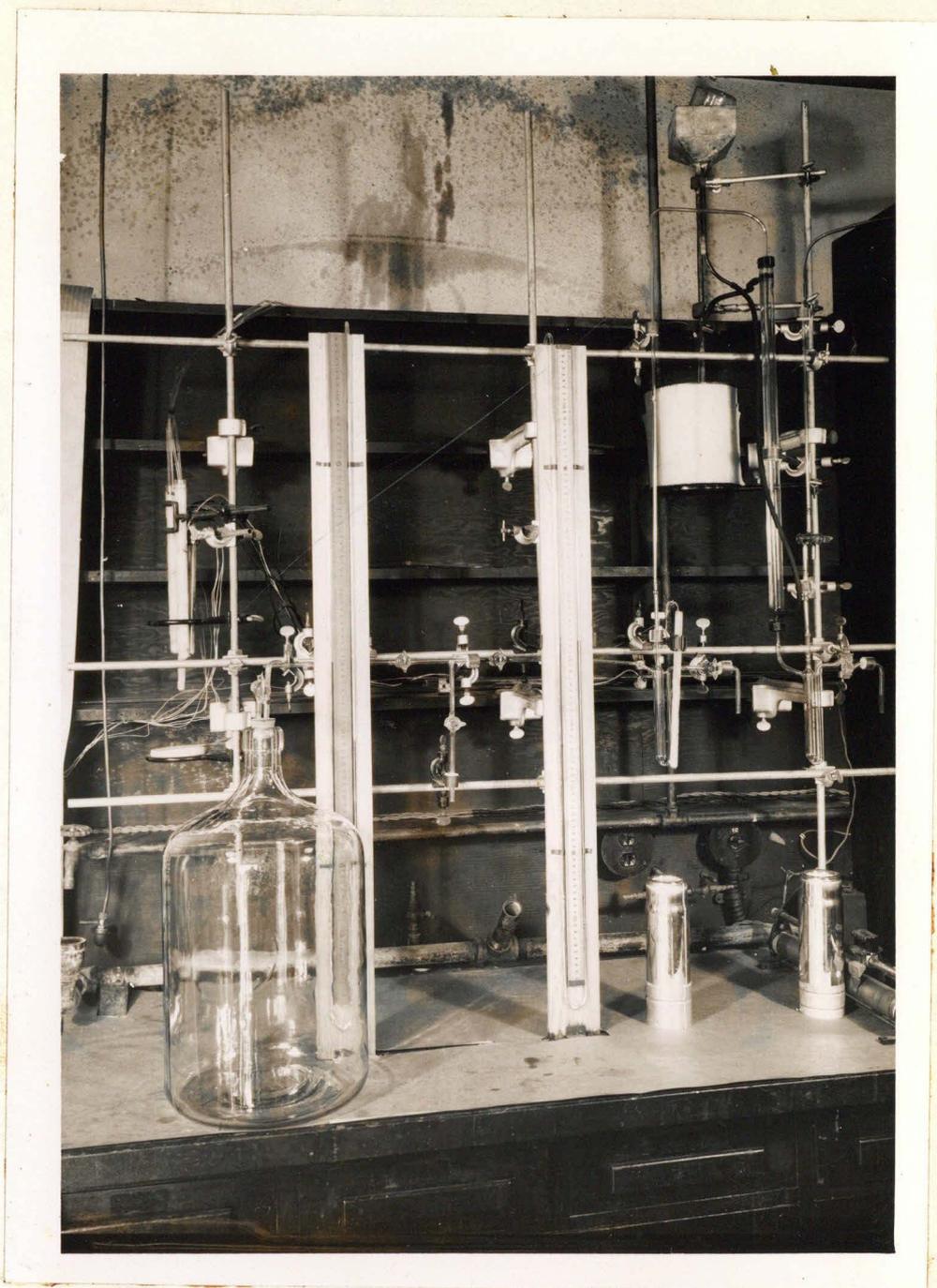


Figure 4. Equipment Used for Sampling the Products of Reaction.

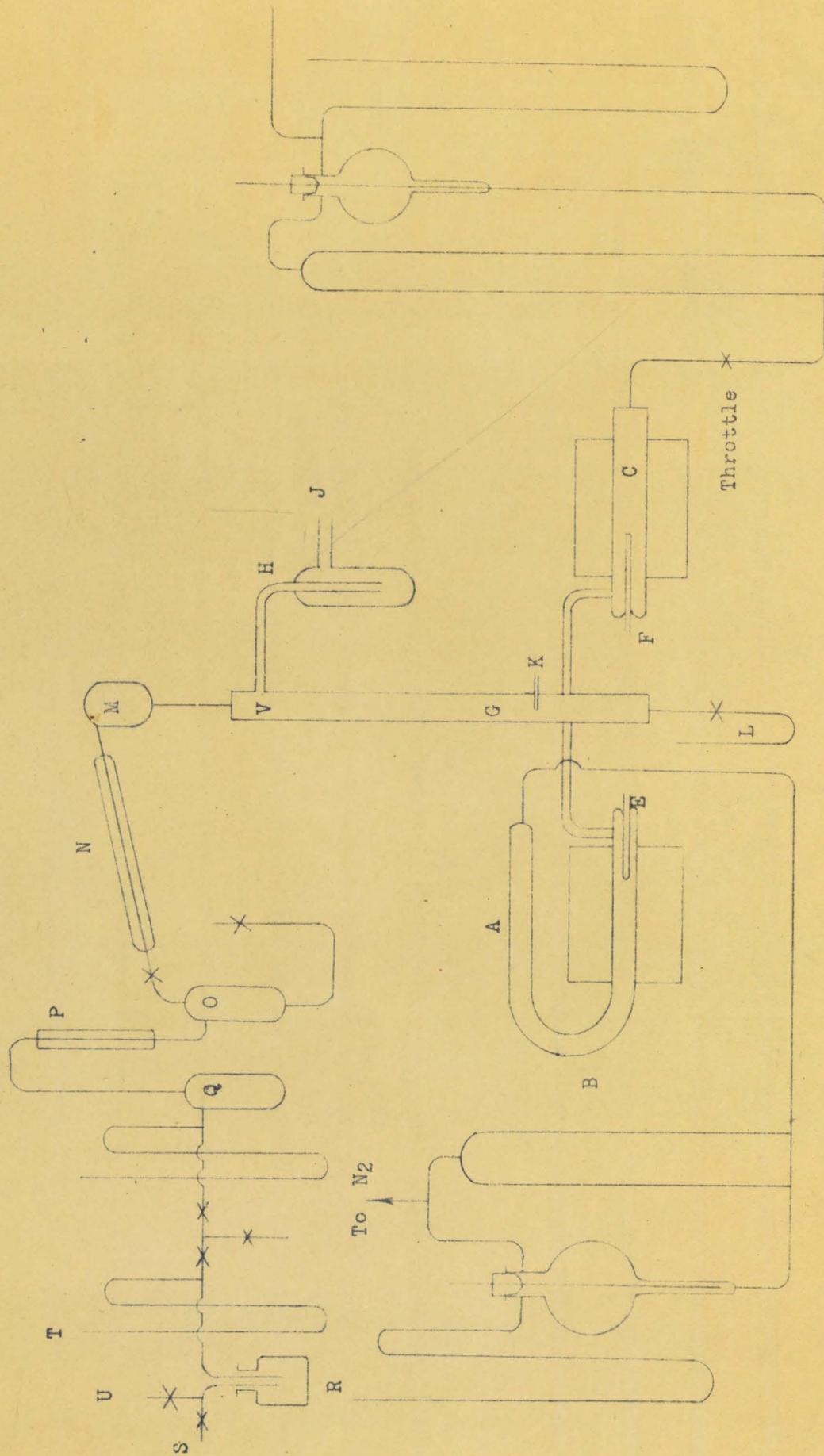


Figure 5
Arrangement of Equipment for Gas-phase Reaction Investigation



Figure 6. Gas Analysis Apparatus.

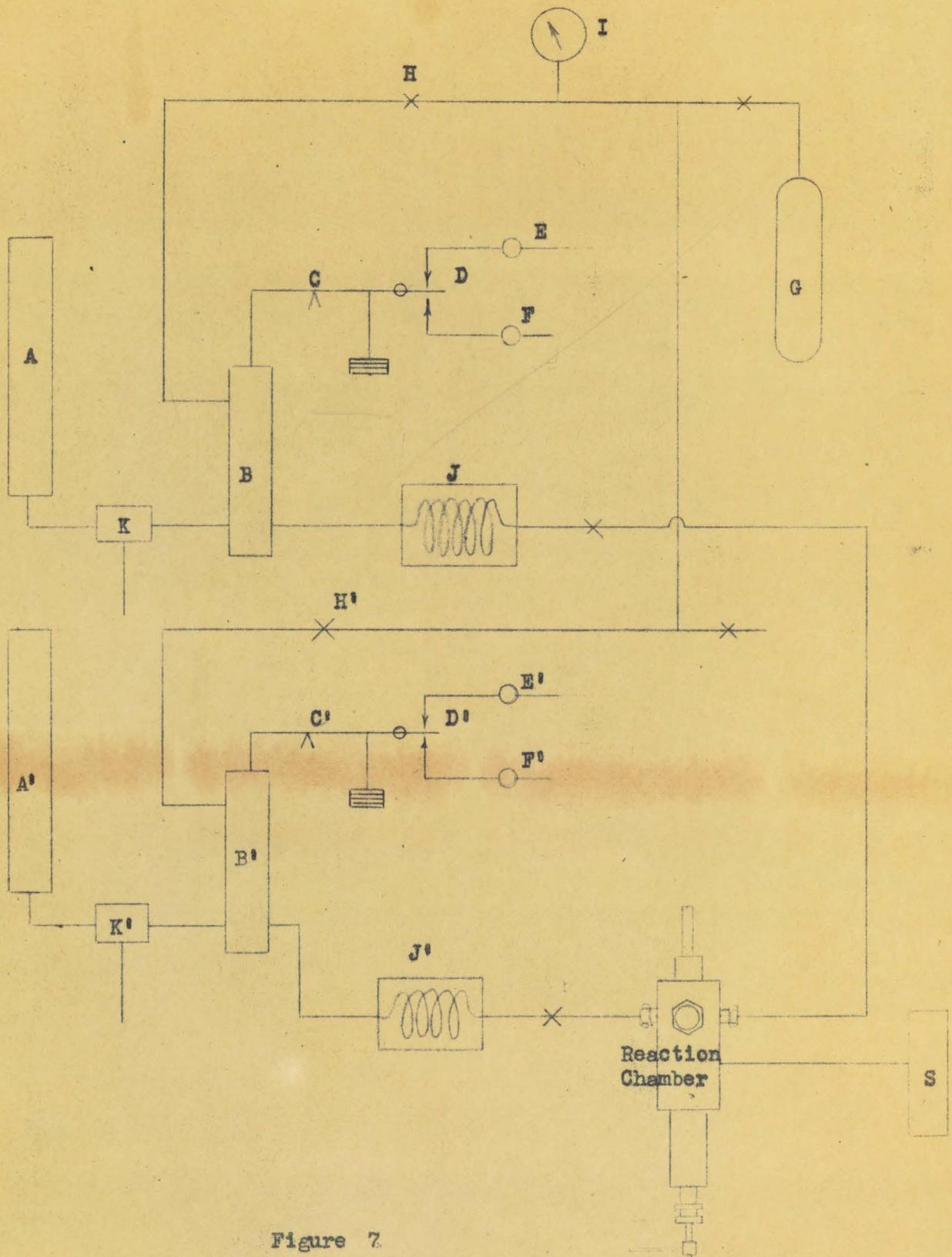


Figure 7

Flow Sheet of Apparatus for Ignition of Nitric Acid and Gasoline Using Opposed Injection Nozzles.

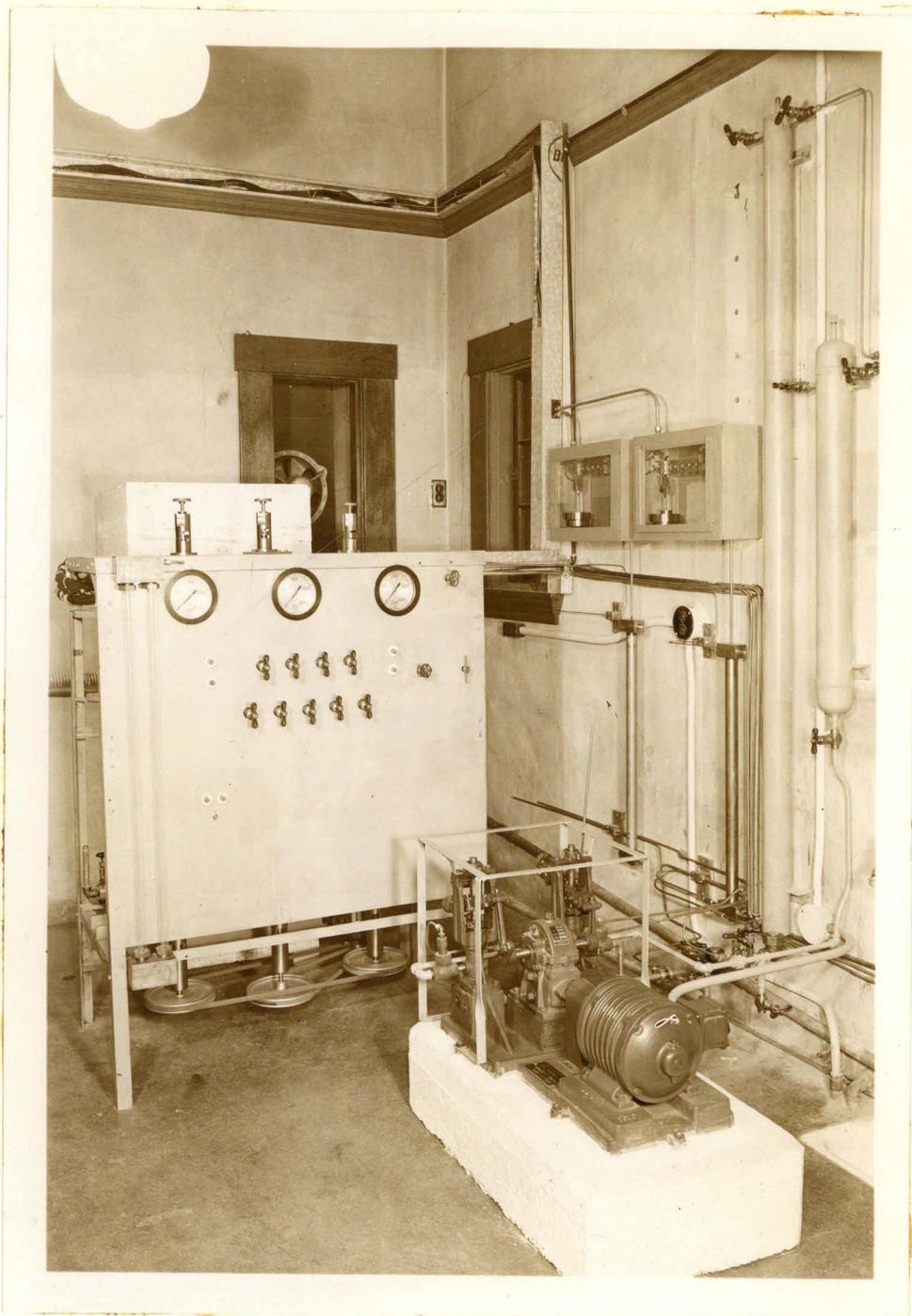


Figure 8. View of Equipment Used to Supply and Measure the Reactants.

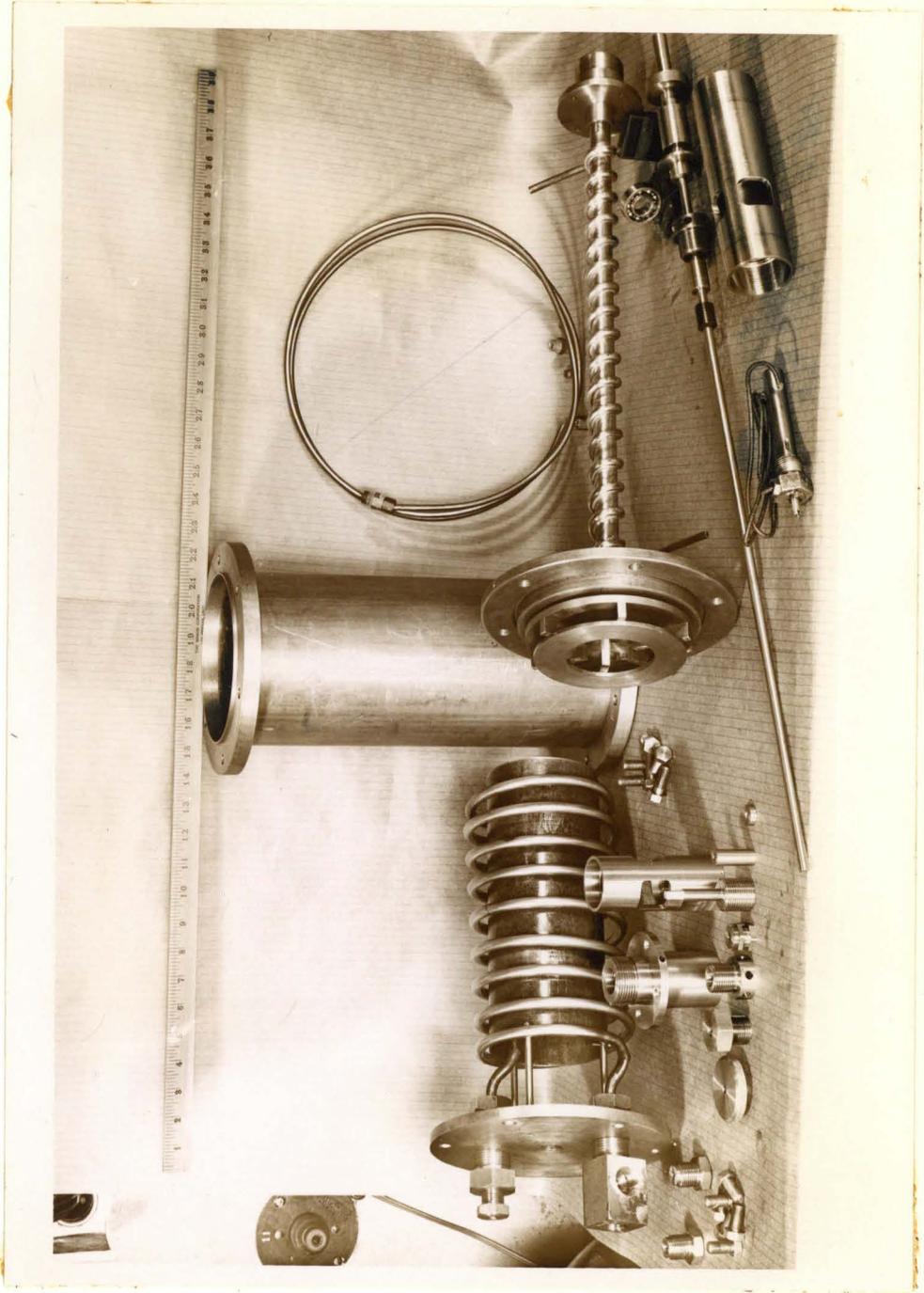


Figure 9. View of Heat Transfer Equipment.

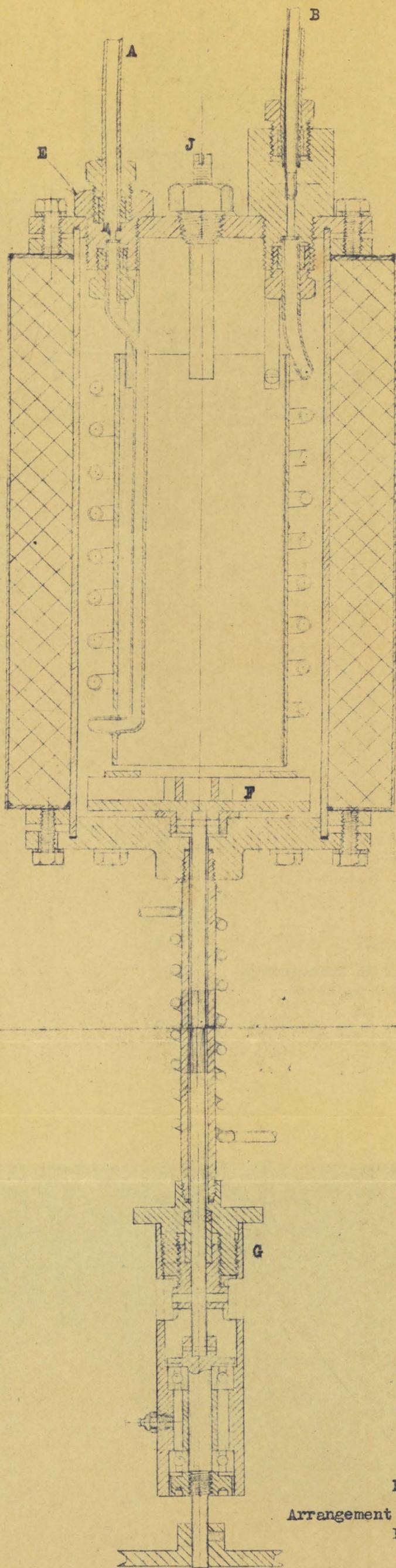


Figure 10
Arrangement of Heat Transfer
Equipment

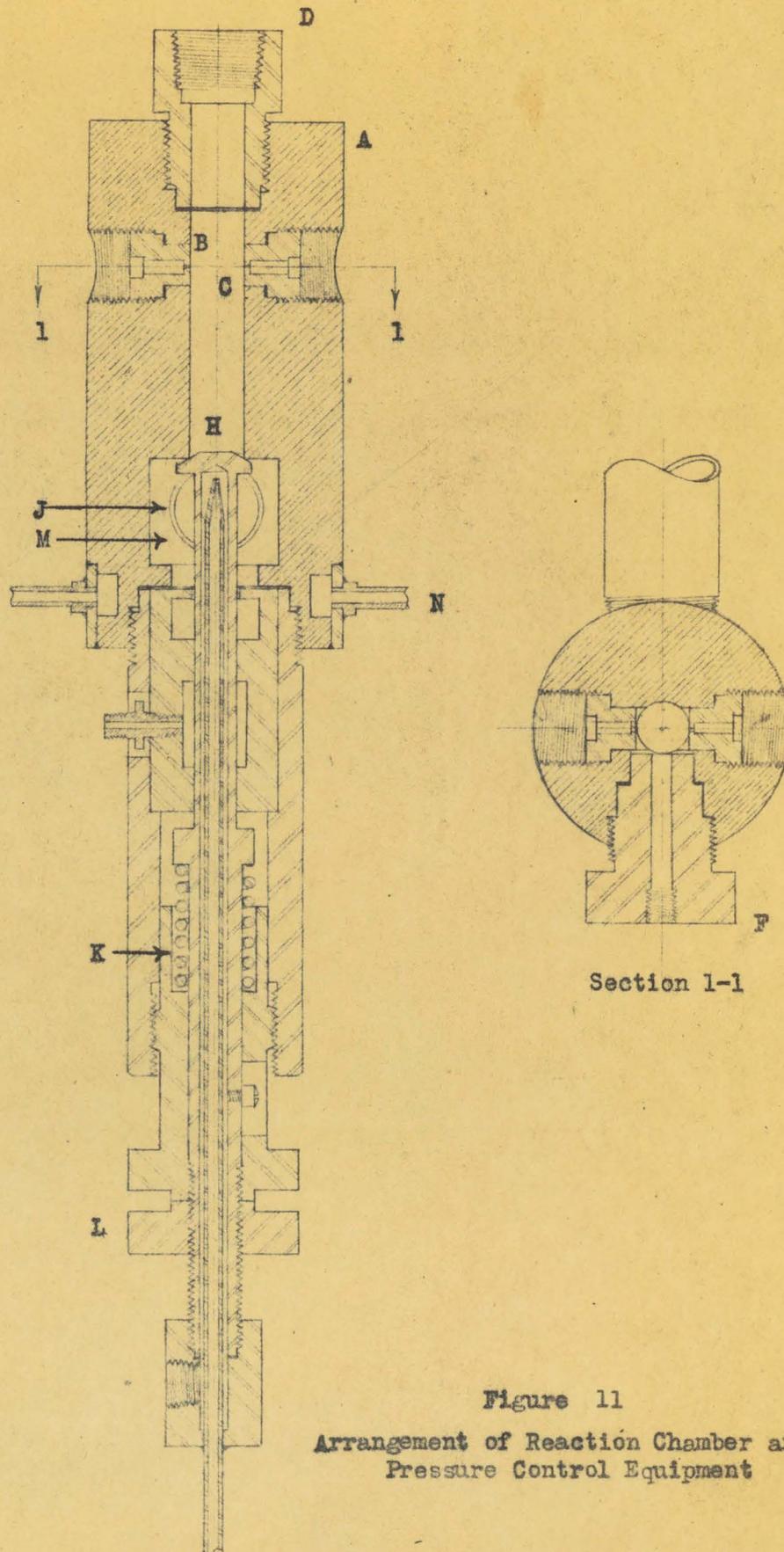


Figure 11
 Arrangement of Reaction Chamber and
 Pressure Control Equipment

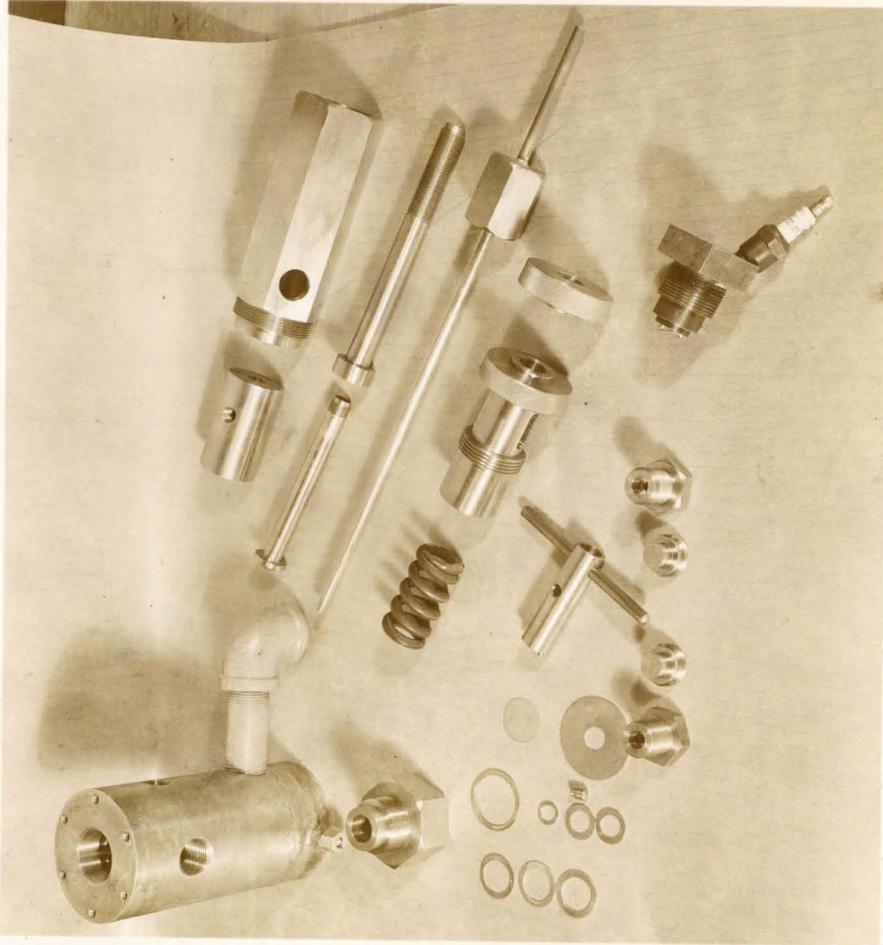


Figure 12. View of Ignition Chamber Using Opposed Jets.

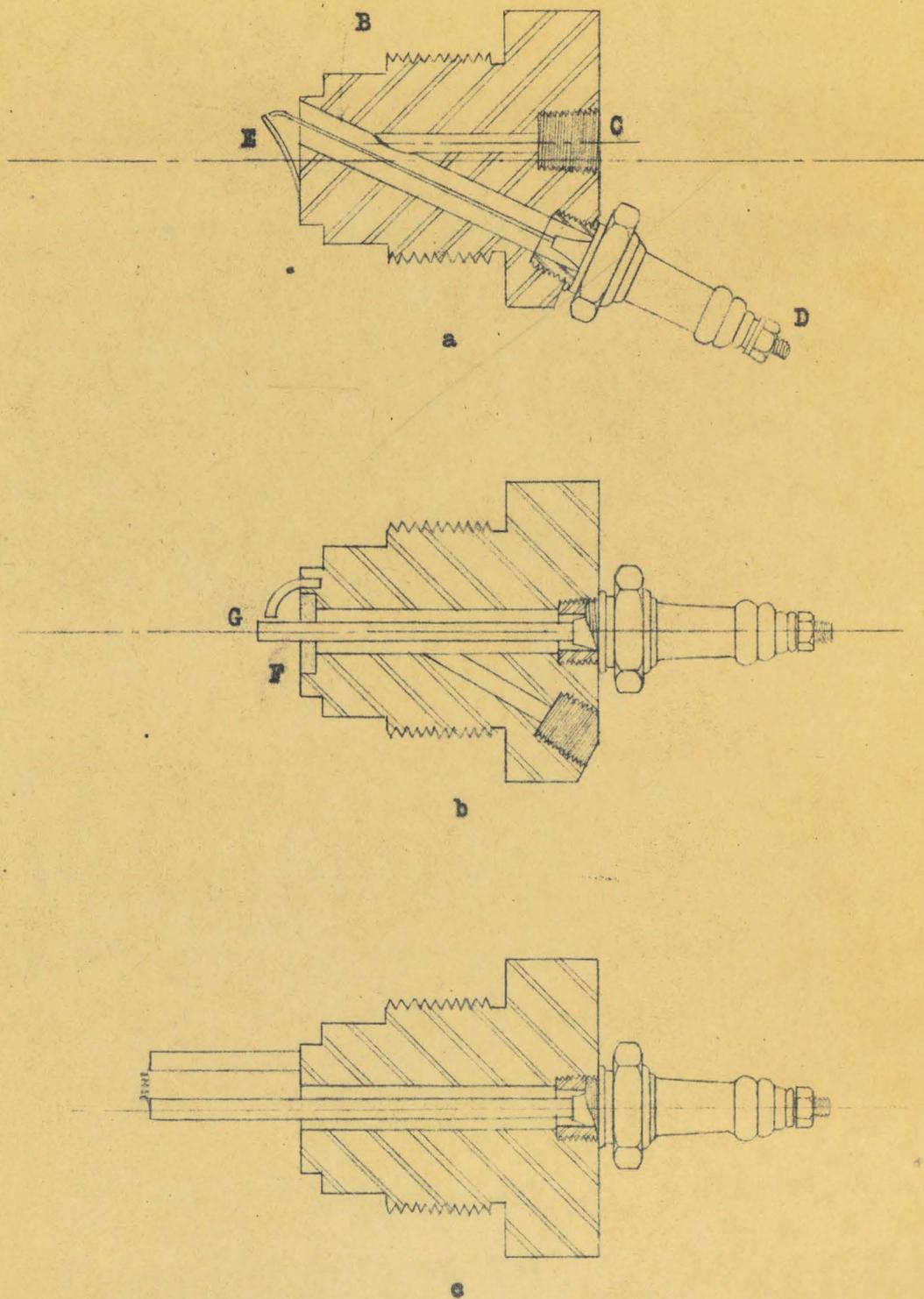


Figure 13.

Arrangement of Ignition Equipment in Reaction Chamber

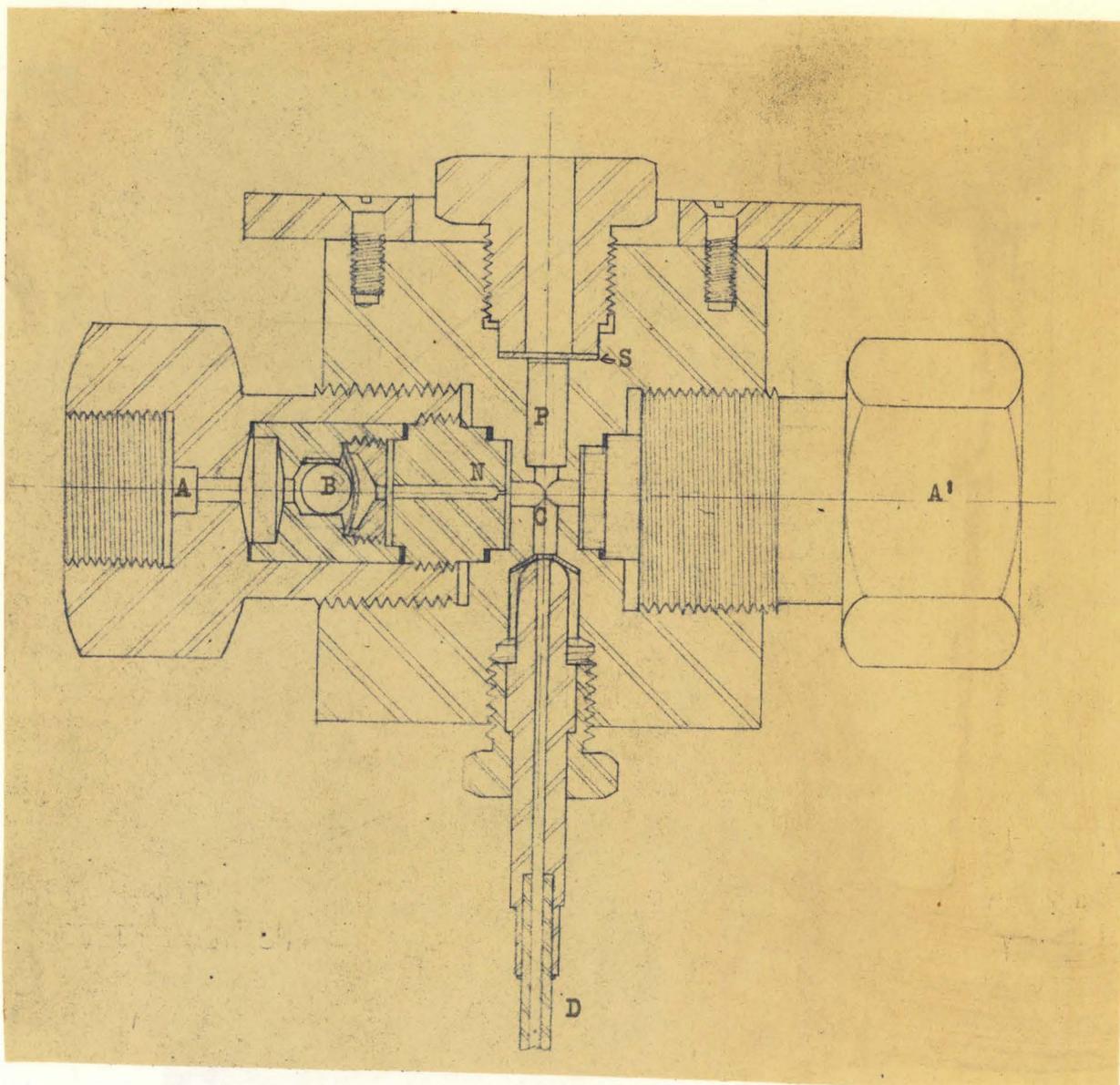


Figure 14. Sketch of Rate of Reaction Equipment.

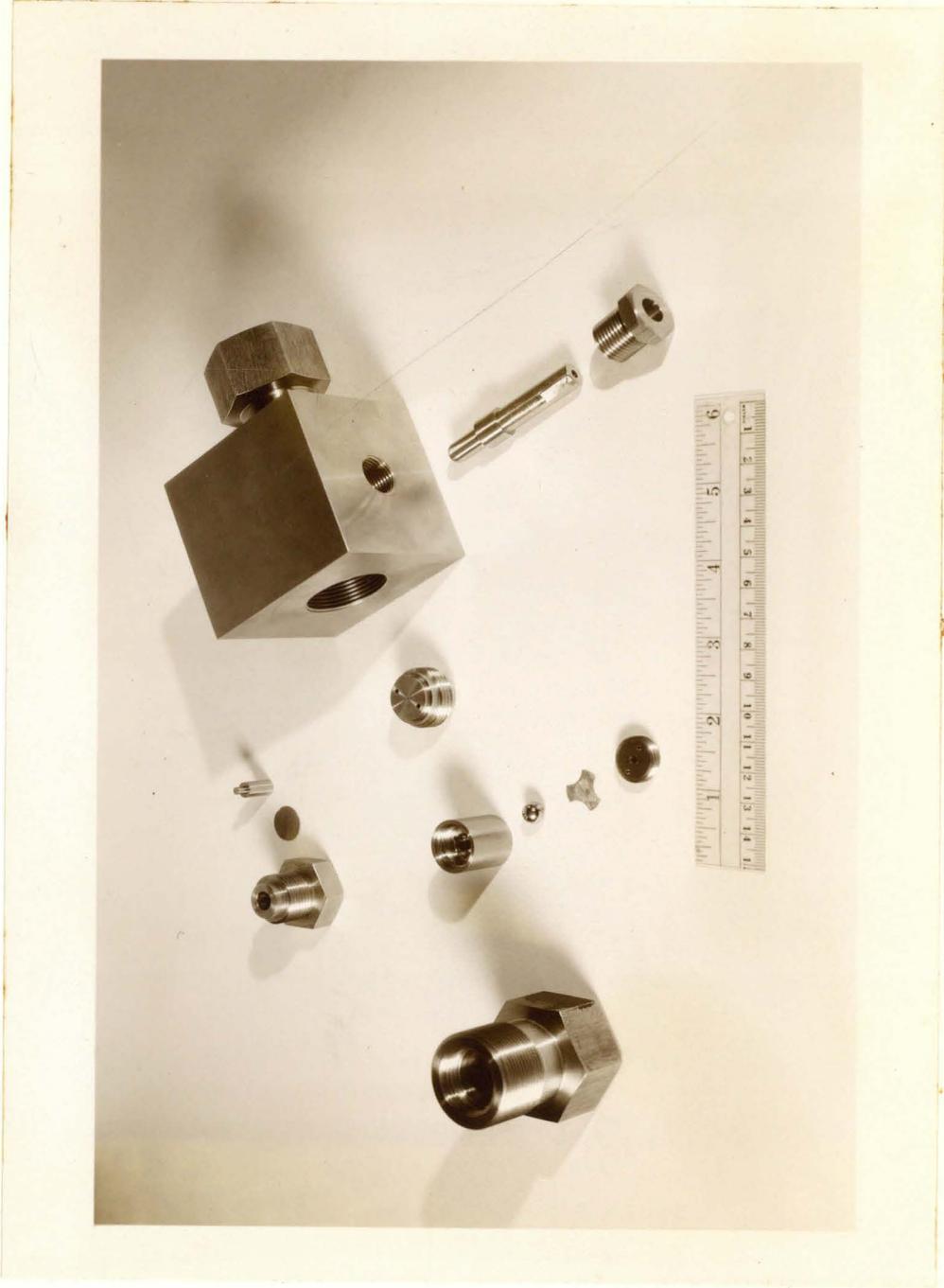


Figure 15. Rate of Reaction Equipment.



Figure 17. View of Continuous Reaction Chamber and Control Valve.

TABLE I. SUMMARY OF RESULTS FOR MINIMUM PREHEATING TEMPERATURES
 FOR THE GAS-PHASE REACTION OF NITRIC ACID AND GASOLINE
 AT ATMOSPHERIC PRESSURE

Nitric Acid			
Sample Number	209	214	213
Weight Fraction Nitrogen Dioxide from Density (2)	--	--	0.17
Weight Fraction Water from Density (1)	0.465	0.156	--
Weight Rate of Flow, lb/sec	1 to 6 x 10 ⁻⁴	4.4 x 10 ⁻⁴	4.2 x 10 ⁻⁴
Weight Fraction in Mixture	0.67 to 0.92	0.844	0.875
Theoretical Weight Fraction Assuming Nitrogen as N ₂	--	0.8650	0.8417
Theoretical Weight Fraction Assuming Nitrogen as NO	--	0.9129	0.9014
Preheating Temperature, °F	750	700	490
Gasoline			
Sample Number	210	210	210
Carbon/Hydrogen Ratio, lb/lb	5.884	5.884	5.884
Weight Rate of Flow, lb/sec	0.5 x 10 ⁻⁴	0.83 x 10 ⁻⁴	0.55 x 10 ⁻⁴
Weight Fraction in Mixture	0.33 to 0.08	0.156	0.125
Preheating Temperature, °F	750	460	490
Flame Volume (visual estimate) cu.ft/lb/sec	No reaction	2.0	1.5

TABLE II. COMPOSITION OF THE PRODUCTS OF REACTION
OF RED FUMING NITRIC ACID AND GASOLINE

Component	Atmospheric Pressure		
	Weight Fraction Gasoline		
	0.120	0.159	0.266
Nitrogen and Hydrogen	0.1483 ^a	0.1430	0.3430
Nitrogen Dioxide ^b	0.1685	0.0442	0.0000
Nitric Oxide	0.0000	0.1410	0.0545
Oxygen	0.0000	0.0000	0.0000
Carbon Dioxide	0.2150	0.2400	0.1195
Carbon Monoxide	0.0000	0.0000	0.1730
Water	0.4381	0.4052	0.3095
Nitric Acid	0.0301	0.0266	0.0005

^a Compositions are expressed as mole fractions.

^b The measurements at 0.266 and 0.120 weight fraction gasoline involved only a measurement of the total quantity of the oxides of nitrogen. The absence of nitrogen dioxide at the higher weight fraction of gasoline was estimated from the colorless nature of the gas while the absence of nitric oxide at the lower weight fraction was indicated by the material balance and by the lack of change of color upon the admission of oxygen.

TABLE III. THE REACTION OF NITRIC ACID AND
GASOLINE AT ATMOSPHERIC PRESSURE

Component	Weight Fraction Gasoline		
	0.120	0.159	0.266
<u>Reactants</u>			
Nitric Acid	5.965 ^a	4.265	2.2094
Nitrogen Dioxide	1.405	1.005	0.5204
Gasoline	1.000	1.000	1.000
<u>Products</u>			
Nitric Oxide ^b	0.000	0.876	0.268
Nitrogen Dioxide ^b	2.700	0.420	0.000
Nitrogen	0.969	0.730	0.505
Carbon Monoxide	0.000	0.000	0.796
Carbon Dioxide	2.160	2.140	0.865
Carbon (free)	0.248	0.259	0.277
Hydrogen (free)	0.000	0.000	0.075
Water	1.849	1.505	0.916
Nitric Acid	0.444	0.340	0.028
Total Weight	8.370	6.270	3.730
Enthalpy Change of Reaction ^c	1570.3	1912	1896
Reaction Temperature, °F	4060	4160	3780

^a All weights are expressed in pounds of reactant or product per pound of gasoline.

^b Only total quantity of oxides of nitrogen was measured at weight fraction of 0.120 and 0.266 gasoline.

^c Enthalpy of reaction is expressed in Btu per pound of reactants for both reactants and products at 64° F and 1 atmosphere pressure, the product water being considered in the liquid state.

TABLE IV. COMPOSITION OF PRODUCTS OF REACTION OF NITRIC ACID
AND GASOLINE WITH FULL-SCALE JET-PROPULSIVE EQUIPMENT

Component	Mole Fraction
Nitrogen Dioxide	0.0625
Nitrogen Tetroxide	0.0475
Carbon Dioxide	0.1619
Oxygen	0.0026
Hydrogen	0.0223
Carbon Monoxide	0.0335
Nitrogen	0.1216
Water	0.4613
Nitric Acid	0.0023
Free Carbon	0.0845

Operating Conditions^a

Reaction Temperature, °F	3880
Exhaust Temperature, °F ^b	2175
Enthalpy Change in Nozzle, Btu/lb	725
Exit Velocity, ft/sec	6014
Specific Thrust, lb.sec/lb	188
Weight Fraction Gasoline in Reactants	0.141

^a These conditions were computed from analysis of the products of reaction.

^b Calculated for isentropic expansion from 300 pounds per square inch to 14.7 pounds per square inch absolute pressure.

TABLE V. THE SPARK IGNITION OF NITRIC ACID AND GASOLINE WITH OPPOSED JETS^a

Acid Jet Diameter (in. x 10 ⁻³)	Gasoline Jet Diam. (in. x 10 ⁻³)	Pressure Acid Jet Above Chamber (lb/in. ²)	Pressure Gasoline Jet Above Chamber (lb/in. ²)	Weight Ratio Acid/Gasoline	Chamber Pressure (lb/in. ²)	Ignition Power (watts)	No. of Trials	Use of Air	Ignition	No Ignition
14	6.3	75	100	6.4	0	16	12	yes	16	6
16.6	6.3	75	100	9.1	0	15	9	no	0	9
16.6	6.3	75	100	9.1	0	15	5	yes	1	4
16.6	6.3	75	100	9.1	0	15	1	no	0	1

^a Nitric acid used contained 0.19 weight fraction NO₂, from specific weight measurements. Reactants at 770 F.

A

TABLE VI. THE HOT WIRE IGNITION OF NITRIC ACID AND GASOLINE WITH OPPOSED JETS^a

Acid Jet Diameter (in. x 10 ⁻³)	Gasoline Jet Diam. (in. x 10 ⁻³)	Pressure Above Chamber (lb/in. ²)	Pressure Gasoline Jet Above Chamber (lb/in. ²)	Weight Ratio Acid/Gasoline	Chamber Pressure (lb/in. ²)	Chamber Pressure above atmosphere (lb/in. ²)	Ignition Power (watts)	Surface Density of Ignition Power (watts/in. ²)	No. of Trials	Use of Air	Ignition	No Ignition
16.6	6.3	75	100	9.1	0	0	60	380	3	no	3	0
16.6	6.3	75	100	9.1	0	0	100	397	14	no	14	0
16.8	6.3	75	100	9.2	0	0	20	392	2	no	2	0
7.5	4.1	250	250	5.01	25	25	20	390	1	no	1	0
7.5	4.1	200	250	4.48	25	25	20	390	1	no	1	0
		200	250	4.48	25	25	20	390	6	no	2	4
		200	250	4.48	0	0	20	390	1	no	1	0
		200	250	4.48	20	20	20	390	1	no	1	0
		200	250	4.48	10	10	20	390	1	no	1	0
		150-250	250	---	---	---	---	---	9	---	0	9

^a Nitric acid used contained 0.19 weight fraction NO₂ from specific weight measurements. Reactants at 770° F.

TABLE VII. THE HOT WIRE IGNITION OF NITRIC ACID AND GASOLINE WITH JETS INTERSECTING AT 90 DEGREES^a.

Acid Jet Diameter (in. x 10 ⁻³)	Gasoline Jet Diam. (in. x 10 ⁻³)	Pressure Above Chamber (lb/in. ²)	Pressure Gasoline Jet Above Chamber (lb/in. ²)	Chamber Pressure above atmosphere	Weight Ratio Acid/Gasoline	Ignition Power (watts)	Surface Density of Power (watts/in. ²)
9.0	5.4	200	200	0	4.12	80	400
9.0	5.4	200	150	0	4.75	80	400
9.0	5.4	200	100	0	5.83	80	400
9.0	5.4	200	150	0	---	80	400
9.0	5.4	150	350	0	2.70	80	400
9.0	5.4	150	250	0	3.20	80	400
9.0	5.4	150	250	0	3.20	80	400
9.0	5.4	200	250	0	3.70	80	400
9.0	5.4	200	250	0	3.70	89	400
9.0	5.4	200	250	0	3.70	80	400
9.0	5.4	200	250	0	3.70	80	400
9.0	5.4	200	250	0	3.70	80	400

^a Nitric acid contained 0.137 weight fraction nitrogen dioxide, from specific weight measurement.

TABLE VII. THE HOT WIRE IGNITION OF NITRIC ACID AND GASOLINE WITH JETS INTERSECTING AT 90 DEGREES

(cont'd)

Acid Jet Diameter (in. x 10 ⁻³)	Gasoline Jet Diam. (in. x 10 ⁻³)	Pressure Acid Jet Above Chamber (lb/in. ²)	Pressure Gasoline Jet Above Chamber (lb/in. ²)	Chamber Pressure (lb/in. ² above atmosphere)	Weight Ratio Acid/gasoline	Ignition Power (watts)	Surface Density of Power (watts/in. ²)
9.0	5.4	200	250	0	3.70	80	400
9.0	5.4	200	250	0	3.70	80	400
9.0	5.4	200	250	0	3.70	80	400
9.0	5.4	200	250	0	3.70	80	400
9.0	5.4	200	250	0	3.70	80	400
9.7	5.9	300	350	0	3.72	80	400
9.7	5.9	300	350	300 ^b	3.72	80	400

^b Unstable.

TABLE VIII. COMPOSITION OF PRODUCTS OF REACTION OF ANILINE
AND RED FUMING NITRIC ACID

Run Number	15a	15b	19	27
Weight Fraction Nitrogen Dioxide in Acid Phase	0.145	0.145	0.153	0.154
Weight Ratio Acid / Fuel by Orifice Measurement	1.57	1.57	2.37	1.89
Weight Ratio Acid / Fuel by Material Balance	1.93	1.93	2.10	1.83
Reaction Pressure (lb/in. ² abs.)	14.7	115	315	515
Dry Gas Analysis (mole fraction)				
Nitric Oxide	0.2435	0.0230	---	---
Carbon Dioxide	0.1830	0.3556	0.1299	0.0900
Hydrogen	0.0429	0.0734	0.2158	0.2385
Carbon Monoxide	0.2321	0.2076	0.4310	0.4573
Nitrogen	0.2985	0.3404	0.1949	0.1889
Hydrocarbons	---	---	0.0284	0.0253
Total Products Analysis (mole fraction)				
Nitric Oxide	0.1237	0.0130	---	---
Carbon Dioxide	0.0929	0.2011	0.1096	0.0783
Hydrogen	0.0218	0.0415	0.1821	0.2076
Carbon Monoxide	0.1179	0.1173	0.3637	0.3980
Nitrogen	0.1517	0.1922	0.1645	0.1644 ^b
Hydrocarbons	---	---	0.0240 ^a	0.0220 ^b
Water	0.4920	0.4349	0.1561	0.1297
Carbon	---	---	---	---
Calculated Reaction				
Temperature (°F)	3940	4800	4270	3857
Exit Velocities (ft/sec)	---	5740	6841	6956
Specific Impulse (lb.sec/lb)	---	178.6	212.7	216.3

^a Assumed equivalent to CH₄

^b Equivalent to C_{1.54}H_{5.07}

TABIE IX. CALCULATED COMPOSITION OF THE PRODUCTS OF REACTION OF ANILINE
AND RED FUMING NITRIC ACID AT EQUILIBRIUM

	300			600				
	1	2	3	5	7	1	2	3
Pressure (lb/in. ²)	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Weight Fraction Nitrogen Dioxide in Acid Phase	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Weight Ratio Acid / Fuel	1	2	3	5	7	1	2	3
Composition of Equilibrium Mixture (mole fraction)								
Oxygen	---	---	0.0037	0.0898	0.1963	---	---	0.0027
Monatomic Oxygen	---	---	0.0020	0.0078	0.0026	---	---	0.0015
Triatomic Oxygen	---	---	---	---	---	---	---	---
Nitrogen	0.1122	0.1551	0.1919	0.2136	0.2246	0.1122	0.1551	0.1930
Nitric Oxide	---	---	0.0036	0.0171	0.0163	---	---	0.0032
Nitrogen Dioxide	---	---	---	---	0.0001	---	---	---
Monatomic Nitrogen	---	---	0.0002	0.0002	---	---	---	0.0002
Hydrogen	0.3446	0.2126	0.0632	0.0105	0.0016	0.3407	0.2126	0.0626
Water	0.0173	0.1594	0.2827	0.2919	0.2898	0.0211	0.1594	0.2881
Monatomic Hydrogen	---	0.0013	0.0114	0.0038	0.0003	---	0.0013	0.0092
Hydroxyl	---	0.0003	0.0316	0.0622	0.0338	---	0.0003	0.0279
Carbon Dioxide	0.0098	0.0550	0.1587	0.2431	0.2265	0.0100	0.0550	0.1622
Carbon Monoxide	0.3466	0.4163	0.2510	0.0601	0.0080	0.3422	0.4163	0.2494
Carbon	0.1695	---	---	---	---	0.1738	---	---
Reaction Temperature (°F)	1950	3710	5065	4930	4320	2015	3710	5150
Exit Velocity (ft/sec)	5207	6514	7091	6688	6192	5658	6998	7694
Specific Impulse (lb.sec/lb)	161.9	202.6	220.5	207.95	192.54	175.9	2176	239.2

TABLE X. COMPOSITION OF THE PRODUCTS OF REACTION OF
ANILINE, ACETONE, AND RED FUMING NITRIC ACID

Run Number	38a	33	30	38b	34
Weight Fraction Nitrogen Dioxide in Acid Phase	0.2137	0.2100	0.1979	0.2137	0.2105
Weight Fraction Acetone in Fuel	0.1875	0.1923	0.2000	0.1875	0.1875
Weight Ratio Acid / Fuel by Orifice Method	2.05	1.93	2.04	2.01	1.86
Weight Ratio Acid / Fuel by Material Balance	1.76	1.88	1.76	2.22	1.79
Reaction Pressure (lb/in. ² abs.)	115	115	315	315	540
Dry Gas Analysis (mole fraction)					
Oxygen	---	---	0.0020	---	---
Nitrogen	0.2410	0.2125	0.1915	0.1750	0.1710
Nitric Oxide	0.0485	0.0703	---	---	---
Hydrogen	0.1580	0.1262	0.1405	0.2300	0.2275
Carbon Dioxide	0.1435	0.1680	0.1330	0.1190	0.1040
Carbon Monoxide	0.3730	0.3520 ^b	0.4515 ^c	0.4470 ^d	0.4505 ^e
Hydrocarbons (C _n H _m)	0.0360 ^a	0.0710 ^b	0.0815 ^c	0.0290 ^d	0.0470 ^e
Total Product Analysis (mole fraction)					
Oxygen	---	---	0.0018	---	---
Nitrogen	0.1386	0.1423	0.1692	0.1568	0.1558
Nitric Oxide	0.0279	0.0471	---	---	---
Hydrogen	0.0909	0.0845	0.1242	0.2061	0.2073
Water ^a	0.2635	0.2331	0.1163	0.1039	0.0888
Carbon Dioxide	0.0825	0.1125	0.1175	0.1066	0.0948
Carbon Monoxide	0.2146	0.2357	0.3890	0.4006	0.4105
Hydrocarbons	0.0207	0.0475	0.0720	0.0260	0.0428
Carbon ^f	0.1613	0.0973	---	---	---
Calculated Reaction Tem- perature (°F)	4640	4395	3500	4035	3580
Exit Velocity (ft/sec) ^g	6082	5966	6048	6730	6762
Specific Impulse (lb.sec/lb) ^g	189.1	185.5	188.0	209.3	210.3

Equivalent to C_{1.39}H_{4.61}

Equivalent to C_{1.21}H_{3.65}

Equivalent to C_{1.90}H_{5.80}

Equivalent to C_{1.36}H_{4.07}

^e Equivalent to C_{1.57}H_{5.15}

^f Determined from material balance.

^g Calculated assuming isentropic expansion through jet to 14.70 pounds per square inch absolute.

TABLE XI. CALCULATED COMPOSITION OF THE PRODUCTS OF REACTION
OF ANILINE, ACETONE, AND RED FUMING NITRIC ACID
AT EQUILIBRIUM

Pressure (lb/in. ²)	500	500	500
Weight Fraction Nitrogen Dioxide in Acid Phase	0.15	0.15	0.15
Weight Fraction Acetone in Fuel	0.10	0.10	0.10
Weight Ratio Acid / Fuel	1	2	3
Composition of Equilibrium Mixture (mole fraction)			
Oxygen	---	---	0.0031
Monatomic Oxygen	---	---	0.0015
Triatomic Oxygen	---	---	---
Nitrogen	0.1081	0.1571	0.1898
Nitric Oxide	---	---	0.0034
Nitrogen Dioxide	---	---	---
Monatomic Nitrogen	---	---	0.0002
Hydrogen	0.3446	0.2053	0.0595
Water	0.0300	0.1763	0.3008
Monatomic Hydrogen	---	0.0010	0.0090
Hydroxyl	---	0.0003	0.0285
Carbon Dioxide	0.0154	0.0600	0.1682
Carbon Monoxide	0.3380	0.4000	0.2360
Carbon	0.1639	---	---
Reaction Temperature (°F)	1940	3780	5100
Exit Velocity (ft/sec)	5868	6998	7543
Specific Impulse (lb.sec/lb)	182.5	217.6	234.5

TABLE XII. COMPOSITION OF THE PRODUCTS OF REACTION
 ORTHO-TOLUIDINE AND RED FUMING NITRIC ACID

Run Number	47	49	50
Weight Fraction Nitrogen Dioxide in Acid Phase	0.2182	0.2163	0.2179
Weight Ratio Acid / Fuel by Orifice Measurement	1.7	2.8	2.8
Weight Ratio Acid / Fuel by Material Balance	2.29	2.33	2.40
Reaction Pressure (lb/in. ² abs.)	315	315	315
Dry Gas Analysis (mole fraction)			
Carbon Dioxide	0.1630	0.1639	0.1540
Oxygen	--	--	0.0020
Hydrogen	0.1620	0.1871	0.1455
Carbon Monoxide	0.3877	0.4091	0.4420
Nitrogen	0.2253	0.2146	0.2100
Nitric Oxide	0.0203	--	--
Hydrocarbons	0.0417 ^a	0.0253 ^b	0.0465 ^c
Total Product Analysis (mole fraction)			
Carbon Dioxide	0.1294	0.1304	0.1224
Oxygen	--	--	0.0015
Hydrogen	0.1286	0.1488	0.1157
Carbon Monoxide	0.3077	0.3254	0.3513
Nitrogen	0.1788	0.1707	0.1669
Nitric Oxide	0.0161	--	--
Hydrocarbons	0.0331 ^a	0.2012 ^b	0.0370 ^c
Water	0.2063	0.2046	0.2052
Calculated Reaction Temperature (°F)	4325	4570	4440
Exit Velocity ^e (ft/sec)	6785	7017	6873
Specific Impulse ^e (lb.sec/lb)	210.7	218.2	213.7

^a Equivalent to C_{1.21}H_{4.78}

^b Equivalent to C_{1.95}H_{5.33}

^c Equivalent to C_{1.29}H_{4.48}

^d Determined from material balance.

^e Calculated assuming isentropic expansion through jet to 14.70 pounds per square inch absolute.

TABLE XIII. CALCULATED COMPOSITION OF THE PRODUCTS OF
REACTION OF ORTHO-TOLUIDINE AND RED FUMING
NITRIC ACID AT EQUILIBRIUM

Pressure (lb/in. ²)	300	300	300
Weight Fraction Nitrogen Dioxide in Acid Phase	0.15	0.15	0.15
Weight Ratio Acid / Fuel	1	2	3
Composition of Equilibrium Mixture (mole fraction)			
Oxygen	---	---	0.0012
Monatomic Oxygen	---	---	0.0007
Triatomic oxygen	---	---	---
Nitrogen	0.1026	0.1505	0.1849
Nitric Oxide	---	---	0.0019
Nitrogen Dioxide	---	---	---
Monatomic Nitrogen	---	---	0.0001
Hydrogen	0.3506	0.2377	0.0765
Water	0.0328	0.1520	0.2972
Monatomic Hydrogen	---	0.0005	0.0088
Hydroxyl	---	0.0001	0.0208
Carbon Dioxide	0.0110	0.0489	0.1486
Carbon Monoxide	0.3146	0.4104	0.2593
Carbon	0.1884	---	---
Reaction Temperature (°F)	1855	3490	4905
Exit Velocity (ft/sec)	5153	6452	7046
Specific Impulse (lb.sec/lb)	160.19	200.62	219.1

TABLE XIV. COMPOSITION OF THE PRODUCTS OF REACTION OF ANILINE, ORTHO-TOLUIDINE, AND RED FUMING NITRIC ACID

Run Number	53
Weight Fraction Nitrogen Dioxide in Acid Phase	0.220
Weight Fraction Ortho-toluidine in Fuel	0.810
Weight Ratio Acid / Fuel by Orifice Measurement	2.53
Weight Ratio Acid / Fuel by Material Balance	2.23
Dry Gas Analysis (mole fraction)	
Carbon Dioxide	0.1523
Oxygen	0.0015
Hydrogen	0.1923
Carbon Monoxide	0.4195
Hydrocarbons	0.0232
Nitrogen	0.2112
Total Product Analysis (mole fraction)	
Carbon Dioxide	0.1214
Oxygen	5 0.0012
Hydrogen	0.1532
Carbon Monoxide	0.3343
Hydrocarbons	0.0184
Water	0.2016
Nitrogen	0.1683
Black Residue ^a	0.00165
Calculated Reaction Temperature (°F)	4290
Exit Velocity (ft/sec)	6834
Specific Impulse (lb.sec/lb)	212.5

^a Composition equivalent to $H_{12.98}C_{25.6}N_1O_{1.75}$

TABLE XV. CALCULATED COMPOSITION OF THE PRODUCTS OF REACTION
 OF ORTHO-TOLUIDINE, ANILINE, AND RED FUMING NITRIC
 ACID AT EQUILIBRIUM

Pressure (lb/in. ²)	300	300	300
Weight Fraction Nitrogen Dioxide in Acid Phase	0.15	0.15	0.15
Weight Fraction Aniline in Fuel	0.19	0.19	0.19
Weight Ratio Acid / Fuel	1	2	3
Composition of Equilibrium Mixture (mole fraction)			
Oxygen	---	---	0.0027
Monatomic Oxygen	---	---	0.0017
Triatomic Oxygen	---	---	---
Nitrogen	0.1043	0.1523	0.1846
Nitric Oxide	---	---	0.0029
Nitrogen Dioxide	---	---	---
Monatomic Nitrogen	---	---	0.0002
Hydrogen	0.3481	0.2327	0.0740
Water	0.0314	0.1533	0.2876
Monatomic Hydrogen	---	0.0007	0.0121
Hydroxyl	---	0.0002	0.0287
Carbon Dioxide	0.0110	0.0499	0.1450
Carbon Monoxide	0.3187	0.4109	0.2606
Carbon	0.1866	---	---
Reaction Temperature (°F)	1845	3540	5040
Exit Velocity (ft/sec)	5127	6476	7142
Specific Impulse (lb.sec/lb)	159.43	201.36	222.09

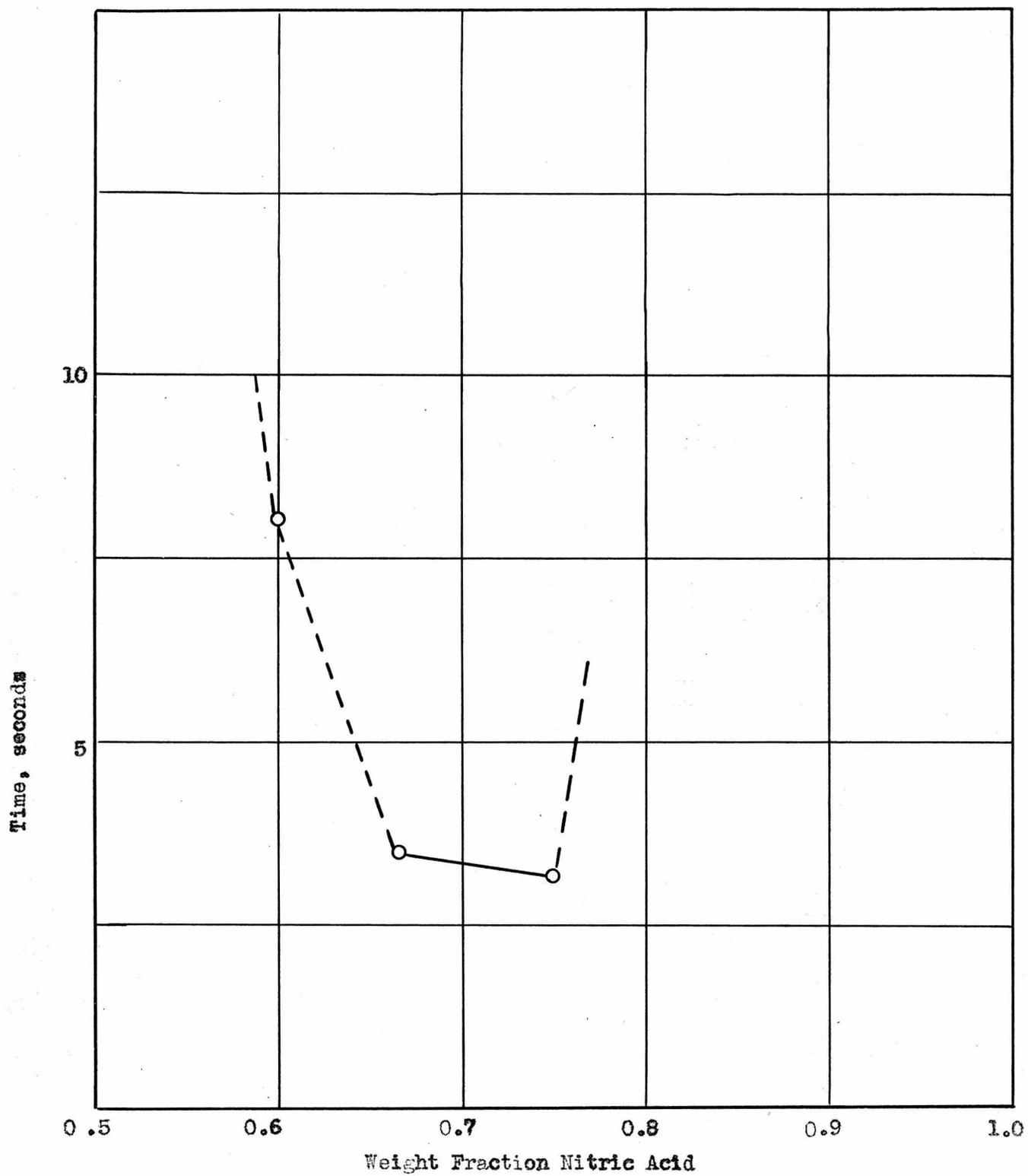


Figure I. Time Delay Associated With the Crucible Ignition of Nitric Acid and Aniline at 77° F.

Figure II

Ignition of Aniline-Acetone-Nitric Acid Mixtures

Figures in parentheses are temperatures of reactants, °F.
Figures preceding parentheses are ignition delay, seconds.

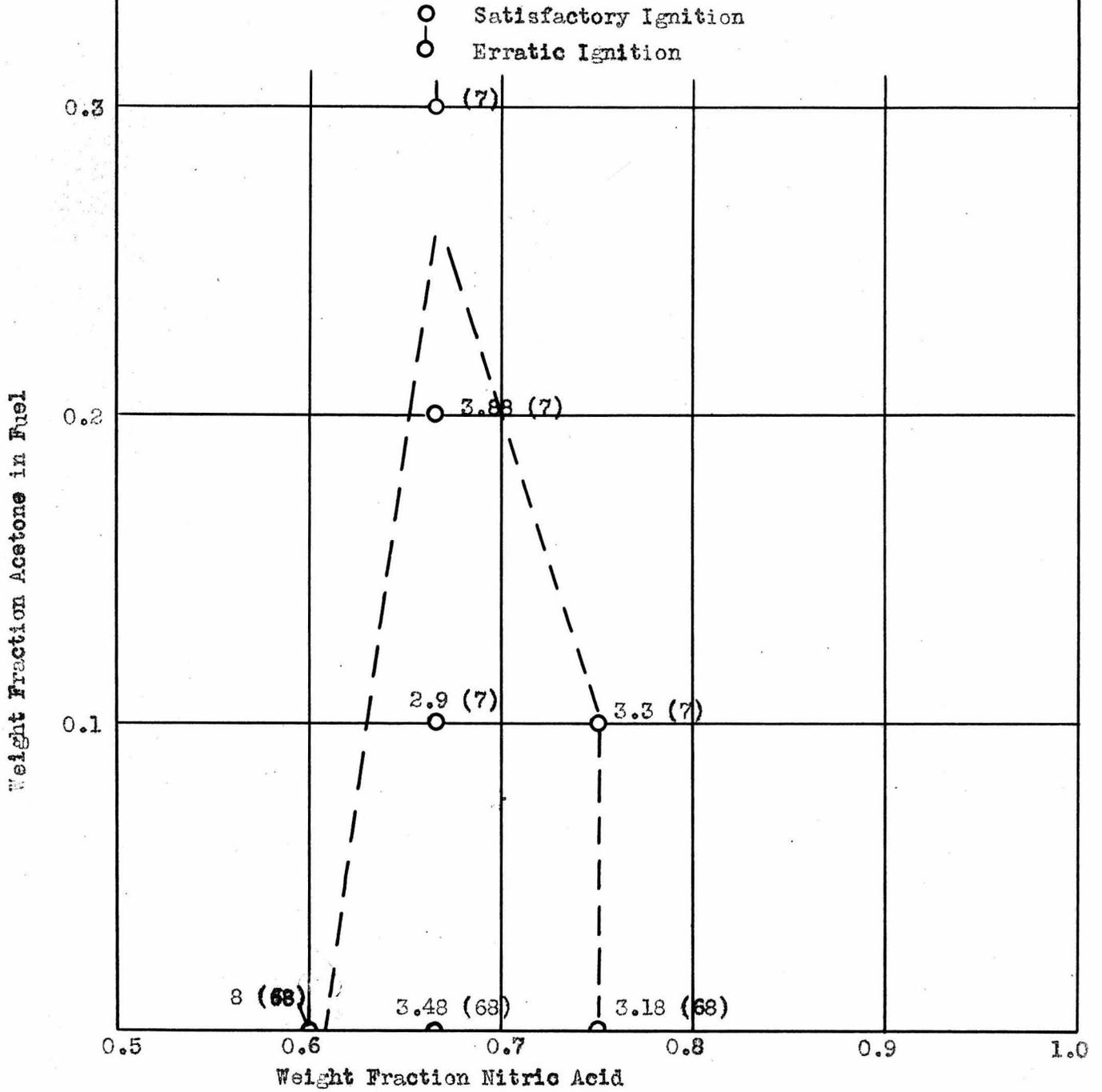
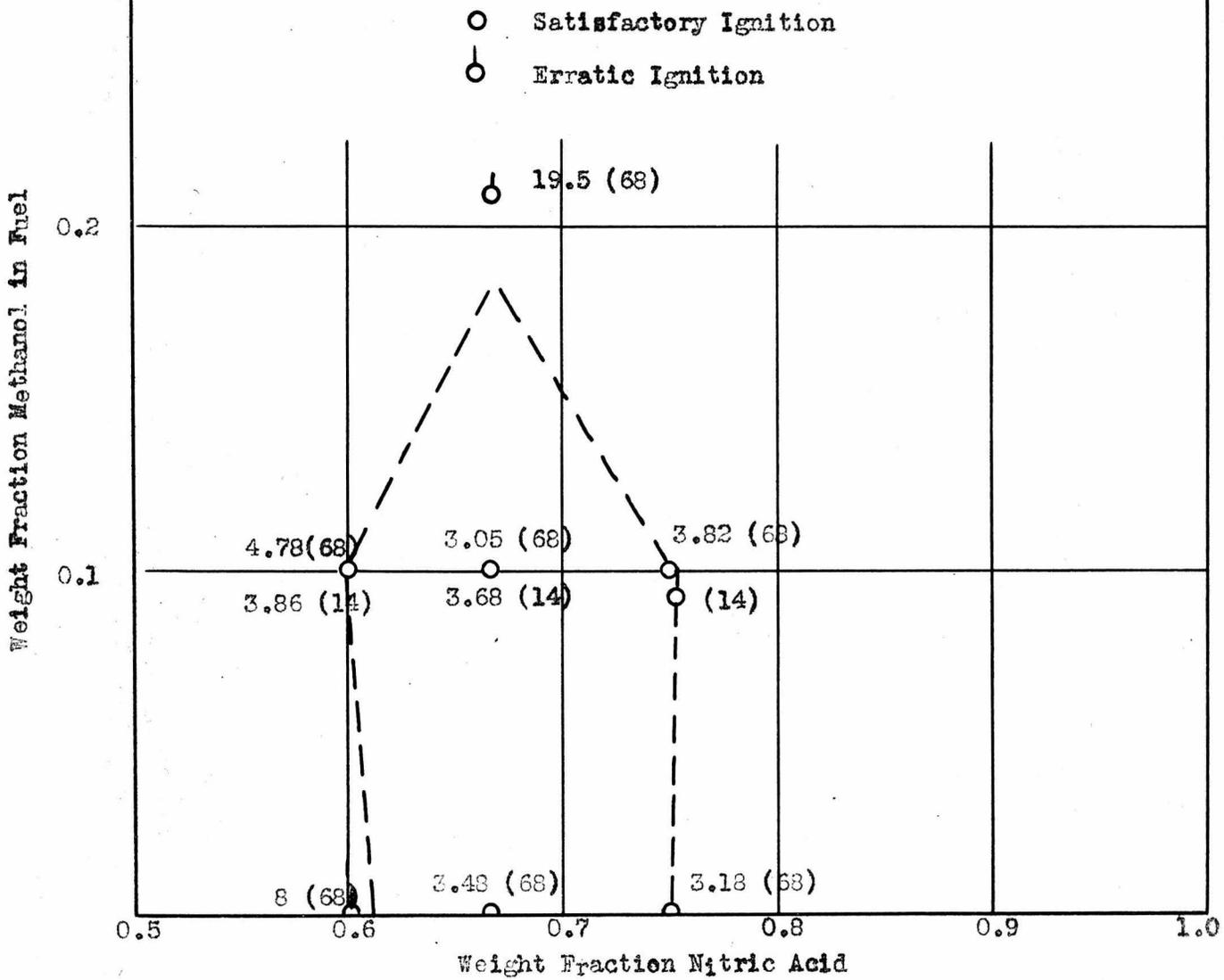
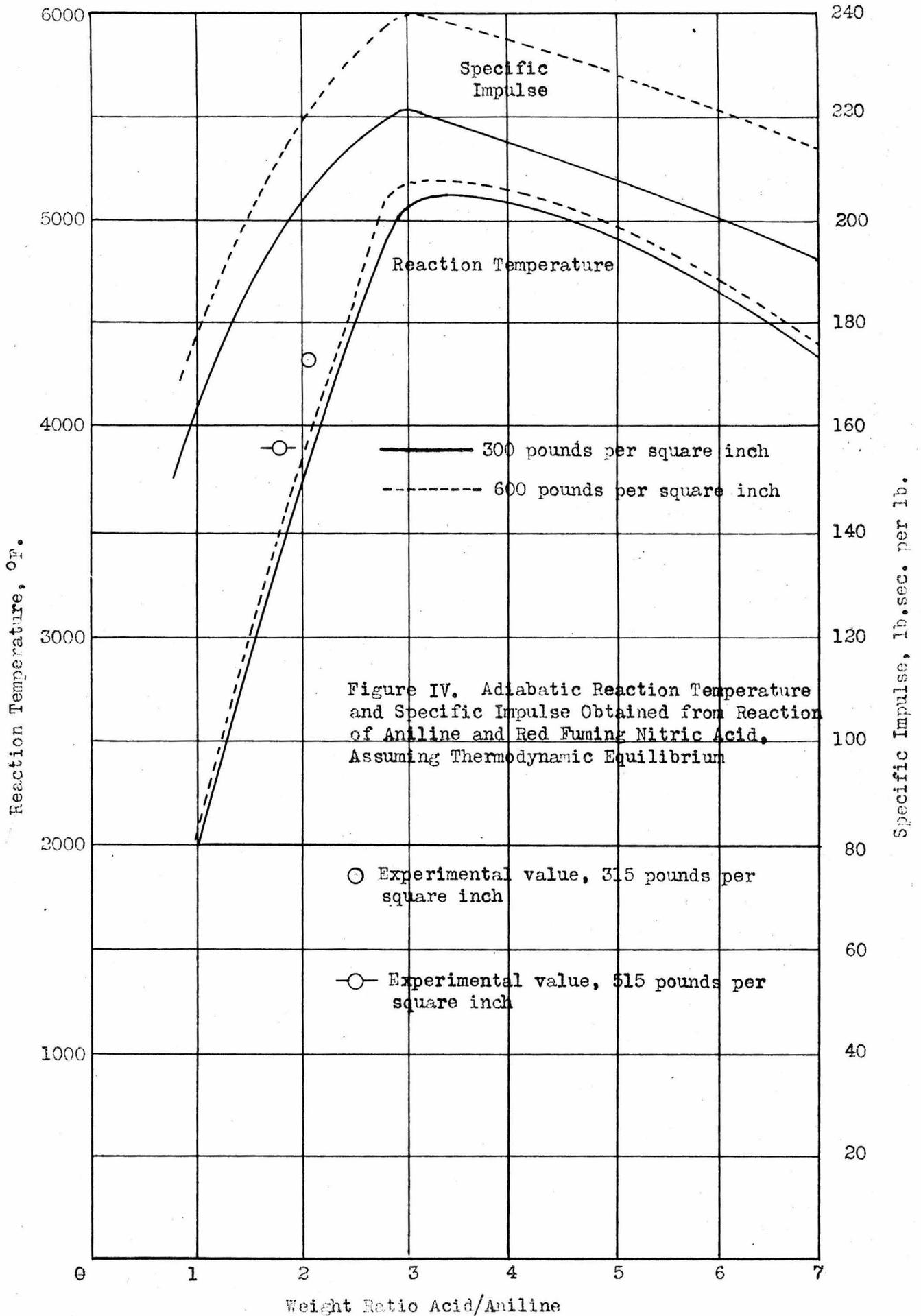


Figure III

Ignition of Aniline-Methanol-Nitric Acid Mixtures

Figures in parentheses are temperatures of reactants, °F.
Figures preceding those in parentheses are ignition delay expressed in seconds.





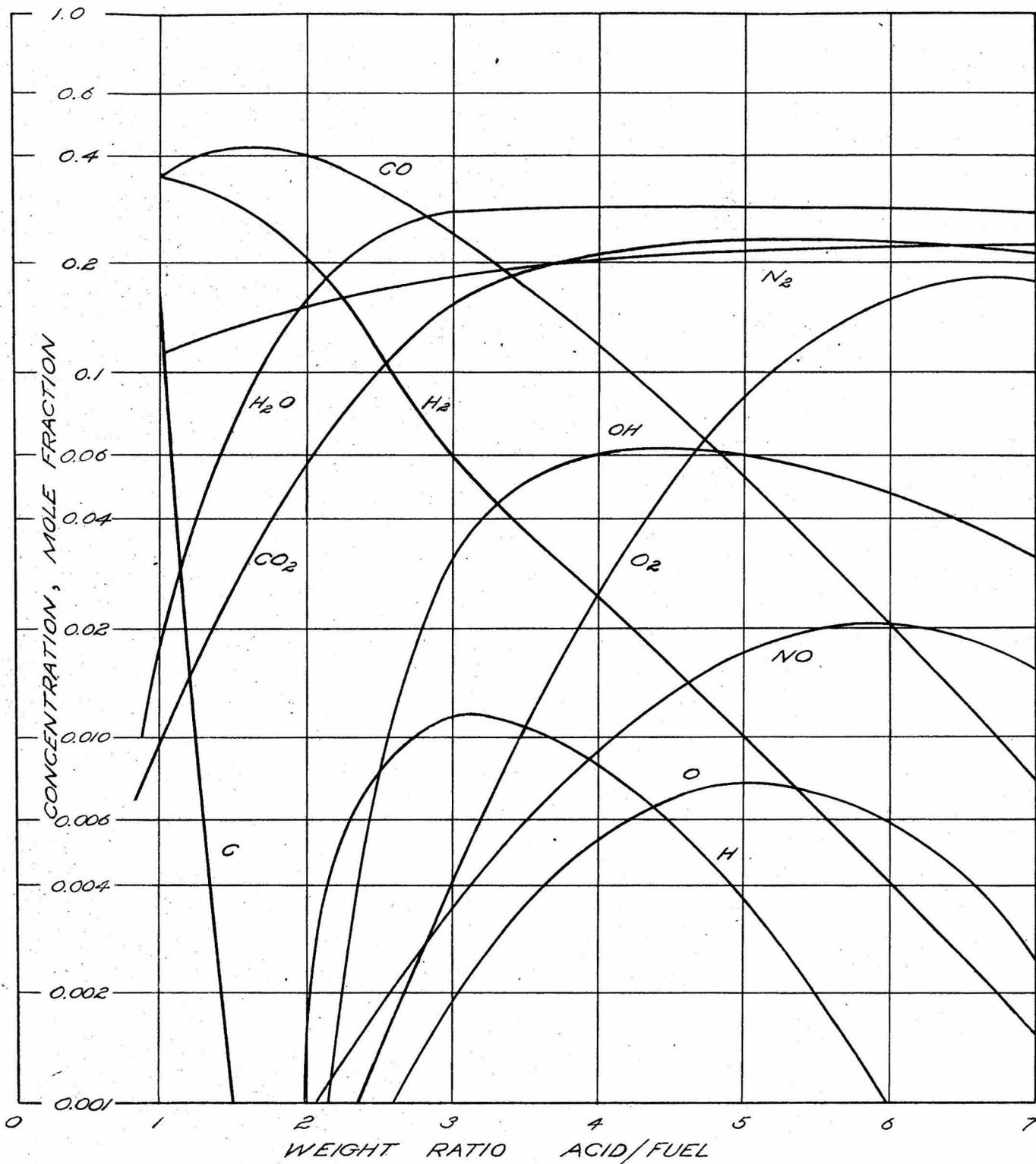


Figure V.

*CALCULATED EQUILIBRIUM COMPOSITION OF
THE REACTION PRODUCTS OF ANILINE AND
RED FUMING NITRIC ACID.*

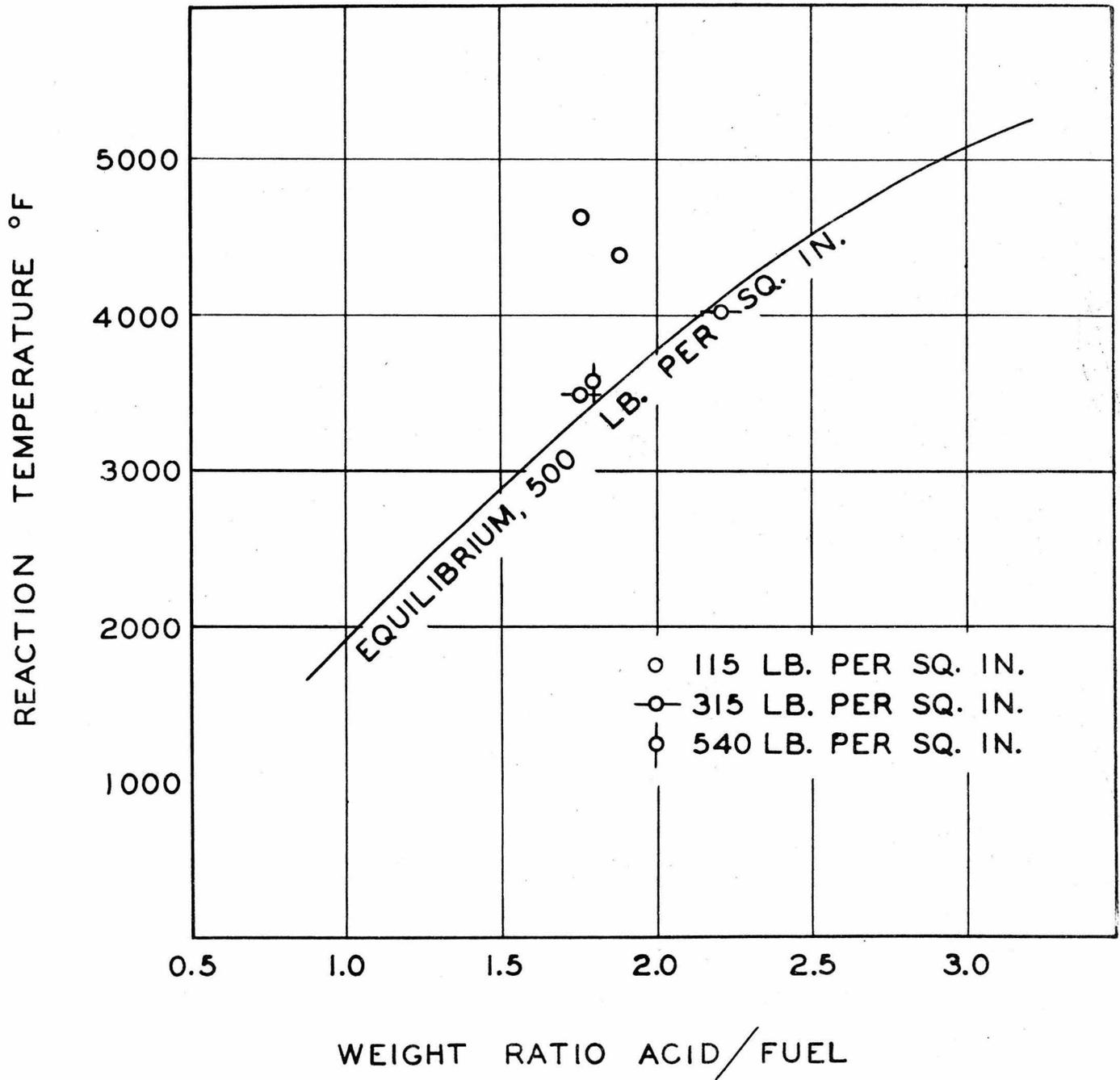
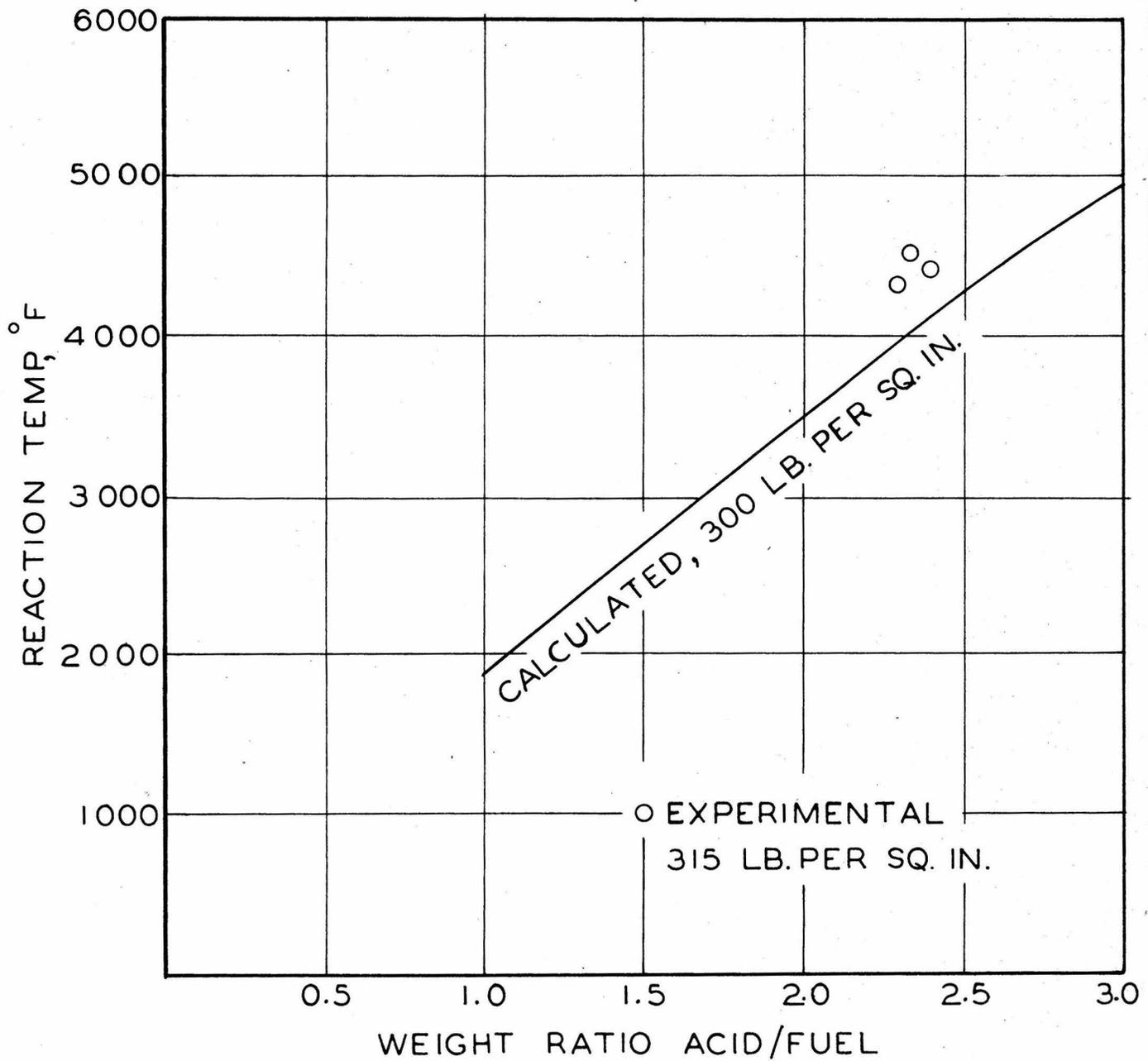
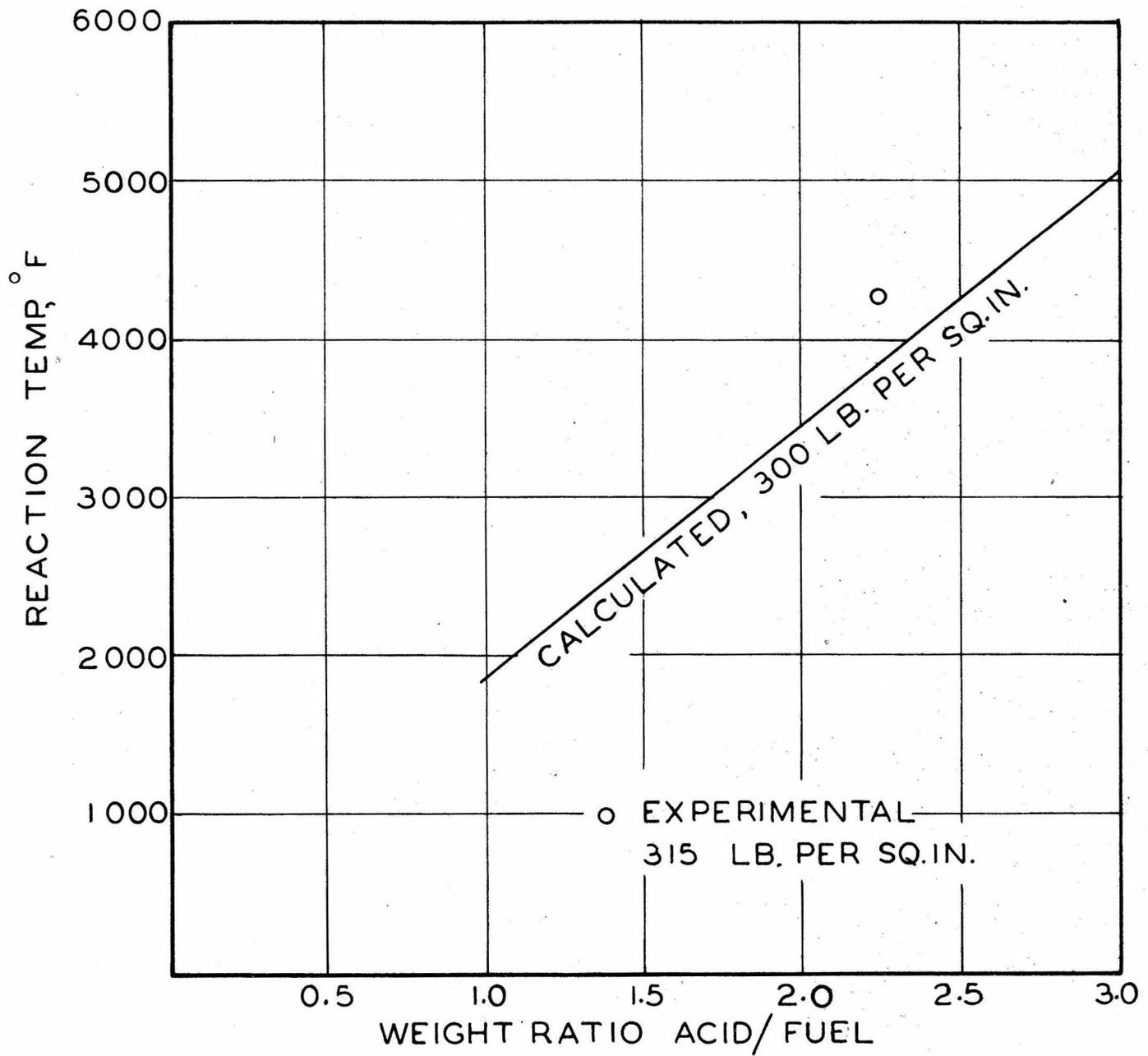


Figure VI. Reaction Temperature of the Aniline-acetone-Red Mining Nitric Acid System.



Influence of Mixture Ratio upon Flame Temperature in
the Orthotoluidine-fueled Burning Nitric Acid System

Figure VII.



Influence of Mixture Ratio upon Flame Temperature in the Orthotoluidine-Aniline-Red Fuming Nitric Acid System

Figure VIII.

Appendix A

THE LOWERING OF THE FREEZING POINT OF ANILINE BY THE ADDITION OF CERTAIN COMPOUNDS

Because the freezing point of aniline, 21.02° F, is well above many temperatures encountered in practice, it is desirable to find the freezing point lowering substance that is best from the points of view (i) of giving the best reaction with red fuming nitric acid and (ii) of giving a vapor pressure at ordinary temperatures when dissolved in aniline such that the presence of air at pressures of atmospheric or above will not introduce the hazard of inflammability.

The apparatus used in determining the freezing points of different mixtures is depicted in Figure A-1. The sample is contained in a small closed test tube A, which contains a stirrer B and a thermocouple C. Surrounding this test tube is a closed air jacket containing a drying agent, phosphorous pentoxide. The outer test tube E is immersed in a bath of acetone cooled by dry ice, which is contained in the transparent Dewar flask D.

The copper-constantan thermocouple employed was calibrated against a Leeds Northrup Platinum Resistance Thermometer which in turn was calibrated by the National Bureau of Standards. It is believed that the uncertainty involved in the temperature of the sample is not more than 0.1° F.

All the reagents employed were of c.p. quality except turpentine, ethyl cellosolve, and methyl-ethyl ketone. No attempts were made to purify any of these substances further, and it is believed therefore that the final results may involve uncertainties up to 2° F.

Because of the pronounced supercooling that occurred, the measurement of the disappearance of the solid phase gave a much more reliable indication of the freezing point than did the reverse procedure. The freezing point was ascertained by the melting-point curve and checked by visual observation.

The results are plotted in Figures A-I, A-II, and A-III, along with the values for acetone, which are available in the literature (1). Table A-I contains the numerical values.

Acetone is the most efficient as a freezing point depressant, as can be seen by Figure A-I, but the fugacity of 0.3 weight fraction acetone in aniline is about 3.85 pounds per square inch at 130° F. This high value of fugacity gives rise to inflammable mixtures with air present, if the total pressure is between 30 and 150 pounds per square inch. This is discussed in Appendix C. Similarly methanol and methyl-ethyl ketone are efficient but have high enough fugacities, when present in aniline to an appreciable extent, to constitute a hazard in use.

Ethyl cellosolve and diacetone alcohol are less efficient but have the virtue of having very low vapor pressures, comparable to that of aniline. The vapor pressures of ethyl cellosolve, diacetone alcohol, and aniline at 130° F are, respectively, 0.039 (2), 0.018 (2), and 6.070 pound per square inch.

Isobutanol, normal butanol, toluene, nitrobenzene, and ethylene glycol are not considered efficient enough in their freezing point depressing capacities to merit further consideration.

All the compounds mentioned above are not spontaneous with red fuming nitric acid under the conditions of use in jet-propulsion apparatus, and hence have a retarding effect on the spontaneity of the reaction of aniline with the acid.

Orthotoluidine reacts spontaneously, has a (stable) freezing point of 3.92° F (3), and forms two eutectics with aniline at 0.20 and 0.82 weight fraction orthotoluidine that exhibit freezing points of about 0.46° and -25° F, respectively. In addition the vapor pressure of orthotoluidine is even lower than that of aniline, and it is readily available.

Other compounds have been considered. Furfuryl alcohol has a low vapor pressure, about 0.156 pound per square inch at 140° F, is available, is spontaneous in reaction, but polymerizes when heated to about 338° F (4). This temperature may be lowered to 176° F if 0.1 per cent hydrochloric acid is present. Metatoluidine, which is spontaneous with red fuming acid, lowers the freezing point of aniline to -76° F if present in concentration of 0.426 mole fraction, according to Linard (5), but it is not available in large quantities.

Orthotoluidine and acetone were selected for the studies presented in the thesis for the reasons here indicated.

Appendix A

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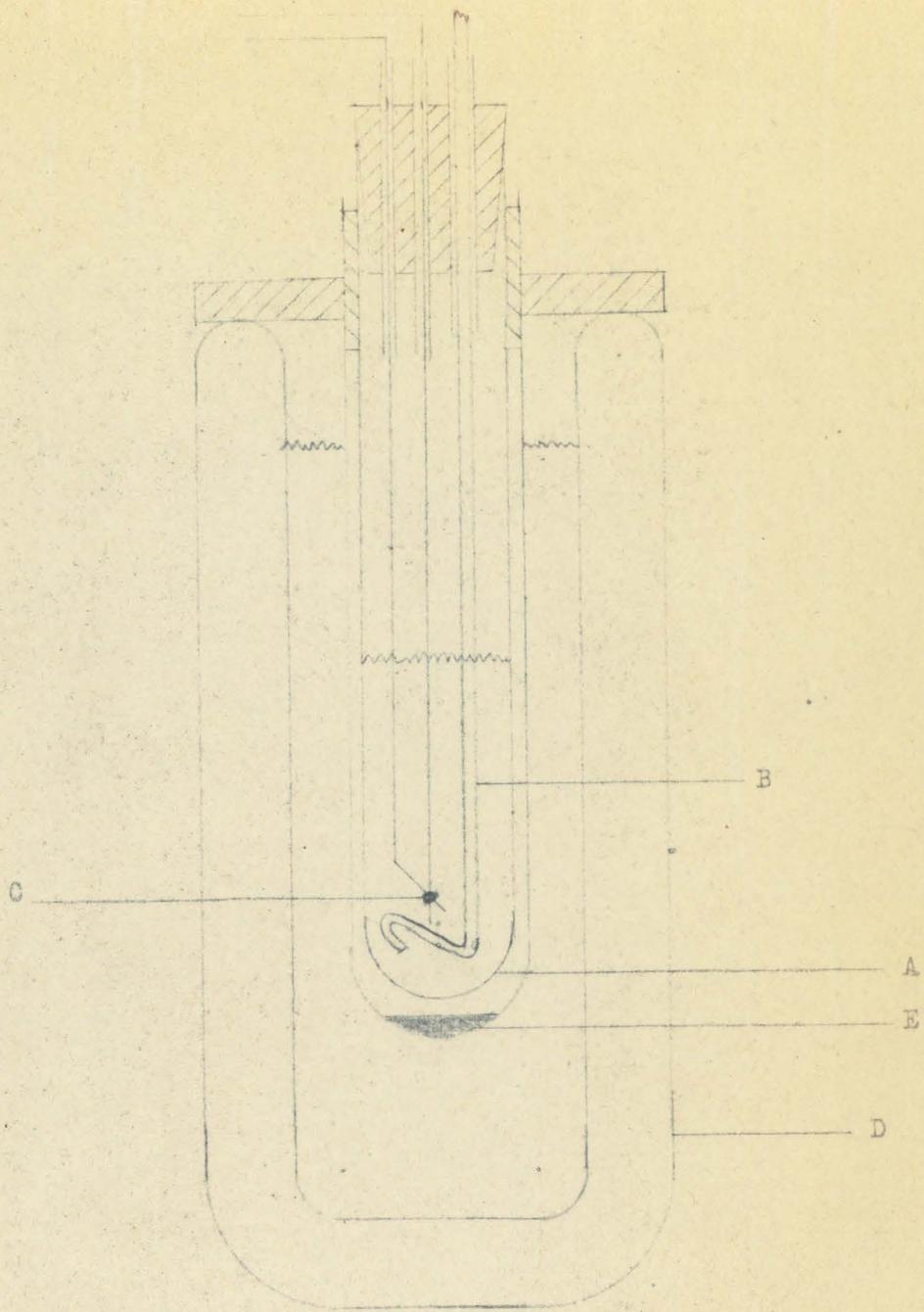


Figure A-1.

Schematic Drawing of Apparatus Used in Determination
of Freezing Point.

TABLE A-I. FREEZING POINTS OF MIXTURES OF ANILINE AND
A NUMBER OF ADDITIVE AGENTS

Added Material	Weight Fraction Added Material	Freezing Point (°F)
o-Toluidine (c.p.)	0.0000	21.02
	0.1021	11.05
	0.1520	6.21
	0.2002	0.46
	0.2538	10.27
	0.2998	12.16
	0.4000	12.78
	0.4999	10.27
	0.6003	4.35
	0.6999	-6.36
	0.8000	-22.36
	0.8999	-18.52
1.0000	-9.48	
o-Toluidine ("practical")	1.0000	-13.26
Acetone (c.p.) (1)	0.078	-1.3
	0.185	-29.2
	0.292	-62.5
	0.425	-103.0
Toluene (c.p.)	0.3000	-4.05
Turpentine	0.3001	*
n-Butanol (c.p.)	0.3001	-3.67
iso-Butanol (c.p.)	0.3000	-3.35
Nitrobenzene (c.p.)	0.3000	-4.32
Ethylene glycol (c.p.)	0.1163	+15.14
	0.2219	18.62
	0.3014	18.83
Diacetone Alcohol (c.p.)	0.0999	10.80
	0.2000	0.51
	0.3000	-15.54

* Forms two liquid phases below 54.2° F.

TABLE A-I. FREEZING POINTS OF MIXTURE OF ANILINE AND

A NUMBER OF ADDITIVE AGENTS

(cont'd)

Added Material	Weight Fraction Added Material	Freezing Point (°F)
Ethyl Cellosolve (technical)	0.0999	+10.27
	0.2005	-1.74
	0.3004	-15.81
Methyl ethyl ketone (technical)	0.0998	+5.41
	0.2002	-12.56
	0.3052	-36.03
Methanol (c.p.)	0.0985	+0.88
	0.2100	-19.05
	0.3025	-33.3

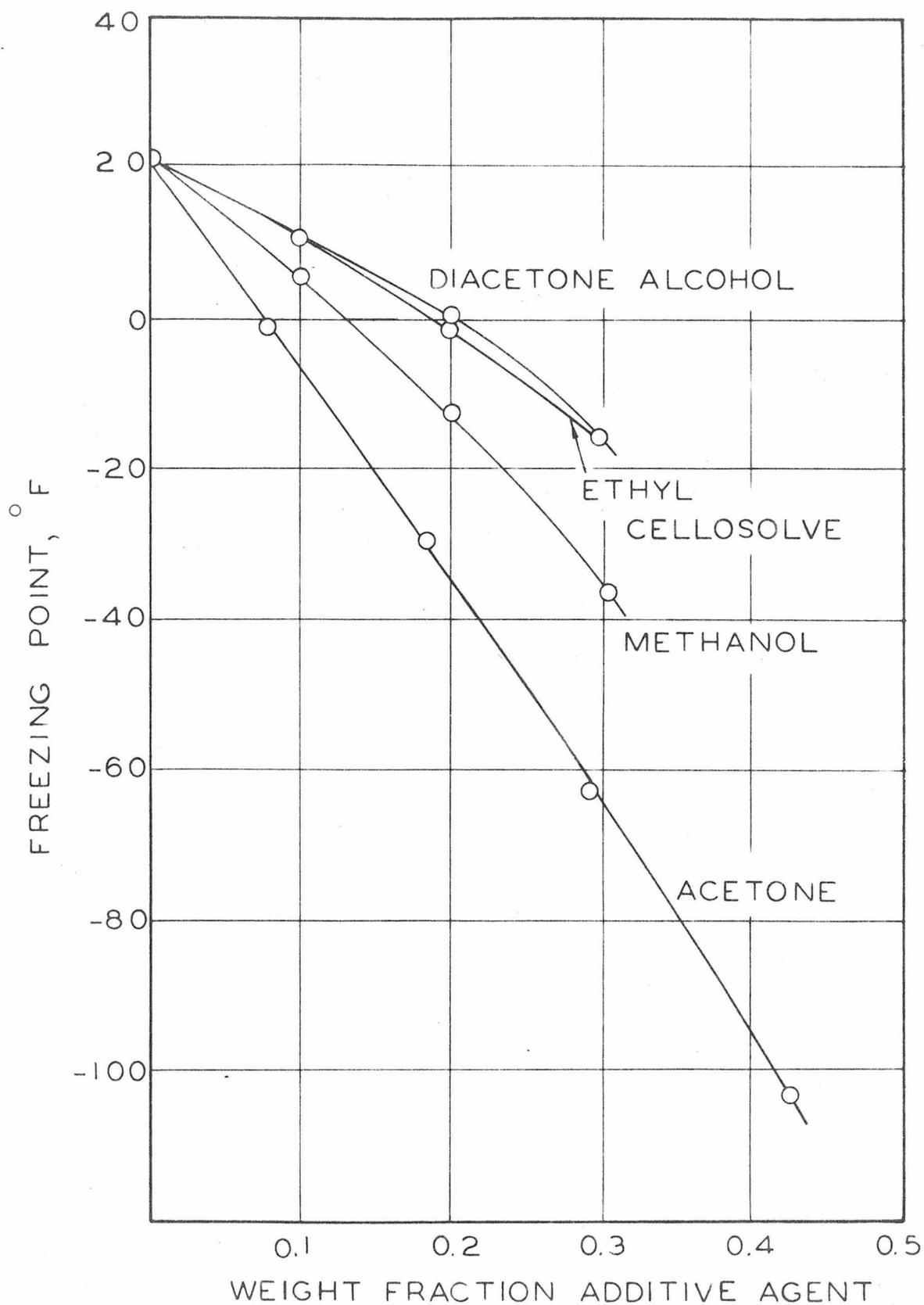


Figure A-I. Freezing Points of Mixtures of Aniline and a Number of Additive Agents.



Figure A-II. The Freezing Points of Aniline-Orthotoluidine System.

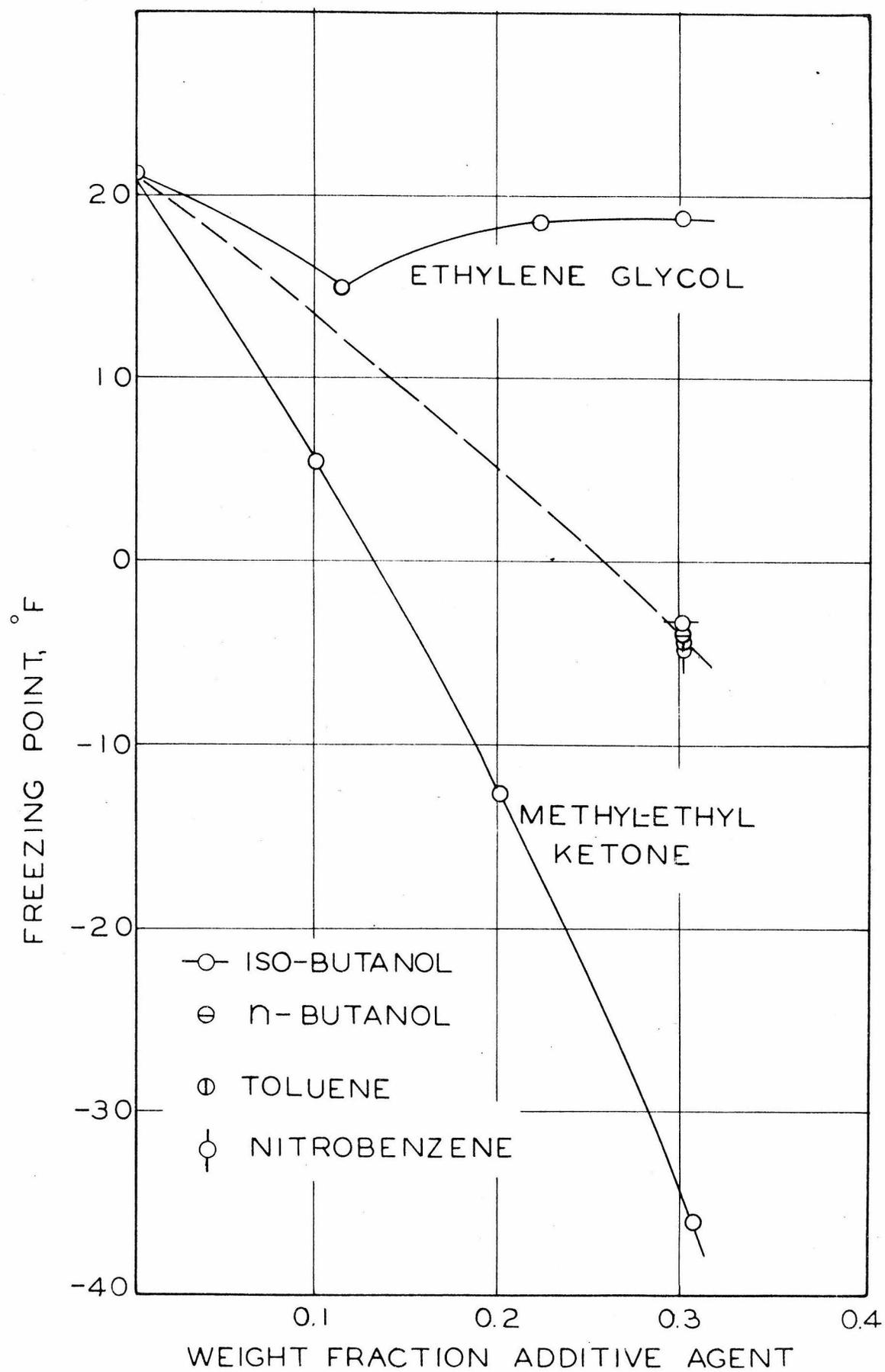


Figure A-III. The Freezing Points of Aniline with Various Compounds.

Appendix B

THE MEASUREMENT OF BUBBLE-POINT PRESSURE, SPECIFIC WEIGHT, AND VISCOSITY OF THE REACTANTS

Purpose: To facilitate the design of units for the exchange of heat between the cold reactants and the hot jet unit, and to assist in the design of pumping equipment for these liquids, a study of the bubble-point pressures, specific weights, and viscosities was undertaken.

Apparatus and Method: Essentially the apparatus used was a glass capillary tube 0.080 inch in inside diameter, surrounded by an ebullioscopic bath. The pressure of the bath was regulated at any desired subatmospheric pressure by means of a manostat. The pressure within the capillary tube was measured by a fluid pressure balance which had been calibrated against the vapor pressure of carbon dioxide at the ice point. The uncertainty of the actual pressure existing within the apparatus was probably less than 0.2 pound per square inch. However, because of the presence of uncondensable gases in the sample, which made the exact bubble point uncertain, the error in the final results may be as much as 10 pounds per square inch. The copper-constantan thermocouple employed was calibrated against a strain-free platinum resistance thermometer which had been calibrated at the Bureau of Standards, and its potential was measured by a White double potentiometer. The actual temperature measured was probably exact to within 0.05° F, but because of variation of the manostat-controlled pressure on the bath and some superheating of the liquid in the bath, the final temperature for one point may be uncertain by as much as 0.3° F.

A small hollow glass cylinder 0.061 inch in diameter and 0.5 inch long, containing an iron needle, was supported within the capillary by means of the field of an axially mounted electromagnet and was used to stir the sample during bubble-point pressure measurements and to ascertain the viscosity of the liquid sample.

Figure B-1 shows a photograph of the assembled apparatus, and Figure B-2 indicates it schematically. The fluid pressure balance was connected to the capillary tube through the oil-mercury-air interfaces in the vessel A. A mercury manometer was attached to ascertain the effective head of the mercury and oil in the apparatus with respect to the pressure balance, and a vacuum system was provided to permit evacuation of the capillary prior to sample introduction. The glass capillary was sealed to the metal part of the system by an unsupported-area packing gland J, and was contained in part in the vacuum-jacketed ebullioscopic bath which is shown within the electromagnet B. The boiler C supplied saturated gas to the upper part of the bath. This fluid was condensed on the inside of the water jacket E and returned to the boiler by the external return F, thus preventing temperature gradients within the tube due to inhomogeneity of the fluid within the bath. A small mercury-sealed stopcock provided at the bottom of the column, cooled by the water jacket D, was used as an inlet for a very small stream of air to prevent superheating of the liquid in the boiler, and also was used to change the fluid in the boiler. The thermocouple was introduced with a well extending down into the bath from the fitting G, and the manostat was connected at H.

Viscosity was measured by ascertaining the limiting rate of fall for the cylinder by measurements of time for different distances of fall, while the fluid was held at the desired pressure and temperature.

Two axially mounted electromagnets were used, the top one to hold the cylinder in the initial position and the bottom one to catch it below the final position. Both magnetic fields were turned off at the beginning of the fall, by a switch which also started an electric timer. When the cylinder had fallen a measured distance, the fields were turned on and the clock stopped simultaneously, while the cylinder was caught in the bottom field, permitting its return to the original position.

The fall time was reproducible to within approximately 5 per cent. At least 60 fall times were measured for each state of the liquid. The instrument was calibrated by the known values for pentane (1) and water (2). It has been found necessary to ascertain the specific weight of the liquid and cylinder in order to obtain the viscosity from this type of instrument (3,4,5). This was done by the usual closed-pycnometer method (6), using a glass-enclosed magnetic agitator to assure equilibrium within the sample.

The equation used to calculate viscosity was

$$\eta = \alpha (\rho - \rho_f) \mathcal{D} - \beta \rho_f / \mathcal{D}$$

where η is the absolute viscosity of the liquid, ρ and ρ_f are, respectively, the specific weights of the cylinder and fluid, \mathcal{D} is the time of fall, and α and β are empirically determined constants. This relation is derived from the usual equation of force that defines viscosity but with the incorporation of a correction for the inertial force exerted on the falling body by the flow of the liquid past it, which is taken as proportional to the density of the fluid times the velocity of the falling cylinder squared. It is estimated that the uncertainty of the viscosities measured, from their absolute value, is about 10 per cent. The temperatures, as described above, are uncertain by about 0.3° F.

Results: The red and white fuming nitric acids used were of compositions shown in Table B-Ib. The oxides of nitrogen present in the samples reported as nitrogen dioxide were determined by oxidation with ceric sulfate, followed by titration of the excess oxidizing agent with ferrous sulfate. The total nitrogen present was ascertained by a nitrometer. The compositions shown in Table B-Ib were calculated on the assumption that only water, nitric acid, and nitrogen dioxide are present in the sample. Correlations of composition with specific weight are available in the literature, assuming, respectively, for red fuming and for white fuming acid that no water is present (7) or that no oxides of nitrogen are present (8). These correlations are also listed in the table. In the case of the red fuming acid the analysis is believed more accurate, but in the case of the white fuming acid the composition determined from the specific weight is probably better.

The bubble-point pressures were determined for the two samples of acid described at a series of temperatures between 100° F and 300° F. Figure B-I and Table B-Ia show the results. In the case of the red fuming acid, decomposition occurred slowly above about 200° F. For this reason a new sample was used for the values above 220° F, and the measurements were made as rapidly as possible. At the low temperatures the bubble point was reversibly reproducible to within about 1 pound per square inch. The white fuming acid did not show appreciable decomposition for temperatures up to 300° F for the times encountered in making these measurements.

The specific weight at the bubble point is shown for various temperatures in Figure B-II and Table B-Ia. Corrections were made for the temperature coefficient expansion of the pycnometer, for the buoyancy of air on the weight of the sample, and for the small amount of acid in the gas phase.

The pycnometer containing the sample was cooled to -60° F and evacuated to remove non-condensable gases. No correction was made for the change of volume of the pycnometer due to pressure. It is believed that these measurements are good to 0.5 per cent.

Viscosity at the bubble-point pressure, over the range of temperature 100° to 300° F, was ascertained. The results are recorded in Table B-Ia and Figure B-III. As mentioned previously, the change in specific weight of the liquid is accounted for in these measurements. The effect of pressure and temperature upon the dimensions of the falling cylinder and the enclosing capillary tubing is not corrected for. The absolute accuracy is estimated to be 10 per cent.

The vapor pressure (9,10,11,12,13,14) and viscosity (15) of aniline are well known. The determination of these properties for one aniline-acetone mixture was made because of interest in acetone as a freezing point depressant in aniline. Table B-II contains the values of bubble-point pressure for an aniline-acetone mixture containing 0.2975 weight fraction acetone. The measured values are from 3 to 25 per cent lower than calculated from Raoult's law. The values shown for 0.10 and 0.20 weight fraction acetone were computed assuming that the deviation from Raoult's law is proportional to the concentration of acetone. The measurements of viscosity of this mixture were carried out. The results are shown in Table B-III and Figure B-IV.

Appendix B

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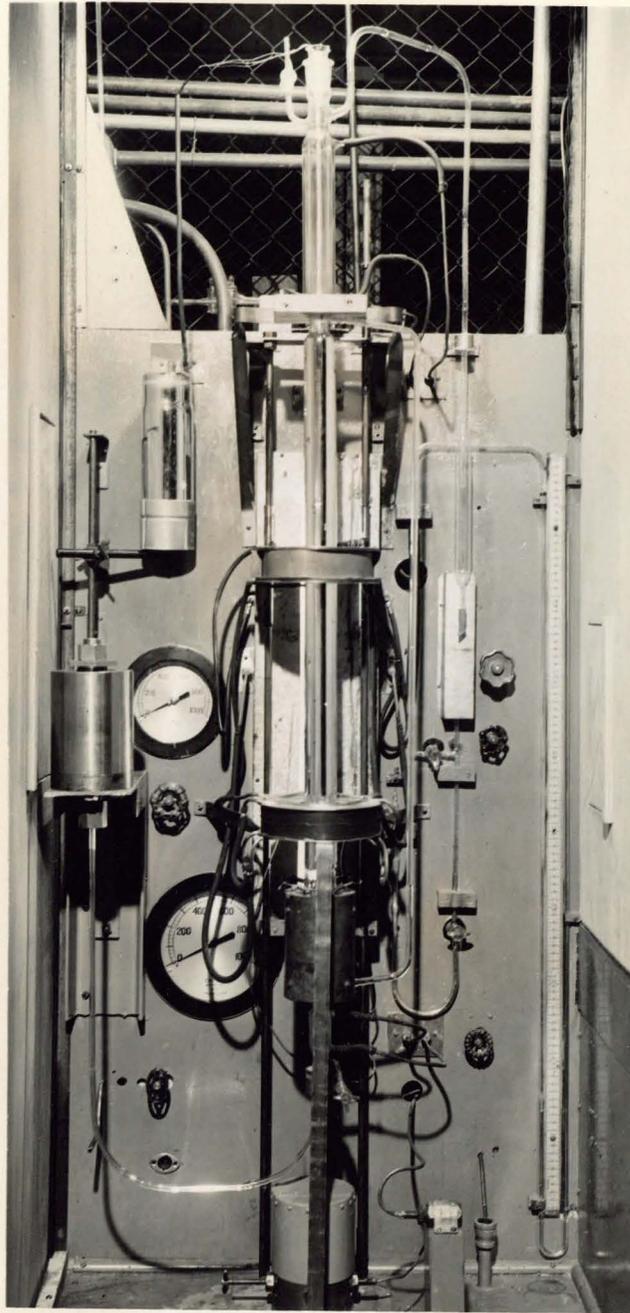


Figure B-1. Bubble-point Pressure and Viscosity Equipment.

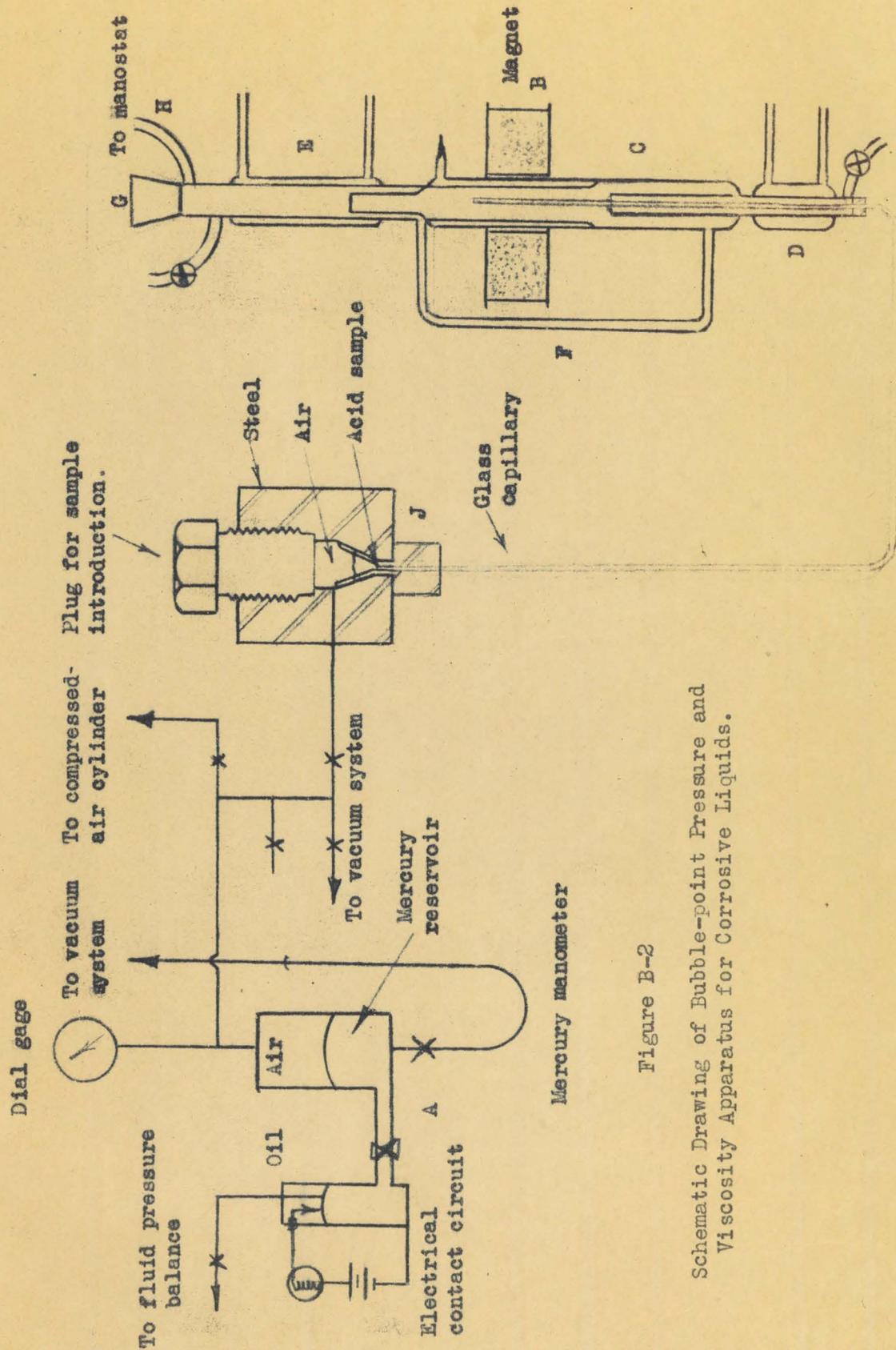


Figure B-2

Schematic Drawing of Bubble-point Pressure and Viscosity Apparatus for Corrosive Liquids.

TABLE B-1a. VOLUMETRIC PHASE BEHAVIOR AND VISCOSITY OF
FUMING NITRIC ACIDS

Bubble Point

Total Pressure (lb/in. ²)	Temperature (°F)	
	White Fuming Acid	Red Fuming Acid
50	204.4	155.8
100	231.5	189.1
200	265.6	228.2
300	290.0	255.2
400	309.9	275.7
500	326.6	292.8
600		308.5

Density

Temperature (°F)	Density (lb/ft. ³)	
	White Fuming Acid	Red Fuming Acid
75	92.20	98.90
100	90.57	97.23
150	87.43	93.45
200	84.25	89.20
250	81.03	84.40
300	77.80	

TABLE B-1a. VOLUMETRIC PHASE BEHAVIOR AND VISCOSITY OF
FUMING NITRIC ACIDS

(cont'd)

Temperature (°F)	Viscosity (centipoises)		Viscosity (lb. sec/ft ²)	
	White Fuming Acid	Red Fuming Acid	White Fuming Acid	Red Fuming Acid
80	1.168	1.525	2.44×10^{-5}	3.187×10^{-5}
100	0.990	1.240	2.07×10^{-5}	2.592×10^{-5}
120	0.842	1.010	1.76×10^{-5}	2.111×10^{-5}
140	0.718	0.835	1.50×10^{-5}	1.745×10^{-5}
160	0.617	0.690	1.29×10^{-5}	1.442×10^{-5}
180	0.536	0.575	1.12×10^{-5}	1.202×10^{-5}
200	0.471	0.485	0.985×10^{-5}	1.014×10^{-5}
220	0.416	0.411	0.870×10^{-5}	0.859×10^{-5}
240	0.371	0.352	0.776×10^{-5}	0.736×10^{-5}
260	0.334	0.308	0.697×10^{-5}	0.644×10^{-5}
280	0.302	0.269	0.632×10^{-5}	0.562×10^{-5}
300	0.277		0.579×10^{-5}	
320	0.255		0.532×10^{-5}	

TABLE B-1b. COMPOSITIONS OF FUMING NITRIC ACIDS

Density (gm/cc)	<u>White Fuming Acid</u>		<u>Red Fuming Acid</u>	
	1.4704 at 23.4° C.		1.5767 at 25° C.	
Composition (wt.fraction)	Analysis	By Density ^a	Analysis	By Density ^c
NO ₂	0.0054	---	0.2401	0.1818
HNO ₃	0.8634	0.8718	0.7259	0.8182
H ₂ O ^b	0.1312	0.1282	0.0340	---

^a Reference (8). Density corrected for NO₂, reference (7).

^b By difference.

^c Assuming only HNO₃ and NO₂ present, reference (7).

TABLE B-II. BUBBLE POINT PRESSURE OF ANILINE-ACETONE MIXTURES

Temperature (°F)	Vapor Pressure, (lb/in. ²)			
	Aniline ^b	0.10 Wt.Frac. Acetone ^a	0.20 Wt.Frac. Acetone ^a	0.2975 Wt.Frac. Acetone
80	0.005	0.373		0.2972
100	0.016	0.622	1.019	1.432
120	0.044	1.006	1.694	3.289
140	0.107	1.567	2.690	5.728
160	0.215	2.356	4.094	8.750
180	0.390	3.392	5.918	12.79
200	0.650	4.779	8.341	18.07
220	1.045	6.589	11.45	24.72
240	1.615	8.908	15.31	32.58
260	2.475	11.80	19.95	42.17
280	3.650	15.46	25.74	53.33
300	5.370	20.10	32.75	67.92
320	7.464	25.47	40.72	81.47
340	10.26	31.97	50.14	99.08
360	13.87	40.04	61.72	119.7
380	18.58	49.75	75.11	142.6
400	24.38	60.78	90.10	168.7
420	31.62	73.81	107.2	199.1
440	40.55	88.80	126.6	233.9

^a Computed values.

^b From references cited in text.

TABLE B-III. VISCOSITY OF ANILINE ACETONE MIXTURES
CONTAINING 0.2975 WEIGHT FRACTION ACETONE

Temperature (°F)	Viscosity (centipoises)	Viscosity (lb.sec/ft. ²)
80	1.32	2.75×10^{-5}
120	0.761	1.59×10^{-5}
160	0.536	1.12×10^{-5}
200	0.423	0.885×10^{-5}
240	0.354	0.740×10^{-5}
280	0.308	0.646×10^{-5}
320	0.278	0.581×10^{-5}
360	0.253	0.532×10^{-5}
400	0.238	0.498×10^{-5}
440	0.224	0.469×10^{-5}

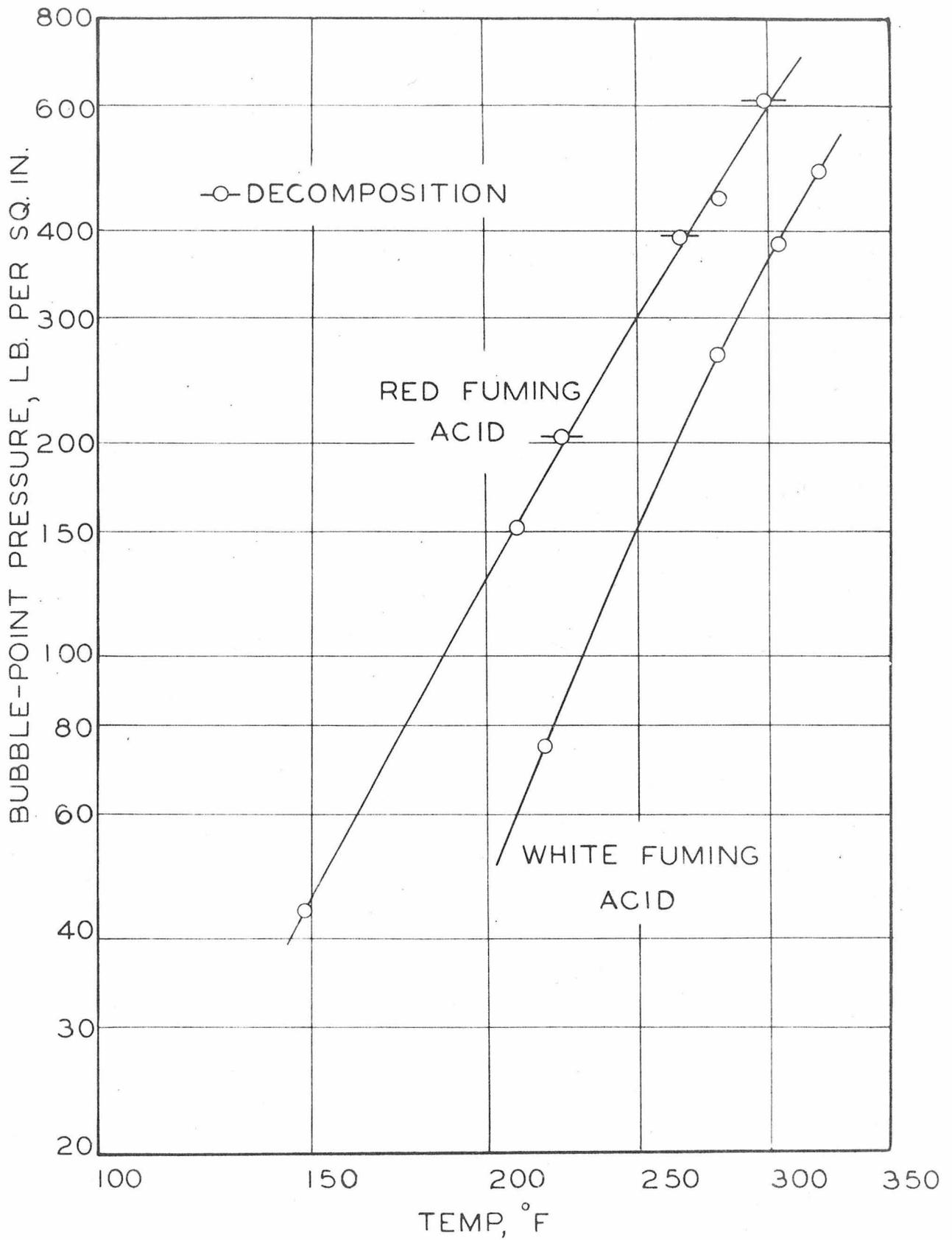


Figure B-I. Bubble-point Pressure of Fuming Nitric Acids.

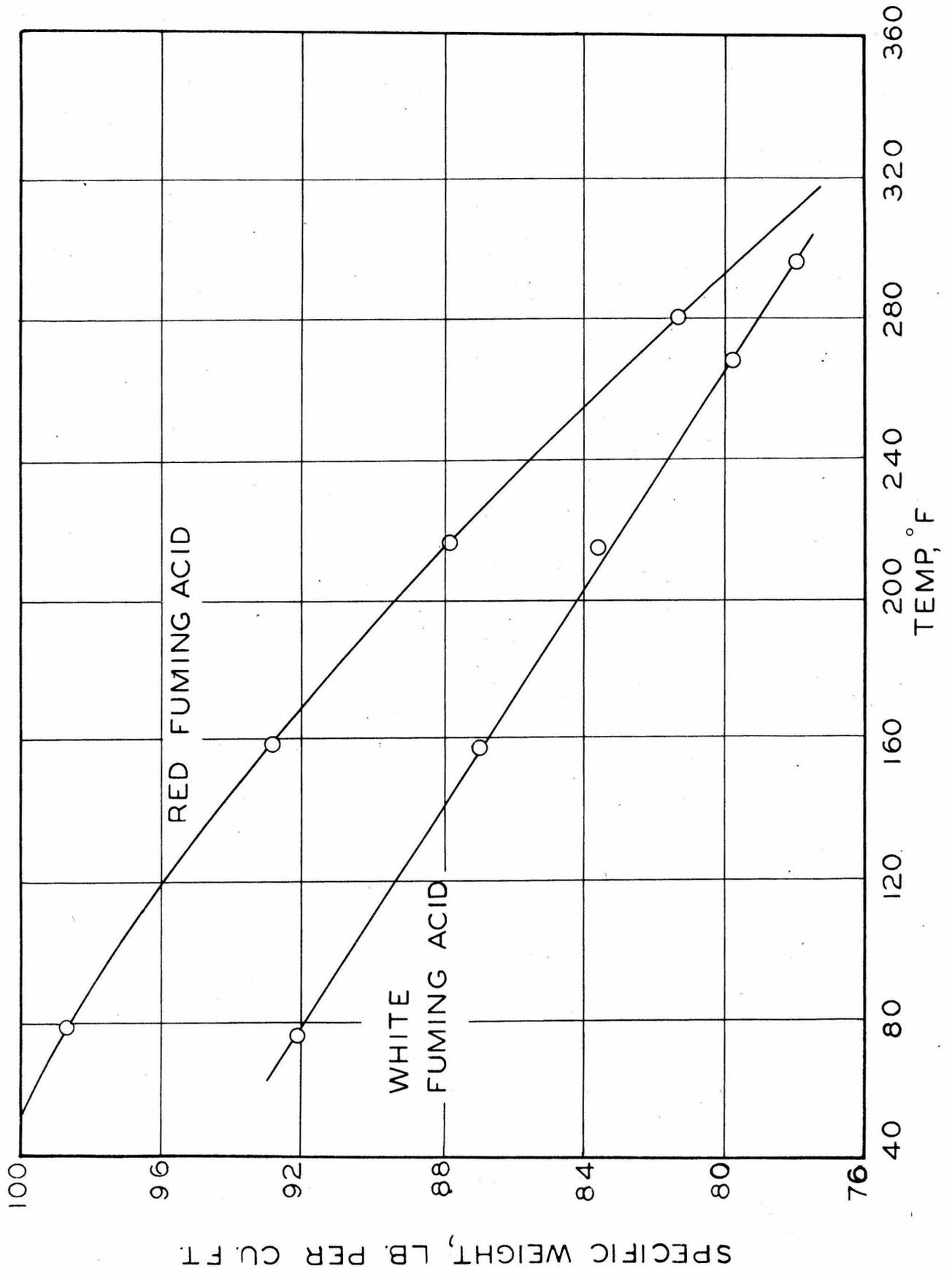
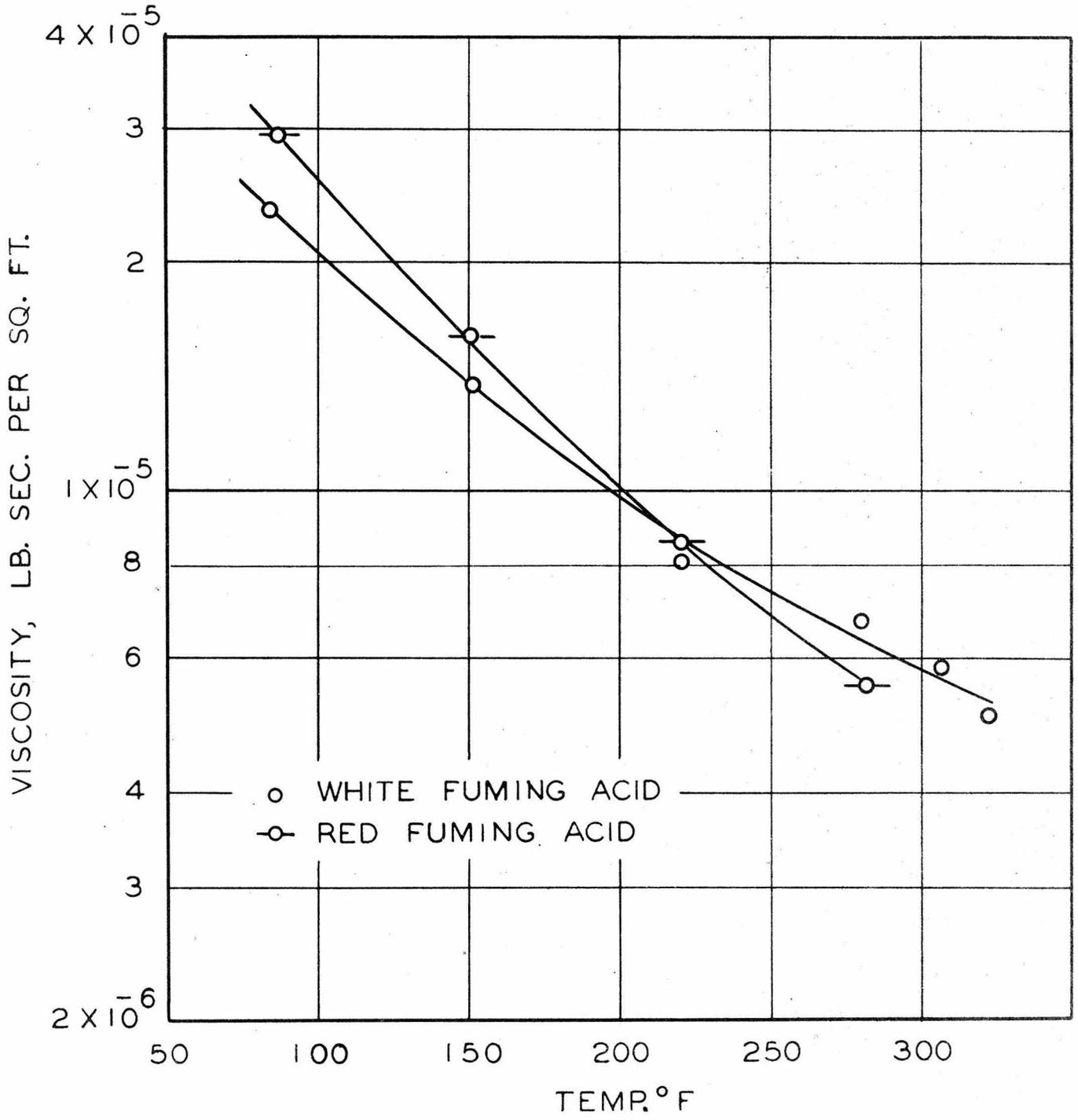


Figure B-II. Specific Weights of Fuming Nitric Acids at the Bubble Point.

Figure B-III.

Viscosity of Fuming Nitric Acids at the Bubble-point Pressure



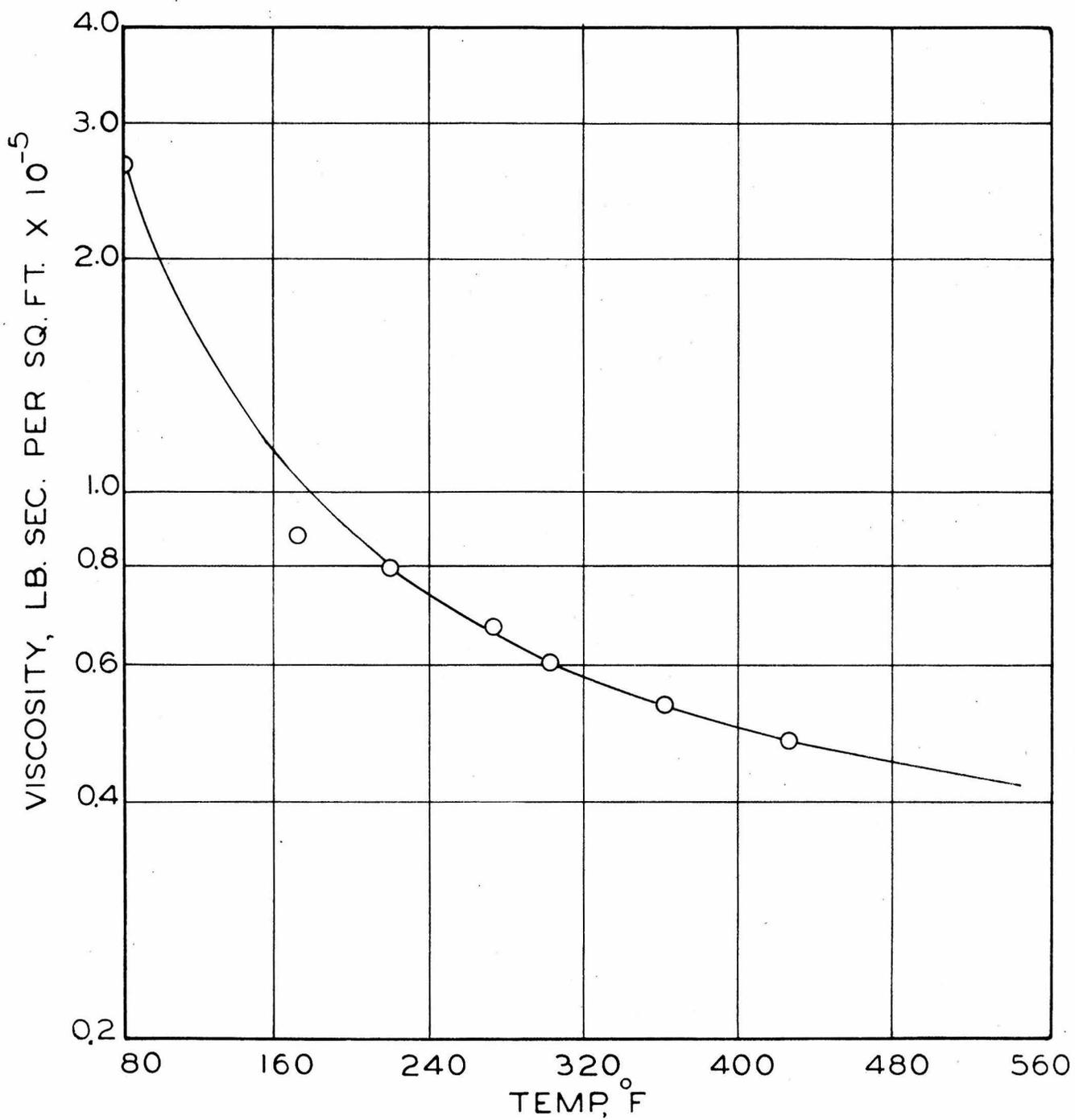


Figure B-IV. Viscosity of Aniline-Acetone Mixture Containing 0.2975 Weight Fraction Acetone at the Bubble Point.

Appendix C

THE IGNITION OF THE ANILINE-ACETONE-AIR SYSTEM

Purpose: One method of transferring the reactants from their respective storage tanks to the jet unit is to maintain approximately constant the pressure of some gas in these containers and to control the flow of the reactants by valves and orifices in the reactant lines. If air is used for the expulsion of these liquids from storage, there is a possible hazard from explosion when acetone is used as a freezing point lowering substance in the aniline. It was desired to study this hazard by experiment and by calculation.

Apparatus: It is known (1) that the geometry of the apparatus employed affects the ignition of mixtures of acetone and air in at least two ways. The experimentally determined limits of composition for ignition may be made slightly wider by permitting upward propagation of the flame because of the gentle turbulence introduced. Also, if the linear dimensions of the combustion chamber are all large, of the order of 0.5 foot or more, there are some borderline gas-phase compositions which will not ignite and propagate throughout the volume but which may show ignition in smaller chambers.

It was desirable to build a small compact apparatus in which the temperature and compositions of gas and liquid phases could be precisely controlled. Preliminary experiments with pure acetone indicated that a chamber 1 inch in diameter and 3 inches long gave ignition limits not appreciably different from those reported for geometry featuring upward propagation of flame and diameters of the order of 0.5 foot (1). This was borne out by comparison of the results for acetone in aniline with calculations.

The apparatus employed is shown in Figure C-1. A steel chamber A is sealed at one end with a blow-out disc B by fitting C and at the other end by a hollow fitting D which contains a spark plug with points shown at F and a connection for the introduction of air and the measurement of pressure at E.

The pressure was measured by a Bourdon-tube pressure gauge, which had been calibrated against a fluid pressure balance standardized by the vapor pressure of carbon dioxide at 32° F.

Temperature was maintained constant by immersion of the pressure chamber in an agitated oil bath. Measurements of temperature were by a mercury-in-glass thermometer in the oil bath, which was checked at intervals by a standard thermocouple, which in turn had been calibrated by the strain-free platinum resistance thermometer from the National Bureau of Standards.

Measurements of composition were checked before and after each series of measurements by ascertaining the index of refraction at 78.44° F on an Abbe refractometer. Chemicals of the c.p. grade were used throughout.

Procedure: A measured quantity of a controlled aniline-acetone mixture to be used was introduced into the chamber by removal of the fitting D of Figure C-1. The chamber was placed in the oil bath and allowed to reach equilibrium at a certain temperature. Air which had been dried and freed from carbon dioxide by passage over calcium chloride, sodium hydroxide, and potassium hydroxide at a pressure above 4000 pounds per square inch was introduced into the chamber to the desired pressure. The ignition attempt was made by applying from 5,000 to 15,000 volts, depending on the pressure, to the spark plug from the secondary of a 60-cycle transformer. The corresponding energy dissipation were about 20 to 40 watts. If no ignition

was obtained, as indicated by a pulse on the Bourdon-tube gauge, the gaseous mixture in the chamber was changed by introducing air to a pressure of at least 100 pounds per square inch absolute and releasing for four times. Then another charge of air was put into the chamber and 1 minute allowed for equilibrium to obtain before the next ignition attempt. In general pressure was controlled so that the range covered went from non-inflammable to inflammable. This avoided introduction of more products of combustion than absolutely necessary. The 1-minute period for attainment of equilibrium was decided on after it had been ascertained that periods up to 10^3 times longer made no measurable difference. Results were distinctly not reproducible if the air-flushing process was omitted, even though ignition as indicated on the gauge had not occurred. Pressure changes of less than 2 per cent of the original absolute pressure were taken as due to heat generated by the spark and by reaction, the rate of which was below the range of practical interest. Each point was repeated using a fresh liquid sample to check the accuracy, and the composition of each liquid sample was checked before and after the point. The composition of the liquid phase for each ignition attempt was estimated by the change in refractive index and the number of air flushes and their pressures.

Results: The experimental results are recorded in Table C-I. The temperatures recorded are believed good to 0.1° F. The weight fractions are probably not in error by more than 0.002 since the change in any one liquid sample due to the introduction of air was not more than 0.0045 weight fraction acetone. The pressures themselves are reliable to about 0.5 pound, lack of resolution of the limits probably being due to non-equilibrium conditions.

The incidental data used for the control measurements on the liquid sample are portrayed in Figure C-III.

Since the vapor pressure of acetone is of about two orders of magnitude larger than that of aniline, and since the explosive limits of acetone-air mixtures are not very dependent on pressure and are known (1), it is possible to calculate the explosive limits of the aniline-acetone-air system if the fugacity of the acetone in the aniline is known at different concentrations and temperatures. These data are available at 68° F (2) and can be extended by calculations to different temperatures, using the heat of mixing given in reference (2), by the methods of Carlson and Colburn (3). These calculations assume that the effect of the dissolved air upon the fugacity of the acetone in the liquid phase is negligible.

The results of these calculations are shown in Table C-II, and comparison with the experiment values is made in Figure C-I.

Figure C-II is derived from Figure C-I by taking the calculated or experimental limits that will give the wider range of inflammability.

Appendix C

Bibliography

1. Jones, Harris, and Miller, U. S. Bureau of Mines, Tech. Paper 544 (1933).
2. Tables Annuelles Internationales de Constantes et Donnees Numeriques, VII, p. 251, Paris (1930).
3. Carlson and Colburn, Ind. Eng. Chem., 34, 588 (1942).

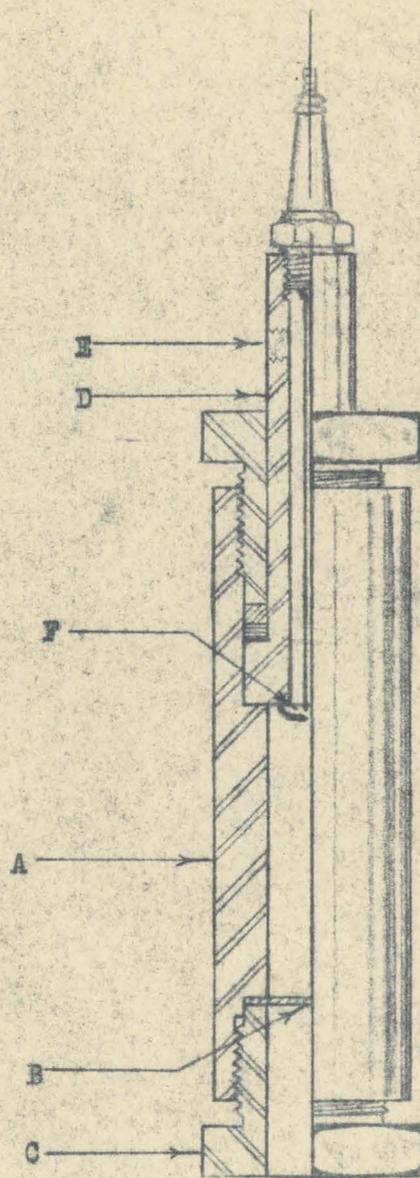


Figure C-1. Diagram of apparatus

TABLE C-I. IGNITION LIMITS FOR THE GAS PHASE OF HETEROGENEOUS MIXTURES OF ANILINE, ACETONE, AND AIR

	Upper Pressure Limit			Lower Pressure Limit		
	Temp. (°F)	Wt.Frac. Acetone in Liquid	Total Pressure (lb/in. ²)	Temp. (°F)	Wt.Frac. Acetone in Liquid	Total Pressure (lb/in. ²)
Ignition	130.54	0.3011	151.8	129.95	0.2993	35.0
No Ignition	130.45	0.3001	162.5	130.00	0.2987	30.3
Ignition	130.00	0.2003	91.3	130.07	0.1999	22.9
No Ignition	130.09	0.1994	100.9	130.05	0.1995	20.8
Ignition	129.86	0.1012	43.2	130.00	0.1013	14.3
No Ignition	129.86	0.1007	53.3	--	--	--
Ignition	80.10	0.3028	43.2	80.30	0.2996	14.3
No Ignition	80.22	0.3022	48.3	--	--	--
Ignition	80.18	0.2006	22.9	80.04	0.1995	14.3
No Ignition	80.18	0.2011	28.0	--	--	--
Ignition	--	--	--	--	--	--
No Ignition	80.00	0.1000	14.3	--	--	--

TABLE C-II. CALCULATED COMPOSITION OF GAS PHASE AND IGNITION LIMITS OF ANILINE-ACETONE-AIR MIXTURES

Weight Fraction Aniline in Liquid Phase	0.1	0.2	0.3
Temperature (°F)	68 100 130	68 100 130	68 100 130
Fugacity of Acetone (lb/in. ²)	0.260 0.598 1.166	0.598 1.284 2.452	1.166 2.047 3.849
Mole Fraction Acetone in Vapor Phase			
Total Pressure 14.7 lb/in. ²	0.0177 0.0407 0.0794	0.0389 0.0874 0.1668	0.0636 0.1392 0.2618
Total Pressure 100 lb/in. ²	0.0026 0.0060 0.0117	0.0057 0.0128 0.0245	0.0093 0.0205 0.0385
Total Pressure 500 lb/in. ²	0.0005 0.0012 0.0023	0.0011 0.0026 0.0049	0.0019 0.0041 0.0077
Upper Pressure Limit of Inflammability (lb/in. ²)	10 24 45	22 50 95	37 80 150
Lower Pressure Limit of Inflammability (lb/in. ²)	---	---	16 30

Limits of inflammability of acetone-air mixtures are reported as 0.0255 - 0.1280 mole fraction at 68° F.

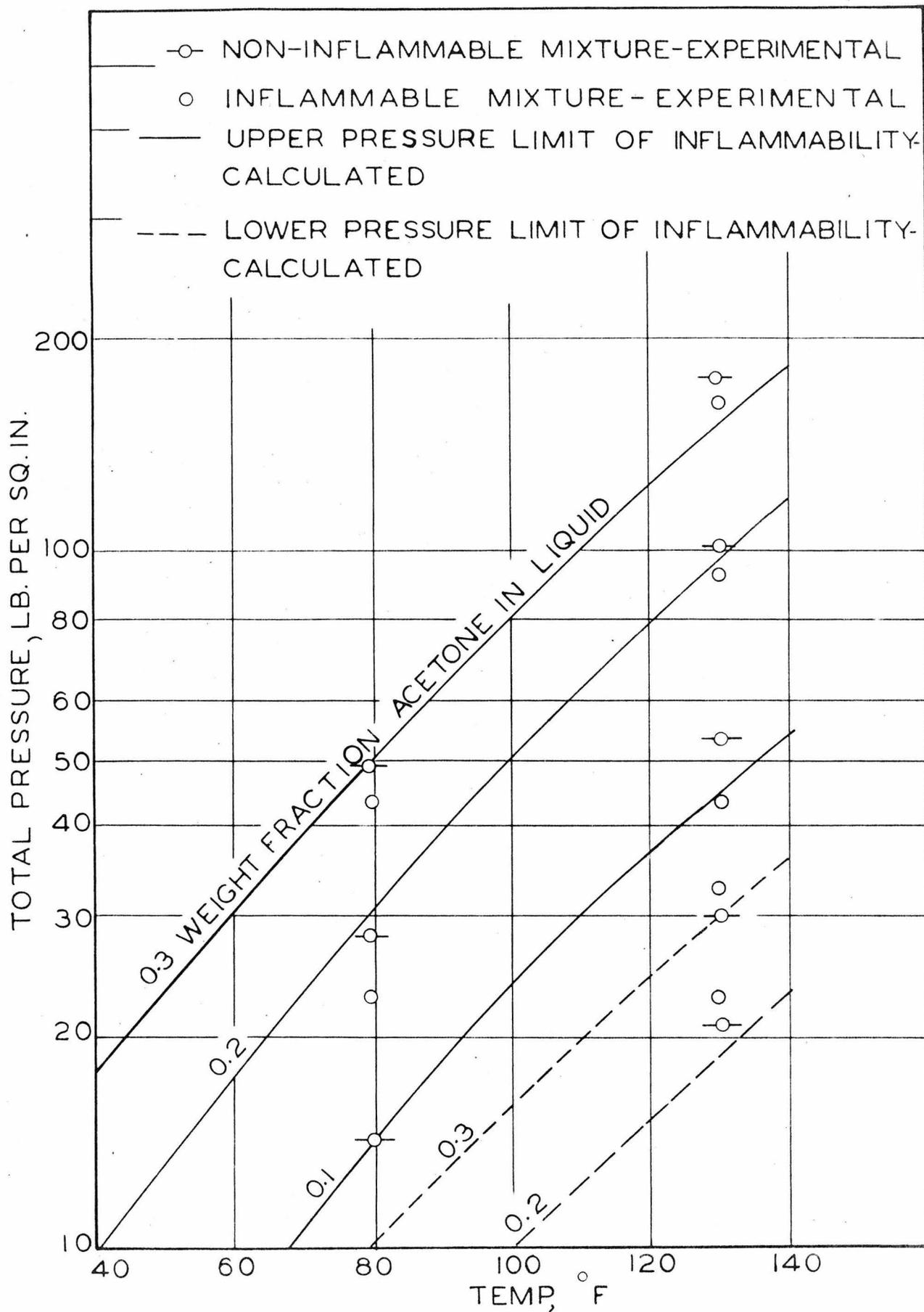


Figure C-I. Experimental and Calculated Pressure Limits of Inflammability for Aniline-Acetone Mixtures in Air at Various Temperatures.

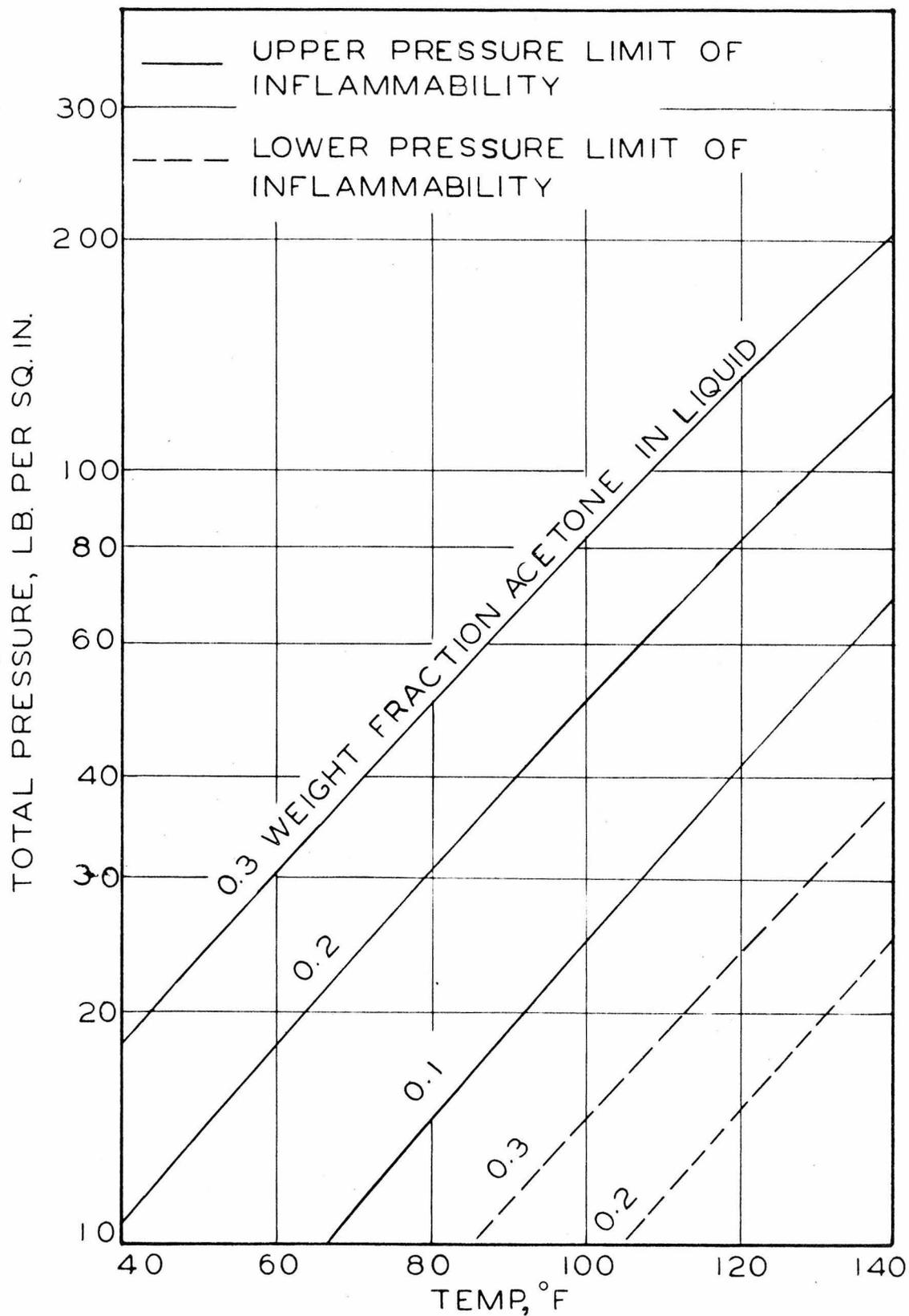


Figure C-II. Critically Chosen Pressure Limits of Inflammability for Aniline-Acetone Mixtures in Air at Various Temperatures.

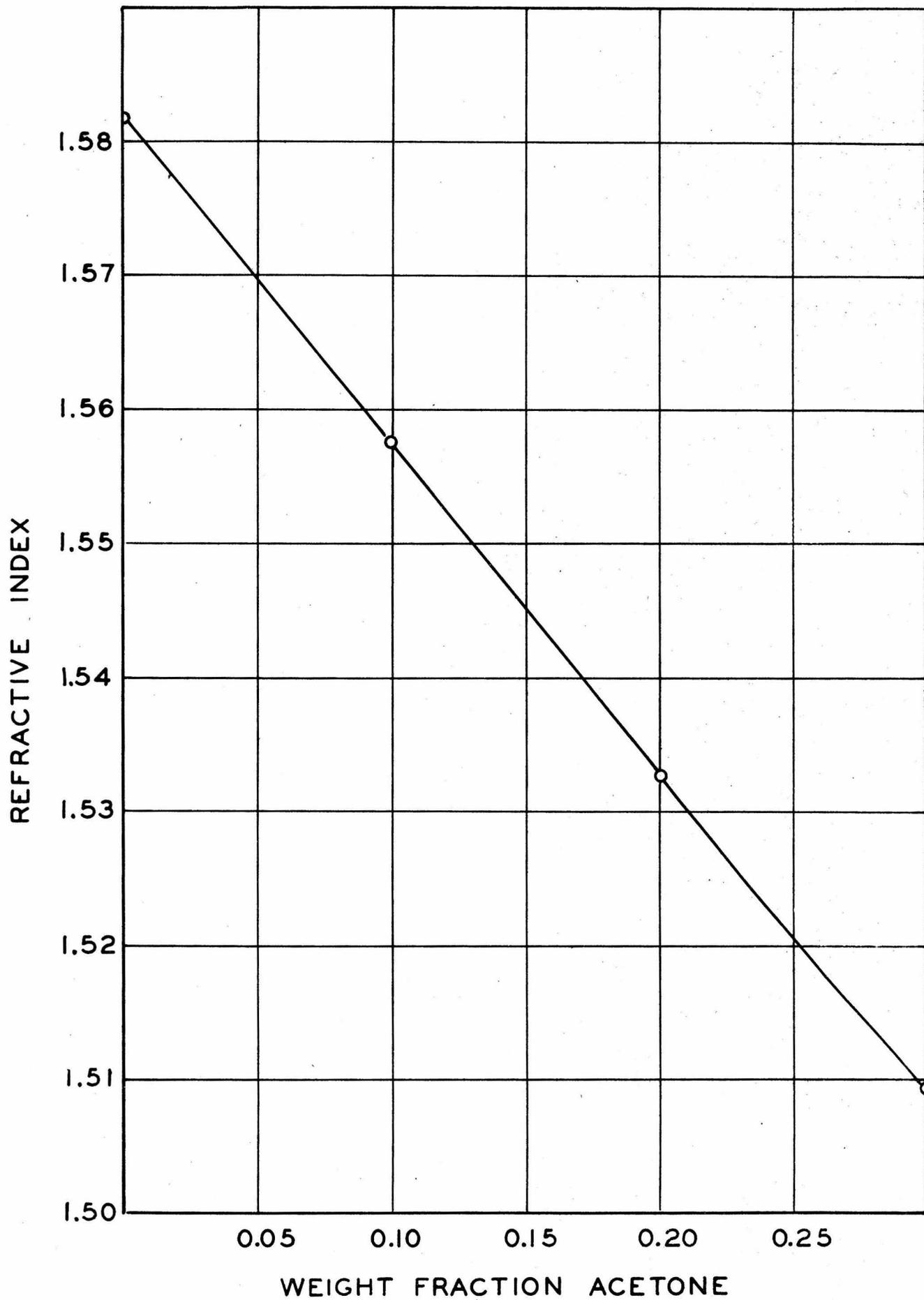


Figure O-III. The Index of Refraction of Aniline-Acetone Mixtures at 78.5° F.