WAR RESEARCH

PART I

THE RECOVERY OF GLACIAL ACETIC ACID FROM THE RESIDUAL LIQUORS OF THE BACHMANN PROCESS

PART II

THE DEVELOPMENT OF A CONTINUOUS REACTOR WITH WHICH TO INVESTIGATE THE BACHMANN REACTION

A. THE U-TUBE REACTOR

B. THE ROTATING TUBE REACTOR

by

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PREFACE

The work reported in this thesis was comprised of two rather distinct investigations, the reason for which should be indicated briefly. Originally it was planned to develop a continuous pilot plant reactor of suitable design to study, in particular the effect of dilution on the preparation of RDX(B) and more generally the influence of other variables on the yield and quality of the product of the Bachmann reaction.

Before these plans had progressed beyond the stage of preliminary development, there intruded the urgent problem of recovering acetic acid from the RDX(B) slurry at St. Maurice Chemicals, the centre of commercial production of RDX(B) in Canada. This investigation proved to be more time-consuming than originally anticipated, and it was not until its successful conclusion several months later that attention could again be given to the development of the pilot plant initially projected. A design of reactor suited to investigation of the problems in mind was finally evolved; it remained however for other investigators in this laboratory to make with it the extended studies of the effect of dilution and other factors on the course of the Bachmann reaction as originally proposed.

Ph.D. Chemistry

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WAR RESEARCH

Part I: THE RECOVERY OF GLACIAL ACETIC ACID FROM THE RESIDUAL LIQUORS OF THE BACHMANN PROCESS.

A process has been devised for the recovery of glacial acetic acid from the waste products of the Bachmann reaction. The method involves the removal of nitric acid as ammonium nitrate, a "fume-off" of the filtrate with sulphuric acid and a distillation in the presence of sulphuric acid. No stainless steel equipment and only a minimum of supervision is required for the process. Oleum and/or sulphuric acid are not practical dehydrating agents in this process.

Part II: THE DEVELOPMENT OF A CONTINUOUS REACTOR WITH WHICH TO INVESTIGATE THE BACHMANN REACTION.

A. THE U-TUBE REACTOR. B. THE ROTATING TUBE REACTOR.

An instrument in the form of a rotating tube has been developed for an accurate determination of the effects of the variables, encountered in the Bachmann reaction, on the yield and quality of RDX(B).

The trends in yield of RDX(B), HMX and BSX, as the input of nitric acid, ammonium nitrate and acetic anhydride were varied, have been established and were shown to conform in general to those established in batch experiments.

PART - I

THE RECOVERY OF GLACIAL ACETIC ACID
FROM THE
RESIDUAL LIQUORS
OF THE
BACHMANN PROCESS

INTRODUCTION

Cyclotrimethylenetrinitramine, familiarly known as RDX or cyclonite, is produced commercially in Canada by the Bachmann or Combination process, at the plant operated by St. Maurice Chemicals, Lac la Tortue, Quebec.

The reagents used in this process, and their approximate molar ratios, are as follows:-

Hexamine:	1.0
Nitric Acid:	4.6
Acetic Anhydride:	8.0
Ammonium Nitrate:	3.2
Acetic Acid:	4.5

Clumsy and inaccurate methods of introducing the solid reagents into the reaction mixture are avoided by using a system of three liquid feeds, consisting of hexamine dissolved in acetic acid, ammonium nitrate dissolved in 98% nitric acid, and acetic anhydride respectively. This procedure ensures the most intimate contact of the reagents.

During the course of the reaction water is liberated which, together with the water initially present in the acids introduced into the reactor, combines with roughly 5.7 times its own weight of acetic anhydride to form acetic acid. Thus more acetic acid emerges from the reactor than enters it per unit time.

A survey of plant data showed that acetic acid is present to the extent of approximately 3.5 pounds per pound of product in the spent liquors emerging from the reactor. It is evident, therefore, that recovery of acetic acid is essential to economic production of RDX by the Bachmann process.

Obviously, distillation of the acetic acid from the undiluted liquors should involve hazard, since an accumulation of explosive materials should occur in the system during such a process. Moreover, it might be expected that certain excess reaction materials, such as nitric acid, should contaminate the distillate. Hence, the impurities remaining in solution, after the main reaction product is filtered off, must be removed before any such distillation procedure may be employed.

Since the explosive is water insoluble, the simplest method of removing the greater part of it involves water dilution of the filtrate to such an extent that only small amounts of impurities remain. Acetic acid of glacial strength may then be recovered by filtration of the precipitated solids, followed by azeotropic distillation of the filtrate in stainless steel equipment. This is essentially the method now in successful operation at the Holston Ordnance Works.

The obvious necessity of introducing acetic acid recovery at the St. Maurice plant as quickly as possible, but without the use of stainless steel equipment which was not available owing to wartime shortages, made an alternative method of recovery essential. Of course, any such method must avoid the previously mentioned hazard of accumulation of explosive at any point in the system, or retention of explosive in the recovered acid itself.

With these limitations in view, research on the problem was begun. The studies made and the results obtained therefrom are presented in two parts:-

<u>Part</u> <u>I</u>: - Recovery of Acetic Acid by Solvent Extraction.

<u>Part</u> <u>II</u>: - Recovery of Acetic Acid by Fume-off of the Mother Liquor followed by Distillation from Sulphuric Acid.

- LITERATURE REVIEW -

The first attempt at recovering acetic acid from the residual liquors of the Bachmann process was reported by Bachmann (1). In brief, the procedure he found successful was as follows:-

The nitric acid in the diluted reaction mixture was neutralized with concentrated ammonium hydroxide, using 0.1% thymolsulphonphthalein indicator solution. The resulting solution was then distilled to dryness under reduced pressure. The distillate obtained in this manner was found to contain no trace of nitric acid and was reported suitable for fractionation.

The work of Bachmann was repeated by Wright (2) a short time later, who made use of thymol blue indicator in partially neutralizing the mother liquor with 28% ammonia. The resulting solution was then vacuum distilled to dryness. The distillate, free of nitric acid, contained 70% of the expected acetic acid as a 24% aqueous solution.

A slight modification in recovery technique was next reported by Whitmore (3). He offered a procedure for recovery, as 31% solution, of 79% of the total acetic acid used in the Bachmann process. This involved dilution of the filtrate (initially at 60°C.) with water. The precipitate which formed on dilution was filtered off, base was added equivalent to the nitrate ion present, and the clear filtrate distilled, at atmospheric pressure to give dilute acetic acid free from nitrates and non-volatile organic impurities. Traces of formaldehyde were detected in the filtrate. During the course of these experiments it was found that dilution of the reaction liquors with water to a concentration of 30% acetic acid gave the maximum amount of solid precipitated out of the mother liquor.

In a second report (4) Whitmore reported that distillation of the liquor at 12 mm. pressure after treatment with ammonium hydroxide yielded 88% of the theoretical acid as a 30% solution containing 25 parts per million of nitrate ion. He found that 3-5% additional RDX was obtained by dilution of the mother liquor, while from the distillation residue crude ammonium nitrate was obtained equivalent in weight to 40% of that used in the reaction.

At this time Wright (5), in studying the spent liquors of the Ross reaction, found that if 3 volume per cent of concentrated sulphuric acid was added to the mother liquor and the solution heated in a large vessel on a hotplate, a sudden evolution of nitrogen oxides occurred after an induction period, the fume-off being complete in ten to fifteen minutes. A distillation of the residue at atmospheric pressure gave a 72% yield of acetic acid of melting point 13°C.

Further experiments (6) showed that the removal of residual RDX and HMX from the Ross reaction liquors could be effected reliably only when 10 volume per cent of concentrated sulphuric acid was added. Here the fume-off was not as violent as when smaller amounts of sulphuric acid were used. The operation was conducted in an inclined, steam-jacketted tube with an indented floor, a slow stream of air being passed counter-current to the acetic acid sulphuric acid mixture to remove the nitrogen oxides. The effluent acids were distilled to remove the acetic acid. The residual sulphuric acid was used five times without loss in effectiveness, but was then discarded because of its extreme viscosity. This viscous residue was found to contain no trace of RDX or HMX. The recovered acetic acid melted at 15.8°C and had a total acidity of 97.3%. It smelled strongly of sulphur dioxide and reduced potassium permanganate.

Dilution of the Ross reaction liquors with petroleum ether (7) was found to precipitate an appreciable amount of water soluble material (6-8 grams per litre) although the removal of this material did not increase the efficiency of the sulphuric acid used to decompose the RDX which remained in solution (1.88 grams per litre). Hence the modification of adding an organic solvent was discarded.

In a search for other means of destroying RDX, oxidizing agents were found ineffective, as was hydrogen sulphide, hydrochloric acid, phosphorous tri - and penta-chloride, phosphoric acid, zinc chloride, thionyl chloride, nitrous acid and sulphurous acid. Reducing agents showed more promise e.g., tin reduced RDX completely after thirty minutes boiling, but iron filings produced incomplete reduction. However, an iron-copper couple rapidly and completely reduced RDX when sulphuric acid (1% of the acetic acid volume) was present. These experiments were made on synthetic mixtures of RDX-ammonium nitrate - acetic acid. In every case the residual acetic acid contained formaldehyde. When this reduction technique was applied to the actual reaction liquors, a fume-off occurred, difficult to control, after ten to thirty minutes. The RDX was only partially reduced unless the reaction was allowed to proceed so far that the mixture became unworkable, owing to the presence of iron salts. As a consequence, this method was abandoned as impractical.

Later, Wright found (8) that the residual RDX in the filtrates from Ross reaction liquors could be destroyed by prolonged heating of these liquors. The same workers, in experimenting with the Bachmann liquors, showed that superheating of these liquors destroyed all traces of residual RDX (9). The following technique was employed.

A Bachmann mixture was filtered without dilution, and the filtrate diluted to an acetic acid concentration of 30%. Before dilution, the filtrate was found to contain 4% RDX. The materials precipitated by the dilution were not removed, but the whole was transferred directly to a bomb tube and heated. When the tube was cooled and opened, a colourless gas was evolved over a period of one-half hour. No solid was precipitated from the liquid upon dilution with ten times its volume of water, and only faint tests for nitric acid and formaldehyde were obtained. The acetic acid recovery was 95% of that originally present, and no ammonium nitrate or other solid remained as residue.

Several other methods of destroying residual explosive in the Bachmann filtrates were developed. The work of Johnson (10) covered two principal variations:

(1) A Bachmann filtrate, with or without the addition of the aqueous washings of the RDX filter cake, was treated with cold concentrated sulphuric acid, and a controlled fume-off effected at 105°C. The residual liquid was distilled to give 75-98% acetic acid free of nitric acid. The overall recovery was 72-80% of that expected.

(2) The filtrate and aqueous washings were diluted to about 40% acetic acid and extracted with ether to remove acetic acid and some RDX. The organic solvent was distilled off and the residual acetic acid, containing a small amount of RDX, but no ammonium nitrate, was

treated with concentrated sulphuric acid. This mixture was fumed off and the acetic acid distilled from the sulphuric acid solution. This method gave a 91.4% recovery of the total input, as 72% acetic acid, with a strong test for formaldehyde.

Experiments were also made on the undiluted mother liquor by Johnson. The mother liquor was allowed to cool to 25°C, and the crude RDX which settled out was filtered off. The filtrate was then treated with 20% of its own weight of cold concentrated sulphuric acid (95%) with cooling. A 10 ml. portion of this solution was placed in a 500 ml. flask fitted with a reflux condenser, thermometer and dropping funnel. The small portion was then heated to 105-110°C, at which point a violent fume-off occurred, lasting about 20 seconds. The resulting liquid was maintained at the reflux temperature (118°C) by external heating and the remainder of the acetic-sulphuric solution was added dropwise over a period of 50 minutes. It was found essential that each increment of solution be caused to fume-off as introduced, so that no accumulation occurred. When completely fumed off, the residual liquid was boiled for ten minutes to ensure destruction of RDX and nitrates. The solution was then distilled at atmospheric pressure and the distillate collected from 115-135°C (vapour temperature). The internal temperature of the liquid rose from 118-190°C during the distillation.

The distillate thus obtained assayed 98-100% acetic acid, was water white and gave no test for nitric acid. The overall recovery amounted to 70-75% of the total acetic acid input.

At this point, acetic acid was being successfully recovered on pilot plant scale, by the Tennessee Eastman Corporation, using the dilution technique followed by an azeotropic distillation of the diluted liquors, the explosive in the still residues being decomposed periodically by treatment with alkali. Hence no further experimental work on acetic acid recovery was attempted in the United States.

EXPERIMENTAL

PART I.

THE RECOVERY OF ACETIC ACID BY SOLVENT EXTRACTION.

(a) From Acetic Acid-Water Solutions:

Customary plant practice for the manufacture of RDX by the Bachmann Process involves water dilution of the slurry (spent reaction liquors before filtration) from the reactor. Solvent extraction of the acetic acid from the diluted liquor, after the RDX had been filtered off, offered a possible basis for a satisfactory recovery method.

However, qualitative experiments with acetic acid-water solutions soon showed that the presence of a small amount of acetic acid increased largely the solubility of water in a solvent in which it is ordinarily insoluble. This was found to be in accord with the results of Campbell (11), who reported that while isopropyl ether was one of the most efficient solvents for the extraction of acetic acid from aqueous solution, it nevertheless gave a solution containing much water. Moreover, since plant filtrates contain explosive and other materials (ammonium nitrate, nitric acid, etc.) in solution, it would be expected that these would pass partially into the acetic acid-water-solvent layer during a solvent extraction process. Hence recovery of the acid would involve presumably a primary distillation to remove these impurities, followed by an azeotropic distillation, to recover glacial acetic acid. Such a procedure could not be considered a satisfactory alternative to the method already in existence.

(b) From Glacial Acetic Acid-RDX Mixtures:

Dilution of the slurry from the reactor has as its main purpose the destruction of BSX by simmering of the diluted mixture and the maximum recovery of RDX. The solubility of RDX in the cold concentrated liquor is not large, however, and if a small reduction (1-2%) in final yield of explosive is permitted, filtration of the undiluted slurry should yield a liquor containing an excess of acetic anhydride, from which the recovery of a highly concentrated acetic acid by solvent extraction might be expected. The slight solubility of RDX, HMX, BSX, etc., in the solvent-acetic solution represented the main difficulty to be overcome.

To this end, the efficiencies of a number of solvents as precipitating agents for RDX were examined, using solutions of glacial acetic acid saturated with RDX. The solubilities of RDX in solutions of acetic acid were determined for various proportions of acetic acid. The results, given in Table I, show that even in highly dilute solutions of acetic acid, small amounts of RDX remain in solution, and that cooling the solution

TABLE I

SOLUBILITY (gms. per 100 ml. solution) OF RDX IN VARIOUS ACETIC ACID SOLUTIONS

Acetic Acid in solution	Petroleum Ether		H_2O	Naphtha	Turpentine	Toluene
	at		at	at	at	at
% by Vol.	18°C	25°C	16°C	20°C	20°C	20°C
100.0	0.417	0.483	0.331	0.419	0.397	0.331
83.3	-	0.336	-	-	-	-
71.4	0.107	0.200	0.139	0.124	0.086	-
66.7	-	-	-	-	-	0.096
50.0	0.038	0.087	0.029	0.041	0.041	0.039
33.3	0.010	0.023	0.007	0.011	0.007	0.012
25.0	-	-	0.004	0.004	0.003	-
20.0	0.002	0.003	0.002	0.003	0.001	-
16.7	-	-	-	-	-	0.004
11.1	0.0006	0.0006	0.0009	0.001	-	-
9.1	-	-	-	-	-	0.0017

to the temperature at which acetic acid begins to crystallize out, does not completely prevent this retention of explosive.

Attempts were then made to obtain pure acetic acid, free of explosive and solvent, by reducing the temperature until the acetic acid was precipitated. Petroleum ether was chosen as a solvent in these experiments since it appeared to have the advantage of low boiling and freezing points as well as a high efficiency in precipitating RDX. The effectiveness of such treatment is indicated by the data in Table II, from which it is evident that the acetic acid recovered by freezing was invariably contaminated with solvent. Moreover, traces of RDX were also detectable with all proportions of acetic acid-petroleum ether used.

Hence it is seen that while simple distillation would serve to remove the acetic acid from the dissolved petroleum ether, this distillation would have to be made in the presence of RDX. In practice, presumably this could be done safely enough if the explosive in the still residues was destroyed periodically with alkali or other suitable means. Since there appeared to be no sufficient grounds for condemning such a process, the method was then applied to undiluted plant filtrates.

TABLE II

THE RECOVERY OF ACETIC ACID BY FREEZING FROM PETROLEUM ETHER SOLUTIONS

Original Acetic Acid			Recovered Acetic Acid		
Acetic Acid Volume %	Pet. Ether Volume %	Freezing Point of Solution °C	Acetic Acid Volume %	Pet. Ether Volume %	Recovery of Acetic Acid %
100.0	0.0	16.6	100.0	0.0	100.0
71.4	28.6	11.4	87.0	13.0	89.6
50.0	50.0	9.5	84.7	15.3	94.1
33.3	66.7	8.6	79.2	20.8	90.8
20.0	80.0	6.3	69.2	30.8	91.7
11.1	89.9	1.8	79.5	20.5	91.7
0.0	100.0	-95.	0.0	100.0	0.0

(c) From Undiluted Plant Filtrates:

Since previous experiments showed petroleum ether to be the most effective of the liquids used for precipitating RDX from glacial acetic acid, this solvent was employed in experiments with undiluted plant liquor.

The addition of petroleum ether to the clear liquor gave a large, white, voluminous precipitate, which was filtered off, and the acetic acid present in the filtrate was recovered by crystallization at 0°C. The petroleum ether was separated from the acetic acid by distillation, yielding an acetic acid from which a considerable amount of curdy, white precipitate (BSX, RDX, etc.) could be thrown down on dilution with water. Nitric acid im small amounts was also present in the acid after removal of the petroleum ether.

It was found impossible to eliminate the impurities in the acetic acid by using very high dilutions with petroleum ether and greatly reduced temperatures (as low as -30°C) for crystallization. It appeared necessary, therefore, to destroy the impurities prior to the extraction of the mother liquor.

(d) From the Fumed off Mother Liquor:

Rough estimates, by microscopic examination * showed that the solids precipitated from the mother liquor by the petroleum ether treatment consisted largely of RDX and BSX. The data are given in Table III.

* Analyses performed by Mr. R. Smart.

TABLE III

WEIGHT AND COMPOSITION OF SOLIDS PRECIPITATED FROM MOTHER LIQUOR BY PETROLEUM ETHER

Composition of Solution			Weight Solids Precipitated	Composition of Solids		
Acetic Acid %	Pet. Ether %	Impurities %	gms.	RDX %	HMX %	BSX, NH_4NO_3, etc. %
90.0	0.0	10.	0.0	60	10	25
53.0	41.1	5.9	0.748	85	0	15
37.6	58.3	4.1	0.682	73	0	27
29.1	67.7	3.2	0.738	55	0	45
22.9	73.6	3.5	0.792	40	0	60
20.0	77.8	2.2	1.100	55	0	45

Several materials were tested, in addition to those reported by Wright (7), for their effectiveness in destroying the impurities present in the mother liquor. No appreciable effect was observed with urea, sulphamic acid, or ammonia, but warm concentrated sulphuric acid gave a very rapid fume-off reaction by which all traces of BSX were destroyed. The nitric acid and ammonium nitrate contents of the liquor were reduced, but no appreciable reduction of RDX content was observed.

Extraction of the fumed off mother liquor with petroleum ether, with subsequent crystallization of the acetic acid, as previously described, gave a recovered acid slightly contaminated with sulphuric acid, nitric acid and RDX, even with high solvent dilution. No curdy precipitate was obtained when the recovered acid was diluted with water, indicating complete destruction of the BSX, but RDX was slowly precipitated on standing for longer periods.

Attempts to remove the sulphuric acid as an insoluble salt by adding acetates of calcium, barium or lead were not successful since the acid was then contaminated with the acetate of the metal.

All experience with the solvent extraction methods discussed above indicated that a distillation process of some kind was essential for the recovery of glacial acetic acid free from contamination by explosive. Effort was next directed, therefore, to the elimination of prior solvent extraction.

Since the fume-off reaction with sulphuric acid served to eliminate BSX from the liquor, it was decided to use the fumed off liquor as a starting point for further investigation. The immediate problems to be solved were two:-

(a) Control of the fume-off reaction.

(b) Complete, rapid and continuous destruction of RDX (B) in the fumed off liquor without the addition of a reagent which would remain in the recovered acid to the detriment of acid quality.

The development of the procedure whereby these objectives were finally obtained is discussed in the following section.

PART II

THE RECOVERY OF ACETIC ACID BY FUME-OFF OF THE MOTHER LIQUOR FOLLOWED BY DISTILLATION FROM SULPHURIC ACID

The Fume-off Reaction with Undiluted Mother Liquor:

The observations made here concerning the fume-off reaction confirm generally those made earlier at Toronto (5) and Cornell (10).

(A) Batch Operation:

(1) General Nature of the Reaction:

When sufficient concentrated sulphuric acid is added to the slurry from the reactor, or to undiluted filtrate from the slurry, and this mixture is heated to approximately 100°C, a violent reaction occurs. The colour of the liquid suddenly changes from a straw colour to deep brown, and large volumes of nitrogen oxide gases begin to be evolved. The violence of the reaction is thought to be due to this gas evolution. The evolution of gas causes considerable foam which, however, is unstable and disappears rapidly as soon as the gas evolution ceases. During the fume-off, the temperature of the solution rises to approximately 106°C.

(2) Sulphuric Acid Concentration Required in the Fume-off.

The amount of sulphuric acid necessary to initiate the fume-off depends on the quality of the filtrate or slurry. The experimental procedure which led to this conclusion was as follows:-

The slurry was cooled to 25°C and the solid which precipitated was filtered off, and air-dried over a period of three days. To a given volume of the filtrate was added varying amounts of this solid, and the amount of concentrated sulphuric acid required to fume-off these synthetic slurries was determined by heating the slurry to 100°C and then adding the sulphuric acid dropwise until a fume-off was initiated. The results of these experiments are presented in Table IV.

The removal of nitric acid and ammonium nitrate prior to the fume-off had a marked effect on the nature and violence of the reaction. The addition of anhydrous ammonia to the liquor served to convert the nitric acid excess to ammonium nitrate, and since this salt is sparingly soluble in the cold (25-30°C) liquor, most of the nitrates are eliminated from the filtrate at ordinary temperatures. When this nitrate deficient filtrate was fumed off very little nitrogen dioxide was formed, but a considerable amount of colourless gas, possibly nitrous oxide, was evolved at a steady rate at 106°C, probably from the decomposition of BSX and related compounds.

A more detailed study of the sulphuric acid requirements necessary to fume-off the nitrate deficient

TABLE IV

THE AMOUNT OF SULPHURIC ACID NECESSARY TO INITIATE THE FUME-OFF OF A GIVEN AMOUNT OF SLURRY

Run No.	Gms. of RDX, HMX, BSX, etc., added per 1000 ml. of Mother Liquor	Ml. of H_2SO_4 to Fume-off 1000 ml. of Mother Liquor
1	83.5	26.7
2	83.5	33.3
3	83.5	33.3
4	143.0	38.7
5	45.5	8.2 + 3 ml. 98% HNO_3
6	154.5	22.7
7	0.0	1.1
8	0.0	2.5 + 2.5 ml. Ac_2O

filtrate was not attempted since it was at that time being undertaken on pilot plant scale at St. Maurice Chemicals.

(3) The Effect of Temperature on the Fume-off Reaction:

The temperature at which the mother liquor is fumed off is important in controlling the violence of the reaction. When the temperature is high enough to promote the rapid fume-off reaction (usually between 95-100°C), the heat of reaction is sufficient to raise the liquid temperature to 106°C. This temperature can be maintained without further external heating, providing fresh mother liquor-sulphuric acid mixture is introduced to the reacting mixture at the proper rate. If heat is applied externally until the liquid temperature rises to approximately 112°C, the evolution of nitrogen oxides ceases, and may or may not be restored by lowering the liquid temperature to its proper range. The reason for this phenomenon is not evident and has not been investigated.

(4) The Role of Nitrogen Dioxide in the Fume-off Reaction:

The part played by nitrogen dioxide in the fume-off reaction is not understood. It was thought that nitrogen dioxide might act as catalyst, but the introduction of nitrogen dioxide from an outside generator had no apparent effect on the initiation of the reaction. Evidently it is one of the products from a decomposition which occurs at a controllable rate in a restricted temperature range of 95-112°C approximately. This decomposition destroys all but traces of ammonium nitrate and nitric acid along with all the BSX originally present in the mother liquor.

(B) Continuous Operation.

While the batch fume-off of even a small volume of mother liquor is rather violent, the continuous reaction was easily controlled. The principle employed was similar to that of the Cornell workers (10), the main difference being that the introduction of fresh liquor to the reaction, and the fume-off were continuous.

The reactor, shown in Fig. 1, consisted of a vertical pyrex glass tube, 4 feet long, 3 inches in diameter, fitted with a condenser at the top and outlet at the bottom. The condenser was installed to reduce loss of acetic acid by entrainment in the gases evolved. The outlet at the bottom led directly to a still in which the acetic acid was separated from the sulphuric acid.

To initiate the reaction, a small volume (100-500 ml.) of mother liquor was introduced into the reactor and heated to 100°C. To this hot liquor was added sulphuric acid (or oleum) until the liquid began to fume-off. Mother liquor containing 6% by weight of sulphuric acid was then run into the reactor at a rate sufficient to maintain the liquid temperature in the reactor at 105-106°C. It was found essential to keep the liquid temperature within this range for continuous, trouble-free operation. When the volume of liquid had reached the desired level in the reactor, the fumed off liquor was drawn off to the still at such a rate as to maintain a constant liquid level in the reactor.

The Impurities in the Fumed off Mother Liquor:

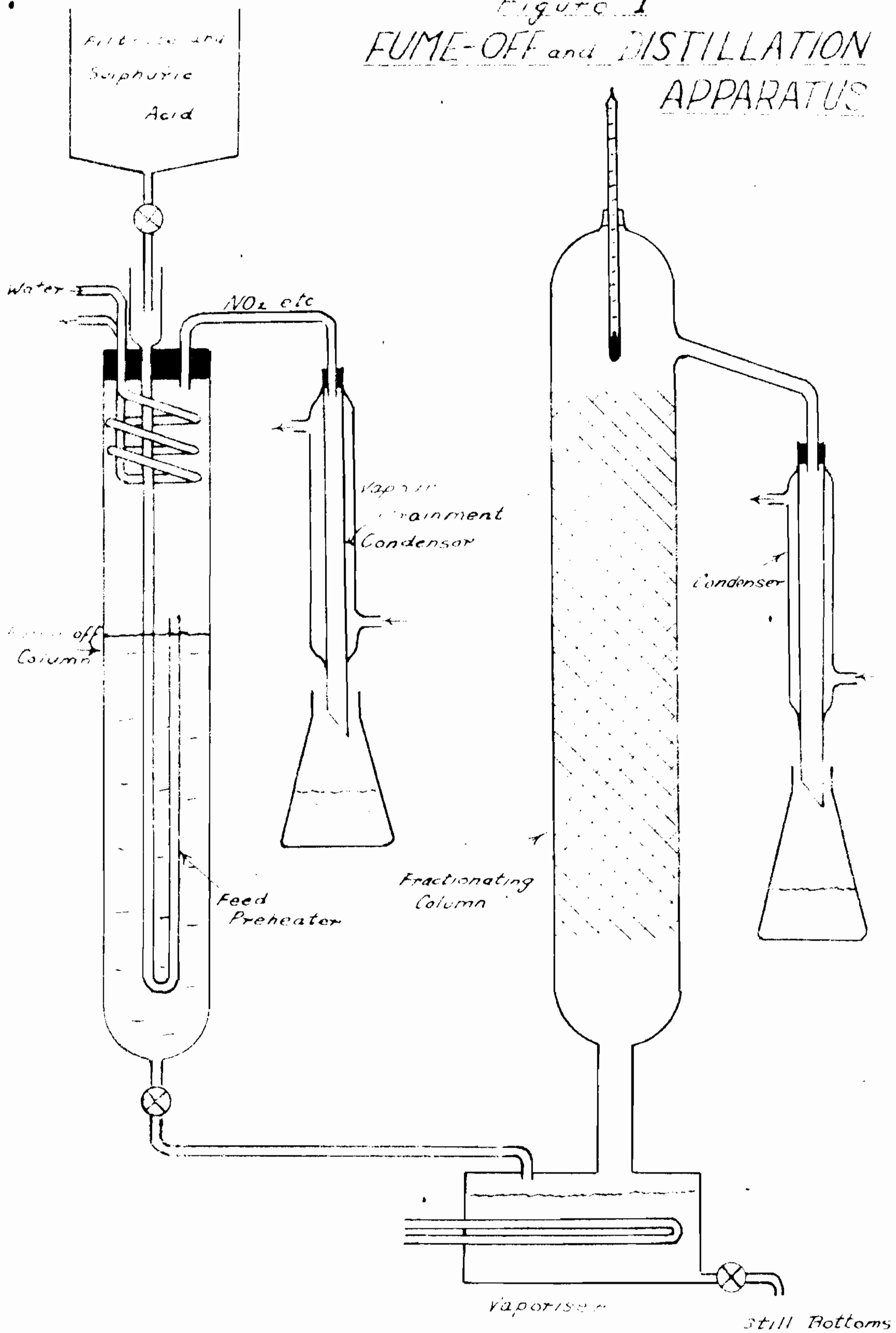
The composition of the fumed off liquor depends largely on the composition of the original liquor. All traces of BSX, etc., are removed in the fume-off, but there remains approximately the same amounts of RDX and HMX in the fumed off liquor as in the original solution. Traces of nitric acid also remain, together with sulphuric acid and water. Recently it has been found that the fumed off liquor also contains formaldehyde and formic acid in small amounts (12). The former may arise from two main sources:-

(a) Residual degradation products of hexamine (usually free formaldehyde).

(b) Destruction of BSX in the fume-off.

It has been shown in this laboratory (12) that a synthetic mixture of BSX in acetic acid when fumed off and distilled in the usual manner, gave a distillate containing roughly 27% of the potential formaldehyde in the BSX. The same workers have found that at least 99%

Figure 1
FUME-OFF and DISTILLATION APPARATUS



of the formaldehyde can be removed by carrying out the fume-off and distillation steps in the presence of aniline (5% in excess over the stoichiometric equivalent).

The formic acid present probably arises from the oxidation of the formaldehyde, and can be kept at a minimum by removing most of the nitric acid prior to the fume-off in the manner described previously, or by refluxing the fumed off liquor for a period of one hour during which the formic acid is destroyed according to the equation:-

$$HCOOH + H_2SO_4 \rightarrow CO + H_2O$$

The water content of the fumed off mother liquor is considerably higher than that of the original liquor. In Table V are shown the results of a series of experiments in which were determined the increase of the water content in the fumed off liquor over that in the mother liquor. The average increase in the water content was approximately 1.6%, regardless of the initial water content of the mother liquor.

In runs 10 and 11, the precipitate, which appeared on addition of sulphuric acid to the mother liquor, was filtered off before the liquid was fumed off, and in these runs the average increase in the water in the fumed off mother liquor was 2.4% over that in the mother liquor. The presence of the precipitate, which was identified as ammonium sulphate, during the fume-off, apparently exerts

TABLE V

THE AMOUNT OF WATER FORMED DURING THE FUME-OFF

Run No.	Vol. Mother Liquor Fumed off ml.	H_2O in Mother Liquor %	Vol. Oleum to Fume-off Mother Liquor ml.	H_2O in Fumed off Liquor %	Increase in H_2O Content %
1	200	2.9	7.0 of 11% Oleum	4.7	1.8
2	200	2.9	8.0 " " "	4.3	1.4
3	200	2.9	9.0 " " "	4.2	1.3
4	200	2.9	10.0 " " "	4.2	1.3
5	200	2.9	11.0 " " "	4.3	1.4
6	100	0.0	3.7 " " "	1.6	1.6
7	100	0.0	5.8 " " "	1.9	1.9
8	100	1.2	3.7 " " "	2.9	1.7
9	100	1.2	5.8 " " "	2.9	1.7
10	100	1.2	3.7 " " "	3.8	2.6
11	100	1.2	3.7 " " "	3.3	2.1
12	100	2.9	3.7 " 23% "	4.7	1.8
13	100	2.9	5.8 " " "	4.3	1.4
14	500	1.5	18.5 " " "	2.7	1.2
15	100	2.9	3.7 " 96% H_2SO_4	5.7	2.8
16	300	2.9	11.1 " " "	4.8	1.9
17	300	2.9	11.1 " 11% Oleum	4.4	1.5
18	300	2.9	11.1 " 23% "	4.2	1.3
19	100	2.9	12.0 " " "	3.7	0.8

a dehydrating effect. At the temperature of the fume-off, ammonium sulphate presumably decomposes into ammonia and sulphuric acid. On the other hand, estimation of the water content in the fumed off liquor, etc., by the acetic anhydride method (Appendix) employed in these studies, gives a figure which includes apparently any water bound as hydrate with the sulphuric acid. If this is true, the presence of the sulphuric acid from the decomposition of the ammonium sulphate should make no difference to the amount of water detected by the analytical method used. No reason can be given for the apparent dehydrating effect of the ammonium sulphate.

No increase was observed in the water content after fuming off the nitrate deficient filtrate obtained by treatment with ammonia. Hence, the water formed during the fume-off of the mother liquor is formed almost entirely from the ammonium nitrate and nitric acid present. Apparently BSX decomposes to formaldehyde and nitrous oxide rather than to water and nitrogen oxides.

A few experiments in which the whole slurry, including all solid products in suspension, was fumed off, produced a filtrate containing approximately 7% water. The solids which precipitated from this fumed off slurry were found to be pure RDX and HMX. The destruction of RDX and HMX in the fume-off is small, hence a very simple method for producing RDX and HMX free of solid impurities is available.

Since control of the fume-off reaction no longer presented a serious problem, attention was next directed to the destruction of residual RDX and HMX in the fumed off liquor.

THE DESTRUCTION OF RDX-HMX RESIDUES IN THE FUMED OFF MOTHER LIQUOR.

The possibility of utilizing the sulphuric acid already present in the fumed off liquor for destroying the RDX-HMX residues was first investigated.

Preliminary experiments indicated that RDX was rapidly and completely destroyed in hot sulphuric acid-acetic acid solutions if the sulphuric acid content was at least 20% by volume. The procedure adopted in these experiments was as follows:-

To a given weight of fumed off mother liquor, containing a known amount of RDX in solution, was added a definite weight of sulphuric acid, and the solution was brought rapidly to its boiling point. After boiling under reflux for varying times, the solution was diluted with ten times its volume of water and allowed to stand in an ice box for 48 hours. The precipitate which formed was filtered off, dried at 110°C, and weighed. The experiment was repeated using varying amounts of sulphuric acid.

The results of these experiments in which the rate of destruction of RDX in sulphuric acid-acetic acid mixtures was determined are given in Table VI and Fig. 2.

Effective destruction of RDX appeared to be possible if the fumed off liquor was distilled from a mixture containing approximately 40% by weight sulphuric acid, 60% by weight acetic acid. For computing the approximate compositions of the mixtures in the still, the boiling curve for sulphuric-glacial acetic mixtures was determined over the complete working range. The data are given in Table VII and Fig. 3.

DISTILLATION OF FUMED OFF LIQUOR FROM A 40% SULPHURIC ACID -60% ACETIC ACID MIXTURE.

Seven litres of fumed off mother liquor (containing 5.4% sulphuric acid) were distilled through 130 ml. sulphuric acid-acetic acid (40-60) mixture using a reflux ratio of 0.1. The distillate was analyzed by the Celanese Corporation of America who reported the following results:-

Acetic Acid	97.7%
Formic Acid	0.3%
Water	1.4%
Esters, as Ethyl Acetate	0.5%
Aldehydes, as acetaldehyde	0.05%
Copper	0.2 p.p.m.
Iron	0.2 p.p.m.
Total Solids	0.008%
Ash	0.003%
Iodine No.	0.08
Saponification No.	3.4
Distillation Range	110.8-118.6°C.

TABLE VI

THE RATE OF DESTRUCTION OF RDX IN FUMED OFF MOTHER LIQUOR BY H_2SO_4

Run No.	% H_2SO_4 by Weight	Boiling Temp. °C	Boiling Time minutes	RDX Destroyed %
1	7.6	121.5	4	19
2	7.6	121.5	10	42
3	7.6	121.5	16	75
4	11.8	125.0	6	60
5	11.8	125.0	10	100
6	22.4	132.0	1	65
7	22.4	132.0	1.5	100

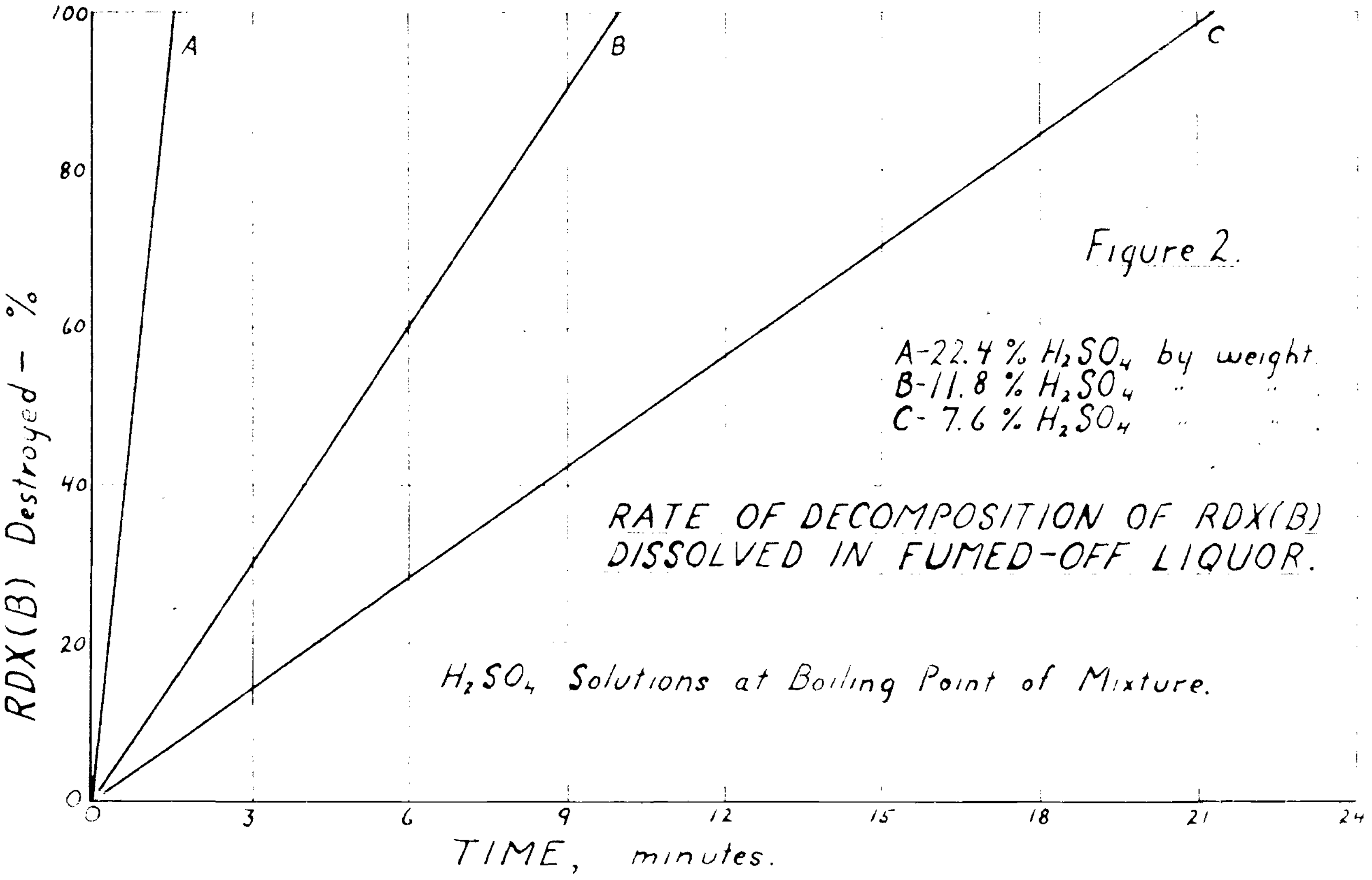


Figure 2.

RATE OF DECOMPOSITION OF RDX(B) DISSOLVED IN FUMED-OFF LIQUOR.

H_2SO_4 Solutions at Boiling Point of Mixture.

TABLE VII

COMPOSITION - BOILING POINT DATA FOR ACETIC ACID - SULPHURIC ACID SOLUTIONS

(A) Technical Acetic Acid:

With 11% Oleum.			With 95% H_2SO_4		
Oleum Volume %	Acetic Acid Volume %	B. Pt. °C	H_2SO_4 Volume %	Acetic Acid Volume %	B. Pt. °C
0.0	100.0	118.0	0.0	100.0	118.0
3.2	96.8	120.5	5.2	94.8	120.5
6.3	93.7	122.5	9.1	90.9	122.0
9.1	90.9	125.0	13.0	87.0	124.4
11.8	88.2	127.0	16.7	83.3	128.0
14.3	85.7	130.0	20.0	80.0	131.5
16.7	83.3	133.0	23.1	76.9	135.0
18.9	81.1	136.0	25.9	74.1	139.4
21.0	79.0	140.0	28.6	71.4	143.8
23.0	76.9	144.5	31.0	69.0	147.5
25.0	75.0	147.5	33.3	66.7	151.3
26.8	73.2	150.0	35.5	64.5	156.1
28.6	71.4	154.2			
30.2	69.8	158.3			
31.8	68.2	163.0			
33.4	66.6	167.0			
34.8	65.2	170.0			
36.2	63.8	172.5			
37.5	62.5	173.7			
38.8	61.2	176.5			

(B) Recovered Acetic Acid (98.4%):

0.0	100.0	115.0	0.0	100.0	115.0
3.3	96.7	117.5	5.2	94.8	118.8
6.2	93.8	119.5	9.1	90.9	121.0
9.1	90.9	121.9	13.0	87.0	123.5
11.8	88.2	124.9	16.7	85.3	127.2
14.3	85.7	127.0	20.0	80.0	131.0
16.7	83.3	131.0	23.1	76.9	135.5
18.9	81.1	134.5	25.9	74.1	140.0
21.0	79.0	138.0	28.6	71.4	145.0
23.1	76.9	142.0	31.0	69.0	149.0
25.0	75.0	146.0	33.3	66.7	154.0
			35.5	64.5	159.0

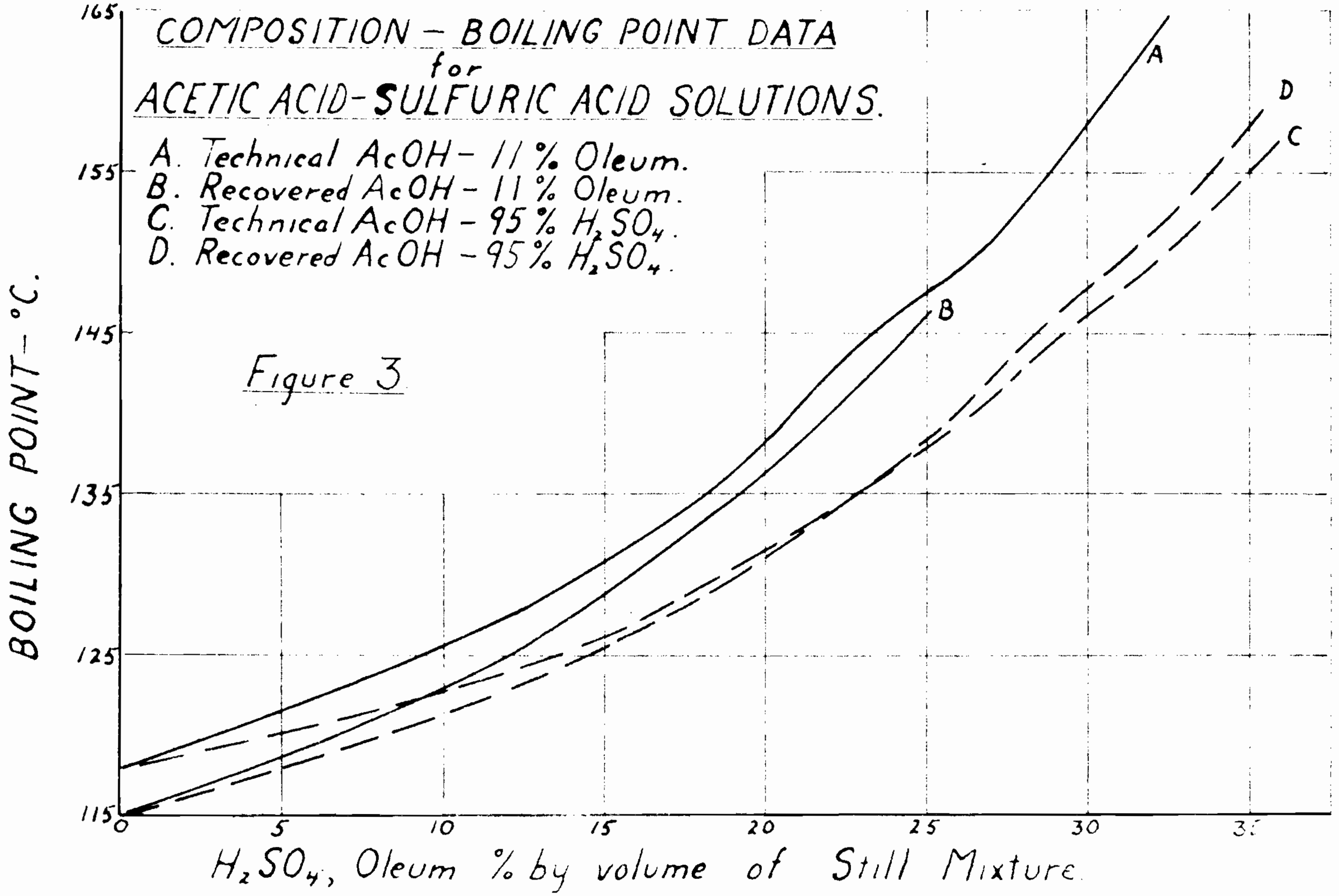

COMPOSITION – BOILING POINT DATA
for
ACETIC ACID-SULFURIC ACID SOLUTIONS.
A. Technical AcOH – 11 % Oleum.
B. Recovered AcOH – 11 % Oleum.
C. Technical AcOH – 95 % H_2SO_4.
D. Recovered AcOH – 95 % H_2SO_4.
BOILING POINT – °C.
165
155
145
135
125
115
0
5
10
15
20
25
30
3
H_2SO_4, Oleum % by volume of Still Mixture
A
B
C
D

Figure 3

This acid was reported to be of sufficiently high quality for the production of acetic anhydride, but it was recommended that, if possible, the water-ester-aldehyde content should be reduced.

A similar distillation of the fumed off liquor without reflux gave a distillate which contained traces of sulphuric acid. Replacing the fractionating column and running at a reflux ratio of 0.1 again gave a distillate free of sulphuric acid, even at elevated stillpot temperatures.

Removal of Water from the Distillate:

The sources of water in the distillate are three:

(1) Water in the fumed off mother liquor.
(2) Water formed by the decomposition of RDX, etc., in the stillpot.
(3) Water formed by the decomposition of acetic acid in the stillpot at elevated temperatures.

(1) Water in the Fumed off Liquor:

The water content of the fumed off liquor, prior to distillation, was finally reduced to a negligible amount by treatment of the mother liquor with anhydrous ammonia. This served to precipitate most of the nitric acid as ammonium nitrate as well as the ammonium nitrate which was already present in the mother liquor before the fume-off operation, and largely reduced the water production from these compounds in the fume-off.

(2) Water Formed by Decomposition of RDX, etc.:

The water formed during distillation from the destruction of RDX residues in the fumed off mother liquor is essentially a constant quantity, and may be removed only by the addition of a dehydrating agent to the stillpot or distillate, or by rectification of the distillate. The possibility of using oleum as a dehydrating agent in the stillpot was investigated. The results from a number of batch distillations in which the oleum was dissolved in the fumed off liquor before distillation of the acetic acid are given in Tables VIII and IX.

At low sulphuric acid concentrations, the destruction of RDX residues occurs comparatively slowly (Fig. 2). Hence under such conditions, the rate of distillation may affect the relative water contents of successive portions of the distillate. This is illustrated in runs 2, 3 and 4, Table IX, where it is seen that the slower distillation rate, permitting more decomposition to occur during the time of collecting the first fractions, increases the water content of these fractions.

Considering the whole series of experiments above, the average increase in the water content of the distillate, due to destruction of RDX residues, was approximately 1.5%.

TABLE VIII

THE DEHYDRATING EFFICIENCY OF OLEUM IN FUMED OFF MOTHER LIQUOR IN A BATCH DISTILLATION

Volume of Fumed Off Liquor ml.	H_2O in Fumed Off Liquor %	Oleum (23%) added to Fumed Off Liquor ml.	B. Pt. of Still Mixture °C	Distillate		Recovery of Acetic Acid %
				Vol. ml.	H_2O %	
100	1.0	10.0	123-35	50.0	0.3	
			135-70	25.5	0.7	80
100	1.0	10.0	123-35	49.5	0.4	
			135-70	25.5	0.7	80
100	1.0	15.0	128-50	50.0	0.03	
			150-80	19.0	0.6	72
1575	2.9	30.0	118	100.0	2.9	
			118-19	100.0	2.9	
			118-19	100.0	2.9	
			119-19.5	100.0	2.9	
			119.5-20	100.0	2.9	
			120	100.0	2.7	
			120-21	100.0	2.6	
			121-22	100.0	2.4	
			122-23	100.0	2.4	
			123-25	100.0	2.2	
			125-27	100.0	1.8	
			127-33	100.0	1.8	
			133-44	100.0	2.1	
			144-49	28.0	2.4	89.5

TABLE IX

WATER FORMED IN THE DISTILLATION OF FUMED OFF MOTHER LIQUOR BY DECOMPOSITION OF IMPURITIES

H_2O in Original Fumed Off Liquor = 0.8%

Fumed Off Mother Liquor = 1 Litre Mother Liquor + 30 ml. H_2SO_4(95%)

Run No.	Volume fumed off Liquor ml.	H_2SO_4(95%) added to fumed off Liquor ml.	% H_2O in the Distillate 1st Fraction 25 ml.	 2nd Fraction 25 ml.	 3rd Fraction 25 ml.	 4th Fraction 25 ml.	Time to Distill 100 ml. Min.
1	200	0	2.4	2.1	1.2	0.7	25.
2	200	6	1.5	1.2	1.1	1.0	4.75
3	200	6	1.9	1.3	1.4	1.0	14.5
4	200	6	3.4	2.1	1.9	0.7	45.
5	200	12	2.5	2.0	1.6	1.0	29.5
6	200	48	2.9	2.1	2.0	1.6	50.
7	200	96	3.3	2.5	3.3	4.0	45.

A series of semi-continuous distillations was made using various strengths of oleum. The oleum was mixed with sufficient fumed off liquor to give a mixture which boiled at 128-130°C. The remaining fumed off liquor was run into this mixture at a rate sufficient to maintain the boiling point of the still mixture constant at 128-30°C. In all these distillations the total volume of fumed off liquor had been added by the time the eighth fraction had been collected. The results are presented in Table X and Fig. 4.

From Fig. 4, it is evident that an essentially water free distillate may be obtained by addition of sufficient sulphur trioxide. However, the amount of trioxide required is prohibitive from the standpoint of maximum acetic acid recovery. It is essential to keep the sulphuric acid content to a minimum, since the loss of acetic acid in the still residues is approximately 1 to 1.5 times the weight of sulphuric acid present (40% sulphuric-60% acetic). Hence the most efficient process would be one in which the feed to the still was an anhydrous fumed off liquor with a minimum amount of sulphuric acid present.

(3) Water Formed by Decomposition of Acetic Acid at Elevated Temperatures.

A noticeable increase of water content in the

TABLE X

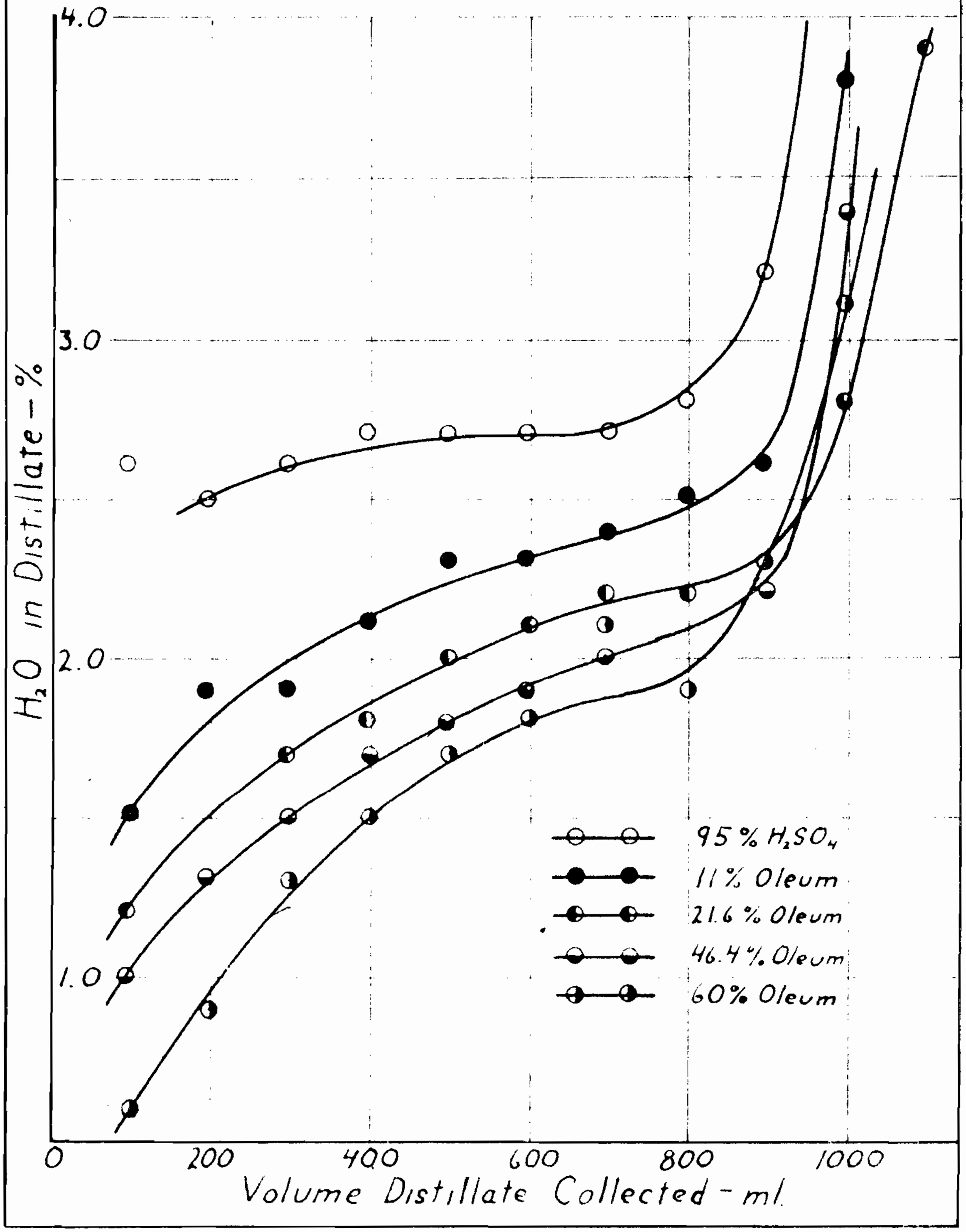
THE DEHYDRATING EFFICIENCY OF OLEUM IN A CONTINUOUS DISTILLATION OF FUMED OFF MOTHER LIQUOR

Water in Distillate - %

Volume Fumed Liquor ml.	Water Content %	Volume Oleum added ml.	100 ml. Fractions.										
			1	2	3	4	5	6	7	8	9	10	11
1120	2.8	30 of 96% H_2SO_4	2.6	2.5	2.6	2.7	2.7	2.7	2.7	2.8	3.2	4.8	-
			←---- B.Pt. = 126-129°C -------→								←129-45°→	←145-69°→	-
1300	2.8	30 of 11% Oleum	1.5	1.9	1.9	2.1	2.3	2.3	2.4	2.5	2.6	3.8	-
			←---- B.Pt. = 127-130°C -------→								←130-46°→	←146-68°→	-
1575	2.9	30 of 21.6% Oleum	1.2	1.3	1.7	1.8	2.0	2.1	2.2	2.2	2.3	2.8	3.9
			←---- B.Pt. = 127-128°C -------→								←128-33°→	←133-48°→	←148-68°→
1190	2.4	30 of 46.4% Oleum	1.0	1.3	1.5	1.7	1.8	1.9	2.0	2.2	2.2	3.4	-
			←---- B.Pt. = 127-128°C -------→								←128-40°→	←140-65°→	-
1185	2.7	30 of 60% Oleum	0.6	0.9	1.3	1.5	1.7	1.8	2.1	1.9	2.3	3.1	-
			←---- B.Pt. = 127-130°C -------→								←130-44°→	←144-67°→	-

Figure 4.

THE DEHYDRATING EFFICIENCY OF OLEUM IN FUMED-OFF MOTHER LIQUOR IN A CONTINUOUS DISTILLATION.



distillate, accompanied by charring of the sulphuric-acetic mixture in the stillpot at high distillation temperatures, indicated that the acetic acid was being cracked at these temperatures. This is readily apparent from Fig. 4, where it is seen that after 800 ml. of distillate had been collected, and addition of fumed off liquor was stopped, while the distillation was continued to a stillpot temperature of 170°C, the distillate contained as much as 5% water, whereas the water content of the original was only 2.9%. The increase in water content is presumably due to decomposition of acetic acid at elevated temperatures.

To determine the temperature at which the acetic acid destruction became significant, an experiment was made on acetic acid-water-sulphuric acid mixtures in which the sulphuric acid content of the still mixture was varied over a fairly wide range. The acetic acid feed contained 5.1% water. The results are given in Table XI and Fig. 5.

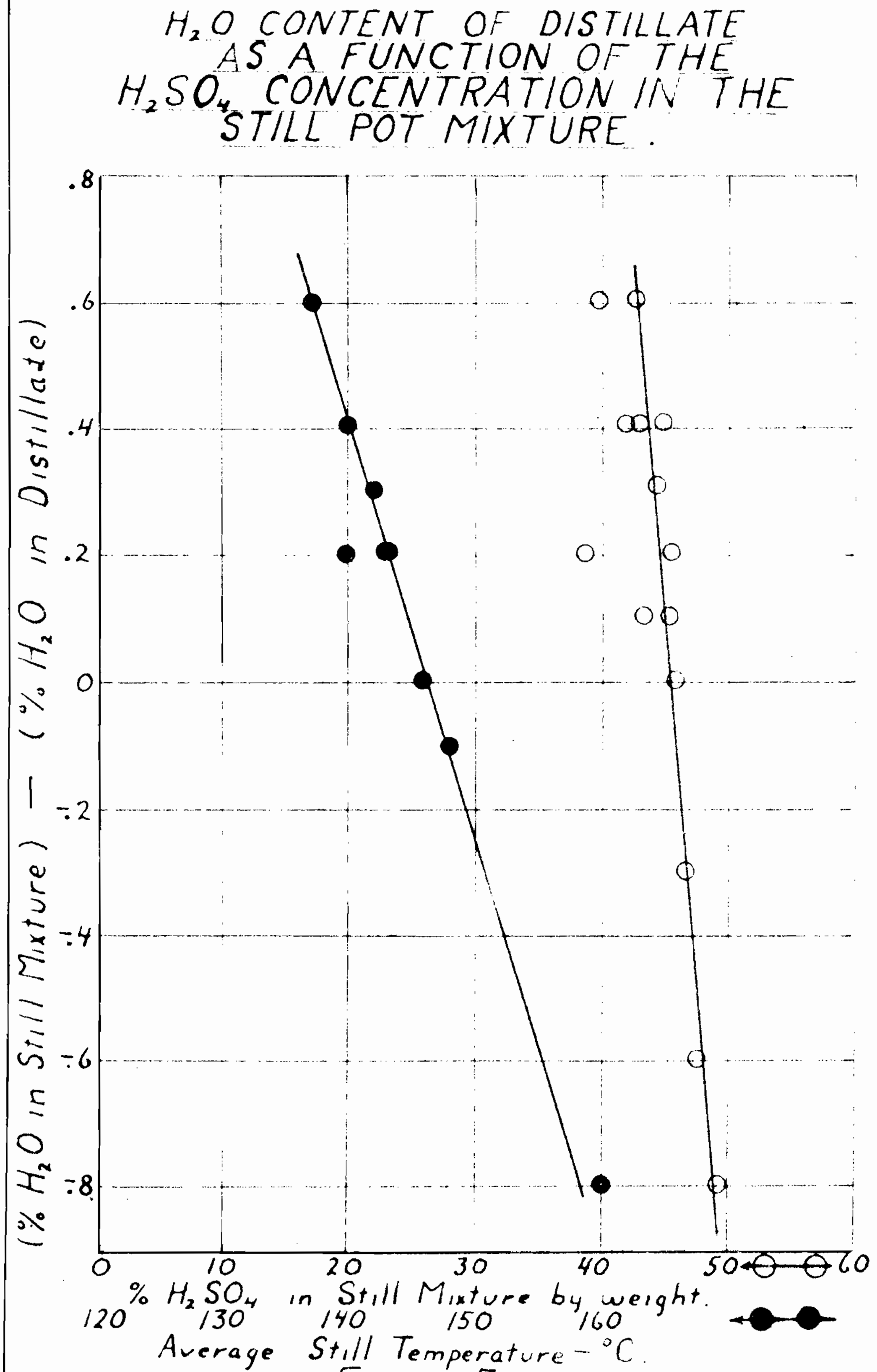
The data indicate that the percentage water in the distillate is less than that in the still mixture up to a well defined limit, represented by 46% sulphuric acid in the still mixture. Beyond this point, i.e., at a temperature greater than 146°C, the water content of the distillate is greater than that of the still mixture. This fact is clearly illustrated in Fig. 5, where the

TABLE XI

H_2O CONTENT OF THE DISTILLATE AS A FUNCTION OF THE H_2SO_4 CONCENTRATION IN THE STILLPOT MIXTURE

Feed: 5.1% Water - 94.9% Acetic Acid

Average Stillpot Temperature °C	H_2SO_4 in Still Mixture (Expressed as 100% H_2SO_4) % by Weight	Water Content % by Weight		(%H_2O in Still) -(%H_2O in Distillate)
		In Still Mixture	In Distillate	
137	40.0	2.8	2.2	+ 0.6
140	43.1	2.4	2.0	+ 0.4
140	42.0	2.5	2.1	+ 0.4
140	43.4	2.2	2.1	+ 0.1
141	45.3	2.1	2.0	+ 0.1
142	44.7	2.4	2.1	+ 0.3
143	45.4	2.3	2.1	+ 0.2
144	42.8	2.9	2.3	+ 0.6
144	45.0	2.6	2.2	+ 0.4
145	46.8	1.8	2.1	- 0.3
146	46.2	1.9	1.9	- 0.0
148	49.8	2.2	2.3	- 0.1
153	47.8	1.8	2.4	- 0.6
160	49.2	1.8	2.6	- 0.8



(%H_2O in still) - (%H_2O in distillate) is plotted against:

(a) The sulphuric acid content of the still mixture.

(b) The average temperature of the still mixture.

The sulphuric acid exhibits a maximal dehydrating efficiency as illustrated in Table XII and Fig. 6. In this experiment, the feed was 1575 ml. of fumed off mother liquor containing 5% sulphuric acid, 2.6% water and 92.4% acetic acid. The distillate was collected in 100 ml. fractions. In Fig. 6 is plotted (%H_2O in still) - (H_2O in distillate) against % H_2SO_4 in the still.

Until a composition of 14.2% sulphuric acid - 2.6% water - 83.2% acetic acid was attained in the stillpot, the sulphuric acid exerted no appreciable dehydrating action. From 15% to approximately 35% sulphuric acid, the dehydrating capacity increased to a maximum, giving a distillate of a progressively higher acetic acid strength. After a maximal dehydrating efficiency at approximately 35% sulphuric acid in the still mixture, the efficiency decreased sharply.

The highest quality acetic acid distillate was obtained at the maximum dehydrating concentration of approximately 35% sulphuric acid in the still mixture, but the total recovery of acetic acid was not maximal under these conditions. With a still mixture of 35% sulphuric acid - 3.3% water - 61.7% acetic acid, a recovery of only 55% of the total acetic acid initially present was obtained.

As a result of the above experiments,

TABLE XII

THE DEHYDRATING EFFICIENCY OF H_2SO_4 IN THE STILL MIXTURE

Original Feed to Still: 2.9% H_2O, 97.1% Acetic Acid

Composition of Still Mixture % by Weight H_2O	H_2SO_4	AcOH	H_2O in Distillate % by Weight	(H_2O in Still) -(%H_2O in Distillate)
2.6	10.0	87.4	2.9	- 0.3
2.6	10.6	86.8	2.9	- 0.3
2.6	11.3	86.1	2.9	- 0.3
2.6	12.2	85.2	2.9	- 0.3
2.6	13.1	84.3	2.9	- 0.3
2.6	14.2	83.2	2.9	- 0.3
2.6	15.5	81.9	2.7	- 0.1
2.6	17.1	80.3	2.6	0.0
2.6	19.0	78.4	2.4	0.2
2.7	21.5	75.8	2.4	0.3
2.8	24.6	72.6	2.2	0.6
3.0	28.8	68.2	1.8	1.2
3.2	34.8	62.0	1.8	1.4
3.3	41.3	55.4	2.1	1.2
3.6	47.1	49.3	2.4	1.2

DEHYDRATING EFFICIENCY of H_2SO_4 IN THE STILL MIXTURE

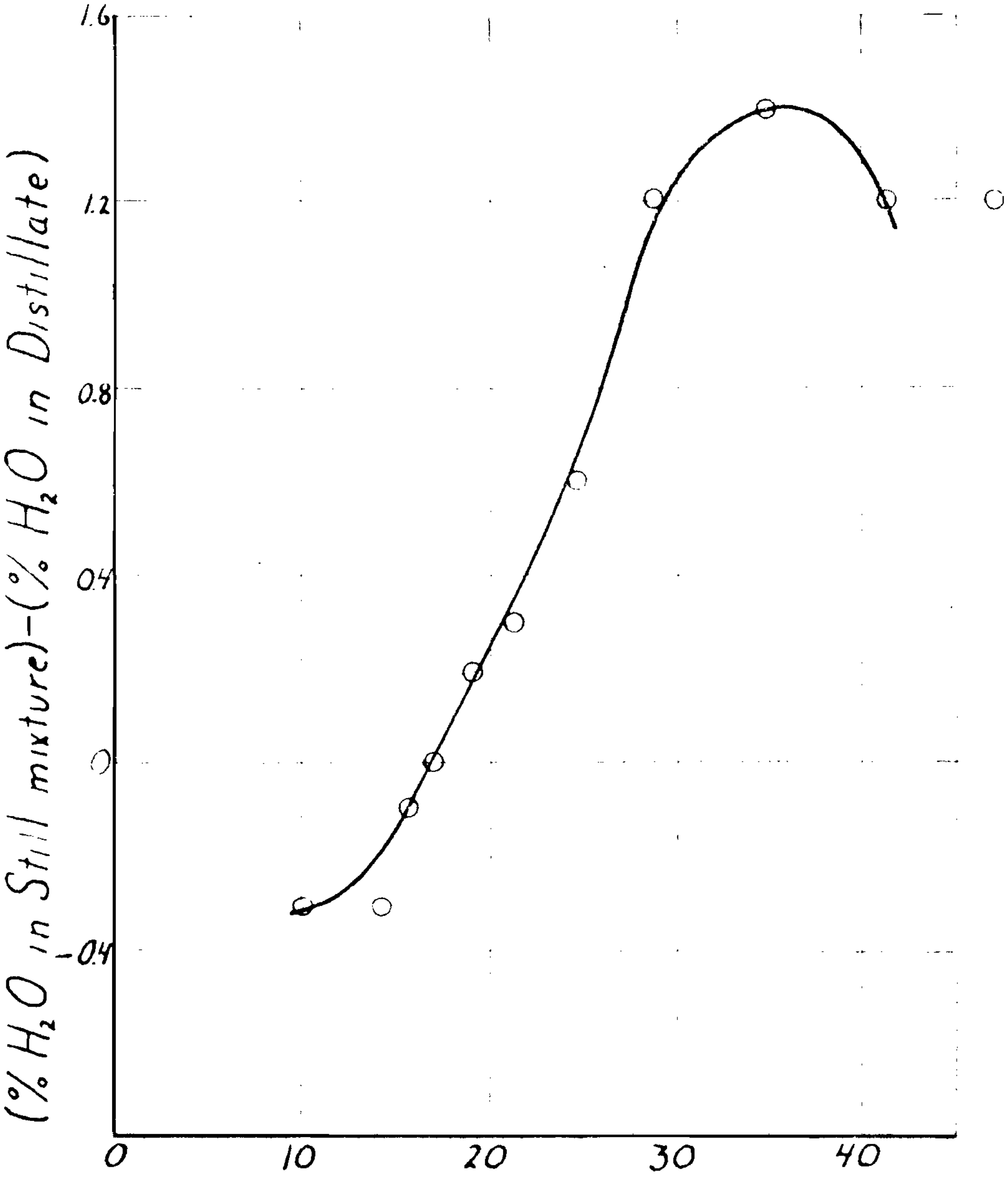


Figure 6

it was concluded that sulphuric acid was inefficient as a dehydrating agent in the acetic acid-water-sulphuric acid system, and, indeed, under certain operating conditions, might exert a harmful effect by decomposing acetic acid.

Summarizing the results of the foregoing experiments, it might be concluded that the water content of the recovered acid may be minimized by the following:

Treatment of the cooled (25-30°C) slurry from the converter with stoichiometric amounts of anhydrous ammonia to minimize the nitric acid and ammonium nitrate contents of the filtered liquor; fume-off of this essentially nitrate free filtrate with a minimum amount of sulphuric acid, to give a nearly anhydrous feed for distillation; distillation of this anhydrous liquor from a 35% sulphuric - 65% acetic acid mixture, keeping the temperature of the still mixture below about 145°C. A slight excess of acetic anhydride in the filtrate, would, of course, serve to reduce or eliminate the small amount of water formed during the distillation.

<u>Losses in the Recovery Process:</u>

A number of experiments was made to obtain some information on the probable extent of losses during the fume-off and distillation operations.

<u>(A) Loss in the Fume-off:</u>

The mother liquor was fumed off in the manner described previously, using the reactor sketched in Fig. 1, except that the fumed off liquor was drained off at the bottom of the reactor into a graduated cylinder, rather than fed directly to the still. In the second batch fumed off, the loss was partially overcome by trapping the vapours evolved in a flask immersed in an ice-water bath. The results are recorded in Table XIII.

(B) Loss in the Distillation:

A number of variations in the distillation were studied.

(a) To 500 ml. of fumed off liquor from Run (a) was added 23 ml. of 11% oleum (sufficient sulphur trioxide to combine with the water present). The resultant solution was then distilled and three fractions were collected over stillpot temperature ranges of 120-125°C, 125-135°C, and 135-145°C respectively. To the residue from this distillation was added another 500 ml. of fumed off liquor, and three more fractions were collected as before. This procedure was repeated with a third 500 ml. batch of fumed off liquor. The residue from the final distillation was diluted ten fold with water and allowed to stand for 24 hours to precipitate any RDX that might have remained undecomposed in the stillpot.

(b) 250 ml. of fumed off liquor from Run (b) was distilled to determine whether the sulphuric acid remaining in the liquor after the fume-off was in sufficient

TABLE XIII

THE EXTENT OF LOSSES IN THE FUME-OFF OPERATION

Original Liquor

Run No.	Volume Fumed off ml.	H_2O Content %	Vol.Oleum to Fume-off ml.	Fume-off Temp. °C.
1	2050	0.0*	64.0	105-6
2	2050	0.0*	64.0	104-5

Fumed off Liquor

Run No.	Volume Recovered ml.	H_2O Content %	Volume Decrease ml.	Vol. Condensed Vapour ml.	Net Loss ml.
1	2026	0.73	88	-	88
2	2022	0.71	92	18	74

RDX in fumed off liquor = 0.485 gms./100 ml. liquor

* Mother liquor contained an excess of anhydride, but this could not be determined since method of analysis for excess anhydride was not available to this laboratory at time of experiment.

amount to decompose all the RDX present. Two fractions were collected over stillpot temperature ranges of 119-122°C and 122-145°C respectively, and the still residues were treated as in (a).

(c) 15 ml. of acetic anhydride was added to 250 ml. of fumed off liquor from Run (b), this quantity of anhydride being in slight excess over that calculated to remove all water present in the fumed off liquor. Two fractions were collected over pot temperature ranges of 121-122.5°C and 122.5-145°C. The residues were treated as in (a). The results of these experiments are presented in Table XIV.

The initial fractions in (a) contained relatively little water, owing to the slow rate at which the residues in the still were being decomposed. As the sulphuric acid concentration increased in the stillpot, so also did the rate of decomposition of the residues, and consequently the water content of the distillate. A limit would have been attained ultimately after the sulphuric acid content in the still had reached a concentration sufficiently high to decompose the residues as fast as they were being added.

In experiment (c), it will be noticed that no water was detected in the first fraction, since all water initially present and all that subsequently formed in the stillpot was removed by the acetic anhydride excess present. Also, it is seen that the formic acid content was reduced to a small value.

TABLE XIV

THE EXTENT OF LOSSES IN THE DISTILLATION OPERATION

Run No.	Liquor Input ml.	Temp. Still Mixture °C.	Volume Collected ml.	Acetic Acid %	H_2O %	HCOOH etc. %	RDX in Residue gms.
(a)	500	120-125	203.0		0.51		
		125-135	140.0		0.53		
		135-145	42.0	99.07	0.80	0.284	0
	500	120-125	217.0		0.86		
		125-135	174.0		0.79		
		135-145	56.5	98.84	0.96	0.294	0
	500	120-125	160.0		0.97		
		125-135	212.5		0.86		
		135-145	74.0	-	1.01	0.316	0
Recovery of Acetic Acid = 89%							
(b)	250	119-122	100.0	98.66	1.06	0.280	
		122-145	123.5	98.96	0.75	0.285	0
Recovery of Acetic Acid = 92%							
(c)	250	121-122.5	102.0	99.99	0.00	0.005	
		122.5-145	138.0	99.84	0.10	0.058	0
Recovery of Acetic Acid = 93%							

The Application of the Recovery Method to Plant Practice.

The studies described in the foregoing pages indicated as essential features of the fume-off sulphuric acid distillation recovery process the necessity for obtaining from the RDX slurry a filtrate as free as possible from nitrates (NH_4NO_3 and HNO_3) and, if possible, one in which the acetic anhydride excess normally required in the manufacture of RDX(B) was retained as such.

Plant reports indicated that the slurry from the convertor was difficult to filter unless diluted with water, followed by a thirty minute simmer period. In this way, clogging of the filter pores by BSX was presumed to be avoided. However, addition of water to the slurry in any amount would be detrimental to acid quality, so that some alternative method of obtaining a relatively rapid filtration rate was obviously necessary.

Following a brief survey of the filtration problem in this laboratory, it became apparent that a solution must be sought in the plant itself, since the slurry, as received at the laboratory, filtered very easily, even when the water dilution and simmer steps were omitted. This difference in behaviour was thought to be due to changes which occurred during aging of the slurry while in transit from plant to laboratory. Accordingly, all further work on the filtration problem was done during two weeks spent at the St. Maurice plant.

Since ammonia treatment of the slurry from the reactor was desirable for reducing the nitrate content of the filtrate, the majority of the experiments were made with ammonia treated material. Experiments on a small scale, using a stainless steel tube, 3 inches in diameter, fitted with a stainless steel 250 x 20 mesh filter, the tube being 26 inches in height to permit a filter bed of thickness comparable with that in the plant, indicated that the filtration time could be kept well within the limits required for practical purposes if two conditions were observed:

(a) The ammonia treated slurry was cooled to 25-30°C before being transferred to the filter.

(b) A settling period of 5 minutes or longer preceded application of suction to the filter.

At this time, it was believed that if the slightly warm (30°C or higher) slurry was poured onto the filter, subsequent slow cooling would cause additional precipitation of materials (NH_4NO_3, BSX, etc) in the body of the filter cake, thus clogging the pores and increasing the difficulty of filtration. The settling period was thought to be advantageous in that it probably permitted a thin layer of relatively coarse crystals of RDX to be deposited initially on the filter, thus providing a favourable bed. (Subsequent work at the plant appears to have

TABLE XV

DATA ON FILTRATION OF UNDILUTED BACHMANN SLURRY (PLANT SCALE)

Filter Temp. °C	NH_3 added lb.	Settling Time min.	Vacuum inches Hg.	Filter Time min.	Wash Time min.	Remarks on handling of Washed Cake	Other Remarks
26	26	5	20	42	25	Easily handled	The acetic acid recovered from these batches by fume-off and distillation was 98.8% to 99.4% strength. These batches boiled to acid specification in normal time with very little frothing.
27	35	5	12	65	30	Easily handled - no odour	
27	25	5	12	120	50	Do	
26	22	15	10	50	20	Do	
27	-	10	10	60	30	Do	
25	30	45	12	65	30	Very easy to handle	
30	29	nil	21	360	45	Easily handled - did not smell strongly. (Note:-this was a large batch - ca. 300 Gal.)	
30	nil	5	?	80	-	Difficult to wash free of acid odour	Boiled to acid specification in 12 hours.
30	nil	5	?	80	-	Do	

It may be noted from Table XV that the filter times are generally well within the three hour limit imposed by the normal operation cycles at the St. Maurice Plant. The resulting cakes of the ammonia treated batches when washed met the approval of experienced operators, as far as handling characteristics were concerned, while the time required to boil the product to acid specification was indicated to be no longer than normal. The filtrates of the ammonia treated batches, containing excess acetic anhydride, but relatively free of nitric acid and ammonium nitrate, were found to fume-off satisfactorily.

In conclusion, it might be noted that, while the studies reported here provided the basis for the design and operation of the units at present in operation at the St. Maurice Plant, a large body of information, not included in this thesis, presumably is now available from the operation of these units. The method has now been patented, both in Canada and the United States.

THE DEVELOPMENT
OF A
CONTINUOUS REACTOR
WITH WHICH
TO
INVESTIGATE THE BACHMANN REACTION

A. THE U-TUBE REACTOR

B. THE ROTATING TUBE REACTOR

INTRODUCTION

Hexamethylenetetramine (hexamine) may be nitrated to cyclotrimethylenetrinitramine by the direct action of sufficient excess of strong nitric acid (>88%), by the action of acetic anhydride on a mixture of formaldehyde and ammonium nitrate, or by the interaction of hexamine with nitric acid (approximately 98%), ammonium nitrate and acetic anhydride in acetic acid medium. These preparative methods may be designated the direct nitrolysis, the Ross or McGill and the Bachmann or Combination reactions respectively. The product from the Ross and Bachmann reactions carries with it some cyclotetramethylenetetranitramine (HMX), and has therefore been designated RDX(B) to distinguish it from the essentially pure product prepared by direct nitrolysis. While the Ross reaction has not attained commercial importance, the other two processes are currently used for the production of large quantities of explosive stores.

The combined efforts of investigators in the United Kingdom, U.S.A., and Canada during the past five years have resulted in a large body of information on the direct nitrolysis and Bachmann reactions particularly, and on the chemistry of nitramines in general. It would serve little purpose to attempt here a comprehensive survey of the available information; two excellent monographs by Linstead (13, 14) give adequate treatment to the majority of the information, and it should suffice to confine these introductory remarks to those facts which are directly relevant to the present studies on the Bachmann reaction. This will exclude many studies whose primary purpose was to develop or test theories for the mechanism of the reaction. It seems desirable, moreover, to bring together the facts pertaining to the influence of each variable, rather than give particular concern to the chronological order in which the facts were established.

There are a number of possible variables which may influence the conversion of hexamine to RDX in the Bachmann reaction. Five of these are the reagents themselves, of which one (acetic acid) may, however, play a part only as a carrier and diluent for the other reactants. Four other variables are temperature, the order of addition, the effect of dilution and the effect of water present as an impurity in small amounts in most of the reagents. There may be other variables such as the type of converter in which the reaction occurs, agitation or mixing of the reaction medium, and still others not obvious.

Effect of Nitric Acid:

Among the variables having greatest influence on the conversion of hexamine to RDX(B) is the molar ratio of nitric acid to hexamine. It will be convenient to express reactant concentrations throughout as mole ratios, that is, moles per mole hexamine. Following immediately upon discovery of the reaction, Bachmann (15) reported the quality of the RDX(B) to depend on the amount of nitric acid introduced and that the yield of RDX(B) depended inversely on the quantity of nitric acid. In a later report (16) this author reported increases in yields of RDX(B) up to approximately 80% by increasing the nitric acid from 4.4 to 4.7 moles per mole hexamine and the ammonium nitrate from 3.4 to 3.9 moles per mole hexamine. A further report (17) illustrated the vital importance of maintaining the proper reagent excesses over those required theoretically. The following data are abstracted from his report.

	Acetic Anhydride Deficiency	Acetic Anhydride Excess
Nitric Acid Deficiency	73% HMX 6% RDX	48% HMX 8% RDX
Nitric Acid Excess	42% HMX 12% RDX	5% HMX 70% RDX

These figures represent the percentage of the theoretical conversion of hexamine to HMX or RDX in each case.

A low or high nitric acid excess was shown to decrease the rate of production of RDX(B) while a low nitric acid excess was found to favor the production of HMX, (18).

A sharply defined optimum value of the nitric acid concentration was observed at 35°C by Williams (18), the optimum being approximately 4 moles of nitric acid per mole hexamine.

In a recent report (19) Bachmann et al also reported the existence of an optimum value of the nitric acid introduced per mole hexamine for optimum conversion of hexamine to RDX(B). The optimum value for their standard batch runs was 4.2 moles of nitric acid per mole hexamine with yields of RDX(B) as high as 85% of the theoretical value at this concentration.

Winkler reported (20) an optimum to exist at 5 moles of nitric acid per mole hexamine when the reaction was studied homogeneously at 45°C. The consumption of ammonium nitrate per mole of RDX produced has been shown to increase as the nitric acid concentration is increased (21).

Laboratory work by Tennessee Eastman Corporation (22) showed the optimal quantity of nitric acid to be 4.45-4.78 moles per mole hexamine. In pilot plant work (22) a yield of 82.5% RDX(B) was obtained with 4.35 moles nitric acid, 2.78 moles ammonium nitrate and 7.84 moles of acetic anhydride per mole hexamine. The nitric acid mole ratio was adjusted slightly in operation to maintain the concentration of free nitric acid in the reaction at 2-2.5% by weight.

Wright (23) investigated the effect of decreasing the mole ratio of nitric acid to ammonium nitrate ratio from 2.3 to 1.4 at a nitric acid to hexamine mole ratio of 4.6. There was a linear increase in yield of RDX(B) from 77% to 80% accompanied by an increase in the HMX content of the RDX(B) from 5% to 7%.

Effect of Ammonium Nitrate.

In the early developmental stages of the "Combination Process" Bachmann noticed that the yield of RDX(B) was markedly increased when excess ammonium nitrate was added above that theoretically required (24). He reported yields as high as 83% using 2.6 moles ammonium nitrate per mole hexamine (25). He reported later (26) that the conversion of hexamine to BSX was inhibited by ammonium nitrate while the conversion to RDX was aided by ammonium nitrate. A more detailed study (27) revealed that a low ammonium nitrate concentration decreased the rate, whereas a higher ammonium nitrate concentration increased the rate of production of RDX(B), the production of HMX being simultaneously decreased.

Kinetic studies (18) at 45°C revealed that an increase in ammonium nitrate concentration had the following effects:

(i) Rate of HMX formation remained constant.

(ii) Yield of HMX decreased slowly

(iii) Rate of formation of RDX passed through a maximum.

(iv) Yield of RDX passed through a maximum

In his studies of the mechanism of the formation of RDX, Carmack (28) was able to verify the conclusion of Davy (29) that the consumption of ammonium nitrate was one mole per mole of RDX produced. This ratio increased as the nitric acid concentration was increased (30). A series of experiments (29) at 70°C in which the ammonium nitrate added was varied from 2.87 moles to 1.04 moles per mole hexamine gave yields of RDX(B) varying from 78.3% to 30.4%. The ratio of RDX(B) produced to ammonium nitrate consumed remained at 1:1 over this whole range. The same series of experiments repeated at 35°C gave inconclusive results which did not conform to any known mechanism postulated for the conversion of hexamine to RDX. Smart (31) was not able to establish a 1:1 ratio between the RDX produced and ammonium nitrate consumed.

Effect of Acetic Anhydride

The course of the reaction in the "Combination Process" is influenced appreciably by the quantity or concentration of acetic anhydride present relative to the theoretically required amount.

Bachmann et al (32) noticed that a product containing as much as 60% HMX could be obtained with an initial deficiency of anhydride, the deficiency being eliminated at the end of the experiment. The same workers (33) investigated the influence of adding different amounts of acetic anhydride at the beginning of the reaction. Starting with 4.63 moles of acetic anhydride per mole hexamine and increasing this ratio to 11, decreased the yield of HMX from 70% to 50% of the theoretical value. They report also (34) a decrease in the rate of production of RDX at low anhydride concentrations.

Some contradictory evidence was presented by Wright (35) who reported exceptionally low yields of HMX on decreasing the amount of acetic anhydride to less than 7 moles per mole of hexamine. He suggested that other factors such as leading the nitric acid-ammonium nitrate concentration ahead of the hexamine concentration might account for this discrepancy. The necessity has been stressed (36) of maintaining at all times an excess of acetic anhydride in the reaction mixture, if maximum production of RDX were to be attained.

A more detailed investigation of the effect of excess acetic anhydride by Whitmore (37) revealed a large increase in the yield of RDX as the acetic anhydride concentration approached 0.5 moles in excess of that theoretically required. From 0.5 to 1.25 moles excess the yield of RDX increased more slowly and beyond this range the yield started to decrease.

At 45°C, in a homogeneous reaction, maximum production of HMX has been found (20) at an acetic anhydride excess of 6 moles per mole hexamine. This large excess had little influence on the rate of production of HMX.

Effect of Temperature:

The effect of temperature on the yield of RDX(B) was first investigated by Bachmann (38). For a standard set of conditions he obtained a maximum conversion of hexamine to RDX(B) at approximately 75°C. Overall conversions of hexamine to RDX(B) as low as 30-49% have been reported (39) at reduced temperatures. The product was estimated to contain more than 50% HMX. In a later investigation Bachmann, et al (33, 34) reported a decrease in the HMX : RDX ratio as the temperature was increased from 25°C to 65°C and an increase in this ratio above 65°C. More careful study of the temperature effect on the conversion of hexamine to RDX(B) by the same workers (40) placed the maximum conversion at around 65°C rather than 75°C. Conversions of hexamine to RDX(B) as high as 85% of the theoretical yield were found at 65°C. Increased consumptions of acetic anhydride and nitric acid were noted as the temperature was increased from 55°C to 75°C. Over this range the HMX production was essentially constant while the "acidity" of the product decreased regularly as the temperature was increased.

The temperature at which hexamine is converted to RDX(B) may alter the value of the optimum concentration of nitric acid at which a maximum yield of RDX(B) is obtained (19).

The obvious necessity of maintaining a given constant temperature throughout the reaction for maximum yields of RDX(B), led to an investigation of methods for dissipating the large quantity of heat evolved in the initial stages of the reaction. Approximately 178,000 calories per mole of hexamine are evolved almost instantaneously when the reactants are mixed rapidly at higher temperatures (41). This primary heat effect is followed by a much smaller one involving approximately 3,600 calories per mole hexamine. The reaction when solid hexamine is introduced into the other Bachmann reagents has been reported to be 140,000 calories per mole hexamine exothermic (42).

In commercial practice, this large amount of heat is removed by causing the reaction to take place in a tubular reactor, jacketed with cooling water, the whole functioning as an efficient heat exchanger. Coating of the heat exchanger, with reduction in its efficiency, has been found a serious technical problem at St. Maurice Chemicals, Canada, although the same type of equipment has functioned with little difficulty from this cause at Holston Ordnance, Tennessee.

A possible method of removing the reaction heat was suggested by Winkler (43), and tested by Nicholls. The method involved the removal of the heat as the latent heat of vaporization of some inert solvent having a boiling point in the range 40°C - 80°C. Nicholls (30) reported adequate cooling by the vaporization of chloroform, 1,2 - dichloro-ethane and dichloromethane but the yields of RDX(B) were in all cases lower than normal, for example 40% instead of 80%. The author then suggested the possibility of removing the heat as the latent heat of vaporization of acetic acid at a reduced pressure. Nicholls (44) tested this method and found it to give excellent control of temperature with yields of RDX(B) as high as 70% compared with the normal yield of 80-85%. The advantage of such a method for controlling the temperature lies in the fact that it is not affected by coating of the convertor. Nicholls (30) reported that coating was less severe, using the method of solvent evaporation, than in a normal batch experiment. A detailed study (45) of the coating has failed to provide a method for its elimination, and it appears that (29) careful control of reagent excesses is the only expedient likely to reduce the extent of coating to the point where it is not a serious handicap to commercial production.

Effect of Order of Time of Addition of the Reagents to the Convertor.

The order of addition of the reagents is determined by which reagent (s) must be maintained in excess of the theoretical requirements throughout that part of the experiment which governs the course of the reaction. The possible variations are summarized by Bachmann, et al (32) who have shown that by leading the hexamine, nitric acid or acetic anhydride or any two of these reagents, it is possible to vary the extent of conversion over the range 73% HMX and 6% RDX to 5% HMX and 70% RDX.

The length of time taken to complete the reaction is reported (32) to influence the production of HMX, the yield of HMX increasing with increased time.

Wright (46) has been able to produce RDX(B) of which HMX comprised 90%. This result was obtained by maintaining a hexamine excess in the reaction mixture and adding the reagents slowly over a period of 30 minutes. Exceptionally low yields of HMX have been found with nitric acid-ammonium nitrate in excess over the hexamine (35).

Ralph and Winkler (47) have studied the effect of maintaining zero excess of ammonium nitrate over a period of hours after the reaction was started. The experiments were made at 35°C. Withholding the ammonium nitrate for several hours did not reduce the yield of RDX below approximately 50% of the value obtained with ammonium nitrate present initially. The greater part of the reduction in yield was caused by the absence of ammonium nitrate for the first 30 minutes after the reaction was started. After the addition of ammonium nitrate the rate of formation of RDX was approximately one half the rate of that in an experiment in which the ammonium nitrate was present initially.

Effect of Water in the Reaction.

Bachmann reported (26) that the presence of water in the nitric acid had little effect on the final yield if sufficient acetic anhydride was added to compensate for the water. In a later investigation the same workers found that an increase in the water content of nitric acid from 0.5% to 2.5% caused a 1% reduction in the yield of RDX(B) (48).

A small percentage of water in the hexamine-acetic acid reagent has been found to cause a 10% decrease in yield of RDX(B) (49).

Effect of Dilution.

Diluting the reaction mixture with an equal volume of acetic acid greatly decreases the rate of formation of RDX. It has also been rsported (33, 34) that dilution increases the yield of HMX, but that the reaction medium can be diluted without reducing the final yield of RDX(B) (50). The rates of formation of RDX and HMX appear to be affected in approximately the same proportions upon dilution with acetic acid (20).

Effect of Reactor Design and Operation.

More success has been reported with a circulating type of reactor ~~U~~ than with a U tube (25), while a continuous process for the production of RDX(B) has been found to give lower yields than batch operations (51).

It is evident from the preceding brief survey that, while there is considerable information available concerning the influence of various factors on the yield of RDX(B) from the Bachmann reaction, there remains much to be done towards the end of increasing the yield above the maximum value of approximately 85-86% attainable at present. It seemed not unlikely that higher yields might be made possible by suitable modification of a continuous process. The present project was undertaken from this point of view, the reactor given first attention being a U-tube design. Owing to certain undesirable features of this type of reactor, particularly its unsuitability for study of the effect of dilution, it was abandoned without comprehensive study, and attention was directed towards the design of a reactor capable of use with wider variety and ranges of operating conditions. The result of this development is the rotating tube reactor described in a later section of the thesis.

A. THE U-TUBE REACTOR

FEED SYSTEM.

The reagents of the Bachmann reaction are generally brought together as three liquid feeds: a solution of hexamine in acetic acid, a solution of ammonium nitrate in nitric acid and acetic anhydride.

The reagent feed system developed was common for all types of convertors used in these investigations. It is shown diagramatically in Fig. 7, which represents one metering unit for one liquid feed, the others being of similar design. The reagent from storage tank A was passed through stopcock P, controlled temperature preheater B and insulated line C to the burette D. This burette, located in an air thermostat I, was fitted with a 3 hole rubber stopper, (protected with polyvinyl chloride polymer) the reagent being introduced through one hole, the second hole serving to apply vacuum above the reagent, while the third hole was fitted with a short length of glass tubing to act as a gland for the tube E which controlled the pressure head of the liquid. A short length of rubber tube was used to make the gland air-tight. A sight tube H was attached to the burette to facilitate accurate adjustment of the head of liquid on the control orifice O. From the burette, the reagent

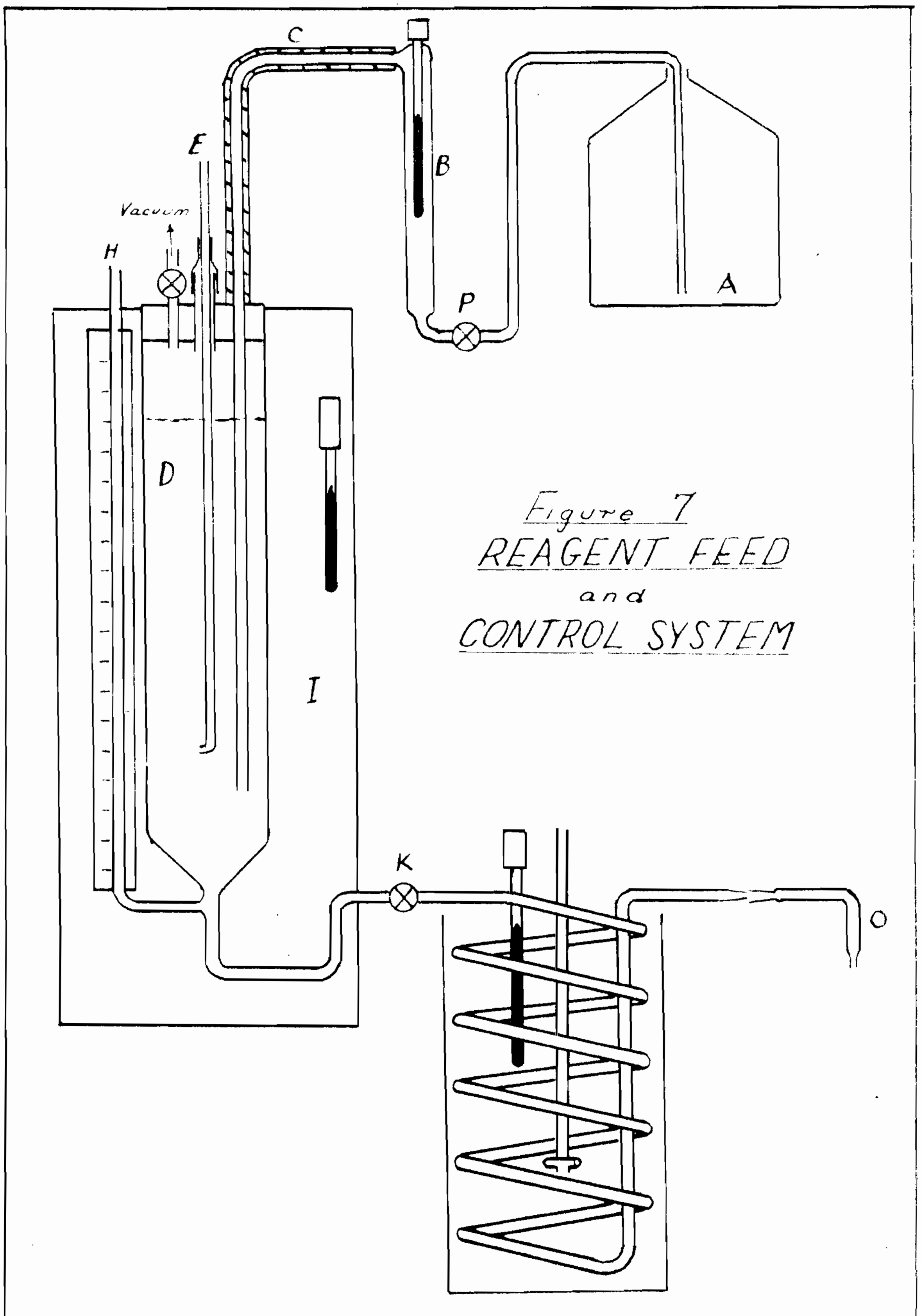


Figure 7
REAGENT FEED
and
CONTROL SYSTEM

was passed through a coil immersed in an oil thermostat, so that the temperature of the reagent was brought to 28°C (± 0.01°).

The metering equipment was operated as follows: The valve on the vacuum line was opened slightly and the syphon from the storage tanks started by momentarily blocking the sight tube and liquid head control tube. When the burette was filled, the stopcock P was shut and the vacuum on the burette adjusted until a slow steady stream of air bubbles rose through the liquid from the lower end of the control tube E. By raising or lowering tube E, the head pressure of the liquid on the metering orifice O could be adjusted to give the desired rate of delivery of reagent, as determined from a calibration curve. When feeding into the reactor, stopcock K was opened wide and stopcock P adjusted to permit the liquid to enter the burette from the storage tank at the same rate as it was being removed to the reactor.

MATERIALS AND METHODS OF ANALYSIS.

All reagents used in the project were of commercial grades. Solutions were made to have the following approximate compositions by weight:

Hexamine in acetic acid - - - - - -	38%
Ammonium nitrate in nitric acid - -	48%

The reagents were introduced into the convertor as liquid feeds, the permitted tolerance in feed rate being not in excess of ± 0.4%.

The product was sampled and analyzed using procedures and methods developed in this laboratory.

The sample for analysis was obtained by collecting over a measured time interval the whole product from the reactor. The yields of RDX, HMX and BSX were calculated on the basis of the hexamine introduced over this same time interval. The rate of flow of all reagents was checked before and after each experiment.

Two 35-45 gram aliquots were taken from each sample, (after cooling to 25°C), diluted with 350 ml. of distilled water and allowed to stand at room temperature for 24 hours. The precipitate was filtered off, washed with distilled water, dried at 100°C, cooled and weighed. The filtrate was evaporated to dryness in a tared beaker. All water solubles present in this filtrate were considered to be ammonium nitrate.

The precipitate at this point in the procedure consisted of all RDX, HMX and BSX from the aliquot except for a small amount dissolved in the filtrate. The precipitate was fumed off with nitric acid according to the following procedure:

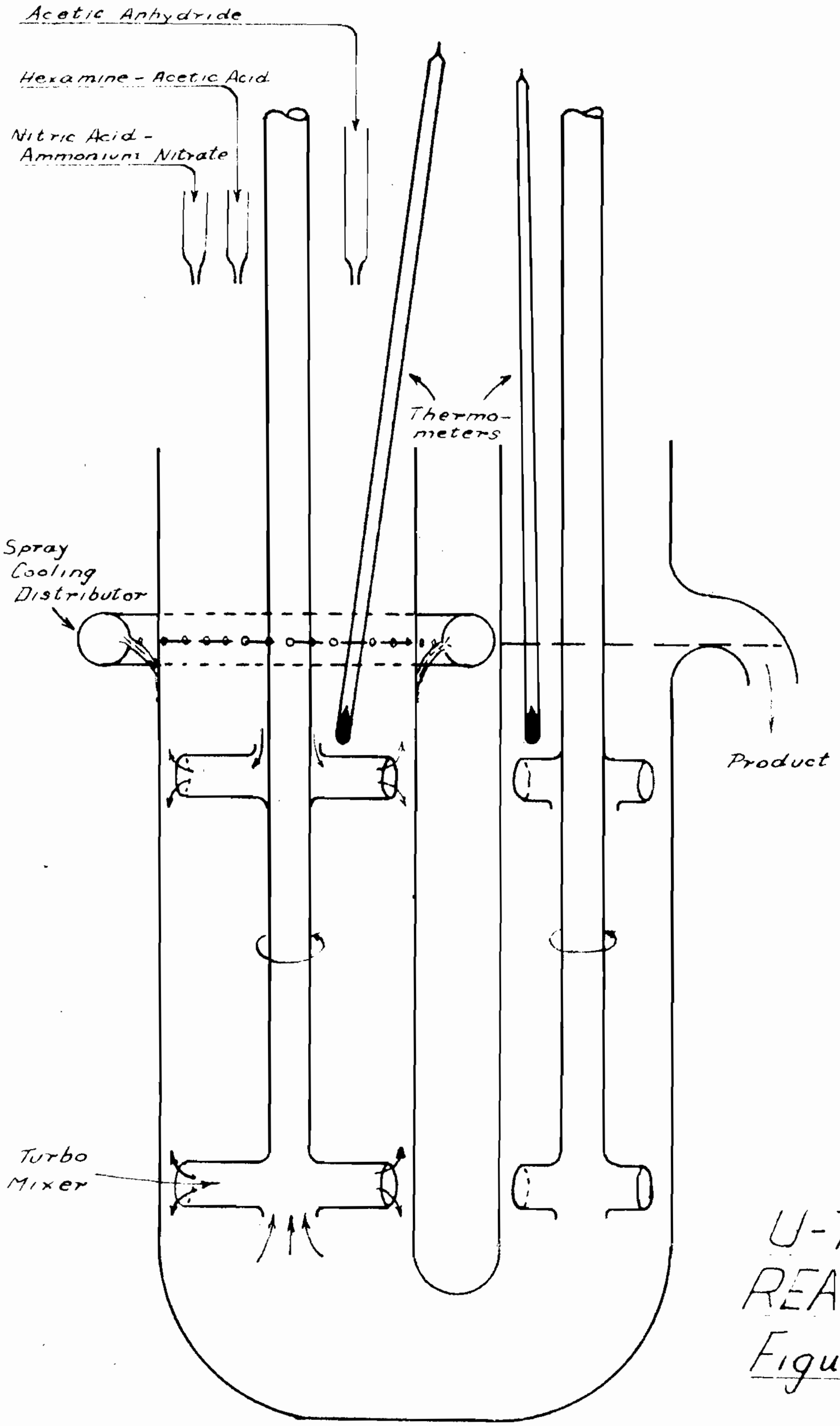
The precipitate was removed from the sintered depends on the resulting temperature rise due to the heat evolved when acetic anhydride is hydrolized with a 10% solution of sulphuric acid in water. The method, being empirical, must be standardized in the equipment to be used for the determinations.

CONSTRUCTION AND OPERATION OF THE U-TUBE CONVERTOR.

The design of this convertor is readily seen from Fig. 8. It was constructed of Pyrex glass, the vertical arms, 4 inches and 3 inches in diameter and 12 inches long, being connected by a crossarm 2 inches in diameter. The outlet, 3 inches from the top of the 3 inch arm, limited the capacity under operating conditions to 2250 ml.

The convertor was supported in a vertical position during operation, high speed stirrers mounted vertically in each arm of the convertor serving to maintain the composition of the slurry essentially constant throughout.

Each experiment was started by introducing approximately 1500 ml. of hot, glacial acetic acid (approximately 75°C) into the convertor and adding the reagent feeds with both stirrers in operation. The temperature of the reaction mixture was controlled manually by adjusting the amount of cooling water passing



U-TUBE
REACTOR
Figure 8

through a cooling coil (experiments 1-8) or, over the outer surface of the reactor (experiment 10). The samples were collected in flasks and allowed to cool to room temperature.

EXPERIMENTAL RESULTS AND DISCUSSION.

Preliminary experiments (1-8) were made using feed rates as follows:

Reagent	Feed Rate grams/second
Hexamine in Acetic Acid (38%)	1.00
Ammonium Nitrate (48%) in Nitric Acid (52%)	1.50
Acetic Anhydride	2.80

Yields of RDX(B) of 81-85% were obtained at temperatures 75-80°C, the HMX content being 3.2-8.5% and the BSX content 3.5-6.0%. In a further experiment using 1.55 grams of nitric acid-ammonium nitrate per second and 2.53 grams of acetic anhydride per second, a yield of 87.5% of RDX(B) was obtained, of which the HMX content was 8.4%. Following these preliminary studies two experiments (No. 6 and No. 8) were made in which samples were collected continuously during 5 minute intervals. The results are shown in Tables XVI and XVII and Fig's. 9 and 10.

In the initial stages of experiments made in the U-tube reactor all of the reaction products produced in

TABLE XVI

PRODUCTION OF RDX(B)
IN
U-TUBE REACTOR

Reagent	Feed Rate grams/second	Reagent	Input moles/mole hexamine
Hexamine (38%)-AcOH(62%)	1.000	NH_4NO_3	3.57
NH_4NO_3(50.3%)-HNO_3(46.8%)	1.547	HNO_3	4.22
Ac_2O	2.534	Ac_2O	8.65

Time	T	Sample Weight	Yield								Excess-% by Weight-of			Initial Acidity
			Uncorrected				Corrected							
minutes	°C	grams	RDX(B) %	RDX %	HMX %	BSX %	RDX(B) %	RDX %	HMX %	BSX %	NH_4NO_3 in slurry	HNO_3 in filtrate	Ac_2O in filtrate	%
7.25	73	679	47.0	39.9	10.6	1.9	63.8- 83.3	54.1- 70.7	14.3- 18.7	2.6- 3.3	4.7	2.06	6.0	
12.25	75	774	71.3	62.0	13.9	16.0	83.5- 93.7	72.0- 80.8	16.3- 18.3		5.4	2.28	8.2	0.45
17.25	75	756	82.2	74.0	12.2	4.4	89.7- 95.3	80.7- 85.8	13.3- 14.1	4.8- 5.1	5.7	2.36	10.0	0.31
22.25	75	753	84.9	78.1	10.2	4.4	88.9- 91.6	81.8- 84.3	10.7- 11.0	4.6- 4.8	5.9	2.48	10.7	0.54
27.25	75	749	85.7	79.6	9.1	4.3	87.9- 89.2	81.8- 82.9	9.3- 9.5	4.4- 4.5	5.7	2.56	10.7	0.19
33.25	75	736	85.6	80.4	7.8	4.2	86.8- 87.8	81.5- 82.4	7.9- 8.0	4.3	5.7	2.48	11.5	0.20
37.25	75	752	87.4	82.2	7.8	4.2	87.4	82.2	7.8	4.2	5.7	2.44	11.6	0.25
42.25	77	753	77.7	72.5	7.8	4.4	77.7	72.5	7.8	4.4	6.0	2.44	11.4	0.22
47.25	79	754	81.3	75.8	8.3	4.4	81.3	75.8	8.3	4.4	6.4	2.44	11.2	0.21
52.25	80	750	80.2	74.8	8.1	4.4	80.2	74.8	8.1	4.4	6.1	2.50	11.1	0.19
57.25	83	773	79.8	74.1	8.5	4.8	79.8	74.1	8.5	4.8	6.7	2.50	10.6	0.27
62.25	88	772	74.0	68.3	8.6	4.8	74.0	68.3	8.6	4.8	6.7	2.54	9.8	0.21
67.25	95	768	66.6	60.9	8.6	5.3	66.6	60.9	8.6	5.3	7.1	2.54	8.7	0.21

Figure 9

EXPERIMENT 6

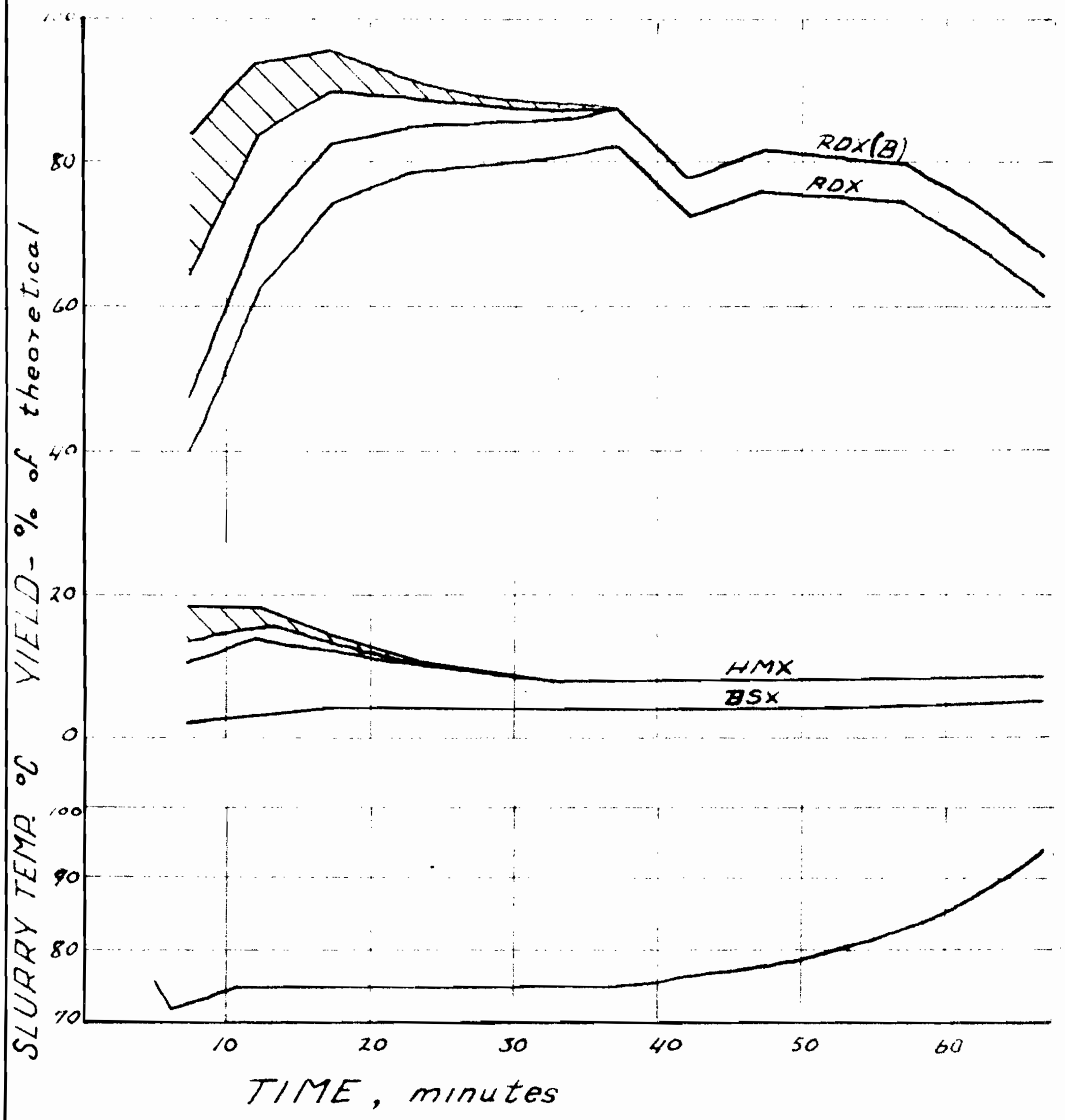


TABLE XVII

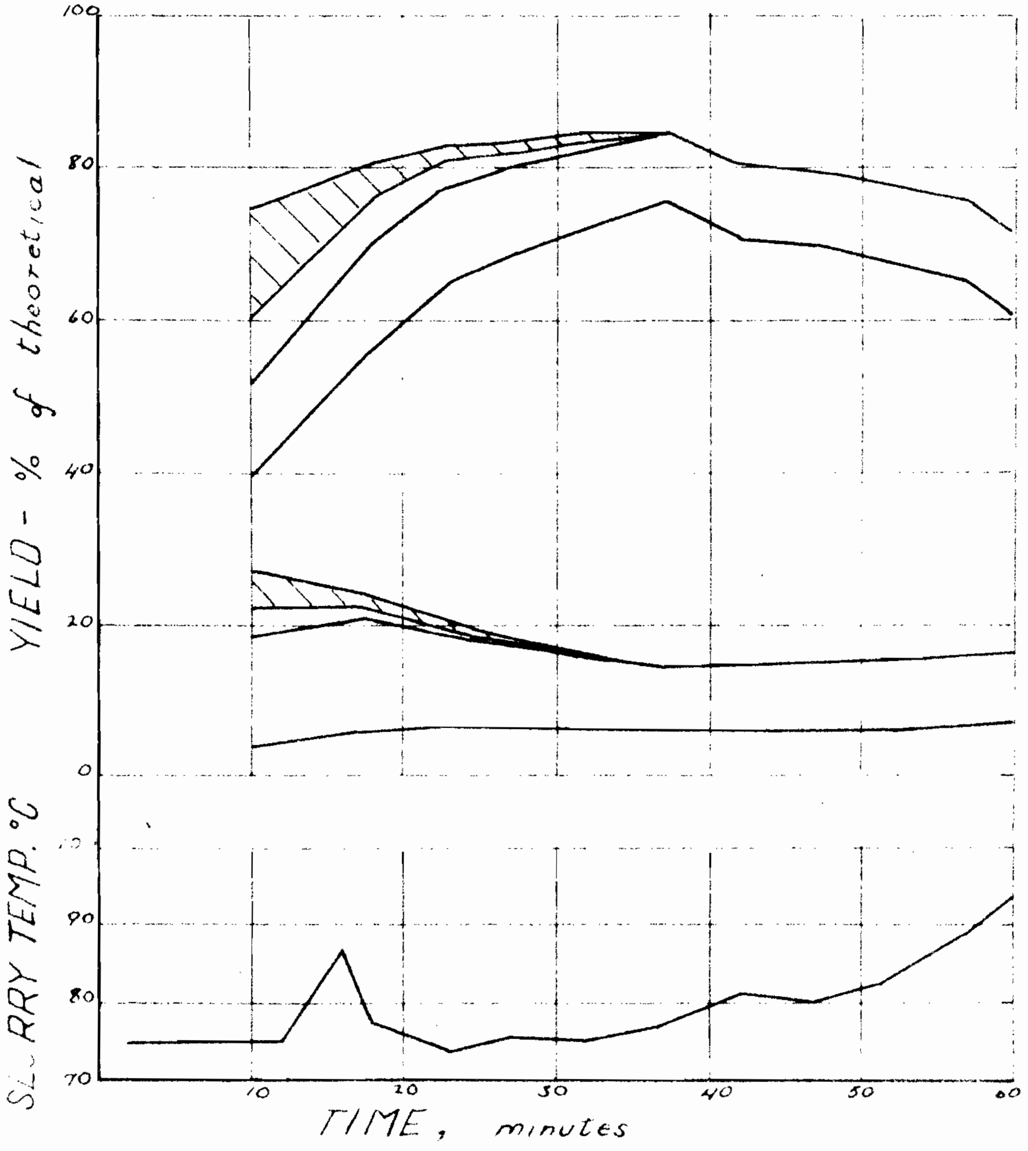
PRODUCTION OF RDX(B)
IN
U-TUBE REACTOR

Reagent	Feed Rate grams/second	Reagent	Input moles/mole hexamine
Hexamine(38%)-AcOH(62%)	1.000	NH_4NO_3	3.57
NH_4NO_3(50.3%)-HNO_3(46.8%)	1.547	HNO_3	4.22
Ac_2O	2.534	Ac_2O	8.65

Time	Temp.	Sample Weight	Yield								Excess-% by Weight-of			Initial Acidity
			Uncorrected				Corrected							
Minutes	°C	grams	RDX(B) %	RDX %	HMX %	BSX %	RDX(B) %	RDX %	HMX %	BSX %	NH_4NO_3 in slurry	HNO_3 in filtrate	Ac_2O in filtrate	%
10	75.0	735.8	52.0	39.4	18.8	3.4	60.7-74.7	46.0-56.6	22.0-27.0	4.0-4.9	3.4	1.63	2.5	-
18	77.0	748.0	69.8	55.9	20.8	5.4	75.7-80.3	60.6-64.3	22.5-24.0	5.8-6.2	4.8	1.69	5.2	-
23	74.5	771.9	77.1	64.3	19.0	6.1	80.8-82.9	67.5-69.2	19.9-20.4	6.4-6.6	5.2	1.73	6.3	-
27	75.5	752.7	79.8	68.6	16.8	6.0	81.6-83.2	70.2-71.5	17.2-17.5	6.1-6.3	5.7	1.73	6.8	-
32	75.0	757.5	82.3	72.0	15.3	5.8	83.5-84.5	73.2-74.1	15.5-15.7	5.9-6.0	5.7	1.84	-	-
37	77.0	761.8	84.4	75.3	14.1	5.3	84.4	75.3	14.1	5.3	5.7	1.88	7.7	-
42	81.5	754.3	80.0	70.2	14.5	5.6	80.0	70.2	14.5	5.6	5.8	1.98	7.3	-
47	80.0	748.0	79.4	69.5	14.8	5.7	79.4	69.5	14.8	5.7	5.7	1.92	-	-
52	82.5	742.1	77.1	67.0	14.9	5.7	77.1	67.0	14.9	5.7	5.8	1.96	5.8	-
57	89.0	748.7	75.3	64.8	15.9	6.6	75.3	64.8	15.9	6.6	6.0	1.98	4.6	-
61	95.5	735.9	69.5	58.8	16.1	7.1	69.5	58.8	16.1	7.1	5.6	1.95	2.8	-

Figure 10

EXPERIMENT 8



unit time do not leave the reactor in the corresponding interval. Only after the steady state has been reached can the yields obtained by analysis represent the overall conversion of hexamine to its various reaction products. This state is reached when the reaction products leaving the reactor in unit time are equivalent to the products formed in the corresponding interval.

The following equation was developed to obtain an estimate of the extent of the conversion of hexamine to its products in the initial stages of an experiment.

Let m = Moles of RDX entering the reactor per minute. Here m is considered to be twice the number of moles of hexamine being introduced per minute.

n = ml. of slurry leaving the reactor per minute.

V = Volume of the reactor (ml.).

Q = Moles of RDX in the reactor at time "t", where "t" is measured from the instant the reactor started to overflow.

Q_o = Moles of RDX in the reactor at "t_o", that is, the time the reactor started to overflow.

Then $$\frac{dQ}{dt} = m - \frac{nQ}{V} \text{ - - - - - - - - - - - - - - } (1).$$

On separating the variables and integrating between limits Q_o and Q, and t_o and t, (1) becomes

$$\ln\left(\frac{mV}{n} - Q\right) - \ln\left(\frac{mV}{n} - Q_o\right) = \frac{-nt}{V} \text{ - - - - } (2)$$

With the above equation (2) the quantity of RDX (theoretically) in the reactor at any time "t" may be calculated. Assuming 100% conversion of hexamine to RDX and a 100% material balance throughout, then since

$m\ (t_b - t_a)$ = moles of RDX introduced in the interval "t_a" to "t_b", and

$Q_b - Q_a$ = moles of RDX which have accumulated in the reactor in the interval "t_a" to "t_b", it follows that

$m\ (t_b - t_a) - (Q_b - Q_a)$ = moles of RDX - - - - - -(3) expelled from the convertor in the interval "t_a" to "t_b".

The per cent conversion of hexamine to RDX is obtained by comparing the actual yield obtained with the yield calculated by (3).

A similar correction must be applied to the yields of HMX and BSX.

In Fig's. 9 and 10, the shaded area above the RDX(B) curve represents the limits between which the true yield curve for RDX(B) should appear, when the yield is corrected for the build-up of products in the reactor in the initial stages of the experiment. Similar areas exist for RDX and BSX (not shown on graph) and also for HMX as indicated. The limits between which the true yields lie are presented in Tables <u>XVI</u> and <u>XVII</u>, under the heading "Corrected Yields". The actual calculation of yields and corrected yields (that is, corrected for the "build-up" of RDX in the convertor) is best illustrated by reference to the next experiment.

The data in Fig's. 9 and 10 are of interest mainly by comparison with other data to be presented later; their immediate significance was to demonstrate that the U-tube convertor could be regarded as a satisfactory means of studying the "Combination Process" only if more continuous operation were possible. In its existing form, this was not possible owing to coating of the cooling coil which it was not practicable to keep clean, even manually. The cooling coil was therefore removed from the reactor, and the loss in available cooling surface compensated by a reduction in total feed rate from approximately 5 grams per second to 1.4 grams per second. At the reduced rate the wall of the convertor provided sufficient cooling surface to maintain a constant temperature in the slurry, and the wall was readily scraped free of coating periodically to maintain efficient cooling for extended periods of time. The cooling water was sprayed over the outer wall of the convertor, the temperature of the slurry being held essentially constant by manual adjustment of the amount of cooling water applied.

Owing to voltage fluctuations in the line, and consequent variations in stirring speed, there was noticeable surging of the slurry as it overflowed to the sampling vessels. Hence the weights of samples collected during a given short interval of time (e.g. 10 minutes) often differed appreciably. The procedure used to obtain the yield figure during a short interval of time was therefore as follows: Each sample was collected during a measured interval of approximately 10 minutes, and samples were taken in immediate succession to one another so that the total weight of slurry collected during a known time of operation at a given temperature was known. The true weight of sample, corresponding to a known collecting time, was then obtained by multiplying the sampling time by the average weight collected per minute. The weights of samples obtained in this way are shown under the heading of "Corrected Weights", in the tables of data. With this method of relating sample weight to time of collecting the sample, errors arising from random surging at the overflow should be minimized.

Any changes in stirring speed, below a critical minimum, would permit the solid particles in suspension in the slurry to settle out. Variations in yield, on analysis, due to this factor cannot be corrected easily, if at all. The larger fluctuations in RDX yield over certain intervals may be due to some settling out, followed by redispersion, of a part of the solid matter in suspension.

The feed rates used throughout were:

Reagent	grams/second
Hexamine in acetic acid (38%)	0.276
Ammonium nitrate (50%) in nitric acid (46.8%)	0.437
Acetic anhydride	0.750

Expressed in molar proportions the input of reagents was:

Reagent	moles/mole hexamine
Nitric Acid	4.3
Ammonium nitrate	3.5
Acetic anhydride	9.8

The slurry was diluted and filtered in the usual way and the filtrate and solids analyzed as outlined previously.

The results of a series of experiments over the temperature range 60^{o} - 85^{o}C are shown in Tables XVIII, XIX, XX and XXI, and in Fig's 11 and 12.

TABLE XVIII

ANALYTICAL DATA FROM EXPERIMENT 10

							Corrected Weights					
Sample Number	Temperature of Slurry °C.	Sampling Time minutes	Rate of Flow of Sample from Convertor grams/minute	Excess of NH_4NO_3 in slurry % by weight of slurry	Excess of Ac_2O in filtrate. % by weight of slurry	Excess of HNO_3 in filtrate. % by weight of filtrate	Weight of Sample grams	Weight of RDX(B) grams	Weight of HMX grams	Weight of RDX grams	Weight of BSX grams	Initial Acidity of RDX(B)
10A	75	7	88.4	5.0	9.2	2.45	603	80.9	7.4	73.5	2.8	.60
B	"	8	85.6	5.6	10.0	2.64	689	108.1	8.7	99.4	4.1	.38
C	"	9	86.3	5.9	11.0	2.60	775	136.0	9.2	126.8	5.0	.29
D	"	7	85.3	5.4	11.8	2.59	603	107.3	6.8	100.5	4.1	.20
E	"	8	89.3	6.1	11.7	2.60	689	123.4	7.2	116.2	4.8	.23
F	"	8	81.6	6.5	11.1	2.64	689	132.4	8.0	124.4	4.8	.15
G	"	9	79.7	6.2	10.8	2.64	775	155.8	8.0	147.8	5.5	.17
H	"	9	89.7	6.3	10.9	2.64	775	162.0	7.6	154.4	5.3	.26
I	"	9	84.9	6.5	10.9	2.61	775	151.7	7.7	144.0	5.3	.22
J	"	8	93.5	6.3	13.0	2.69	689	132.2	6.5	125.7	5.2	.33
K	"	8	94.0	6.8	13.3	3.10	689	137.0	6.0	131.0	4.3	.22
L	"	8	84.7	7.2	13.4	3.07	689	132.2	6.1	126.1	5.0	.23
M	70	11	83.0	7.9	13.9	3.06	927	191.8	7.7	184.1	6.3	.23
N	"	9	83.0	7.8	14.3	3.04	758	155.2	6.5	148.7	5.9	.25
O	"	10	80.8	8.1	14.4	3.06	842	174.0	7.1	166.9	7.2	.24
P	"	10	86.6	8.4	14.3	3.05	842	192.1	6.3	184.8	7.3	.21
Q	70	11	89.0	8.0	14.3	2.77	927	196.5	8.3	188.2	8.3	.23
R	"	10	72.7	7.9	14.2	2.60	842	175.0	7.5	167.5	7.2	.22
S	"	10	86.4	7.9	14.5	2.53	842	189.1	7.2	181.9	6.9	.20
T	"	9	88.2	7.9	14.5	2.56	750	169.2	6.0	162.8	5.6	.22
U	"	10	90.0	7.6	14.8	2.62	842	194.2	7.3	166.9	6.3	.28
V	"	10	87.2	7.6	15.2	2.63	842	171.9	7.2	164.7	6.2	.22
W	65	10	84.6	8.0	15.4	2.67	872	178.8	7.9	170.9	6.5	.23
X	"	9	89.2	7.6	15.9	2.68	785	159.1	6.1	153.0	6.1	.35
Y	"	10	87.1	7.6	16.2	2.67	872	179.0	7.0	172.0	7.3	.30
Z	"	10	89.5	7.6	16.3	2.69	872	177.9	6.9	171.0	7.5	.26
AA	"	13	82.4	7.7	16.9	2.69	1132	226.1	9.5	216.6	10.2	.30
AB	"	11	87.1	7.7	16.7	2.69	960	192.2	-	-	8.9	.48
AC	"	9	88.2	7.6	17.3	2.69	785	155.1	5.9	149.2	7.2	.28
AD	"	9	87.5	7.9	17.0	2.92	785	152.2	-	-	7.4	.29
AE	"	9	88.6	7.8	17.1	2.90	785	153.7	5.8	147.9	7.5	.31
AF	"	9	88.9	7.8	17.1	2.90	785	156.0	-	-	7.4	.26
AG	60	9	86.5	8.1	17.3	2.85	791	156.5	5.5	151.0	8.6	.27
AH	"	9	88.6	8.0	17.2	2.83	791	155.0	-	-	9.2	.42
AI	"	9	85.6	7.9	17.2	2.82	791	152.1	-	-	9.5	.41
AJ	"	9	89.4	7.8	17.1	2.82	791	149.7	5.7	144.0	10.6	.48
AK	"	9	88.3	7.7	17.6	2.81	791	150.3	-	-	10.9	.45
AL	"	10	89.8	7.8	17.2	2.74	879	168.3	5.4	162.9	12.4	.37
AM	"	9	87.5	7.9	17.2	2.68	791	152.6	-	-	11.2	.41
AN	"	9	88.3	7.7	17.5	2.64	791	151.3	5.8	145.5	11.5	.41
AO	"	10	86.2	7.7	17.5	2.60	879	169.2	-	-	12.1	.44
AP	"	10	89.2	7.9	17.1	2.73	879	172.4	6.7	165.7	12.0	.43
AQ	80	11	86.2	7.5	16.4	2.64	852	170.0	-	-	10.9	.43
AR	"	7	86.8	6.9	15.9	2.81	596	112.8	3.8	109.1	6.5	.32
AS	"	8	92.8	6.7	14.6	2.83	681	127.7	-	-	6.8	.29
AT	"	6	88.1	6.1	11.3	2.65	511	100.5	4.4	96.1	4.6	.30
AU	"	10	74.8	6.7	11.9	2.63	852	163.5	-	-	7.7	.30
AV	"	8	85.0	7.1	12.6	2.93	681	127.4	6.1	121.3	5.5	.28
AW	"	8	79.5	7.0	13.0	3.08	681	132.2	-	-	5.2	.27
AX	"	8	80.2	7.3	12.8	3.20	681	130.9	5.4	125.5	5.1	.22
AY	"	6	84.6	7.7	12.8	3.32	511	97.1	-	-	3.9	.28
AZ	"	6	91.9	7.9	12.9	3.42	511	96.1	3.9	92.2	3.6	.33
BA	"	10	84.7	8.0	12.5	3.46	852	156.9	6.1	150.8	6.1	.33
BB	"	9	79.1	8.0	12.6	3.54	766	136.3	5.3	131.0	5.4	.27
BC	85	10	86.1	7.8	12.3	3.57	870	150.7	-	-	6.2	.22
BD	"	10	89.0	8.1	11.9	3.44	870	156.3	5.5	150.8	5.7	.20
BE	"	12	88.0	7.7	11.4	3.26	1043	186.0	-	-	7.3	.15
BF	"	9	80.9	8.0	11.1	3.18	783	117.4	4.6	112.8	4.9	.15
BG	"	9	87.8	7.6	10.9	3.16	783	150.5	-	-	5.2	.23
BH	"	11	94.5	7.1	9.9	3.19	957	180.9	6.3	174.6	6.5	.27
BI	"	10	93.3	6.6	8.0	2.61	870	168.8	7.4	161.4	6.7	.20
BJ	"	9	88.6	6.8	8.8	2.82	783	134.9	6.9	128.0	5.6	.15
BK	"	10	84.6	6.9	9.5	2.99	870	143.4	7.9	135.3	7.0	.23
BL	"	10	85.9	7.0	10.1	2.97	870	152.2	7.8	144.4	6.7	.19

NOTE: Weight of sample = Average rate of flow X Sampling time.

Weight of RDX(B) = Weight of sample X % by weight RDX(B) in sample.

Weight of HMX = Weight of RDX(B) X % by weight HMX in RDX(B)

Weight of BSX = Weight of sample X % by weight BSX in sample.

TABLE XX

INITIAL ACIDITY OF CRUDE PRODUCT AS A FUNCTION OF TEMPERATURE

Experiment 10

Temperature °C	Initial Acidity % of Crude Product as AcOH
60	0.42
65	0.28
70	0.22
75	0.22
80	(0.25)
85	(0.2)

Figure 11
EXPERIMENT 10

TABLE XXI

YIELD AVERAGES FROM TABLE XIX

Temp.		Yield, moles per mole hexamine		
oC	RDX(B)	RDX	HMX	BSX
60	1.70	1.64	0.048	0.077
65	1.75	1.69	0.048	0.052
70	1.79	1.72	0.054	0.040
75	1.83	1.71	0.081 (0.057)	0.041 (0.039)
80	1.61	1.54	0.050	0.038
85	1.54	1.45	0.059	0.042

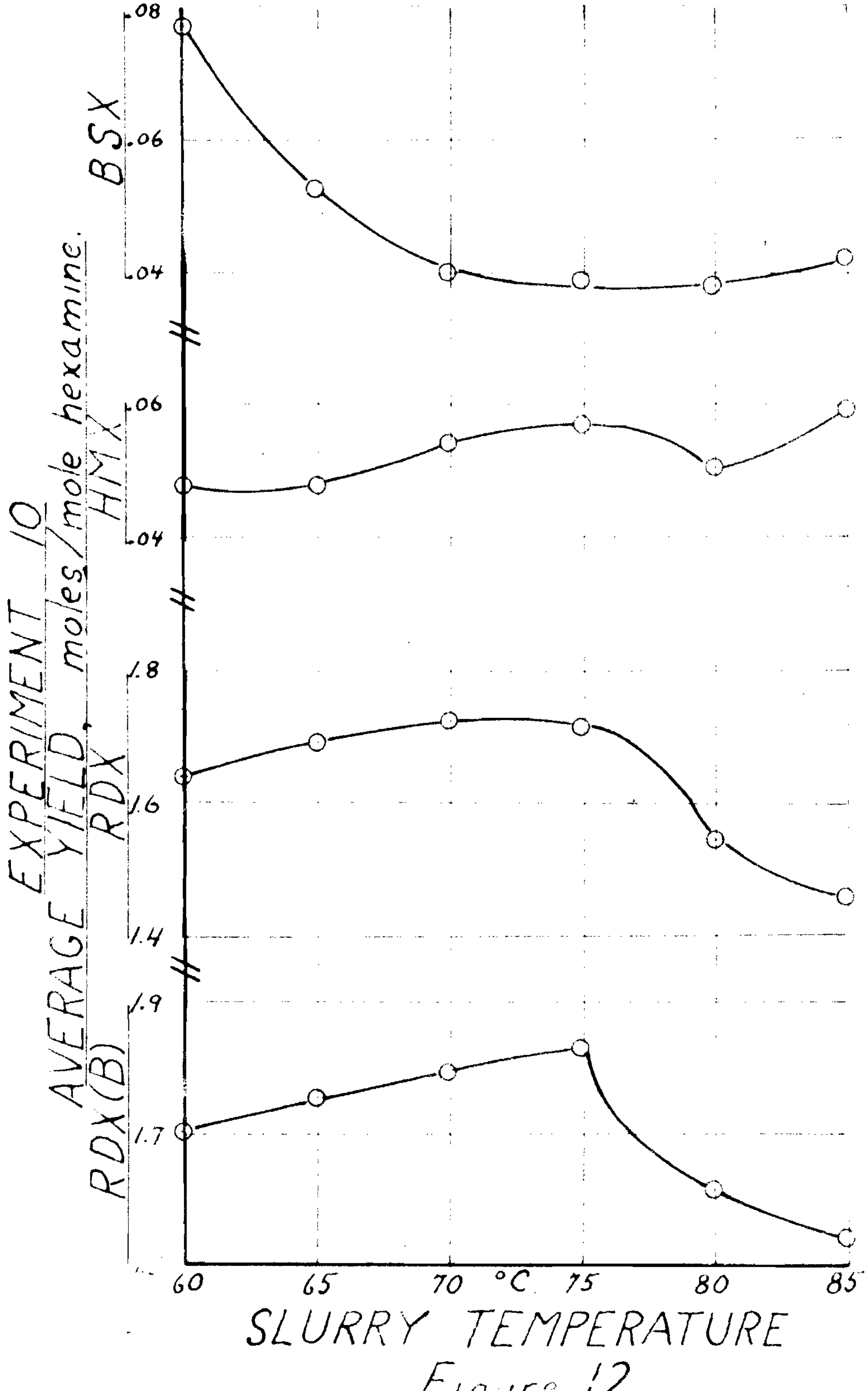

EXPERIMENT 10
AVERAGE YIELD, moles/mole hexamine.
BSX
.08
.06
.04
HMX
.06
.04
RDX
1.8
1.6
1.4
RDX(B)
1.9
1.7
60
65
70
°C
75
80
85
SLURRY TEMPERATURE

Figure 12.

The method of calculating the yields of RDX(B), RDX, BSX and HMX may be illustrated by the following example:

Sample 10-K.		grams
A	Wt. of slurry from convertor corrected for surging	689
B	Wt. of aliquot of A	34.954
C	Wt. of water insoluble solids in B	7.173
D	Wt. of RDX(B) in C	6.932
E	Wt. of BSX in C (C-D)	0.241

F Total wt. of RDX(B) in A $= \frac{D(A)}{B} = \frac{6.932(689)}{34.954} =$ 136.2

G. Total wt. of BSX in A $= \frac{E(A)}{B} = \frac{0.241(689)}{34.954} =$ 4.82

H % HMX in RDX(B) = 4.4

Total grams of HMX in A = H(F) $= \frac{4.4(136.2)}{100} =$ 6.0

I Total grams of RDX in A = F - H = 136.2 - 6.0 = 130.2

J Moles of Hexamine introduced 0.360

moles/mole Hexamine

K Yield of RDX $= \frac{I}{J(222)} = \frac{130.2}{0.360(222)} =$ 1.64

L Yield of HMX $= \frac{H}{0.360(296)} = \frac{6.0}{0.360(296)} =$ .056

M Yield of BSX $= \frac{G}{0.360(354)} = \frac{4.82}{0.360(354)} =$ .039

The calculation of yields during the initial stages of reaction may also be illustrated as follows:

Sample 10-A.

Time of start of overflow	16.5 minutes
Time of start of hexamine flow	1.5 minutes
Moles of RDX introduced per minute = m =	0.090

$n = 75.3$ ml./minute

$V = 2250$ ml.

$Q_o = (16.5 - 1.5)\ m = 15\ m =$ 1.347 moles

By equation (2)

$$\ln\left(\frac{mV}{n} - Q\right) - \ln\left(\frac{mV}{n} - Q_o\right) = - \frac{nt}{V}$$

If $t_a = 2.5$ minutes = time measured from the instant the slurry started to overflow from the convertor, then

$t_b = 9.5$ minutes, and

$Q_a = 1.455$ moles

$Q_b = 1.711$ moles

$Q_b - Q_a = 0.256$ moles

$m(t_b - t_a) = 0.630$ moles

Then RDX theoretically produced in effluent from reactor in the interval "t_a" to "t_b":

$m(t_b - t_a) - (Q_b - Q_a) = 0.374$ moles.

Experimentally the yield was 0.331 moles or 88.5% of the theoretical yield.

A correct estimate for the amount of RDX produced in the initial stages of experiment 10, as determined experimentally, required the density of the slurry sample to be known. The variations in density of slurry with the RDX(B) content were determined (54) and the density may be deduced from the following relation:

If d = slurry density, grams/ml.
b = % RDX(B) by weight of slurry
Then $d = 1.020 + 0.007\ B.$

The correct yield of RDX(B) is then obtained as follows, employing the same terminology as before:

$$\frac{ndb(t_b - t_a)100/222}{m(t_b - t_a) - (Q_b - Q_a)} = \text{Yield of RDX(B)},$$

expressed as per cent of the theoretical yield.

The trends shown by the data in Tables XVIII and XIX may be discussed with reference primarily to changes wrought by temperature variations. The discussion follows the chronological order in which the temperature changes were made.

Operation at 75°C.

The convertor was operated at 75°C for the first 140 minutes of the experiment.

(a) Yield of RDX(B) and RDX:

The "build-up" of RDX(B) in the slurry (broken line, Fig. 11) followed the theoretical "build-up" (dot-dash line, Fig. 11) for 40 minutes after the experiment started. At 40 minutes there was a sudden drop in the yield of RDX and RDX(B), followed immediately by rapid increases in the concentrations of nitric acid and acetic anhydride in the slurry. The yield of RDX(B) dropped from approximately 1.95 at 24 minutes to approximately 1.75 moles per mole hexamine at 140 minutes. (Table XIX). The corresponding yields of RDX were approximately 1.80 and 1.65 moles per mole hexamine respectively.

These large decreases in RDX(B) and RDX yields over the 140 minute interval accompanied the large increases in reagent concentrations (in the reaction medium) that must have occurred during the initial stages of the experiment. It would appear, then, that at 75°C the conversion of hexamine to RDX(B) was practically quantitative in the dilute reaction medium.

The yield of RDX was decreased proportionately less than for RDX(B) over the corresponding 140 minute interval, as a consequence of the high initial yield of HMX.

(b) Yield of HMX: The yield of HMX declined steadily during the interval 24 to 140 minutes from 0.134 to 0.057 moles per mole hexamine. (Table XIX). This 57% decrease in yield of HMX was probably due to an increasing concentration in the reaction medium of ammonium nitrate and perhaps nitric acid. Throughout the entire experiment, irrespective of temperature, a decreased concentration of ammonium nitrate in the filtrate coincides with an increased yield of HMX. This behavior was also noticed in experiments 6 and 8, Tables XVI and XVII, the concentrations of ammonium nitrate, nitric acid and acetic anhydride being lower in experiment 8 than in experiment 6.

(c) Yield of BSX: The yield of BSX decreased steadily from 40 minutes to 90 minutes. The random variations in the yield of BSX after 90 minutes coincided with a sudden decrease in the consumption of nitric acid and acetic anhydride. (Fig. 11). The inexplicable decrease in the concentration of acetic anhydride in the slurry from 40 minutes to 90 minutes may have been responsible for the steady decline in the yield of BSX over this interval. The probable yield of BSX at the steady state was estimated to be about 0.040 moles per mole of hexamine at 75°C.

(d) Initial acidity of the crude product: As the concentrations of the reagents in the reaction medium increased during the initial stages of the experiment, the "initial acidity" decreased rapidly, (Fig. 11). It is difficult to explain this behavior in relation to the trends of the other properties, since no parallel exists throughout the entire experiment.

Operation at 70°C.

The convertor was operated at 70°C over the interval from 140 to 240 minutes.

(a) Yield of RDX(B) and RDX: The RDX(B) and RDX yields were random , the average yield being 1.79 and 1.72 moles per mole hexamine respectively. (Table XIX). The increased yield of RDX at 210 minutes may be real, a reflection of the increased consumption of nitric acid, as indicated by the decreased concentration of nitric acid in the filtrate, from 170 to 210 minutes. More probably these high yields are only apparent and result from settling and redispersion of solids in the convertor as explained previously.

(b) Yield of HMX: The yield of HMX was nearly constant at 0.055 moles per mole hexamine. (Table XIX). Since HMX is probably all in solution and since correction can be made for surging, settling of the solids in the slurry should have little or no effect on the yields of HMX, but may alter largely the yield of RDX. The essentially constant yield of HMX, with variable RDX yields, may therefore be taken as further indication that settling and redispersion of solids is responsible for the variable RDX yield.

The fairly wide variations in the concentrations of nitric acid and acetic anhydride had no noticeable effect on the yield of HMX.

(c) Yield of BSX: The yield of BSX appears to have been dependent mainly upon two factors, slurry temperature and nitric acid concentration in the reaction medium. As the temperature and consumption of nitric acid decreased the yield of BSX increased. With the temperature and other factors constant the yield of BSX decreased as the nitric acid in the filtrate decreased, that is, as the consumption of nitric acid increased, up to 210 minutes. The increased consumption of nitric acid is not apparent as an increase in the yield of RDX, HMX or BSX, and has not, in fact, been explained.

(d) Initial acidity of crude product: At 70°C the "initial acidity" remained essentially constant at approximately 0.22. (Table XX).

Operation at 65°C.

The reactor was operated at 65°C from 240 to 350 minutes.

(a) Yield of RDX(B) and RDX: The yield of RDX(B) and

and RDX decreased slightly as the temperature was decreased from 70°C to 65°C. (Table XXI) The decreased yield of RDX(B) was accompanied by a greater decrease in the consumption of acetic anhydride than accounted for by the increased yield of BSX. This fact would indicate that at temperatures above 65°C (perhaps 70°C) some acetic anhydride is consumed in a side reaction. Since there is no proportionate change in the consumption of nitric acid or ammonium nitrate, this side reaction probably does not involve RDX, HMX, BSX or their precursors.

(b) Yield of HMX: The yield of HMX decreased slightly from 0.054 to 0.28 moles per mole hexamine as the operating temperature was decreased from 70°C to 65°C. (Table XXI).

(c) Yield of BSX: The yield of BSX increased by almost 40%, from 0.039 to 0.052 moles per mole hexamine, for a drop in the operating temperature of 5°C, from 70°C to 65°C. (Table XXI)

(d) Initial acidity of the crude product: The "initial-acidity" increased to 0.28 at 65°C from 0.22 at 70°C, (Table XX), in line with the results obtained by Bachmann (55).

Operation at 60°C.

Over the interval from 350 to 455 minutes the reactor was operated at 60°C.

(a) Yield of RDX(B) and RDX: The yield of RDX(B) and RDX decreased slightly from those at 65°C. (Table XXI). These decreased yields were a reflection of the greater conversion of hexamine to BSX. The rate of this latter reaction apparently decreases less rapidly with decrease of temperature than the rate of conversion of hexamine to RDX(B).

(b) Yield of HMX: The yield of HMX remained essentially constant over the range 65°C to 60°C.

(c) Yield of BSX: The yield of BSX increased by 50% over the yield at 65°C. The effect of temperature on the yield of BSX is well illustrated in Fig. 12 and Table XXI.

(d) Initial acidity of crude product: As with the BSX content, the "initial acidity" at 60°C increased by nearly 50% over its value at 65°C. (Table XX). This result corroborates the findings of Bachmann (55).

Operation at 80°C.

The reactor was operated at 80°C from 455 to 570 minutes.

(a) Yield of RDX(B) and RDX: After 455 minutes the slurry temperature was increased from 60° to 80°C. Coincident with this alteration, large variations in the yield of RDX(B) were obtained. It is impossible to ascribe these variations to any one of the changes in the consumptions of nitric acid, ammonium nitrate and acetic amhydride that accompanied the temperature shift from 60°C to 80°C.

The yield of RDX decreased from approximately 1.6 to 1.5 moles per mole hexamine in more or less random manner. This may be a reflection of the decreased consumption of nitric acid as evinced by the increased concentration of nitric acid in the reaction medium over the 80°C operating period. It may also be a reflection of the "fume-off" which occurred at 485 minutes, with its ensuing variations in reagent concentrations in the slurry.

(b) Yield of HMX: The yield of HMX increased from 0.049 to 0.056, (Table XIX, Fig. 11), and then decreased to 0.044 moles per mole of hexamine. The increase was more or less coincident with increased consumptions of acetic anhydride and ammonium nitrate from the slurry. Generally the yield of HMX decreased slightly at the higher operating temperature of 80°C.

(c) Yield of BSX: The conversion of hexamine to BSX was apparently decreased by 50% at 80°C from its value at 60°C. It is impossible to ascribe this decrease to the shift in operating temperature or the alterations in the reagent concentrations in the reaction medium. The increased consumption of acetic anhydride is not reflected in an increase in yield of RDX, HMX or BSX. As postulated previously, this increase in consumption of acetic anhydride is considered to be the result of a side reaction involving acetic anhydride (but not nitric acid), which becomes noticeable at temperatures above 65°C. The decreased consumption of nitric acid, as reflected in the increase in concentration of nitric acid in the slurry, more or less parallels the decreased production of RDX, HMX and BSX. The "fume-off" at 485 minutes did not affect noticeably the decline in the curve, Fig. 11, representing the yield of BSX.

(d) Initial acidity of crude product: The interdependence between slurry temperature and "initial-acidity" is illustrated clearly by the large drop (approximately 50%) in the "initial-acidity" as the temperature was raised from 60°C to 80°C. It is possible that the large changes in reagent concentrations introduced by this temperature shift also affected the "initial acidity".

Operation at 85°C.

During the balance of the experiment the reaction medium was maintained at 85°C.

(a) Yield of RDX(B) and RDX: The yields of RDX(B) and RDX were too random at this temperature for any conclusions to be drawn concerning the effect of temperature on the conversion of hexamine to RDX(B) and RDX.

(b) Yield of HMX: The yield of HMX tended to increase slightly at this higher temperature, perhaps owing to the increased consumption of ammonium nitrate (decreased concentration of ammonium nitrate in the slurry, Fig. 11).

(c) Yield of BSX: The yield of BSX tended to increase slightly at 85°C, a rise which may not be attributed with certainty to any one of the changing variables. (Fig. 11).

(d) Initial acidity of crude product: The "initial acidity" declined further from 0.25 at 80°C to 0.2 at 85°C. (Table XX).

Considering the data as a whole, several rather well-defined generalizations appear to be possible. It appears that increased dilution with respect to nitric acid, ammonium nitrate and acetic anhydride may make the conversion of hexamine to RDX(B) more nearly quantitative.

On the same basis the yield of HMX is dependent on the concentration, in the reaction medium, of one or more of the reagents, particularly ammonium nitrate. The yield of HMX varies inversely as the concentration of ammonium nitrate.

The yield of BSX appears to vary directly as the concentration of nitric acid and/or acetic anhydride in the reaction medium, whereas the concentration of ammonium nitrate, over the range investigated, has no apparent influence on the yield of BSX.

The optimal temperature for a maximal conversion of hexamine to RDX(B) is 75°C, under the operating conditions prevailing throughout this experiment.

The effect of temperature, over the range 60°C to 85°C, on the yield of HMX was slight but the yield of BSX was highly dependent on temperature, increasing very rapidly as the temperature decreased below 70°C. The yield of RDX tends to decrease below 70°C, this decrease being paralleled by increased production of BSX at the lower temperatures. The rate of the competing reaction to produce BSX decreases less rapidly than the rate of the RDX reaction as the temperature is lowered below 70°C.

The consumption of nitric acid is fairly constant up to 80°C. At this temperature there is a sudden decrease in the consumption of nitric acid owing to a decreased conversion of hexamine to RDX, HMX and BSX. At 85°C there is apparently an increased consumption of nitric acid probably as a result of its destruction in a side reaction of the type:

$$2Ac_2O + 4HNO_3 \rightarrow 4AcOH + 4NO_2 + O_2$$

This reaction is postulated only to represent a probable type of reaction that occurs during the "fume-off".

The consumption of acetic anhydride varies directly as the temperature of the reaction medium over the range 60°C. The increased consumption of acetic anhydride above 65°C may be accounted for partly by reactions leading to the production of RDX, HMX and BSX but may also be due in part to reactions of the type:

$$NH_4NO_3 + 2Ac_2O \rightarrow 4AcOH + N_2O.$$

Between 60°C and 85°C the consumption of ammonium nitrate is practically constant.

The "initial acidity" of the crude product is a function of both temperature and dilution. At high dilution, during the initial stages of the experiment, the "acidity" was very high but decreased rapidly as the concentrations of the various reagents built up to their steady state values. The effect of temperature on the "initial acidity" is apparent, the "initial acidity" increasing rapidly as the temperature was reduced below 70°C.

No parallel, consistent throughout the entire range covered, is evident between the "initial acidity" and any other measured value. Over certain regions a parallel exists, for example, between HMX yield and "initial acidity" in the initial stages of the experiment, but this correlation no longer exists when the steady operating state is reached.

It is of interest that the hexamine conversion up to 40 minutes is over 100% on the basis of the following commonly accepted equations:

$$(CH_2)_6N_4 + 4HNO_3 + 2NH_4NO_3 + 6Ac_2O \rightarrow 2RDX + 12AcOH$$

$$(CH_2)_6N_4 + \text{- - - - - - - - - - - - - - -}\rightarrow 1HMX$$

$$(CH_2)_6N_4 + \text{- - - - - - - - - - - - - - -}\rightarrow 1BSX$$

Thus from Table XIX, converting to per cent of theoretical yields, the data are:

Sample No.	Yield Percent of Theoretical RDX	 HMX	 BSX	Total Hexamine Converted %
10-A	88.5	13.4	4.2	106.1
10-B	90.0	11.8	4.6	106.4
10-C	91.0	9.9	4.5	105.4

On the other hand, the equations:

1 hexamine → 2RDX

2 hexamine → 3HMX

2 hexamine → 3BSX

lead to the following figures for hexamine conversion.

Sample No.	Yield Percent of Theoretical RDX	 HMX	 BSX	Total Hexamine Converted %
10-A	88.5	8.9	2.8	100.2
10-B	89.8	7.9	3.1	100.8
10-C	91.0	6.6	3.0	100.6

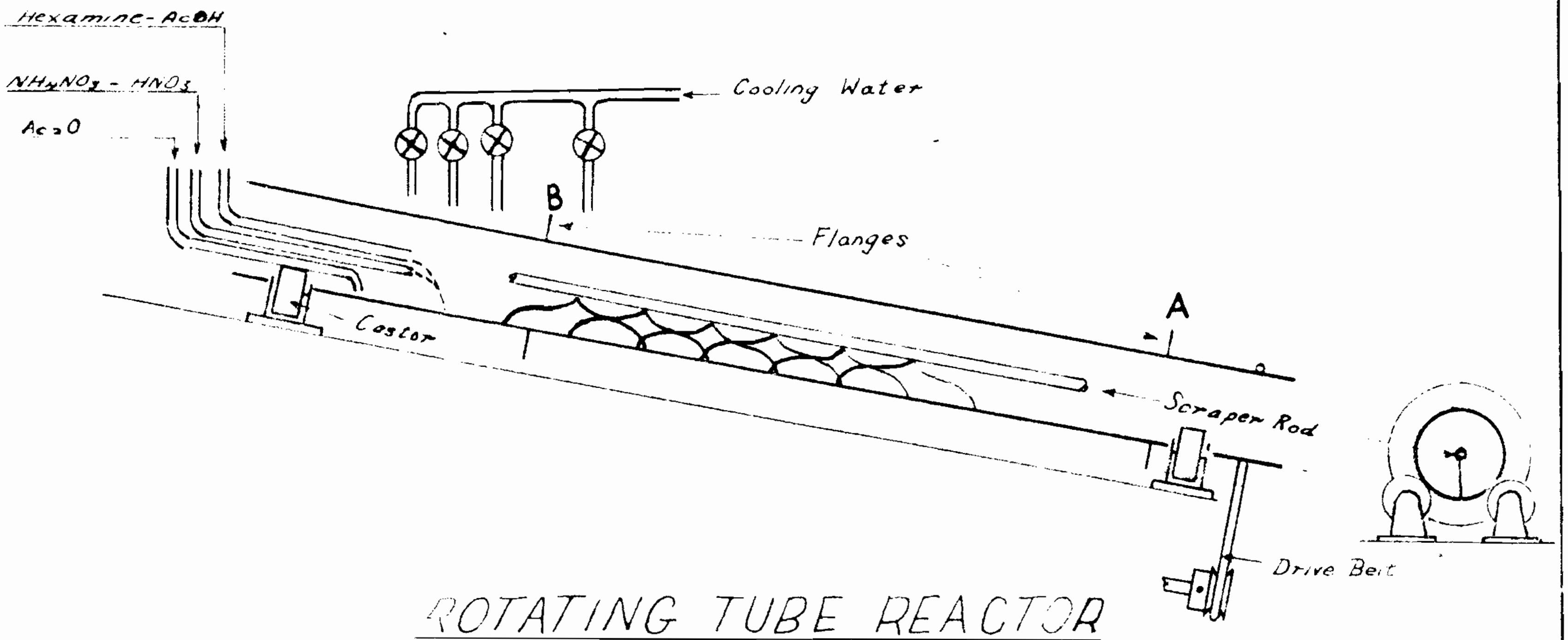
B. THE ROTATING TUBE CONVERTOR

A major disadvantage of the U-tube convertor was revealed by the experiments described in the previous pages. While temperature control was very satisfactory with such a reactor, the time required for the system to reach a steady state following any alteration of the variables was too great to permit adequate examination of the effect of several variables on the course of the reaction without undue expenditure of time and reagents. Furthermore, it became of major interest, as indicated by the data obtained during the early stages of reaction in the U-tube to investigate the effect of dilution on the reaction, a problem to which this type of reactor did not satisfactorily lend itself. It was decided, therefore, to attempt the development of a reactor in which the hold-up of reaction slurry was minimal. It was recognized from experience gained with the U-tube, however, that attainment of this objective would be difficult in view of the necessity for dissipating the large heat of reaction in the absence of a considerable body of liquid to act as heat reservoir. It seemed not unlikely that sufficiently rapid removal of the heat might be effected if the reaction proceeded in a thin film of the reaction medium dispersed over a large cooling surface, for which purpose a rotating tube carrying the film on its inner surface appeared to offer greatest promise of successful operation. It was realized that the large temperature gradient across the wall of the tube would lead inevitably to coating of the inner surface, but this problem seemed capable of solution by mechanically removing the coating, an operation to which a rotating tube, unlike the cooling surface in the U-tube reactor, seemed to be well suited. With these points in mind, development of a rotating tube convertor was undertaken and finally brought to a successful conclusion.

The feed system, the reagents and methods of analysis were similar to those described in the preceding discussion of the U-tube reactor.

CONSTRUCTION, OPERATION AND DEVELOPMENT OF THE CONVERTOR.

The rotating tube reactor in its simplest form consisted of a Pyrex tube 4 feet long, 3 inches inside diameter, supported at an incline of about 20 degrees on 4 castors and rotated by a rubber belt passing around the tube (Fig. 13). A fifth castor bearing against the face of flange A prevented the tube from sliding downward during rotation. The reagents were introduced at the upper end through three separate feed lines. Adjustable cold



ROTATING TUBE REACTOR

Type A

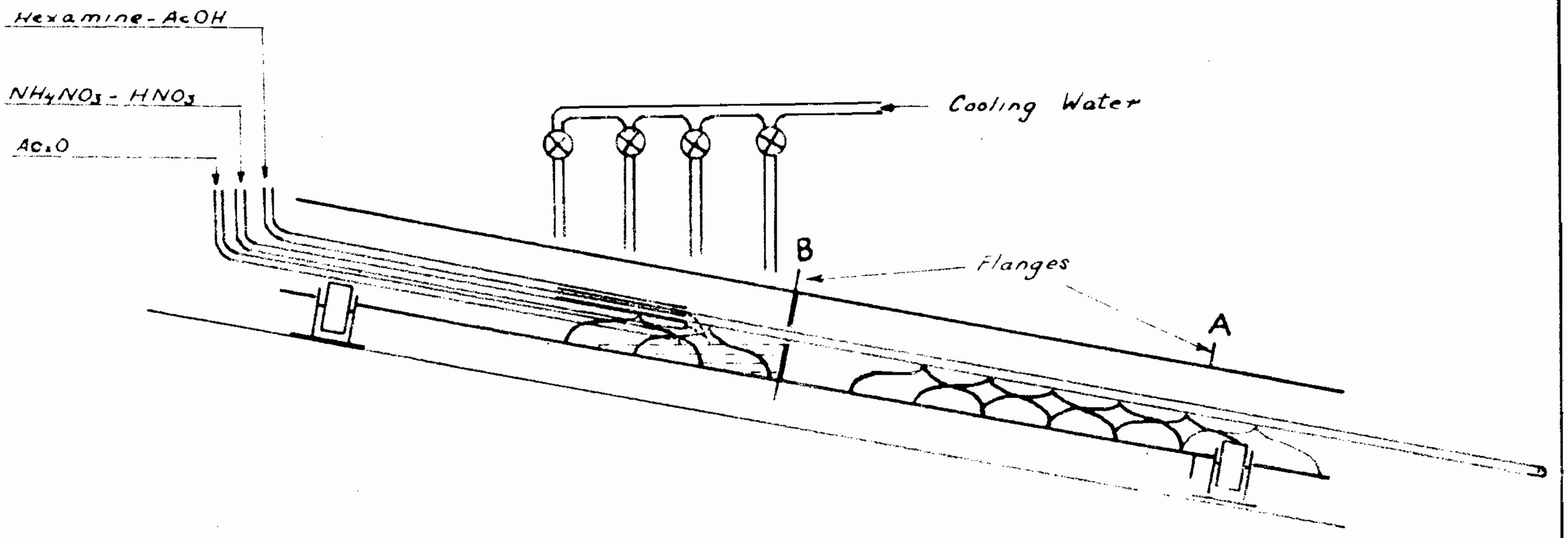
Figure 13

water jets playing over the external surface cooled the reaction mixture.

Excessive cooling towards the bottom end was prevented by a flange located near the upper end (as in diagram) to divert the cold water stream, and permit the use of warm water streams over the lower portion if desired. By adjusting the position of this flange, a fairly constant temperature could be maintained throughout most of the length of the convertor, but a region of somewhat higher temperature did persist at the point of juncture of the feeds. Temperatures were measured by a roving thermocouple in the film of slurry on the inner wall of the tube. A fixed thermocouple was also used at the point at which the feeds were mixed.

Since there was a tendency for coating to occur on the inner wall, a scraper, consisting of long flexible Nichrome strips attached to an aluminium or stainless steel rod, was driven slowly back and forth inside the reactor. The Nichrome strips had sufficient spring tension when bearing on the inner wall of the tube to prevent accumulation of coating on the wall.

Accurate temperature control throughout the length of the convertor was found to be possible by modifying slightly the simple design to include a diaphragm inside the tube near its upper end. (Fig. 14). This diaphragm had a



ROTATING TUBE REACTOR

Type 3

Figure 14

hole at the centre slightly larger than required to pass the scraper rod. A small pool of liquid was therefore permitted to accumulate above the diaphragm into which the liquid feeds were introduced. When the surface of the pool reached the central hole in the diaphragm the slurry overflowed into the bottom section of the tube and formed a film which traversed the length of the convertor until it finally spilled into a vessel at the lower end. By suitable adjustment of cold water streams at the upper end and warm water streams at the lower end, on the outer wall of the tube, very satisfactory temperature control was readily obtained.

The sample collected at the lower end of the convertor was transferred to a thermostatted bath, and maintained at a temperature of 70°C, for 20 minutes after leaving the reactor. At the end of this interval the sample was cooled rapidly to 20°C, having been stirred continuously up to this point.

Development of the rotating tube convertor to the form described above resulted from a series of experiments in which alterations of the reactor were dictated by observations of the Bachmann reaction under various conditions. In the first of these experiments, a taut wire, stretched along the inner surface of the tube, was used to remove the greater proportion of the coating that formed on the convertor wall. The reagents were introduced to the convertor in the order (proceeding along the tube from the upper end) hexamine-acetic acid, nitric acid-ammonium nitrate and acetic anhydride. There was approximately 2 inches between each feed jet. The feed proportions were, in molar ratios:

Hexamine - - - - - - - 1.0
Ammonium nitrate - - - 3.5
Nitric acid - - - - - - 4.5
Acetic anhydride - - - 9.0

A survey of the temperature in the liquid film along the convertor revealed a sharp peak between 1 and 2 inches below the point at which all three liquid reagent feeds came together. Excess cooling water, from the area in which this peak occurred, ran down the exterior surface of the tube and cooled the slurry, as it passed along the convertor, to an outlet temperature of 35-40°C. The temperature peak could not be maintained below 90°C.

Addition of the reagents in the order used in this experiment caused a voluminous white precipitate at the junction of the hexamine-acetic acid and nitric acid-ammonium nitrate liquid feeds. This precipitate was sticky and did not flow at a uniform rate along the convertor, hence wide fluctuations occurred in the rate of flow from the convertor.

Refinements in the design and operation of the

An alternative method of feed was therefore devised in which the hexamine-acetic acid and the nitric acid-ammonium nitrate liquid feeds were mixed in mid air, and fell into a film of acetic anhydride on the wall. This procedure solved the problem of a constant mass velocity through the convertor.

It was then observed that, owing to irregularities in the glass surface, the taut wire type of scraper was not completely satisfactory as a method of keeping the convertor wall free of coating. The introduction of the oscillating scraper (Fig's 13 and 14) was found to give completely satisfactory results.

Three experiments were made to determine whether any order of addition of reagents other than that mentioned above was preferable from yield and operational points of view. The order was varied so that two of the liquid feeds mixed in mid-air before falling into a film of the third liquid feed on the wall of the convertor. The variations tested were:

(1) HNO_3 - NH_4NO_3 and hexamine - AcOH falling into a film of Ac_2O.

(2) HNO_3 - NH_4NO_3 and Ac_2O falling into a film of hexamine - AcOH.

(3) Hexamine - AcOH and Ac_2O falling into a film of HNO_3 - NH_4NO_3.

The results of these tests are presented in Table XXII, in the order outlined above.

TABLE XXII

EFFECT OF ORDER OF ADDITION OF REAGENTS
ON
YIELD OF RDX(B) AND BSX.

Order of Addition	Yield, moles/mole hexamine	
	RDX(B)	BSX
(1)	1.18	.082
(2)	1.12	.088
(3)	1.14	.155

The operational behavior as well as the yield figures indicated that the most satisfactory mode of reagent feed was to introduce the mixed nitric acid-ammonium nitrate and hexamine-acetic acid solutions into a film of acetic anhydride and this procedure was adopted for further investigational purposes.

The final problem was elimination of the temperature peak and the maintenance of constant temperature throughout the entire course of the reaction.

The temperature peak resulted directly from the fact that the rate of heat evolution, corresponding to the high rate of reaction in undiluted medium, was too great to maintain optimal slurry temperature with the small amount of cooling surface available immediately below the point at which the reagents mixed (Appendix II). It was evident that only by decreasing the rate of reaction by dilution of the reagents would it be possible to attain the optimal slurry temperature (65-75°C). Dilution of the reagents with acetic acid, introduced into the falling mixture of hexamine-acetic acid and nitric acid-ammonium nitrate, did reduce the rate of reaction to some extent as indicated in Table XXIII, with some corresponding reduction in the temperature peak.

TABLE XXIII.

EFFECT OF DILUTION ON RATE OF BACHMANN REACTION
IN
ROTATING CONVERTOR

Dilution with AcOH moles/mole hexamine	Yield of RDX(B) At Exit from Convertor	Final
37	0.01	1.40
9.6	1.36	1.40

If excessive dilution (Table XXIII) of the slurry was used, it became necessary to apply heat to the external surface of the convertor, to maintain the optimal slurry temperature. Obviously the bulk of the reaction occurred after such highly diluted slurry left the convertor.

Even with dilution however, the temperature of the slurry varied over a fairly wide range. Increasing dilution shifted and broadened the temperature peak in such a random manner that it was practically impossible to maintain a constant slurry temperature throughout the entire length of the convertor. The results of a typical experiment (39) are presented in Tables XXIV, XXV, XXVI, XXVII, XXVIII, and Fig.'s 15 and 16.

These investigations showed that accurate temperature control is difficult, even impossible, with such small volumes of reaction liquor as were involved in the liquid film itself. A compromise between the U-tube and simple straight tube types of reactors was finally evolved to a point of successful operation consistent with rapid attainment of steady state conditions and small consumption of reagents. As mentioned previously, a diaphragm, (Fig. 14), with a central hole large enough to pass the scraping rod and allow the slurry to overflow freely, was fitted into the convertor at the point where the three feeds mingled. This diaphragm inside the convertor provided, by means of the pool of slurry, a heat reservoir with sufficient heat capacity and cooling surface to permit temperature control within ± 0.5°C. The slurry temperature in the pool was determined with a calibrated thermometer.

Experiments 47-52 (Tables XXIX, to XLVIII and

TABLE XXIV

ANALYTICAL DATA FROM EXPERIMENT 39

Composition of Reagents, % by Weight
Hexamine(38.7) in Acetic Acid(61.3)
Ammonium Nitrate(48.2) in Nitric Acid(50.8)
Acetic Acid, diluent, 1.023 grams per second.
Acetic Acid, total input, 11.6 moles per mole hexamine.

Sample No.	Convertor Temperature °C	Input moles/mole hexamine			Reagent Excesses % by weight		
		HNO_3	NH_4NO_3	Ac_2O	HNO_3	NH_4NO_3	Ac_2O
39-1	7 0	5.75	4,30	11.0	4.9	11.59	6.7
2	"	"	"	"	5.0	-	10.7
3	"	5.39	4.04	"	3.9	9.80	10.3
4	"	"	"	"	4.3	-	6.8
5	"	5.01	3.74	"	3.0	8.19	8.3
6	"	"	"	"	3.0	-	8.5
7	"	4.59	3.43	"	1.9	6.32	6.8
8	"	"	"	"	1.9	-	8.9
9	"	6.41	4.79	"	5.8	12.30	11.9
10	"	"	"	"	6.5	-	10.5
11	"	6.34	4.74	10.3	6.7	13.24	9.3
12	"	"	"	"	6.9	-	8.3
13	"	5.67	4.24	"	5.2	11.29	9.3
14	"	"	"	"	5.0	-	8.8
15	"	5.33	3.98	"	4.8	11.91	2.5
16	"	"	"	"	3.9	-	9.0
17	"	4.96	3.71	"	3.2	8.86	4.7
18	"	"	"	"	4.0	-	0.8
19	"	4.53	3.38	"	2.3	7.77	2.0
20	"	"	"	"	2.0	-	8.1

(No pool present).

TABLE XXV

CONSUMPTION OF REAGENTS

A. MOLES PER MOLE HEXAMINE

B. MOLES PER MOLE RDX(B)

Sample No.	Consumption moles/mole hexamine			Consumption moles/mole RDX(B)		
	HNO_3	NH_4NO_3	Ac_2O	HNO_3	NH_4NO_3	Ac_2O
39-1	4.37	1.43	9.80	4.05	1.32	9.07
2	4.25	-	8.98	3.83	-	8.09
3	4.30	1.52	9.13	3.55	1.26	7.55
4	4.33	-	9.92	3.61	-	8.27
5	4.25	1.86	9.69	3.08	1.35	7.02
6	4.30	-	9.69	3.12	-	7.02
7	4.13	2.01	9.92	2.87	1.40	6.89
8	4.13	-	9.61	2.81	-	6.54
9	4.45	1.18	8.43	4.32	1.14	8.18
10	4.45	-	8.98	4.59	-	9.26
11	4.41	1 .41	8.75	4.70	1.50	9.31
12	4.41	-	8.94	4.80	-	9.71
13	4.17	1.34	8.70	3.90	1.25	8.13
14	4.25	-	8.82	3.86	-	8.02
15	4.25	0.95	10.1	3.48	0.78	8.28
16	4.25	-	8.82	3.35	-	6.94
17	4.22	1.77	9.73	3.22	1.35	7.43
18	4.17	-	10.3	3.26	-	8.05
19	4.10	2.94	10.2	3.04	2.18	7.55
20	4.06	-	9.18	2.98	-	6.75

(No pool present).

TABLE XXVI

YIELD AND QUALITY OF PRODUCTS

Sample No.	Yield of Products moles/mole hexamine RDX(B)	HMX	RDX	BSX	H_2CO Accounted for as Products %	Initial Acidity %
39-1	1.08	.045	1.02	.254	72.5	0.38
2	1.11	-	-	.284	73.8	0.45
3	1.21	.049	1.15	.167	73.8	0.39
4	1.20	-	-	.171	71.2	0.35
5	1.38	.059	1.30	.091	76.5	0.43
6	1.38	-	-	.088	74.5	0.45
7	1.44	.053	1.37	.050	77.8	0.38
8	1.47	-	-	.054	77.2	0.33
9	1.03	.039	0.97	.351	76.5	0.55
10	0.97	-	-	.351	71.9	0.42
11	0.94	.039	0.89	.303	69.3	0.49
12	0.92	-	-	.306	66.7	0.48
13	1.07	.046	1.01	.272	74.0	0.50
14	1.10	-	-	.222	70.6	0.38
15	1.22	.051	1.15	.180	74.9	0.48
16	1.27	-	-	.159	74.5	0.46
17	1.31	.054	1.23	.103	74.2	0.44
18	1.28	-	-	.084	70.6	0.46
19	1.35	.051	1.29	.042	71.7	0.42
20	1.36	-	-	.055	72.5	0.43

(No pool present).

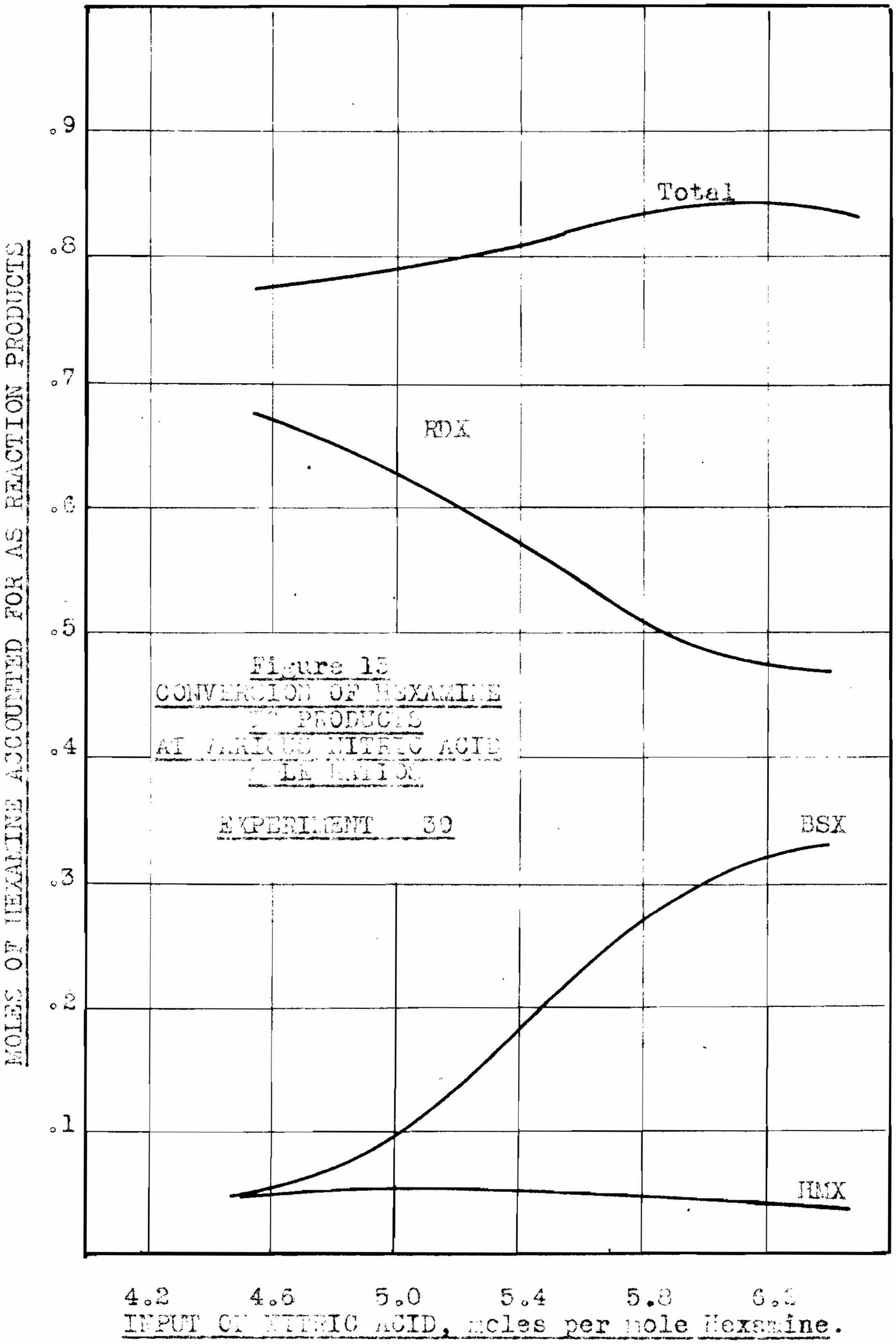


Figure 13
CONVERSION OF HEXAMINE TO PRODUCTS AT VARIOUS NITRIC ACID MOLE RATIO

EXPERIMENT 39

TABLE XXVII

DISTRIBUTION OF NITRIC ACID

Sample	Moles of Nitric Acid						
No.	Introduced	Recovered	Consumed	Converted to RDX	HMX	BSX	Unaccountable
39-1	1.46	.35	1.11	.51	.03	.17	.40
2	"	.38	1.08	-.56-		.19	.33
3	1.37	.28	1.09	.58	.03	.11	.37
4	"	.27	1.10	-.61-		.12	.37
5	1.27	.19	1.08	.66	.04	.06	.32
6	"	.18	1.09	-.70-		.06	.33
7	1.17	.12	1.05	.70	.03	.03	.29
8	"	.12	1.05	-.75-		.04	.26
9	1.63	.50	1.13	.50	.03	.24	.36
10	"	.50	1.13	-.49-		.24	.40
11	1.63	.50	1.13	.46	.03	.21	.43
12	"	.50	1.13	-.47-		.21	.45
13	1.46	.39	1.07	.52	.03	.19	.33
14	"	.39	1.09	-.57-		.15	.37
15	1.37	.28	1.09	.59	.03	.13	.34
16	"	.28	1.09	-.65-		.11	.33
17	1.27	.19	1.08	.63	.04	.07	.34
18	"	.20	1.07	-.66-		.06	.35
19	1.16	.11	1.05	.67	.03	.03	.32
20	"	.12	1.04	-.70-		.04	.30

Note- To convert to moles per mole hexamine multiply by 3.94

(No pool present).

TABLE XXVIII

DISTRIBUTION OF AMMONIUM NITRATE

Sample No.	Moles of Ammonium Nitrate						
	Introduced	Recovered	Consumed	Converted to			Unaccountable
				RDX	HMX	BSX	
39-1	1.09	.65	.44	.26	.02	.02	.14
2							
3	1.02	.56	.46	.29	.02	.01	.14
4							
5	0.95	.41	.54	.33	.02	.01	.18
6							
7	0.87	.31	.56	.35	.02	0	.19
8							
9	1.22	.84	.38	.25	.01	.03	.09
10							
11	1.22	.78	.44	.23	.01	.03	.17
12							
13	1.09	.67	.42	.26	.02	.02	.12
14							
15	1.02	.56	.46	.30	.02	.02	.12
16							
17	0.95	.42	.53	.32	.02	.01	.18
18							
19	0.87	.30	.57	.33	.02	0	.22
20							

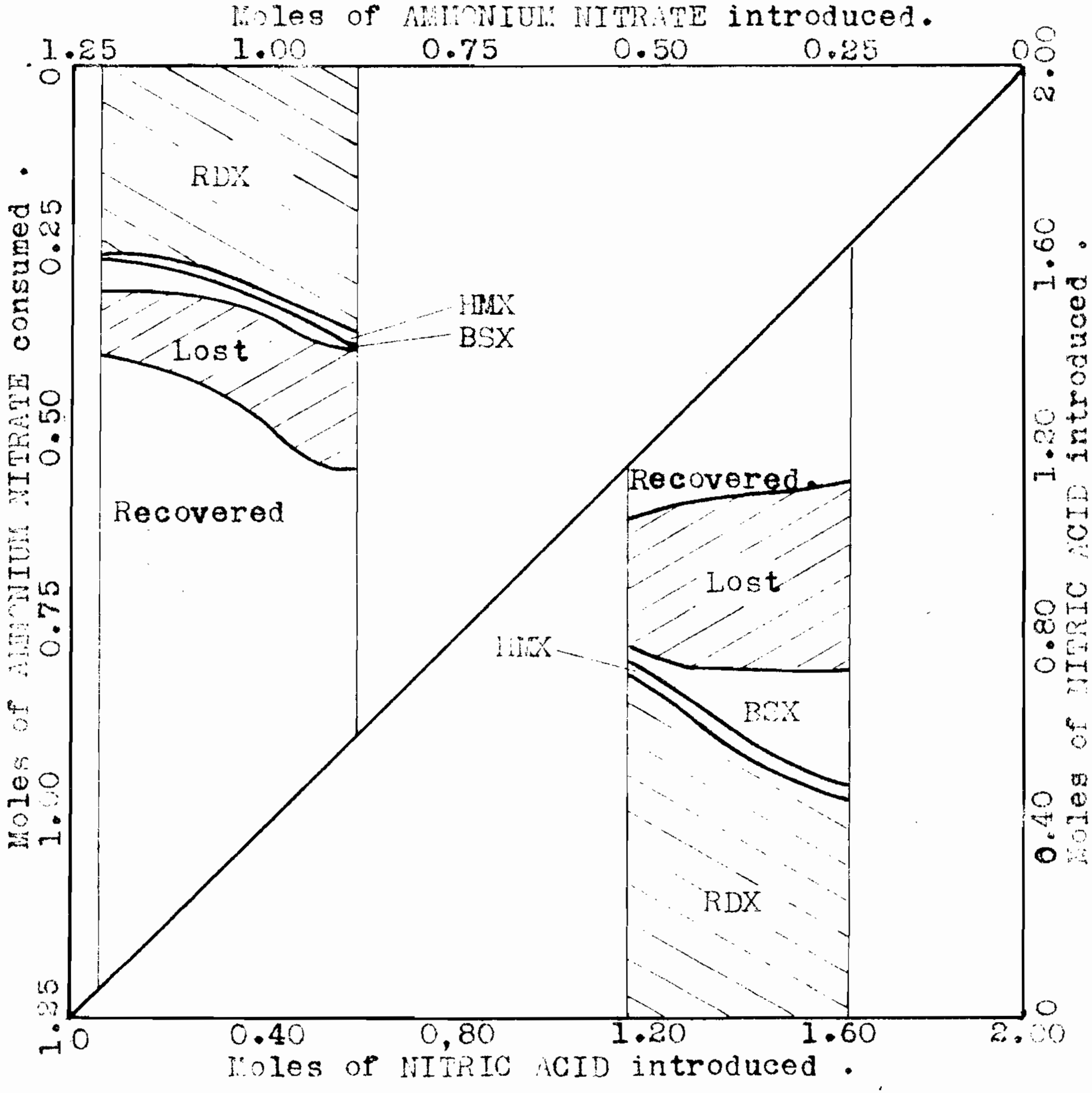
Note- To convert to moles per mole hexamine multiply by 3.94.

(No pool present).

Figure 16

DISTRIBUTION OF

NITRIC ACID AND AMMONIUM NITRATE



Experiment 39

(Note: To convert to moles/mole hexamine multiply by 3.94)

TABLE XXIX

ANALYTICAL DATA FROM EXPERIMENT 47

Composition of Reagents, % by Weight

Hexamine(38.0%) in Acetic Acid (62.0%)

Ammonium Nitrate(48.3%) in Nitric Acid(50.8%)

Acetic Acid, diluent, 2.475 grams/second

Acetic Acid, total input 24.2 moles/mole hexamine

Sample No.	Convertor Temperature °C	Input Moles/mole hexamine			Reagent Excesses % by weight		
		HNO_3	NH_4NO_3	Ac_2O	HNO_3	NH_4NO_3	Ac_2O
47-1	70	4.73	3.54	10.2	2.5	5.02	-
2	70	4.73	3.54	10.2	2.3	4.38	-
3	70	4.24	3.17	10.2	1.4	3.03	-
4	70	4.24	3.17	10.2	1.5	3.38	-
5	70	4.55	3.40	10.2	2.2	4.11	-
6	70	4.55	3.40	10.2	2.3	4.32	-
7	70	5.20	3.89	10.2	3.4	5.52	-
8	70	5.20	3.89	10.2	3.4	5.98	-
9	70	6.04	4.51	10.2	5.2	8.07	-
10	70	6.04	4.51	10.2	5.3	-	-
11	70	6.75	5.05	10.2	6.5	9.68	-
12	70	6.75	5.05	10.2	7.1	10.4	-
13	70	4.55	3.40	10.2	2.3	4.68	-
14	70	4.55	3.40	10.2	2.2	4.35	-

(Pool present).

TABLE XXX

CONSUMPTION OF REAGENTS

A. MOLES PER MOLE HEXAMINE

B. MOLES PER MOLE RDX(B)

Sample	Consumption moles/mole hexamine			Consumption moles/mole RDX(B)		
No.	HNO_3	NH_4NO_3	Ac_2O	HNO_3	NH_4NO_3	Ac_2O
47-1	3.78	1.93	-	2.49	1.27	-
2	3.87	2.00	-	2.60	1.34	-
3	3.70	2.13	-	2.55	1.47	-
4	3.72	2.11	-	2.48	1.41	-
5	3.73	2.04	-	2.48	1.34	-
6	3.79	2.12	-	2.48	1.39	-
7	3.86	1.94	-	2.56	1.28	-
8	3.90	1.80	-	2.59	1.18	-
9	3.94	1.61	-	2.61	1.16	-
10	3.98	-	-	2.64	-	-
11	4.02	1.48	-	2.67	1.19	-
12	3.90	1.34	-	2.59	1.10	-
13	3.78	1.98	-	2.39	1.25	-
14	3.79	2.05	-	2.49	1.35	-

(Pool present).

TABLE XXXI

YIELD AND QUALITY OF PRODUCTS

Sample	Yield of Products moles/mole hexamine				H_2CO Accounted for as products	Initial Acidity
No.	RDX(B)	HMX	RDX	BSX	%	%
47-1	1.52	.083	1.41	.018	77.2	.49
2	1.49	.080	1.39	.046	78.0	.53
3	1.45	.103	1.32	.013	73.8	.33
4	1.50	.108	1.36	.024	76.6	.32
5	1.52	.088	1.40	.025	78.0	.48
6	1.53	.090	1.41	.030	78.6	.47
7	1.51	.064	1.43	.055	79.3	.52
8	1.53	.067	1.44	.050	79.3	.54
9	1.39	.049	1.32	.131	78.6	.47
10	1.39	.049	1.33	.132	78.6	.46
11	1.24	.039	1.19	.192	75.2	.46
12	1.22	.043	1.16	.179	72.4	.49
13	1.58	.092	1.45	.031	80.7	.47
14	1.52	.088	1.40	.027	78.6	.47

(Pool present).

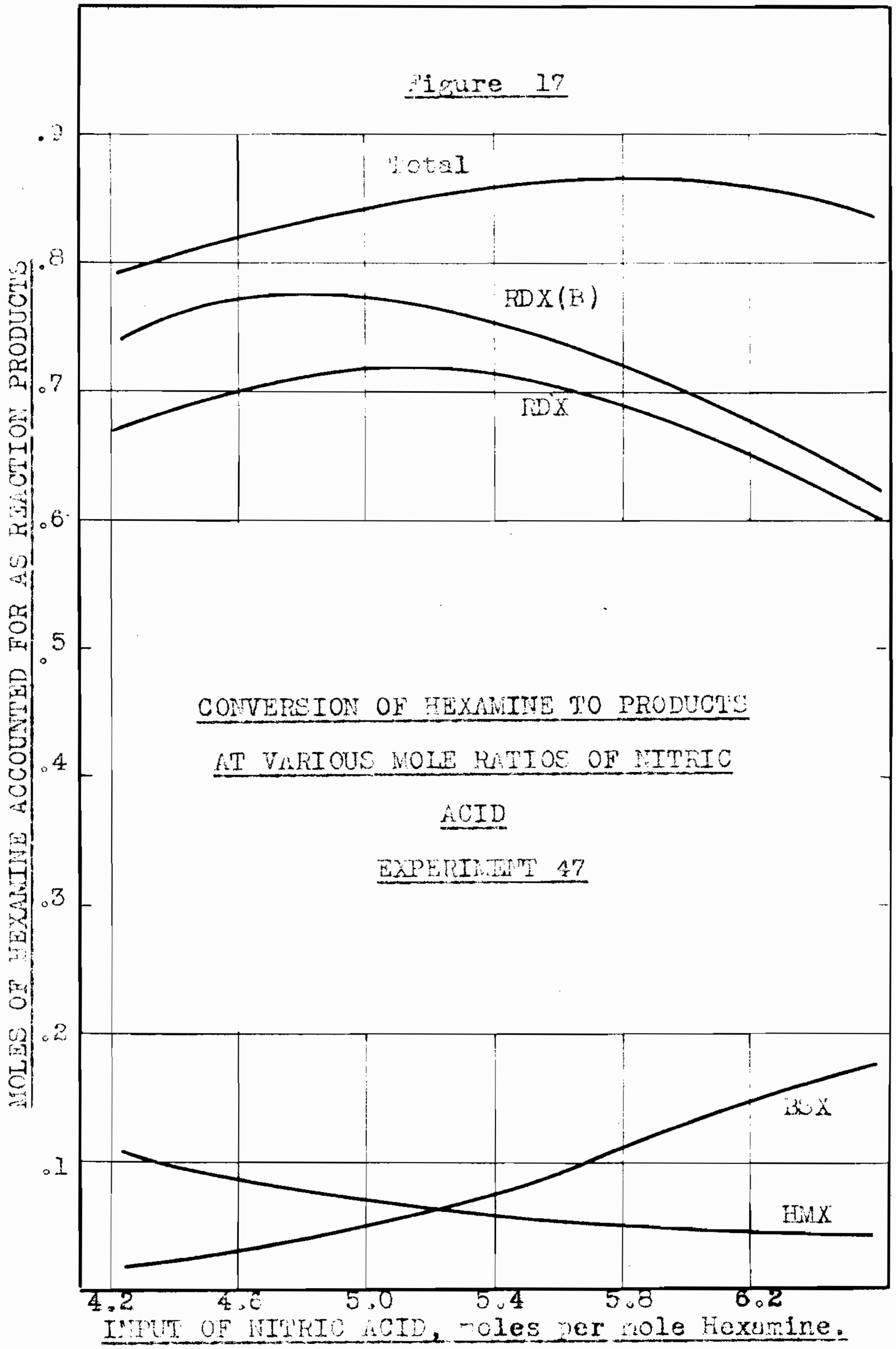


Figure 17

CONVERSION OF HEXAMINE TO PRODUCTS AT VARIOUS MOLE RATIOS OF NITRIC ACID

EXPERIMENT 47

TABLE XXXII

DISTRIBUTION OF NITRIC ACID

Sample	Moles of Nitric Acid						
	Introduced	Recovered	Consumed	Converted to			Unaccountable
No.				RDX	HMX	BSX	
47-1	1.14	.20	.94	.68	.05	.01	.20
2	1.14	.21	.93	.67	.05	.03	.18
3	1.02	.12	.90	.64	.07	.01	.18
4	1.02	.12	.90	.66	.07	.01	.16
5	1.10	.20	.90	.68	.06	.01	.15
6	1.10	.18	.92	.68	.06	.02	.16
7	1.26	.33	.93	.69	.04	.03	.17
8	1.26	.32	.94	.70	.04	.03	.17
9	1.46	.51	.95	.64	.03	.09	.19
10	1.46	.50	.96	.64	.03	.09	.20
11	1.63	.66	.97	.57	.03	.13	.24
12	1.63	.69	.94	.56	.03	.11	.24
13	1.10	.18	.92	.70	.06	.02	.14
14	1.10	.18	.92	.68	.06	.02	.16

Note: To convert to moles/mole hexamine multiply by 4.15

(Pool present).

TABLE XXXIII

DISTRIBUTION OF AMMONIUM NITRATE

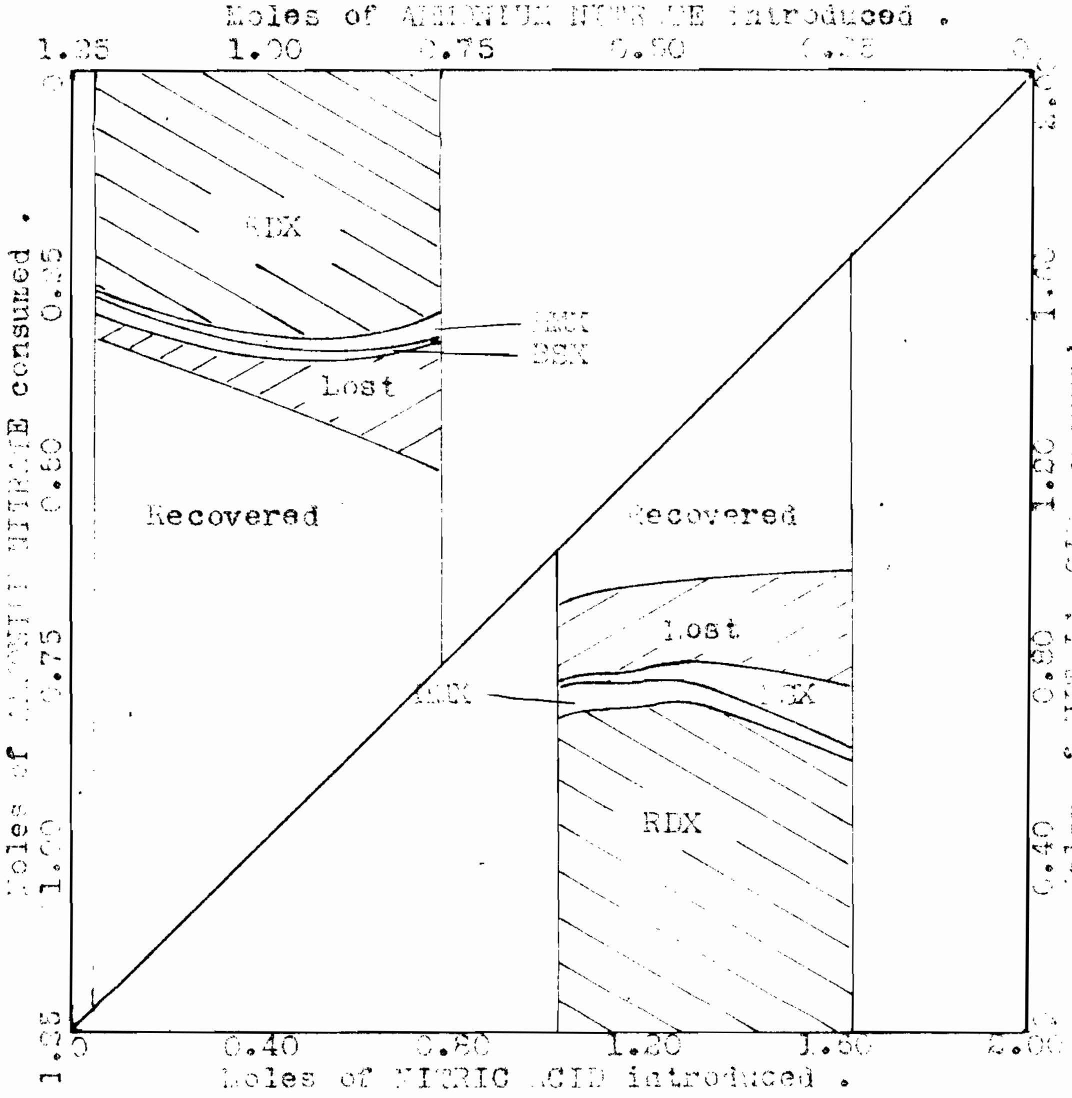
Sample	Moles of Ammonium Nitrate						
	Introduced	Recovered	Consumed	Converted to			Unaccountable
No.				RDX	HMX	BSX	
47-1	.86	.39	.47	.34	.03	0	.10
2	.86	.37	.49	.34	.03	0	.12
3	.77	.25	.52	.32	.03	0	.17
4	.77	.26	.51	.33	.03	0	.15
5	.82	.32	.50	.34	.03	0	.13
6	.82	.31	.51	.34	.03	0	.14
7	.94	.47	.47	.35	.02	0	.10
8	.94	.50	.44	.35	.02	0	.07
9	1.09	.70	.39	.32	.02	.01	.04
10	1.09	-	-	.32	.02	.01	(.04)
11	1.22	.86	.36	.29	.01	.02	.04
12	1.22	.89	.33	.28	.01	.01	.03
13	.82	.34	.48	.35	.03	0	.10
14	.82	.32	.50	.34	.03	0	.13

Note: To convert to moles/mole Hexamine multiply by 4.15 (Pool present).

Figure 18

DISTRIBUTION OF

NITRIC ACID AND AMMONIUM NITRATE



Experiment 47

(Note: To convert to moles/mole hexamine multiply by 4.15)

TABLE XXXIV

ANALYTICAL DATA FROM EXPERIMENT 48

Composition of Reagents, % by Weight.

Hexamine (38.0) in Acetic Acid (62.0)

Ammonium Nitrate (48.3) in Nitric Acid(50.8)

Acetic Acid, diluent, 2.475 grams per second.

Acetic Acid, total input, 24.2 moles per mole hexamine

Sample	Convertor Temperature	Input moles/mole hexamine			Reagent Excesses % by weight		
No.	°C	HNO_3	NH_4NO_3	Ac_2O	HNO_3	NH_4NO_3	Ac_2O
48-1	70	5.51	4.12	10.6	3.7	5.53	9.4
2	"	"	"	"	3.7	-	9.0
3	"	4.28	3.20	"	1.2	2.10	9.0
4	"	"	"	"	1.2	-	9.4
5	"	4.77	3.57	"	2.2	3.95	10.7
6	"	"	"	"	2.2	-	9.8
7	"	6.09	4.55	"	4.8	-	9.8
8	"	"	"	"	4.8	7.22	10.7
9	"	6.85	5.12	"	6.3	8.94	11.1

(Pool present).

TABLE XXXV

CONSUMPTION OF REAGENTS

A. MOLES PER MOLE HEXAMINE

B. MOLES PER MOLE RDX(B)

Sample	Consumption moles/mole hexamine			Consumption moles/mole RDX(B)		
No.	HNO_3	NH_4NO_3	Ac_2O	HNO_3	NH_4NO_3	Ac_2O
48-1	3.80	1.86	8.05	2.46	1.21	5.22
2	"	-	8.13	"	-	5.31
3	3.76	2.38	8.22	2.44	1.69	5.84
4	"	-	8.10	"	-	5.70
5	3.76	2.03	7.76	2.44	1.33	5.04
6	"	-	8.01	"	-	5.20
7	3.80	-	7.85	2.46	-	5.60
8	"	1.65	7.64	"	1.21	5.61
9	3.64	1.33	7.27	2.35	1.17	6.37

(Pool present).

TABLE XXXVI

YIELD AND QUALITY OF PRODUCTS

Sample	Yield of Products moles/mole hexamine				H_2CO Accounted for as products	Initial Acidity
No.	RDX(B)	HMX	RDX	BSX	%	%
48-1	1.54	.041	1.49	.027	79.3	0.23
2	1.53	.062	1.45	.056	80.0	0.28
3	1.41	.116	1.26	.010	71.0	0.58
4	1.42	.036	1.37	.019	72.4	0.31
5	1.53	.052	1.46	.013	77.3	0.30
6	1.54	.076	1.44	.013	77.3	0.30
7	1.40	.070	1.31	.116	78.0	0.32
8	1.36	.043	1.30	.111	75.2	0.30
9	1.14	.028	1.10	.227	72.4	0.39

(Pool present).

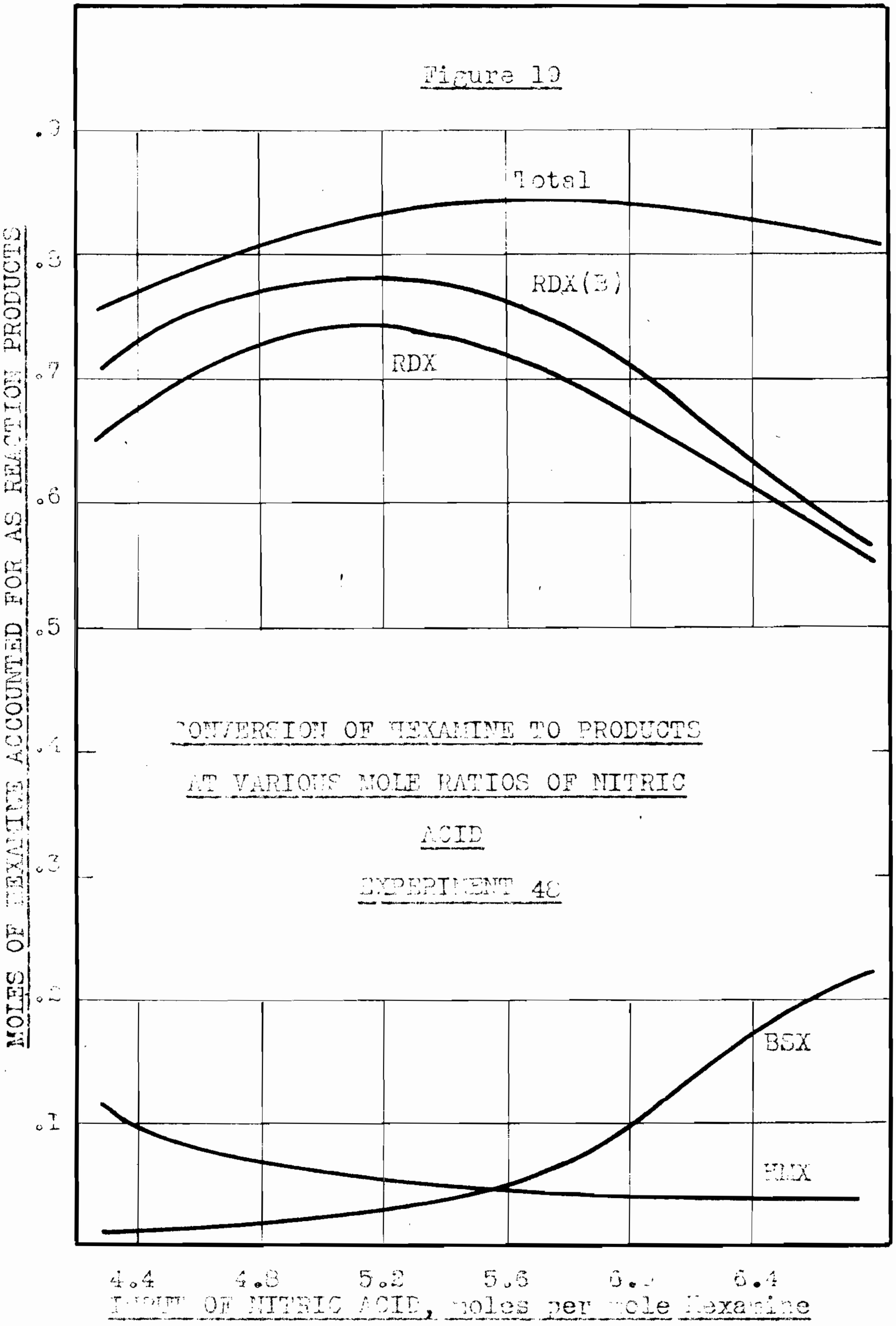


Figure 10

CONVERSION OF HEXAMINE TO PRODUCTS AT VARIOUS MOLE RATIOS OF NITRIC ACID

EXPERIMENT 48

TABLE XXXVII

DISTRIBUTION OF NITRIC ACID

Sample	Moles of Nitric Acid						
	Introduced	Recovered	Consumed	Converted to			Unaccountable
No.				RDX	HMX	BSX	
48-1	1.33	.41	.92	.72	.03	.02	.15
2	"	.41	.92	.70	.04	.03	.15
3	1.03	.12	.91	.61	.07	.01	.22
4	"	.12	.91	.66	.03	.01	.21
5	1.15	.24	.91	.71	.03	.01	.16
6	"	.24	.91	.70	.05	.01	.15
7	1.46	.54	.92	.63	.05	.07	.17
8	"	.54	.92	.63	.03	.07	.19
9	1.64	.76	.88	.53	.02	.15	.18

Note- To convert to moles per mole hexamine multiply by 4.14.

(Pool present).

TABLE XXXVIII

DISTRIBUTION OF AMMONIUM NITRATE

Sample	Moles of Ammonium Nitrate						
	Introduced	Recovered	Consumed	Converted to			Unaccountable
No.				RDX	HMX	BSX	
48-1	.99	.54	.45	.36	.01	0	.08
2	-	-	-	-	-	-	-
3	.77	.20	.57	.30	.04	0	.23
4	-	-	-	-	-	-	-
5	.86	.37	.49	.35	.02	0	.12
6	-	-	-	-	-	-	-
7	-	-	-	-	-	-	-
8	1.10	.70	.40	.31	.01	.01	.07
9	1.23	.91	.32	.27	.01	.02	.02

Note- To convert to moles per mole hexamine multiply by 4.14.

(Pool present).

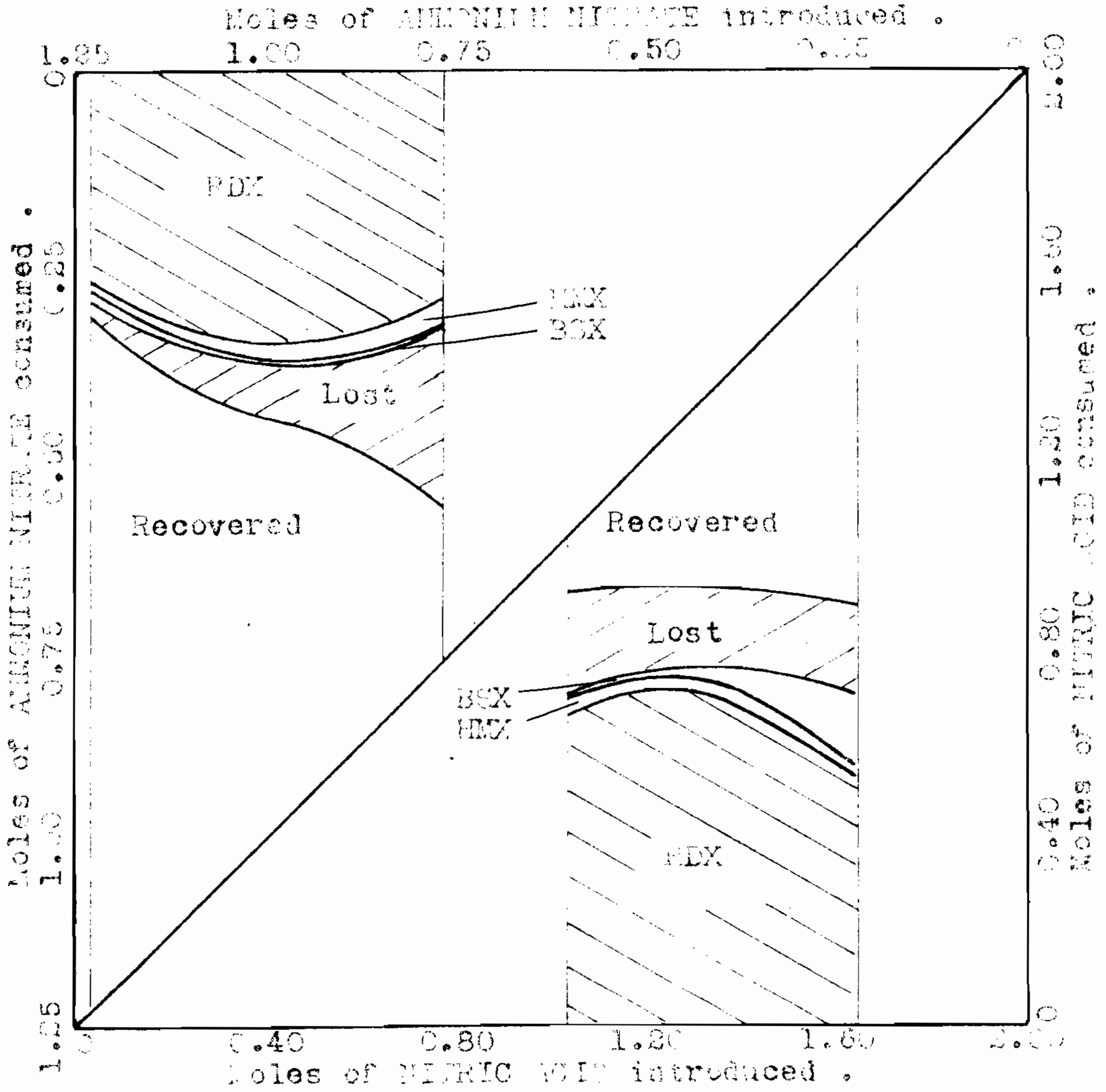


Figure 20

DISTRIBUTION OF

NITRIC ACID AND AMMONIUM NITRATE

Experiment 48

(Note: To convert to moles/mole hexamine multiply
by 4.14)

TABLE XXXIX

ANALYTICAL DATA FROM EXPERIMENT 50

Composition of Reagents, % by Weight.

Hexamine(38.0) in Acetic Acid(62.0)

Ammonium Nitrate(48.3) in Nitric Acid(50.8)

Acetic Acid, diluent, 2.475 grams/second.

Acetic Acid, total input, 24.1 moles/mole hexamine.

Sample	Convertor	Input			Reagent Excesses		
	Temperature	moles/mole hexamine			% by weight		
No.	°C	HNO_3	NH_4NO_3	Ac_2O	HNO_3	NH_4NO_3	Ac_2O
50-1	70	4.26	3.19	10.2	1.17	-	6.2
2	"	"	"	"	1.16	1.9	6.2
3	"	4.39	3.28	"	1.88	-	7.0
4	"	"	"	"	1.91	-	7.8
5	"	4.46	3.34	"	1.50	2.3	7.2
6	"	"	"	"	1.46	-	7.4
7	"	4.64	3.47	"	1.38	-	8.0
8	"	"	"	"	1.24	-	8.2
9	"	4.25	3.18	"	1.20	0.66	6.6
10	"	"	"	"	1.18	-	6.2
11	"	4.08	3.05	"	0.82	1.08	6.8
12	"	"	"	"	0.85	-	5.8

(Pool present).

TABLE XL

CONSUMPTION OF REAGENTS

A. MOLES PER MOLE HEXAMINE

B. MOLES PER MOLE RDX(B)

Sample	Consumption			Consumption		
	moles/mole hexamine			moles/mole RDX(B)		
No.	HNO_3	NH_4NO_3	Ac_2O	HNO_3	NH_4NO_3	Ac_2O
50-1	3.76	-	8.55	2.83	-	6.43
2	3.76	2.46	8.55	2.87	1.88	6.53
3	3.56	-	8.30	2.56	-	5.97
4	3.54	-	8.10	2.60	-	5.95
5	3.81	2.46	8.27	2.72	1.76	5.90
6	3.82	-	8.18	2.75	-	5.88
7	4.04	-	8.05	2.75	-	5.48
8	4.08	-	7.97	2.82	-	5.50
9	3.75	2.94	8.43	2.95	2.31	6.63
10	3.76	-	8.55	2.96	-	6.73
11	3.72	2.65	8.39	3.12	2.23	7.05
12	3.72	-	8.64	3.12	-	7.26

(Pool present).

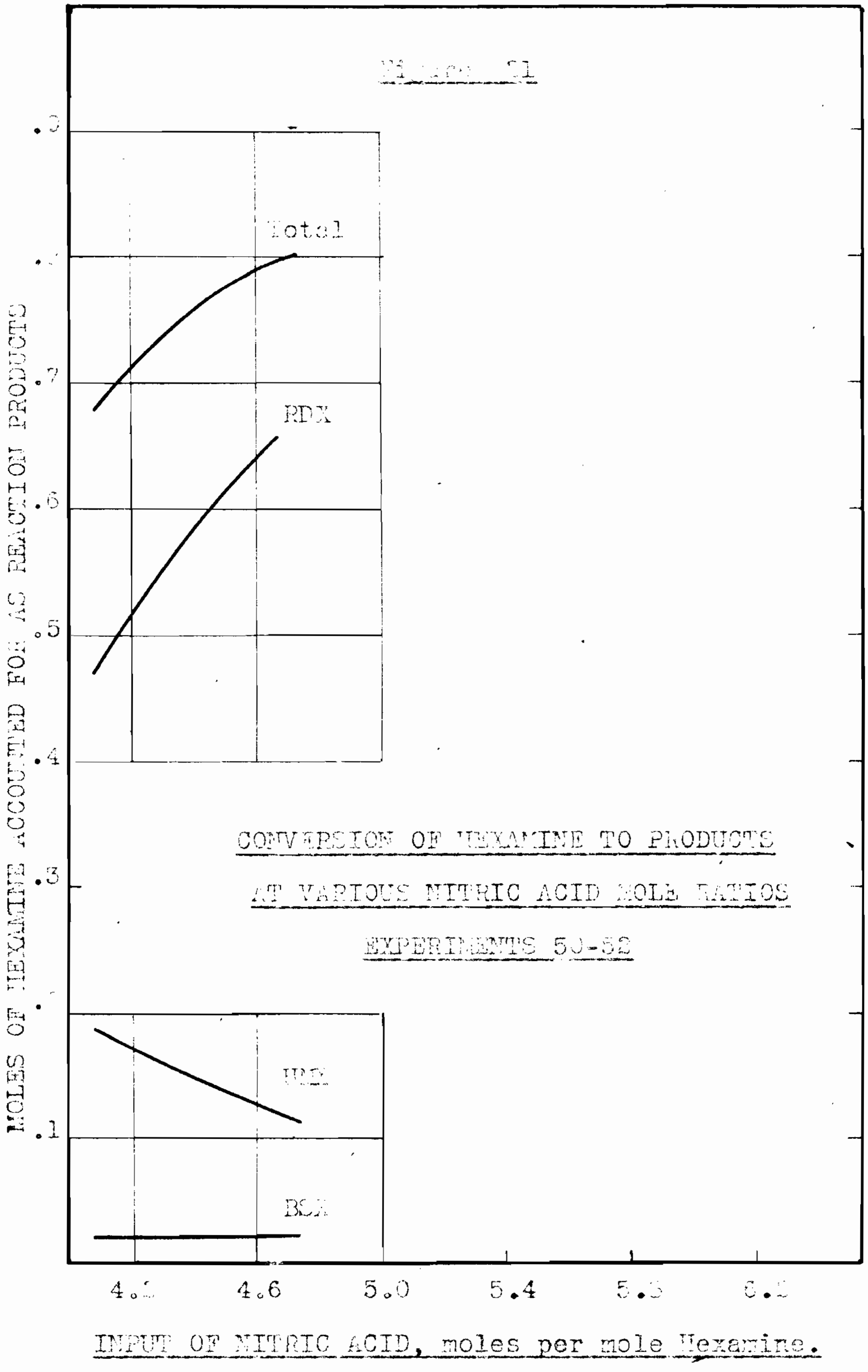
TABLE XLI

YIELD AND QUALITY OF PRODUCTS

Sample	Yield of Products moles/mole hexamine				H_2CO Accounted for as products	Initial Acidity
No.	RDX(B)	HMX	RDX	BSX	%	%
50-1	1.33	.150	1.13	.032	69.0	.50
2	1.31	.163	1.09	.024	67.6	.62
3	1.39	.218	1.10	.027	71.7	.56
4	1.36	.145	1.17	.024	69.7	.61
5	1.40	.148	1.21	.026	72.5	.77
6	1.39	.142	1.20	.022	71.0	.63
7	1.47	.120	1.31	.030	76.6	.50
8	1.45	.114	1.30	.025	74.5	.55
9	1.27	.181	1.03	.025	65.5	.63
10	1.27	.181	1.03	.021	65.5	.48
11	1.19	.182	0.94	.024	61.4	.64
12	1.19	.187	0.94	.017	61.4	.93

(Pool present).

Figure [illegible]



CONVERSION OF HEXAMINE TO PRODUCTS
AT VARIOUS NITRIC ACID MOLE RATIOS
EXPERIMENTS 50-52

TABLE XLII

DISTRIBUTION OF NITRIC ACID

Sample	Moles of Nitric Acid						
	Introduced	Recovered	Consumed	Converted to			Unaccountable
No.				RDX	HMX	BSX	
50-1	1.03	.12	.91	.54	.10	.02	.25
2	"	"	.91	.53	.11	.01	.26
3	1.06	.20	.86	.53	.14	.02	.17
4	"	"	.86	.57	.09	.01	.19
5	1.08	.16	.92	.59	.09	.02	.22
6	"	"	.92	.58	.09	.01	.24
7	1.12	.14	.98	.64	.08	.02	.24
8	"	.13	.99	.63	.07	.01	.28
9	1.03	.12	.91	.50	.12	.01	.28
10	"	"	.91	.50	.12	.01	.28
11	0.99	.09	.90	.46	.12	.01	.31
12	"	"	.90	.46	.12	.01	.31

Note- To convert to moles per mole hexamine multiply by 4.13.

(Pool present).

TABLE XLIII

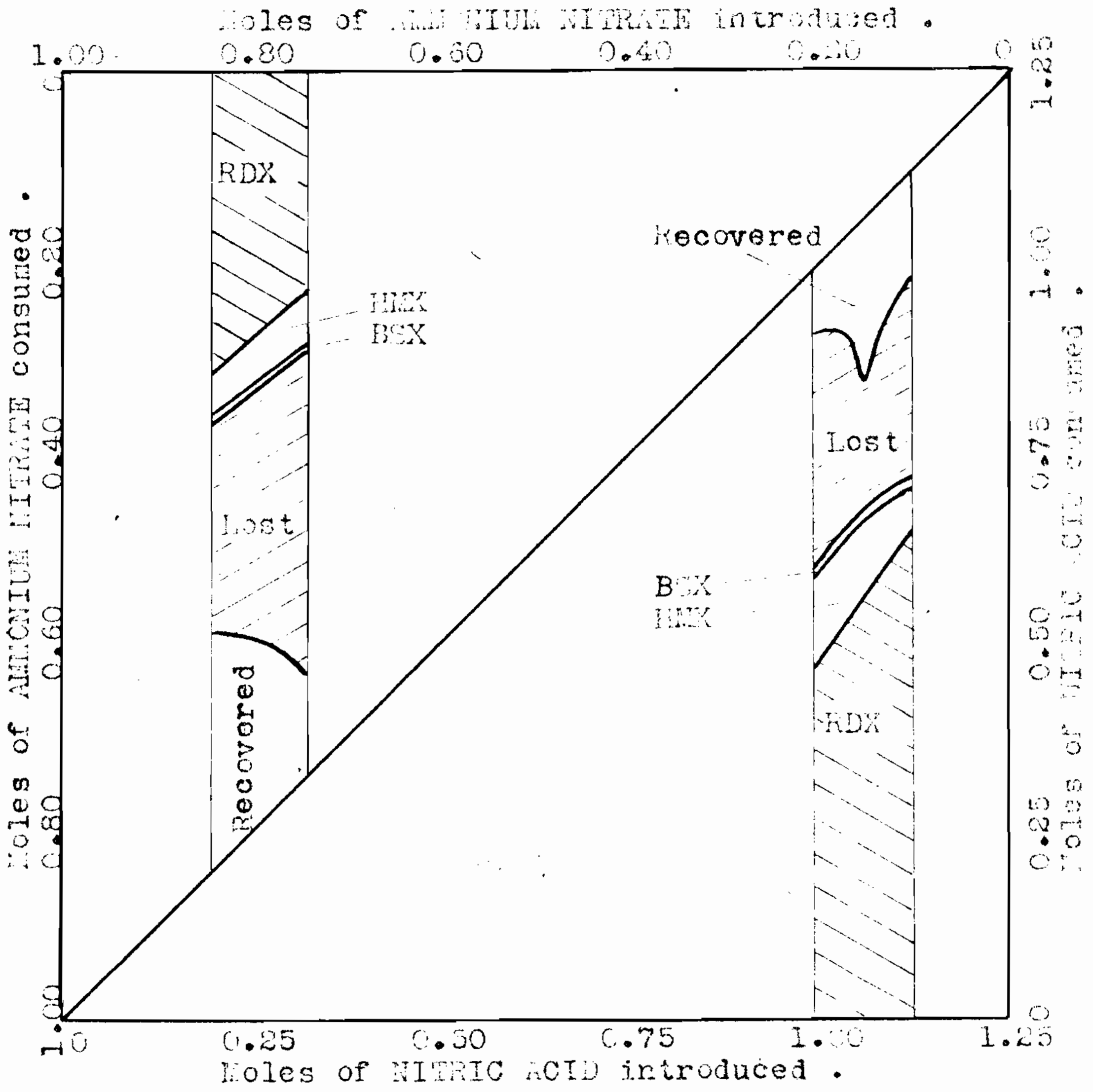
DISTRIBUTION OF AMMONIUM NITRATE

Sample	Moles of Ammonium Nitrate						
	Introduced	Recovered	Consumed	Converted to			Unaccountable
No.				RDX	HMX	BSX	
50-1	.77	-	-	.27	.05	0	-
2	.77	.17	.60	.27	.05	0	.28
3	.79	-	-	.27	.07	0	-
4	.79	-	-	.28	.05	0	-
5	.81	.21	.60	.29	.05	0	.26
6	.81	-	-	.29	.05	0	-
7	.84	-	-	.32	.04	0	-
8	.84	-	-	.32	.04	0	-
9	.77	.06	.71	.25	.06	0	.40
10	.77	-	-	.25	.06	0	-
11	.74	.10	.64	.23	.06	0	.35
12	.74	-	-	.23	.06	0	-

Note: To convert to moles/mole hexamine multiply by 4.13 (Pool present).

Figure 22

DISTRIBUTION OF NITRIC ACID
AND AMMONIUM NITRATE



Experiment 50

(Note: To convert to moles/mole hexamine multiply
by 4.13)

TABLE XLIV

ANALYTICAL DATA FROM EXPERIMENT 52

Composition of Reagents, % by Weight

Hexamine(38.0) in Acetic Acid(62.0)

Ammonium Nitrate(48.3) in Nitric Acid(50.8)

Acetic Acid, diluent, 2.485 grams/second

Acetic Acid, total input, 23.9 moles/mole hexamine

Sample	Convertor	Input			Reagent Excesses		
	Temperature	moles/mole hexamine.			% by weight		
No.	°C	HNO_3	NH_4NO_3	Ac_2O	HNO_3	NH_4NO_3	Ac_2O
52-1	70	4.66	3.49	8.69	2.04	3.35	0
2	70	4.66	3.49	8.69	2.02	3.35	0
3	70	4.66	3.49	8.69	1.91	3.60	0
4	70	4.66	3.49	8.69	1.96	3.40	0
5	70	4.55	3.41	8.69	1.71	2.80	0
6	70	4.55	3.41	8.69	1.76	3.25	0
7	70	4.55	3.41	8.69	2.28	2.85	0
8	70	4.80	3.59	8.69	1.66	4.15	0
9	70	4.80	3.59	8.69	2.22	4.15	0
10	70	4.80	3.59	8.69	2.32	4.00	0

(Pool present).

TABLE XLV

CONSUMPTION OF REAGENTS

A. MOLES/MOLE HEXAMINE

B. MOLES/MOLE RDX(B)

Sample	Consumption moles/mole hexamine			Consumption moles/mole RDX(B)		
No.	HNO_3	NH_4NO_3	Ac_2O	HNO_3	NH_4NO_3	Ac_2O
52-1	3.85	2.31	-	2.71	1.63	-
2	3.86	2.30	-	2.61	1.55	-
3	3.89	2.19	-	2.65	1.49	-
4	3.88	2.28	-	2.66	1.56	-
5	3.86	2.40	-	2.68	1.67	-
6	3.87	2.28	-	2.74	1.62	-
7	3.62	2.38	-	2.50	1.64	-
8	4.13	2.10	-	2.66	1.35	-
9	3.88	2.06	-	2.47	1.30	-
10	3.86	2.14	-	2.44	1.35	-

(Pool present).

TABLE XLVI

YIELD AND QUALITY OF PRODUCTS

Sample	Yield of Products moles/mole hexamine				H_2CO Accounted for as products	Initial Acidity
No.	RDX(B)	HMX	RDX	BSX	%	%
52-1	1.42	.139	1.23	.006	72.3	-
2	1.48	.138	1.29	.006	75.0	-
3	1.47	.143	1.28	.017	74.3	-
4	1.46	.142	1.27	.018	73.7	-
5	1.44	.147	1.24	.016	73.0	-
6	1.41	.145	1.22	.024	71.0	-
7	1.45	.142	1.26	.019	73.7	-
8	1.55	-	-	.023	79.1	-
9	1.58	-	-	.016	80.4	-
10	1.58	-	-	.020	80.4	-

(Pool present).

TABLE XLVII

DISTRIBUTION OF NITRIC ACID

Sample	Moles of Nitric Acid						
	Introduced	Recovered	Consumed	Converted to			Unaccountable
No.				RDX	HMX	BSX	
52-1	1.15	.20	.95	.61	.09	.01	.24
2	1.15	.20	.95	.64	.09	.01	.21
3	1.15	.19	.96	.63	.09	.01	.23
4	1.15	.19	.96	.63	.09	.01	.23
5	1.12	.17	.95	.61	.10	.01	.23
6	1.12	.16	.96	.60	.09	.01	.26
7	1.12	.22	.90	.62	.09	.01	.18
8	1.19	.17	1.02	-.77	-	.01	.24
9	1.19	.23	.96	-.78	-	.01	.17
10	1.19	.24	.95	-.78	-	.01	.16

Note: To convert to moles/mole hexamine multiply by 4.05

(Pool present).

TABLE XLVIII

DISTRIBUTION OF AMMONIUM NITRATE

Sample No.	Moles of Ammonium Nitrate Introduced	Recovered	Consumed	Converted to RDX	HMX	BSX	Unaccountable
52-1	.86	.29	.57	.31	.05	0	.21
2	.86	.29	.57	.32	.05	0	.20
3	.86	.32	.54	.32	.05	0	.17
4	.86	.30	.56	.31	.05	0	.20
5	.84	.25	.59	.31	.05	0	.23
6	.84	.28	.56	.30	.05	0	.21
7	.84	.25	.59	.31	.05	0	.23
8	.89	.37	.52	-.38 -		0	.14
9	.89	.38	.51	-.39 -		0	.12
10	.89	.36	.53	-.39 -		0	.14

Note: To convert to moles/mole hexamine multiply by 4.05 (Pool present).

Figure 23

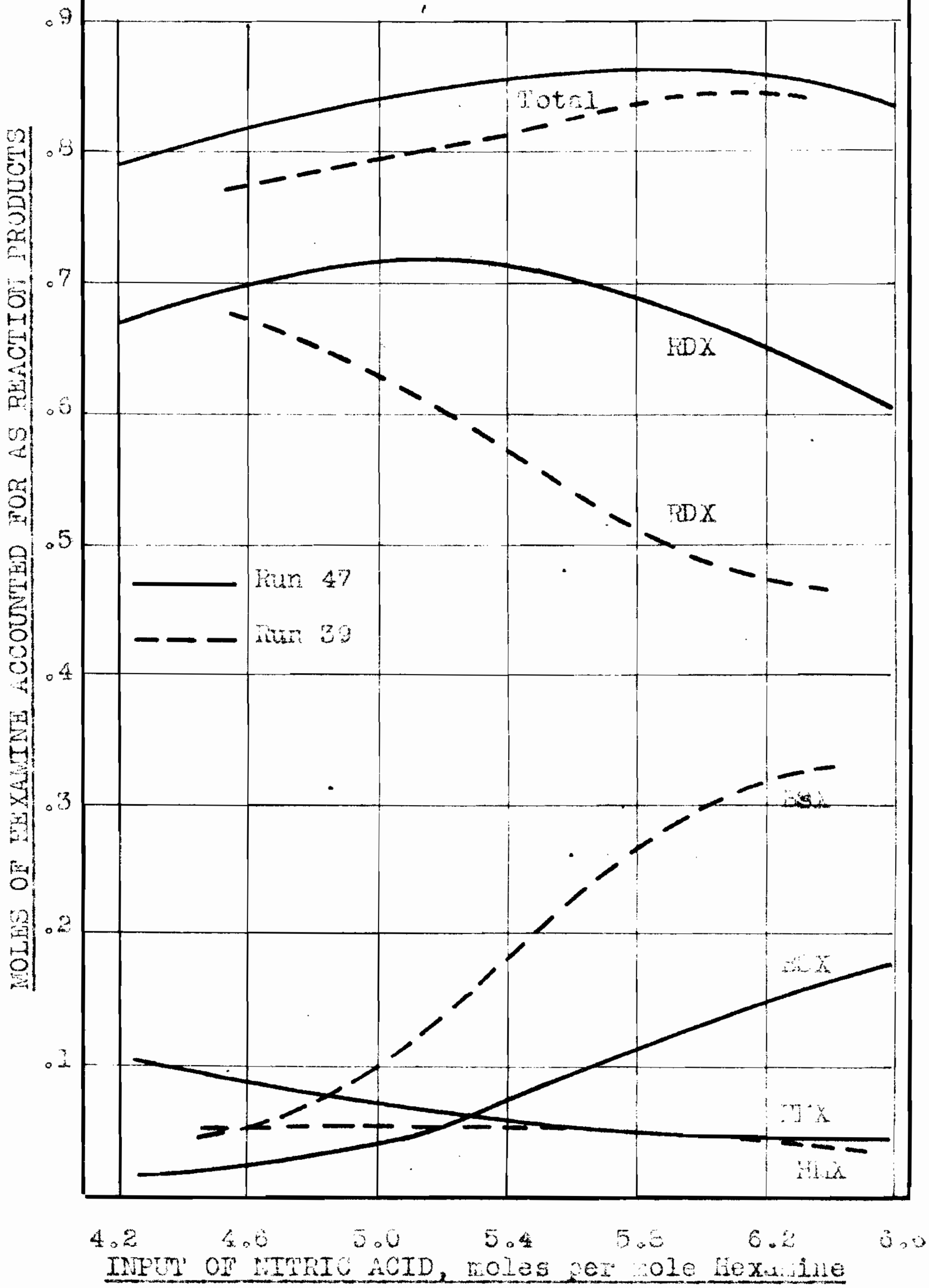
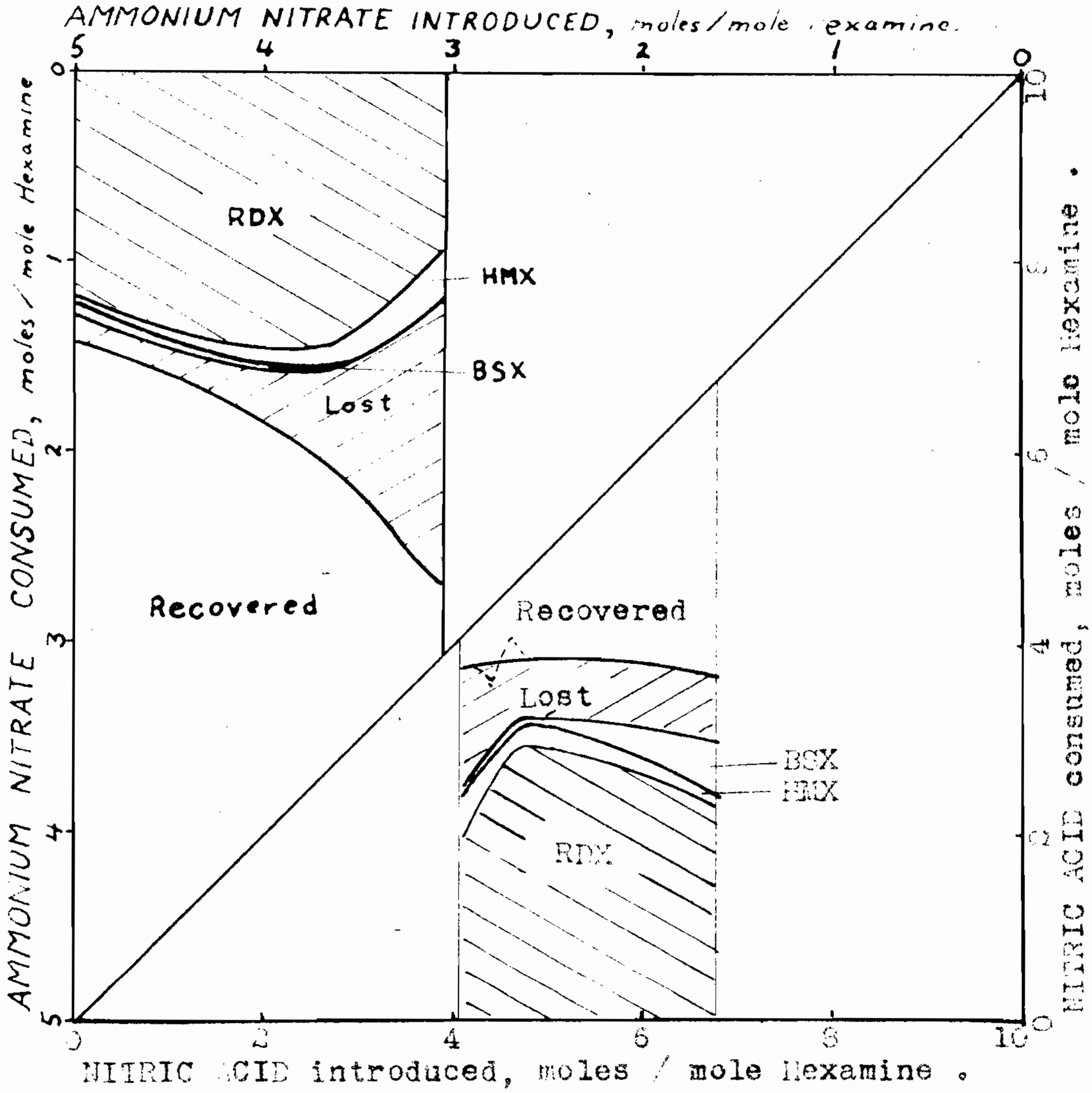

.9
.8
.7
.6
.5
.4
.3
.2
.1
MOLES OF HEXAMINE ACCOUNTED FOR AS REACTION PRODUCTS
Total
RDX
RDX
Run 47
Run 39
BSX
BSX
HMX
HMX
4.2
4.6
5.0
5.4
5.8
6.2
6.6
INPUT OF NITRIC ACID, moles per mole Hexamine

Figure 24

DISTRIBUTION OF
NITRIC ACID AND AMMONIUM NITRATE



Experiments 47,48,50 and 52.

Fig's. 17-24) were made with the pool present in the convertor, as illustrated in Fig. 14, with the tube rotating at 100 revolutions per minute. The reagents were fed directly into this pool, the slurry being maintained at a temperature of 70°C ± 0.5°C in the convertor. The results of these experiments are of interest mainly by comparison with those obtained in the absence of the pool of slurry, but also serve to illustrate to some extent the effect of certain variables on the yield and quality of the product from the Bachmann reaction. The results are calculated on the basis of the following commonly accepted relations:

1 mole of hexamine → 2 moles of RDX
1 mole of hexamine → 1 mole of HMX
1 mole of hexamine → 1 mole of BSX

In Fig's. 15, 17, 19, 21 and 23 the yield of RDX and/or RDX(B), expressed as moles/mole hexamine, is obtained by multiplying by 2 the moles of hexamine accounted for as RDX and/or RDX(B).

Yield of RDX(B).

The optimal yield of RDX(B) was approximately 1.52 moles per mole hexamine in experiments 47-52 at a nitric acid input of 5.2 moles per mole hexamine. At a corresponding nitric acid input in the absence of a pool in the convertor the yield of RDX(B) was 1.20 moles per mole hexamine, (Fig.15), while the optimal yield of RDX(B) in such a reactor, at a comparable input of acetic anhydride, was 1.36 moles per mole hexamine, obtained at a nitric acid input of 4.5 moles per mole hexamine. The increased dilution and better temperature control obtained with the pool therefore effected an 8% increase in the yield of RDX(B), (Fig. 23) while the optimal input of nitric acid was increased from 4.5 to 5.3 moles per mole hexamine at the higher dilution. The yield of RDX(B) decreased more rapidly in the more concentrated reaction mixture as the input of nitric acid was increased beyond the optimal value. (Fig. 23).

Yield of RDX:

The effect on the yield of RDX of the increased dilution in the pool is well illustrated in Fig. 23. The same general behavior as described for RDX(B) was obtained. The optimal yield was increased from 1.36 moles per mole hexamine with no pool to 1.44 in the presence of the pool. The input of nitric acid for these optimal yields increased from 4.5 to 5.2 moles per mole hexamine as the dilution was increased.

Yield of HMX.

As the slurry became more dilute with respect to nitric acid and ammonium nitrate the yield of HMX increased. In experiments in the presence of a pool the yield of HMX at an input of 4.2 moles of nitric acid per mole hexamine was nearly double that when the pool was absent at the same input of nitric acid. The yield of HMX at higher inputs of nitric acid (above 5.4 moles per mole hexamine) was the same in both types of reactors. (Fig. 23).

Yield of BSX.

The yield of BSX was decreased by approximately 50% by the introduction of the pool and higher dilutions in the convertor. (Fig. 23).

MATERIAL BALANCES.

Approximately 5% more of the hexamine introduced into the convertor was accountable as RDX, HMX and BSX in the more dilute system. The milder conditions existing in the more dilute slurry apparently decreased appreciably the side reactions in which hexamine is destroyed. The reagent concentrations were still appreciably greater than those existing in the U-tube reactor discussed previously which might account for a 10% greater loss of hexamine in the rotating convertor.

Losses of nitric acid and ammonium nitrate also occurred in the rotating reactor as seen from Fig's. 16, 18, 20, 22 and 24. The loss of nitric acid on the basis of the following equations:

$1\ \text{hexamine} + 4HNO_3 + 2NH_4NO_3 + 6Ac_2O \rightarrow 2RDX + 12AcOH$

$2\ \text{hexamine} + 8HNO_3 + 4NH_4NO_3 + 12Ac_2O \rightarrow 3HMX + 24AcOH$

$2\ \text{hexamine} + 8HNO_3 + 1NH_4NO_3 + 9Ac_2O \rightarrow 3BSX + 12AcOH$

was approximately 50% less with the more dilute conditions existing in a pool of reaction medium, (Fig's 13 and 14), then in the absence of a pool in the convertor (Fig's 16, 18, 20, 22 and 24, and Tables XXVII, XXVIII, XXXII, XXXIII, XXXVII, XXXVIII, XLII, XLIII, XLVII, and XLVIII). Above a nitric acid input of approximately 4.5 moles per mole hexamine the loss of nitric acid was essentially constant. (Fig. 24). Below an input of 4.5 moles of nitric acid per mole hexamine the nitric acid not accountable as RDX, HMX and BSX and not recovered from the slurry, increased greatly.

The amount of ammonium nitrate, not accountable as RDX, HMX and BSX (on the basis of the above equations) nor as ammonium nitrate in the slurry, was decreased greatly at the higher dilutions and more constant temperature conditions existing throughout the experiment made with the pool present in the rotating convertor.(Fig. 24).

The loss of ammonium nitrate was practically constant in the rotating convertor without the pool. (Fig. 16). With the pool present, the loss of ammonium nitrate decreased to practically zero as the input of ammonium nitrate was increased tp 5 moles per mole hexamine, while with an input of 3 moles per mole hexamine the loss was practically 50% of the ammonium nitrate introduced. (Fig. 24). The disappearance of this ammonium nitrate is not explained nor is a satisfactory explanation available to account for the reduction in loss of ammonium nitrate from 50% to about 2% as the input was increased from 3 to 5 moles of ammonium nitrate per mole hexamine.

CONCLUSIONS.

A satisfactory instrument with which to investigate the Bachmann reaction has been developed. The system permits control of the reagent feed rates and temperature with an accuracy of ± 0.5%, with a mass velocity through the convertor constant within 1%. The overall precision of operation is estimated to be within 1%.

The yield of RDX and RDX(B) is maximal at an optimal concentration of nitric acid. This optimal concentration may be maintained, as dilution of the reaction medium is increased, by increasing the input of nitric acid.

The maximal yield of RDX and RDX(B) is increased as the reaction medium becomes more dilute. The greatest effect is probably due to change in nitric acid concentration, but ammonium nitrate and acetic anhydride concentrations may also be of importance.

The yield of HMX increases as dilution of the reaction mixture is increased, while the yield of BSX is decreased greatly as the reagent concentrations are decreased by dilution with acetic acid.

The recovery of hexamine as RDX, HMX and BSX is increased as the reagent concentrations in the reaction mixture are decreased, probably because of more constant temperature conditions.

The loss of nitric acid and ammonium nitrate is decreased appreciably in the more dilute reaction mixture, with the better temperature control.

The development of the rotating tube reactor in the final form described in this thesis has since permitted detailed study, by other workers, of the factors influencing the Bachmann reaction, particularly the effect of dilution. The equipment has not been found wanting in either precision or versatility. Yields of RDX(B) of 1.76 moles per mole hexamine, obtained consistently (56), are equal to and in most cases superior to any obtainable in present commercial installations.

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SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

A process has been devised for the recovery of glacial acetic acid from the waste products of the Bachmann reaction. The method involves the removal of nitric acid as ammonium nitrate, a "fume-off" of the filtrate with sulphuric acid and a distillation in the presence of sulphuric acid. No stainless steel equipment and only a minimum of supervision is required for the process.

The recovered acid is sufficiently pure to permit its conversion to acetic anhydride in existing commercial units.

The efficiency of sulphuric acid and oleum as dehydrating agents has been investigated and it was concluded that the use of these reagents in this role was not practical from the point of view of a maximum recovery of acetic acid of glacial strength.

The method has been patented in the United States and Canada and has been in operation at the St. Maurice Chemicals Company plant since 1943.

A rotating reactor has been devised to investigate the Bachmann reaction. This instrument, permitting control of all variables within 1%, was demonstrated to be superior to a U-tube type of reactor in respect of both versatility and conversation of reagents and time. Yields of RDX(B) as high as 1.76 moles per mole hexamine have been obtained consistently with the rot~~at~~ing tube reactor in which a pool of slurry had been incorporated. The effect, of varying the input of nitric acid-ammonium nitrate and acetic anhydride, on the yields of RDX(B), RDX, HMX and BSX and on the consumption of nitric acid and ammonium nitrate has been established. Also, dilution of the reaction mixture with acetic acid has been shown to increase the overall conversion of hexamine to explosive products, RDX and HMX. In general the trends established with this continuous process confirm those established in batch processes, especially the existence of an optimal concentration of nitric acid for a conversion of hexamine to RDX(B).

APPENDIX I

THE CALORIMETRIC DETERMINATION OF WATER IN ACETIC ACID SOLUTIONS

The method used to determine the water content of the acetic acid solutions under investigation is based on an estimate of the heat evolved by the hydrolysis of acetic anhydride in the presence of sulphuric acid, and is similar in most respects to the method developed by the Tennessee Eastman Corporation. The procedure adopted was as follows:-

25.0 millilitres of the acid sample to be tested was cooled to approximately 25°C and poured into a small, narrow-necked Dewar flask. To this was added 0.75 millilitres of 95% sulphuric acid, cooled to about 20°C, and the resultant solution stirred with a thermometer until its temperature became constant. Then 15.0 millilitres of acetic anhydride, cooled to the temperature of the mixture in the flask, was then rapidly poured into the Dewar, and the mixture was stirred vigoursly to constant temperature. Noting the temperature rise, the percentage of water in the sample was read directly from a calibration curve previously obtained using solutions of known water content. The agreement of these results with those obtained by titration was well within the results of experimental error.

Determination of Calibration Curve:

Glacial acetic acid assaying 99.5% in acetic acid was concentrated to 100% acid by the addition of a calculated amount of acetic anhydride, the final acidity being checked by titration with standard alkali. Aqueous solutions of this acid were made containing various known percentages of water (by weight), and their concentrations checked by titration. Using the anhydride method outlined above, the temperature rise was determined for each of the known solutions. The water content of the solutions was then plotted against the corresponding temperature rise. The results are presented numerically in Table XVI, and graphically in Fig. 7. It is seen that each 7°C rise in temperature corresponds to a 1% water content.

The solutions were cooled prior to the hydrolysis to avoid the occurrence of a fume-off when analysing original mother liquor, and thus prevent expulsion of the mixture from the Dewar owing to the rapid evolution of gas.

TABLE - XLIX

THE CALORIMETRIC DETERMINATION OF WATER IN ACETIC ACID SOLUTIONS

Water Content % by Weight	Temperature Rise °C
0.5	3.0
1.0	6.5
1.5	10.0
2.0	15.1
3.0	20.5
5.0	36.3
7.0	49.5

APPENDIX II

In an effort to learn more concerning the "temperature peak" encountered in the rotating tube (Fig. 13), a series of experiments was made in which the three liquid reagent feeds used in the "Combination Process" were made to flow over a surface before falling into ice water. Examination was made of the effect on the behaviour of the reaction of

(a) the distance of free fall of the reagents after mixing,

(b) the length of surface over which the reacting mixture passed,

(c) the material constituting the surface, and

(d) the distance of free fall after leaving the surface.

The feeds were mixed by injecting the nitric acid-ammonium nitrate solution into a falling stream of the hexamine-acetic acid solution, and injecting, 0.01 seconds later, a stream of acetic anhydride into the falling mixture. The final mixture was allowed to fall through various distances and over various lengths of a surface interposed between the falling stream and a quenching mixture of ice and water.

The results and experimental details from three experiments are presented in Tables L, LI and LII.

TABLE L

EFFECT ON THE YIELD OF RDX(B)
OF
A. TYPE OF SURFACE
B. LENGTH OF SURFACE

The three feeds of the Bachmann reaction were mixed in mid-air and allowed to fall 1.75 inches to a surface of glass or aluminium of various lengths held at a fixed angle of 45° to the horizontal. The slurry fell 4 inches from the surface into ice-water. Slurry temperaure, leaving the surface, 130°C.

Surface Material	Length of Surface Inches	Yield of RDX(B) %
Glass	0.3	5.1
Glass	0.5	16.1
Glass	1.0	20.2
Glass	1.5	26.4
Glass	2.0	32.0
Glass	2.5	37.4
Glass	3.0	40.0
Aluminium	1.5	20.2
Aluminium	2.0	22.4
Aluminium	2.5	26.0
Aluminium	3.5	34.6
Aluminium	4.0	38.8
Aluminium	5.0	42.1
Aluminium	8.0	50.4

TABLE LI

EFFECT ON YIELD OF RDX(B) OF A. ANGLE OF SURFACE TO HORIZONTAL B. DISTANCE OF FREEFALL OF MIXED REAGENTS

The three feeds of the Bachmann reaction were mixed together in mid-air and allowed to fall onto a smooth aluminium surface 2.5 inches in length, held at various angles and distances below the point of mixing of the feed solutions. Slurry running off the end of the surface was collected in ice-water held at a fixed distance of 26.5 inches below the point of mixing of the feed solutions. Slurry temperature, leaving the surface, 130°C.

Sample No.	Vertical Distance Free Fall inches	Angle of the Surface from the Horizontal degrees	Yield of RDX(B) %
10	3	15	47.4
11	3	15	46.3
12	3	15	45.8
13	3	45	38.6
14	3	45	38.0
1	3	75	34.2
2	3	75	33.8
9	3	75	34.8
3	9	75	40.4
4	9	75	40.2
8	9	75	42.9
5	16.5	75	39.3
6	16.5	75	40.4
7	16.5	75	40.2

TABLE LII

EFFECT ON YIELD OF RDX(B)
OF
A. TYPE OF SURFACE
B. DISTANCE OF FREEFALL OF SLURRY

The three feeds of the Bachmann reaction were mixed in mid-air and fell 1.75 inches to a surface of carbon or aluminium held at a fixed angle of 45°. After travelling a given distance on the surface the slurry fell freely various distances into ice-water. Slurry temperature, leaving the surface, 130°C.

Surface Material	Length of Surface inches	Distance of Free Fall from Surface inches	Yield of RDX(B) %
Aluminium	4	10	43.0
Aluminium	4	22	44.5
Carbon	3	1.8	24.2
Carbon	3	10.8	32.3
Carbon	5.5	1.8	37.4
Carbon	5.5	9.5	44.9
Aluminium	4	10	43.0
Carbon	4	10	39.4

From Table L it appears that the rate of the Bachmann reaction is higher on a glass surface then on aluminium, but it is possible that the higher yield of RDX(B) on glass may be due to a longer reaction period if the rate of flow of slurry over a glass surface is slower than over an aluminium surface. The length of time taken by the slurry to flow across the surface could not be measured or even estimated accurately because of the precipitation of a sticky white solid immediately the reaction mixture came into contact with the surface. This precipitate moved unevenly along the surface, and in general appeared to cross the surface in less than 2 seconds.

The yield of RDX(B) was proportional to the reaction time which was varied by either lengthening the surface or by changing the angle of the surface to the horizontal plane. (Tables L, LI and LII).

The time interval between the injection of acetic anhydride into the falling stream and the instant the reaction mixture came in contact with the surface appears to have influenced the yield of RDX(B). Distances of free fall of the reaction mixture greater than 9 inches had no noticeable effect on the yield of RDX(B).

The rate of the Bachmann reaction at 130°C was estimated by permitting the reaction mixture to fall various distances on leaving the surface. The increased yield of RDX(B) with increased distances of free fall of the reacting mixture gave the rate of the reaction to be 1.16 moles of RDX per mole hexamine per second. The overall time of reaction was estimated to be less than 3 seconds and the final yield was approximately 0.8 moles of RDX(B) per mole hexamine. (Table LII).

This high rate of reaction when the undiluted reagents were made to react on a surface, combined with the very great heat of reaction encountered in the Bachmann reaction, readily explained the "temperature peak" found in the rotating reactor. (Fig. 13). These investigations illustrated the necessity for reducing the rate of the Bachmann reaction and for introducing a heat reservoir into the system to obtain the accuracy of temperature control required in this project. This accuracy of control was obtained through the introduction of a small pool of slurry into the rotating convertor. (Fig. 14).

This investigation was terminated with a qualitative experiment which proved that at approximately 75°C the induction period in the Bachmann reaction, if it exists at all, must be very small in the undiluted system. The reagents were preheated to 70°C before mixing and no surface was interposed between the point of mixing and the quenching mixture of ice and water. A free fall of 26 inches, equivalent to a reaction time of approximately 0.35 seconds, produced a small yield of RDX(B).

The method is limited as a means for studying the Bachmann reaction because of the impossibility of exerting any measure of control over the temperature of the reacting mixture.