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EVALUATION OF THE MECHANISM OF CORROSION IN CAPILLARIES

DSR S 11047 FINAL REPORT

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FOREWORD

This document is submitted under Paragraph 3.14.2 of contractor's Data Specification BMS-TII-CD-71,000 (Rev. 2), as incorporated in Contract AF04(647)-576

This is the Final Report to DSR S 11047

INTRODUCTION

This program[1] was initiated to develop an understanding of the mechanisms by which corrosion can occur in a capillary of 2014 aluminum. Both experimental and theoretical techniques are employed in the program. The corrosive media are products of the reaction between:

1. Water and fuel (a mixture of hydrazine and dimethyl hydrazine).
2. Water and oxidizer (nitrogen tetroxide).

With each of these two reacting systems, one may form two displacement systems. In one case the capillary is initially filled with water which is later displaced by propellant. In the other case the capillary is initially filled with propellant which is later displaced by water.

The word capillary in this report refers to a crevice of small diameter open at one end to a propellant tank but closed at the other end. This is intended to include weld cracks, weld porosity, or huckbolt patches. For the purposes of this study two configurations were considered in detail:

1. A uniform cylindrical hole
2. A large cavity connected to a propellant tank by a relatively narrow hole.

Because of the vast difference between liquid and vapor densities of the above reactants, it is obvious that liquid filled capillaries offer greater potential for serious corrosion than do vapor filled capillaries. Thus emphasis is placed upon liquid phase reactions.

Some aspects of the problem are not particularly new. Our literature survey shows that Joseph Priestly[2] studied the reaction between nitrogen tetroxide and water in 1786.

CONCLUSIONS AND RECOMMENDATIONS

1. No evidence of significant corrosion was found in specimens exposed to fuel and water.
2. Of 89 specimens exposed to oxidizer and water, 60 showed no significant corrosion.
3. The oxidizer corrosion process formed localized pits which ranged from 0.0004" to 0.012" deep. No intergranular corrosion was found.
4. The oxidizer corrosion was more severe in the large cavity than in the uniform hole.
5. Diffusion theory shows that corrosive media will not remain in capillaries more than two weeks. Experimental verification was obtained by both corrosion data and liquid analysis.

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[1] DSR 11047 - Evaluation of the Mechanism of Corrosion in Capillaries

[2] Priestley, J., Experiments and Observations Relating to Various Branches of Natural Philosophy, vol. III, section XIX, Pearson and Rollason, London, England (1786).

6. Significant corrosion in closed capillaries initially filled with water in a missile propellant tank is unlikely. Even if it should occur, the results will become apparent within two weeks after filling the tanks.

7. All available evidence refutes the hypothesis that extensive and continuing corrosion in capillaries can be catalysed by water.

8 Present drying procedures following hydrostatic testing in producing Titan II missile propellant tanks are adequate since complete drying of capillaries is not necessary.

CHEMISTRY OF CORROSION PROCESSES

In general, the principal factors influencing the rate of reaction between a corrosive liquid phase and metal include: 1) the chemical nature of the reactants, solid and liquid, 2) the physical nature of the metal surface, 3) the impurities present on the surface of the metal, 4) the activation energy of reactions taking place between the metal and liquid phase, and 5) the rate of transfer of liquid phase reactant to the surface of the metal through films of inert liquid, layers of solid reaction products, and by the diffusion coefficient of the reactive liquid component through inert liquid component.

A Oxidizer Systems

Corrosion which takes place in a water-filled dead-end crack or pore below the liquid level in an oxidizer tank would involve some and possibly all of the reactions that are known to take place between nitrogen tetroxide and water, and between the oxidizer hydrolysis products and the tank material, 2014 aluminum alloy. The following reactions appear to be the most important.

1) hydrolysis of nitrogen tetroxide:

$$N_2O_4 + H_2O \rightarrow HNO_3 + HNO_2$$

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

or

$$3N_2O_4 + 2H_2O \rightarrow 4HNO_3 + 2NO$$

2) dissolution of the air-formed oxide film

$$Al_2O_3 + 6H^{+} \rightarrow 2Al^{+3} \quad H_2O$$

3) corrosion attack

$$Al + 6H^{+} + 3NO_3^{-} \xrightarrow{\text{(concentrated)}} Al^{+3} + 3NO_2 + 3H_2O$$

(relatively slow)

$$Al + 4H^{+} + NO_3^{-} \xrightarrow{\text{(dilute)}} Al^{+3} + NO + 2H_2O$$

finally as the pH approaches 6

$$2Al^{+3} + 6OH^{-} \longrightarrow Al_2O_3 \cdot H_2O + 2H_2O$$

The hydrolysis reactions are known to be relatively rapid and the rate of the N_2O_4 hydrolysis is apparently controlled by the first reaction of the two step sequence indicated above.[3]

The above equations account for the corrosion process in aqueous systems. There are considerable data available on the effect of nitric acid concentration on the corrosion rate of aluminum and aluminum alloys.[4] In general, the attack rate is low for acid concentrations above 70% by weight. Below 70% by weight the corrosion rate increases sharply with decreasing acid concentration and goes through a maximum at a concentration between 15 and 20% by weight.

Consideration of corrosion mechanisms in the "binary" system N_2O_4-H_2O is complicated by chemical reaction between these substances which introduces the additional components HNO_3, HNO_2, NO, and N_2O_3. Furthermore the resulting mixtures of compounds are not miscible in all proportions at ambient temperatures. Examination of the phase diagram for the system (Figure 1) reveals a region characterized by the appearance of two liquid layers within the composition range 52 - 98% N_2O_4 at 20°C.[5] Over most of this composition range the more dense lower layer consists mainly of a mixture of nitrogen tetroxide and dinitrogen trioxide (N_2O_3); the upper layer is mainly aqueous nitric acid with some dissolved HNO_2, N_2O_4, and N_2O_3.

Materials compatibility experience with the oxidizer MON, mixed oxides of nitrogen,(N_2O_4 containing up to 30% NO) suggested that a mixture of N_2O_4 and N_2O_3 (as in the dense lower layer referred to above) is no more corrosive than NO-free nitrogen tetroxide.

B. Fuel Systems

Corrosive attack by fuel-water mixtures in cracks or capillaries in the fuel tank wall would appear to involve the following.

1) some reaction between the fuel components N_2H_4 and $(CH_3)2\ N_2H_2$, and H_2O at all concentrations and consisting of

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3. Wendel, M. M. and Pigford, R.L., A.I.Ch.E. Jour. 4, p 249, September (1958)
4. Lyman, T.,Metals Handbook, Am.Soc.for Metals, 8th ed., Novelty, Ohio, p. 927, (1961)
5. Lowry and Lemon, Jour. Chem. Soc., p. 6, (1936)

a) limited formation of the ionic species,

$N_2H_5^+$ (hydrazonium ion), $(CH_3)_2\ N_2H_3^+$, and OH^- ion;

$$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH^-$$

$$(CH_3)_2\ N_2H_2 + H_2O \rightleftharpoons (CH_3)_2\ N_2H_3^+ + OH^-$$

b) hydrogen bonding between simple and polymerized molecular species of N_2H_4, UDMH, and water.

2. corrosive attack by the OH ion

$$Al + 3OH^- + 3N_2H_5^+ \longrightarrow Al\ (OH)_3 + \frac{3}{2}\ H_2 + 3N_2H_4$$

As in the case of solutions of ammonia in water, the concentration of hydroxyl ions in aqueous hydrazine solutions is always small and is given by the equilibrium constant for the reaction.

$$N_2H_4 + H_2O \rightleftharpoons N_2H_5^+ + OH$$

$$K_b = \frac{[N_2H_5^+\ \ OH^-]}{[N_2H_4]} = 8.5(10^{-7}) \qquad (25^\circ C)$$

pH = 11.0 for 1 molar solution

Since the corresponding constant for the basic ionization of ammonia in water is

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = \frac{[NH_4^+\ \ OH^-]}{[NH_3]} = 1.77\ (10^{-5}) \qquad (25^\circ C)$$

pH = 11.6 for 1 molar solution

hydrazine is a somewhat weaker base than ammonia. A given concentration of hydrazine, therefore, produces fewer OH⁻ ions in aqueous solutions than an equivalent concentration of ammonia.

For aluminum the minimum in the corrosion rate vs pH relationship occurs on the acid side of neutrality and the rise on the alkaline side can be very marked. While the rate of attack depends, in general, on the pH there are other factors which can exert a strong influence. In aqueous solutions of pH above 8.5 for example, the resistance of aluminum to attack depends to a large degree on the nature of the compound or compounds causing the high pH. Although sodium hydroxide and sodium carbonate solutions cause severe attack, ammonium hydroxide solutions are not particularly corrosive[4] (Figure 2). Also, the rate of attack is increased by impurities of low hydrogen overpotential (e.g. Cu, Fe, and Pt).

Aluminum is rapidly attacked and dissolved by sodium hydroxide and sodium carbonate solutions. The rate of attack by ammonium hydroxide solutions, however, is low for all concentrations even at temperatures up to $120^\circ F$. This difference has been attributed to the low solubility of $Al(OH)_3$ in ammonium hydroxide solutions. While sodium hydroxide, sodium carbonate, and other strong bases readily dissolve the corrosion product $Al(OH)_3$ according to the reaction

$$Al + OH^- + H_2O \rightarrow AlO_2^- + 3/2\ H_2$$

in the case of ammonium hydroxide solutions, $Al(OH)_3$ is coprecipitated with other insoluble minor constituents on the metal surface. This precipitate presumably hampers the diffusion of fresh solution to the aluminum surface and accounts for the distinct tendency of the attack rate in NH_4OH to gradually decrease with time.

Another school of thought holds that the attack or dissolution of aluminum in alkaline solution proceeds by an electrochemical mechanism. The impurities in aluminum or the alloying constituents in aluminum alloys form the cathodes of local cells of which the aluminum matrix is the anode. The initial attack or dissolution rate is the result of the action of these and other cells, e.g., those caused by grain boundaries. At anodes aluminum goes into solution or is converted to $Al(OH)_3$, while at the cathodes an equivalent quantity of hydrogen is evolved. As the aluminum metal is dissolved by a solution such as sodium hydroxide, a precipitate forms on the surface of the metal. This precipitate, consisting of impurity compounds, e.g., hydroxides of iron and copper possibly interspersed with metallic deposits of these metals, can act as a cathode as corrosive attack progresses. In ammonium hydroxide solutions, the precipitate on the metal surface consists mainly of $Al(OH)_3$. This electrochemical process depends on the presence of a conducting solution and may be limited by accessibility of fresh solution to the metal surface. Also, this mechanism would be favored by increasing water content which gives a solution of higher conductivity and by dissolution of $Al(OH)_3$ which improves the accessibility of the conducting solution to the metal surface.

Although the mechanisms of the corrosion of aluminum discussed above are based on observations made in studies using ammonium hydroxide and other common alkaline solutions, it appears reasonable to assume that the limited corrosive attack observed for aqueous solutions of hydrazine and UDMH proceeds by a mechanism similar to that for ammonium hydroxide solutions because of the marked similarities in the chemical behavior of ammonia, hydrazine, and UDMH. The hydrazine molecule may be thought of as an ammonia molecule in which one of the hydrogen atoms has been replaced by the more electronegative $-NH_2$ group. This substitution has the effect of somewhat reducing the basicity of the resulting molecule. It is apparent that in fuel-water mixtures corrosive attack by either an electrochemical mechanism or one governed by the hydroxyl ion concentration will be dependent to a large degree on the concentration of water present. This is borne out by results of corrosion rate studies on aluminum alloys in, for example, mixtures of UDMH and deionized water. In studies carried out at 30° and $63^\circ C$ the alloy specimen weight gain or rate of scale buildup was proportional to the water content and below 20% water no noticeable effect was observed.[6]

C. Estimation of Diffusion Coefficients

The diffusion coefficients of reactive liquid phase components through inert liquid components were mentioned earlier as one of the factors influencing the rate of transfer of liquid phase reactant to the surface of the metal.

In the absence of experimental diffusion coefficient data for the pertinent species in oxidizer-water and fuel-water mixtures it becomes necessary to make estimates for these physical constants. Fortunately, it has been shown that for a wide variety of solutes and solvents, values of the diffusion coefficient, D, fall within the relatively narrow range 0.5 to 4 x 10^{5} cm^2/sec.[7] In Table I examples of literature values of diffusion coefficients for two substances in aqueous solution are given.

TABLE I

HNO_3 in H_2O	0.1 g-mole/liter	68°F	D = 2.6 x 10^{-5} cm^2/sec.
CH_3COOH in H_2O	0.5 g-mole/liter	63°F	D = 0.96 x 10^{-5} cm^2/sec.

The diffusion coefficient D increases with temperature, is larger for small molecules, and decreases usually with the concentration of solute.

For the purposes of this analytical study calculations of values of D for various species occurring in oxidizer-water and fuel-water mixtures were made using an empirical equation.[8] Results are given in Table II.

TABLE II

H_2O in N_2O_4	20°C	D = 0.85 x 10^{-4} cm^2/sec.
N_2O_4 in H_2O	20°C	D = 1.3 x 10^{-5} cm^2/sec.
N_2H_4 . H_2O in Aerozine 50	20°C	D = 2.35 x 10^{5} cm^2/sec

Since there are probably association effects in these systems which cannot be estimated accurately and certainly changes in the actual values of the diffusion coefficients accompanying changes in concentrations of the diffusing species, it seemed desirable to use a single value for the diffusion coefficient D of all the liquid species considered in calculations based on analytical models. The value taken was 2.0 x 10^{-5} cm^2/sec.

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6. Raleigh and Deer, Corrosion, p. 115, October, (1960)
7. Sherwood, T. K. and Pigford, R. L., Absorption and Extraction, McGraw-Hill, 1952)
8. Wilke, C. R. and Chang, P., A.I.Ch. E., Jour., 1, p. 270, (1955)

DIFFUSION IN CAPILLARIES

Some of the above reactions show that either fuel or oxidizer may react with water to form products which are corrosive to aluminum. Since the extent of corrosion is critical in predicting wall penetration, both the length of time a capillary is filled with corrosive fluids and the corrosion rate are important. The capillary residence time will be estimated by calculations of diffusion rates.

In view of the size of capillaries it would seem that the dominant mode of mass transport is molecular diffusion. By estimating capillary depth, diffusion constants, and reactions, one may solve the diffusion equation. Such solutions give the concentration anywhere in the capillary as a function of time - thus indicating how long a capillary is filled with a corrosive media. Because of the number of assumptions, the results are to be regarded only as approximations. However, one may assume a sequence of worst case situations and obtain the longest time for a capillary to be filled with corrosive media. The longest time is of the order of a week or two.

The rate of diffusion of some species i is usually written as

$$F_i = -D \text{ grad } C_i \qquad (1)$$

Using the above expression to write a material balance around a small volume leads to the classical diffusion equation

$$\frac{\partial C_i}{\partial t} = D \text{ div } \left[\text{grad } C_i \right] \qquad (2)$$

where constant diffusivity has been assumed. To simplify the problem assume the capillary is a straight hole of uniform cross section. In this case the right hand side of (2) is D times the second partial derivative of C_i with respect to x. Solutions of (2) are developed for varying degrees of complexity in the material below.

In the simplest case, assume the capillary is filled with substance one at time zero and, as time passes, this material diffuses out of the capillary. Carslaw and Jaeger,[9] p. 100, have found the solution to be

$$C_i = \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left[\frac{D(2n+1)^2 \pi^2 t}{\text{[illegible]}} \right] \cos (2n+1)\pi x / 2L \qquad (3)$$

Boundary and initial conditions are

$$C_i (x, 0) = 1 \qquad (4)$$

$$\frac{C_i}{\partial} (0, t) = 0 \quad (x = 0 \text{ is closed end}) \qquad (5)$$

$$C_i (L, t) = 0 \quad (x = L \text{ is open end}) \qquad (6)$$

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[9] Carslaw, H. S., and Jaeger, J.C., Conduction of Heat in Solids, Oxford Press, 2nd ed. (1959)

Figure 3 shows the results from (3) for the closed end of the capillary as a function of time for assumed capillary depths of 0.1" and 0.4". (A diffusivity of 2.0 x 10^{-5} cm^2/sec is assumed in this work). Since 0.4" would seem to be an extremely long capillary and since it is depleted to 10% of the original concentration in 3.7 hours, it is evident that the aluminum is exposed to a corrosive media for a relatively short time. Because of the exponential character of (3), one expects a decay to 1% of the original concentration in another 3.7 hours etc. Estimates above show that the diffusivity for fuel-water and oxidizer-water are about the same. Thus the above result applies to either case.

Equation (3) is deficient in that it does not account for the formation of the corrosive media in the capillary. It is imagined that initially the capillary is filled with water (substance 1) and the main tank contains either fuel or oxidizer (substance 2). These materials react to form substance 3 at a rapid rate. If this reaction rate is large compared with diffusion rates, the process may be described as a moving boundary problem. Assume, now, the pore opening is at x = 0. Initially the materials react at the boundary, x_b, which is at x = 0. As time passes this boundary moves deeper into the pore. Between the pore opening and the boundary only substances 2 and 3 exist. Substance 2 is diffusing toward the boundary as substance 3 diffuses toward the opening. Between the boundary and the pore end, only substances 3 and 1 exist. In this region substance 1 diffuses toward the boundary as substance 3 diffuses toward the pore end. Two parts comprise this analysis; a reacting part in which the boundary moves from x = 0 to x = L; and a depletion part in which substance 3 is replaced by substance 2 via diffusion. The only exact solution for the reacting part of the problem is that of Neumann, see p. 285 of Carslaw and Jaeger.[9] Unfortunately, this applies for an infinitely long capillary. By using the Neumann solution only until the moving boundary strikes the capillary end, and then using the usual diffusion solution for removal of component 3 the deficiency in Neumann's solution causes little error. For the first part of the process the Neumann solution is

$$\begin{aligned} C_2 &= 1 - 2\,\mathrm{erf}\left(\frac{x}{2\sqrt{Dt}}\right), & 0 \le x \le x_b \\ C_2 &= 0 & , x_b \le x \le L \end{aligned} \qquad (7)$$

$$\begin{aligned} C_1 &= 1 - 2\,\mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right), & x_b \le x \le L \\ C_1 &= 0 & , 0 \le x \le x_b \end{aligned} \qquad (8)$$

$$x_b = 0.954\sqrt{Dt} \qquad , 0 \le t \le \left(\frac{L}{0.954\sqrt{D}}\right)^2 \qquad (9)$$

Figure 4 illustrates the concentration distribution 3.8 hours after filling the propellant tank. At this time the boundary is half-way through the capillary. Concentrations of components 1 and 2 are labeled on the figure and one may estimate the concentration of component 3 by noting the difference between the curves and the horizontal line, C = 1. In this connection one may say that the moving boundary is a source of species 3 which then diffuses away from the boundary. After 15.7 hours the boundary reaches the end of the capillary and only species 2 and 3 remain. Figure 5 shows the concentration of species 3 at this time. Further time lapse implies diffusion of species 3 out of the pore; see the result for 23.5 hours, also on Figure 5. In round numbers, this study shows that species 1 and 2 react in a diffusion limited process in about 16 hours. In a total time of 24 hours, 90% of the product species has diffused from the capillary.

Emphasis is now placed on the N_2O_4 - H_2O system as this seems to posses the greatest potential for corrosion. Assume N_2O_4 and water react to produce HNO_2 and HNO_3 and that this is the only chemical reaction occurring. Wendel[3] has measured the appropriate rate constant for N_2O_4 reacting with water at very low N_2O_4 concentrations. His results, reported for a first order reaction, was a rate constant of 290 sec^{-1}. In the present application a second order model would be more appropriate since the reaction rate must vanish if either water or N_2O_4 disappears. Thus Wendel s constant is divided by 55 (the molar concentration of pure water) to obtain the estimated second order constant of 5.3 liters/mol. sec.

Two equations are now necessary to describe the process

$$\frac{\partial C_1}{\partial t} = D \frac{\partial^2 C_1}{\partial x^2} - k C_1 C_2 \qquad (10)$$

$$\frac{\partial C_2}{\partial t} = D \frac{\partial^2 C_2}{\partial x^2} - k C_1 C_2 \qquad (11)$$

Let subscripts 1 and 2 denote water and N_2O_4 respectively, then the boundary and initial conditions are:

$$C_1 (x, 0) = 1 \qquad (12)$$

$$C_2 (x, 0) = 0 \qquad (13)$$

$$C_1 (0, t) = 0 \qquad (14)$$

$$C_2 (0, t) = 1 \qquad (15)$$

$$\frac{\partial C_1}{\partial x} = \frac{\partial C_2}{\partial x} = 0 \text{ at } x = L \qquad (16)$$

Since (10) and (11) are nonlinear, exact methods of solution do not apply. By using the numerical technique of Saul'ev[10], solution was effected using an IBM 1620 computer. Twenty space increments were employed. Results are presented for the reacting part in Figure 6, and for the depleting part in Figure 7 for a uniform capillary. About 5 hours are necessary for the reaction to reach completion. After about 24 hours, the closed end of the pore contains only about 5% reaction

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10. Larkin, B. K., Math. of Comp., #86, April, (1964)

products, see Figure 7.

The final case which was treated was the restricted capillary. This capillary has a large inner pore (a cavity) connected to a propellant tank by a smaller pore. In this case each pore was 0.2" long and the cross-sectional area of the cavity was 30 times that of the small pore. Equations (10) through (16) still apply, but in addition one must use continuity of concentration and flux at the junction between large and small pores to complete the problem. Figures 8 and 9 show that this change in geometry has increased the time scale considerably. In Figure 8 we note that after 36 hours the reaction zone has not reached the large pore. Because of the longer time, concentrations are nearly uniform within the large pore. After 78 hours the reaction portion of the process ends as the water disappears. The depletion of the products also is slowed, see Figure 9, by the restriction. It takes 270 hours for the large pore to reach 84% C_2 concentration.

Although the above results contain many questionable approximations, the conclusions concerning the general time scale are unavoidable. Nearly all liquid phase diffusion constants are within an order of magnitude of 10^{-5} cm^2/sec. Regardless of what reactions do occur within a capillary, any corrosive products must diffuse out of the pore in about the times described above. Thus corrosion within a closed capillary can only last, at most, about two weeks after filling the propellant tanks.

EXPERIMENTAL - CORROSION STUDY

An experimental corrosion study was performed to test the results of the analysis. This was done by subjecting capillaries to three different environments. The first environment consisted of having liquid nitrogen tetroxide in the capillary, while the exterior of the capillary was an "infinite" supply of water. An "infinite" supply is so large that concentration changes are negligible. The second condition was a reverse of the first, that is, the capillary was filled with water and the exterior was an "infinite" supply of liquid nitrogen tetroxide. Finally, the capillary was filled with water and then surrounded by an "infinite" supply of liquid Aerozine-50. The specimens were subjected to these environments for periods of one, two, three and four weeks.

The capillaries were machined in two different types of blocks. One block was machined from 2014-T6 to a size of 8" x 3" x 1". The second block was made by U-butt welding two blocks (8" x 1 1/2" x 1") to create a block 8" x 3" x 1". The weld bead was then ground flush. There were three different types of capillaries in the parent metal block. Two capillaries were straight blind holes which were 0.046" and 0.020" in diameter. The third capillary was made by plug welding over a hole 0.250" in diameter and then drilling an 0.046" D hole through the plug weld to create a capillary with cavity. (See Figures 10 and 11). All capillaries in the welded blocks were .046" D blind holes. These were staggered such that they penetrated weld metal, heat affected metal, and parent metal. (See Figure 12). Specimens were also created by lockbolting two 6" squares of 2014-T6 together with five lockbolts. The lockbolts were found to leak helium in excess of 2×10^{-5} atm cc/sec, as determined with a helium mass spectrometer.

The specimens were filled by first heating to 250°F and then immersing them in water. In filling the capillaries with nitrogen tetroxide the blocks and panels were heated to 90°F and then immersed. This method of filling created, approximately, a 30% air pocket in the uniform capillary. The cavities were completely filled with liquid, however. Such a procedure would seem to duplicate conditions in a blind defect in a propellant tank

After filling, the blocks were placed in a closed system of about five gallons liquid volume. The blocks were placed so that the capillary opening was pointed up. Exposure temperature varied from 60 to 80°F.

After exposure the specimens were evaluated. The acid concentration of both the cavity liquid and surrounding water was determined by titration. The water content of the surrounding N_2O_4 was determined by a conductivity method. The liquid in fuel exposed specimens was analyzed by a gas chromatograph. The specimens were then randomly sectioned and polished for a metallographic examination. The sectioned specimens were first examined with a stereomicroscope at 7x to 30x magnification for evidence of corrosion. After examining the surface, the specimens were then polished and lightly etched so as to allow examination of the hole for any appreciable depth of corrosion. The lockbolt specimens were examined metallographically in the same manner. The results of the metallographic examination are presented in Tables 3, 4, and 5. The results of the analysis of the entrapped liquids are listed in Table 6.

The tabulated metallographic data indicates that the corrosion is no worse at the end of the fourth week than it is after the second week. This is also substantiated by the weekly analysis of the acid concentrations. Due to the small amount of corrosion, and inherent mechanical damage, corrosion of the lockbolt specimens proved to be indeterminate The surfaces of the 2014-T6 sheet were very irregular and gouged from the intentionally improper installations

The tabular data contains a "worst case" descriptive analysis of the specimens. Along with the description there is a fractional number, the denominator of this number is the number of specimens examined and the numerator is the number that exhibited corrosion. A percentage figure is also listed. This figure presents the relative depth in the capillary of the corrosion pit location. The decimal figure is the distance of the pit into the capillary wall

In the welded block, the only capillaries that are listed are those that penetrate both weld metal and heat-affected parent metal. The data pertaining to the large cavity is taken only from the lower portion of that cavity. This was done so that the effects of plug welding would not confuse the corrosion data.

These data lend strong support to the conclusions from diffusion theory concerning the residence time of corrosive fluids in a capillary. Both corrosion data and chemical analysis of liquids show little difference during the last two weeks of the test.

That the more severe attack was noted in the cavities may be explained in several ways. Because of the flow restriction, the residence time of the corrosive fluids was much longer than in the uniform holes. The cavities, because of their larger diameter, contained more corrosive fluid per unit metal surface area than did the uniform holes. Thus there was more fluid available to corrode in the large cavity.

H_2O IN CAPILL

Weeks Exposure	Parent Meta	
	Large Cavity	0.046" D
1	Some pitting Approx .0004" to .006" 1/3	No evidence of light film on s
2	Average pit depth .002" Some pits at bottom .004" .008" 3/4	Moderate pitting mately .0004" t 84%
3	Fairly severe pitting .0004" to .003" occurring at bottom and at corners 4/4	Some moderate pi fairly uniform pit at a depth 19%
4	Uniform pitting over surface 0.001" 0.005" 2/4	Some moderate p large pit to 0.0 60%

The tabular data contains a "worst case" description and
is a fractional number; the denominator of this number
the number that exhibited corrosion. A percentage figure
in the capillary of the corrosion pit location the
wall.

TABLE III

LARY [illegible] SURROUNDING

tal Block		Welded Block All Holes 0.046" D
D Hole	0.020" D Hole	
corrosion surface 0/4	No evidence of corrosion 0/2	Some slight pitting in heat affected zone 0/2
ng approxi- to .0012" 1/2	No evidence of corrosion 0/2	No strong evidence of corrosion. Some superficial in heat affected zone 0/2
pitting one large of .004" 1/4	One possible pit to about .0002" 42% 1/2	Some localized pitting 0.004" - 0.008" 75% & 42% 2/2
pitting one 005" 1/4	No evidence of corrosion 0/2	No corrosion 0/2

nalysis of the specimens. Along with the description there is the number of specimens examined and the numerator is [illegible] listed. This figure represents the relative depth [illegible] figure is the distance [illegible]

N_2O_4 IN CAPILL

Weeks Exposure	Parent Met	
	Large Cavity	0.046" D
1	Some localized pitting 0.006" depth mostly on sides 2/3	No evidence of
2	Localized pitting 0.004" to 0.010" on sides 1/3	No evidence of
3	Large pits at corners 0.012" deep surface pitting to 0.00 3/3	Localized pitti to 0.010"
4	No large pits 0/4	Some local pitt .004" 90%

TABLE IV

LARY - H_2O SURROUNDING

tal Block		Welded Block All
D Hole	0.020" D Hole	Holes 0.046" D
corrosion 0/4	No evidence of corrosion 0/2	No corrosion 0/2
corrosion 0/2	One pit to a depth of 0.006" 70% 1/2	Some localized pitting 0.001" 58% 1/2
ing 0.001" 2/3	No evidence of corrosion 0/2	Slight pitting approximately .0004" to .0008" 1/3
ting up to 1/5	One small pit 0.0002" maximum depth 62% 1/2	Localized pitting up to 0.004" 55% 1/2

H_2O IN CAPIL

Weeks Exposure	Parent Me	
	Large Cavity	0.046"
1	No evidence of corrosion	No evidence of
2	No evidence of corrosion	One pit to 0.0
3	No evidence of corrosion	No evidence of
4	Slight pit at bottom 0.0006" maximum depth	No evidence of

* No data taken

TABLE V

ILLARY – A 50 SURROUNDING

etal Block		Welded Block - All Holes - 0.046" D
' D Hole	0.020" D Hole	
of corrosion	No evidence of corrosion	No evidence of corrosion
.001"	*	Some slight pitting
of corrosion	No evidence of corrosion	*
of corrosion	No evidence of corrosion	*

TABLE VI

CONCENTRATION DATA

Week	NTO in Capillary - H_2O Surrounding		H_2O in Capillary - NTO Surrounding	
	Cavity	Bath	Cavity	Bath (Water Content)
1	0.006N (pH = 2.22)	0.0001N (pH = 4)	0.6N (pH = .22)	0.11%
2	0.023N (pH = 1.64)	0.0152N (pH = 1.82)	0.53N (pH = 0.4)	0.14%
3	0.038N (pH = 1.43)	0.0152N (pH = 1.82)	0.72N (pH = 0.143)	0.14%
4	0.14N (pH = 0.96)	0.019N (pH = 1.72)	0.504N (pH = 0.301	

EXPERIMENTAL - WATER, TETROXIDE REACTIONS

Mixtures of water and nitrogen tetroxide were prepared and examined in a test cell, see Figure 16. The cell was made using two 6" x 16" x 1/2" stainless steel plates. A 4" x 14" x 1/2" glass plate, which allowed visual observation of the mixtures, was held between the metal plates by 24 bolts. A polyethelene gasket was used to effect the necessary gas tight glass to metal seal. In the back metal plate a milled channel of 3" x 12" x 1/8" held the mixtures. In preparing a mixture in the vertical test cell, a small quantity of water was introduced from a burette, see Figure 16, into the bottom of the cell. Next the system was opened to a water aspirator to remove most of the residual air. The tetroxide supply was contained in a pressure bomb which was submerged in a water bath at 120°F. After evacuation of the test cell, the tetroxide valve was slowly opened, allowing liquid tetroxide to enter the test cell. Initially the oxidizer liquid fell to the bottom of the water and the reaction seemed to occur very rapidly with considerable gas evolution. As no gas was vented, the pressure in the cell increased with addition of tetroxide. With increasing amounts of oxidizer the cell liquid changed color from light blue to very dark blue. Finally two liquid layers were formed, a light green and a dark blue layer as described above.

In the initial design phase of the project it was intended to take conductivity measurements through the glass cell. By relating conductivity to concentration. one could then use such data to determine diffusion coefficients for the tetroxide-water system. For two reasons, this technique was impossible. In the early stages, when a single liquid phase existed, gas evolution provided turbulent mixing. Thus diffusion was not an important mixing mechanism. Later, as gas evolution stopped, the existence of two liquid phases made it impossible to relate conductance measurements to concentration.

SYMBOLS

C	Concentration, moles/liter
D	Diffusivity, cm^2/sec.
F	Flux, moles/cm^2, sec.
k	Reaction rate constant, liter/mole, sec.
L	Capillary length, cm (or inches)
t	Time, sec.
x	Distance variable from capillary end, cm.
x_b	Moving boundary position, cm.

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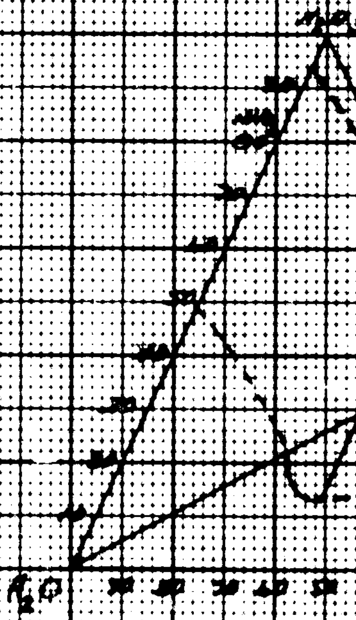
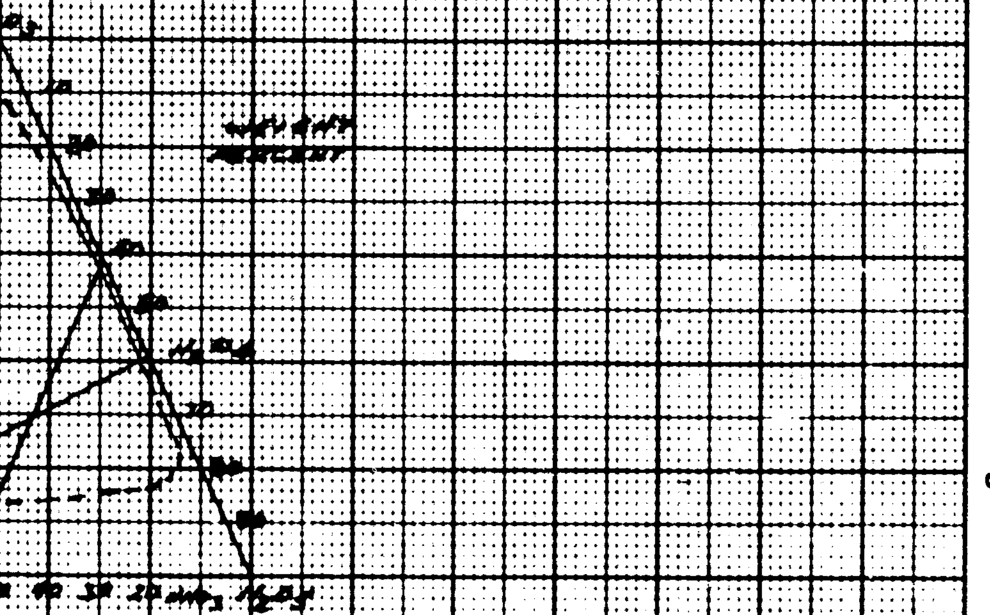


Figure 1 - Water-Oxides of Nitrog



an Phase Diagram

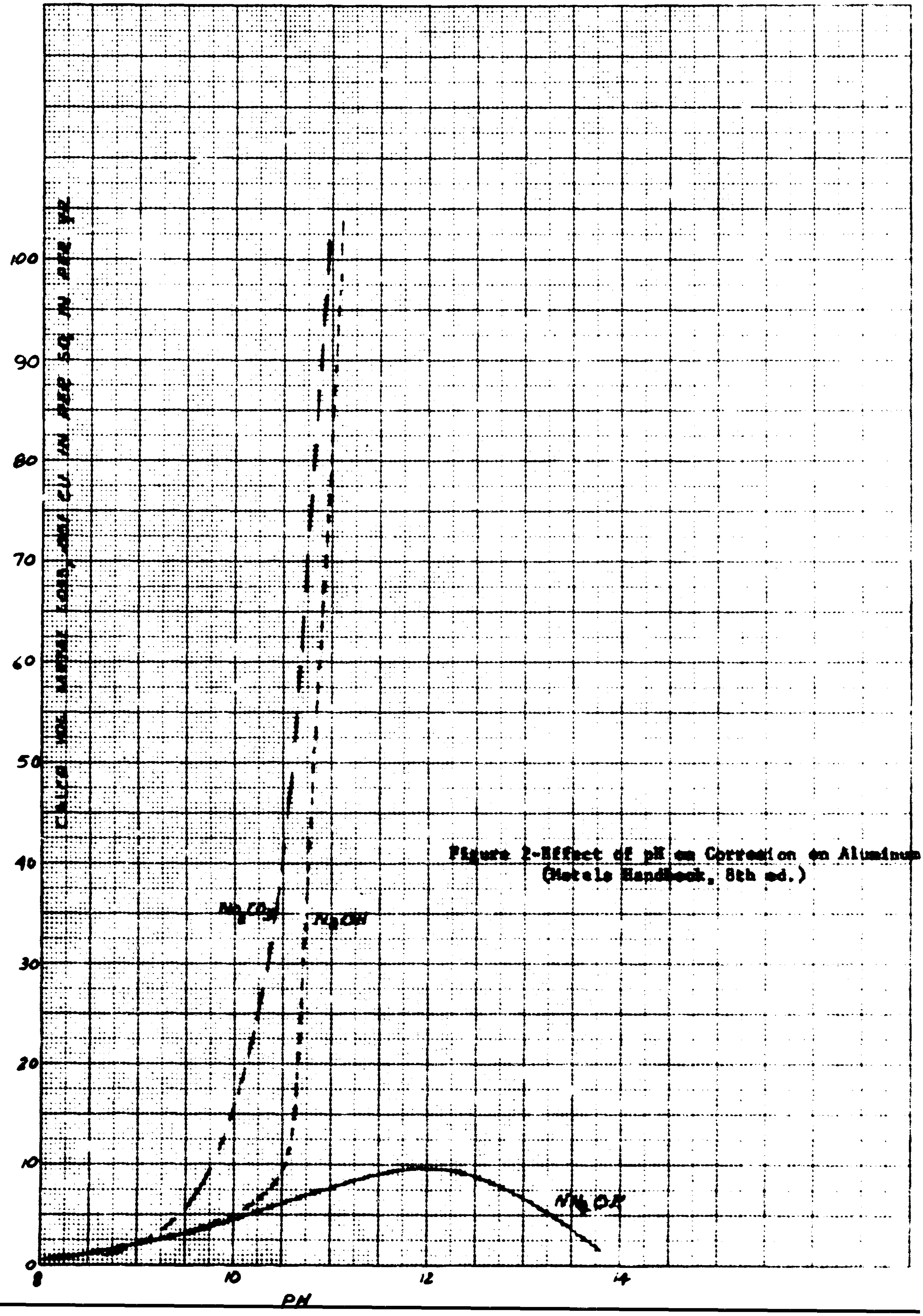


Figure 2-Effect of pH on Corrosion on Aluminum
(Metals Handbook, 8th ed.)

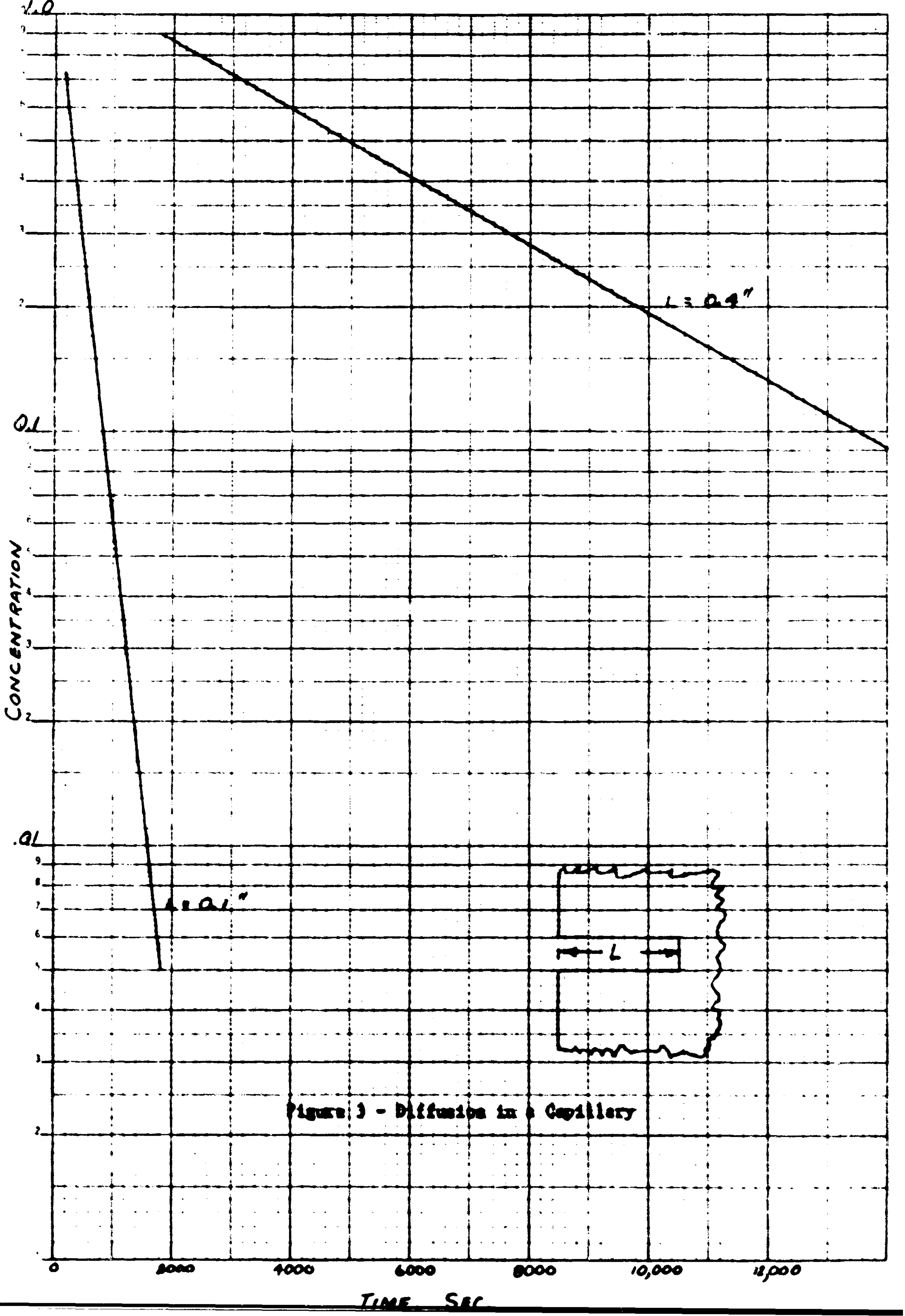


Figure 3 - Diffusion in a Capillary

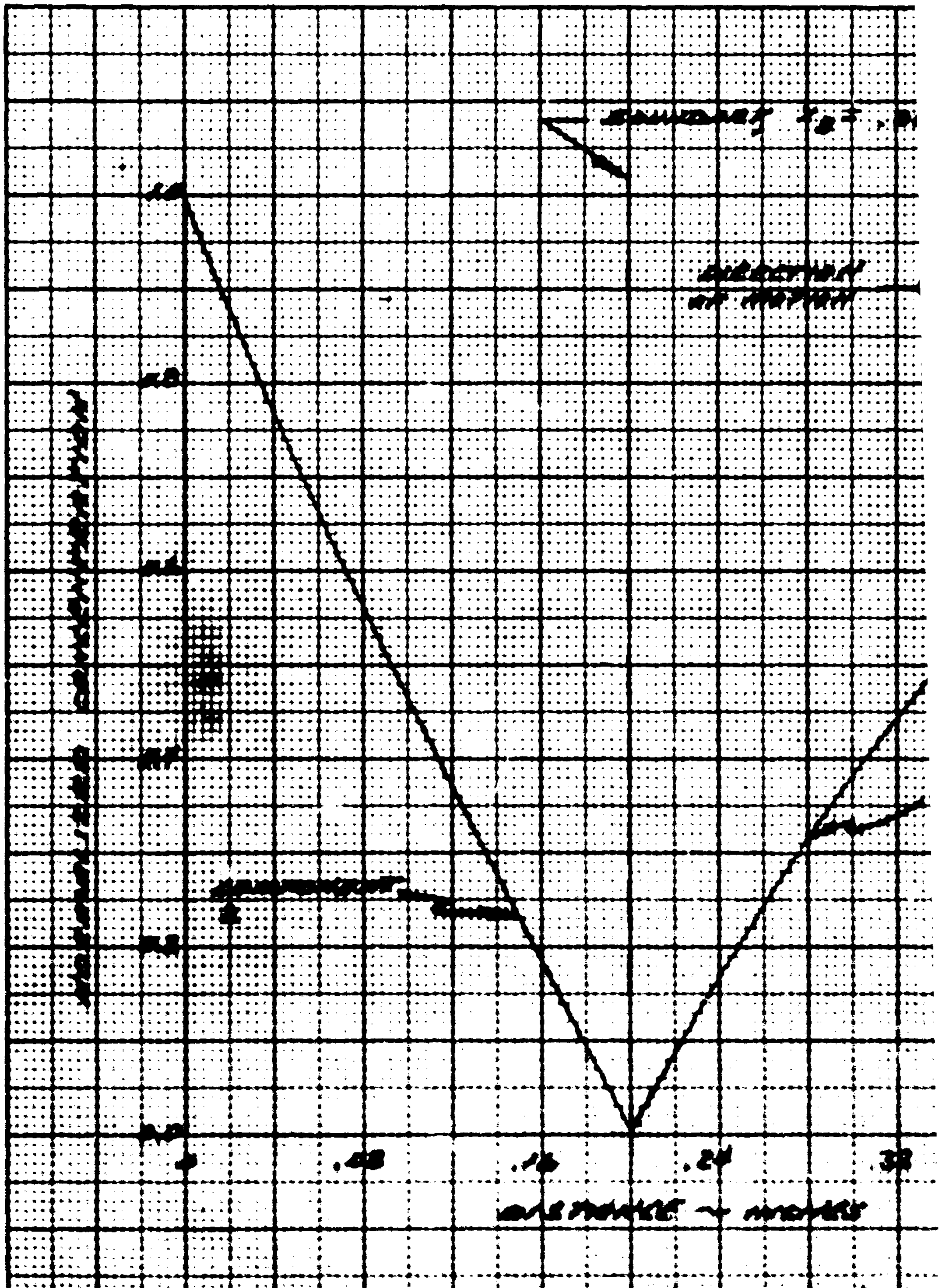
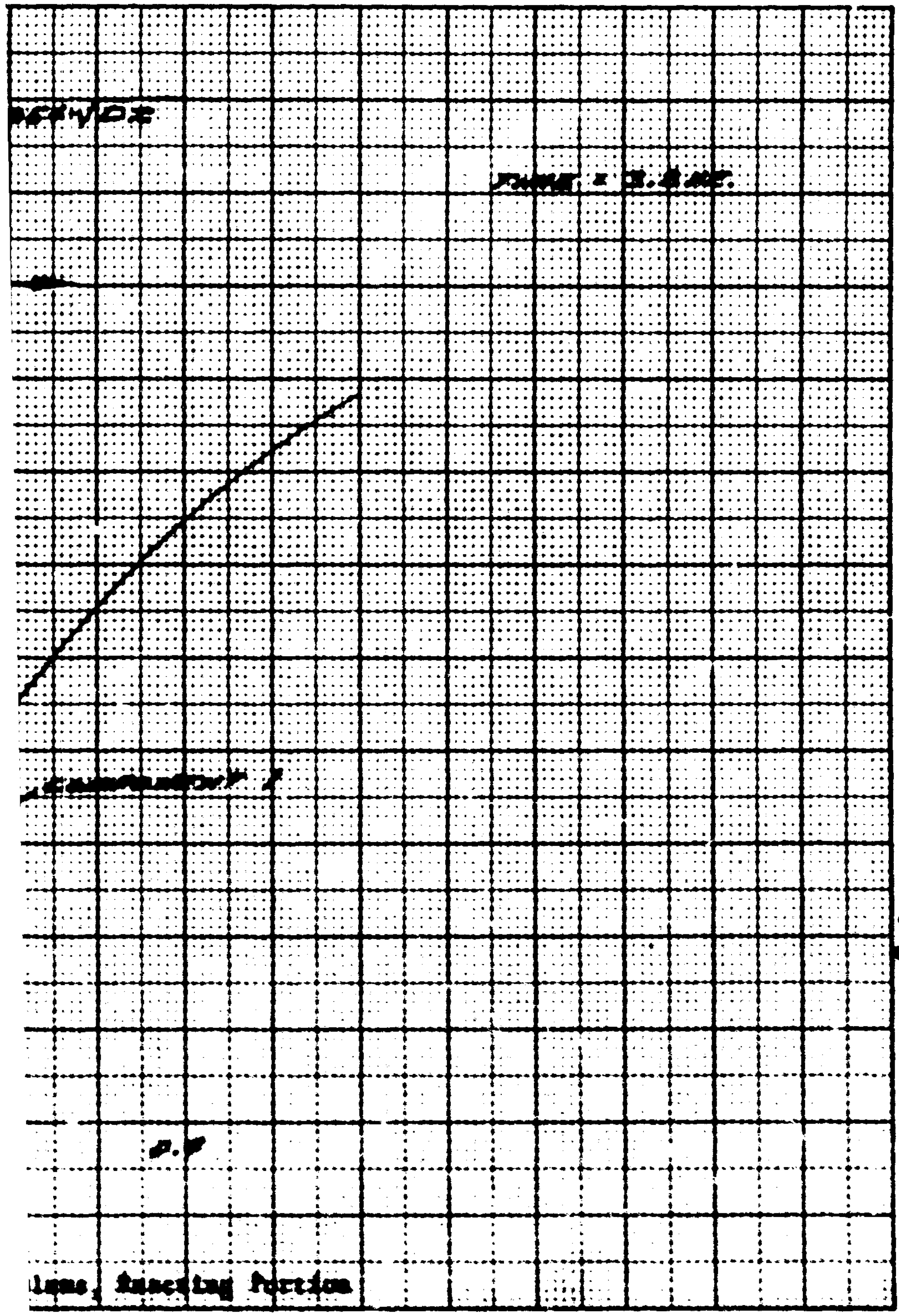


Figure 4 - Moving Boundary Probl



lane, Reacting Portion

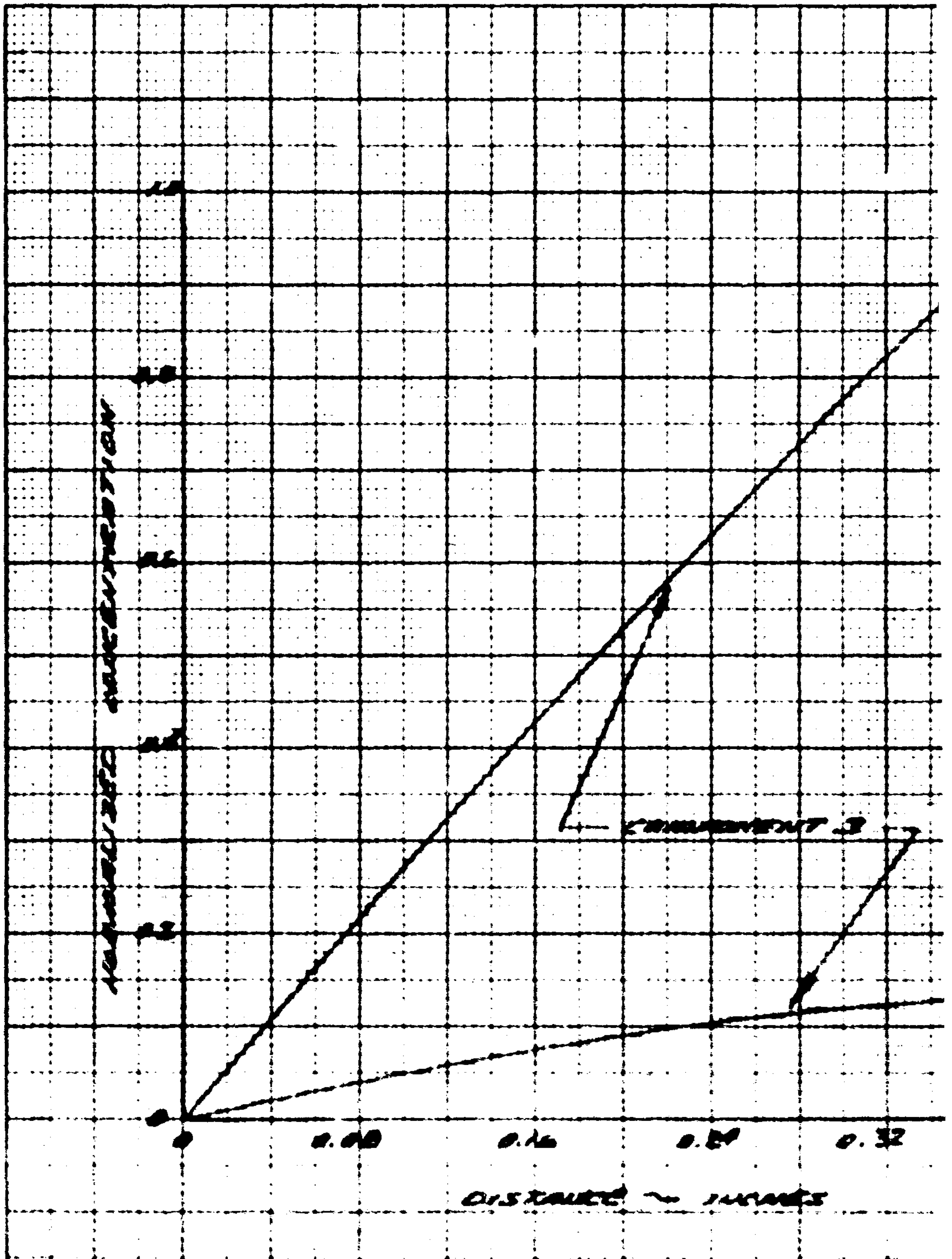
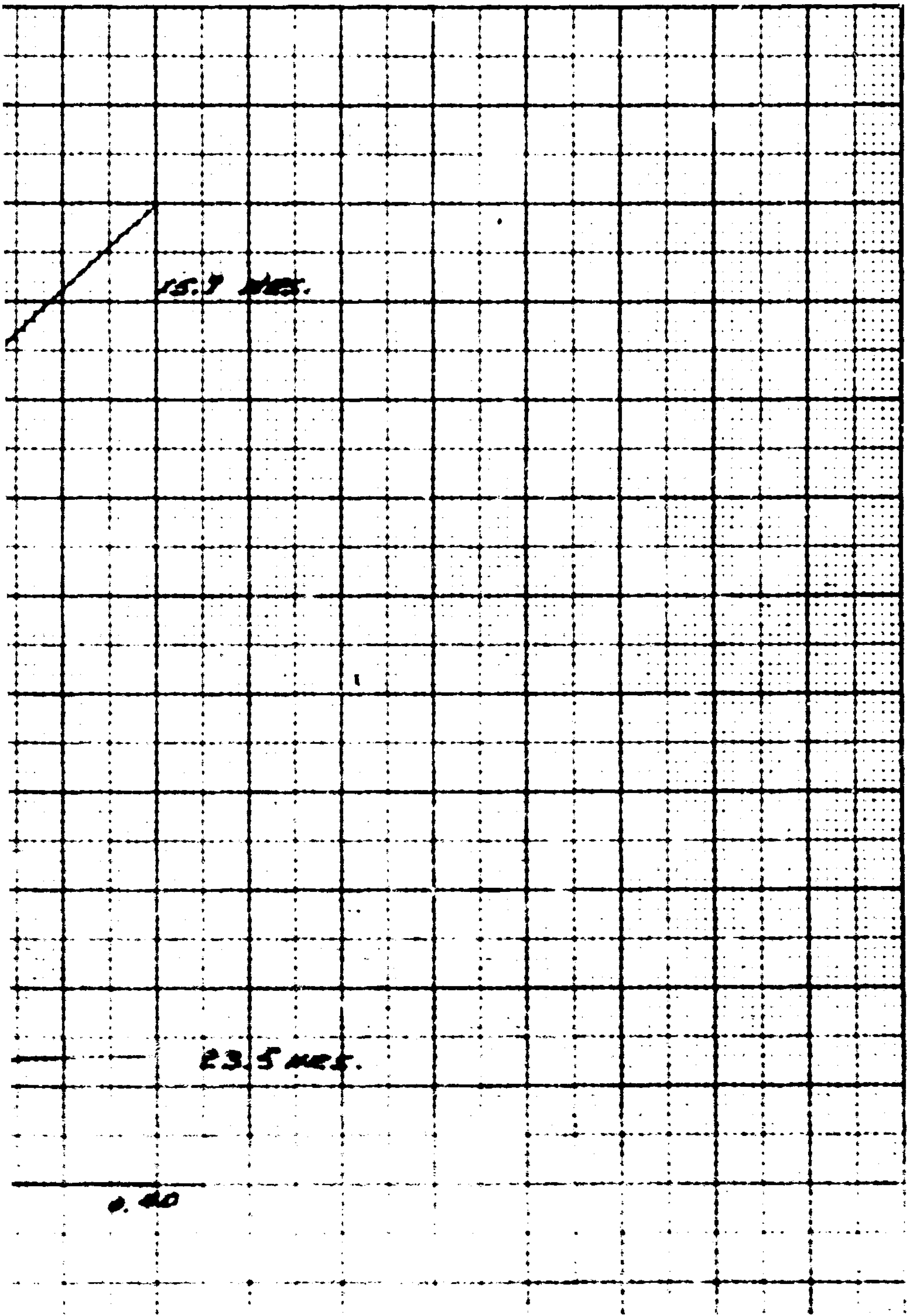


Figure 5 - Moving Boundary Problem



n, Depleting Portion

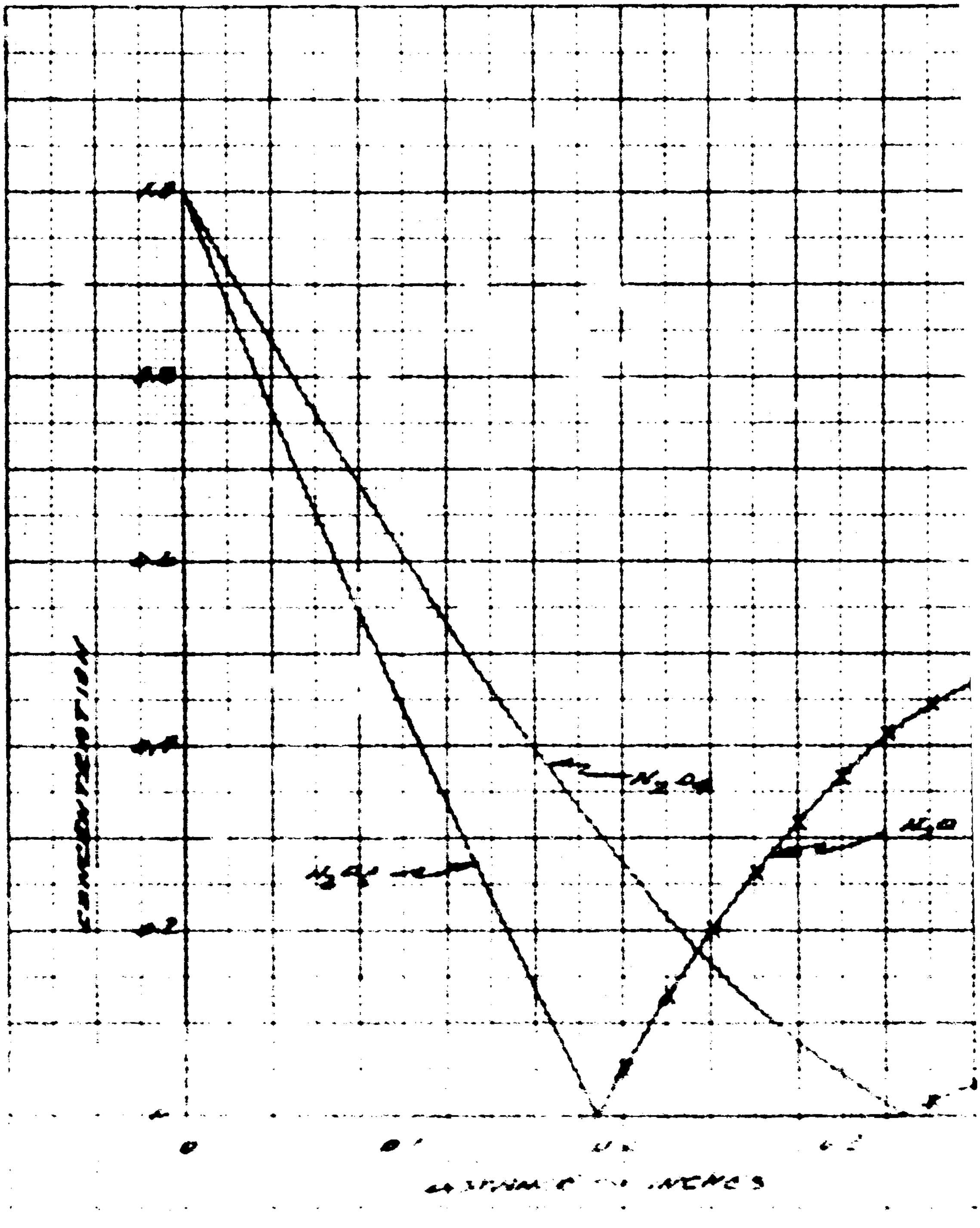
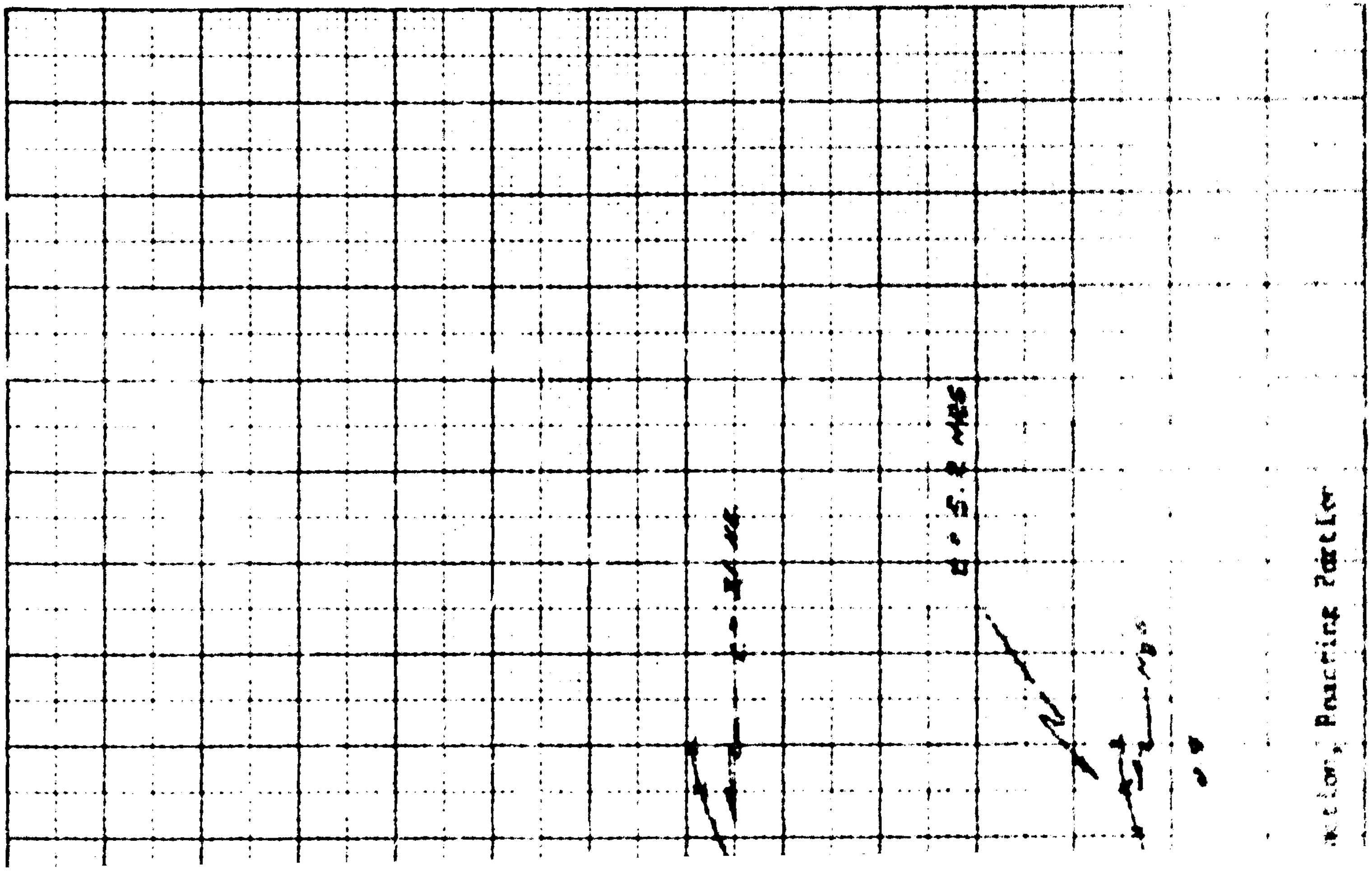


Figure 6 - Diffuser with Pitot R



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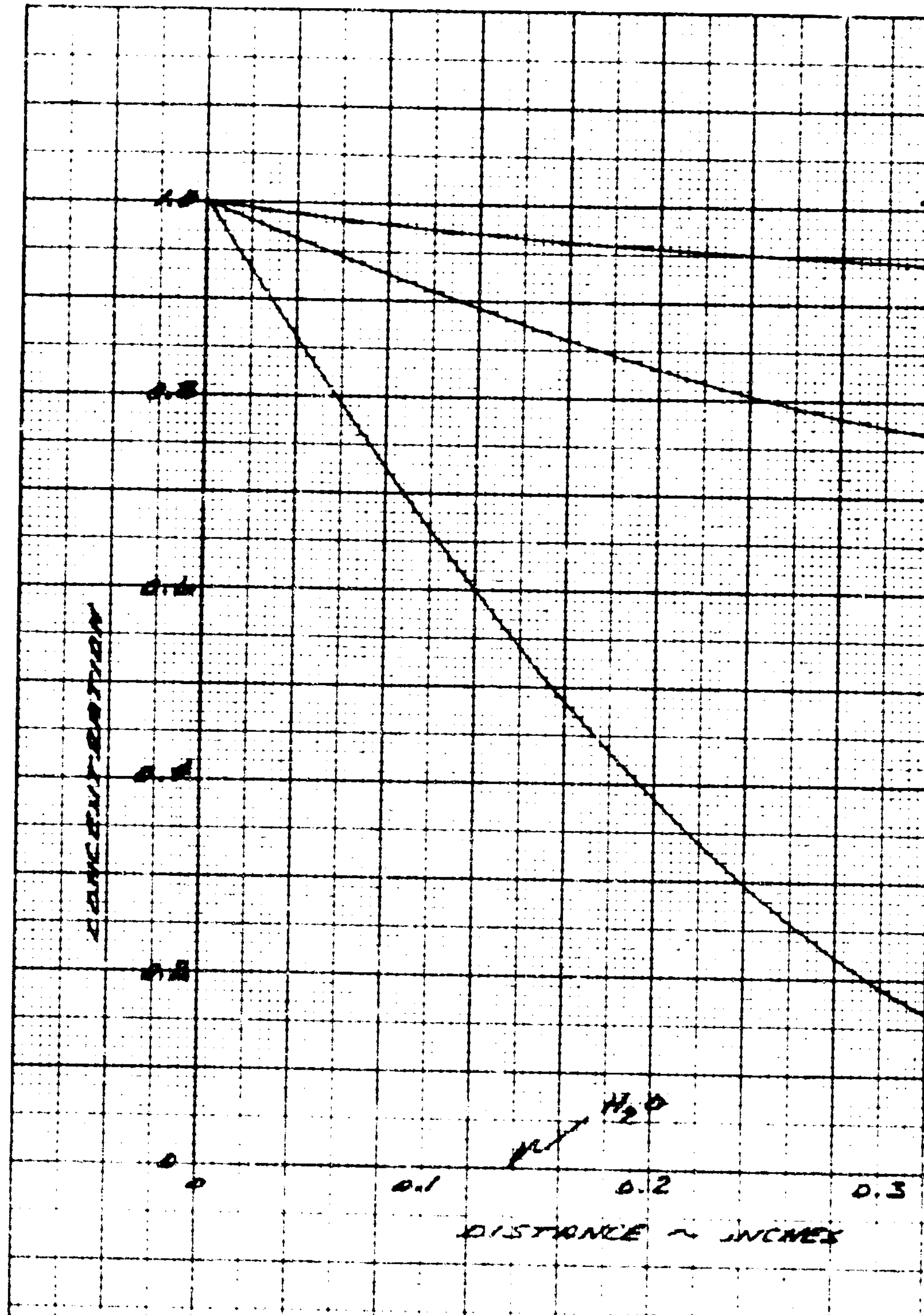
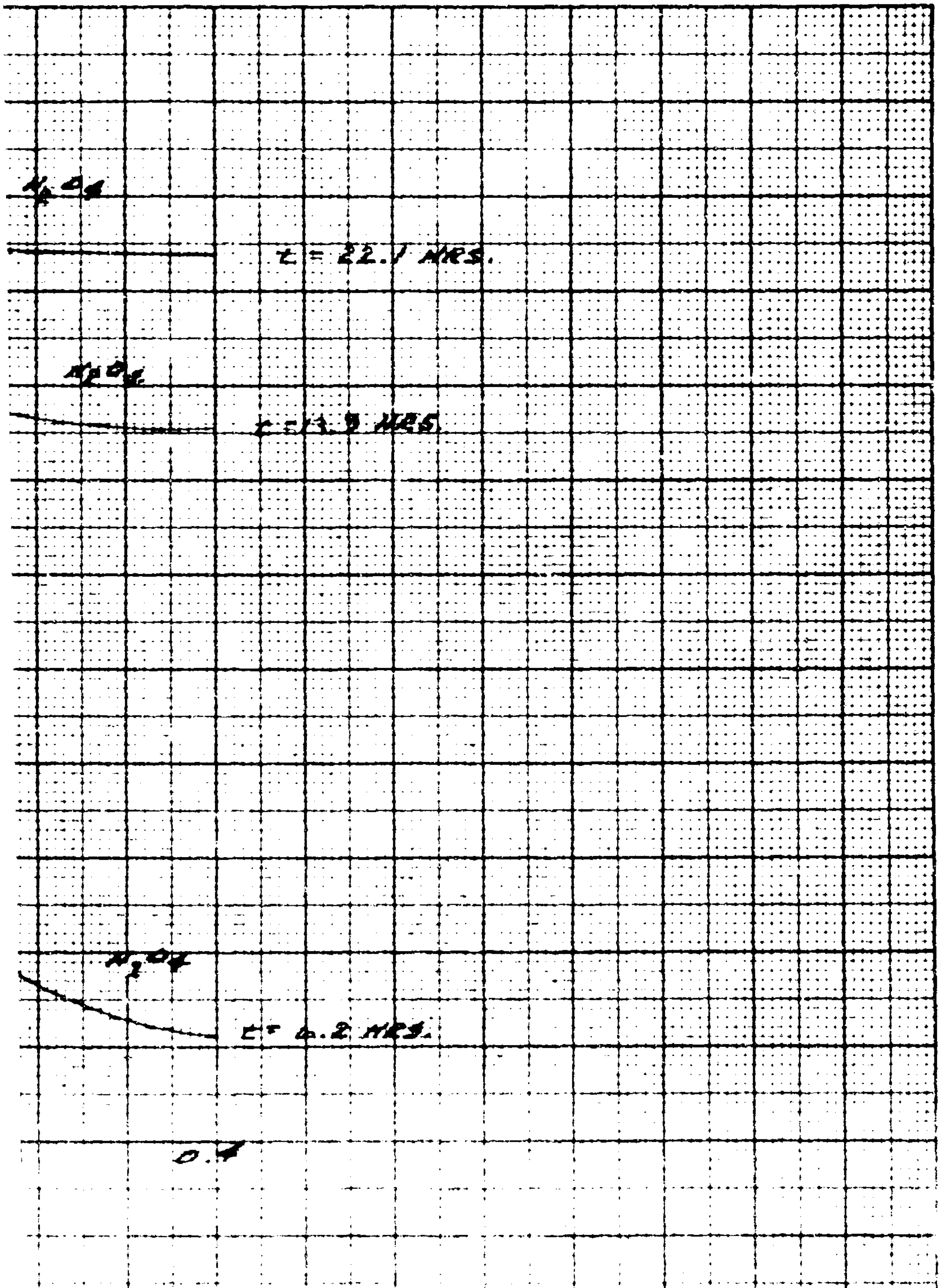


Figure 7 - Diffusion with Finit



ite Reaction, Depleting Portion

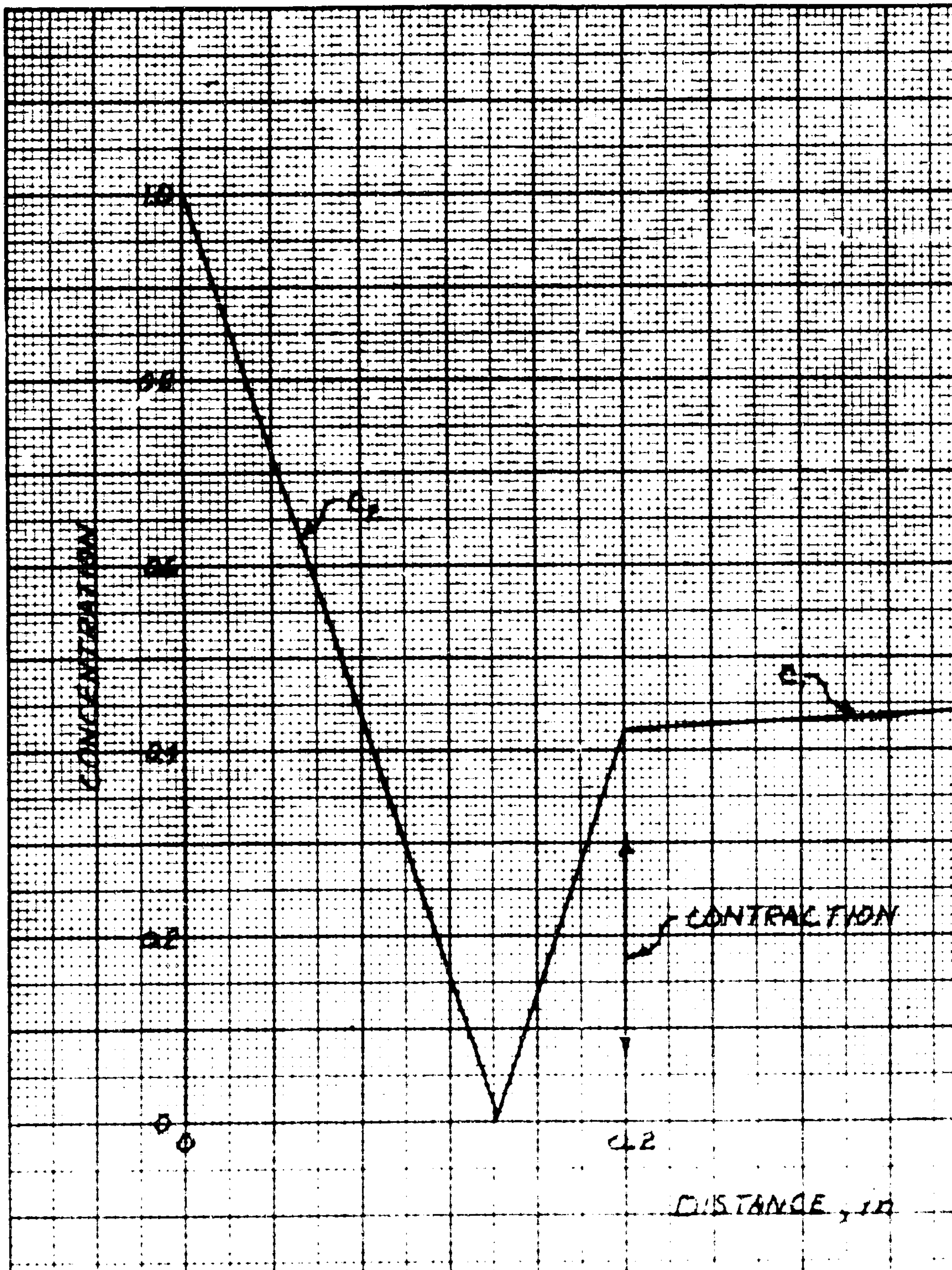
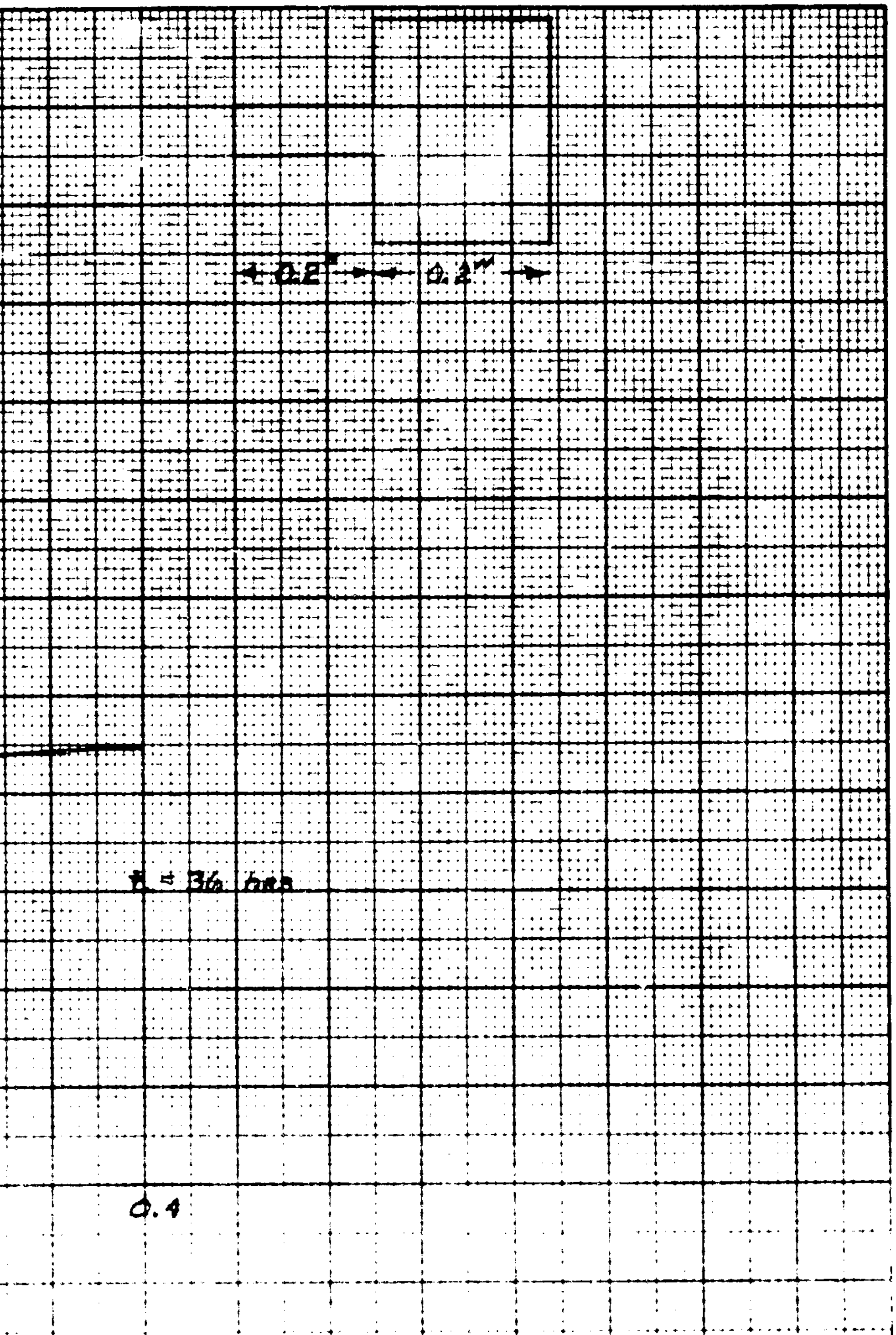


Figure 8 - Diffusion with Restrict



cted Capillary, Reacting Portion

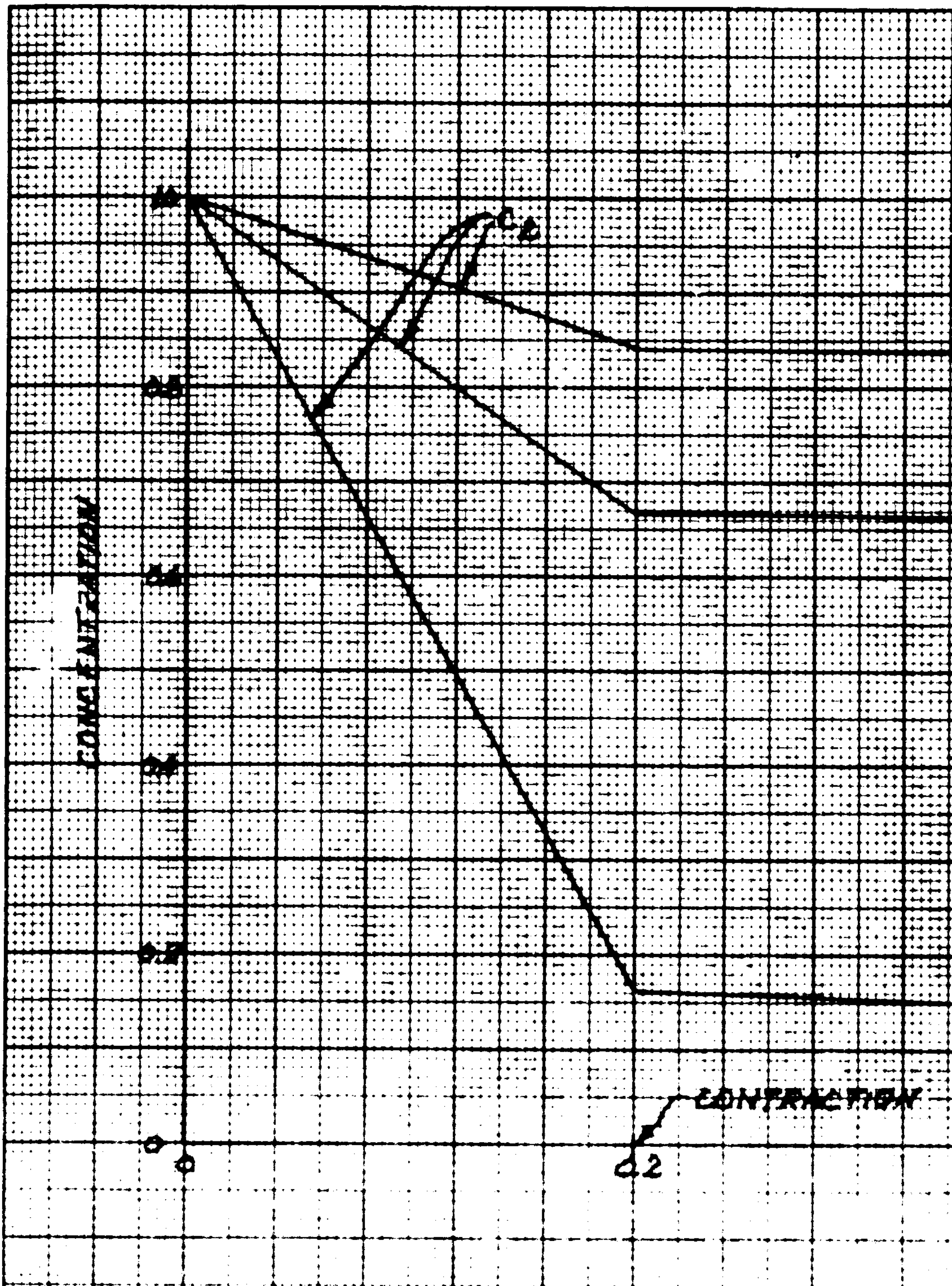
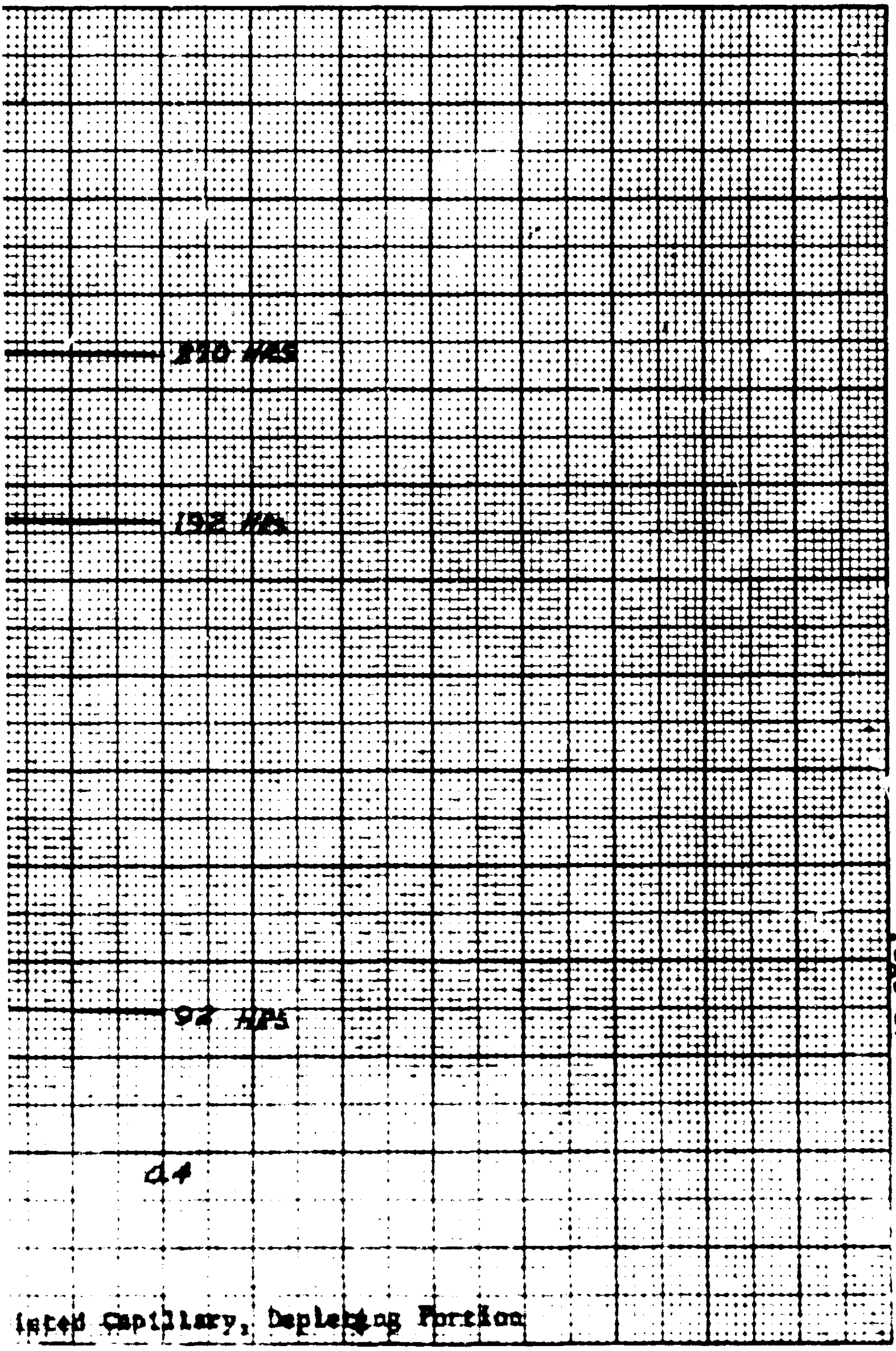


Figure 9 - Diffusion with Restri



isted Capillary, Depleting Portion

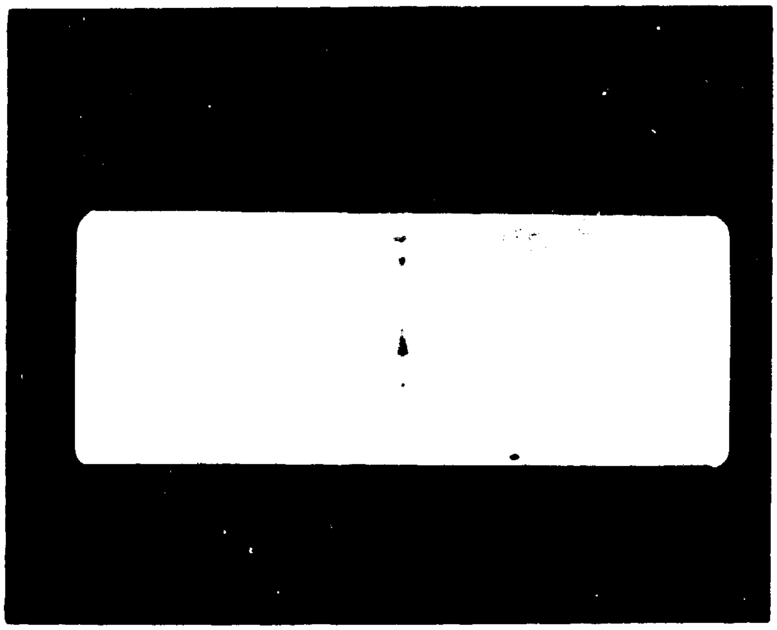


Figure 10 - Cross Section of Specimen Showing Large Cavity and Two 0.020" Holes Mag 1X

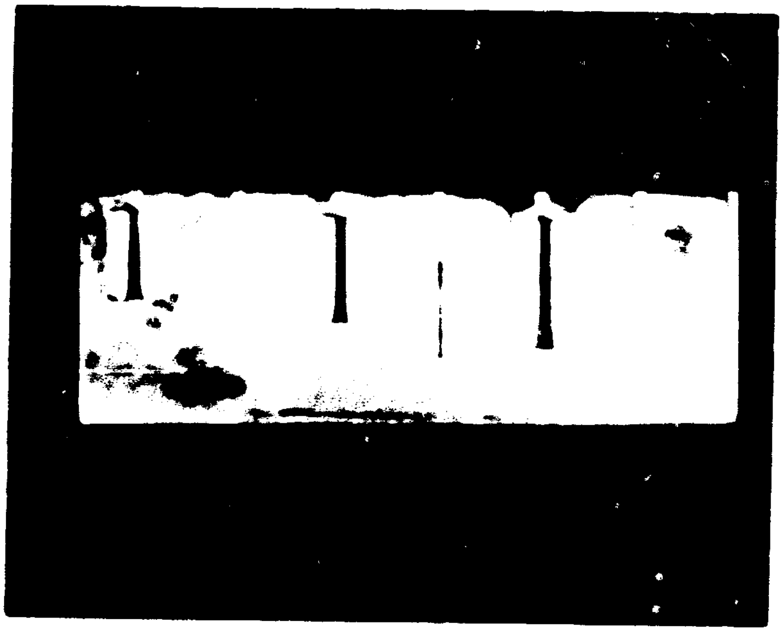


Figure 11 - Longitudinal Cross Section Through Specimen - Showing Varying Depths of Holes Mag 1X

Figure 12 - Transverse Cross Section Through Weld Specimen Mag 1X

Figure 13 - Showing Pit Corrosion in Cavity to a Depth of 0.0048". NTO in Cavity H_2O Surrounding. One Week Exposure Mag 400X

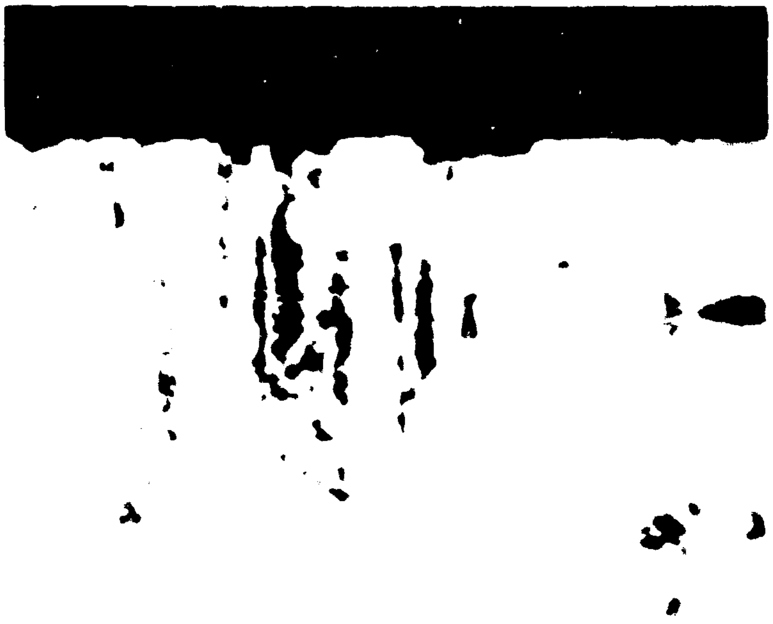


Figure 14 - Showing Pit Corrosion - 0.0025" H_2O in Cavity. NTO Surrounding Three Week Exposure Mag 400X

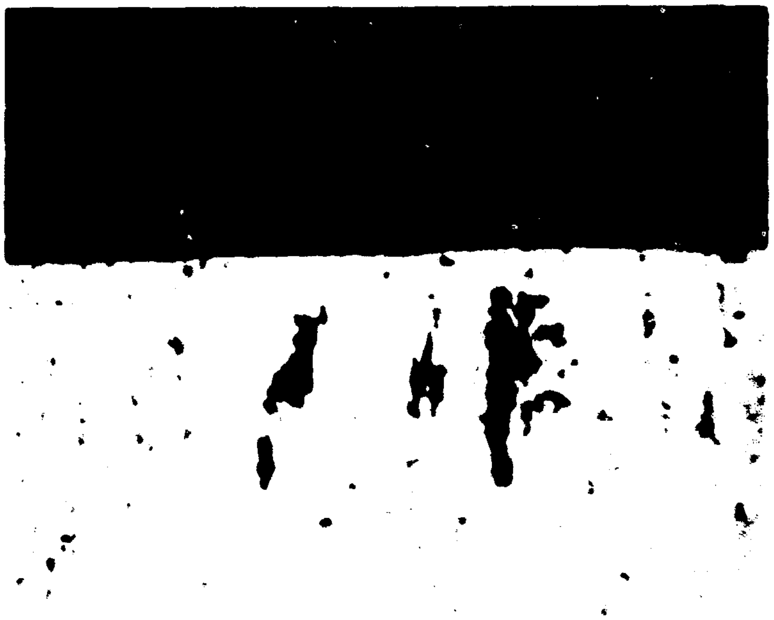


Figure 15 - Showing Pit Corrosion - 0.002" NTO in Cavity - H_2O Surrounding Two Weeks Exposure Mag 400X

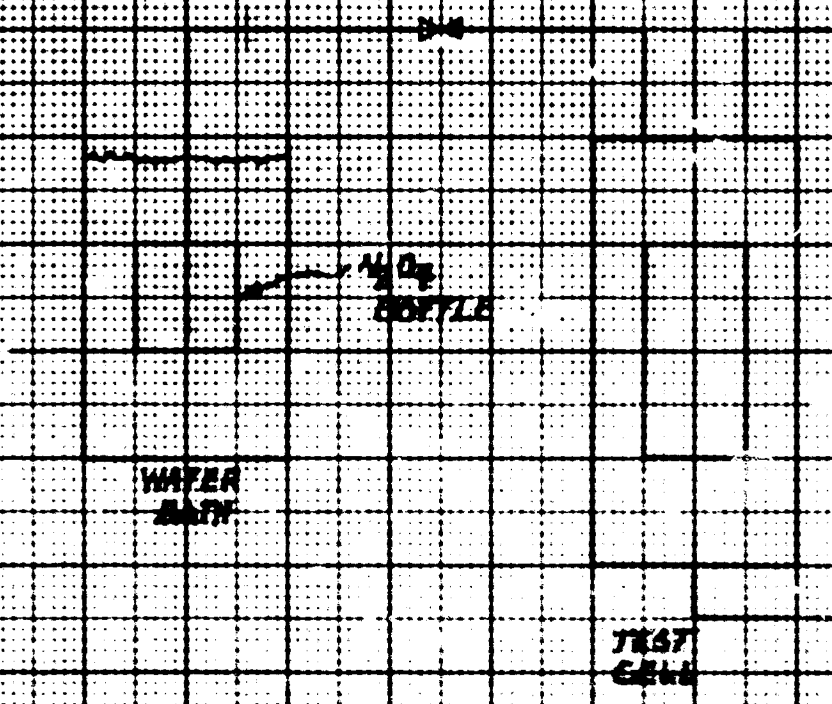
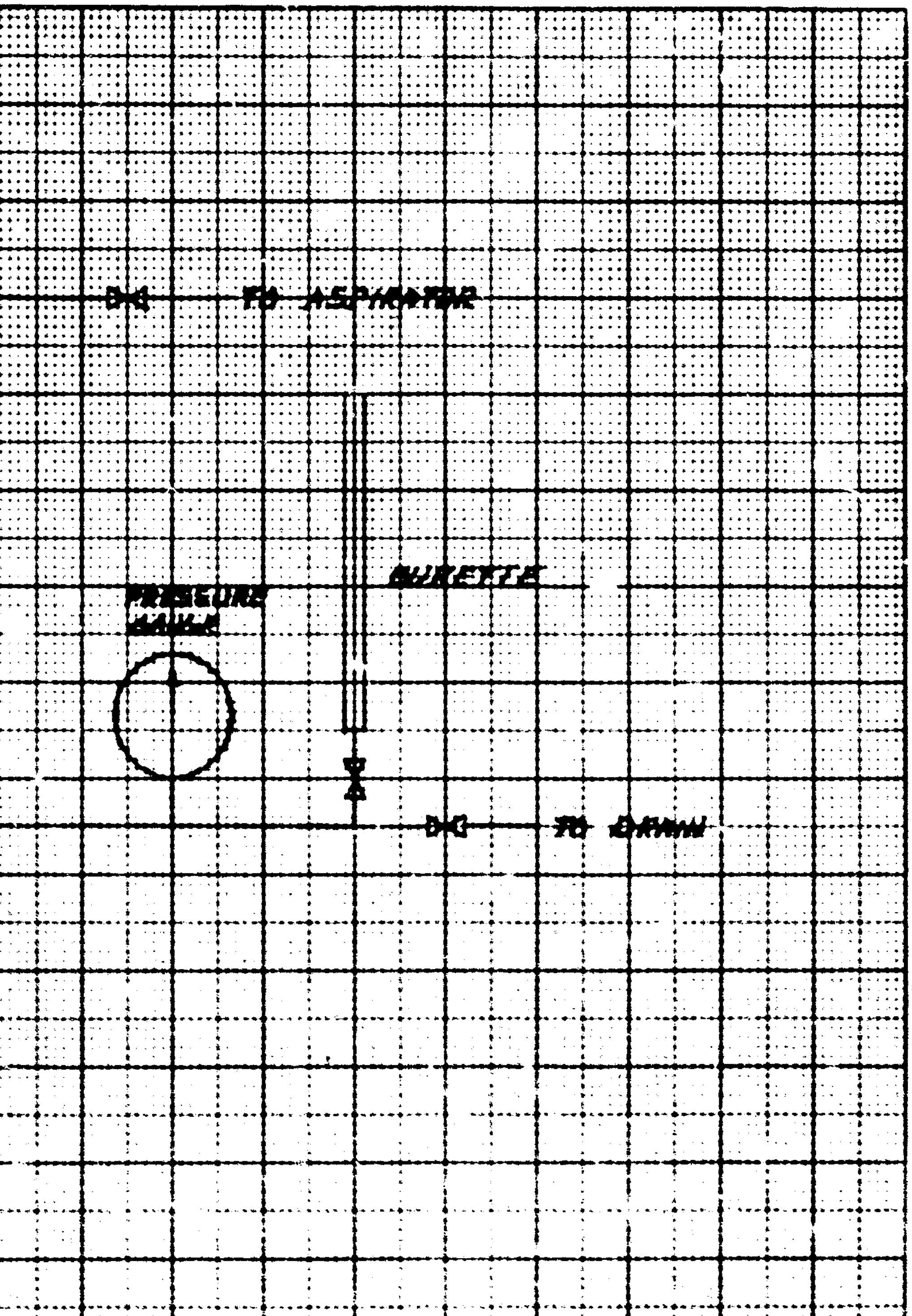


Figure 14 - Water - Nitrogen Te



atroxide Mixing Apparatus