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ABSTRACT

The objective of this program was to obtain data to assess the probability of N_2O_4 iron induced flow decay occurring in liquid propulsion feed systems. Data were obtained for the rate of dissolution of iron in N_2O_4, for the solubility limit as a function of temperature, and for the effects on the rate and solubility of adding small amounts of the impurities H_2O, NOCl and NO.

A radioactive tracer technique was developed to make the necessary measurements at the low concentrations encountered. The results obtained followed basically a solubility-type behavior. The iron build-up was initially rapid and leveled off to an equilibrium value in a few hours. Solubilities increased linearly with temperature typically from about 0.3 PPM at 32°F to 1 PPM at 116.6°F. Water in 0.1% by weight concentration increased the solubility to about 2 PPM at 116.6°F. NO (0.8% by weight) and NOCl (0.07% chlorine as NOCl) had little effect on the solubility limits although some effect on the rate was apparent when NOCl was added.

The mechanism suggested from the results is one in which N_2O_4 reacts initially with the iron to form a surface layer of iron nitrate whereupon the iron nitrate dissolves in N_2O_4.

KEY WORDS

Flow Decay
Radioactive Tracer
Iron Solubility
Solubility Rate Apparatus
Nitrogen Tetroxide
Nuclear Counting Equipment

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1.0 INTRODUCTION

Flow decay, and resulting thrust degradation in liquid rocket engine systems, has been a problem since the German Wasserfall Program, but only within the past few years has the origin of the phenomenon been understood. Recent performance anomalies attributed to flow decay, have been reported on Transtage, S-IVB, Gemini, and ground flow tests (References 1, 2, and 3), and there is concern that the problem might occur in Apollo systems.

Both NASA and the Air Force have sponsored research programs (Reference 4 and 5) to identify the causes and elimination of flow decay. It was found that the degradation of flow results from the buildup of solvated metallic compounds in the N_2O_4 oxidizer, which deposit at flow constrictions in the flow system.

It was the main objective of this program to obtain data necessary for assessing the probability of N_2O_4-iron-induced flow decay occurring in liquid propulsion feed systems. The scope of the work necessary to make a preliminary assessment was reasoned to include measurement of Fe/N_2O_4 reaction rate and solubility for the following conditions:

- Versus temperature in the range of 30 - 140°F
- With 0.8 wt. percent of NO added at the highest temperature
- With 0.08 wt. percent of Cl added as NOCl at the highest temperature
- With 0.1 wt. percent H_2O added at the highest temperature

To obtain these data, an accurate measurement technique was required for the measurement of solubility rates at low concentrations. A technique based on radioactive tracing was developed at Boeing for this purpose. In this technique, a known element is activated and then traced in solution to determine the rate of transfer. The technique was found to be sensitive at low concentrations, unambiguous, and rapid to apply. Excellent rate and solubility data were obtained for the dissolution of iron in N_2O_4.

2.0 THEORETICAL APPROACH

The dissolution rate of iron in N_2O_4 was obtained by measuring the rate of transfer of radioactive iron (Iron-59) into solution. This procedure involved three essential steps: 1) activation of the iron sample to produce the radioactive species, 2) reaction of the sample in N_2O_4 to transfer iron into solution, and 3) determination of the amount of iron transferred into solution to obtain the rate.

Natural iron consists of four isotopes: Fe^{54}, Fe^{56}, Fe^{57}, and Fe^{58}. Of these, the isotope, Fe^{58}, is the most useful for activation studies. This isotope can be transformed in a thermal neutron flux into the radioactive species, Fe^{59}, according to the nuclear reaction:

$$Fe^{58} + {}_{o}n' \longrightarrow Fe^{59}$$

The iron-59 decays to Co^{59} mostly by the following schemes:

$$Fe^{59} \begin{cases} \longrightarrow Co^{59} + \beta^- + \ (1.10) \\ \longrightarrow Co^{59} + \beta^- + \ (1.29) \end{cases}$$

Since the half-life of the decay is 45 days and the gamma ray energies are 1.10 and 1.29 Mev, the isotope is easily traced. The cross section of the neutron reaction with Fe^{58} is approximately 0.9 barns. With this cross section, it can be shown theoretically that it is relatively easy to detect a dissolution rate of about 10^{-12} gms iron/cm^2-sec when irradiating with a nuclear reaction of thermal flux of about 10^{13} n/cm^2-sec for a period of about 10 hours.

Quantitative counting of the activity transferred to solution involves the proper calibration of the nuclear detector, which will be described below, and the application of appropriate corrections to obtain the dissolution rate. The activity transferred to solution can be used to measure the total number of iron atoms transferred. If N_{TS} is the total atoms transferred after an immersion time t, the concentration in PPM (Parts per Million by weight) is given for low concentrations by the equation:

$$PPM = \frac{10^6 N_{TS} A_{Fe}}{N_A V_{NTO} \rho_{NTO}} \qquad (1)$$

N_{TS} is related to the ratio of radioactive to nonradioactive atoms by the equation:

$$N_{TS} = \frac{N_{59S}}{\left(\frac{N_{59}}{N_T}\right)} \qquad (2)$$

where N_{59S} is the total atoms of radioactive iron-59 present in solution after an immersion time t, and $\left(\frac{N_{59}}{N_T}\right)$ is the ratio of radioactive atoms of iron-59 to total atoms in the iron sample. This approach assumes that the rate of dissolution of iron-59 is the same as for the other iron isotopes, a very good assumption.

The total atoms of iron-59 present in solution, N_{59S}, is given by

$$N_{59S} = \frac{S_{59S}}{\lambda_{59}} \qquad (3)$$

where S_{59S} is the total activity of iron-59 in solution and λ_{59} is the decay constant for iron-59. Since the counting equipment is not perfect, it must be calibrated before S_{59S} can be accurately determined. If ϵ is the efficiency of the instrument, S_{59S} is found from the equation

$$S_{59S} = \frac{(CPM)_{BG}}{\epsilon} \qquad (4)$$

where $(CPM)_{BG}$ is the actual count rate obtained by use of the instrument corrected for background count rate. Thus the equation to calculate PPM is

$$PPM = \frac{10^6 (CPM)_{BG} A_{Fe}}{\lambda_{59} \epsilon \left(\frac{N_{59}}{N_T}\right) N_A V_{NTO} \rho_{NTO}} \qquad (5)$$

The quantities which must be measured experimentally to determine the PPM are the activity in solution $(CPM)_{BG}$, the instrument efficiency (ϵ), and the ratio of radioactive iron-59 atoms to total iron atoms in the activated iron sample (N_{59}/N_T).

3.0 EXPERIMENTAL

3.1 ACTIVATION

Iron samples were irradiated in the Washington State University reactor. This reactor is of the swimming pool type with a Triga-core having a maximum thermal neutron flux of about 3.0×10^{13} n/sec-cm^2.

The iron samples were prepared from 2-mil iron foil purchased from Inorganics Chemical Corporation, Sunnyvale, California. This iron had a composition as specified by the manufacturer of 99.56 percent iron, 0.44 percent normal impurities. The iron samples were prepared by rolling strips of metal one inch wide and 15 inches long into a spiral of cylindrical shape. Final dimensions of the cylinder were approximately 1/2 inch diameter by one inch long. In preliminary tests, it was found that very little space remained between layers of the spiral after rolling. To provide spacing, which was necessary for proper circulation of the N_2O_4, hundreds of dents were impressed with a dull pointer on each strip before rolling. This had the effect of creating "small mounds" on the opposite side of the identations, which served as spacers. Examination of the samples prepared in this manner showed that light readily transmitted between the layers, indicating that there was indeed a space between. Six samples were prepared for irradiation, and these had the following characteristics:

Sample No.	Size	Area (in^2)	No. of Dents	(Untied) Mass (gms)	(Tied)* Mass (gms)
1	0.99" x 15"	29.7 ± 0.2	350	3.07445	3.13346
2	1" x 15"	30 ± 0.2	300	3.13809	3.20048
3	1" x 15"	30 ± 0.2	310	3.12856	3.18297
4	0.99" x 15"	29.7 ± 0.2	300	3.11438	3.17342
5	0.99" x 15"	29.7 ± 0.2	300	3.11826	3.17802
6	1" x 15"	30 ± 0.2	250	3.10053	3.16275

*Sample was tied with a piece of iron wire (99.9+ percent iron) to hold spiral together.

The samples were irradiated for 10 hours on October 14 and 15, 1968 with irradiation time split about evenly during these days, respectively. The samples were enclosed in polyethylene containers during irradiation. Since not all the samples could be accommodated in the position of maximum flux, some were irradiated at a flux of less than 10^{13} n/cm^2-sec Samples 1, 4, 5, and 6 were irradiated at a flux of 1.2×10^{13} n/cm^2-sec; samples 2 and 3 at a flux of 8×10^{12} n/cm^2-sec. Following irradiation the samples were allowed to cool for about two days to permit short-lived radioisotopes to decay before shipment to Boeing Examination of the samples showed that 1, 3, and 6 had rusted. These samples were not used in the experiments

3.2 SAMPLE CALIBRATION

Before a dissolution experiment, the iron sample was calibrated to determine its activity; i.e., the ratio of radioactive iron-59 to total iron (N_{59}/N_T). This quantity was necessary in calculating the dissolution rate (see above under Theoretical Approach). To calibrate the iron samples, the "point-source geometry" experiment (shown in Figure 1) was set up to compare the activity of the iron with that of a standard Co-60 source The shield pig and detector setup was the same as that used for dissolution experiments, which will be described in detail below.

The following procedure was used to calibrate a sample. A collimator with a hole of approximately 1/8 inch diameter was placed in the shield pig. A light was shined through the hole and, with the room dark, the centerline from the detector to the shelf wall, 9 feet 6 inches away, was determined from the image of the hole on the shelf wall. The center of the image, which was approximately circular, was marked with a cross mark. With the collimator removed, the standard Co-60 source, which was a vial filled with $CoCl_2$ solution, was positioned over the cross mark and a count taken. The unknown iron sample was then positioned over the cross mark and a count taken.

The activity of the iron sample was calculated by comparing the iron to the standard Co-60 count. This is given by the equation

$$S_{Fe} = 2S_{Co}\frac{I_{Fe}}{I_{Co}} = 2(S_{Co})_0 \frac{(CPM)_{Fe}}{(CPM)_{Co}} e^{-\lambda_{60} t_{60}}$$

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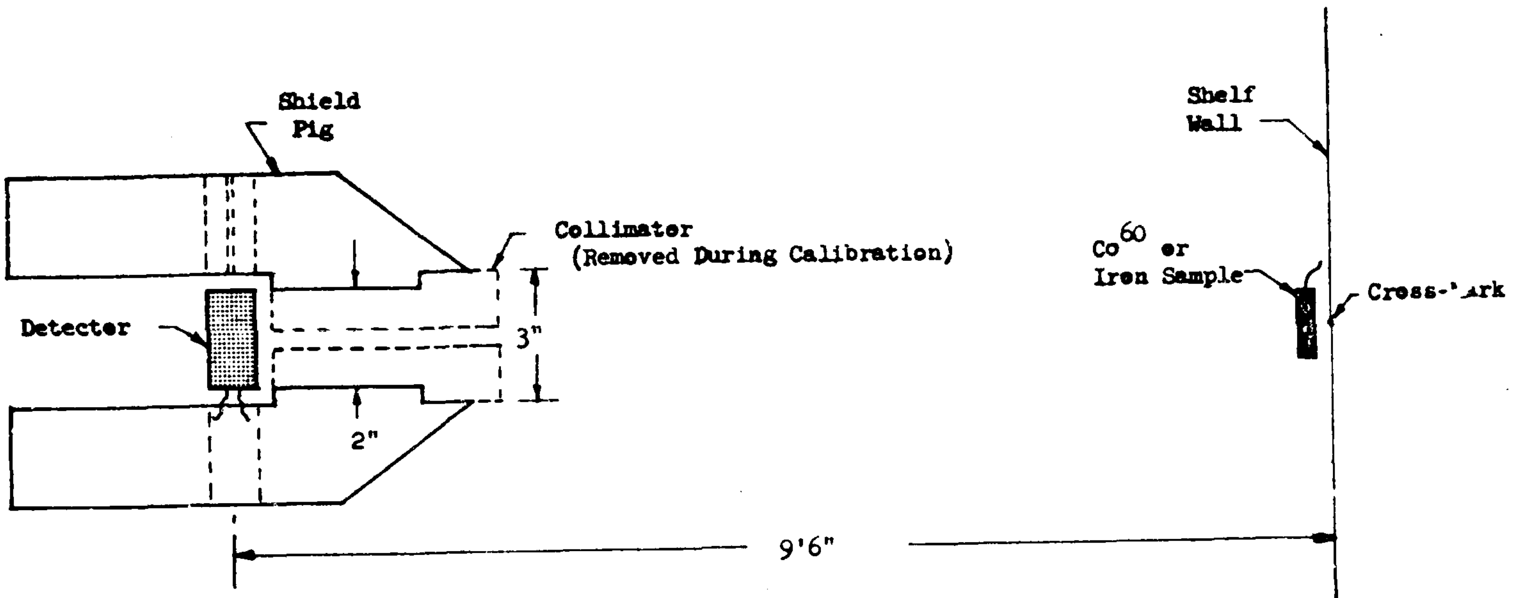


FIGURE 1. Point Source Geometry Set-Up

The factor of 2 results from the mode of the decay of Fe-59 when compared to Co-60. The Fe-59 decays in parallel while the Co-60 decays in cascade. Thus it takes twice the iron activity to produce the same intensity as a cobalt source. A correction for the decay of Co-60 was necessary becuuse the Co-60 had been standardized several months prior to these experiments.

The ratio of radioactive iron-59 to total iron is now easily found. N_{59}, the total atoms of iron-59 in the sample, is given by $N_{59} = S_{Fe}/\lambda_{59}$. The total number of iron atoms is given by $N_T = M_{Fe}N_A/A_{Fe}$. The ratio is

$$\left(\frac{N_{59}}{N_T}\right)_0 = \frac{S_{Fe}A_{Fe}}{\lambda_{59}M_{Fe}N_A}$$

Since an experiment was usually conducted a few days after the iron sample was calibrated, the following correction for the decay of the iron was necessary.

$$\left(\frac{N_{59}}{N_T}\right) = \left(\frac{N_{59}}{N_t}\right)_0 e^{-\lambda_{59}t_{59}}$$

To determine the sensitivity of the calibration to improper positioning of the sources over the cross mark; i.e., to slight misalignments, the following experiments were performed. The Co-60 source was purposely positioned one inch to the right, to the left, and below the cross mark. The following results were obtained:

Positon of Source	CPM (Corrected for B.G.)
Centered on X mark	776
One inch to right of X mark	749
One inch to left of X mark	750
One inch below X mark	735

These results indicate that misalignment of the source by as much as one inch causes an error of the order of ± 4 percent. In actual experiments, the misalignment is much less, probably never greater than 1/8 inch from the cross mark, so that the error introduced by misalignment should be negligible.

3.3 DISSOLUTION RATE APPARATUS AND PROCEDURE

Dissolution rate experiments were conducted in a specially designed glass reaction tube which was made from a one inch outside diameter, heavy-wall, Pyrex glass tube. Figure 2 is a schematic, and Figure 3 a photograph of this tube. The tube was bent at an angle of approximately 25 degrees. The bottom arm (shorter end) contained the N_2O_4 and fitted into the well of a NaI scintillation detector. The upper arm (longer end) was used as a recession place for the iron sample when the sample was not immersed in the N_2O_4. A Teflon stopcock was provided in the upper part of the bend to transfer N_2O_4 into the tube.

To run a rate experiment, a calibrated, activated iron sample, to which a Teflon-covered, magnetic stirrer had been attached with a piece of platnium wire, was placed inside the tube and the tube end (right end in Figure 2) sealed. The tube was then connected to a vacuum apparatus and evacuated, whereupon 15 cu cm of N_2O_4 were transferred into it. The stopcock was then tightly closed, and the tube was immersed in a constant temperature bath. When thermal equilibrium was reached, the iron sample was immersed in the N_2O_4 for a predetermined time, after which it was again removed from solution. During the immersion the N_2O_4 was agitated with a small, Teflon-covered, spherical, magnetic stirrer. The sample was manipulated in and out of the N_2O_4 by the use of a small U magnet which acted on the magnetic stirrer attached to the sample -- all done externally.

After an immersion, the reaction tube was positioned in the NaI detector well to determine the activity transferred to solution. To reduce the count from the activated sample which would otherwise swamp the count from the solution, a large amount of shielding was required between the sample and the detector. This shielding was provided by an existing lead shield pig, which was modified to provide about 10 inches of shield between the sample and the detector. Figure 4 shows a cross-sectional view of the shielding arrangement with the reaction tube in place. Figure 5 shows a side view photograph of the lead pig, and Figure 6 a front view showing the reaction tube entering into the shield inside of which was the detector. With this arrangement, the background from the activated iron sample was reduced to some 5 to 10 CPM above normal background.

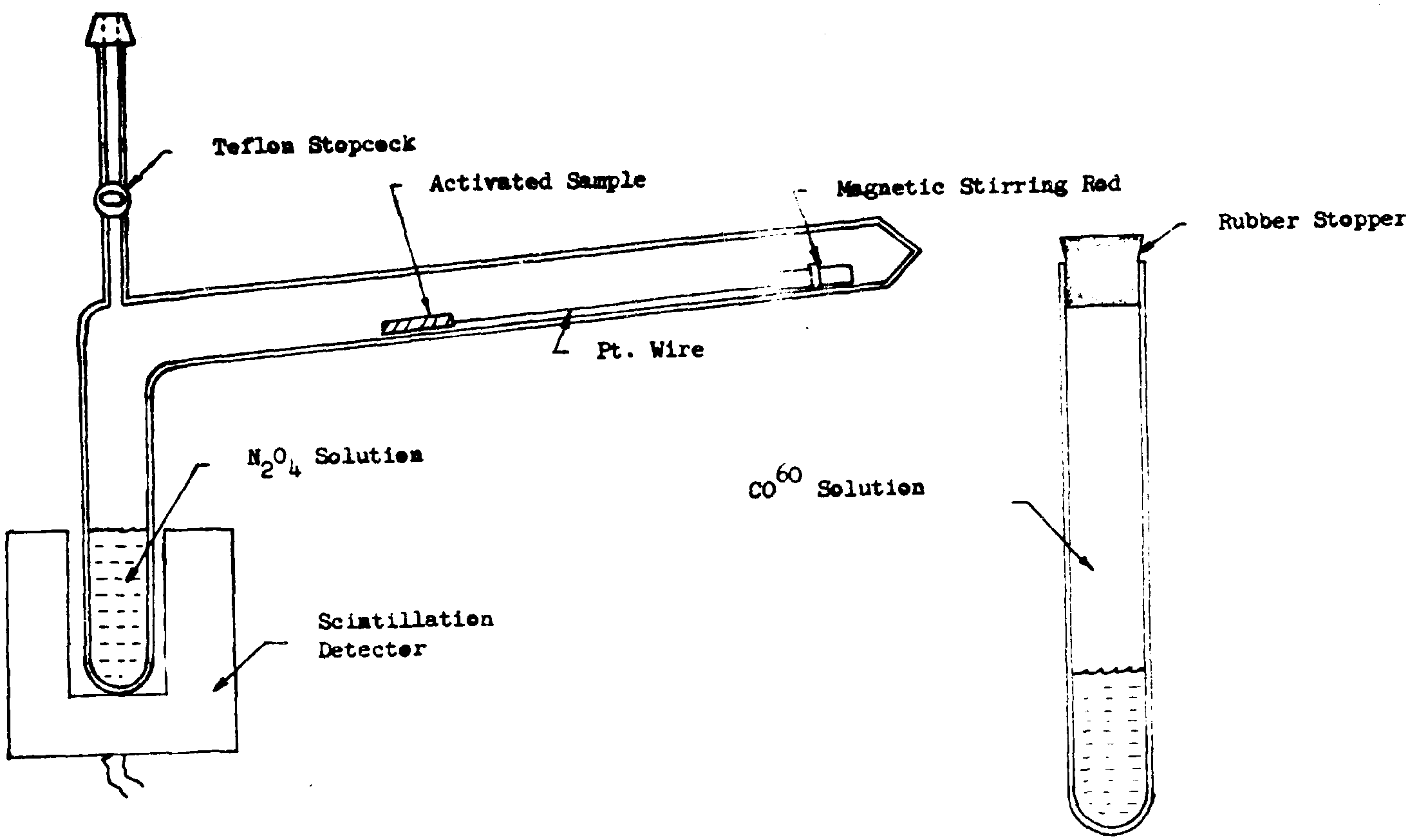


FIGURE 2. Schematic of Dissolution Rate Reaction Tube

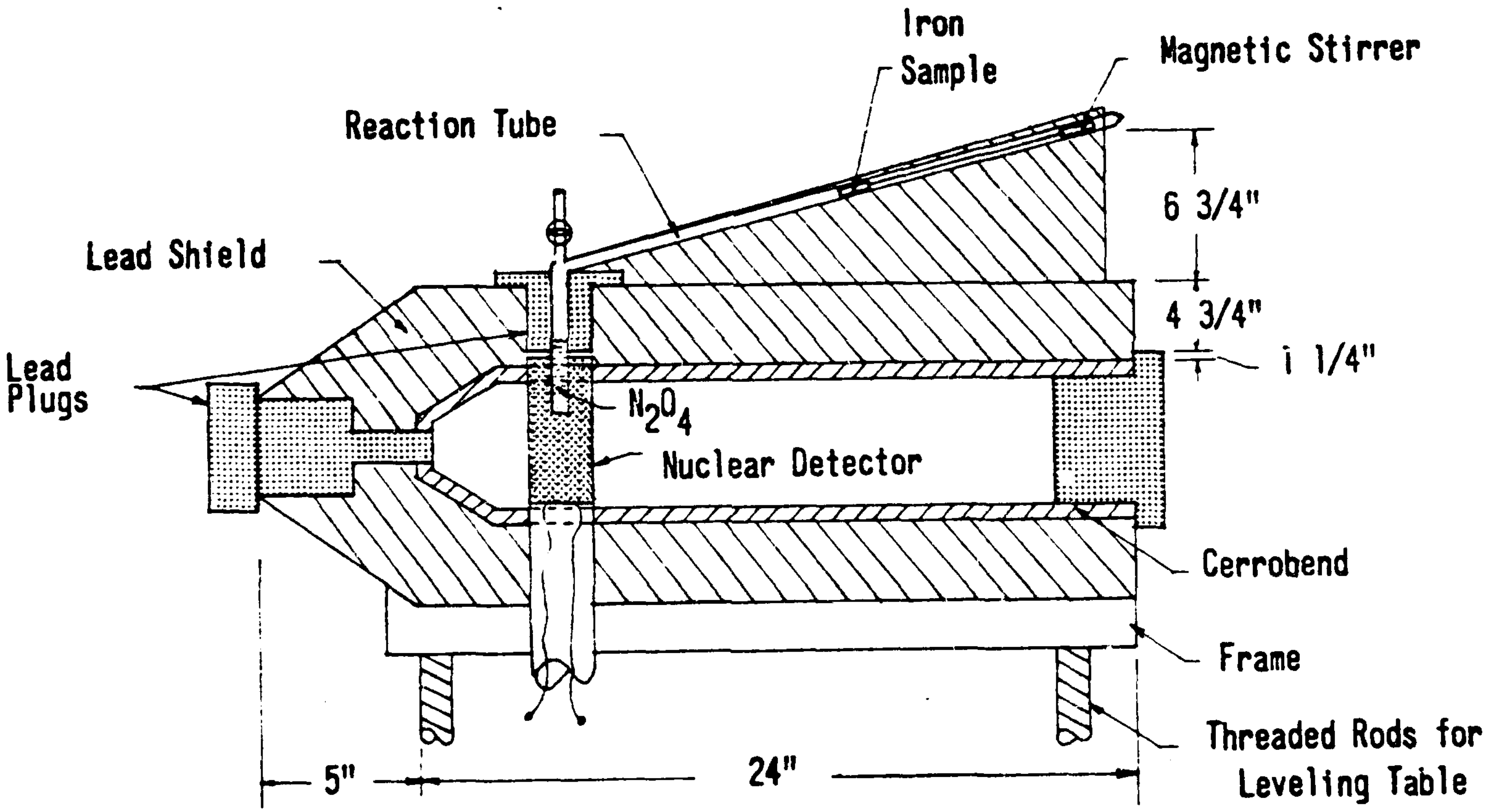


FIGURE 4. Cross-Section of Shielding Arrangement

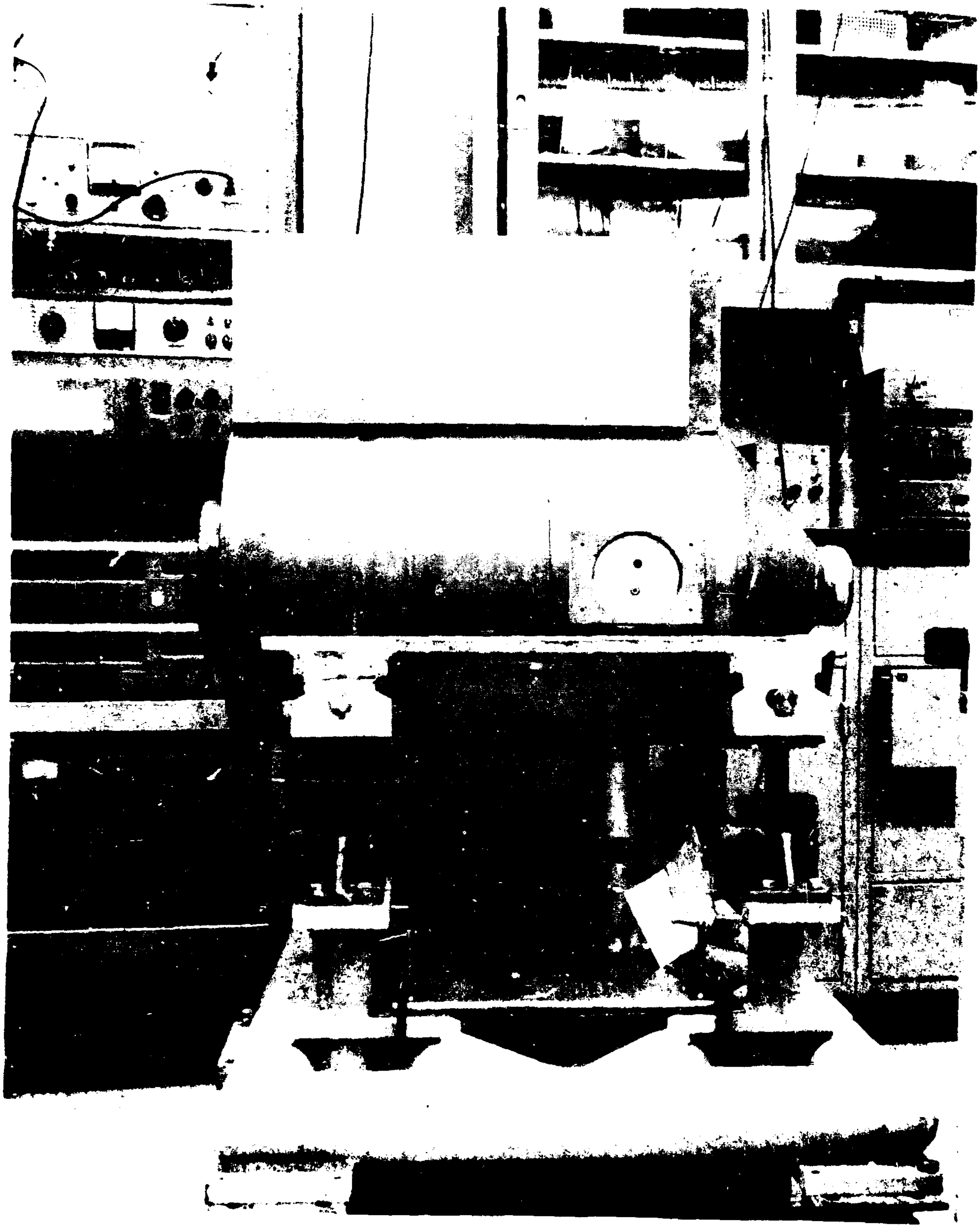


FIGURE [illegible]. Side-View of Shield Rig

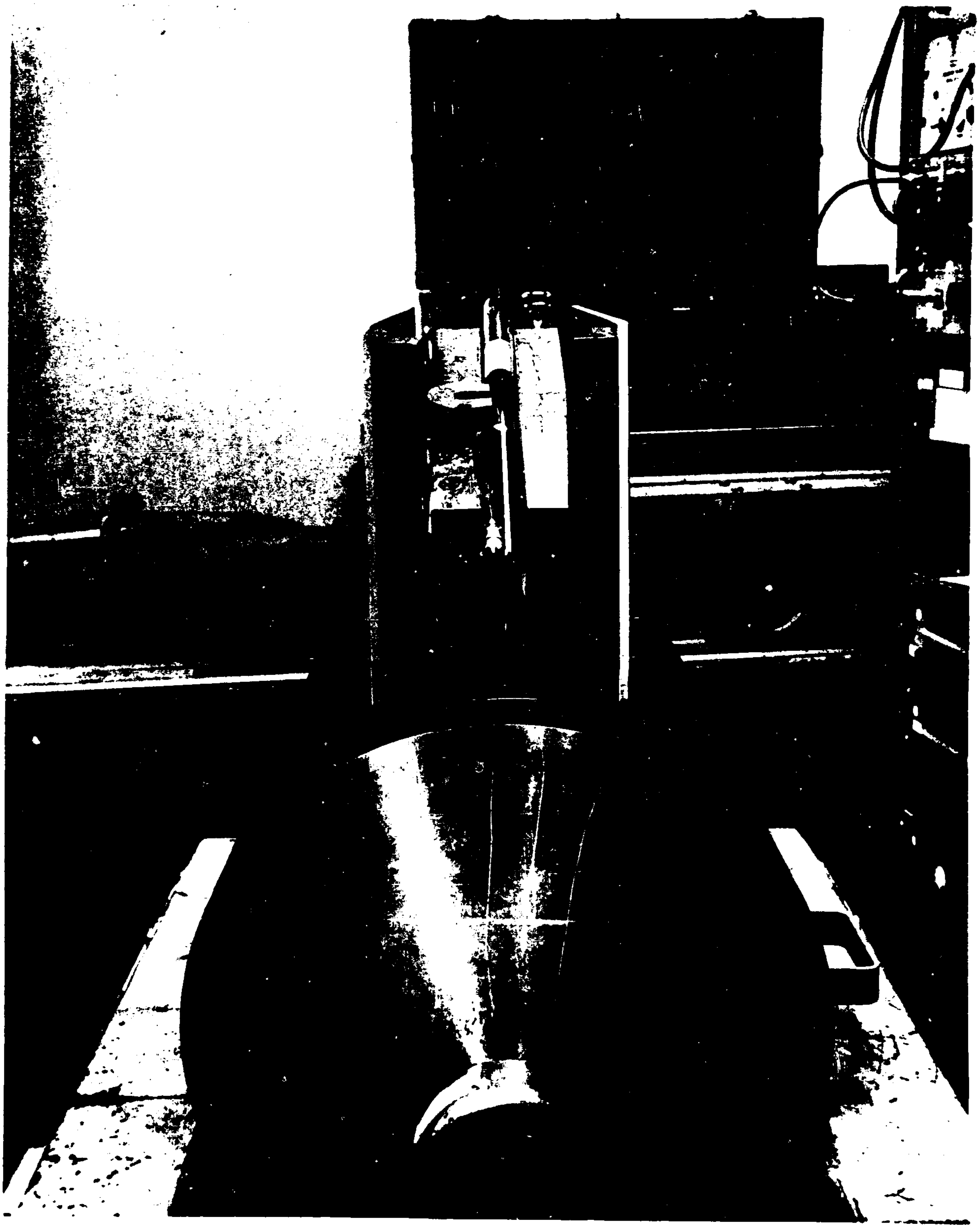


FIGURE 6. Front-View of Shield Pig with Reaction Tube in Place

The radiation counting equipment used in the study consisted of a 3" x 3" sodium iodide scintillation counter with a 1 1/16" x 1 1/2" well, supplied by the Harshaw Company. The multiple phototube output was amplified by a charge-sensitive preamplifier of Boeing's own design, followed by a Hammer, Model N685 single-channel discriminator, a Baird-Atomic, Model CS101 scaler, and a Baird-Atomic, Model CS905 timer. The single-channel discriminator was adjusted to accept only those pulses resulting from the photoelectric absorption of the two Fe-59 gammas in the sodium iodide crystal. A Technical Measurements, Model CN1024 multichannel analyzer, with punch tape readout, was used to check the operation of the system and to set the single-channel discriminator. A general view of the counting and multichannel analyses equipment is shown in Figure 7.

3.4 INSTRUMENT CALIBRATION

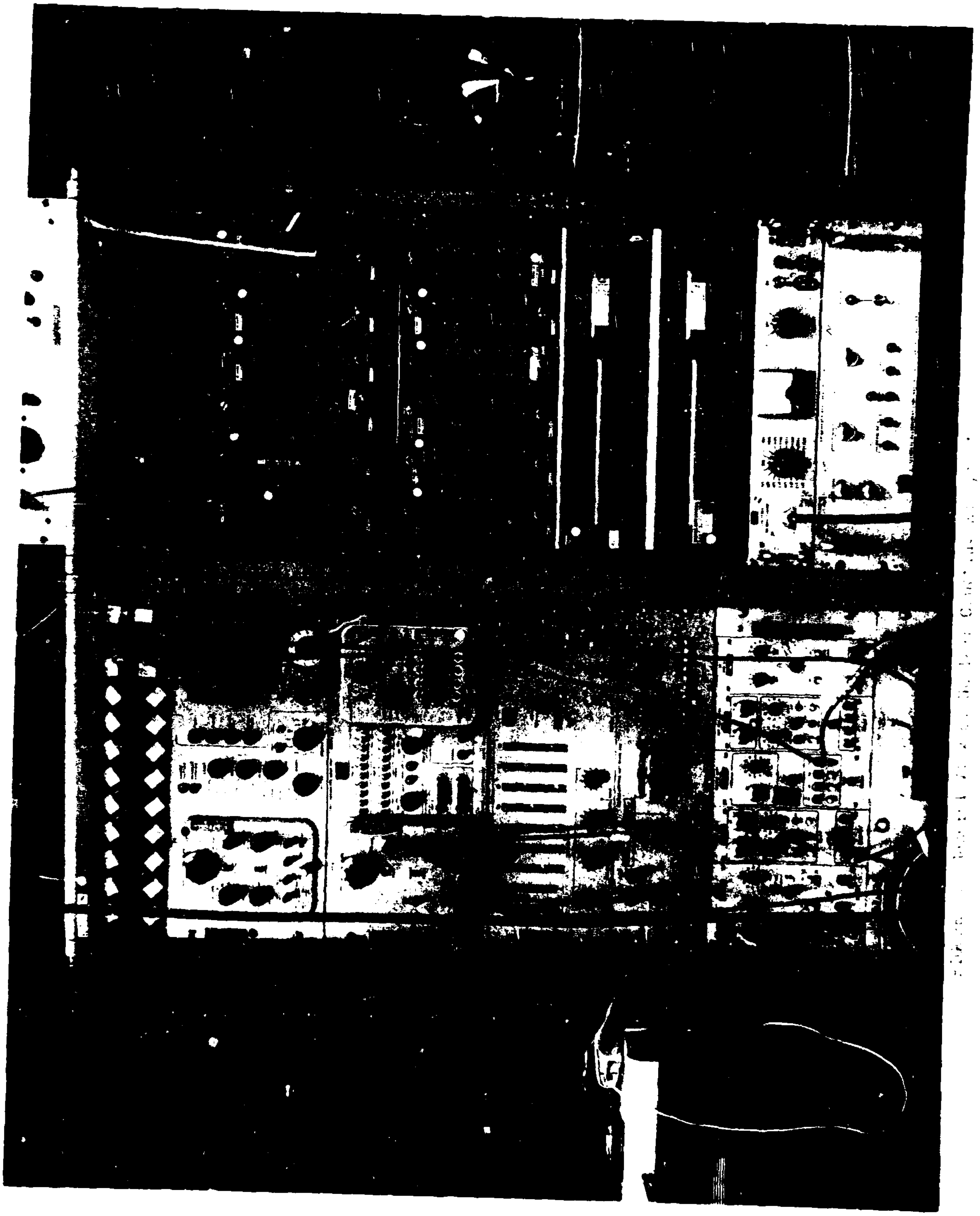
To calibrate the nuclear counting equipment, a nonvariable geometry approach was used. This approach had the advantage of eliminating many of the counting errors introduced by changes in geometry. To accomplish this, calibration tubes having the same size and volume as the reaction tube were used (Figure 2). Ten such tubes, about 7 inches long each, were made from one inch O.D., heavy-wall, glass tube of the same type as that used to make the reaction tubes. Fifteen cubic centimeters of solution of known activity were placed in each tube. Thus, the effective geometry of each tube was of the same size, volume, wall thickness, etc., as the reaction tubes. These tubes were used to determine the efficiency of the counting equipment and for occasional checks of instrument drift.

The solutions used in the tubes were prepared from a standard Co-60 ($CoCl_2$) vial having the following characteristics as given by the supplier:

Activity: 0.124×10^5 d/sec-ml ± 3 percent. Date: December 3, 1962

Volume: 2.85 ± 0.02 ml

The activity on October 17, 1968, when the calibration tubes were made, was calculated as 5.70×10^3 d/sec-ml. The calibration tubes were prepared as follows: First, the solution in the vial was diluted to 30 cu cm. Fifteen cubic centimeters were then



removed with a burette and transferred to one of the empty calibration tubes. The remaining solution was then again diluted to 30 cu cm by the addition of 15 cu cm of water. After proper mixing, another 15 cu cm were removed and transferred to a second calibration tube. This procedure was repeated until ten tubes were prepared. Each succeeding tube prepared in this manner had a decreasing known activity, which is shown in Table 1, Column 2. The reading obtained from the instrument is shown in Column 3, and Column 4 shows the counter efficiency on October 17, 1968.

During the course of various experiments the instrument was checked for efficiency, and if a drift was noted, an appropriate correction was made. To compare the instrument readings with those obtained on October 17, 1968, a correction was made for the decay of the Co-60; that is, all readings were referred back to October 17, 1968 when the instrument was calibrated. Thus, if t_{17} is the time after October 17th, a correction, $e^{\lambda_{60} t_{17}}$, was applied to the reading to refer it back to this date.

The slight decrease in efficiency with decreasing count rate was not explained satisfactorily. The effect was repeatable, so apparently it was the result of instrumentation characteristics. For the rate runs the count rate was not higher than 1000 CPM, and in this range the efficiency was nearly constant. Thus, an average efficiency for this range was used in the calculations.

3.5 PREPARATION AND HANDLING OF N_2O_4

Considerable effort was devoted to obtaining N_2O_4 in a state of high purity. All N_2O_4 used in the experiments was prepared as needed by the reaction of NO with excess O_2:

$$2\,NO + O_2 \longrightarrow N_2O_4$$

Distillation of slightly impure N_2O_4 was rejected as a means of purification, since common impurities such as HNO_3 and NOCl are difficult to remove completely from N_2O_4. HNO_3 and NOCl can, however, be easily separated from NO and O_2 by low temperature distillation.

The volatile substances (NO, O_2, N_2O_4, NOCl, and H_2O) used in this project were handled in the glass vacuum apparatus illustrated in Figure 8. The glass

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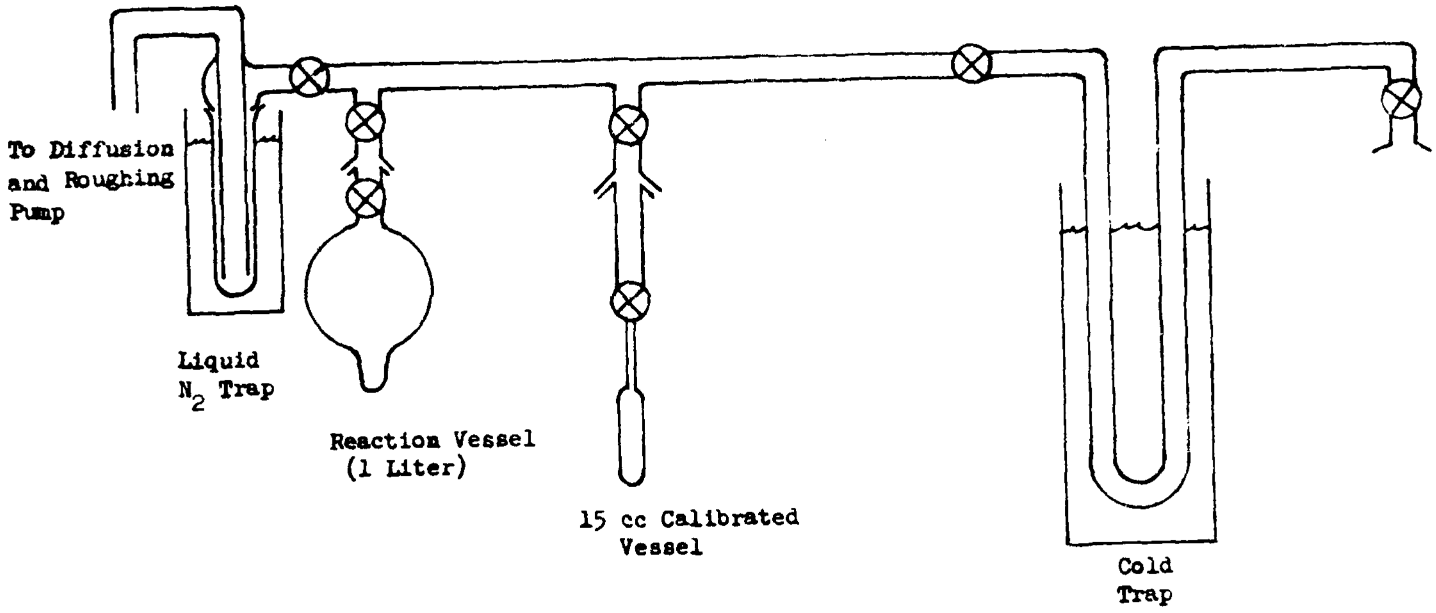
TABLE 1. Instrument Calibration Data

Instrument Settings:

Pulse Height Analyzer Settings:	400 (Left), 432 (Right)
Amplifier Setting:	1 (Coarse), 48 (Fine)
High Voltage Setting:	700 Volts

Date: October 17, 1968

Tube Number	True Activity (CPM)	Instrument Reading (CPM	Efficiency (Percent)
1	488, 200	80,830	16. 56
2	244, 100	40, 416	16. 56
3	122, 050	19, 980	16. 37
4	61, 025	9,836	16. 12
5	30, 513	4,892	16. 03
6	15, 257	2, 414	15. 82
7	7, 629	1, 199	15. 72
8	3, 815	584	15. 31
9	1, 908	290	15. 20
10	954	145	15. 20



Note: Main Tubing, Std. 15 mm
All Joints, Std. 10/30
All Stopcocks Fischer-Porter Teflon Type

FIGURE 8. Apparatus for Preparation of High-Purity N_2O_4

vacuum line was equipped with Fischer-Porter Teflon stopcocks in order to minimize use of stopcock grease. Connections to the vacuum line were made through 10/30 ground glass joints lubricated with Kel-F No. 90 grease. Two traps were incorporated into the line: a liquid, nitrogen-cooled trap which separated the vacuum manifold from the diffusion pump and a "U"-trap employed in low temperature distillation. Prior to admitting a substance, all glass apparatus was thoroughly flamed out under dynamic vacuum.

The reaction between NO and O_2 was carried out in the one-liter reaction vessel pictured in Figure 8. About 15 grams of gaseous NO (99%, The Matheson Company) was slowly passed through the "U"-trap cooled with a trichlorofluoromethane slush bath (-112°C). The NO was condensed in the reaction vessel with the aid of liquid nitrogen. Oxygen was then added to the reaction vessel in 1.0 - 1.5 gram portions. The O_2 was passed through a drying tube prior to passage through the -112°C trap. Upon slight warming the reaction occurred readily. The mixture was refrozen at -196°C, and another 1.0 - 1.5 gram portion of O_2 was added. This procedure was repeated until the reaction was complete. (Caution: NO has a vapor pressure of 1 atm at -152°C. When appreciable quantities of NO are in the vessel, the temperature must not be allowed to rise much above -152°C, to avoid a dangerously high pressure.)

The reaction was judged to be essentially complete when the N_2O_4 could be frozen to a white solid showing no trace of color. At this point excess O_2 (about 1.5 grams) was added to the N_2O_4, and the contents of the vessel were allowed to stand at room temperature for a few hours with occasional shaking. The unreacted excess O_2 was then removed by pumping at -196°C.

Measurement of the desired amount (15 cc) of N_2O_4 was accomplished by distilling the liquid into a calibrated 15 cc vessel. The N_2O_4 was then distilled from the calibrated vessel to the reaction tube.

Nitrosyl chloride, required in one of the experiments, was prepared by the reaction of NO with Cl_2. The product was purified by low temperature vacuum distillation.

4.0 RESULTS

Figures 9 to 14 summarize the dissolution data obtained as a function of temperature and with various impurities added. Besides the precautions taken in calibration to minimize errors, each point in these figures represents at least a total count of 5000. This count corresponds to a statistical error of about 3 percent at a 95 percent confidence level. All the rate results obtained exhibited the same general behavior — a rapid, almost linear initial rate of dissolution followed by a leveling-off of the rate. The figures show that the dissolution was 70 - 80 percent complete after one hour, with another 15 - 20 hours required to reach essentially complete saturation of the N_2O_4.

4.1 EFFECTS OF TEMPERATURE

Figure 9 presents data obtained when a sample (Sample No. 5) was carried through a step temperature change. Since the immersion time at each of the four temperatures was only 2 to 3 hours, complete saturation was not reached, and the four level portions of the curve should be regarded as corresponding to about 80 percent of saturation. In Figure 10 the four levels of Figure 9 are plotted as a function of temperature. The solubility is seen to vary linearly with temperature in the range 32 - 117°F.

The data of Figure 9 were obtained by carrying the same iron sample through the various temperature changes, and there is the question of the effect of prior reaction at lower temperature on succeeding reactions at higher temperature. To obtain some idea of this effect, a second iron sample (Sample No. 2) was studied at 75°F. The results obtained are presented in Figure 11. Comparing these results with the 74°F curve of Figure 9, it is seen that the solubility limits are about the same for both curves.

4.2 EFFECTS OF WATER

Several studies were conducted on the effects of addition of water. A rate curve at 116.6°F was run with a water concentration of 0.107 percent (Figure 12). In addition, miscellaneous studies were made in which water was added to two samples after completion of runs with pure N_2O_4.

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The results of Figure 12 indicate that 0.107 percent water increased considerably the solubility of iron in N_2O_4. The solubility limit increased by a factor of about two, being about 1.2 PPM for pure N_2O_4 at 116.6°F and about 2 PPM when water was added at the same temperature. From the data taken it is difficult to make a quantitative comparison of the effects on the dissolution rate.

In one miscellaneous study, water was added to sample No. 2 (Figure 11) after completion of the high purity N_2O_4 run. Initially, 15 PPM of water was added, with no resulting increase in count over the saturation level with pure N_2O_4. Then the water concentration was increased to 460 PPM, and an increase in concentration by about 30 percent over saturation resulted. In a second related experiment, 1 percent by weight water was added to sample No. 5 after completion of the run with pure N_2O_4. A large increase in the amount of dissolved iron was noted after a few minutes immersion time at room temperature. After a few hours immersion, the amount of iron in the N_2O_4 was found to be about 10 PPM. The iron sample was then immersed in the N_2O_4 for about a month. At the end of this period, the reaction tube was found to contain many colorless transparent crystals. Some of the crystals were about 2 mm long, and had the shape of rectangular plates.

4.3 EFFECTS OF NO AND NOCL

Figure 13 presents results obtained upon addition of 0.83 percent NO at 116.6°F. The rate curve followed the normal trends, but the solubility limit was depressed by about 20 percent when compared with the high purity N_2O_4 run of Figure 9.

Figure 14 presents results obtained at 116.6°F when 0.07 percent chlorine as NOCl was added. In this case the curve deviated somewhat from the norm in that the leveling-off was much more gradual.

4.4 VOLATILITY

Since during the rate experiments radioactive iron had gone into solution in N_2O_4, an excellent opportunity was provided to test the volatility of the iron compound upon distillation. The N_2O_4 in two of the reaction tubes used was subsequently distilled into clean tubes and a count taken of the distillate as well as the residue. It was found that all the radioactivity remained in the residue. It was concluded that the iron compound in solution was not volatile.

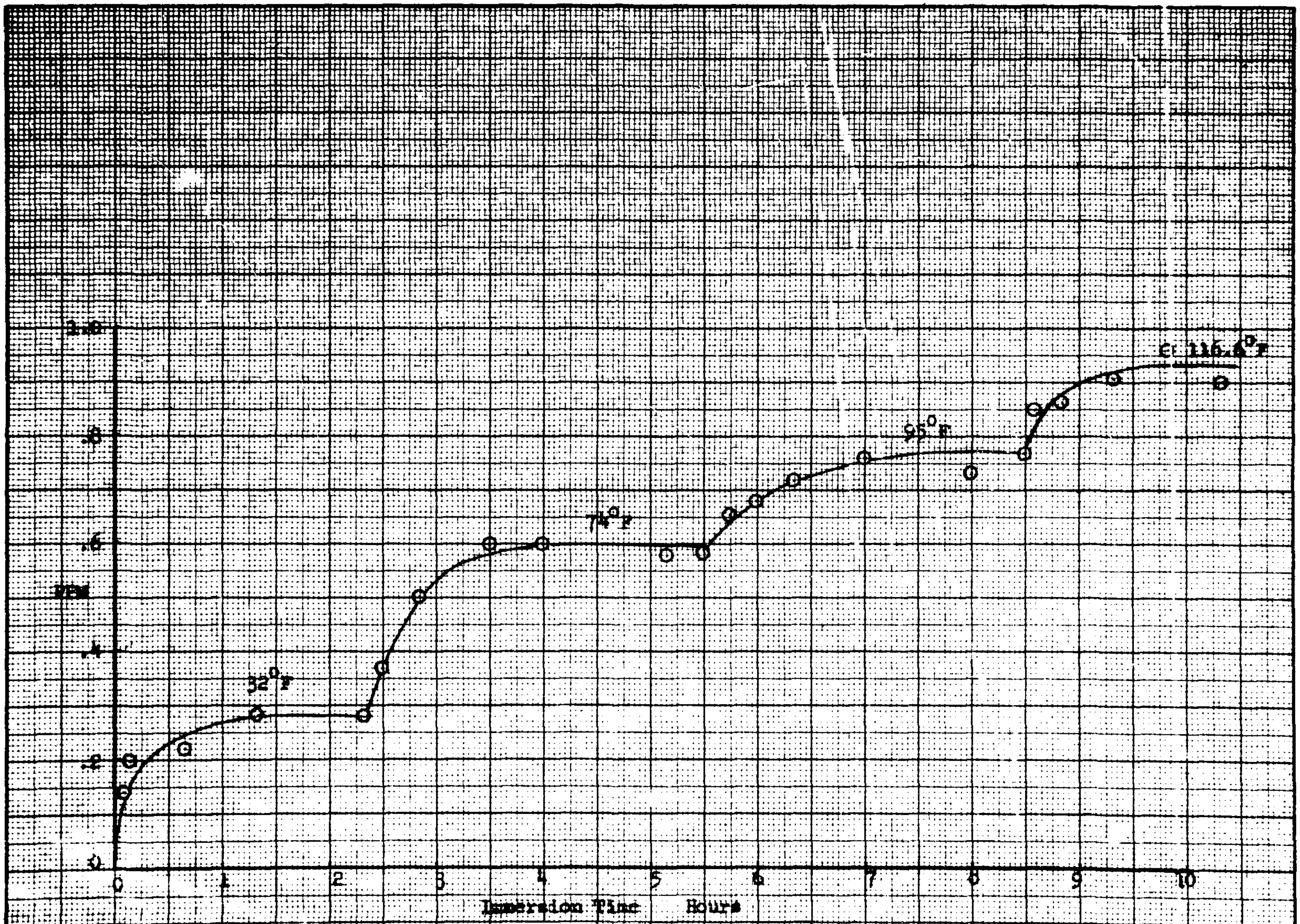

FIGURE 9. Effect of Temperature on the Solubility of Iron In Nitrogen Tetroxide (Sample No. 5)

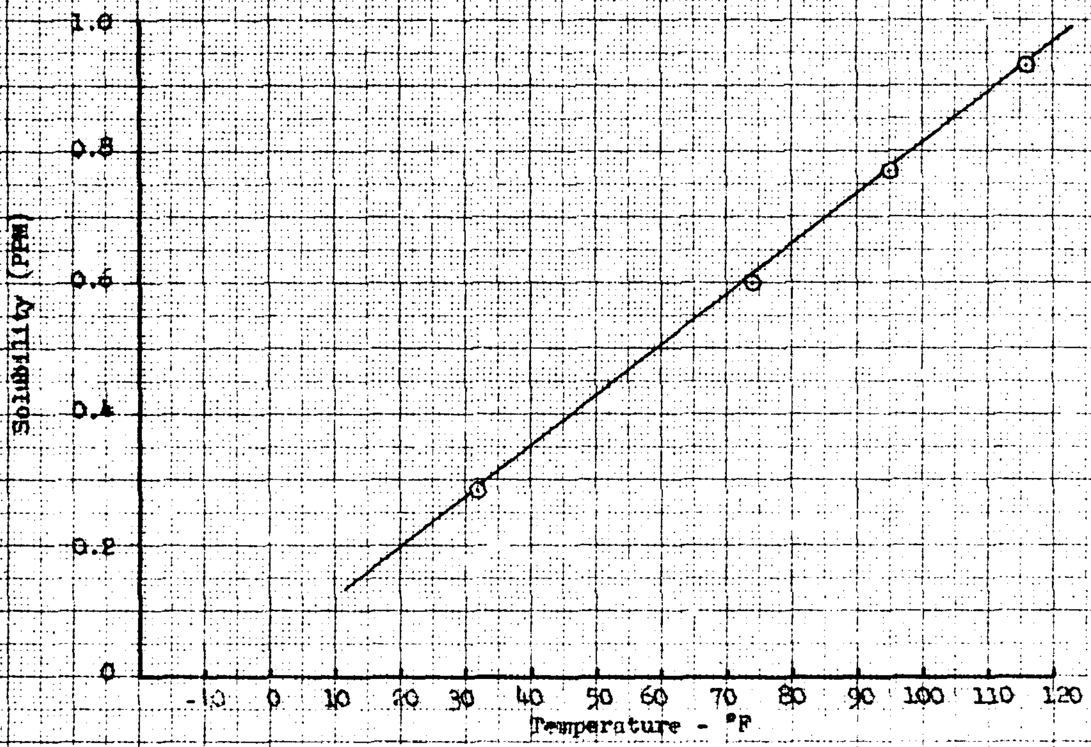

FIGURE 10. Solubility as a Function of Temperature

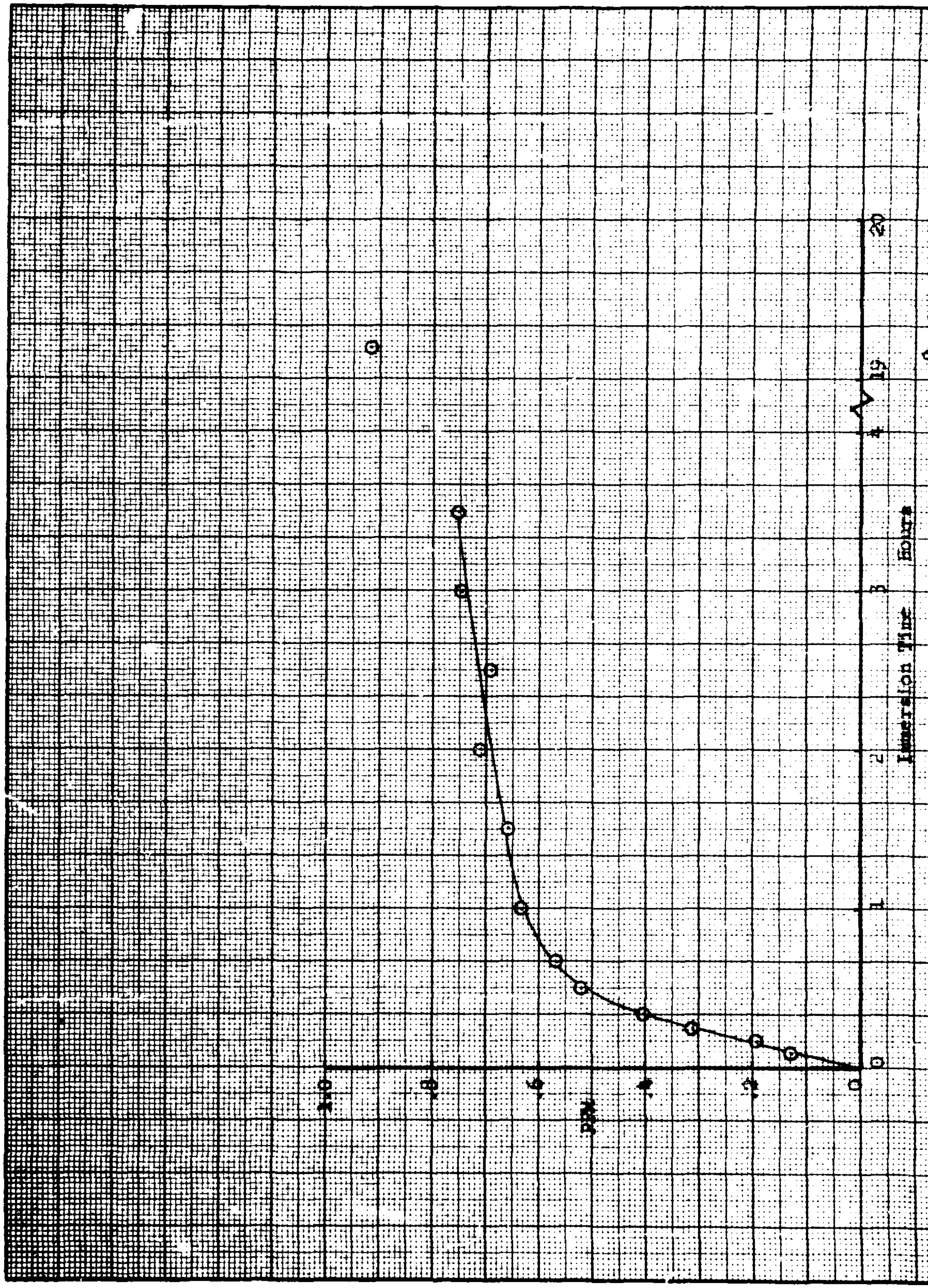

FIGURE 11. Dissolution of Iron in Pure N_2O_4, T = 75°F (Sample No. 2)

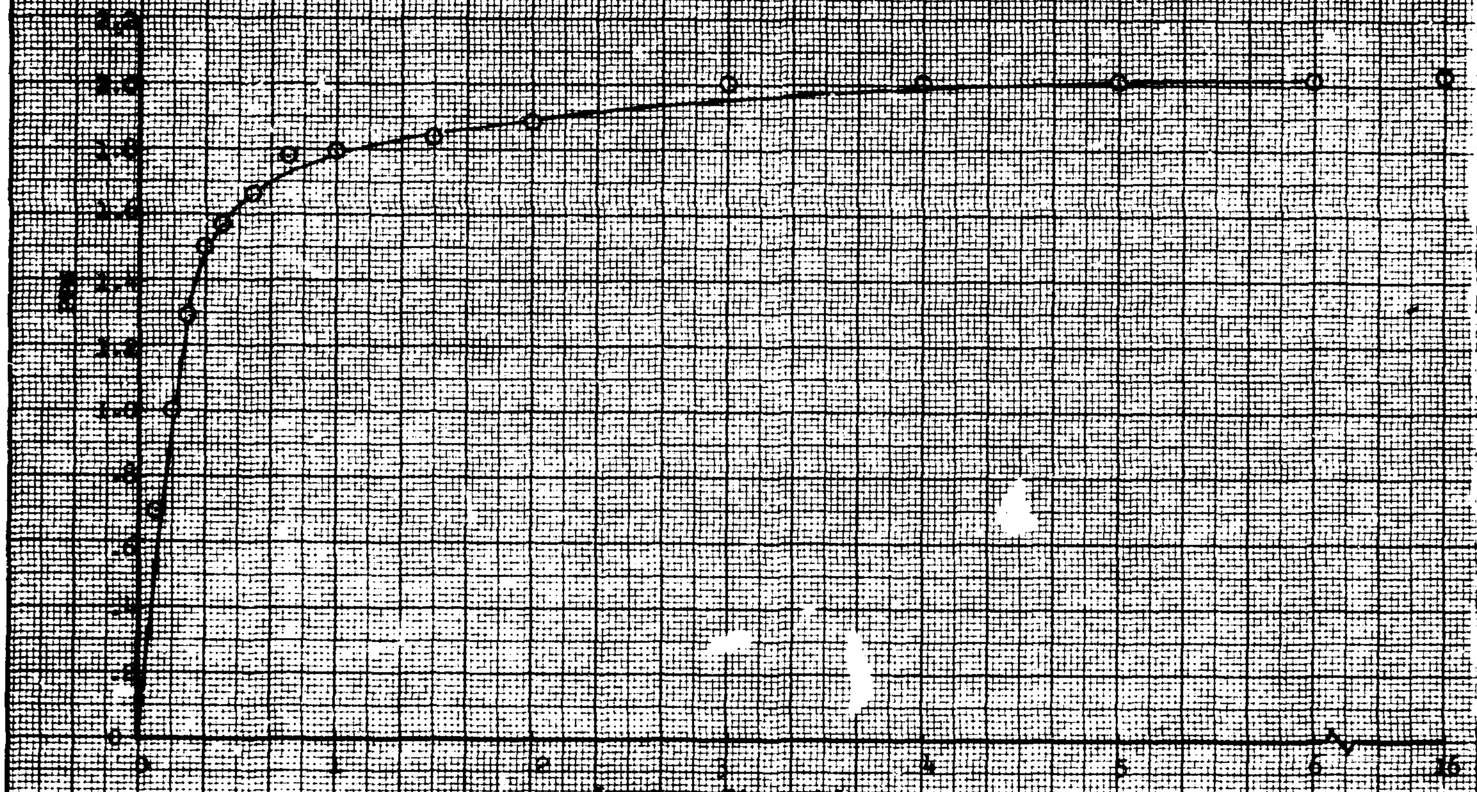

FIGURE 12. Dissolution of Iron in N_2O_4 Containing 0.107% H_2O, T = 116°F (Sample No. 2)

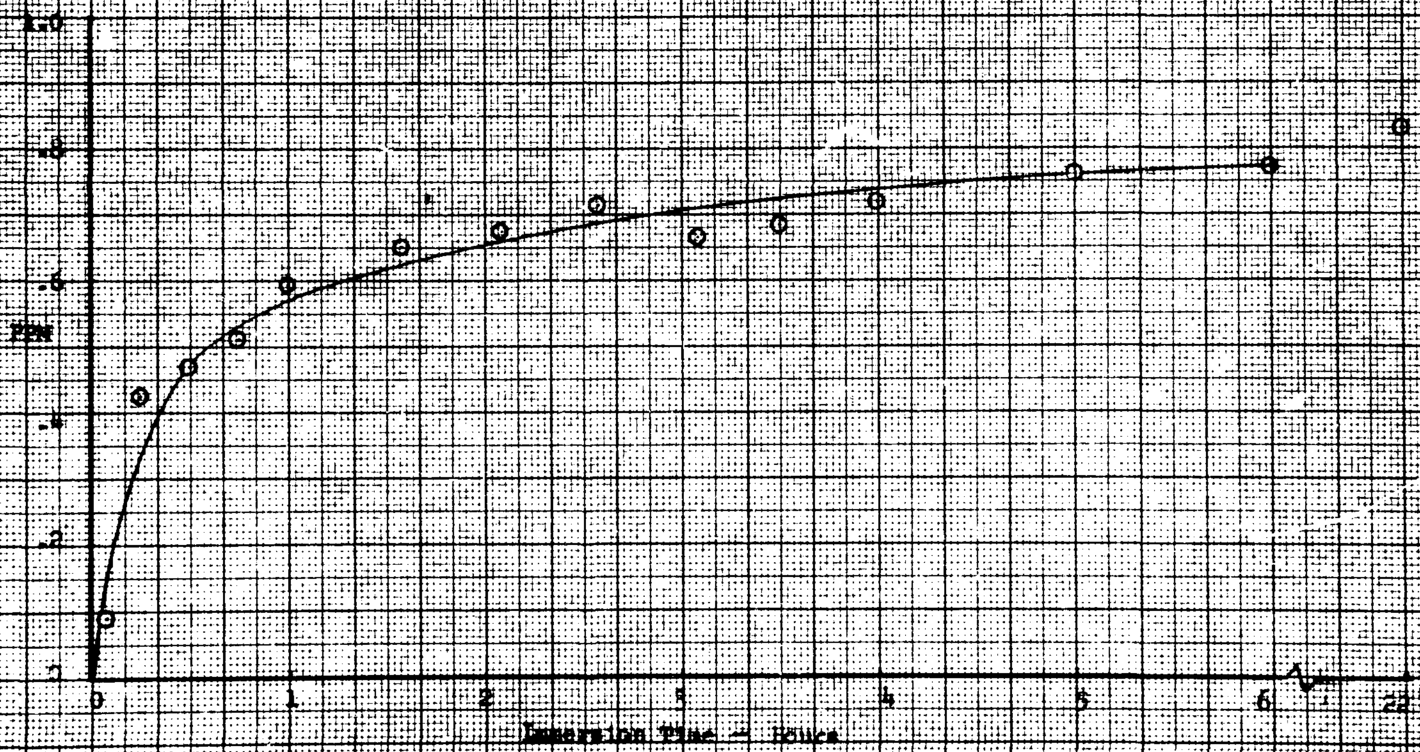

FIGURE 13. Dissolution of Iron in N_2O_4 Containing 0.83% NO, T = 116.6°F (Sample No. 4)

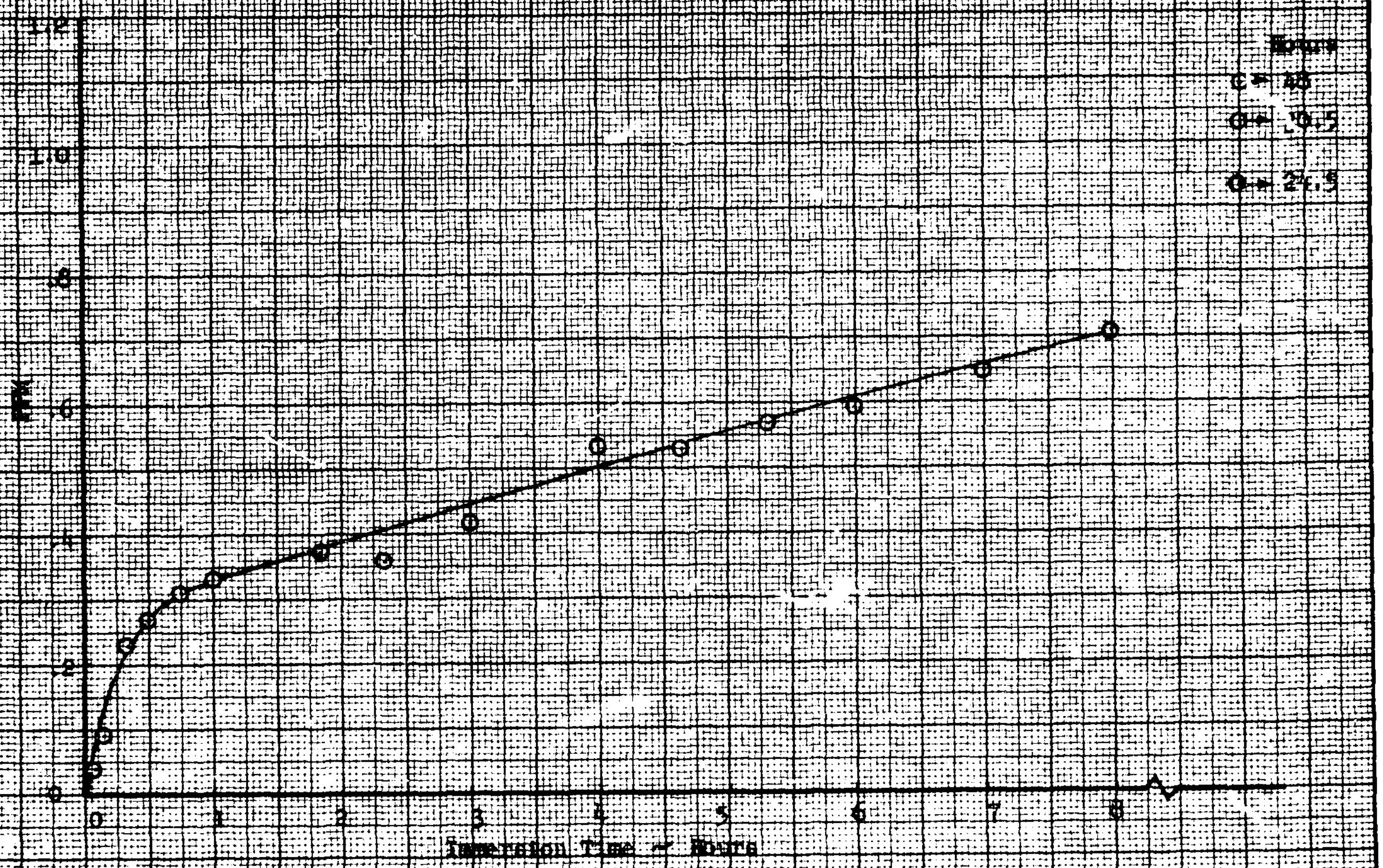

FIGURE 14. Dissolution of Iron in N_2O_4 Containing 0.47% Chlorine as NOCl, T = 116.6°F (Sample No. 4)

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5.0 DISCUSSION

The results of Figures 9 to 14 show that the radioactive tracer technique provides a powerful, accurate method for the study of dissolution. Besides its inherent sensitivity at low concentrations, the method has the advantage of being independent of the chemistry of the system. Thus, it can be extended to a large number of related studies.

Perhaps the most outstanding features of the results obtained are the leveling-off of the iron concentration in solution and the nearly linear increase of saturation concentration with temperature. This behavior is reminiscent of the solubility of a salt in a solvent; and in fact, a solubility mechanism is consistent with the observations.

Another mechanism that would be consistent with the results obtained is one in which a reactant is exhausted with time It has been suggested that water, perhaps in the form of nitric acid, may play a key role as a reactant. If this mechanism were involved one would not expect the increase of solubility noted with temperature, unless the reactant was also somehow produced as a function of temperature. Other evidence also suggests that this mechanism was not at play. When water was added at a concentration of the order of 15 PPM no noticeable change in reaction rate was observed. Yet this water concentration would be sufficient to cause a large increase in rate if indeed water were a reactant.

Perhaps a more plausible mechanism is one involving reaction at the iron surface followed by dissolution of the product formed. In this mechanism, N_2O_4 would react rapidly with the surface to form a ferric compound (probably $Fe(NO_3)_3$) with the reaction subsiding when the surface was covered with a ferric nitrate layer. If the compound formed then dissolved in N_2O_4 in true solubility fashion, the behavior observed would result.

It is quite possible that the role played by water in this mechanism is more of a secondary type -- as an agent that breaks up the protective layer. Exactly how the layer is broken up is not known, but the adsorption of nitric acid or water onto the

$Fe(NO_3)_3$ surface may well make the protective layer less adherent. (Although water reacts with N_2O_4 to form HNO_3, $Fe(NO_3)_3$ may be capable of dehydrating HNO_3 to form a ferric nitrate hydrate. It is well known that $Fe(NO_3)_3$ cannot be obtained in pure form; it always has water of hydration. Thus anhydrous $Fe(NO_3)_3$ would be expected to have a very strong affinity for water.) As the layer breaks up, a colloidal suspension would be expected initially. With further break-up of the layer, some coagulation would eventually occur, resulting in the formation of a precipitate. This would explain the precipitate sometimes observed in N_2O_4 systems. It would also explain the results noted in this study; that is, when one percent by weight of water was added to the iron - N_2O_4 system, colorless crystals formed after a few weeks.

For immediate application to spacecraft systems, some practical use can be made of the rate and solubility data obtained. For example, as a means of alleviating the flow decay problem, it might be desired to keep the N_2O_4 unsaturated above a given temperature. Referring to Figure 10, it is seen that if N_2O_4 can be obtained with an initial (at time of flight) iron concentration of less than 0.4 PPM, it will be unsaturated above about 40°F. If in addition the water content is kept less than 400 PPM, its effect on the solubility is only about 20 percent. For these conditions it is seen that the chances of iron-induced, flow decay occurring for a lunar mission of short duration are small, if indeed, the N_2O_4 must be saturated before the iron precipitates.

The rates of dissolution can be easily calculated, taking into account the surface area of the iron samples (30 sq in) and the weight of the propellant (15 cc of N_2O_4 = 21.6 gms). In the case of pure N_2O_4 at room temperature, the rate of dissolution initially is of the order of 10^{-8} gms iron/in^2-min. At this rate many propellant tanks will saturate in less than a month's time. For example, in the case of a steel tank having a surface area of 25,000 in^2 and loaded with 14,000 lbs. of N_2O_4, it would take about 12 days to reach saturation at a constant dissolution rate of 10^{-8} gms iron/in^2-min. Actual saturation time would of course be somewhat longer because of the leveling of the rate of dissolution. Thus, the chances of flow decay occurring if the N_2O_4 were purified before the flight would be greatly reduced. These results are subject to the constraints of the experimental work; e.g., the effects of water, the use of iron rather than stainless, etc., which need further investigation.

Another result of considerable practical importance is the volatility of the iron in solution. In a few experiments the N_2O_4 was distilled from the reaction tube to determine the iron carryover. In no case did iron carry over. It was concluded that the iron compound was nonvolatile, and thus distillation is an excellent purification scheme.

6.0 CONCLUSIONS AND RECOMMENDATIONS

The dissolution of metallic iron in N_2O_4 is consistent with a solubility-type mechanism. The iron build-up in solution increased rapidly with time and levels off to a saturation limit in a few hours. The saturation level increases linearly with temperature over the range of 32 - 117°F.

The addition of the impurities H_2O, NO and NOCl in small quantities had varying effects on the dissolution. Water at concentrations of about 0.1% by weight had the effect of increasing the solubility by a factor of about two. At concentrations of 15 PPM, water had no effect on solubility over that of pure N_2O_4, while at concentrations of 1% a very large increase in solubility resulted followed by degradation of the sample and formation of colorless, transparent crystals. Neither the addition of NO (0.8%) or NOCl (0.07% chlorine) had much effect on the solubility limit, although the presence of NO depressed the solubility slightly. The presence of NOCl apparently changed the nature of the dissolution rate, since the leveling-off occurred more gradually.

Previous work has implied that the rate of dissolution is fast, although no quantitative data have been reported. Data taken from Figure 11 indicate that a dissolution rate of 10^{-8} gms. iron/in^2-min is of the correct order of magnitude in the case of high purity N_2O_4 at room temperature. This implies that for many propellant tanks, it will take several days to saturate with iron. For example, it is estimated that a cylindrical steel tank fully loaded with 14,000 lbs. of N_2O_4 will take about 12 days to saturate assuming initial iron-free N_2O_4. However, these results are subject to change, if one accounts for the effects of other variables such as the presence of water. Volatility studies, conducted as a side-line to the main experimental work, indicate that the iron compound in solution is non-volatile so that purification by distillation of N_2O_4 should be practical. However, in applications to spacecraft it might be just as important to reduce the water content since water has a large effect on solubility above 0.1%.

The radioactive tracer technique has proven to be an excellent tool for the study of dissolution, and it is recommended that the technique be exploited in future related studies. There are various directions which these studies can take, but it is recommended that obtaining basic data on flow data should take priority. Recommended problems for study are the following:

- Extension of the present work to other temperatures and concentrations.
- Study of the dissolution of stainless steel.
- Accurate analysis of water in propellants.
- A program for analyses of impurities in N_2O_4 using the tracer technique
- Extension of the above to other propellants.
- Engineering applications for diagnostics of flow decay.

7.0 NOMENCLATURE

A_{Fe}	Atomic Mass Number of Iron, g/g-mole
$(CPM)_{BG}$	Count Rate of Solution Corrected for Background
$(CPM)_{Fe}$	Count Rate with Iron Sample in Place Corrected for Background
$(CPM)_{Co}$	Count Rate with Co-60 Standard in Place Corrected for Background
I_{Co}	Radiation Intensity of Co-60 Standard, d/m-cm^2
I_{Fe}	Radiation Intensity of Fe-59 Sample, d/m-cm^2
M_{Fe}	Mass of Iron Sample, Gms
N_A	Avogadro's Number, atoms/g-mole
N_T	Total Atoms of Iron Present in Sample
N_{TS}	Total Atoms of Iron Transferred to Solution After Immersion Time t
N_{59}	Total Atoms of Iron-59 Present in Sample
N_{59S}	Total Atoms of Iron-59 Transferred to Solution after Immersion Time t
PPM	Parts per Million by Weight
$(S_{Co})_o$	Initial Activity of Standard Co-60 Solution, d/s
S_{Co}	Activity of Standard Co-60 Solution at Calibration, d/s
S_{Fe}	Activity of Iron Sample at Calibration, d/m
S_{59S}	Total Activity of Iron-59 in Solution, d/m
t	Immersion Time, min
t_R	Irradiation Time, hr
t_{17}	Time from October 17, 1968, days
t_{59}	Time from Calibration of Iron Sample to Dissolution Experiment, days
t_{59}^R	Time from Irradiation of Iron to Dissolution Experiment, days
t_{60}	Time from Calibration of Standard Co-60 Solution to Calibration
V_{NTO}	Volume of N_2O_4 used in Experiments, cc

Greek Symbols

ρ_{HTO}	Density of N_2O_4, g/cc
λ_{59}	Disintegration Constant of Fe-59, min^{-1}
λ_{60}	Disintegration Constant of Co-60, yr^{-1}
ϵ	Instrument Efficiency

8.0 REFERENCES

1. "Project Gemini - A Technical Summary," McDonnell Douglas Corporation, June 1968, NASA CR-1106

2. "The Nitrogen Tetroxide Flow Decay - Final Report," Rocketdyne Report R-6385, June 1966

3. "Investigation of the Formation and Behavior of Clogging Material in Earth - and Space-Storable Propellants," TRW Quarterly Progress Report, 08113-6013-R000, March 9, 1968 to June 9, 1968.

4. "Methods for Elimination of Corrosion Products of Nitrogen Tetroxide," Technical Report AFRPL - TR-67-277, July 1967.

5. "Investigation of the Formation and Behavior of Clogging Material in Earth- and Space-Storable Propellants," TRW Report 08113-6007-R000, October 1967.

LIMITATIONS

This document describes processes and equipment which are being considered for possible patent protection by The Boeing Company Reference: Patent Disclosure Number 69-7 "Process and Equipment for Diagnostics of Flow Decay and Related Problems," by J. B. Romero. Release of the document outside should first be cleared by the Patent Staff.

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