

**INVESTIGATION OF THE EFFECTS OF PRESSURE AND HYDROGEN  
CONCENTRATION ON AMMONIA SYNTHESIS  
UNDER NEUTRON IRRADIATION**

by

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## I. INTRODUCTION

The study of chemical reactions induced or accelerated by nuclear radiations is important to the fields of nuclear physics, physical chemistry, and all branches of nuclear engineering. Studies of nuclear structure, reaction kinetics, and nuclear reactor poisoning and burnup are, at present, only beginning to uncover the large amount of useful information concerning these reactions.

From the standpoint of the nuclear reactor design engineer, some very important reactions take place as results of irradiation of the materials of construction, fuel, and coolant inside a nuclear reactor. One such reaction is the formation of nitric acid and ammonia by the action of thermal neutrons on water vapor. Any buildup of acid or base in an aqueous system creates corrosion problems, and the reactor design engineer has to solve these problems either by gas removal or by some other procedure.

The above mentioned reaction involves competition between water and hydrogen for gaseous nitrogen, but the mechanism of the

reaction is not fully understood. The reaction appears to involve a direct combination of hydrogen and nitrogen to form ammonia after decomposition of water to hydrogen and oxygen or after the reaction combining water vapor and nitrogen to form nitric acid and gaseous hydrogen.

The purpose of this investigation was to determine the effects of mild pressures and hydrogen concentration on the formation of ammonia by slow neutron irradiation of a gaseous nitrogen-hydrogen system.

## II. LITERATURE REVIEW

With the advent of the nuclear reactor as a primary power source, increasing attention has been focused on nuclear radiation as it affects materials used in the reactors. Radioactivity presents hazards in the investigations of these effects; and, although much research has been done in this field, the effects of nuclear radiation do not follow any ordinary scheme of chemical reaction except that the irradiation adds energy to the reaction system. Some of the reports of that group of investigations which have direct or indirect bearing on the problem of this investigation will be discussed in the following sections.

Much of this work, especially that which pertains directly to nuclear reactor design, is still classified material; but there is much literature in reactor and radiation chemistry which is helpful to the understanding of the problem. Because this investigation is included in the relatively new field of nuclear chemistry, a large section of this review contains the fundamental terms used in this field. Also, included in the review are discussions of chemical

analysis used in quantitative determination of ammonia in water and factors to be considered in the design, construction, and operation of the experimental apparatus.

### Definitions and Concepts

The following definitions and concepts are in general use in radiochemistry and nuclear physics, and they are used frequently in this discussion.

Activation Energy. The activation energy <sup>(34)</sup> of a system is defined as the minimum energy a system must acquire before any reaction can occur. The energy of a system can be increased in many ways; the method of increasing the energy which is most important in this investigation is the addition of energy in the form of energetic nuclear particles. Reaction between two molecules occurs in this case when the original energy of the molecules supplemented by energy added to the molecules or to a reaction surface by radiation equals or exceeds the activation energy of the two molecules.

Neutron. The neutron is defined by Halliday <sup>(19)</sup> as an electrically neutral nuclear particle of mass approximately one

atomic mass unit. Neutrons are torn away from a nucleus by physical reactions such as fission or the action of an alpha particle (helium nucleus) on a nucleus. Neutrons generally react with nuclei more easily than charged particles because of the absence of electrical repulsion. Thermal neutrons, or neutrons in thermal equilibrium, travel relatively slowly and, consequently, are more reactive with nuclei than fast neutrons.

Gamma Ray Emission. Gamma radiation <sup>(18)</sup>, or gamma rays, is quantized electromagnetic radiation differing from light only in that its wavelength is much shorter. This radiation represents a method of emission of excitation energy by a nucleus. Gamma radiation produces ionization reactions in matter, and a gamma ray can be stopped by one interaction with a nucleus.

Electron Volt. The most convenient unit of energy <sup>(35)</sup> for use in the study of nuclear reactions is the electron volt (symbol: ev). The electron volt is defined as the amount of kinetic energy acquired by a unit electronic charge from passage through an electrical potential of one volt.

Conversion units and multiples in use are:

$$1 \text{ ev} = 1.60 \times 10^{-12} \text{ erg}$$

$$1 \text{ mev} = 10^6 \text{ ev}$$

$$1 \text{ kev} = 10^3 \text{ ev.}$$

Isomeric Transition. Isomeric transition (7, 18) is a process by which nuclear excitation energy is emitted from a nucleus, the reaction producing a gamma ray and an isomer of the excited nucleus at a lower energy state. It has been proposed (5, 17, 26, 30) that this process produces activation energy for many chemical reactions which are induced or accelerated by neutron capture.

Neutron Capture. The capture of a neutron by a nucleus may produce many different reactions depending on the nucleus and the energy of the captured neutron. For slow neutrons, probable reactions (31) are radiative capture and the (n, p) reaction in which the products are a proton and a nucleus of the same mass number and with atomic number greater by one from the original. Radiative capture involves the collision of a nucleus with a slow neutron with subsequent formation of a nucleus of the same element with mass number one unit greater and the emission of gamma radiation. Both the (n, p) reaction, which is exothermic, and the gamma emission represent means of adding energy to an enclosed system.

Neutron Scattering. Neutrons are scattered by elastic collisions with nuclei in which the neutrons are not captured. The collisions cause the neutrons to lose energy or to be slowed down. If very slow

neutrons are desired, the neutrons should have to pass through a large amount of scattering (or slowing down) material. Nuclei of low atomic weight are the best scatterers (or moderators) because they do not, as a rule, capture many neutrons and because it requires few collisions for the neutron to lose a large amount of energy.

Neutron Cross Section. The description of interaction of neutrons with matter can be made quantitative by the use of the concept of cross section (12, 13). The neutron cross section,  $\sigma$ , of a nucleus is a measure of the probability of interaction of a neutron with the nucleus. Another concept is that the cross section is the area of the wave function of the nucleus which is seen by an approaching neutron. Cross sections are measured in units of barns, where one barn is defined to be  $10^{-24}$  square centimeters.

Generally, the total cross section of a nucleus corresponding to all interactions with a nucleus can be divided into the following cross sections:

$$\sigma_t = \sigma_a + \sigma_f + \sigma_s$$

where:

$\sigma_a$  = cross section for neutron absorption (capture), barns

$\sigma_s$  = cross section for neutron scattering, barns

$\sigma_f$  = cross section for fission, barns

$\sigma_t$  = cross section for all interactions, barns.

Neutron Flux. The concept of neutron flux, or flow, involves the current of neutrons in a given volume of material. Neutron flux is defined <sup>(14)</sup> by the following equation, which has been derived for monoenergetic neutrons:

$$\phi = nv$$

where:

$\phi$  = neutron flux, neutrons per square centimeter-second

$n$  = neutron density, neutrons per cubic centimeter

$v$  = neutron velocity, centimeters per second.

Since  $\phi$  is the sum of the distances traveled by the neutrons in one cubic centimeter in one second, it is not a true flux and is sometimes called the track length. The more general definition <sup>(14)</sup>, for neutrons of many different energies, is:

$$\phi = \int_0^{\infty} n(E) v dE$$

where:

$\phi$  = flux, neutrons per square centimeter - second

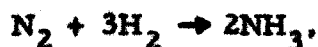
$n(E) dE$  = number of neutrons of energy from  $E$  to  $E + dE$ ,  
neutrons per cubic centimeter

$v$  = neutron velocity corresponding to neutron velocity  $E$ ,  
centimeters per second.



### The Ammonia Synthesis Reaction

Because of the great importance of ammonia in the chemical processing and manufacturing industries, the ammonia synthesis reaction,



has been studied extensively with regard to the kinetics, catalysis, and thermodynamics of the reaction.

Mechanism. The generally accepted statement <sup>(22)</sup> regarding the ammonia synthesis reaction is that it is a surface activated reaction. Molecular hydrogen is adsorbed on the surface as atomic hydrogen. This very active form of hydrogen then reacts with nitrogen to form the ammonia or to form an activated intermediate compound which, in turn, reacts with molecular hydrogen to form the ammonia molecule.

Catalysis. The catalysis most used in the synthesis of ammonia is a form of iron promoted by some other material. Commercial catalysts cited by Hein <sup>(24)</sup> include iron promoted with alkali metal oxides, iron promoted with an amphoteric metal oxide, and iron promoted with a metal cyanide. These catalysts provide the adsorption and reaction surface, and they are employed in the form of packed beds through which the mixture of hydrogen and nitrogen to be reacted flows.

In this manner, a large surface area for reaction is presented to the synthesis gases.

Reaction Rates. Inspection of the equation for the ammonia synthesis reaction as presented above reveals that the reaction involves a reduction in volume, from four moles to two, in a gaseous system. This means that an increase in pressure will tend to force the reaction toward the right, or toward completion. For this reason, many industrial ammonia synthesis processes <sup>(36)</sup> involve pressures up to 1000 atmospheres of pressure; these include the modified Haber process at 250 atmospheres, 550 degree Centigrade, and 20 per cent conversion with recirculation; the DuPont process at 1000 atmospheres, 500 degree Centigrade, and good conversion with recirculation; and the Mont Cenis process at 100 atmospheres, 425 degree Centigrade, and about 15 per cent conversion with recirculation.

The equilibrium constant, K, is a thermodynamic measure of the completeness of a reaction. The expression which defines K thermodynamically is <sup>(22)</sup>:

$$\Delta F = -RT \ln K$$

where:

$\Delta F$  = free energy of reaction, calories per mol

R = molar gas constant, 1.987 cal/mol-°K

T = absolute temperature, °K

K = equilibrium constant, dimensionless.

It is to be expected that the completeness of the ammonia synthesis reaction decreases with increasing temperature because the reaction is exothermic.

It has been reported by Harrison and Kobe<sup>(22)</sup> that, for the ammonia synthesis reaction, the equilibrium constant decreases with increasing temperature up to a temperature of about 1100 degrees Centigrade; at temperatures higher than this, the equilibrium constant increases. The variation of the equilibrium constant with temperature for the ammonia synthesis at one atmosphere pressure is shown on Figure 1, page 12.

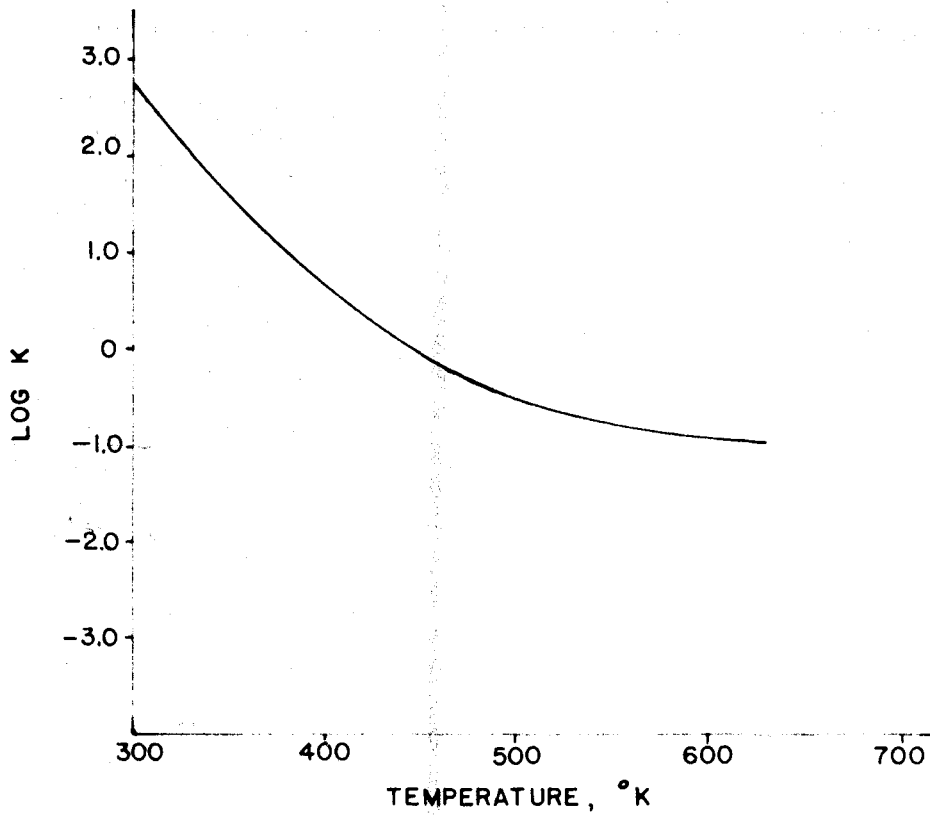


FIGURE 1. VARIATION OF EQUILIBRIUM CONSTANT, K, WITH  
TEMPERATURE AT ONE ATMOSPHERE PRESSURE FOR  
THE AMMONIA SYNTHESIS REACTION

HARRISON, R. H., AND K. A. KOBE: THERMODYNAMICS OF AMMONIA SYNTHESIS AND OXIDATION, CHEM. ENG. PROGRESS, 49, 349-58 (1953).

### Neutron Radiation Chemistry

Neutron radiation chemistry concerns the effects of neutron irradiation on chemical reactions and chemical species. A review of some radiation chemistry research, in the portion of this field which pertains to reactions induced or accelerated by neutron capture, is presented in the following section.

Isomeric Transition. It has been proposed by many researchers<sup>(5, 10, 11, 30)</sup> that reactions observed under neutron bombardment may depend, to a large extent, on isomeric transition for their activation energy. The gamma radiation produced in this process can be absorbed by atoms in a system and thereby may increase their individual energies. Increased activity of alkyl bromides containing radioactive  $\text{Br}^{80}$  indicates<sup>(8, 10, 11)</sup> that gamma rays from the isomeric transition of  $\text{Br}^{80*}$  to  $\text{Br}^{80}$  (where \* indicates an excited state of an atom) tend to concentrate  $\text{Br}^{80}$  in a combined state. The radiobromine atoms have been found<sup>(5, 21, 30)</sup> to replace other halogen atoms easily; this the stable  $\text{Br}^{79}$  will not do.

Ionization Reactions. According to Libby<sup>(30)</sup>, phosphorus and arsenic in the plus five valence state expel divalent oxygen ions and halate ions are reduced by expulsion of atomic oxygen, under neutron

irradiation. Libby<sup>(30)</sup> also states that there is a possibility of a rough rule that electrons will be distributed in the decomposition products of such reactions in about the same order as in the original molecule. It is suggested by Wahl and Bonner<sup>(40)</sup> that the transfer of electrons and other charged particles from reactions in a gaseous phase may be hampered by the essentially electrically neutral nature of the gas mixture used. It is significant to this investigation that one of the reactions cited in this discussion was the  $N^{14} (n, p) C^{14}$  reaction.

Effects of Phase and Concentration in Hot Atom Chemistry. The Szilard-Chambers reaction has been studied by Libby<sup>(30)</sup> and others<sup>(5)</sup> with respect to the effects of phase, concentration, and temperature. This reaction involves the separation of radioactive  $Br^{80}$  from neutron irradiated bromine by the selective replacement of another halogen atom. The  $Br^{80}$  will replace chlorine from carbon tetrachloride in the liquid phase but not in the gaseous phase. Carbon tetrachloride is stable to attack by the  $Br^{79}$  and  $Br^{81}$  isotopes present in naturally occurring bromine. A linear increase in  $Br^{80}$  concentration caused a linear increase in the amount of chlorine replaced. It was also found that an increase in temperature had a negligible effect on the

amount of chlorine replaced by  $\text{Br}^{80}$ . These experiments indicate that both phase and concentration affect reactions initiated or accelerated by neutron bombardment.

Reactions of Nitrogen with Neutrons. The total thermal neutron cross section for nitrogen is reported <sup>(15)</sup> to be 12.7 barns, and the absorption cross section under the same conditions is reported <sup>(15)</sup> to be 1.5 barns. The scattering cross section is given by Glasstone and Edlund <sup>(15)</sup> to be 11.2 barns. This nitrogen is composed almost entirely of  $\text{N}^{14}$ ; the atmospheric abundance of  $\text{N}^{15}$ , the only other isotope of nitrogen occurring naturally, is only about 0.365 per cent <sup>(32)</sup>. The thermal neutron absorption cross section for  $\text{N}^{15}$  is reported <sup>(15)</sup> to be less than 0.025 barns.

The  $\text{N}^{14}$  isotope has reported <sup>(32)</sup> cross sections for the  $\text{N}^{14}$  (n, p)  $\text{C}^{14}$  reaction and the  $\text{N}^{14}$  (n,  $\gamma$ )  $\text{N}^{15}$  reaction of about 1.75 and 0.1 barns, respectively. According to Johnson and Barschell <sup>(28)</sup>, 60 per cent of the energy released in irradiated gaseous nitrogen is from the exothermic  $\text{N}^{14}$  (n, p)  $\text{C}^{14}$  reaction.

Nitrogen bombarded with fast neutrons was reported by Johnson and Barschell <sup>(28)</sup> to possess gamma radiation resonance peaks at 499 and 600 kev. Millar and Bartholomew <sup>(32)</sup>, upon irradiation of nitrogen with slow neutrons, observed resonance peaks at 6.1 mev, 6.133 mev,

and 7.1 mev. The 6.1 mev resonance peak corresponds to the  $N^{14}(n, p)C^{14}$  reaction, and the other two high energy peaks correspond to two gamma rays from unstable  $N^{16}$  formed by the neutron capture reaction of  $N^{15}$ .

Reactions of Hydrogen with Neutrons. According to Glasstone and Edlund<sup>(14)</sup> and Hamermesh, Rings, and Wexler<sup>(20)</sup>, the thermal neutron scattering cross section for atomic hydrogen varies greatly with the neutron energy; over the thermal range,  $\sigma_s$  for hydrogen varies from 20 barns to 80 barns. The thermal neutron capture cross section for hydrogen is reported<sup>(14, 20)</sup> to be about 0.33 barns. The absorption of a neutron by a hydrogen atom produces a deuteron, which is stable; and this reaction is slightly exothermic. Neutrons are thus seen to have little effect on hydrogen atoms except to add energy by elastic collisions.

#### Chemical Reactions under Nuclear Reactor Conditions

The high intensities of different kinds of radiation inside a nuclear reactor produce many different types of reactions in the reactor coolant, moderator, and fuel. Many materials cannot be used inside a reactor because of radiation effects. One of the best reactor coolants has



proved to be water, but even water is attacked by radiation to some extent. The reactor design engineer must take into account neutron induced reactions in water systems in order to lessen the danger of rapid corrosion, fuel poisoning, and explosions within a reactor which is cooled by water.

Radiation Induced Reactions in Water. Hochanadel <sup>(25)</sup> has reported reactions of hydrogen and oxygen under reactor conditions. The combination of hydrogen and oxygen in water, under ionizing radiation of electrons, protons, and gamma rays to form hydrogen peroxide, reaches an equilibrium value as the peroxide decomposition rate becomes large. In the gaseous phase, hydrogen and oxygen also react to form water with the release of a large amount of energy. This reaction has nearly the same free energy change as does the nitrogen-hydrogen reaction to form ammonia.

Hart, McDonell, and Gordon <sup>(23)</sup> have found that ionizing radiation fails to decompose pure, air-free, liquid-water; but heavy particles, such as neutrons, decompose water into atomic hydrogen and oxygen. Water vapor in air is quite subject to ionisation by gamma radiation, and intense gamma irradiation of liquid water produces hydrogen peroxide.

Neutron Irradiation of an Air-Water System. The British researchers Bates, Linacre, Marsh, and Wright<sup>(2)</sup> have investigated the effects of reactor radiation on two-phase systems of water and air. Their experiments were performed in sealed, heated, 50 milliliter, silica tubes placed in the BEPO experimental pile at Harwell, England. The conditions in this reactor were a flux of approximately  $5 \times 10^{14}$  neutrons per square centimeter-second and very little ionizing radiation. The experiments were conducted at atmospheric pressure.

Results of Two-Phase Air-Water System Irradiation.

Analysis of the experiments mentioned above indicate formation of both nitric acid and ammonia in the gas phase. Nitric acid seems to have been formed by the overall reaction:



A large part of the energy into the system was accomplished by the  $\text{N}^{14}(\text{n}, \text{p})\text{C}^{14}$  reaction. Hydrogen produced in the formation of nitric acid combined, by unknown mechanism, with nitrogen in the gaseous phase to form ammonia.

Graphical results of the experiments by Bates, Linacre, Marsh, and Wright are presented in Figure 2, page 19, and on Figure 3, page 20.

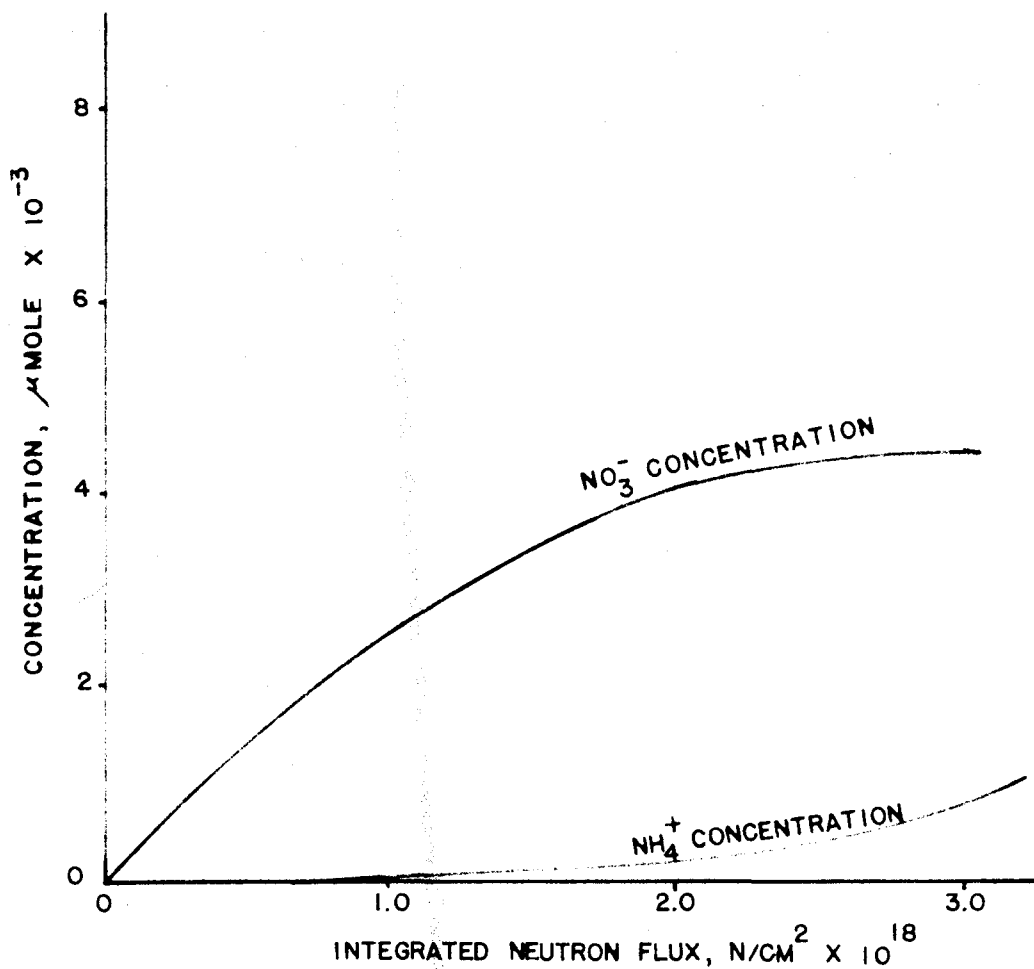


FIGURE 2. VARIATION OF  $NO_3^-$  AND  $NH_4^+$  CONCENTRATION WITH  
FLUX AT GAS-LIQUID VOLUME RATIO OF 2.0, CONSTANT  
VOLUME OF 50 MILLILITERS, AND  
ATMOSPHERIC PRESSURE

BATES, T. H. ET AL: EFFECT OF RADIATION ON HETEROGENEOUS SYSTEMS OF AIR AND NITROGEN AND WATER, PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON THE PEACEFUL USES OF ATOMIC ENERGY, 1, 560-568 (1955).

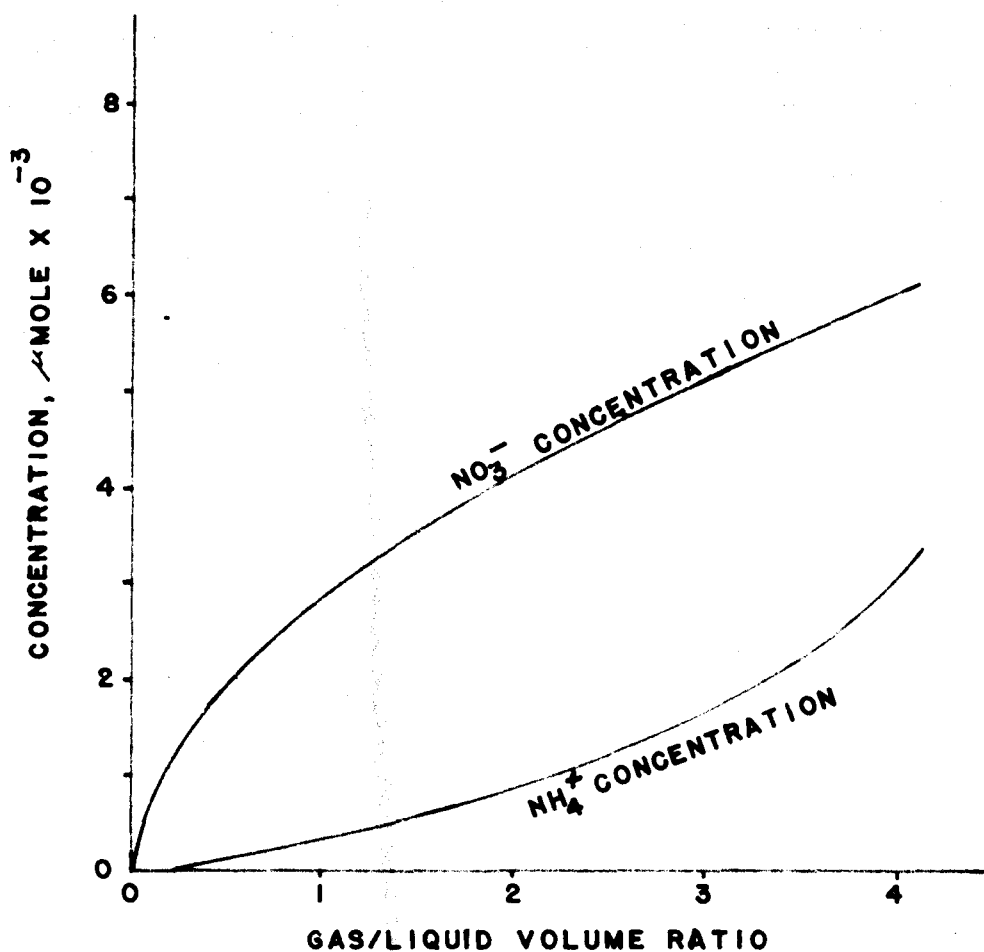


FIGURE 3. VARIATION OF  $\text{NO}_3^-$  AND  $\text{NH}_4^+$  CONCENTRATION WITH  
GAS-LIQUID VOLUME RATIO AT AN INTEGRATED FLUX OF  
 $2.92 \times 10^{18}$  NEUTRONS/ $\text{CM}^2$ , CONSTANT VOLUME OF  
50 ML, AND ATMOSPHERIC PRESSURE

BATES, T. H. ET AL: EFFECT OF RADIATION ON HETEROGENEOUS SYSTEMS OF AIR AND NITROGEN AND WATER, PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON THE PEACEFUL USES OF ATOMIC ENERGY, 1, 560-568 (1955).

Discussion<sup>(2)</sup> of Experimental Curves. The fact that the ammonia formation was negligible below an integrated flux of  $0.7 \times 10^{18}$  neutrons per square centimeter in Figure 2, page 19, has been explained by the low concentration of hydrogen formed by the reaction forming nitric acid; the hydrogen had not been produced for a long enough time for ammonia to appear in the results. Both curves indicate, by the leveling off of the  $\text{NO}_3^-$  concentration curves, that there is competition for nitrogen between the nitric acid reaction and the ammonia formation. Figure 3, page 20, indicates that equilibrium between the competing reactions for nitrogen would be reached when the ammonia reaction would use all the hydrogen formed in the formation of nitric acid. Figure 3 also shows that there is no formation of either nitric acid or ammonia in the liquid phase.

The concentration of hydrogen peroxide, although not plotted on the above graphs, was linear on both plots; this indicates that the formation of neither nitric acid nor ammonia depended in any way on the formation of hydrogen peroxide. It is very significant that no traces of nitrites or any other oxygen-nitrogen compounds were found in the reaction products; this fact clearly indicates a direct combination of nitrogen and water vapor to form the nitric acid.

### Neutron Flux Measurement

The method found by experimenters<sup>(4)</sup> to be most reliable in the measurement of a constant neutron flux employs a calibrated gold or silver foil. This foil is irradiated in the flux to be measured and then counted in a beta counter<sup>(14)</sup>. The activation, or neutron absorption as measured by the counting technique, of the calibrated foil is compared to the values used to obtain the calibration;

In a body of cylindrical shape, the neutron flux should follow a cosine distribution<sup>(16)</sup> along the axis perpendicular to the neutron sources; and the distribution along an axis parallel to the sources should be a Bessel function of zero order<sup>(16)</sup>. For a meaningful flux measurement, the flux at different points throughout the reactor (or reaction) space should be plotted; and a mean value taken from the plot should be used as the average flux.

### Neutron Behavior in Paraffin Wax

Paraffin is composed of carbon and hydrogen atoms linked through carbon-carbon coordinate covalent bonds. Paraffin is mostly eleven or twelve carbon chain molecules called saturated hydrocarbons. The rule<sup>(15)</sup> that atoms of low atomic weight slow down neutrons

effectively holds in the case of bonded hydrogen; a hydrogen atom can remove all the kinetic energy of a neutron in just one elastic collision.

Paraffin is as good a neutron moderator, or slowing down material, as water because <sup>(3)</sup> there is about the same density of hydrogen atoms in a given volume of paraffin as there is in water. Also, paraffin can be shaped while water is liquid at ordinary temperatures.

Paraffin Neutron Absorption and Moderation. Goldhaber and Briggs <sup>(3)</sup> have shown that the absorption of neutrons in paraffin wax can be attributed almost entirely to the hydrogen. Values given by Glasstone and Edlund <sup>(15)</sup> for the neutron absorption cross sections of hydrogen and carbon are 0.32 barns and 0.0045 barns, respectively. It may be deduced from these low values of  $\sigma_a$  that there is very little absorption of neutrons in paraffin. Values for scattering cross sections of hydrogen and carbon are given <sup>(3)</sup> to be 47.5 barns and 4.8 barns, respectively. However, it has been pointed out by Cohen, Goldsmith, and Schwinger <sup>(6)</sup> and by Glasstone and Edlund <sup>(15)</sup> that the scattering property of hydrogen varies greatly with neutron energy, even in the thermal range.

Use of Paraffin as a Moderator. There is evidence<sup>(3, 15)</sup> that the hydrogen atoms in paraffin can be considered as free protons only if the energy of the incident neutrons is large compared to the energy of the lowest vibrational level in the paraffin molecules, or about three or four mev. The low absorption cross section and high scattering cross section of paraffin cause it to be considered an almost ideal solid state moderator at low temperatures. The use of paraffin howitzers in the irradiation of foils by neutrons is a common laboratory procedure.



### Colorimetric Analysis

An outline of the colorimetric quantitative analysis of ammonia by the use of Nessler's reagent is presented in the following paragraphs.

Beer's Law<sup>(37)</sup>. Beer's law states that the probability of light absorption is directly proportional to the concentration of the absorbing molecules. Expressed in a useful form, Beer's law becomes:

$$\log \frac{I_0}{I} = D = a_M bc$$

where:

$I_0$  = incident intensity, photons/cm<sup>2</sup>

$I$  = final intensity, photons/cm<sup>2</sup>

$D$  = optical density, dimensionless

$a_M$  = molar absorbancy index, lit/mol-cm

$b$  = cell thickness, cm

$c$  = concentration of absorber, mol/lit.

Use of Colorimeter. A colorimeter is an instrument which employs a light-sensitive device, such as a photocell, to detect changes in color of solutions<sup>(39)</sup> which obey Beer's law. The reading of optical density may be calibrated to give a direct reading of concentration for a given solution. In the use of the colorimeter, light of the same wave length

as the color of the solution is passed through a cell of solution. Distilled water is used as the absolute standard; but, if a certain reagent is used, a sample of this reagent in distilled water is then used as the standard.

Turbidity Measurements. According to Snell<sup>(37)</sup>, turbid solutions and colloids which do not obey Beer's law may still be analyzed by means of a colorimeter if the turbidity conditions at a given concentration are reproducible.

Colorimetric Determination of Ammonia by Nessler's Reagent. There are many methods given<sup>(33, 38, 39)</sup> for the use of Nessler's reagent in the colorimetric analysis of ammonia in water. These methods differ mainly in the preparation of the reagent. The method outlined by Snell<sup>(38)</sup>, which produces color for concentrations as low as 0.01 parts per million of ammonia in water, appears to be a simple and accurate ammonia determination. Nessler's reagent, a potassium-mercuric iodide complex, forms a reddish-brown colloidal complex<sup>(39)</sup> when it is reacted with ammonia. This colloid in water obeys Beer's law for concentrations of ammonia in water of lower than about 0.01 moles per liter. The wavelength of the color produced by the reaction of Nessler's reagent with ammonia is 4100 angstrom units.

### III. EXPERIMENTAL

This section contains information related to the experimental phase of this investigation. Subjects discussed include purpose of investigation, plan of experimentation, materials, apparatus, method of procedure, and data and results.

#### Purpose of Investigation

The purpose of this investigation was to determine the effects of pressure and concentration on the formation of ammonia by slow neutron irradiation of a gaseous nitrogen-hydrogen system.

#### Plan of Experimentation

The plan of experimentation followed in this investigation consisted of a review of available literature concerning chemical reactions which are induced or accelerated by irradiation with slow neutrons, the design and construction of experimental apparatus, and preparation and analysis of test samples.

Literature Review. A search of the literature was made to acquaint the author with what work has been done in the field of neutron

radiation chemistry concerning specific reactions, materials used in previous investigations, and methods of chemical analysis for the test samples. Also included was a study of the specific reaction to be investigated as it occurs under non-irradiated conditions.

Design and Construction. The experimental apparatus was designed, the equipment and materials were collected, and the apparatus was assembled. The system which was constructed consisted of two parallel reaction tubes, one of which was enclosed in a paraffin neutron howitzer, and the other of which was used as a control experiment and was not irradiated.

Sample Preparation and Analysis. It was decided that effects of pressure and concentration on the system of nitrogen and hydrogen could be adequately described by reaction tests using hydrogen-nitrogen ratios of 3 to 1 and 6 to 1 irradiated at absolute pressures of 5, 4, and 3 atmospheres. It was recognized that the limiting factor in the investigation would be the number of neutrons available; therefore, the irradiation time was set at 24 hours in order to supply an integrated neutron flux of about  $10^{10}$  neutrons per square centimeter for the tests. Because of possible absorption on the tube walls, the tubes were to be washed off, and the amount of ammonia added from the washing was to

be calculated. Because of the possibility of very low concentrations of ammonia in the test samples, it was necessary to use the most accurate method of chemical analysis available. From information in the literature, it was found that the most accurate practical method available was colorimetric analysis using Nessler's reagent.

### Materials

The materials used in the investigation are presented in the following section.

Ammonium Chloride. Reagent grade, lot No. 2247 . Obtained from J. T. Baker Chemical Company, Phillipsburg, New Jersey. Used in standard solutions for calibration of colorimeter.

Hydrochloric Acid. Dilute. Obtained from the chemical stockroom of the Chemistry Department of Virginia Polytechnic Institute, Blacksburg, Virginia. Used to aid in absorption of ammonia from test samples.

Hydrogen. Electrolytic, cylinder size 1-A. Obtained from the Matheson Company, Incorporated, East Rutherford, New Jersey. Used as a component in the test samples.

Mercuric Chloride. Reagent grade. Obtained from J. T. Baker Chemical Company, Phillipsburg, New Jersey. Used in preparation of Nessler's reagent.

Nitrogen. Commercial grade, cylinder size 1. Obtained from Southern Oxygen Company, Roanoke, Virginia. Used as a component in the test samples and to purge the reaction tubes.

Paraffin Wax. Formula 3512, 133/135 AMP refined wax. Obtained from Esso Standard Oil Company, Roanoke, Virginia. Used as a neutron moderator.

Potassium Iodide. Reagent grade. Obtained from J. T. Baker Chemical Company, Phillipsburg, New Jersey. Used in the preparation of Nessler's reagent.

Potassium Permanganate. Reagent grade. Obtained from General Chemical Division, Allied Chemical and Dye Corporation, New York, New York. Used in the preparation of ammonia-free water.

Sodium Carbonate. Reagent grade, lot No 31148. Obtained from J. T. Baker Chemical Company, Phillipsburg, New Jersey. Used in the preparation of ammonia-free water.

Sodium Hydroxide. Reagent grade pellets, lot No 6429. Obtained from General Chemical Division, Allied Chemical and Dye Corporation, New York, New York. Used in the preparation of Nessler's reagent and for aiding desorption of ammonia from test samples.

Water, Ammonia-Free. Prepared in the Unit Operations Shop of the Chemical Engineering Department, Virginia Polytechnic Institute,

Blacksburg, Virginia. Used in the preparation of Nessler's reagent, in flushing the reaction tubes, and for absorption of ammonia from the test samples.

Water, Distilled. Obtained from the still of the Chemistry Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used in the preparation of ammonia-free water and for standardization of the colorimeter.

### Apparatus

The apparatus used in the investigation is presented in the following section.

Adapters. Nylon, 3/8 in. tube to 1/4 in. pipe, 24 used. Obtained from Fogleman Company, Incorporated, Charleston, West Virginia. Used in the system tubing.

Adapters. Black iron, 1/8 in. pipe to 1/4 in. pipe, 2 used. Obtained from the piping storeroom of the Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used in gas bleed line.

Air Pump. Vacuum and pressure; Cenco Pressevac; serial No 30431; single stage, 115 v, ac, 60 cy motor. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to evaporate water from the system.

Balance. Analytical. Serial No 11 G 30 39, capacity 100 grams, graduations of 0.1 milligram. Manufactured by Will Corporation, Rochester, New York. Used to weigh chemicals in preparation of Nessler's reagent and ammonia-free water.

Clamps. Fisher Castaloy tube clamps, 2 required. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to regulate flow in gas exhaust lines.

Clock. Electric wall clock with sweep second hand. Manufactured by General Electric Company, Poughkeepsie, New York. Used to measure times in irradiation tests.

Colorimeter. Bausch and Lomb "Spectronic 20", serial No ED-6955. Manufactured by Bausch and Lomb Optical Company, Rochester, New York.

Connector. Fisher Castaloy soft tubing connector, Y-shape. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to join gas exhaust lines.

Drum Liner. Polyethylene, 55 gallon drum size. Obtained from Delaware Barrel and Drum Company, Wilmington, Delaware. Used to contain paraffin neutron howitzer.



Elbow. Black iron, 1/8 in. ell, Obtained from pipe supply room of the Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used in the vacuum pump line.

Flange. Corning style, for 2 in. standard flanged glass pipe, made of cast iron, 4 required. Obtained from Sentinel Glass Company, Hatboro, Pennsylvania. Used as flanges on the reaction tubes.

Flange Bolts. Steel, 5/16 in. bolts 3 in. long. Obtained from Sentinel Glass Company, Hatboro, Pennsylvania. Used to bolt the Corning flanges.

Flange Blanks. Type 316 stainless steel, 4-9/16 in. diam. by 1/4 in. thick, 4 required. Obtained from Whitehead Metal Company, Baltimore, Maryland. Used as ends of the reaction tube.

Gage. Gas pressure; range 0-60 psig in calibrations of 2 psi. Manufactured by Leeds and Northrup Company, Philadelphia, Pennsylvania. Used to measure pressure in the blank reaction tube.

Gage. Gas pressure; range 0-100 psig in calibrations of 2 psi. Manufactured by Taylor Instrument Company, Rochester, New York. Used to measure pressure in the irradiated reaction tube.

Gaskets. Molded teflon, type T for 2 in. glass pipe, 4 required. Obtained from Sentinel Glass Company, Hatboro, Pennsylvania. Used as flange gaskets on the reaction tubes.

Miscellaneous Glassware. Laboratory glassware obtained from Fisher Scientific Company, Silver Spring, Maryland. Used for standard analytical and laboratory purposes.

Neutron Sources. Pu-Be sources with surface flux of  $1 \times 10^7$  neutrons/sq cm-sec, 4 required. Obtained under AEC specifications from Mound Laboratory of Monsanto Chemical Company, Miamisburg, Ohio. Used as neutron sources in the howitzer.

Nipples. Black iron, 1/8 in. pipe by 1 in. long, 4 required. Obtained from piping storeroom of Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used in gas bleed line.

Tees. Nylon, 3/8 in. tubing tees, 8 required. Obtained from Fogleman Company, Incorporated, Charleston, West Virginia. Used in the tubing of the system.

Tees. Black iron, 1/8 in. piping tees, 2 required. Obtained from piping storeroom of the Chemical Engineering Department, Virginia Polytechnic Institute, Blacksburg, Virginia. Used in pressure gage lines from gas bleed lines.

Tubing. Nylon, 1/4 in. outside diameter tubing, 8 ft. required. Obtained from Phipps and Bird Company, Richmond, Virginia. Used in system tubing.

Tubing. Polyethylene, 3/8 in. outside diameter, 20 ft. required. Obtained from Sentinel Glass Company, Hatboro, Pennsylvania. Used in system tubing.

Tubing. Saran, 3/8 in. outside diameter, 20 ft. required. Obtained from Sentinel Glass Company, Hatboro, Pennsylvania. Used in the gas exhaust line.

Tubing. Pyrex, double strength, 2 in. flanged tubes, 4 ft. long, 2 required. Obtained from Sentinel Glass Company, Hatboro, Pennsylvania. Used as reaction tubes.

Valve. Hydrogen automatic single stage regulator; range 5-3000 psig. Obtained from the Matheson Company, Incorporated, East Rutherford, New Jersey. Used to regulate the flow of hydrogen to the reaction tubes.

Valve. Range 0-500 psig, N<sub>2</sub> regulator to fit standard N<sub>2</sub> cylinder connection. Obtained from the Matheson Company, Incorporated, East Rutherford, New Jersey. Used to regulate the flow of nitrogen to the reaction tubes.

Valves. Hoke needle valves, brass with stainless steel insets, with 1/4 in. female fittings, 7 required. Obtained from Sentinel Glass Company Hatboro, Pennsylvania. Used to direct and regulate the flow pattern of the system.

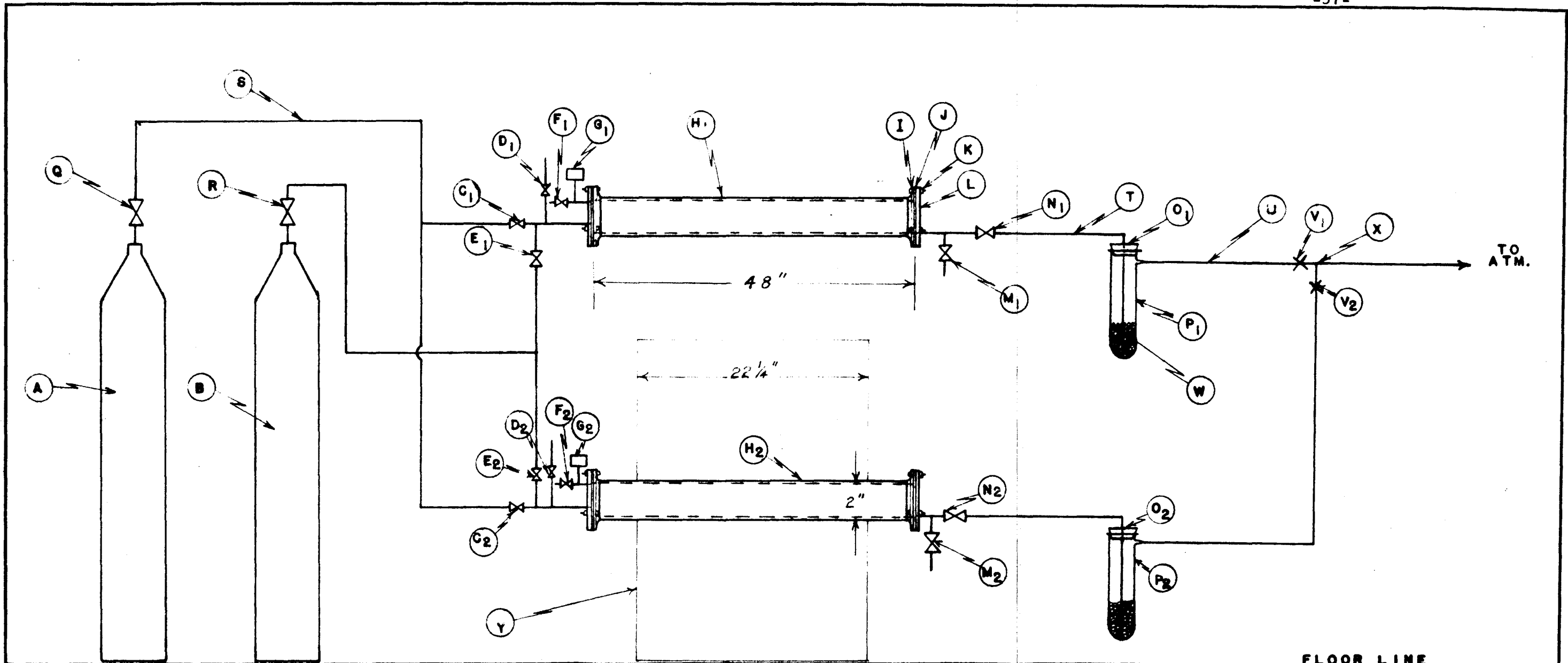
Valves. Hoke needle valves, type 303 stainless steel with 1/4 in. male fittings, 5 required. Obtained from Sentinel Glass Company, Hatboro, Pennsylvania. Used to direct and regulate the flow pattern of the system.

### Method of Procedure

The method of procedure followed in this investigation consisted of the construction of the experimental system, the experimental tests, and the analysis of the test samples.

Construction of Experimental System. The construction work on the apparatus was performed in the Unit Operations Shop of the Chemical Engineering Department, Virginia Polytechnic Institute. When the construction had been completed, the apparatus was moved to the south corner of Room 102 of Davidson Hall, which is the Nuclear Reactor Laboratory of the Physics Department, Virginia Polytechnic Institute, Blacksburg, Virginia. The flow diagram of the equipment as it was set up is shown on Figure 4, page 37. The methods used in the construction of the apparatus is presented in the following paragraphs.

Construction of Neutron Howitzer. The design of the paraffin neutron howitzer is shown on Figure 5, page 38. Paraffin wax



LEGEND

- 1 - BLANK SYSTEM
- 2 - IRRADIATED SYSTEM
- A - NITROGEN SUPPLY
- B - HYDROGEN SUPPLY
- C - N<sub>2</sub> LEAD-IN VALVE
- D - WATER INLET LINE AND VALVE
- E - H<sub>2</sub> LEAD-IN VALVE
- F - GAS BLEED LINE AND VALVE
- G - GAS PRESSURE GAGE
- H - PYREX GLASS TUBE, 2 IN.

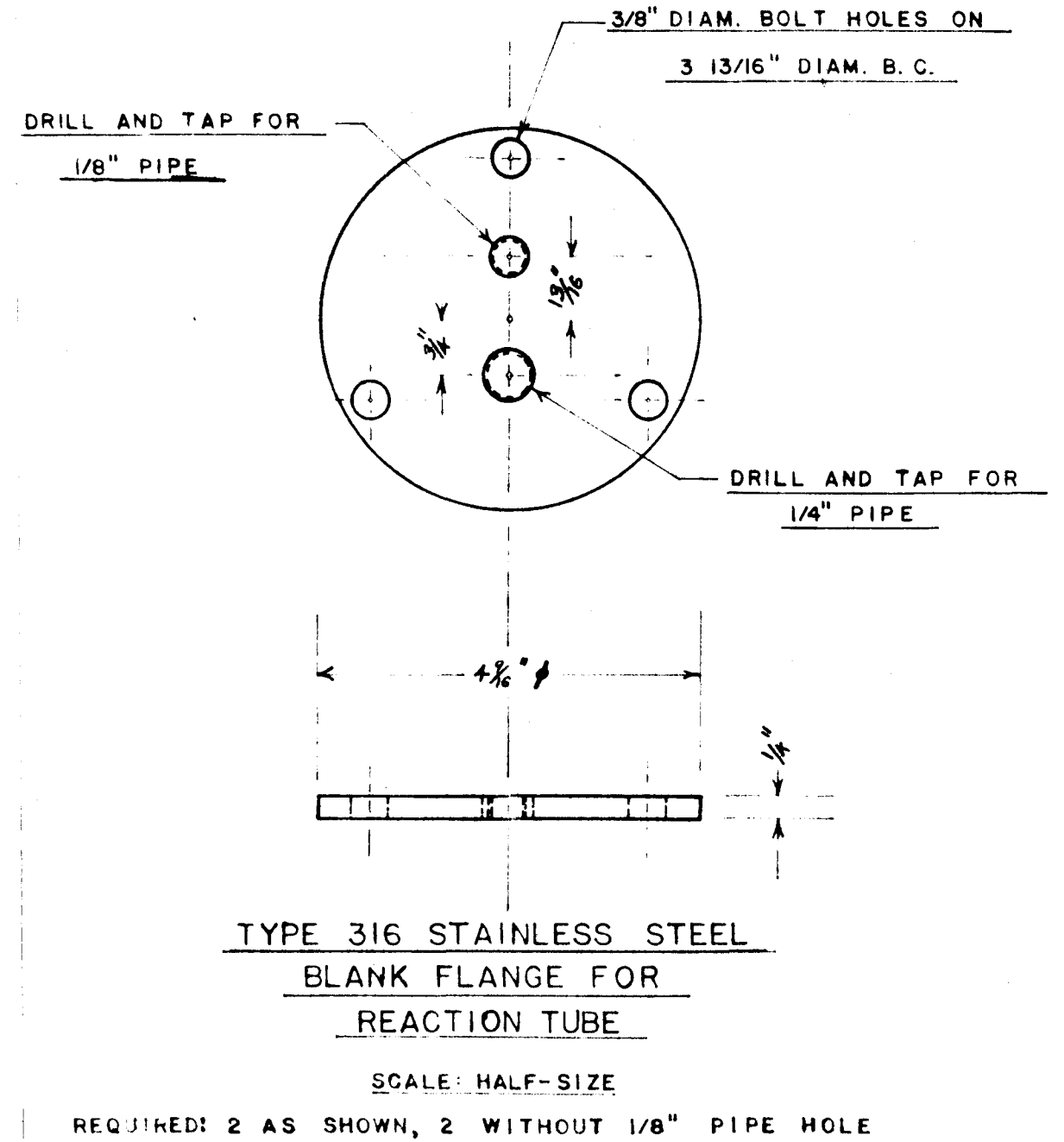
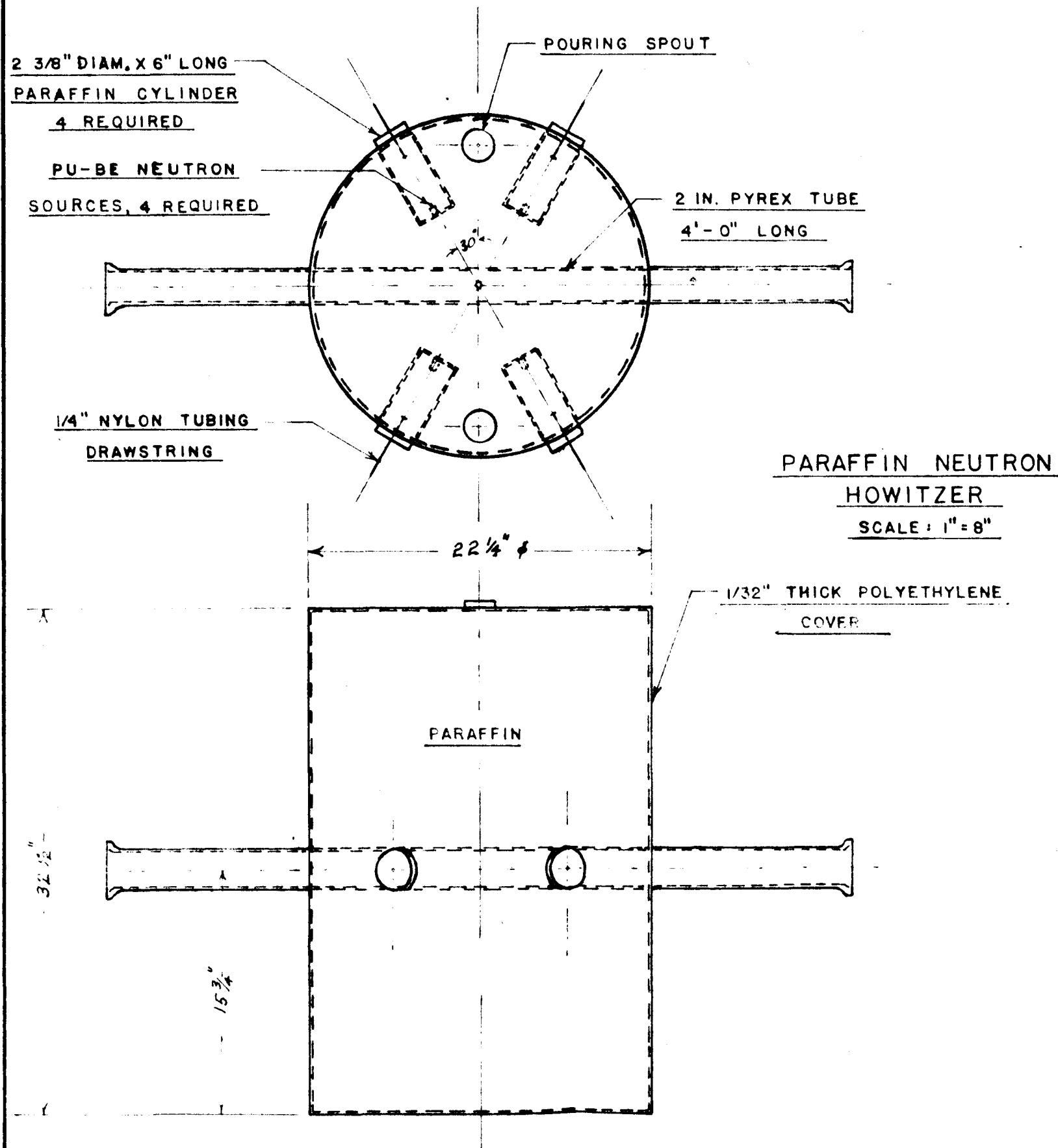
- I - CORNING STYLE 2" C. I. FLANGE
- J - TEFLON FLANGE GASKET
- K - FLANGE BOLTS, 3/16 IN.
- L - BLANK FLANGE, TYPE 316 S. S.
- M - WATER DRAIN LINE AND VALVE
- N - SAMPLING LINE VALVE
- O - RUBBER STOPPER, NO. 4
- P - SIDE-NECK TEST TUBE, 100 ML
- Q - N<sub>2</sub> REDUCING VALVE
- R - H<sub>2</sub> REDUCING VALVE

- S - POLYETHYLENE TUBING, 3/8 IN.
- T - NYLON TUBING, 1/4 IN.
- U - TYGON TUBING, 3/8 IN.
- V - HOSECOCK
- W - GLASS BEADS, 5MM
- X - HOSE CONNECTOR
- Y - PARAFFIN HOWITZER

DEPARTMENT OF CHEMICAL ENGINEERING  
 VIRGINIA POLYTECHNIC INSTITUTE  
 BLACKSBURG, VIRGINIA

FLOW DIAGRAM FOR NEUTRON  
 IRRADIATION EXPERIMENT

SCALE: NONE      DATE: 7-9-58      CASE NO:  
 DRAWN BY: RLB      FILE NO:  
 CHECKED BY:      FIGURE NO: 4  
 APPROVED BY:      SHEET NO:



DEPARTMENT OF CHEMICAL ENGINEERING  
VIRGINIA POLYTECHNIC INSTITUTE  
BLACKSBURG, VIRGINIA

HOWITZER AND BLANK FLANGE  
FOR IRRADIATION EXPERIMENT

SCALE: AS SHOWN	DATE: 7-11-58	CASE NO:
DRAWN BY: RCB		FILE NO:
CHECKED BY:		FIGURE NO: 5
APPROVED BY:		SHEET NO:

was melted in buckets placed on hot plates and was poured into the polyethylene drum liner through the pouring spouts. After the paraffin in the drum had reached a depth of 14-1/2 inches, holes were cut in the polyethylene, and the pyrex reaction tube was placed in position. Holes were also cut for closed, iron tubes of 2-3/8 inches diameter; and these tubes were placed into position by means of small paraffin blocks. Molten paraffin in which incipient solidification was taking place was poured over these inserted pieces to seal the holes in the polyethylene. Paraffin was then melted and poured into the polyethylene liner until it was full.

Construction of Source Plugs. Paraffin was then poured into tubing molds of 2-3/8 inches inside diameter to a solidified depth of six inches. Short lengths of polyethylene tubing, with otherwise unusable tubing fittings on one end, were placed into the molten paraffin to be used as drawstrings upon solidification. Holes of 1-1/4 inch diameter were then bored into the solidified paraffin to a depth of 1-3/4 inch. These cylinders of paraffin, or plugs, provided the means of inserting neutron sources into the howitzer in holes formed by removal of the tubes inserted before the paraffin was poured.

Assembly. Flange blanks were prepared according to Figure 5, page 38. These blanks, along with Corning style flanges and teflon gaskets, closed the pyrex tubes. The piping and tubing systems were then constructed according to the flow diagram on Figure 4, page 37. The reaction tube in the blank system, all tubing on which valves had been placed, and the absorption tubes were supported by means of laboratory ringstands. The entire apparatus was tested for leaks for 24 hours at nitrogen pressure of 70 pounds per square inch, gage. The entire system was then partially disassembled, moved to Room 102 of Davidson Hall, and reassembled.

The Experimental Tests. The experimental tests were performed at hydrogen-nitrogen ratios of 6 to 1 and 3 to 1 under pressures of 5, 4, and 3 atmospheres in a gaseous system of nitrogen and hydrogen. The procedure followed in the performance of these tests is presented in the following paragraphs. The apparatus referred to in this procedure appears on Figure 4, page 37.

Volume Measurement. The volume of the blank system was measured by closing all valves but the gas bleed valve,  $F_1$ , and the water inlet line valve,  $D_1$ . Distilled water was then introduced through  $D_1$  until water ran out of  $F_1$ . The water was then drained



from the system through the water drain valve, M<sub>1</sub>, into a large graduated cylinder. The same procedure was followed for the measurement of the volume of the irradiated system. Both systems were dried by the same method. A vacuum pump was attached to M, all valves were closed except M, and the system was evacuated. Valve M was then closed, valve C was opened, and nitrogen was introduced into the system by opening regulator valve Q slightly. Valves Q and C were then closed, valve M was opened, and the system was again evacuated. This procedure was also used to dry the system after each test.

Insertion of Neutron Sources. The neutron sources were taken from the wax drum in Room 102 of Davidson Hall and placed into the holes cut into the paraffin plugs. The sources were handled with tongs. The plugs were then inserted into their respectively numbered holes in the neutron howitzer, Y.

Test Procedure. For each test, the test procedure was the same for both the blank and the irradiated systems. All valves were closed except C and N, and the rubber stopper, Q, was removed from the absorption tube, P. The system was purged with nitrogen for 20 minutes by the opening of regulator valve Q. Valve N was then closed, and the pressure of nitrogen was allowed to increase until the pressure gage, G, indicated that the

desired amount of nitrogen was present at the correct pressure for the specified test. Valves Q and C were then closed. Valve E was then opened, and hydrogen was allowed into the system by the opening of regulator valve R until the pressure gage, G, indicated that the test pressure had been reached. Valves R and E were then closed.

After a period of 24 hours had passed, ten milliliters of distilled water made slightly acid with hydrochloric acid were placed in the absorption tube, P, and the stopper, O, was replaced. Cock V was opened as was valve N. After the pressure inside the system had reduced to atmospheric pressure, valves C and Q were opened, and the remaining gas was forced out by nitrogen. Valves C, Q, and N were then closed, valves F and D were opened, and the system was filled with slightly acid distilled water. Valve M was then opened, and the water was drained and collected. After the sample collected in tube P had been analyzed, it was again placed into P. Tube T was removed, and the absorption tube, P, was attached to a one liter flask by means of a glass tube through a stopper such as O. The collected wash water was placed into the one liter flask, and the solution was made basic by the addition of sodium hydroxide. The solution was heated to boiling

so that any ammonia present in the wash water would be absorbed in the sample which had been analyzed. The enriched sample was then analyzed. After each test the system was dried according to the procedure given in the paragraph Volume Measurement, page 40.

Sample Analysis. The sample analysis consisted of the preparation of Nessler's reagent, calibration of the colorimeter, preparation of the test samples, and operation of the colorimeter. The procedure suggested by Snell<sup>(38)</sup> was used in the preparation of Nessler's reagent and in the calibration of the colorimeter. This procedure was deviated from only slightly in that the samples were not distilled. The operation of the colorimeter was according to the Leeds and Northrup Instruction Manual for the "Spectronic 20" colorimeter.

### Data and Results

The data and results of this investigation are presented in the following sections.

Volumes of Reaction Spaces. The volumes of the reaction spaces of the irradiated and the blank systems were found to be 2580 and 2490 cubic centimeters, respectively.

Colorimeter. The data taken in the calibration of the colorimeter used in sample analysis are presented on Table I, page 45. These data were taken using standard solutions of ammonium chloride prepared according to the method suggested by Snell and Snell<sup>(38)</sup> for standardizing Nessler's reagent prepared and used within less than two weeks. The calibration curve for the colorimeter is presented on Figure 6, page 46.

Product Analysis. The conditions and results of the reaction tests are presented on Table II, page 47, and in Table III, page 48. The results of each test are expressed as the ratio of the ammonia concentration in the sample taken from the irradiated system to the concentration of ammonia in the sample taken from the blank system. The variations of the ratios of concentrations with pressure which resulted from the tests performed in this investigation are presented graphically on Figure 7, page 49.

**TABLE I**

**Calibration of Bausch and Lomb Colorimeter for**  
**Determination of Ammonia in Chloride Solution**

<b>Wavelength</b>	<b>Ammonia Concentration</b>	<b>Optical Density<sup>a</sup></b>
<b>millimicrons</b>	<b>grams/liter</b>	<b>dimensionless</b>
410	0.0005	0.369
410	0.000375	0.278
410	0.00025	0.218
410	0.000125	0.172
410	0.00005	0.138
410	0.000025	0.105
410	0.0	0.101

<sup>a</sup> Nessler's reagent was added to the samples, in a 1 to 50 ratio, at 27°C

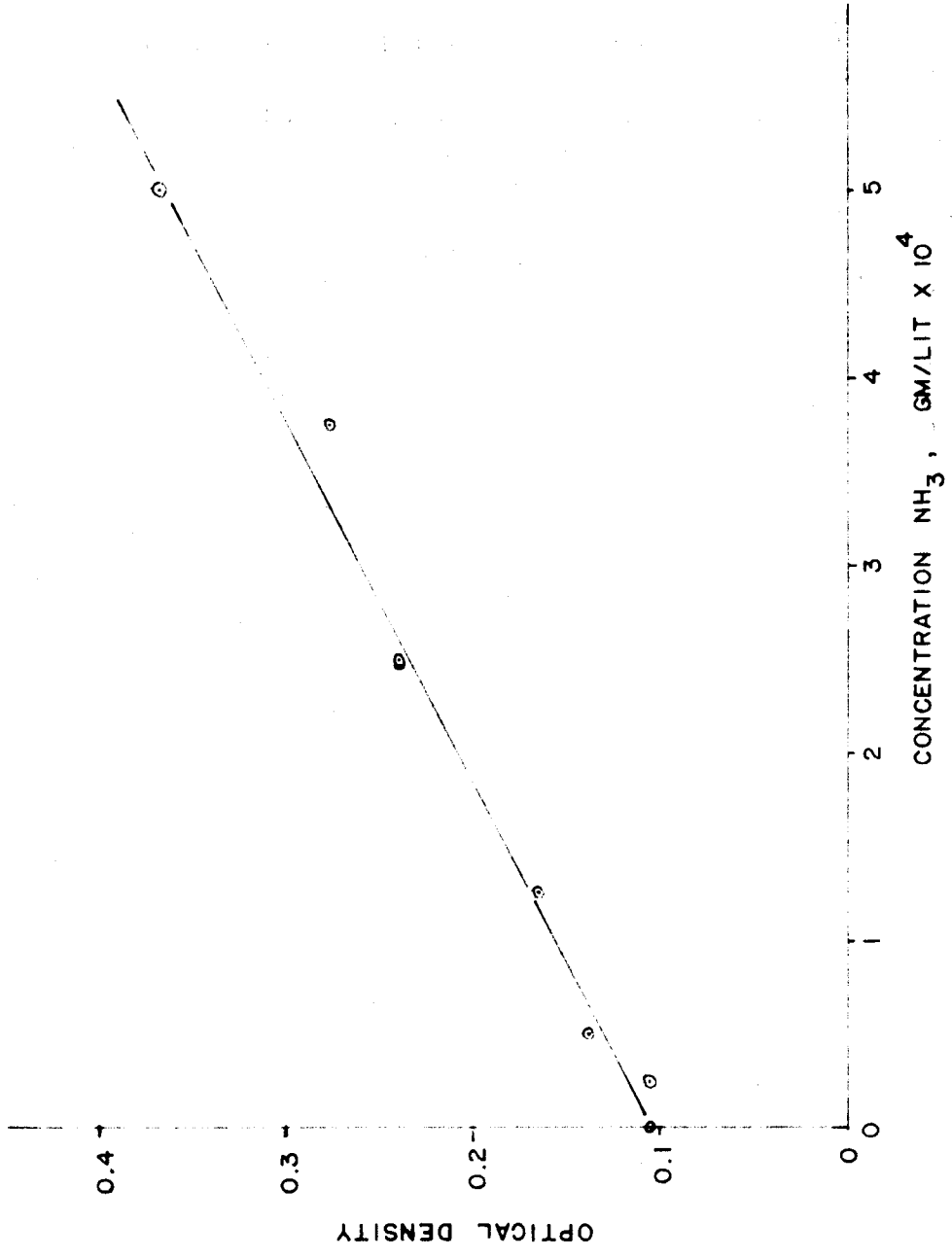


FIGURE 6. CALIBRATION CURVE FOR BAUSCH & LOMB COLORIMETER USING

NESSLER'S REAGENT

**FOR DETERMINATION OF AMMONIA IN CHLORIDE SOLUTIONS**

TABLE II

Conditions and Analyses of Samples for Ammonia Synthesis

With and Without Neutron Irradiation

Pressure	N <sub>2</sub> -N <sub>2</sub> Ratio	Temperature	Analyses of Absorbent by Optical Density			
			Irradiated <sup>a</sup>		Nonirradiated	
			B. W. <sup>b</sup>	A. W. <sup>c</sup>	B. W.	A. W.
atm.		°C				
5.0	3.0	32	0.259	0.345	0.252	0.309
5.0	6.0	30	0.329	0.527	0.433	0.453
4.0	3.0	28	0.103	0.259	0.161	0.247
4.0	6.0	30	0.330	0.517	0.440	0.502
3.0	3.0	30	0.509	0.527	0.248	0.347
3.0	6.0	28	0.314	0.314	0.163	0.263

<sup>a</sup> The irradiated system was bombarded by an average total flux of  $6.05 \times 10^7$  neutrons/sq cm

<sup>b</sup> B. W. stands for the sample before the washings from the tube were added to the absorbent

<sup>c</sup> A. W. stands for the sample after the washings from the tube were added to the absorbent.

TABLE III

Effects of Neutron Irradiation on  
Ammonia Synthesis

Pressure H <sub>2</sub> -N <sub>2</sub>		Sample Analysis				Conc. Ratio <sup>a</sup>
		Total Optical Density		Corrected <sup>b</sup> Optical Density		
atm.		Irradiated <sup>c</sup>	Non-irradiated	Irradiated	Non-irradiated	
5.0	3.0	0.345	0.309	0.244	0.208	1.17
5.0	6.0	0.527	0.453	0.426	0.352	1.21
4.0	3.0	0.259	0.247	0.158	0.146	1.08
4.0	6.0	0.517	0.502	0.416	0.401	1.04
3.0	3.0	0.527	0.347	0.426	0.246	1.73
3.0	6.0	0.314	0.266	0.213	0.165	1.29

<sup>a</sup> Conc. Ratio = Corrected optical density of irradiated sample divided by corrected optical density of the nonirradiated sample

<sup>b</sup> Corrected optical density is the total optical density of a sample with Nessler's reagent less the optical density of Nessler's reagent in pure water (0.101)

<sup>c</sup> The irradiated system was bombarded by a total flux of  $6.05 \times 10^7$  neutrons/cm<sup>2</sup>



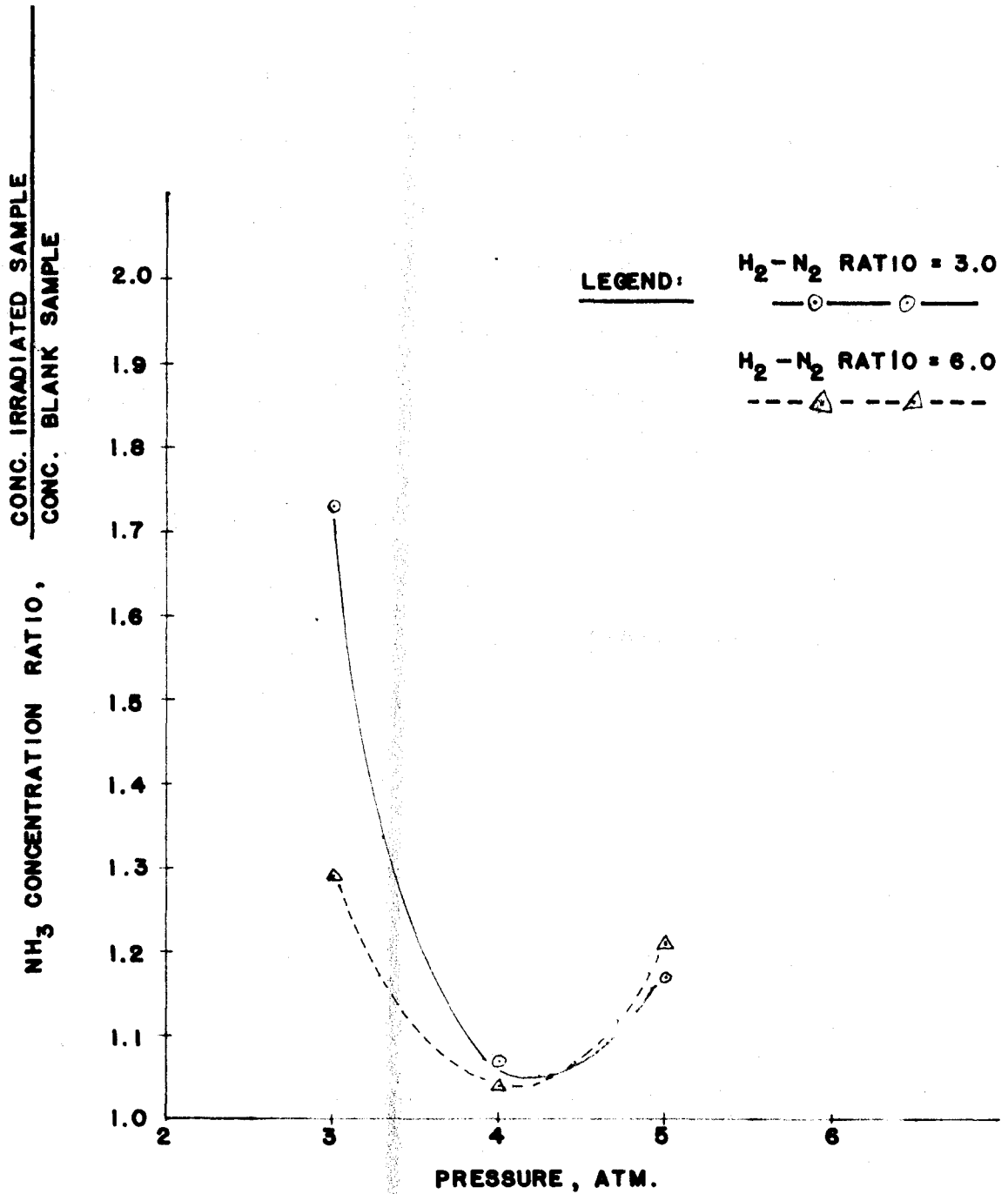


FIGURE 7. VARIATION OF CONCENTRATION RATIO WITH  
PRESSURE AT AN INTEGRATED FLUX OF  
 $6.05 \times 10^7$  N/CM<sup>2</sup>

Qualitative Analysis of the Product. The data from the spectroscopic analyses of standard ammonium chloride solution and of a sample of reaction products is given in Table IV, page 51. The spectra are compared in Figure 8, page 52.

Determination of Neutron Flux. The average thermal neutron flux was determined over the total length of the reaction tube. Flux determination data can be found on Table V, page 53, and the flux plot is shown on Figure 9, page 54.

TABLE IV

Spectroscopic Analysis of Reaction Products  
and of Ammonium Chloride Standard

Wavelength millimicrons	Optical Density	
	Sample dimensionless	Standard dimensionless
360	1.25	1.35
380	0.74	0.80
390	0.577	0.604
400	0.430	0.450
410	0.349	0.368
420	0.284	0.309
440	0.211	0.240
460	0.157	0.185
480	0.114	0.128
500	0.093	0.097

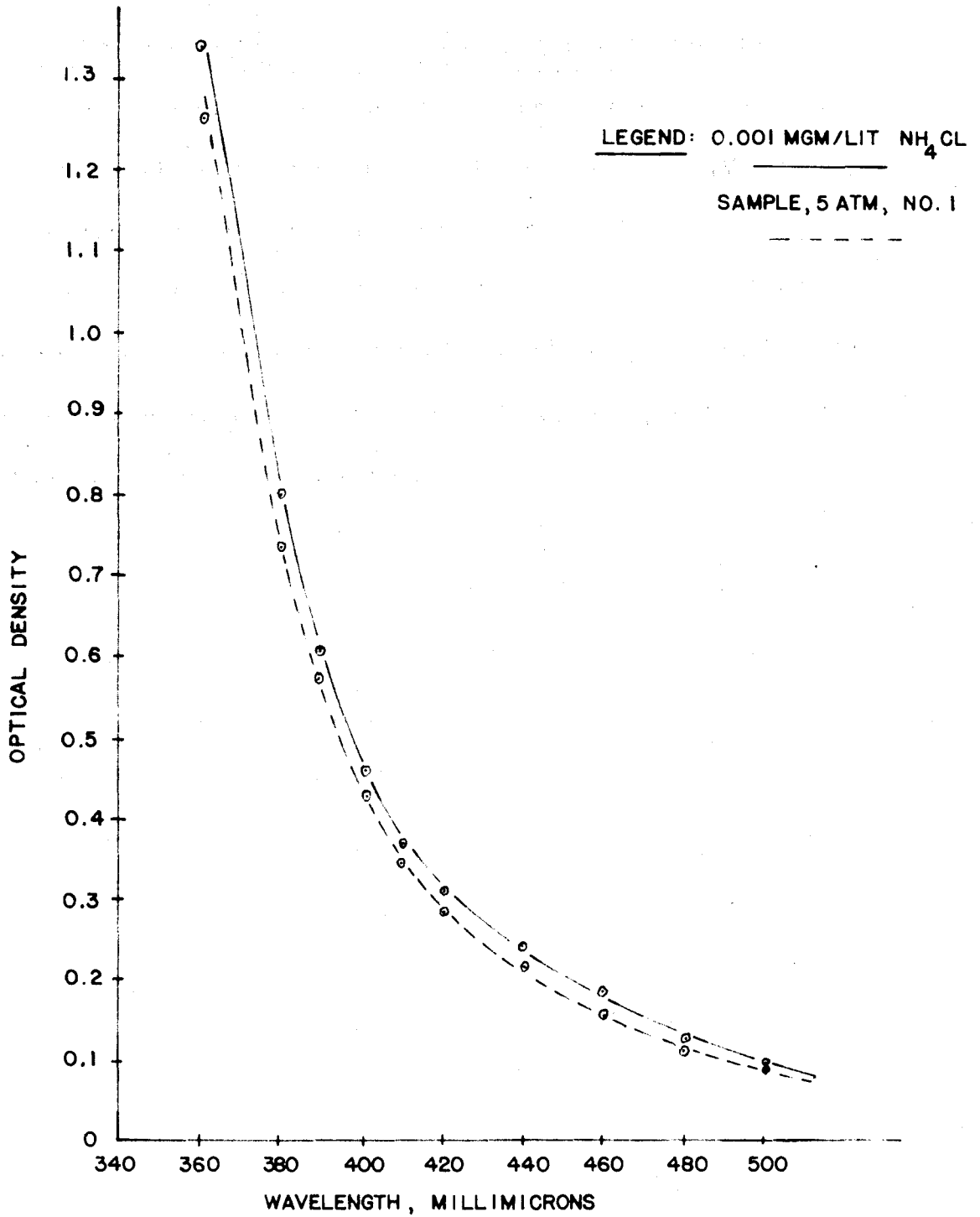


FIGURE 8. SPECTRA OF AMMONIA-NESSLER'S REAGENT

STANDARD AND SAMPLE

TABLE V

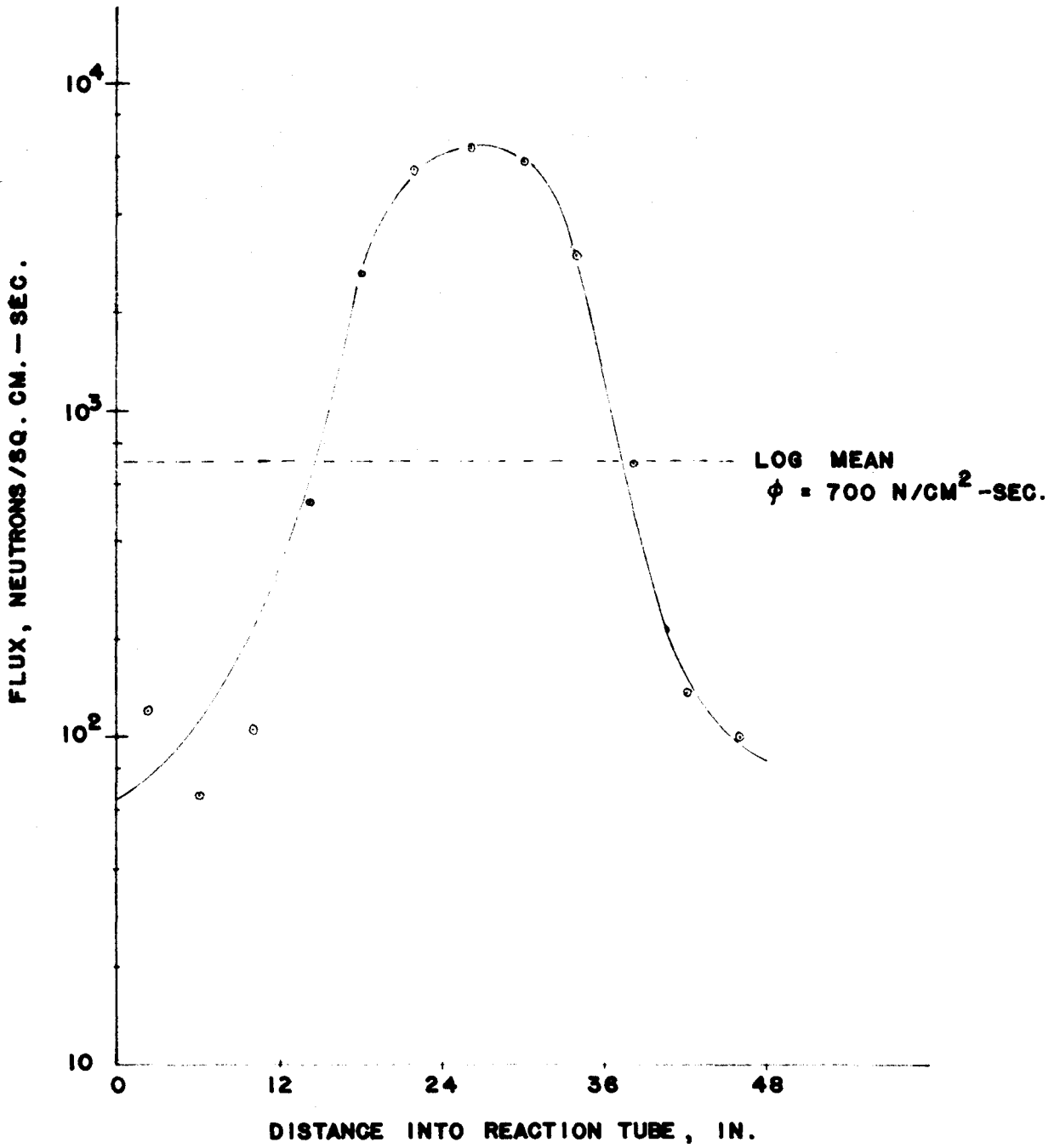
Flux Distribution in the Neutron Howitzer<sup>a</sup>

Distance In Tube	Time	Counts	Counts/Sec.	Corrected cps <sup>b</sup>	Flux <sup>c</sup> n/cm <sup>2</sup> -sec
in.	min.				
2	1	1299	22	100	121
6	1	768	12	55	67
10	1	1153	19	87	106
14	1	5800	97	441	531
18	1	28537	475	2160	2603
22	1	59486	990	4500	5420
26	1	68538	1142	5250	6330
30	1	62290	1038	4720	5690
34	1	32458	541	2460	2970
38	1	7544	126	573	691
42	1	1475	25	114	138
46	1	1102	18	82	99

<sup>a</sup> Data taken with RCL Model 10503 BF<sub>3</sub> counter

<sup>b</sup> Counter efficiency taken as 22 per cent

<sup>c</sup> Counter sensitivity taken to be 0.83 counts/sec. per unit neutron flux



**FIGURE 9. FLUX PLOT FOR NEUTRON HOWITZER**

#### IV. DISCUSSION

In the following sections the results of this investigation are reviewed, recommendations for future work are presented, and the limitations imposed upon the investigation are stated.

##### Discussion of Results

The discussion of results deals with the design and construction, safety considerations, and test results of the experimental system used in this investigation.

Design and Construction of the System. The design and construction of the system consisted of providing a reaction chamber which could be irradiated with an appreciable neutron flux and from which samples could be taken for colorimetric analysis for ammonia concentration. An identical, but non-irradiated, parallel system was provided so that the effects of neutrons on the ammonia synthesis could be compared (see Figure 4, page 51).

Neutron Howitzer. The only two methods of slow neutron irradiation available were a subcritical graphite reactor<sup>(42)</sup> and a paraffin howitzer. It was decided that a howitzer should be used

because of the problems involved in constructing a large reaction system inside the reactor. There was also some danger of explosion from pressure; this was highly undesirable inside an expensive reactor.

Reaction Tubes. It was at first decided that fused silica reaction tubes should be used. Silica has a low neutron absorption cross section and provides catalytic surface for the ammonia synthesis reaction. However, the silica tubes obtained proved to be incapable of holding pressures over a few atmospheres. These tubes were therefore discarded, and thick pyrex tubes were used instead. The pyrex tubes were more easily sealed than were the silica tubes, and they held six atmospheres pressure easily. The only drawback to glass tubes was that they contained boron, which has a very high thermal neutron absorption cross section.

Safety Considerations. Hydrogen was passed into the atmosphere outside of the building to decrease the danger of a gas explosion. There was no smoking allowed in the reactor laboratory; this is a standing rule. The howitzer was designed so that there was enough paraffin between the neutron sources and the outside of the howitzer to reduce the neutron flux below 100 neutrons per square centimeter-second at the surface. The sources were only handled by the instructor



in charge of the laboratory, and radiation warning signs were placed on the hewitzer when the sources were inside. Dosimeters were worn at all times inside the reactor laboratory.

Colorimetry. The calibration of the colorimeter was made with newly-made Nessler's reagent. The stability<sup>(38)</sup> of Nessler's reagent for more than five days is questionable. From Figure 6, page 46, optical density of a sample of ammonia solution and Nessler's reagent is directly proportional to the concentration of ammonia in the solution. The optical density of Nessler's reagent in water was found to be 0.101. The ratio of corrected optical densities of two samples is therefore equal to the ratio of the ammonia concentrations in the samples, for samples of equal volume (see Table III, page 48). The volume of the samples was ten milliliters, and the volumes of the reaction tubes were within four per cent of each other.

Production of Ammonia. Although the purpose of this investigation was to determine effects of pressure and hydrogen concentration on ammonia synthesis under neutron irradiation, the investigation was exploratory in that the production of ammonia had to be ascertained. This production had to include not only ammonia produced by the

amount of synthesis occurring in a static mixture of hydrogen and nitrogen but also ammonia synthesized by the catalysis of neutron irradiation in the same system.

The spectra of one sample compared with a prepared ammonium chloride standard, shown on Figure 8, page 52, proves that the product of the reaction was ammonia. The sample spectrum was checked with a sample of lower optical density, and the shapes of the curves were the same. Because the concentration of the ammonium chloride standard was known and the optical density of this standard was very close to that of the sample at all wavelengths, the concentration of ammonia was shown to be the only coloring agent responsible for the optical density of the sample. The mixed but unreacted gases were tested for ammonia at five atmospheres pressure. The optical density was 0.102, which shows that a negligible amount of ammonia was introduced into the system with the reactants.

Flux Determination. The magnitude of the thermal neutron flux may or may not have a determining part as a catalyst for the formation of ammonia. The flux plot found on Figure 9, page 54, is typical for the inside of a neutron howitzer taken along a horizontal axis. More than half of the synthesis gas mixture was outside of the howitzer and was not subjected to a high neutron flux. A logarithmic mean was taken in the case of the flux plot on Figure 9 to give an

average thermal neutron flux of 700 neutrons per square centimeter-second. This is a low flux for the sources used, but the boron and other impurities in the pyrex tube probably absorbed most of the neutrons before they reached the gas mixture. Flux measurements were taken by means of a boron trifluoride counter<sup>(41)</sup> because the more accurate method of using a calibrated foil<sup>(4)</sup> was not available. Background radiation was included in the flux measurement, but an attempt was made to provide the same surroundings for the flux determination as had been present during the actual tests.

Effects of Pressure. No conclusions can be made concerning the effects of pressure on ammonia synthesis under neutron irradiation. The curves on Figure 7, page 49, indicate that the results of this investigation are meaningless for indicating the direct action of neutrons on the reacting gases except that more ammonia was formed in the irradiated than in the non-irradiated system in every test.

Effects of Hydrogen Concentration. No conclusions can be made concerning the effects of hydrogen concentration on ammonia synthesis under neutron irradiation. The curves on Figure 7, page 49, do not show any effects of concentration at the conditions of ammonia synthesis given on Table II, page 47.

Duplication of Tests. Although it is evident that the tests should have been duplicated, duplication was not feasible because of the length

of each test and because the neutron sources used in the tests were not available when they were used in laboratory experiments.

Surface Catalysis. There is some evidence presented in the results of this investigation that the catalysis by neutron irradiation is concentration at the surface. In the tests made at four and five atmospheres pressure, the additional ammonia obtained by rinsing the walls of the reaction tubes was greater for the irradiated than for the non-irradiated tube. This surface activity may arise from (a) formation of catalysts by transmutation, from (b) direct action of neutrons on molecules of gas, or from (c) exchange of energy at the surface of the tube.

Based on the absorption cross sections of the materials in the glass and on the flux, the transmutation effected would be negligible. Since about  $10^4$  atoms of ammonia were formed for each neutron available, the possibility of action of the neutrons directly on the gas molecules is very unlikely because it would involve a chain-type transfer of energy. A possible explanation for the increased yield under radiation is the transfer of energy from the neutrons to the surface of the tube, increasing its catalytic activity. However, further experiments would be necessary to substantiate this idea.

In terms of nitrogen, molar conversion to ammonia varied from  $8 \times 10^{-4}$  per cent to  $2.5 \times 10^{-3}$  per cent. It is obvious from Table III, page 48, that the molar conversions do not follow a general pattern. The highest conversion,  $2.5 \times 10^{-3}$  per cent, occurred at the lowest pressure, three atmospheres.

#### Recommendations

The following recommendations are made concerning the procedure and the problem of this investigation.

Nessler's Reagent. It is recommended that the Nessler's reagent, for the sake of surety, be prepared not more than four or five days before use.

Duplication. It is recommended that, hereafter, any tests made on this problem be duplicated at least once.

Shorter Tubes. If a howitzer is to be used it is recommended that the reaction tubes not extend beyond the surface of the howitzer.

Catalysts. It is recommended that catalysts be added to the reaction vessels as a part of further tests. Addition of catalyst to the reaction system would give an indication of possible surface catalysis caused by neutrons; this would also increase the concentrations of ammonia to be analyzed.

Higher Pressures. It is recommended that ammonia synthesis under neutron irradiation be studied at pressures higher than those used in this investigation.

Higher Fluxes. It is recommended that ammonia synthesis be studied at neutron fluxes higher than the flux used in this investigation.

#### Limitations

The limitations imposed upon this investigation are given in the following paragraphs.

Reactants. The reacting gases were electrolytic hydrogen and commercial grade nitrogen.

Pressure. The gases were reacted at pressures of 3.0, 4.0, and 5.0 atmospheres.

Hydrogen-Nitrogen Ratio. The gases were reacted at hydrogen-nitrogen molar ratios of 3.0 and 6.0.

Temperature. The gases were reacted and the samples were analysed at ambient temperature.

Reactor Tubes. The hydrogen and nitrogen were reacted in pyrex tubes of two inches inside diameter and four feet long. The volumes of the blank and irradiated reaction spaces were 2490 and 2580 cubic centimeters, respectively. The tubes were sealed with Type 316 stainless steel blank flanges and teflon gaskets.

Neutron Flux. Neutrons were provided by four plutonium-beryllium sources with a surface strength of  $10^7$  neutrons per square centimeter-second. The average neutron flux at the center of the reaction tube was 700 neutrons per square centimeter-second.

Reaction Time. The gas mixtures were allowed to react for 24 hours; this gave a total neutron flux of  $6.05 \times 10^7$  neutrons per square centimeter.

Moderator. The neutrons were slowed by at least 5.5 inches of 133 AMP paraffin wax.

Amount of Absorbent. Ammonia was collected in ten milliliter portions of distilled water made slightly acid with hydrochloric acid.

Washing of Tubes. The ammonia on the walls of the tubes was washed off with distilled water made slightly acid with hydrochloric acid.



## V. CONCLUSIONS

From tests of ammonia synthesis in irradiated and non-irradiated, static mixtures of hydrogen and nitrogen contained in pyrex reaction tubes, at an average total neutron flux of  $6.05 \times 10^7$  neutrons per square centimeter, ambient temperature ranging from 27 to 32 degrees centigrade, pressures of 3.0, 4.0 and 5.0 atmospheres, hydrogen-nitrogen molar ratios of 3.0 and 6.0, and reaction time of 24 hours, the following conclusions may be drawn:

1. The amount of ammonia formed in the irradiated reaction tube was from 4 per cent to 73 per cent greater than the amount formed without irradiation.
2. The results for testing the effect of ratio of reactants and of pressure were too scattered to permit any valid conclusions.
3. Ammonia synthesis under neutron irradiation is worthy of further study as a possible industrial process.

## VI. SUMMARY

The purpose of this investigation was to determine the effects of mild pressures and hydrogen concentrations on the formation of ammonia by slow neutron irradiation of gaseous hydrogen-nitrogen systems. A secondary purpose of this investigation was to determine the effects of neutron irradiation on ammonia synthesis.

Apparatus consisted of two parallel reaction tubes identical except that one was under an average neutron flux of 700 neutrons per square centimeter-second in a paraffin howitzer. The reaction tubes were of pyrex with inside diameter of two inches and length of four feet. Ammonia produced was absorbed in ten milliliter portions of very dilute hydrochloric acid, and the rinsings from the tube walls were added to the sample. Analyses of the samples were made with Nessler's reagent and a colorimeter.

Tests were performed at pressures of 3.0, 4.0, and 5.0 atmospheres and at hydrogen-nitrogen molar ratios of 3.0 and 6.0. Reaction time was 24 hours, and average total flux was  $6.05 \times 10^7$  neutrons per square centimeter.

It was found that the amount of ammonia formed in the irradiated reaction tube was from 4 per cent to 73 per cent greater than the amount formed without irradiation, the results for testing the effects of ratio of reactants and of pressure were too scattered to permit any valid conclusions, and that ammonia synthesis under neutron irradiation is worthy of further study as a possible industrial process.

## VII. BIBLIOGRAPHY

1. Allen, A. O., C. J. Hechanadel, J. Gardner, and T. W. Davis: Decomposition of Water and Aqueous Solutions Under Mixed and Fast Neutron and Gamma Radiation, *J. Phys. Chem.*, 56, 575-586 (1952).
2. Bates, T. H., J. K. Linacre, W. R. Marsh, and J. Wright: Effect of Radiation on Heterogeneous Systems of Air and Nitrogen and Water, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, 1, 560-568 (1955).
3. Briggs, G. H. and M. Goldhaber: Scattering of Slow Neutron, *Proc. Roy. Soc.*, 162, 127-129 (1937).
4. Cain, V. M.: Personal Communication, March 26, 1958. Oak Ridge, Tennessee.
5. Chaing, J., M. Goldhaber, and J. E. Willard: Some Effects of Temperature, Phase, and Nature of Chemical Species on Halogen Atom Reactions Irradiated by Radiative Neutron Capture and by Isomeric Transition, *J. Am. Chem. Soc.*, 73, 2271-2274 (1951).
6. Cohen, V. W., H. H. Goldsmith, and J. Schwinger: The Neutron-Proton Scattering Cross Section, *Phys. Rev.*, 55, 106 (1939).
7. Cook, G. B., and J. F. Duncan: "Modern Radiochemical Practice," pp 91-112. The Clarendon Press, Oxford University Press, London, England, 1952.
8. DeVault, D. C., and W. F. Libby: Evidence of Gamma-Radioactivity of 4.5-hour  $\text{Br}^{80}$  from Radiobromate, *Phys. Rev.*, 55, 321 (1939).

9. Dolin, P.I., and B.V. Ershler: Radiolysis of Water in the Presence of  $H_2$  and  $O_2$  due to Reactor Radiation, Fission Fragments, and X-Radiation, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, 1, 564-72 (1955).
10. Fox, O.M., and W.F. Libby: The Hot Atom Chemistry of the Propyl Bromides; Effect of Phase and Recoil Energy on Retentions, J. Chem. Phys., 20, 487-90 (1952).
11. Friedman, L., and W.F. Libby: The Hot Atom Chemistry of Propyl Bromides, J. Chem. Phys., 17, 647-56 (1949).
12. Glasstone, S., and M.C. Edlund: "The Elements of Nuclear Reactor Theory," pp. 27-29. D. Van Nostrand Company, Inc., Princeton, N. J., 1952.
13. *ibid*, pp. 43-46.
14. *ibid*, pp. 48-59.
15. *ibid*, pp. 161-165.
16. *ibid*, pp. 211-213.
17. Halford, R.S., G.T. Seaborg, and E. Segre: Chemical Separation of Nuclear Isomers, Phys. Rev., 55, 321-44 (1939).
18. Halliday, D.: "Introductory Nuclear Physics," pp. 89-113. John Wiley and Sons, Inc., New York, N. Y., 1955. 2 ed.
19. *ibid*, pp. 214-243.
20. Hamermesh, B., G.R. Rings, and S. Wexler: Thermal Neutron Cross Section for Atomic Hydrogen, Phys. Rev., 90, 603-6 (1953).
21. Hamill, H.W., and R.R. Williams: Chemical Kinetics of Bromine Following Neutron Capture, J. Chem. Phys., 16, 1171-9 (1948).

22. Harrison, R. H., and K. A. Kobe: Thermodynamics of Ammonia Synthesis and Oxidation, *Chem. Engr. Prog.*, 49, 349-58 (1953).
23. Hart, E. J., W. R. McDonell, and S. Gordon: The Decomposition of Light and Heavy Water Boric Acid Solutions by Nuclear Reactor Radiations, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, 1, 593-8 (1955).
24. Hein, L. B.: Three New Processes for Ammonia Synthesis, *Pet. Proc.*, 7, 1462-77 (1952).
25. Hechanadel, C. J.: Radiation Induced Reactions in Water, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, 1, 521-25 (1955).
26. Hornig, J. F. and J. E. Willard: Effect of Bromine Concentration on the Products of the Reaction of Carbon Tetrachloride with Bromine Activated by Radiative Neutron Capture and Isomeric Transition, *J. Am. Chem. Soc.*, 75, 461-6 (1955).
27. Humphreys, J. R.: The Effects of Reactor Radiation Upon High Temperature Static Water Systems, *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, 1, 583-90 (1955).
28. Johnson, C. H., and H. H. Barschell: Energy Spectra for the Nitrogen (n, p) Reaction, *Phys Rev.*, 80, 818-23 (1950).
29. Kilpatrick, M. L., and F. O. Rice: Decomposition Reactions of Hydrogen Peroxide, *J. Phys. Chem.*, 31, 1507-13 (1927).
30. Libby, W. F.: Reactions of High Energy Atoms Produced by Slow Neutron Capture, *J. Am. Chem. Soc.*, 62, 1930-43 (1940).
31. Massey, H. S. W., and N. F. Nott: "The Theory of Atomic Collisions," p. 308. Oxford at the Clarendon Press, London, England, 1949. 2 ed.

32. Millar, C. H., and G. A. Bartholomew: The Nitrogen (n, p) Reaction Under Slow Neutrons, *Phys. Rev.*, 81, 150-2 (1951).
33. Rosin, J.: "Reagent Chemicals and Standards," pp. 5-7. D. Van Nostrand Co., Inc., New York, N. Y., 1937.
34. Rossini, F. D.: "Thermodynamics and Physics of Matter," pp. 52-71. The University Press, Princeton, N. J., 1955.
35. Semat, H.: "Introduction to Atomic and Nuclear Physics," pp. 63-4. Rinehart and Co., Inc., New York, N. Y., 1956. 3 ed.
36. Shreve, R. N.: "The Chemical Process Industries," pp. 399-410. McGraw-Hill Book Co., Inc., New York, N. Y., 1956. 2 ed.
37. Snell, F. D., and Cornelia T. Snell: "Colorimetric Methods of Analysis," Vol. II, pp. 7-12. D. Van Nostrand Co., Inc., New York, N. Y., 1949. 3 ed.
38. *ibid*, pp. 808-824.
39. Thompson, F. J., and G. R. Morrison: Determination of Organic Nitrogen; Control of Variables in the Use of Nessler's Reagent, *Anal. Chem.*, 23, 1153-7 (1951).
40. Wahl, A. C., and N. A. Benner: "Radioactivity Applied to Chemistry," pp. 24-6. John Wiley and Sons, Inc., New York, N. Y., 1951.

ADDENDA

41. Price, W. J.: "Nuclear Radiation Detection," pp. 261-3.  
McGraw-Hill Book Co., Inc., New York, N. Y., 1958.
42. Schuler, T.M.: The Design and Construction of a  
Subcritical Nuclear Reactor. Unpublished M.Sc. Thesis,  
Library, Virginia Polytechnic Institute, Blacksburg,  
Virginia, (1957).



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**ABSTRACT**

**INVESTIGATION OF THE EFFECTS OF PRESSURE AND HYDROGEN  
CONCENTRATION ON AMMONIA SYNTHESIS**

**UNDER NEUTRON IRRADIATION**

by

**Robert Lewis Durfee**

**A Thesis Submitted to the Graduate Faculty of  
the Virginia Polytechnic Institute in Candidacy  
for the Degree of Master of Science**

in

**NUCLEAR ENGINEERING PHYSICS**

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Blacksburg, Virginia**

**1958**

## ABSTRACT

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