FC

~~CONFIDENTIAL~~

UNCLASSIFIED
AUTHORITY: LTR DATED [illegible] 55
DUNHAM, WCLPF-3 REF:
AFR 205-1, PAR. 26A

AD NO. 65100
ASTIA FILE COPY

WADC TECHNICAL REPORT 54-380

Preparation of Nitric Oxide - Nitrogen Dioxide Mixtures From The FMC Nitrogen Fixation Furnace By Chilling

fmc

FOOD MACHINERY
AND CHEMICAL
CORPORATION

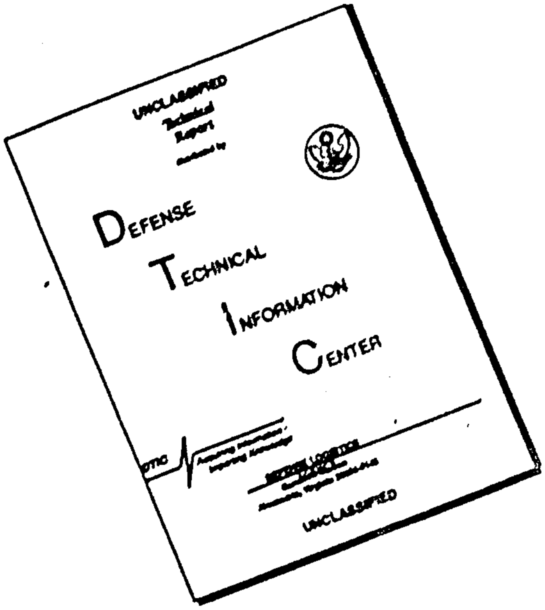
DONAT B. BRICE

OCTOBER 1954

WRIGHT AIR DEVELOPMENT CENTER

UNCLASSIFIED
AUTHORITY: LTR DATED 18 FEB 55
DUNHAM, WCLPF-3 REF.
AFR 205-1, PAR. 26A

[redacted]



~~CONFIDENTIAL~~ UNCLASSIFIED

[illegible] UNCLASSIFIED
AUT[illegible] LTR DATED 18 FEB 55
DUNHAM, WCLPF-3 REF:
AFR 205-1, PAR. 26A

WADC Technical Report 54-380

PREPARATION OF NITRIC OXIDE - NITROGEN DIOXIDE MIXTURES FROM THE FMC NITROGEN FIXATION FURNACE BY CHILLING

Donat B. Brice
Food Machinery and Chemical Corporation

October 1954

Power Plant Laboratory
Contract No. AF 18(600)-34
Supplemental Agreement No. S3 (53-908)
RDO No. 531-373-H

Wright Air Development Center
Air Research and Development Command
United States Air Force
Wright-Patterson Air Force Base, Ohio

CO[redacted]TIAL

FOREWORD

Food Machinery and Chemical Corporation has investigated different means of producing liquid mixtures of nitric oxide and nitrogen dioxide from the standard high-temperature adsorption (HTA) recovery system. The aim of this specific project, under Contract AF 18(600)-34, Supplemental Agreement No. S3(53-908), has been to develop a process to rapidly cool the nitric oxide-oxygen gas mixture, as obtained from the regular HTA process, condense nitric oxide-nitrogen dioxide, and allow the excess oxygen to escape. Five bimonthly progress reports have been issued describing the research on this project from 1 March 1953 to 1 March 1954. This is a final report prepared from the earlier reports to cover the work completely.

The contract was administered under Forrest S. Forbes, Project Engineer, Fuel and Oil Branch, Power Plant Laboratory, Wright Air Development Center.

Donat B. Brice, assisted by Norman Fishman, was responsible for planning of experiments and for process calculations. Norman Fishman made the majority of the sorption and condensation tests, and William J. Gowans, the analytical determinations. Supervision of the project was under Wesley N. Lindsay, Chief, Chemical Research Section, Central Research Department, Food Machinery and Chemical Corporation, under the general direction of Paul C. Wilbur, Vice President and Director of Research.

This document is classified CONFIDENTIAL in its entirety because of the nature of, and potential military application of, the research work and data described herein.

ABSTRACT

The production of liquid mixtures of nitric oxide and nitrogen dioxide useful as a rocket fuel oxidant is shown to be practical on a laboratory scale by the rapid chilling of gaseous nitric oxide, nitrogen dioxide and oxygen mixtures. Liquid mixed oxides freezing at -101°F. (28.6% NO) and at -117°F. (30.0% NO) are obtained by film-type condensation of gaseous mixtures (NO, NO_2 and O_2) equivalent to N_2O_3 and N_2O_4, respectively.

Sorption of gaseous nitric oxide by liquid mixed oxides is sufficiently rapid to indicate the possible recovery of nitric oxide from HTA process gas by use of this property. Maximum sorption of about 29% of the nitric oxide as nitric oxide is obtained, with the rest oxidized to nitrogen dioxide and condensed.

Experimental data are reported on vapor pressure, viscosities, densities, surface tensions, and specific heats of liquid mixed oxides over pertinent concentration and temperature ranges, and refrigeration requirements are estimated for a commercial sized plant. A flow sheet for a commercial plant is presented.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

for E. C. Phillips
NORMAN C. APPOLD
Colonel, USAF
Chief, Power Plant Laboratory
Directorate of Laboratories

TABLE OF CONTENTS

Page

ABSTRACT. iii

INTRODUCTION. 1
  Objectives. 2
  Laboratory Processes. 2
  Physical Data. 3
  Commercial Process 3

EXPERIMENTAL:

Production of Mixed Oxides by Bubbling Techniques 4
  Apparatus. 4
  Preparation 4
  Bubbling Process 5

Film-Type Condensation of Process Gas 5
  Apparatus 5
  Condensation Process.. 6

RESULTS:

Bubbling Gases through Liquid Mixed Oxides. 8
Film-Type Condensation of Process Gas 13
Process Heat Requirements. 17
Carbon Dioxide as a Process Contaminant 17

DISCUSSION:

Bubbling Gases through Liquid Mixed Oxides. 19
Film-Type Condensation of Process Gas 21
  Glass Condenser Coils. 21
  Stainless Steel Condenser Coil 23
Calculations for Nitric Oxide Sorbed and Condensed. 24
Comparison of Freezing Point and Chemical Analysis Methods. 25
Carbon Dioxide as a Process Contaminant. 27
Physical Data. 27
Process Heat Requirements 27

PLAN FOR COMMERCIAL PROCESS. 28

SUMMARY AND CONCLUSIONS. 29

TABLE OF CONTENTS

Page

APPENDICES:

I ANALYSES:

Analysis of Liquid Mixed Oxides by Freezing Point Method. 31
Chemical Analysis of Liquid Mixed Oxides. . . 31
Analysis of Stack Gases for Nitrogen Dioxide. 33

II PHYSICAL PROPERTY MEASUREMENTS:

Vapor Pressure. 35
Viscosity. 37
Density 37
Surface Tension 39
Specific Heat. 40

III KINETIC CALCULATIONS:

Oxidation of Nitric Oxide in Bubble Tip . . . 42
Velocities and Reynolds Number for NO-NO_2 Condenser. 44
Reaction Rate Constant. 46
Effective Fluid Temperatures Inside Condenser Coil. 47

IV SORPTION AND CONDENSATION CALCULATIONS:

Calculation of Per cent Nitric Oxide Sorbed . 52
Calculation of Per cent Nitric Oxide Condensed and Exhausted. 53

V HEAT LOADS AND REFRIGERATION REQUIREMENTS:

Measurement of Heat Evolved in Condensation of Mixed Gases 54
Calculation of Theoretical Heat Evolution in Condensation of Mixed Gases. 55
Refrigeration Requirements for a Commercial Sized Plant. 56

LITERATURE CITED. 58

GENERAL REFERENCES 58

ILLUSTRATIONS

Figure		Page
1	Apparatus for Purification of Nitrogen Dioxide by Distillation.	59
2	Stainless Steel Reservoir for Storage of Liquid Mixed Oxides.	60
3	Bubbling Assembly for Series "A" Runs	61
4	Schematic Cross-Sectional Sketches of Bubbling Tips "A" and "B"	62
5	Bubbling Assembly for Series "C" Runs	63
6	Equipment Set Up for Series "C" Bubbling Runs	64
7	Glass Condenser for Series "D" Condensation Runs.	65
8	Glass Condenser, Transfer Tubing and Sample Flask for Series "E" Condensation Runs.	66
9A	Stainless Steel Condenser Coil.	67
9B	Diagram of Flows in Stainless Steel Condenser	68
10	Stainless Steel Condenser with Gas Preheater Attached	69
11A	Calibration Curves of Rotameter 02 F 1/8-16-5/25 for Nitrogen Dioxide Gas.	70
11B	Calibration Curve of Rotameter BIB-25 for Nitrogen Dioxide Gas.	71
11C	Calibration Curve of Rotameter 2F 1/4-16-5 for Nitrogen Dioxide Gas.	72
12	Diagram of Flow of Gases to Glass Condenser.	73
13	Estimation of Temperature of Heated Gases Prior to Mixing with Oxygen.	74
14	Nitric Oxide Sorption Isotherms Using Single Orifice Bubbler Tip.	75
15	Relation Between Nitric Oxide Flow Rate and Per Cent Sorption Using Fritted Glass Bubbler Tip.	76

Page

16 Effect of Bath Temperature on Concentration of Nitric Oxide in Liquid Product. 77

17 Variation of Nitric Oxide Concentration in the Product with Changing $NO:NO_2$ Proportions in the Reactant Gases 78

18 Effect of Carbon Dioxide on Vapor Pressure of Mixed Oxides 79

19 Comparison of Calculated Per Cent Nitric Oxide Condensed with Theoretical Values. 80

20 Schematic Flowsheet for Commercial Manufacture of Mixed Oxides. 81

21 Freezing Point Curve of Nitric Oxide - Nitrogen Dioxide Mixture vs Weight Per Cent of Nitric Oxide. 82

22 Typical Tracing of Cooling Curve of Nitric Oxide - Nitrogen Dioxide Liquid Mixture. 83

23 Freezing Point Apparatus Consisting of Double-Wall Glass Container, Glass Stirrer and Thermocouple. 84

24 Apparatus for Evacuation of Sample Flask 85

25 Apparatus for Measurement of Vapor Pressure. 86

26 Vapor Pressure of Mixed Oxides. 87

27 Viscosity of Mixed Oxides. 88

28 Apparatus for Measurement of Density 89

29 Density of Mixed Oxides. 90

30 Isotherms of Density for Mixed Oxides. 91

31 Apparatus for Measurement of Surface Tension 92

32 Surface Tension of Mixed Oxides 93

33 Reaction Rate Constant, k_c, for the Nitric Oxide Oxidation Reaction $2NO + O_2 = NO_2$ vs. Reciprocal of the Absolute Temperature 94

34 Reaction Rate Constant, k_p, for the Nitric Oxide Oxidation Reaction $2NO + O_2 = NO_2$ vs. Reciprocal of the Absolute Temperature 95

LIST OF TABLES

TABLE		PAGE
1	Loss of Nitric Oxide in Liquid Mixed Oxides by Bubbling Oxygen or Nitrogen	8
2	Experimental Data and Calculated Results, Single Orifice Bubbler Tips.	10
3	Experimental Data and Calculated Results, Fritted Glass Bubbler Tip.	12
4	Results of Film-Type Condensation, Glass Coil - "D"	14
5	Results of Film-Type Condensation, Glass Coil - "E"	15
6	Results of Film-Type Condensation, Stainless Steel Coil - "F"	16
7	Heat Evolved in the Condensation Process.	18
8	Comparison between Nitric Oxide Concentrations from Freezing Point Measurements and Results of Analyses of Multiple Samples	26
9	Vapor Pressure of Mixed Oxides.	36
10	Density of Mixed Oxides.	38
11	Surface Tension of Mixed Oxides.	39
12	Specific Heat of Mixed Oxides	41

INTRODUCTION

INTRODUCTION

Many forms of rockets are under intensive development in this country and many combinations of fuels and oxidizers for these devices have been examined. A 30-70 weight per cent mixture of nitric oxide and nitrogen dioxide appears well suited for use as an oxidizer. It has the same desirable properties of nitrogen dioxide plus the added feature of a low freezing point (under -100°F) which is a requirement for use in rockets which must perform in arctic climates as well as high altitudes where the temperature is low. Sources of supply for mixed oxides have therefore become important to the Armed Forces.

The effluent gases from the Food Machinery and Chemical Corporation high-temperature nitrogen-fixation furnace offer a potential source of mixed oxides. As produced these gases contain about 2% nitric oxide, 2% carbon dioxide, 5% water vapor, 17% oxygen and the rest nitrogen. Various methods of concentrating the dilute nitric oxide to useful values have been examined. One such method investigated in the laboratory under Contract AF 18(600)-34 over the period January 1, 1952, through February 28, 1953, is described fully in WADC TR 54-378 (FMC Final Report CR-CH 2065.) (1) These tests involved modifications of the so-called high temperature adsorption (HTA) process, represented by the equation:

$$2NO + 3/2\ O_2 + Na_2Fe_2O_4 \underset{750^\circ C}{\overset{400^\circ C}{\rightleftarrows}} 2NaNO_3 + Fe_2O_3$$

The earlier laboratory and pilot-plant investigations indicated the feasibility of recovering a 4:3 mol mixture of nitric oxide and oxygen from a two per cent nitric oxide gas, as obtained from the nitrogen fixation furnace using the standard HTA recovery process. Calculations were made to determine if this 4:3 mol mixture could be cooled rapidly enough in a conventional heat exchanger to prevent excessive oxidation of nitric oxide to nitrogen dioxide and thus produce a 30-70 weight per cent $NO-NO_2$ mixture (mixed oxides). These calculations indicated that upon cooling the nitric oxide and oxygen, a 30-70 $NO-NO_2$ mixture would be reached at about 160°F. By increasing the rate of chilling, it appeared possible to avoid going beyond the desired state of oxidation at a lower temperature.

It was reasoned that if this partially cooled gas were bubbled into cold mixed oxides (30-70 $NO-NO_2$), the nitrogen oxides would be condensed and the excess oxygen would escape. In order to limit nitrogen oxide losses to about 15%, the liquid temperature would have to be below -60°F.

OBJECTIVES

This investigation involves different means of producing $NO-NO_2$ mixtures from the HTA recovery system. It was anticipated that the process developed would rapidly cool the nitric oxide-nitrogen dioxide-oxygen gas mixture obtained from the regular HTA process, condense $NO-NO_2$ in liquid form and allow the excess oxygen to escape. Included are:

1. A demonstration of the process on a laboratory scale by mixing nitric oxide and oxygen gas streams together, suddenly cooling the mixture either by passing it into cold liquid $NO-NO_2$ or by condensing it on a cold surface to determine the practicability of the operation.
2. A study of the efficiency of stripping the entering gases, the degree of oxidation ocurring in the liquid, and the allowable state of oxidation of the inlet gases.
3. Measurement of physical properties of the mixed oxides.

Runs of an exploratory nature show the efficiency of sorption of nitric oxide by this process. The workability of a process based on the principle of chilling a gaseous mixture of $NO-NO_2-O_2$ by bubbling it through a $NO-NO_2$ liquid mixture is affected by the following:

1. The tendency of oxygen in the gaseous mixture to oxidize the nitric oxide in the liquid $NO-NO_2$ mixture as the gases were bubbled through the liquid mixture.
2. The efficiency of recovery (or sorption) of nitrogen oxide gases by the liquid $NO-NO_2$ mixture.
3. The amount of nitrogen dioxide formed from the oxidation of nitric oxide by oxygen in the bubbles during their rise through the liquid.

LABORATORY PROCESSES

The laboratory experimentation is presented in two separate phases. Phase one involves production of mixed oxides by bubbling techniques and is concerned with effects of depth of liquid column, reaction temperature, gas flow rate and type of bubbling tip. Phase two, an outgrowth of phase one, involves direct film-type condensation of mixed oxides by passing process gas at high velocity through a coil immersed in a low temperature bath and is concerned with studies of such variables as bath temperature, dilution of the gaseous mixture with inerts, and preheat of the inlet gases. In both phases special efforts are made to prevent excessive oxidation of nitric oxide to nitrogen dioxide, in order to obtain the desired 30 weight per cent nitric oxide in the liquid product. Descriptions of analytical procedures and discussions of pertinent analyses are given in Appendix I.

PHYSICAL DATA

In order to permit more detailed chemical engineering calculations of the proposed method for manufacture of mixed oxides, data were desired on the physical properties of the liquid $NO-NO_2$ system such as vapor pressure, viscosity, density, surface tension and specific heat. Since these data were for the most part unknown, they were determined experimentally over the pertinent temperature and concentration ranges. Appendix II contains procedures used and results of physical property measurements.

COMMERCIAL PROCESS

Various calculations were made to determine the efficiency of recovery of nitrogen oxides in the laboratory process and to estimate the probable efficiency of operation of a larger scale process. Appendices III, IV and V contain examples of kinetic calculations, sorption and condensation calculations, and data on heat loads and refrigeration requirements. These calculations serve as the basis for the proposed commercial process.

EXPERIMENTAL

Page

Production of Mixed Oxides by Bubbling Techniques. 4

Film-Type Condensation of Process Gas 5

EXPERIMENTAL

PRODUCTION OF MIXED OXIDES BY BUBBLING TECHNIQUES

Liquid mixed oxides were produced by bubbling various gaseous mixtures of oxygen and nitric oxide through cold liquid mixed oxides. The gases were obtained in commercial cylinders. The initial charge of liquid oxides was made by adding nitric oxide gas to liquid nitrogen dioxide in a pressure vessel. The nitrogen dioxide was from commercial cylinders and was distilled over phosphorus pentoxide prior to use.

Apparatus

Apparatus shown in Figure 1 for the purification of commercial nitrogen dioxide by distillation comprises a 500 ml flask, a glass reservoir fabricated from 41 mm OD pyrex tubing, and a liquid nitrogen condensate bath.

The stainless steel reservoir shown in Figure 2, used to prepare stock quantities of liquid mixed oxides, was fabricated from a short length of one-inch schedule 40, type 304, stainless steel pipe, and was hydraulically tested to 800 psi. before use.

The first bubbling apparatus (Figure 3) comprised a glass sample container, a thermocouple well, and a concentric tube bubbler. Figure 4 is a schematic drawing of bubbler tip "A", and the revised bubbler tip "B". The revised bubbler was made somewhat longer to permit bubbling through greater depths of liquid, and the concentric orifices were arranged so that nitric oxide and oxygen gases would not mix until they were bubbled into the mixed oxides. In both bubblers, oxygen flowed through the inner tube and nitric oxide through the annular space between the tubes.

Another concentric tube apparatus (Figure 5), used in the last series of bubbling tests, consisted of a fritted glass tip for more efficient distribution of gas bubbles. The equipment set up for a bubbling run, including apparatus used to collect samples of the exhaust gas, is shown in Figure 6.

Preparation

Nitrogen dioxide crystals from the condenser of the purification apparatus were thawed, transferred to the evacuated steel reservoir (Figure 2), frozen by immersion of the reservoir in liquid nitrogen, and freed of impurities by further evacuation of the reservoir. With the reservoir still in liquid nitrogen, nitric oxide was added to the nitrogen dioxide through a 1/4-inch stainless steel tube from a nitric oxide cylinder. The nitric oxide was transferred at a pressure of 20 to 40 psig. as observed by a pressure gage attached to the transfer line, and the time of flow was controlled to limit the transfer at any one time to 10 to 15 grams. These small increments were used to avoid the possibility of excessive pressures if all the nitric oxide should gasify when the reservoir was allowed to warm. After each increment the reservoir was removed from the liquid nitrogen and the contents were allowed to melt. Nitric oxide and nitrogen dioxide appeared to react rapidly to form liquid mixed oxides under these conditions. The chilling and melting cycle was repeated until weighings indicated that the desired amount of nitric oxide had been added. The steel reservoir was then cooled to about -60°F. and the liquid mixture was transferred through a glass tube into a glass sample flask--immersed in a dry ice-acetone mixture to minimize vaporization. The composition of the sample was obtained from its freezing point, using the method presented in Appendix I.

Bubbling Process

Process gases were bubbled through a charge of liquid mixed oxides in a glass sample flask, under prescribed conditions of gas flow rate, bath temperature and run duration. Gas flows were measured with Fisher-Porter precision bore rotameters and controlled by means of 1/8-inch stainless steel needle valves. Dry ice was added as necessary to maintain the dry ice-acetone bath at the prescribed temperature.

Sorption efficiencies were calculated as illustrated in Appendix IV, using material balances based on liquid weights and compositions before and after bubbling. Sample flasks were calibrated to give volume for measured height of liquid, and density data were used to convert to sample weight. Liquid compositions were determined from freezing point data.

During the later tests, samples of exhaust gases were retained for analysis by freezing them with liquid nitrogen using the apparatus shown in Figure 6. The sampling and analysis procedures are described in Appendix I.

FILM-TYPE CONDENSATION OF PROCESS GAS

Apparatus

Apparatus used in the investigation of film-type condensation of process gas comprised a condensing coil, a reservoir for condensed liquid, and an exhaust stack for escape of uncondensed gases. The first condenser coil (Figure 7) was fabricated from 5 mm ID pyrex tubing, wound in three turns of approximately 1.5 inch ID.

Figure 8 shows the second condenser in position for transfer of liquid sample. The coil was made of 5 mm. ID pyrex tubing, wound in eight turns of approximately 3 inch ID. The auxiliary tubing and sample flask were used to transfer condensate from the condenser reservoir for freezing point determinations.

Results of condensation tests with the glass coils led to fabrication of a condenser coil of stainless steel tubing. This coil (Figures 9A and 9B) consisted of 9 1/2 turns of 3 3/8 inch mean diameter, 1/4 inch OD, 20 gauge, type 304, stainless steel tubing. Liquid condensate was separated from uncondensed gases in a tee-shaped vapor separator, from which the condensate flowed through a U-tube liquid trap into the upper reservoir. Uncondensed gases passed through the upper arm of the vapor separator to the lower reservoir from which they were allowed to vent to the atmosphere. A stainless steel coil wrapped with Nichrome wire (Figure 10) was used to preheat the gaseous NO-NO_2 stream. The dip-tube used for the transfer of condensate was the same as that used with the glass condensers. (Figure 8).

Condensation Process

A mixture of three gases was used. Nitrogen dioxide gas was added to nitric oxide and oxygen in such proportions as to simulate HTA process gas after it had been cooled and a portion of the nitric oxide had been oxidized. Gas flows were metered by rotameters and controlled by 1/8 inch stainless steel needle valves. The nitrogen dioxide rotameter and its inlet line were heated by Nichrome wire windings to prevent condensation. The three rotameters used for nitrogen dioxide at various flow ranges were calibrated directly by condensing nitrogen dioxide gas and weighing the liquid condensate, giving the calibration curves in Figures 11 (A, B and C). To prevent condensation of nitrogen dioxide downstream from its rotameter, it was mixed immediately with metered nitric oxide. Oxygen was mixed into the gas stream immediately upstream from the point where the gas flowed into the low temperature bath. Figure 12 shows flows of these three gases.

Starting procedures were varied somewhat for tests with the different condensers. In the experiments with the smallest coil, the flow of nitric oxide and nitrogen dioxide was started prior to immersion, and the oxygen flow was begun immediately after immersion. This technique was employed to lessen oxidation of the nitric oxide at the start of the experiment before a low temperature surface was available for condensation.

When the larger glass condenser came into use, the starting procedure was modified in that only nitric oxide or nitrogen gas was flowed prior to immersion. The timed run was commenced by introducing the other gases simultaneously after immersion of the condenser into the bath. Nitrogen gas was flowed into the reservoir through a tube inserted into the exhaust vent at a rate approximately twice that of the existing gases to minimize condensation of gases in the reservoir or in the stack.

The starting procedure remained essentially unchanged with the stainless steel condenser. However, due to the condensate trapping arrangement, it was not necessary to flow nitrogen into the reservoir.

In those runs in which the gas preheater was used, the stainless steel condenser was first filled with nitrogen gas and immersed in the bath. Air was flowed through the preheater until temperature equilibrium had been reached. Then the air flow was stopped and the flow of nitric oxide and nitrogen dioxide commenced. The discharge from the preheater was then coupled to the condenser coil and the oxygen flow quickly started. The gas temperature at the discharge from the preheater was measured with a Chromel-Alumel thermocouple attached to the metal wall. The temperature of the mixed gases at the entrance to the condenser was then estimated from air-flow calibration data in this same range of mass flow rates (Figure 13).

Upon cessation of gas flows the glass condensers were removed from the low temperature bath and weighed to determine the quantity of product condensed. The product was then transferred to the freezing-point-determination flask by means of nitrogen gas pressure and the transfer dip-tube. Because of the double reservoir system employed by the stainless steel condenser, it was found more convenient to weigh the product after transfer to the freezing point flask.

For the determination of the heat load involved in the condensation process, the procedure was modified. To avoid dissolved carbon dioxide in the acetone coolant bath, the acetone was precooled indirectly by surrounding its container with dry ice. The chilled acetone was then transferred to the insulated bath vessel, the mixed gases were flowed through the immersed condenser, and the time for the bath temperature to change an arbitrary number of degrees was recorded.

RESULTS

Page

Bubbling Gases through Liquid Mixed Oxides. 8

Film-Type Condensation of Process Gas 13

Process Heat Requirements 17

Carbon Dioxide as a Process Contaminant 17

RESULTS

BUBBLING GASES THROUGH LIQUID MIXED OXIDES

Preliminary tests involved bubbling a pure gas (nitrogen, oxygen, or nitric oxide) through liquid mixed oxides. Early results showed that at -60°F., oxygen bubbled through the mixed oxides did not readily oxidize the nitric oxide present. Later results, presented in Table 1, showed that though the oxidation rate was small at lower temperatures, it increased appreciably as the liquid temperature was raised.

TABLE 1

Loss of Nitric Oxide in Liquid Mixed Oxides by Bubbling Oxygen or Nitrogen

Bath Temp. °F.	Oxygen Gas Bubbled Weight % NO Initial	Oxygen Gas Bubbled Weight % NO Final	Oxygen Gas Bubbled %NO Loss [a]	Nitrogen Gas Bubbled Weight % NO Initial	Nitrogen Gas Bubbled Weight % NO Final	Nitrogen Gas Bubbled % NO Loss
-60	28.4	27.1	5.2	28.3	27.9	2.8
-40	27.1	23.4	12.5	27.9	27.1	5.3
-30	23.4	20.2	14.1	27.1	26.3	5.4

[a] Loss either by evaporation or oxidation to nitrogen dioxide.

In an experiment in which nitric oxide gas was bubbled through a 2.5 inch depth of liquid mixed oxides at -60°F., more than 60% of the gas was sorbed. Other preliminary work in which 4:3 molar mixtures of nitric oxide and oxygen were bubbled through a small sample of liquid mixed oxides resulted in only small amounts of nitric oxide being sorbed. The rest of the nitric oxide introduced was either oxidized and condensed as nitrogen dioxide or passed out of the surface of the liquid unreacted. Calculations shown in Appendix III indicated that about 40% of the nitric oxide could be oxidized in the free volume of the bubbler tip at -60°F.

Results of experiments with this first single-orifice bubbler are presented in Table 2 as Series-A runs. Also presented in Table 2 as Series-B runs are the experimental results of investigations conducted with the modified bubbler having the reduced premixing volume in the tip. A bubbling time of 60 minutes was used for all runs except B-15. Nominal column heights were 2, 4, 6, or 8 inches, and the liquid temperature was -60°F. or -90°F. (with two exceptions). Flow rates of the NO-O_2 gas mixture varied from 17.5 to 192.5 std. cc/min. (70°F. and 14.7 psia). Initial liquid concentrations varied from 25.5 to 30.3 wt. % nitric oxide.

Data obtained in the "A" series runs suggested trends and directions for subsequent experimentation. Evidence was obtained to show an increase in nitric oxide sorption with greater column depths and greater flow rates. Later runs yielded more complete data which allowed determination of actual percentages of nitric oxide sorbed, confirmed trends indicated by earlier tests, and showed optimum flow rates for each sample depth. Figure 14 shows the relationship between nitric oxide flow rate and the percentage of nitric oxide sorbed, based on the calculation method illustrated in Appendix IV. Sorption isotherms are drawn for liquid temperatures of -60° and -90°F. for a nominal liquid depth of six inches.

Table 3 presents experimental data and calculated results for work done with the fritted glass bubbler. Reaction temperatures were -60°F. and -90°F. Flow rates, as indicated in Table 3, ranged from 220 to 480 std. cc. per minute for the nitric oxide and all flows were in a 4:3 molar ratio of nitric oxide to oxygen. Column heights were measured with a cathetometer before and after bubbling, the sample being thermostated at -60°F. Conversion to sample weights were made using density data presented in Appendix II. Figure 15 shows the relationship between nitric oxide flow rate and nitric oxide sorbed by means of sorption isotherms at temperatures of -60° and -90°F.

TABLE 2

Experimental Data and Calculated Results
Single Orifice Bubbler Tips 1/

Per Cent Nitric Oxide Sorbed[a]	Liquid Conc., Weight % NO Initial	Liquid Conc., Weight % NO Final	Initial Sample, Weight Grams[b]	Final Sample Weight Grams[b]	Liquid Temp., °F.	Nominal Column Height, Inches	Nitric Oxide Flow, Std. cc /min.	Oxygen Flow, Std. cc /min.	Run Number
-	25.5	23.8	21.0[c]	-	-60	2	11	6.5	A-5
-	25.8	25.0	51.2[c]	-	-60	6	30	22.5	A-6
-	25.8	24.5	-	-	-75	6	30	22.5	A-7[d]
-	27.0	25.0	33.3[c]	-	-60	4	20	15.0	A-8
-	26.5	24.1	-	-	-45	4	20	15.0	A-9[e]
-	26.7	25.0	35.1[c]	-	-60	4	20	15.0	A-10
-	25.9	24.7	39.8[c]	-	-60	4	30	22.5	A-11
-	27.0	24.0	18.5[c]	-	-60	2	30	22.5	B-1
-0.2	26.7	24.0	22.3	24.6	-60	2	30	22.5	B-2
-	27.3	26.1	67.1[c]	-	-60	8	40	30.0	B-3
-	26.5	25.5	-	-	-60	8	40	30.0	B-4[d]
-	28.7	26.2	-	-	-60	4	40	30.0	B-5[f]
0	29.0	26.5	35.0	38.2	-60	4	50	37.5	B-6
15.1	30.1	28.5	41.6	45.9	-90	4	50	37.5	B-7
-	29.6	28.8	-	-	-90	6	70	52.5	B-8[g]
26.9	28.7	26.8	47.3	55.9	-60	6	70	52.5	B-9
23.9	27.8	26.0	52.7	62.5	-60	6	90	67.5	B-10
27.7	29.7	28.5	47.0	55.5	-90	6	90	67.5	B-11
22.4	28.7	27.7	51.9	60.4	-90	6	110	82.5	B-12
29.7	30.2	29.7	46.4	50.9	-90	6	50	37.5	B-13
-	-	-	-	-	-90	6	30	22.5	B-14[h]
22.9	30.2	28.5	29.0	55.5	-90	6	30	22.5	B-15[i]
-	29.8	29.0	-	-	-90	6	70	52.5	B-16[j]

1/ See end of table for lettered footnotes.

TABLE 2

Experimental Data and Calculated Results
Single Orifice Bubbler Tips (Continued)

Per Cent Nitric Oxide Sorbed[a]	Liquid Conc. Weight % NO		Initial Sample, Weight Grams[b]	Final Sample, Weight Grams[b]	Liquid Temp., °F.	Nominal Column Height, Inches	Nitric Oxide Flow, Std.cc /min.	Oxygen Flow, Std.cc /min.	Run Number
	Initial	Final							
-	30.5	29.2	-	-	-90	6	70	52.5	B-17[j]
-	29.5	28.5	-	-	-90	6	70	52.5	B-18[j]
-	29.2	27.5	-	-	-60	6	50	37.5	B-19[j]
21.7	28.9	28.0	48.6	56.5	-90	6	110	82.5	B-20
29.4	29.5	28.7	49.1	55.8	-90	6	70	52.5	B-21
26.2	29.7	28.8	47.2	53.4	-90	6	70	52.5	B-22
25.2	30.3	28.8	46.9	52.6	-60	6	50	37.5	B-23
16.7	28.3	26.9	33.7	37.9	-60	4	50	37.5	B-24

Notes for Table 2:

[a] Sample calculation in Appendix IV.

[b] The conversion from volume of sample to weight in grams is based on density data presented in Appendix II.

[c] Weights by reservoir difference, no final sample weights.

[d] Freezing of the bubbler tip in runs A-7 and B-4.

[e] No sample weights were obtained in run A-9.

[f] Faulty pressure regulator in run B-5.

[g] Probable error in column height measurement in run B-8.

[h] Quantities too small in run B-14. Conditions repeated in run B-15, using bubbling time of 2.0 hours.

[i] Bubbling time of 2.0 hours in run B-15.

[j] Contaminated sample in runs B-16 through B-19.

TABLE 3

Experimental Data and Calculated Results, Fritted Glass Bubbler Tip
(All flows based on 4:3 molar ratio of $NO:O_2$, equiv. to N_2O_5)

Per Cent Nitric Oxide Sorbed[a]	Liquid Conc. Wt. % NO		Sample Weight Grams		Liquid Temp., °F.	Nominal Height Inches	NO Flow, Std.cc. /min.	NO in Exhaust Gases, as % of NO Flow[b]	Run No.
	Initial	Final	Initial	Final					
24.9	30.6	28.8	143.5	166.6	-90	6	220	----------	C-2
27.3	30.2	28.6	137.0	162.4	-90	6	250	----------	C-3
31.1	29.0	27.6	154.3	185.6	-90	6	280	----------	C-4
26.6	30.1	28.1	149.4	181.9	-90	6	310	----------	C-5
29.1	30.6	28.5	148.9	185.7	-90	6	340	1.3, 1.5	C-6
14.1	28.0	24.8	149.0	180.1	-60	6	280	2.5, 2.5, 3.0	C-7
19.8	28.0	25.1	150.6	188.0	-60	6	340	2.3, 2.5, 3.1	C-8
24.1	29.2	26.5	149.7	190.7	-60	6	380	1.9, 2.6, 2.8	C-9
26.5	29.2	26.5	152.5	200.0	-60	6	430	2.3, 2.6, 3.0	C-10
21.4	28.2	25.0	147.1	196.5	-60	6	480	2.4, 2.4, 2.4	C-11
16.6	33.1	27.4	137.7	184.4	-90	6	400	4.0, 3.0 1.9	C-12

[a] Calculation illustrated in Appendix IV. Bubbling time of 60 minutes for all runs.

[b] Determined by chemical analysis. Triplicate analyses shown were made on samples taken at different time intervals during the run.

FILM-TYPE CONDENSATION OF PROCESS GAS

Tables 4, 5, and 6, respectively, present experimental data and calculated results for condensation tests with the three condenser coils used. Except as noted, the gas proportions flowed are based on a 4:3 molar ratio of nitric oxide to oxygen corresponding to N_2O_5. Data of doubtful accuracy are indicated by explanatory footnotes. In order to compare the results with those from bubbling tests, the amount of nitric oxide condensed or exhausted is expressed as a percentage of the total flow of nitrogen oxides as nitric oxide. A sample calculation is shown in Appendix IV.

All test work with the small glass coil was conducted using a bath temperature of -60°F. Variables studied with the large glass coil included bath temperature and the addition of an inert diluent to the gas mixture. Experiments with the stainless steel coil included effects of changing the $NO:NO_2$ ratio flowed and preheating the entering gases, as well as changing the bath temperature and introducing an inert diluent (nitrogen) into the flowing stream.

Figure 16 illustrates the effect of bath temperature on the condensation of mixed oxides for the large glass coil and the stainless steel coil--with added parameters of gas preheat and inert diluent. Figure 17 shows the effect of changes in the $NO:NO_2$ proportion on the nitric oxide concentration of the product.

TABLE 4

Results of Film-Type Condensation, Glass Coil-"D"
(Bath Temperature - 60°F.)
(All flows based on 4:3 molar ratio of $NO:O_2$, equiv. to N_2O_5)

Liquid Product		Per Cent Nitric Oxide [a]		Nitric Oxide Flow Gm/Hr.	Weight Ratio $NO:NO_2$	Gas Entrance Velocity, Ft/Sec.	Run No.
Freezing Point °F	Concentration Weight % NO	Condensed	Exhausted				
-	<16	-	1.2[b]	40	50:50	-	D-1
-58	23.3[c]	-	-	100	40:60	-	D-2[c]
-38	19.3	26.2	3.8[b]	120	50:50	10	D-3
-34	18.3	25.0	2.0	140	40:60	14	D-4
-40	19.8[d]	-	-	80	40:60	-	D-5[d]
-33	18.0	25.3	4.0[b]	120	60:40	10	D-6
-47	21.4	29.8	-	120	60:40	8	D-7[e]
-31	17.5	-	-	150	70:30	-	D-8[f]
-29	16.7	22.8	3.1	180	40:60	18	D-9
-29	16.7	22.5	4.4	200	40:60	20	D-10
-31	17.3	17.3	28.9	425	50:50	37	D-11

[a] As Calculated in Appendix IV, except as indicated by superscript b.

[b] Determined by chemical analysis.

[c] Doubtful data due to faulty thermocouple wiring.

[d] Doubtful data due to supercooling and resulting poor cooling curve.

[e] Gas flows proportional to N_2O_4 rather than N_2O_5.

[f] Error in nitrogen dioxide rotameter setting; excess oxygen gave the ratio shown which is approximate.

TABLE 5

Results of Film-Type Condensation, Glass Coil-"E"
(All flows based on 4:3 molar ratio of $NO:O_2$, equiv. to N_2O_5)

Liquid Product Freezing Point °F	Liquid Product Concentration Wt. % NO	Bath Temp. °F	Per Cent NO[a] Condensed	Per Cent NO[a] Exhausted	N_2 Diluent, Mole % of Combined NO and O_2 Flows	NO Flow Gm/Hr.	Weight Ratio $NO:NO_2$	Gas Entrance Velocity Ft/Sec.	Run No.
-36	18.7	-60	26.3	0.9	0	425	50:50	37	E-2
-37	19.0	-60	26.6	-	0	500	50:50	44	E-3[b]
-48	21.5	-60	28.4	4.0	0	750	60:40	60	E-4
-37	19.1	-60	-	18.9	0	1200	60:40	96	E-6[c]
-50	22.0	-60	30.2	30.6	0	1200	60:40	96	E-7[d]
-50	22.0	-60	30.2	34.1	0	1260	60:40	84	E-8[e]
-20.5	14.0	-30	30.2	52.9	0	1200	60:40	96	E-9
-74	25.8	-87	34.8	9.5	0	1200	60:40	96	E-10
-83	26.8	-116	36.0	8.1	0	1260	60:40	101	E-11
-66	24.7	-60	33.4	27.2	25	1200	60:40	117	E-12
-86.5	27.1	-83	36.3	17.2	25	1200	60:40	117	E-13
-93.5	27.9	-114	37.3	13.5	25	1200	60:40	117	E-14
-79	26.4	-111	35.5	21.0	50	1200	60:40	138	E-15
-86	27.1	-111	36.3	12.0	20	1200	60:40	113	E-16
-93	27.8	-111	37.1	5.3	0	1200	60:40	96	E-17

[a] As calculated in Appendix IV.

[b] Run time doubtful.

[c] NO condensation data doubtful due to secondary condensation in exhaust stack at high input rates.

[d] Nitrogen purge gas (1530 grams/hour) to reservoir to improve operation over run E-6.

[e] Gases flowed equivalent to N_2O_4.

TABLE 6

Results of Film-Type Condensation, Stainless Steel Coil- "F"
(All flows based on 4:3 molar ratio of $NO:O_2$, equiv. to N_2O_5)

Liquid Product		Bath	Per Cent NO[a]		N_2 Diluent, Mole % Comb.	Approx.		Weight	Entrance	
Freezing Point, °F.	Conc'n. Wt. % NO	Temp. °F	Condensed	Exhausted	NO and O_2 Flows	Preheat Temp. °F	NO Flow Gm/Hr.	Ratio $NO:NO_2$	Velocity Ft/Sec	Run No.
-68.5	25.0	-60	33.9	11.7	0	-	1000	60:40	96	F-1
-95.5	28.0	-83	37.3	12.1	0	-	1200	60:40	96	F-2
-	-	-114	-	-	0	-	1200	60:40	-	F-3[b]
-	-	-111	-	-	20	-	1410	60:40	-	F-4[c]
-95.5	28.0	-91	37.3	16.6	0	-	1410	60:40	136	F-5
-91	27.6	-89.5	-	-	20	-	1410	60:40	160	F-6[d]
-91	27.6	-88.5	37.0	28.8	20	-	1200	60:40	135	F-7
-79	26.4	-60	35.5	11.9	0	110	1000	60:40	107	F-8
-101	28.6	-89	38.0	14.2	0	125	1410	60:40	155	F-9
-102.5	28.7	-114	28.2	14.8	0	135	1410	60:40	157	F-10
-99	28.4	-85	37.8	13.9	0	170	1410	60:40	172	F-11
-67	24.8	(-60)	33.7	18.7	0	-	1000	60:40	96	F-12[e]
-73.5	25.7	-60	34.6	10.2	0	-	900	50:40	94	F-13
-60	23.8	-60	32.4	11.3	0	-	770	40:60	90	F-14
-68.5	25.0	-60	33.8	12.1	0	-	860	47:53	93	F-15
-87	27.2	-89.5	36.4	13.2	0	-	1260	50:50	132	F-16
-102.5	28.7	-115	38.3	10.0	0	170	1480	65:35	188	F-17
(-48)	(21.6)	(-61)	-	-	0	-	1000	60:40	96	F-18[e]
(-48.5)	(21.7)	(-57)	-	-	0	-	1000	60:40	96	F-19[e]
-117	30.0	-88.5	-	-	0	160	1700	60:40	153	F-20[f,g]
(-69.5)	(25.2)	(-71)	-	-	0	-	1000	60:40	96	F-21[e]
-109	29.6	-88.5	39.2	16.7	0	185	1410	60:40	109	F-22[f]
-100	28.5	-90	38.0	7.7	18	170	1000	60:40	142	F-23

[a] As calculated in Appendix IV.
[b] Product solidified in coil.
[c] Product solidified in line to upper reservoir. All condensate collected in lower reservoir.
[d] Diluent carried approximately half of condensate over into lower reservoir.
[e] Calorimetric measurements. Bath temperatures average over range.
Concentrations and freezing points in parentheses are for combined product.
[f] Gas flows equivalent to N_2O_4.
[g] Pressure drop through preheater too great to support these flows. Flow rates not known accurately.

PROCESS HEAT REQUIREMENTS

Four measurements were made of the heat load involved in the condensation process. The first was a preliminary trial during run F-12, and the other three were experiments employing more adequate bath agitation and increased bath capacity to improve the precision and reliability of measurement (see Table 7). A sample calculation is given in Appendix V.

CARBON DIOXIDE AS A PROCESS CONTAMINANT

To determine the solubility of carbon dioxide in the mixed oxides, carbon dioxide was bubbled at -60°F. into a liquid containing 27.7% nitric oxide until saturated. By weighing the sample before and after bubbling, it was found that carbon dioxide was soluble to the extent of about five per cent at -60°F. This amount of carbon dioxide, also served to lower the freezing point of the mixture by 3.5°F., from -91.5°F. to -95°F.

To determine the effect that the solution of carbon dioxide in liquid mixed oxides would have on the vapor pressure of the mixture, the vapor pressure was measured before and after addition of carbon dioxide. A sample of mixed oxides (32.3% NO) was frozen into a stainless steel reservoir. Its vapor pressure was measured with a Bourdon gauge over a temperature range of about 30°F. to 65°F. This measurement was repeated after an amount of carbon dioxide equal to four per cent by weight of the mixture had been added to the reservoir. Figure 18 presents the vapor pressure curves for the liquid sample with and without added carbon dioxide over the temperature range measured.

TABLE 7

Heat Evolved in the Condensation Process[a]

B.t.u. per Minute						
Experimental	Calculated[b]	Deviation, Per Cent	Wt. % NO in Combined Product	Temperature Change of Bath, °F	Average Temp. of Bath, °F	Duration of Run, Seconds
39.2	38.8	-1.0	21.6	28	-61	170
33.0	34.7	+5.1	21.7	24.5	-57	180
37.7	38.4	+1.8	25.2	16	-71	360

[a] All flows were $NO\text{-}NO_2\text{-}O_2$ mixtures; 1000 gm/hr of NO; $NO:NO_2$ equal to 60:40 weight ratio.

[b] Neglects heat required to cool the uncondensed gases.

DISCUSSION

Page

Bubbling Gases through Liquid Mixed Oxides. 19

Film-Type Condensation of Process Gas 21

Calculations for Nitric Oxide Sorbed and Condensed 24

Comparison of Freezing Point and Chemical Analysis Methods 25

Carbon Dioxide as a Process Contaminant 27

Physical Data 27

Process Heat Requirements 27

DISCUSSION

BUBBLING GASES THROUGH LIQUID MIXED OXIDES

Preliminary bubbling tests using pure gases (nitrogen, oxygen, or nitric oxide) gave information on the general mechanism of recovering nitrogen oxides by bubbling HTA process gas through liquid mixed oxides. When pure nitric oxide was bubbled through a 2.5 inch depth of liquid mixed oxides at -60°F., the sorption of more than 60% of the input as nitric oxide indicated that sorption of this type was sufficiently rapid to make possible efficient recovery by bubbling.

Results presented earlier in Table 1 indicate that when pure oxygen was bubbled through liquid mixed oxides, oxidation of nitric oxide in the liquid was not rapid at -60°F., but became appreciable at higher temperatures. The differences shown in the table for the effects of bubbling oxygen and nitrogen on nitric oxide losses are a measure of the NO oxidized. These data are conservative because of differences in liquid composition. For example, if nitrogen were bubbled through a 23.4% NO mixture at -30°F., instead of through a liquid containing 27.1% NO, the loss would be less because of the difference in vapor pressures of the two mixtures. Similarly, bubbling oxygen through a 27.1% NO mixture at -30°F. would result in a greater loss than that experienced by using the liquid containing 23.4% NO.

Without an attempt to offer any theoretical explanation, we interpret the performance of the system to indicate that the oxidation of nitric oxide in liquid mixed oxides occurs in the gas phase. As the bubble of gas passes up through the liquid, NO is evaporated from the liquid and passes through the gas-liquid interface. If the bubble contains oxygen, the NO is rapidly oxidized. The liberation of heat and the reduction in the partial pressure of NO in the bubble allow more NO to be vaporized. If the bubble is composed of an inert gas, the NO content of the bubble is limited by the vapor pressure of the NO dissolved in the liquid only and this amount of NO is lost as the bubble passes out of the surface of the liquid.

Upon bubbling a 4:3 molar mixture of nitric oxide and oxygen gases, as would be supplied by the HTA recovery process, it was found that only a small amount of nitric oxide was sorbed as nitric oxide. Calculations showed that about 40% of the nitric oxide could be oxidized in the bubbler tip at -60°F. Further oxidation of the nitric oxide was assured inside the bubble as it rose through the liquid.

The oxidation of nitric oxide in the tip was reduced by modifying the bubbler so that the free volume in the bubbler tip became negligible. Oxidation inside the bubble could not be controlled, therefore studies were undertaken to determine conditions for maximum recovery of nitric oxide as nitric oxide.

Results of bubbling a 4:3 molar mixture of nitric oxide and oxygen gases through liquid NO-NO_2 mixtures showed that (1) an optimum gas flow rate existed for each column height for maximum sorption of nitric oxide, and (2) that sorption increased at lower reaction temperatures. From Figure 14, the maximum percentage of nitric oxide sorbed as nitric oxide, about 29.5%, was obtained at -90°F. with a column height of six inches. The existence of optimum flow rates is compatible with reasoning from which one can deduce that increases in bubble velocity will increase condensation or mass transfer while oxidation rate is presumed to remain constant. The optimum flow rate is exceeded when a velocity is reached that causes uncondensed and unoxidized nitric oxide to be released from the surface of the liquid.

A rapid rate of condensation or sorption of NO by the mixed oxides favors the production of a mixture rich in NO. In calculating the bubble area per unit column height, the gas flow rate, bubble diameter and ascending velocity are important. The bubble diameter varies inversely with bubble surface area per unit column height, and is dependent on surface tension, density of the liquid and orifice diameter. Only the orifice diameter can be changed to influence the bubble diameter since the other factors are physical properties of the mixture and their values cannot be expected to change greatly in the temperature range of interest. A smaller orifice diameter results in smaller bubbles and an increase in the surface area under any given flow conditions. Since mass transfer under constant gas flow increases directly as surface area increases, a larger interfacial area results in more transfer of nitric oxide into the liquid. Since the best nitric oxide sorption experience was about 29.5 weight per cent of the amount bubbled, it was expected that an improvement in transfer rate would increase the percentage of nitric oxide sorbed.

The fritted glass bubbler (Figure 5) was then fabricated with the expectation of increasing nitric oxide sorption by passing the mixed gases through a fritted glass diffuser tip to introduce smaller bubbles into the liquid sorbent. Sorption isotherms obtained with this apparatus, shown in Figure 15, resembled those obtained previously in that the maximum percentage of nitric oxide sorbed was approximately the same for the same liquid column height (six inches). The greatest difference between these results and the previous data was the four to fivefold increase in flow rate at which this maximum (or optimum) sorption occurred. The relative sample weights were such that a 2-1/2 fold increase in flow rate would be expected to give maximum sorption based on sample size alone. This increase in optimum flow rate can be accounted for by greater efficiency in gas distribution brought about by the fritted glass diffuser tip. Since considerably more interfacial area was produced but no increase in percentage recovery of nitric oxide was observed, it was indicated that considerable oxidation was occurring in the free volume available in the tip and in the gas bubbles.

These results are explained on the basis that the controlling step was the oxidation of nitric oxide, which is extremely rapid under the experimental conditions of low temperature and high partial pressure of nitric oxide and oxygen.

Other methods of attack were also considered such as studying the effect of large changes in bubbling depths, of bubbling warm gases to lower the oxidation rate and collapse the bubble, and of bubbling mixtures of NO, NO_2 and O_2 to induce more rapid condensation in addition to slowing the oxidation and collapsing the bubble.

This last approach of bubbling a mixture of NO, NO_2 and O_2 gases in proportions based on the 4:3 molar ratio of NO to O_2 was attempted. Condensation of liquid inside the fritted tip stopped the flow of gas. The rapidity with which the liquid mixture condensed prompted early study of the condensation of such mixtures in a heat exchanger designed for condensation of product direct from gases. Prior to the fabrication of the apparatus, a mixture of the gases was passed through a short glass U-tube immersed in a -60°F. bath. The rapidity of condensation of the intensely colored blue liquid characteristic of N_2O_3 was encouraging and the condensation runs were initiated.

FILM-TYPE CONDENSATION OF PROCESS GAS

Glass Condenser Coils

Results of film-type condensation with the smaller glass condense (Table 4) demonstrated only fragmentary trends. Most gas flows were in the streamline region. When the flow rates were increased to add turbulence, the capacity of the condenser was exceeded such that 30% of the unreacted nitric oxide was lost to the stack. One run was made in which the gas flows were in proportions equivalent to N_2O_4, rather than the 4:3 molar ratio of nitric oxide and oxygen which is equivalent to N_2O_5. The nitric oxide concentration in the product was increased from 18.0% to 21.4% by this reduction in excess oxygen.

The larger area glass condenser (Figure 8) was then constructed to investigate flow rates in the turbulent region. It was felt that increasing the velocity of flow would demonstrate two main advantages.

First, the heat transfer rate would increase as the velocity increased. This would speed condensation of gases where the nitric oxide concentration in the gas phase was still high. Second, increasing the velocity would decrease retention time for oxidation of nitric oxide and maintain a higher effective temperature of the main gas stream. Since the reaction rate constant for the oxidation of nitric oxide decreases with increase in temperature, the higher effective temperature would reduce the quantity of nitric oxide oxidized. Typical calculations are shown in Appendix III.

Keeping these advantages of higher gas velocity in mind, a discussion of the probable mechanism or mechanisms for the condensation of mixed oxides is appropriate. Of the constituents present in the mixed gas stream, it is known that nitrogen dioxide is readily condensed at the temperatures under consideration. As the NO_2 condenses it may carry with it, in solution, either NO or N_2O_3. Therefore, a high NO concentration is beneficial at the entrance to the condenser where the entering NO_2 condenses. Then as the gases progress down the tube and more NO_2 is formed by the oxidation of NO, it is presumed that N_2O_3, even if in small amount, is also formed and is condensed with the NO_2. Though the equilibrium concentration for N_2O_3 is purportedly very low, it forms extremely rapidly. A balance of condensation rate and oxidation rate of the nitric oxide would be expected to exist under certain conditions so as to produce a maximum concentration of nitric oxide in the condensed liquid.

Visual observations of experimental runs using the larger glass condenser with an entrance velocity of about 100 ft/sec., showed that a major part of the condensate was formed in the exhaust stack under low velocity conditions with a relatively small amount of liquid flowing in the coil. Therefore, it was necessary to dilute the gases in the reservoir and increase the exhaust gas velocity by the injection of nitrogen gas into the reservoir. This procedure was used with good results. The maximum nitric oxide concentration of 22.0% reported is believed representative of the liquid formed in the coil. It is noted that this concentration of product is defined by calculation as 30.2 per cent of the nitric oxide condensed. (See Appendix IV). This was only slightly higher than the maximum of 29.5 per cent sorbed achieved by bubbling experimentation.

Other means of increasing the amount of nitric oxide condensed as nitric oxide were tried. Flows equivalent to N_2O_4 were introduced with no effect. Under these conditions, it was concluded that the actual amount of excess oxygen present in the gas stream was of minor importance.

The bath temperature was reduced to obtain a colder surface for condensation. This resulted in a liquid mixture which had a freezing point of -83°F. (26.8 per cent nitric oxide). The bath temperature in which this product was condensed was -116°F. From the shape of the curves of Figure 16, it can be seen that this variation and others to be discussed below served to increase the quality (lower the freezing point) of the liquid product but that this increase levels off as the condensing bath temperature is reduced below about -90°F.

An inert gas, nitrogen, was introduced with the reactants to diminish the partial pressures of nitric oxide and oxygen and in so doing reduce the oxidation rate of the nitric oxide. Results were as expected; the use of diluent nitrogen improved the product quality appreciably for bath temperature of -60°F. and -90°F. (See Figure 16). However, the improvement in product quality was again less pronounced for bath temperatures below -90°F.

Stainless Steel Condenser Coil

The stainless steel condenser coil (Figure 9) was introduced as another method of lowering the temperature of the condensing surface. The double reservoir system was incorporated into this condenser to separate condensate produced in the coil from low velocity stack condensate. Therefore, it was no longer necessary to flow nitrogen gas into the product reservoir through the exhaust stack.

Since the thermal conductivity of stainless steel is approximately 15 times that of Pyrex glass, it was expected that this condenser would be more efficient than one made of glass. Difficulties were encountered in that the wall temperature and hence the effective temperature in the coil was reduced to the point where freezing occurred in the coil (Table 6). Increasing the gas flow rate served to increase the effective temperature in the coil and the difficulty was partially overcome. With the stainless steel coil in a bath at -91°F., an improved liquid product freezing at -95.5°F. (28.0% nitric oxide) was obtained. Further improvement was attempted with the addition of an inert diluent as before, but no change was observed. Thus, nitrogen gas dilution apparently improved the nitric oxide concentration in the liquid product with the glass condenser coil, but not with the steel coil.

The next modification involved preheating the reactant gases to make the process more nearly representative of a commercial installation where gases will come from a heat exchanger at 150°F. to 200°F. The warmer gases served to reduce the initial oxidation of nitric oxide and keep the effective temperature higher so that a greater overall temperature difference was maintained. In addition, the higher effective temperature prevented solidification in the condenser coil. Measurement of the actual temperature of the mixed gases at the entrance of the condenser coil was difficult, but the approximations (Figure 13) were considered sufficiently accurate for the purpose. Liquid condensates with the lowest freezing points were obtained with preheated gases. Gases preheated to about 125°F. and condensed at a bath temperature of -89°F. yielded a product freezing at -101°F. (28.6% nitric oxide). The reduced significance of lowering the bath temperature below -90°F. is clearly indicated by the flatness of the curves in Figure 16. An important operating advantage is realized at the -90°F. bath temperature in that the resulting liquid product has a lower freezing point than the bath and cannot freeze in the coil.

The effect of changing the proportion of nitric oxide to nitrogen dioxide in the entering gases is plotted in Figure 17. These curves show that at the highest bath temperature, -60°F., the greatest nitric oxide concentration was obtained with gases in the approximate $NO:NO_2$ proportion of 52:48. As the bath temperature is reduced, the amount of nitric oxide present in the incoming gases must be increased to maintain product quality. In a commercial installation, the flow of gases with a higher proportion of nitric oxide would be accompanied by a higher gas temperature. Though this would necessitate greater refrigeration capacity, it would be beneficial for the condensation of liquid mixtures richer in nitric oxide.

The results of flowing a mixture of preheated gases in the proportion of N_2O_4 into the stainless steel condenser (Table 6) show that the amount of excess oxygen is a factor in the condensation process. The nitric oxide content of the liquid product was increased from 28.5% to 30% by this reduction in excess oxygen. Thus the concentration of the liquid product can be controlled to a moderate degree by controlling both the rate of chilling of the gases and the amount of excess oxygen present in the gas stream. For the condition of constant chilling rate, a decrease in excess oxygen in the gas stream will result in the condensation of a mixed oxide richer in nitric oxide.

In earlier work with the glass condenser coil, nitrogen had been added to the gas mixture as a diluent to reduce the partial pressures of the reactant gases in the oxidation of nitric oxide. This change resulted in the condensation of a liquid product richer in nitric oxide. With the stainless steel coil condenser, there was no improvement in nitric oxide concentration in the product by dilution with nitrogen. From data in Table 6, it is evident that also in flowing preheated gases, no effect is observed due to dilution.

CALCULATIONS FOR NITRIC OXIDE SORBED AND CONDENSED

The two sets of calculations shown in Appendix IV for nitric oxide sorbed and nitric oxide condensed are parallel in that they represent the same quantity for the two systems of $NO-NO_2$ recovery. Stoichiometric calculations show that in either case 39.6% of the incoming nitric oxide must be condensed as nitric oxide to achieve a 30% NO- 70% NO_2 liquid mixture.

Figure 19 is a plot of the per cent of entering nitric oxide from an HTA process gas mixture that is condensed versus the concentration of nitric oxide in the liquid product as determined experimentally and by stoichiometric calculation. The experimental points show good agreement with each other and with the calculated curve.

COMPARISON OF FREEZING POINT AND CHEMICAL ANALYSIS METHODS

Table 8 compares nitric oxide concentrations determined by the freezing point method and the chemical analysis method, both of which are described in Appendix I. The calculated weight of analytical sample and the excess sodium hydroxide used in the determinations are also listed. In general, results from the two methods show fair to good agreement, thus attesting to the reliability of the freezing point method.

The analytical results were influenced by the weight of sample taken and the amount of excess sodium hydroxide present in the determination. Small samples (0.1-0.2 gms) produced higher values of per cent nitric oxide than larger samples. These higher values were considered less accurate because of the nature of the sampling procedure. Just before the liquid NO-NO$_2$ sample was withdrawn into the glass bulblet, a small amount of vapor appeared in the bulblet. This vapor was richer in NO than the liquid sample because of the higher vapor pressure of NO. Consequently, the smaller samples appeared to contain percentagewise a greater amount of NO.

The values for NO concentration determined from large samples (0.6-0.9 gms) are lower than the true values, since insufficient excess sodium hydroxide was present in the flask when the bulblet was broken. This was readily seen by the large amount of vapor evolved when the liquid NO-NO$_2$ reacted with the sodium hydroxide. It appears that fairly accurate values of NO concentration can be determined using the analytical method if a large enough sample (0.5 gms) is taken and a sufficient excess (200%) of sodium hydroxide is present.

TABLE 8

Comparison Between Nitric Oxide Concentrations from Freezing Point Measurements and Results of Chemical Analyses of Multiple Samples

Run No.	NO Concentration by Freezing Point Method, Wt. %	NO Concentration by Chemical Analysis,		Wt. Analytical Sample, Grams[a]	Excess NaOH in Analytical Determination, %
		Wt. %	Ave. Wt. %		
D-3	19.3	17.7	19.1	0.5576	68
		19.7		.3701	150
		19.9		.2653	249
D-5	19.8	14.7	18.5	.3824	151
		17.3		.2812	233
		23.6		.1319	589
D-6	18.0	18.6	18.4	.1046	610
		18.2		.2109	395
D-7	21.4	23.7	22.2	.1560	551
		20.8		.2637	290
		22.2		.2730	274
D-9	16.7	14.9	17.1	.4793	129
		16.8		.4560	139
		19.5		.3713	189
D-11	17.3	15.3	16.0	.7775	41
		16.4		.6333	72
		16.2		.6356	72
E-2	18.7	15.2	18.0	.9508	16
		20.2		.2964	261
		18.7		.5844	84
E-3	19.0	20.1	20.3	.3419	213
		20.5		.2483	545
		20.3		.3366	625
E-4	21.5	21.9	20.9	.3804	319
		20.8		.4307	272
		20.0		.6938	132

[a] Calculated

CARBON DIOXIDE AS A PROCESS CONTAMINANT

Since carbon dioxide is likely to be present as a process contaminant, information was desired as to any effects it might have on the process. Test results showed that carbon dioxide was soluble in the mixed oxides to the extent of about five per cent at -60°F., and this quantity of CO_2 served to lower the freezing point of the liquid mixture by 3.5°F., from -91.5°F. to -95°F. Other tests showed that four per cent by weight of carbon dioxide raised the vapor pressure of the mixed oxides at 32°F. from 35 psig. to 70 psig.

The slight lowering in freezing point is beneficial, but the increase in vapor pressure is detrimental. This increase in vapor pressure can be explained by the decrease in the constant-pressure solubility of carbon dioxide in the mixed oxides as the temperature is increased.

PHYSICAL DATA

Procedures for and results of physical property measurements are given in Appendix II, together with estimations of the probable accuracies of the data. The plots of vapor pressure, viscosity, density, and surface tension versus temperature over the pertinent concentration ranges are of value for design calculations of larger scale equipment. Of prime importance for the experimental work were the density-temperature plots, since these data were required to determine sample weights from cathetometer readings. Experimental specific heat data were used in the calculation of refrigeration requirements in Appendix V.

PROCESS HEAT REQUIREMENTS

The experimental results of the process heat measurements are in good agreement with the calculated values of the refrigeration requirements for the process (Table 7). The calculated refrigeration requirement of 116 tons for a commercial plant (Appendix V) is of value in process equipment design.

PLAN FOR COMMERCIAL PROCESS

PLAN FOR COMMERCIAL PROCESS

A proposed commercial process for the manufacture of mixed oxides from the hot gases produced in the HTA regenerator is shown schematically in Figure 20. The mixed oxides are produced essentially by cooling and condensing. The hot mixture of nitric oxide and oxygen is cooled to about 200°F. in a heat exchanger where sensible heat and some heat of oxidation are removed; then the partially cooled gases are quick chilled in another heat exchanger using Freon 11 coolant (trichlorofluoromethane) at -90°F. In this second exchanger additional sensible heat is removed along with heats of oxidation, polymerization and condensation.

The Freon 11 coolant is pumped through an indirect heat exchanger where its temperature is reduced to -90°F. by a 116 ton refrigeration system operating at -95°F.

An alternate plan and one that is portable involves starting with liquid nitrogen tetroxide. The design is similar in that quick chilling is employed after the liquid nitrogen tetroxide is passed through a heater. In this preheater its temperature is raised to 1200°F at which temperature about 90 per cent of the nitrogen dioxide is dissociated into nitric oxide and oxygen. These hot gases can then be quick-cooled to produce mixed oxides essentially as described above. With less excess oxygen present (excess based on a production of a 30-70 mixed oxide) the production of mixed oxides is more easily accomplished.

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

1. Process gas condensation as mixed oxides rich in nitric oxide is readily accomplished in coil-type heat exchangers. Liquid mixtures freezing at -101°F. (28.6% NO) and at -117°F (30.0% NO) are obtained by film-type condensation using gaseous mixtures ($NO-NO_2-O_2$) equivalent to N_2O_5 and N_2O_4, respectively, at bath temperatures of about -90°F.

2. The concentration of nitric oxide in the liquid mixed oxides produced in the laboratory condensation tests is increased by:

   a. Increased gas entrance velocity to the condenser,
   b. Reduced condensation temperature,
   c. Dilution of the gases with nitrogen,
   d. Preheat of the gases.

3. Sorption of pure gaseous nitric oxide by liquid mixed oxides is sufficiently rapid to indicate the possible recovery of nitric oxide from HTA process gas by utilization of this property. Maxima of about 29% nitric oxide sorption as nitric oxide are obtained, with the rest oxidized to nitrogen dioxide and condensed, when HTA process gases equivalent to N_2O_5 are bubbled through six-inch depths of liquid mixed oxides at -90°F. (39.6% of the incoming nitric oxide must be condensed as nitric oxide to achieve a 30-70 $NO-NO_2$ liquid mixture). Sorption is noted to increase as reaction temperatures are lowered and liquid depths are increased. Optimum flow rates for maximum sorption are shown to exist and to be four to five times greater with a fritted glass bubbler tip than with a single orifice bubbler, due to the greater efficiency of gas distribution with fritted tip.

4. Oxidation of nitric oxide, which is extremely rapid under the experimental conditions of low temperature and high partial pressure of nitric oxide and oxygen, is shown to be the controlling step in the sorption of gases equivalent to N_2O_5.

5. The agreement between experimental measurements and calculated values for the heat evolved in the condensation of mixed oxides is good (± 5%), indicating that the reactions chosen for thermodynamic calculations correctly represent the actual system, and may be used with assurance for engineering design. A refrigeration requirement of 116 tons is estimated for a 40 ton per day nitric acid plant.

6. Experimental results are reported for physical properties of mixed oxides containing 20 to 30 weight per cent of nitric oxide. Viscosity, density, and surface tension data are given in the temperature range of -80°F. to 0°F., vapor pressure data are given from -90°F. to +50°F., and the specific heat is reported as 0.6 ± 0.1 BTU/(lb)(°F.), measured at -70°F.

7. Carbon dioxide is soluble in the mixed oxides to the extent of about five weight per cent at -60°F. This addition of carbon dioxide approximately doubles the vapor pressure in the temperature range 10° to 50°F.

8. For the system under study, the oxidation rate of liquid mixed oxides by oxygen bubbling is shown to increase from 0.06 grams NO oxidized per gram of oxygen bubbled at -60°F. to 0.26 grams per gram at -30°F.

APPENDIX I

ANALYSES

Page

Analysis of Liquid Mixed Oxides by Freezing Point Method. . . . 31

Chemical Analysis of Liquid Mixed Oxides 31

Analysis of Stack Gases for Nitrogen Dioxide 33

APPENDIX I

ANALYSES

ANALYSIS OF LIQUID MIXED OXIDES BY FREEZING POINT METHOD

The laboratory investigation required a reliable method of analysis of liquid mixed oxides, which would also be considerably more rapid than time-consuming chemical analysis. A study of available freezing-point data (Figure 21) showed a rapid decrease in freezing point temperatures with increase in nitric oxide content. This suggested a trial of the freezing-point method for determining weight per cent nitric oxide. After several exploratory runs with a student potentiometer setup, a Leeds and Northrup recorder (Speedomax, type G, adjustable-range, adjustable-zero) was installed to record continuously the emf from a copper-constantan thermocouple placed in the mixture. This recorder gave a good indication of the freezing point. A typical tracing is shown in Figure 22.

A double-walled glass container immersed in a Dewar flask of liquid nitrogen was used for the freezing point determination. A glass stirrer and a thermocouple housed in a glass well were placed in the liquid before the start of a run. Figure 23 shows glass container, stirrer and thermocouple used.

The procedure was to assemble the apparatus while holding the liquid NO-NO_2 mixture at the dry ice - acetone slush temperature (approximately -115°F.). The container with contents was removed from the acetone slush, the outer jacket put on, and the contents allowed to warm to a temperature (followed on the recording potentiometer) well above the freezing point. The container was then placed in the Dewar of liquid nitrogen, and stirred continuously while the mixture was cooling. The inflection in the cooling curve (Figure 22) was interpreted as the freezing point of the mixture, and the weight per cent nitric oxide was read from Figure 21.

CHEMICAL ANALYSIS OF LIQUID MIXED OXIDES

A method of chemical analysis was developed and tried out as a check on the freezing point method. A sample for analysis was collected in a glass bulblet directly from the coil condenser reservoir prior to liquid transfer for freezing point determination. After sealing, the bulblet was placed in a flask containing an excess of standard sodium hydroxide solution and broken to release the sample. Total nitrogen was determined by back titration with standard acid solution, and nitrite was determined by adding excess potassium permanganate solution and back titrating with standard sodium thiosulfate solution. Nitric, oxide and nitrogen dioxide were then calculated, as illustrated below:

Equations and Calculations

For this method to be applicable, it is necessary that the NO_2 content of the liquid NO-NO_2 mixture be at least 50 mol per cent. It is assumed that all of the NO present in the mixture is in the molecular form of N_2O_3. As the liquid mixture of nitrogen oxides reacts with sodium hydroxide, the excess NO_2 is converted to sodium nitrate and sodium nitrite.

$$2NO_2 + 2\ NaOH = NaNO_3 + NaNO_2 + H_2O$$

Sodium hydroxide converts N_2O_3 to sodium nitrite only.

$$N_2O_3 + 2\ NaOH = 2NaNO_2 + H_2O$$

Nitric oxide does not react with sodium hydroxide.

The amount of sodium hydroxide used can thus be represented,

$$\text{mols } NO_2 + 2(\text{mols } N_2O_3) = \text{total mols sodium hydroxide used.} \qquad (1)$$

After the solution has been neutralized and potassium permanganate added, only nitrite reacts with permanganate.

$$1/2\ (\text{mols } NO_2) + 2\ (\text{mols } N_2O_3) = \text{mols potassium permanganate used.} \qquad (2)$$

Subtracting equation (2) from (1) gives

$$1/2\ (\text{mols } NO_2) = \text{mols NaOH} - \text{mols } KMnO_4 \qquad (3)$$

N_2O_3 can be determined from equation (1)

$$\text{mols } N_2O_3 = \frac{\text{mols NaOH} - \text{mols } NO_2}{2} \qquad (4)$$

also

$$N_2O_3 = NO + NO_2 \qquad (5)$$

Total NO_2 present in sample can then be calculated from (3), (4) and (5), and

$$\text{Wt. \% } NO_2 = \frac{\text{m.e. } NO_2 \times 46\ (\text{eq. wt. } NO_2)}{\text{total wt. } (NO + NO_2)}$$

Total NO can be determined from (4) and (5) and

$$\text{Wt. \% NO} = \frac{\text{m.e. NO} \times 30\ (\text{eq. wt. NO})}{\text{total wt. } (NO + NO_2)}$$

ANALYSIS OF STACK GASES FOR NITROGEN DIOXIDE

Gases normally lost through the stack can be recovered for analysis by freezing out with liquid nitrogen. The gases collected in this manner are a mixture of oxygen and nitrogen dioxide, with traces of nitric oxide. The oxygen is boiled off by evacuation and the nitrogen dioxide is allowed to vaporize in the presence of sodium hydroxide solution. The sodium hydroxide reacts with nitrogen dioxide and the amount reacted can be determined by back titration with standard acid solution.

Procedure

The stack gas samples are collected in U-tubes immersed in liquid nitrogen contained in a clear pint Dewar flask. A calcium chloride drying tube is used for removal of moisture, and the period of collection is timed with a stop watch. Figure 6 is a photograph of the apparatus while a sample was being collected.

As the gases are collected, the U-tubes containing the frozen gases are stoppered and stored in a 2-quart Dewar flask which contains liquid nitrogen. Traces of nitric oxide are known to be present by the slight amount of blue color (N_2O_3) formed on the collection arm of the U-tube. However, the samples are analyzed only for nitrogen dioxide, neglecting any small amount of nitric oxide.

The oxygen is evacuated from the U-tube with a water aspirator connected to the U-tube by a stopcock, the other end being stoppered. The U-tube is immersed in liquid nitrogen in a clear pint Dewar flask during the evacuation, care being taken to keep all solid material below the liquid nitrogen level. It is possible by means of the clear walled Dewar to observe when the oxygen has been removed from the system. After the oxygen has been completely evaporated, the stopper is removed from the U-tube and a 250 ml. flask containing an excess of sodium hydroxide solution is connected to the U-tube. Again the system is evacuated, making sure the liquid nitrogen is at the same level as before. Figure 24 shows this apparatus during an evacuation.

After the evacuation, the U-tube with the attached flask is quickly transferred to an ice bath, where only the U-tube is kept immersed. Under these conditions the solid NO_2 melts and vaporizes, and is partly absorbed by the sodium hydroxide solution. After a few minutes, the assembly is removed from the ice bath and rotated so that all of the nitrogen dioxide reacts with the sodium hydroxide solution. The solution is transferred to a 500 ml. Erlenmeyer flask, phenolphthalein indicator added, and the contents back-titrated with 0.5 N sulfuric acid solution. The amount of NO_2 present in the sample can then be calculated.

Calculations

Two moles of nitrogen dioxide react with sodium hydroxide to form one mole of sodium nitrate and one mole of sodium nitrite.

$$2\ NO_2 + 2\ NaOH = NaNO_3 + NaNO_2 + H_2O$$

Let **A** = milliequivalents of total sodium hydroxide used and B = milliequivalents of total sulfuric acid used. Then **A** - B = milliequivalents of NO_2 present in sample. Therefore,

$$\text{Wt. } NO_2 \text{ lost from stack/min.} = \frac{(A - B) \times 46(\text{eq. wt. } NO_2)}{\text{collection time (minutes)}}.$$

APPENDIX II

PHYSICAL PROPERTY MEASUREMENTS

Page
Vapor Pressure. 35
Viscosity 37
Density 37
Surface Tension 39
Specific Heat 40

APPENDIX II

PHYSICAL PROPERTY MEASUREMENTS

The NO-NO_2 mixtures used for these measurements were made by condensing gaseous mixtures of nitric oxide (Commercial grade, 98% NO) and nitrogen dioxide (distilled from commercial grade liquid), flowed in the proper proportions. Concentrations of nitric oxide were obtained by freezing point determinations.

VAPOR PRESSURE

The sample for the vapor pressure determination was transferred to a steel reservoir and frozen in liquid nitrogen (See Figure 25). The reservoir was connected to a mercury manometer and evacuated, then transferred to an acetone-dry ice bath and thawed at the lowest temperature at which the vapor pressure was to be measured. The liquid material was allowed to come to equilibrium at each successively higher temperature prior to reading the vapor pressure. Data are presented in Table 9, and Figure 25 is a plot of the log of vapor pressure in psia versus the reciprocal of the absolute temperature in °R.

It can be seen from the shapes of the curves of Figure 26, that the log of the vapor pressure deviates from the straight line relationship with reciprocal temperature as the liquid temperature approaches the freezing point. This is explained by the possibility that at temperatures near freezing, N_2O_3 is more stable as a compound and therefore less pressure is exerted. As the temperature is raised, the stability of N_2O_3 decreases and NO is released to status as a solute and can exert increased pressure.

Temperature measurements were accurate to 0.5°F. Manometer readings could be made to within 0.5 mm. Therefore, it can be assumed that the accuracy of these measurements was limited only by the maximum deviation of the data points in Figure 26. This maximum uncertainty is considered to be five per cent.

TABLE 9

Vapor Pressure of Mixed Oxides

21.6 Wt. % Nitric Oxide		28.5 Wt. % Nitric Oxide		29.2 Wt. % Nitric Oxide	
T°F.	Psia.	T°F.	Psia.	T°F.	Psia.
-45	2.63	-91	1.07	-90	1.12
-35	3.12	-70	1.49	-80	1.28
-25	3.80	-61	1.88	-70	1.57
-15	4.79	-49	2.71	-60	1.99
0	7.19	-37	3.53	-50	2.55
+10	9.38	-23	5.85	-39	3.40
+21	12.9	-10	9.09	-30	4.66
+30	16.4	+ 2	12.7	-20	6.46
+41	21.9	+ 9	16.3	-10	8.88
+48	27.0	+20	21.8	+ 3	13.5
+19	12.1	+30	28.7	+15	18.8
-10	5.49			+29	27.8
-33	3.23				

VISCOSITY

Viscosities were measured with an Ostwald viscosimeter, an instrument used to compare the viscosities of two liquids. If the coefficient of one is known, the other can be evaluated. This method eliminates the tedious experimental work involved in the direct measurement of viscosity which requires the determination of the rate of flow of a liquid through a capillary tube of known dimensions. Comparison was made with di-ethyl ether measured over the same range of temperature using viscosity data obtained from the International Critical Tables. Figure 27 shows viscosity of mixed oxides in centipoises plotted against temperature. It can be seen from these data, that the viscosities of mixed oxides vary only slightly with composition changes between 20 per cent NO and 30 per cent NO.

The densities of mixed oxides and ether are known with a maximum uncertainty of one per cent. Since the remaining sources of error, measurement of time of efflux and viscosimeter height effects, cumulatively can account for no more than one per cent error, these measured data are considered to have a maximum uncertainty of three per cent.

DENSITY

Densities were determined by weighing a glass hydrometer float of known volume and mass, immersed in a flask of liquid mixed oxides using the apparatus illustrated in Figure 28. Determinations were made over a range of temperature from 0°F. to -110°F. for four different compositions. Data are presented in Table 10 and illustrated in Figures 29 and 30.

The measurements were made with ease and the results obtained were consistent. The most probable sources of error are errors in weighing and temperature measurement. Since the magnitudes of these are small, the maximum uncertainty, as determined by the deviation of data points, is one per cent.

TABLE 10

Density of Mixed Oxides

21.4 Wt. %
Nitric Oxide

T°F.	ρ (gm/cc)
-0.5	1.490
-13	1.501
-37	1.521
-44	1.534

25.6 Wt. %
Nitric Oxide

T°F.	ρ (gm/cc)
-30	1.505
-36	1.511
-45	1.516
-60	1.532

28.6 Wt. %
Nitric Oxide

T°F.	ρ (gm/cc)
-45	1.507
-60	1.519
-75	1.536
-85	1.548

29.6 Wt. %
Nitric Oxide

T°F.	ρ (gm/cc)
-36.5	1.494
-42	1.495
-109	1.567

SURFACE TENSION

Surface tension determinations were made using a du Nouy ring tensiometer, (Figure 31), and thermostatting the sample for each measurement at each temperature. The ring was suspended by a wire through a small opening in the cap of the sample flask to prevent excessive exposure to the atmosphere. Results of measurements for four compositions are presented in Table 11 and Figure 32.

Difficulties in handling contributed to the inconsistency of the surface tension data. No means were provided for mixing of the sample to insure constant surface composition. Despite precautions taken, atmospheric moisture condensed on the inside wall of the sample flask making visibility poor and causing further uncertainties in the surface composition. From consideration of the maximum possible error in the results obtained as demonstrated by the reversal of the curves for 21.1% NO and 23.4% NO, it is estimated that the data of Figure 32 have an uncertainty of about five per cent.

TABLE 11

Surface Tension of Mixed Oxides

21.1 Wt. %
Nitric Oxide

T°F.	σ (dyne/cm)
-10	33.9
-17	34.5
-23	35.5
-31	36.2
-39	37.4
-44	37.9

23.4 Wt. %
Nitric Oxide

T°F.	σ (dyne/cm)
-11	33.5
-20	34.5
-31	35.5
-40	36.3
-45	37.0
-50	37.5
-55	38.4

27.5 Wt. %
Nitric Oxide

T°F.	σ (dyne/cm)
-20	36.0
-41	39.1
-50	39.7
-60	40.3
-70	41.5

28.3 Wt. %
Nitric Oxide

T°F.	σ (dyne/cm)
-34	38.5
-43	39.0
-50	39.8
-60	40.6
-70	41.5
-76	42.1

SPECIFIC HEAT

Values for specific heat of liquid mixed oxides were obtained by comparison of cooling curves, using the same apparatus and procedure which were used in the freezing point determinations. The sample flask was filled to a specified depth with the material whose cooling curve was to be obtained and the sample was weighed. The jacketed flask was then immersed in liquid nitrogen and the cooling curve was recorded on the Leeds and Northrup type G recording potentiometer. This procedure was duplicated for each material which was used for comparison purposes.

The method of calculation illustrated below compares slopes of cooling curves for the liquids under measurement, assuming equal heat flux for each cooling curve obtained. The data in Table 12 are scattered over a rather large range and no distinction can be noted for variations in composition. The probable difficulty with this method is a variation of heat flux from one cooling run to the next.

Method of Calculation of Specific Heat

If $Q = H\theta$, where H = rate of heat loss, Btu/second
θ = time, seconds.

Then $dQ = H d\theta$

$$Cp = \left(\frac{dQ}{dt}\right)_p = \frac{H}{dt/d\theta}$$

where t = temperature, °F.
$dt/d\theta$ = the slope of the cooling curve.

If the slopes of the cooling curves for two liquids, A and B, are found, and if the heat flux in each case is the same, then a comparison of the specific heats of the two liquids may be made.

$$w_A \, (Cp)_A \left(\frac{dt}{d\theta}\right)_A = w_B \, (Cp)_B \left(\frac{dt}{d\theta}\right)_B$$

$$(Cp)_B = \left(\frac{w_A}{w_B}\right) \frac{(dt/d\theta)_A}{(dt/d\theta)_B} (Cp)_A$$

Various standards were used for comparison. The first part of Table 12 demonstrates how the values of specific heat obtained by this method for certain liquids compare with known values. The second part presents the specific heat obtained for NO-NO_2 mixtures.

TABLE 12

Specific Heat of Mixed Oxides

	Comparison Liquid				
	Diethyl Ether	Toluene	Carbon Disulfide	Acetone	Actual Values Btu/(lb)(°F.)
Diethyl Ether	-	0.88	0.75	0.81	0.93 at -70°F.
Toluene	0.69	-	0.56	-	0.65 at -70°F.
Carbon Disulfide	0.49	0.46	-	-	0.40 at -70°F.
Acetone	1.01	-	-	-	0.87 at -30°F.

	Comparison Liquid			
Wt. % NO	Diethyl Ether	Toluene	Carbon Disulfide	Acetone
21.1	0.71	-	-	0.61
26.3	0.73	0.70	-	-
28.2	0.62	0.58	0.50	-
28.3	0.55	-	-	-

Average specific heat of NO = 0.6 ± 0.1 Btu/(lb)(°F.).

APPENDIX III

KINETIC CALCULATIONS

Page

Oxidation of Nitric Oxide
in Bubble Tip. 42

Velocities and Reynolds Number
for NO-NO_2 Condenser 44

Reaction Rate Constant. 46

Effective Fluid Temperatures
Inside Condenser Coil 47

APPENDIX III

KINETIC CALCULATIONS

OXIDATION OF NITRIC OXIDE IN BUBBLE TIP

This section presents a calculation of the probable amount of oxidation of nitric oxide to nitrogen dioxide in the bubble tip, before introduction of the $NO-O_2$ gas mixture into the liquid $NO-NO_2$ mixture. The bubble tip is the one used for obtaining the preliminary experimental data and has an internal volume of 0.043 cc. The gaseous mixture contains 28 std. cc/min. of nitric oxide and 20 std. cc/min. oxygen, giving a total nitric oxide + oxygen flow of 48 std. cc/min. and a residence time of 0.054 seconds in the bubble tip. Since the reaction rate constant is known at several temperatures a plot of k_c vs. 1/T °R can be made. Figure 33 based on International Critical Tables, (2) contains such a plot.

The oxidation of nitric oxide to nitrogen dioxide is considered to be the third order reaction:

$$2NO + O_2 = 2NO_2.$$

For a constant-pressure process, assuming no mixing,

$$-\frac{d(NO)}{dt} = \frac{k_c\,(NO)^2\,(O_2)}{V^2}, \qquad (1)$$

$$\text{or } -\int_1^2 \frac{V^2\,d(NO)}{(NO)^2\,(O_2)} = k_c \int_1^2 dt = k_c\,t. \qquad (2)$$

On the basis of one mol of gaseous mixture (S.T.P.),

$(NO)_o$ = initial mols of NO = 0.583

$(O_2)_o$ = initial mols of O_2 = 0.417

(NO) = mols of NO at any time

(O_2) = mols of O_2 at any time

N = total mols at any time

V = total volume in liters = 22.4 N.

$$\text{Then } N = 1.000 - \frac{(NO)_o - (NO)}{2} = 0.708 + \frac{(NO)}{2}$$

$$\text{and } (O_2) = 0.417 - \frac{(NO)_o - (NO)}{2} = 0.126 + \frac{(NO)}{2}$$

Substituting values in equation (2),

$$-\int_{0.583}^{(NO)} \frac{(22.4)^2(0.708 + 0.5\ NO)^2\ d(NO)}{(NO)^2\ (0.126 + 0.5\ NO)} = k_c\ t \qquad (3)$$

Expanding and integrating,

$$-250.9 \left[6.530 + \ln (NO + 0.252) + 11.238 \ln \frac{(NO)}{(NO) + 0.252} - \frac{7.952}{(NO)} + 31.557 \ln \frac{(NO) + 0.252}{(NO)} \right] = k_c\ t \qquad (4)$$

Solving equation (4) by trial, using the reaction-rate data from Figure 33, the following relationships are obtained:

Assumed Temperature, °F.	Reaction Rate Constant k_c, $(\text{liters})^2/(\text{g-mol})^2(\text{sec})$	Final Nitric Oxide, Mols (NO)	Fraction of NO Oxidized in tip. $\frac{(NO)_o - (NO)}{(NO)_o}$
-60	25,600	0.355	0.39
32	17,400	0.404	0.31

These calculations indicate that about 40% of the nitric oxide in the gaseous NO - O_2 mixture could be oxidized in the bubble tip at the low temperature of -60°F. At higher temperatures the amount oxidized would be less.

VELOCITIES AND REYNOLDS NUMBER FOR NO-NO_2 CONDENSER

(Data from Run E-4)

Entrance Conditions:

Gas flow is in proportion $NO:NO_2$, 60:40

NO = 750 gm./hr.
NO_2 = 500 gm./hr.
O_2 = 685 gm./hr.
Total 1935 gm./hr.

Assume mixed gases enter coil at 77°F. The molar volume at that temperature = 24,500 cc/gm. mol.

Since NO_2 is approx. 68% polymerized at 77°F, the ave. mol. wt. of $NO_2 - N_2O_4 = 92 \times 0.68 + 46 \times 0.32 = 77$.

If gas flow is W gm./hr., then

$$\text{for } NO, \quad \text{cc/min.} = \frac{W \times 24{,}500}{30 \times 60} = 10{,}200$$

$$NO_2, \quad \text{cc/min.} = \frac{W \times 24{,}500}{77 \times 60} = 2{,}650$$

$$O_2, \quad \text{cc/min.} = \frac{W \times 24{,}500}{32 \times 60} = 8{,}740$$

21,590 cc/min.

I.D. of 7 mm O.D. pyrex tubing = 0.197 in.

Cross sectional area of pyrex tubing = 0.000212 sq. ft.

Gas flow rate = 21,590/28,320 = 0.761 cfm.

Entrance velocity = 0.761/(60) (0.000212) = 60 ft/sec.

To calculate Reynolds number

$$Re = \frac{6.32\ W}{d\mu}$$ (Crane Co. "Fluid Flow" page 80)

W = rate of flow, lbs./hr.
d = I.D., inches
μ = absolute viscosity, centipoises

Assume μ = 0.017 c_p, then

$$Re = \frac{6.32 \times 1935}{454 \times 0.197 \times 0.017} = \underline{8{,}060}$$

Exit Velocity and Reynolds Number

Out exhaust	43 gm./hr. NO	=	1.43 gm. mol./hr.
	471 gm./hr. O_2	=	14.7 gm. mol./ hr.
Total	514 gm./hr.		16.13 gm. mol./hr.

At -60°F. Molal volume = 18,260 cc/min.

$$V_f = \frac{16.13 \times 18{,}260/28{,}320}{3600 \times 0.000212} = \underline{\underline{13.7 \text{ ft./sec}}}.$$

$$Re = \frac{6.32 \times 514}{454 \times 0.197 \times 0.017} = \underline{\underline{2140}}$$

REACTION RATE CONSTANT

For the purpose of computing the reaction rate constant for the NO oxidation reaction in the condenser coil, certain assumptions must be made:

1. All NO_2 introduced is immediately condensed.

2. Any NO_2 formed is immediately condensed so that the NO_2 exerts no pressure in the coil.

3. The disappearance of NO due to sorption has no effect on the reaction rate constant (k_p). The rate changes as the NO concentration changes since it is proportional to $k(p_{NO})^2(p_{O_2})$.

The reaction rate constant for the reaction $2\ NO + O_2 = 2NO_2$ may be expressed as follows:

$$-\frac{d(p_{NO})}{dt} = k_p\ (p_{NO})^2\ (p_{O_2})$$

$$\int_1^2 \frac{d(p_{NO})}{(p_{NO})^2\ (p_{O_2})} = -k_p t$$

where p_{NO} = Partial pressure NO, atm.
p_{O_2} = Partial pressure O_2, atm.
k_p = Reaction rate constant, $1/(\text{atm.})^2$ (sec.)
t = time, seconds.

Since neither (p_{NO}) nor (p_{O_2}) is constant, we must express (p_{O_2}) in terms of (p_{NO}).

Let $(p_{O_2}) = 1 - (p_{NO})$, then

$$-k_p t = \int_1^2 \frac{d(p_{NO})}{(p_{NO})^2 - (p_{NO})^3} = -\left[\frac{1}{(p_{NO})} + \ln\frac{1-(p_{NO})}{(p_{NO})}\right]_1^2$$

Figure 34, based on I.C.T. data (2), consists of a plot of this reaction rate constant, k_p, vs. reciprocal of the absolute temperature in °R.

EFFECTIVE FLUID TEMPERATURES INSIDE CONDENSER COIL

The reaction rate equation derived in the previous section is used to calculate values for k_p and effective fluid temperatures for the two runs E-4 and E-7.

Nomenclature Used in Calculation

V_o = initial gas velocity

V_f = final or exit gas velocity

$$V_{ave.} = \frac{V_o + V_f}{2}$$

V_{eff} = mean or effective velocity calculated at $T_{eff.}$

T_{eff} = temperature defining average k_p

Example 1 (Run E-4)

Entrance conditions (assume 77°F.):

$$\begin{aligned} NO &= 750 \text{ gm./hr.} = 25.0 \text{ gm. mol./hr.} \\ O_2 &= 685 \text{ gm./hr.} = 21.4 \text{ gm. mol./hr.} \\ & \qquad\qquad\qquad\quad \overline{46.4} \text{ gm. mol./hr.} \end{aligned}$$

$$(p_{NO})_1 = \frac{25.0}{46.4} = 0.539 \text{ atm.}$$

$$V_o = \frac{46.4 \times 24{,}500/28{,}320}{3600 \times 0.000212} = 52.5 \text{ ft./sec.}$$

1st Trial

Exit conditions (assume -60°F.):

$$\begin{aligned} NO &= 43 \text{ gm./hr.} = 1.43 \text{ gm. mol./hr.} \\ O_2 &= 471 \text{ gm./hr.} = \underline{14.7} \text{ gm. mol /hr.} \\ & \qquad\qquad\qquad\quad 16.13 \text{ gm. mol./hr.} \end{aligned}$$

$$(p_{NO})_2 = \frac{1.43}{14.7} = 0.0972 \text{ atm.}$$

$$V_f = \frac{16.13 \times 18{,}260/28{,}320}{3600 \times 0.000212} = 13.7 \text{ ft./sec.}$$

Assume V is linear, and $V_{ave.} = \frac{V_o + V_f}{2}$

$$V_{ave.} = 33.1 \text{ ft./sec.}$$

$$\text{Coil length} = 8\pi \times 3/12 = 6.3 \text{ ft.}$$

$$t = \frac{6.3}{33.1} = 0.190 \text{ sec.}$$

$$\text{and } k_p t = \left[\frac{1}{0.0972} + \ln\frac{0.9028}{0.0972}\right] - \left[\frac{1}{0.539} + \ln\frac{0.461}{0.539}\right] = 10.8(\text{atm})^{-2}$$

$$k_p = 10.8/0.190 = 56.7(\text{atm})^{-2}(\text{sec})^{-1}.$$

From Figure 34, this indicates an effective temperature in the coil of of -13°F.

For the next trial, use an effective velocity that is proportional to the relative temperatures rather than an average velocity.

2nd Trial

$$V_o - V_f = 38.8 \text{ ft./sec.}$$

$$V_{eff} = 52.5 - 38.8\left[\frac{77-(-13)}{77-(-60)}\right] = 27.0 \text{ ft./sec.}$$

$$t = \frac{6.3}{27.0} = 0.233 \text{ sec.}$$

$$k_p = 10.8/0.233 = 46.4(\text{atm})^{-2}(\text{sec})^{-1}$$

$$T_{eff} = +5°\text{F.}$$

3rd Trial

$$V_{eff} = 52.5 - 38.8\left[\frac{77-(+5)}{77-(-60)}\right] = 32.1 \text{ ft./sec.}$$

$$t = \frac{6.3}{32.1} = 0.196 \text{ sec.}$$

$$k_p = 10.8/0.199 = 55.0(\text{atm})^{-2}(\text{sec})^{-1}$$

$$T_{eff} = -9°\text{F.}$$

4th Trial

$$V_{eff} = 52.5 - 38.8 \left[\frac{77-(-9)}{77-(-60)}\right] = 28.1 \text{ ft./sec.}$$

$$t = \frac{6.3}{28.1} = 0.224 \text{ sec.}$$

$$k_p = 10.8/0.224 = 48.2(\text{atm.})^{-2}(\text{sec})^{-1}$$

$$T_{eff} = +1°\text{F.}$$

It is felt that a sufficiently accurate value of T_{eff} for this calculation can be found by using an average "t" from trials 3 and 4.

$$t = \frac{0.196 + 0.224}{2} = 0.210 \text{ sec.}$$

$$k_p = \frac{10.8}{0.210} = 51.4(\text{atm})^{-2}(\text{sec})^{-1}$$

$$T_{eff} = \underline{\underline{-4°\text{F}}}.$$

Example 2 (Run E-7)

Entrance conditions (assume 77°F):

$$\begin{aligned} NO &= 1200 \text{ gm./hr.} = 40.0 \text{ gm. mol./hr.} \\ O_2 &= 1095 \text{ gm./hr.} = \underline{34.2} \text{ gm. mol./hr.} \\ & \qquad\qquad\qquad\quad\;\; 74.2 \text{ gm. mol./hr.} \end{aligned}$$

$$(p_{NO})_1 = \frac{40.0}{74.2} = 0.539 \text{ atm.}$$

$$V_o = \frac{74.2 \times 24{,}500/28{,}320}{3600 \times 0.000212} = 84.0 \text{ ft./sec.}$$

Exit conditions (assume -40°F.):

$$\begin{aligned} NO &= 527 \text{ gm./hr.} = 17.6 \text{ gm. mol./hr.} \\ O_2 &= 929 \text{ gm./hr.} = \underline{29.0} \text{ gm. mol./hr.} \\ & \qquad\qquad\qquad\;\; 46.6 \text{ gm. mol./hr.} \end{aligned}$$

$$(p_{NO})_2 = \frac{17.6}{46.6} = 0.376 \text{ atm.}$$

$$V_f = \frac{46.6 \times 19{,}130/28{,}320}{3600 \times 0.000212} = 41.3 \text{ ft./sec.}$$

$$V_{ave} = 62.6 \text{ ft./sec.}$$

$$t = \frac{6.3}{62.6} = 0.1005 \text{ sec., and}$$

$$k_p t = \left[\frac{1}{0.376} + \ln\frac{0.624}{0.376}\right] - \left[\frac{1}{0.539} + \ln\frac{0.461}{0.539}\right] = 1.47\ (\text{atm})^{-2}$$

$$k_p = \frac{1.47}{0.1005} = 14.6(\text{atm})^{-2}(\text{sec})^{-1}$$

From Figure 34, $T_{eff} = \underline{\underline{138°\text{F}.}}$

This indicates an effective temperature in the coil higher than the entrance temperature. The effective velocity must also be higher, and a linear $V_{ave.}$ is no longer valid. Therefore, in succeeding trials the effective velocity will be used in the same proportions as the relative temperatures.

2nd Trial

$$V_{eff} = \frac{598°\text{R}}{537°\text{R}} \times 84 = 93.5 \text{ ft./sec.}$$

$$t = \frac{6.3}{93.5} = 0.0675 \text{ sec.}$$

$$k_p = \frac{1.47}{0.0675} = 21.8(\text{atm})^{-2}(\text{sec})^{-1}$$

$$T_{eff} = 84°\text{F}$$

3rd Trial

$$V_{eff} = \frac{544}{537} \times 84 = 85 \text{ ft./sec.}$$

$$t = \frac{6.3}{85} = 0.074 \text{ sec.}$$

$$k_p = \frac{1.47}{0.074} = 19.8(\text{atm})^{-2}(\text{sec})^{-1}$$

$$T_{eff} = 95°\text{F}$$

4th Trial

$$V_{eff} = \frac{555}{537} \times 84 = 86.8 \text{ ft./sec.}$$

$$t = \frac{6.3}{86.8} = 0.0726 \text{ sec.}$$

$$k_p = \frac{1.47}{0.0726} = 20.2(\text{atm})^{-2}(\text{sec})^{-1}$$

$$T_{eff} = \underline{\underline{94°\text{F}.}}$$

Example 1 (Run E-4) for which the effective temperature is -4°F, represents a heat exchanger running at full capacity. Example 2 (Run E-7) demonstrates a heat exchanger running about 100% over capacity; or the first 1/2 of an hypothetical heat exchanger coil is under investigation. The effective temperature in this case was 94°F. From the results of the above calculations, one can conclude that the temperature profile through the length of the coil is such that a rapid rise in temperature occurs immediately after mixing, due to the oxidation of a large quantity of NO. This is followed by a decrease in temperature as the quantity of NO available for oxidation decreases, and heat is lost to the surrounding bath.

APPENDIX IV

SORPTION AND CONDENSATION CALCULATIONS

Page

Calculation of Per Cent Nitric Oxide Sorbed. 52

Calculation of Per Cent Nitric Oxide Condensed and Exhausted . . . 53

APPENDIX IV

SORPTION AND CONDENSATION CALCULATIONS

PER CENT NITRIC OXIDE SORBED

This calculation of the per cent gaseous nitric oxide sorbed by the liquid mixture requires initial and final weights and nitric oxide concentrations of the liquid mixture. The difference between the initial and final weights of nitric oxide gives the weight of nitric oxide sorbed. This weight, divided by the weight of nitric oxide bubbled, gives the per cent nitric oxide sorbed.

The procedure followed is to calculate grams of liquid sample from the measured heights of liquid in the sample flask, using flask calibration data and the temperature-density curves in Appendix II. These weights multiplied by the nitric oxide concentrations from freezing point determinations give the weight of nitric oxide in the liquid sample before and after bubbling. The weight input of nitric oxide is calculated from the volume of gas bubbled. A sample calculation follows, using data from Run B-23:

Experimental Data

Nominal column height = 6 inches.
Liquid temperature = -60°F.
Bubbling time = 60 minutes
Freezing point before bubbling = 7.27x(-0.4) = -2.91 mv; equiv. to -120°F or 30.3% NO
Freezing point after bubbling = 6.49x(-0.4) = -2.60 mv; equiv. to -102.5°F or 28.8% NO.
Density of liquid before bubbling: 1.509 gm/cc
Density of liquid after bubbling: 1.519 gm/cc
Liquid heights before bubbling = 5-1/4 inches, equivalent to 46.9 gm.
Liquid height after bubbling = 5-13/16 inches, equivalent to 52.6 gm.
Nitric oxide bubbled = 50 std. cc/min., equiv. to $\frac{50 \times 30 \times 60}{24,200}$ or 3.72 gm.
Oxygen bubbled = 37.5 std. cc/min., equiv. to $\frac{37.5 \times 32 \times 60}{24,200}$ or 2.98 gm.

Calculation

Nitric oxide present after bubbling = 52.6 x 0.288 = 15.15 gm.
Nitric oxide present before bubbling = 46.9 x 0.303 = 14.21 gm.
Nitric oxide sorbed = 15.15 - 14.21 = 0.94 gm.

$$\text{Percentage of nitric oxide sorbed} = \frac{0.94}{3.72} = \underline{\underline{25.2\%}}$$

CALCULATION OF PER CENT NITRIC OXIDE CONDENSED AND PER CENT NITRIC OXIDE EXHAUSTED.

Sample Calculation for Run E-7

Flow Rates:

NO = 1200 gm./hr.
NO_2 = 800 gm./hr.
O_2 = 1095 gm./hr.

Running time = 7 min.
Product Weight = 191 gm.
Conc. by freezing pt. = 22.0 wt. % NO

Product = 191 x 60/7 = 1640 gm./hr.
NO in product = 1640 x 0.220= 361 gm./hr.

If X = gm./hr. NO exhausted, then

$$(1200-361-X)\ (46/30) + 800 + 361 = 1640$$

Solving for X,

$$(1200-361)\ (46/30) + 800 + 361 = 1640 + (46/30)X$$

X = 527 gm./hr. NO exhausted.

Flow of nitrogen oxides as NO

$$= (1200) + (800)\ (30/46) = 1721 \text{ gm./hr.}$$

Per Cent NO exhausted (expressed as % of total nitrogen oxides as NO)
= 527/1721 = 30.6%.

Per Cent NO condensed (calculated from the net flow of nitric oxide into the condenser to compare with bubbling runs)
=361/(1721-527) = 30.2%.

APPENDIX V

HEAT LOADS AND REFRIGERATION REQUIREMENTS

Page

Measurement of Heat Evolved in Condensation of Mixed Gases. 54

Calculation of Theoretical Heat Evolution in Condensation of Mixed Gases 55

Refrigeration Requirements for a Commercial Sized Plant 56

APPENDIX V

HEAT LOADS AND REFRIGERATION REQUIREMENTS

MEASUREMENT OF HEAT EVOLVED IN CONDENSATION OF MIXED GASES (RUN F-21)

Flow rate of entering gases:

NO = 1000 gm/hr
NO_2 = 667 gm/hr
O_2 = 915 gm/hr

Product: (Upper and lower reservoirs combined)

1830 gm/hr 25.2% NO

Time - Temperature:

0 min -79°F
6.0 min -63°F
Temperature span = 16°F
Ave. Temperature = -71°F

Wt. of Acetone in Bath: 31.75 lb.

Calorimeter constant:

$$\frac{(31.75 \text{ lb. Acetone})(0.467 \text{ Btu/lb-°F})(7.4\text{°F/hr})}{60 \text{ min/hr}} = 1.8 \text{ Btu/min}$$

Reaction heat load:

$$\frac{(31.75)(0.467)(16\text{°F})}{6.0 \text{ min}} = 39.5 \text{ Btu/min}$$

Net Heat load: 39.5 - 1.8 = $\underline{\underline{37.7 \text{ Btu/min}}}$

CALCULATION OF THEORETICAL HEAT EVOLUTION IN THE CONDENSATION OF MIXED GASES (RUN F-21)

Entering flow rates at 70°F.:

NO = 1000 gm/hr = 0.0368 lb/min
NO_2 = 667 gm/hr = 0.0245 lb/min
O_2 = 915 gm/hr = 0.0337 lb/min

Product (liquid at -71°F):

NO = (1830) (0.252) = 461 gm/hr = 0.01696 lb/min
NO_2 = 1830-461 = 1369 gm/hr = 0.0502 lb/min

NO oxidized: (0.0502 - 0.0245) 30/46 = 0.01675 lb/min

The following calculation is made using the thermodynamic values indicated:

1. Heat of reaction $NO(g) + 1/2\ O_2(g) = NO_2\ (g)$ (70°F)
   - 24,400 Btu/#mole [K. K. Kelley, U. S. Bur. of Mines, RI 3776 (1944)] (3)
2. Heat of polymerization $2NO_2\ (g) = N_2O_4\ (g)$ (70°F)
   - 12,300 Btu/#mole [K. K. Kelley, U. S. Bur. of Mines, RI 3776 (1944)] (3)
3. Pseudo-Heat of vaporization of Nitric Oxide at 70°F:
   2,480 Btu/#mole [I.C.T. VII, pg. 239] (4)
4. Heat of vaporization of N_2O_4 at 70°F:
   16,400 Btu/#mole [Giauque and Kemp, J. Chem. Phys., 6, 40 (1938)] (5)
5. Specific heat of liquid NO-NO_2 mixture from 70°F to -71°F = 0.6 Btu/lb-°F

1. (24,400) (0.01675) 1/30 = 13.6 Btu/min
2A. (12,300) (0.0245) (0.28) 1/46 = 1.8 "
2B. (12,300) (0.0502 - 0.0245) 1/46 = 6.9 "
3. (2,480) (0.01696) 1/30 = 1.4 "
4. (16,400) (0.0502) 1/92 = 9.0 "
5. (0.6) (141) (0.0672) = 5.7 "

38.4 Btu/min

REFRIGERATION REQUIREMENTS FOR A COMMERCIAL SIZED PLANT

Basis: 40 ton/day HNO_3, 90% recovery.

Assume a liquid product at -90°F with 28.5% NO

$$NO = \frac{(30)\,(40)\,(2000)}{(63)\,(24)\,(60)\,(0.9)} = 29.4 \text{ lb/min} = 0.979\# \text{ moles/min}$$

$$O_2 = \frac{(3)\,(0.979)}{4} = 0.734\# \text{ moles/min} = 23.5 \text{ lb/min}$$

Assume that these gases are cooled in a heat exchanger to 200°F, and that the composition of the gases at the entrance to the condenser is:

NO = 20.5 lb/min
NO_2 = 13.7 lb/min
O_2 = 18.7 lb/min

10% NO exhausted (and returned to process) = 0.1 X 29.4 = 2.94 lb/min

38% NO condensed (From Figure 34) = (0.38) (0.9) (29.4) = 10.05 lb/min

Liquid Product:

NO = 10.05 lb/min
NO_2 = 25.20 lb/min

NO oxidized = 30/46 (25.2 - 13.7) = 7.5 lb/min

(Neglect the cooling of unreacted gases)

1. Cool gases from 200°F to 70°F: — Btu/min

$(20.5)\ (0.23)\ (130) = 615$
$(13.7)\ (0.27)\ (130) = 480$
$(18.7)\ (0.22)\ (130) = 535$

2. Heat of oxidation of NO at 70°F:

$(24{,}400)\ (7.5)\ (1/30) = 6{,}100$

3. Heat of polymerization of NO_2 at 70°F (No N_2O_4 at 200°F):

$(12{,}300)\ (25.2)\ 1/46 = 6{,}740$

4. Heat of condensation of NO at 70°F

$(2480)\ (10.05)\ (1/30) = 830$

5. Heat of condensation of N_2O_4 at 70°F:

$(16{,}400)\ (25.2)\ (1/92) = 4{,}500$

6. Cool liquid from 70°F to -90°F:

$(0.6)\ (35.25)\ (160) = \underline{3{,}390}$

Total 23,190 Btu/min

$$\text{Tons of refrigeration} = \frac{(23{,}190)\ (60)}{12{,}000} = \underline{\underline{116\ \text{Tons}}}$$

LITERATURE CITED

1 Lindsay, W. N., Preparation of Nitric Oxide - Nitrogen Dioxide Mixtures from the FMC Nitrogen Fixation Furnace. WADC TR 54-378, 1954, 179.pp. (FMC Final Report CR-CH 2065)

2 International Critical Tables. McGraw-Hill Book Co., New York, Vol. 7, 1930, p. 117.

3 Kelley, K. K., Energies and Equilibria in the Decomposition of Nitrates of Manganese, Magnesium, Calcium, Barium, and Aluminum and Reactions of Nitrogen Dioxide. U. S. Bur. Mines, Rept. of Investigations 3776, 1944, 33 pp.

4 International Critical Tables. Vol. 7, 1930, p. 239.

5 Giauque, W. F. and Kemp, J. D., The Entropies of Nitrogen Tetroxide and Nitrogen Dioxide. The Heat Capacity from 15°K. to the Boiling Point. The Heat of Vaporization and the Vapor Pressure. The Equilibria $N_2O_4 = 2NO_2 = 2NO + O_2$. J. Chem. Phys. Vol. 6, 1938, pp. 40-52.

GENERAL REFERENCES

Brice et al, Preparation of Nitric Oxide - Nitrogen Dioxide Mixtures from the FMC Nitrogen Fixation Furnace by Chilling. Food Machinery & Chemical Corp. Bimonthly Progress Reports under Contract AF 18(600)-34,, Supplemental Agreement No. S3(53-908): No. 1, CR-CH 2051, July 1953; No. 2, CR-CH 2052, Sep. 1953; No. 3, CR-CH 2058, Nov. 1953; No. 4, CR-CH 2063, Jan. 1954; No. 5, CR-CH 2142, March 1954.

UNCLASSIFIED

~~CONFIDENTIAL~~

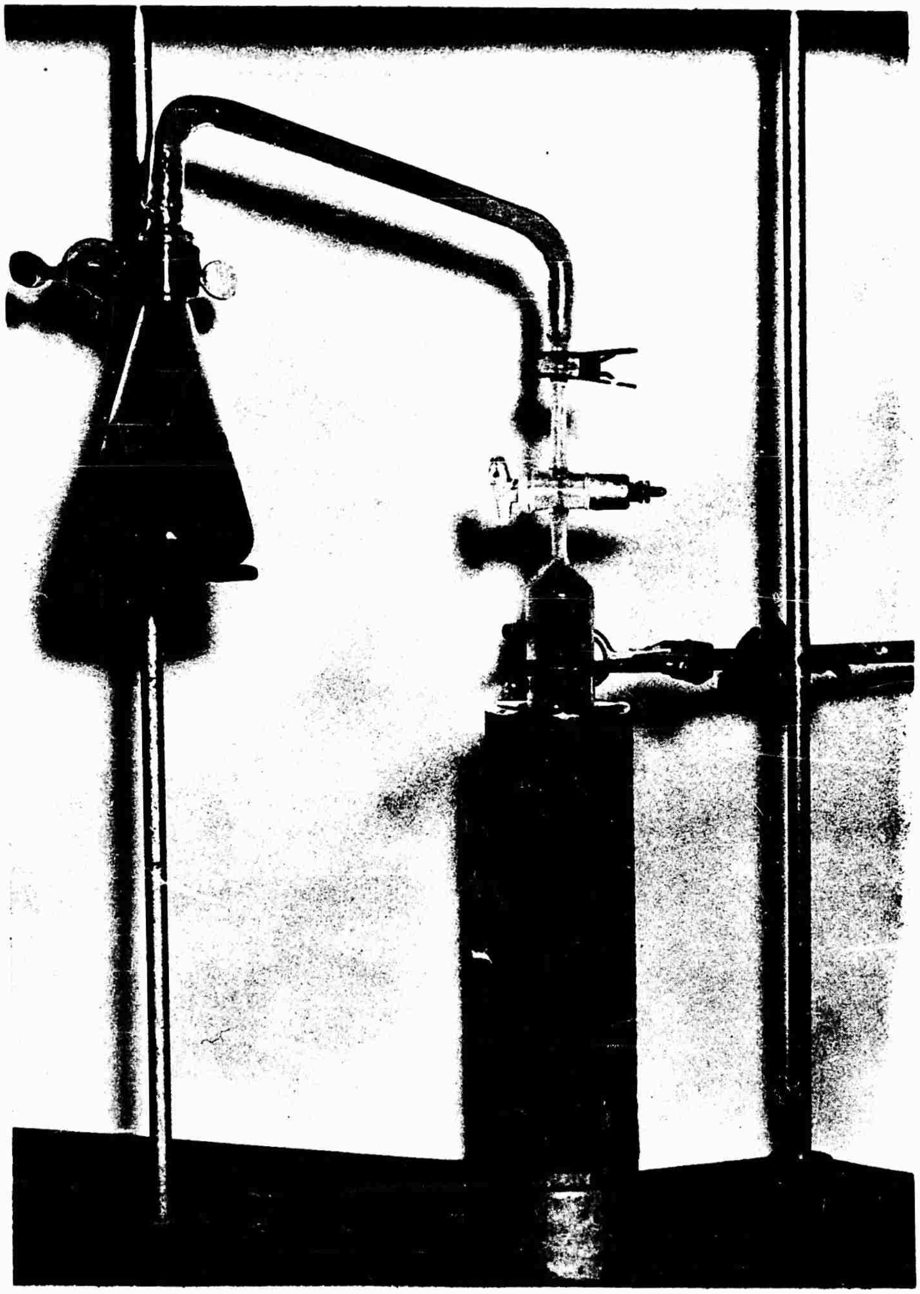


FIG. 1. APPARATUS FOR PURIFICATION OF NITROGEN DIOXIDE BY DISTILLATION.

CON[redacted]L

FIG. 2. STAINLESS STEEL RESERVOIR FOR STORAGE OF LIQUID MIXED OXIDES.

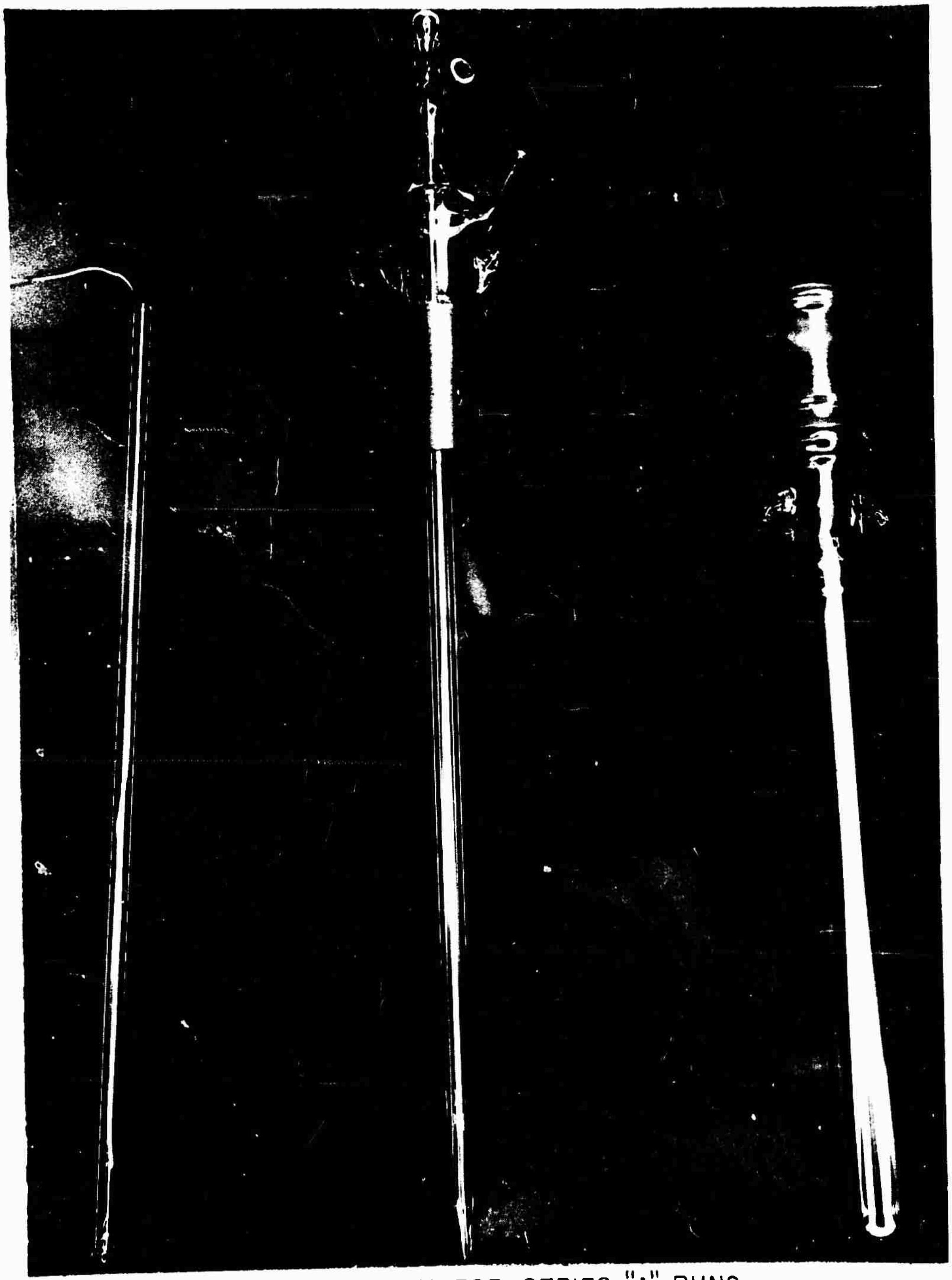


FIG. 3. BUBBLING ASSEMBLY FOR SERIES "A" RUNS.
THERMOCOUPLE - LEFT, BUBBLING TIP - CENTER, AND GLASS CONTAINER

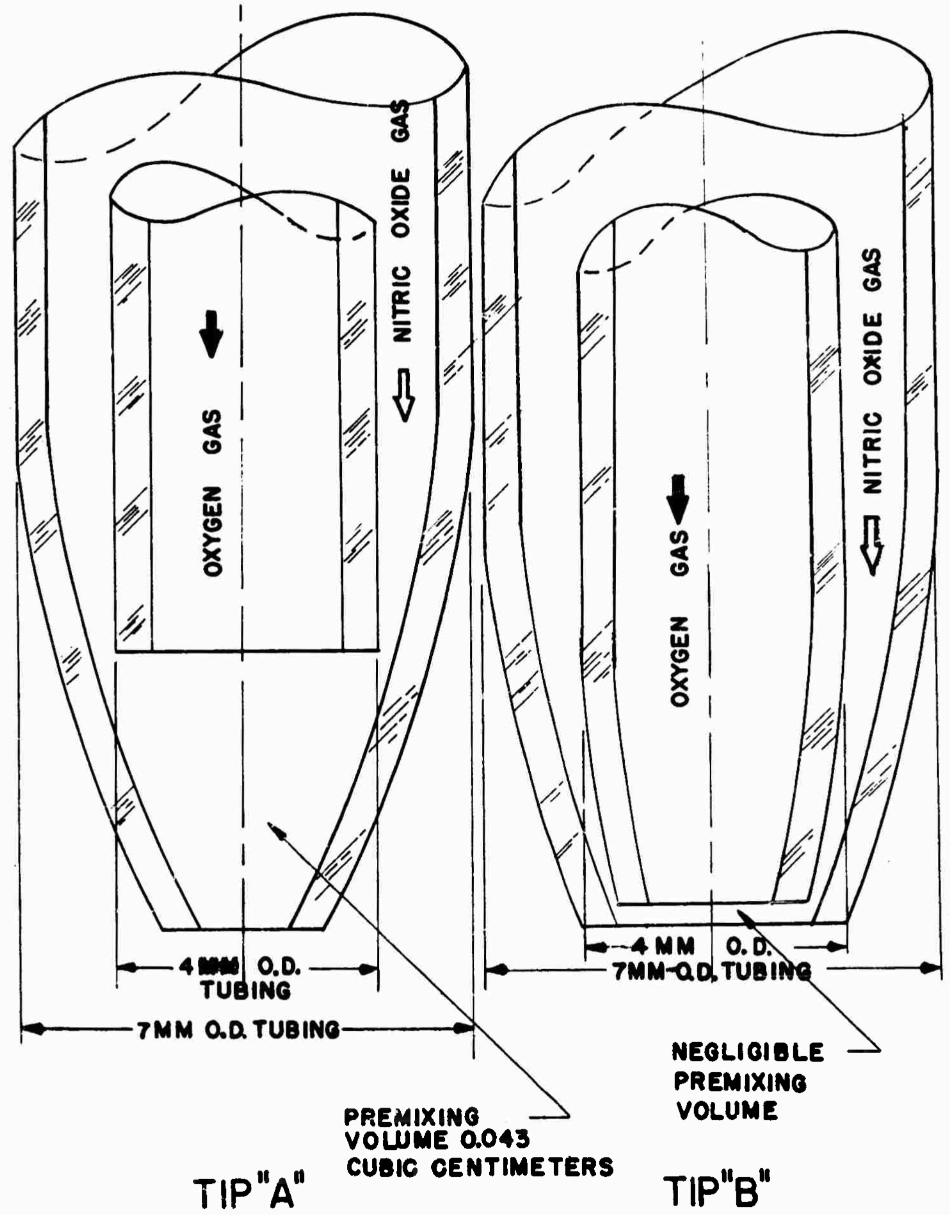


FIG. 4. SCHEMATIC CROSS-SECTIONAL SKETCHES OF BUBBLING TIPS "A" AND "B".

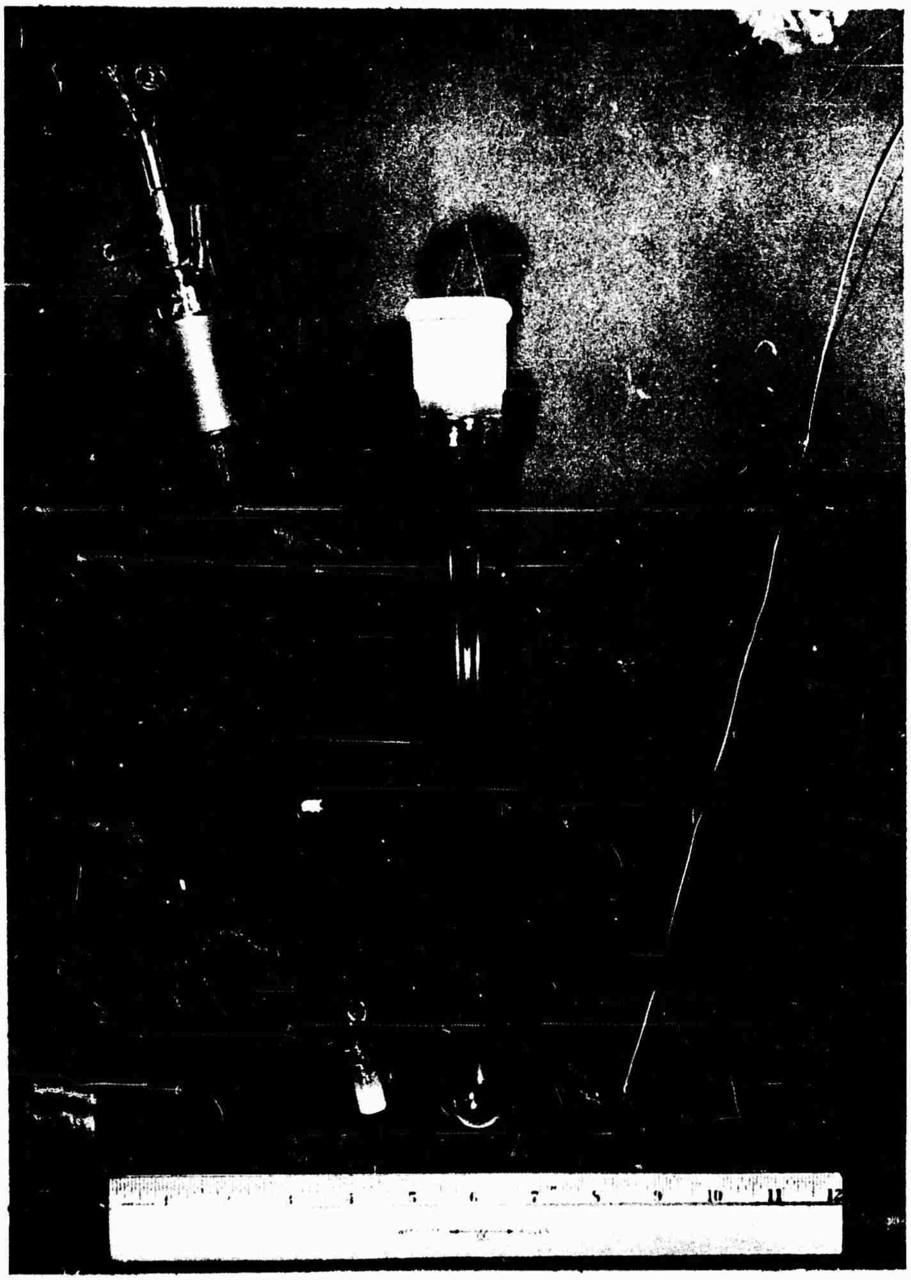


FIG. 5. BUBBLING ASSEMBLY FOR SERIES "C" RUNS.

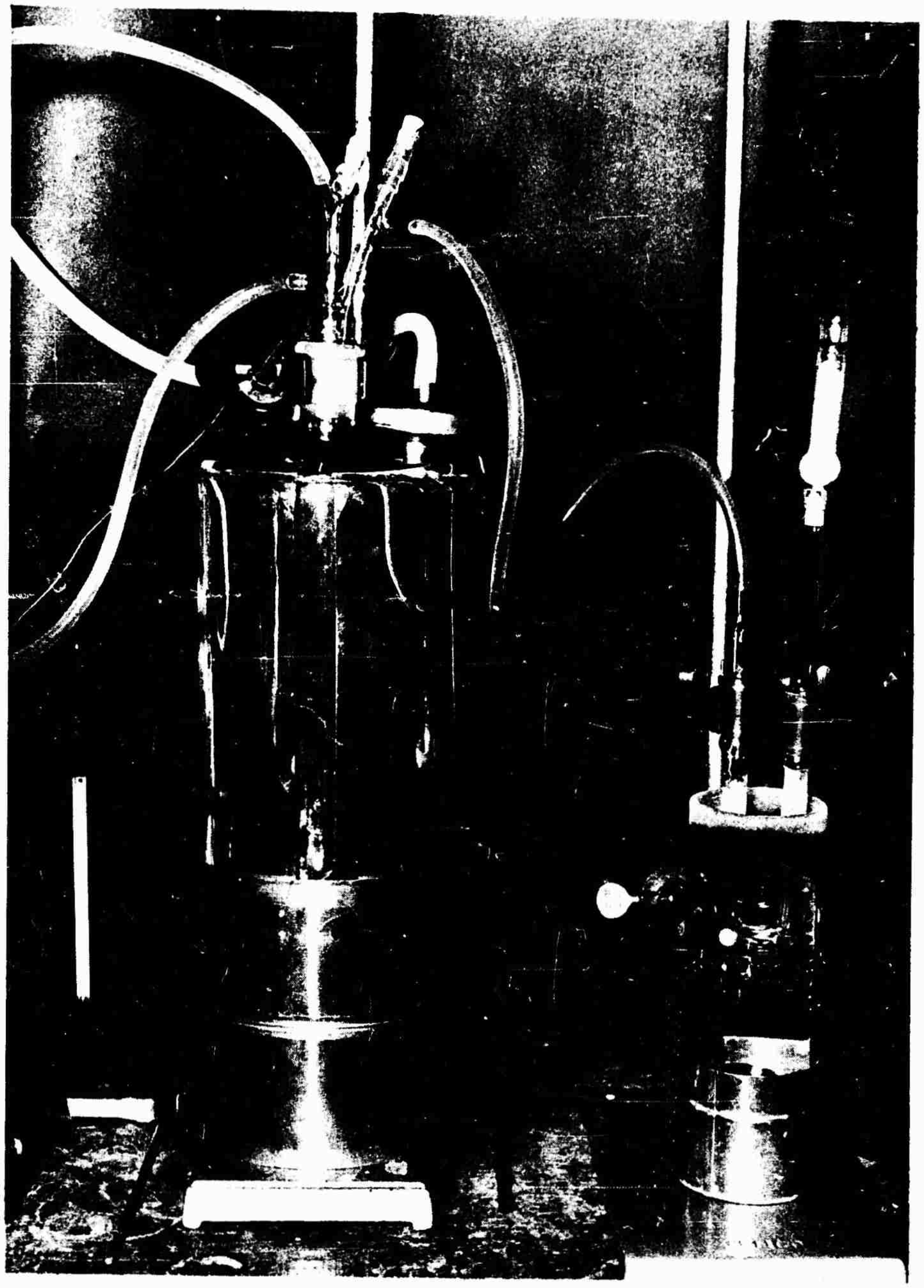


FIG. 6. EQUIPMENT SET UP FOR SERIES "C" BUBBLING RUNS.

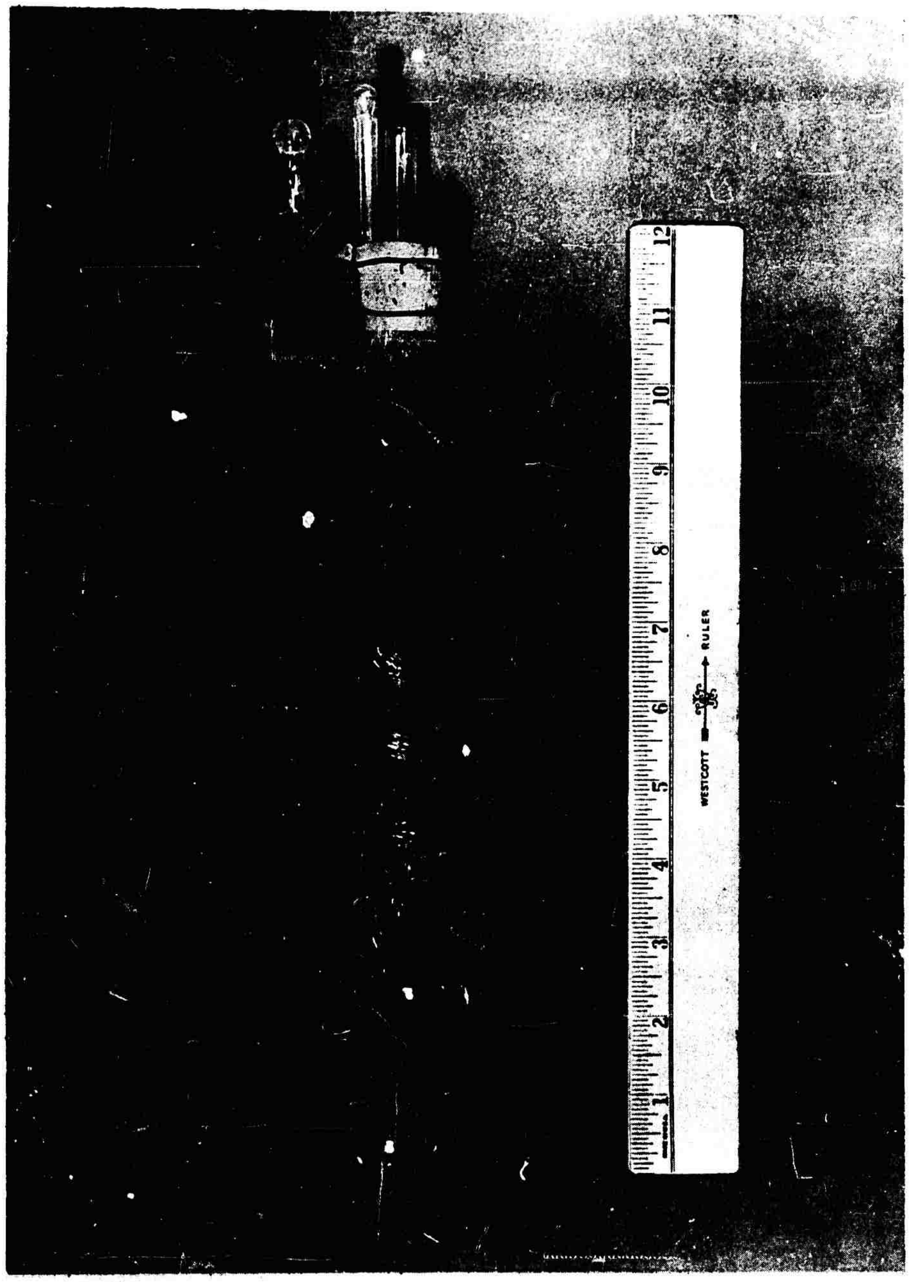


FIG. 7. GLASS CONDENSER FOR SERIES "D" CONDENSATION RUNS.

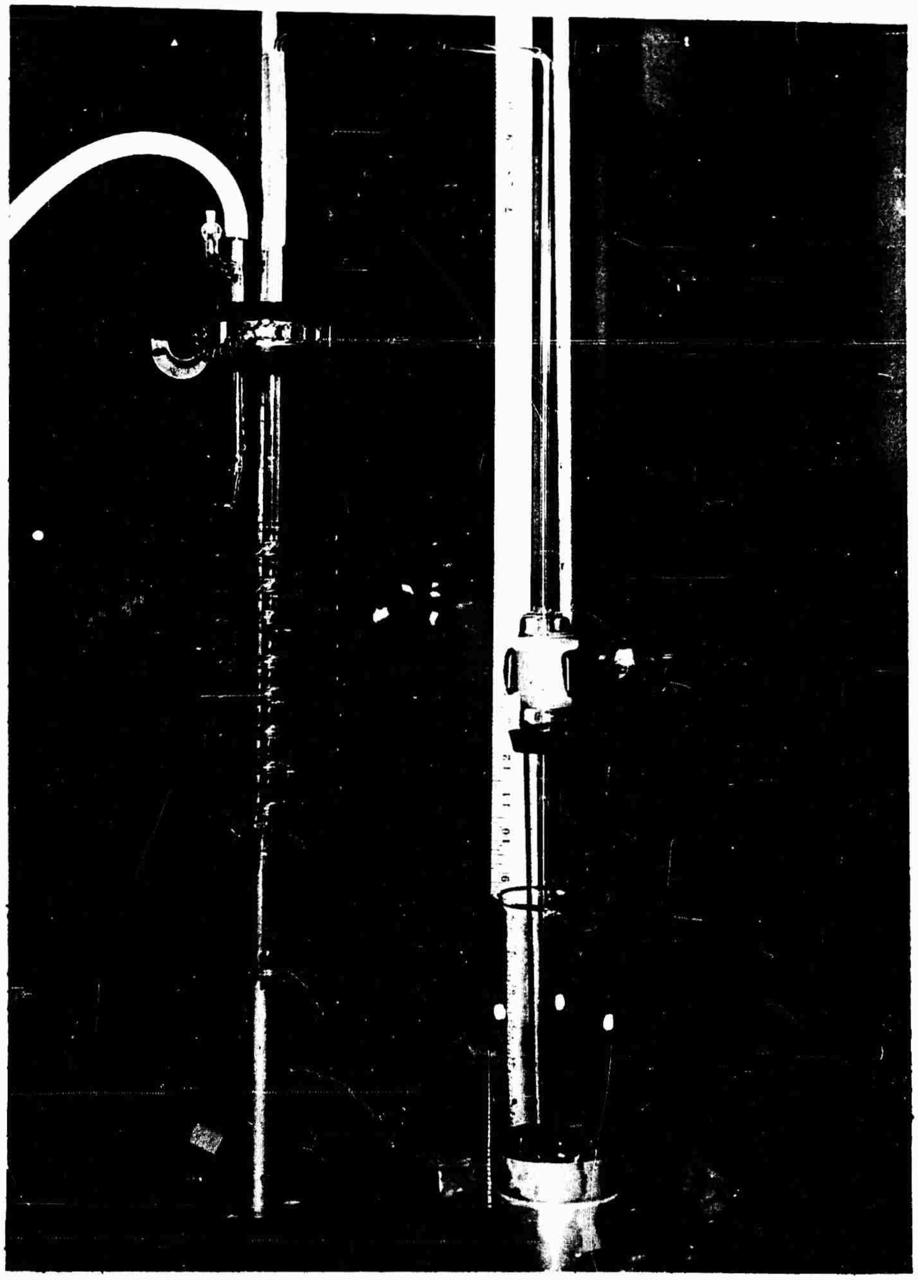


FIG. 8. GLASS CONDENSER, TRANSFER TUBING AND SAMPLE FLASK FOR SERIES "E" CONDENSATION RUNS.

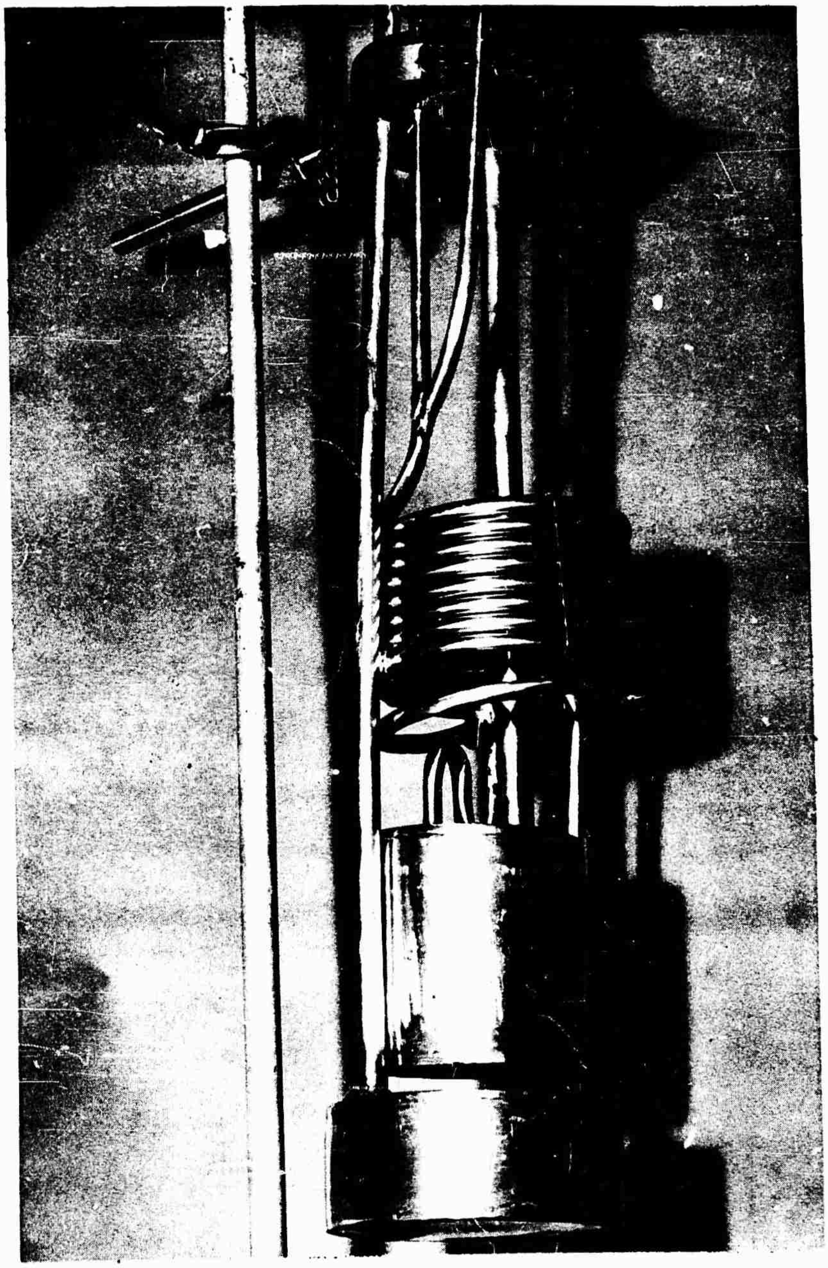


FIG. 9A. STAINLESS STEEL CONDENSER COIL.

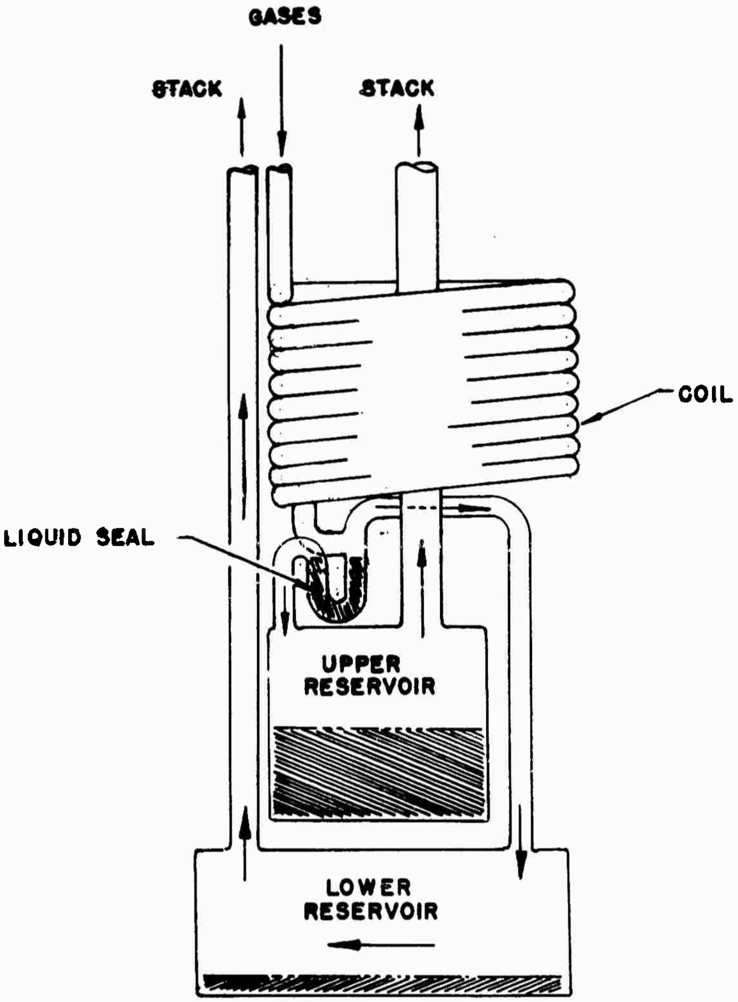


FIG. 9B. DIAGRAM OF FLOWS IN STAINLESS STEEL CONDENSER.

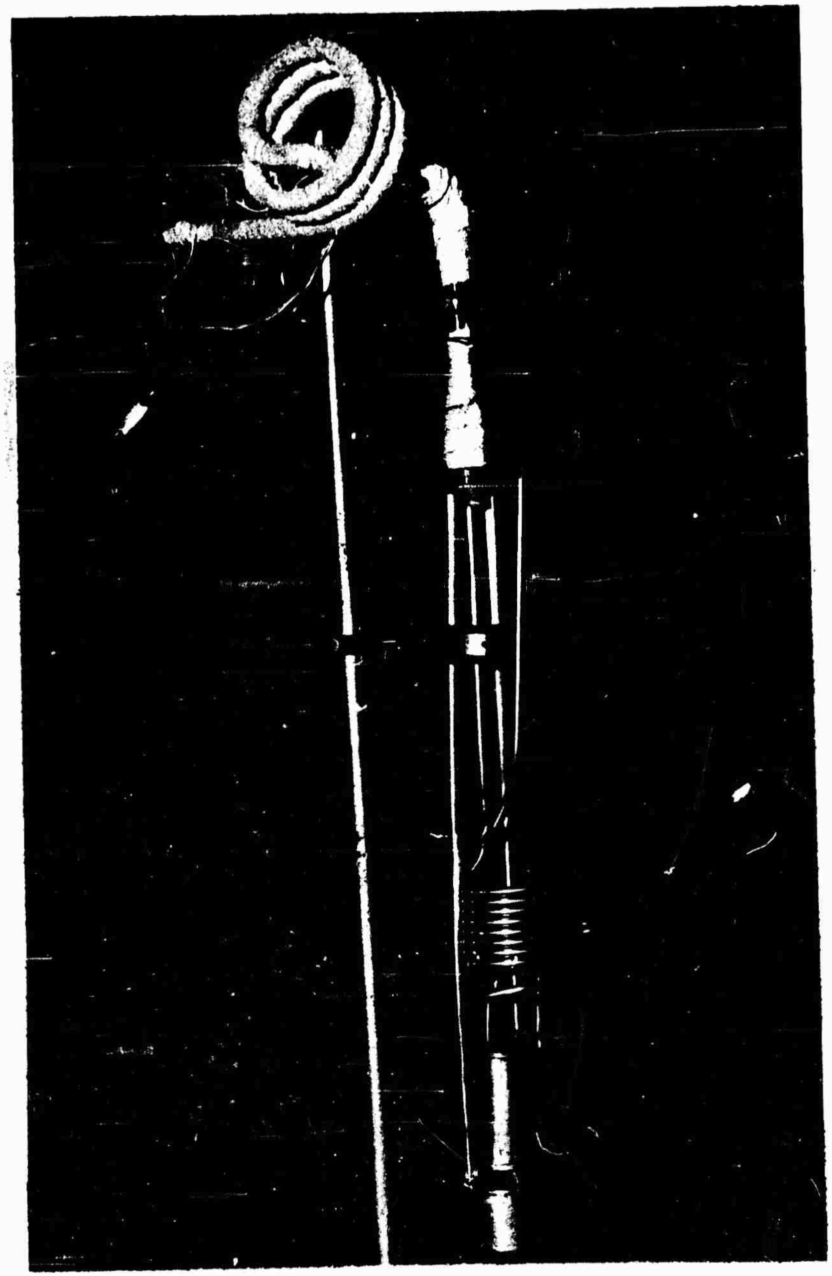


FIG. 10. STAINLESS STEEL CONDENSER WITH GAS PREHEATER ATTACHED.

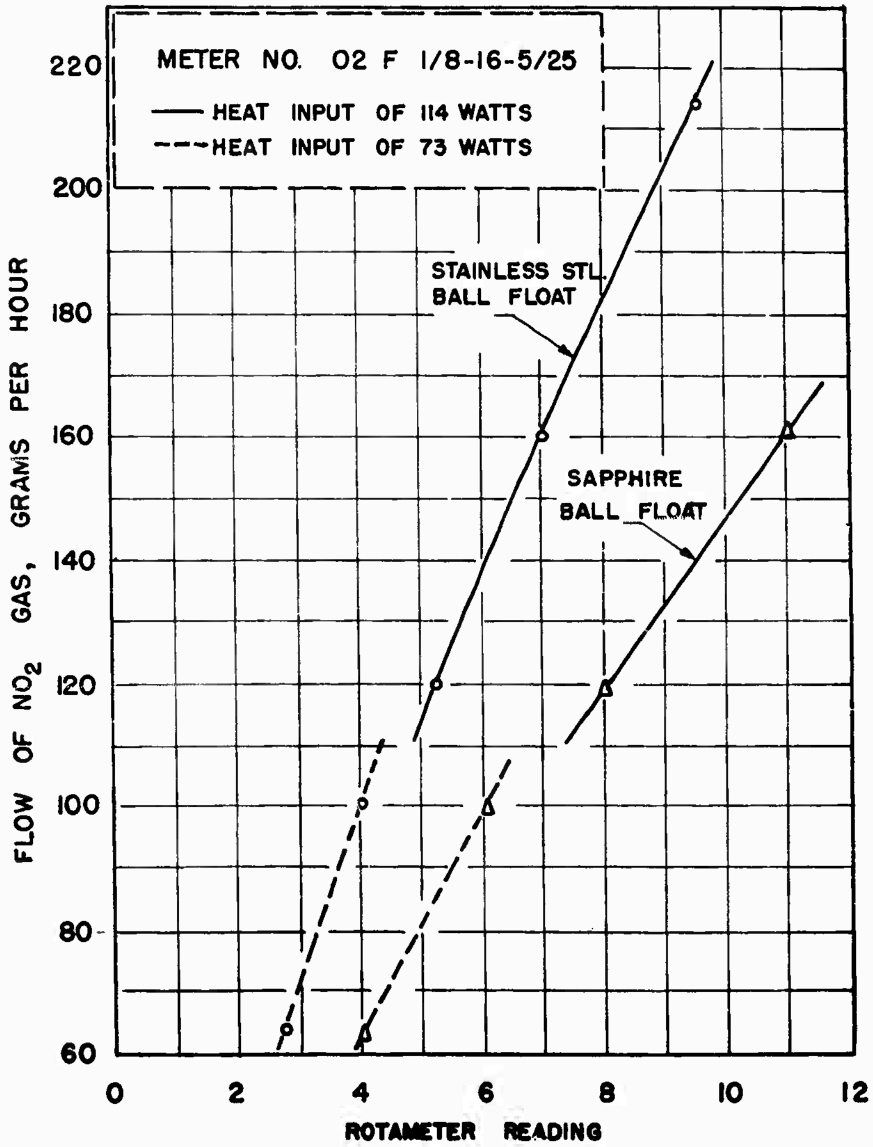


FIG. 11 A. CALIBRATION CURVES OF ROTAMETER 02 F 1/8-16-5/25 FOR NITROGEN DIOXIDE GAS.

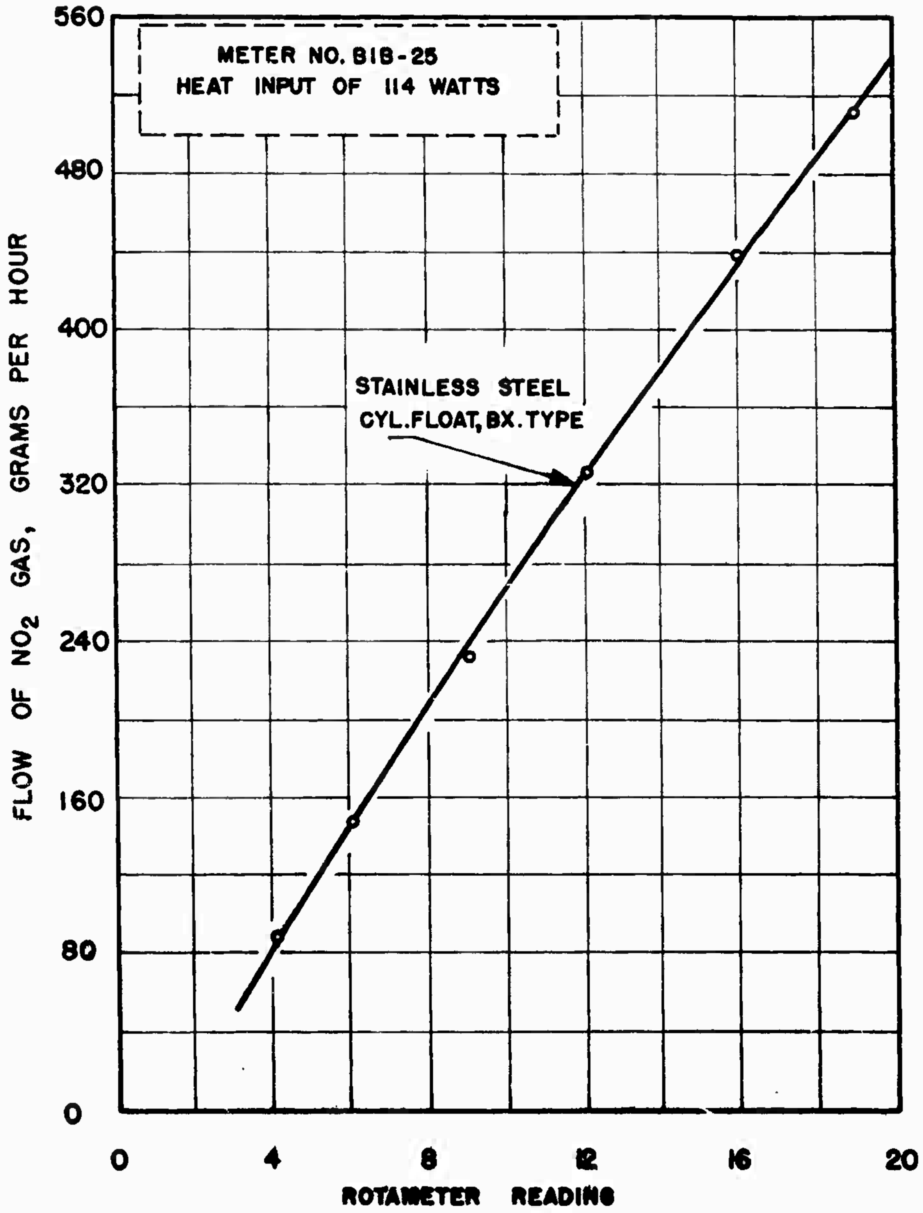


FIG. 11B. CALIBRATION CURVE OF ROTAMETER B1B-25 FOR NITROGEN DIOXIDE GAS.

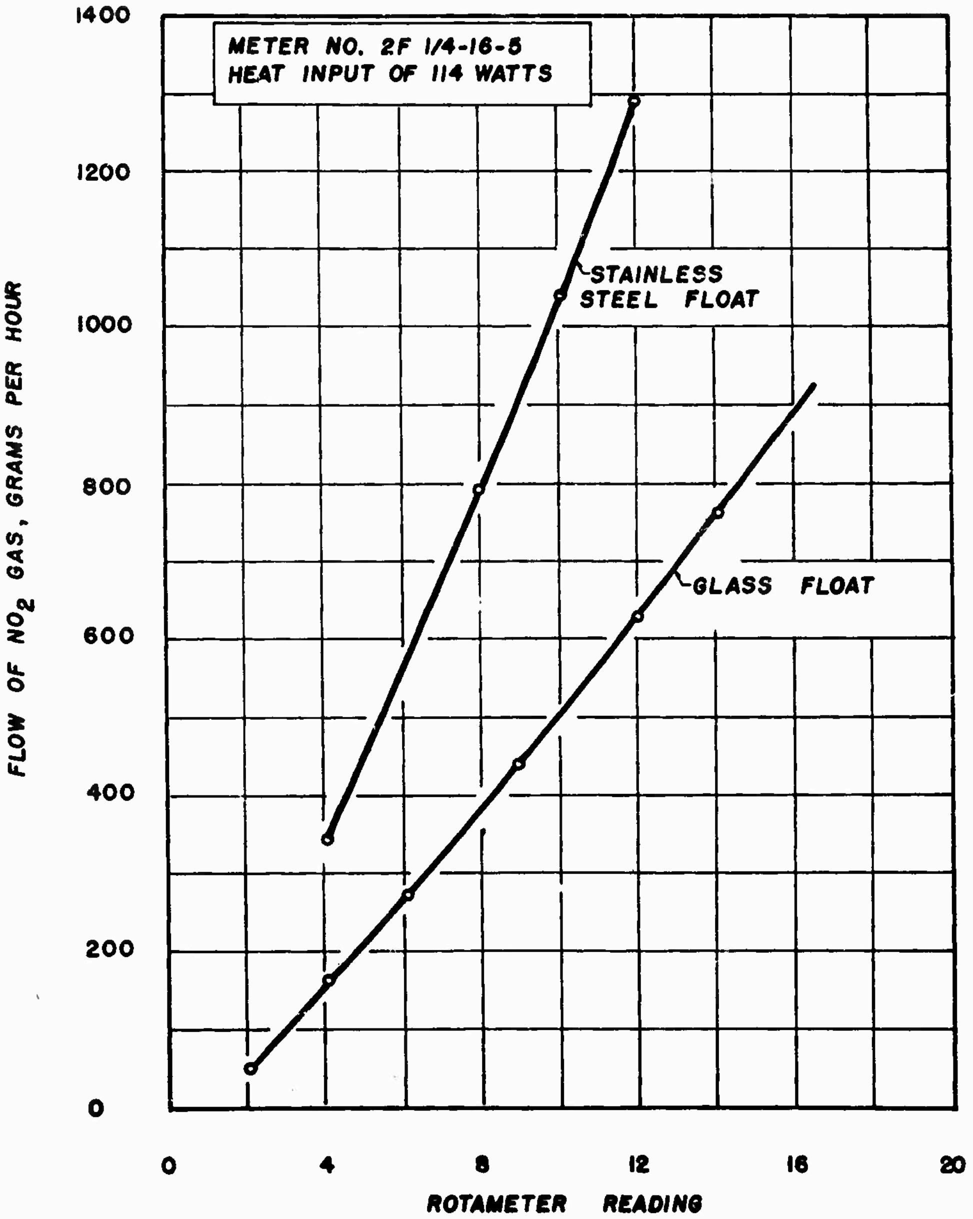


FIG. 11C. CALIBRATION CURVE OF ROTAMETER 2F 1/4-16-5 FOR NITROGEN DIOXIDE GAS.

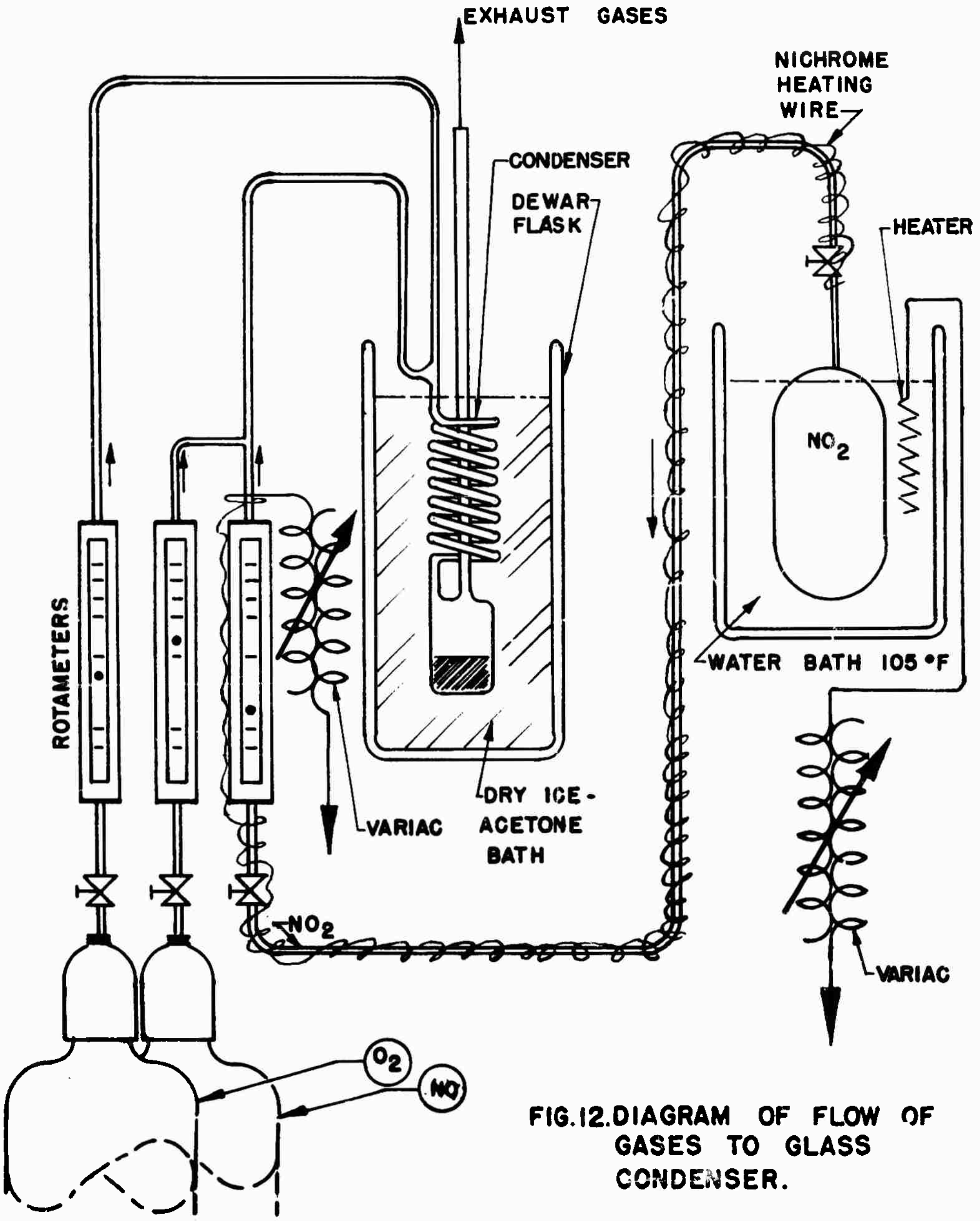


FIG. 12. DIAGRAM OF FLOW OF GASES TO GLASS CONDENSER.

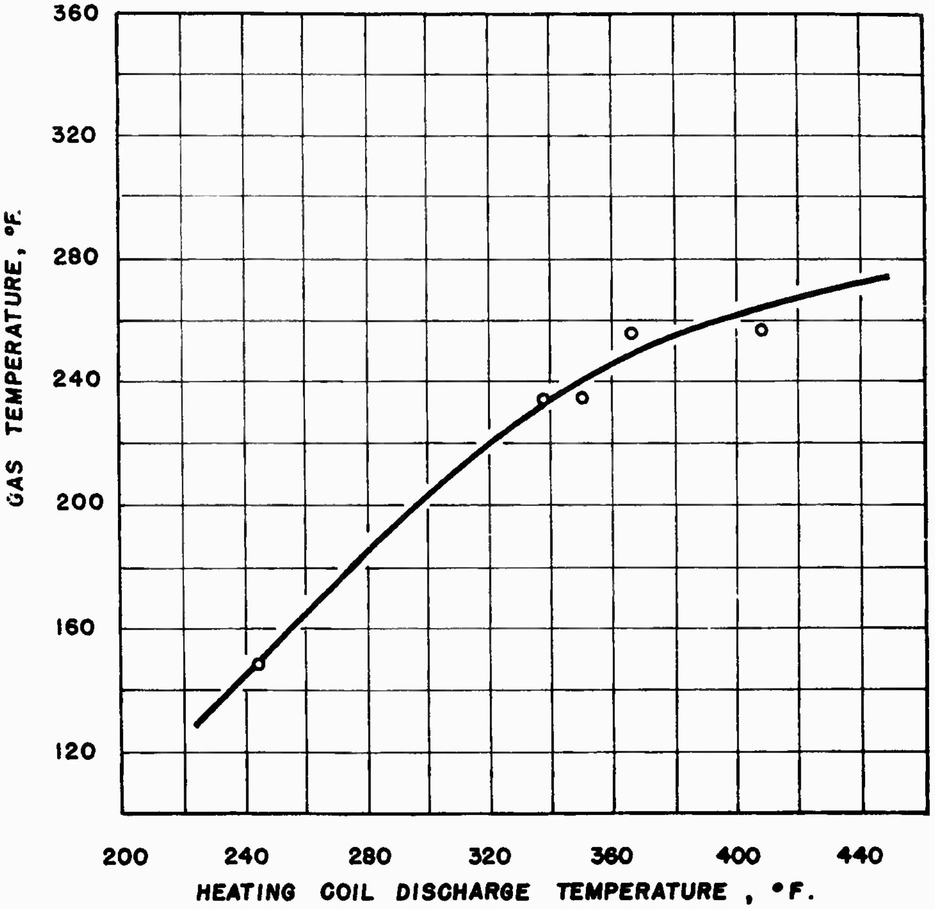


FIG. 13. ESTIMATION OF TEMPERATURE OF HEATED GASES PRIOR TO MIXING WITH OXYGEN.

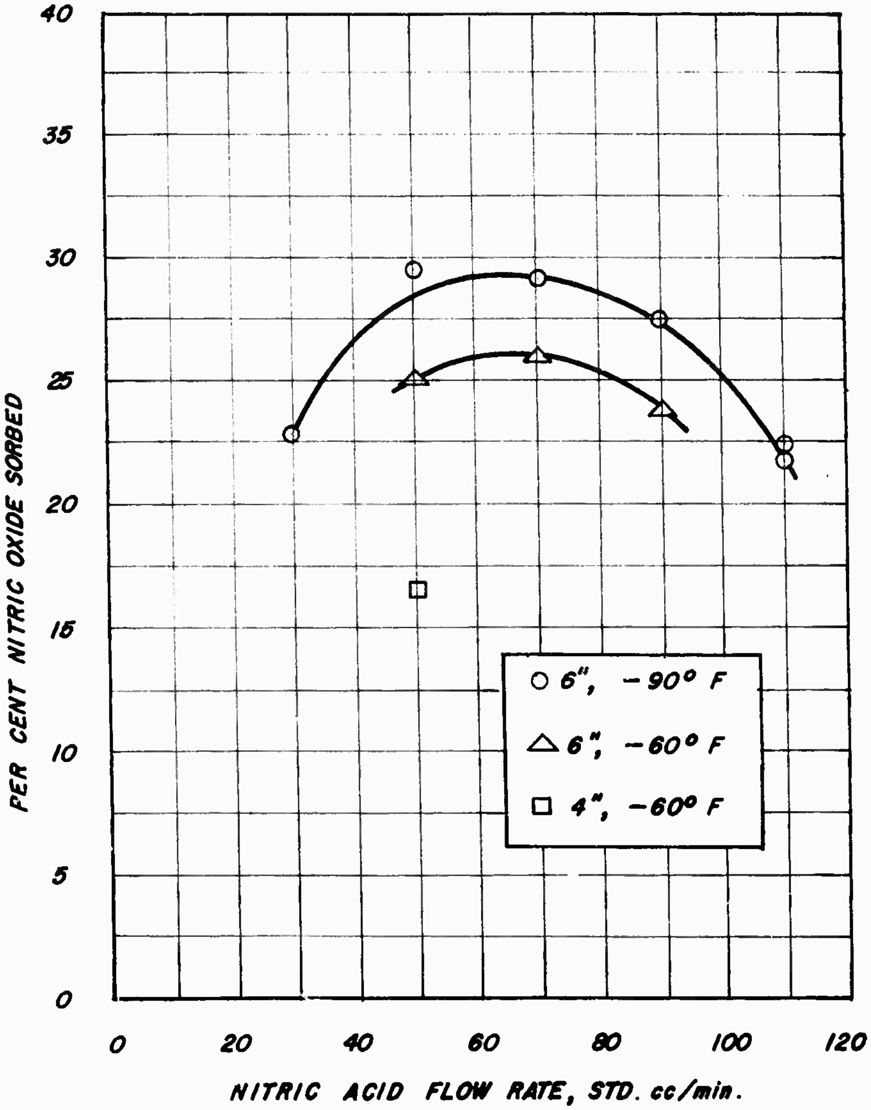


FIG. 14. NITRIC OXIDE SORPTION ISOTHERMS USING SINGLE ORIFICE BUBBLER TIP.

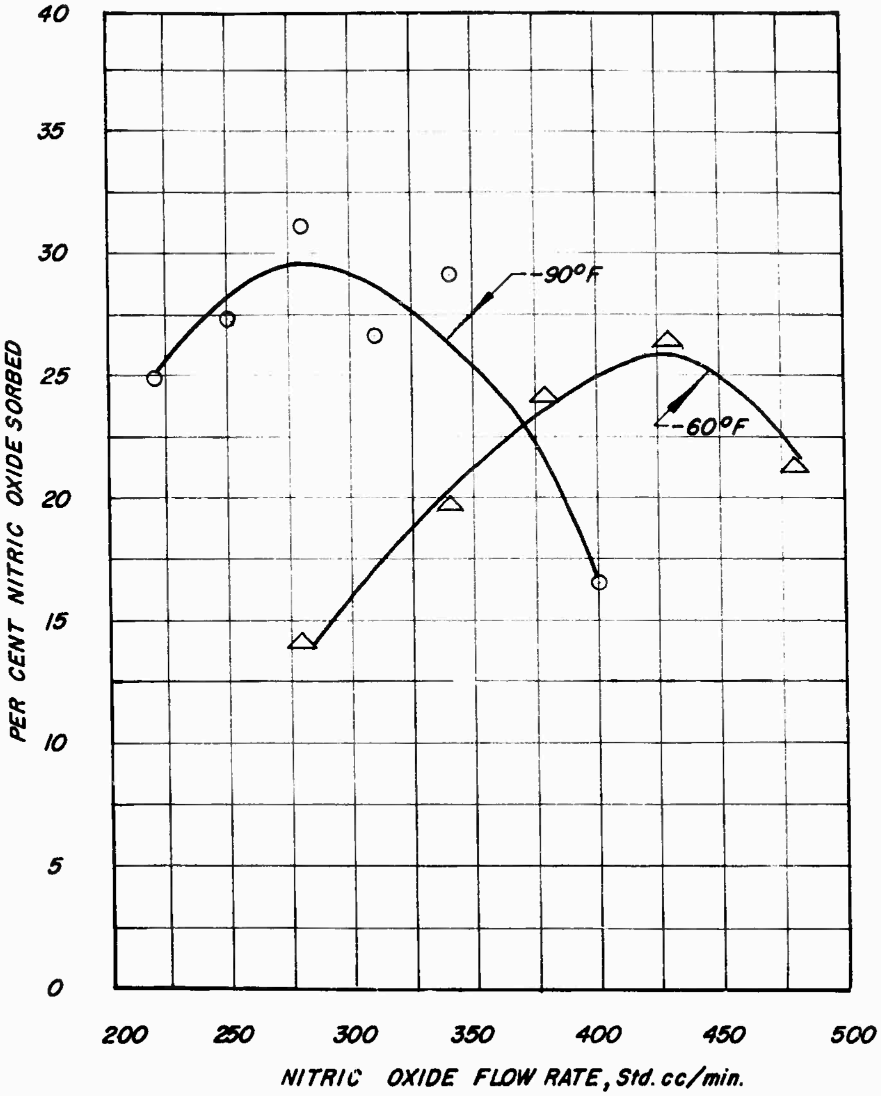


FIG. 15. RELATION BETWEEN NITRIC OXIDE FLOW RATE AND PER CENT SORPTION USING FRITTED GLASS BUBBLER TIP.

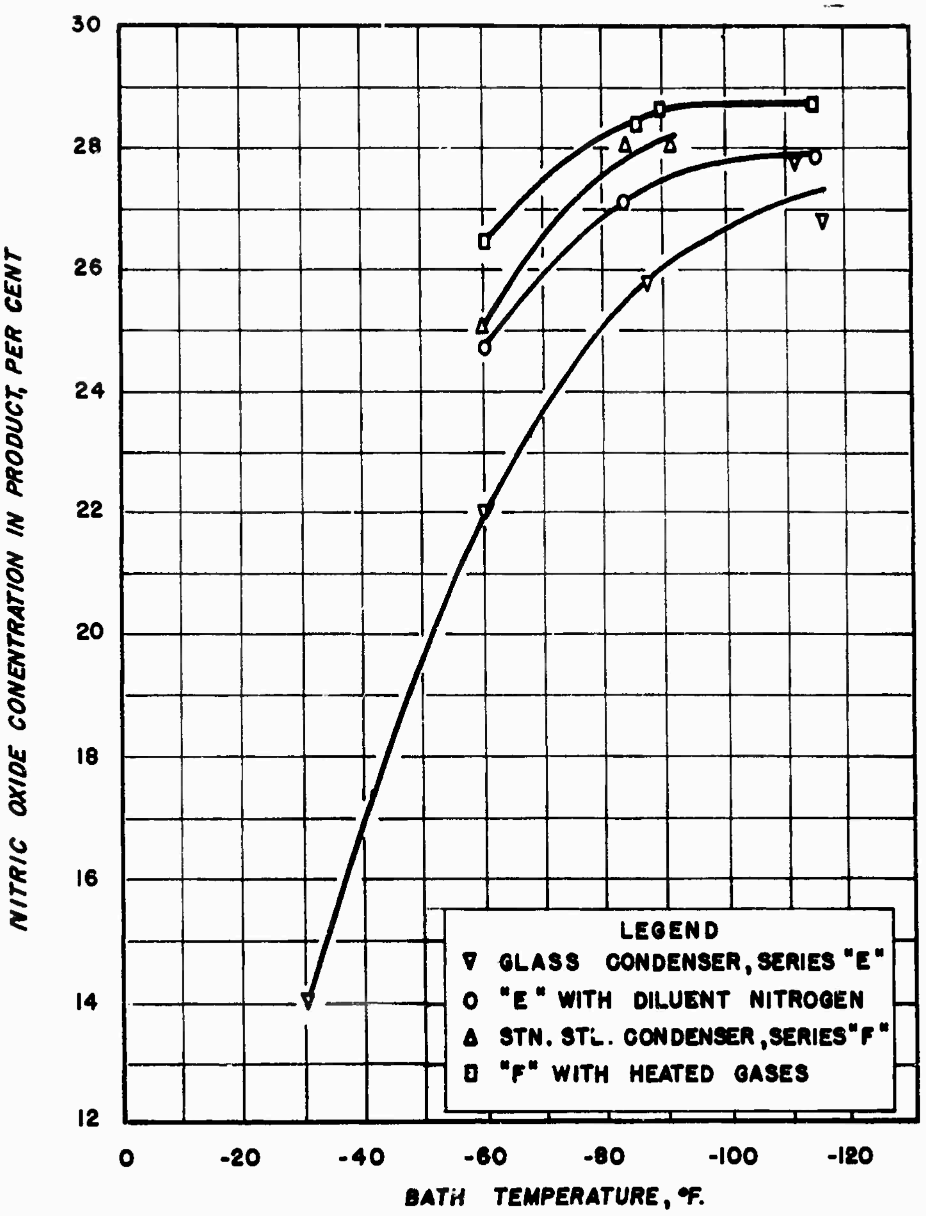


FIG. 16. EFFECT OF BATH TEMPERATURE ON CONCENTRATION OF NITRIC OXIDE IN LIQUID PRODUCT.

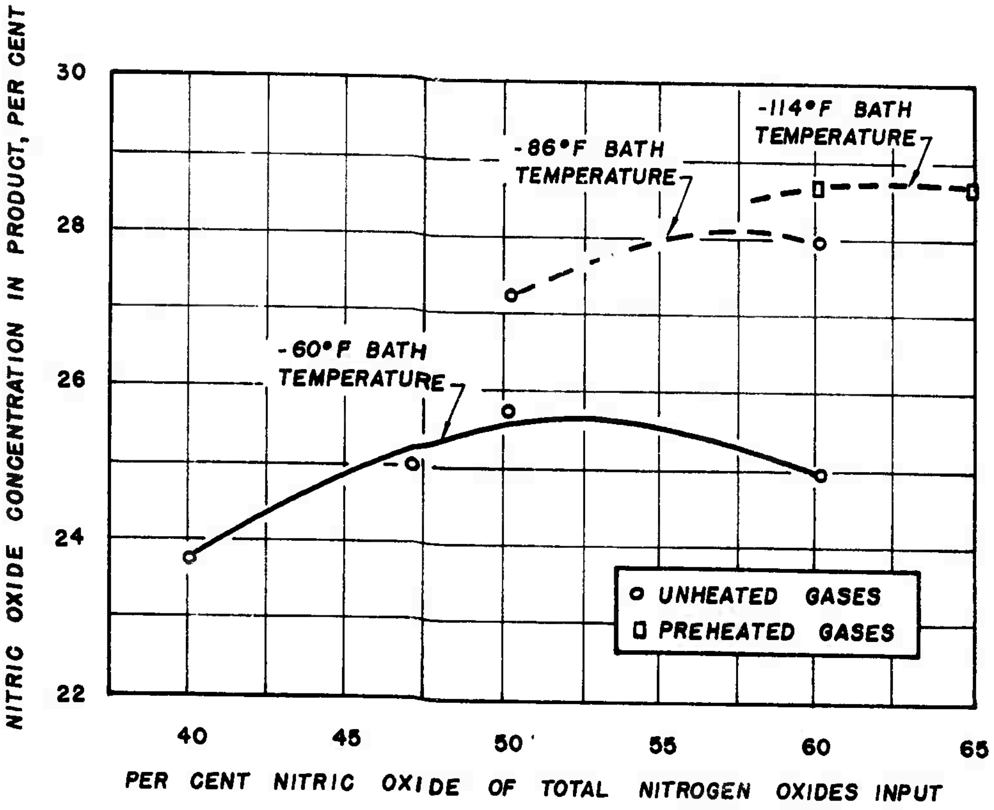


FIG.17. VARIATION OF NITRIC OXIDE CONCENTRATION IN THE PRODUCT WITH CHANGING NO:NO_2 PROPORTIONS IN THE REACTANT GASES.

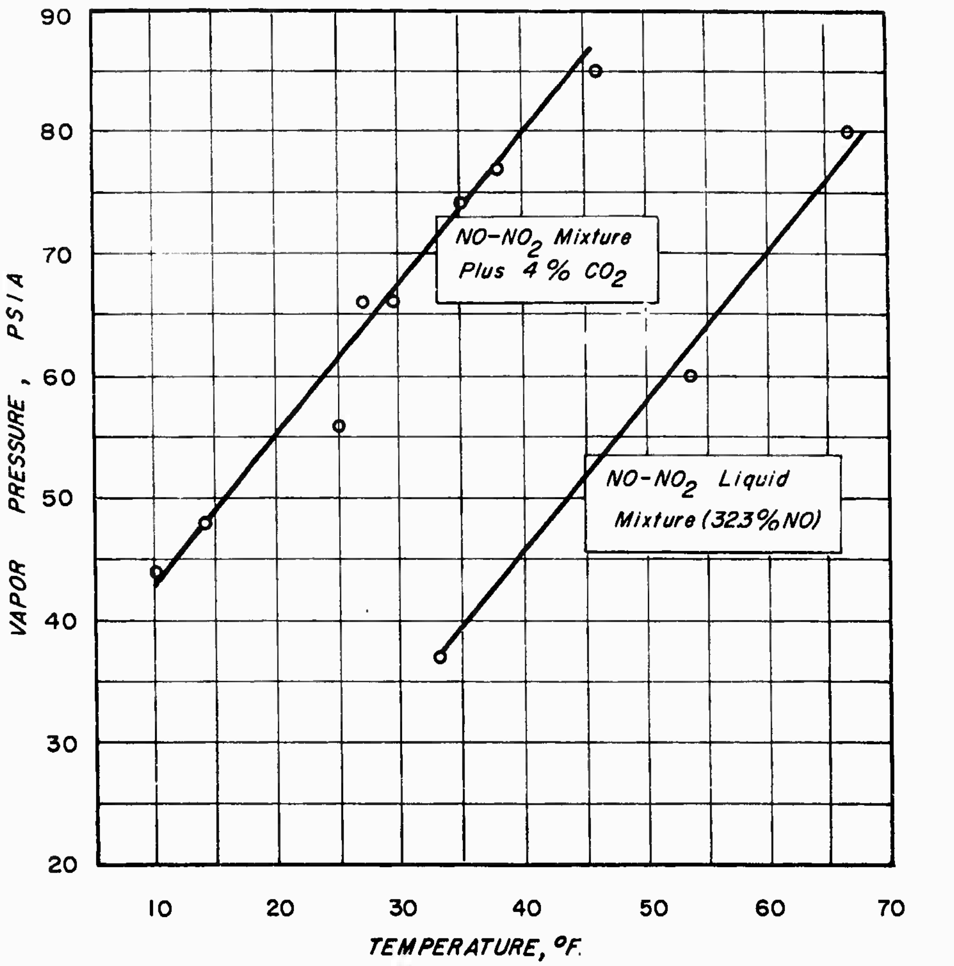


FIG. 18. EFFECT OF CARBON DIOXIDE ON VAPOR PRESSURE OF MIXED OXIDES.

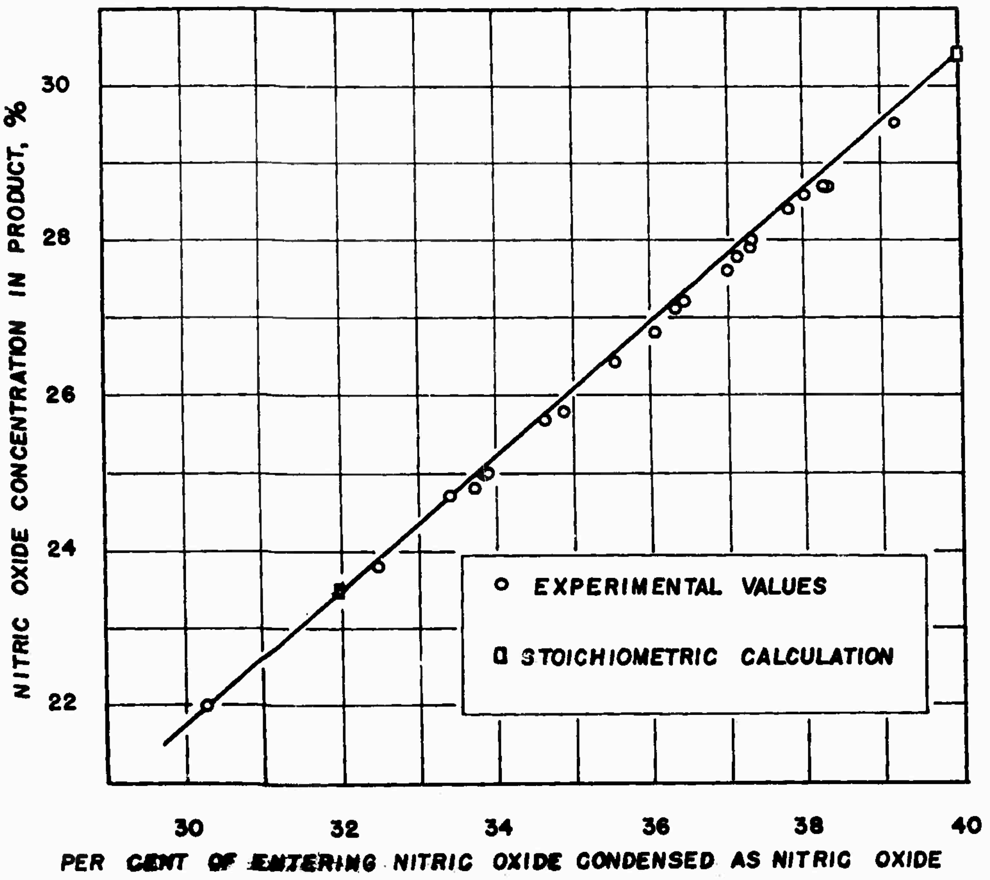


FIG. 19. COMPARISON OF CALCULATED PER CENT NITRIC OXIDE CONDENSED WITH THEORETICAL VALUES.

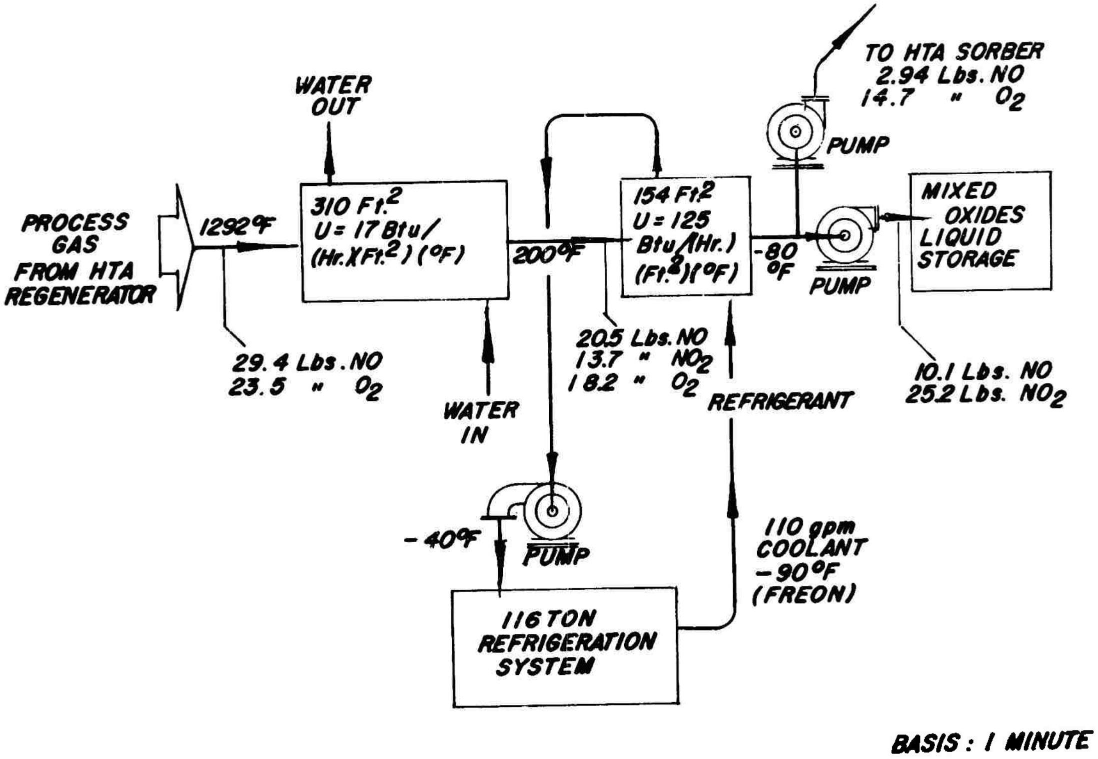
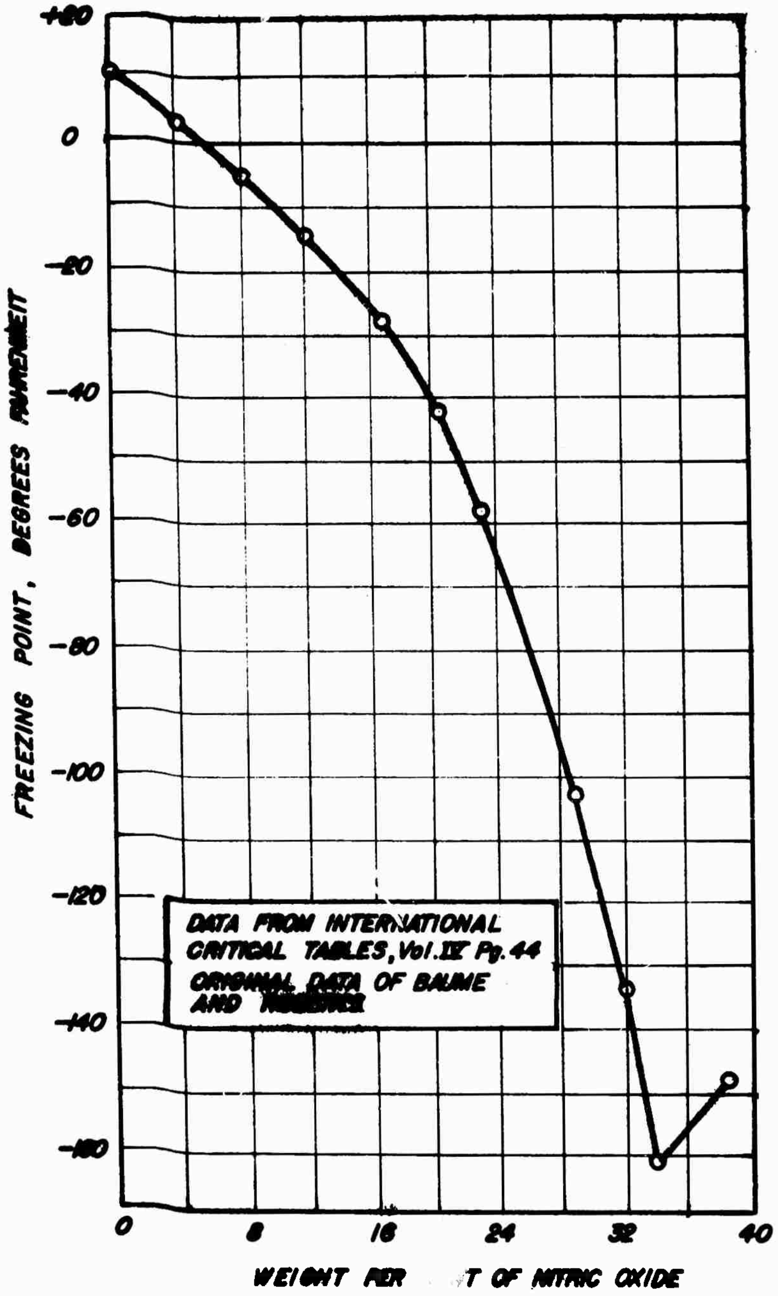


FIG. 20. SCHEMATIC FLOWSHEET FOR COMMERCIAL MANUFACTURE OF MIXED OXIDES.



DATA FROM INTERNATIONAL CRITICAL TABLES, Vol. IV Pg. 44
ORIGINAL DATA OF BAUME AND [illegible]

FIG. 21. FREEZING POINT CURVE OF NITRIC OXIDE-NITROGEN DIOXIDE MIXTURE vs. WEIGHT PER CENT OF NITRIC OXIDE.

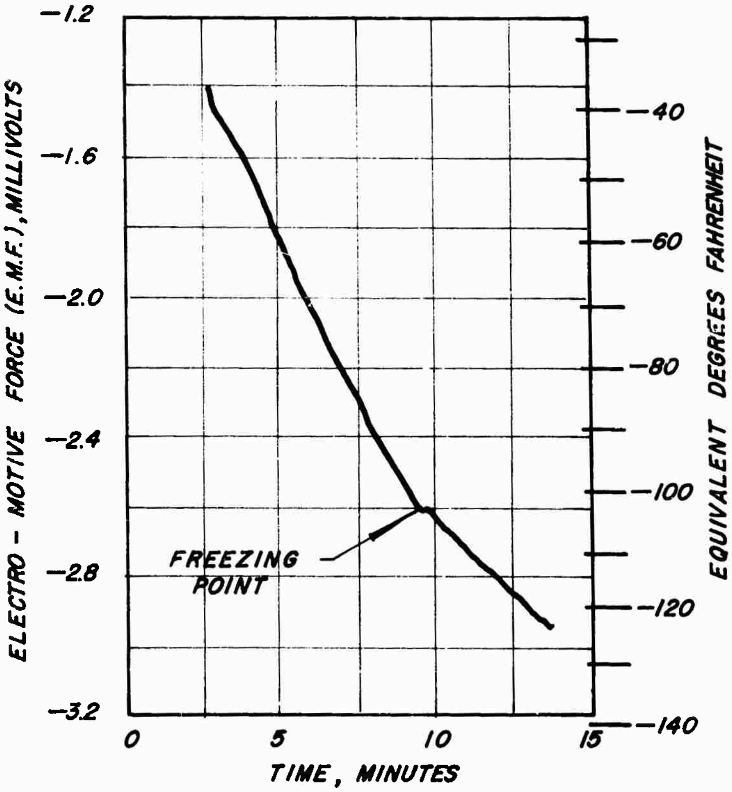


FIG. 22. TYPICAL TRACING OF COOLING CURVE OF NITRIC OXIDE—NITROGEN DIOXIDE LIQUID MIXTURE.

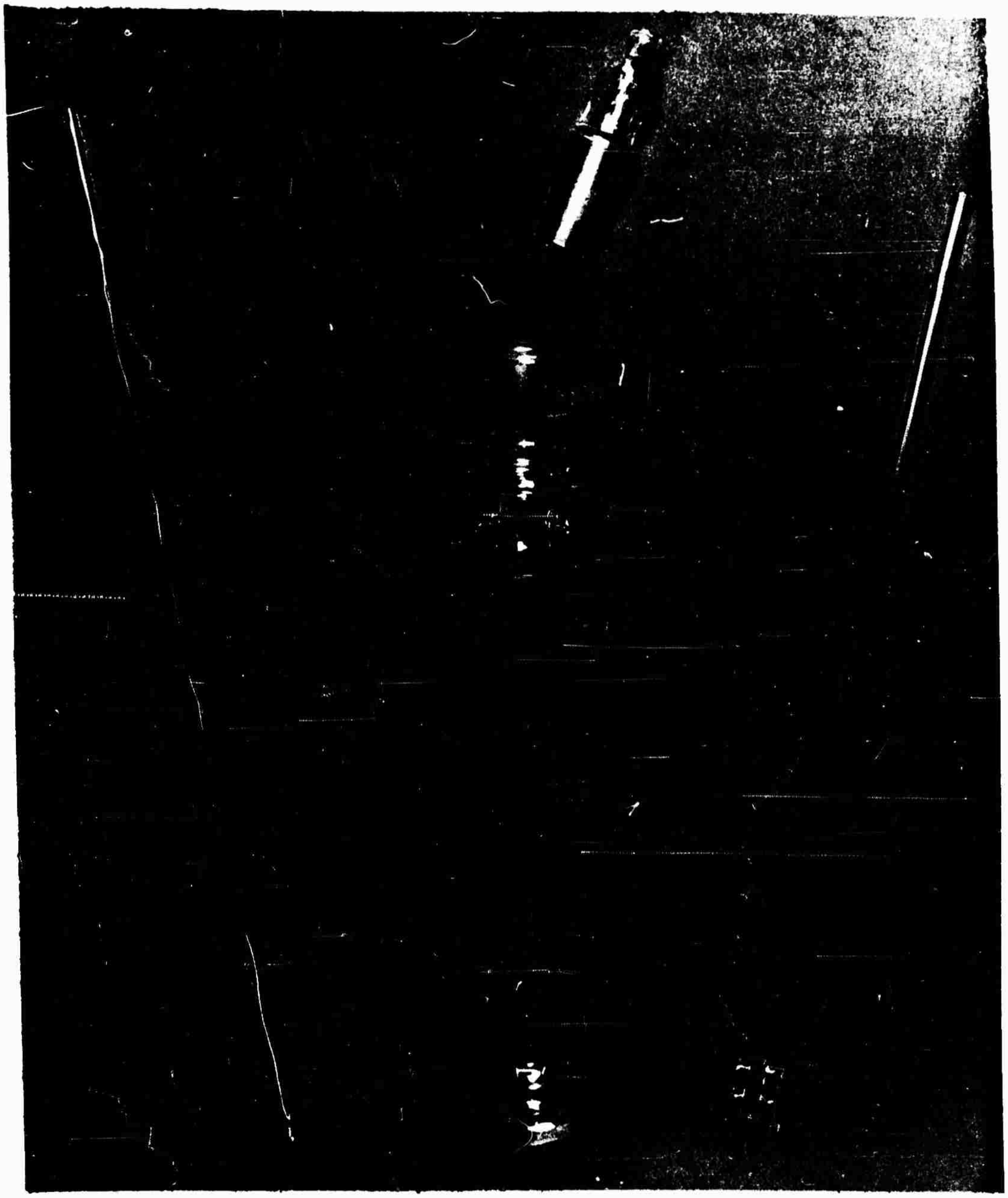


FIG. 23. FREEZING POINT APPARATUS CONSISTING OF DOUBLE-WALL GLASS CONTAINER, GLASS STIRRER AND THERMOCOUPLE.

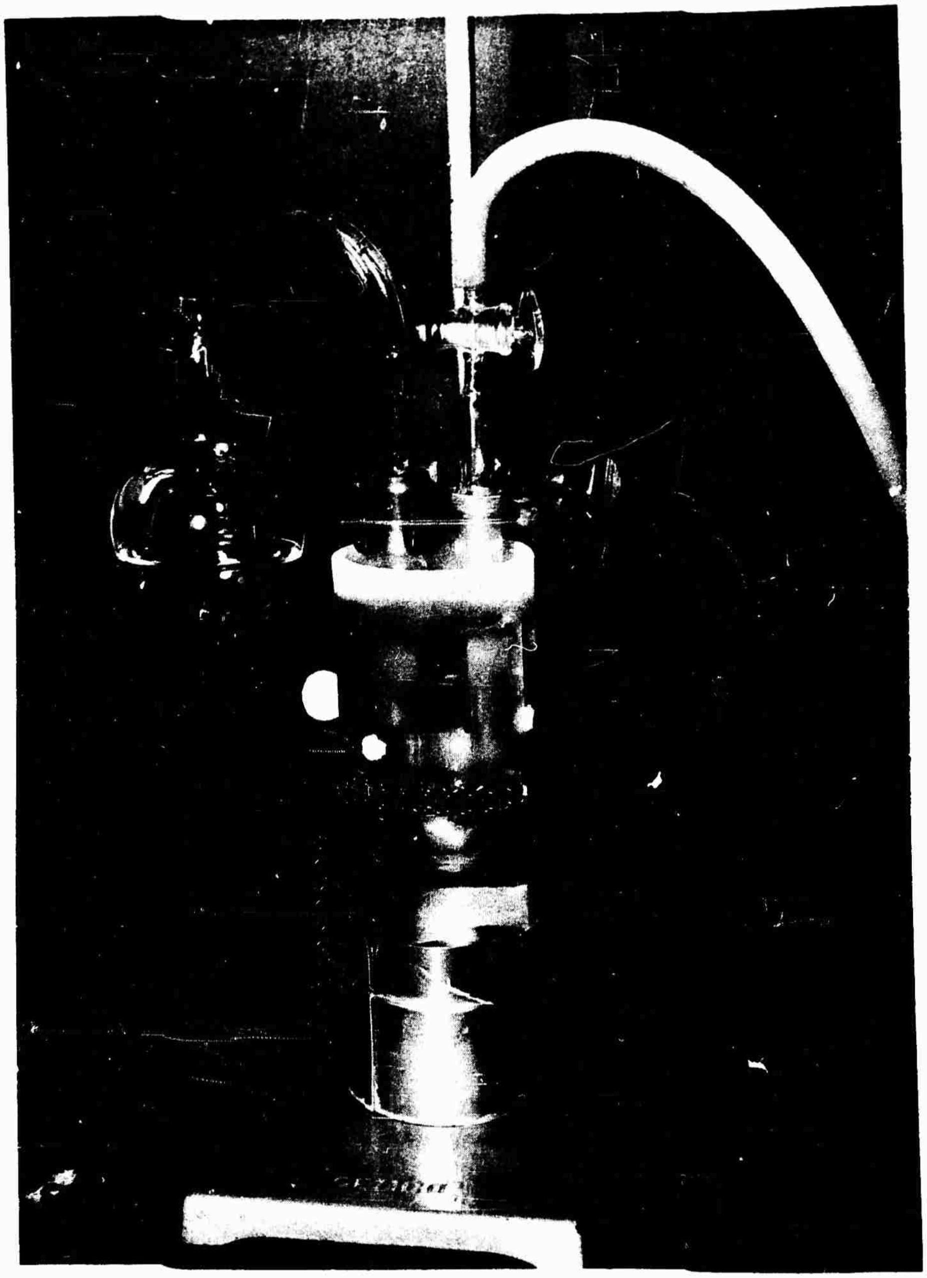


FIG. 24. APPARATUS FOR EVACUATION OF SAMPLE FLASK.

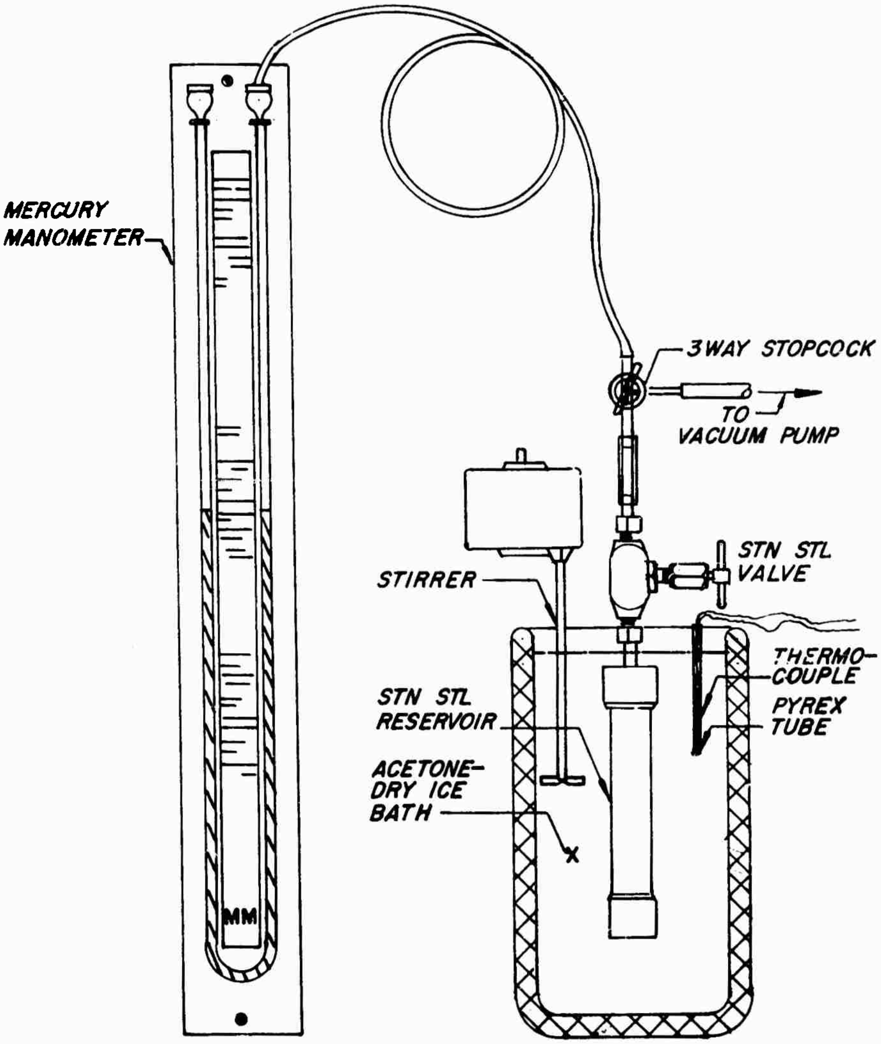


FIG. 25. APPARATUS FOR MEASUREMENT OF VAPOR PRESSURE.

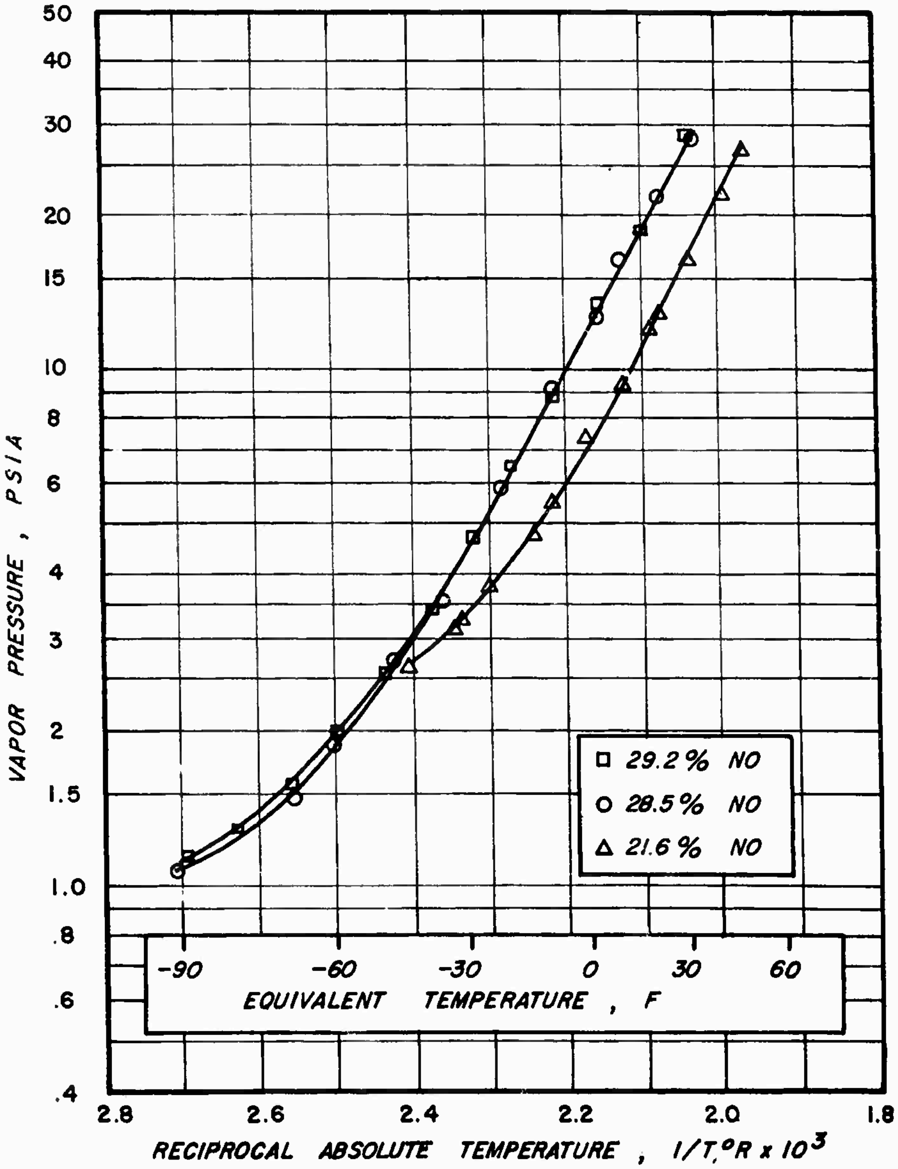


FIG. 26. VAPOR PRESSURE OF MIXED OXIDES.

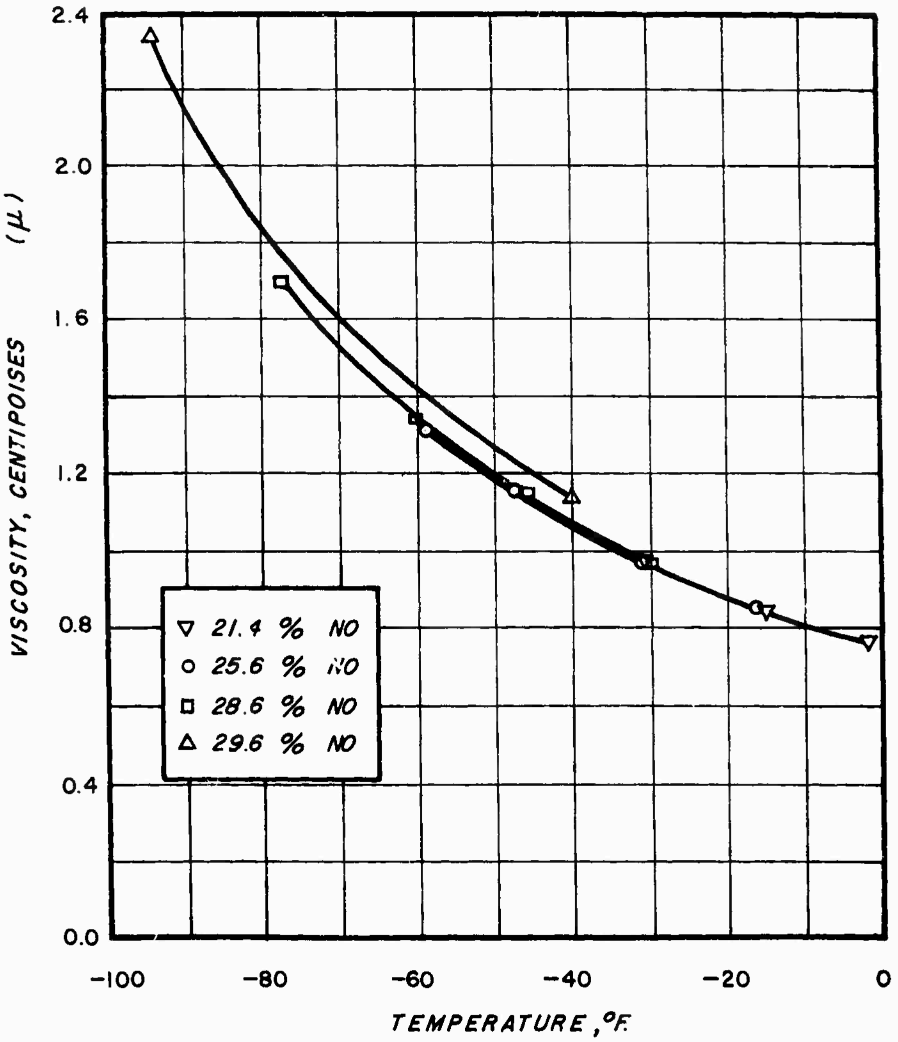


FIG. 27. VISCOSITY OF MIXED OXIDES.

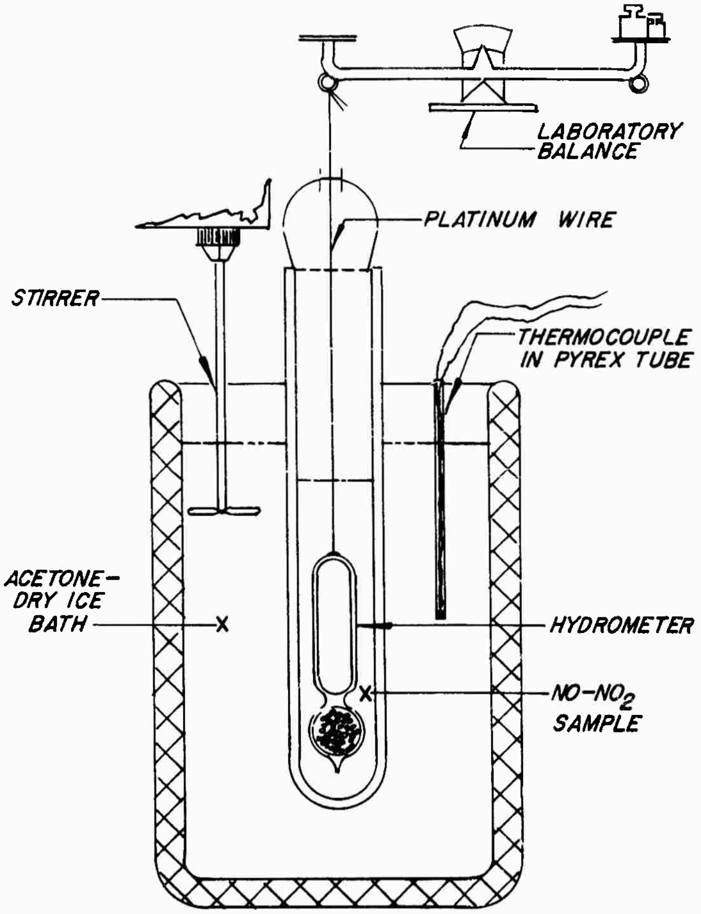


FIG. 28. APPARATUS FOR MEASUREMENT OF DENSITY.

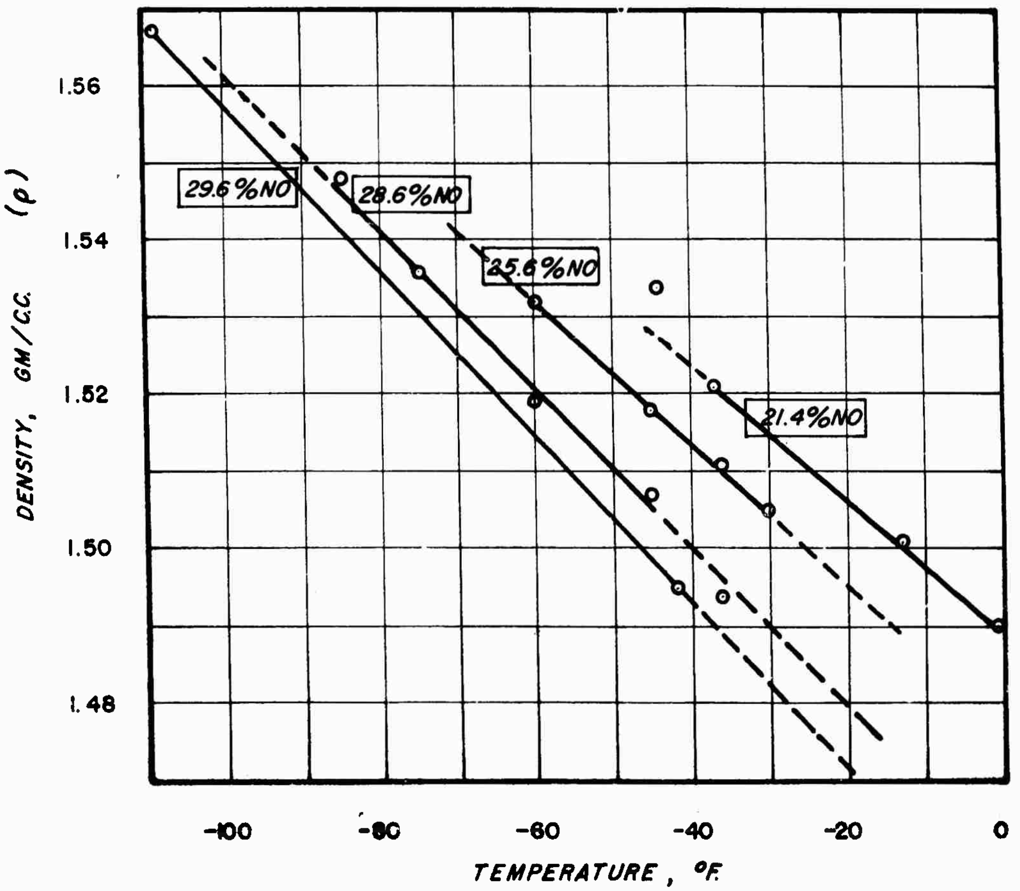


FIG. 29. DENSITY OF MIXED OXIDES.

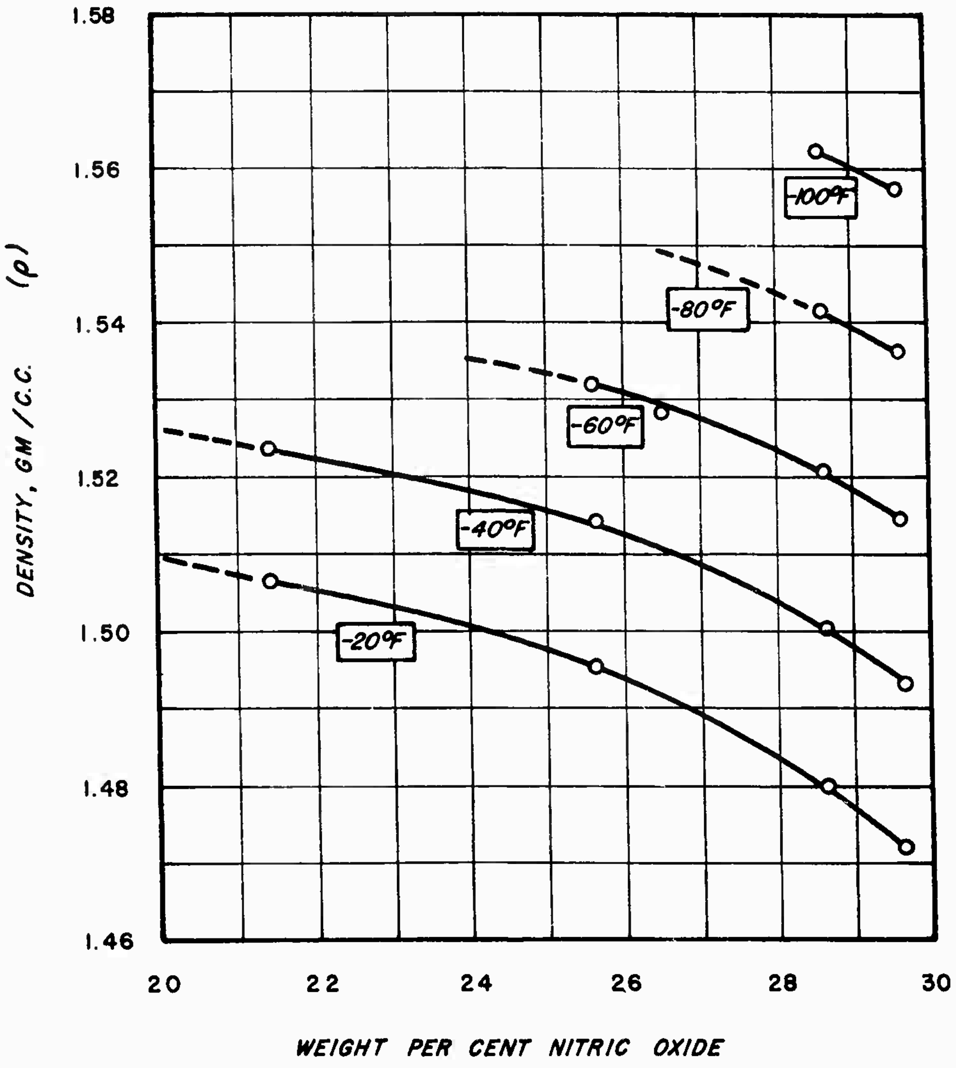


FIG. 30. ISOTHERMS OF DENSITY FOR MIXED OXIDES.

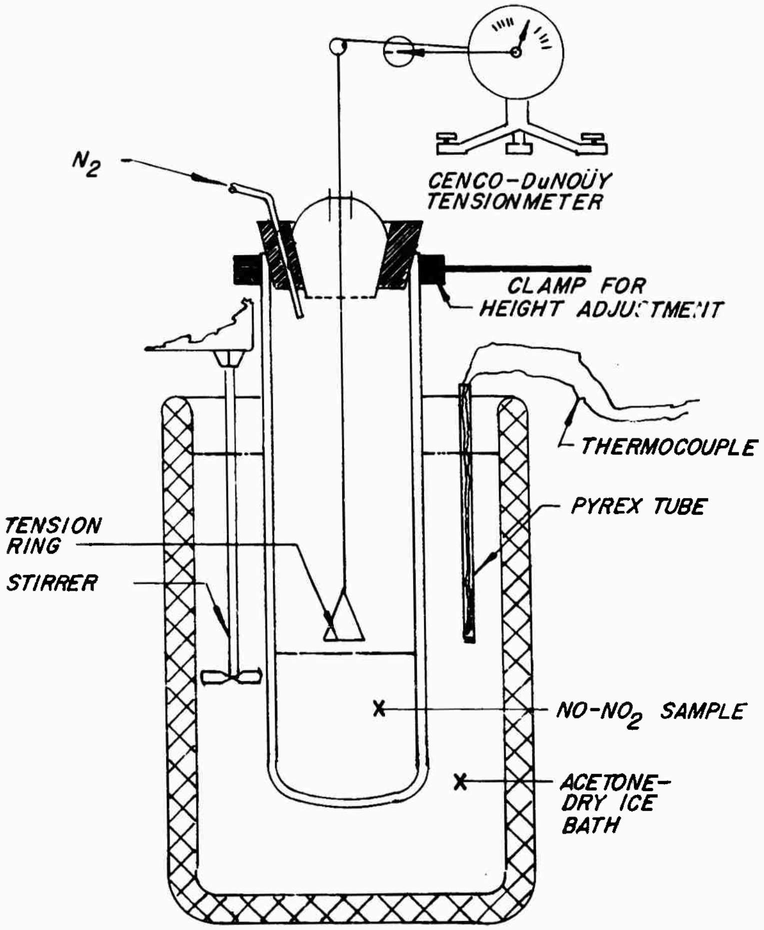


FIG. 31. APPARATUS FOR MEASUREMENT OF SURFACE TENSION.

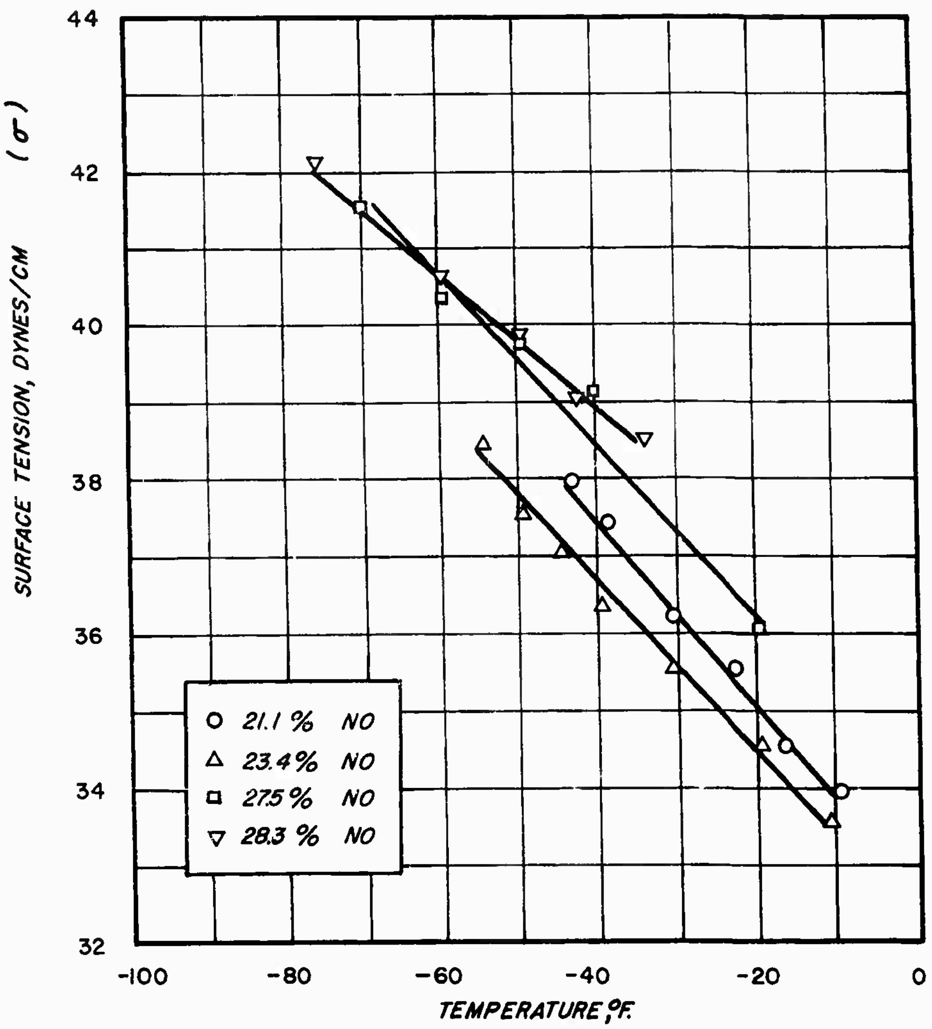


FIG. 32. SURFACE TENSION OF MIXED OXIDES.

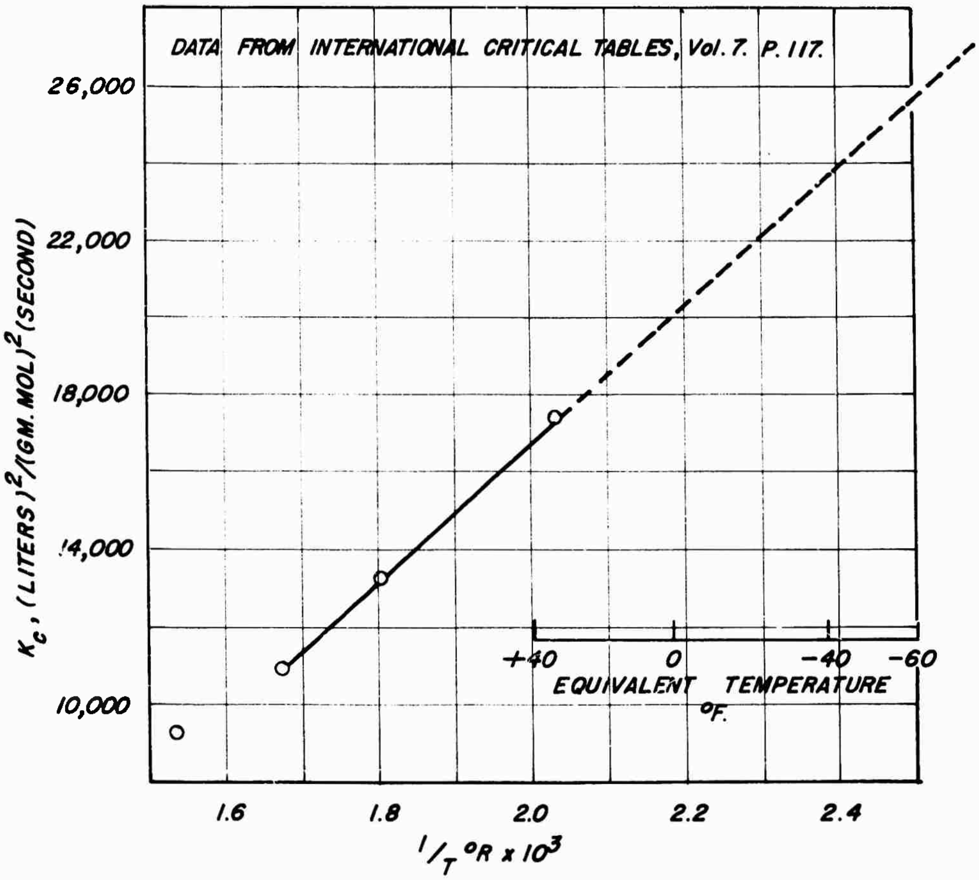


FIG. 33. REACTION RATE CONSTANT, k_c, FOR THE NITRIC OXIDE OXIDATION REACTION $2NO + O_2 = 2NO_2$ vs. RECIPROCAL OF THE ABSOLUTE TEMPERATURE.

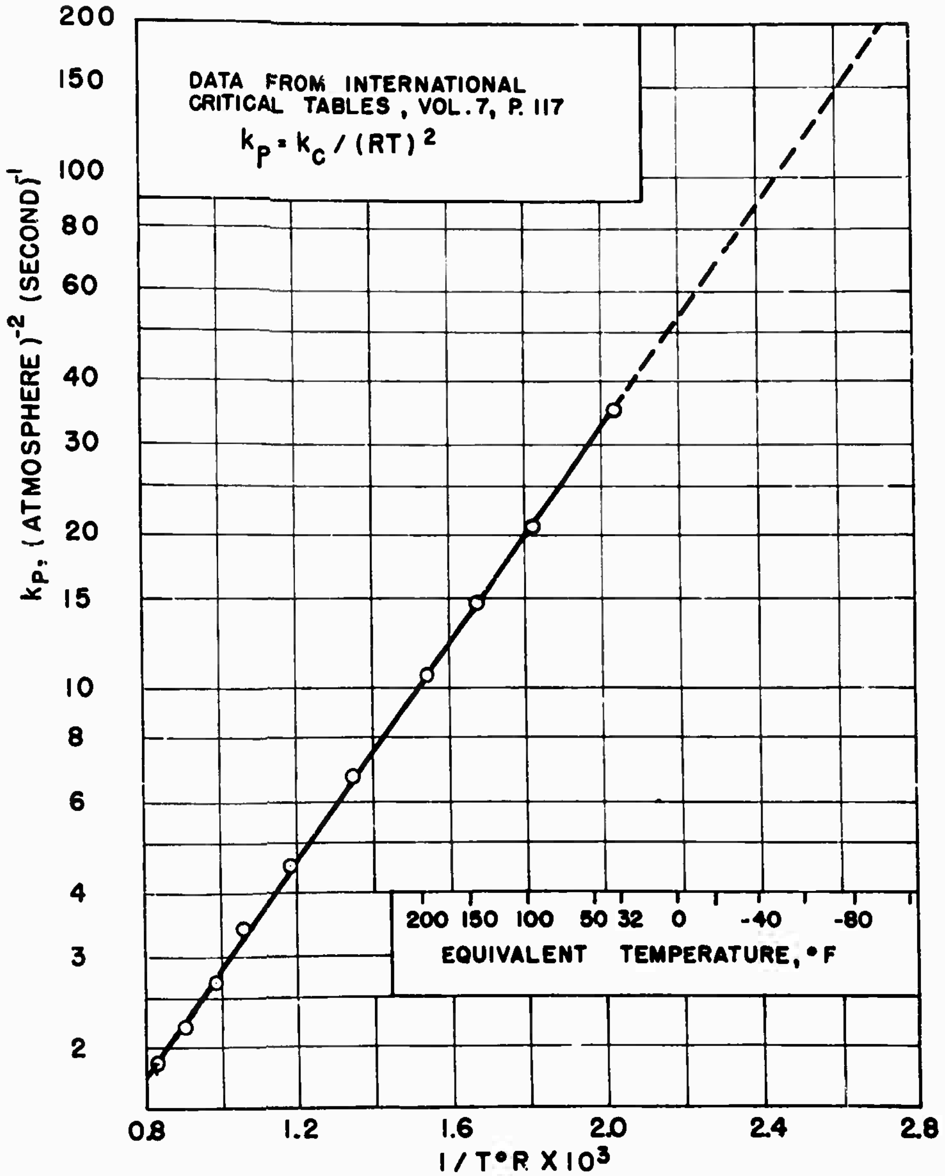


FIG. 34. REACTION RATE CONSTANT, k_p, FOR THE NITRIC OXIDE OXIDATION REACTION $2NO + O_2 = 2NO_2$ VERSUS RECIPROCAL OF THE ABSOLUTE TEMPERATURE.