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Temperature kinetics of nitrogen dioxide-ammonia reactions

George Dillender Jr.

TEMPERATURE KINETICS OF NITROGEN DIOXIDE-
AMMONIA REACTIONS

BY

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A

THESIS

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Approved by-___*Robert R Russell*_____
Professor of Organic Chemistry

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The author gratefully acknowledges the suggestions of Dr. Walter T. Schrenk and the helpful time contributed by Mr. Randolph R. Cornwall.

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INTRODUCTION

The purpose of this project was to study the rapid rate of reaction of nitrogen dioxide and ammonia and if possible to determine the mechanism of the reaction.

The author became interested in this project through his interest in rockets, jets, and the types of fuel that are used to propel them.

The prospect of using nitrogen dioxide and ammonia as a possible fuel was the basic reason for the selection of this project.

Very little has been done in the study of the reaction of nitrogen dioxide and ammonia, although the reaction seems to be a simple one.

How fast does the reaction go to completion and what are the products of the reaction? What path does the reaction follow when an excess of nitrogen dioxide or ammonia is used and what effect does temperature have upon the formation of the reaction products? These are some of the unanswered questions for which the author has tried to find an answer.

The author feels that this project is of importance, because as mentioned before, very little has been done on the reaction and there is a possibility that the reaction may be of some economic value as a rocket propellant.

It is essential that the fuel used in rockets and jets be cheap and that the products of combustion of the

oxidant and the reductant be gaseous.

Such is the case in the reaction of nitrogen dioxide and ammonia.

Nitrogen dioxide and ammonia are very cheap to produce. Nitrogen dioxide is produced by oxidation of atmospheric nitrogen. Reduction of nitric oxide, nitrous oxide, and nitrogen dioxide produces ammonia.

Neither nitrogen dioxide nor ammonia is very difficult to handle and neither is as susceptible to chance detonation as many other oxidants and reductants.

It is believed that much has been learned from the study of the reaction between nitrogen dioxide and ammonia concerning the amount and type of gaseous products formed, the amount and type of solid products formed from the reaction, and the possibility of using the reaction in a commercial application.

It is the author's intention to arrive at an overall balanced equation for the reaction of nitrogen dioxide and ammonia, and to give some definite conclusions regarding the reaction.

REVIEW OF LITERATURE

A thorough review of the literature indicates that very little information is available concerning the reaction of nitrogen dioxide and ammonia.

Several authors have reported[1] that the reaction of

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(1)
Ephraim, F., Inorganic Chemistry. 5th ed. N. Y., Interscience Publishers, Inc., 1948. p. 181
---

nitrous oxide and ammonia occurs with explosive violence when heated but that nitric oxide and ammonia react less vigorously and only at higher temperatures. The equations for the reactions are assumed to be as follows:

$$3N_2O + 2NH_3 = 4N_2 + 3H_2O$$
and
$$6NO + 4NH_3 = 5N_2 + 6H_2O$$
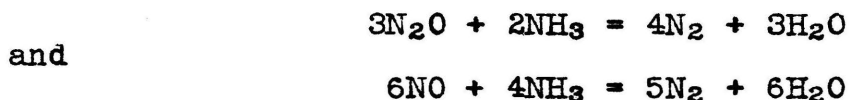
with nitrogen being liberated only at high temperatures in the second reaction.

Nitrogen dioxide is not only a good oxidant[2] for

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(2)
J. Am. Rocket Soc., 80, 1 (1951)
---

ammonia but for many metals[3] and for other organic[4] and inorganic compounds.

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(3)
Oza, M. T., J. Indian Chem. Soc. 22, 173-80 (1945)

(4)
Gee, K. W., U. S. 2,464,572, Mar. 15, 1946

The use of several different oxidants[5] (nitrous

(5)
Zachringer, A. J., J. Space Flight. 2, 1-4 (1950)

oxide, nitric oxide, nitrogen dioxide, nitrogen trioxide,

and nitrogen pentoxide) have been used with various reduc-

tants (PhNH$_2$, EtOH, N$_2$H$_4$, LiH, and several others) and the

theoretical exhaust velocities have been calculated. But,

none of the oxidants, including nitrogen dioxide, have been

used with ammonia.

It has been reported that nitrogen dioxide and ammo-

nia[6] react with a violent explosion with the formation of

(6)
Besson and Rosset, Action du peroxyde d'azote sur l'ammo-
niac et quelques sais ammoniacaux; Compt. Rend., 142,
633-634 (1906)

several products; liquid, gaseous, and solid. The products

formed were assumed to be nitric acid, ammonium nitrite,

ammonium nitrate, and nitric oxide. The possible equation

for the reaction being

$$3NO_2 + 4NH_3 = 7N + 6H_2O$$

and

$$3NO_2 + 2NH_3 + H_2O = NO + 2NH_4NO_3$$
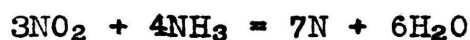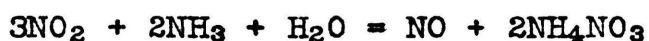
with ammonium nitrite formed in the reaction not being

considered. No data were presented to support the results

of the assumptions.

In the reaction of nitrogen dioxide and ammonia, hydra-

zine has been reported[7] as one of the possible products.

(7)
Patry, Garlet, and Pupko, Compt. Rend., 225, 941-942
(1947)

The analysis showed about 0.6% of this material. The above authors also reported the following products from the reaction: ammonium nitrite, ammonium nitrate, nitrous oxide, nitric oxide, and nitrogen. The oxides of nitrogen were reacted with ammonia and the following results reported: nitrous oxide and nitric oxide reacted with ammonia at a fairly fast rate and a temperature of 100°C. Nitrogen dioxide and dinitrogen tetroxide reacted with ammonia to form the products mentioned above. It was also suggested that the ammonium nitrite formed in the reaction reacted with nitrogen dioxide according to the following equation:
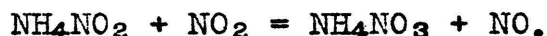
$$NH_4NO_2 + NO_2 = NH_4NO_3 + NO.$$

The hydrazine formed in the reaction of nitrogen dioxide and ammonia was assumed to be a secondary reaction with nitrous and nitric oxide also being formed.

The data for the reaction of nitrogen dioxide and ammonia were not presented by these authors, but the results of the reaction of other oxides of nitrogen with ammonia were reported.

The results of several determinations of the reaction of nitrogen dioxide and ammonia have been reported.[8]

(8)
Cooley, R. A., Annual Report On Study Of Chemical Kinetics Of Rapid Reactions, Atomic Energy Commission. Unpublished. August, 1951.

Quantitative analyses of the solid and gaseous products were reported.

Physical constants of the reactants and products were obtained from the standard sources. [9, 10]

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(9)
Lange, Handbook of Physical Chemistry. 6th ed. Ohio, Handbook Publishers, Inc., 1946.

(10)
Handbook of Chemistry and Physics. 31st ed. Ohio, Chemical Rubber Publishing Co., 1949.

DISCUSSION OF METHODS

Samples for the study of the rapid rate of reaction of nitrogen dioxide and ammonia were prepared in glass ampoules made of no. 4 glass tubing.

The ampoules were prepared by cutting the glass tubing into approximately six-inch lengths. The cut lengths were heated at the mid point and drawn into a fine capillary. The ends were then cut to a suitable size to allow the admission of a previously prepared capillary. The bottom end of the ampoule was then shaped and sealed, the completed ampoule being shown in Figure 1.

The completed ampoules were cleaned with acetone which was then evaporated on the sand bath. The ampoules were then desiccated at room temperature to remove any moisture which may have collected on the external or internal surfaces of the ampoule. The finished ampoules were desiccated for a minimum of twenty-four hours, removed, and carefully weighed on an analytical balance to an accuracy of $\pm$ 0.1 mg.

The weighed ampoules were then filled with liquid ammonia and liquid nitrogen dioxide.

The ammonia was obtained from the Ohio Chemical and Manufacturing Co. The analysis given was 99$^+$ % ammonia.

An ampoule was placed in a no. 41k weighing bottle which had been filled with acetone. A freezing solution
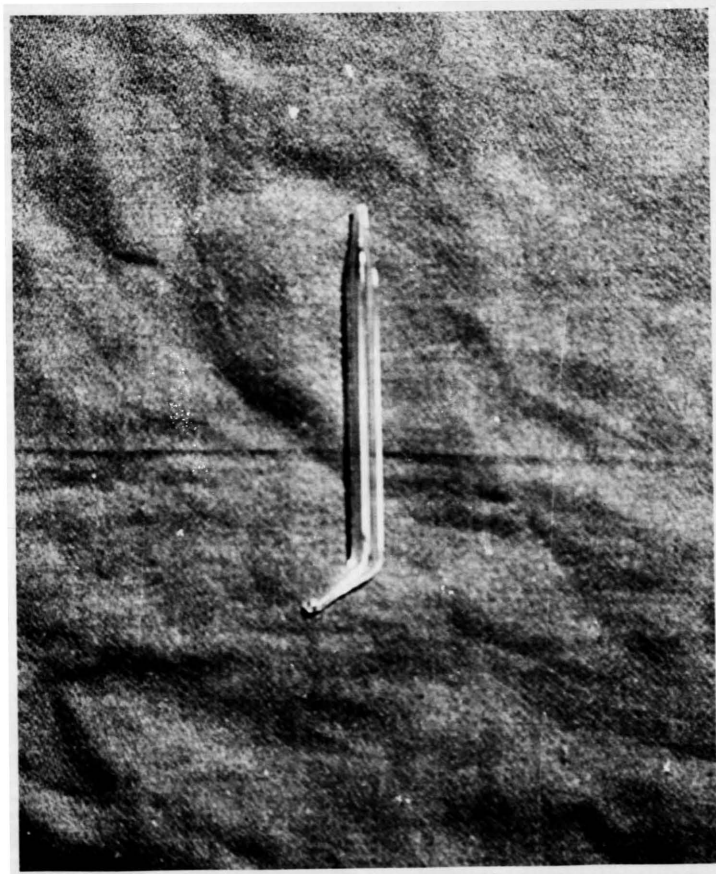
Figure 1

Ampoule used for quantitative
samples of liquid nitrogen dioxide
and ammonia.

was prepared by filling a vacuum bottle with dry ice and then with acetone, the temperature being approximately -86°C. The weighing bottle, used as a support for the ampoule and contents, was placed in the freezing solution.

A finely drawn capillary was placed inside of the ampoule from one-half to three-quarters of an inch from the tip and ammonia led into the ampoule and condensed. A rubber tube connection was used to lead the ammonia from the ammonia tank to the capillary and ampoule.

After the ampoule had been filled to the desired level with liquid ammonia the capillary was removed and the end of the ampoule sealed with a micro-burner flame. The ampoules were easily sealed due to the low temperature of the contents.

After filling, the ampoule was removed from the freezing solution and allowed to warm to room temperature. The external surface was then thoroughly cleaned and the filled ampoule weighed to an accuracy of ± 0.1 mg. The weight of condensed ammonia was taken as the difference of the filled and unfilled ampoule weight.

Procuring of nitrogen dioxide samples proved to be a more difficult task than was anticipated.

Nitrogen dioxide used was obtained from the Matheson Chemical Company and was assumed to be at least 99% nitrogen dioxide and was at a pressure of 1.8 atmospheres at room temperature.

The nitrogen dioxide was dried by a bank of U tubes

containing phosphorous pentoxide. All necessary connections were made of Tygon tubing with glass to glass connections being made as closely as possible.

The gaseous nitrogen dioxide was condensed in the ampoules with the aid of an ice-water mixture.

Dry ice placed in acetone was first used as a cooling solution but the temperature was very difficult to control and the nitrogen dioxide froze in the ampoules making it difficult to estimate the correct amount of nitrogen dioxide desired.

After being filled, the ampoule was removed from the cooling solution and immediately placed in the dry ice-acetone mixture to freeze the nitrogen dioxide. This made sealing of the ampoule very easy. In several cases the nitrogen dioxide froze at the bottom of the ampoule first forcing liquid nitrogen dioxide from the ampoule. This necessitated refilling the ampoule. The method was consequently soon discarded.

As an alternative method the ampoules were sealed while in the ice-water mixture. Care must be taken at this point to seal the ampoules as quickly as possible, otherwise the heat is not dissipated quickly enough; thus, the contents will warm up and exert enough vapor pressure to blow out the ends of the hot glass ampoules.

After filling, the ampoule was removed from the condensing bath, allowed to warm to room temperature, thoroughly cleaned, and the filled weight recorded to an ac-

curacy of $\pm$ 0.1 mg. The weight of liquid nitrogen dioxide was taken as the difference in the filled and unfilled weight of the ampoule.

As all rapid rate determinations were made in an identical manner, a typical run at 35°C will be thoroughly explained. It should be noted at this point that the following procedure was used for taking "still" pictures. The method for continuous motion pictures follows this procedure.

A merc to merc water bath regulator was set for 35°C and placed in the water bath. The water bath, with continuous stirring, was allowed to reach a temperature of 35°C and was controlled to an accuracy of $\pm$ 0.03°C by the merc to merc regulator.

As the water bath was heating, the Camera Recording Oscilloscope was grounded, turned on, and allowed to warm for a minimum of one hour before being used.

Next, the D.C. amplifier was grounded, plugged into a 110 volt A.C. current supply and allowed to warm for one hour before being used.

After these two instruments had warmed for approximately forty-five minutes the positive and negative terminals of a forty-five volt B battery were connected to the correct terminals of the D.C. amplifier. Next, the 13.5 volt supply, supplied by nine one and a half volt telephone batteries, was connected to the positive and negative terminals of the Statham Pressure Gage indicator

pick up and the output terminals of the pressure indicator were connected to the correct terminals of the D.C. amplifier. The output signal terminal of the D.C. amplifier was then connected to the Y amplitude terminal of the oscilloscope.

The wiring diagram of the oscilloscope was changed in order that the pressure changes would be noted on the X axis and the time sweep would be noted on the Y axis in order to accommodate the film motion.

Five 600 volt 5 mfd condensers were connected to the oscilloscope, one terminal was connected to the X amplitude and the other terminal was connected to the ground wire. The condensers were used to give a sweep time of 4.3 seconds with the oscilloscope trace covering a distance of 4.05 inches. The time sweep and distance were controlled by manipulation of the X amplitude and sweep time knobs.

The camera unit was then mounted. Figure 2 shows the complete apparatus assembly for rapid rate reaction determinations.

The sweep time and sweep distance was determined by counting a unit number of sweeps and recording the time. The length of sweep distance is shown in Run A_5.

The instruments were calibrated by applying positive pressure to the Statham Gage and noting the deflection of the oscilloscope electron beam. The increasing pressure calibration deflection was checked by noting the deflection of the oscilloscope electron beam during decreasing
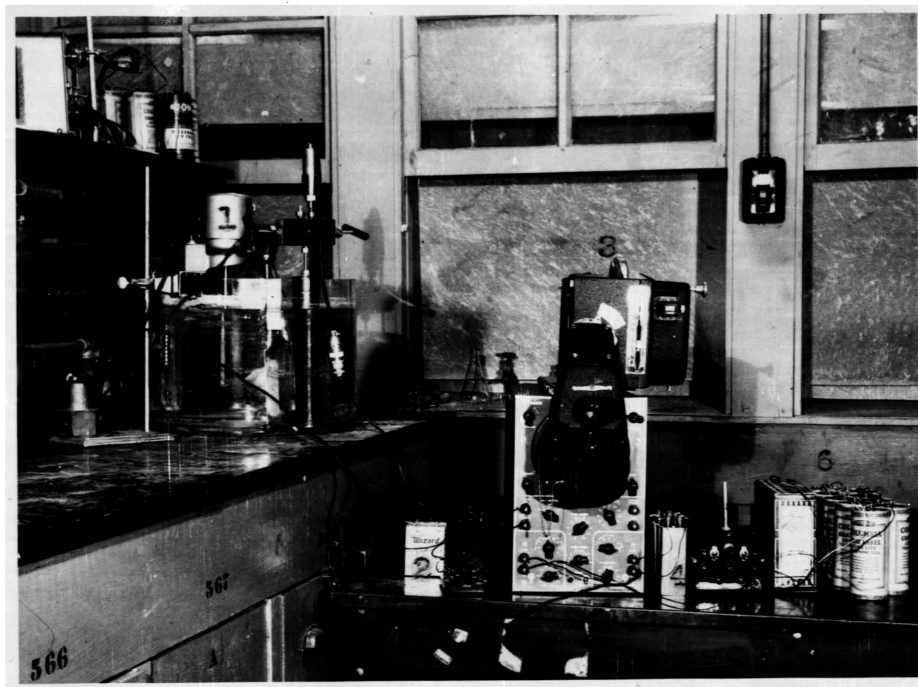
Figure 2

Experimental apparatus for still pictures of
rapid rate determinations. Reading from left to
right: (1) constant temperature water bath con-
taining reactor, (2) battery, condensers, and tap-
ping key for external excitation of oscilloscope
electron tube, (3) oscilloscope with camera and
camera attachment mounted, (4) condensers for con-
trolling sweep time, (5) D.C. amplifier, and (6)
batteries for D.C. voltage supply to D.C. ampli-
fier and Statham Pressure Gage Indicator.

positive pressure.

All calibrations were recorded on film.

An ampoule of nitrogen dioxide and an ampoule of ammonia, containing known amounts of oxidant and reductant, were placed in the ampoule breaker as shown in Figure 3. The breaker was designed and made by the author and is of stainless steel.

The breaker and contents were then placed in the stainless steel reactor while in a horizontal position and gently pushed to the bottom of the reactor. The Statham Gage and assembly were then securely tightened to the stainless steel reactor. The completed assembly is shown in Figure 4. By means of an oil vacuum pump the pressure on the inside of the reactor was reduced to one millimeter of of mercury. The stainless steel reactor and assembly was then connected to the remaining apparatus by means of an electrical coupling and placed in the constant temperature bath.

As the reactor was warming to the desired temperature a picture was made of the oscilloscope screen. The time-distance base line was placed on the same negative. After this, the sweep control knob was placed on "continuous sweep" for visual observation during reactor heating to make sure the reactor was not leaking and allowing air to reenter the reactor.

After the reactor was heated for one-half hour, at which time it was assumed to be at water bath temperature,
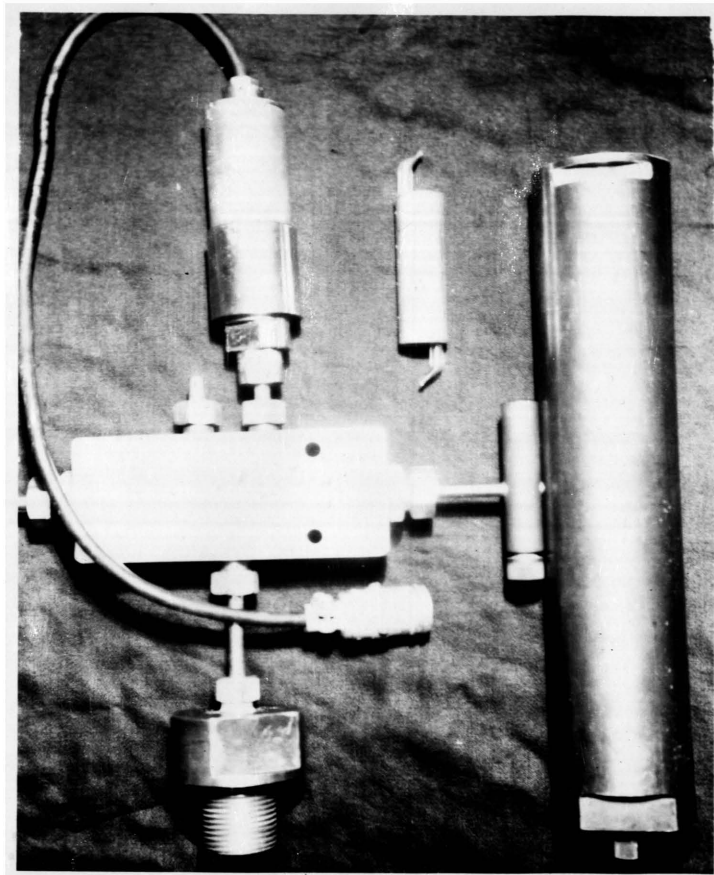
Figure 3

Disassembled reactor. Reading from
left to right: Statham Pressure Gage
Indicator and reactor attachment, ampoule
breaker containing ampoules of liquid
nitrogen dioxide and ammonia, and stain-
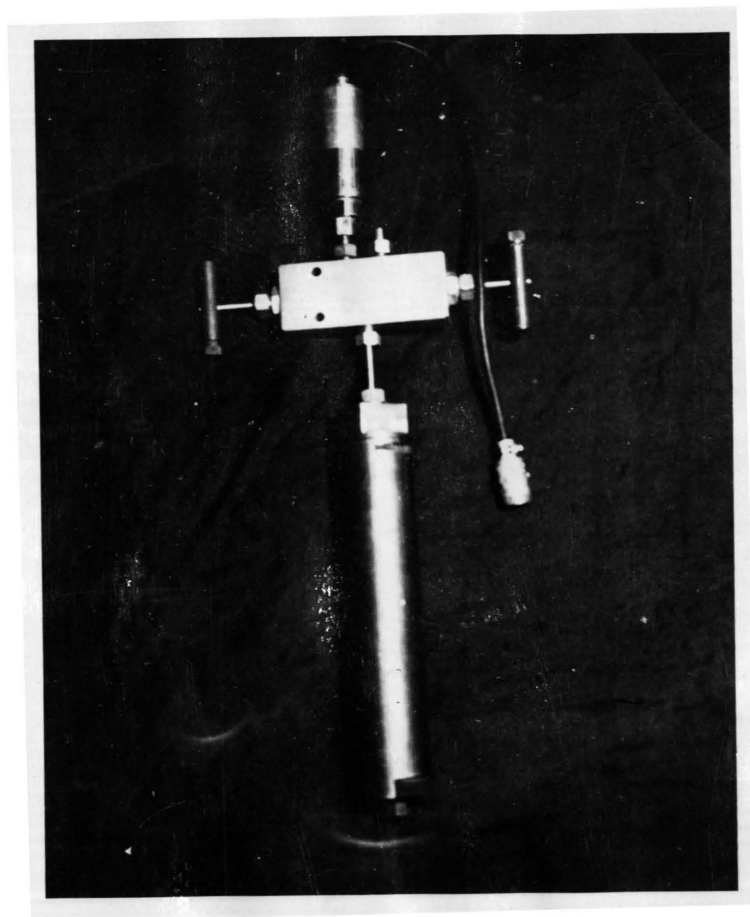less steel reactor.

Figure 4

Assembled reactor for determining
the rapid rate of reaction of nitrogen
dioxide and ammonia.

it was removed from the water bath and nitrogen dioxide-ammonia reaction determined photographically.

The electron oscilloscope tube was excited by external means thus making it possible to start the electron tube sweep at any desired time and position.

After removing the reactor from the water bath, the electron tube sweep was started and the reactor manipulated to break the nitrogen dioxide ampoule. The results of the breakage were recorded on film as well as visually to insure the breakage of the ampoule. The electron tube sweep was again started and the reactor manipulated for breakage of the ammonia ampoule. The results of the breakage and reaction were recorded on film as well as visually. After the reaction had been recorded the reactor and assembly was disconnected from the system, disassembled, and thoroughly cleaned to remove all possible traces of reactants and reaction products.

The above procedure was then followed for the determination of another reaction.

Continuous motion pictures of reactions were also taken. This necessitated a few minor changes as follows: removal of the five condensers used for the sweep time control, removal of the external excitation unit from the oscilloscope electron tube, and placing the X amplitude on zero. The control unit was grounded and then plugged into a 110 volt A.C. supply and turned on. The unit was connected to the camera by means of a suitable electrical

connection. After the control unit had warmed for about fifteen minutes the motor control switch was placed in the "on" position. The motor control switch controlled the motor in the camera. Next, the film rate knob was placed in the correct position to give the rate of film speed desired. A control knob on the camera was placed "in" or "out" depending on the film rate desired. Figure 5 shows the apparatus hookup used for continuous motion pictures. The experimental procedure for reaction preparation was used as previously described for still pictures.

When continuous motion pictures were taken an external time base was used. This was achieved by allowing a swinging pendulum to come into contact with a drop of mercury and thus completing the electrical circuit to a neon tube inside of the camera. A tapping key was also placed in the circuit to activate the neon tube at the time desired. The neon tube was activated by the use of a 110 volt line supply. Electrical connections for the time baselight unit were made according to instructions received with the Electronic Control Unit.

Ten rapid rate determinations were made at each temperature starting at 35° C, and with ten degree increment increases, and ending with the reactions being run at 93° C.

Five determinations were made at each temperature in which an ampoule of nitrogen dioxide was broken in an atmosphere of ammonia and five determinations made in which an ampoule of ammonia was broken in an atmosphere of nitrogen
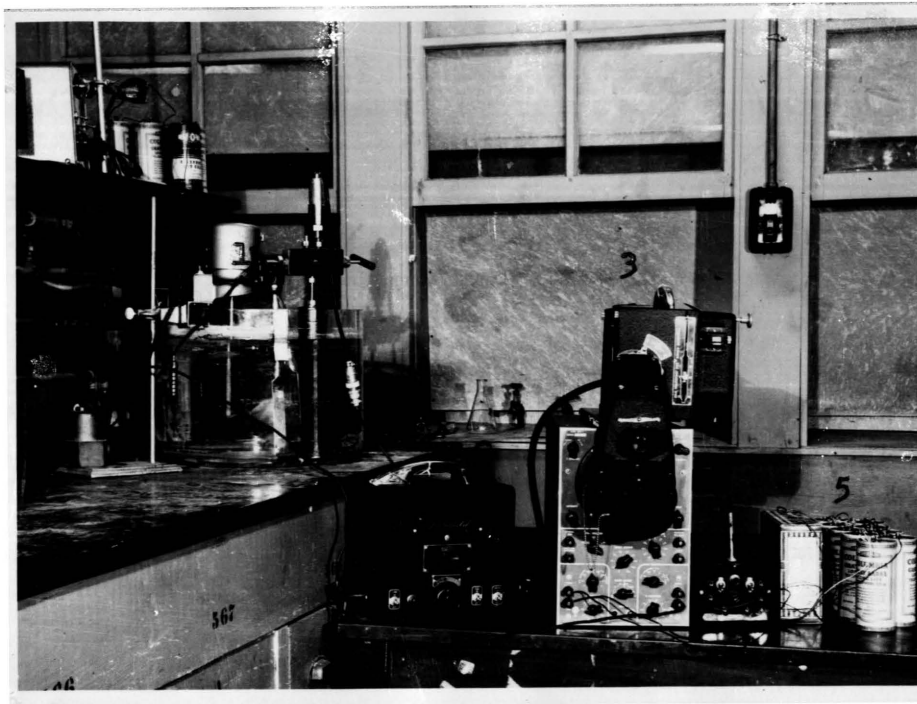
Figure 5

Experimental apparatus for continuous motion
pictures of rapid rate determination. Reading
from left to right: (1) constant temperature wa-
ter bath containing reactor, (2) Fairchild Camera
Control unit, (3) oscilloscope with camera and
camera attachment mounted, (4) D.C. amplifier,
and (5) batteries for D.C. voltage supply to D.C.
amplifier and Statham Pressure Gage Indicator.

dioxide. The results of these determinations were recorded
on film. At each temperature three gas analyses were made
and accompanying solids formed from the reactions were
analyzed. The method of gas and solids analysis follows
in the next section.

When continuous motion pictures were made of the reac-
tions a film rate of one inch per minute was used, with a
few runs being made at a film rate of one inch per second.

Four runs at 85°C were made in which the ampoule of
ammonia was broken in an atmosphere of nitrogen dioxide
and the result of the reaction recorded at a film rate of
one inch per second. Four runs at 60°C and three runs at
35°C were also made at the fast film rate. No attempt was
made to analyze the gaseous or solid products formed from
the reaction.

The results of the reactions are found in tabulated
data.

All films and photographs used in the development of
this project were processed by the author.

A list of all equipment used is as follows:

A) Burrell Gas Analysis Apparatus.

B) Stainless steel bomb reactor, 15,000 psi pressure.

C) Statham Gage Pressure Indicator, 0-50 psi and time
resolution of 10,000 cycles per second, and attach-
ment.

D) Dumont 304H Cathode-Ray Oscillograph.

E) Fairchild 314A Oscillograph Record Camera Control.

F) Fairchild 314A Oscillograph Record Camera and attachment.

G) Precision Scientific Co. water bath and control unit.

PROCEDURE FOR GAS ANALYSIS

A Burrell Gas Analyzer was used for the analysis of the gaseous products formed from the reaction of nitrogen dioxide and ammonia. All analyses were made at a room temperature of 70°F and atmospheric pressure.

Air was first removed from the Burrell Gas Analyzer by means of a mercury column attached to the gas analyzer. After the air had been removed, the mercury column was manipulated to the top of the gas burette attached to the gas analyzer.

After a reaction had been recorded on film, a dry ice trap, which had been previously evacuated by use of an oil vacuum pump to a pressure of 1 millimeter of mercury, was attached to the external outlet of the reactor assembly. The connection was made by use of Tygon tubing. The outlet of the dry ice trap was then connected to the inlet of the burette by the use of rubber tubing.

The dry ice trap was then placed in the dry ice-acetone mixture and allowed to cool. Pinch clamps closing the tubing were loosened and the outlet valve of the reactor opened to allow the gaseous products to enter the dry ice trap. The inlet stop cock valve of the burette was then opened and the gaseous products slowly drawn into the burette until a 50 milliliter sample had been obtained. It was necessary to draw the gas stream slowly into the burette so that excess ammonia or nitrogen dioxide was trapped in the dry ice

trap. After procuring the required gas sample, the stop cock was closed and the volume of gas sample was measured and recorded at room temperature and atmospheric pressure. The burette was water jacketed to insure that the gas sample was at room temperature. The gas analyzer was then manipulated to determine the percent by volume of nitrous oxide, nitric oxide, oxygen, with the remaining unabsorbed volume assumed to be nitrogen.

The gas sample to be analyzed was bubbled through each specific solution five times before recording the volume decrease.

All gas analyses were made in an identical manner.

Care was taken to keep the level of the mercury column constant when drawing the gas sample into the burette after one constituent had been absorbed to insure a proper analysis of the gas sample.

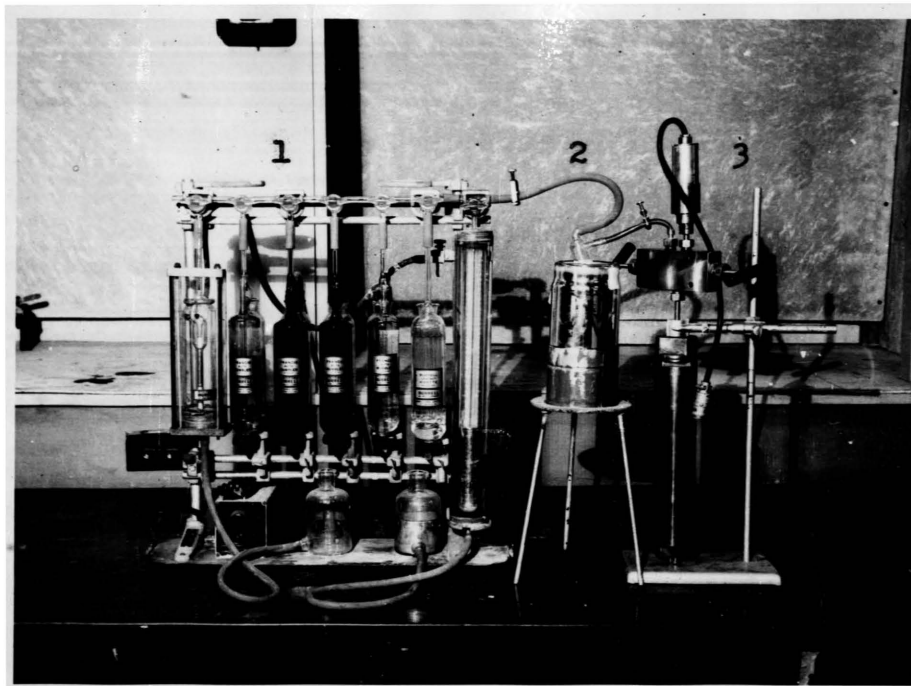Figure 6 illustrates the apparatus arrangement used for the gas analysis.

Figure 6

Apparatus used for gas analysis. Reading
from left to right: (1) Burrell Gas Analyzer,
(2) dry ice trap in mixture of dry ice and ace-
tone, and (3) stainless steel reactor and assembly.

PROCEDURE FOR ANALYSIS OF SOLID PRODUCTS

After making the gas analysis, the solid products were removed from the reactor and the reactor assembly by washing with four twenty-five milliliter portions of distilled water to insure the complete removal of the solid products formed from the reaction. The resulting solutions were placed in a one hundred twenty-five milliliter Erlenmeyer Flask.

The solutions for solids analysis were all obtained for the seven temperature determinations before being analyzed.

To a three hundred milliliter flask there was added thirty to thirty-five milliliters of standardized potassium permanganate solution, ten milliliters of one to four sulfuric acid, and seventy-five milliliters of distilled water. The sample to be analyzed was added dropwise with constant stirring to this solution. The one hundred twenty-five milliliter flask was washed with four portions of distilled water which were added to the three hundred milliliter flask. The flask was continuously stirred for several minutes to insure the complete oxidation of the nitrite ion to nitrate ion. The equation for the reaction being

$$2KMnO_4 + 3H_2SO_4 + 5NO_2^- = K_2SO_4 + 2MnSO_4 + 5NO_3^- + 3H_2O$$

The excess potassium permanganate solution was then titrated to the end point with standardized ferrous sulfate solution and several milliliters excess added. The excess ferrous sulfate solution was then titrated to the end point with

the potassium permanganate solution. The total volume of ferrous sulfate and potassium permanganate used was recorded.

This solution was then placed in a Kjeldahl Flask, and the flask containing the unknown sample was carefully washed and the washings added to the Kjeldahl Flask. To a three hundred milliliter flask there was added fifty milliliters of standardized hydrochloric acid, fifty milliliters of distilled water, and four drops of methyl red indicator. This solution was then placed at the receiving end of a water cooled condenser, the end of which was placed below the solution level to insure complete absorption of expelled ammonia from the unknown sample. A Kjeldahl Trap was then connected to the water cooled condenser and the cooling water turned on.

To the Kjeldahl Flask there was added approximately twenty grams of sodium hydroxide pellets to insure the formation of a basic solution. The Kjeldahl Flask was quickly connected to the water condenser by means of the trap and the sodium hydroxide allowed to dissolve. The Kjeldahl Flask was then gently heated until the contents began to boil. This solution was then heated for one-half hour to remove all the ammonia which may have been present in the solution. After one-half hour the collecting flask was lowered until the end of the condenser was above the solution level, the Bunsen Burner was removed from below the Kjeldahl Flask and the contents allowed to cool for at least fifteen minutes.

The Kjeldahl Trap was then removed and cleaned with distilled water for the next determination. The Kjeldahl Flask was tested for complete removal of ammonia by smelling the vapors from the solution.

The receiving flask was removed and marked as the ammonia analysis.

To the Kjeldahl Flask there was added approximately twenty more grams of sodium hydroxide pellets, which were then dissolved and the solution allowed to cool. During this time a second receiving flask was prepared as previously described, attached to the condenser and the Kjeldahl Trap put in place. Next, two grams of pure aluminum were added to the Kjeldahl Flask and the flask quickly attached to the Kjeldahl Trap. The aluminum was then allowed to thoroughly dissolve. After the aluminum had dissolved, the flask and contents were gently heated until the contents began to boil. The contents of the flask were then boiled for one-half hour to remove all possible traces of ammonia.

It should be noted at this point that the addition of aluminum to the basic solution converted the nitrate ion to ammonia which was distilled over and collected in the receiving solution, the equations being

$$2Al + 6NaOH = 2Na_3AlO_3 + 3H_2$$

and

$$NO_3^- + 3H^+ = NH_3 + 3O.$$
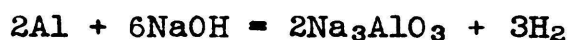
After one-half hour the receiving flask was lowered and the Kjeldahl Flask allowed to cool. The condenser was rinsed with distilled water and the receiving solution

marked as the nitrate ion determination.

The Kjeldahl Flask and Trap were removed from the system, cleaned with distilled water, and assembled for another unknown sample determination.

The solutions marked ammonium and nitrate ion analysis were titrated to a yellow end point with standardized sodium hydroxide, the volume required for each solution being recorded.

The results of all titrations are shown in tabulated data.

TABLE 1

REACTION PRODUCTS OF NO_2-NH_3 REACTIONS

Note: See page 40, item 12, for units on table.

Run No.	Reactants A NO_2	Reactants B NH_3	Ratio C NO_2/NH_3	D % N_2	E % O_2	F % NO	G % N_2O
A_5	8.730	10.400	0.8407	93.90	2.63	0.00	3.47
A_6	7.780	8.810	0.8829	77.86	0.00	19.28	2.86
A_8	7.710	12.000	0.6419	79.05	0.89	17.67	2.39
B_{13}	8.670	9.320	0.9299	91.22	0.00	4.88	3.90
B_{14}	9.760	9.710	1.0040	89.19	0.00	9.66	1.15
B_{15}	6.545	11.680	0.5615	85.57	0.00	12.37	2.06
C_{10}	8.130	9.570	0.8499	96.45	1.01	0.50	2.04
C_{11}	8.393	9.823	0.8541	85.17	0.00	14.35	0.48
C_{12}	7.126	10.410	0.6841	81.15	5.46	12.56	0.83
D_{10}	4.820	5.200	0.9277	90.34	0.00	9.66	0.00
D_{11}	6.932	5.637	1.2290	97.79	0.00	1.57	0.64
D_{12}	5.956	7.017	0.8480	83.34	4.26	11.63	0.77
E_7	7.758	7.404	1.0476	96.05	0.00	2.19	1.76
E_8	7.258	8.103	0.8955	98.68	0.00	0.00	1.32
E_9	11.770	10.520	1.1180	92.99	1.32	4.47	1.22
F_8	6.358	9.307	0.6830	93.80	0.00	0.69	5.51
F_9	6.330	9.271	0.6826	84.46	0.00	14.32	1.22
F_{10}	6.706	9.377	0.4394	60.98	0.00	38.32	0.70
G_1	6.265	9.307	0.6730	98.43	0.98	0.00	0.59
G_2	5.541	9.113	0.6078	71.38	0.00	27.11	1.51
G_3	6.823	8.637	0.7896	88.50	0.00	10.00	1.50

TABLE 1 (continued)

REACTION PRODUCTS OF NO_2-NH_3 REACTIONS

Run No.	Reaction Solid Products			Total
	H	I	J	K
	NO_2^-	NO_3^-	NH_4^+	$NO_2^- + NO_3^-$
A_5	1.164	2.712	6.176	3.876
A_6	1.257	3.314	7.444	4.571
A_8	1.164	3.708	9.104	4.872
B_{13}	1.093	3.875	5.640	4.968
B_{14}	1.460	3.925	6.604	5.385
B_{15}	1.029	3.185	6.491	4.214
C_{10}	0.795	2.320	3.460	3.115
C_{11}	1.106	4.235	6.155	5.341
C_{12}	0.976	2.783	5.309	3.759
D_{10}	0.036	4.419	2.739	4.455
D_{11}	0.628	2.636	3.278	3.264
D_{12}	0.669	2.168	4.669	2.837
E_7	0.612	2.157	3.759	2.770
E_8	0.670	2.426	5.123	3.096
E_9	0.910	1.067	2.694	1.977
F_8	0.865	2.063	4.256	2.928
F_9	0.755	2.553	4.237	3.308
F_{10}	0.978	2.224	4.545	3.202
G_1	0.315	2.289	2.928	2.604
G_2	0.667	1.643	3.258	2.310
G_3	0.667	1.729	3.400	2.407

TABLE 2

MATERIAL BALANCE OF GASEOUS PRODUCTS

Note: See page 40, item 12, for units on table.

Run No.	Reactants A NO$_2$	Reactants B NH$_3$	Excess Reactant C NO$_2$	Excess Reactant D NH$_3$	Excess E N$_2$	Excess F H$_2$
A$_5$	8.730	10.400	0.000	1.670	0.835	2.505
A$_6$	7.780	8.810	0.000	1.030	0.515	1.545
A$_8$	7.710	12.000	0.000	4.290	2.145	6.435
B$_{13}$	8.670	9.320	0.000	0.650	0.325	0.975
B$_{14}$	9.760	9.710	0.050	0.000	0.025	0.000
B$_{15}$	6.545	11.680	0.000	5.135	2.568	7.703
C$_{10}$	8.130	9.570	0.000	1.440	0.720	2.160
C$_{11}$	8.393	9.823	0.000	1.430	0.715	2.145
C$_{12}$	7.126	10.410	0.000	3.284	1.642	4.926
D$_{10}$	4.820	5.200	--	--	--	--
D$_{11}$	6.932	5.637	1.295	0.000	0.648	0.000
D$_{12}$	5.956	7.017	0.000	1.061	0.531	1.592
E$_7$	7.758	7.404	0.354	0.000	0.177	0.000
E$_8$	7.258	8.103	0.000	0.845	0.423	1.268
E$_9$	11.770	10.520	1.250	0.000	0.625	0.000
F$_8$	6.358	9.307	0.000	2.949	1.475	4.424
F$_9$	6.330	9.271	0.000	2.941	1.471	4.412
F$_{10}$	6.706	9.377	0.000	2.671	1.336	4.007
G$_1$	6.265	9.307	0.000	3.042	1.521	4.563
G$_2$	5.541	9.113	0.000	3.572	1.786	5.358
G$_3$	6.823	8.637	0.000	1.814	0.907	2.721

TABLE 2 (continued)

MATERIAL BALANCE OF GASEOUS PRODUCTS

Run No.	H2 In G Solids	H2 H In H_2O	H2 I Entering	N2 J Entering	H2 Available K For Reaction
A_5	7.752	5.343	15.600	9.565	13.095
A_6	9.141	2.534	13.220	8.295	11.675
A_8	9.744	1.821	18.000	9.855	11.565
B_{13}	9.937	3.068	13.980	8.995	13.005
B_{14}	10.770	3.795	14.565	9.735	14.565
B_{15}	8.428	1.389	17.520	9.113	9.817
C_{10}	6.229	5.966	14.355	8.850	12.195
C_{11}	10.681	1.904	14.735	9.108	12.590
C_{12}	7.517	3.172	15.615	8.768	10.689
D_{10}	--	--	--	--	--
D_{11}	6.528	1.928	8.456	6.932	8.456
D_{12}	5.673	3.261	10.526	6.487	8.934
E_7	5.539	5.567	11.106	7.581	11.106
E_8	6.193	4.694	12.155	7.681	10.887
E_9	3.952	11.828	15.780	11.145	15.780
F_8	5.857	3.680	13.961	7.833	9.537
F_9	6.616	2.879	13.907	7.801	9.495
F_{10}	6.404	3.655	14.066	8.043	10.059
G_1	5.208	4.190	13.961	7.786	9.398
G_2	4.619	3.693	13.670	7.327	8.312
G_3	4.813	5.422	12.956	7.730	10.235

TABLE 2 (continued)

MATERIAL BALANCE OF GASEOUS PRODUCTS

Run No.	O_2 In M H$_2$O	N_2 Available N For Reaction	N_2 In Gas O Phase	Total Gaseous P Products
A_5	2.672	8.730	4.854	5.168
A_6	1.267	7.780	3.209	4.122
A_8	0.911	7.710	2.838	3.732
B_{13}	1.534	8.670	3.702	3.058
B_{14}	1.898	9.710	4.325	4.684
B_{15}	0.695	6.545	2.331	2.724
C_{10}	2.983	8.130	5.015	5.199
C_{11}	0.955	8.393	3.052	3.584
C_{12}	1.586	7.126	3.367	4.149
D_{10}	--	--	--	--
D_{11}	0.964	6.284	2.373	2.485
D_{12}	1.631	5.956	3.120	3.744
E_7	2.784	7.464	4.694	4.324
E_8	2.347	7.258	4.162	4.218
E_9	5.914	10.520	8.544	7.943
F_8	1.840	6.358	3.430	3.657
F_9	1.439	6.330	3.022	3.578
F_{10}	1.828	6.707	3.505	5.748
G_1	2.095	6.265	3.661	3.719
G_2	1.847	5.541	3.231	4.526
G_3	2.711	6.823	4.417	4.991

TABLE 3

MATERIAL BALANCE OF REACTANTS, SOLIDS ANALYSIS,

AND REMAINING GASEOUS PRODUCTS

Note: See page 40, item 12, for units on table.

Run No.	Reactants		Total	Entering Elements		
	A	B	C	D	E	F
	NO_2	NH_3	A + B	N_2	O_2	H_2
A_5	8.730	10.400	19.130	9.565	8.730	15.600
A_6	7.780	8.810	16.590	8.295	7.780	13.220
A_8	7.710	12.000	19.710	9.855	7.710	18.000
B_{13}	8.670	9.320	17.990	8.995	8.670	13.980
B_{14}	9.760	9.710	19.470	9.735	9.760	14.565
B_{15}	6.545	11.680	18.255	9.113	6.545	17.520
C_{10}	8.130	9.570	17.700	8.850	8.130	14.355
C_{11}	8.393	9.823	18.210	9.108	8.393	14.735
C_{12}	7.126	10.410	17.536	8.768	7.126	15.615
D_{10}	4.820	5.200	10.020	5.010	4.820	7.800
D_{11}	6.932	5.637	12.569	6.285	6.932	8.456
D_{12}	5.956	7.017	12.973	6.487	5.956	10.526
E_7	7.758	7.404	15.162	7.581	7.758	11.106
E_8	7.258	8.103	15.361	7.681	7.258	12.155
E_9	11.770	10.520	22.290	11.145	11.770	15.780
F_8	6.358	9.307	15.665	7.833	6.358	13.961
F_9	6.330	9.271	15.601	7.801	6.330	13.907
F_{10}	6.706	9.377	16.083	8.043	6.706	14.066
G_1	6.265	9.307	15.572	7.786	6.265	13.961
G_2	5.541	9.113	14.654	7.327	5.541	13.670
G_3	6.823	8.637	15.460	7.730	6.823	12.956

TABLE 3 (continued)

MATERIAL BALANCE OF REACTANTS, SOLIDS ANALYSIS,
AND REMEINING GASEOUS PRODUCTS

Run No.	Solids		Solids Analysis		
	G	H	I	J	K
	NH_4NO_3	NH_4NO_2	N_2	O_2	H_2
A_5	2.712	1.164	3.876	5.232	7.752
A_6	3.314	1.257	4.571	6.227	9.141
A_8	3.708	1.164	4.872	6.726	9.744
B_{13}	3.875	1.093	4.968	6.906	9.937
B_{14}	3.925	1.460	5.385	7.347	10.770
B_{15}	3.185	1.029	4.214	5.807	8.428
C_{10}	2.320	0.795	3.115	4.275	6.229
C_{11}	4.235	1.106	5.341	7.458	10.681
C_{12}	2.783	0.976	3.759	5.150	7.517
D_{10}	4.419	0.036	4.455	6.665	8.910
D_{11}	2.636	0.628	3.264	4.582	6.528
D_{12}	2.168	0.669	2.836	3.920	5.673
E_7	2.157	0.612	2.770	3.848	5.539
E_8	2.426	0.670	3.096	4.309	6.193
E_9	1.067	0.910	1.976	2.509	3.952
F_8	2.063	0.865	2.928	3.960	5.857
F_9	2.553	0.755	3.308	4.584	6.616
F_{10}	2.224	0.978	3.202	4.314	6.404
G_1	2.289	0.315	2.604	3.749	5.208
G_2	1.643	0.667	2.310	3.131	4.619
G_3	1.729	0.677	2.406	3.271	4.813

TABLE 3 (continued)

MATERIAL BALANCE OF REACTANTS, SOLIDS ANALYSIS,
AND REMAINING GASEOUS PRODUCTS

Run No.	Elements Remaining In Gaseous Products		
	L N_2	M O_2	N H_2
A_5	5.689	3.498	7.848
A_6	3.724	1.553	4.079
A_8	4.983	0.984	8.256
B_{13}	4.027	1.764	4.043
B_{14}	4.350	2.413	3.795
B_{15}	4.899	0.738	9.092
C_{10}	5.735	3.855	8.126
C_{11}	3.767	0.935	4.054
C_{12}	5.009	1.976	8.098
D_{10}	0.555	-1.845	-1.110
D_{11}	3.021	2.350	1.928
D_{12}	3.651	2.036	4.853
E_7	4.811	3.910	5.567
E_8	4.585	2.949	5.962
E_9	9.169	9.261	11.828
F_8	4.905	2.398	8.104
F_9	4.493	1.746	7.291
F_{10}	4.841	2.392	7.662
G_1	5.182	2.516	8.753
G_2	5.017	2.410	9.051
G_3	5.324	3.552	8.143

TABLE 4

MATERIAL BALANCE OF OVERALL REACTION

Note: See page 40, item 12, for units on table.

Run No.	Reactants		Total	Gaseous Products		
	A	B	C	D	E	F
	NO_2	NH_3	Gaseous Products	% N_2	N_2	% O_2
A_5	8.730	10.400	5.168	93.90	4.854	2.63
A_6	7.780	8.810	4.122	77.86	3.208	0.00
A_8	7.710	12.000	3.732	79.05	2.951	0.89
B_{13}	8.670	9.320	4.058	91.22	3.702	0.00
B_{14}	9.760	9.710	4.684	89.19	4.178	0.00
B_{15}	6.545	11.680	2.724	85.57	2.331	0.00
C_{10}	8.130	9.570	5.199	96.45	4.937	1.01
C_{11}	8.393	9.823	3.584	85.17	3.053	0.00
C_{12}	7.126	10.410	4.149	81.15	3.367	5.46
D_{10}	4.820	5.200	--	90.34	--	0.00
D_{11}	6.932	5.637	2.485	97.79	2.430	0.00
D_{12}	5.956	7.017	3.744	83.34	3.120	4.26
E_7	7.758	7.404	4.324	96.05	4.155	0.00
E_8	7.258	8.103	4.218	98.68	4.163	0.00
E_9	11.770	10.520	7.943	92.99	7.386	1.32
F_8	6.358	9.307	3.657	98.80	3.431	0.00
F_9	6.330	9.271	3.578	84.46	3.022	0.00
F_{10}	6.706	9.377	5.748	60.98	3.505	0.00
G_1	6.265	9.307	3.719	98.43	3.661	0.98
G_2	5.541	9.113	4.526	71.38	3.231	0.00
G_3	6.823	8.637	4.991	88.50	4.417	0.00

TABLE 4 (continued)

MATERIAL BALANCE OF OVERALL REACTION

Run No.	Gaseous Products				
	G O_2	H % NO	I NO	J % N_2O	K N_2O
A_5	0.136	0.00	0.000	3.47	0.179
A_6	0.000	19.28	0.794	2.86	0.118
A_8	0.033	17.67	0.659	2.39	0.089
B_{13}	0.000	4.88	0.198	3.90	0.158
B_{14}	0.000	9.66	0.453	1.15	0.054
B_{15}	0.000	12.37	0.337	2.06	0.056
C_{10}	0.052	0.50	0.026	2.04	0.104
C_{11}	0.000	14.35	0.514	0.48	0.017
C_{12}	0.226	12.56	0.522	0.83	0.034
D_{10}	--	9.66	--	0.00	--
D_{11}	0.000	1.57	0.039	0.64	0.016
D_{12}	0.159	11.63	0.436	0.77	0.029
E_7	0.000	2.19	0.095	1.76	0.074
E_8	0.000	0.00	0.000	1.32	0.055
E_9	0.105	4.47	0.355	1.22	0.097
F_8	0.000	0.69	0.025	5.51	0.201
F_9	0.000	14.32	0.512	1.22	0.044
F_{10}	0.000	38.32	2.203	0.70	0.040
G_1	0.036	0.00	0.000	0.59	0.022
G_2	0.000	27.11	1.227	1.51	0.068
G_3	0.000	10.00	0.499	1.50	0.075

TABLE 4 (continued)

MATERIAL BALANCE OF OVERALL REACTION

| Run No. | Excess Reactant | | Solid Products | | P |
| | L | M | N | O | |
	NO_2	NH_3	NH_4NO_3	NH_4NO_2	H_2O
A_5	0.000	1.670	2.712	1.164	5.343
A_6	0.000	1.030	3.314	1.257	2.534
A_8	0.000	4.290	3.708	1.164	1.821
B_{13}	0.000	0.650	3.875	1.093	3.068
B_{14}	0.050	0.000	3.925	1.460	3.795
B_{15}	0.000	5.135	3.185	1.029	1.389
C_{10}	0.000	1.440	2.320	0.795	5.966
C_{11}	0.000	1.430	4.235	1.106	1.904
C_{12}	0.000	3.284	2.783	0.976	3.172
D_{10}	0.000	0.380	4.419	0.036	--
D_{11}	1.295	0.000	2.636	0.628	1.928
D_{12}	0.000	1.061	2.168	0.669	3.261
E_7	0.354	0.000	2.157	0.612	5.567
E_8	0.000	0.845	2.426	0.670	4.694
E_9	1.250	0.000	1.067	0.910	11.828
F_8	0.000	2.949	2.063	0.865	3.680
F_9	0.000	2.941	2.553	0.755	2.879
F_{10}	0.000	2.671	2.224	0.978	3.655
G_1	0.000	3.042	2.289	0.315	4.190
G_2	0.000	3.572	1.643	0.667	3.693
G_3	0.000	1.814	1.729	0.677	5.422

NOMENCLATURE FOR TABLES AND PHOTOGRAPHS

(1)   Runs A_5, A_6, and A_8 were made at a temperature of 35°C.

(2)   Runs B_{13}, B_{14}, and B_{15} were made at a temperature of 45°C.

(3)   Runs C_{10}, C_{11}, and C_{12} were made at a temperature of 55°C.

(4)   Runs D_{10}, D_{11}, and D_{12} were made at a temperature of 65°C.

(5)   Runs E_7, E_8, and E_9 were made at a temperature of 75°C.

(6)   Runs F_8, F_9, and F_{10} were made at a temperature of 85°C.

(7)   Runs G_1, G_2, and G_3 were made at a temperature of 93°C.

(8)   Run 1 was made at a temperature of 35°C.

(9)   Run 2 was made at a temperature of 60°C.

(10)   Runs 3 and 4 were made at a temperature of 85°C.

(11)   Capitol letters at the head of each column of a table refer only to that column.

(12)   The units for Tables 1, 2, 3, and 4 are in millimoles except those columns which are marked as percent of an element. The percent of an element, in the gaseous product, is reported as percent by volume. Calculations for converting percent by volume to milli-

NOMENCLATURE FOR TABLES AND PHOTOGRAPHS (cont.)

moles are shown in the METHOD OF CALCULATIONS.

(13) In Table 1, columns H, I, and J were obtained by the Kjeldahl method of analysis.

(14) Column P, Table 2 for Total Gaseous Products does not include the amount of Excess Reactant present in the gas phase. The Excess Reactant present was determined by assuming equal millimoles of nitrogen dioxide and ammonia reacted. Refer to Table 2, Columns C and D.

(15) The results of the nitrite and nitrate ion determinations, Columns H and I, Table 1, were used as the basis of calculations for Tables 2, 3, and 4.

(16) Water formed as a result of the reaction, Column H, Table 2, was calculated by assuming H_2 not present in the solids or excess reactant was present as water.

(17) Run D_{10} was not completed for calculations as preliminary calculations indicated more oxygen and hydrogen were present in the solid products than that which was available for reaction.

METHOD OF CALCULATIONS

Sample calculations for runs in which NH_3 was in excess in Table 2.

Run A_5: NO_2 = 8.730 NH_3 = 10.400 N_2 = 93.90%

excess NH_3 = 10.400 − 8.730 = 1.670

excess N_2 = 1.670/2 = 0.835

excess H_2 = (1.670)(1.5) = 2.505

H_2 in solids (Table 3) = 7.752

H_2 entering (Table 3) = 15.600

N_2 entering (Table 3) = 9.565

Calculations:

H_2 available for reaction = 15.600 − 2.505 = 13.095

H_2 in water = 13.095 − 7.752 = 5.343

O_2 in water = 5.343/2 = 2.672

N_2 available for reaction = 9.565 − 0.835 = 8.730

N_2 in gaseous product (except N_2 in excess NH_3) =

$$8.730 - 3.876 = 4.854$$

total gaseous product = 4.854/0.939 = 5.168

* All units in METHOD OF CALCULATION are in millimoles except N_2 reported as %, which is % by volume.

By multiplying the amount of the total gaseous product by the percent of each element as reported in the gas phase, the amount of each element, by weight is found. Refer to Table 4 for complete analysis of the gaseous product as reported in weight units.

METHOD OF CALCULATIONS

Sample calculations for runs in which NO_2 was in excess in Table 2.

Run B_{14}:

reactants: NO_2 = 9.760 NH_3 = 9.710

gas analysis: N_2 = 89.19% O_2 = 0.00%

NO = 9.66% N_2O = 1.15%

O_2 in gas phase (Table 3, after reaction) = 2.413

O_2 balance:

O_2 entering reaction (Table 3) = 9.760

O_2 in solids after reaction (Table 3) = 7.347

O_2 in H_2O (Table 3) = 1.898

O_2 in gases other than H_2O =

$$9.760 - 7.347 - 1.898 = 0.515$$

N_2 balance:

N_2 entering reaction (Table 3) = 9.735

N_2 in solids after reaction (Table 3) = 5.385

N_2 in gas phase (Table 3, after reaction) = 4.350

calculation of N_2, N_2O, NO, NO_2, and O_2 in gas phase after reaction (except excess NO_2):

$$O_2 \text{ balance} = 0.515 = (0 + \frac{0.015}{2} + \frac{0.0966}{2})X + Y$$

$$N_2 \text{ balance} = 4.350 = (0.8919 + 0.0115 + \frac{0.0966}{2})X + \frac{Y}{2}$$

where: X is the total amount of NO_2 free gas phase,

Y is the total amount of NO_2 in excess.

METHOD OF CALCULATIONS (continued)

Solving the above equations, the total amount of gas phase (except NO_2) was found to be as follows:

$$X = 4.684$$

By multiplying the value of X by the percents of the elements as reported in the gas phase, the amount of each element, by weight, is found. Refer to Table 4 for complete analysis of the gaseous product as reported in weight units.

* All units in METHOD OF CALCULATIONS are in millimoles except the gas analysis reported as %, which is % by volume.

RESULTS

Twenty-one rapid rate determinations of nitrogen dioxide and ammonia were successfully completed. A temperature range of 35-93°C was covered, three determinations being made at each temperature; twenty material balances were calculated on the reaction. The tabulated data are shown in Tables 1 to 4..

A visual inspection of the solid products formed after each reaction showed a white colored product deposited on the ampoule breaker and the inside of the reactor. This product was found to be readily soluble in water.

A white cloud was observed to be suspended in the gaseous reaction products when a sample of the gaseous products was being removed from the stainless steel reactor prior to making the gas analysis. The white cloud suspension was removed from the gas stream by the dry ice trap; no attempt was made to analyze the product.

The products formed from the reaction of nitrogen dioxide and ammonia are primarily nitrogen, ammonium nitrate, and water. The amount of nitrogen formed in the gaseous products was found to increase slightly with an increase in the temperature of the reaction. The amount of nitric oxide formed in the gaseous product was found to vary considerably with temperature, and in some cases to form a greater percent at the higher temperatures than at the lower temperatures. The amount of nitrous oxide formed in the reaction was found to decrease with an increase in temperature.

Ammonium nitrate was formed in the solid products at

all temperatures but the amount decreased with an increase
in temperature. This was also found to be true for the
amount of ammonium nitrate formed.

The water formed in the reaction varies considerable
over the entire temperature range. A greater quantity of
water is formed at higher temperatures than at lower tem-
peratures.

The following photographs correspond to runs in which
the products of the reaction were analyzed. The axes are
labeled as P and T where P refers to the Y axis and denotes
pressure units in psi. T refers to the X axis and denotes
sweep time in inches per second.

Run A8   Ratio NO2/NH3 = 0.6419
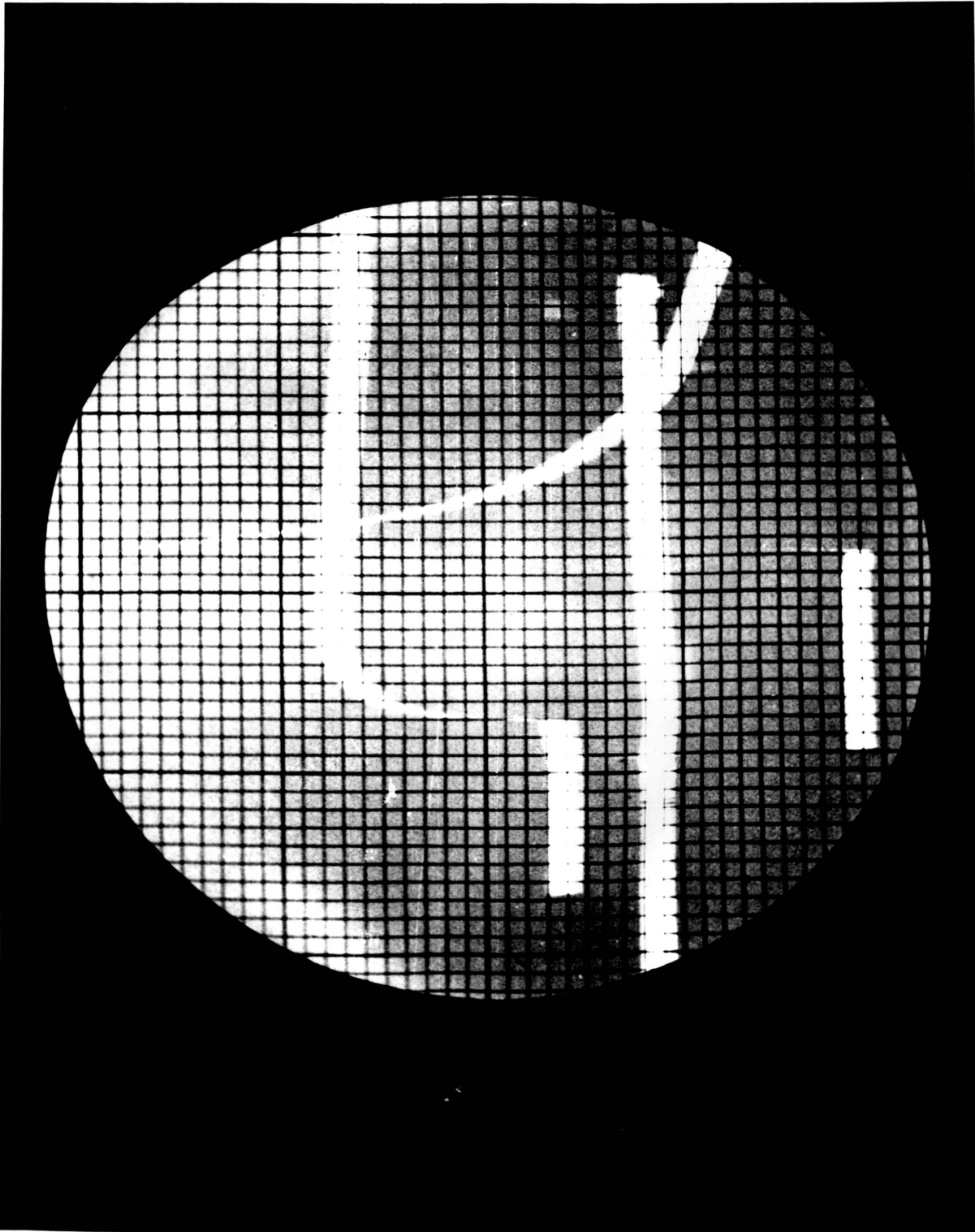
Run B₁₅   Ratio NO₂/NH₃ = 0.6515
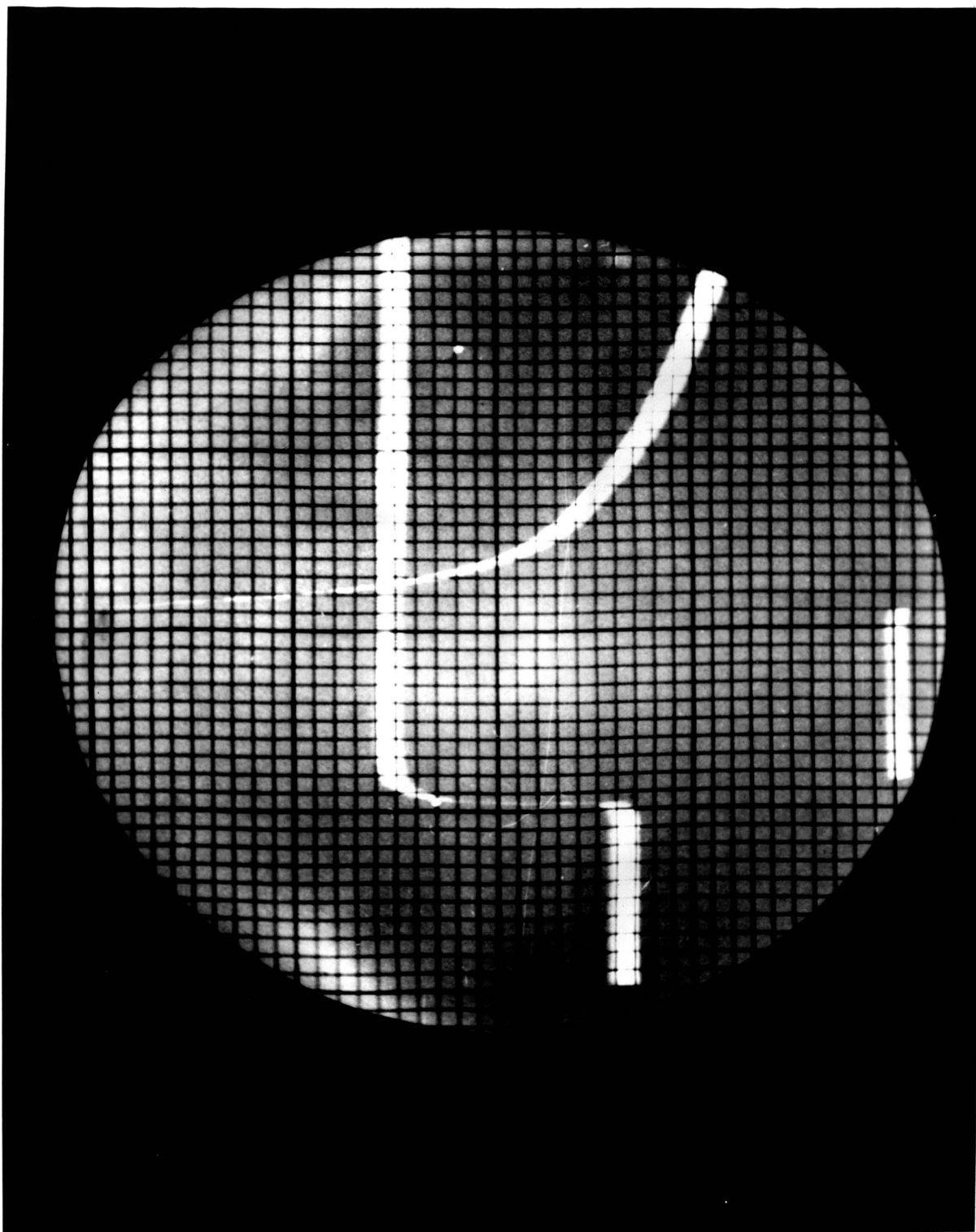
P

Run C_{12} Ratio $NO_2/NH_3 = 0.6841$
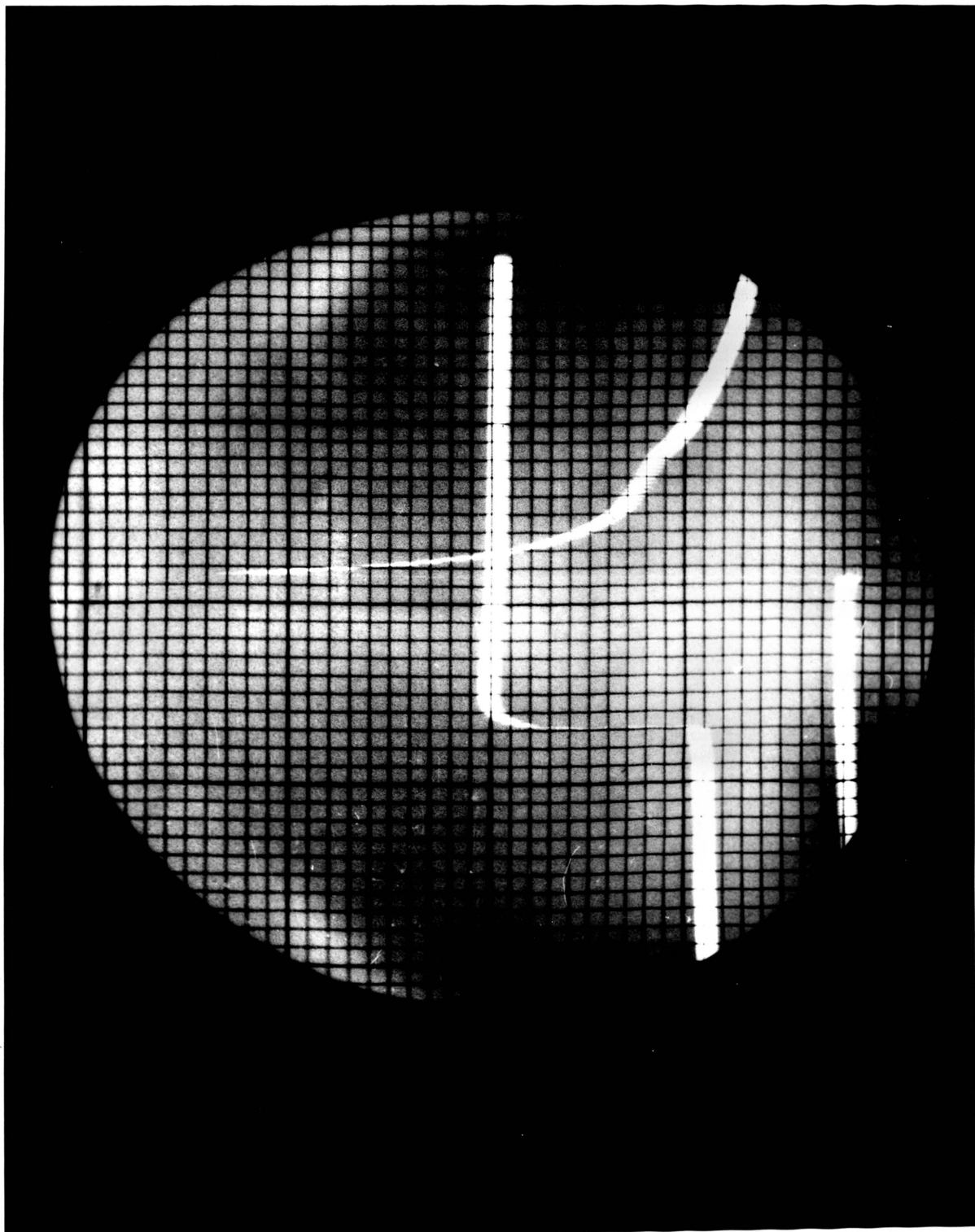
Run D_{11} Ratio NO_2/NH_3 = 1.2290
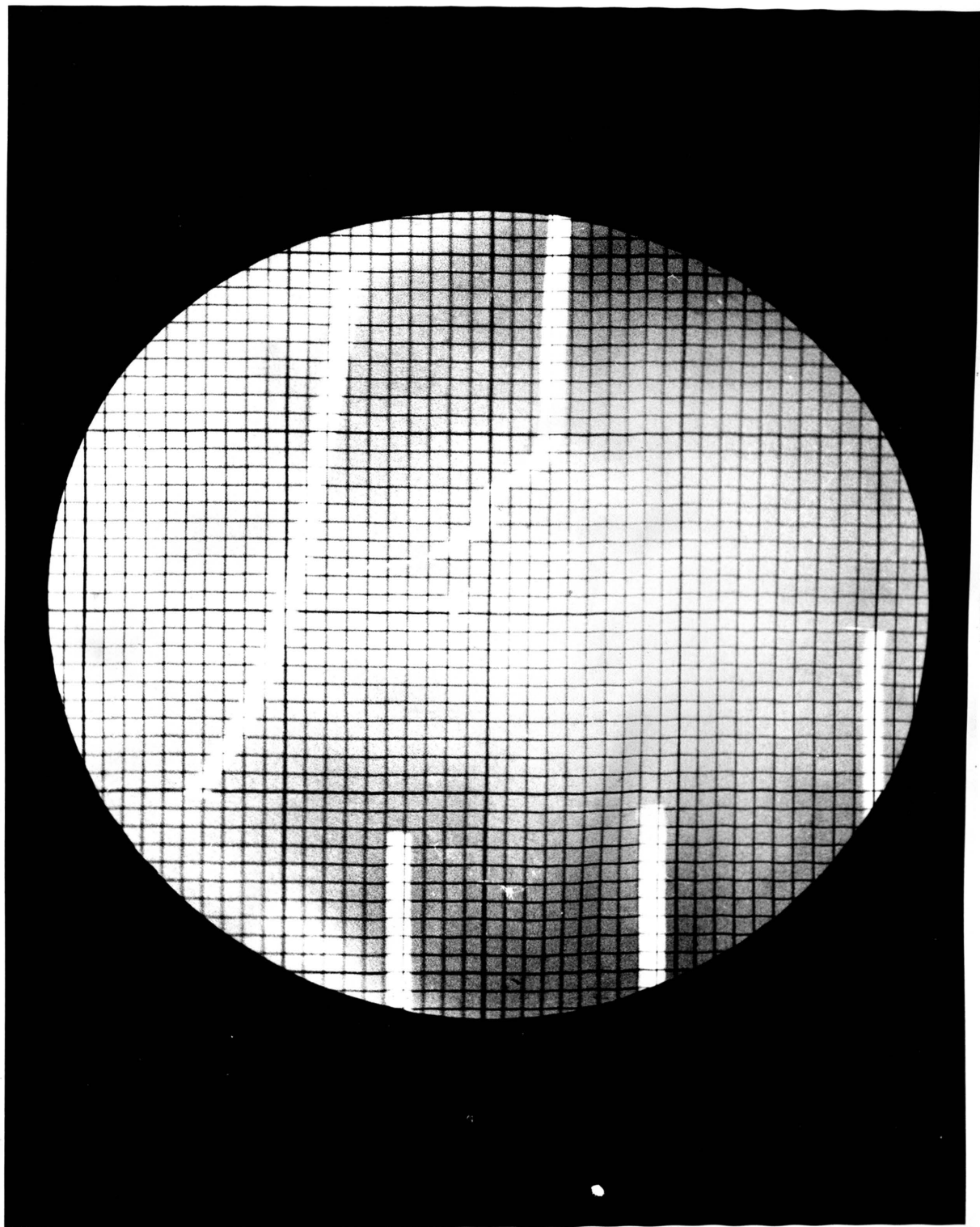
Run D_{12} Ratio $NO_2/NH_3 = 0.8480$
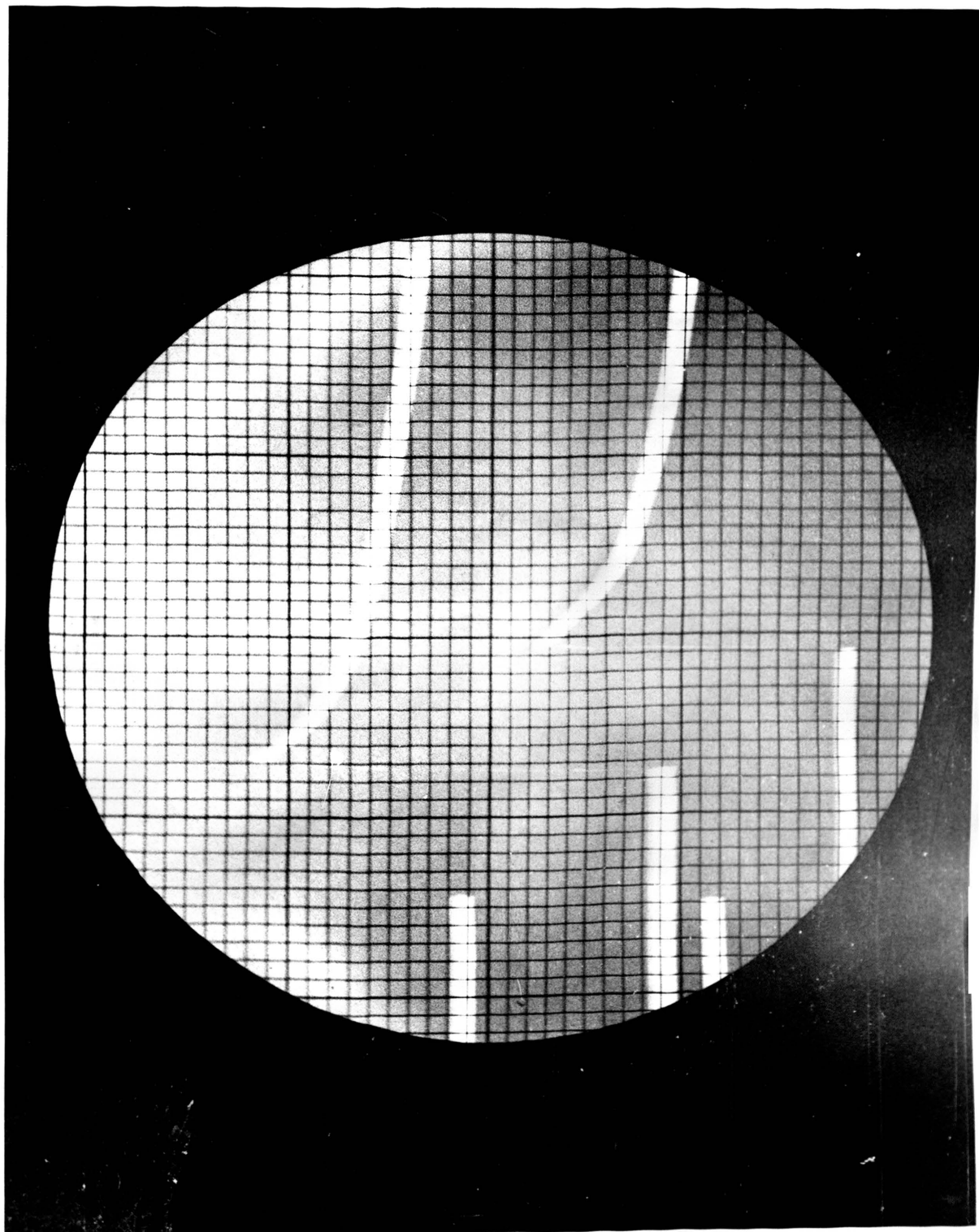
Run E$_8$ Ratio NO$_2$/NH$_3$ = 0.8955

T

P

Run F_{10} Ratio NO_2/NH_3 = 0.4394
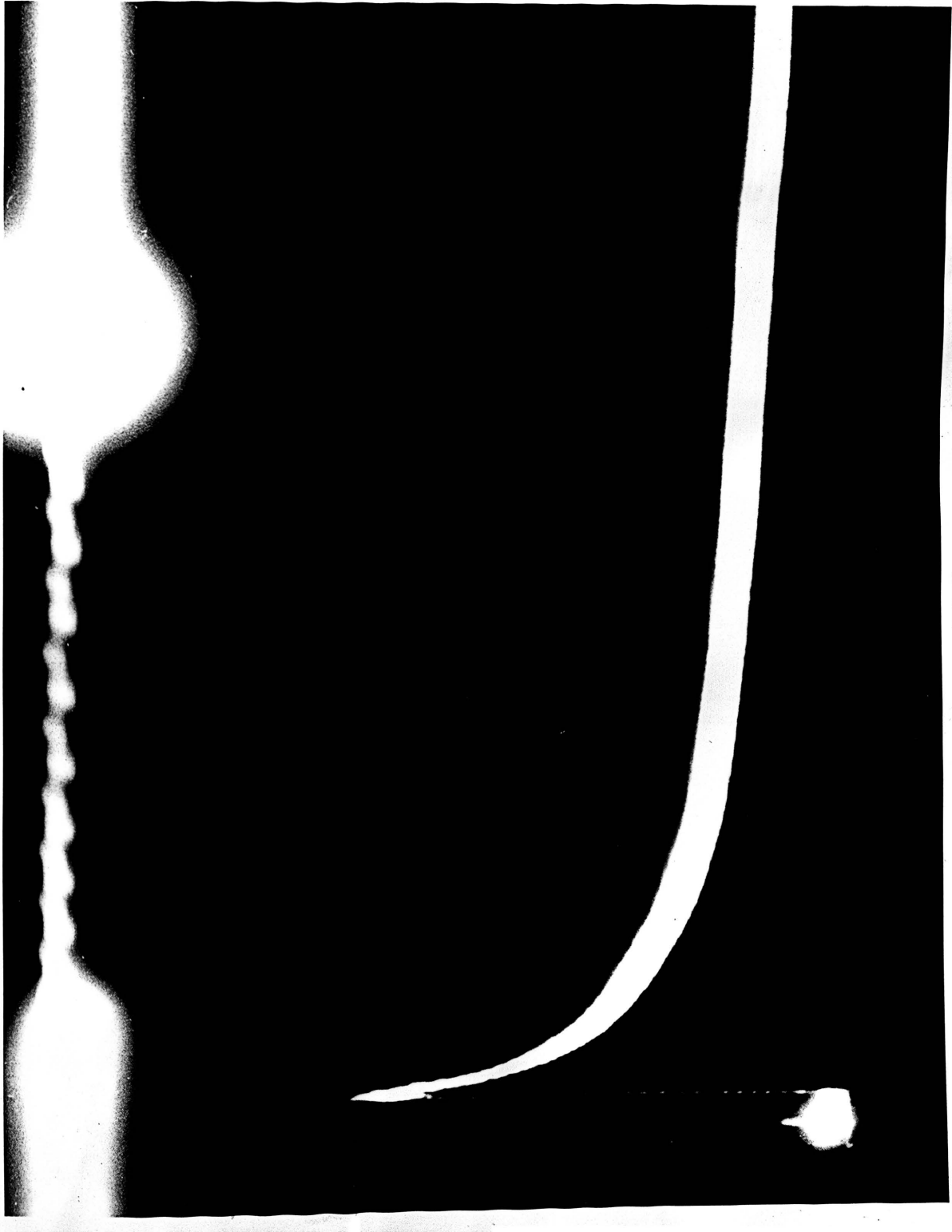
Run G_1 Ratio NO_2/NH_3 = 0.6730
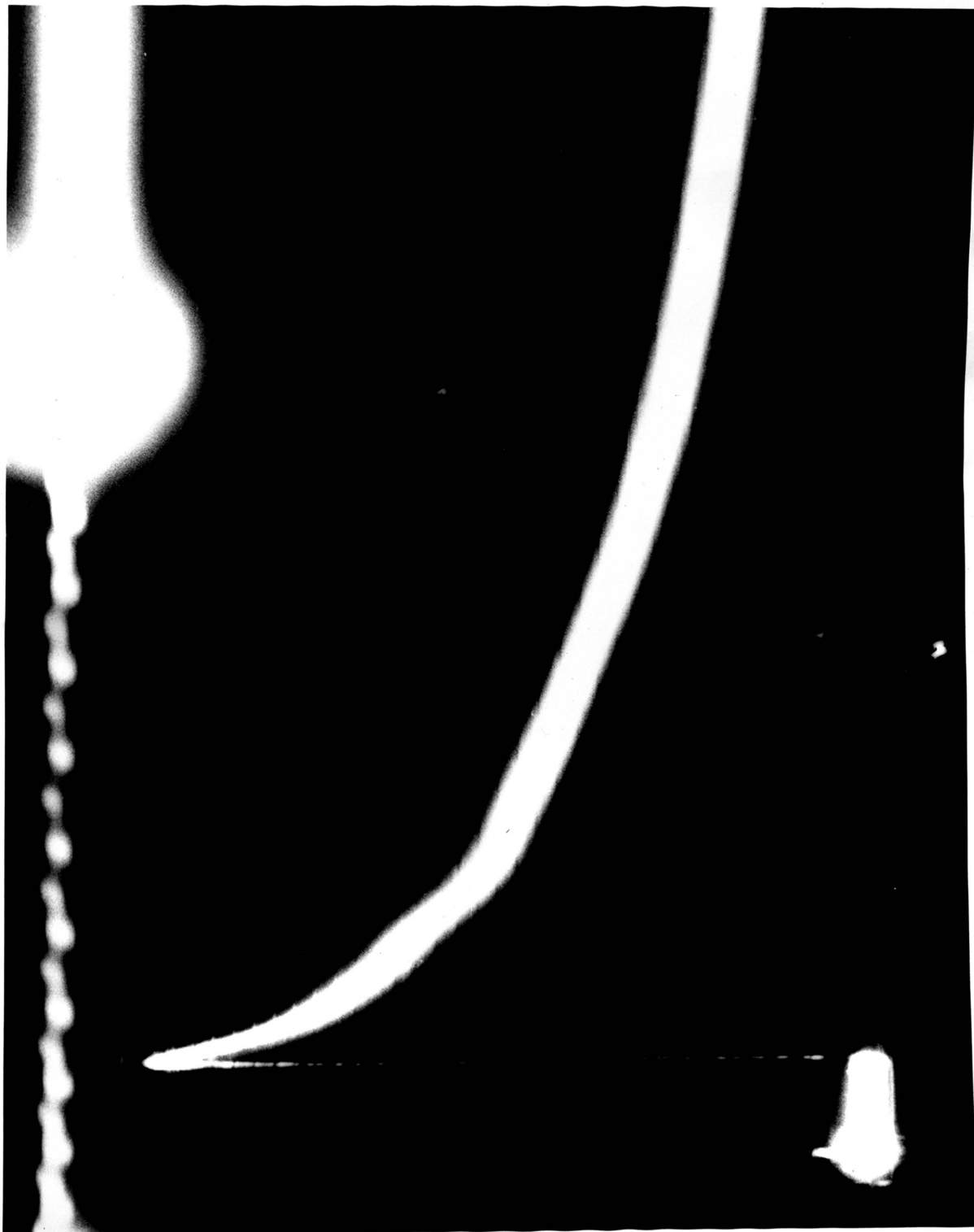
P

Run 1   Ratio NO_2/NH_3 = 0.6141
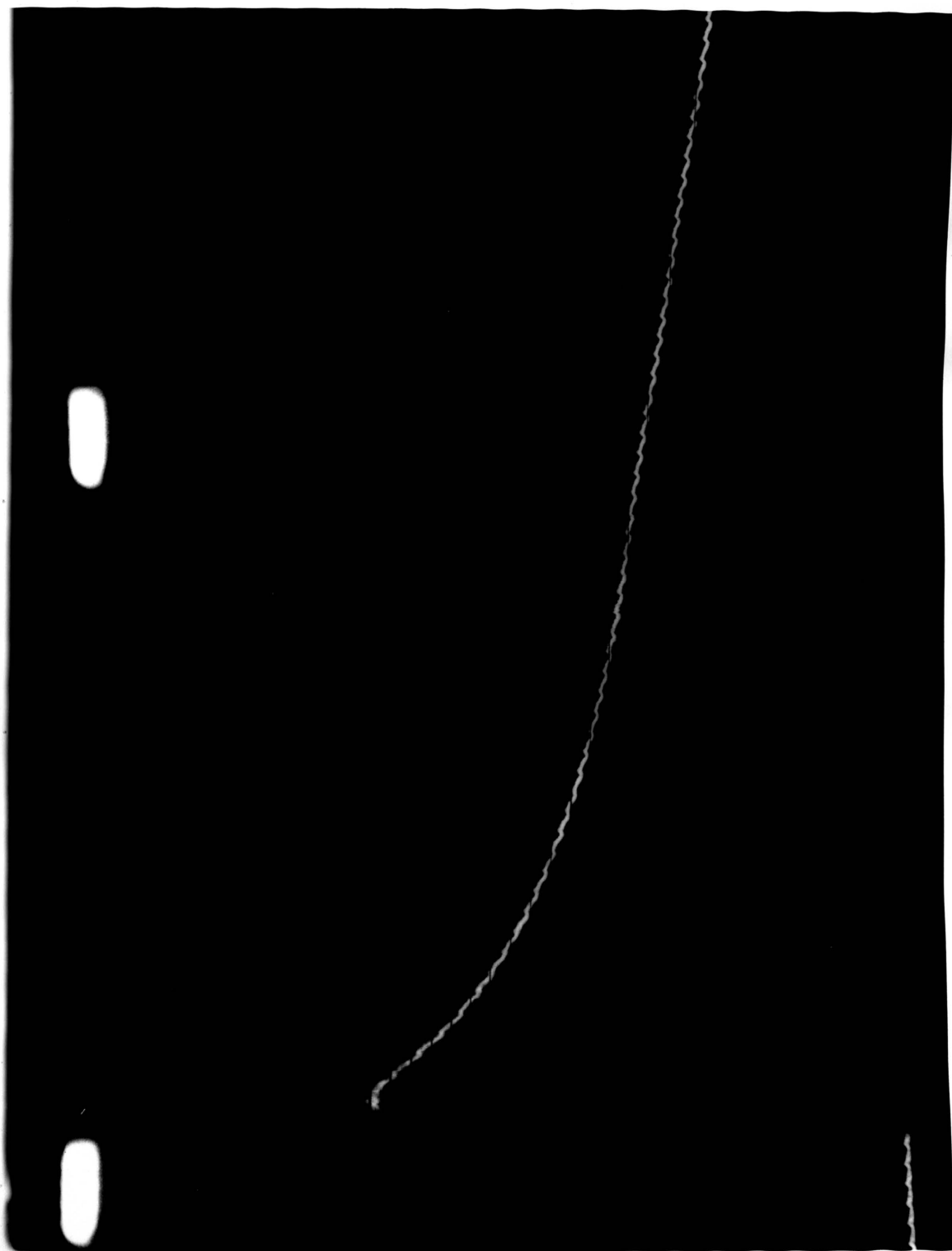
Run 2   Ratio NO_2/NH_3 = 0.6315

P
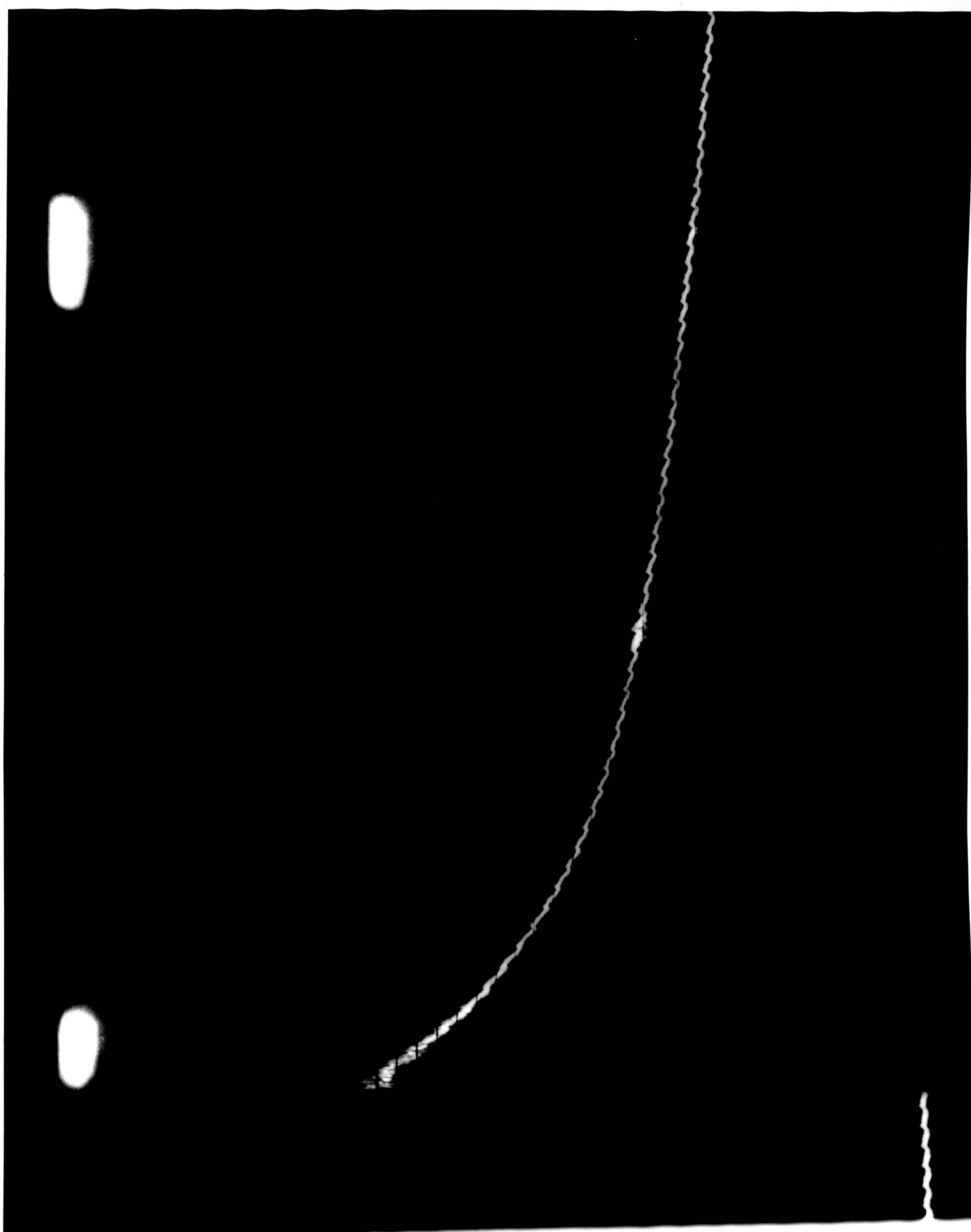
Run 3   Ratio NO_2/NH_3 = 0.6745
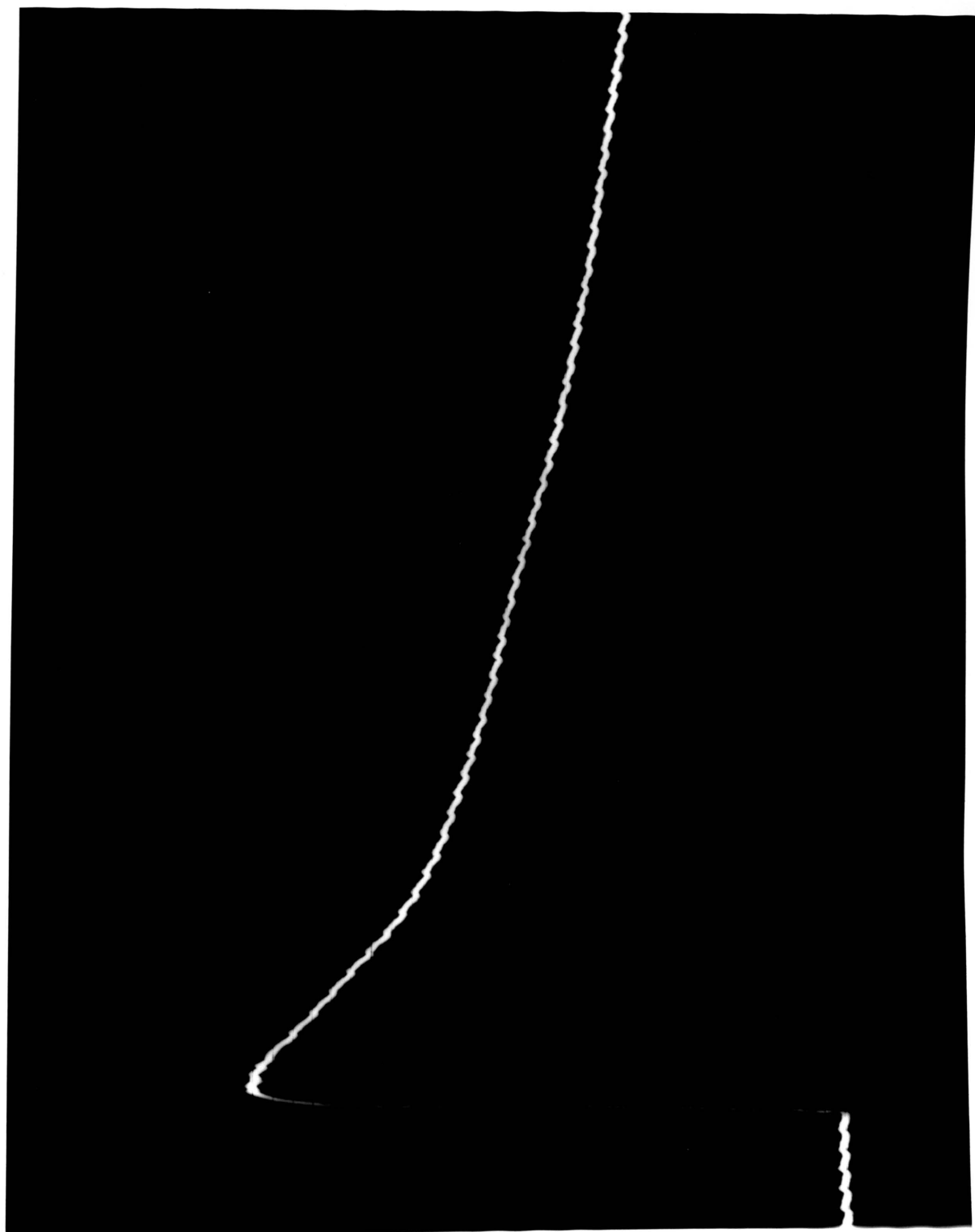
P

T

Run 4   Ratio NO_2/NH_3 = 0.6807
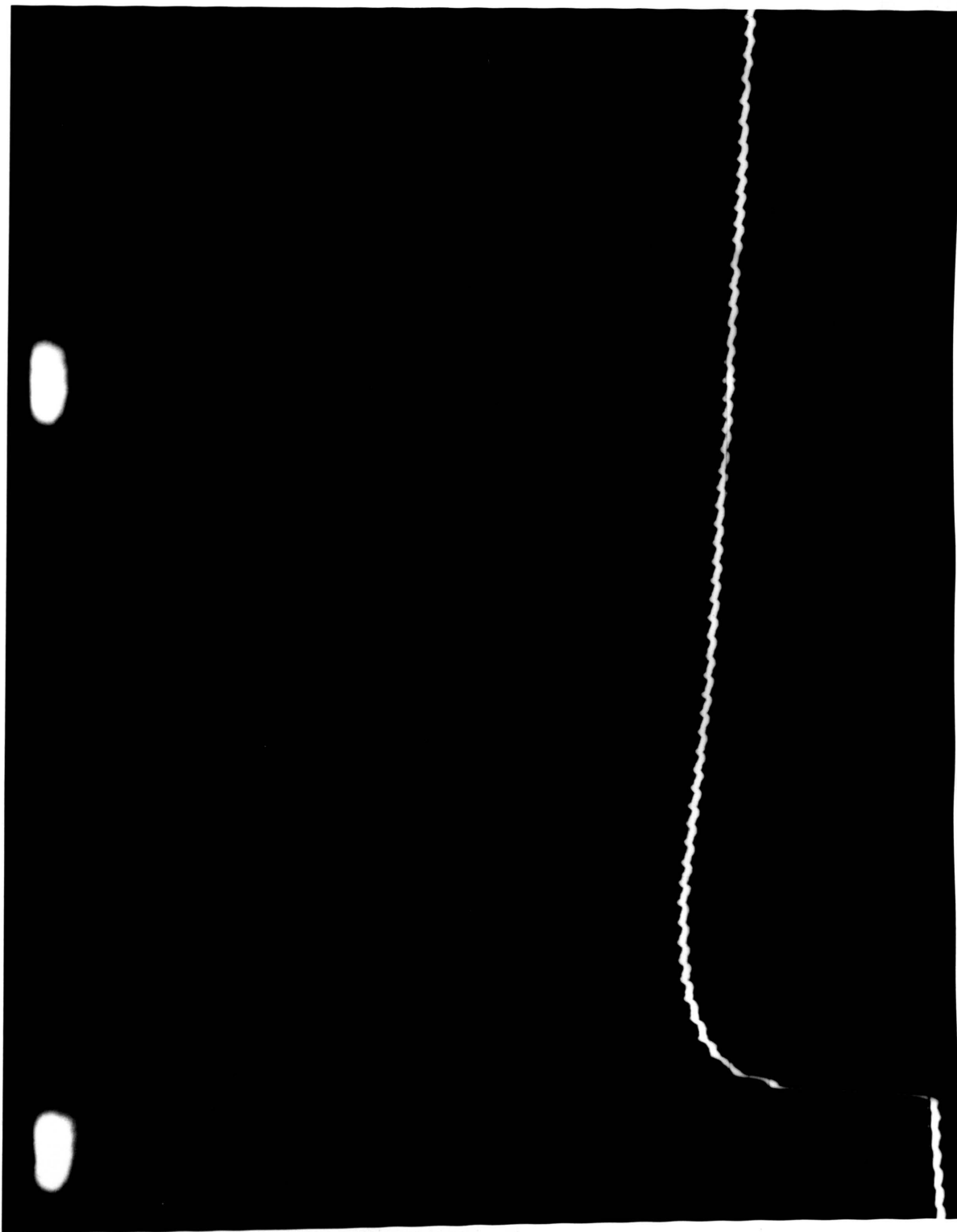
DISCUSSION OF RESULTS

During the filling of the nitrogen dioxide ampoules it was noted that various colored samples were collected. This can be explained by showing that various other colored[11]

(11)
Curtis, H. A., Fixed Nitrogen. N. Y., The Chemical Catalog Co., Inc., 1932. pp. 383-384.

compounds were present. Sesqui-oxide which has been carefully dried has an almost pure blue color at ordinary temperature but upon warming the color changes to green and is due to yellow nitrogen dioxide formed from the dissociation of the sesqui-oxide as shown by the equation

$$N_4O_6 = N_2O_3 + NO_2 + NO.$$

The wet sesqui-oxide is green due to a large amount of nitrogen dioxide being present, but at low temperatures the sesqui-oxide is blue. In relation to the sesqui-oxide, the tri-oxide will also dissociate into the following

$$N_2O_3 = NO_2 + NO$$
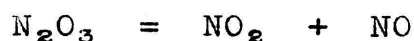
and the nitrogen dioxide will establish the equilibrium

$$2NO_2 = N_2O_4$$

and also

$$NO_2 = NO + \tfrac{1}{2}O_2$$
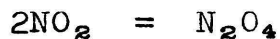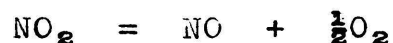
This result may be used to explain the reason for side reactions occuring when it is assumed that only nitrogen dioxide and ammonia react. The formation of the gaseous products may indicate that this assumptiom is true.

The possibilities of side reaction of ammonia and the

nitrogen dioxide will be undertaken from a theoretical standpoint.

The principal products of reaction of nitrogen dioxide and ammonia were nitrogen, nitrous oxide, nitric oxide, ammonium nitrate, ammonium nitrite, water, and in some cases oxygen. It has been previously reported[12] that hydrazine is also a product formed in this reaction.

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[12] Besson and Rosset, op. cit., p.4.

A summary of possible reactants and reactions follows.

(a) Oxides of nitrogen possible: NO_2, NO, N_2O

(b) Other reactant (original): NH_3

(c) Possible intermediates: HNO_2, HNO_3, N_2, O_2, H_2, NH_4NO_2, NH_4NO_3, N_2H_4.

This could very well complicate the theoretical reaction of nitrogen dioxide and ammonia.

It should be noted at this point that no attempt is being made to list the possible reactions in order, but. only those which may and could occur during the time the reaction is going to completion.
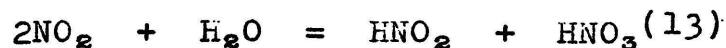
$$2NO_2 + H_2O = HNO_2 + HNO_3 \quad (13)$$
$$NO + NO_2 + H_2O = 2HNO_2$$
$$3HNO_2 = HNO_3 + 2NO + H_2O$$
$$2HNO_3 = NO + NO_2 + O_2 + H_2O \ (80°C)$$
$$N_2 + O_2 = 2NO$$

---

[13] Martin, G. and Barbour, W., Industrial Nitrogen Compounds and Explosives. N. Y., D. Appleton and Co., 1915. p. 117.

$$2NO + O_2 = 2NO_2$$

$$2NO = N_2O + \tfrac{1}{2}O_2$$

$$\tfrac{1}{2}O_2 + N_2O = 2NO$$

$$NO_2 = NO + \tfrac{1}{2}O_2$$

$$NH_4NO_2 + \tfrac{1}{2}O_2 = NH_4NO_3$$

$$NH_3 + H_2O = NH_4OH$$

$$NH_3 + HNO_2 = NH_4NO_2$$

$$NH_3 + HNO_3 = NH_4NO_3$$

$$N_2 + 3H_2 = 2NH_3$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

$$3NO_2 + H_2O = 2HNO_3 + NO$$

$$2NH_4NO_3 = 2N_2 + 4H_2O + O_2$$

$$NH_4NO_3 = N_2O + 2H_2O$$

$$N_2H_4 + HNO_2 = N_2O + NH_3 + H_2O$$

$$N_2H_4 + HNO_3 = N_2H_4HNO_3$$

$$N_2H_4 + HNO_2 = N_3H + 2H_2O$$

$$4NH_3 + 6NO = 5N_2 + 6H_2O$$
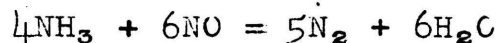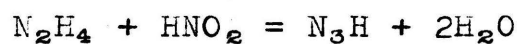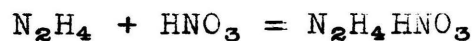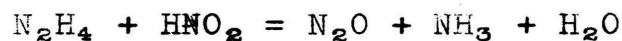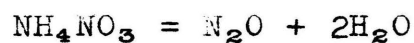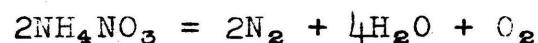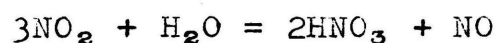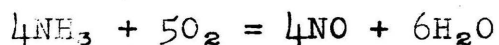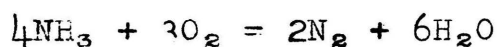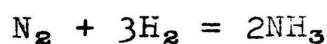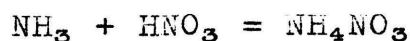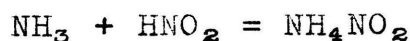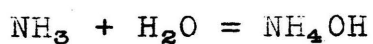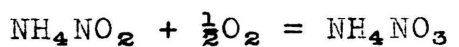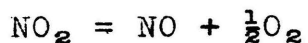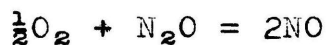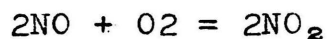
It may appear that the above number of equations represents a considerably greater number than are possible as conditions of pressure and temperature are different in each case. But, when the ampoules of reactants are broken, pressure is built up, and in the formation of the solid products a large quantity of heat is evolved. On the basis of this observation it can be assumed that all of the above equations are possible.

The data in Table 4, giving material balances on the respective runs, indicates the presence of side reactions.

Analysis of Runs A_5, A_6, and A_8 at 35°C:

In Run A_5, for a ratio of NO_2/NH_3 of 0.847, ammonia being in excess by 1.670 mM., the reaction favored the formation of the gaseous product nitrogen, 93.90%, a large excess of water, 5.343mM., and the formation of the smallest amount of solid products. The suggested side reactions are:

$$4NH_3 + 6NO = 5N_2 + 6H_2O$$

$$NH_4NO_3 = N_2 + \tfrac{1}{2}O_2 + 2H_2O$$

$$NH_4NO_3 = N_2O + 2H_2O$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

and

$$2NH_3 + 7H_2O + 8NO = 5NH_4NO_3$$
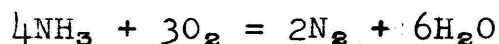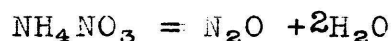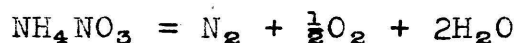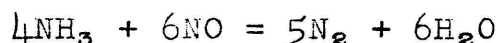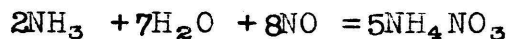
Nitric oxide was found to be present in the gaseous product. In Runs A_6 and A_8, ratio of NO_2/NH_3 being 0.8829 and 0.6419 respectively, the reaction favored the formation of solid products. About half as much water as in Run A_5 was produced. The formation of nitric oxide, and a reduction in the amount of nitrogen was noted. The possible side reactions are:

$$NH_3 + HNO_3 = NH_4NO_3$$

$$NH_3 + HNO_2 = NH_4NO_2$$

$$3HNO_2 = HNO_3 + 2NO + H_2O$$

$$N_2 + O_2 = 2NO$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$
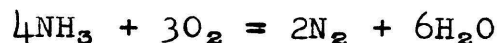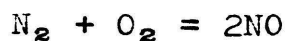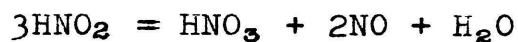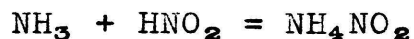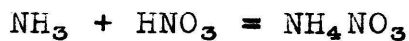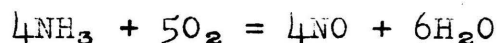
Analysis of Runs B_{13}, B_{14}, and B_{15} at $45°C$:

In Run B_{15} it again appears that a large excess of ammonia, ratio of NO_2/NH_3 being 0.8499, the reaction is favored toward the formation of a large amount of solid products, a small amount of water and reduction in the percent of nitrogen, and the formation of a large amount of nitric oxide. The side reactions in this case being the same as for runs A_6 and A_8.

In Run B_{13} the ratio of NO_2/NH_3 being 1.0040, and a small excess of ammonia, 0.650 mM., the reaction is favored toward the formation of a large amount of water, solid products, and a large amount of nitrogen. But some nitric oxide was produced, indicating the reaction

$$NO_2 = NO + \tfrac{1}{2}O_2$$
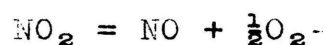
being possible.

Side reactions as for Run A_6 would be possible in this case also.

For Run B_{14} a slight excess of nitrogen dioxide was present leading to the formation of a considerable amount of water and solids. Nitric oxide was formed to some extent with a decrease in percent of nitrogen as compared to Run B_{15} by the following equations:

$$NO_2 = NO + \tfrac{1}{2}O_2$$

$$N_2 + O_2 = 2NO.$$
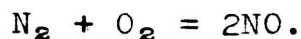
The side reactions in this case could be compared to those in Run A_5.

Analysis of Runs C_{10}, C_{11}, and C_{12} at 55°C:

Run C_{10} is again similar to Run A_5 in an overall comparison of gaseous and solid products, except the amount of ammonium nitrate is decreased and there is an increase in the amount of water formed from the reaction.

This may be explained by the reaction:

$$5NH_4NO_3 = 2NH_3 + 7H_2O + 8NO$$
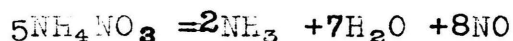
Runs C_{10} and C_{11} are again similar to other runs at different temperatures in which ammonia is in great excess, although the amount of ammonium nitrate produced in the solids decreases, indicating the side reaction

$$2NH_3 + NO_2 + NO = 2N_2 + 3H_2O$$

for Run C_{10} and

$$4NH_3 + O_2 + 5NO_2 = 3NH_4NO_3 + 3NO$$
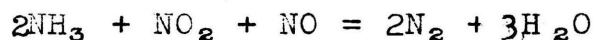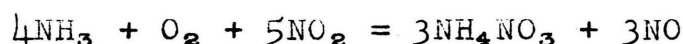
for Run C_{11}.

Analysis of Runs D_{10}, D_{11}, and D_{12} at 65°C:

The material balance for Run D_{10} was not calculated as previous calculations indicated more oxygen and hydrogen were present in the reaction products than were available for reaction.

Run D_{11} indicated an excess of nitrogen dioxide present after the reaction was over, with the main gaseous product formed being nitrogen, with trace amounts of nitric oxide and nitrous oxide. Water and nitrites were again formed in small amounts, suggesting the equations for C_{11} which holds for this case also.

Run D_{12} was observed to have an excess of ammonia,

showing a decrease in the percent of nitrogen formed in the gaseous products, an increase in the amount of water formed, and a smaller amount of nitrates being in the solids, suggesting the possible side reactions:

$$NH_4NO_3 = N_2O + 2H_2O$$

$$4NH_3 + 5O_2 = 4NO_2 + 6H_2O$$

$$N_2O + \tfrac{1}{2}O_2 = 2NO$$

and

$$N_2 + O_2 = 2NO$$
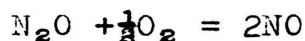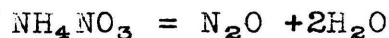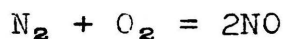
Analysis of Runs E_7, E_8, and E_9 at $75°C$:

In comparison of Runs E_7 and E_9 in which there was an excess of nitrogen dioxide, E_9 containing the larger amount, Run E_9 favored the formation of water and gave a small amount of nitrates in the solids suggesting

$$NH_4NO_3 = N_2O + 2H_2O$$

$$2NO_2 + H_2O + 2NH_3 = NH_4NO_3 + N_2 + 2H_2O$$

and

$$NH_4NO_3 = N_2 + \tfrac{1}{2}O_2 + 2H_2O.$$
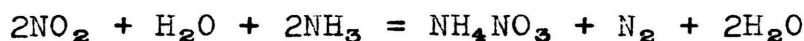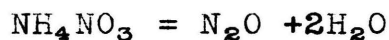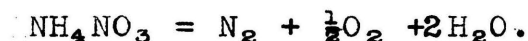
Run E_7 favored the formation of water with the nitrites being formed suggesting in a small amount

$$5NH_4NO_3 = 2NH_3 + 7H_2O + 8NO$$

$$2NO_2 + H_2O + 2NH_3 = NH_4NO_3 + N_2 + 2H_2O$$

and

$$4NH_3 + 6NO = 5N_2 + 6H_2O..$$
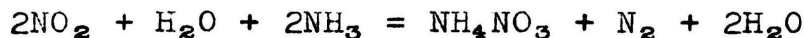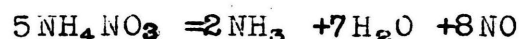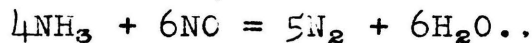
Run E_8 suggests the above equations as ammonia was in excess but the reaction also favored the formation of gaseous products and water.

Analysis of Runs F_8, F_9, and F_{10} at $85°C$:

Runs F_8, F_9, and F_{10} contained a large excess of ammonia giving a variety of results. Run F_8 had a 2.949mM.

excess of ammonia and favored the formation of nitrogen and water over ammonium nitrate, expressing the equations

$$2NH_4NO_3 = N_2 + \tfrac{1}{2}O_2 + 2H_2O$$

$$N_2 + O_2 = 2NO$$

$$N_2O + \tfrac{1}{2}O_2 = 2NO$$

$$NH_4NO_3 = N_2O + 2H_2O$$

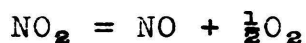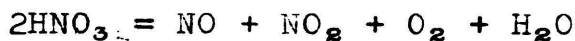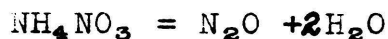$$2NO_2 + H_2O + 2NH_3 = NH_4NO_3 + N_2 + 2H_2O$$

and

$$4NH_3 + 6NO = 5N_2 + 6H_2O.$$
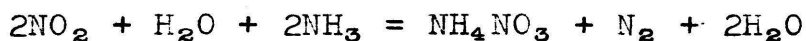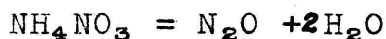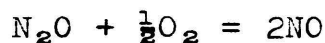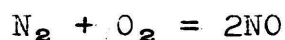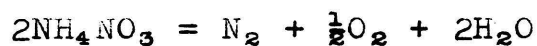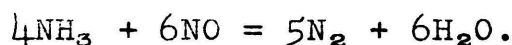
Run F_9 contained 2.941 mM. excess ammonia and favored the reaction of ammonium nitrate and nitric oxide, decreasing the amount of water and nitrogen, suggesting the side reactions

$$NH_4NO_3 = N_2O + 2H_2O$$

$$NO_2 = NO + \tfrac{1}{2}O_2$$

$$N_2O + \tfrac{1}{2}O_2 = 2NO$$

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

$$4NO_2 + 2NH_3 + 2H_2O = 2NH_4NO_3 + 2NO + H_2O$$

and

$$N_2 + O_2 = 2NO.$$
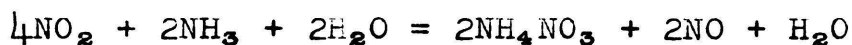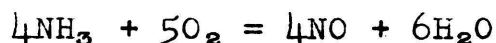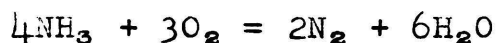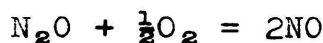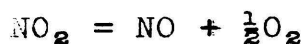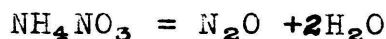
Run F_{10}, 2.671 mM. excess ammonia, favored the formation of a considerable amount of nitric oxide and showed a slight decrease in the amount of nitrates formed. This could be caused by the side reactions

$$NH_4NO_3 = N_2O + 2H_2O$$

$$2HNO_3 = NO + NO_2 + O_2 + H_2O$$

$$NO_2 = NO + \tfrac{1}{2}O_2$$

$$N_2O + \tfrac{1}{2}O_2 = 2NO$$

and

$$4NH_3 + 5O_2 = 4NO + 6H_2O.$$
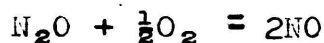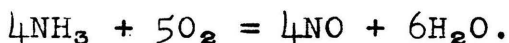
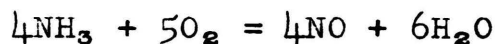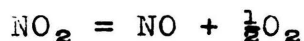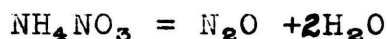Analysis of Runs G_1, G_2, and G_3 at 93°C:

Runs G_1, G_2, and G_3 were carried out with an excess of ammonia also.

Run G_1 had 3.042 mM. excess of ammonia with nitrogen being present in the gas product to an extent of 98.43%. A small amount of nitrites were formed, no nitric oxide was formed, and considerable water was formed. As no nitric oxide was formed, the reaction
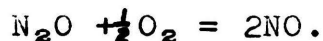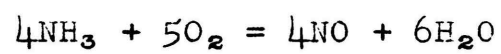
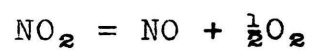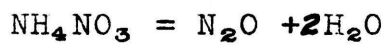$$4NH_3 + 6NO = 5N_2 + 6H_2O$$
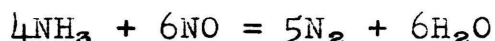
may have been possible.

Run G_2 had 3.572 mM. excess of ammonia, causing the nitric oxide to be present to an extent of 27.11% and decreasing the nitrogen to 71.38%. As a low amount of ammonium nitrate was formed, the following reactions may account for the excess nitric oxide:
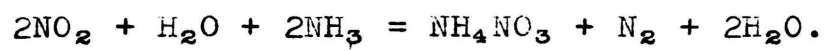
$$NH_4NO_3 = N_2O + 2H_2O$$

$$NO_2 = NO + \tfrac{1}{2}O_2$$

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

$$N_2 + O_2 = 2NO$$

and

$$N_2O + \tfrac{1}{2}O_2 = 2NO.$$
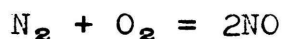
Run G_3 had an excess of 1.014 mM. of ammonia with ammonium nitrate being formed in smaller amount than Run G_1, with water being formed in a greater amount than Run G_1. The nitrogen dioxide content of Run G_3 was greater than that of G_1. Possible side reactions occurring are:

$$NH_4NO_3 = N_2O + 2H_2O$$

$$NO_2 = NO + \tfrac{1}{2}O_2$$

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

and

$$2NO_2 + H_2O + 2NH_3 = NH_4NO_3 + N_2 + 2H_2O.$$

CONCLUSIONS

The reaction of nitrogen dioxide and ammonia appears to be more complicated than would be expected.

The data collected indicates that the amount of ammonium nitrate formed in the reaction decreases with an increase in temperature. The amount of ammonium nitrite formed in the reaction also decreases with an increase in temperature. The amount of nitrous oxide in the gaseous product decreases with an increase in temperature while the amount of nitric oxide formed in the reaction increases. This appears reasonable, as nitric oxide is more stable at higher temperatures than nitrous oxide.
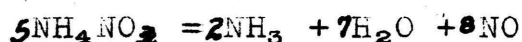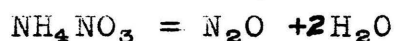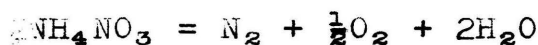
The ammonium nitrate formed in the reaction decreases as the temperature of the reaction increases. The volume of total gaseous product from the reaction increases as the temperature increases. This may be due to the decomposition of the ammonium nitrate and the ammonium nitrite.

Excess ammonia present during and after the reaction tends to alter the quantities of products formed. An optimum amount of ammonia is necessary to favor the production of gaseous products high in nitric oxide, and to decrease the amount of ammonium nitrate, ammonium nitrite, and water formed by the reaction. Illustrations of this conclusion are Runs F_8, F_9, and F_{10}.
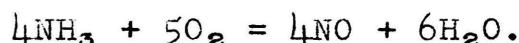
Both high and low ratios of ammonia produce an increased amount of nitrogen up to a temperature of 55°C. Above this

temperature, lower ammonia ratios give increasing amounts of nitric oxide and water, and decreased amounts of ammonium nitrate and ammonium nitrite. Runs A_5, A_6, and A_8 lead to this conclusion.
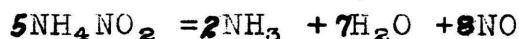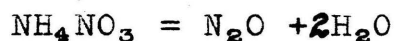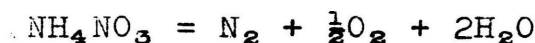
In one case it appears that the following side reactions are possible:

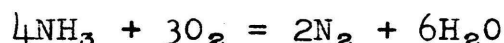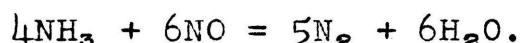$$NH_4NO_3 = N_2 + \tfrac{1}{2}O_2 + 2H_2O$$

$$NH_4NO_3 = N_2O + 2H_2O$$

$$5NH_4NO_2 = 2NH_3 + 7H_2O + 8NO$$

and

$$4NH_3 + 5O_2 = 4NO + 6H_2O.$$

In case two the equilibrium shift may be caused by the following side reactions:

$$NH_4NO_3 = N_2 + \tfrac{1}{2}O_2 + 2H_2O$$

$$NH_4NO_3 = N_2O + 2H_2O$$

$$5NH_4NO_2 = 2NH_3 + 7H_2O + 8NO$$

and

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

but as a general rule, very little nitrous oxide was formed, suggesting the following reaction:

$$4NH_3 + 6NO = 5N_2 + 6H_2O.$$

The amount of excess ammonia, necessary to the formation of gaseous products tends to increase as the reaction temperature is increased.

It is of interest to note that in the runs in which nitrous oxide was in considerable excess the amount of nitrogen present in the gaseous products was considerably decreased. This may be due to oxygen, available from the decomposition of the ammonium nitrate and ammonium nitrite,

reacting with the nitrogen to form nitric oxide. Also, the nitrogen dioxide may react with ammonia giving nitric oxide and ammonium nitrate, which decomposes.
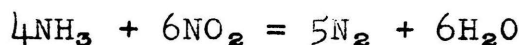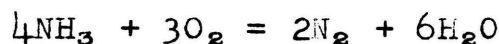
Several runs were made in which nitrogen dioxide was in excess. The general tendency was that the ammonium nitrate was readily decomposed with the formation of a considerable amount of water. In all cases in which nitrogen dioxide was in excess the nitrogen content of the gaseous product was above 90%. The gaseous product contained a small amount of nitrous oxide and nitric oxide. The excess nitrogen dioxide may force the final product to decompose according to the equations

$$NH_4NO_3 = N_2 + O + 2H_2O$$
and
$$NH_4NO_3 = N_2O + 2H_2O$$
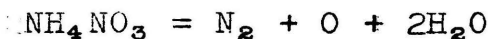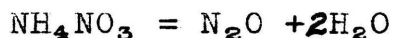
and leaving the nitrous oxide and oxygen free to react as follows:

$$4NH_3 + 3O_2 = 2N_2 + 6H_2O$$

$$4NH_3 + 6NO_2 = 5N_2 + 6H_2O$$
and to some extent
$$4NH_3 + O_2 = 4NO + 6H_2O.$$
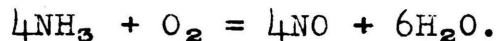
In referring to the photographs of Runs C_{12}, E_8, and G_1, it is noted that after the maximum reaction pressure increase was obtained, the total pressure in the reactor decreased and then showed an increase after approximately 0.6 of a second. In Runs E_8 and G_1 a large excess of ammonia was present and the reaction favored the formation of nitrogen in the gaseous product, decomposition of ammonium nitrate and ammonium nitrite, and

the formation of water. The maxima which occurred after the initial reaction could well be caused by the decomposition of the solid products to form gases.

In Run C_{12} a maxima occurred after the initial reaction and the reaction favored the formation of water, decomposition of the ammonium nitrate, but the formation of nitrous oxide. This would indicate that the oxygen produced in the decomposition of ammonium nitrate reacted with ammonia to form the principle products water and nitrous oxide.

In the case of Runs E_8 and G_1, assuming decomposition of the ammonium nitrate, the oxygen could have reacted with ammonia to form water and nitrogen or with nitrous oxide to give nitric oxide.

In reference to the runs made at $45°$ and $55°C$ it is noted that there is a marked decrease in the amount of ammonium nitrite formed by the reaction, indicating that a considerable amount of nitrous oxide is formed.

The photograph of Run D_{12} proves to be very interesting as far as the formation of the reaction products are concerned and clearly indicates that the reaction is very complex. Approximately fifty milliseconds after the reaction of nitrogen dioxide and ammonia had started, the maximum reaction pressure was obtained and a pressure decrease was noted for approximately two hundred milliseconds. After this time the reaction products decomposed to give such a pressure increase that the electron tube sweep was

thrown completely off the oscillograph screen. The pressure then decreased for approximately 3.5 seconds and leveled off for about 0.2 seconds, indicating that an equilibrium may have been reached. The pressure then decreased for about 0.4 seconds indicating that solid products may have been formed again. The total pressure then leveled off and remained constant.

Run D_{10} was made with an excess of ammonia. The nitrogen dioxide was allowed to react with ammonia by breaking the ammonia ampoule first. The top curve represents the breakage of the ammonia ampoule and the bottom curve the reaction of nitrogen dioxide and ammonia.

Runs one and two were photographed at a fast film rate of one inch per second. It appears that the reaction was complete in approximately fifty-three milliseconds.

Runs three and four were photographed at a temperature of 85°C. Run three was photographed as an ampoule of ammonia was broken in an atmosphere of nitrogen dioxide. The maximum total reaction pressure was reached in fifty milliseconds and the reaction appeared to be complete. The ratio of nitrogen dioxide to ammonia in this case was 0.6745.

Run four was made at a temperature of 85°C in which an ampoule of nitrogen dioxide was broken in an atmosphere of ammonia. The photograph indicates that by the time the reaction pressure had reached a maximum the reaction had reached an equilibrium. This is due to the fact that a

greater time is required for the nitrogen dioxide to vaporize than for the reaction to go to completion. The ratio of NO_2/NH_3 was 0.6807. It appears that this would not be a good method to study the reaction photographically.
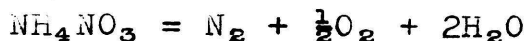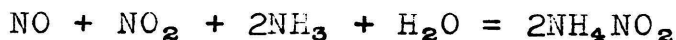
Run three shows clearly the pressure decrease after the reaction was complete.

It should be noted that as the temperature of the reaction is increased the maxima do not appear as great as those which appear at a temperature of 35°C. This could be due to the fact that the reaction products decompose immediately upon formation or that they are not formed at all.
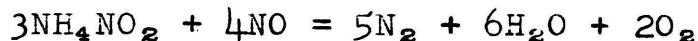
Although the main reaction is considered to be between nitrogen dioxide and ammonia it appears that after the reaction starts it could be considered as being multiphase. After the reaction starts, nitrous oxide, nitrogen, ammonium nitrate, nitric oxide, and water are formed. This may account for the side reaction products. It could be concluded that the main reaction is

$$5NO_2 + 4NH_3 = -N_2 + 3NH_4NO_3 + -NO.$$

The side reactions possible are as follows:

$$NO + NO_2 + 2NH_3 + H_2O = 2NH_4NO_2$$

$$NH_4NO_3 = N_2 + \tfrac{1}{2}O_2 + 2H_2O$$

and

$$3NH_4NO_2 + 4NO = 5N_2 + 6H_2O + 2O_2$$
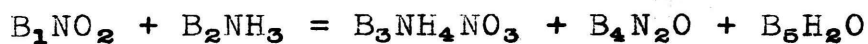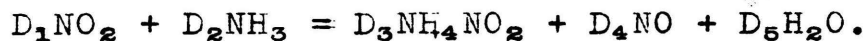
when nitrates, nitrites, and nitrogen appear at the lower temperatures. Thus at low temperatures it appears that possible overall reactions are:
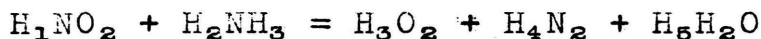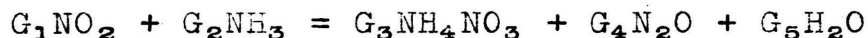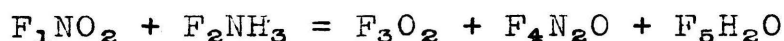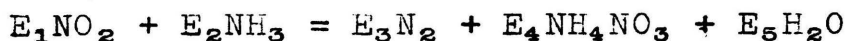
$$A_1NO_2 + A_2NH_3 = A_3O_2 + A_4N_2O + A_5H_2O$$

$$B_1NO_2 + B_2NH_3 = B_3NH_4NO_3 + B_4N_2O + B_5H_2O$$

$$C_1NO_2 + C_2NH_3 = C_3O_2 + C_4N_2 + C_5H_2O$$

and

$$D_1NO_2 + D_2NH_3 = D_3NH_4NO_2 + D_4NO + D_5H_2O.$$
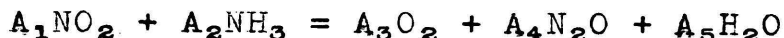
Between 55 to 65°C the reactions appear to be:

$$E_1NO_2 + E_2NH_3 = E_3N_2 + E_4NH_4NO_3 + E_5H_2O$$

$$F_1NO_2 + F_2NH_3 = F_3O_2 + F_4N_2O + F_5H_2O$$

$$G_1NO_2 + G_2NH_3 = G_3NH_4NO_3 + G_4N_2O + G_5H_2O$$

$$H_1NO_2 + H_2NH_3 = H_3O_2 + H_4N_2 + H_5H_2O$$

and

$$I_1NO_2 + I_2NH_3 = I_3N_2 + I_4NO + I_5H_2O.$$
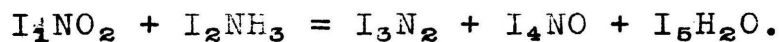
It had been the author's intention to arrive at an overall balanced equation for the reaction of nitrogen dioxide and ammonia. As the tabulations show varied results, it appears that it may be impractical to suggest an overall equation for the reaction. As noted in the tabulated data, between a temperature of 45 and 65°C there is a noted change in the reaction as far as the solid reaction products are concerned. It may well appear that no single overall equation will hold for the reaction of nitrogen dioxide and ammonia. It appears that several overall equations are necessary at each specific temperature level and that the overall equation tends to change as reaction temperature is changed. **It should be noted that the above equations are balanced by the method of standard nomenclature.**

SUGGESTIONS FOR FUTURE WORK

It was the author's intentions, had time allowed, to construct a suitable apparatus for measuring the temperature inside of the reactor from the time the reaction of nitrogen dioxide and ammonia was started until the reaction was complete. One could then determine the exact temperature at which the reaction was carried out instead of assuming the temperature of the reactants and reactor remained constant.

Another possible object of future work would be to construct a reactor of larger size, and while remaining in a constant temperature bath, to break the separate ampoules by automatic means.

It would also be advantagous to investigate the reaction at higher temperatures, say, above the temperature at which ammonium nitrate and ammonium nitrite are known to decompose.

If time allowed, the author had intended to break an ampoule of ammonia and an ampoule of nitrogen dioxide at the same instant to determine what effects this procedure would have on the results of the reaction.

The oxidation of other inorganic and organic compounds by nitrogen dioxide could be studied.

A favorable suggestion would be the construction of a small rocket motor, using ammonia and nitrogen dioxide as a fuel, and allow the oxidizer and reductant to react in the combustion chamber. The rate of oxidizer and reductant could be controlled and the amount of thrust produced could be measured.

Equilibrium constants and the order of the reaction might also be determined.

SUMMARY

1. The apparatus for the determination of the rapid rate of reaction between nitrogen dioxide and ammonia has been assembled.

2. The operation of the apparatus and its use has been explained.

3. The results of the reaction of nitrogen dioxide and ammonia has been studied at seven different temperatures levels with the results being recorded photographically.

4. Three separate gas analyses were made of the reaction at the seven different temperature levels with the percent by volume of nitrous oxide, nitric oxide, nitrogen, and oxygen being determined.

5. Three separate solids analyses were determined for the reaction at the seven different temperature levels with the results of ammonia, nitrite ion, and nitrate ion being recorded in millimoles.

6. The reaction was studied from 35°C to 93°C at ten degree increments.

7. Still photographs of the reaction were taken.

8. Continuous motion pictures of the reaction were taken.

9. The reaction was studied at 85°C, 60°C, and 35°C at a fast film rate of one-inch per second.

10. The balanced equation for the reaction between nitrogen dioxide and ammonia was predicted from the experimental results obtained.

11. A complete material balance for the reaction has been

calculated.

12. The reaction has been studied at a ratio of oxidant to reductant varing from 0.4394 to 1.8690.

13. The reaction has been studied by allowing the nitrogen dioxide to react in an atmosphere of ammonia.

14. The reaction has been studied by allowing the ammonia to react in an atmosphere of nitrogen dioxide.

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