MITNE-2

UNCLASSIFIED NYO - 2347

AMMONIA DISTILLATION FOR DEUTERIUM SEPARATION

by

G. T. Petersen and M. Benedict

Massachusetts Institute of Technology
Nuclear Engineering Department
Contract No. AT (30-1)2249
May 16, 1960
July, 1958 - May, 1960

UNCLASSIFIED NYO - 2347

AMMONIA DISTILLATION FOR DEUTERIUM SEPARATION

by

G. T. Petersen and M. Benedict

Massachusetts Institute of Technology
Nuclear Engineering Department
Contract No. AT (30-1)2249
May 16, 1960
July, 1958 - May, 1960

UNCLASSIFIED NYO-2347

Distribution	No. of Copies
A.E.C. New York Operations Office	8
A.S. Friedman. A. E. C. Washington	2
Nuclear Engineering Department, M. I. T.	10
Industrial Liaison Office, M. I. T.	50
M. Benedict	1
J. E. Bigelow	1
Contractors John Brown	1
W. P. Drews	1
W. Hinkle	1
M. P. Kalman	1
B. Lazard, French A. E. C.	1
P. Lualdi	1
J. Moss	1
J. Neill	1
G. T. Petersen	9
D. F. Stedman, National Research Labs., Canada	1
Total Distribution	90

The contents of this report have been submitted by Mr. G. T. Petersen to the Massachusetts Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

"AMMONIA DISTILLATION FOR DEUTERIUM SEPARATION"

by

GERALD THORNTON PETERSEN

Submitted to the Department of Nuclear Engineering on May 16, 1960 in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Nuclear Engineering.

ABSTRACT

The relative volatility or separation factor for deuterium enrichment in ammonia distillation was measured at several pressures and deuterium concentrations. Over the range of pressure (250 mm - 760 mm Hg.) and the range of composition 0.10 - 0.58 mole fraction deuterium, the measurements are adequately expressed by the following equation:

$$\ln(\alpha) = (0.0395 \pm 0.0004) - (0.0128 \pm 0.0029)(x - 0.424) - (0.01246 \pm 0.00065)\left(\ln \frac{\pi}{760\text{mm}} \text{ Hg.}\right)$$

α = separation factor

π = system pressure mm Hg.

x = liquid composition, mole fraction deuterium.

It is interesting to note that a dependence on the composition was observed. Although this is not predicted by the normal method of calculating the separation factor from the vapor pressure ratio

$$\alpha = \sqrt[3]{P_{NH_3} / P_{ND_3}} ,$$

its existence has been postulated due to the asymmetry of the partially deuterated ammonia molecule. However, the magnitude of the separation factor as well as its dependence on pressure were in good agreement with the vapor pressure ratio predictions. ($\alpha = 1.042$ at 1 atm.)

The knowledge of this information is very helpful in predicting costs of heavy water production by the ammonia distillation process. It has been stated by others, that the ammonia distillation process of heavy water production would be competitive with other developed methods only if the actual separation factor was at least 1.062 at low deuterium concentration. Unfortunately, the measurements do not indicate that the separation factor at low deuterium composition differs greatly from the vapor pressure prediction. ($\alpha = 1.042$)

Deutero-ammonia was synthesized by isotopic exchange between natural ammonia and heavy water. Equilibrium determinations were made using an Othmer still, modified for low temperature operation, and a concentric tube fractionating column. The ammonia samples were analyzed for deuterium content by converting them to water by flow through hot copper oxide, followed by a differential density determination using the falling drop method.

Thesis Supervisor: Professor Manson Benedict
Title: Head of Department, Nuclear Engineering

Acknowledgement

The authors wish to thank the following men who have been of invaluable help in performing this work: Mr. John Neill for his assistance and advice in the early stages of the investigations and Messrs. William Hinkle, John Moss, and Paul Lualdi for their untiring efforts in taking experimental measurements. The financial support of the U. S. Atomic Energy Commission is acknowledged with gratitude.

TABLE OF CONTENTS

Figures, Tables, Graphs and Plates

Figures | Page

Tables

Graphs

Plates

I. Introduction

The current rapid development of nuclear power reactors seems destined to require a continued expansion of heavy water production facilities. It has been estimated that heavy water requirements for power reactors will be 480 tons per year in 1960 and increase to 35,600 tons per year in 1978. (11, 32) Further expansion may be required if the fusion process becomes a reality in the next few years.

Since the main stimulus for the development of commercial nuclear power is its competitive potential with fossil fuels, every effort is being made to reduce the cost of the nuclear components essential for the operation of power reactors. Since a single heavy water moderated reactor requires about 100 tons of heavy water, at a current value of about $6,000,000, it becomes evident that a reduction in heavy water cost would significantly effect the economics of nuclear power. The incentive for the work done on this thesis stems from the economic promise of a proposed method of heavy water production.

Heavy water has been manufactured by several processes: distillation of ordinary water, electrolysis of water, exchange reactions between hydrogen compounds, distillation of hydrogen, and distillation of other hydrogen compounds.(6) During World War II, the crash program necessitated the construction of several plants with little research and development work on the various methods available. Economically it is now important to study all the feasible methods of production to determine the most inexpensive process.

Recently Barr and Drews have surveyed all the promising heavy water production techniques from the economic point of view. (3, 13) Drews used the hydrogen sulfide-water dual temperature exchange process as a target for comparison. This process is currently being used by the Atomic Energy Commission for heavy water production. A detailed description of the process and its economics are found in an A.E.C. report by Bebbington and Thayer (4). The current A.E.C. heavy water price is $28.00 per pound.

The potential advantages of the ammonia distillation techniques are (compared to water distillation):

1. Relatively low latent of vaporization
2. Reasonably good separation factor
3. Relatively high vapor pressure for reasonable separation factor.

Its major disadvantage is that unless a large stream of ammonia is available some means of introducing deuterium feed in the form of natural water must be supplied.

If heavy water were produced as a by product at all the ammonia plants in the U.S.A., a total of about 1000 tons of heavy water could be produced per year. However, the maximum practical yield of heavy water from any one ammonia plant is only about 35 tons per year. This figure is small when compared to the large amount of heavy water (about 100 tons) used in a single large heavy water nuclear power reactor.

The most favorable cost estimates of heavy water production by ammonia distillation are than based on the parasitic type of plant using an ammonia stream already in existence. When additional equipment must be added to introduce deuterium feed as water, the costs become appreciably higher.

Cost figures are given by Barr and Drews for three ammonia distillation plants:

a) A base plant

b) A parasitic plant

c) A very optimistic parasitic plant

In the very optimistic case, it was assumed that several savings could be attained in equipment costs by novel techniques not demonstrated to date.

Cost Analysis of Barr and Drews (3, 13)

		Ammonia Distillation Plants		
			Parasitic Plants	
Cost	Target H_2S	Base Plant	Realistic	Very Optimistic
On Site Investment per ton D_2O year	$250,000	$365,000	$290,000	$247,000
Operating Costs per pound D_2O				
Interest, Depreciation	$20,90	$29.95	$23.25	$19.80
Utilities	7.10	33.85	17.65	9.10
Total	$28.00	$63.10	$40.90	$28.90

In addition to plants using ammonia distillation as the sole method of deuterium enrichment, others including additional techniques have been studied. One such combination has been proposed by a British firm and includes ammonia distillation as the intermediate enrichment step following dual temperature exchange between ammonia synthesis gas and liquid ammonia and preceeding water distillation. (18)

The economics of these proposals are dependent on the relative volatility or separation factor for deuterium separation in the distillation of ammonia. Barr and Drews' cost estimates have been based on the assumption that this relative volatility may be evaluated from the vapor pressure ratio. ($\alpha = \sqrt[3]{\text{vapor pressure } NH_3 \text{ / vapor pressure } ND_3}$) This assumption is based on ideal solution theory and does not allow for any anomalies in the volatility relation.

The relative volatility of the components to be separated is basic to any distillation design. The relative volatility for a binary system is defined as:

$$\alpha = \frac{y_A / x_A}{y_B / x_B} \qquad (1.1)$$

x = mole fraction in liquid

y = mole fraction in vapor

A = more volatile component

B = less volatile component

For special cases, the liquid may follow Raoult's law which states that the partial pressure exerted by a component in solution is equal to the full vapor pressure of the component multiplied by the mole fraction of the respective component. For a binary system:

$$p_A = P_A x_A \qquad (1.2)$$

$$p_B = P_B (1 - x_A) \qquad (1.3)$$

where: p = partial pressure

P_A = total vapor pressure of component A

P = total pressure

$P = p_A + p_B = P_A x_A + P_B (1 - x_A)$

Assuming the mole fraction of component "A" in the vapor is equal to the ratio of the partial pressure of "A" to the total pressure,

$$y = \frac{p_A}{p_A + p_B} = \frac{P_A x_A}{P_A x_A + P_B (1 - x_A)} = \frac{P_A x_A}{P} \qquad (1.4)$$

If in addition to the liquid following Raoult's law, the vapor follows Dalton's law,

Dalton's law states:

$p_A = y_A P$

$p_B = y_B P$

then the relative volatility can be directly calculated from the vapor pressures of the pure components for a binary system.

Since $y_A = \frac{P_A x_A}{P}$ and $y_B = (1 - y_A) = \frac{P_B x_B}{P}$

Substitution in $\alpha = \frac{y_A / x_A}{y_B / x_B}$ (1.1)

Gives $\alpha = \frac{P_A}{P_B}$ (1.5)

For the deuterated ammonia system the relative volatility or separation factor for deuterium enrichment in ammonia distillation is defined as:

$$\alpha = \frac{y_H / x_H}{y_D / x_D} \qquad (1.6)$$

Where: x = mole fraction in liquid

y = mole fraction in vapor

H = hydrogen

D = deuterium

The ammonia system is not binary, but consists of the four species in equilibrium: NH_3, NH_2D, NHD_2, and ND_3. As written above the separation factor does not depend on the concentration of the individual species, but on the over-all deuterium enrichment.

When a system contains more than two components it becomes necessary to make further assumptions about the behavior of the components to be able to estimate the volatility from vapor pressure data. If one assumes that in the ammonia system under consideration, equilibrium is maintained in the liquid phase between the species: NH_3, NH_2D, NHD_2, and ND_3, and in addition:

1. Gaseous, and liquid mixtures follow Dalton's and Raoult's laws respectively (Ideal Solutions).
2. The vapor pressure ratios are equal.

$$\frac{P_{NH_3}}{P_{NH_2D}} = \frac{P_{NH_2D}}{P_{NHD_2}} = \frac{P_{NHD_2}}{P_{ND_3}}$$

3. A random distribution of deuterium and hydrogen atoms at equilibrium among the species.

Then the following relationship between relative volatility and vapor pressure is valid.

$$\alpha = \frac{y_H / x_H}{y_D / x_D} = \sqrt[3]{\frac{P_{NH_3}}{P_{ND_3}}}$$ (See Appendix Section F1 for derivation) (1.7)

Where P = vapor pressure

By extrapolation of the sub-atmospheric data of Kirshenbaum and Urey (26) $\alpha = 1.041$ at the normal boiling point. By interpolation between the low pressure data of Kirshenbaum and Urey (26) and Taylor and Jungers (33) and the high pressure data of Groth (17) one obtains $\alpha = 1.042$ at the normal boiling point. (See Graph 6)

The validity of the above assumptions is questionable when applied to the ammonia system. In fact, it has been shown by infra-red analysis that the species are not randomly distributed in a 0.50 mole fraction deuterium gaseous ammonia sample. (31) It was found that the end members NH_3 and ND_3 were highly favored. The preference for the end members can also be shown from calculations of the partition functions for each of the species. (24) The calculations do not, however, predict the asymmetry to be as severe as the measurements indicate. It has been further observed that the boiling point elevation caused by increasing the deuterium concentration from 0.00 to 0.33 mole fraction is higher than that caused by increases from 0.33 to 0.67 and from 0.67 to 1.00 mole fraction deuterium. (30) These effects are attributable to the asymmetry of the partially deuterated molecule, and could cause a definite deviation in the relative volatility from the vapor pressure prediction. In fact, one investigator estimated that a relative volatility as high as 1.088 is possible at low deuterium concentrations. (30) Barr and Drews (3) have estimated that if this were true, the cost of producing heavy water by distillation of ammonia would be reduced to 50 percent of that given in the preceding table, thus making this process economically preferable to the H_2S process presently used by the U.S. A.E.C.

The purpose of the investigation described in this thesis has been to make a direct experimental measurement of the relative volatility, or separation factor, in the distillation of ammonia, to determine whether this property may be estimated reliably from the ratio of vapor pressures of NH_3 to ND_3. The separation factor has been measured at deuterium mole fractions ranging from 0.10 to 0.58 and at pressures of 250, 375, 500, 600, and 760 mm. Hg. This work extends and refines a preliminary study of this system reported in a Master's thesis by Kalman and the author. (22)

II. Apparatus and Procedure

A. Single Stage Equilibrium Devices

Vapor liquid equilibria have been determined by several techniques. Among the more familiar is the circulation method, in which vapor is continuously recirculated through the liquid until no further change occurs in either the composition of the liquid or the vapor. This method requires a pump to circulate the vapor and demands that the liquid and vapor be analyzed frequently to determine whether equilibrium has been attained.

Another method referred to as the "Bomb" method, consists in placing liquid in an evacuated container and agitating it in a constant temperature bath until equilibrium is reached. The taking of samples is rather difficult and the method is prone to large experimental errors. The dew and boiling point method is one in which liquid of known composition is charged to a variable volume apparatus. The pressure is measured at which vaporization and condensation occur for a given temperature. The apparatus, however, is difficult to construct and operate.

A dynamic distillation method is one in which a small amount of liquid is distilled from a large volume of liquid of known composition, and the distillate analyzed. This method is relatively simple, and simulates actual operating conditions. However, it requires a large amount of initial inventory. One of the most widely used methods is referred to as the continuous distillation method. It involves the distillation of a liquid, condensing of the vapor sample, and recycling the condensate back into the still. After a steady state is reached, samples of residue and distillate are withdrawn.

Of the above methods, the most practical for the ammonia system was the continuous distillation procedure. The apparatus is simple, compact, easy to operate, and accurate results can be obtained in a relatively short time. The volume of the still charge is smaller than the volume required for most of the other methods. Another advantage is the fact that this method simulates conditions encountered in the actual industrial operations, and therefore provides a good basis for process evaluation.

Robinson and Gilliland (29) give concise descriptions of each of the above mentioned methods as well as numerous references to original experimenters. They also state that from the analysis of the published data obtained by the continuous distillation method, it appears that this method gives data which is within 10 percent among investigators using essentially the same technique.

Ebeling (14) also describes the various techniques, and also enumerates the sources of inaccuracies inherent in each method. Williams (35) describes a continuous distillation still designed expressly for the purpose of obtaining equilibrium data at low temperatures (-40°C.). He suggests that his still or some modification of it would be applicable to the deuteroammonia-ammonia system.

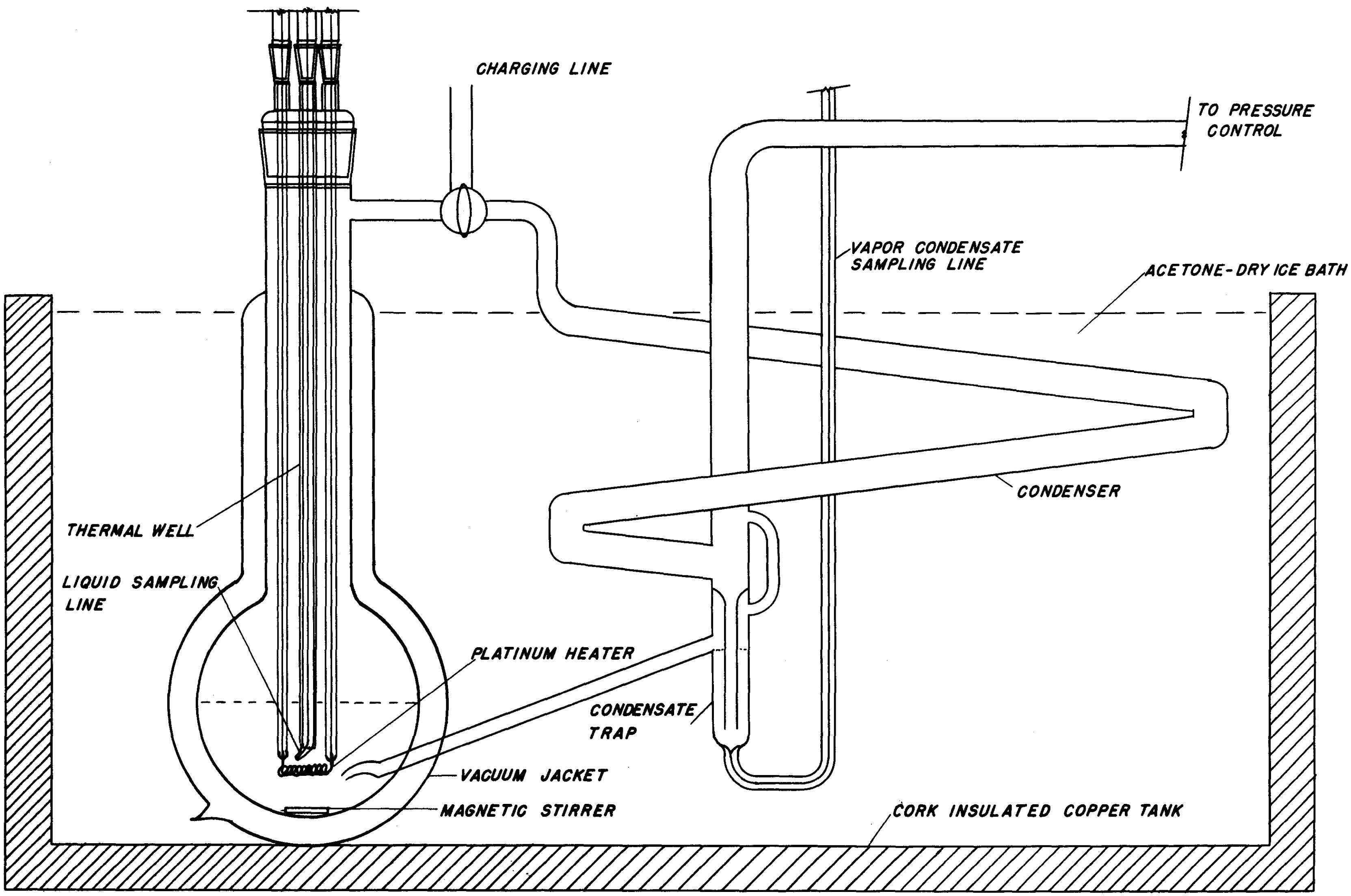
A modification of the continuous distillation still described by Williams was chosen for the present investigation of the deuteroammonia-ammonia system. It was felt that it incorporated more of the desirable features than the other alternatives.

B. The Equilibrium Still

The equilibrium still used in this work is shown in Figure 1. The still consisted of a 1000 ml. boiling flask, a condenser, a condensate trap, and a condensate return line, all made of Pyrex glass. The boiling flask was insulated by encasement in a vacuum jacket of about one-half inch greater radius. During operation of the still, liquid ammonia was boiled in the flask. The vapor then passed up and out of the flask into the condenser where it was condensed and ran down into the condensate trap. A vent line was attached to the top of the condensate trap. to provide for the escape and entrance of non-condensable gases during the still operation to keep the still pressure constant.

The condensate trap provided a reservoir of freshly distilled material which could easily be sampled without disturbing the operation of the still. The center tube in the condensate trap assured that fresh material would continuously pass the sampling point at the bottom of the trap. From the bottom of the trap samples could be drawn through the capillary sampling line.

During operation, all but the neck of the still and the vapor delivery line were immersed in an acetone bath, cooled with dry ice to 10°C below the boiling temperature inside the still. The still was operated with the boiling flask approximately half full of liquid ammonia. Liquid was boiled by an immersion electric heater constructed of 50 cm. of 0.2 mm. platinum wire. The ends of the platinum wire were connected to tungsten leads and these in turn were sealed into the bottom of Pyrex glass tubes which entered the still through the large inner, 45/50



EQUILIBRIUM STILL
FIG. 1

ground glass joint in the neck of the boiling flask. During normal operation, the heater was submerged one inch below the liquid ammonia.

Copper leads were connected to the tungsten leads on the upper side of the glass seals and were carried through the tube and out of the flask. The heater was designed for a maximum power of 200 watts, but was never operated over 80 watts. Two hundred watts corresponded to a heat flux of 2 x 10^5 BTU/hr. $ft.^2$ and 18 volts across the heater. During normal operation the power was adjusted to 34 watts corresponding to one ml. of of liquid vaporizing per minute.

To facilitate fabrication of the large, 45/50, inner joint, as well as to simplify modification, the Pyrex tubes containing the heater leads were fitted with 10/30 ground glass fittings that formed the seal with the 45/50 joint. The liquid sampling capillary line, which also pierced the 45/50 joint, was similarly sealed with a 10/30 fitting. This proved to be very fortunate since this sampling line was modified several times. The thermowell, located on the center line between the three 10/30 fittings was made as an integral part of the 45/50 fitting.

Vapor was removed from the boiling flask through a side arm located above the refrigerant level on the neck of the flask. This vapor was condensed in about 60 cm. of 16 mm. Pyrex tubing which was coiled below the level of the acetone refrigerant. The diameter of the condenser as well as its pitch was increased from Williams' design to permit operation at higher boiling rates and lower pressures. The condensate trap at the lower end of the condenser maintained a small volume (3 ml.) of condensate for sampling. The condensate entered the trap from the top and flowed down the central tube, delivering fresh condensate to the bottom of the trap well at all times. The condensate left the trap by overflowing into the condensate return line, which returned it to the center of the boiling flask. The upper portion of the trap was connected to the vent line of the still so that free flowing of liquid ammonia would not be restricted. The still vent line attached to both the top of the condensate trap and the condenser was attached to a manostat for pressure control. The insertion of a dry ice cooled trap in this line prevented moisture from entering the still.

The refrigerant which surrounded the condenser and (insulated) still was contained in a copper tank, 27 x 12 x 7 inches, insulated with one-inch of pressed cork. Galvanized steel could not be used because it would block the magnetic field of the stirrer.

The equilibrium still provided reservoirs of liquid ammonia very near its boiling point to be sampled. In sampling these reservoirs, it was important to insure the fact that all the liquid drawn from the reservoir was fully vaporized and that no partially vaporized material returned to the reservoir. This problem was in mind when, in the original design, the sampling lines were made of small 0.3 mm capillary tubing. The reason partial vaporization of the samples could not be tolerated is that if more partial vaporization occurredin one sample line than the other, the composition difference between the liquid and vapor samples would have been in error.

It was not until Runs 1 thru 15 had been made with the equilibrium still that it was realized that even the capillary lines were not sufficient to prevent the partial vaporization of the samples. In these early runs, as in the preliminary results quoted by Kalman and the author in their master's dissertation, there was apparently more partial vaporization in the liquid sampling line than in the condensate sampling line leading to low values of the separation factor.

To eliminate the partial vaporization of samples, constrictions were placed in the capillary sampling lines just before the capillary was fused to standard 7 mm. tubing. The point of transfer from capillary tubing to standard tubing was placed as close to the still as possible, but far enough away so that the segment of standard tubing immediately adjacent to the constriction could be heated with a Nichrome resistance heating coil. At the constriction a pressure drop of at least 1 cm. Hg. was maintained during sampling to prevent any back flow of liquid. Furthermore, any liquid entering this heated section of large diameter tubing was totally vaporized. A mercury manometer was used to measure the pressure drop across the capillary. After these precautions were taken, very little difficulty was encountered due to partial vaporization.

Any continuous distillation equilibrium still has several possible sources of error:

a. Condensation and refractionation of vapor on vapor space walls. This would cause the concentration of the more volatile component in the vapor to be greater than it would be at true equilibrium, since a second stage of fractionation would have taken place.

b. Complete vaporization of liquid splashed on over-heated vapor space wall. In this case, the liquid would be totally vaporized, causing a lower concentration of the more volatile component in the vapor.

c. Entrainment of liquid in the vapor. This also would result in a decrease in the concentration of the more volatile component in the vapor.

d. Reaction with materials of construction.

e. Improper return of condensate to the still. If this occurs, vaporization of the condensate may take place before it is entirely mixed with the contents of the still. This would cause the vapor to be rich in the more volatile component.

In the operation of the modified Othmer still, used in this work, the possibility of complete vaporization of liquid splashed on overheated walls, as well as partial condensation and revaporization was minimized. The vapor space walls were vacuum jacketed and the outer surface was maintained at a temperature (10°C less) than the boiling point of ammonia. The entrainment of liquid in the vapor was very unlikely due to the fact that the still was operated at a low boiling rate. The fifth possible error was eliminated by using a magnetic stirrer to mix the return condensate with the contents of the still.

Because this is an isotopic separation study, isotopic exchange with materials of construction becomes an important problem. The basic problem was to eliminate any hydrogeneous materials from the system. The entire still and its associated tubing were constructed from Pyrex glass, and all ground glass fittings were lubricated with a completely halogenated grease.

Temperature measurements within the equilibrium still were made with a chromel-alumel thermocouple; E.M.F. readings being made with a Leeds and Northrup type "K" potentiometer. Since the potentiometer indicated the potential to the nearest tenth of a microvolt, errors in voltage measurement should have been negligible. All measurements were made with a reference junction maintained at 0.00°C. in an ice bath.

The thermocouple was calibrated at the following reference points: (See Appendix Sec. B5)

Carbontetrachloride Freezing Point	-22.9 °C.
Natural Ammonia Boiling Point (26)	-33.48°C.
Mercury Freezing Point	-38.87°C.
Chlorobenzene Freezing Point	-45.2 °C.
Chloroform Freezing Point	-63.5 °C.

There were two possible sources of error in measuring temperatures in the equilibrium still which should be considered. Since the platinum heater was relatively close to the thermowell in which the thermocouple was located there was the possibility of the well being overheated. Also since the top of the well and the thermocouple lead were at room temperature, conduction down the thermowell could introduce additional temperature elevation at the measuring point. Fortunately, these errors did not appear to be significant, since the calibration point obtained by boiling natural ammonia in the still agreed excellently with the other points.

During the sub-atmospheric pressure runs pressure measurements were made with a closed end mercury manometer accurate to 0.5 mm Hg. This accuracy was verified by pressure comparison with barometric pressure readings published by the U.S. Weather Bureau. For the atmospheric pressure runs, the barometric pressure readings available from the M.I.T. Meteorological Department were used. In this case, the variation of the barometric readings during a run were important for accurate temperature correction to one standard atmosphere (760 mm Hg.), and for this reason the time was noted whenever temperature measurements were made and the readings corrected with the pressure reading at that time. The effect of this small pressure variation on the separation factor was much smaller than the other errors introduced and was neglected.

C. Multi-Stage Fractionating Devices

The single-stage equilibrium still described in Section B above was used to measure the separation factor at deuterium mole fractions between 0.58 and 0.10. At these compositions, the difference in deuterium mole fraction between liquid and vapor samples (at 760 mm. Hg.) was 0.010 and 0.004, respectively. At deuterium mole fractions below 0.10, the difference in mole fraction becomes so small that reliable measurement of the separation factor in a single-stage device becomes very difficult.

Yet the composition range below 0.10 mole fraction deuterium is the range of greatest practical interest, because in a plant to concentrate deuterium by distillation of natural ammonia, 99 percent of the cost of production is incurred while concentrating deuterium from 0.00014 mole fraction in the feed to 0.10 mole fraction.

To supplement the measurement of separation factor made with the single-stage equilibrium still with others at deuterium mole fractions below 0.10, it was decided to use a multi-stage device for this low composition range, in order to increase the difference in deuterium content of liquid and vapor samples.

In the choice of a multi-stage unit it was realized that the following features would be desirable:

1. Availability
2. Basic design that would allow estimation of the effect of mole fraction on the number of stages.
3. Low pressure drop
4. Low hold up

5. Small equilibrium times
6. Small charge
7. Compact size
8. Reliable operation

There are several types of multi-stage devices which satisfy most of the above criteria. Packed towers are probably the simplest to construct, and are therefore readily available, but are less desirable than other types from most other points of view. They are not well suited to theoretical analysis, have high pressure drop and hold up, and require a relatively large change of material. A sieve plate tower has the same disadvantages.

Bubble-cap columns are more difficult to construct and are not so readily available in the small laboratory size. They also are unattractive from the point of view of the large hold up and pressure drop and the relatively large charge required. Equilibrium times would be relatively long due to the comparatively large hold up and the over-all size would be considerable for the desired number of stages (approximately 50). Theoretical analysis would, however, be straight forward and not present any problem. Furthermore, bubble cap columns have the very desirable property of being rather insensitive to operating variables such as thruput and system properties such as wetting, viscosity and density. The achievement of the reliable performance should, therefore be assured.

Rotating packed columns are very compact and are available in small laboratory size. They are, however, difficult to theoretically analyze, and their sensitivity to operating conditions makes them rather unreliable for a separation study.

Concentric - tube columns are relatively difficult to construct but satisfy almost all the desired criteria. They are especially well suited for theoretical analysis due to the uniformly constant contact area for mass transfer between phases. They also are desirable because of their low pressure drop and hold up, small equilibrium times, and compact size. They may be operated with an extremely small charge. (as little as 10 ml) Their major disadvantage is their sensitivity to variables of operation and system properties, the most important single variable being wetting of the active zone walls where mass transfer occurs.

Of the above multi-stage devices, the two that were the most attractive were the bubble-cap tower and the concentric tube column. The bubble-cap tower is very desirable because of its insensitivity to operating variables and system properties, in spite of the other disadvantages. The concentric-tube column satisfies all criteria except it is rather more sensitive to operating variables and system properties.

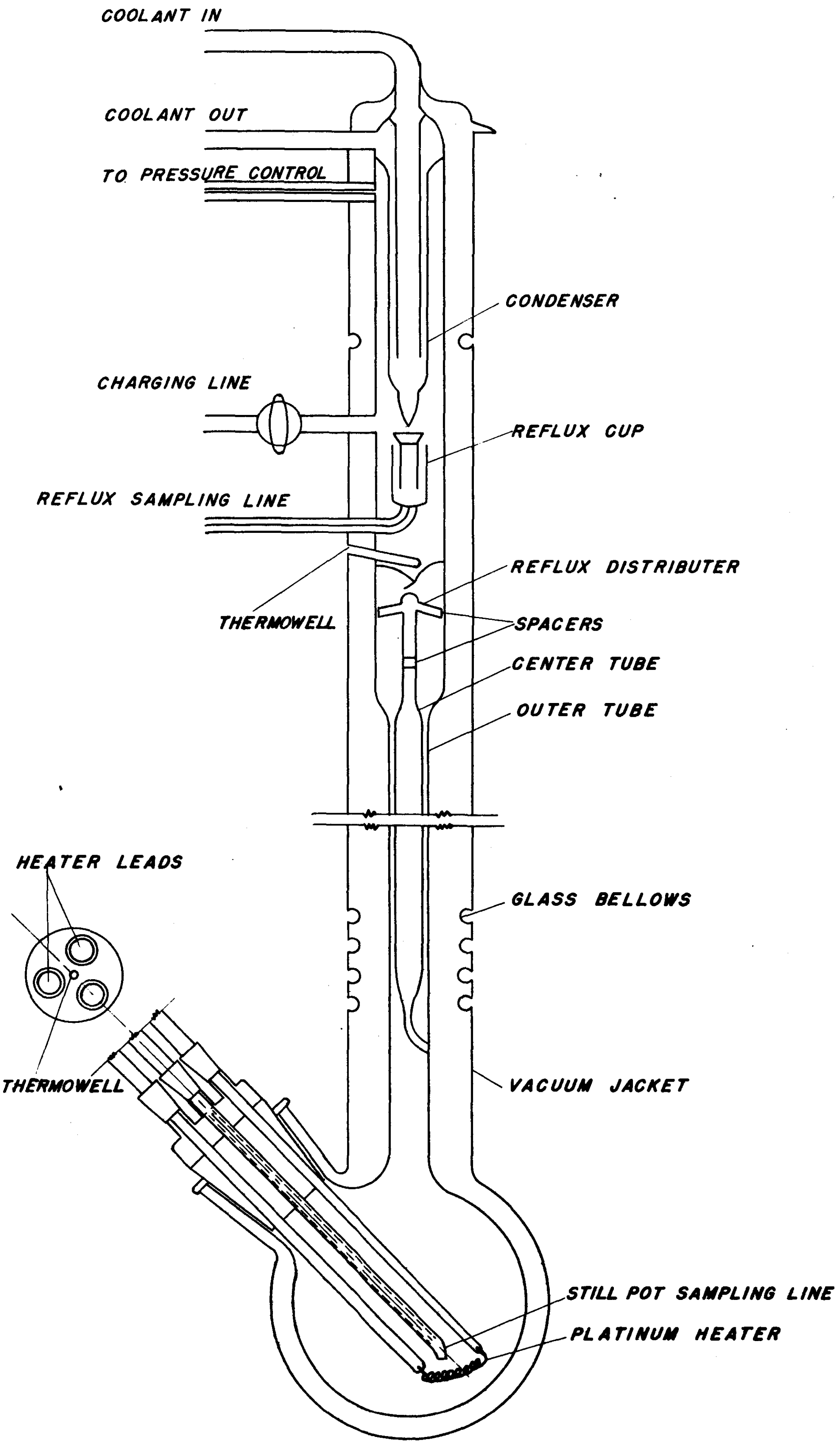
Naragon and Lewis (27) describe a small concentric-tube column that they quite successfully operated with the system n-heptane-methylcyclohexane ($\alpha = 1.08$) with the highest of a theoretical stage as small as 0.4 cm. giving up to 75 stages in a 30.5 c. active zone. On the basis of their favorable results and the availability of such a design, it was decided to use the concentric-tube column if the wetting of glass by ammonia could be demonstrated. When visual observations of the ammonia-glass interface within the equilibrium still consistently indicated contact angles of greater than 90 degrees, the final decision to use the concentric-tube column was made.

Certain modification of the design described by Naragon and Lewis were, however, incorporated in the column used for this work. Ground glass joints were eliminated wherever possible by fabricating kettle, active column zone, and condenser in one piece and providing an integral vacuum jacket covering all these components.

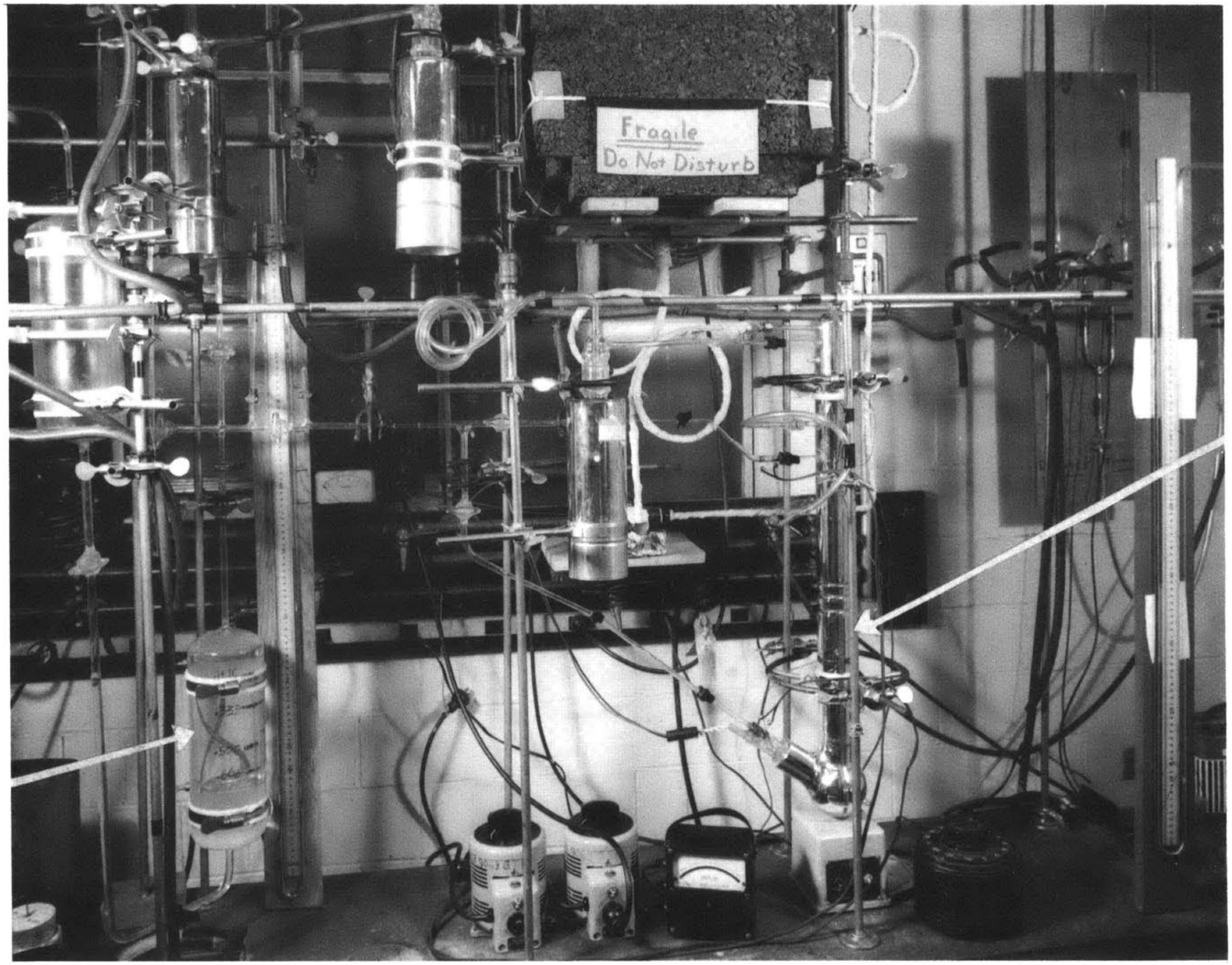
Figure 2 is a sketch of the column and Plate 1 is a photograph showing the set up of the column in the experimental train of equipment. The column itself consisted of an active portion 30.5 cm. long formed as an annular passage between an 8 mm. inside diameter outside tube, and a 6.5 mm. outside diameter center tube. Above the active zone were located the reflux condenser, reflux sampling cup, and the reflux distributer. Below the active zone a kettle was attached as an integral part of the column. The entire column, including the kettle and reflux condenser was encased in a vacuum jacket to minimize heat transfer to the column.

The two critical tubes forming the annular passage were Pyrex Trubore tubing. One end of the inner tube was drawn down and sealed to an 8 mm ball. To this ball were attached two troughs formed by cutting 7 mm outside diameter tubing lengthwise with a diamond saw. These troughs together with the ball formed the reflux distributer.just above the active zone of the column. The function of this distributer was to divide the liquid stream between the inner and outer tubes.

The bottom of the inner tube was drawn down to 2 mm outside diameter and attached to the outer tube below the active zone. During fabrication the two tubes were accurately spaced by a wrapping of 0.75 mm.



CONCENTRIC TUBE COLUMN
FIG. 2



COLUMN

BURETTE

PLATE I

CONCENTRIC TUBE COLUMN AND SAMPLING SYSTEM diameter copper wire on the inner tube. After fabrication and annealing, the wire was removed by solution in sulfuric acid and potassium dichromate.

The kettle was an integral part of the column and was fully vaquum jacketed. An opening in the kettle, inclined upward at about 45°, received a standard taper 29/42 male fitting. The inner 29/42 fitting had a central thermowell fabricated of 4 mm Pyrex tubing. Around this tube there were symmetrically spaced three openings to receive the two heater heads and the liquid sampling line. A seal was made between these lines and the 29/42 fitting by 10/30 standard taper fittings.

The two heater leads passed through 7 mm. tubing attached to the 10/30 standard tapers and terminated with tungsten seals at the bottom. The liquid sampling line was a 0.3 mm. capillary with a constriction to 0.1 mm. at the point it joins the 10/30 fitting. The lower end of the sampling capillary was also slightly constricted and offset. The heater, identical to that used in the equilibrium still, was fabricated as a coil of 0.2 mm. platinum wire of about 50 cm. in length. The platinum heater was spot welded to the tungsten seals.

In addition to the vent line and the reflux sample line leaving the upper portion of the column, another tube pierced the vacuum jacket between the active zone of the column and the condenser. This line permitted charging the column. A 4 mm. reflux thermowell was provided just above the reflux distributer. The reflux sampling cup held about 2 ml. of liquid. A central funnel was provided within the cup to insure continuous flushing of the sample. To allow for temperature differentials between the inner tubes and the outside of the vacuum jacket, several glass bellows were included in the jacket for expansion. Acetone refrigerant for the condenser was provided at -70°C. The acetone was cooled in a coil of 1/4 inch copper tubing submerged in an acetone-dry ice bath contained in an insulated sheet metal tank. The acetone flowed from an expansion tank through the cooling coil, through the column, then through a small centrifugal pump and back through a filter to the expansion tank. (Fig. 6) All lines were insulated to conserve dry ice and prevent excessive ice formation. Seals were made between the 1/4 inch copper tubing and the 1/4 inch glass tubing at the column with "Swage-Lock" fittings with Teflon inserts.

The column was charged by injecting gaseous ammonia through the charging line at a rate of about 1.5 liters per minute. As the ammonia was condensed and flowed down the column, it cooled the column internals and accumulated in the kettle. The column was supported by 8 coil springs to provide flexibility.

During operation the kettle was filled about half way with liquid ammonia. Care was taken to keep the level constant since separation occurred on the wetted walls exposed. Liquid samples could be taken at will, but a minimum of 90 minutes of continuous operation was allowed for equilibrium to be attained before drawing reflux samples. (Sampling of the reflux was performed with the column operation halted, to prevent contamination with material obtained under non-equilibrium conditions.) All reflux samples were then representative of the total reflux operation of the column. (Experience with partially vaporized samples taken from the equilibrium still dictated the necessity of providing capillary constrictions and heated zones in the sampling lines for the complete vaporization of the samples. Again the pressure drop through the constrictions during the sampling was observed on a mercury manometer and the heat supplied by Nichrome resistance heaters wrapped around the 7 mm. Pyrex lines and insulated with glass tape.

Since all the column runs were carried out at one atmosphere, the barometer pressure readings available from the M.I.T. Meteorological Department were used for pressure determinations. The values reported in Table 2 were obtained by averaging the reported readings during the interval of a run.

Temperature measurement was, as in the equilibrium still, carried out with a Chromel-Alumel thermocouple; E.M.F. measurements being made with a Leeds and Northrup type "K" potentiometer. The errors introduced in temperature measurement were the same ones discussed in equilibrium still section. The important differences with the column were:

1. The kettle thermowell was overheated about 0.3°C. when the platinum kettle heater was operated.
2. The reflux thermowell was not reliable since it was not normally covered with liquid reflux.

The first error was uncovered when it was observed that the indicated temperature of the kettle charge dropped 0.3°C. immediately after shutting the heater off. The most obvious explanation is that the platinum heater was overheating the thermowell since the contents of the kettle continued to boil very slowly even after the heater was shut off due to heat leakage from the surroundings to the low temperature charge. This drop was not observed when the heater of the equilibrium still was shut off, and furthermore, the readings obtained from the column when the heater was not operating agreed well with the still measurements. However, since most of the temperature measurements from the column kettle were made with the heater operating, they were corrected by arbitrarily subtracting 0.3°C. This source of error was not serious since accurate temperature measurements had already been obtained over a wide composition range with the equilibrium still.

The reflux thermowell was not situated exactly as specified in the design of the column, and as a result the stream of reflux returning to the column did not always pass over it. This would not have been a serious error if the boiling point of the column contents was above the surrounding temperature, for then some condensation would have occurred on the thermowell keeping it at the boiling point. This was not the case with the ammonia system and whenever liquid reflux was not flowing over the reflux thermowell, the indicated temperature rose considerably above the boiling point due to heat conduction down the thermowell. This clearly indicates the necessity of keeping a reflux thermowell submerged in liquid when sub-room temperatures are to be measured. Because of this limitation, no reflux temperatures are reported in this investigation.

Unfortunately, the column did not operate reliably with the ammonia system due to incomplete wetting of the active walls of the column. Because the walls were not fully wetted, any change in flow regime changed the area for mass-transfer and hence the effective number of stages obtained.

After it was realized that wetting had become a problem several attempts to establish uniform wetting were carried out. The column was cleaned with hot sulfuric acid - potassium dichromate solution, followed by distilled water and pure acetone rinses. Then it was dried by a stream of purified nitrogen passed first through a liquid nitrogen trap. Little improvement was noted. The column was again cleaned as above, except acetone was omitted since it was felt that it could have left a film of grease on the walls, but uniform wetting was never obtained with ammonia.

The effect of boil-up rate was observed from the point where reflux just began to the flooding point. Better separation was encountered at the low boil-up rates but results were less reproducable than at higher rates near the flooding point despite the lower separation encountered. This is probably due to the better wetting at this condition. The highest number of stages obtained for the column operated on ammonia was four at the lowest thruput, and the number decreased to 2.6 at the flooding point.

A check was made of the column performance with the system n-heptane-methylcyclohexane since Naragon and Lewis (27) had reported up to 75 theoretical stages for a similar column on this system. Complete wetting was visually observed and up to 28 theoretical stages were obtained (see Appendix Sec. B3). The reason for the poor performance of the column with this system is not completely certain, but evidently the tolerance on dimensions and alignment of the concentric tube in this design is so small that even with reasonable care, it is difficult to reproduce the column specifications stated by Naragon and Lewis. This result does, however, indicate the strong effect of wetting since under similar operating conditions only 4 theoretical stages were obtained with the ammonia system.

Knowing that the results would be questionable, it was nevertheless decided to carry out a limited number of runs with the column. These were all performed at atmospheric pressure and at the three concentrations 0.57, 0.23, and 0.04 MFD. Since the best reproducibility of the column stages seemed to occur near the flooding point, it was decided to operate there during these runs. The performance of the column was erratic, however, and no reliable measurements were obtained.

D. Analysis for Deuterium Content

Since the difference in composition between liquid and vapor samples in the single-stage still was in the range 0.004 to 0.010 mole fraction deuterium, it was necessary to have an analytic method whose precision was of the order of 0.0001 mole fraction deuterium. Many methods of analyzing for deuterium have been developed. Due to the different refractive indices of compounds where hydrogen has been replaced by deuterium, interferometry can be used to measure changes in deuterium concentration. Since this method depends on the difference in refractive index of the mediums through which light travels, it can be used to measure the difference in composition of two samples. This method has been used successfully by several investigators. Ingelstam et al. (21) have developed an instrument for heavy water analysis that is capable of measuring compositions within ± 0.00002 mole fraction, at all concentrations, with a sample of one ml. Gas phase interferometry is complicated due to the long paths required for sufficient accuracy.

Using a differential method of infra-red analysis, deuterium concentrations in heavy water can be measured to a probable precision of ±0.00003 mole fraction in concentrations either very rich or very lean in deuterium. Patterson (28) has developed a method using 0.5 mm. calcium fluoride cells which yields an accuracy of ± 0.00003 mole fraction, but he felt that if the scattered light problem which he encountered could be solved, an accuracy of ± 0.00001 mole fraction would not be unreasonable. Very small samples suffice.

Thermal conductivity measurements of the gas phase of a hydrogen compound would allow composition measurements to be made. However, to get sufficient accuracy, measurements should be made on mixtures of hydrogen and deuterium to take advantage of the maximum conductivity difference. Heumann (20) has demonstrated accuracies of ± 0.0005 mole fraction using a Gow-Mac model 60S flow type cell with hydrogen deuterium mixtures. Small samples are sufficient for this method also.

The mass spectrometeric method makes use of the fact that atomic deuterium has approximately twice the mass of the normal hydrogen atom. Heavy water to be analyzed is first decomposed into hydrogen and then the hydrogen gas is bombarded by electrons to produce hydrogen ions. These ions are then accelerated by an electric field to produce a beam of ions. This beam of ions is dispersed into a mass spectrum by a magnetic field, and each separate portion of the spectrum having a different mass is segregated by means of parallel slits. A great deal of work has been done with this type of apparatus, and it can be used to measure heavy water concentration to within ± 0.0001 mole fraction for samples containing about equal proportions of hydrogen and deuterium. (19) The elaborate equipment required, however, makes this method prohibitively expensive.

Among the analytic techniques which makes use of the fact that heavy water is approximately 10 percent more dense than light water is the standard pycnometer method. This consists essentially of determining the weight of a known volume of water. Another familiar density technique is referred to as the temperature float method. The principle upon which the temperature float method is based is quite simple. The temperature at which a small quartz or glass float has the same density as an unknown water sample (i.e. the float neither rises or falls) is compared with the temperature at which the float has the same density as standard water. This temperature difference, together with the data on the coefficients of expansion of water, quartz, and heavy water, permit calculation of the density difference between the unknown and standard waters. Kirshenbaum (25) gives complete descriptions of all these various techniques. The disadvantage of these methods is that large amounts of water are needed.

The falling drop method for determining the density of a liquid was first used by Barbour and Hamilton (2) who utilized it in the determination of the density of blood. This method, which is based on Stokes' law, consists of allowing a small drop of liquid sample to fall through an immiscible fluid having a density only slightly less than that of the sample. After the drop reaches terminal velocity, its rate of fall is measured by timing its passage between two scratch marks with a stopwatch. The terminal velocity of a falling sphere is given by Stokes' law as a function of the density difference between the two fluids. Although Stokes' law is not obeyed exactly in the case of a falling liquid drop, it does show a functional relationship between the density difference and the time of fall, therefore indicating how the density of a sample can be determined so precisely.

Keston and Rittenberg (23) refined the technique by careful temperature control and thus were able to analyze low concentration heavy water samples to within ± 0.0002 mole fraction. Frillette and Hanle (15) using a mixture of alphamethylnaphthalene and phenanthrene were able to determine within ± 0.0001 mole fraction the heavy water content of samples which contained between 0.10 and 0.42 mole fraction heavy water.

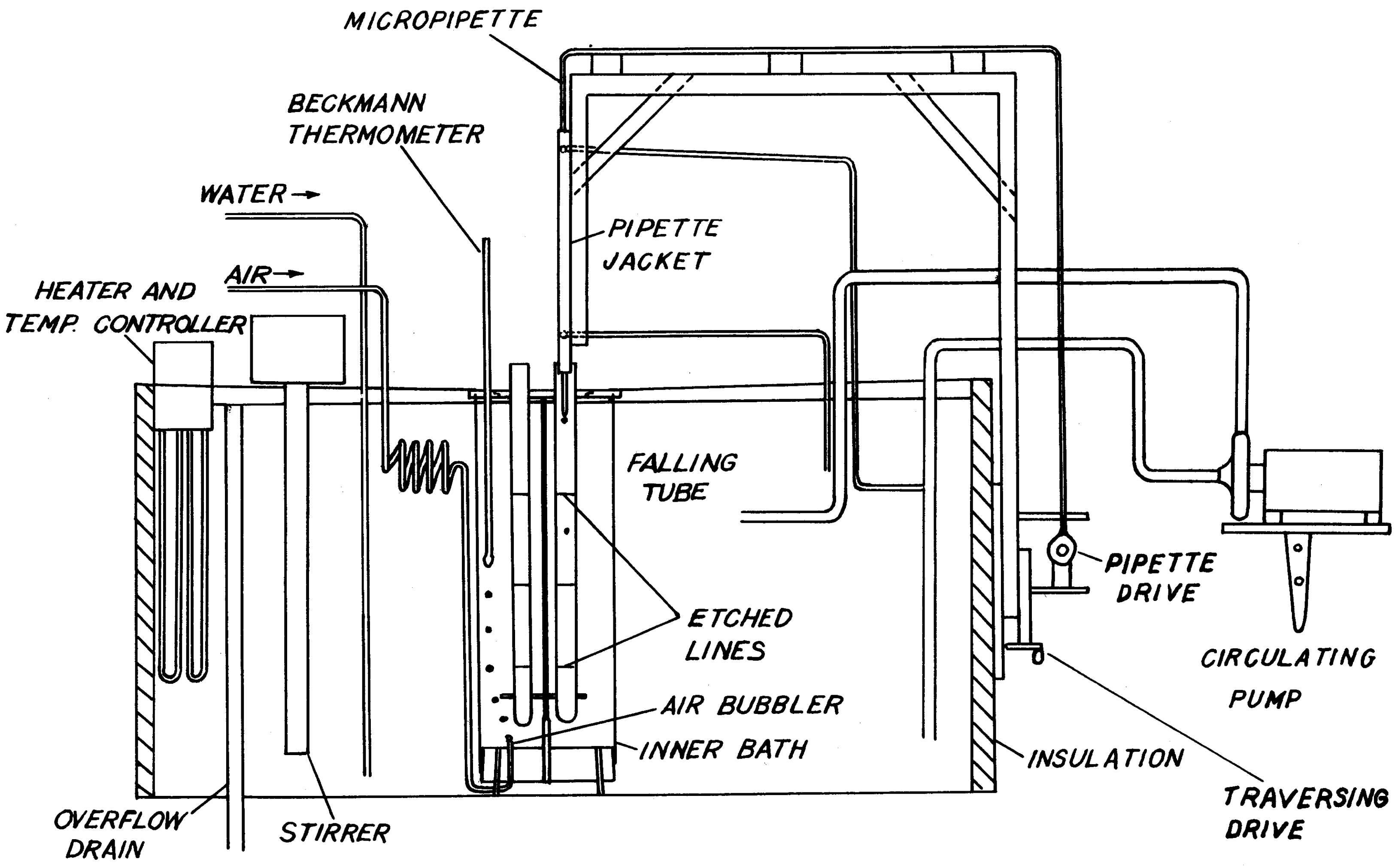
These limits of concentration depend on the density of alphamethylnaphthalene and the solubility of phenanthrene. The falling drop method has been used by Bigelow, (8) who determined heavy water concentrations in the range of 0.0001 to 0.05 mole fraction, to within ± 0.0002 to ± 0.0004 mole fraction using o-fluorotoluene as the immiscible fluid. He states that this substance is inadequate above 0.05 mole fraction because of the increasing difference between the sample density and the o-fluorotoluene density.

One distinct advantage of the falling drop method is the fact that very small samples suffice (0.1 to 0.5 ml.). It requires less time and less water than the temperature float method. As in all density measurements it requires a very sensitive thermostat capable of maintaining the temperature constant to within ± 0.001°C. In spite of this fact, density methods in general all probably require less expensive apparatus than the interferometric, spectographic, or mass-spectrometric methods. Density measurements, based on heavy water standards, have the disadvantage, however, that the sample of deuterated ammonia must be quantitatively converted to water with no hydrogen contamination. This can be accomplished by passing the ammonia over copper oxide at 700°C. (16)

Due to the precision, low cost, and small samples required, the falling drop method was adopted for the measurements of the deuterium concentration in the water samples which could be obtained by quantitative oxidation of the ammonia samples. In addition, the bath, used by Bigelow (8) and set up during preliminary measurements by Kalman and the author, was available. After an extensive literature search for the best possible fluid mixtures to cover a wide concentration range, the ~~mixture~~ alpha-methylnaphthalene and methoxynaphthalene was chosen to cover the range from 0.10 to 0.80 mole fraction deuterium. This had the advantage over the mixture of alpha-methylnaphthalene and phenanthrene used in the preliminary work, in that the upper concentration that could be analyzed was 0.80 rather than 0.42 mole fraction deuterium. For the very low deuterium concentrations the mixture alpha-methylnaphthalene and 1, 2, 3, 4 tetrahydronaphthalene was chosen.

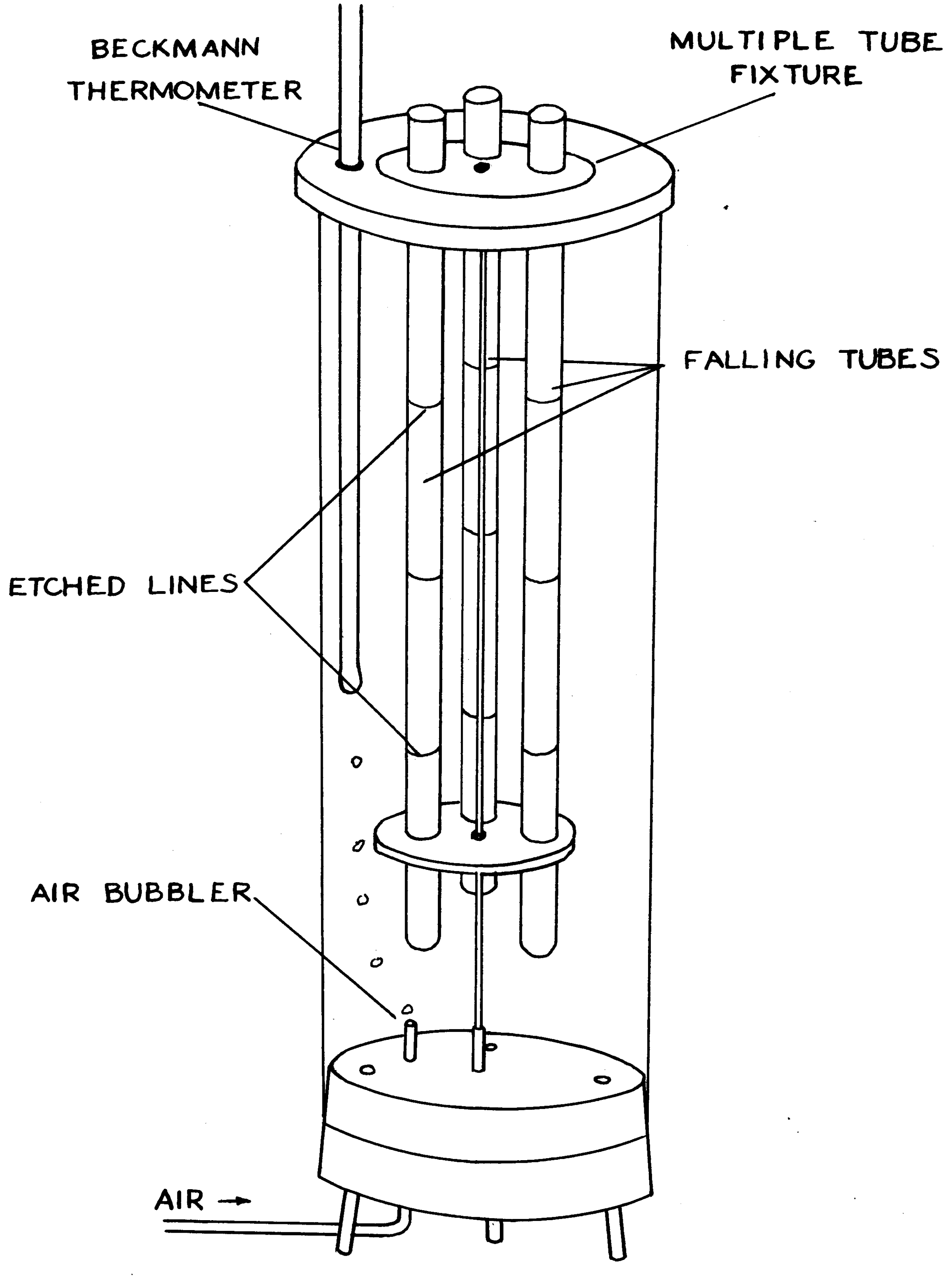
The falling drop apparatus consisted of a large constant temperature water bath which was maintained within ± 0.001°C of the set temperature (35°C.). It is shown in Figs. 3 and 4, and Plates 2 and 3. Within the large bath was a smaller inner bath in which three falling tubes were supported in a fixture which permitted selection of one tube for a particular density. The outer bath was stirred by two centrifugal stirrers. The inner bath was stirred by an air bubbler. Due to the thermal inertia of the inner bath and the falling tubes, their temperature could be maintained nearly constant. Variation of the inner bath temperature was less than 0.002°C over a 24 hour period. The temperature of the inner bath was measured by a Beckmann Thermometer.

The falling tubes were made of 24 mm Pyrex tubing about 40 cm long. A scratch mark was made completely around the tube about 7 cm from the bottom. A second scratch mark was made 10.00 cm. above the first, and a third 10.00 cm. above the second. The first and third marks were used in timing of the drops.



FALLING DROP ANALYSIS

FIG. 3



DETAIL OF INNER BATH

FIG. 4

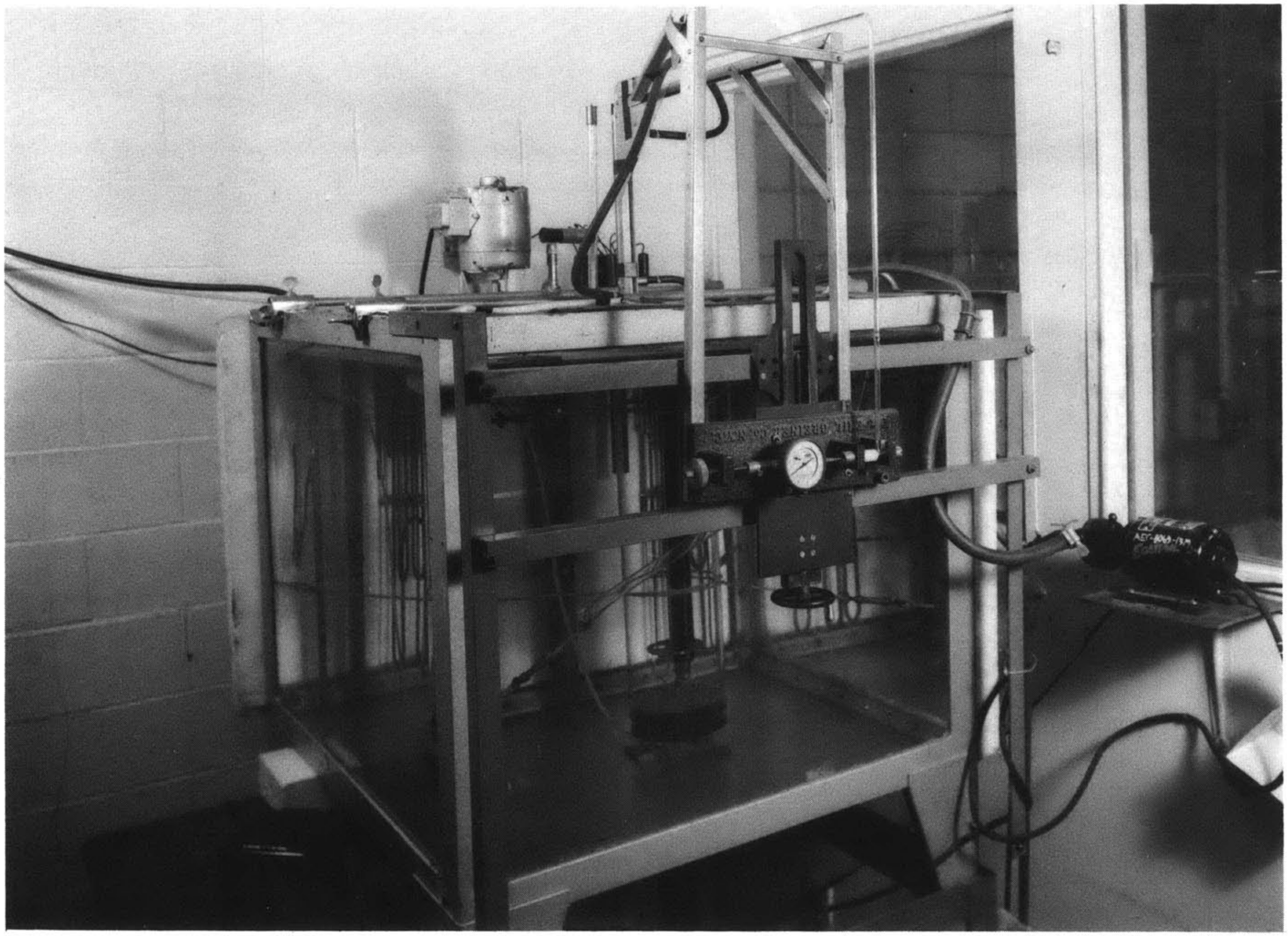


PLATE 2
GENERAL VIEW OF FALLING DROP APPARATUS
(INSULATION REMOVED FROM TWO SIDES)

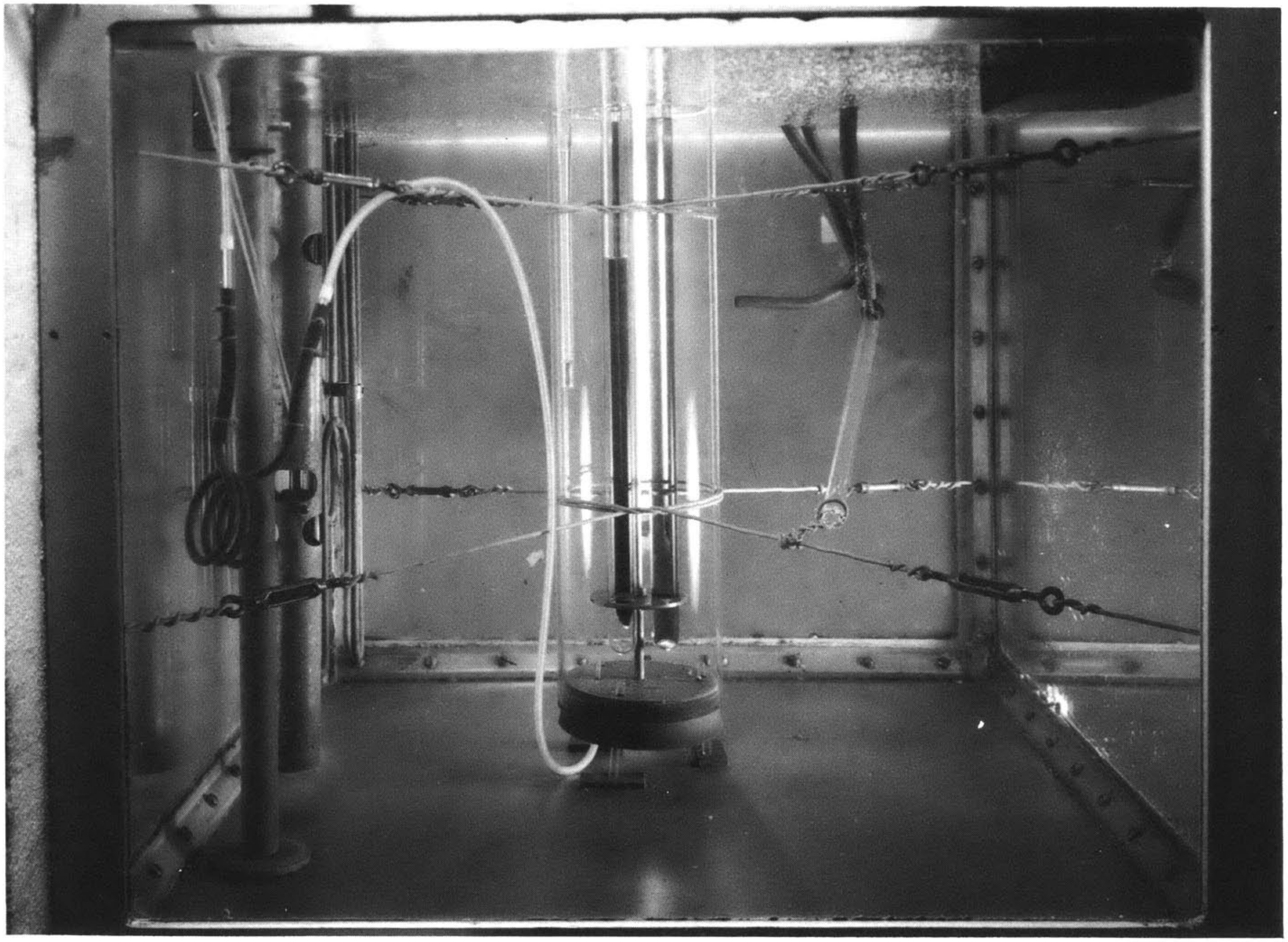


PLATE 3
FRONT VIEW OF FALLING DROP APPARATUS
(INSULATION REMOVED)

The pipette was fabricated from 0.3 mm. Pyrex capillary tubing and is the same in principle as that used by Frillette (15). Mercury was used as the displacement liquid within the pipette. The tip was hand ground to a fine point to deliver drops of uniform size. The capillary tubing was continuous from the tip, up through the water jacket, horizontally across the bath, and down the side of the bath to a point 4 inches below the tip. At this point the capillary tubing was attached to a small glass cylinder which was traversed by a stainless steel piston of 0.040 inches in diameter. The piston seal was located at a lower level than the pipette tip to prevent inleakage of air. The piston was driven by a screw drive with a micro-dial indicator. The displacement of one drop represented one revolution or 100 units on the dial. The entire pipette assembly including its jacket and piston drive was mounted on a vertical traversing plate. This plate could be traversed over a ten-inch range with a screw drive. The horizontal section of the pipette and the pipette jacket were supported from the traversing plate with aluminum channel brackets.

A centrifugal pump mounted at the side of the bath served to circulate the water in the bath as well as to circulate water from the bath through the pipette jacket. A second centrifugal stirrer was submerged within the bath. The bath was insulated with three inches of plastic foam, and the top was fitted with an air-tight polyethylene cover to limit evaporation of water and to keep out dust. A small rack was provided in one corner of the bath, capable of holding three standard water bottles and eight sample bottles to allow all samples analyzed to come to temperature equilibrium with the bath before transfer to the pipette.

The four principal sources of error in the falling drop technique are: temperature variations within the falling fluid, changes in composition and hence density of the falling fluid, variations in the size of drops, and errors in timing. Temperature control is important for two reasons. Due to the difference in the coefficients of expansion of water and the falling fluid, their density difference can be altered by small temperature changes. In addition, temperature changes can set up convection currents within the dropping tube, which would superimpose a velocity on the falling drop. Previous investigators (8) using ortho-fluoro-toluene as a falling medium have determined from the coefficients of expansion that a variance of ± 0.001°C. would not cause errors greater than ± 0.0001 mole fraction deuterium due to changes in density. In this regard, alpha-methylnapthalene is even better than ortho-fluoro-toluene since its coefficient of expansion is much nearer that of water. Temperature variations of ± 0.010°C. with alpha-methylnapthalene correspond to ± 0.0001 mole fraction deuterium. (See Appendix Sec. B8) It was found, however, that with the apparatus used, the error due to convection currents was more serious than the error due to changes in the density difference. Small temperature transients set up convection flow within the falling tube and superimposed a velocity on the falling velocity of the drop in the falling medium. For this reason it was desirable to use a viscous oil as the falling medium to dampen the convection currents. Alpha-methylnapthalene was a good choice in this regard since its viscosity was higher than other fluids having the same density and being immiscible with water. It was observed that analytic precision of ± 0.0001 mole fraction deuterium could be obtained if the rate of temperature change was less than 0.001°C./hour, using alpha-methylnapthalene. With the same temperature control, ortho-fluorotoluence gave a precision of about ± 0.0004 mole fraction deuterium due to its lower viscosity. It was found experimentally that, except during the hottest summer days, during any 24 hour period, the temperature could be maintained constant within ± 0.002°C.

Because the square of the drop diameter appears in Stokes' equation, it is necessary to keep the volume of the drop uniform. The diameter of a spherical drop is proportional to the two-thirds power of the volume, so that an error of three percent in volume causes an error of only two percent in the terminal velocity. The displacement of the sample was accomplished by piston displacement of mercury in the body of the pipette and indicated on a micro dial. Displacement of one drop represented one rotation of the micro dial, divided into 100 intervals. Due to compressibility of air, it is important to keep the contents of the pipette air free at all times. For this reason, the pipette was constructed so that the seal around the piston would not be under a vacuum. Errors due to volume of the drop should have been less than 0.2 percent or less than 0.00005 mole fraction deuterium.

Errors in the falling time should have been negligible since an electric stopwatch measuring to 0.001 of a minute was used to measure times greater than one minute. At regular intervals this watch was compared with others and was found to be reliable.

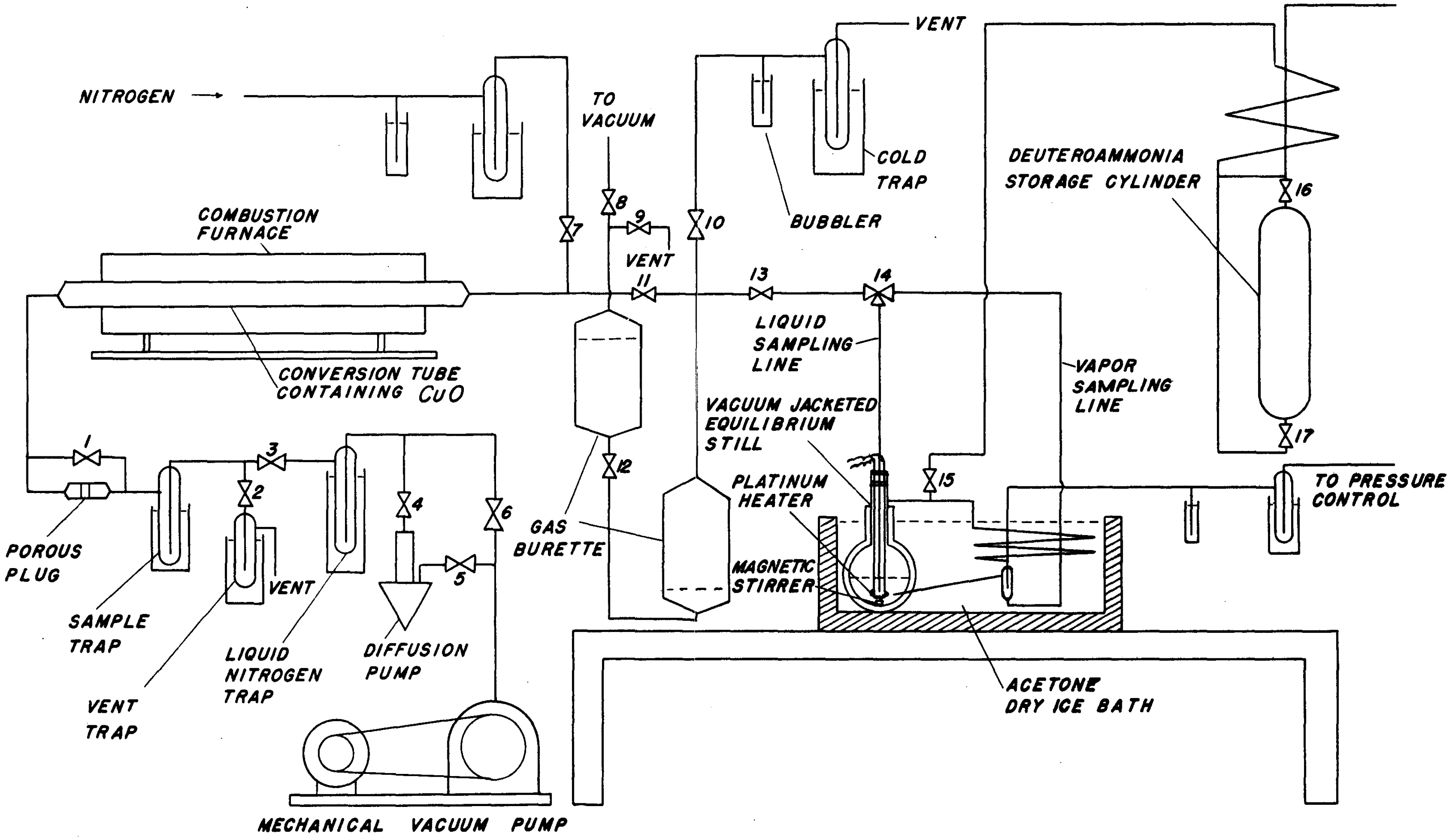
Due to the slow falling velocities, Stokes' Law was approximated and a linear relation between the rate of fall and the mole fraction deuterium was attainable. A calibration curve of falling velocity as a function of the deuterium content of the samples for each dropping fluid mixture allowed precise determination of composition. (See Graph 9)

Before each determination, the pipette was flushed twice with the sample to be analyzed. After the third falling, the pipette was lowered so that the tip was submerged about one-fourth of an inch in the dropping fluid. With the pipette in the position at least five minutes were allowed for the temperature of the sample to come into temperature equilibrium with the falling medium. Drops were then formed by traversing the piston 100 units and each given an additional 90 seconds to attain temperature equilibrium before discharge. Drops were discharged by raising the pipette tip above the surface. As the pipette tip left the surface, surface tension would pull the drop off. After discharge, the pipette was immediately submerged in the falling fluid to prevent any contamination of the sample by moisture in the air. Uniformly of the procedure for every sample prevented introducing unknown perturbations.

E. Conversion of Deuterated Ammonia And Deuterated Water

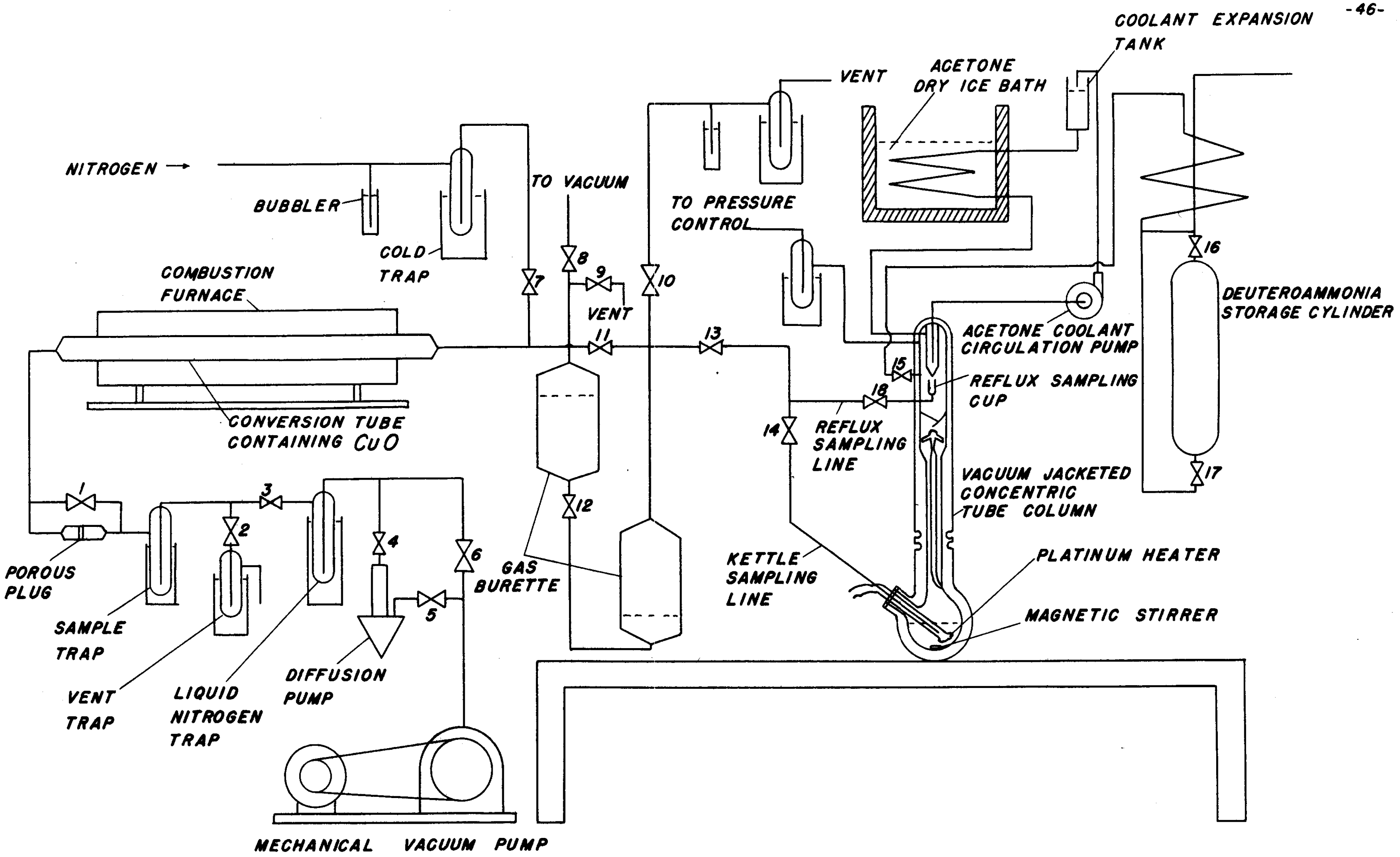
Since water was chosen as the medium for deuterium analysis, a method of quantitatively converting the deuterated ammonia samples from the equilibrium still of the column to water was required. Several methods of direct oxidation of ammonia are possible, but oxidation over copper oxide was preferred to oxidation with gaseous oxygen due to the explosive character of oxygen-ammonia mixtures. At high temperatures (above 650°C) copper oxide is very effective for ammonia oxidation and it can easily be regenerated by passing air over it at 700°C. It was therefore chosen for the oxidizing agent.

The conversion apparatus contained a two liter gas burette, a conversion tube containing copper oxide, a water sample trap and a high vacuum system. Figure 5 is a flow sheet showing the assembly of the single-stage equilibrium still and the conversion equipment. Figure 6 is a similar diagram for the concentric-tube column and the conversion equipment. Plate 4 is a photograph of the conversion equipment and high vacuum system. The gas burette served as an ammonia pump and as a volumetric measuring device. Ammonia samples were drawn from the capillary sampling lines into the gas burette. A completely halogenated oil (Kel-F medium oil) was used as the displacement medium. Mercury was originally used with a much smaller burette, but due to the large number of fillings required to get one gram of ammonia when operating at subatmospheric pressure, it was replaced by the large two-liter burette. Two liters of mercury would have been much too heavy to be contained in a glass burette, and since the glass burette was desirable because it gave a visual observation of the level and flow, a completely halogenated



EQUILIBRIUM STILL - SAMPLING FLOW SHEET

FIG. 5



CONCENTRIC TUBE COLUMN- SAMPLING FLOW SHEET

FIG. 6

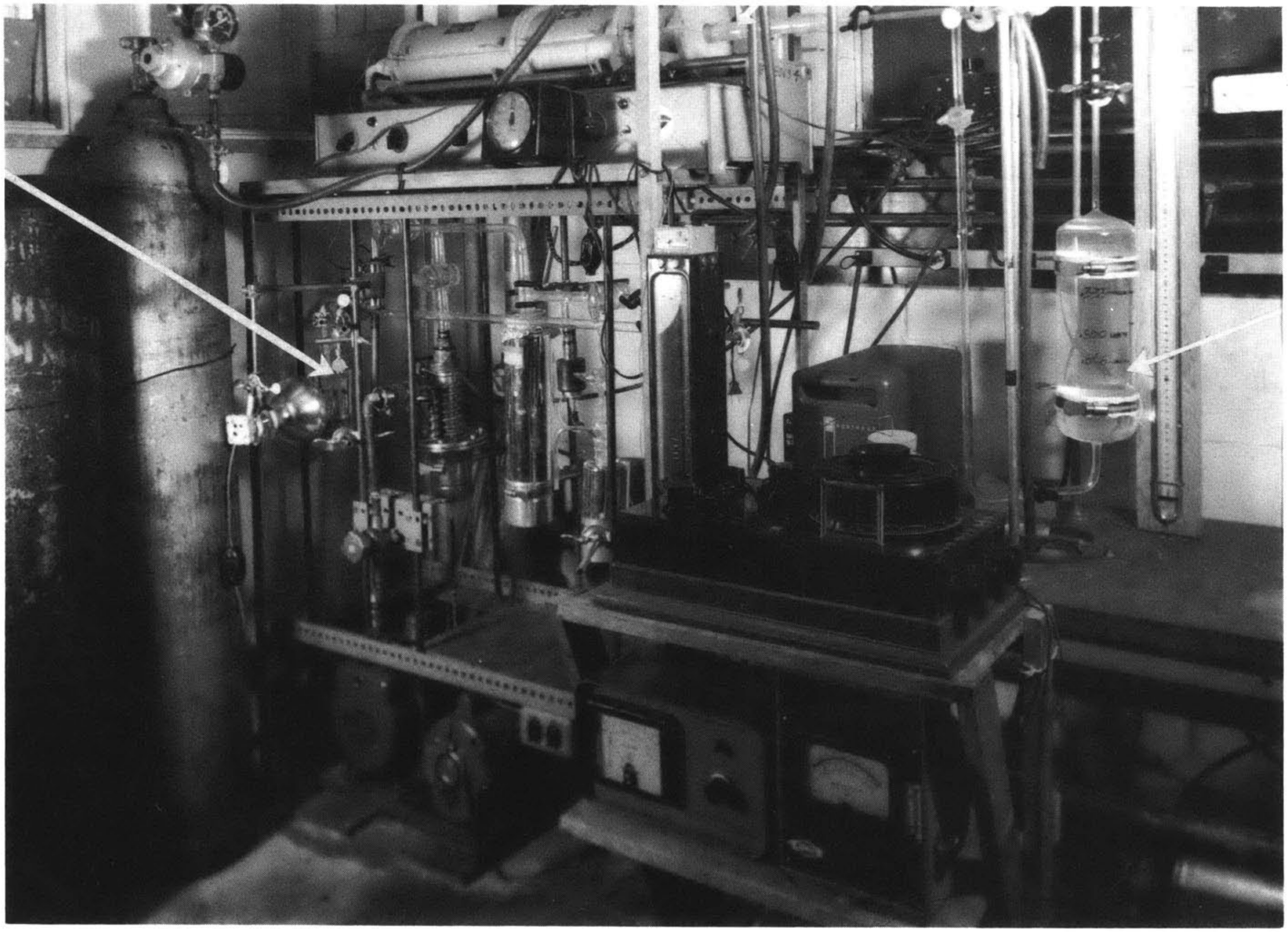


PLATE 4
CONVERSION AND HIGH VACUUM SYSTEM

oil was chosen as a substitute for the mercury.

Kel-F medium oil has a relatively low vapor pressure (about 1 micron Hg. at 25°C) and contains no hydrogen, so there was no chance of sample contamination with oil vapor or isotopic exchange. The oil was drawn from the lower burette chamber to the upper reservoir by a vacuum of about 1 mm. Hg. above the oil in the upper reservoir. Flow was throttled by a stopcock placed in the oil line (No. 12, Figs. 5 and 6). To discharge the ammonia sample, the oil was allowed to flow undergravity from the upper reservoir into the lower burette. When drawing samples at subatmospheric pressure, they were compressed to a pressure of one atmosphere before discharge from the burette to the conversion tube.

After it was found that the solubility of ammonia in the halogenated burette oil was 0.16g. per liter at one atmosphere there was some concern about sample exchange with the dissolved ammonia. Since a high vacuum was maintained above the oil in the reservoir, most of the ammonia dissolved was removed between samples. To check the possible memory of the system, several analyses of the deuterated ammonia drawn from the equilibrium still were performed. After running several deuterated samples, a natural ammonia sample was run through the burette and conversion tube to contaminate the system with light hydrogen, followed by another deuterated sample from the equilibrium still. The deuterium content of the final sample from the still did not differ significantly from that of the initial samples. (See Appendix Sec. B6). Contamination of samples by ammonia dissolved in the burette oil was thus proved not to occur.

The reaction tube in which the ammonia was oxidized to water consisted of Vycor tubing 30 mm. in diameter and 28 inches long. The tube was filled with 900 grams of copper oxide, which was sufficient to convert 25 ammonia samples to water before regeneration was necessary. The reaction tube was heated by a standard laboratory furnace of the type used in organic combustion analyses. The Vycor tube and the furnace were each capable of operation at temperatures up to 1000°C.

During conversion, the maximum ammonia flow rate was one standard liter per minute. The temperature of the copper oxide was carefully controlled between 650° and 720°C. This is essential, because at lower temperatures, oxidation is incomplete, and at higher temperatures, oxides of nitrogen are formed. These would dissolve in the water and change its density. Both possible sources of error were shown to be absent at the operating conditions chosen.

The copper oxide was prepared from precipitated copper hydroxide as described in Appendix Sec. C3. It was activated by reduction in hydrogen at 400°C. The porous metallic copper was reoxidized by passing air at 700°C over it for several hours before initial use, and was regenerated in this way after each experimental run. This method of preparing copper oxide gives much more surface area for reaction than would be obtained by oxidizing copper wire.

The exit of the reaction tube was attached to a vertical section of 7 mm. Vycor tubing which was connected to a sample trap assembly. The sample trap assembly had two parallel paths, one through a porous plug, and the other, a bypass, through unrestricted tubing with a shut-off stopcock. The porous plug filtered out any copper oxide dust from the sample, but the bypass permitted evacuation with little restriction to gas flow. The sample trap itself was made from a 24/40 standard taper joint. The entire sample path from the reaction tube to the trap was trace heated with Nichrome resistance wire and kept above 150°C. to prevent condensation. The trap was maintained at -70°C. with a dry ice-acetone mixture during conversion. The exit of the sample trap was connected to an atmospheric vent line and to a high vacuum system. Both paths contain cold traps to prevent ingress of moisture.

A sample was drawn into the burette and then allowed to flow at atmospheric pressure through the reaction tube no matter what the operating pressure of the equilibrium still or the column. (See Fig. 5 or 6) Once the sample had been entirely introduced into the reaction tube, the inlet stopcock (No. 11) and vent stopcock (No. 2) were closed and slow evacuation started. Evacuation continued to a pressure of 5 microns Hg drawing all of the sample into the sample trap. The reaction tube and the sample trap were than pressurized with dry nitrogen passed through a liquid air trap. The system was once again evacuated to 5 microns Hg and pressurized with dry nitrogen to sweep any residual traces of the sample into the trap. The sample was then melted and transferred to a small vial with a clean, dry hypodermic syringe. The sample vials were stored in a dessicator when not being analyzed. (Appendix A1 contains a more detailed description of the procedure).

Between samples, the conversion tube and sample trap assembly were evacuated to a pressure less than one micron Hg for a period of at least ten minutes. To provide maximum flexibility, the vacuum system, consisting of a two-stage mechanical pump and a three-stage oil diffusion pump, was hooked up with a bypass around the diffusion pump and with valves to isolate the diffusion pump. This enabled "roughing down" without disturbing the diffusion pump operation. A liquid nitrogen trap upstream of the diffusion pump was provided to trap any condensables. To this trap was connected a manifold with an ionization gauge and valves to the conversion system. When isolated, manifold pressure of as low as 10^{-7} mm. Hg. were attained. Within two minutes, the pressure with the entire conversion system evacuated could be reduced to 0.2 microns at the manifold.

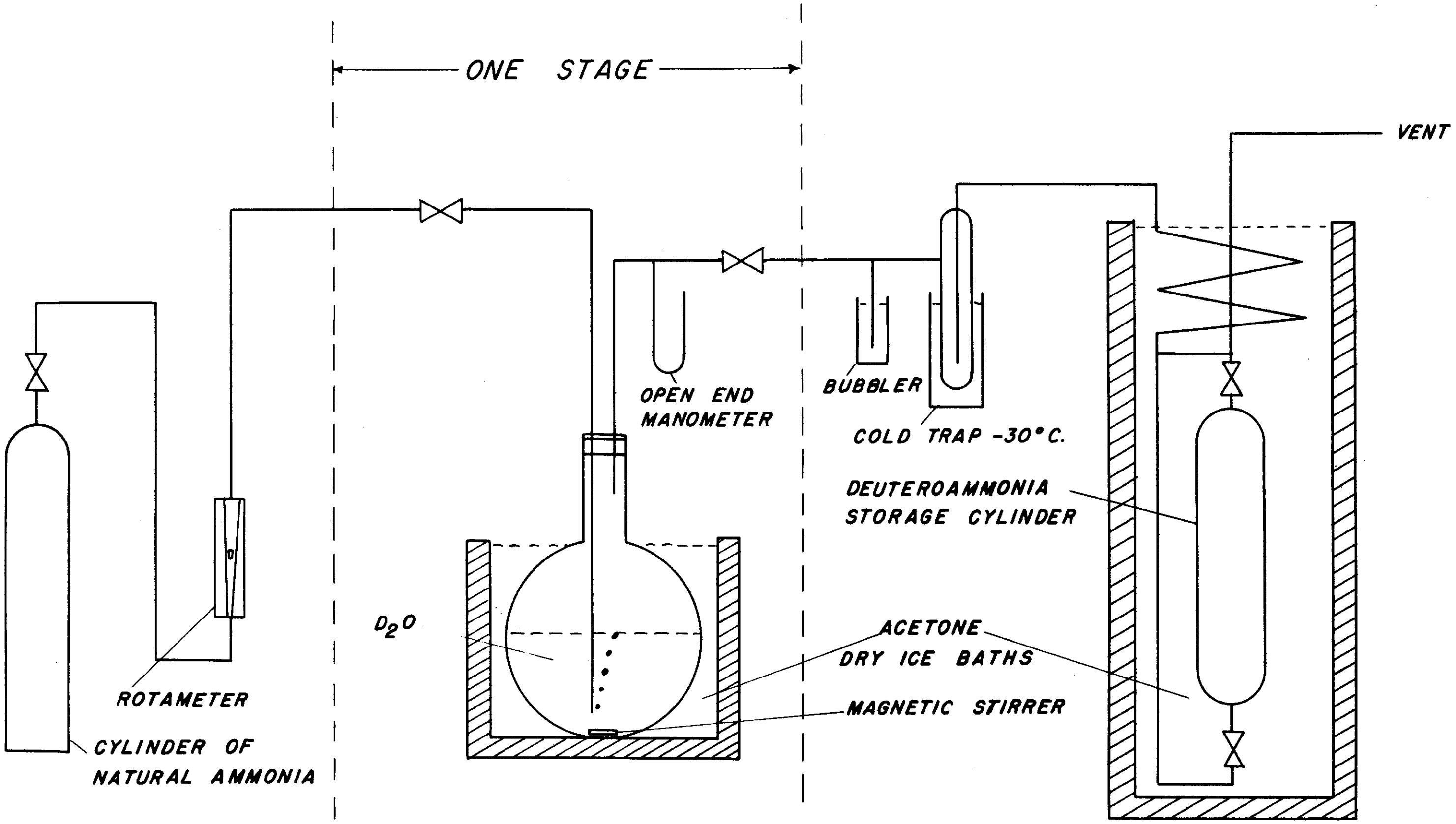
To verify the absence of oxides of nitrogen, unconverted ammonia and chlorine in the water sample its neutrality was periodically checked with "pH paper". In addition, the non-condensable gases leaving the conversion system were frequently checked with Nessler's reagent for traces of ammonia, and with silver nitrate for chlorine. When the precautions described previously in this section were taken, none of these contaminants was found to be present.

F. Manufacture of Deuterated Ammonia

The standard method of manufacturing deuterated ammonia, described by Kirshenbaum and Urey (26), involves the reaction of heavy water with magnesium nitride. This process is capable of producing very pure ND_3, the purity limited only by the purity of the heavy water used. However, for this work, deuterium enrichments over 80 percent were not required, and it was therefore possible to produce the desired partially deuterated ammonia by direct exchange reaction with heavy water and natural ammonia.

The apparatus used in the manufacture of deuterated ammonia was very simple in design. (Fig. 7) A contact stage consisted of a three-liter, round-bottom, long-neck flask, fitted with a rubber stopper through which passed two glass tubes. One tube extended nearly to the bottom of the flask while the other terminated very near the stopper. The flask was immersed in a five-gallon earthenware pot containing acetone refrigerant chilled with dry ice. To facilitate mixing, a magnetic stirrer was used. Through the glass tube that extended to the bottom of the flask gaseous ammonia was bubbled. A rotameter was used in this line to indicate flow rate. The other glass tube leaving the flask was attached to an open u-tube mercury manometer and to the next stage.

During ammonia addition, the line to the next stage was closed and the flask chilled to dissolve the ammonia. After the desired ammonia had been added, the inlet line was closed and the outlet opened and the flask warmed to discharge the deuterated ammonia. Using three stages, two pounds of deuterated ammonia of 0.80 mole fraction deuterium were obtained.



MANUFACTURE OF DEUTEROAMMONIA

FIG. 7

A stainless-steel, high-pressure cylinder fitted with needle valves at both ends and with stainless steel tubing that served as a condenser and vent was used to store the deuterated ammonia. When charging this cylinder with deuterated ammonia, it was suspended by a spring scale in a galvanized tank which contained acetone chilled with dry ice to -60°C. The ammonia from the last stage was passed through traps at -30°C. to remove traces of water before entering the cylinder. Precautions not to fill the cylinder more than half way with liquid ammonia were taken by noting the change in weight as ammonia was distilled into it. Closing the valves of the cylinder filled completely with liquid ammonia, could cause an explosion due to thermal expansion as the cylinder and the ammonia warmed to room temperature.

III. Results

Measurements of the deuterium separation factor in the distillation of ammonia obtained with the single-stage equilibrium still are given in Table 1. Runs have been listed in the order in which they were conducted. Measurements were taken at four deuterium mole fractions (MFD), namely 0.58, 0.40, 0.23 and 0.10. The pressure range covered was from 250 to 760 mm. Hg. The experimental error assigned to each MFD includes uncertainties introduced through variations in both the analytic and sampling procedure. The procedure for working up the data is described in Section IVD and Appendix E1.

The values of the separation factor obtained in the single-stage equilibrium still were represented by an equation of the form

$$\ln \alpha = a + bx + c \ln (\pi/\pi_0) \qquad (3.1)$$

where:

x = mole fraction deuterium in liquid

π = pressure mm. Hg. π_0 = 760 mm. Hg.

α = deuterium separation factor

and a, b and c are constants determined by the method of weighted least squares. The procedure for fitting this equation is described in Section IVA and the Appendix Section E2. The result is:

$$\ln \alpha = (0.0395 \pm 0.0004) - (0.0128 \pm 0.0029)(x - 0.424)$$
$$-(0.01246 \pm 0.00065) \ln (\pi/760) \qquad (3.2)$$

SUMMARY OF SINGLE STAGE MEASUREMENTS

TABLE 1

Run # *	MFD Liquid	MFD Vapor	Pressure MM Hg.	Separation Factor = α	ln α	Temp. °C.
16	0.5817 ± 0.0003	0.5729 ± 0.0002	765.5	1.0369 ± 0.0017	0.0362	-31.67
17	0.5810 ± 0.0005	0.5699 ± 0.0003	250.0	1.0466 ± 0.0023	0.0456	-50.82
18	0.5821 ± 0.0003	0.5725 ± 0.0001	761.3	1.0393 ± 0.0014	0.0385	-31.60
19	0.5812 ± 0.0004	0.5716 ± 0.0001	600.0	1.0404 ± 0.0017	0.0396	-36.36
20	0.5816 ± 0.0001	0.5713 ± 0.0001	500.0	1.0429 ± 0.0006	0.0420	-39.59
21	0.5796 ± 0.0001	0.5664 ± 0.0002	250.0	1.0552 ± 0.0010	0.0538	-50.82
22	0.5803 ± 0.0001	0.5689 ±.0.0001	375.0	1.0480 ± 0.0007	0.0469	-44.69
23	0.4203 ± 0.0002	0.4108 ± 0.0001	751.8	1.0399 ± 0.0008	0.0391	-32.41
24	0.4221 ± 0.0004	0.4112 ± 0.0003	500.0	1.0457 ± 0.0020	0.0447	-40.05
25	0.4223 ± 0.0001	0.4122 ± 0.0001	600.0	1.0425 ± 0.0008	0.0416	-36.73
26	0.4230 ± 0.0001	0.4097 ± 0.0002	250.0	1.0562 ± 0.0010	0.0547	-51.53
27	0.4235 ± 0.0003	0.4138 ± 0.0002	769.4	1.0407 ± 0.0015	0.0399	-32.04
28	0.4231 ± 0.0002	0.4115 ± 0.0002	375.0	1.0491 ± 0.0010	0.0480	-45.27
29	0.2371 ± 0.0002	0.2296 ± 0.0002	763.8	1.0429 ± 0.0015	0.0420	-32.60
30	0.2374 ± 0.0001	0.2287 ± 0.0001	500.0	1.0501 ± 0.0007	0.0489	-40.62
31	0.2370 ± 0.0002	0.2273 ± 0.0002	250.0	1.0563 ± 0.0016	0.0541	-52.16
32	0.2374 ± 0.0002	0.2276 ± 0.0001	250.0	1.0564 ± 0.0013	0.0548	-52.23
33	0.1011 ± 0.0000	0.0970 ± 0.0002	765.8	1.0474 ± 0.0019	0.0463	-32.97
34	0.1007 ± 0.0002	0.0965 ± 0.0001	500.0	1.0489 ± 0.0018	0.0478	-41.05
36	0.1014 ± 0.0001	0.0966 ± 0.0001	250.0	1.0547 ± 0.0018	0.0533	-52.59

* Runs 1 through 15 are not included due to the difficulty with sampling noted in Section II B.

Table 2 lists the over-all column separation factor observed in runs made with the concentric-tube column. The over-all separation factor is defined as:

$$\beta = \frac{(x_k)(1 - x_r)}{(1 - x_k)(x_r)} \qquad (3.3)$$

where x_k = mole fraction deuterium in kettle or still

x_r = mole fraction deuterium in reflux or distillate

The over-all column separation factor is related to the deuterium separation factor in simple distillation by

$$\beta = \alpha^{n + 1} \qquad (3.4)$$

where n is the number of theoretical plates in the column.

Table 2 indicates that n was far from constant in successive runs. In the first three runs at 0.57 MFD, the over-all separation factor, which should have remained constant within ± 0.0025, the variance of individual runs, varied over a range of 0.0124. In the second three runs at 0.23 MFD, the over-all separation factor should have been higher than the first three, because α at 0.23 MFD is greater than at 0.57 MFD, but the over-all separation factor at 0.23 MFD actually was less than at 0.57 MFD. The final run at 0.23 MFD, gave an over-all separation factor much less than in the three previous runs at 0.23 MFD, made before an intervening series at 0.04 MFD.

Because of this evidence for changes in the number of equivalent plates in the column, little significance can be attached to the over-all separation factor measured at 0.04 MFD, which was the main object

SUMMARY OF COLUMN RUNS

TABLE 2

Kettle Composition MFD	Overall Column Separation Factor	Pressure mm Hg.	Temperature °C. *
0.57	1.1396 - 0.0022	768.1	-31.6
0.57	1.1499 - 0.0022	764.6	-31.7
0.57	1.1520 - 0.0025	760.0	-31.8
0.23	1.1483 - 0.0038	762.0	-32.5
0.23	1.1453 - 0.0008	767.1	-32.3
0.23	1.1443 - 0.0009	764.6	-32.2
0.04	1.1398 - 0.0039	754.9	-33.4
0.04	1.1318 - 0.0059	768.6	------
0.23	1.1353 - 0.0016	753.9	-32.8

* These temperatures are not as accurate as those obtained from the equilibrium still since a correction of (-0.30°C.) had to be applied to compensate for the heating effect of the platinum heater which was near by. (This error is discussed in Section II G.)

of this series of experiments. It is possible that α at 0.04 MFD is actually less than at 0.23, but this series of runs cannot be considered to have established this fact.

A second reason for having little confidence in these results is the very low number of equivalent theoretical plates implied by them. The value of n inferred from the first three runs at 0.23 MFD is 2.3. This is so much less than the 75 plates observed by Naragon and Lewis (27) that it is evident that the column was not performing satisfactorily. The behavior of the column is discussed in Section IIC and IVC4. Because of the erratic behavior of the column results obtained with it have been disregarded in the interpretation of the measurements on the system NH_3 - ND_3 to be given in section IVA.

IV. Discussion of Results

A. Correlation of Data

To correlate the values of α determined in the single-stage experiments, it was assumed that the effects of composition and pressure were additive and of the form:

$$\ln \alpha = f(x) + c \ln (\pi/\pi_0) \qquad (4.1)$$

where: x = mole fraction deuterium in liquid

$f(x)$ is a function of x to be determined

π = pressure mm. Hg.

π_0 = 760 mm. Hg.

c = is a constant, to be determined.

The first step in correlating the data was to determine, by the method of weighted least squares, the best value of c and f(x), weighting each observed value of α inversely as the square of the experimental standard deviation. The results of this least square fit were:

$$c = -0.01246 \pm 0.00065$$

and

x	f(x)
0.57	0.0376 ± 0.0007
0.40	0.0394 ± 0.0006
0.23	0.0427 ± 0.0010
0.10	0.0426 ± 0.0016

Graphs 1, 2, 3 and 4 compare the values of α predicted by the above correlation with the observed values at 0.58, 0.42, 0.24, and 0.10 MFD, respectively. The length of the stroke through each point represents the experimental standard deviation. The line shown on each graph represents the equation:

$$\ln \alpha = f(x) + c \ln (\pi/\pi_0) \qquad (4.1)$$

From the slope of the line, it is evident that the value of c determined in this way represents the effect of pressure on α within two standard deviations of the experimental points.

f(x) in the above correlation is the value of ln α at 760 mm evaluated from all experimental measurements at each MFD. Graph 5 is a plot of f(x) against x, the mole fraction deuterium. f(x) clearly varies with mole fraction deuterium to an extent substantially greater than the experimental error. The straight line drawn through the four points was determined by the method of least squares, and is represented by the equation

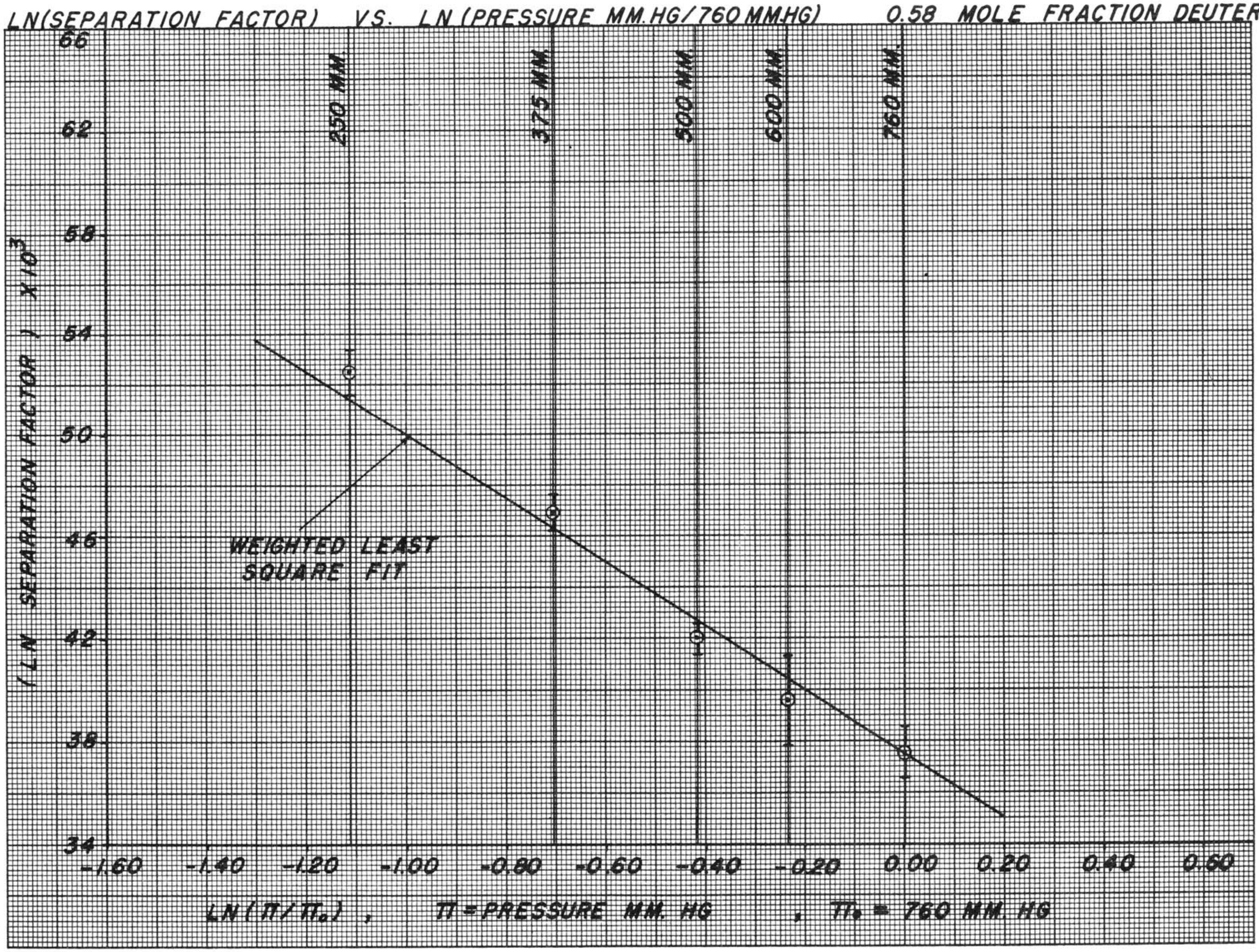
$$f(x) = 0.0395 \pm 0.0004 - (0.0128 \pm 0.0029)(x - 0.424) \qquad (4.2)$$

It is evident that this linear equation represents the points within the experimental uncertainty of each, so that no more involved dependence on x can be supported by these data. The complete equation for the dependence of α on MFD and pressure is

$$\begin{aligned} \ln \alpha = {} & (0.0395 \pm 0.004) - (0.0128 \pm 0.0029)(x - 0.424) \\ & -(0.01246 \pm 0.00065) \ln (\pi/\pi_0) \qquad (4.3) \end{aligned}$$

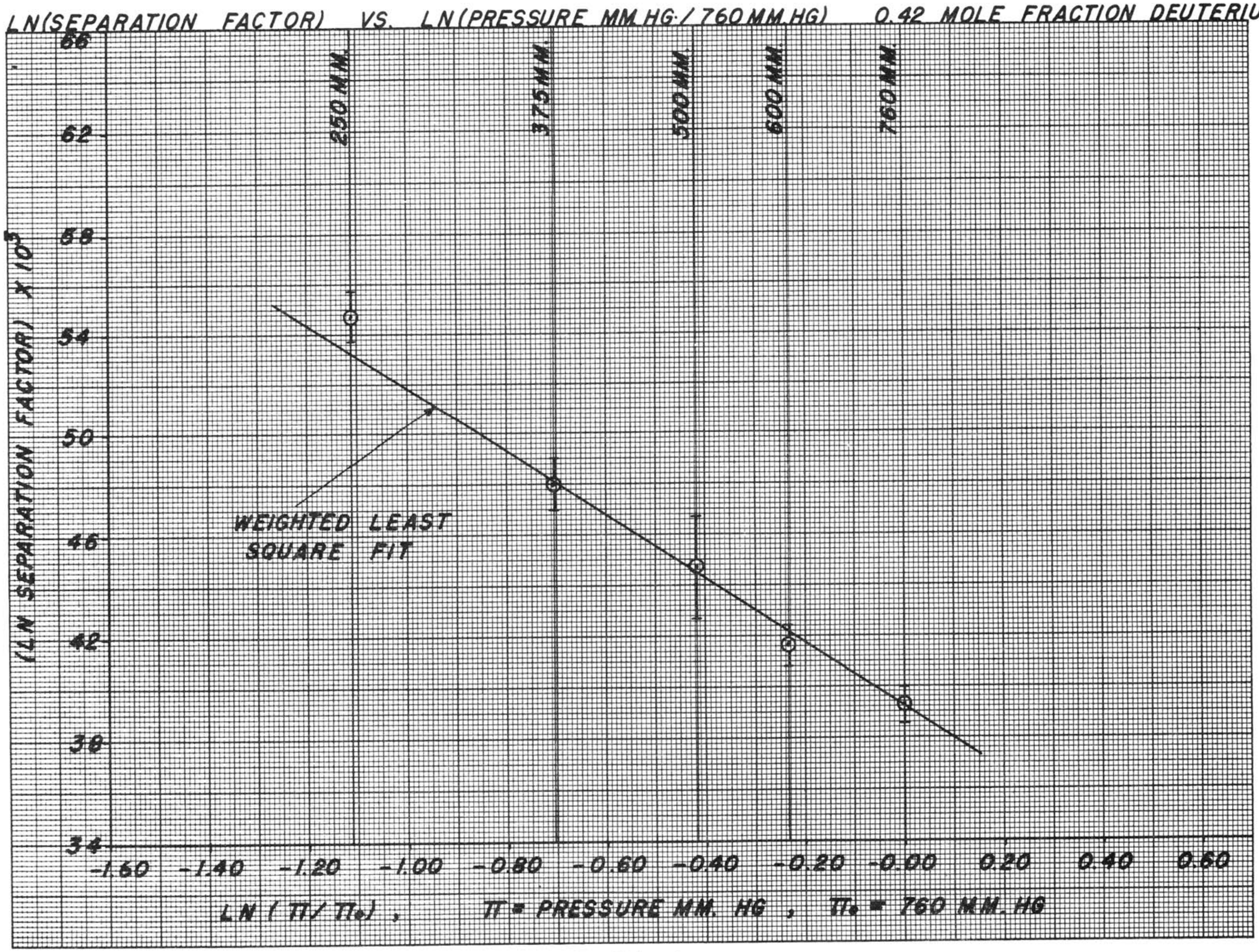
However, the theoretical analysis of the effect of preferential disproportionation of mixed deuteroammonias into NH_3 and ND_3 given in the Appendix Section F2 suggests that the value of ln α at a given pressure should reach a maximum at some MFD between 0.0 and 1.0,

LN(SEPARATION FACTOR) VS. LN (PRESSURE MM.HG/760 MM.HG) 0.58 MOLE FRACTION DEUTERIUM



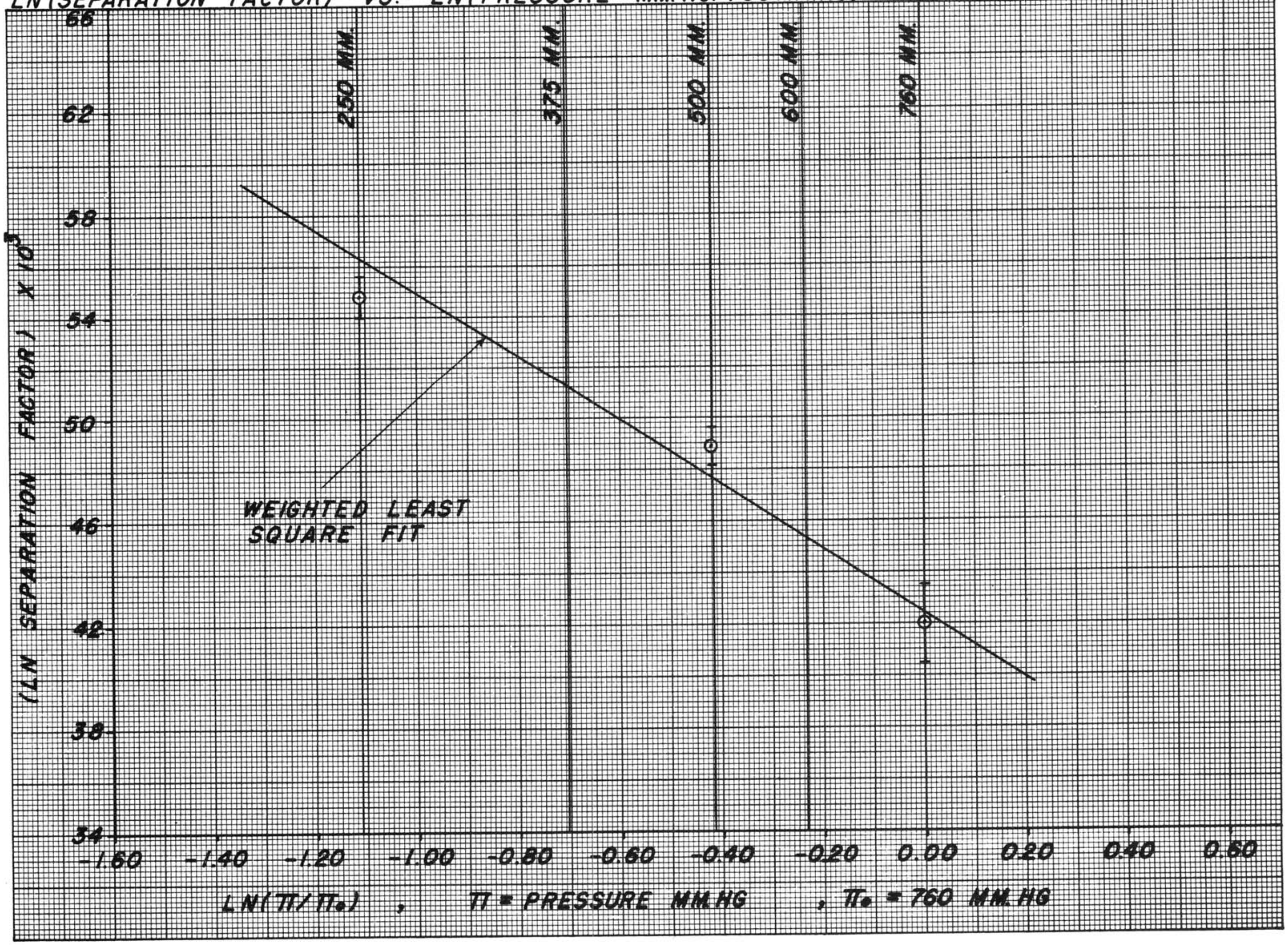
GRAPH I

LN(SEPARATION FACTOR) VS. LN(PRESSURE MM.HG/760 MM.HG) 0.42 MOLE FRACTION DEUTERIUM



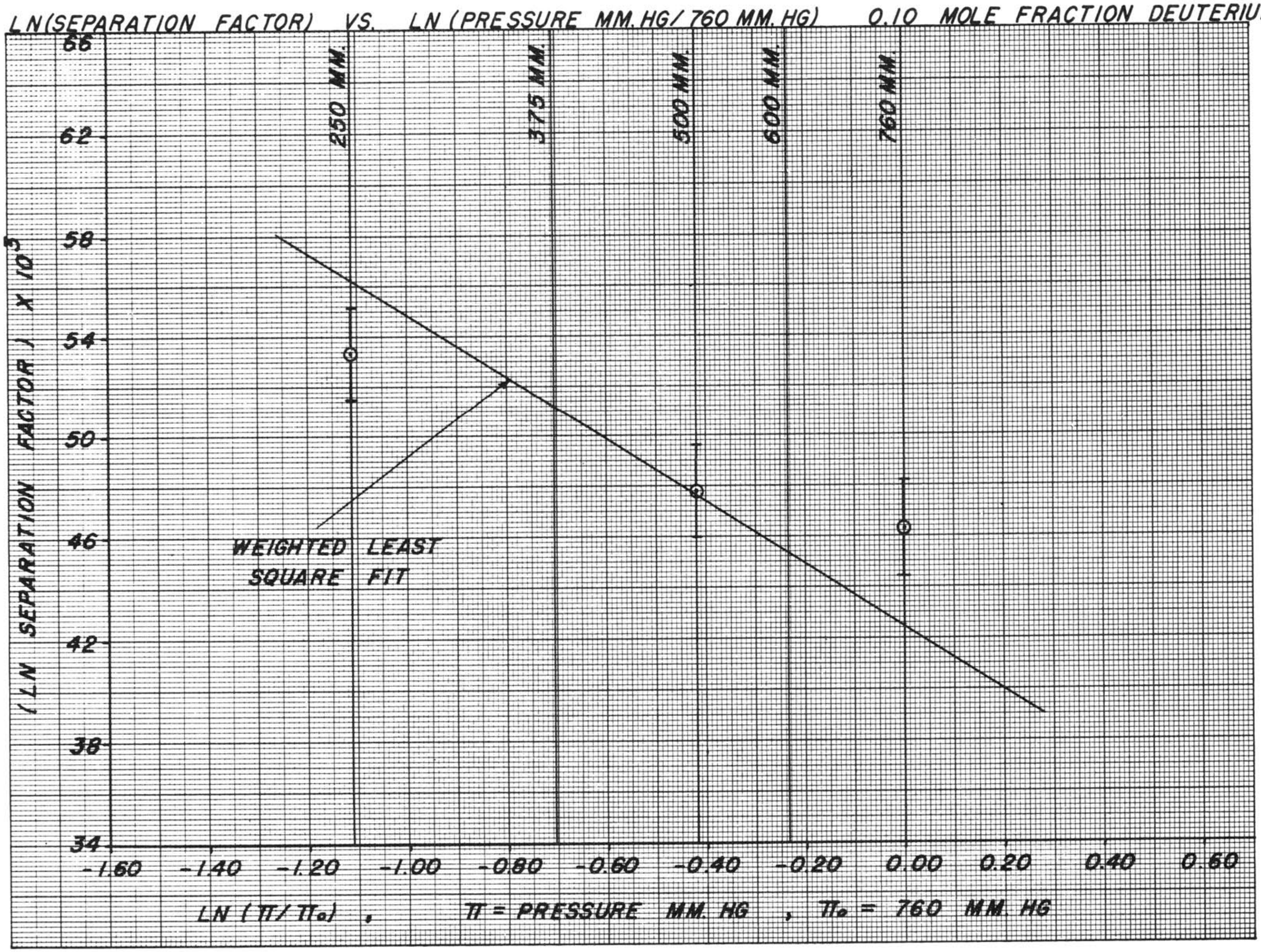
GRAPH 2

LN(SEPARATION FACTOR) VS. LN(PRESSURE MM.HG/760 MM.HG) 0.24 MOLE FRACTION DEUTERIUM



GRAPH 3

LN(SEPARATION FACTOR) VS. LN (PRESSURE MM.HG/760 MM.HG) 0.10 MOLE FRACTION DEUTERIUM



GRAPH 4

should drop off as the MFD approaches 0.0 and 1.0, and should approach the value

$$\ln \alpha = \ln \left(\frac{P_{NH_3}}{P_{ND_3}} \right)^{1/3} \qquad (4.4)$$

at the MFD's of 0.0 and 1.0. The dashed line on Graph 5 shows that the experimental results for $\ln \alpha$ at 760 mm. Hg. are not inconsistent with such behavior, and might predict a value of $\ln \alpha$ at 760 mm. Hg. and 0.0 MFD of 0.039, corresponding to $\alpha = 1.040$ instead of the value of $\ln \alpha = 0.045$ corresponding to $\alpha = 1.046$ obtained by linear extrapolation. In fact, the most probable value of α at 760 mm. and 0.0 MFD inferred from these measurements appears to be 1.043 ± 0.003, a value selected to have its limits at the intercepts of the solid and dashed lines of Graph 5. This value of 1.043 agrees almost exactly with the value of α interpolated from the vapor pressure data of Kirshenbaum and Urey (28) Taylor and Jungers (33), and Groth (17) for NH_3 and ND_3 by means of

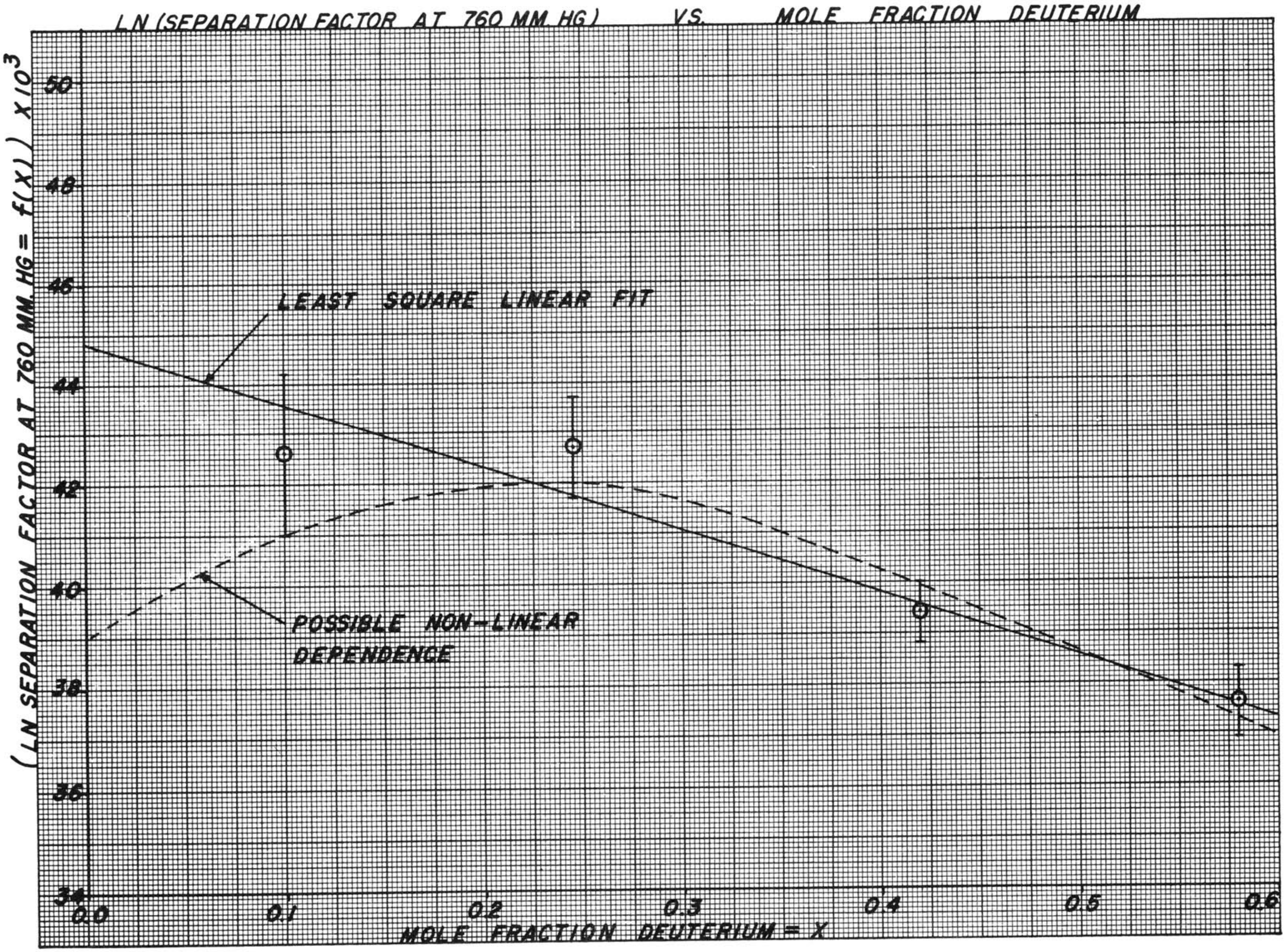
$$\alpha = \sqrt[3]{P_{NH_3} / P_{ND_3}} \qquad (4.5)$$

namely 1.0420.

Graph 6 is a plot of $\ell n \, \alpha$ computed by this cube-root relation from the vapor pressure ratio data of Kirshenbaum and Urey (28), Taylor and Jungers (33), and Groth (17) versus $\ell n \, (\pi/\pi_0)$. The slope of the line is 0.01286, which agrees almost exactly with the value of c in the equation (4.1).

$$\ell n \, \alpha = f(x) + c \ln (\pi/\pi_0) \qquad (4.1)$$

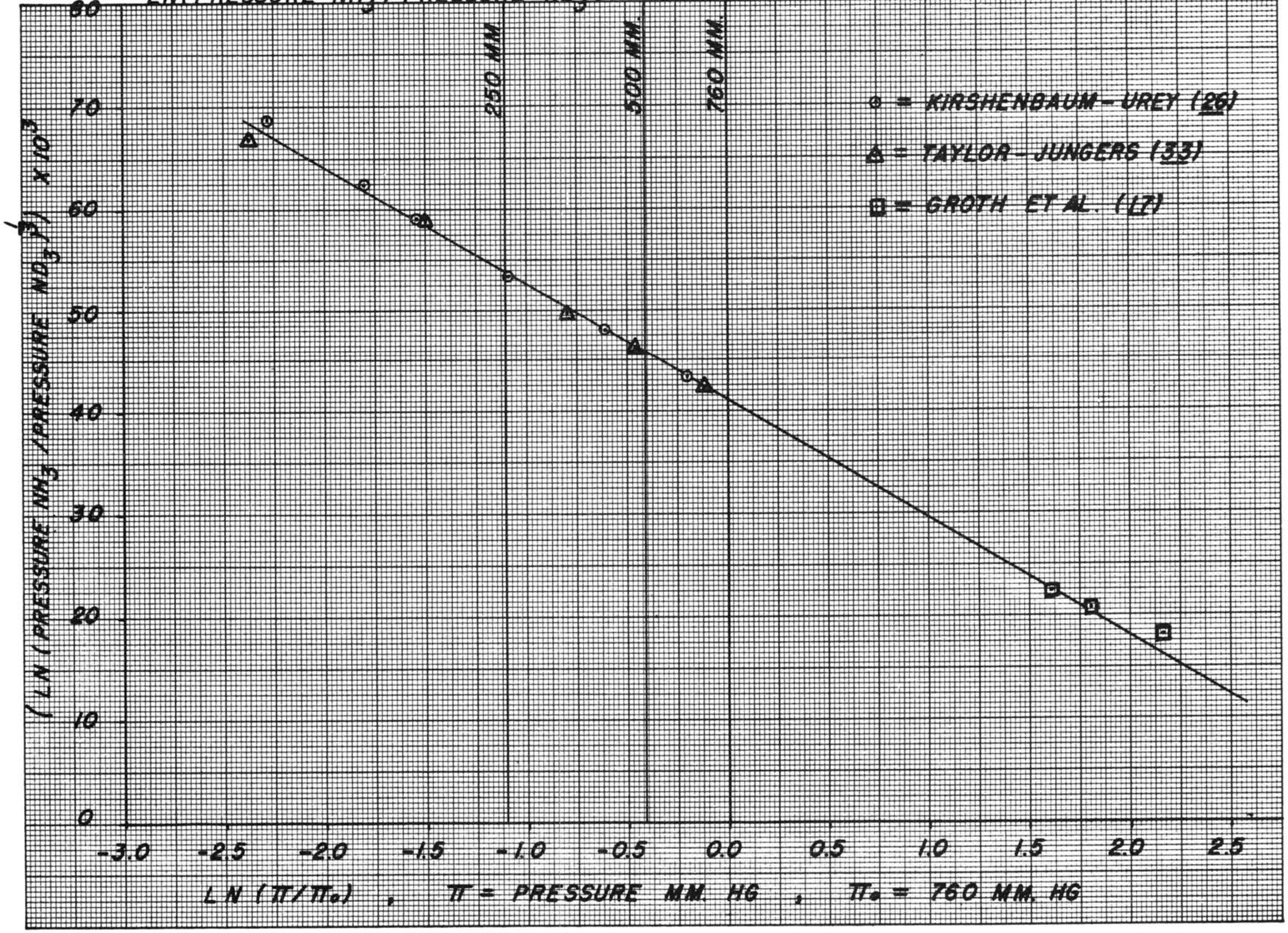
determined from the measurements of this thesis.


LN (SEPARATION FACTOR AT 760 MM. HG) VS. MOLE FRACTION DEUTERIUM
(LN SEPARATION FACTOR AT 760 MM. HG = f(X)) X 10^3
50
48
46
44
42
40
38
36
34
0.0
0.1
0.2
0.3
0.4
0.5
0.6
MOLE FRACTION DEUTERIUM = X
LEAST SQUARE LINEAR FIT
POSSIBLE NON-LINEAR DEPENDENCE

GRAPH 5

VAPOR PRESSURE RATIO PREDICTION OF THE DEUTERIUM SEPARATION FACTOR, $\alpha = (P_{NH_3}/P_{ND_3})^{1/3}$

$LN(PRESSURE\ NH_3 / PRESSURE\ ND_3)^{1/3}$ VS. LN(PRESSURE MM.HG/760 MM. HG)



GRAPH 6

Table 3 compares the experimental values of ln α with those computed from the least squares equation

$$\ell n\ \alpha = 0.0395 - 0.0128\ (x - 0.424) - 0.01246\ \ln\ (\pi/\pi_0) \qquad (4.6)$$

and with the equation fitted to the vapor pressure ratios of Graph 6.

$$\ell n\ \alpha = 0.0415 - 0.01286\ \ \ell n\ (\pi/\pi_0) \qquad (4.7)$$

The root mean square deviation from equation (4.6) is somewhat smaller than from (4.7).

R.M.S. Eq. (4.6) = 0.0020

R.M.S. Eq. (4.7) = 0.0035

This indicates that the variation of α with deuterium content is significant and should be taken into account in design studies in the ammonia distillation process.

Graph 7 is a plot of the boiling temperature observed for deuterated ammonia at 760 mm Hg as a function of mole fraction deuterium in the liquid. These measurements were made in the single-stage equilibrium still operating at atmospheric pressure. Excellent agreement was obtained with the values reported for the pure species NH_3 and ND_3 by Krishenbaum and Urey (26).

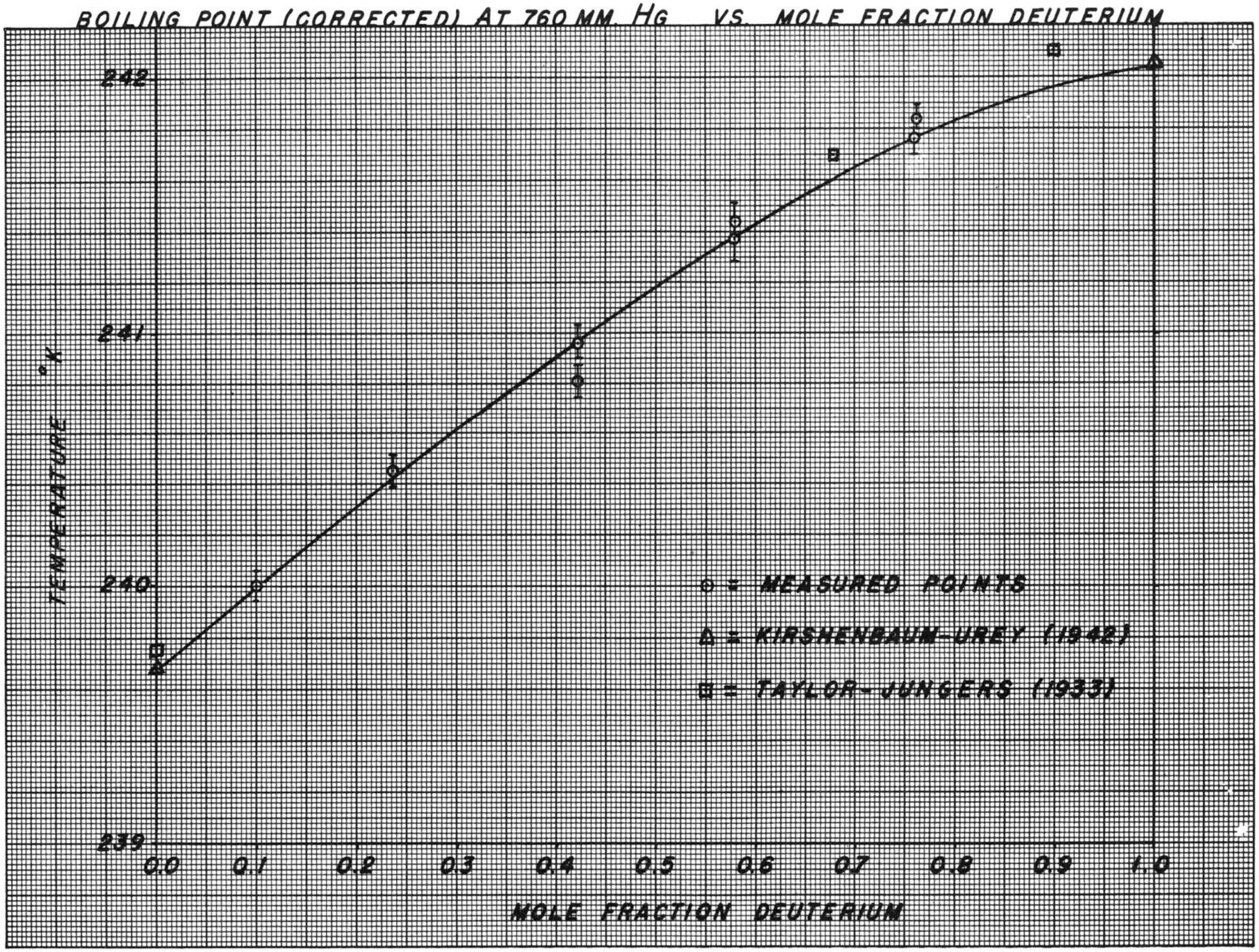
COMPARISON OF EXPERIMENTAL VALUES OF SEPARATION FACTOR WITH EQUATIONS

TABLE 3

		ln α			Deviations		Sq. Deviations	
MFD	π mm Hg.	Observed	Eq. 4.6	Eq. 4.7	Eq. 4.6	Eq. 4.7	Eq. 4.6	Eq. 4.7
					x10^4	x10^4	x10^8	x10^8
0.582	765.5	0.0362	0.0375	0.0412	-13	-50	169	2500
0.581	250.0	0.0456	0.0514	0.0555	-58	-99	3364	9801
0.582	761.3	0.0385	0.0375	0.0412	+10	-27	100	729
0.581	600.0	0.0396	0.0404	0.0442	- 8	-46	64	2116
0.582	500.0	0.0420	0.0427	0.0466	- 7	-46	49	2116
0.580	250.0	0.0538	0 0514	0.0555	+24	-17	576	289
0.580	375.0	0.0469	0.0463	0.0503	+ 6	-34	36	1156
0.420	751.8	0.0391	0.0395	0.0412	- 4	-21	16	441
0.422	500.0	0.0447	0.0447	0.0466	0	-19	0	361
0.422	600.0	0.0416	0.0424	0.0442	- 8	-26	64	676
0.423	250.0	0.0547	0.0534	0.0555	+13	- 8	169	64
0.424	769.4	0.0399	0.0395	0.0412	+ 4	-13	16	169
0.423	375.0	0.0480	0.0483	0.0503	- 3	-23	9	529
0.237	763.8	0.0420	0.0419	0.0412	+ 1	+ 8	1	64
0.237	500.0	0.0489	0.0471	0.0466	+18	+23	324	529
0.237	250.0	0.0547	0.0558	0.0555	-11	- 8	121	64
0.237	250.0	0.0548	0.0558	0.0555	-10	- 7	100	49
0.101	765.8	0.0463	0.0436	0.0412	+ 27	+ 51	729	2601
0.101	500.0	0.0478	0.0488	0.0466	-10	+12	100	144
0.101	250.0	0.0533	0.0575	0.0555	-42	-22	1764	484
							$\Sigma = 7771$	$\Sigma = 24882$

RMS Eq. $4.6 = \frac{1}{\sqrt{n}}\sqrt{\sum^{n}(\alpha_o-\alpha_e)^2} = \frac{1}{\sqrt{20}}\sqrt{7771 \times 10^{-8}} = 19.7 \times 10^{-4}$

RMS Eq. $4.7 = \frac{1}{\sqrt{20}}\sqrt{24882 \times 10^{-8}} = 35.2 \times 10^{-4}$


BOILING POINT (CORRECTED) AT 760 MM. HG VS. MOLE FRACTION DEUTERIUM

GRAPH 7

B. Effect of the Results on Economics of Heavy Water Production

Barr and Drews (3, 13) have estimated that an increase of the separation factor at one atmosphere pressure and low deuterium concentration from 1.042 to 1.084 would approximately cut all the cost figures in half for the ammonia distillation process. (These figures are given in Section I). The highest possible value found in this thesis at one atmosphere pressure, 1.047 would lower the cost of heavy water produced through ammonia distillation by no more than 15 percent. With so little reduction in cost indicated over the data given in Section 1, it must be concluded that distillation of ammonia, even in a parasitic plant, is not competitive with the H_2S process for primary concentration of deuterium. Ammonia distillation, however, may be useful as an intermediate concentration step, as in the plant proposed by a British engineering firm (18).

C. Accuracy (Sources of Error)

1. Single-Stage Measurements

Any continuous distillation equilibrium still has several inherent errors:

a. Condensation and refractionation of vapor or vapor space walls.

b. Complete vaporization of liquid splashed on over-heated vapor space walls.

c. Entrainment of liquid in the vapor.

d. Reaction with material of construction.

e. Improper return of condensate to the still.

In the design and operation of the continuous distillation equilibrium still used in this work every precaution was taken to minimize the above errors. The detailed steps taken in this regard are discussed in Section IIB. Robinson and Gilliland (29) state that from the analysis of the published data obtained by the continuous distillation method, it appears that this method gives data which is within 10 percent in (α-1) among investigators using essentially the same technique. Due to the extensive precautions taken in this investigation, the resultant error, due to the above causes should have been less than 10 percent.

2. Sampling and Conversion

In sampling the reservoirs of liquid ammonia in either the single or multi-stage investigations it was important to eliminate errors that would affect the composition of deuterium reported from the falling drop analysis. Some of the possible errors were:

a. Partial vaporization of samples

b. Contamination with light hydrogen.

c. Incomplete conversion of ammonia to water

d. Contamination from previous sample "Memory"

e. Contamination of water samples with foreign substance such as N_2O_3 or chlorine

f. Incomplete collection of the water sample

To minimize or eliminate all of the above errors the sampling and conversion system was designed and operated in such a manner that these errors were avoided. The detailed steps taken are described in detail in Section II B and E. The statistical evaluation of the variance introduced into the reported separation factors by errors in sampling and conversion indicated that an uncertainty of from 2 to 5 percent in $(\alpha-1)$ could be assigned to this effect. (Section IVD and Appendix Section E2 and 3 contain details of the statistical evaluation of these errors)

3. Analysis

The falling drop analytic device had four major sources of error:

a. Temperature fluctuations within the falling fluid.

b. Composition and hence density changes of the falling fluid.

c. Fluctuation in drop size.

d. Errors in timing.

The temperature fluctuations which gave use to convection currents within the falling fluid were found to be the limiting source of uncertainty. The steps taken to minimize this effect along with others are described in detail in Section IID. Statistical analysis of the performance of the falling drop apparatus indicated that it introduced an uncertainty in the composition of each sample analyzed of 0.0001 mole fraction deuterium. (See Appendix El) This uncertainty was found to be considerably less than that introduced by sampling and conversion errors and was therefore not the prime source of uncertainty in the reported separation factors.

4. Column

Unfortunately, the column did not operate reliably with the ammonia system due to incomplete wetting of the active walls of the column. Several attempts to correct this malfunction were unsuccessful. (See Section IIC). Because the walls were not fully wetted, any change in flow regime changed the area for mass-transfer and hence the effective number of stages obtained. Due to this erratic behavior the results obtained with it have been disregarded in the interpretation of the measurements on the system NH_3 - ND_3.

D. Statistical Evaluation of Data

The first step in the evaluation of the experimental data for any run was to establish a calibration curve from which sample compositions could be determined. The method used to determine this curve is given in Appendix Section El. Due to the number and wide composition range of the standards used for this calibration the error introduced into the separation factor by its uncertainty was negligible. Each sample was determined by averaging the rate of fall of six or more drops. From the fluctuation in the time of fall of these drops the variance or the standard deviation assigned to analyze uncertainties could be calculated. This standard deviation σ_a was found to be a good estimate of the precision with which a given sample could be analyzed.

From the fluctuations of the indicated compositions for a series of samples, either liquid or vapor, the total composition variance or standard deviation of the mean could be calculated. From these variances $\sigma_{\bar{x}}^2$ and $\sigma_{\bar{y}}^2$, the variance of the separation factor was calculated ($\sigma_{\bar{\alpha}}^2$). (See Appendix Section E2)

For the equilibrium still runs it was interesting to determine what fraction of the total composition variance $\sigma_{\bar{x}}^2$ or $\sigma_{\bar{y}}^2$ was due to uncertainties in the analytic technique, and what fraction to sampling errors and still fluctuations. The analytic variance $\sigma_{a\bar{x}}^2$ and $\sigma_{a\bar{y}}^2$ could be calculated directly from the fluctuations in time of fall for drops of a given sample and the total sample variance $\sigma_{\bar{x}}^2$ and $\sigma_{\bar{y}}^2$ could be calculated from the reported composition fluctuations. It was therefore possible to estimate the sample variance $\sigma_{s\bar{x}}^2$ and $\sigma_{s\bar{y}}^2$ from:

$$\sigma_{\bar{x}s}^{2} = \sigma_{\bar{x}}^{2} - \sigma_{\bar{x}a}^{2} \qquad (4.8)$$

As it can be seen from Table 5 in the Appendix, the analytic variance was consistently less than ten percent of the total variance. This means that the precision in composition determination, and hence separation factor, was not limited by the analytic technique, but by sampling errors and fluctuations in the still operation.

V. Conclusions

The separation factor or relative volatility for deuterium enrichment in ammonia distillation over the range of pressure 250 mm. to 760 mm. Hg. and the range of deuterium concentration 0.10 to 0.58 mole fraction deuterium is in good agreement with the value predicted from an interpolation of the low vapor pressure data of Kirshenbaum and Urey (26) and the high vapor pressure data of Groth (17). ($\alpha = 1.042$ at one atmosphere) However, a weak dependence of the separation factor on deuterium concentration was observed over this composition range. The highest values were obtained at 0.23 and 0.10 mole fraction deuterium ($\alpha = 1.044$ at one atmosphere) compared to ($\alpha = 1.040$ at 0.42 mole fraction deuterium, one atmosphere) and ($\alpha = 1.038$ at 0.58 mole fraction deuterium, and one atmosphere). (See Graph 1, 2, 3, 4, 5, and 6)

The practical consequences of this result is that there is little hope that ammonia distillation will offer a truly competitive process for heavy water manufacture when compared to the other existing techniques such as the hydrogen sulfide-water dual temperature exchange process.

In addition to separation factor measurements the boiling temperature of partially deuterated ammonia was determined as a function of the deuterium concentration. Good agreement with the boiling points of the pure and species NH_3 and ND_3, as reported by Kirshenbaum and Urey (26), was obtained. (See Graph 7)

VI. Recommendations

Since there seems to be little doubt that other processes of heavy water production will be more competitive than ammonia distillation, it is not suggested that further investigations be carried out with the hope of achieving a low-cost source of deuterium. This work did, on the other hand, uncover an interesting dependence of separation factor on composition which for theoretical reasons could be the basis of further research. It would be desirable to have values of the separation factor over as wide a composition range as possible, since from a theoretical point of view, the behavior at high deuterium concentrations is just as important as at low concentrations. Low concentrations received more attention in this work since the economics of a deuterium enrichment process depends only on the values of the separation factor at low deuterium compositions.

Due to the accuracy limitation of analytic devices it appears that a multi-stage device would be preferable to a single-stage device for any further investigations. The most important attribute of such a device would be that it be as insensitive as possible to all variables other than the separation factor. Although the concentric tube fractionating column had many advantages, the effect of external variables such as wetting and thruput proved to be so large and unpredictable that any changes in the over-all separation factor of the column could not be assigned to changes in the separation factor for deuterium enrichment. Although a bubble cap column would have a larger pressure drop, and much larger hold up, and would require much more deuterated ammonia charge, its efficiency would not be as severely effected by variables such as wetting and thruput. A bubble cap column would, therefore, appear promising and is suggested for further investigation of the concentration dependence of the separation factor for deuterium enrichment in the distillation of ammonia.

VII. Appendix

A. Detailed Procedure

1. Equilibrium Still

Prior to a run, the equilibrim still, the connecting lines, and the conversion system were cleaned and dried. Old grease was removed from the ground glass fittings with acetone and fresh halogenated grease applied. The conversion tube containing copper oxide was regenerated by passing air through it at 700°C. Finally the entire apparatus was swept with a stream of dry nitrogen for over an hour to remove all traces of moisture. This nitrogen was first passed through a liquid nitrogen trap to prevent ingress of moisture or grease. A cleaned and dried trap and a rotameter were connected in series to the still charging stopcock No. 15 (See Figure 5) from the deutero-ammonia storage cylinder. The still vent line was then closed to prevent ingress of moisture.

The evening previous to a run, the high vacuum system was turned on. This consisted of starting the mechanical and diffusion pumps and installing a Dewar reservoir of liquid nitrogen on the trap connecting the vacuum manifold to the diffusion pump. After one hour, the diffusion pump would normally be operating efficiently and the vacuum manifold pressure reduced to less than 10^{-5} mm Hg. pressure. If the manifold remained isolated for eight hours or more, pressures as low as 10^{-7} mm Hg. were attained. Once the diffusion pump was operating efficiently, however, the entire conversion system was normally evacuated.

During "roughing down" the conversion system, a procedure designed to keep the pressure within the diffusion pump below a few microns, was followed. The diffusion pump was isolated under low pressure by closing valves Nos. 4 and 5 (Fig. 5 or 6). The diffusion pump by-pass valve No. 6 was then opened. This allowed gases drawn into the vacuum manifold to pass directly into the mechanical pump. With valves Nos. 7, 11, 1 and 2 closed, the "roughing down" of the conversion system could be started. Valves Nos. 7 and 2 opened the system to atmospheric pressure, while valve No. 11 connected the conversion system with the sample burette. Since during "roughing down" some fine copper oxide dust was often blown out of the conversion tube, a porous plug was placed in the exit line of the conversion tube. It was desired, however, to be able to have a minimum pressure drop during final evacuation and for this reason a by-pass around this porous plug (valve No. 1) was provided. This valve was closed only while "roughing down" and when purging with nitrogen.

After the aforementioned valves Nos. 7, 11, 1, and 2 were closed and the diffusion pump isolated by closing valves Nos. 4 and 5 and the by-pass valve No. 6 opened, evacuation was accomplished by opening valve No. 3. Within one minute the pressure of the system was reduced to a few microns of mercury pressure and the porous plug by-pass valve No. 1 was opened. An ionization gauge located between the liquid nitrogen trap and the diffusion pump valve No. 4 was then turned on to determine the system pressure. As soon as the system pressure was less than 25 microns, the diffusion pump valves Nos. 4 and 5 were opened and the by-pass No. 6 closed. The lowest possible pressure of the entire conversion system could then be attained. Unless there was a leaking gound glass fitting, the pressure of the entire system would drop below 0.5 micron within one-half hour. If it did not, the leak was located and corrected. The system was then continuously evacuated in this manner for 12 hours previous to a run. Care was taken not to allow the liquid nitrogen trap to lose all of its refrigerant during this time.

After all the above preparations had been completed the actual run was started. A Dewar flask containing solid dry ice and acetone (-78°C) was placed on the still vent trap shown beneath the deuteroammonia storage cylinder in Figure 1. The vent line marked "to pressure control" was then opened. This line was previously closed to prevent entrance of moisture after the still was dried. The insulated copper tank surrounding the equilibrium still was filled with acetone to a level covering all of the condenser shown on the right side of the boiling flask in Figures 1 and 5. The temperature of this acetone was then lowered to approximately -70°C. by lowering dry ice in a wire basked into the bath. The basket was necessary to prevent pieces of dry ice from falling on the fragile still, and to limit the rate of gaseous carbon dioxide release. A Dewar flask containing acetone cooled to -30 to -32°C was placed on the trap inserted in the still charging line. The magnetic stirrer in the still was started.

The still charging stopcock, valve No. 15 was then opened and the ammonia flow from the storage cylinder to the still started by opening valve No. 16. The flow rate for the first ten minutes was kept below one liter per minute since the inner boiling flask of the still was still warm, being insulated by its vacuum jacket. The ammonia condensed, flowed down through the condensate trap into the still, and flashed out to the condenser again. After ten minutes the internal still flask was cooled to the ammonia boiling point, and the flow rate of ammonia from the storage cylinder was increased to five litres per minute for the remainder of the charging. The amount of ammonia charged was noted by a decrease in weight of the storage cylinder. Seven ounces were found to be optimum. Additional charge caused the loss of so much heat that it was impossible to maintain the flow of condensate from the condensate trap to the boiling flask without the backing up of liquid from the still.

Once charging was completed, valves No. 15 and 16 were closed and the charging trap was dismantled. Any condensed ammonia and water was discharged. If the run was to be carried out at sub-atmospheric pressure, the still was adjusted to the desired pressure, otherwise, the still vent line marked "to pressure control" was left open to the atmosphere during the run. The still pressure was controlled during the sub-atmospheric pressure runs by an automatic manostat. (See Appendix Section C1)

After the equilibrium still was adjusted to the proper pressure, boiling was started by turning on the platinum heater. The heater power was set at 34 watts corresponding to a boil-up rate of approximately one ml per minute. The magnetic stirrer operated continuously to insure complete mixing of the condensate and the contents of the still. The still was operated for at least two hours before sampling was commenced to allow equilibrium to be established.

The conversion apparatus had been evacuated continuously for over 12 hours before sampling was started and was maintained at 650 - 700°C. The trace heater on the exit line from the conversion tube was turned on to keep the temperature of this line over 150°C. during sampling. To prepare for sampling, a Dewar flask containing liquid nitrogen was placed on the nitrogen purge line (See Figure 5) and another Dewar flask with solid dry ice and acetone was placed on the vent trap from the gas burette. Two more Dewar flasks were prepared with solid dry-ice and acetone for use at the sample trap and the sample vent trap below valve No. 2. Previous to drawing a sample, the gas burette upper reservoir was evacuated to a pressure of about 1 mm Hg.

The type of sample to be drawn was chosen and the trace heater on this line turned on. Trace heaters were provided on both sampling lines to insure complete vaporization of the liquid ammonia drawn from the capillary sampling lines into the large diameter connecting tubing. After a few minutes to allow the trace heater to warm up, valve No. 14 was opened to the desired sampling line. Valves No. 10, 11 and 13 were closed to the gas burette. A small flow of oil was started from the gas burette up to the reservoir. Immediately after starting this flow, valve No. 13 was opened. A U-tube mercury manometer connected between the bas burette and the vent line of the still indicated the pressure drop across the sampling capillary. This pressure drop was kept above 10 mm Hg. at all times and usually at about 3-5 cm Hg. This prevented any ammonia from returning to the still once it left the sampling capillary.

Partial vaporization of the samples and return of the unvaporized samples to the still would have introduced serious errors.

After the desired volume of ammonia had been drawn from the equilibrium still (about 1 liter at S.T.P.), valves No. 12 and 13 were closed and the vent to the oil reservoir valve No. 9 was opened, and vacuum valve No. 8 closed. The drawn sample was first brought to one atmosphere pressure by allowing oil to flow from the reservoir into the burette, throttling the flow with valve No. 12. Once at atmospheric pressure, the sample could be discarded by opening valve No. 10 and allowing it to flow out the vent line. After the first sample drawn had been discarded, valves No. 10 and 12 were closed and the sampling procedure repeated a second time.

Following the drawing of a second burette filling of the desired sample and pressure adjustment to one atmosphere, the conversion tube was prepared to accept the sample. The evacuation was terminated by closing valves No. 3 and No. 1 and dry nitrogen was allowed to fill the conversion system by opening valve No. 7. The Dewar flasks prepared with solid dry ice and acetone were placed on the sample trap and on the sample vent trap beneath valve No. 2.

After the system pressure reached one atmosphere, valve No. 7 was closed and the vent valve No. 2 opened. The conversion tube was now ready to accept ammonia. Valve No. 11 was opened and ammonia flow was started by throttling the oil flow in the gas burette with valve No. 12. About 3-5 minutes were allowed for all the ammonia to enter the conversion apparatus, then valves No. 12, No. 11, and No. 2 were closed.

A heat lamp was focused on the upper portion of the sample trap to prevent condensation at this point and a slow evacuation of the system to 1-3 microns mercury pressure was started. As previously described when "roughing down" valves No. 7, 11, 1, 2, 4, 8, 5 were closed, No. 6 was opened. Throttling was accomplished by just cracking valve No. 3. After evacuation, valve No. 3 was closed, the heat lamp turned off, and dry nitrogen introduced through valve No. 7 to bring the system pressure to one atmosphere. A second evacuation to 1-5 microns Hg. pressure and a dry nitrogen filling was performed. The Dewar flask was then lowered from the sample trap and the frozen sample allowed to melt.

During conversion, the exit gas was periodically checked with Nessler's reagent for traces of unconverted ammonia and with silver nitrate solution for chlorine. In addition to these steps to insure sample purity, the pH of the sample was also checked to confirm its neutrality.

A sample vial was dried with dry nitrogen and numbered. Then a 2 ml hypodermic syringe was cleaned and dried. The sample trap was lowered and the melted sample transferred with the hypodermic syringe to the sample vial. Except during analysis, the sample vials were stored in a desiccator to prevent contamination with moisture.

The sample trap was then cleaned, dried, and replaced. The conversion system evacuated, "roughing down" first, and then using the diffusion pump for at least 10 minutes between samples. The trace heater was again turned on, on the desired sampling line, and sampling of another sample started. Sampling continued until from 5 to 7 samples of each type were obtained.

The boiling temperature in the still was noted at several times during the run and the pressure recorded for each temperature reading. For the runs at atmospheric pressure, the time was noted and the barometer readings were obtained later for these times from the M.I.T. Meteorological Department.

After sampling was terminated, the ammonia remaining in the still was returned to the storage cylinder. This was accomplished by chilling the storage cylinder in an acetone bath, cooled with dry ice to -60°C., and distilling the ammonia from the still into the cylinder. Once the cylinder was cooled below -33°C., valves No. 16 and 17 could be opened without losing ammonia. The still charging valve No. 15 was then connected to the condensing coil provided above the cylinder which was submerged in the -60°C. acetone. The still was brought to atmospheric pressure if it was under a vacuum. Valve No. 15 was opened and the still sampling lines and the vent line disconnected and corked. The acetone bath which had surrounded the still during the run was lowered. The still heater was turned on to about 40 watts and two infrared lamps were focused on the contents of the still and the ammonia distilled into the storage cylinder. The still heater was turned off before it was exposed above the liquid level and the remaining ammonia distilled by the two heat lamps alone.

When all the ammonia was returned to the storage cylinder, the heat lamps were turned off. The cylinder was removed from the acetone bath, valves 16 and 17 closed, and the cylinder was allowed to warm to room temperature.

Finally, the last step in the run was to start the regeneration of the copper oxide in the conversion tube. To accomplish this the vacuum system was shut down and valves No. 7, 1, and 2 were opened. Valves No. 11 and 3 remained closed. A slow flow of air was introduced into the nitrogen purge line while the furnace remained set at 650-700°C. Regeneration was continued overnight for at least eight hours. This was found to regenerate the copper oxide completely.

2. Column

Previous to a column run, the column, sample lines, traps, and connecting tubing were cleaned and dried. Old grease was replaced by fresh halogenated grease on all the ground glass fittings. The conversion tube was regenerated by passing a stream of air through it at 700°C for at least eight hours. The column and the sampling lines were swept with dry nitrogen for over an hour to remove all traces of moisture. This nitrogen was first passed through a liquid nitrogen trap to prevent ingress of moisture or grease. A cleaned and dried trap and a rotameter were connected in series between the deuterated ammonia storage cylinder and the column charging line. (Valve No. 15 - see Figure 6) The column vent line marked "to pressure control" was corked to prevent ingress of moisture until the actual run was started.

The column charging valve No. 15 was then opened and the ammonia flow from the storage cylinder started by cracking valve No. 16. The flow rate for the first ten minutes was kept below one liter per minute since the column internals were still at room temperature, with the exception of the reflux condenser. Ammonia condensed on the reflux condenser and flowed down into the warm column. Upon entering the warm column the ammonia flashed and was recondensed at the condenser only to flash again. However, after ten minutes all the column internals were chilled to the ammonia boiling point and liquid ammonia had started to accumulate in the kettle. The flow rate was then increased to five liters per minute for the remainder of the charging. Since an observation window was provided in the silvering of the vacuum jacket, the liquid ammonia level could be visually determined. Charging was terminated when the liquid ammonia level reached a mark about two-thirds up from the bottom of the kettle. This corresponded to about 100 ml of charge. Since mass transfer occurred on wetted kettle walls during column operation, it was necessary to keep the ammonia level constant from run to run.

Once charging was complete, valves No. 15 and 16 were closed, and the charging trap dismantled. Any condensed ammonia and water was discarded. Since all the column runs were carried out at one atmospheric pressure, the column vent line marked "to pressure control" remained open to the atmosphere during all the runs. Barometric pressure readings at intervals throughout the run were obtained from the M.I.T. Meteorological Department.

Once the column charging had been completed, the kettle heater was started at 10 volts, which corresponds to about 2 ml/min. boil up rate. This rate was above the column flooding point so flooding soon occurred. Before the flooding became severe, the heater power was reduced to 6.9 volts which corresponded to a boil-up rate of 0.9 ml/min. and was below the flooding point. The purpose of flooding the column was to promote wetting of the active zone walls. The magnetic stirrer operated continuously to insure mixing of the column down flow with the kettle contents. The column was operated under invariant conditions at least two hours before sampling was started to allow time for equilibrium to be established.

The conversion apparatus was operated in an identical manner in the column runs as in the equilibrium still runs. The oxidation tube had been evacuated hot for over 12 hours before the run was commenced. The trace heater on the exit line from the conversion tube was turned on to keep this line over 150°C. during sampling. To prepare for sampling, a Dewar flask containing liquid nitrogen was placed on the nitrogen purge line (See Figure 6) and another Dewar flask with solid dry ice and acetone was placed on the vent trap from the gas burette. Two more Dewar flasks were prepared with solid dry ice and acetone for use at the sample trap and the sample vent trap below valve No. 2. Previous to drawing a sample, the gas burette upper reservoir was evacuated to a pressure of about 1 mm Hg.

The type of sample to be drawn was chosen and the trace heater on this line was turned on. These heaters were provided on both sampling lines to insure complete vaporization of the liquid ammonia samples drawn from the capillary sample lines into the large diameter tubing. The manner in which the samples were drawn differed depending on whether they were kettle or reflux samples. The kettle samples were drawn in the same manner as the samples were drawn from the equilibrium still, but the reflux samples were treated specially due to the problem of disturbing the column operation.

Kettle samples were drawn in the following fashion. After a few minutes were allowed for the trace heater to warm up, valve No. 14 was opened, valve No. 18 remained closed. Valves No. 10, 11 and 13 were closed to the burette. A small flow of oil was started from the gas burette to the reservoir. Immediately after starting this flow, valve No. 13 was opened. A U-tube mercury manometer connected between the gas burette and the vent line of the column indicated the pressure drop across the sampling capillary. Partial vaporization of the sample and return of unvaporized liquid would have introduced serious errors. After the desired volume of ammonia had been drawn from the kettle (about 1 liter at S.T.P.), valves No. 12, 8, and 13 were closed and the vent valve No. 9 to the oil reservoir opened. The drawn sample was first brought to one atmospheric pressure by allowing oil to flow from the oil reservoir into the burette, throttling the oil flow with valve No. 12. Once at atmospheric pressure, the sample could be discarded by opening valve No. 10 and allowing it to flow out the vent line. After the first sample drawn had been discarded, valves No. 10 and 12 were closed, and the sampling procedure repeated a second time.

The reflux sampling, on the other hand, had to be performed with the column operation halted, to prevent sample contamination with material not obtained under total reflux conditions. The column was always operated at least 90 minutes without interruption previous to drawing a reflux sample. To sample the reflux, the trace heater was turned on, and a few minutes were allowed for it to warm up. Valve No. 15 was opened, and No. 14 was closed. The oil reservoir of the gas burette was evacuated and the valves No. 10, 11, 12 and 13 were closed. Just before sampling, the column heater was shut off and 30 seconds allowed for reflux to stop. Then valve No. 13 was opened and oil flow from the burette started by throttling with valve No. 12. As soon as all the liquid was drawn from the reflux cup (about $1\frac{1}{2}$ ml) valves No. 13 and 12 were closed. The column was started up again as described previously (flooding first). Once this point was reached, the reflux sample was treated just as the kettle samples. The first filling of the burette from the reflux cup was not discarded, however, since a second 90 minute period would have had to elapse before drawing the second burette filling to allow the column to attain equilibrium. This omission should not have introduced significant error since the memory checks were made without flushing, and did not show appreciable contamination of the drawn sample with residual ammonia in the conversion system. (See Appendix Sec. B6).

Following the final burette filling and the pressure adjustment to one atmosphere, the conversion tube was prepared to accept the sample. The steps of conversion and sample transfer were the same for the column runs as for the still runs described in Appendix Sec. A1, above. The appropriate cold traps were installed, the conversion system filled with dry nitrogen and the samples passed through. Two evacuations were performed to carry all traces of the sample to the sample trap. The sample was melted and transferred to a clean sample vial with a dry hypodermic. (See the corresponding steps in the equilibrium still procedure for details). Sampling continued until seven samples of each type were obtained.

The boiling temperature in the kettle was noted at regular intervals during the run and the time was recorded for each temperature reading. The barometric pressures were obtained from the M.I.T. Meteorological Department for the corresponding times. Due to an error in placement of the reflux thermowell, reliable reflux temperature readings were not available (See Section IIC).

After sampling was terminated, the ammonia remaining in the column kettle was returned to the storage cylinder. This was accomplished by chilling the storage cylinder in an acetone bath cooled with dry ice to -60°C. and distilling the ammonia from the kettle into the cylinder. Once the cylinder was cooled below -33°C., valves No. 16 and No. 17 could be opened without losing ammonia. The column charging valve No. 15 was opened, and the coolant circulating pump, which supplied coolant to the reflux condenser, was shut off. The column vent line was corked, and the kettle heater turned on to about 50 watts corresponding to a liquid boil-up rate of $1 \frac{1}{2}$ ml/minute. Distillation was terminated when the kettle heater was no longer fully submerged in the liquid ammonia.

After the distillation was terminated, the storage cylinder was removed from the acetone bath and valves No. 16 and No. 17 closed. The cylinder was allowed to warm to room temperature. Any remaining ammonia in the column was allowed to slowly distill out through the charging valve No. 15 to a vent line which led outside the building. Only a few milliliters of ammonia were lost in this manner during each run.

The last step in the run, as with the still runs, was to start the regeneration of the copper oxide in the conversion tube. To accomplish this, the vacuum system was shut down and valves No. 7, No.1, and 2 were opened. Valves No. 11 and No. 3 remained closed. A slow flow of air was introduced into the nitrogen purge line while the furnace remained set at 650 - 700°C. Regeneration was continued for at least eight hours. This was found to regenerate the copper oxide completely.

3. Analysis

Analysis of the deuterated water samples obtained by quantative oxidation of the ammonia samples was carried out with the falling drop apparatus. (Figures 3 and 4). At least 12 hours before analysis was to begin, both stirrers were turned on in the large water bath. This bath provided a constant temperature environment for the falling media. The temperature controller operated continuously even on days when no analyses were performed. This greatly simplified start-up prodedures. Due to its large thermal inertia, it would have required a long time for the water bath to reach operating temperature had it been allowed to cool to room temperature. The temperature chosen for operation (35°C.) was sufficiently high so that even on the warmest days little or no cooling was required to maintain this temperature.

The water bath was sealed with a polyethylene sheet at the top that contained an opening to a sample rack in which samples could be immersed in the bath prior to analysis. The inner bath containing the falling tubes was continuously stirred with an air bubbler, and a small stream of water was continuously added to the main bath to compensate for any evaporation.

At the beginning of a run the first three calibration standards to be run were chosen and placed in the rack prior to introduction into the pipette in order to minimize temperature disturbance of the pipette and the falling fluid. After the 90 minute warm-up, the pipette was raised by means of the traversing drive to its highest point. This raised the pipette tip about four inches above the top of the falling tube and permitted introduction of the sample. A small square of clean cotton towel was used to absorb water remaining in the pipette. This water was driven out by running the piston drive in, forcing mercury from the cylinder into the capillary of the pipette. The mercury was run out to the point where a small drop of mercury was exposed at the end of the pipette tip.

A standard water vial was taken from the rack in the outer bath, its top removed, and the pipette tip, which had been wiped with a dry cotton cloth, submerged about 1/4 inch in the standard water. Care was taken not to get excessive water on the outside of the pipette, or to touch the tip of the standard vial with the pipette tip since this tip was covered with a film of halogenated grease. A filling of the standard water was drawn into the pipette by withdrawing the piston from the pipette cylinder. The vial was then lowered from the pipette tip, closed, and returned to the rack. The filling was then expelled onto a cotton towel and the filling procedure repeated. The second filling was expelled and a third filling performed. After the third filling the falling tube containing the fluid of the correct density range was positioned beneath the pipette and the pipette lowered with the traversing drive until the tip was submerged in the falling fluid. Another standard of sample was then placed in the warm-up rack in place of the one removed. The two flushings of the pipette were required to assure that all traces of the previous sample were removed. To prevent contamination from the towel squares used to wipe the tip, a fresh, clean square was used for each filling.

Once the pipette was filled and submerged in the correct falling tube, a stop watch was started to indicate the submersion warm-up time. At the end of five minutes a drop was formed by driving the piston in 100 units on the pipette drive micro dial. The drop of water remained suspended from the pipette tip. After an additional minute, this drop was detached by slowly raising the pipette tip above the surface of the falling fluid. As the tip broke the surface, surface tension pulled the drop from the tip. The pipette tip was then immediately lowered once again beneath the surface of the falling fluid. The rate of fall of the first drop was never timed.

When the first drop reached the mid-point of the falling tube, a second drop was formed and the stopwatch reset. This drop was released when the first drop reached the lowest mark on the falling tube. The temperature was then read on the Beckmann thermometer and the stopwatch started when the drop passed the upper mark on the falling tube. Again, as this drop passed the mid-point of the falling tube, another drop was formed. When the falling drop reaching the lowest mark, the stopwatch was stopped and the time of fall recorded. Another drop was released and the same timing procedure repeated. The temperature was read during the fall of each drop and each drop was given an equal submersion warm-up time.

When six or seven drops had been timed, the pipette tip was raised from the falling tube and the next standard or sample introduced. Depending on the rate of fall, from 30 to 45 minutes were required to analyze each sample. Four standards were normally timed on the day of a run to determine the intercept of the calibration curve of reciprocal falling time versus deuterium composition. The slope of this calibration curve was previously determined by running six or more standards and found to be constant over periods of time as long as three months. (See Graph 9). By the time the fourth standard had been run, the first equilibrium sample was normally ready for pipette filling. Samples analyzed in this method could be determined to 0.0001 mole fraction deuterium.

Precautions were taken to clean and refill the pipette with clean mercury before it became sufficiently dirty to cause the mercury column to separate. This regular refilling, which occurred every 2 to 3 weeks, also precluded the chance of air bubbles developing in the pipette body. (See Appendix Sec. C2) Between runs the pipette tip was submerged in the falling fluid to prevent ingress of moisture or air. The stirrers were turned off when the bath was not in use, but the temperature controls remained on to facilitate start-up.

B. Calibrations and Related Measurements

1. Column Calibrations

Since reliable measurements of the separation factor for deuterium enrichment in ammonia distillation had been made with the single-stage equilibrium still in the composition range 0.10 to 0.58 mole fraction deuterium, these results could be used to determine the number of equilibrium stages obtained with the concentric tube column for the ammonia system. Graph 8 shows the variation of kettle and reflux samples during Run No. 4. It is interesting to note the slight deuterium enrichment of both samples during the run, which was caused by removal of the hydrogen rich overhead stream in the form of reflux samples. The separation obtained remained relatively constant during a given run as shown on Graph 8, but unfortunately a change in wetting regime between runs made it difficult to reproduce any given results exactly.

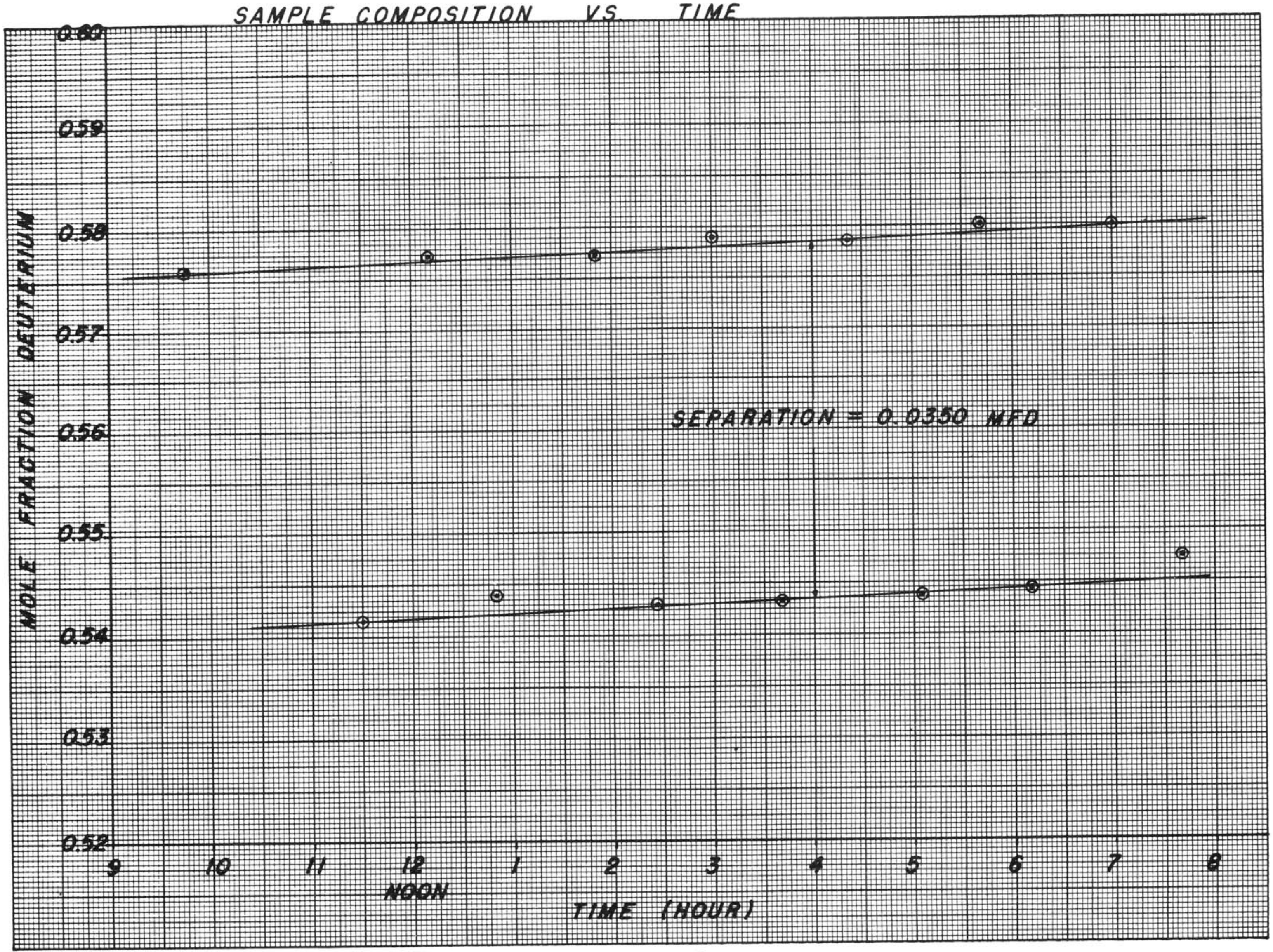
Under the condition of Run No. 4, graphical analysis of the separation gives a value of 0.0350 MFD as shown on Graph 8. Using this value, the number of equilibrium stages can be calculated as follows:

Using the following equation relating the number of stages to the deuterium separation factor and the kettle and reflux compositions for total reflux conditions:

$$(n + 1) = \frac{\ln \dfrac{x_k}{1 - x_k} \; \dfrac{1 - x_r}{x_r}}{\ln \alpha} \qquad (7.1)$$

COLUMN PERFORMANCE RUN 4

SAMPLE COMPOSITION VS. TIME



GRAPH 8

where:

n = number of equilibrium stages in the column at total reflux

x_k = kettle composition-mole fraction deuterium

x_r = reflux composition-mole fraction deuterium

α = separation factor for deuterium enrichment

and a value of (α = 1.037) at 0.54 to 0.58 mole fraction deuterium and k = 0.5785 MFD, r = 0.5435 MFD from Graph 8,

$$n + 1 = \frac{\ln \frac{(0.5785\quad)}{(1-0.5785)} \frac{1-0.5435}{0.5435}}{\ln (1.037)} = \frac{0.142}{0.0363} = 3.91$$

one arrives at the result: 2.91 equilibrium stages in the column. One can directly compare the over-all column separation factor:

$$\beta = \frac{x_k}{(1 - x_k)} \frac{(1 - x_r)}{x_r} \qquad (7.2)$$

for each run in Table No. 2 to see the relative separation obtained for the various runs.

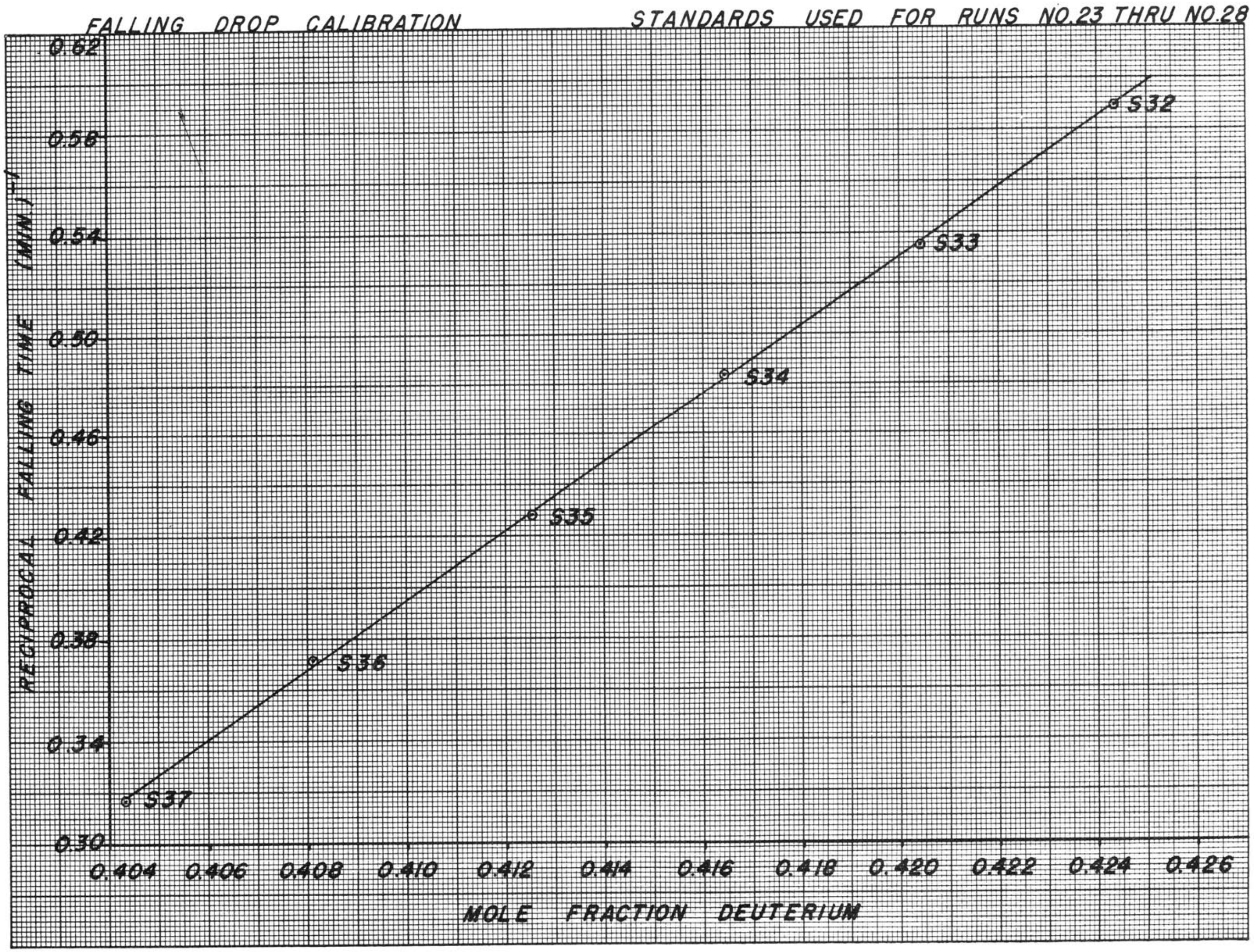
2. Falling Drop Analysis Calibration

Previous to any series of runs at a given deuterium concentration a calibration of at least six standard samples was performed. A curve of the reciprocal falling time versus the mole fraction deuterium was then prepared. The slope of this curve was found to be constant for periods of time as long as three months. The intercept was found, however, to shift slightly from one run to another and was therefore determined for each run by timing four or more standard samples on the day of the run.

The calibration of the falling fluid used for the equilibrium still runs No. 23 thru 28 at 0.42 mole fraction deuterium is given below as an example. The specific calibration points used for each run are listed in Table 4 and 6 (Appendix Sec. D1 and D3)

Standard	Mole Fraction Deuterium	Reciprocal Falling Time $(\text{min})^{-1}$
S32	0.42433	0.5892 ± 0.0010
S33	0.42042	0.5349 ± 0.0014
S34	0.41643	0.4833 ± 0.0012
S35	0.41256	0.4280 ± 0.0013
S36	0.40814	0.3716 ± 0.0011
S37	0.40433	0.3163 ± 0.0003

The results of this calibration are shown on the following graph (Graph 9).


FALLING DROP CALIBRATION
STANDARDS USED FOR RUNS NO.23 THRU NO.28
RECIPROCAL FALLING TIME (MIN.)$^{-1}$
0.62
0.58
0.54
0.50
0.46
0.42
0.38
0.34
0.30
0.404
0.406
0.408
0.410
0.412
0.414
0.416
0.418
0.420
0.422
0.424
0.426
MOLE FRACTION DEUTERIUM
S32
S33
S34
S35
S36
S37

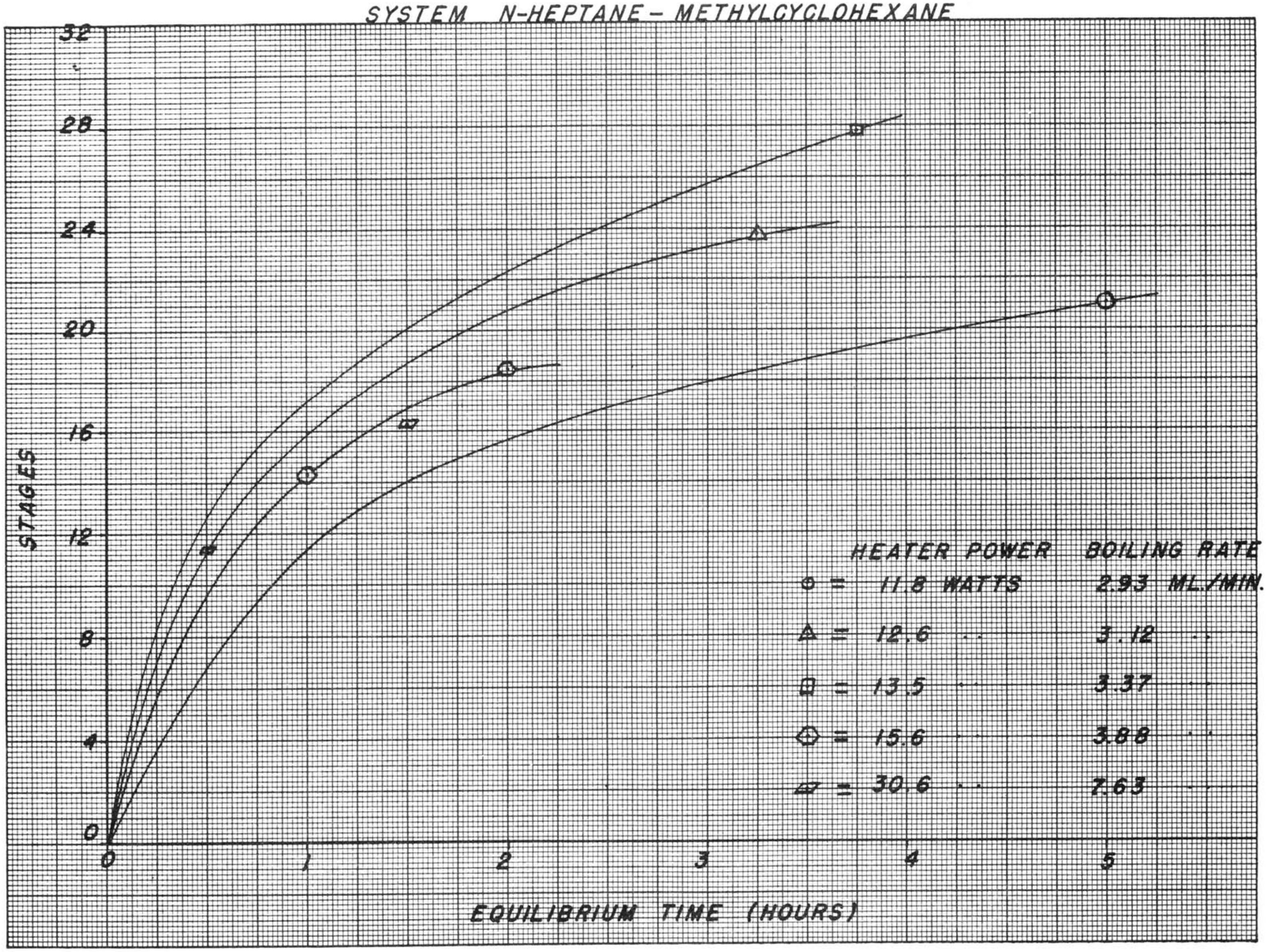
GRAPH 9

3. Column calibration-n-heptane-methylcyclohexane-system

The column was operated with the system n-heptane-methylcyclohexane to determine whether or not the poor results obtained with deuterated ammonia were due to the lack of ammonia wetting the walls. The results indicated that wetting was indeed the major difficulty since up to 28 stages were obtained with the organic system, while a maximum of five stages were obtained under similar conditions with the ammonia systems. These results do, however, indicate a somewhat lower number of stages with the n-heptane-methylcyclohexane system than Naragon and Lewis (27) reported for a similar design. They were able to obtain up to 75 equilibrium stages.

Graph 10 shows the effect of thruput and equilibrium time on the effective number of equilibrium stages for the system n-heptane-methylcyclohexane. It is interesting to note that there is an intermediate thruput for which separation was highest (3.37 ml/min). Below this boil-up rate too thin a liquid film probably caused a loss of efficiency. The data obtained with this system is summarized in Table 7. In calculating the equilibrium stages, a relative volatility of 1.085 was assumed.

COLUMN STAGES AT TOTAL REFLUX VS. EQUILIBRIUM TIME
SYSTEM N-HEPTANE - METHYLCYCLOHEXANE



GRAPH 10

4. Refractive Index Analytic Calibration for n-Heptane-Methylcyclohexane.

Refractive index measurements were used for the analysis of the samples of n-Heptane-Methylcyclohexane obtained from the column calibration with this system. The values for the pure components agreed well with the literature values:

	Refractive Index at 20°C.	
	Literature (9)	Observed
n-Heptane-		
Methylcyclohexane	1.3877	1.3876
	1.4230	1.4229

The calibration results are shown on Graph No. 11.

5. Thermocouple Calibration

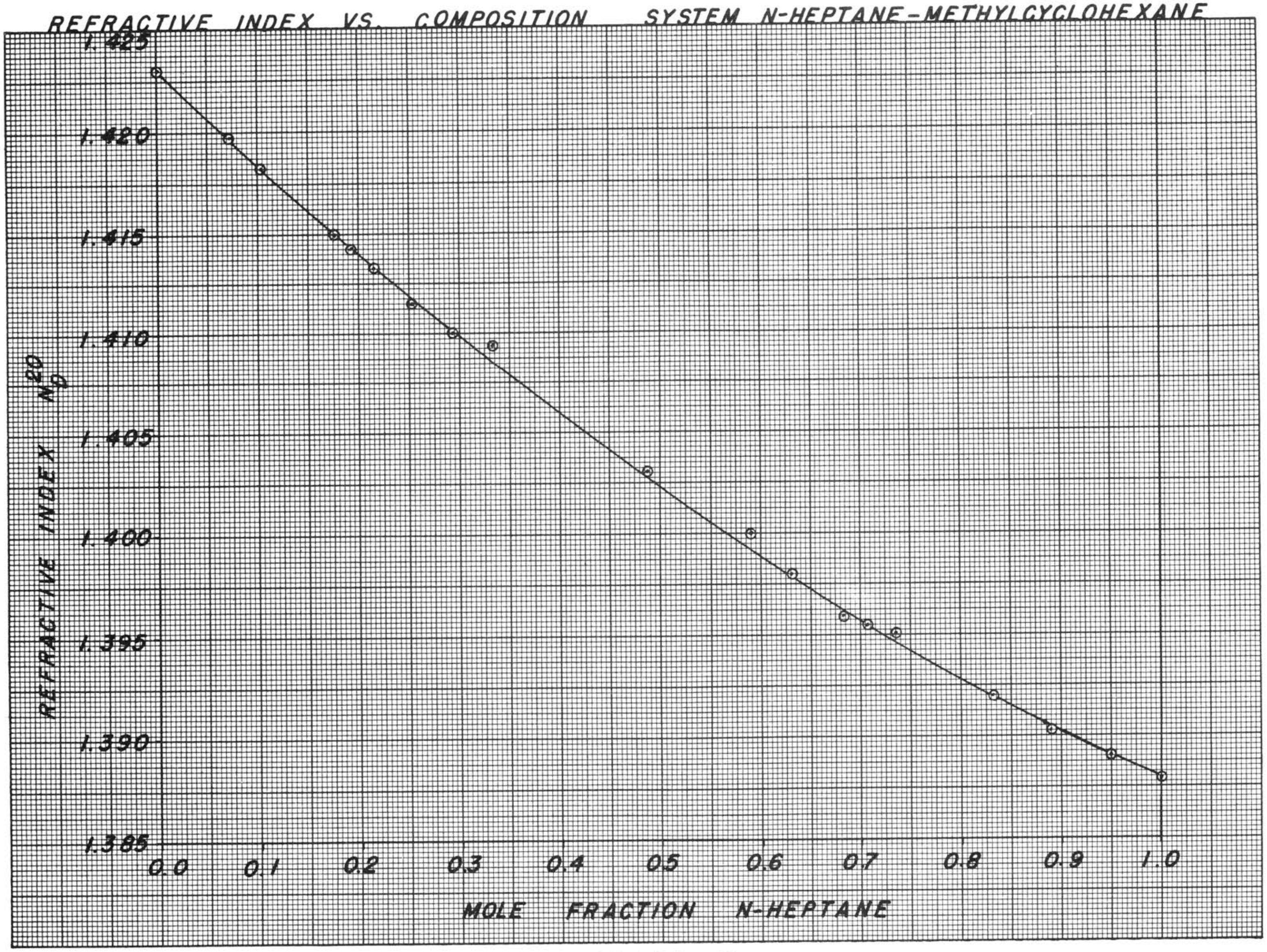
The Chromel-Alumel thermocouple used for all the temperature measurements was calibrated at the following reference points:

Carbontetrachloride freezing point	-22.9 °C.
Natural ammonia boiling point	-33.48°C. (26)
Mercury freezing point	-38.87°C.
Chlorobenzene freezing point	-45.2 °C.
Chloroform freezing point	-63.5 °C.

The natural ammonia boiling point was determined with the thermocouple placed in the equilibrium still thermowell, and the still operated under normal conditions with a natural ammonia charge. The freezing points were determined in a freezing point apparatus.

CALIBRATION CURVE

REFRACTIVE INDEX VS. COMPOSITION SYSTEM N-HEPTANE-METHYLCYCLOHEXANE



GRAPH II

A reference junction was maintained at 0.00°C. in a crushed ice bath at all times. The freezing point apparatus consisted of a Dewar flask with a centrally placed well for the sample. The thermocouple was placed in the well. By adjusting the temperature of an acetone bath placed in the Dewar flask to either just slightly below or above the freezing point, the sample could be frozen or melted respectively.

The E.M.F. readings used were average values for the freezing and melting cycles. All E.M.F. readings were obtained on a Leeds and Northrup type "K" potentiometer capable of reading to a tenth of a microvolt. The observations were as follows:

Point	E.M.F. (millivolts)	Temp. °C.
Carbon tetrachloride freezing point	0.870	-22.9 °
Natural ammonia boiling point (corrected to 760 mm Hg.)	-1.2581	-33.48°
Mercury freezing point	-1.4539	-38.87°
Chlorobenzene freezing point	-1.6851	-45.2 °
Chloroform freezing point	-2.3332	-63.5 °

The above values are probably accurate to within ± 0.0007 MV or ± 0.02°C. Some difficulty was encountered in reading the precision galvanometer since a vibration free support for it was not available.

To prepare a calibration curve, reference was made to the Bureau of Standards Circular No. 508 giving the E.M.F. as a function of temperature for a Chromel-Alumel thermocouple with the reference junction at 0.00°C. Values were given at every degree Centigrade and over the temperature range -20° to -50°C. A linear variation could be assumed. To have a precise reference curve, the values stated at -20, -30, and -50°C. were assumed exact. (See Graph 12)

Temp. °C.	MV(Circular No. 508)
-30°	- 1.14
-40°	- 1.50
-50°	- 1.86

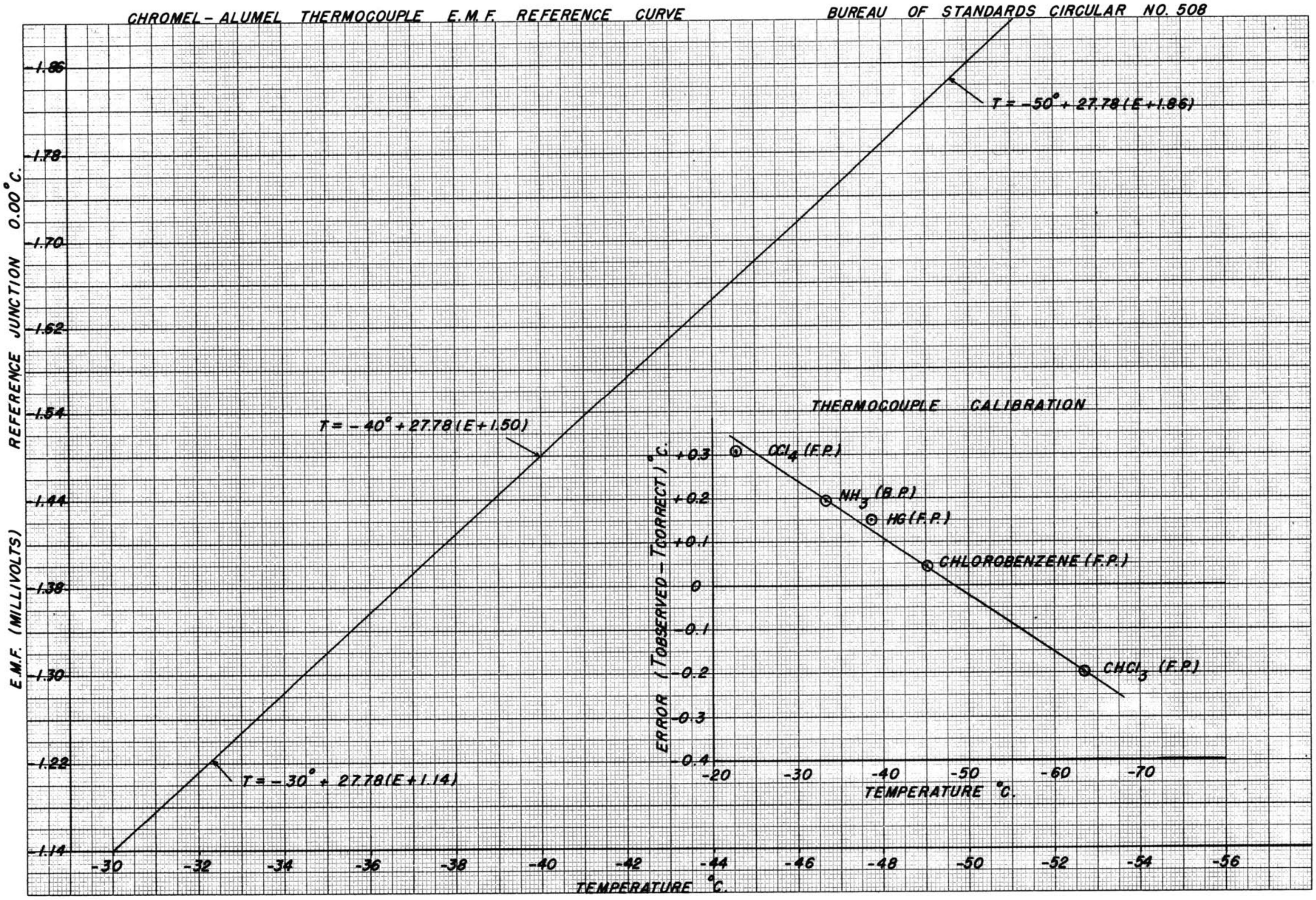
A change of 0.036 MV is observed per degree in this range. The following equations were used for calculation:

$$T = -30^\circ + 27.78 \; (E + 1.14)$$
$$T = -40^\circ + 27.78 \; (E + 1.50)$$
$$T = -50^\circ + 27.78 \; (E + 1.86)$$

and the calculated temperatures compared to the reported correct temperatures. The error stated as (T° observed–T° correct) is given on Graph 12 and it varied from 0.30 at -25°C. to -0.20 at -63.5°C. The above equations and this error graph were than used to calculate all the reported temperatures.

6. Memory Measurements of the Conversion System (Notebook No. 1, Pages 66 - 68)

To check the memory of the conversion system, a sample of light ammonia was introduced into the system between two samples of deuteroammonia from the equilibrium still. A series of samples of condensate had given the following results:


CHROMEL - ALUMEL THERMOCOUPLE E.M.F. REFERENCE CURVE
BUREAU OF STANDARDS CIRCULAR NO. 508
E.M.F. (MILLIVOLTS) REFERENCE JUNCTION 0.00 °C.
-1.86
-1.78
-1.70
-1.62
-1.54
-1.44
-1.38
-1.30
-1.22
-1.14
-30
-32
-34
-36
-38
-40
-42
-44
-46
-48
-50
-52
-54
-56
TEMPERATURE °C.
T = -50° + 27.78 (E + 1.86)
T = -40° + 27.78 (E + 1.50)
T = -30° + 27.78 (E + 1.14)
THERMOCOUPLE CALIBRATION
ERROR (TOBSERVED - TCORRECT) °C.
+0.3
+0.2
+0.1
0
-0.1
-0.2
-0.3
-0.4
-20
-30
-40
-50
-60
-70
TEMPERATURE °C.
CCl4 (F.P.)
NH3 (B.P.)
HG (F.P.)
CHLOROBENZENE (F.P.)
CHCl3 (F.P.)

GRAPH 12

No. 61	0.75574 MFD
No. 62	0.75412 MFD
No. 63	0.75566 MFD
No. 64	0.75583 MFD
No. 66	0.75579 MFD
No. 67	0.75728 MFD

The observed spread in the compositions of these samples is assigned to random sampling errors and fluctuations in the operation of the still. Following sample No. 67, a sample of light ammonia was introduced into the system and treated as any other sample. Then another condensate sample was drawn from the still and analyzed. (No. 68)

No. 68	0.75602 MFD

Since sample No. 68 was even richer in deuterium content than the average of the previous series, it proves that there was negligible contamination from the previous sample occurring.

To verify the necessity of the high vacuum maintained in the conversion system for at least 10 minutes between samples, the memory test was repeated without evacuation between the light ammonia sample and the following condensate sample. The result

No. 69	0.724 MFD

indicated an appreciable contamination with light hydrogen. The evacuation between samples was, therefore, necessary to eliminate contamination.

7. Ammonia Solubility in Halogenated Kel-F Oil

The ammonia solubility of Kel-F medium oil was determined. Ammonia at one atmosphere was bubbled for an hour through a small volume of the oil to saturate it. Then 50 ml of the oil was washed with 50 ml of distilled water in a separatory funnel. After settling for 20 minutes, 25 ml of the aqueous phase was decanted. To this aliquot 25 ml of distilled water was added and the solution was titrated with 0.01 normal sulfuric acid solution. The end point was determined by a direct reading pH meter.

Ml of 0.01066 NH_2SO_4	pH
0.0	8.50
1.0	8.45
2.0	8.40
7.0	8.25
10.0	8.12
19.0	7.70
23.35	6.85

The end point was taken as 23.0 ml.

This indicated an ammonia solubility of:

$$\text{Solubility} \cong 0.16 \text{ g./liter}$$

8. Falling Fluid Temperature Coefficients

To determine the effect of a shift in the absolute temperature of the falling fluid on the rate of fall for given standard samples of heavy water, two standards were run at 30.0°C. and at 31.2°C. The difference in the rate of fall at these two temperatures is due to the different coefficients of thermal expansion for the falling fluid and the deuterated water sample. The falling media used was an equal volume mixture of alphamethylnapthalene and methoxynapthalene, but should be representative of other ratios of these fluids as well, since their properties are so similar. It is important to differentiate this effect of temperature from the transient effect. The transient effect depends on the rate of temperature change. As the temperature changed, convection currents were set up within the falling tube. These currents then superimposed a velocity on the falling drop causing an error in the time of fall.

Sample	Temp.	Falling time $\bar{t}$	1/t min^{-1}	$\sigma_{1/\bar{t}}$ min^{-1}
A	31.2	1.668 min.	0.5995	± 0.0026
A	30.0	1.967 min.	0.5084	± 0.0012
B	31.2	1.850 min.	0.5405	± 0.0015
B	30.0	2.221 min.	0.4502	± 0.0014

Sample A gives a coefficient of 0.0795 ± 0.0024 min^{-1}/°C., and Sample B gives 0.0752 ± 0.0018 min^{-1} / °C. Since the slope of the calibration curve of reciprocal falling time versus composition was found to be 14 min^{-1} mole fraction deuterium, this coefficient corresponds to a composition coefficient of about 0.0054 mole fraction deuterium per °C. This means that a temperature change of 0.010°C. corresponds to an error in composition of only 0.00005 mole fraction deuterium. Finally, since the temperature fluctuations during any run were not greater than ± 0.002°C., the error from this effect should have been negligible, ± 0.00001 mole fraction deuterium.

9. Effect of Deuterium Composition on Column Stages

Since the purpose of the multi-stage measurements was to measure the composition dependence of the separation factor for deuterium enrichment, it was necessary to be able to show that the observed changes in the over-all separation factor of the column were not due to changes in the number of stages in the column. Unfortunately there is insufficient data available on the properties of deuterated ammonia to directly calculate the effect of composition in the number of stages. An estimate of the order of magnitude of this effect was therefore made by calculating the effect for heavy water-light water mixtures.

The H.T.U. (height of transfer unit or stage) for a concentric tube fractionating column can be estimated by the following formula:

$$HTU = 10.9 \; D_d \left(\frac{\mu}{\rho c_p}\right)^{0.67} \left(\frac{D_v \rho}{\mu}\right)^{0.2} \qquad (7.3)$$

where:

D_d = diffusion coefficient for the system.
μ = viscosity
ρ = density
c_p = specific heat
v = velocity (superfied based on entire cross section)
D = effective column diameter.

The effect of composition can then be estimated by taking a ratio of H.T.U.'s for light and heavy water, assuming that the column parameters remain constant.

$$\frac{HTU_{H2O}}{HTU_{D2O}} = \left(\frac{\mu_{H2O}}{\mu_{D2O}} \right)^{0.47} \left(\frac{\rho_{D2O}}{\rho_{H2O}} \right)^{0.47} \left(\frac{C_{pD2O}}{C_{pH2O}} \right)^{0.67} \qquad (7.4)$$

These ratios were evaluated from data in Kirshenbaum (25).

$$\left(\frac{\mu_{H2O}}{\mu_{D2O}} \right) = 1.232, \quad \left(\frac{\rho_{D2O}}{\rho_{H2O}} \right) = 1.1076, \quad \left(\frac{C_{pD2O}}{C_{pH2O}} \right) = 1.100$$

Then

$$\frac{HTU_{H2O}}{HTU_{D2O}} = \left(\frac{1.1076}{1.232} \right)^{0.47} (1.100)^{0.067} = 1.014$$

This indicates that 1.4 percent more stages would be obtained with pure D2O that with pure H2O, since the stages are obtained by dividing the active height of the column by the H.T.U. value.

It was felt that this result indicated that the effect of a change in the nuclear mass of 10 percent should cause less than 2 percent change in the number of stages for chemical isotopes. Extrapolating to the deuterated ammonia system where the nuclear mass change is about 17 percent, the effect of composition on the number of stages should have been less than 3 percent. Further, since the composition range investigated was only from 0.57 to 0.04, only about half this change should have occurred (i.e. 1 $\frac{1}{2}$ percent).

C. Associated Apparatus, Procedure, and Measurements

1. Pressure Control System

The pressure control system was used to maintain constant subatmospheric pressures during the low pressure equilibrium still runs. It consisted of a vacuum pump, a ballast tank, a solenoid valve, a mercury differential pressure switch, and a closed-end mercury manometer. Whenever the pressure in the system rose above the set point, the differential mercury pressure switch activated the solenoid valve, opening a line between the system and the vacuum pumps, hence lowering the system pressure.

The differential mercury pressure switch consisted of a glass U-tube with a mercury fill line attached at the bottom. Electrical leads were placed in each leg of the U-tube. One lead extended all the way to the bottom of the U-tube, but the other terminated in a sharp point half way down. A connecting line containing a stopcock joined the top of the two tubes. The top of the leg with the long lead was also connected to the system. The entire switch assembly was mounted on a rotating frame which allowed fine pressure adjustment. A six-volt battery operated a relay which was controlled by this switch. To prevent excessive sparking, a diode was placed in parallel with the switch to carry the current caused by the inductive voltage surge at the instant the switch opened. This relay in turn operated the solenoid valve with 110 volts A.C. A manual switch was provided to control the valve during pressurizing or evacuation of the system.

To set the system pressure, the vacuum pump was started and the by-pass opened on the differential mercury pressure switch. Controlling the solenoid valve manually, the system pressure was reduced until 2 mm Hg. above the desired set point. The by-pass valve was then closed and the automatic control turned on. Fine pressure adjustment was then made by rotating the differential pressure switch. The drift rate from the set point was less than 0.1 mm Hg. per hour.

The ballast tank dampened any severe pressure fluctuation caused by evacuation pulses or still oscillation. The closed-end mercury manometer was accurate to 0.2 mm Hg. as confirmed by comparison of barometric pressure readings to the published weather bureau values.

2. Pipette Mercury Filling

The micro-pipette used to deliver drops of uniform size to the falling tube of the falling drop apparatus was periodically cleaned and refilled with triple distilled mercury. This periodic cleaning prevented the accumulation of dirt, moisture or air within the body of the pipette. Dirt accumulation in the pipette would eventually cause the mercury column to separate, moisture would contaminate the sample, and air bubbles would cause fluctuations in the drop size.

The cleaning procedure included the following steps. The pipette piston drive was detached and the hose lines attached to the water jacket were removed. The tape holding the pipette to the aluminum traversing plate and angle support was removed, and the pipette removed from the apparatus. The Teflon piston seal was opened and all the old mercury was withdrawn. A rubber bulb was then placed over the cylinder opening and hot cleaning solution (sulfuric acid-potassium dichromate) drawn through the pipette capillary to remove any dirt. This cleaning was followed by a rinse of distilled water and pure acetone. The acetone was used as a drying agent. Following the acetone rinse, dry nitrogen passed through a liquid nitrogen trap was passed through the pipette for at least half an hour. The Teflon piston seal and the piston were cleaned with acetone to remove the old grease and dried by dry nitrogen.

After cleaning and drying the pipette, piston seal, and piston were replaced, a grease seal being formed with Dow Corning High Vacuum Grease. A filling device consisting of a mercury reservoir and vacuum lines was then attached to the tip of the pipette. Evacuation to a pressure less than 0.5 micron mercury was performed and continued for one hour. During this step the mercury reservoir, containing triple distilled mercury, was evacuated as well as the pipette body. After one hour of evacuation, the mercury reservoir was raised and mercury ran under gravity into the pipette. Only after the pipette was entirely filled, was evacuation terminated and air allowed to enter the filling device. By following this procedure, the possibility of air bubbles being trapped in the pipette was precluded. After filling, the pipette was returned to the falling drop apparatus. Finally the piston drive and hose lines were replaced, and the pipette was then ready for use.

3. Copper Oxide Preparation

The copper oxide used in the conversion of ammonia to water was prepared by a precipitation method to give the maximum surface area per gram. The following steps produced sufficient oxide to fill the conversion tube. A slight excess of 30 percent NaOH solution was added to a solution of 915 grams of Cu $(NO3)_2$. 3H20 and 15 grams of $Fe(NO3)_3$. 9H20 dissolved in 9 liters of water. The slurry formed was boiled gently for 20 minutes, cooled, decanted, and filtered, the filtrate being discarded. The filter cake was dried and crushed. The portion retained on a 20 Tyler mesh screen, but able to pass through a 6 Tyler mesh screen, was reduced by hydrogen at 400°C. and re-oxidized by passing air over it at 700°C. A second screening to remove fines on a 20 mesh screen was made. The retained copper oxide was packed into the Vycor-conversion tube. Burke (10) gives further information about oxide preparation.

4. Standard Sample Preparation

Standard samples of deuterated water were used to calibrate the falling drop analytic apparatus. Usually six standards were prepared to cover a range of 0.02 mole fraction deuterium, spaced at 0.004 mole fraction. The standards were made up by delivering a prescribed quantity of light water from a pipette and of 99.8 percent heavy water from a burette to a 20 mm. weighing bottle fitted with a ground glass stopper. The weighing bottle was weighed before and after each addition to determine accurately the amount of heavy and light water added. From these weights the mole fraction was calculated to the nearest 0.00001 mole fraction deuterium. When not being analyzed, the standards were stored in a desicator to prevent contamination by light water from the air.

Large errors can result in the calculated mole fraction if splashes occurred on delivering the waters to the weighing bottle, since the splashes did not mix with the bulk of the standard, but tended to evaporate. As long as sufficient care was taken to prevent this, no difficulty in getting excellent agreement between the standards was encountered. (See the calibration shown on Graph 9).

D. Data and Calculated Values

1. Single-Stage Equilibrium Data (Table 4)

The following table gives the raw equilibrium data obtained from the experimental runs carried out with the single-stage equilibrium still. The data for Runs 1 thru 15 are given, although due to sampling errors which occurred during these runs, they were not used in correlating the data. The sampling errors are discussed in Section IIB. The samples are given in the order obtained.

The symbols used are defined as:

S = standard water sample used for calibration. These standards were used for several runs at the same deuterium concentration.

L = liquid sample. The number merely refers to the order in which the samples were drawn.

V = vapor sample. The number indicates the order of sampling.

$1/\bar{t}$ = reciprocal of mean falling time for drops of specified sample $(\text{min})^{-1}$

$\sigma_{1/\bar{t}}$ = standard deviation of $1/\bar{t}$

MFD = mole fraction deuterium

σ_{MFD} = standard deviation of MFD

Table 4

Single-Stage Equilibrium Data

Run No. 1, 1 Atm., 6/9/59 Notebook No. 1 p. 40-44*

Run terminated when samples were found to be contaminated with N_2O_3, hence no samples were analyzed.

Run No. 2, 1 Atm., 6/11/59 Notebook No. 1 p. 45-49

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S20	0.5378	0.0011	0.76986	-	Calibration
S21	0.5043	0.0012	0.76600	-	"
S23	0.4727	0.0007	0.76276	-	"
S19	0.4461	0.0007	0.76021	-	"
L1	0.4987	0.0019	0.76542	0.00019	
L2	0.4933	0.0012	0.76487	0.00012	
L3	0.4909	0.0007	0.76461	0.00007	
L4	0.4965	0.0012	0.76520	0.00013	
V1	0.4289	0.0009	0.75865	0.00009	
V2	0.4420	0.0016	0.75986	0.00016	
V3	0.4356	0.0013	0.75927	0.00013	
V4	0.4333	0.0006	0.75905	0.00007	
L5	0.4951	0.0013	0.76504	0.00013	
V5	0.4116	0.0005	(Samples believed contaminated		
V6	0.4263	0.0009	with light water)		
V7	0.4355	0.0010	0.75926	0.00011	

* Location of Original Data

Run No. 3, 500 mm Hg., 6/18/59 Notebook No. 1, Pages 50-54

Sample	$(1/\bar{t})\text{min}^{-1}$	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S23	0.4719	0.0011	0.76276	-	Calibration
S20	0.5340	0.0015	0.76986	-	"
S21	0.4984	0.0011	0.76600	-	"
S19	0.4441	0.0008	0.76021	-	"
L1	0.4653	0.0008	0.76233	0.00008	
L2	0.4827	0.0004	0.76403	0.00004	
L3	0.4742	0.0016	0.76322	0.00016	
V1	0.3947	0.0010	0.75545	0.00011	
V2	0.3907	0.0015	0.75506	0.00015	
V3	0.3989	0.0013	0.75585	0.00013	
V4	0.4065	0.0018	0.75659	0.00019	
L4	0.4813	0.0013	0.76394	0.00013	
L5	0.4857	0.0019	0.76439	0.00019	
V5	0.4017	0.0013	0.75612	0.00013	
V6	0.3932	0.0008	0.75532	0.000078	
L6	0.4731	0.0007	0.76312	0.000075	

Run No. 4, 250 mm Hg., 7/2/59 Notebook No. 1, pages 56-57

Run terminated when liquid sampling line became clogged.

Run No. 5, 250 mm Hg., 7/4/59 Notebook No. 1 , Pages 58-62

Sample	$(1/\bar{t})\ \mathrm{min}^{-1}$	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S33	0.5164	0.0021	0.76009	-	Calibration
S32	0.4968	0.0011	0.75693	-	"
S34	0.5755	0.0010	0.76562	-	"
S35	0.4010	0.0011	0.74896	-	"
S31	0.4582	0.0007	0.75354	-	"
L1	0.5277	0.0010	0.76026	0.00011	
L2	0.5436	0.0019	0.76197	0.00022	
L3	0.5341	0.0012	0.76095	0.00014	
V1	0.4332	0.0010	0.75156	0.00009	
V2	0.4542	0.0011	0.75332	0.00009	
V3	0.4526	0.0012	0.75318	0.00010	
L4	0.5293	0.0020	0.76044	0.00024	
V4	Samples believed contaminated				
V5	0.4506	0.0012	0.75301	0.00010	
V6	0.4519	0.0011	0.75311	0.00009	
L5	0.5195	0.0013	0.75945	0.00011	
V7	Samples believed contaminated				
V8	0.4351	0.0012	0.75170	0.00010	
L6	0.5112	0.0015	0.75862	0.00018	

Run No. 6, 1 Atm., 7/7/59 Notebook No. 1, Pages 63-68

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S32	0.4876	0.0020	0.75693	-	Calibration
S33	0.5063	0.0017	0.76009	-	"
S34	0.5673	0.0015	0.76562	-	"
S31	0.4453	0.0011	0.75354	-	"
S35	0.3919	0.0007	0.74896	-	"
L1	0.5180	0.0012	0.76009	0.00014	
L2	0.5373	0.0011	0.76210	0.00014	
L3	0.5376	0.0011	0.76213	0.00013	
L4	0.5411	0.0007	0.76252	0.00009	
L5	0.5275	0.0011	0.76106	0.00013	
L6	0.5338	0.0017	0.76173	0.00020	
V1	0.4728	0.0019	0.75574	0.00019	
V2	0.4542	0.0021	0.75412	0.00021	
V3	0.4718	0.0017	0.75566	0.00017	
V4	0.4737	0.0011	0.75583	0.00011	
V5	0.4732	0.0015	0.75579	0.00015	
V6	0.4730	0.0012	0.75577	0.00012	

Run No. 7 250 mm Hg., 7/9/59 Notebook No. 1, Pages 69-70

Run discontinued due to oil in conversion tube. In addition, falling fluid was darkening very greatly.

Run No. 8, 1 Atm, 7/27/59, Notebook No. 1, Pages 72-73

Run discontinued due to oil in still vapor phase trap.

Run No. 9, 1 Atm, 7/30/59, Notebook No. 2, Pages 4-7

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S51	0.5037	0.0008	0.57279	-	Calibration
S52	0.4399	0.0005	0.56751	-	"
S53	0.4015	0.0009	0.56403	-	"
S50	0.5321	0.0010	0.57570	-	"
S44	0.5718	0.0008	0.57977	-	"
L1	0.5189	0.0013	0.57452	0.00012	
L2	0.5257	0.0012	0.57512	0.00010	
L3	0.5405	0.0038	0.57642	0.00033	
L4	0.5301	0.0003	0.57500	0.00003	
L5	0.5317	0.0008	0.57565	0.00007	
V1	0.4448	0.0008	0.56810	0.00007	
V2	0.4422	0.0012	0.56787	0.00010	
V3	0.4457	0.0006	0.56818	0.00005	
V4	0.4570	0.0008	0.56916	0.00007	
V5	0.4528	0.0009	0.56879	0.00008	
L6	0.5486	0.0006	0.57711	0.00005	

Run No. 10 500 mm Hg., 8/18/59, Note book No. 2, Pages 8 - 12

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S51	0.5077	0.0010	0.57279	-	Calibration
S50	0.5389	0.0007	0.57570	-	"
S52	0.4421	0.0006	0.56751	-	"
S53	0.4108	0.0011	0.56403	-	"
L1	0.5386	0.0011	0.57568	0.00010	
L2	0.5320	0.0005	0.57505	0.00004	
L3	0.5373	0.0007	0.57558	0.00006	
L4	0.5296	0.0017	0.57483	0.00015	
L5	0.5351	0.0003	0.57537	0.00003	
V1	0.4365	0.0010	0.56661	0.00008	
V2	0.4370	0.0003	0.56666	0.00003	Same CuO Dust
V3	0.4390	0.0010	0.56681	0.00008	
V4	0.4323	0.0008	0.56628	0.00007	
V5	0.4456	0.0005	0.56740	0.00004	
V6	0.4344	0.0021	0.56644	0.00019	

Run No. 11 250 mm Hg., 8/20/59, Notebook No. 2, Pages 12-16

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S50	0.5352	0.0006	0.57570	-	Calibration
S51	0.5105	0.0006	0.57279	-	"
S52	0.4411	0.0011	0.56751	-	"
S53	0.4078	0.0007	0.56403	-	"
S54	0.3793	0.0009	0.56128	-	"
L1	0.5429	0.0006	0.57618	0.00005	
L2	0.5375	0.0004	0.57565	0.00004	
L3	0.5509	0.0011	0.57698	0.00010	
L4	0.5414	0.0005	0.57604	0.00005	
L5	0.5607	0.0010	0.57796	0.00009	
V1	0.4227	0.0008	0.56521	0.00007	Some CuO Dust
V2	0.4471	0.0006	0.56735	0.00005	present
V3	0.4207	0.0008	0.56505	0.00007	
V4	0.4439	0.0008	0.56705	0.00007	
V5	0.4438	0.0011	0.56705	0.00010	
V6	0.4426	0.0006	0.56695	0.000052	
V7	0.4474	0.0006	0.56738	0.000055	

Run No. 12, 250 mm Hg., 8/24/59 Notebook No. 2, Pages 17-18

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S50	0.5255	0.0009	0.57570	-	Calibration
S51	0.5035	0.0011	0.57279	-	"
S52	0.4361	0.0006	0.56751	-	"
S53	0.4028	0.0012	0.56403	-	"
S44	0.5819	0.0012	0.57977	-	"
L1	0.5425	0.0004	0.57659	0.00004	
L2	0.5463	0.0010	0.57698	0.00009	
V1	0.4284	0.0021	0.56643	0.00018	

Run terminated when oil entered conversion tube.

Run No. 13, 250 mm Hg., 8/26/59, Notebook No. 2, Pages 19-22

Sample	$(1/\bar{t})\ \text{min}^{-1}$	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S50	0.5286	0.0009	0.57570	-	Calibration
S51	0.5019	0.0006	0.57279	-	"
S53	0.3996	0.0006	0.56403	-	"
S52	0.4337	0.0012	0.56751	-	"
S44	0.5833	0.0014	0.57977	-	"
L1	0.5393	0.0009	0.57628	0.00008	
L2	0.5415	0.0010	0.57649	0.00009	
V1	0.4292	0.0004	0.56653	0.00003	
V2	0.4548	0.0004	0.56870	0.00004	
L3	0.5499	0.0006	0.57727	0.00005	
L4	0.5527	0.0004	0.57754	0.00003	
V3	0.4328	0.0011	0.56683	0.00010	
V4	0.4457	0.0009	0.56795	0.00008	
L5	0.5519	0.0009	0.57746	0.00008	
V5	0.4341	0.0004	0.56696	0.00003	
V6	0.4363	0.0007	0.56714	0.00006	

Run No. 14, 375 mm Hg., 9/1/59 Notebook No. 2, Pages 24-28

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S2	0.5550	0.0005	0.57627	-	Calibration
S3	0.5046	0.0005	0.57277	-	"
S4	0.4586	0.0007	0.56878	-	"
S5	0.4255	0.0007	0.56506	-	"
S1	0.6027	0.0009	0.58085	-	"
L1	0.5058	0.0006	0.57220	0.00005	believed contamination
L2	0.5396	0.0005	0.57533	0.00005	
V1	0.4211	0.0006	0.56480	0.00005	
V2	0.4237	0.0005	0.56501	0.00005	
L3	0.5523	0.0010	0.57655	0.00009	
L4	0.5527	0.0011	0.57658	0.00009	
V3	0.4317	0.0005	0.56568	0.00004	
V4	0.4314	0.0007	0.56565	0.00068	
L5	0.5617	0.0007	0.57748	0.00006	
L6	0.5706	0.0007	0.57835	0.00006	
V5	0.4310	0.0008	0.56562	0.00007	
V6	0.4365	0.0006	0.56610	0.00006	

Run No. 15, 500 mm Hg., 9/3/59, Notebook No. 2, Pages 29-33

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S3	0.5005	0.0012	0.57277	-	Calibration
S2	0.5570	0.0007	0.57627	-	"
S4	0.4554	0.0013	0.56878	-	"
S5	0.4213	0.0005	0.56506	-	"
S1	0.5978	0.0011	0.58085	-	"
L1	0.5341	0.0012	0.57511	0.00010	
L2	0.5286	0.0005	0.57460	0.00005	
V1	0.4055	0.0007	0.56383	0.00006	
V2	0.4184	0.0007	0.56493	0.00006	
L3	0.5468	0.0005	0.57630	0.00004	
L4	0.5394	0.0006	0.57560	0.00005	
V3	0.4148	0.0009	0.56461	0.00008	
V4	0.4159	0.0004	0.56470	0.00004	
L5	0.5497	0.0008	0.57657	0.00007	
V5	0.4281	0.0009	0.56574	0.00008	
V6	0.4372	0.0007	0.56642	0.00006	Drawn fast
V7	0.4437	0.0012	0.56706	0.00010	
V8	0.4332	0.0006	0.56619	0.00006	

Run No. 16, 765.5 mm Hg., 9/29/59 Notebook No. 2, Pages 47-53

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S7	0.5778	0.0013	0.58584	-	Calibration
S8	0.5155	0.0020	0.58108	-	"
S9	0.4709	0.0027	0.57748	-	"
S10	0.3996	0.0009	0.57273	-	"
S11	0.3643	0.0015	0.56956	-	"
L1	0.5288	0.0030	0.58202	0.00023	1st Run with still
	0.5170	0.0023	0.58110	0.00018	modified
L2	0.5333	0.0005	0.58240	0.00004	
V1	0.4067	0.0018	0.57263	0.00012	
V2	0.4067	0.0008	0.57262	0.00006	
L3	0.5136	0.0005	0.58084	0.00004	
L4	0.5299	0.0015	0.58211	0.00011	
V3	0.4089	0.0014	0.57279	0.00010	
V4	0.4041	0.0025	0.57247	0.00017	
	0.4091	0.0041	0.57280	0.00029	Line out
L5	0.4919	0.0039	0.57911	0.00030	of liquid?
	0.4873	0.0011	0.57877	0.00009	
V5	0.4213	0.0018	0.57370	0.00012	

Run No. 17, 250 mm Hg., 10/3/59, Notebook No. 2, Pages 54-58

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/t}$	MFD	σ_{MFD}	Remarks
S7	0.5456	0.0041	0.58584	-	Calibration
S8	0.5006	0.0014	0.58108	-	"
S9	0.4518	0.0012	0.57748	-	"
S10	0.3884	0.0012	0.57273	-	"
S11	0.3472	0.0019	0.56956	-	"
S7	0.5588	0.0021	0.58584	-	"
L1	0.5102	0.0008	0.58190	0.00006	
L2	0.4843	0.0018	0.57993	0.00014	
V1	0.3393	0.0022	0.56902	0.00017	
V2	0.3516	0.0011	0.56995	0.00008	
L3	0.5061	0.0010	0.58160	0.00008	
L4	0.4945	v0.0018	0.58070	0.00014	
V3	0.3548	0.0014	0.57018	0.00010	
V4	0.3585	0.0016	0.57047	0.00012	

Run No. 18, 761.3 mm Hg., 10/6/59 Notebook No. 2, Pages 59-64

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S7	0.5326	0.0010	0.58584	-	Calibration
S8	0.4670	0.0024	0.58108	-	"
S9	0.4417	0.0013	0.57748	-	"
S10	0.3784	0.0013	0.57273	-	"
S11	0.3183	0.0023	0.56956	-	"
S7	0.5442	0.0012	0.58584	-	"
L1	0.4855	0.0014	0.58099	0.00011	
L2	0.4982	0.0007	0.58200	0.00005	
V1	0.3725	0.0021	0.57232	0.00014	
V2	0.3782	0.0011	0.57271	0.00007	
L3	0.4968	0.0008	0.58190	0.00007	
L4	0.5077	0.0010	0.58278	0.00008	
V3	0.3763	0.0016	0.57258	0.00011	
V4	0.3761	0.0015	0.57256	0.00010	
L5	0.5072	0.0008	0.58274	0.00007	
V5	0.3749	0.0008	0.57248	0.00005	

Run No. 19, 600 mm Hg., 10/8/59 Notebook No. 2 Pages 65-70

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S7	0.5310	0.0040	0.58584	-	Calibration
S8	0.4934	0.0011	0.58108	-	"
S11	0.3337	0.0015	0.56956	-	"
S10	0.3818	0.0010	0.57273	-	"
S7	0.5421	0.0021	0.58584	-	"
L1	0.4896	0.0006	0.58106	0.00005	
L2	0.4909	0.0007	0.58119	0.00005	
V1	0.3623	0.0016	0.57140	0.00011	
V2	0.3598	0.0011	0.57121	0.00008	
L3	0.4780	0.0010	0.58015	0.00008	
L4	0.4922	0.0040	0.58130	0.00032	
V3	0.3643	0.0020	0.57152	0.00016	
V4	0.3720	0.0021	0.57206	0.00017	
L5	0.5068	0.0014	0.58247	0.00011	
V5	0.3654	0.0017	0.57162	0.00013	

Run No. 20, 500 mm Hg, 10/13/59, Notebook No. 2, Pages 71-75

Notebook No. 3, Page 1

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S10	0.3701	0.0010	0.57273	-	Calibration
S11	0.3296	0.0012	0.56956	-	"
S8	0.4648	0.0015	0.58108	-	"
S7	0.5281	0.0006	0.58584	-	"
S8	0.4683	0.0014	0.58108	-	"
L1	0.4808	0.0010	0.58154	0.00008	opened contraction on liquid sampling line.
L2	0.4851	0.0009	0.58190	0.00007	
V1	0.3499	0.0017	0.57139	0.00012	
V2	0.3453	0.0011	0.57108	0.00008	Calibration
L3	0.4794	0.0011	0.58144	0.00009	in question
L4	0.4785	0.0009	0.58315	0.00007	New stds.
V3	0.3475	0.0010	0.57123	0.00007	weighed
V4	0.3495	0.0016	0.57137	0.00012	out
L5	0.4826	0.0014	0.58169	0.00011	
V5	0.3533	0.0011	0.57164	0.00008	

Run No. 21, 250 mm Hg., 10/15/59, Notebook No. 3, Pages 3-8

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S12	0.5541	0.0013	0.58534	-	Calibration
S13	0.5231	0.0005	0.58199	-	"
S15	0.3916	0.0003	0.57264	-	"
S16	0.3500	0.0008	0.56934	-	"
S14	0.4513	0.0008	0.57757	-	"
L1	0.4649	0.0010	-	-	partial vaporization
L2	0.5217	0.0016	-	-	partial vaporization
V1	0.3153	0.0013	0.56623	0.00016	
V2	0.3255	0.0014	0.56695	0.00017	
L3	0.4818	0.0017	-	-	partial vaporization
L4 *	o.4868	0.00017	0.57948	0.00021	run later
V3	0.3256	0.0009	0.56696	0.00012	
V4	0.3104	0.0025	0.56588	0.00032	
L5 *	0.4842	0.0018	0.57930	0.00023	run later
V5	0.3128	0.0009	0.56602	0.00011	
L6 *	0.4914	0.0014	0.57982	0.00019	run later
L7 *	0.4881	0.0012	0.57960	0.00016	run later

* Run after still pressurized. (used for $\bar{x}$)

Run No. 22, 375 mm Hg., 10/17/59 Notebook No. 3, Pages 9-14

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S12	0.5470	0.0022	0.58534	-	calibration
S16	0.3481	0.0011	0.57264	-	"
S13	0.5155	0.0009	0.58199	-	"
S17	0.2930	0.0008	0.56483	-	"
S15	0.3861	0.0011	0.57264	-	"
L1	0.4700	0.0028	0.57880	0.00021	
L2	0.4843	0.0013	0.57992	0.00010	
V1	0.3386	0.0006	0.56860	0.00005	
V2	0.3455	0.0002	0.56910	0.00002	
L3	0.4923	0.0006	0.58050	0.00004	
L4	0.4901	0.0013	0.58035	0.00010	
V3	0.3427	0.0002	0.56892	0.00002	
V4	0.3435	0.0009	0.56898	0.00087	
L5	0.4931	0.0001	0.58055	0.00008	
V5	0.3393	0.0012	0.56868	0.00004	

Run No. 23, 751.8 mm Hg., 10/27/59, Notebook No. 3, Pages 23-28

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S18	0.7223	0.0007	0.43222	-	calibration
S19	0.6946	0.0009	0.43017	-	"
S23	0.4751	0.0007	0.41381	-	"
S22	0.5336	0.0011	0.41755	-	"
S21	0.6043	0.0008	0.42228	-	"
S30	0.3436	0.0011	0.40704	-	"
L1	0.5800	0.0009	0.42074	0.00007	
L2	0.5821	0.0016	0.42090	0.00011	
V1	0.4346	0.0006	0.41067	0.00005	
V2	0.4371	0.0008	0.41082	0.00006	
L3	0.5662	0.0012	0.41979	0.00009	
L4	0.5711	0.0009	0.42012	0.00006	
V3	0.4360	0.0010	0.41074	0.00007	
V4	0.4408	0.0009	0.41108	0.00007	
V5	0.4374	0.0010	0.41087	0.00008	
L6	0.5764	0.0011	0.42050	0.00008	
L5	0.5680	0.0008	0.41992	0.00005	

Run No. 24, 500 mm Hg., 10/29/59, Notebook No. 3, Pages 29-34.

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S32	0.6229	0.0022	0.42433	-	calibration
S34	0.5050	0.0012	0.41643	-	"
S33	0.5591	0.0015	0.42042	-	"
S35	0.4535	0.0008	0.41256	-	"
S36	0.3936	0.0009	0.40814	-	"
S37	0.3403	0.0007	0.40433	-	"
L1	0.5693	0.0012	0.42110	0.00008	
L2	0.5732	0.0015	0.42140	0.00011	
V1	0.4409	0.0007	0.41168	0.00005	
V2	0.4210	0.0008	0.41022	0.00006	
L3	0.5854	0.0009	0.42228	0.00007	
L4	0.5870	0.0005	0.42238	0.00004	
V3	0.4331	0.0010	0.41113	0.00007	
V4	0.4381	0.0011	0.41149	0.00008	
L5	0.5984	0.0025	0.42320	0.00018	
V5	0.4385	0.0017	0.41152	0.00012	

Run No. 25, 600 mm Hg., 11/3/59, Notebook No. 3, Pages 35-39

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S36	0.3809	0.0013	0.40814	-	calibration
S34	0.4910	0.0018	0.41643	-	"
S37	0.3267	0.0006	0.40433	-	"
S33	0.5459	0.0014	0.42042	-	"
L1	0.5732	0.0034	0.42225	0.00024	
L2	0.5720	0.0020	0.42218	0.00015	
V1	0.4364	0.0023	0.41224	0.00017	
V2	0.4301	0.0014	0.41178	0.00010	
L3	0.5691	0.0008	0.42196	0.00006	
L4	0.5745	0.0011	0.42233	0.00008	
V3	0.4347	0.0020	0.41212	0.00014	
V4	0.4411	0.0011	0.41258	0.00006	
L5	0.5807	0.0012	0.42280	0.00008	
V5	0.4355	0.0004	0.41218	0.00003	

Run No. 26, 250 mm Hg., 11/5/59, Notebook No. 3, Pages 40 - 44

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S33	0.5382	0.0005	0.42042	-	calibration
S34	0.4868	0.0012	0.41643	-	"
S35	0.3778	0.0005	0.47042	-	"
S37	0.3212	0.0006	0.40433	-	"
V1	0.3918	0.0020	0.40952	0.00015	
V2	0.4031	0.0016	0.41037	0.00011	
V3	0.3996	0.0013	0.41009	0.00009	
V4	0.3893	0.0014	0.40938	0.00010	
V5	0.3856	0.0014	0.40908	0.00010	
L1	0.5723	0.0016	0.42285	0.00012	
L2	0.5742	0.0015	0.42300	0.00011	
L3	0.5723	0.0013	0.42286	0.00010	
L4	0.5758	0.0012	0.42309	0.00009	
L5	0.5751	0.0010	0.42307	0.00007	

Run No. 27, 769.4 mm Hg., 11/10/59, Notebook No. 3, Pages 45-50

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S33	0.5349	0.0014	0.42042	-	calibration
S34	0.4833	0.0012	0.41643	-	"
S36	0.3716	0.0012	0.40814	-	"
S37	0.3163	0.0003	0.40433	-	"
L1	0.5666	0.0011	0.42270	0.00008	
L2	0.5678	0.0010	0.42279	0.00007	
V1	0.4442	0.0004	0.41372	0.00003	
V2	0.4367	0.0008	0.41317	0.00006	
L3	0.5743	0.0007	0.42329	0.00005	
L4	0.5818	0.0012	0.42382	0.00009	
V3	0.4472	0.0006	0.41397	0.00004	
V4	0.4504	0.0011	0.41345	0.00008	
V5	0.4566	0.0007	0.41464	0.00005	
L5	0.5878	0.0010	0.42427	0.00007	
L6	0.5860	0.0010	0.42412	0.00007	

Run No. 28, 375 mm Hg., 11/12/59, Notebook No. 3, Pages 51-55

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S33	0.5392	0.0011	0.42042	-	calibration
S34	0.4867	0.0013	0.41643	-	"
S36	0.3766	0.0009	0.40814	-	"
S37	0.3181	0.0011	0.40433	-	"
L1	0.5724	0.0012	0.42270	0.00009	
L2	0.5816	0.0026	0.42337	0.00020	
V1	0.4158	0.0007	0.41127	0.00005	
V2	0.4110	0.0012	0.41092	0.00009	
L3	0.5725	0.0007	0.42270	0.00005	
L4	0.5781	0.0005	0.42311	0.00004	
V3	0.4211	0.0012	0.41165	0.00009	
V4	0.4206	0.0009	0.41162	0.00007	
V5	0.4220	0.0009	0.41173	0.00007	
L5	Sample believed contaminated.				

Run No. 29, 763.8 mm Hg., 11/21/59 Notebook No. 3, Pages 61-66

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S1	0.6284	0.0018	0.24187	-	calibration
S3	0.5044	0.0033	0.23174	-	"
S4	0.4336	0.0010	0.22957	-	"
S3	0.4919	0.0022	0.23174	-	"
S5	0.3799	0.0024	0.22630	-	"
L1	0.5493	0.0013	0.23691	0.00008	
L2	0.5478	0.0018	0.23680	0.00011	
V1	0.4323	0.0011	0.22956	0.00007	
V2	0.4236	0.0012	0.22897	0.00007	
L3	0.5349	0.0023	0.23599	0.00015	contaminated
L4	0.5475	0.0009	0.23678	0.00006	
V3	0.4338	0.0012	0.22962	0.00007	
V4	0.4392	0.0015	0.22997	0.00009	
V5	0.4388	0.0011	0.22995	0.00007	
L5	0.5626	0.0012	0.23773	0.00008	
L6	0.5569	0.0013	0.23738	0.00008	

Run No. 30, 500 mm Hg., 11/24/59, Notebook No. 3, Pages 67-71

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S5	0.3836	0.0023	0.22630	-	calibration
S4	0.4333	0.0007	0.22957	-	"
S3	0.4977	0.0010	0.23174	-	"
S1	0.6231	0.0013	0.24187	-	"
L1	0.5555	0.0020	0.23747	0.00013	
L2	0.5515	0.0010	0.23720	0.00006	
V1	0.4184	0.0010	0.22865	0.00006	
V2	0.4180	0.0020	0.22861	0.00013	
L3	0.5579	0.0017	0.23759	0.00010	
L4	0.5511	0.0014	0.23716	0.00009	
V3	0.4184	0.0014	0.23863	0.00009	
V4	0.4183	0.0015	0.22862	0.00009	
V5	0.4228	0.0008	0.22892	0.00005	
L5	0.5595	0.0014	0.23772	0.00009	

Run No. 31, 250 mm Hg., 12/1/59, Notebook No. 3, Pages 72 - 75
Notebook No. 4, Pages 1 - 2

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S1	0.6092	0.0012	0.24187	-	calibration
S3	0.4884	0.0016	0.23174	-	"
S4	0.4246	0.0018	0.22957	-	"
S5	0.3691	0.0012	0.22630	-	"
S1	0.6122	0.0023	0.24187	-	"
V1	0.3789	0.0011	0.22665	0.00007	
V2	0.3828	0.0018	0.22690	0.00012	
V3	Sample believed to be contaminated				
V4	0.3928	0.0015	0.22756	0.00010	
V5	0.3961	0.0008	0.22780	0.00005	
V6	0.3902	0.0015	0.22748	0.00010	
L1	0.5258	0.0009	0.23648	0.00006	contamination suspected
L2	0.5337	0.0011	0.23702	0.00007	
L3	0.5379	0.0018	0.23730	0.00012	
L4	0.5328	0.0010	0.23698	0.00007	
L5	0.5398	0.0023	0.23744	0.00015	

Run No. 32, 250 mm Hg., 12/3/59, Notebook No. 4, Pages 3 - 7

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S1	0.6214	0.0015	0.24187	-	calibration
S3	0.4909	0.0023	0.23174	-	"
S4	0.4291	0.0022	0.22957	-	"
S5	0.3747	0.0013	0.22630	-	"
V1	0.3939	0.0020	0.22736	0.00013	
V2	0.4056	0.0027	0.22810	0.00017	discarded pressure disturbed
V3	0.3981	0.0009	0.22762	0.00006	
V4	0.4003	0.0015	0.22778	0.00010	
V5	0.4017	0.0016	0.22785	0.00011	
V6	0.3963	0.0012	0.22750	0.00008	
L1	Not Run				
L2	0.5505	0.0012	0.23748	0.00008	
L3	0.5596	0.0014	0.23807	0.00012	
L4	0.5409	0.0015	0.23689	0.00009	
L5	0.5441	0.0014	0.23703	0.00009	
L6	0.5520	0.0013	0.23758	0.00008	

Run No. 33, 765.8 mm Hg., 12/10/59, Notebook No. 4, Pages 12 - 18

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S7	0.6997	0.0018	0.10512	-	calibration
S8	0.6214	0.0011	0.10099	-	"
S9	0.5631	0.0010	0.09800	-	"
S10	0.4712	0.0014	0.09226	-	"
S11	0.4047	0.0011	0.08789	-	"
L1	0.6193	0.0019	0.10103	0.00011	
L2	0.6223	0.0018	0.10123	0.00011	
V1	0.5742	0.0017	0.09831	0.00010	still not in
V2	0.5689	0.0029	0.09801	0.00017	equilibrium
L3	0.6208	0.0027	0.10109	0.00016	
L4	sample discarded due to contamination				
V3	0.5527	0.0025	0.09704	0.00015	
V4	0.5473	0.0026	0.09671	0.00016	
L5	0.6193	0.0029	0.10104	0.00018	
L6	0.6223	0.0024	0.10123	0.00015	
V5	0.5471	0.0024	0.09670	0.00015	
V6	0.5609	0.0022	0.09752	0.00013	

Run No. 34, 500 mm Hg., 12/12/59, Notebook No. 4, Pages 19 -24

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S7	0.5784	0.0009	0.10512	-	calibration
S8	0.5093	0.0013	0.10099	-	"
S9	0.4435	0.0011	0.09800	-	"
S10	0.3445	0.0012	0.09226	-	"
S10	0.3463	0.0011	0.09226	-	"
S11	0.2683	0.0015	0.08789	-	"
L1	0.4737	0.0023	0.09999	0.00013	discarded-believed contaminated
L2	0.4818	0.0009	0.10048	0.00005	
V1	0.4156	0.0015	0.09651	0.00008	
V2	0.4139	0.0015	0.09640	0.00008	
L3	0.4862	0.0014	0.10076	0.00008	
L4	0.4808	0.0016	0.10047	0.00009	
V3	0.4152	0.0019	0.09648	0.00011	
V4	0.4114	0.0018	0.09628	0.00010	
V5	0.4173	0.0013	0.09662	0.00007	
L5	0.4916	0.0012	0.10108	0.00007	

Run No. 35, 250 mm Hg., 12/15/59, Notebook No. 4, Pages 25 - 30

Sample	$(1/\bar{t})\,\mathrm{min}^{-1}$	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S7	0.5421	0.0010	0.10512	-	calibration
S8	0.4793	0.0019	0.10099	-	"
S9	0.4250	0.0011	0.09800	-	"
S10	0.3219	0.0011	0.09226	-	"
S11	0.2486	0.0011	0.08789	-	"
V1	sample discarded - believed contaminated				
V2	0.4036	0.0023	0.09684	0.00014	
V3	0.3880	0.0013	0.09594	0.00007	
V4	0.3973	0.0023	0.09645	0.00013	
V5	0.4028	0.0025	0.09680	0.00015	
V6	0.3977	0.0017	0.09649	0.00010	
L1	0.4751	0.0021	0.10101	0.00014	partial
L2	0.4715	0.0027	0.10081	0.00016	vaporization
L3	0.4619	0.0007	0.10024	0.00004	suspected
L4	0.4689	0.0019	0.10066	0.00011	
L5	0.4750	0.0016	0.10100	0.00009	

Run No. 36, 250 mm Hg., 12/17/59, Notebook No. 4, Pages 31 - 37

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S8	0.4700	0.0019	0.10099	-	calibration
S9	0.4134	0.0008	0.09800	-	"
S10	0.3164	0.0010	0.09226	-	"
S7	0.5410	0.0015	0.10512	-	"
S11	0.2319	0.0015	0.08789	-	"
V1	0.3890	0.0020	0.09639	0.00012	
V2	0.3937	0.0024	0.09667	0.00014	
V3	0.3987	0.0020	0.09696	0.00012	
V4	0.3983	0.0015	0.09692	0.00009	
V5	0.3915	0.0007	0.09652	0.00004	
V6	0.3873	0.0010	0.09630	0.00006	
L1	0.4799	0.0021	0.10165	0.00012	
L2	0.4745	0.0020	0.10135	0.00012	
L3	0.4719	0.0012	0.10120	0.00007	
L4	0.4788	0.0017	0.10158	0.00010	
L5	0.4704	0.0020	0.10110	0.00011	

2. SUMMARY OF SINGLE STAGE MEASUREMENTS

TABLE 5

Run #	Date	Pressure π mm. Hg.	ln (π)	$\bar{x}$	$\sigma_{a\bar{x}}$	$\sigma_{s\bar{x}}$ Estimate	$\sigma_{\bar{x}}$	$\bar{y}$	$\sigma_{a\bar{y}}$	$\sigma_{s\bar{y}}$ Estimate	$\sigma_{\bar{y}}$	$\bar{x}-\bar{y}$	$\bar{\alpha}$	$\sigma_{\bar{\alpha}}$	ln $\bar{\alpha}$	$\bar{Mv}$	T°C.
(1) 16	9/29/59	765.5	6.633	0.58173	0.00005	0.00034	0.00034	0.57288	0.00005	0.00020	0.00021	0.00885	1.0369	0.0017	0.0362	1.1922	-31.67 (2)
17	10/3/59	250.0	5.521	0.58103	0.00006	0.00045	0.00045	0.56991	0.00006	0.00031	0.00031	0.01112	1.0466	0.0023	0.0456	1.8908	-50.82 (3)
18	10/6/59	761.3	6.633	0.58208	0.00004	0.00033	0.00033	0.57253	0.00004	0.00005	0.00007	0.00955	1.0393	0.0014	0.0385	1.1930	-31.69
19	10/8/59	600.0	6.397	0.58123	0.00007	0.00036	0.00037	0.57156	0.00006	0.00013	0.00014	0.00967	1.0404	0.0017	0.0396	1.3635	-36.36
20	10/13/59	500.0	6.214	0.58158	0.00004	0.00009	0.00010	0.57134	0.00005	0.00009	0.00009	0.01024	1.0429	0.0006	0.0420	1.4812	-39.59
21	10/15/59	250.0	5.521	0.57955	0.00009	Negative	0.00009	0.56641	0.00009	0.00021	0.00023	0.01314	1.0552	0.0010	0.0538	1.8911	-50.82
22	10/17/59	375.0	5.927	0.58033	0.00004	0.00014	0.00014	0.56886	0.00003	0.00009	0.00009	0.01147	1.0480	0.0007	0.0469	1.667	-44.69
23	10/27/59	751.8	6.633	0.42033	0.00003	0.00018	0.00019	0.41084	0.00003	0.00006	0.00007	0.00949	1.0399	0.0008	0.0391	1.219	-32.41
24	10/29/59	500.0	6.214	0.42207	0.00004	0.00037	0.00038	0.41121	0.00004	0.00026	0.00026	0.01086	1.0457	0.0020	0.0447	1.498	-40.05
25	11/3/59	600.0	6.397	0.42230	0.00006	0.00012	0.00014	0.41218	0.00005	0.00012	0.00013	0.01012	1.0425	0.0008	0.0416	1.377	-36.73
26	11/5/59	250.0	5.521	0.42297	0.00004	0.00003	0.00005	0.40969	0.00005	0.00023	0.00024	0.01328	1.0562	0.0010	0.0547	1.917	-51.53
27	11/10/59	769.4	6.633	0.42350	0.00003	0.00028	0.00028	0.41379	0.00002	0.00023	0.00023	0.00971	1.0407	0.0015	0.0399	1.2056	-32.04
28	11/12/59	375.0	5.927	0.42312	0.00006	0.00016	0.00017	0.41146	0.00003	0.00015	0.00016	0.01166	1.0491	0.0010	0.0480	1.6888	-45.27
29	11/21/59	763.8	6.633	0.23712	0.00004	0.00018	0.00019	0.22961	0.00003	0.00018	0.00018	0.00751	1.0429	0.0015	0.0420	1.2264	-32.60
30	11/24/59	500.0	6.214	0.23743	0.00004	0.00010	0.00011	0.22869	0.00004	0.00004	0.00006	0.00874	1.0501	0.0007	0.0489	1.5188	-40.62
31	12/1/59	250.0	5.521	0.23704	0.00005	0.00016	0.00017	0.22728	0.00004	0.00021	0.00022	0.00976	1.0563	0.0016	0.0547	1.9399	-52.16
32	12/3/59	250.0	5.521	0.23741	0.00004	0.00021	0.00021	0.22762	0.00004	0.00008	0.00009	0.00979	1.0564	0.0013	0.0548	1.9423	-52.23
33	12/10/59	765.8	6.633	0.10112	0.00006	Negative	0.00004	0.09699	0.00007	0.00013	0.00015	0.00413	1.0474	0.0019	0.0463	1.2395	-32.97
34	12/12/59	500.0	6.214	0.10070	0.00004	0.00014	0.00015	0.09646	0.00004	0.00004	0.00006	0.00424	1.0489	0.0018	0.0478	1.5345	-41.05
35	12/15/59	250.0	-----	-------	-------	-------	-------	-------	-------	-------	-------	-------	------	------	------	------	-52.57 (4)
36	12/17/59	250.0	5.521	0.10138	0.00005	0.00010	0.00011	0.09663	0.00004	0.00010	0.00011	0.00475	1.0547	0.0018	0.0533	1.9551	-52.59

$\bar{x}$ = mean liquid composition, mole fraction deuterium
$\sigma_{a\bar{x}}$ = standard deviation of $\bar{x}$, due to analytic uncertainty
$\sigma_{s\bar{x}}$ = Standard deviation of $\bar{x}$, due to sampling uncertainty
$\bar{y}$ = mean condensate composition, mole fraction deuterium
α = separation factor for deuterium enrichment
Mv = average thermocouple E.M.F. reading
T°C = observed boiling temperature °C.

(1) The results for Runs 1 - 15 were omitted due to sampling errors which invalidated the results.
(2) Possible liquid sampling error.
(3) Liquid sampling line lengthened.
(4) Run discarded due to malfunction of liquid sampling line. (Partial vaporization occurred)

3. Weighted least square analysis of single-stage measurements

The following table gives the intermediate values used to determine the least square lines shown on Graphs No. 1, 2, 3 and 4. It was assumed at a given concentration

$$\ln(\alpha) = f(x) + \ln(\pi/\pi_o) \qquad (7.5)$$

where x = mole fraction deuterium in liquid

π = pressure mm Hg.

π_o = 760 mm Hg.

The constant "c" was determined by

$$c = \frac{\sum^{i} \omega_i (\delta_i - \bar{\delta}_\omega)(\gamma_i - \bar{\gamma}_\omega)}{\sum_{i} \omega_i (\delta_i - \bar{\delta}_\omega)^2} \qquad (7.6)$$

where δ_i = $(\ln \pi)\, i$

γ_i = $(\ln \alpha)\, i$

and ω_i = weight assigned to $\gamma_i = \frac{1}{\sigma_{\gamma_i}^2}$

In addition to determining "c", f(x) in the above equation was determined for four values of x, namely 0.58, 0.42, 0.24 and 0.10 by determining the 760 mm Hg. intercept of a line drawn with slope "c" through the weighted center of gravity of the points at a given concentration. $(\bar{\delta}\,\omega)\, j$ and $(\bar{\gamma}\,\omega)\, j$.

The results:

x = MFD	$f(x) = \ln(\alpha)$ 760 mm Hg
0.58	0.0376 ± 0.0007
0.42	0.0394 ± 0.0006
0.24	0.0427 ± 0.0010
0.10	0.0426 ± 0.0016

This composition dependence was shown on Graph 5. Finally to fit $f(x)$ to a linear function and hence determine a and b in the equation

$$\ln(\alpha) = a + b(x - \bar{x}_\omega) + c \ln(\pi/\pi_o) \qquad (7.7)$$

$\bar{x}_\omega$ = reference composition, MFD

π = pressure mm Hg

π_o = 760 mm Hg

another weighted least square fit was was performed.

$f(x)$ i	σ $f(x)$ i	x_i	$\omega_i \times 10^{-6}$
0.0376	0.0007	0.580	2.04
0.0394	0.0006	0.420	2.78
0.0427	0.0010	0.245	1.00
0.0426	0.0016	0.100	0.39
		Σ =	6.21

x10^{-6} $\omega_i\, x_i$	x10^{-6} $\omega_i\, f(x)\, i$	$x - \bar{x}_\omega$	x10 $f(x)-\overline{f(x)}_\omega$	x10^{-6} $\omega_i(\bar{x} - \bar{x}_\omega)$
1.182	0.0767	0.156	-0.019	0.318
1.168	0.1096	-0.004	-0.001	-0.011
0.245	0.0427	-0.179	+0.032	-0.179
0.039	0.0166	-0.324	+0.031	-0.126
2.634	0.2456			

x10^{-6} $\omega_i(x - \bar{x}_\omega)^2$	x 10^{-6} $\omega_i(x - \bar{x}_\omega)(f(x) - \overline{f(x)}_\omega)$
0.0496	-0.000605
0.0000	-0.000001
0.0320	-0.000573
0.0409	-0.000390
0.1225	-0.001569

Giving

$$\bar{x}_\omega = \frac{2.634}{6.21} = 0.424$$

$$a = \overline{f(x)} = \frac{0.2456}{6.21} = 0.0395$$

$$b = \frac{\sum \omega_i(x-\bar{x}_\omega)\ (f(x)-\overline{f(x)}\omega)}{\sum\ \omega_i(x-\bar{x}_\omega)^2} = \frac{-0.001569}{0.1225} = -0.0128$$

$$Se^2(b) = \frac{1}{\sum \omega_i(x-\bar{x}_\omega)^2} = \frac{1}{0.1225\text{x}10^6} = 8.16 \times 10^{-6}, \quad Se\ b = 2.86 \times 10^{-3}$$

This least square line is shown on Graph 5.

$$Se^2(a) = Se^2 \quad f(x) = \frac{1}{\sum \omega_i} = \frac{1}{6.21x10^6} = 1.9 \times 10^{-8}$$

$$Se(a) = 4 \times 10^{-4}$$

Therefore the final result is

$$\ln(\alpha) = (0.0395 \pm 0.0004) - (0.0128 \pm 0.0029)\ (x - 0.424)$$
$$-(0.01246 \pm 0.00065)\ (\ln \frac{\pi}{\pi_o})$$

3. WEIGHTED LEAST SQUARE ANALYSIS OF SINGLE STAGE RUNS (SEE GRAPHS 1,2,3,& 4)

TABLE 6

Run #	$\ln(\alpha)_i$ γ_i	σ_{γ_i}	$\ln(\pi)_i$ δ_i	$(\bar{\delta}_\omega)_j$	$\delta_i - \bar{\delta}_\omega$	$(\bar{\gamma}_\omega)_j$	$\gamma_i - \bar{\gamma}_\omega$	$\times 10^{-6}$ W_i	$\times 10^{-6}$	$\times 10^{-3}$		$\times 10^{-5}$	$W_i \delta_i$	$W_i \gamma_i$	$W_i \delta_i^2$	$W_i \delta_i \gamma_i$
	1	2	3	4	5	6	7	8	5x8	5x7x8	5^2	5x8	13	14	15	16
16	0.0362	0.0017	6.633	6.081	0.552	0.0445	-0.0083	0.346	+0.191	-1.588	0.305	1.055	2.30	0.0125	15.26	0.0832
17	0.0456	0.0023	5.521	↓	-0.560	↓	0.0011	0.189	-0.106	-0.117	0.314	0.594	1.04	0.0086	5.75	0.0475
18	0.0385	0.0014	6.633	↓	0.552	↓	-0.0060	0.510	+0.282	-1.691	0.305	1.554	3.38	0.0196	22.40	0.1300
19	0.0396	0.0017	6.397	↓	0.316	↓	-0.0049	0.346	+0.109	-0.534	0.100	0.346	2.22	0.0137	14.20	0.0885
20	0.0420	0.0006	6.214	↓	0.133	↓	-0.0025	2.780	+0.370	-0.925	0.018	0.500	17.29	0.1168	107.30	0.7260
21	0.0538	0.0010	5.521	↓	-0.560	↓	0.0093	1.000	-0.560	-5.205	0.314	3.140	5.52	0.0538	30.50	0.2970
22	0.0469	0.0007	5.927	↓	-0.154	↓	0.0024	2.040	-0.314	-0.490	0.024	0.490	12.10	0.0956	71.80	0.5675
												Σ_i = 7.679				
23	0.0391	0.0008	6.633	6.240	0.393	0.0443	-0.0052	1.560	+0.613	-3.190	0.154	2.400	10.36	0.0610	68.80	0.4050
24	0.0447	0.0020	6.214	↓	-0.026	↓	0.0004	0.250	-0.007	-0.003	0.007	0.018	1.55	0.0112	9.65	0.0693
25	0.0416	0.0008	6.397	↓	0.157	↓	-0.0027	1.560	+0.245	-0.662	0.025	0.390	9.98	0.0650	63.90	0.4151
26	0.0547	0.0010	5.521	↓	-0.719	↓	0.0104	1.000	-0.719	-7.460	0.517	5.170	5.52	0.0547	30.50	0.3020
27	0.0399	0.0015	6.633	↓	0.393	↓	-0.0044	0.444	+0.174	-0.766	0.154	0.684	2.94	0.0177	19.50	0.1172
28	0.0480	0.0010	5.927	↓	-0.313	↓	0.0037	1.000	-0.313	-1.159	0.098	0.980	5.93	0.0480	35.18	0.2842
												Σ_i = 9.642				
29	0.0420	0.0015	6.633	6.078	0.555	0.0496	-0.0076	0.444	+0.246	-1.870	0.308	1.369	2.94	0.0186	19.50	0.1236
30	0.0489	0.0007	6.214	↓	0.136	↓	-0.0007	2.040	+0.278	-0.195	0.019	0.388	12.69	0.0996	79.00	0.6200
31	0.0547	0.0016	5.521	↓	-0.557	↓	0.0051	0.390	-0.217	-1.106	0.310	1.210	2.16	0.0214	11.92	0.1181
32	0.0548	0.0013	5.521	↓	-0.557	↓	0.0052	0.591	-0.330	-1.718	0.310	1.832	3.27	0.0324	18.07	0.1791
												Σ_i = 4.799				
33	0.0463	0.0019	6.633	6.114.	0.519	0.0491	-0.0028	0.277	+0.144	-0.403	0.269	0.745	1.84	0.0127	12.20	0.0851
34	0.0478	0.0018	6.214	↓	0.100	↓	-0.0013	0.308	+0.031	-0.040	0.010	0.031	1.92	0.0147	11.94	0.0918
36	0.0533	0.0018	5.521	↓	-0.593	↓	0.0042	0.308	-0.183	-0.769	0.352	1.085	1.70	0.0164	9.41	0.0907
								Σ = 17.383				$\Sigma_j \Sigma_i$ = 23.981 Σ_i = 1.861				

$$c = \frac{\sum_i W_i (\delta_i - \bar{\delta}_\omega)(\gamma_i - \bar{\gamma}_\omega)}{\sum_i W_i (\delta_i - \bar{\delta}_\omega)^2} = -\frac{29.891}{23.981} \times 10^{-2} = -0.01246 \pm 0.00065$$

$$Se^2 c = \frac{1}{\sum_i W_i (\delta_i - \bar{\delta}_\omega)^2} = \frac{1}{23.981} \times 10^{-5} = 0.416 \times 10^{-6}$$

$$Sec = \pm 0.645 \times 10^{-3} = \pm 0.00065$$

Kirshenbaum-Urey(26)
c =-0.01355

Kirshenbaum-Urey(26)-Groth(17)
c =-0.01286

4. Concentric-tube fractionating column data (Table 7)

The following table gives the raw data obtained from the experimental runs carried out with the concentric-tube column. The symbols used are defined as:

S = standard water sample used for calibration. These standards were used for several runs at the same deuterium concentration.

K = kettle sample. The number indicates the order of sampling

R = reflux sample. The number indicates the order of sampling

$1/\bar{t}$ = reciprocal of mean falling time for drops of specified sample $(\text{min})^{-1}$

$\sigma_{1/\bar{t}}$ = standard deviation of $1/\bar{t}$

MFD = mole fraction deuterium

σ_{MFD} = standard deviation of MFD

Falling tube 1 was for the reflux samples, while tube 2 was used for kettle samples during Runs 1 thru 4. For Runs 4 thru 11 only one tube was used. The samples were drawn in the order given.

Table 7

Concentric-Tube Column Data

Run No. 1, 758.5 mm Hg., 2/23/60, Notebook No. 4, Pages 63 - 68.

Sample	Falling Tube No.	$(1/\bar{t})\ \text{min}^{-1}$	$\sigma_{1/t}$	MFD	σ_{MFD}	Remarks
S36	1	0.6463	0.003	0.53890	-	calibration
S34	1	0.3605	0.0016	0.51690	-	"
S26	2	0.2955	0.0017	0.56152	-	"
S29	2	0.3824	0.0013	0.56776	-	"
S20	2	0.5145	0.0022	0.57987	-	"
S28	2	0.4383	0.0018	0.57316	-	"
K1	2	0.4906	0.0026	0.57760	0.00021	
R1	1	0.5138	0.0014	0.52885	0.00011	
K2	2	0.4942	0.0016	0.57794	0.00013	
R2	1	0.5653	0.0035	0.53300	0.00029	
K3	2	0.5176	0.0018	0.57985	0.00015	
R3	1	0.6107	0.0006	0.53650	0.00005	
K4	2	0.5171	0.0012	0.57980	0.00010	
R4	1	0.6311	0.0029	0.53810	0.00024	
K5	2	0.5386	0.0018	0.58158	0.00015	
R5	1	0.6472	0.0023	0.53945	0.00019	
R6	1	0.6599	0.0024	0.54040	0.00020	

Run No. 2 , 768.1 mm Hg., 2/25/60, Notebook No. 4, Pages 69 - 75

Sample	Falling Tube No.	$(1/\bar{t})$ min^{-1}	$\sigma_{1/t}$	MFD	σ_{MFD}	Remarks
S34	1	0.3624	0.0019	0.51690	-	calibration
S36	1	0.6264	0.0013	0.53890	-	"
S20	2	0.5110	0.0011	0.57987	-	"
S26	2	0.3000	0.0014	0.56152	-	"
S28	2	0.4364	0.0015	0.57316	-	"
S29	2	0.3762	0.0018	0.56776	-	"
K1	2	0.4927	0.0021	0.57780	0.00017	
R1	1	0.6947	0.0025	0.54390	0.00020	
K2	2	0.4874	0.0010	0.57736	0.00008	
R2	1	0.7003	0.0016	0.54440	0.00014	
K3	2	0.4982	0.0023	0.57827	0.00019	
R3	1	0.7232	0.0019	0.54630	0.00016	
K4	2	0.5007	0.0007	0.57847	0.00006	
R4	1	0.7249	0.0027	0.54638	0.00023	
R5	1	0.7399	0.0014	0.54760	0.00012	
K5	2	0.5135	0.0021	0.57955	0.00017	
R6	1	0.7491	0.0017	0.54838	0.00014	
R7	1	0.7686	0.0027	0.54990	0.00022	
K6	2	0.5255	0.0012	0.58055	0.00010	

Run No. 3, 764.6 mm Hg., 3/1/60, Notebook No. 5, Pages 2 - 8

Sample	Falling Tube No.	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S36	1	0.6093	0.0009	0.53890	-	calibration
S34	1	0.3509	0.0018	0.51690	-	"
S26	2	0.2981	0.0019	0.56152	-	"
S28	2	0.4511	0.0014	0.57316	-	"
S20	2	0.5258	0.0014	0.57987	-	"
S36	1	0.6211	0.0020	0.53890	-	"
K1	2	0.4931	0.0028	0.57725	0.00023	
R1	1	0.7551	0.0034	0.54985	0.00028	
K2	2	0.4936	0.0012	0.57728	0.00010	
R2	1	0.7312	0.0017	0.54788	0.00013	
K3	2	0.5057	0.0012	0.57782	0.00010	
R3	1	0.6905	0.0019	0.54464	0.00015	
K4	2	0.5176	0.0003	0.57792	0.00003	
R4	1	0.6957	0.0026	0.54500	0.00022	
K5	2	0.5287	0.0019	0.58008	0.00016	
R5	1	0.6946	0.0038	0.54495	0.00032	
K6	2	0.5437	0.0020	0.58130	0.00016	
R6	1	0.7347	0.0014	0.54812	0.00011	
R7	1	0.7323	0.0032	0.54796	0.00026	

Run No. 4, 760.0 mm Hg., 3/3/60, Notebook No. 5, Pages 9 - 15

Sample	Falling Tube No.	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S36	1	0.6269	0.0020	0.53890	-	calibration
S34	1	0.3649	0.0036	0.51690	-	"
S20	2	0.5310	0.0027	0.57987	-	"
S28	2	0.4584	0.0030	0.57316	-	"
S26	2	0.3131	0.0016	0.56152	-	"
S29	2	0.3927	0.0005	0.56776	-	"
K1	2	0.4908	0.0018	0.57605	0.00015	
R1	1	0.6629	0.0017	0.54160	0.00014	
K2	2	0.5076	0.0019	0.57743	0.00016	
R2	1	0.6983	0.0023	0.54424	0.00019	
K3	2	0.5062	0.0015	0.57734	0.00013	
R3	1	0.6816	0.0032	0.54286	0.00027	
K4	2	0.5310	0.0019	0.57938	0.00015	
R4	1	0.6859	0.0035	0.54320	0.00029	
K5	2	0.5193	0.0031	0.57840	0.00026	
R5	1	0.6928	0.0017	0.54380	0.00014	
K6	2	0.5422	0.0026	0.58030	0.00022	
R6	1	0.7020	0.0023	0.54447	0.00019	
K7	2	0.5514	0.0020	0.58105	0.00017	
R7	1	0.7407	0.0031	0.54760	0.00026	

Run No. 5, 762 mm Hg., 3/10/60, Notebook No. 5, Pages 20 -25

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S42	0.3923	0.0009	0.21762	-	calibration
S44	0.5976	0.0008	0.23160	-	"
S45	0.6907	0.0014	0.23829	-	"
S41	0.3005	0.0008	0.21172	-	"
K1	0.6761	0.0023	0.23717	0.00015	
R1	0.3387	0.0005	0.21415	0.00003	
K2	0.6651	0.0057	0.23650	0.00037	contamination suspected
R2	0.3326	0.0009	0.21370	0.00006	contamination suspected
K3	0.6737	0.0027	0.23705	0.00018	
R3	0.3081	0.0014	0.21210	0.00009	
K4	0.6743	0.0022	0.23708	0.00016	
R4	0.3465	0.0019	0.21462	0.00013	
K5	0.6774	0.0009	0.23726	0.00006	
R5	0.3379	0.0009	0.21408	0.00006	
K6	0.6934	0.0016	0.23840	0.00011	
R6	0.3302	0.0013	0.21351	0.00009	
K7	0.7060	0.0028	0.23910	0.00018	
R7	0.3047	0.0004	0.21178	0.00002	

Run No. 6, 767.1 mm Hg., 3/15/60, Notebook No. 5, Pages 26 - 32

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S44	0.5988	0.0042	0.23160	-	calibration
S41	0.2813	0.0012	0.21172	-	"
S42	0.3600	0.0025	0.21762	-	"
S45	0.6751	0.0026	0.23829	-	"
K1	0.6888	0.0040	0.23890	0.00016	
R1	0.3454	0.0015	0.21630	0.00010	
K2	0.7331	0.0021	0.24185	0.00014	
R2	0.5162	0.0015	0.22690	0.00010	
K3	0.8318	0.0039	0.24830	0.00026	
R3	0.6116	0.0017	0.23380	0.00011	
K4	0.8186	0.0020	0.24740	0.00013	
R4	0.4426	0.0016	0.22275	0.00010	
K5	0.8146	0.0031	0.24720	0.00020	
R5	0.4555	0.0025	0.22345	0.00016	
K6	0.8242	0.0015	0.24775	0.00010	
R6	0.4593	0.0024	0.22380	0.00016	
K7	0.8332	0.0019	0.24840	0.00012	
R7	0.4609	0.0038	0.22395	0.00025	

Run No. 7, 764.6 mm Hg., 3/17/60, Notebook No. 5, Pages 33 ~~p~~ 41

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S45	0.6841	0.0020	0.23829	-	calibration
S41	0.2744	0.0018	0.21172	-	"
S42	0.3688	0.0016	0.21762	-	"
S44	0.5888	0.0020	0.23160	-	"
K1	0.7088	0.0016	0.23995	0.00010	
R1	0.3431	0.0014	0.21610	0.00009	
K2	0.7079	0.0016	0.23990	0.00011	
R2	0.3534	0.0012	0.21670	0.00008	
K3	0.7137	0.0013	0.24025	0.00009	
R3	0.3410	0.0017	0.21600	0.00011	
K4	0.6937	0.0013	0.23900	0.00009	
R4	0.3212	0.0017	0.21470	0.00011	samples con-
K5	0.6824	0.0029	0.23820	0.00019	taminated by
R5	0.3663	0.0007	0.21760	0.00005	unoxidized
K6	0.6721	0.0024	0.23760	0.00016	ammonia
R6	0.3109	0.0019	0.21400	0.00012	(short Eq. time)
K7	0.5358	0.0017	0.22880	0.00011	

Run No. 8, 751.9 mm Hg., 3/22/60, Notebook No. 5, Pages 44 - 48

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S47	0.3243	0.0029	0.03372	-	calibration
S50	0.5407	0.0035	0.04581	-	"
S48	0.4051	0.0013	0.03826	-	"
S51	0.6176	0.0014	0.05036	-	"
K1	0.5101	0.0028	0.04360	0.00016	
R1	0.4330	0.0031	0.03980	0.00017	
K2	0.4830	0.0030	0.04265	0.00017	
R2	0.3927	0.0016	0.03788	0.00009	
K3	0.4791	0.0028	0.04240	0.00016	
R3	0.3880	0.0035	0.03722	0.00020	

Run terminated when ammonia was detected in samples.

Run No. 9, 754.9 mm Hg., 3/24/60, Notebook No. 5, Pages 49 - 56

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S48	0.4186	0.0041	0.03826	-	calibration
S50	0.5316	0.0026	0.04581	-	"
S51	0.6005	0.0033	0.05036	-	"
S47	0.3054	0.0011	0.03372	-	"
S48	0.3823	0.0016	0.03826	-	"
S50	0.5246	0.0008	0.04581	-	"
K1	0.4767	0.0029	0.04340	0.00016	
R1	0.3625	0.0013	0.03695	0.00007	
K2	0.4426	0.0020	0.04150	0.00011	contaminated
R2	0.3654	0.0046	0.03730	0.00026	
K3	0.4708	0.0031	0.04305	0.00018	
R3	0.3819	0.0033	0.03800	0.00019	
K4	0.4618	0.0020	0.04255	0.00011	
R4	0.3802	0.0023	0.03795	0.00013	
K5	0.4656	0.0022	0.04275	0.00012	
R5	0.3837	0.0015	0.03815	0.00008	
K6	0.4738	0.0027	0.04325	0.00015	
R6	0.3768	0.0020	0.03775	0.00011	
K7	0.4753	0.0048	0.04330	0.00027	
R7	0.3922	0.0038	0.03860	0.00022	

Run No. 10, 768.6 mm Hg., 3/29/60, Notebook No. 5, Pages 57 - 63

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S48	0.3904	0.0022	0.03826	-	calibration
S47	0.3040	0.0017	0.03372	-	"
S51	0.5963	0.0022	0.05036	-	"
S50	0.5197	0.0021	0.04581	-	"
K1	0.4447	0.0025	0.04155	0.00014	
R1	0.3587	0.0029	0.03665	0.00017	
K2	0.4354	0.0021	0.04102	0.00012	
R2	0.3604	0.0029	0.03670	0.00017	
K3	0.4373	0.0040	0.04110	0.00022	
R3	0.3562	0.0028	0.03648	0.00016	
K4	0.4400	0.0025	0.04129	0.00014	
R4	0.3663	0.0025	0.03702	0.00014	
K5	0.4465	0.0032	0.04165	0.00018	
R5	0.3678	0.0030	0.03715	0.00017	
K6	0.4531	0.0017	0.04203	0.00009	
R6	0.3660	0.0026	0.03700	0.00015	
K7	0.4542	0.0019	0.04211	0.00011	
R7	0.3727	0.0020	0.03740	0.00011	

Run No. 11, 753.9, 3/31/60, Notebook No. 5, Pages 64 - 69

Sample	$(1/\bar{t})$ min^{-1}	$\sigma_{1/\bar{t}}$	MFD	σ_{MFD}	Remarks
S44	0.5738	0.0020	0.23160	-	calibration
S41	0.2566	0.0028	0.21172	-	"
S45	0.6717	0.0025	0.23829	-	"
S42	0.3583	0.0023	0.21762	-	"
K1	0.6419	0.0030	0.23638	0.00020	
R1	0.3262	0.0022	0.21560	0.00015	
K2	0.6829	0.0036	0.23908	0.00023	
R2	0.3441	0.0018	0.21668	0.00012	
K3	0.6848	0.0014	0.23920	0.00009	
R3	0.2592	0.0029	0.21768	0.00019	
K4	0.6761	0.0030	0.23865	0.00020	
R4	0.3480	0.0029	0.21705	0.00019	
K5	0.6930	0.0017	0.23975	0.00011	
R5	0.3571	0.0017	0.21762	0.00011	
K6	0.7162	0.0039	0.24130	0.00025	
R6	0.3622	0.0032	0.21798	0.00021	
K7	0.7252	0.0033	0.24190	0.00022	
R7	0.3939	0.0019	0.22005	0.00013	

5. Column calibration with system n-heptane-methylcyclohexane (Table 8)

The following table gives the results of a series of measurements with the system n-heptane-methylcyclohexane carried out with the concentric-tube fractionating column. The refractive indices given (n_D^{20}) were measured at 20°C with an Abbe refractometer.

Column Calibration with System n-Heptane-Methylcyclohexane

Table 8

Kettle η_D^{20} Ref. Index	Kettle Comp. Mole Fr. Heptane	Reflux η_D^{20} Ref. Index	Reflux Comp Mole Fr. Heptane	Thruput ml/min	Equilibrium time hours	Stages
1.4192	0.080	1.4129	0.248	7.63	1.50	16.3
1.4194	0.078	1.4108	0.278	3.88	2.00	18.6
1.4193	0.079	1.4149	0.178	7.63	0.50	11.3
1.4197	0.070	1.4142	0.195	3.88	1.00	14.3
1.4200	0.063	1.4110	0.273	2.93	5.00	21.0
1.4200	0.063	1.4064	0.396	3.37	3.75	27.8
1.4200	0.063	1.4092	0.320	3.12	3.00	23.8

E. Sample Calculations

1. Determination of Falling Drop Calibration and Sample Compositions.

Previous to a series of runs at a given mole fraction deuterium a precise calibration of the falling drop apparatus with six or more standards was determined. Over a composition range of 0.020 MFD the composition of the sample analyzed was related to the mean falling time for drops of the sample by:

$$1/\bar{t} = g + h(x - \bar{x}) \qquad (7.8)$$

where: $\bar{t}$ = mean falling time, min

x = mole fraction deuterium

$\bar{x}$ = average mole fraction deuterium for all standards

g = constant to be determined

h = slope of calibration, constant to be determined

The value of "h" was found to be constant for given falling fluid for periods as long as three months, but "g" was found to vary slightly from run to run, due to slight composition changes within the falling fluid. To allow for the slight changes in "g" from run to run four standards were timed on the day of a run and used together with the value of "h", previously determined by a calibration of six or more standards, to determine a value of "g" for the particular run.

The precise calibration of the standards used for the equilibrium still runs 23 thru 28 is given below as an example. Six standards were timed and their mean falling times least square fitted to the equation

$$Z = 1/\bar{t} = g + h\,(x - \bar{x}) \qquad (7.9)$$

where Z = predicted value of $1/\bar{t}$

z = experimental value of $1/\bar{t}$

Least Square Fitting

Standard	MFD=x	$1/\bar{t}=z(\text{min})^{-1}$	$(x-\bar{x})\mathrm{x}10^2$	$(x-\bar{x})^2\mathrm{x}10^4$	$(x-\bar{x})z\mathrm{x}10^2$
S32	0.42433	0.5892	+ 0.996	0.991	+ 0.586
S33	0.42042	0.5349	+ 0.605	0.365	+ 0.325
S34	0.41643	0.4833	+ 0.206	0.042	+ 0.100
S35	0.41256	0.4280	- 0.181	0.033	- 0.077
S36	0.40814	0.3716	- 0.623	0.388	- 0.230
S37	0.40433	0.3163	- 1.004	1.008	- 0.317
				$\Sigma = 2.827\mathrm{x}10^{-4}$	$\Sigma = +\,0.387\mathrm{x}10^{-2}$

$$x = \frac{\sum^{n} x_i}{n} = 0.41437 \text{ MFD}, \quad g = \frac{\sum^{n} z_i}{n} = 0.4539 \text{ min}^{-1}$$

$$h = \text{slope} = \frac{\sum^{n} (x-\bar{x})z}{\sum^{n} (x-\bar{x})^2} = \frac{+\,0.387\mathrm{x}10^{-2}}{2.827\mathrm{x}10^{-4}} = 13.71 \text{ min}^{-1}/\text{ MFD}$$

Therefore

$$Z = 1/t = 0.4539 + 13.71\,(x - 0.41437)$$

$$Z = 13.71\,x - 5.2272 \qquad (7.10)$$

Using this equation and the $(1/\bar{t})$ for any sample the composition (x) could be determined.

To calculate the error introduced through uncertainty in the slope of this calibration "h", the following analysis was performed.

$$Se^2(h) = \frac{Se^2\,(y_i)}{\sum^{n_i} (x_i-\bar{x})^2} \qquad (7.11)$$

where $$Se^2\,(y_i) = \frac{\sum^{n_i} (Z_i - z_i)^2}{n_i - 2}$$

$n_i - 2$ degrees of freedom

z_i	x_i	$13.71\ x_i$	Z_i	$(Z_i - z_i)^2 \times 10^6$
0.5892	0.42433	5.8171	0.5899	0.49
0.5349	0.42042	5.7634	0.5362	1.69
0.4833	0.41643	5.7089	0.4817	2.56
0.4280	0.41256	5.6559	0.4287	0.49
0.3716	0.40814	5.5952	0.3680	12.96
0.3163	0.40433	5.5430	0.3158	0.25
			$\sum =$	18.44×10^{-6}

$$Se^2(h) = \frac{18.44\text{x}10^{-6}}{4(2.827\text{x}10^{-4})} = 1.63 \times 10^{-2}$$

$$Se(h) = 1.28 \times 10^{-1} = 0.13$$

Therefore h = $13.71 \pm 0.13\ \text{min}^{-1}$ / MFD

This uncertainty in "h" will introduce an uncertainty in the separation factor determined since:

$$\alpha - 1 = \frac{x - y}{y(1-x)} = \frac{(1/\bar{t})_x - (1/\bar{t})_y}{\left[h \; \frac{(1/\bar{t})_y + h\bar{x} - g}{h}\right]\left[1 - \frac{(1/\bar{t})_x + hx - g}{h}\right]} \tag{7.12}$$

$\bar{x}$, refers to the mean composition of the standards used in determining the calibration. The major source of uncertainty arises in the numerator of this expression where a small difference between two numbers is taken. Since this difference is inversely proportional to the slope of calibration "h", the percent error in $(\alpha - 1)$ is about the same as in "h".

$$\text{Percent error "h"} = \frac{\pm 0.13}{13.71} \times 100 = \pm 0.95 \text{ percent}$$

This error was small compared to the 3 to 5 percent error introduced through sample variance and was therefore neglected in calculating the uncertainty of the separation factor.

An uncertainty in $(1/\bar{t})$ was, however, determined for every sample analyzed and used as an estimate of the analytic variance for that specific sample. An example, taken from Run 28 is given in the following Section E2.

2. Determination of the separation factor by the single-stage measurements.

The equilibrium still run No. 28 will be used as an example. This run was one of a series at 0.42 MFD based on the calibration given in the previous Section E1.

Run No. 28 was made on November 12, 1959. The pressure was adjusted to 375 ± 0.2 mm Hg. Four standards were timed and the results given on the next page.

Standard	$Z_i = (1/\bar{t})(\text{min})^{-1}$	x = MFD
S33	0.5392	0.42042
S34	0.4867	0.41643
S36	0.3766	0.40814
S37	0.3181	0.40433
	$\sum =$ 1.7206	$\sum =$ 1.64932

The first step was to fit the above standards to the calibration equation.

$$1/\bar{t} = g + h\,(x - \bar{x}) \qquad (7.8)$$

"h" had been previously determined as 13.71 min^{-1}/ MFD for this fluid by the calibration given in Section E1.

$$g = \frac{\sum^{n_i} z_i}{n_i} = \frac{1.7206}{4} = 0.4302 \text{ min}^{-1}$$

$$x = \frac{\sum^{n_i} x_i}{n_i} = \frac{1.64932}{4} = 0.41233 \text{ MFD}$$

Therefore for this run:

$$1/\bar{t} = 0.4302 + 13.71\,(x - 0.41233) \text{ min}^{-1}$$

$$1/\bar{t} = 13.71x - 5.2228 \qquad (7.13)$$

When this equation is compared to the one determined in Section E1, namely (Eq. 8.10)

$$1/\bar{t} = 13.71\, x - 5.2272 \qquad (7.14)$$

the change in the intercept is seen. This change took place over several weeks. The rate of change was, therefore, not of sufficient magnitude to cause noticeable error on any one day. But, nevertheless, to determine the absolute composition accurately the intercept change was taken into account. The intercept was determined for every run from the mean time of fall for four standards. It should be noted that small changes of the intercept do not affect the reported separation factor since it depends on the difference in composition and hence only on "h".

Once the calibration was determined samples could be analyzed. The samples timed during Run No. 38 gave the times, and indicated composition shown below; compositions being determined by

$$1/\bar{t} = 13.71\, x - 5.2228 \qquad (7.15)$$

Sample	$1/t\ (\text{min})^{-1}$	$\sigma_{1/\bar{t}}$	MFD = x	$\sigma_{MFD} = \sigma_a$
L1	0.5724	0.0012	0.42270	0.00009
L2	0.5816	0.0026	0.42337	0.00020
V1	0.4158	0.0007	0.41127	0.00005
V2	0.4110	0.0012	0.41092	0.00009
L3	0.5725	0.0007	0.42270	0.00005
L4	0.5781	0.0005	0.42311	0.00004
V3	0.4211	0.0012	0.41165	0.00009
V4	0.4206	0.0009	0.41162	0.00007
V5	0.4220	0.0009	0.41173	0.00007
L5	Sample believed contaminated			

where: V = vapor sample, L = liquid sample.

The analytic variance σ_a was calculated in the following manner. The uncertainty in the mean falling time $\bar{t}$ was determined. This was then converted to an uncertainty in $(1/\bar{t})$ and finally to an uncertainty in composition. The individual times are given below for sample V4 as an example.

Observed Falling Times for Vapor Sample 4, Run No. 28

t(min)	$\lvert t - \bar{t} \rvert \times 10^3$	$\lvert t - \bar{t} \rvert^2 \times 10^6$
2.364	14	196
2.384	6	36
2.388	10	100
2.360	18	324
2.390	12	144
2.381	3	9
	$\sum$	$= 809 \times 10^{-6}$

$\bar{t} = 2.3778$ min.

$$\sigma^2_{\bar{t}} = \frac{\sum^{n} (t-\bar{t})^2}{n(n-1)} = \frac{809}{30} \times 10^{-6} = 27 \times 10^{-6}$$

$$\sigma_{\bar{t}} = 5.2 \times 10^{-3}, \quad \sigma_{1/t} = \frac{\sigma_{\bar{t}}}{\bar{t}^2} = 0.00092$$

$1/\bar{t} = 0.42056 \pm 0.00092 \text{ min}^{-1}$

Converting to composition using:

$$1/\bar{t} = 13.71\,x - 5.2228 \tag{7.15}$$

$$x = 0.41162$$

$$\sigma_{ax}^2 = \left(\frac{\partial x}{\partial(1/\bar{t})}\right)^2 \sigma_{1/\bar{t}}^2 = \frac{1}{h^2}\sigma_{1/\bar{t}}^2 = \frac{1}{(13.71)^2}(0.00092)^2 \tag{7.16}$$

$\sigma_{ax} = \pm 0.00007$

Therefore the reported composition becomes

$$x = 0.41162 \pm 0.00007$$

From the individual compositions the mean liquid and vapor compositions were determined,

$$\bar{x} = \frac{\sum^{n_i} x_i}{n_i} \quad , \quad \bar{y} = \frac{\sum^{n_i} y_i}{n_i}$$

along with the variance of the mean.

$$\sigma_{\bar{x}}^2 = \frac{\sum^{n_i} (x_i-\bar{x})^2}{n_i\,(n_i - 1)} \quad , \quad \sigma_{\bar{y}}^2 = \frac{\sum^{n_i} (y_i - \bar{y})^2}{n_i\,(n_i - 1)}$$

Liquid Samples

x_i	$\lvert x_i-\bar{x}\rvert \times 10^4$	$\lvert x_i-\bar{x}\rvert^2 \times 10^8$
0.42270	2.7	7.3
0.42337	4.0	16.0
0.42270	2.7	7.3
0.42311	1.4	2.0
Σ = 1.69188		Σ = 32.6 x10^{-8}

$$\bar{x} = \frac{\sum^{n} x_i}{n} = \frac{1.69188}{4} = 0.42297$$

$$\sigma_{\bar{x}}^2 = \frac{\sum^{n_i} \lvert x_i-\bar{x}\rvert^2}{n_i(n_i-1)} = \frac{32.6 \times 10^{-8}}{12} = 2.72 \times 10^{-8}$$

$\sigma_{\bar{x}} = 1.65 \times 10^{-4}$

Therefore $\bar{x} = 0.42297 \pm 0.00017$

Vapor Samples

y_i	$\lvert y_i-\bar{y}\rvert \times 10^4$	$\lvert y_i-\bar{y}\rvert^2 \times 10^8$
0.41127	1.7	2.9
0.41092	5.2	27.0
0.41165	2.1	4.4
0.41162	1.8	3.2
0.41173	2.9	8.4
$\sum = 2.05719$		$\sum = 45.9 \times 10^{-8}$

$$\bar{y} = \frac{\sum^{n_i} y_i}{n_i} = \frac{2.05719}{5} = 0.41144$$

$$\sigma_{\bar{y}}^2 = \frac{\sum^{n_i} \lvert y_i-\bar{y}\rvert^2}{n_i(n_i-1)} = \frac{45.9 \times 10^{-8}}{20} = 2.295 \times 10^{-8}$$

$\sigma_{\bar{y}} = 1.52 \times 10^{-4}$

Therefore $\bar{y} = 0.41144 \pm 0.00015$

The separation factor is defined as:

$$\bar{\alpha} = f(\bar{x},\bar{y}) = \left(\frac{\bar{x}}{1-\bar{x}}\right)\left(\frac{1-\bar{y}}{\bar{y}}\right) \tag{7.17}$$

Substituting the above values for $\bar{x}$, $\bar{y}$,

$$\bar{\alpha} = \frac{(0.42297)\ (0.58856)}{(0.41144)\ (0.57703)} = 1.049$$

The variance of $\bar{\alpha}$ is defined as:

$$\sigma^2\ (\bar{\alpha}) = \left(\frac{\partial \bar{\alpha}}{\partial \bar{x}}\right)^2 \sigma_{\bar{x}}^{\ 2} + \left(\frac{\partial \bar{\alpha}}{\partial \bar{y}}\right)^2 \sigma_{\bar{y}}^{\ 2} \qquad (7.18)$$

where $$\frac{\partial \bar{\alpha}}{\partial \bar{x}} = \frac{1-\bar{y}}{\bar{y}(1-\bar{x})^2}, \qquad \frac{\partial \bar{\alpha}}{\partial \bar{y}} = \frac{-\bar{x}}{\bar{y}^2(1-\bar{x})} \qquad (7.19)$$

Substituting the above values for $\bar{x}$, $\bar{y}$, $\sigma_{\bar{x}}$ and $\sigma_{\bar{y}}$, in equation (8,11)

$$\sigma^2(\bar{\alpha}) = 18.2\ (2.72 \times 10^{8}) + 18.6\ (2.295 \times 10^{-8})$$

$$\sigma^2(\bar{\alpha}) = (49.5 + 55.8) \times 10^{-8} = 105.3 \times 10^{-8}$$

$$\sigma\ (\bar{\alpha}) = 10.3 \times 10^{-4}$$

Finally, therefore, the reported separation factor was

$$\bar{\alpha} = 1.049 \pm 0.001$$

3. Determination of the Over-all Column Separation Factor β for the Multi-Stage Runs

Since the composition of both the kettle and reflux samples changed during a run the over-all column separation factor β was determined separately for every reflux sample. (See Graph 8)

$$\beta = \frac{x_K \qquad (1-x_R)}{(1-x_K) \qquad x_R} \qquad (7.2)$$

where x_K = mole fraction deuterium in kettle.
x_R = mole fraction deuterium in reflux

Further, since the kettle and reflux samples were not drawn at the same time, the average of the kettle sample drawn before and after a given reflux sample was used along with the reflux sample to calculate an individual β.

For example, Column Run No. 4 gave the following results:

where x_{K_i} = mole fraction deuterium in ith kettle sample
x_K = average of two successive kettle samples
x_{R_i} = mole fraction deuterium in ith reflux sample.
β = over-all column separation factor.

Data, Column Run No. 4

x_{K_i}	x_K	$\left(\frac{x_K}{1-x_K}\right)$	x_{R_i}	$\frac{1-x_{R_i}}{x_{R_i}}$	β_i
0.57605	0.57674	1.36261	0.54160	0.84638	1.1533
0.57743	0.57648	1.36116	0.54424	0.83742	1.1399
0.57734	0.57836	1.37169	0.54286	0.84210	1.1551
0.57938	0.57889	1.37468	0.54320	0.84094	1.1560
0.57840	0.57935	1.37727	0.54380	0.83891	1.1554
0.58030	0.58067	1.38476	0.54447	0.83665	1.1586
0.58105	0.58105	1.38692	0.54760	0.82615	1.1458

$\bar{\beta}$ and its variance were than calculated

β_i	$\lvert\beta_i-\bar{\beta}\rvert \times 10^3$	$\lvert\beta_i-\bar{\beta}\rvert^2 \times 10^6$
1.1533	1	1
1.1399	12	144
1.1551	3	9
1.1560	4	16
1.1554	3	9
1.1586	7	49
1.1458	6	36
$\bar{\beta} = 1.1520$		$\sum = 264 \times 10^{-6}$

$$\sigma^2_{\bar{\beta}} = \frac{\sum^{n} \lvert\beta_i-\bar{\beta}\rvert^2}{n(n-1)} = \frac{264 \times 10^{-6}}{42} = 6.29 \times 10^{-6} \quad \sigma_{\bar{\beta}} = 2.5 \times 10^{-3}$$

Therefore $\bar{\beta} = 1.1520 \pm 0.0025$

F. Derivations

1. Separation Factor Predicted from Vapor Pressure Ratio

Assumptions:

1. Liquid and vapor phases form ideal solutions

2. $$\frac{P_{ND_3}}{P_{ND_2H}} = \frac{P_{ND_2H}}{P_{NDH_2}} = \frac{P_{NDH_2}}{P_{NH_3}}$$

3. Equilibrium in the liquid phase

   $NH_3 + ND_3 \rightleftharpoons NH_2D + ND_2H$

   $NH_3 + ND_2H \rightleftharpoons 2\ NH_2D$

   $ND_3 + NDH_2 \rightleftharpoons 2\ ND_2H$

4. There is a random distribution of deuteriated atoms in the solution.

The first step in the derivation is to calculate the relative amounts of each species assuming a random distribution of deuterated atoms.

Assume x = over-all mole fraction deuterium

$(1-x)$ = over-all mole fraction hydrogen

Consider a bare nitrogen atom. The probability for a deuterium atom being attached = x. The probability for a hydrogen atom being attached = $(1-x)$.

Below are listed the probabilities for the formation of the successive species:

$ND = x$
$NH = (1-x)$

$NDD = x^2$
$NDH = x(1-x)$
$NHH = (1-x)^2$
$NHD = (1-x)x$

$NDDD = x^3$
$NDDH = x^2\ (1-x)$
$NDHH = x(1-x)^2$
$NDHD = x^2(1-x)$
$NHHD = (1-x)^2x$
$NHHH = (1-x)^3$
$NHDD = (1-x)x^2$
$NHDH = (1-x)^2\ x$

Therefore the probability for formation of

$ND_3 = x^3$
$NH_3 = (1-x)^3$
$NH_2D = 3(1-x)^2x$
$ND_2H = 3x^2(1-x)$

For the equilibrium $NH_3 + ND_3 = NH_2D + ND_2H$

$$K_1 = \frac{(NH_2D)(ND_2H)}{(NH_3)(ND_3)} = \frac{[3(1-x)^2x]\ [3x^2(1-x)]}{x^3\ (1-x)^3} = 9 \tag{7.20}$$

For the equilibrium $NH_3 + ND_2H = 2\ NH_2D$

$$K_2 = \frac{(NH_2D)^2}{(NH_3)(ND_2H)} = \frac{[3(1-x)^2x]^2}{3(1-x)^3\ \ x^2(1-x)} = 3 \tag{7.21}$$

Similarly for the equilibrium $ND_3 + NDH_2 = 2\ ND_2H$

$$K_3 = \frac{(ND_2H)}{(ND_3)(NDH_2)} = \frac{[3x^2(1-x)]^2}{3x^2\ \ (1-x)^2\ x} = 3 \tag{7.22}$$

The separation factor is defined $\alpha = \frac{x_D/y_H}{x_H/y_D}$

Let the concentration of

$NH_3 = x_o$ $\qquad$ $NH_3 = y_o$

$NH_2D = x_1$ $\qquad$ $NH_2D = y_1$

$NHD_2 = x_2$ in liquid $\qquad$ $NHD_2 = y_2$ in vapor.

$ND_3 = x_3$ $\qquad$ $ND_3 = y_3$

$$\alpha = \frac{3x_3 + 2x_2 + x_1}{3x_o + 2x_1 + x_2} \cdot \frac{3y_o + 2y_1 + y_2}{3y_3 + 2y_2 + y_1} \qquad (7.23)$$

From equilibrium 1

$$x_2x_1 / x_3x_o = 9$$

From equilibrium 2

$$x_1^2 / x_2x_o = 3$$

From equilibrium 3

$$x_2^2 / x_3x_1 = 3$$

Solving for x_1 and x_2 in terms of x_o and x_3

$$x_1 = 3x_3^{1/3} \; x_o^{2/3} \qquad (7.24)$$

$$x_2 = 3x_3^{2/3} \; x_o^{1/3} \qquad (7.25)$$

Assuming Raoult's law is valid

$$y_A = \frac{P_A\, x_A}{\pi}$$

and

$$P_o / P_1 = P_1 / P_2 = P_2 / P_3$$

substitution in equation (7.23) gives,

$$\alpha = \frac{\left[3x_3 + 6x_3^{\frac{2}{3}}\, x_o^{\frac{1}{3}} + 3x_3^{\frac{1}{3}}\, x_o^{\frac{2}{3}}\right]\left[3P_o x_o + 6x_3^{\frac{1}{3}}\, P_3^{\frac{1}{3}}\, x_o^{\frac{2}{3}}\, P_o^{\frac{2}{3}} + 3x_o^{\frac{1}{3}}\, P_o^{\frac{1}{3}}\, x_3^{\frac{2}{3}}\, P_3^{\frac{2}{3}}\right]}{\left[3x_o + 6x_3^{\frac{1}{3}}\, x_o^{\frac{2}{3}} + 3x_3^{\frac{2}{3}}\, x_o^{\frac{1}{3}}\right]\left[3P_3 x_3 + 6x_o^{\frac{1}{3}}\, P_o^{\frac{1}{3}}\, x_3^{\frac{2}{3}}\, P_3^{\frac{2}{3}} + 3x_3^{\frac{1}{3}}\, P_3^{\frac{1}{3}}\, x_o^{\frac{2}{3}}\, P_o^{\frac{2}{3}}\right]}$$

Factoring out $\sqrt[3]{\frac{P_o}{P_3}}$ and simplifying (7.26)

$$\alpha = \sqrt[3]{\frac{P_o}{P_3}} = \sqrt[3]{\frac{P_{NH_3}}{P_{ND_3}}} \qquad (7.27)$$

2. Derivation of Disproportionation Effect on Separation Factor

It was observed by Stedman et. al. (31) that the four ammonia species were about equally occurrent in a gaseous sample of ammonia having an over-all deuterium content of 0.50 MFD. This shows a decided preference for the end members NH_3 and ND_3 since an entirely random distribution of deuterium atoms would have lead to only 12.5 percent of the end species and 37.5 percent of the intermediate species NH_2D and NHD_2. The following derivation will show what effect this disproportionation of the ammonia species should have on the vapor pressure prediction of the separation factor

$$\alpha = \sqrt[3]{P_{NH_3} / P_{ND_3}}$$

Three equilibria are maintained in the ammonia system.

$$NH_3 + ND_3 \rightleftharpoons NH_2D + ND_2H$$
$$NH_3 + ND_2H \rightleftharpoons 2NH_2D$$
$$ND_3 + NDH_2 \rightleftharpoons 2ND_2H$$

Let x_o, x_1, x_2 and x_3 be the atom fractions of NH_3, NH_2D, NHD_2 and ND_3 in the liquid phase respectively, and y_o, y_1, y_2 and y_3 the similar atom fractions in the vapor phase.

If the species were entirely randomly distributed the equilibrium constants for the three above equilibria would be determined as in the preceeding derivation from probability of occurances. However, since the probability of occurance for each of the four species is known to be 1/4 when the atom fraction is 0.50 MFD these equilibrium constants must differ from their previously assumed values. They are determined as follows:

It is assumed that a preference for the end members alters their probability in the following way.

Probability of formation:

ND_3: $(1 + C_o)\, x^3$ NH_3: $(1 + C_o)(1 - x)^3$

ND_2H: $3(x^2)(1 - x)$ NH_2D: $3(x)(1 - x)^2$

where x = over-all atom fraction deuterium

C_o = constant of preference.

In order that all species be equally occurrent when $x = 0.50$, C_o must equal 2. With this value the equilibrium constants can be calculated:

$$K_1 = \frac{NH_2D \quad ND_2H}{NH_3 \quad ND_3} = \frac{[3x(1-x)^2][3x^2(1-x)]}{[3x^3]\,[3(1-x)^3]} = 1 \qquad (7.28)$$

$$K_2 = \frac{NH_2D}{NH_3 \quad ND_2H} = \frac{[3x(1-x)^2]^2}{[3(1-x)^3][3x^2(1-x)]} = 1 \qquad (7.29)$$

and

$$K_3 = \frac{ND_2H}{ND_3 \quad NDH_2} = \frac{[3x^2\,(1-x)]^2}{[3(x)^3]\,[3x(1-x)^2]} = 1 \qquad (7.30)$$

The separation factor is defined:

$$\alpha = \frac{(y/x)_H}{(y/x)_D} = \frac{x_D\, y_H}{x_H\, y_D}$$

$$\alpha = \frac{3x_3 + 2x_2 + x_1}{3x_o + 2x_1 + x_2} \quad \frac{3y_o + 2y_1 + y_2}{3y_3 + 2y_2 + y_1} \qquad (7.23)$$

Using the above K's

$$K_1 = \frac{x_1\, x_2}{x_3\, x_o} = 1 \qquad x_1 = \frac{x_3\, x_o}{x_2}$$

$$K_2 = \frac{x_1^{\,2}}{x_o\,x_2} = 1\,, \qquad x_1^{\,2} = x_o\,x_2 = x_o\left(\frac{x_3\,x_o}{x_1}\right)$$

$$K_3 = \frac{x_2^{\,2}}{x_1\,x_3} = 1\,, \qquad x_2^{\,2} = x_3\,x_1 = x_3\left(\frac{x_3\,x_o}{x_2}\right)$$

and

$$x_1 = x_o^{2/3}\;x_3^{1/3} \tag{7.26}$$

$$x_2 = x_3^{2/3}\;x_o^{1/3} \tag{7.27}$$

Let P_i = the vapor pressure of the ith species

π = total system pressure.

Assuming Raoult's and Dalton's Laws

$$\pi = \sum P_i$$

$$y_i = P_i\,x_i\,/\,\pi$$

and $P_o/P_i = P_1/P_2 = P_2/P_3$

Substitution in the above expression for α gives; eq. (7.23)

$$\alpha = \frac{\left[3x_3+2x_3^{\frac{2}{3}}\,x_o^{\frac{1}{3}}+x_3^{\frac{1}{3}}\,x_o^{\frac{2}{3}}\right]\left[3x_oP_o+2x_3^{\frac{1}{3}}P_3^{\frac{1}{3}}x_o^{\frac{2}{3}}\,P_o^{\frac{2}{3}}+x_3^{\frac{2}{3}}\,P_3^{\frac{2}{3}}\,x_o^{\frac{1}{3}}\,P_o^{\frac{1}{3}}\right]}{\left[3x_o+2x_3^{\frac{1}{3}}\,x_o^{\frac{2}{3}}+\,x_3^{\frac{2}{3}}\,x_o^{\frac{1}{3}}\right]\left[3x_3P_3+2x_3^{\frac{2}{3}}\,P_3^{\frac{2}{3}}x_o^{\frac{1}{3}}\,P_o^{\frac{1}{3}}+x_3^{\frac{1}{3}}\,P_3^{\frac{1}{3}}\,x_o^{\frac{2}{3}}\,P_o^{\frac{2}{3}}\right]} \tag{7.31}$$

Multiplying out and factoring out $\sqrt[3]{\frac{P_o}{P_3}}$

$$\alpha = \sqrt[3]{\frac{P_o}{P_3}} \left\{ \frac{3x_3^{\frac{5}{3}} x_o^{\frac{1}{3}} + x_3^{\frac{4}{3}} x_o^{\frac{2}{3}} \left[6 \left(\frac{P_o}{P_3}\right)^{\frac{1}{3}} + 2 \right] + x_3 x_o \left[9 \left(\frac{P_o}{P_3}\right)^{\frac{2}{3}} + 4 \left(\frac{P_o}{P_3}\right)^{\frac{1}{3}} + 1 \right] + x_3^{\frac{2}{3}} x_o^{\frac{4}{3}} \left[6 \left(\frac{P_o}{P_3}\right)^{\frac{2}{3}} + 2 \left(\frac{P_o}{P_3}\right)^{\frac{1}{3}} \right] + 3x_3^{\frac{1}{3}} x_o^{\frac{5}{3}} \left(\frac{P_o}{P_3}\right)^{\frac{2}{3}}}{3x_3^{\frac{5}{3}} x_o^{\frac{1}{3}} + x_3^{\frac{4}{3}} x_o^{\frac{2}{3}} \left[2 \left(\frac{P_o}{P_3}\right)^{\frac{1}{3}} + 6 \right] + x_3 x_o \left[\left(\frac{P_o}{P_3}\right)^{\frac{2}{3}} + 4 \left(\frac{P_o}{P_3}\right)^{\frac{1}{3}} + 9 \right] + x_3^{\frac{2}{3}} x_o^{\frac{4}{3}} \left[2 \left(\frac{P_o}{P_3}\right)^{\frac{2}{3}} + 6 \left(\frac{P_o}{P_3}\right)^{\frac{1}{3}} \right] + 3x_3^{\frac{1}{3}} x_o^{\frac{5}{3}} \left(\frac{P_o}{P_3}\right)^{\frac{2}{3}}} \right\} \qquad (7.32)$$

Note that, except for their coefficients the terms in the numerator and denominator of the bracketed ratio are identical. If the four species were randomly distributed this bracket would be unity for all x's because these terms would all cancel. It is interesting to observe the behavior of the bracketed quantity with composition.

Kirshenbaum and Urey give (26)

$$\left(\frac{P_o}{P_3}\right) = 1.1150, \quad \left(\frac{P_o}{P_3}\right)^{\frac{2}{3}} = 1.0753, \quad \left(\frac{P_o}{P_3}\right)^{\frac{1}{3}} = 1.0370$$

at one atmosphere system pressure.

The result of calculating the bracketed quantities for several compositions gives

MFD	$\{\ \}$	α
0.0 or 1.0	0.0000	1.0370
0.10 or 0.90	1.0064	1.0436
0.50	1.0245	1.0624

This result states that the separation factor attains a maximum value at 0.50 MFD and decreases toward the value predicted by

$$\alpha = \sqrt[3]{\frac{P_{NH_3}}{P_{ND_3}}}$$

as the composition either approaches 0.00 or 1.00 MFD. One would therefore not hope to gain any elevation in the separation factor at low deuterium enrichment from the disproportionation effect.

G. Location of Original Data

The original data are located in five research notebooks on file in the Nuclear Engineering Office at the Massachusetts Institute of Technology. Reference to book and page number has been given in Tables 4 and 7.

H. Nomenclature

Symbol		Dimensions
a =	constant	none
b =	constant	$(MFD)^{-1}$
c =	constant	none
C_p =	specified heat at constant pressure	cal/g °C
D =	effective column diameter	cm
D_d =	diffusion coefficient	cm^2/sec.
$f(x)$=	composition dependence of $\ln \alpha$	none
g =	constant,	$(min)^{-1}$
h =	constant,	$(min)^{-1}/MFD$
HTU=	height of a transfer unit or stage,	cm.
MFD=	mole fraction deuterium	none
MFH=	mole fraction heptane	none
MV.=	thermocouple potential	millivolts
n =	number of stages in column	none
η_D^{20}=	refractive index, 20°C	none
P =	total pressure	mm Hg
p =	partial pressure	mm Hg
Se^2=	variance	-
T =	temperature	°C or °K
t =	time	min.
v =	velocity	cm/sec
W_i =	weight of the ith value $= 1/\sigma_i^2$	-

x	=	mole fraction in liquid	none
x_K	=	mole fraction in kettle	none
x_R	=	mole fraction in reflux	none
y	=	mole fraction in vapor	none
Z	=	predicted value of $(1/\bar{t})$	min^{-1}
z	=	experimentally determined value of $1/\bar{t}$	min^{-1}
α	=	relative volatility or separation factor	none
β	=	over-all column separation factor	none
γ	=	$\ln(\alpha)$	none
δ	=	$\ln(\pi)$	none
μ	=	viscosity	g/cm/sec
π	=	system pressure	mm Hg.
π_o	=	reference pressure	mm Hg.
ρ	=	density	g/cm^3
σ	=	standard deviation	-
σ_a	=	standard deviation due to analytic error	-
σ_s	=	standard deviation due to sampling error or equilibrium fluctuations	-
$\sigma_{\bar{x}}$	=	standard deviation of the mean of x	none
$\sigma_{\bar{y}}$	=	standard deviation of the mean of y	none

Subscripts

A = more volatile component

B = less volatile component

D = deuterium

H = hydrogen

I. Literature Citations

1. Armstrong, G. T., "A Critical Review of the Literature Relating to the Vapor Pressure of Ammonia and Tridenteroammonia", NBS-2626 June 30, 1953.
2. Barbour, H. G. and Hamilton, W. F., Am. J. Physiol, 69 : 654 (1924)
3. Barr, F. T. and W. P. Drews, "The Future for Cheap Heavy Water", Chem. Eng. Progress 56, 49 (1960).
4. Bebbington, W. P., Thayer, V. R., eds., Proctor J. F., Comp., "Production of Heavy Water Savannah River and Dana Plants", DP-400, July, 1959).
5. Bebbington, W. P. and Thayer, V. R., "Production of Heavy Water", Chem. Eng. Progress, 55 No. 9 ; 70, (September, 1959).
6. Benedict, M., "Review of Heavy Water Production Processes", Proceedings of the International Conference on Peaceful Uses of Atomic Energy, Vol. 8, p. 377, United Nations N. Y. (1956)
7. Benedict, M, "Heavy Water Production", Lecture Delivered at Reykjavik, September 6, 1956, Mass. Institute of Technology NP-6975 (1956).
8. Bigelow, J. E., "The Catalytic Effect of Structual Materials on the Exchange of Deuterium from Steam to Hydrogen". ScD thesis M.I.T., Ch. E., (1956).
9. Bromiley, E. C., and Quiggle, D., "Vapor-Liquid Equilibria of Hydrocarbon Mixtures". Ind. Eng. Chem. 25, 1136-8 (1933)
10. Burke, O. W. Jr., "Light Hydrocarbon Analysis", Reinhold Corp., p. 137, (1951).

11. Cohen, K., "Charting a Course for Nuclear Power Development", Nucleonics, 16-1, p. 66, (January, 1958).

12. Doss, M. P., "Physical Constants of the Principal Hydrocarbons" New York, Texas Co., (1943).

13. Drews, William, "Deuterium Separation Study, Distillation of Ammonia and Methane", Esso Research and Eng. Co., NYO-7522. Progress Report No. 3, (October, 1955).

14. Ebeling, R. M., S.M. thesis, Ch. E., M.I.T., (1954)

15. Frillette, V. J., and Hanle, J., Anal. Chem. 19. p. 984-87, (1947)

16. Gilliland, R. M. , Cowen, L. M., Curtis, J. E., "Oxidation of Ammonia in a Fluidized Bid of Metallic Oxides", B. S. thesis Ch. E., M.I.T. (1950)

17. Groth, W., Ihle. H., und Murrenhoff, A., "Bestimmung des Dampfdruckverhaltmisses von NH_3/ND_3 zwischen 0^oC und 20^oC", Angew Chem. 68-19. p.605, (January, 1956)

18. "Heavy Water Production; The C.J.B. Process" Published by C.J.B. House, Eastbourne Terrace, Paddington, W.2. England, (1958).

19. Herndon, J. "Progress Report" Y-453, Oak Ridge Assay Lab., (1949).

20. Heumann, F. K., "Analysis of Hydrogen-Deuterium Mixtures by the Thermal Conductivity Method", KAPL-755, (June, 1952).

21. Ingelstam, E., Juilo, E. D., Johnson, J., "Precision Concentration Analysis of D_2O/H_2O by Means of Phase Contrast Refractometry", J. Am. Optical Soc., 44-6, p.472. (June, 1954).

22. Kalman, M. P. and Petersen, G. T., "Relative Volatility of the System Deuteroammonia-Ammonia", S.M. thesis Nuclear Eng., M.I.T. (August, 1958).

23. Keston, A. S., Rittenburg, D, and Schoenheimer, R., J. Biol. Chem. 122 p. 227-237. (1937)

24. Kimball, G. E., and Stockmayer, W. H., "Partition Functions for Distribution of Deuteriated Ammonia Species", S.A.M. Report 100XR-1657, (October, 1942)

25. Kirshenbaum, I., "Physical Properties and Analysis of Heavy Water", McGraw Hill, (1951).

26. Kirshenbaum, I., and Urey, H. C., "The Difference in the Vapor Pressures, Heats of Vaporization and Triple Points of Nitrogen (14) and Nitrogen (15) and of Ammonia and Trideuteroammonia", J. Chem. Physics 10, p 7, (December, 1942).

27. Naragon, E. A., and Lewis, C. J., "Small Glass Center-Tube Fractionating Column", Ind., Eng.. Chem. 18-7, p. 448 (July, 1946).

28. Patterson, W. A., "Final Report Covering the Period 6/15/48 to 12/31/53." Baird Assoc., J. O. 5044, p. 75-85.

29. Robinson, C. S., and Gilliland, E. R., "Elements of Fractional Distillation" Fourth Edition, McGraw-Hill. p. 14 (1950).

30. Stedman, D. F., "Possible Distillation or Similar Methods for Recovery of D_2O". National Research Labs. of Canada, C50-49S (June, 1949).

31. Stedman, D. F., Palmer, J. B. and Ogden, B., "Disproportionation in Deuterated Ammonia". National Research Labs. of Canada. C165-50P (October, 1950)

32. "Studies of the Market for Nuclear Materials, II Moderators, B Heavy Water" Paris, Organization for European Economic Cooperation. (1959).

33. Taylor, H. S. and Jungers, J. C., "Communications to the Editor"- The Deuteroammonias"., J. Am. Soc. 55, p. 5057 (1933).

34. Taylor, H. S., and Jungers, J. C., "The Mercury Photosensitized Decomposition of the Deuteroammonias", J. Chem., Physics 2. p. 373, (1934).

35. Williams, P. M., "Relative Volatility of the Propane-Propene System at Atmospheric Pressure" S.M. thesis Ch. E., M.I.T., (1957).