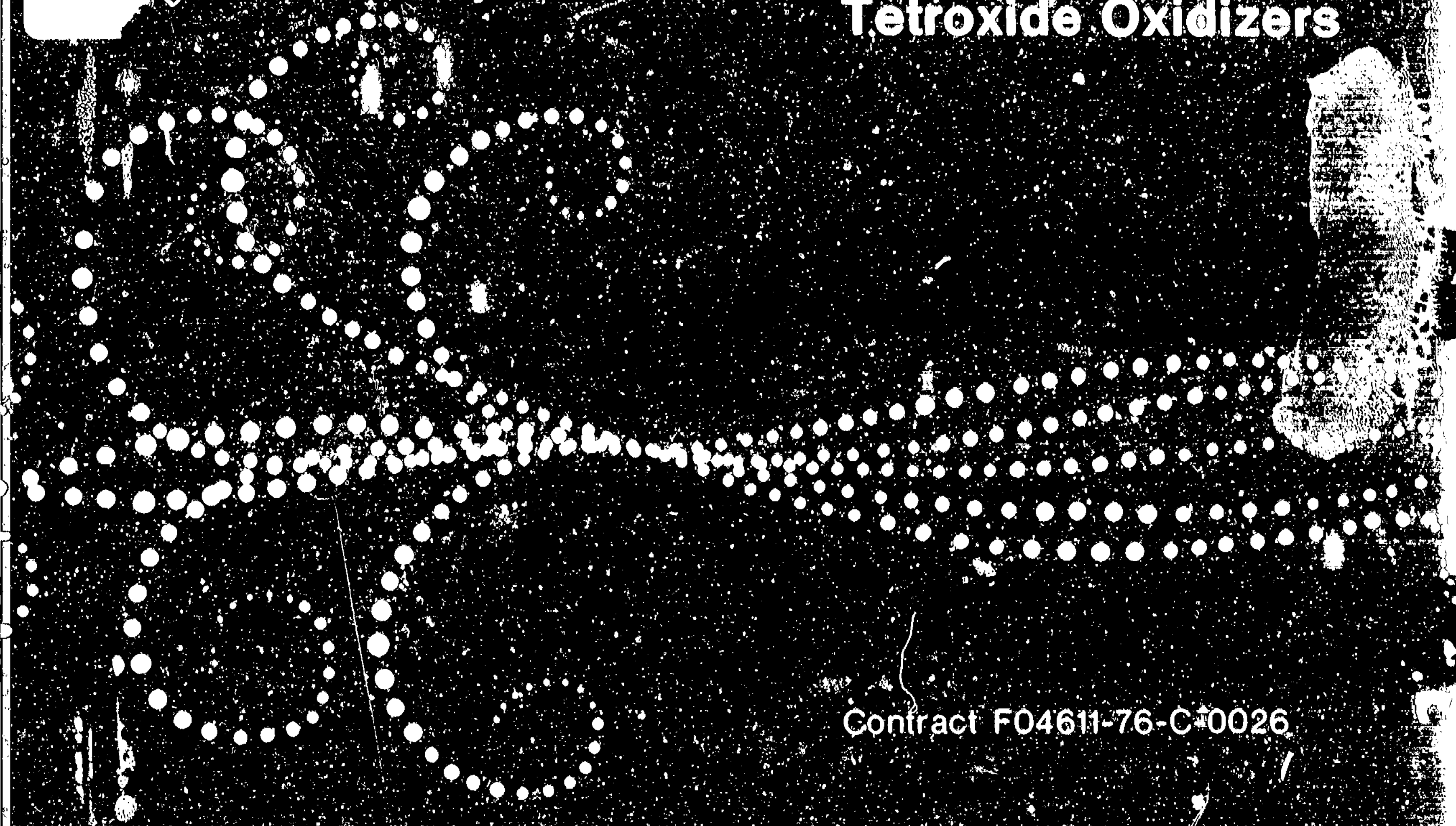
12

AFRPL-TR-76-76

Volume II

USAF
Propellant Handbooks

Nitric Acid/Nitrogen Tetroxide Oxidizers



Contract F04611-76-C-0026

MARTIN MARIETTA

AFRPL-TR-76-76

12

USAF PROPELLANT HANDBOOKS
NITRIC ACID/NITROGEN TETROXIDE OXIDIZERS

VOL II

MARTIN MARIETTA CORPORATION
DENVER DIVISION
P.O. BOX 179
DENVER, COLORADO 80201

AUTHOR: AFRED C. WRIGHT

FEBRUARY 1977

DDC
MAR 11 1977
C

APPROVED FOR PUBLIC RELEASE
DISTRIBUTION UNLIMITED

Prepared for:

AIR FORCE ROCKET PROPULSION LABORATORY
DIRECTOR OF SCIENCE AND TECHNOLOGY
AIR FORCE SYSTEMS COMMAND
EDWARDS AFB, CALIFORNIA 93523

NOTICES

FOREWORD

This propellant handbook is the product of a program sponsored by the Propellants Branch of the Air Force Rocket Propulsion Laboratory. The objection of this program was to provide a comprehensive and systemized text of the properties, handling procedures, compatibility and safety of nitric acid and nitrogen tetroxide and selected blends of these oxidizers.

The program was initiated in February 1976 and was conducted by Martin Marietta Corporation, Aerothermal and Propulsion Engineering Department for the AFRPL, under contract F04611-76-C-0026. Lt. R. Butts served as the Air Force Project Engineer. Mr. A. C. Wright was the Martin Marietta Program Manager.

This report has been reviewed by the Information Office/DOZ and is releaseable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication; it is unclassified and suitable for general public release.

Rodney G. Butts
RODNEY G. BUTTS, 2nd Lt., USAF
Project Engineer

Forrest S Forbes
FORREST S. FORBES, Chief
Propellants Section

FOR THE COMMANDER

Edward E Stein
EDWARD E. STEIN, Deputy Chief
Liquid Rocket Division

(9)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Final rept. Mar-Dec 76,

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER (19 (18) AFRPL-TR-76-76	2. GOVT ACCESSION NO. -	3. RECIPIENT'S CATALOG NUMBER -
4. TITLE (and Subtitle) (6) USAF PROPELLANT HANDBOOKS. NITRIC ACID/NITROGEN TETROXIDE OXIDIZERS. Vol II		5. TYPE OF REPORT & PERIOD COVERED FINAL March-December 1976
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) (10) Alfred C./Wright		8. CONTRACT OR GRANT NUMBER(s) (15) F04611-76-C-0026 Now
9. PERFORMING ORGANIZATION NAME AND ADDRESS Martin Marietta Corporation Denver Division P. O. Box 179, Denver, CO 80201		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS JON: 305810 PR
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Rocket Propulsion Laboratory/LKDP Edwards AFB, California 93523		12. REPORT DATE (11) Feb[redacted] [redacted]77
		13. NUMBER OF PAGES (12) 205 p.
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (16) 3058 (17) 10		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release - Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

- Liquid Rocket Oxidizers
- Nitric Acid
- Nitrogen Oxides
- Nitrogen Tetroxides
- Nitrogen Dioxide
- IRFNA
- Inhibited Red Fuming Nitric Acid
- High Density Acids
- Safety
- Handbooks
- HDA
- Liquid Rocket Propellants
- Chemical Properties
- Physical Properties
- WFNA

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The Nitric Acid/Nitrogen Tetroxide Oxidizer Handbook is a compilation of engineering information on the physical and chemical properties, storage and handling, production, transportation, safety, and material compatibility of the nitric acid/nitrogen tetroxide family of oxidizers and their blends. It contains information on the following propellants:

403225

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. Abstract (Cont'd)

Nitric Acid (IRFNA),
High Density Acid,
Nitrogen Tetroxide,
MON-1,
MON-3,
MON-10,
MON-25,
Minuteman Grade N_2O_4.

The propellant handbook is intended to be used for R&D personnel and test engineers who are directly involved in the utilization of liquid rocket propellants and the design of liquid rocket propulsion systems and facilities.

ACKNOWLEDGEMENTS

During the course of the compilation of data the following individuals and organizations contributed to this handbook. Their cooperation is hereby gratefully acknowledged with thanks.

Name	Organization
Lt. R. Butts	AFRPL/LKDP, Edwards AFB, California
Mr. F. Forbes	AFRPL/LKDP, Edwards AFB, California
Ms. J. Trent	Air Products, Allentown, Pennsylvania
Mr. A. Follows	Allied Chemical, Solvoy, New York
Mr. H. Ph. Heubusch	Bell Aerospace, Buffalo, New York
Mr. L. Thompson	Bell Aerospace, Buffalo, New York
Mr. K. Pullen	Boeing Co., Seattle, Washington
Mr. D. Evans	JPL, Pasadena, California
Mr. W. Watge	Kelly AFB, San Antonio, Texas
Mr. R. F. Hausman	Lockheed Missiles & Space Co., Inc. Sunnyvale, California
Mr. D. F. Stone	McDonnell-Douglas, St. Louis, Missouri
Dr. M. Faget	NASA, Houston, Texas
Mr. H. Brasseaux	NASA, Houston, Texas
Dr. S. Wood Mr. G. W. Burdette	Naval Weapons Center, China Lake, California
Mr. M. Constantine Mr. J. Weber	Rocketdyne Division of Rockwell International, Canoga Park, California
Mr. G. Caton	Thiokol Corporation, Newton, Pennsylvania
Mr. E. Sutton	Thiokol Corporation, Elkton, Maryland
Mr. R. Vaughn	TRW Systems, Inc., Redondo Beach, California
Mr. R. Schmitt	United Technologies, Sunnyvale, California
Dr. H. Sisler	University of Florida, Gainesville, Florida

Special thanks are also extended by the author to the following personnel at Martin Marietta Corporation, Denver, Division, who contributed to this work.

Dr. R. Anselmi
Mr. J. Kling
Mr. R. Herzog
Mr. D. Ong
Mr. G. Roum
Mr. R. VandeKoppel
Mr. L. Williams

TABLE OF CONTENTS

Section **Page**

1.0 Introduction

2.0 Properties and Logistics

2.1 Nitric Acid (Types IIIA, IIIB, and IIILS

2.2 Nitric Acid, Type IV (HDA) and Modified HDA (PF_6)

2.3 Nitrogen Tetroxide (NTO, MON-1, MON-3, MON-10, MON-25)

3.0 Handling, Storage and Compatibility

TABLE OF CONTENTS (cont.)

LIST OF ILLUSTRATIONS

LIST OF TABLES

1.0 INTRODUCTION

1.1 GENERAL

1.2 SCOPE AND CONTENT

1.3 INSTRUCTIONS TO USER

TABLE 1.1-1 INDEX OF SUBJECT MATTER

*HDA = High Density Acid (IRFNA)
**MON = Mixed Oxides of Nitrogen

1.1 GENERAL

The purpose of this Handbook is to provide, in an accessible and convenient manner, as much information as possible on the characteristics of nitric acid and nitrogen tetroxide, their derivitives, related compounds and blends, pertinent to their use as oxidizers for rocket engines, attitude control systems and chemical gas generators. The information presented herein has been collected and correlated from books, published papers and reports, manufacturers' literature, government specifications and private communications. The author and other members of the Martin Marietta organization have carefully reviewed and evaluated this information and have attempted to resolve all disagreements, with the aid of their own considerable experience in the use of these oxidizers.

Since 1942 nitric acids and their derivatives have become increasingly important as rocket engine oxidizers due to their high performance and storability. During World War II, engineers at Peenemunde began work on an anti-aircraft missle in parallel with their development of the famous V2. The oxidizer selected for this missle was nitric acid because the important requirements were simplicity and constant operational readiness. The ethanol/liquid oxygen combination used in the V2 was therefore out of the question. This missle, which became the "Wasserfall," used pure (98%) nitric acid in the early stages of development. Later, nitric acid diluted with a 10% admixture of sulpheric acid was used.

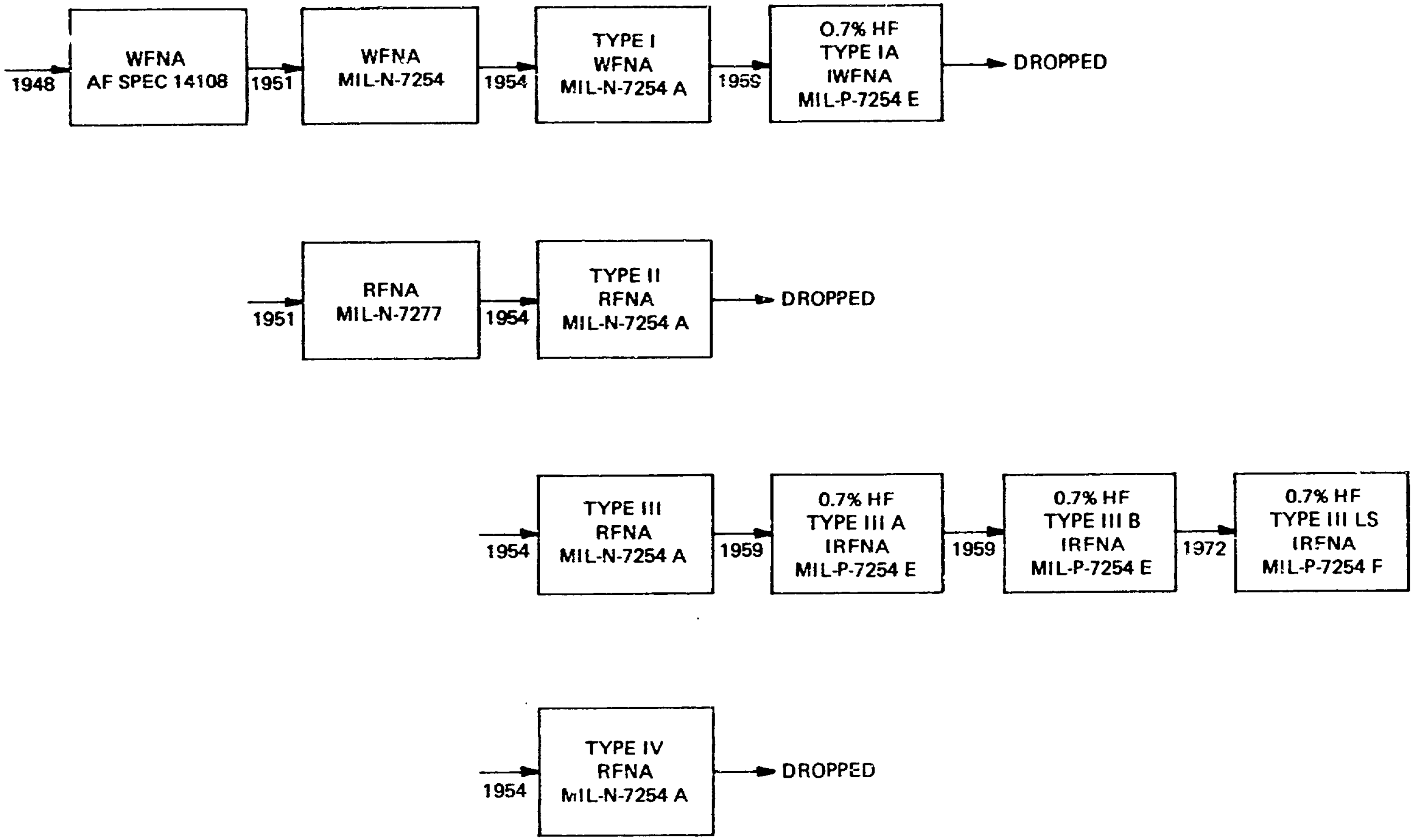
In the United States, nitric acid oxidizer was used in a liquid rocket-assisted take-off unit developed in 1942 by the Jet Propulsion Laboratory. Later, the "WAC Corporal," a meteorological sounding rocket, was developed using nitric acid.

Much of the early effort expended on nitric acid technology was spent in the area of material compatibility. The previously mentioned "Wasserfall" units originally had to be launched within a few days after oxidizer loading because of this problem. The development of nitric acid usage in the United States can be traced by reviewing the changes in the military specifications as depicted in Figure 1.1-1. Originally, there were four types of nitric acid defined in MIL-N-7254A. These were:

1. Type I (WFNA) White Fuming Nitric Acid –97.5% by weight HNO_3, 2.0% by weight H_2O, 0-0.5% by weight NO_2.
2. Type II (RFNA) Red Fuming Nitric Acid –6% by weight NO_2.
3. Type III (RFNA) Red Fuming Nitric Acid –14% by weight NO_2.
4. Type IV (RFNA) Red Fuming Nitric Acid –22% by weight NO_2.

The Type II and Type IV Nitric Acids were dropped from the Mil-Spec because they were no longer used. The Type I and III oxidizers were retained but an inhibitor, hydrogen fluoride (HF), was added which caused them to be called Type IA and Type IIIA.

FIGURE 1.1-1 NITRIC ACID HISTORY



Type IIIA became Type IIIB when the amount of solids was reduced from 0.10% to 0.04%, percent by weight. Type IIILS came into existence because of problems with the Agena upper stage which were attributed to the iron content of the oxidizer. Type IIILS allows a maximum of .002% Fe_2O_3, percent by weight. Type IIILS also has a reduced water content which improves engine performance, slightly, and reduces its storability.

A Type IV Nitric Acid was added to MIL-P-7254F by Amendment 2 which specified a nitric acid/nitrogen tetroxide blend; known as "High Density Acid." The High Density Acid (HDA) was formulated to increase the performance of the Agena. It is defined in MIL-P-7254F as a mixture of inhibited red fuming nitric acid (IRFNA) and nitrogen tetroxide (N_2O_4). It is nominally a 55/44% mix (IRFNA/N_2O_4) which contains the IRFNA inhibitor, hydrogen fluoride (HF). To further decrease the corrosiveness of the oxidizer, a new inhibitor PF_5 has been proposed and tested, but has not been incorporated into the Mil-Spec. The Figure 1.1-2 depicts the history of this oxidizer. This IRFNA/N_2O_4 blend is discussed in detail in Section 2.2 of this Handbook.

A nitric acid oxidizer is being evaluated by the Navy at China Lake for application to a liquid gun program. The composition of this oxidizer, called "90% nitric acid," is as follows:

HNO_3 –89.5 wt. %

H_2O–9.86 wt. %

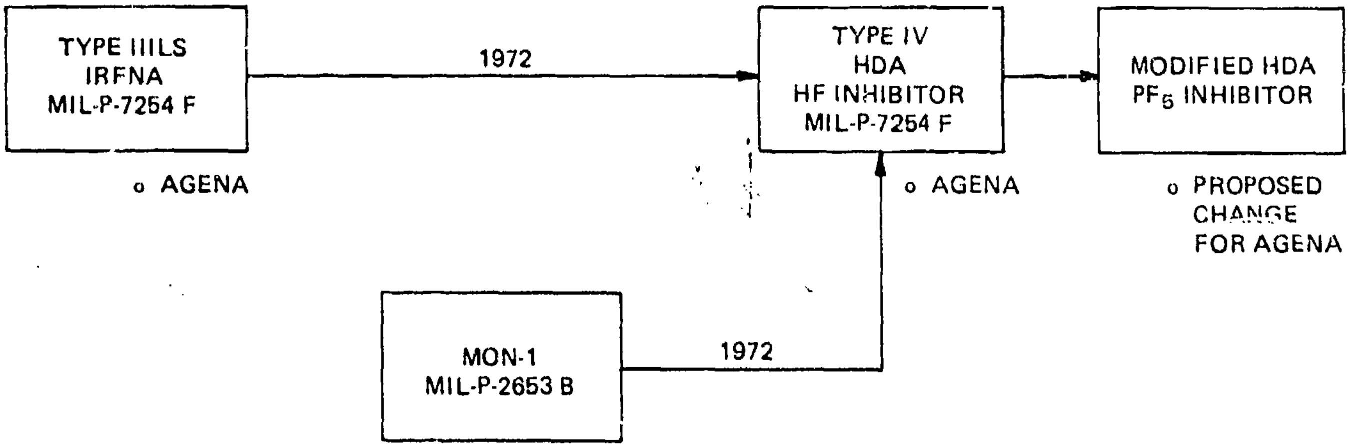
HF –0.62 wt. %

NO_2 –0.02 wt. %

Data from this program are included in the materials compatibility section (3.4).

Approximately 90 percent of the nitric acid is made by the catalytic oxidation of ammonia with air or oxygen to yield nitric oxide (NO). This is oxidized to N_2O_4 which, when treated with water, yields nitric acid (HNO_3). HNO_3 may then be concentrated by distillation with sulphuric acid.

FIGURE 1.1-2 HDA HISTORY



The inorganic chemistry of nitrogen tetroxide and its monomer, nitrogen dioxide, has been the subject of many investigations since Priestley first carried out his laboratory preparation in 1777. The rise to prominence of nitrogen tetroxide as one of the most useful storable liquid propellant ingredients for aerospace work created a demand for additional knowledge on all aspects of nitrogen tetroxide.

Nitrogen Tetroxide began to replace nitric acid in the late 1950s and early 1960s because it gave higher performance and presented less of a corrosion problem. As a storable liquid oxidizer, nitrogen tetroxide offers for liquid-fueled rockets the readiness approaching that of solid-fueled rockets. The development of the Titan II ICBM required that nitrogen tetroxide be developed and explored fully, and be available in large quantities at a reasonable price.

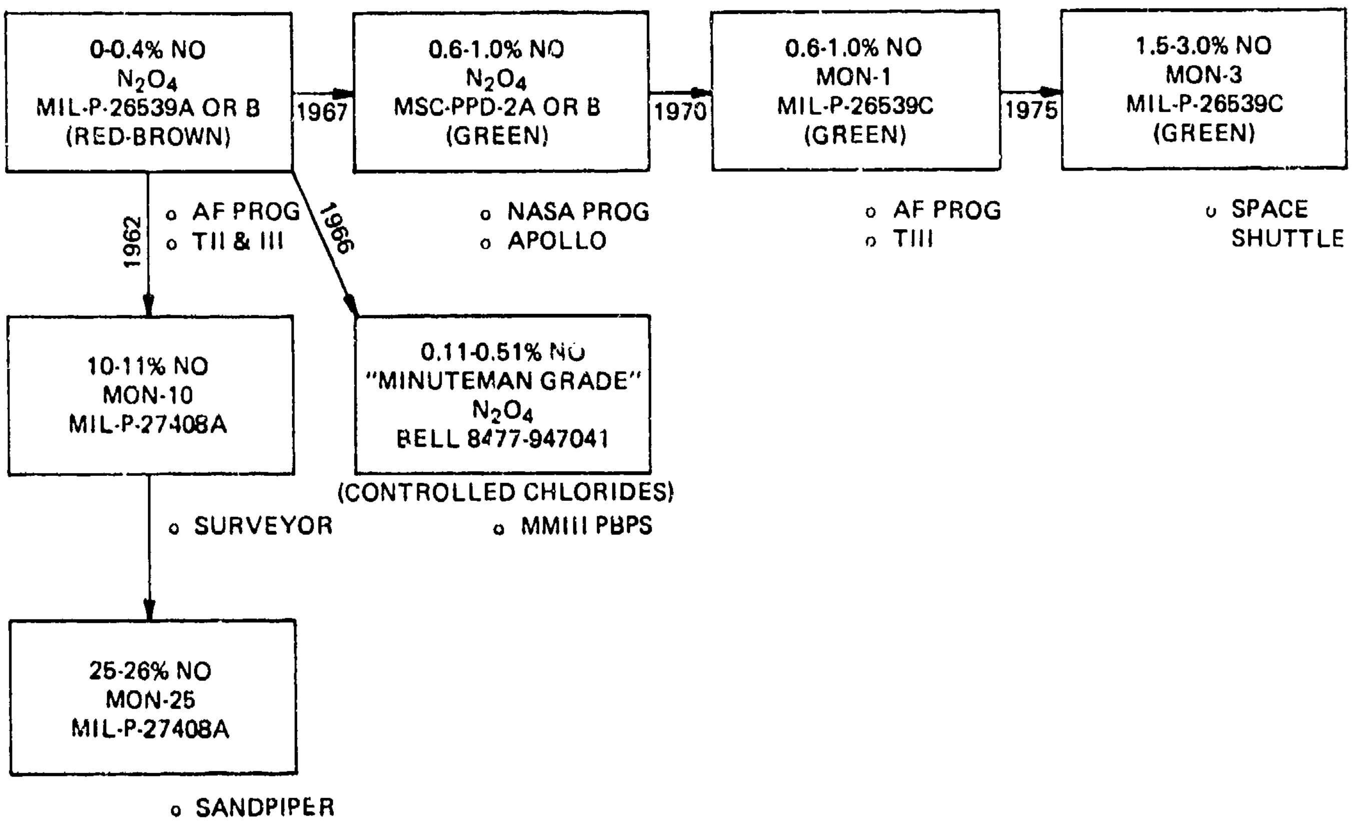
Prior to 1958 the Nitrogen Division of Allied Chemicals was the sole commercial producer of liquid nitrogen tetroxide. This process produced high quality nitrogen tetroxide in connection with production of sodium nitrate and nitric acid. After 1958, Hercules Incorporated produced many tons annually of nitrogen tetroxide in its California plant. Most of that production was used by the U.S. Air Force and NASA as an oxidizer in rocket propulsion systems. This plant is now owned by Valley Nitrogen. At the present time the bulk of the propellant grade N_2O_4 produced in this country is produced by Vicksburg Chemical Company, Vicksburg, Mississippi.

To depress the freezing point of nitrogen tetroxide, nitric oxide (NO) is added. Solutions of NO in nitrogen tetroxide are called mixed oxides of nitrogen (MON) and have been used as oxidizers in rocket engines. Various concentrations have been considered. However, the high vapor pressure of MON limits the concentration of NO in N_2O_4 to about 30 percent. Aside from the high vapor pressure of MON, the material is quite similar to nitrogen tetroxide.

The history of the usage of nitrogen tetroxide as specified in military specifications is very interesting and is shown in Figure 1.1-3. The basic nitrogen tetroxide was used for many years in the red-brown form known as NTO. Problems occured in two programs in about the 1966-67 time period which caused the N_2O_4 to be changed. NASA experienced stress corrosion problems on an Apollo tank with the red-brown NTO. They solved the problem by adding the inhibitor NO. This addition is documented in NASA MSC-PPD-2A which is the specification for green N_2O_4. The Air Force was also concerned about possible corrosion problems on the post-boost propulsion system (PBPS) for Minuteman III. The contractor, Autonetics Division, North American Rockwell ended up with a propellant specification which included controls on NO and chlorides. The control of chlorides was to prevent attack on the 0.030" thick steel bellows in the PBPS tanks.

MIL-P-26539 was modified to specify MON-1, which is the Air Force designation for green N_2O_4. The Space Shuttle Program forced a new look at the N_2O_4 specifications because NASA determined from venting analyses that the NO content of the initial N_2O_4 should be increased to assure that the final or operational oxidizers always had greater than 0.5% NO. Therefore, MON-3 was born. This was incorporated into MIL-P-26539C by Amendment 3. The slight addition of NO does not change the thermal-physical properties of N_2O_4 drastically; therefore, the listed properties for N_2O_4 are applicable to MON-1 and MON-3.

FIGURE 1.1-3 N_2O_4 HISTORY



In 1962, the Surveyor Program wanted to depress the freezing point of N_2O_4 and chose to do so by increasing its NO content. They chose MON-10. The Sandpiper Program chose MON-25 for an even lower freezing point. These variations on N_2O_4 were documented in MIL-P-27408.

1.2 SCOPE AND CONTENT

This Handbook is a comprehensive compilation of all available data pertaining to oxidizers composed of nitric acid and nitrogen tetroxide. An extensive treatment of the physical, chemical, thermodynamic and electrical properties of the oxidizer is combined here, in a single volume, with a survey of the available information on storage, handling, safety, materials compatibility and availability. Also included are sections describing the variation of properties with the composition of blends.

1.3 USER INSTRUCTIONS

1.3.1 FORMAT

This Handbook is divided into five major sections (1.0-5.0). Each major section is then subdivided into subsections by decimal numbers (i.e., 3.1, 2.7 etc.). Each subsection is further divided by three and four digit decimal numbers (i.e., 3.4.1 or 4.2.6.1).

Major sections are separated by tabbed dividers. Each tabbed divider has an index listing the subsections contained after that section tab. Each major subsection has a separator (untabbed) which has an index of minor subsections contained therein.

The indices on each section divider provide a detailed breakdown of the contents of each section and subsection. An index to propellants, acronyms, composition and the relevant properties sections is found after the Section 5.0 divider.

Wherever possible, within a major section, a particular subsection number (three, and four-integer decimals) will always pertain to the same or a similar property or propellant. For example, the numerals 2.1.3.3 denote the following information:

> The first numeral, 2, denotes major section 2, properties. The second numeral, .1, denotes the propellant. The third numeral, .3, denotes that this subsection deals with a physical property. Finally, the fourth numeral, .3, denotes the particular property, "sonic velocity." Within section 2, all sub-sections ending in .3.3 denote "sonic velocity."

In subsections where data on some properties are not available, the corresponding integers will be missing from the sequence, to maintain the meaning of the last two digits.

1.3.2 USE OF INDEX AND REFERENCES

Each section contains on the first page an index to the contents of that section. This page lists the doubly numbered sections within that section. Each doubly numbered section divider contains an index of all subsections within that section. An index showing the location within Section 2, the compositions, and acronyms of the propellants appears on the first page after the Section 5 tabbed divider. This indicates where the properties and logistics of specific propellants may be found.

The location of other types of information is listed alphabetically in Table 1.1-1, located on the first page following the tabbed divider preceding this section.

Each propellant subsection in Section 2 contains a list of references pertaining to the propellant. Each of the remaining major sections (3.0 and 4.0) contains a reference list at the end of the section. The reference numbers in these sections pertain only to the reference list at the end of that section.

1.3.3 UPDATING PROVISIONS

Sections dealing with propellants for which further data is expected to be obtained have been arranged so that missing subsections can be inserted later without disturbing the numbering sequence or the order in which subsections appear. When a gap in data exists for these propellants, the subsection following the gap begins at the top of a new page. If existing subsections must be updated, the appropriate pages can be replaced by the updated page. New or updated pages will be distributed to recipients of this Handbook when they become available.

2.0 PROPERTIES AND LOGISTICS

2.1 NITRIC ACID (TYPE IIIA, IIIB, AND IIILS)

2.2 NITRIC ACID (TYPE IV) (HDA)

2.3 NITROGEN TETROXIDE (NTO, MON-1, MON-3, MON-10, MON-25, AND MM GRADE

2.1 NITRIC ACID, TYPE IIIA, TYPE IIIB, AND TYPE IIILS

2.1.1 PROPERTY SUMMARY SHEET

Chemical Name: RFNA (IRFNA) Type III, IIIA, IIIB, IIILS **Common Name:** Red (Inhibited) Fuming Nitric Acid

Chemical Formula: $H_{0.8894} N_{0.9366} O_{2.6989}$ **Formula Weight:** 57.2 (O^{16}) - Nominal

Property	Value	Units	Temp (°K)	Reference	Figure
Melting Point	221.15 -52 398.07 -61.6	°K °C °R °F		1	
Heat of Fusion	2503±2*	cal/mole	231.56	14	
Normal Boiling Point	337.34 64.19 607.21 147.5	°K °C °R °F		Calc	
Heat of Vaporization	140.4 252.8	cal/g BTU/lb	337.34	Calc	
Heat of Disassociation	Not Available				
Critical State Constants Temperature	546.48 273.33 983.67 524	°K °C °R °F		Calc	
Pressure	95.35 1401.2	atms psia		Calc	
Density	0.55 34.60	g/cc lb/ft^3		Calc	
Vapor Pressure of Liquid	138.7 2.68	mm Hg psia	298.15 298.15	Calc	2.1-1
Density of Liquid	1.55 96.76	g/cc lb/ft^3	298.15	4	2.1-2
Sonic Velocity	1379.0 4526.0	m/sec ft/sec	not given	2, 6	
Compressibility of Liquid Adiabatic	3.563×10^{-5} 2.425×10^{-6}	atm^{-1} psi^{-1}	298.15 298.15	Calc	
Isothermal	Not Available				
Viscosity of Liquid	1.231 0.8282×10^{-3}	cp lb/ft/sec	298.15 298.15	Calc	2.1-4
Heat Capacity of Liquid	0.420 0.420	cal/g-°K BTU/lb-°R	298.15	2, 7	2.1-7
Thermal Conductivity of Liquid	6.968×10^{-4} 4.844×10^{-5}	cal/cm-sec-°K BTU/ft-sec-°R	298.15	2, 7	2.1-6
Surface Tension	40.13 3.089×10^{-3}	dynes/cm lb/ft	298.15	Calc	2.1-5
Refractive Index	1.3970*	–	297.15	14	
Dielectric Constant	Not Available				
Dipole Moment	2.16*	Debyes	Not Reported	14	
Entropy (Gas)	63.62*	cal/°K-mole			
Entropy (Liquid)	37.19*	cal/°K-mole	298.15	14	
Heat of Formation (liquid)	-37.7 1186	Kcal/mole BTU/lb	298.15	Calc	
Specific Heat	0.417	cal/g	293.15	3	

*Pure HNO_3

2.1.2 GENERAL

2.1.2.1 Introduction

Nitric acid is one of the most commonly used oxidizers for rocket engines. It is a readily commercially available chemical. Nitric acid is made by the catalytic oxidation of ammonia with air or oxygen to yield nitric oxide (NO). The latter is oxidized to N_2O_4 which when treated with water, yields nitric acid (HNO_3). HNO_3 may be concentrated by distillation with sulfuric acid. There are three forms in which nitric acid is used:

(1) Anhydrous nitric acid
(2) Red fuming nitric acid (RFNA)
(3) White fuming nitric acid (WFNA)

The fuming nitric acids are produced by passing gaseous N_2O_4 into nitric acid. The fuming nitric acids, as specified in Military Specification MIL-P-7254F, Amendment 2 (9), are identified by chemical composition (percentage of weight) with the limits as listed in Table 2.1-1. The Type I nitric acids have been declared obsolete for military usage as a rocket oxidizer.

Red fuming nitric acid is a highly corrosive, toxic, nonflammable liquid mixture. Its color is light orange to orange-red, depending upon the amount of dissolved NO_2. RFNA will vigorously attack most metals. Addition of 0.7 percent by weight hydrogen fluoride (HF) inhibits corrosion of container materials by RFNA.

The acid reacts with many organic materials spontaneously causing fire. In rare instances, on gross contact with certain materials (e.g., hydrazine) and when spontaneous ignition is delayed because of degraded materials, an explosion may occur. The nitric acids will react with sea water, releasing large quantities of nitrogen oxides which are toxic.

Since the composition of RFNA is variable, all values of physical constants listed in the literature are considered approximate or have been calculated herein based on the following nominal chemical composition:

HNO_3, percent by weight, 84
NO_2, percent by weight, 14
H_2O, percent by weight, 2
HF, percent by weight, 0
Solids, percent by weight, 0

The apparent formula weight for nominal RFNA is 57.2 with a chemical formula $H_{0.8894} N_{0.9365} O_{2.6989}$.

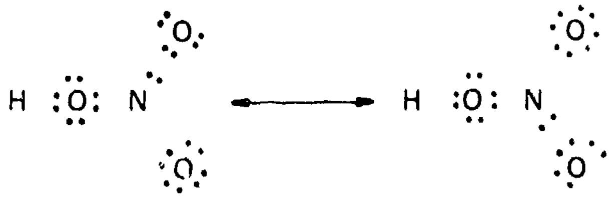
TABLE 2.1-1 FUMING NITRIC ACIDS–CHEMICAL COMPOSITION LIMITS (PERCENTAGE BY WEIGHT)

Type	Common Name	Nitrogen Dioxide (NO_2)	Water (H_2O)	Nitric Acid (HNO_3)	Solids as Nitrates	Hydrogen Fluoride Inhibitor
I[1]	White fuming nitric acid (WFNA)	0.5 max.	2.0 max.	97.5	0.10 max.	--
IA[1]	Inhibited white fuming nitric acid (IWFNA)	0.5 max.	2.0 max.	96.8	0.10 max.	0.7 ± 0.1
III	Red fuming nitric acid (RFNA)	14 ± 1.0	1.5 to 2.5	82.4 to 85.4	0.10 max.	–
IIIA	Inhibited red fuming nitric acid (IRFNA)	14 ± 1.0	1.5 to 2.5	81.6 to 84.8	0.10 max.	0.7 ± 0.1
IIIB	Inhibited red fuming nitric acid (IRFNA)	14 ± 1.0	1.5 to 2.5	81.6 to 84.8	0.04 max.	0.7 ± 0.1
IIILS	Limited Storage red fuming nitric acid (IRFNA)	14 ± 1.0	0.5 max.	83.7 to 86.4	0.04 max.	0.7 ± 0.1

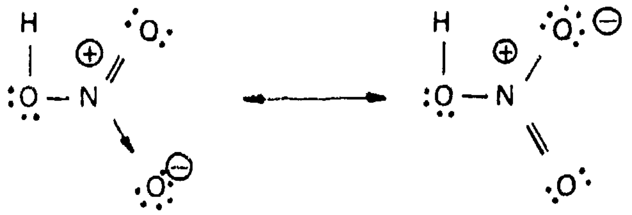
Note: [1] Declared obsolete for military usage.

2.1.2.2 Structure of Nitric Acid

The HNO_3 molecule is planar and may be represented as a resonance hybrid.



or



The "best" bond distances and angles based on the study of Stern, Mullhaupt, and Kay (14) listed below: (Their work should be referred to if a more complete description is required).

N-O length	1.22 Å
N-OH length	1.41 Å
O-N-O angle (degrees)	135
O-N-OH angle (degrees)	115

The molecular dipole moment is 2.16 debyes.

2.1.2.3 Specification

The procurement of RFNA as a propellant is covered by MIL-P-7254F, Amendment 2 (18 January 1972).

2.1.3 PHYSICAL PROPERTIES OF NITRIC ACID

2.1.3.1 Vapor Pressure and Normal Boiling Point

Vapor pressure values found in the literature were few. The decomposition and corrosive nature of nitric acid precludes accurate measurement of vapor pressure. Vapor pressure is defined as the pressure exerted by a vapor when a state of equilibrium has been reached between a liquid, or solid, and its vapor. The data points (1, 2, 5, 6) are plotted and shown in Figures 2.1-1 and 2.1-1a. Rocketdyne (4) prepared a data sheet citing their source from a National Advisory Committee for Aeronautics research memoranda (E53L14, February 1954). Curve-fitted equations are presented for vapor pressure values in the temperature range of 10 to 57°C (50 to 135°F) and a composition range of RFNA as follows:

10 to 17 percent by weight N_2O_4

1 to 6 percent by weight H_2O

77 to 86 percent by weight HNO_3

The equations are: (2.1-1)

$$\log_{10} P(\text{atm}) = 6.447\text{-}2.24 \times 10^{-2} N_{w/o} + 1.72 \times 10^{-3} N_{w/o} \cdot \frac{2250.5}{(T, °K)} + \frac{13.55 N_{w/o}}{(T, °K)}$$

where:

$N_{w/o}$ = weight percent of N_2O_4

$W_{w/o}$ = weight percent of H_2O

P = vapor pressure, atm

T = temperature, °K

(2.1-1a)

$$\log_{10} P(\text{psia}) = 7.6444\text{-}2.24 \times 10^{-2} N_{w/o} + 1.72 \times 10^{-3} N_{w/o} W_{w/o} \cdot \frac{4050.8}{(T, °R)} + \frac{24.39 N_{w/o}}{(T, °R)}$$

where

$N_{w/o}$ = weight percent of N_2O_4

$W_{w/o}$ = weight percent of H_2O

P = vapor pressure, atm

T = temperature, °R

The equations for the nominal RFNA become:

$$\log_{10} P\ (\text{atm}) = 6.182 - \frac{2060.8}{(T, °K)} \qquad (2.1\text{-}2)$$

$$\log_{10} P\ (\text{psia}) = 7.3786 - \frac{3709.34}{(T, °R)} \qquad (2.1\text{-}2a)$$

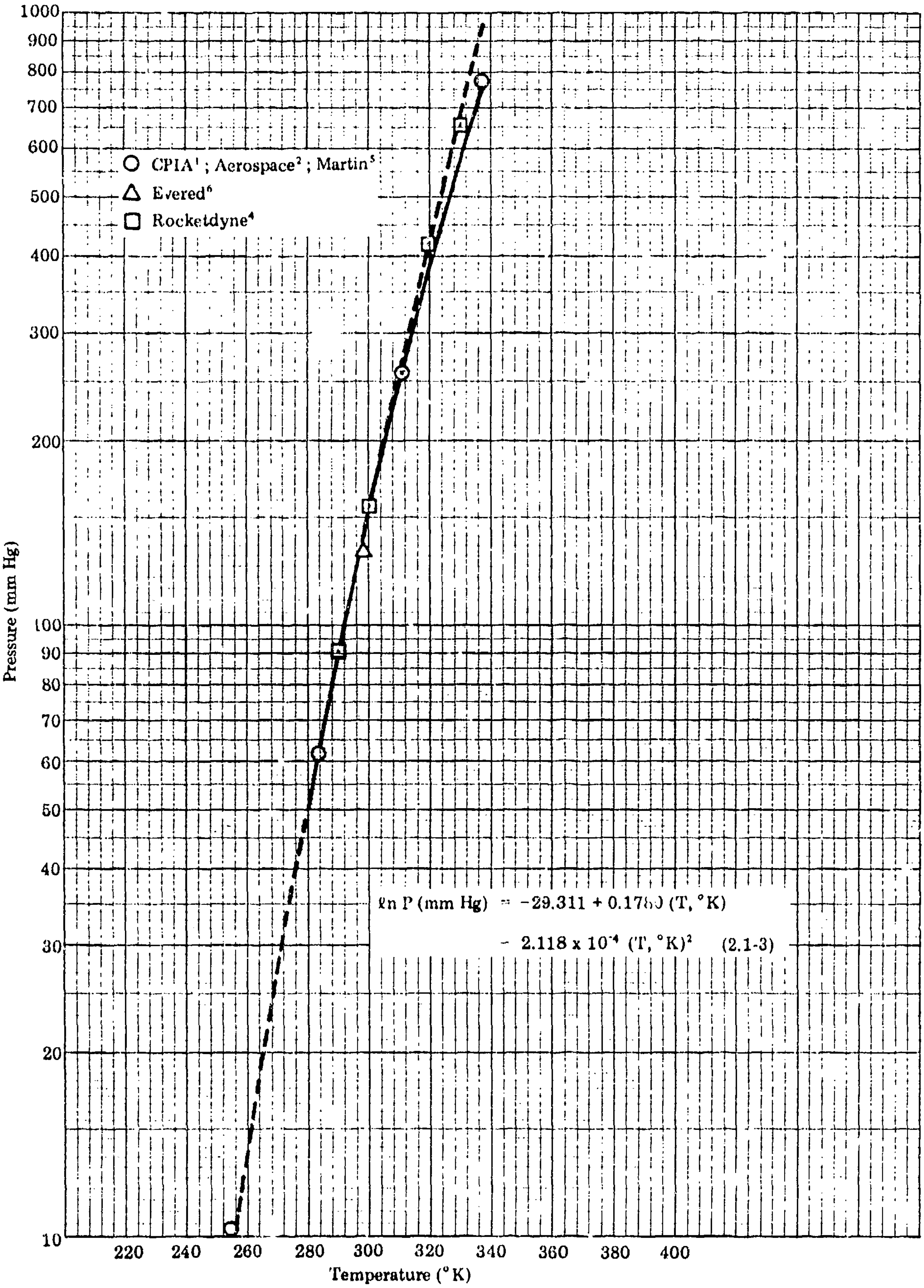
Rocketdyne's standard error of estimate for P is 2.8%. Rocketdyne's values are also plotted in Figures 2.1-1 and 2.1-1a. In this study, equations were determined by the least-squares method due to the divergence noted as the values approached the vapor pressure of 15.0 psia at 775.7 mm Hg (1, 2). They are:

$$\ln P\ (\text{mmHg}) = -29.311 + 0.1780\ (T, {}^\circ K) - 2.118 \times 10^{-4}\ (T, {}^\circ K)^2 \qquad (2.1\text{-}3)$$

$$\ln P\ (\text{psia}) = -33.257 + 0.0989\ (T, {}^\circ R) - 6.539 \times 10^{-5}\ (T, {}^\circ R)^2 \qquad (2.1\text{-}3a)$$

The standard deviation calculated from equation 2.1-3 is 1.2 percent in P and the average deviation is 0.62 percent.

From equation 2.1-3 a normal boiling point value of 337.34°K (64.19°C or 147.5°F) is obtained. CPIA (1) reports a value of 140°F. Aerospace (2) reports a value of 148°F as well as does Aerojet (7). The Propellant Handbook (AFRPL-TR-66-4) (3) reports a value of 65.6°C (150.1°F) for IRFNA.



$$\ell n\, P\ (\text{mm Hg}) = -29.311 + 0.1780\ (T, {}^\circ K) - 2.118 \times 10^{-4}\ (T, {}^\circ K)^2 \qquad (2.1\text{-}3)$$

Figure 2.1-1. Vapor Pressure of RFNA versus Temperature

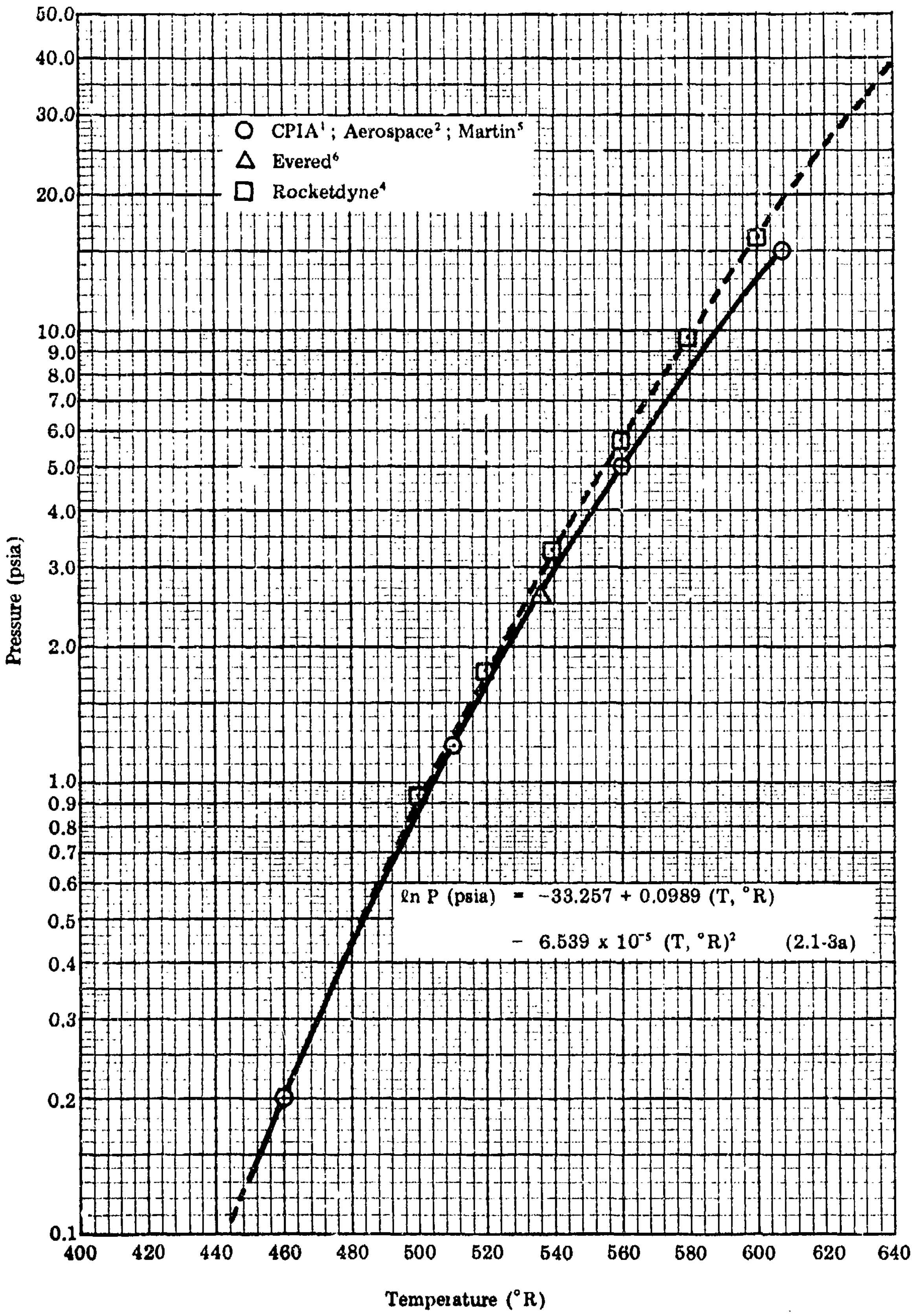


Figure 2.1-1a. Vapor Pressure of RFNA versus Temperature

2.1.3.2 Density of Red Fuming Nitric Acid

Density values of RFNA are listed by Aerospace (2). One point value (1.551 g/cc at 25°C) was listed by CPIA (1) and Evered (6). A value of 1.564 g/cc at 16°C (289.15°K) was listed in the Propellant Handbook/RPL (3) for IRFNA.

Rocketdyne (4) prepared a current data sheet showing the following curve-fitted equations:

$$\begin{aligned}\rho\ (\text{g/cc}) = {} & 1.5340 - 1.694 \times 10^{-3} t_c + 6.06 \\ & \times 10^{-3} N_{w/o} - 3.05 \times 10^{-3} W_{w/o} \\ & - 7.92 \times 10^{-5} N^2{}_{w/o} \\ & - 1.13 \times 10^{-4} N_{w/o} W_{w/o} \end{aligned} \qquad (2.1\text{-}4)$$

$$\begin{aligned}\rho\ (\text{lb/cuft}) = {} & 97.65 - 5.87 \times 10^{-2} t_F \\ & + 0.378 N_{w/o} - 0.190 W_{w/o} \\ & - 4.95 \times 10^{-3} N^2{}_{w/o} \\ & - 7.1 \times 10^{-3} N_{w/o} W_{w/o} \end{aligned} \qquad (2.1\text{-}4a)$$

where:

ρ = density, g/cc or lb/cuft
t = temperature, °C or °F
$N_{w/o}$ = N_2O_4, percent by weight
$W_{w/o}$ = H_2O, percent by weight

Temperature range: 0 to 40°C
(32 to 104°F)
273.15 to 313.15°K
(491.67 to 559.67°R)

Composition Range: 8 to 20 w/o N_2O_4
0 to 6 w/o H_2O
72 to 92 w/o HNO_3

Standard error of estimate: 0.0021 g/cc
(0.13 lb/cuft)

For the nominal RFNA composition, Rocketdyne equations reduces to:

$$\rho\ (\text{g/cc}) = 2.0568 - 1.694 \times 10^{-3}\ (T, ^\circ K) \qquad (2.1\text{-}5)$$

$$\rho\ (\text{lb/ft}^3) = 128.37 - 5.87 \times 10^{-2}\ (T, ^\circ R) \qquad (2.1\text{-}5a)$$

T = temperature, °K or °R

Figures 2.1-2 and 2.1-2a show the density values plotted from the mentioned literature sources. There isn't good agreement between the data of the Aerospace Handbook and Rocketdyne's work. But because there are point values that fall within Rocketdyne's equation, Rocketdyne's equations are recommended for usage since their work is based on the listing of seven documents.

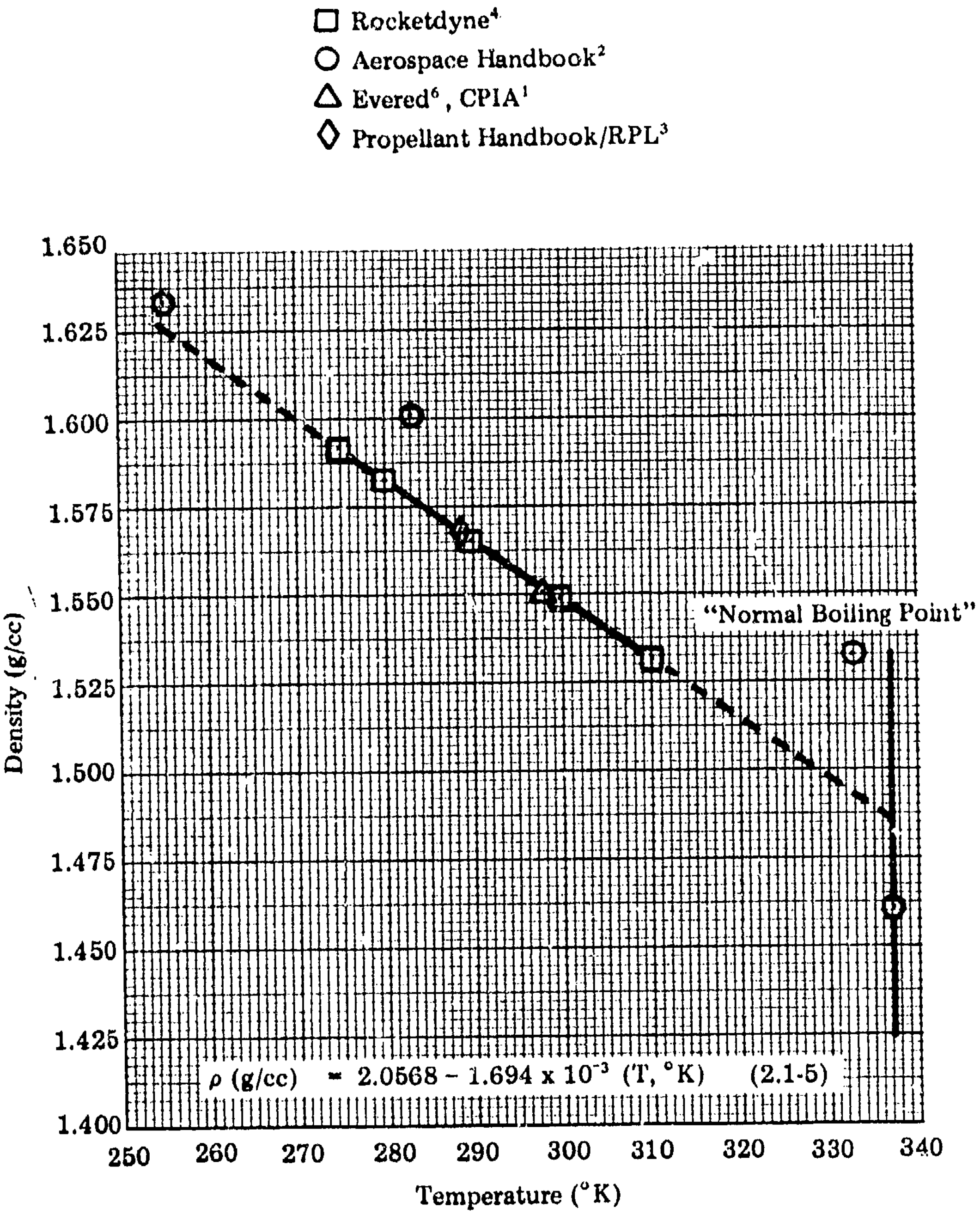


Figure 2.1-2. Density of RFNA

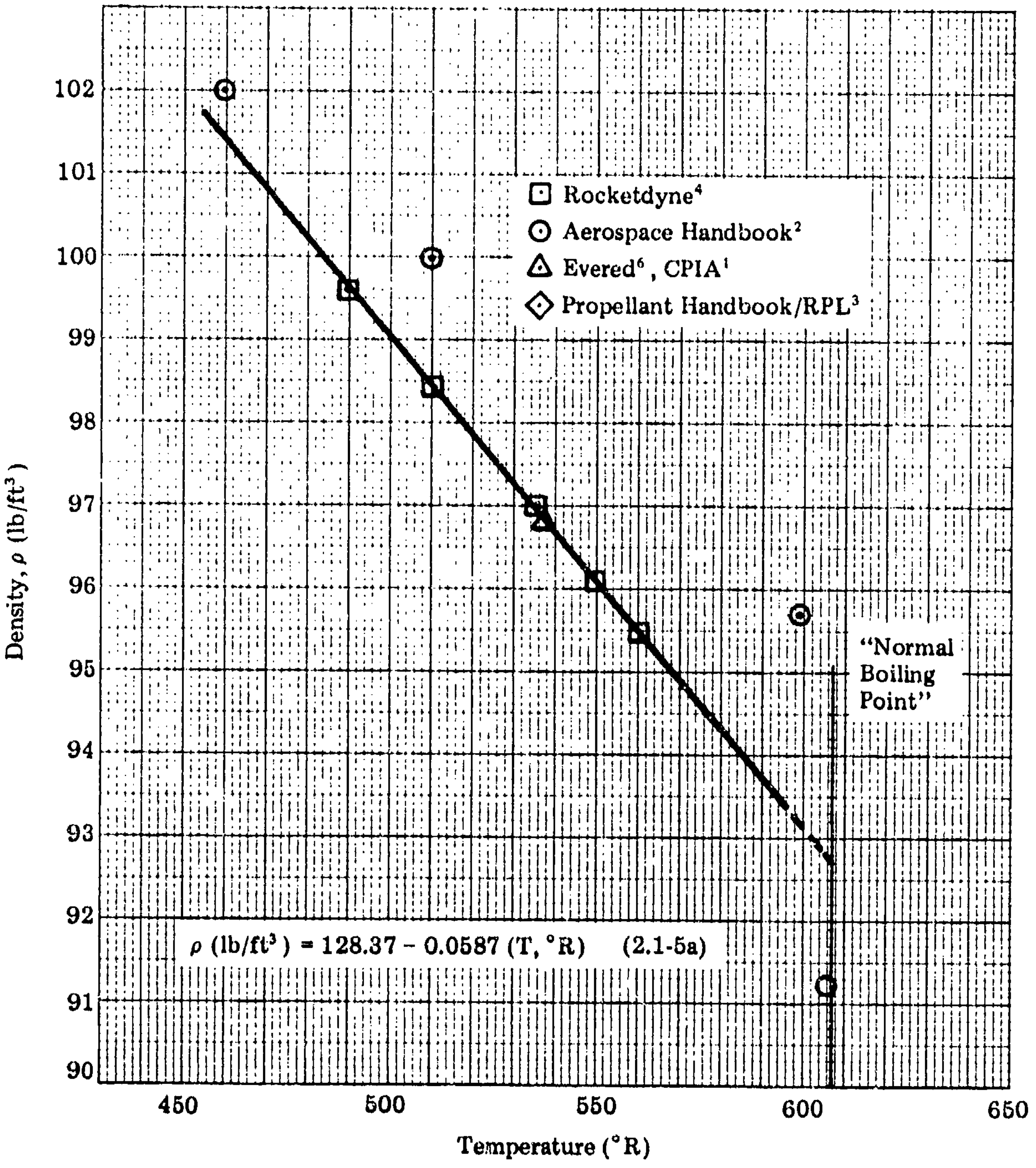


Figure 2.1-2a. Density of RFNA

2.1.3.3 Sonic Velocity in Red Fuming Nitric Acid

Evered (6) listed the velocity of sound value of 4525.0 ft/sec (1379.0 m/sec) in RFNA whose composition was 77.5% HNO, 20% N_2O_4, and 2.0% H_2O. No temperature was given. The same value was quoted by Aerospace (2).

2.1.3.4 Compressibility of Red Fuming Nitric Acid

There is one measurement of the sonic velocity in RFNA listed and it is given in section 2.1.3.3. The adiabatic compressibility β_s can be determined using sonic velocity data and the acoustical equation:

$$\beta_s = \frac{1}{\rho c^2} \qquad (2.1\text{-}6)$$

where: ρ = density
c = sonic velocity

An estimated compressibility value was computed for RFNA with the following assumptions:

1. The velocity was measured at 298.15°K (536.67°R)
2. The velocity was interpolated from a rough plot of velocity, Figure 2.1-3, as a function of percent N_2O_4 in HNO_3 solution. The value was 1354 m/sec.
3. The density at 298.15°K was 1.551 g/cc.

The estimated computed value is 2.425×10^{-6} psi^{-1} or 3.563×10^{-5} atm^{-1} at 298.15°K (536.67°R).

Isothermal cmpressibility β_i could not be estimated as there were no density change measurements as a function of pressure for the same temperature readily listed in the literature.

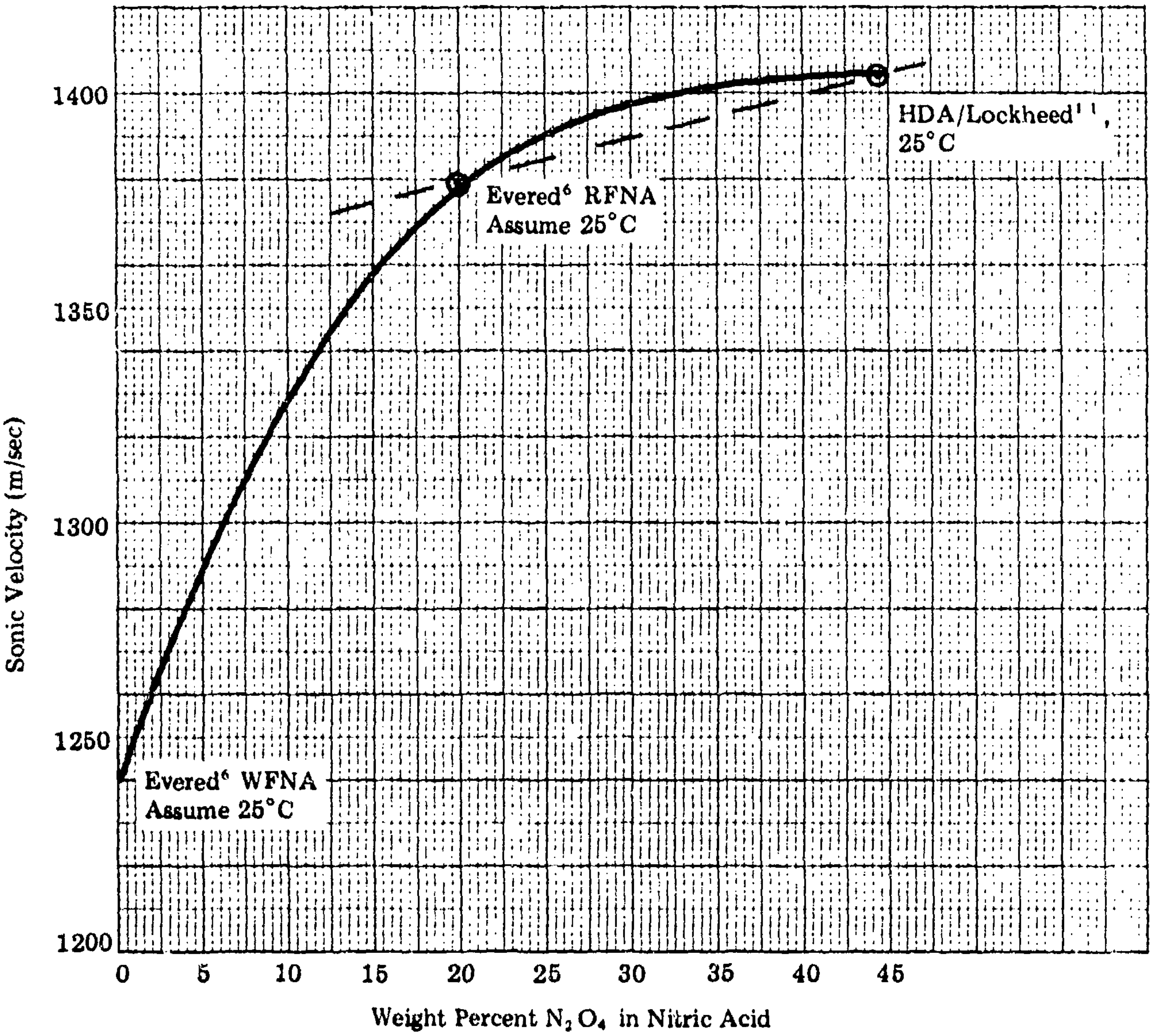


Figure 2.1-3. Rough Estimate of Sonic Velocity as a Function of % N_2O_4

2.1.3.5 Viscosity of Red Fuming Nitric Acid

Viscosity values are tabulated in the Aerospace Handbook (2) for the temperature range 0 to 148°F (459.67 to 607.67°R). Values were also tabulated by Evered (6) from 23 to 113°F. These values are plotted in Figures 2.1-4 and 2.1-4a. A third-order equation was determined from the least-squares method that would pass the temperature limits of 0°F and 148°F for the data listed.

$$\begin{aligned} \ln \mu \text{ (centipoise)} = {} & 11.761 - 3.286 \times 10^{-2} (T, ^\circ K) \\ & - 1.075 \times 10^{-4} (T, ^\circ K)^2 \\ & + 2.943 \times 10^{-7} (T, ^\circ K)^3 \end{aligned} \tag{2.1-7}$$

$$\begin{aligned} \ln \mu \text{ (lb}_m\text{/ft-sec)} = {} & 11.793 - 2.090 \times 10^{-2} (T, ^\circ R) \\ & - 2.781 \times 10^{-5} (T, ^\circ R)^2 \\ & + 4.687 \times 10^{-6} (T, ^\circ R)^3 \end{aligned} \tag{2.1-7a}$$

The standard deviation of the reported data as deter-from equation 2.1-7 was 9 percent in μ.

Rocketdyne (4) presented equations for viscosity as a function of temperature and composition for the red fuming nitric acid. They cited literature sources which Evered (6) listed. The equations were expressed in terms of the weight percent of N_2O_4 and H_2O as follows:

$$\begin{aligned} \log_{10}\mu\text{(cp)} = {} & -3.262 - 0.1084\, N_{w/o} \\ & - 2.66 \times 10^{-2} W_{w/o} \\ & + 3.602 \times 10^{-3} N^2_{w/o} \\ & + \frac{1678.3}{(T, ^\circ K)} + \frac{3.11\, N_{w/o}}{(T, ^\circ K)} \\ & + \frac{11.8 W_{w/o}}{(T, ^\circ K)} - \frac{148760}{(T, ^\circ K)^2} \end{aligned} \tag{2.1-8}$$

$$\begin{aligned} \log_{10}\mu\text{(lbM/ft-sec)} = {} & -6.435 - 0.1084 N_{w/o} \\ & - 2.66 \times 10^{-2} W_{w/o} \\ & + 3.602 \times 10^{-3} N^2_{w/o} \\ & + \frac{3020.8}{(T, ^\circ R)} + \frac{5.6 N_{w/o}}{(T, ^\circ R)} \\ & + \frac{21.3 W_{w/o}}{(T, ^\circ R)} - \frac{482000}{(T, ^\circ R)^2} \end{aligned} \tag{2.1-8a}$$

where:

$N_{w/o}$ = weight percent of N_2O_4

$W_{w/o}$ = weight percent of H_2O

Composition range: 11 to 20 w/o N_2O_4
0 to 6 w/o H_2O
76 to 89 w/o HNO_3

Temperature range: 0 to 116°C
(273.15 to 389.15°K)
32 to 240°F
(491.67 to 599.67°R)

Standard error of estimate: 3 percent in μ.

For the nominal RFNA, the equations reduce to:

$$\log_{10}\mu\text{(cp)} = -4.127 + \frac{1745.4}{(T, ^\circ K)} - \frac{148760}{(T, ^\circ K)^2} \tag{2.1-9}$$

$$\log_{10}\mu\text{(lb}_m\text{/ft-sec)} = -7.300 + \frac{3141.8}{(T, ^\circ R)} - \frac{482000}{(T, ^\circ R)^2} \tag{2.1-9a}$$

The two curves (Aerospace and Rocketdyne data) plotted on Figures 2.1-4 and 2.1-4a indicate divergences at the lower and higher ranges of temperature. When calculating the viscosity, use equation 2.1-7 or 2.1-7a for temperatures below 260°K (468°R). No experimental data was reported beyond 337.59°K (2), however, equations 2.1-9 and 2.1-9a may be used.

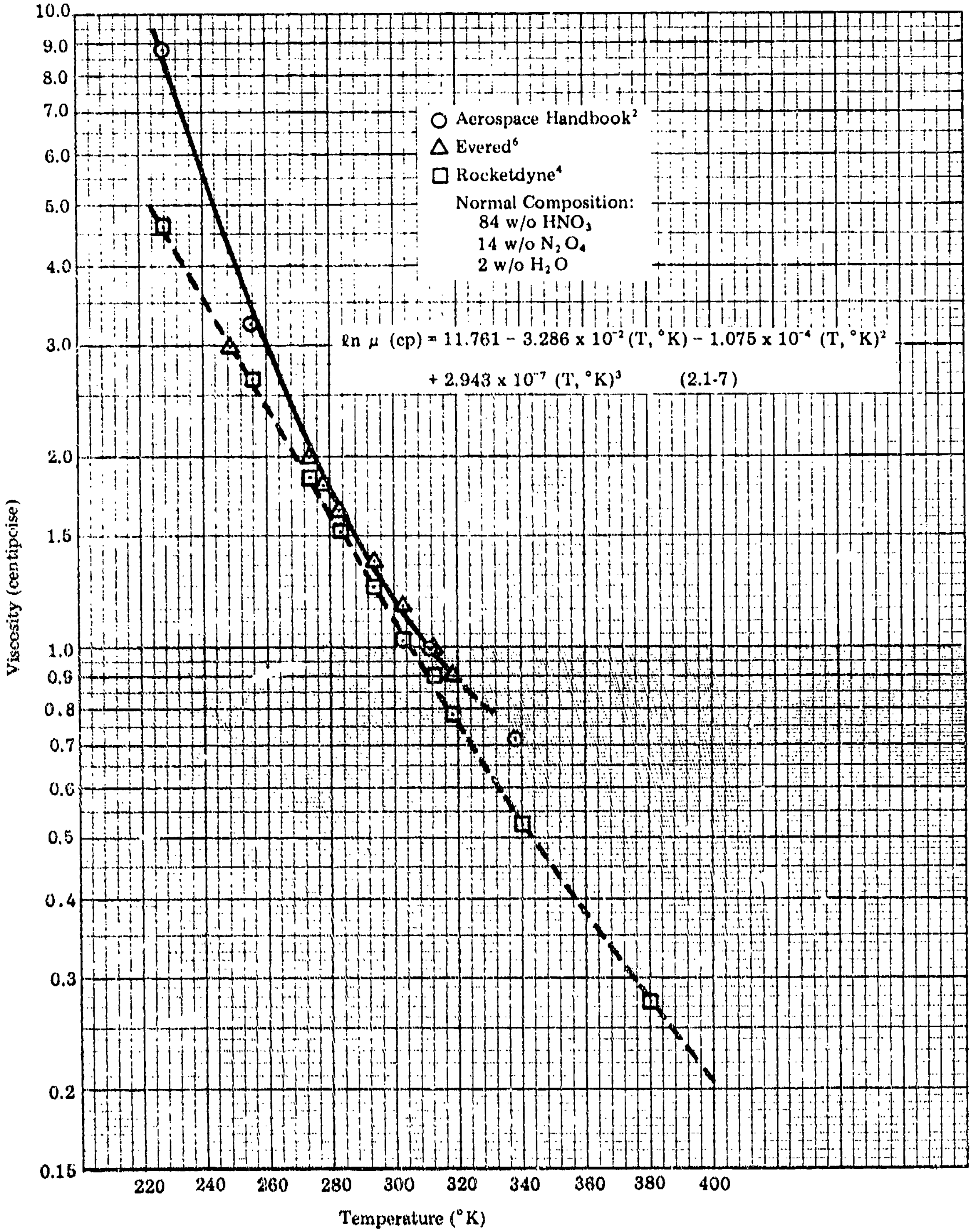
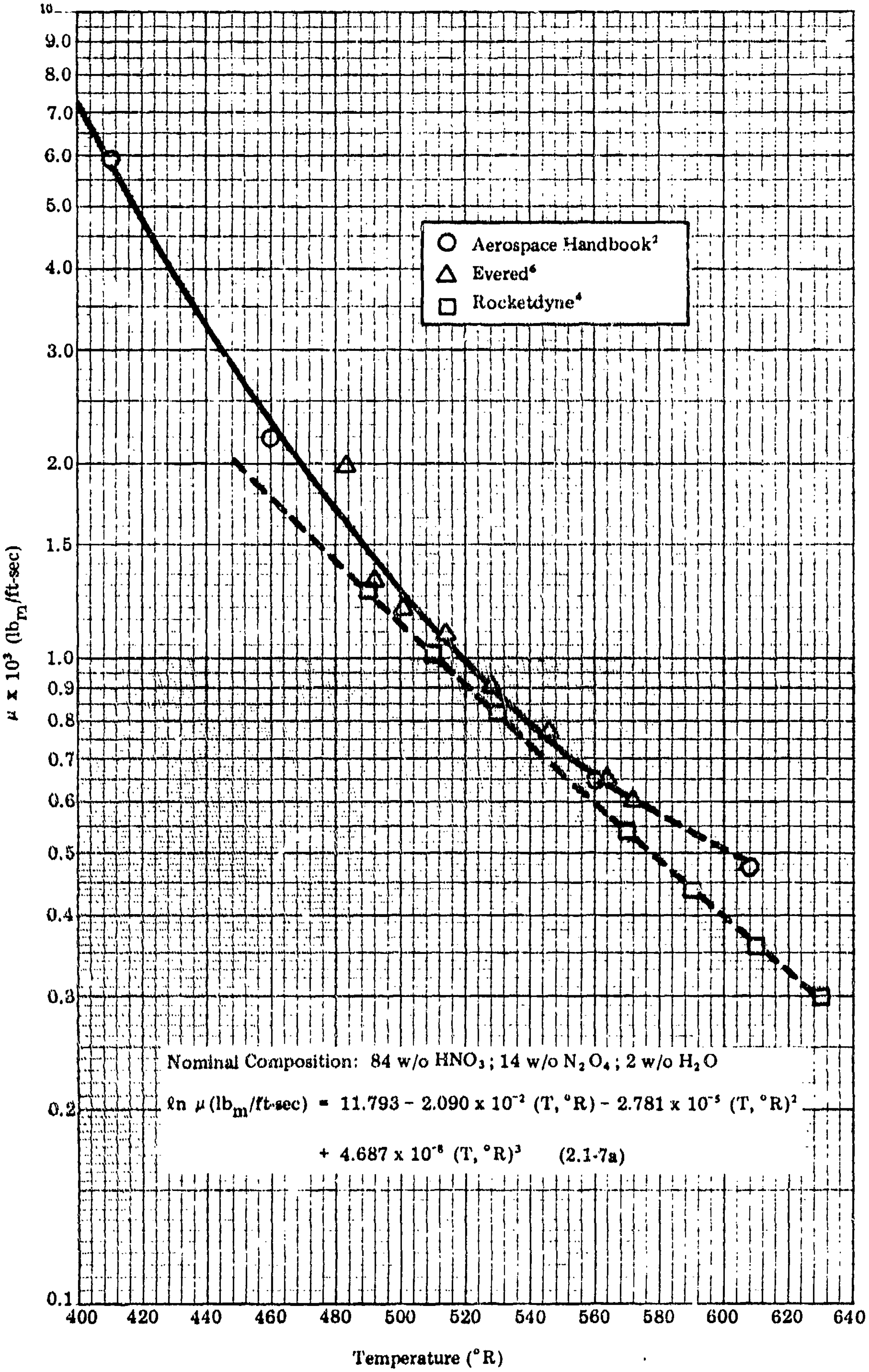


Figure 2.1-4. Viscosity of RFNA versus Temperature



Nominal Composition: 84 w/o HNO_3; 14 w/o N_2O_4; 2 w/o H_2O

$$\ell n\ \mu\,(lb_m/ft\text{-}sec) = 11.793 - 2.090 \times 10^{-2}\,(T, {}^\circ R) - 2.781 \times 10^{-5}\,(T, {}^\circ R)^2 + 4.687 \times 10^{-8}\,(T, {}^\circ R)^3 \qquad (2.1\text{-}7a)$$

Figure 2.1-4a. Viscosity of RFNA versus Temperature

2.1.3.6 Surface Tension of Red Fuming Nitric Acid

Measurements of the surface tension of RFNA were not listed in the literature reviewed from 1960 to the present. Tabulated are the following values found for other forms of the fuming nitric acid.

TABLE 2.1-2 REPORTED SURFACE TENSION VALUES FOR THE NITRIC ACIDS

Temp/ Surface Tension	Anhydrous HNO_3		White Fuming HNO_3		High Density Acid[f]	
	Dynes/cm	Lb_f/Ft	Dynes/cm	Lb_f/Ft	Dynes/cm	Lb_f/Ft
0°C	43.56[4]	.00298[4]	--	–	36.4[11]	.00249
11.6°C	42.7[10]	.00293	–	–	–	–
20°C	41.15[4]	.00282[4]	–	–	31.1[11]	.00214
78.2	32.6[10]	.00223	–	–	–	–
Unknown	–	–	40.99	.002809[2]	–	–

Superscript is literature source.

[f] Included for comparison and trend.

The surface tension of all liquids decreases as the temperature is increased and becomes zero at the critical temperature. The variation of surface tension with temperature may be represented by the Ramsay-Shields equation (8), namely,

$$\gamma\left(\frac{M}{\rho_l}\right)^{2/3} = K(t_c - t - 6) \qquad (2.1\text{-}10)$$

where:

γ = surface tension, dynes/cm

t = temperature, °C

M = molecular weight

ρ_l = density, g/cc

t_c = critical temperature, °C

K = constant, supposedly independent of temperature

For many liquids K has been found to be nearly the same and equal approximately to 2.12. However, using K equal to 2.12, calculated values of surface tension (γ) for the anhydrous nitric acid were high. Thus the K value was derived using the reported surface tension values for 0°C and 20°C in the Ramsay-Shields equation. A value of 1.85 was arbitrarily assigned since the derived value of K was 1.85 at 0°C and 1.91 at 20°C.

Values of surface tension were calculated for the nominal RFNA using these values:

M = 57.2 g/mole

ρ_l = calculated from equation 2.1-5

t_c = 271.11°C

K = 1.85

The calculated values from 0 to 57°C (32 to 134.6°F) on Figures 2.1-5 and 2.1-5a. The graphical data may be expressed as a curve-fit equation, namely:

$$\gamma\ (\text{dynes/cm}) = 98.361 - 0.1953\ (T\ ^\circ K) \qquad (2.1\text{-}11)$$

$$\gamma\ (lb_f/ft) = 6.7574 \times 10^{-3} - 7.4611 \times 10^{-6}\ (T, ^\circ R) \qquad (2.1\text{-}11a)$$

The standard deviation calculated from equation 2.1-11 is 0.0456 dynes/cm.

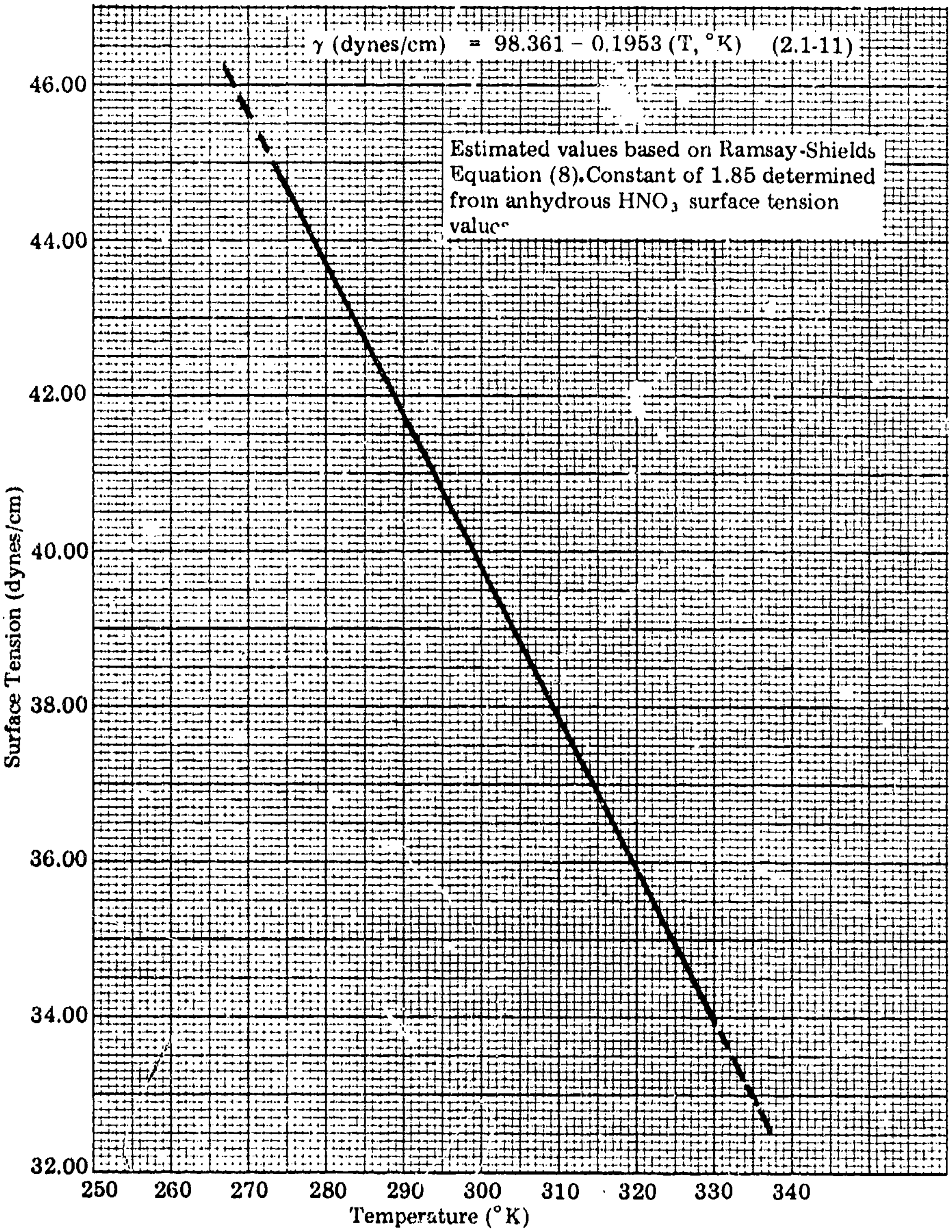


Figure 2.1-5. Estimated Values of Surface Tension RFNA versus Temperature

Estimated values based on Ramsay-Shields Equation (8). Constant of 1.85 determined from anhydrous HNO_3 surface tension values.

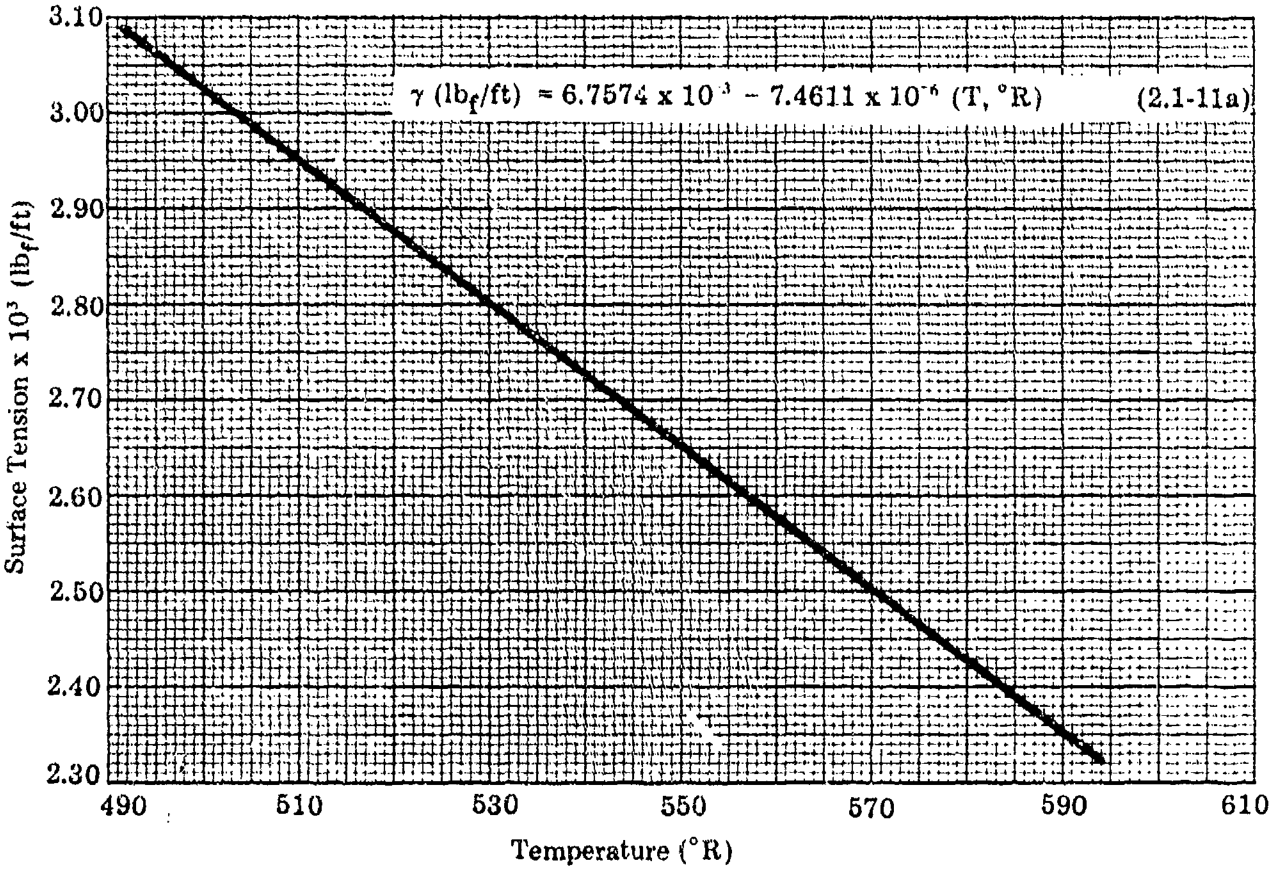


Figure 2.1-5a. Estimated Values of Surface Tension RFNA versus Temperature

2.1.3.7 Thermal Conductivity of Red Fuming Nitric Acid

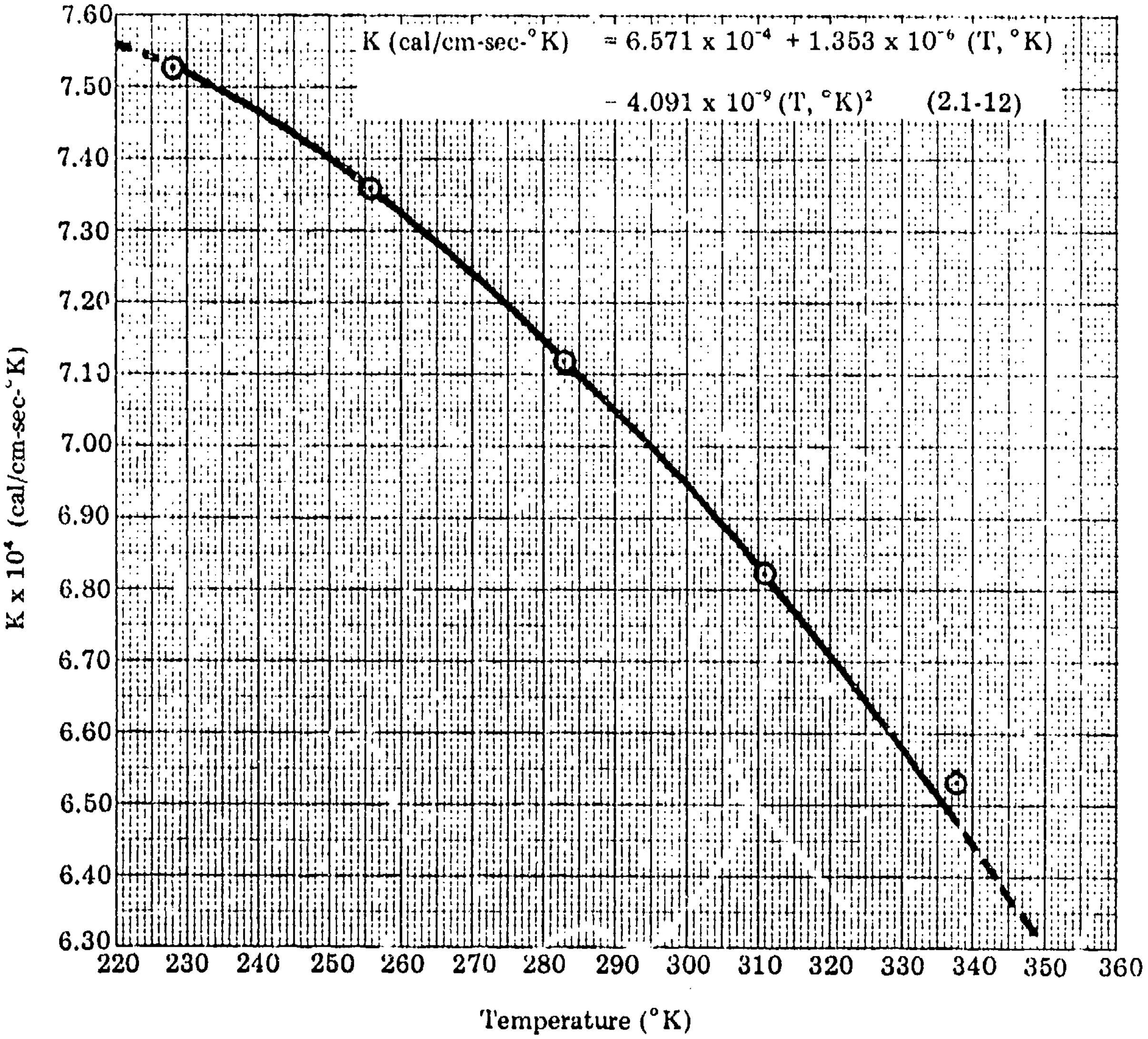
The Aerospace Handbook (2) reported thermal conductivity values from -50° to 148°F. Aerojet-General (7) showed a curve plot of thermal conductivity versus temperature identifying the curve as extrapolated data citing two sources for their presentation of RFNA (85% HNO_3, 15% NO_2 by weight) (12, 13). Aerospace's and Aerojet's data are apparently identical.

The reported values are given in Figures 2.1-6 and 2.1-6a. The expressions of thermal conductivity as a function of temperature by the least square curve fit method as follows:

$$K(\text{cal/cm-sec-°K}) = 6.571 \times 10^{-4} + 1.353 \times 10^{-6} (T, °K) - 4.091 \times 10^{-9} (T, °K)^2 \quad (2.1\text{-}12)$$

$$K(\text{BTU/ft-sec-°R}) = 4.453 \times 10^{-5} + 4.876 \times 10^{-8} (T, °R) - 8.300 \times 10^{-11} (T, °R)^2 \quad (2.1\text{-}12a)$$

The equations are applicable for the temperature range 227.59 to 337.59°K (409.67 to 607.67°R). The standard deviations obtained from equations 2.1-12 and 2.1-12a are 1.043×10^{-6} cal/cm-sec-°K and 5.59×10^{-8} BTU/ft-sec-°R respectively with an average deviation of 0.06 percent.



$$K\ (\text{cal/cm-sec-°K}) = 6.571 \times 10^{-4} + 1.353 \times 10^{-6}\ (T, °K) - 4.091 \times 10^{-9}\ (T, °K)^2 \qquad (2.1\text{-}12)$$

Figure 2.1-6. Thermal Conductivity of RFNA versus Temperature

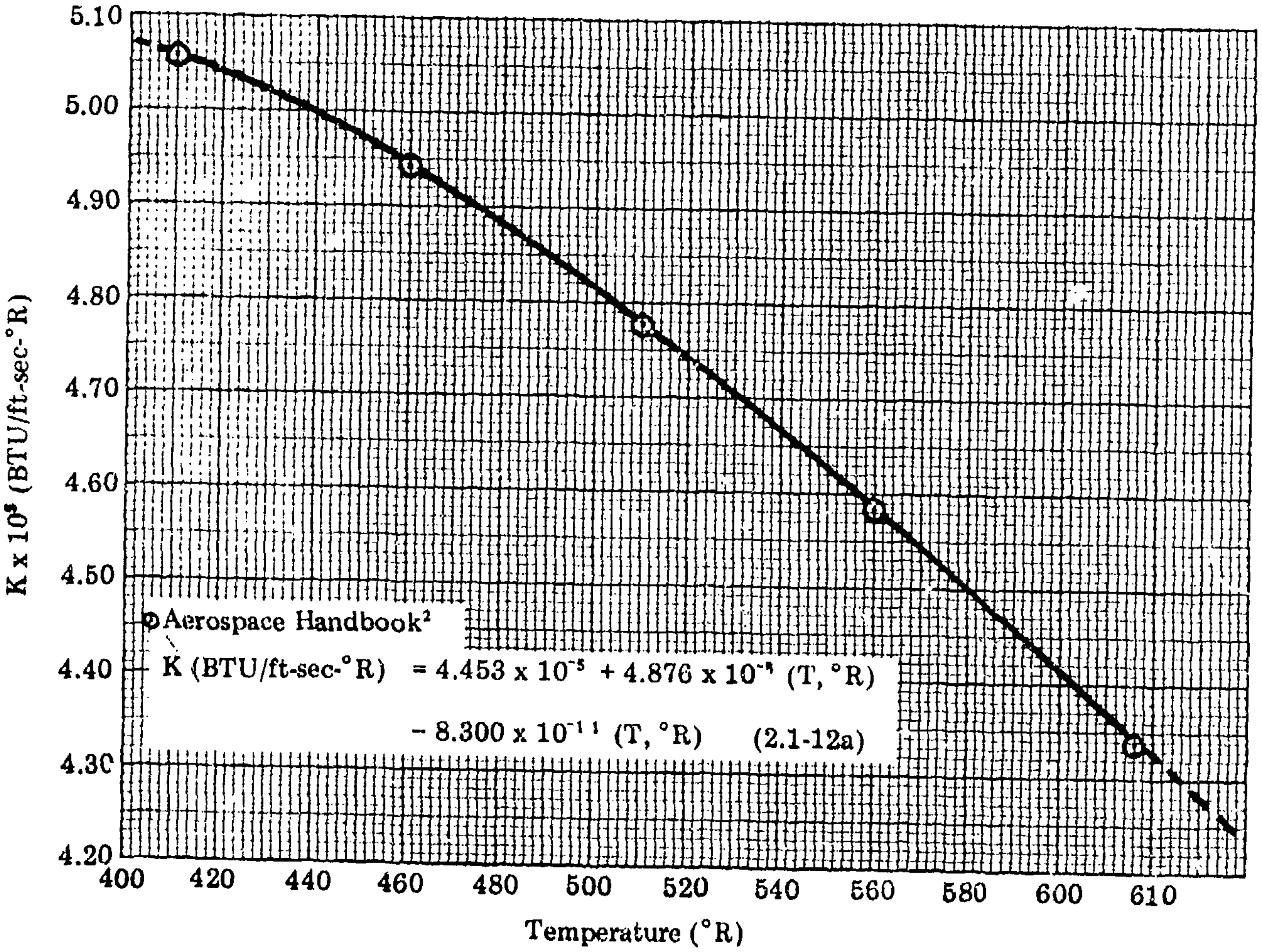


Figure 2.1-6a. Thermal Conductivity of RFNA versus Temperature

2.1.4 CHEMICAL PROPERTIES OF NITRIC ACID, TYPE III (RED FUMING NITRIC ACID)

2.1.4.1 Chemical Reactions

Nitric acid is a powerful oxidizing agent; it oxidizes most nonmetals (generally to oxides or oxyacids of their highest oxidation state) and all metals with the exception of a few of the noble metals. Many unreactive metals, such as silver and copper, that do not react to yield hydrogen with non-oxidizing acids, such as HCl, dissolve in nitric acid.

In nitric acid oxidations, hydrogen is almost never obtained; instead a variety of nitrogen-containing compounds of lower oxidation state is produced; such compounds like NO_2, NO, N_2O, HNO_2. The product to which HNO_3 is reduced depends on the concentration of the acid, the temperature, and the nature of the material being oxidized. Generally, a mixture of products is obtained, but the principal product, in many cases, is NO when diluted HNO_3 is employed and the nitrogen oxides when concentrated HNO_3 is used. Commercially 70 percent by weight HNO_3 is known as concentrated; thus RFNA is in this category.

RFNA reaction:

$$
\begin{aligned}
&Cu_{(s)} + 4H^+_{(aq)} \\
&+ 2\,NO_3^-{}_{(aq)} \rightarrow Cu^{++}_{(aq)} \\
&+ 2\,NO_2\,_{(g)} + 2\,H_2O
\end{aligned}
$$

2.1.4.2 Inert Gas Solubility in Red Fuming Nitric Acid

Lockheed (11) reports two temperature points for the solubility of helium and nitrogen in IRFNA at one atm in parts per million (ppm).

	0°C	25°C
Helium	0.73	0.86
Nitrogen	24	62.8

2.1.5 THERMODYNAMIC PROPERTIES OF NITRIC ACID, TYPE III (RED FUMING)

2.1.5.1 Heat of Formation

From the literature, several values for the heat of formation of nitric acid were reported. The values varied due to differences in temperature, state of aggregation, and state of combination. Although it is understood that standard state conditions are at room temperature and one atmosphere pressure for the formation of the compound, the temperature could be 18°C or 25°C.

TABLE 2.1-3 HEAT OF FORMATION, VARIOUS NITRIC ACIDS

Type of Nitric Acid	H_f Value cal/mole	Temperature °K	Reference
Pure HNO_3	-41,349	298.15	Stern, Mulhanpt, and Kay (14) Evered (6)
IRFNA	-41,000	Not reported	Propellant Handbook/RPL (3)
RFNA (85 w/o HNO_3 15 w/o NO_2)	-33,500	298.15	Aerojet-General (7)
RFNA (Nominal)	-37,700	298.15	Estimated, this work

The heat of formation for nominal RFNA was estimated by summing the heat of formation due to each of the fractional products that make up an apparent molecular mole of the substance plus the heat of solution of water.

Basis: 100 g

Constituent	Weight, g	g-moles	mole-fraction	ΔH_f of Constituent cal/mole	$\Delta H_f(i)$ cal/mole
HNO_3	84	1.333	0.7624	-41,349 (14)	-31,525
NO_2	14	0.304	0.1741	- 7,431 (6)	- 1,294
H_2O	2	0.111	0.0635	-68,400 (8)	- 4,343
Integral heat of solution (0.08 mole H_2O per mole HNO_3) (15)					-500 est.
				Total	-37,662

2.1.5.2 Melting Point and Heat of Fusion

According to Stern, Mullhaupt, and Kay (14) the value reported by Forsythe and Giauque, namely, -41.59°C, for the melting point for pure nitric acid is considered the best in the literature. Penner listed -41.64°C (10). But for the other forms of nitric acid, there are varied values as shown below:

TABLE 2.1-4 MELTING POINT OF VARIOUS FORMS OF NITRIC ACID

Type	Temperature		Reference
	°C	°F	
Pure HNO_3	-41.59	-42.9	Stern, Mullhaupt, and Kay (14) Evered (6)
99.65 w/o HNO_3, .35 H_2O	-42.1	-43.7	Evered (6)
RFNA	-52	-61	CPIA (1)
85 w/o HNO_3, 15 w/o NO_2	-48.9	-56	Aerojet-General (7)
RFNA	-48.9	-56	Aerospace Handbook (2)
IRFNA	-50	-58	Propellant Handbook/RPL (3)

The range may vary from -48 to -52°C depending upon the composition of the RFNA. Both Aerojet-General's and the Aerospace Corporation's value may be based on Elverum's effort in a 1954 Cal. Int. Tech publication (16).

Stern, Mullhaupt, and Kay (14) report that the value, 2503 ± 2 cal/mole, determined calorimetrically by Forsythe and Giauque is considered the most reliable for the heat of fusion of pure nitric acid.

2.1.5.3 Critical State Constants

Experimental values for the critical constants of RFNA do not exist. Even such data for anhydrous nitric acid could not be found. It is quite probable that experimental data do not exist because of not being able to maintain pure HNO_3 at elevated temperature without the HNO_3 decomposing. Therefore, pseudocritical properties are estimated.

Gambill (17,18) outlines various methods for predicting pseudocritical values when no experimental data are available. He includes the method of Kay (19) for determining the pseudocritical temperature and pressure of a mixture, which is summing the contribution of the product of the mole-fraction of the constituent and its critical temperature or pressure, namely, $T_{pc} = x_i T_{ci}$ or $P_{pc} = x_i P_{ci}$.

For the nominal RFNA, the recommended pseudocritical value of temperature is 524°F. This compares favorably with the value of 520°F estimated by Aerojet (7) for RFNA (85 w/o HNO_3, 15 w/o NO_2). CPIA (1) and Aerospace (2) also cite 520°F for RFNA. The temperature of 524°F is the average of the values determined for RFNA having all N_2O_4 or all NO_2 existing along with HNO_3. The values are given below:

TABLE 2.1-5 PSEUDOCRITICAL CONSTANTS OF NOMINAL RFNA

Constituent	Mole-fraction, x_i		T_{ci}, °R	P_{ci}, psia	$x_c T_c$		$x_i P_c$	
	NO_2	N_2O_4			NO_2	N_2O_4	NO_2	N_2O_4
HNO_3	0.7624	0.8351	1003.67	1240	765.2	838.2	945.4	1035.5
NO_2	0.1741		776.16	1466	135.1		255.2	
N_2O_4		0.0953	776.47	1470		74.0		140.1
H_2O	0.0635	0.0695	1165.2	3204	74.0	81.0	203.4	222.7
				Total	974.3	993.2	1404.0	1398.3
					514.6	533.5		
i = individual constituent				Average	T_{pc} = 524°F		P_{pc} = 1401.2 psia	

The recommended pseudocritical pressure for nominal RFNA is 1401.2 psia. It is higher than Aerojet's value of 1286 psia for RFNA (85 w/o HNO_3, 15 w/o NO_2) because of the influence of water in the nominal mixture.

Gambill (18) cites a simple relationship for calculating V_c proposed by Benson (20), namely:

$$V_c/V_b = 2.68 \qquad (2.1\text{-}13)$$

V_c = critical volume, cc/g-mole

V_b = volume at normal boiling point, cc/g-mole

$$= \frac{1\ (57.2)\ \frac{g}{g\text{-mole}}}{1.486} \quad \begin{array}{l}\text{at } 337.34°K \\ \text{From Figure 2.1-2}\end{array}$$

Thus:

$$V_c = \left(\frac{57.2}{1.486}\right)(2.68) = 103.2 \text{ cc/g-mole for nominal RFNA}$$

2.1.5.4 Heat Capacity of Red Fuming Nitric Acid

The heat capacity of RFNA (85 w/o HNO_3, 15 w/o NO_2) was plotted by Aerojet-General (7) citing the work of Mason, Booman, and Elverum (21) as their source. Some of the same values are apparently reported by the Aerospace Handbook (2).

The values are plotted in Figure 2.1-7.

Using the least square method, the following equations are presented to calculate heat capacity as a function of temperature for the range -50 to 148°F:

$$C_p\ (\text{cal/g-°K}) = 0.3779 + 1.406 \times 10^{-4}\ (T, °K) \qquad (2.1\text{-}14)$$

$$C_p\ (\text{BTU/lb-°R}) = 0.3779 + 7.800 \times 10^{-5}\ (T, °R) \qquad (2.1\text{-}14a)$$

The standard deviation is 5.85×10^{-4} cal/g-°K for equation 2.1-14. The average deviation is 0.83 percent.

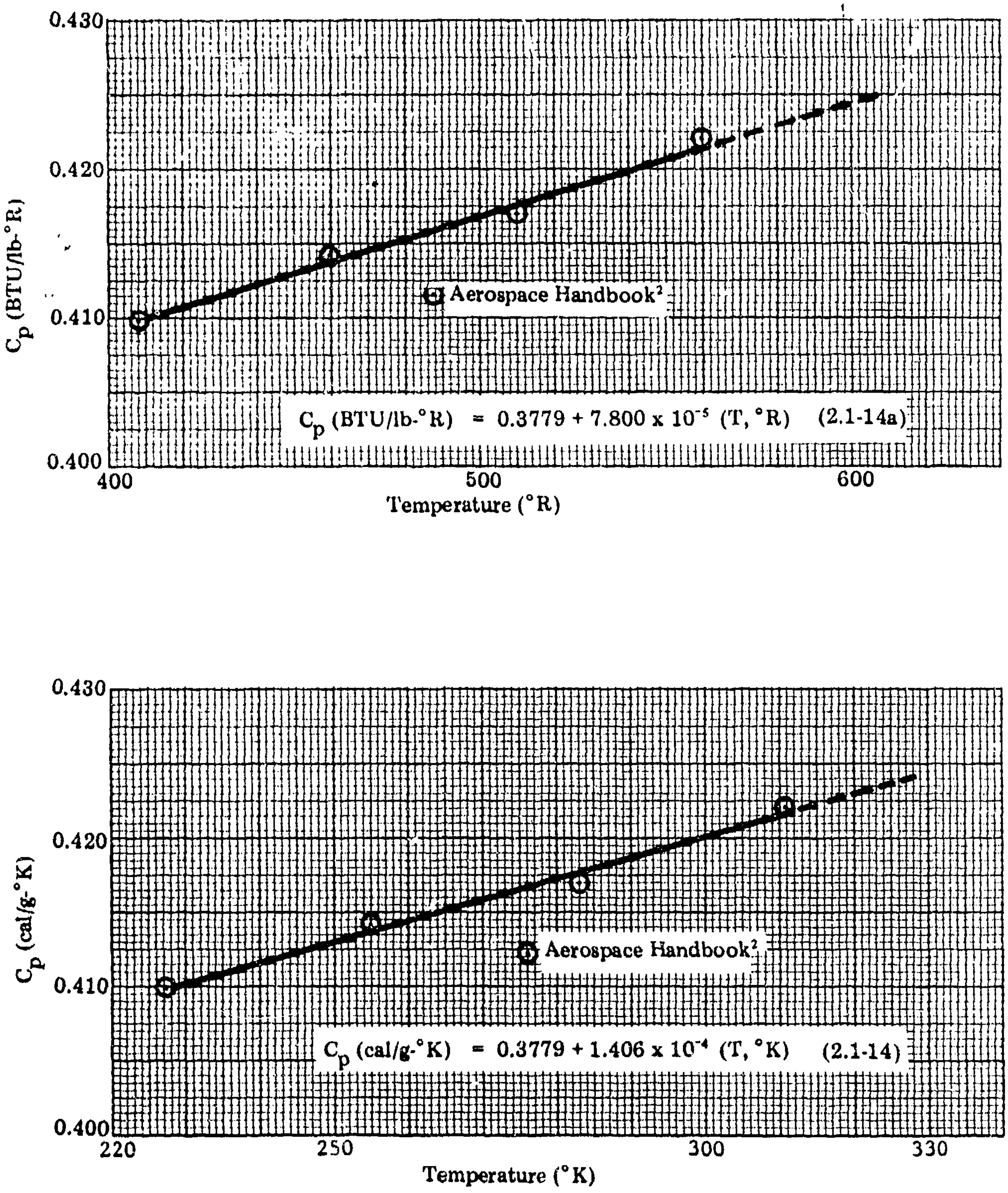


Figure 2.1-7. Heat Capacity of RFNA versus Temperature

2.1.5.5 Latent Heat of Vaporization

The heat of vaporization at the normal boiling point for nominal RFNA is calculated to be 8032 cal/mole (140.4 cal/g or 252.8 BTU/lb) from the Clausius-Clapeyron equation,

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_v}{1.987} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \qquad (2\ 1\text{-}15)$$

P_2 = vapor pressure, atm or mm Hg, (1 atm)

P_1 = vapor pressure, atm or mm Hg, (.945 atm)

ΔH_v = heat of vaporization, cal/mole

R = 1.987 = gas constant, cal/°K-g-mole

T_2 = temperature, °K, (337.34°K)

T_1 = temperature, °K, (336.34°K)

The molecular weight was 57.2 g/mole.

The vapor pressure is calculated from equation 2.1-3.

2.1.6 LOGISTICS OF NITRIC ACID, TYPE III (RED FUMING)

2.1.6.1 Manufacture

The principal supplier of IRFNA at the present time is the Allied Chemical Corporation in Buffalo, New York. Allied's IRFNA manufacturing process is as follows:

Ammonia, produced at another Allied plant, is oxidized by air in a stainless steel oxidizer unit. The oxidation product, NO, is oxidized further by air to NO_2 that is then absorbed by condensate water in a 400 series chrome steel tower to produce a nitric acid of about 65 percent HNO_3. The nitric acid is concentrated in an aluminum Pauling tower, using concentrated sulfuric acid that is also an Allied product. Nitric acid of 97 percent concentration is obtained from the Pauling tower. Allied anhydrous hydrogen fluoride, Hercules nitrogen dioxide, and water are added to the concentrated nitric acid in an adjustment tank to blend an acid meeting the MIL-SPEC demands.

The process equations are as follows:

$$4\,NH_3 + 5\,O_2\ (\text{air}) \longrightarrow 4\,NO + 6\,H_2O$$

$$2\,NO + O_2\ (\text{air}) \longrightarrow 2\,NO_2$$

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO$$

Another method of manufacture was the process used by Hercules Chemical Company, Hercules, California. Their IRFNA manufacturing process is:

Hydrogen gas, obtained from the cracking of natural gas, is combined with nitrogen from the air to produce ammonia. The ammonia produced by the direct synthesis process is then converted to nitric acid by catalytic air oxidation. The nitric acid thus produced is concentrated in a reboiler, using sulfuric acid obtained from the Stauffer Chemical Company. Aqueous hydrogen fluoride, NO_2, and condensate water are added to the concentrated acid to produce an acid conforming to the Military Specification. Quality control tests are made on all starting materials. The equations for the process are:

$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3$$

$$2\,NH_3 + 3\,O_2\ (\text{air}) \xrightarrow{Pt} NO + NO_2 + 3\,H_2O$$

$$2\,NO_2 + H_2O + \tfrac{1}{2}\,O_2\ (\text{air}) \longrightarrow 2\,HNO_3$$

2.1.6.2 Analysis

The analysis of propellant grade IRFNA is covered in MIL-P-7254F (30 April 1970) including Amendment 2 dated 18 January 1972. Only Type IIIB and Type IIILS are currently being procured.

The acid sample is analyzed by first neutralizing the sample and then performing additional analyses.

The nitrogen dioxide content is determined using a 0.1N ceric solution, a 1 N H_2SO_4 solution, a standardized 0.05 N ferrous ammonium sulfate reagent, and a pH meter. The NO_2 content is calculated from the following formula:

$$\text{Weight \%}\ NO_2 = \frac{(\text{ml } Ce^{4+} \times N) - (\text{ml } Fe^{2+} \times N_1) \times 4.601}{W \times 0.2}$$

N = normality of the ceric solution

N_1 = normality of the ferrous ammonium sulfate

W = original weight in grams

The hydrogen fluoride content of the oxidizer is measured by adjusting the pH of the solution to 5.5 by the addition of citrate buffer and then calculating the ppm of fluoride.

The specific gravity shall be as follows:

Type IIIB	1.564 - 1.575 at 60°F
Type IIILS	1.572 - 1.582 at 60°F

The total solids as nitrates of all types in the propellant shall not exceed 0.04 percent by weight. In addition, the iron oxide content of Type IIILS propellant shall not exceed .0020 percent by weight. The iron content may be determined by ASTM D-1068, Method A, paragraph 12 or using a suitable atomic absorption spectrophotometer.

2.1.6.3 Cost and Availability

Inhibited Fuming Nitric Acid (IRFNA) is readily available in large quantities for aerospace industries. The principal use of IRFNA is the rocket engine oxidizer for the Bullpup A and Lance missiles and as a constituent in the oxidizer for the Agena vehicle.

At the present time, IRFNA is being supplied to the government by Allied Chemical Company. The unit price for Type IIIB or IIILS is $0.22/

pound from the government. The government procured 600,000 pounds of nitric acid, Types IIIB and LS, in 1976 (22).

2.1.6.4 Shipping and Transportation

The requirements for shipping and transportation of nitric acid are specified in Reference (9). Excerpts are included here for information.

The product furnished under this specification is a hazardous material as defined and regulated by the Department of Transportation (DOT) regulations. All packaging and shipping commercially by any mode of transportation shall comply with the requirements of DOT regulations 49 CFR 171-190, or DOT special permit obtained in accordance with 49 CFR 170.13 by the shipper in conjunction with the Commander, Headquarters Military Traffic Management and Terminal Service, Attn: Safety Division (TES), Washington, D.C. 20315. All packaging to be shipped by military air shall comply with DSAM 4145.3 (AFM 71-4).

The following listed containers are considered acceptable for military use and are approved for nitric acid by DOT regulations as specified in 49 CFR 173.268 or DOT special permits as stated. Types IIIA and IIIB propellant should be, on a preferential basis and to the greatest extent feasible, shipped in aluminum containers; however, stainless steel (300 series) may be used. Types IIILS propellant should be shipped exclusively in aluminum containers.

a) Sample quantities as specified in DOT special permit no. 2100.

b) Aluminum drums of specification DOT 42B and conforming to MIL-D-4303.

c) Tank cars of specifications DOT 103A-AL-W, 103C-W, or 103C-AL.

d) Cargo tanks of specifications DOT MC 310, MC 311, or MC 312.

2.1.7 REFERENCES

1. Chemical Propulsion Information Agency, *Chemical Rocket/Propellant Hazards, Liquid Propellant Handling, Storage and Transportation, Vol. III,* CPIA No. 194 Change 1, (1 July 1972).
2. Aerospace Corporation, *Aerospace Fluid Component Designers Handbook,* TRW Systems Group, AFRPL TDR 64-25, (February 1970).
3. Von Dochren, Paul J., *Propellant Handbook,* AFRPL-TR-66-4, Edwards, Calfornia, January 1966.
4. Constantine, M.T., *Engineering Property Determination of Rocket Propellants,* Rocketdyne Division of North American Rockwell Corp., Final Report, AFRPL-TR-70-147, (November 1970).
5. Hamilton, William R. and Wolf, Carl J., *Propellant Performance Data,* Martin Company, Denver, Colorado. Report 1362-07-61 (June 1961).
6. Evered, D. and Kit, Boris, *Rocket Propellant Handbook,* The MacMillan Company, New York. 1960.
7. Petrozzi, P.J., Dean, L.E., *Physical Properties of Liquid Propellants,* Report No. LRP 178, Aerojet-General Corp., Liquid Rocket Plant, Sacramento, California, (13 July 1960).
8. Prutton, Carl, *Fundamental Principles of Physical Chemistry,* The MacMillan Company, New York. Revised Ed. 1951.
9. Department of Defense, *Military Specification, Propellants, Nitric Acid,* MIL-P-7254F (30 April 1970) Amendment 2, GPO, (18 January 1972).
10. Penner, S.S. and J. Ducarme, *The Chemistry of Propellants,* Pergamon Press, Inc., New York. 1960.
11. Lockheed Missiles and Space Company, *High Density Acid (HDA) Physical Properties Handbook,* LMSC/D538660, 3rd Edition, (22 July 1976).
12. Eisenschitz, R., Proc. Phys. Soc. (London), 59, 1030, (1947).
13. Weter, H.F., Wiedemann's Ann., Ann. Phys. Chem., 10, 103, (1880).
14. Stern, S.A., J.T. Mullhaupt, and W.B. Kay, *The Physicochemical Properties of Pure Nitric Acid,* Chemical Review, 185-227, 60 (1960).
15. Hougen, O.A. and Watson, K.M., *Industrial Chemical Calculations,* John Wiley & Sons, Inc., New York, 2nd Ed. (1947).
16. Elverum, G.W., Jr., Calif. Institute of Tech., PR 20-224, (24 May 1954).
17. Gambill, W.R., *How to Predict Critical Temperature,* Chem. Engr., 181-184, (June 15, 1959).
18. Gambill, W.R., *How to Predict Critical Pressure,* Chem. Engr., 157-160, (July 13, 1959).
19. Kay, W.B., Ind. and Engr. Chem., 28, 1014 (1936).
20. Benson, S.W., J Phys. and Colloid Chem., 52 1060-1074 (1948).
21. Mason, D.M., Booman, K., and Elverum, G.W., Jr., Calif. Instit. Tech., Jet Propulsion Laboratory PR 20-216, (January 29, 1954).
22. Personal Communication with Mr. W. Watje, Kelly AFB, San Antonio, Texas.

2.2 NITRIC ACID, TYPE IV (HDA) AND MODIFIED HDA (PF_5)

2.2.1 PROPERTY SUMMARY SHEET

2.2.2 GENERAL
  2.2.2.1 Introduction
  2.2.2.2 Structure of Nitric Acid, Type IV (HDA) and Modified HDA (PF_5)
  2.2.2.3 Specification

2.2.3 PHYSICAL PROPERTIES OF HDA
  2.2.3.1 Vapor Pressure and Normal Boiling Point
  2.2.3.2 Density of Liquid HDA
  2.2.3.3 Sonic Velocity in Liquid HDA
  2.2.3.4 Compressibility of Liquid HDA
  2.2.3.5 Viscosity of Liquid HDA
  2.2.3.6 Surface Tension of Liquid HDA
  2.2.3.7 Thermal Conductivity of Liquid HDA

2.2.4 CHEMICAL PROPERTIES OF HDA
  2.2.4.1 Chemical Reactions
  2.2.4.2 Inert Gas Solubility in Liquid HDA

2.2.5 THERMODYNAMIC PROPERTIES OF HDA
  2.2.5.1 Heat of Formation of Liquid HDA
  2.2.5.2 Melting Point and Heat of Fusion
  2.2.5.3 Critical State Constants
  2.2.5.4 Heat Capacity of Liquid HDA
  2.2.5.5 Latent Heat of Vaporization

2.2.6 LOGISTICS OF HDA
  2.2.6.1 Manufacture
  2.2.6.2 Analysis
  2.2.6.3 Cost and Availability
  2.2.6.4 Shipping and Transportation

2.2.7 REFERENCES

2.2.1 PROPERTY SUMMARY SHEET

Chemical Name: HDA – Type IV – IMDFNA

Common Name: High Density Acid: Inhibited Maximum Density Fuming Nitric Acid

Chemical Formula: $H_{.6806} N_{1.2945} O_{3.2254} F_{.0248}$

Formula Weight: 70.897 (nominal) (O^{16})

Property	Value	Units	Temp (°K)	Reference	Figure
Melting Point	235.95 -37.2 424.67 -35	°K °C °R °F		3	
Heat of Fusion	116.3* 209	cal/g BTU/lb	235.95 (MP)	1	
Normal Boiling Point	297.85 24.7** 536.17 76.5**	°K °C °R °F		3	
Heat of Vaporization	7.0** 270**	Kcal/mole BTU/lb	NBP 297.8	3	
Heat of Disassociation	Not available				
Critical State Constants Temperature	540.15 267* 972.27 512.6*	°K °C °R °F		3	
Pressure	97.5* 1428*	atm psia		3	
Density	0.6837* 42.68*	g/cc lb/ft^3		3	
Vapor Pressure of Liquid	1.01 14.9	atm psia		1	2.2-2
Density of Liquid	1.624 101.4	g/cc lb/ft^3	298.15	3	2.2-3
Sonic Velocity (liquid)	1403 4635	m/sec ft/sec	298.15	3	2.2-4
Compressibility of Liquid Adiabatic	3.157×10^{-5} 2.148×10^{-6}	atm^{-1} psi^{-1}		3	2.2-5
Isothermal	Not available				
Viscosity of Liquid	2.28 1.54×10^{-3}	Centipoise lb_m/ft-sec	298.15	3	2.2-6
Heat Capacity of Liquid	0.4435* 0.4435*	cal/g-°C BTU/lb-°F	298.15	1	2.2-10
Thermal Conductivity of Liquid	7.27×10^{-4}* 0.1771*	cal/sec-cm-°K BTU/hr-ft-°F	298.15	1	2.2-8
Surface Tension	29.9 2.04×10^{-3}	dynes/cm lb_f/ft	298.15	2	2.2-7
Refractive Index	Not available				
Dielectric Constant	Not available				
Entropy (Gas)	Not available				
Entropy (Liquid)	Not available				
Heat of Formation (Liquid)	-31.678* -779.4*	Kcal/mole BTU/lb	298.15	3	

*Estimated Value

**Calculated from vapor pressure equation

2.2.2 GENERAL

2.2.2.1 Introduction

Early rocket engines such as the Agena were developed using fuming nitric acid as the oxidizer. It was discovered that by increasing the nitrogen tetroxide content in nitric acid, performance could be increased (specifically for the Agena engine) thus creating the requirement for what is known as high density acid. Nitric acid readily dissolves N_2O_4 to form a mixture that reaches maximum density for a particular temperature. Lockheed (1) has compiled and evaluated the most recent data on HDA. A phase diagram study of Elverum (4) was documented by Lockheed and is reproduced herein as Figure 2.2-1. This provides some of the data describing the physical characteristics of the mixture of nitric acid and N_2O_4 making up HDA.

The nominal composition of HDA is:

54.8 w/o HNO_3
44.0 w/o N_2O_4
0.5 w/o H_2O
0.7 w/o HF

The addition of HF was found to inhibit the corrosive action of nitric acid and N_2O_4 on the rocket container materials. Another inhibitor, Phosphorous Pentafluoride (PF_5), has been found to be a superior inhibitor (17) but has not been incorporated into the military specification.

From the phase diagram, there exists a compound with the composition 2 $HNO_3 \cdot N_2O_4$. The compound $2HNO_3 \cdot N_2O_4$ has a N_2O_4 content of 42 percent, slightly lower than the 44 percent N_2O_4 content of the nominal high density acid. Thus, the HDA mixture can be approximated by the chemical formula, $2HNO_3 \cdot N_2O_4$. The empirical formula is $H_{0.9602}N_{1.8261}O_{4.5495}F_{0.0350}$ g-atoms/100g mixture. The apparent molecular weight is 70.897 for the nominal composition of 1 g-mole.

2.2.2.2 Structure

High density acid is a mixture with two major components, HNO_3, and N_2O_4. The structure of HNO_3 is discussed in section 2.1.2.2. The structure of N_2O_4 is discussed in section 2.3.2.2.

2.2.2.3 Specification

The procurement and analysis of HDA are controlled under Military Specification MIL-P-7254F (30 April 1970), Amendment 2 (18 January 1972). This specification defines the composition range for HDA as follows:

HNO_3	percent by weight	52.7-57.4
NO_2	percent by weight	44 ± 2
HF	percent by weight	0.7 ± 0.1
H_2O	percent by weight	0.5 max.
Fe_2O_3	percent by weight	0.002 max.
Solids w/o as nitrate		0.04 max.
Specific gravity, 60 °F/60 °F		1.642 min – 1.652 max.

No specification exists for the Modified HDA with the PF_5 inhibitor.

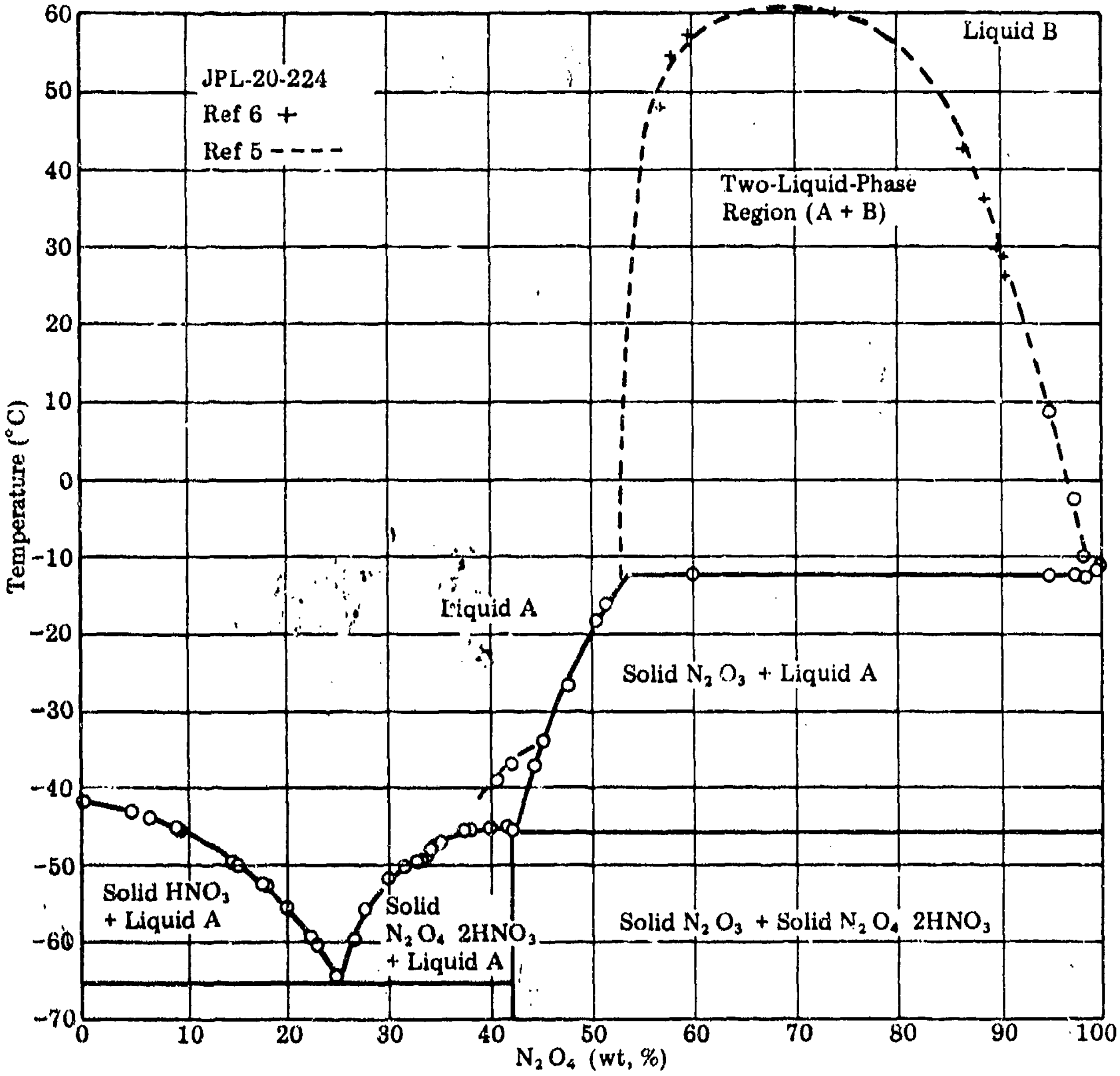


Figure 2.2-1. Phase Diagram for HNO_3 – N_2O_4 System (From JPL-20-224, 24 May 1954)

2.2.3 PHYSICAL PROPERTIES OF HDA

2.2.3.1 Vapor Pressure and Normal Boiling Point of HDA

Lockheed (1) documented that vapor pressure and equilibrium pressure measurements have been made at the laboratories of Bell and Rocketdyne (2,3). They noted a disagreement of vapor pressure data exists at temperatures below 54°C (130°F); the Rocketdyne (3) pressures being greater than those reported by Bell (2). By comparing N_2O_4 data at the lower temperature, Lockheed recommends that Bell data be used for temperatures below 54°C (130°F) and the Rocketdyne data be used for the higher temperatures.

Rocketdyne produced the following equations by correlating their vapor pressure data (108 points) by use of the least-squares curve-fit technique:

$$\begin{aligned}\log_{10}P(\text{atm}) = {} & 10.7662 - \frac{4702.28}{(T,\ ^\circ K)} \\ & - 5.43556 \times 10^{-2} N_{(w/o)} \\ & + 2.5549 \times 10^{-2} W_{(w/o)} \\ & + 28.5036 \frac{N_{(w/o)}}{(T,\ ^\circ K)} \\ & + \frac{282926}{(T,\ ^\circ K)^2} \qquad (2.2\text{-}1)\end{aligned}$$

$$\begin{aligned}\log_{10}P(\text{psia}) = {} & 11.9347 - \frac{8464.86}{(T,\ ^\circ R)} \\ & - 5.43838 \times 10^{-2} N_{(w/o)} \\ & + 2.5548 \times 10^{-2} W_{(w/o)} \\ & + 51.3221 \frac{N_{(w/o)}}{(T,\ ^\circ R)} \\ & + \frac{916700}{(T,^\circ R)^2} \qquad (2.2\text{-}1a)\end{aligned}$$

The experimental data included four compositions of mixture, a temperature ramge of -17 to 129°C (1 to 264°F), NO_2 (N) ranges of 43.2 to 45.6 w/o NO_2, and H_2O (W) ranges of 0.4 to 1.7 w/o H_2O. The standard error estimate is equivalent to 4.0 percent in pressure.

Equations 2.2-1 and 2.2-1a reduce to the following expressions for the nominal composition:

$$\log_{10}P(\text{atm}) = 8.3872 - \frac{3448.12}{(T,\ ^\circ K)} + \frac{282926}{(T,\ ^\circ K)^2} \qquad (2.2\text{-}2)$$

$$\log_{10}P(\text{psia}) = 9.5545 - \frac{6206.69}{(T,\ ^\circ R)} + \frac{916700}{(T,\ ^\circ R)^2} \qquad (2.2\text{-}2a)$$

Graphs for the nominal values by Rocketdyne are shown in Figures 2.2-2 and 2.2-2a. Bell tabulated test data (2) as dashed lines are also plotted.

The normal boiling point of HDA was calculated by Rocketdyne (3) based on their vapor pressure correlations. The normal boiling point of the nominal HDA (54.8 w/o HNO_3, 44.0 w/o NO_2, 0.5 w/o H_2O, 0.7 w/o HF) was calculated at 24.7°C (76.5°F) for 1 atm.

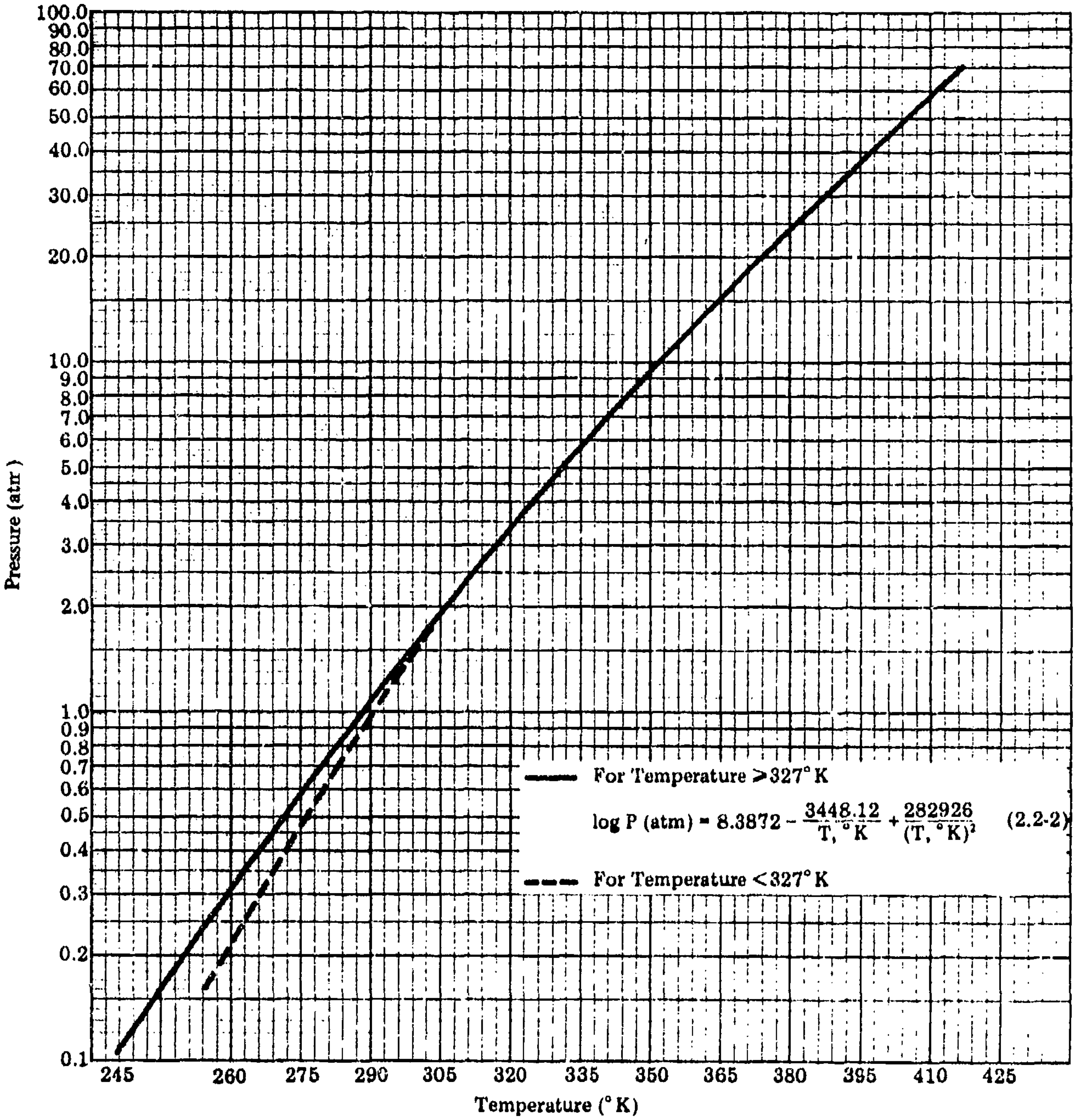


Figure 2.2-2. Vapor Pressure of HDA versus Temperature

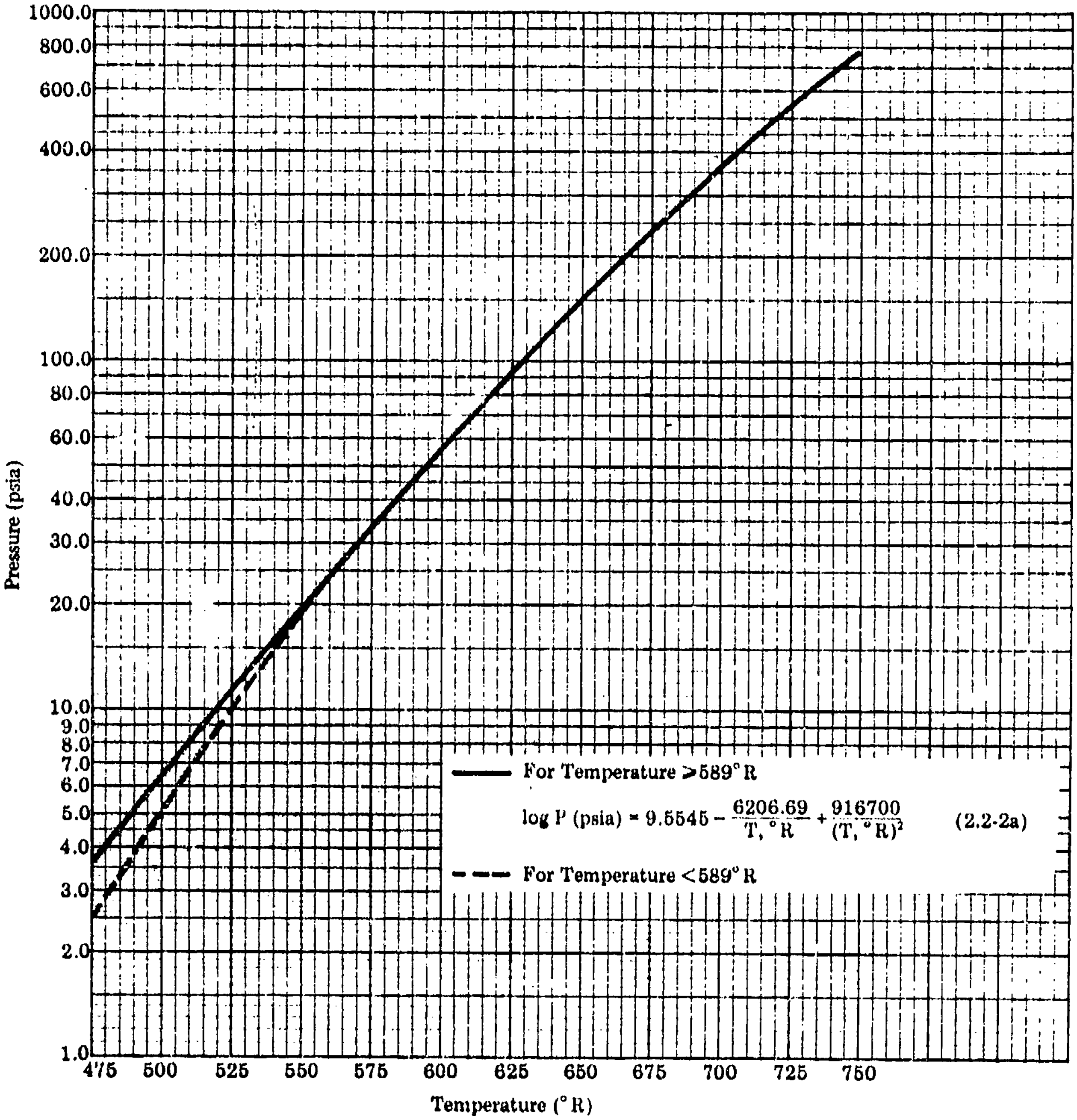


Figure 2.2-2a. Vapor Pressure of HDA versus Temperature

2.2.3.2 Density of Liquid HDA

Density measurements were made by Rocketdyne (3, 5) of liquid HDA using the Poole-Nyberg densimeter. Bell (2) made specific gravity measurements using a capillary pycrometer. Lockheed (1) documents Rocketdyne's recent (3) correlations of denisty measurements. Rocketdyne derived the following expressions of density as a function of temperature and composition by use of a least-squares curve fit computer program:

$$\begin{aligned}\rho\,(\mathrm{g/cc}) = {} & 1.7889 - 1.8391 \times 10^{-3}\,(t, {}^\circ\mathrm{C}) \\ & - 5.82 \times 10^{-6}\,(t, {}^\circ\mathrm{C})^2 \\ & - 2.420 \times 10^{-3}\,N_{(w/o)} \\ & - 1.750 \times 10^{-2}\,W_{(w/o)} \qquad (2.2\text{-}3)\end{aligned}$$

$$\begin{aligned}\rho\,(\mathrm{lb/ft^3}) = {} & 113.61 - 5.66 \times 10^{-2}\,(t, {}^\circ\mathrm{F}) \\ & - 1.12 \times 10^{-4}\,(t, {}^\circ\mathrm{F})^2 \\ & - 0.1511\,N_{(w/o)} - 1.093\,W_{(w/o)} \qquad (2.2\text{-}3a)\end{aligned}$$

The earlier data (5) were not used by Rocketdyne because earlier HDA compositions were not as accurately controlled as the more recent measurements (3). The standard error of estimate of these equations are 0.0017 g/cc and 0.106 lb/cuft respectively, over a temperature range of 1 to 68°C (34 to 155°F) and composition variations of 43.5 to 45.6 w/o NO_2 and 0.4 to 1.7 w/o H_2O.

For the nominal composition of HDA and in terms of absolute temperatures, density values are expressed as follows:

$$\begin{aligned}\rho\,(\mathrm{g/cc}) = {} & 1.7418 + 1.3404 \times 10^{-3}\,(T, {}^\circ\mathrm{K}) \\ & - 5.82 \times 10^{-6}\,(T, {}^\circ\mathrm{K})^2 \qquad (2.2\text{-}4)\end{aligned}$$

$$\begin{aligned}\rho\,(\mathrm{lb/ft^3}) = {} & 108.78 + 4.64 \times 10^{-2}\,(T, {}^\circ\mathrm{R}) \\ & - 1.12 \times 10^{-4}\,(T, {}^\circ\mathrm{R})^2 \qquad (2.2\text{-}4a)\end{aligned}$$

These correlations are shown graphically in Figures 2.2-3 and 2.2-3a.

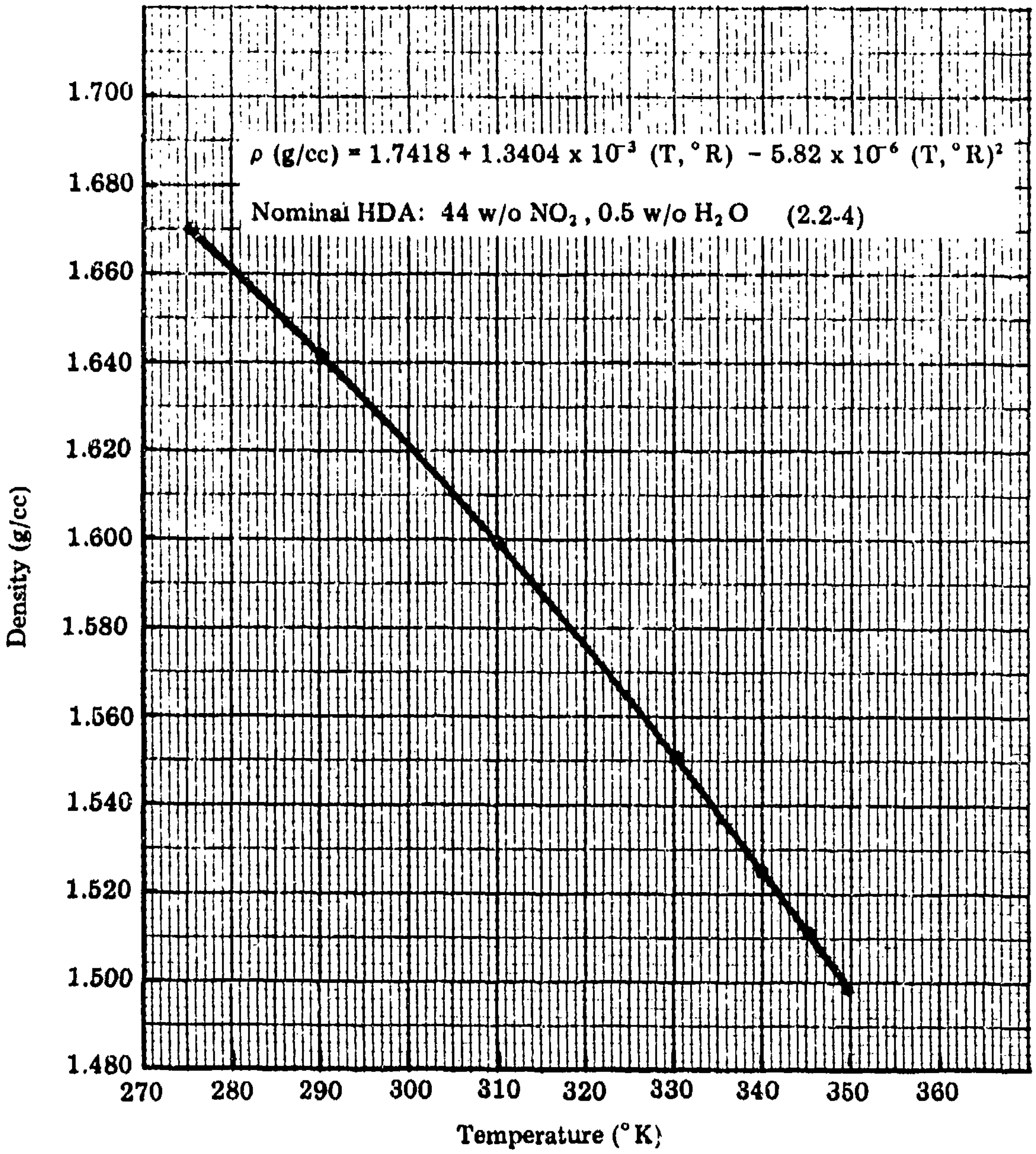


Figure 2.2-3. Density of Liquid HDA versus Temperature

ρ (lb/ft^3) = 108.78 + 4.64 x 10^{-2} (T, °R) − 1.12 x 10^{-4} (T, °R)^2

Nominal HDA: 44 w/o NO_2, 0.5 w/o H_2O (2.2-4a)

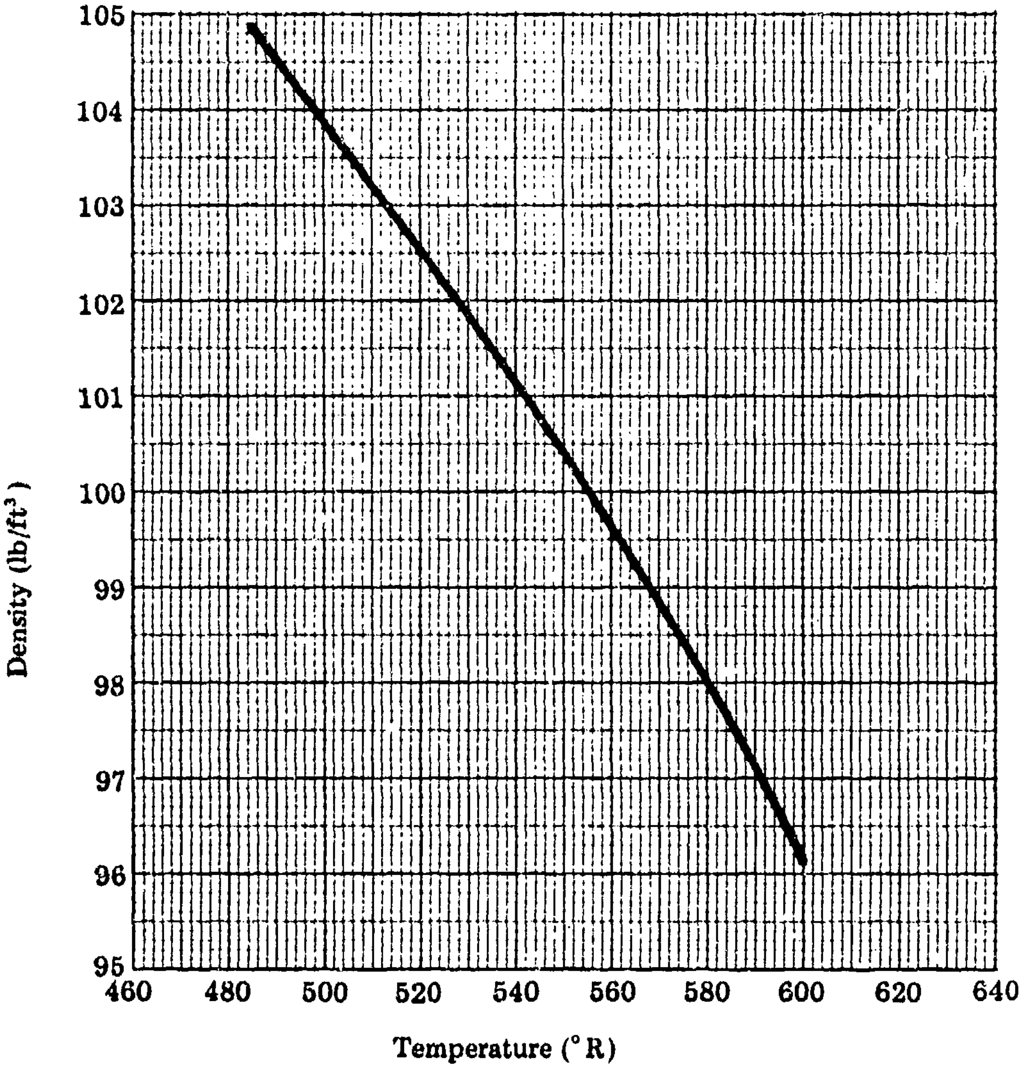


Figure 2.2-3a. Density of Liquid HDA versus Temperature

2.2.3.3 Sonic Velocity in Liquid HDA

Rocketdyne (3), provides the sonic velocity measurements for three different HDA formulations over a temperature range of 1 to 60°C (34 to 140°F) under saturated liquid conditions. Composition ranges were 43.4 to 46.6 w/o NO_2, and 0.4 to 1.7 w/o H_2O. The resulting data were curve-fitted and yielded the following expressions for sonic velocity as a function of temperature and composition:

$$c(\text{m/sec}) = 2180.0 - 3.523\ (T, °C) - 1.45 \times 10^{-2}\ (T, °C)^2 - 14.977 N_{(w/o)} - 40.6 W_{(w/o)} \qquad (2.2\text{-}5)$$

$$c(\text{ft/sec}) = 7343 - 5.482\ (T, °F) - 1.47 \times 10^{-2}\ (T, °F)^2 - 49.14 N_{(w/o)} - 133 W_{(w/o)} \qquad (2.2\text{-}5a)$$

The standard errors of estimate of the just-mentioned equations are 6.3 m/sec and 20.6 ft/sec respectively. For the nominal composition of HDA and in terms of absolute temperature, the above equations reduce to:

$$c(\text{m/sec}) = 1381.161 + 4.398\ (T, °K) - 1.45 \times 10^{-2}\ (T, °K)^2 \qquad (2.2\text{-}6)$$

$$c(\text{ft/sec}) = 4558.202 + 8.032\ (T, °R) - 1.47 \times 10^{-2}\ (T, °R)^2 \qquad (2.2\text{-}6a)$$

These correlations are presented graphically in Figures 2.2-4 and 2.2-4a.

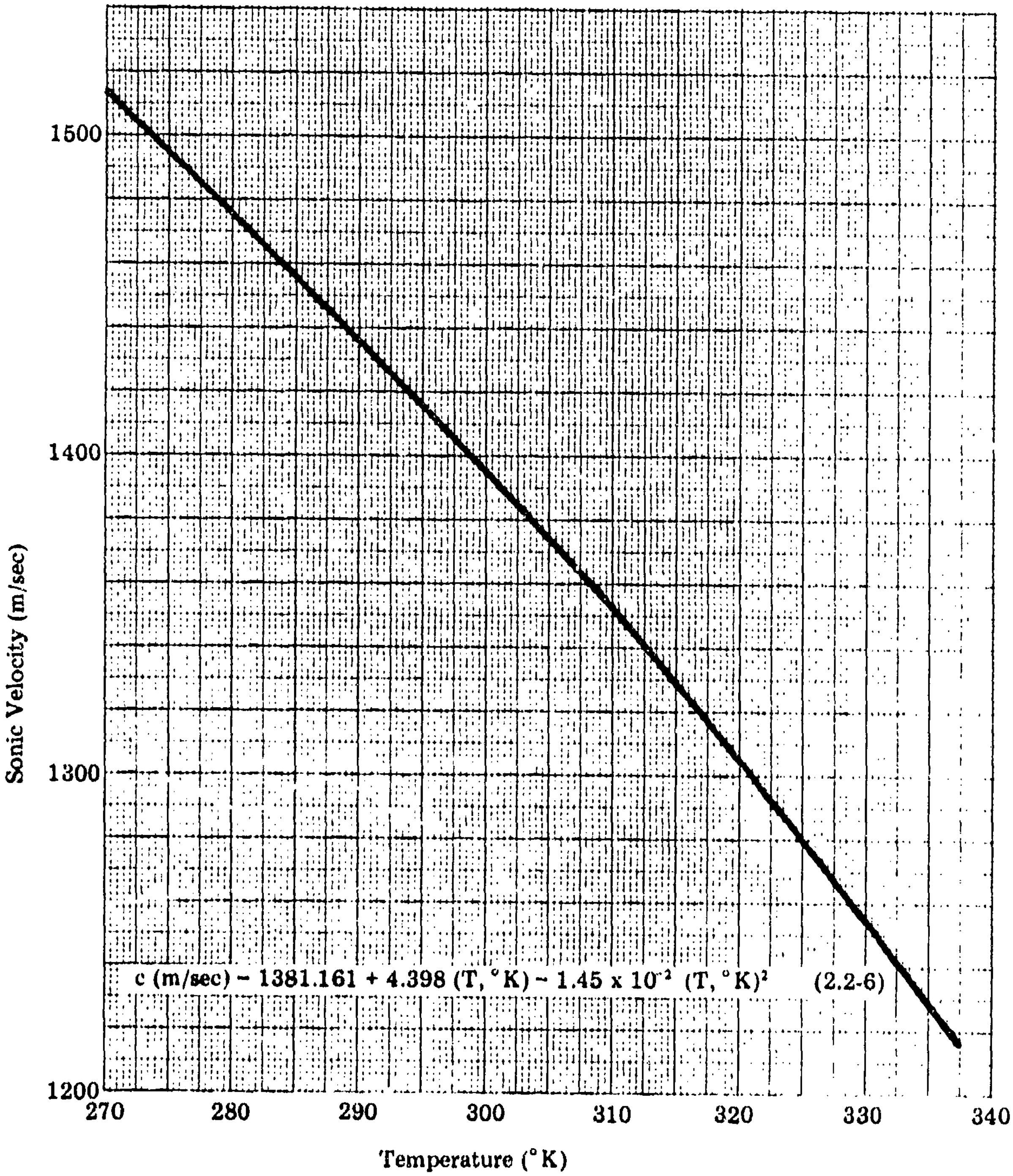


Figure 2.2-4. Sonic Velocity in HDA versus Temperature

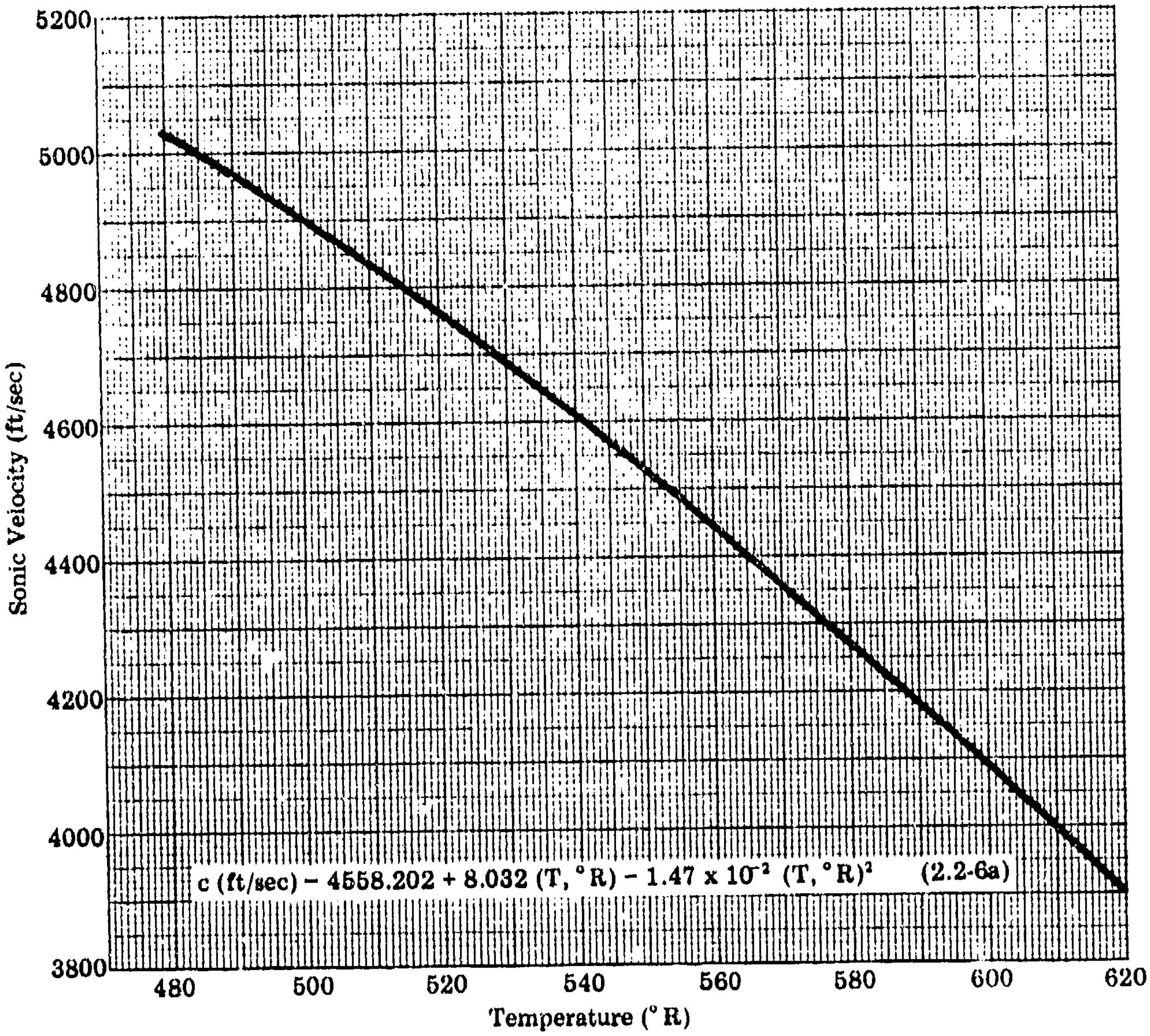


Figure 2.2-4a. Sonic Velocity in HDA versus Temperature

2.2.3.4 Compressibility of Liquid HDA

The adiabatic compressibility of HDA was calculated from the equation:

$$\beta_a = \frac{1}{\rho c^2} \qquad (2.2\text{-}7)$$

where:

β_a = adiabatic compressibility of the liquid
ρ = density of the liquid
c = velocity of sound in the liquid

Rocketdyne used their experimental data for liquid density (Section 2.2.3.2) and sonic velocity (Section 2.2.3.3) in the calculation of the adiabatic compressibility. The resulting correlation is given by the following equations:

$$\begin{aligned}\beta_a\ (\text{atm}^{-1}) = {} & 6.097 \times 10^{-7} \\ & - 2.9506 \times 10^{-7}\ (T, {}^\circ C) \\ & + 9.126 \times 10^{-10}\ (T, {}^\circ C)^2 \\ & + 1.718 \times 10^{-11}\ T, {}^\circ C)^3 \\ & + 5.794 \times 10^{-7} N_{(w/o)} \\ & + 1.727 \times 10^{-6} W_{(w/o)} \\ & + 9.808 \times 10^{-9} N_{(w/o)}\ (T, {}^\circ C) \\ & + 2.84 \times 10^{-8} W_{(w/o)}\ (T, {}^\circ C)\end{aligned} \qquad (2.2\text{-}8)$$

$$\begin{aligned}\beta_a\ (\text{psi}^{-1}) = {} & 4.115 \times 10^{-7} \\ & - 1.1765 \times 10^{-8}\ (T, {}^\circ F) \\ & - 8.107 \times 10^{-14}\ (T, {}^\circ F)^2 \\ & + 2.005 \times 10^{-13}\ (T, {}^\circ F)^3 \\ & + 2.755 \times 10^{-8} N_{(w/o)} \\ & + 8.318 \times 10^{-8} W_{(w/o)} \\ & + 3.708 \times 10^{-10} N_{(w/o)}\ (T, {}^\circ F) \\ & + 1.074 \times 10^{-9} W_{(w/o)}\ (T, {}^\circ F)\end{aligned} \qquad (2.2\text{-}8a)$$

The standard errors of estimate for these equations are 8.7×10^{-8} atm^{-1} and 5.9×10^{-9} psi^{-1}, respectively. These expressions are valid for temperatures from 1 to 60°C (34 to 140°F), N_2O_4 concentrations from 43.4 to 45.6 w/o, and H_2O concentrations from 0.4 to 1.7 w/o.

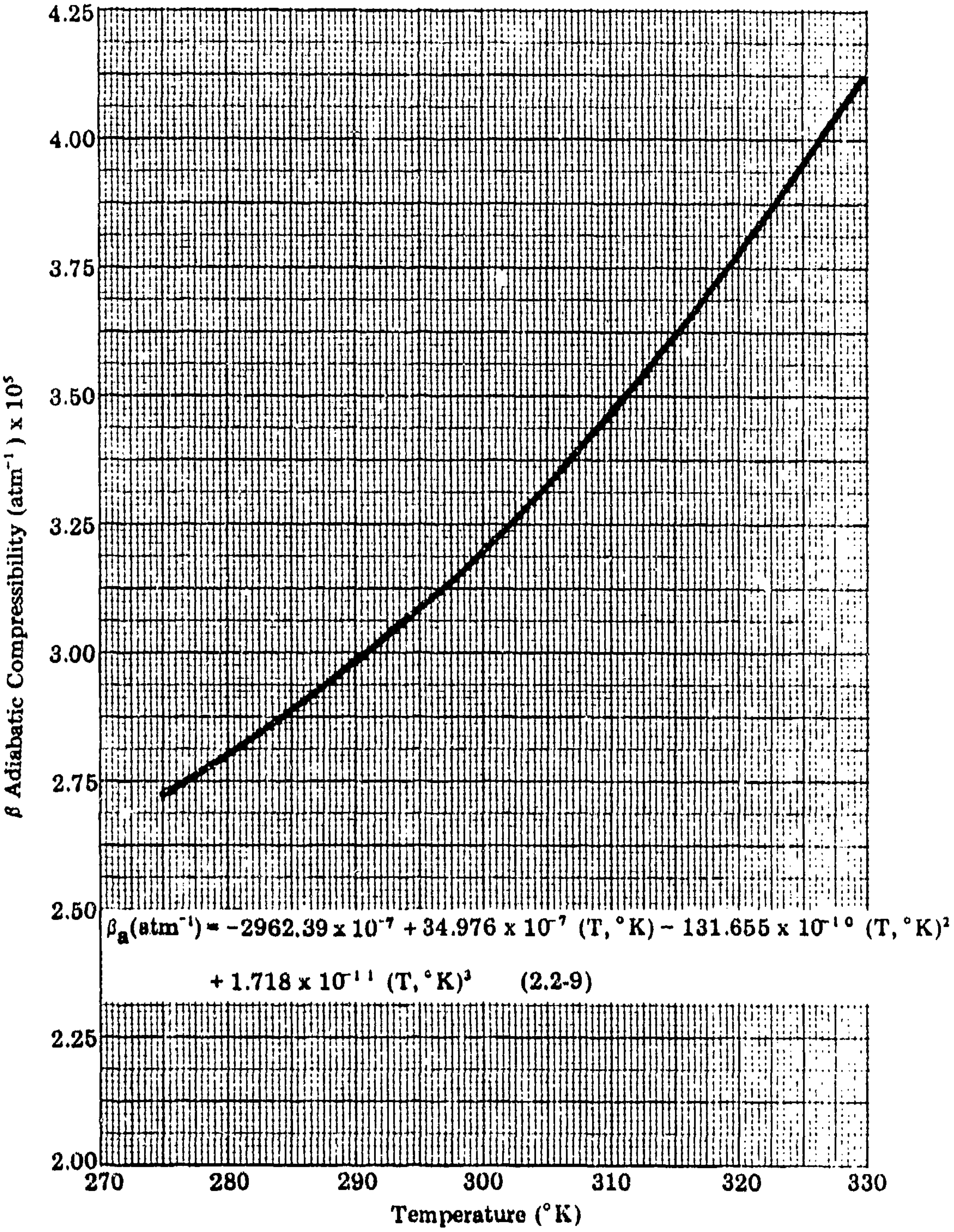
For nominal HDA and in terms of absolute temperatures, the aforementioned equations reduce to:

$$\begin{aligned}\beta_a\ (\text{atm}^{-1}) = {} & - 2962.39 \times 10^{-7} \\ & + 34.976 \times 10^{-7}\ (T, {}^\circ K) \\ & - 131.655 \times 10^{-10}\ (T, {}^\circ K)^2 \\ & + 1.718 \times 10^{-11}\ (T, {}^\circ K)^3\end{aligned} \qquad (2.2\text{-}9)$$

$$\begin{aligned}\beta_a\ (\text{psi}^{-1}) = {} & -201.641 \times 10^{-7} \\ & + 1.3225 \times 10^{-7}\ (T, {}^\circ R) \\ & - 2.7657 \times 10^{-10}\ (T, {}^\circ R)^2 \\ & + 2.005 \times 10^{-13}\ (T, {}^\circ R)^3\end{aligned} \qquad (2.2\text{-}9a)$$

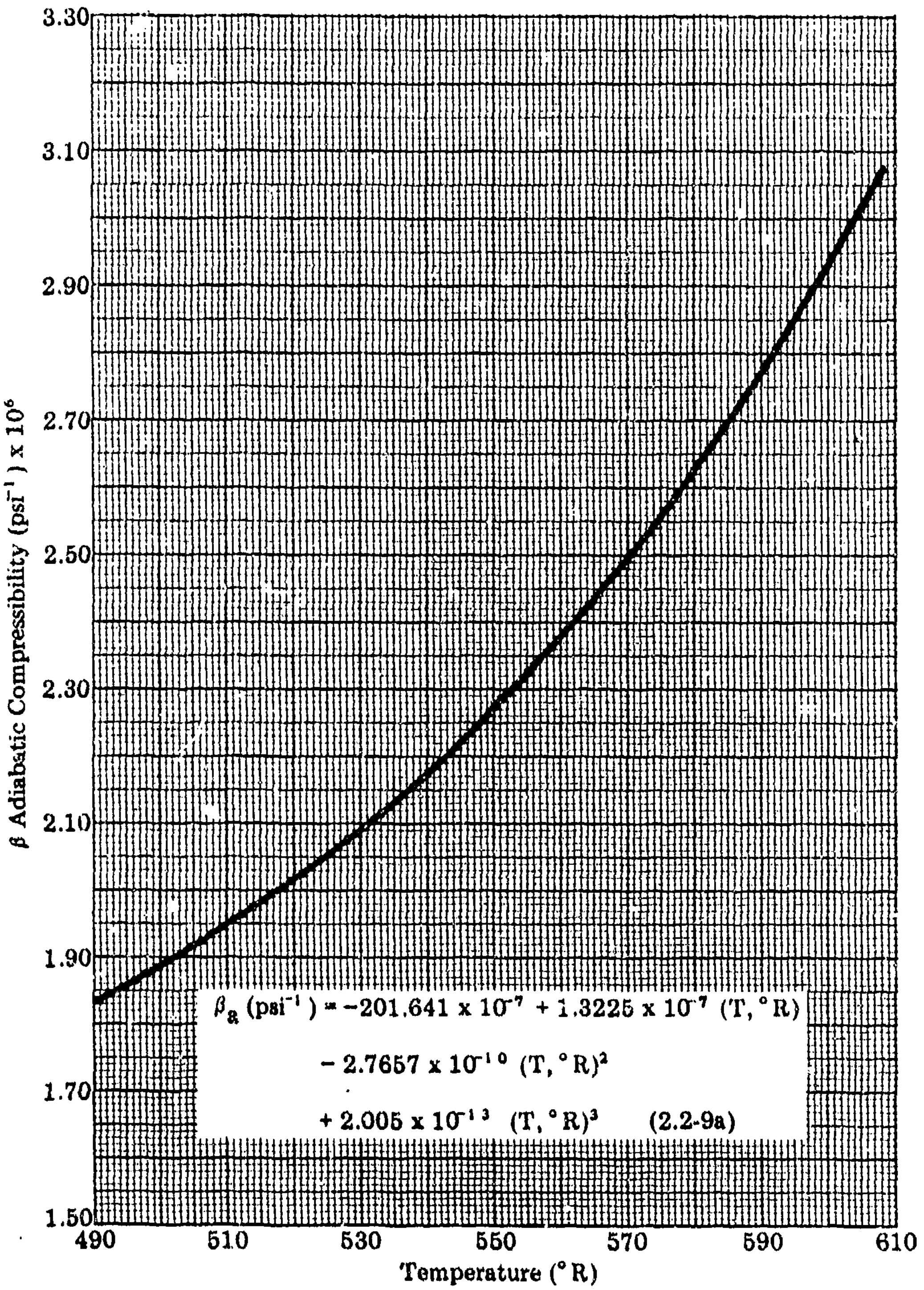
The calculated data is graphically presented in Figures 2.2-5 and 2.2-5a.

Experimental data for the isothermal compressibility of liquid HDA does not appear in the literature.



$$\beta_a(\mathrm{atm}^{-1}) = -2962.39 \times 10^{-7} + 34.976 \times 10^{-7}\ (T, {}^\circ K) - 131.655 \times 10^{-10}\ (T, {}^\circ K)^2 + 1.718 \times 10^{-11}\ (T, {}^\circ K)^3 \qquad (2.2\text{-}9)$$

Figure 2.2-5 Adiabatic Compressibility of Liquid HDA versus Temperature



$$\beta_a\,(\mathrm{psi}^{-1}) = -201.641 \times 10^{-7} + 1.3225 \times 10^{-7}\,(T, {}^\circ R) - 2.7657 \times 10^{-10}\,(T, {}^\circ R)^2 + 2.005 \times 10^{-13}\,(T, {}^\circ R)^3 \qquad (2.2\text{-}9a)$$

Figure 2.2-5a. Adiabatic Compressibility of Liquid HDA versus Temperature

2.2.3.5 Viscosity of Liquid HDA

Viscosity measurements were made on three HDA formulations over a temperature range of 1.1 to 54.4°C (34 to 130°F) using a modified Ostwald glass capillary viscometer (3). Curve-fitted correlations were developed for the range of temperature as well as the composition range of 42.5 to 45.6 w/o NO_2, 0.4 to 2.0 w/o H_2O. These equations are:

$$\log \mu \text{ (cp)} = 0.27546 - \frac{470.888}{(T, {}^\circ K)} + \frac{216430}{(T, {}^\circ K)^2} - 1.70171 \times 10^{-2} N_{(w/o)} - 4.6580 \times 10^{-2} W_{(w/o)} \qquad (2.2\text{-}10)$$

$$\log \mu \text{ (lb}_m\text{/ft-sec)} = -2.89701 - \frac{847.874}{(T, {}^\circ R)} + \frac{701369}{(T, {}^\circ R)^2} - 1.70171 \times 10^{-2} N_{(w/o)} - 4.6580 \times 10^{-2} W_{(w/o)} \qquad (2.2\text{-}10a)$$

where:

μ = absolute viscosity, centipoise or lb_m/ft-sec
T = absolute temperature, Kelvin or Rankine
N = NO_2 concentration, weight percent
W = water concentration, weight percent

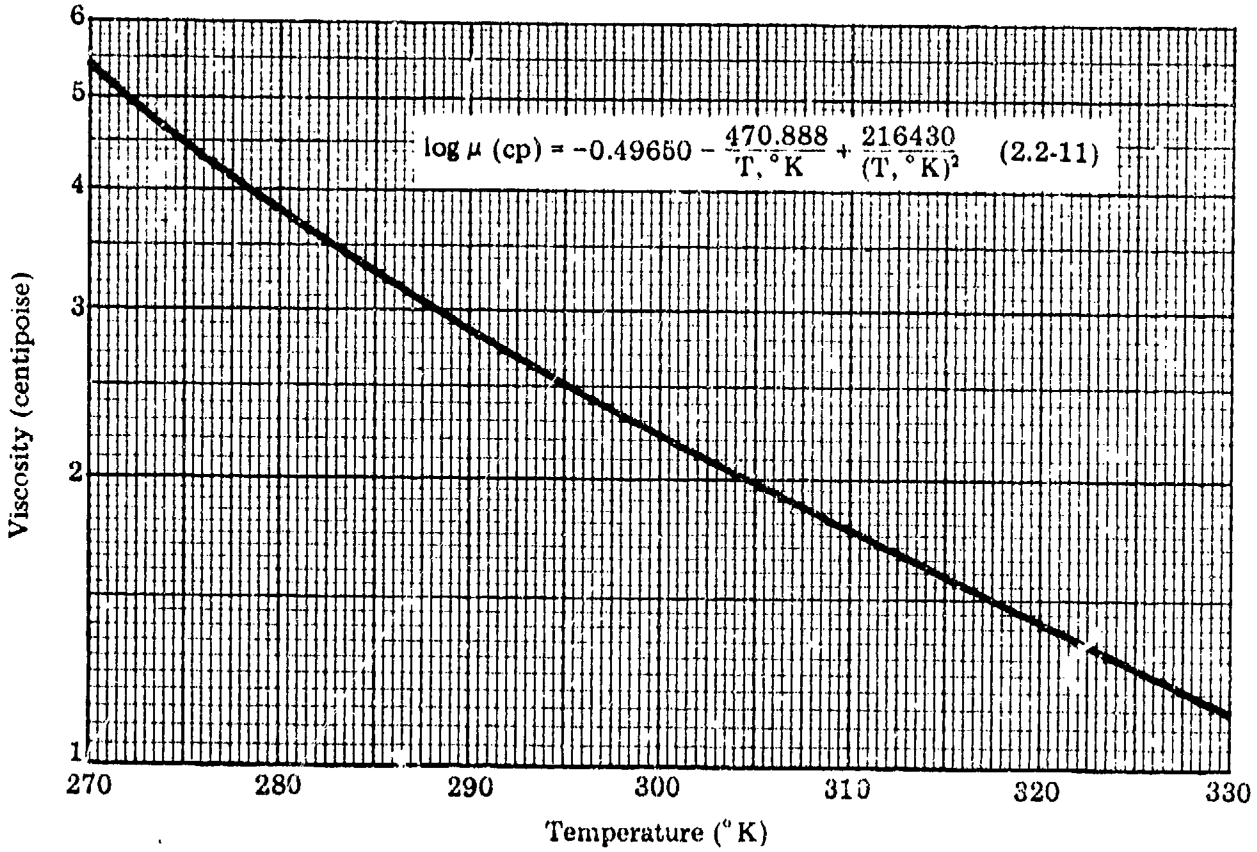
The standard error of estimate of the aforementioned equations is 1.6 percent in absolute viscosity.

For the nominal composition of HDA, the equations reduce to:

$$\log \mu \text{ (cp)} = -0.49650 - \frac{470.888}{(T, {}^\circ K)} + \frac{216430}{(T, {}^\circ K)^2} \qquad (2.2\text{-}11)$$

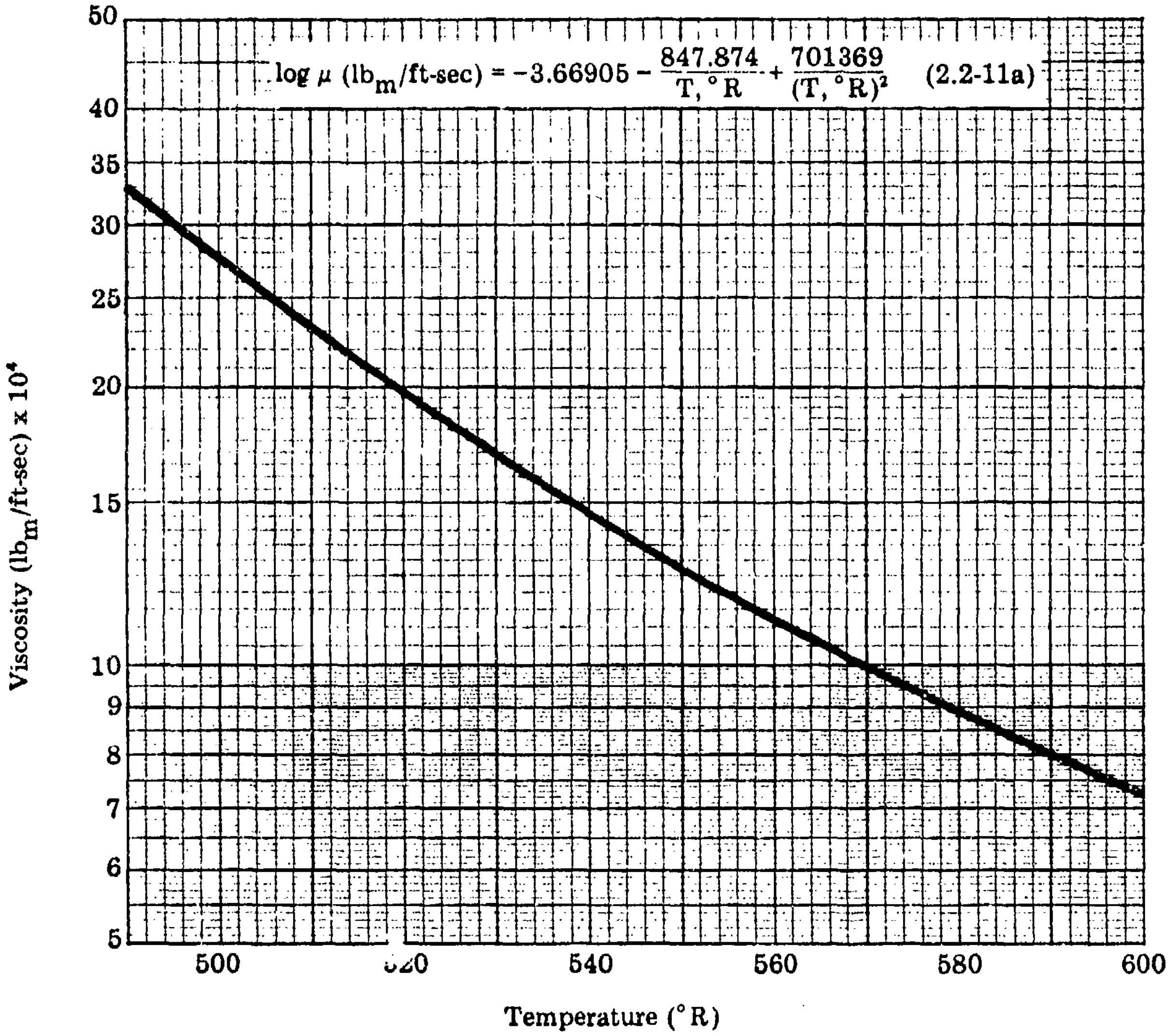
$$\log \mu \text{ (lb}_m\text{/ft-sec)} = -3.66905 - \frac{847.874}{(T, {}^\circ R)} + \frac{701369}{(T, {}^\circ R)^2} \qquad (2.2\text{-}11a)$$

The relationships are plotted in Figures 2.2-6 and 2.2-6a.



$$\log \mu \text{ (cp)} = -0.49650 - \frac{470.888}{T, °K} + \frac{216430}{(T, °K)^2} \qquad (2.2\text{-}11)$$

Figure 2.2-6. Liquid Viscosity of HDA versus Temperature



$$\log \mu\ (\mathrm{lb_m/ft\text{-}sec}) = -3.66905 - \frac{847.874}{T,\ ^\circ R} + \frac{701369}{(T,\ ^\circ R)^2} \qquad (2.2\text{-}11a)$$

Figure 2.2-6a. Liquid Viscosity of HDA versus Temperature

2.2.3.6 Surface Tension of Liquid HDA

The surface tension of liquid HDA has been experimentally determined by Bell Aerospace (2). Measurements were made using sapphire capillaries and surface tension values were computed from the capillary rise formula. The composition of HDA tested was as follows (approximated the nominal composition).

54.6 w/o HNO_3
44.3 w/o NO_2
0.4 w/o H_2O
0.8 w/o HF

The temperature range was from -20°F to 100°F. The surface tension values for HDA are plotted on Figures 2.2-7 and 2.2-7a. Using the least-squares curve fit method, surface tension as a function of temperature is given as follows:

$$\gamma\,(\text{dynes/cm}) = 107.33 - 0.2597\,(T, °K) \tag{2.2-12}$$

$$\gamma\,(\text{lb}_f/\text{ft}) = 7.359 \times 10^{-3} - 9.895 \times 10^{-6}\,(T, °R) \tag{2.2-12a}$$

Standard deviations for equations 2.2-12 and 2.2-12a are 0.68 dynes/cm and 4.522 x 10^{-5} lb_f/ft respectively.

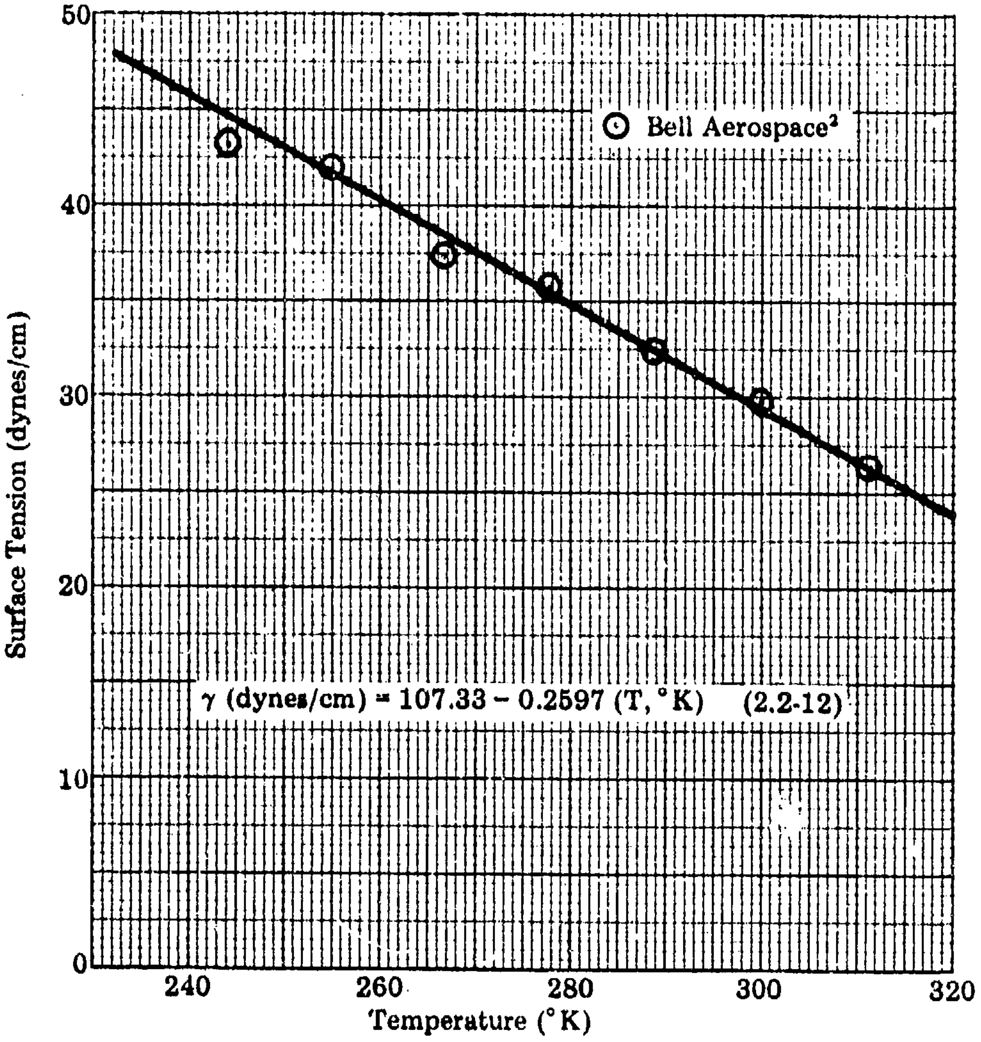


Figure 2.2-7. Experimental Values of Surface Tension of HDA versus Temperature

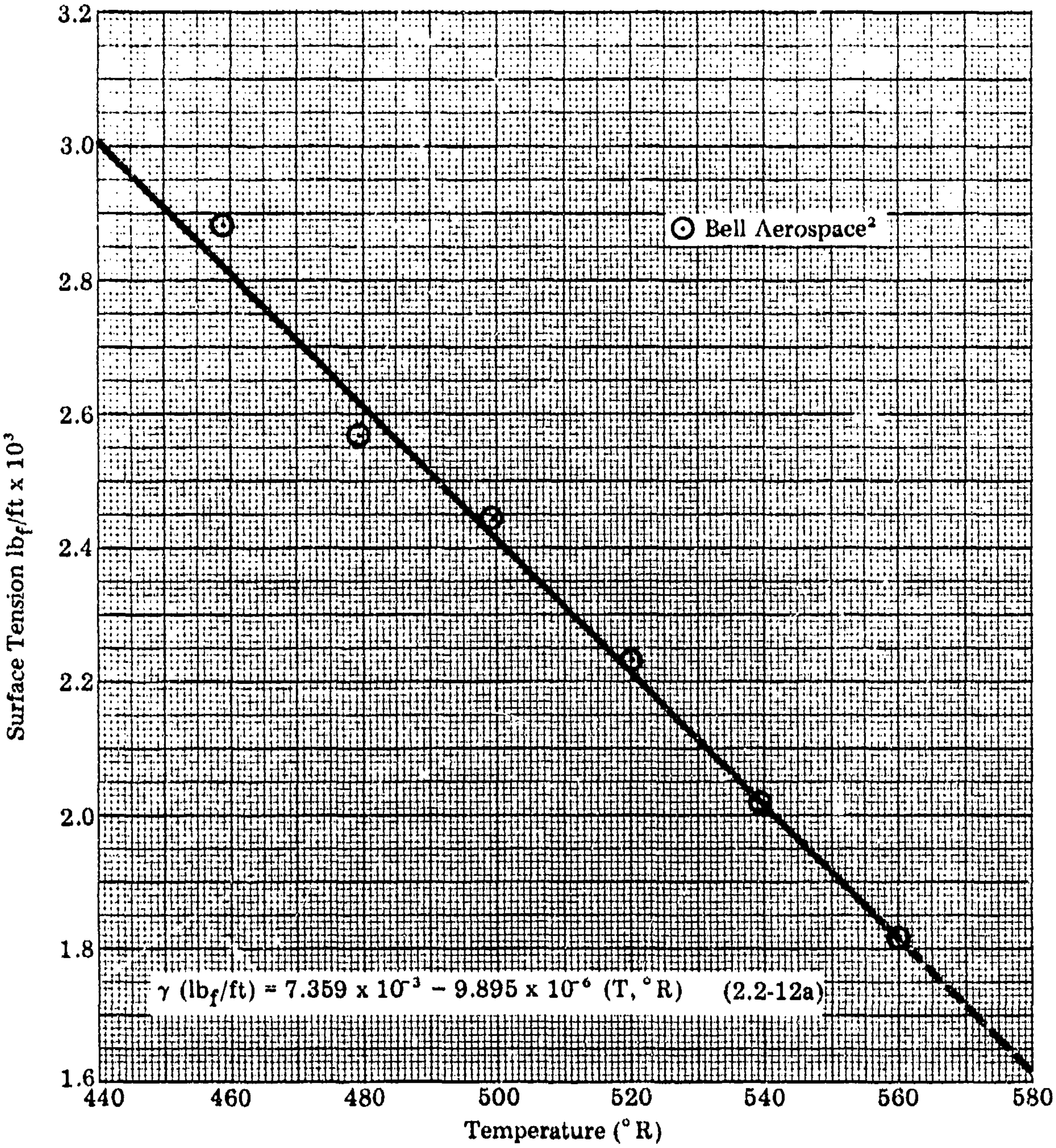


Figure 2.2-7a. Experimental Values of Surface Tension of HDA versus Temperature

2.2.3.7 Thermal Conductivity of Liquid HDA

Lockheed (1) calculated estimated thermal conductivity values of liquid HDA as a function of temperature using Weber's relation (6):

$$K = 3.59 \times 10^{-3}\ Cp\ \rho(\rho/M)^{1/3} \qquad (2.12\text{-}13)$$

where:

K = thermal conductivity, cal/sec - cm - °C
C_p = heat capacity, cal/gm-°C
ρ = density, gm/cm^3
M = molecular weight
$M = 73.16$ (Section 2.2.2.1)

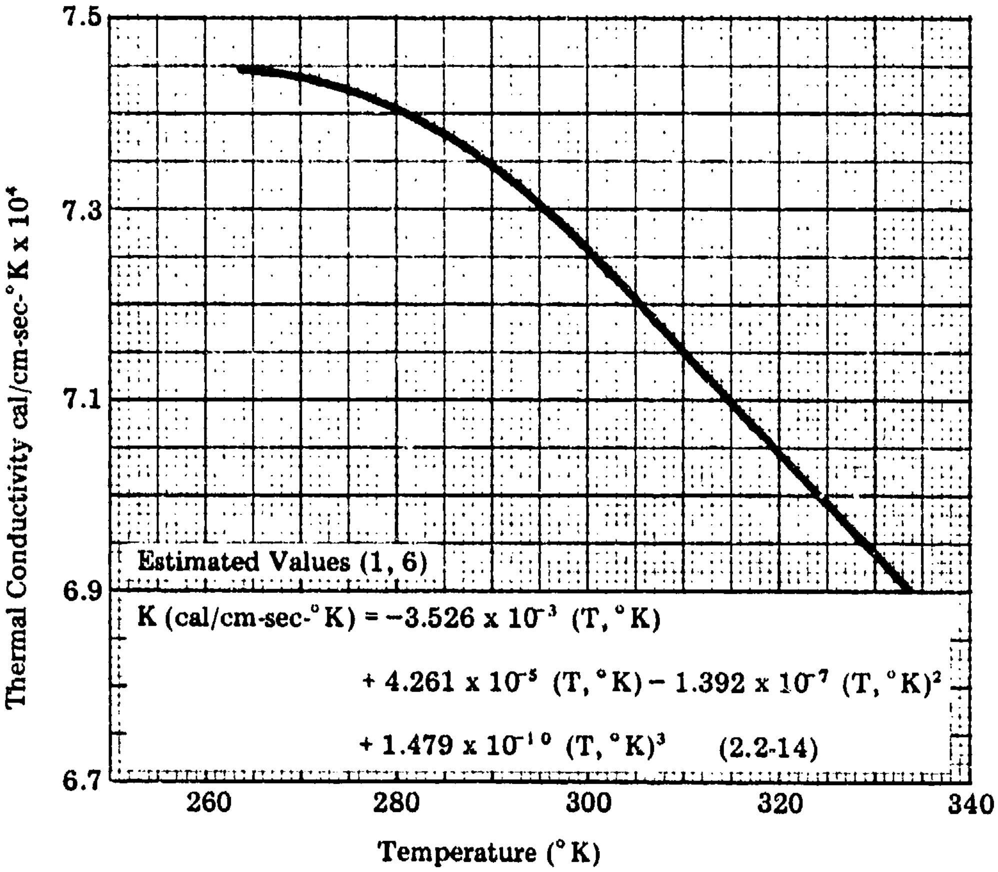
The heat capacity and density values used by Lockheed were the recent empirically-derived data discussed in Section 2.2.4.4 and 2.2.3.2, respectively.

Using the least-squares curve-fit method, estimated thermal conductivity of nominal HDA may be expressed as follows:

$$\begin{aligned} K\,(\text{cal/cm-sec-°K}) = &-3.526 \times 10^{-3} \\ &+ 4.261 \times 10^{-5}\,(T,\text{°K}) \\ &- 1.392 \times 10^{-7}\,(T,\text{°K})^2 \\ &+ 1.479 \times 10^{-10}\,(T,\text{°K})^3 \end{aligned} \qquad (2.2\text{-}14)$$

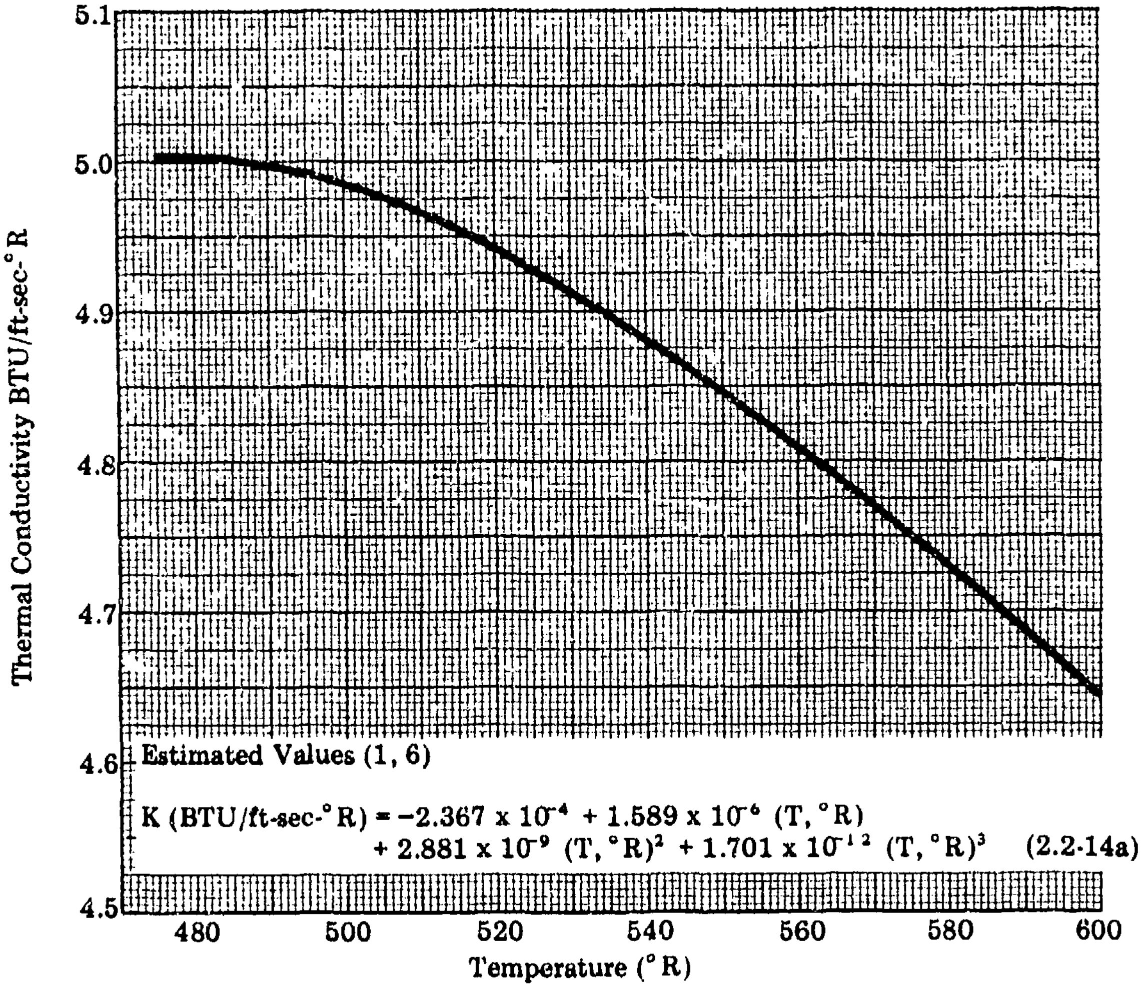
$$\begin{aligned} K\,(\text{BTU/ft-sec-°R}) = &-2.367 \times 10^{-4} \\ &+ 1.589 \times 10^{-6}\,(T,\text{°R}) \\ &- 2.881 \times 10^{-9}\,(T,\text{°R})^2 \\ &+ 1.701 \times 10^{-12}\,(T,\text{°R})^3 \end{aligned} \qquad (2.2\text{-}14a)$$

From equation 2.2-14 a standard deviation of 2.449×10^{-7} cal/cm-sec-°K is obtained. The estimated thermal conductivity values are plotted on Figures 2.2-8 and 2.2-8a.



$$K\,(\text{cal/cm-sec-}^\circ\text{K}) = -3.526 \times 10^{-3}\ (T, {}^\circ\text{K}) + 4.261 \times 10^{-5}\ (T, {}^\circ\text{K}) - 1.392 \times 10^{-7}\ (T, {}^\circ\text{K})^2 + 1.479 \times 10^{-10}\ (T, {}^\circ\text{K})^3 \qquad (2.2\text{-}14)$$

Figure 2.2-8. Thermal Conductivity of Liquid HDA versus Temperature



$$K\ (\mathrm{BTU/ft\text{-}sec\text{-}^\circ R}) = -2.367 \times 10^{-4} + 1.589 \times 10^{-6}\ (T, {}^\circ R) + 2.881 \times 10^{-9}\ (T, {}^\circ R)^2 + 1.701 \times 10^{-12}\ (T, {}^\circ R)^3 \qquad (2.2\text{-}14a)$$

Figure 2.2-8a. Thermal Conductivity of Liquid HDA versus Temperature

2.2.4 CHEMICAL PROPERTIES OF HDA

2.2.4.1 Chemical Reactions

High density acid is basically a mixture of nitric acid and nitrogen dioxide or nitrogen tetroxide; thus, the chemical reactions of HDA are those which nitric acid and NO_2 (N_2O_4) will undergo. The reactions of nitric acid are discussed in Section 2.1.4.1 and the reactions of N_2O_4 in Section 2.3.4.1.

2.2.4.2 Inert Gas Solubility in Liquid HDA

Lockheed (1) estimated solubilities of helium and nitrogen in HDA by assuming HDA to be a mixture of IRFNA and N_2O_4. Experimental data of solubilities of helium and nitrogen and IRFNA and in N_2O_4 at 0°C and 25°C were reported by Chang (7) and Lockheed based their calculations from Chang's work. Solubility isotherms for 0°C and 25°C are plotted on Figures 2.2-9 and 2.2-9a. Curves are extrapolated beyond two atmospheres since experimental work was not in that range. Henry's Law is valid because of low solubilities.

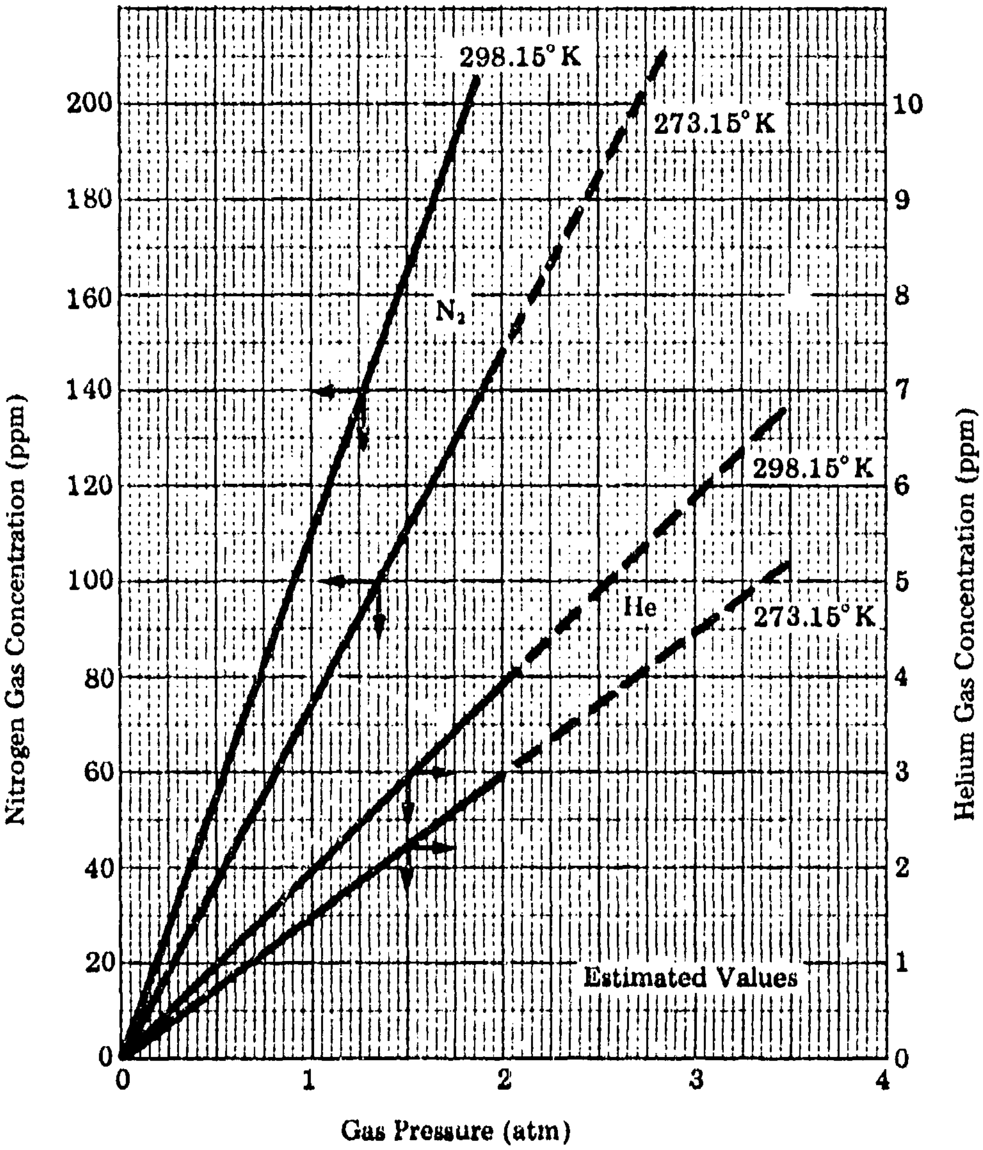


Figure 2.2-9. Helium and Nitrogen Gas Solubilities in HDA

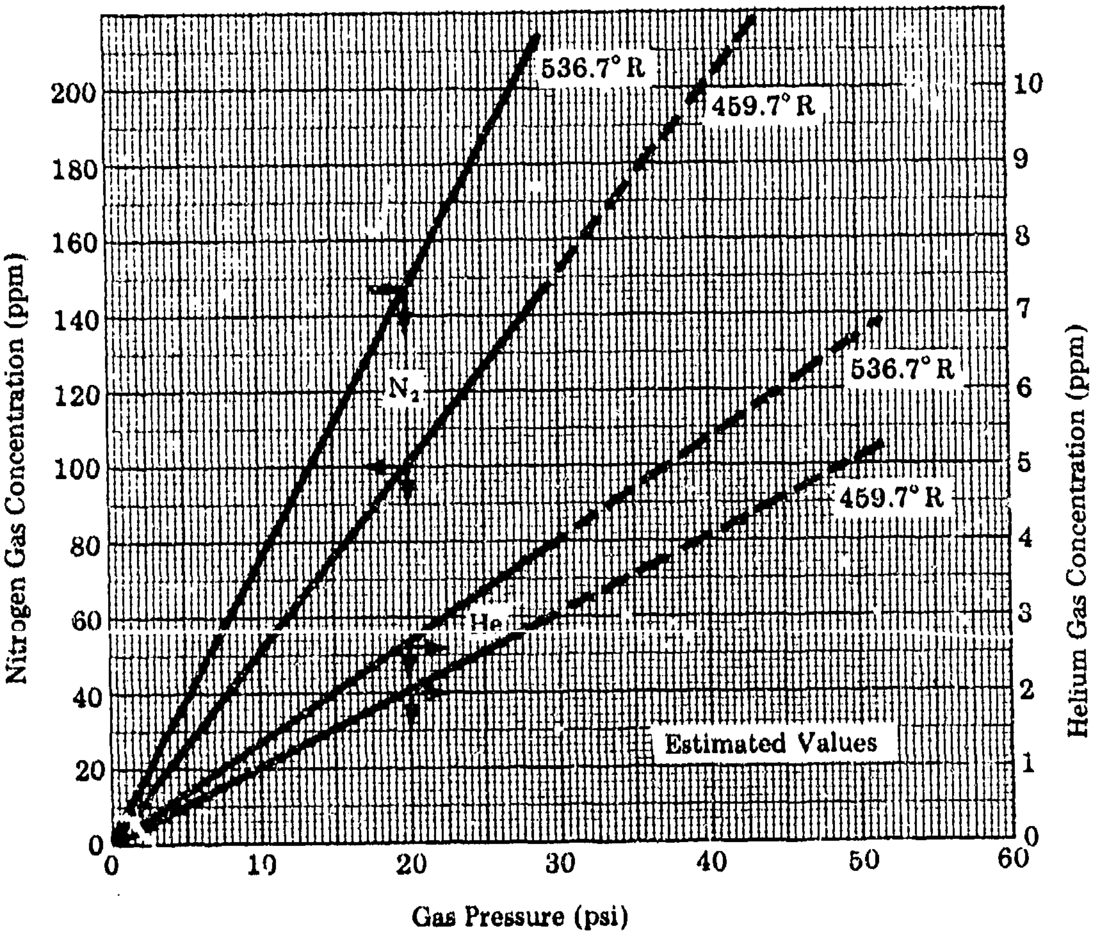


Figure 2.2-9a. Helium and Nitrogen Gas Solubilities in HDA

2.2.5 THERMODYNAMIC PROPERTIES OF HDA

2.2.5.1 Heat of Formation of Liquid HDA

No experimental determination for the heat of formation of HDA is noted in the current literature. Rocketdyne (3) presents a well constructed case for the estimated value in lieu of making an experimental determination. It is summarized in the following paragraphs.

The heat of formation of HDA (54.8 w/o HNO_3, 44.0 w/o N_2O_4, 0.5 w/o H_2O, 0.7 w/o HF) was estimated using the heats of formation of the components, N_2O_4, H_2O, and HF, and their heats of solution with each other. An estimate was made of the possible uncertainty in the calculation, using a conservative approach to arrive at the greatest possible uncertainty. Where uncertainties in individual enthalpies had to be estimated, unusually large values were chosen. Absolute values of the individual uncertainities were summed to calculate the total uncertainty. It should be noted that enthalpy values associated with H_2O and HF are not very critical since these components are present in small quantities.

The heat of formation of HDA was found to be 43.3 ± 0.8 Kcal/100g, where 0.8 Kcal/100g is the estimate of the maximum uncertainty that could be expected.

The individual values used in preparing the estimate are summarized in the following table:

TABLE 2.2-1 ENTHALPY CONTRIBUTIONS OF HDA COMPONENTS AND THE HEAT FORMATION OF HDA

Component	Composition w/o	Molecular Weight	Moles/100 g HDA	Enthalpy Contribution (Kcal/100 g HDA) Low	Nominal	High
HNO_3	54.8	63.0129	0.86966	-36.14	-36.06	-35.97
N_2O_4	44.0	92.011	0.47820	-3.41	-2.98	-2.55
H_2O	0.5	18.0153	0.02775	-1.83	-1.62	-1.51
HF	0.7	20.0064	0.03499	-2.68	-2.59	-2.51
HDA Heat of Formation (Kcal/100 g)				-44.06	-43.25	-42.54
Selected Value of HDA Heat of Formation:				-43.3 ± 0.8 Kcal/100 g		
Empirical Formula (basis of 100 g HDA): $H_{0.96015}N_{1.82606}O_{4.54953}F_{0.03499}$						

The general approach employed by Rocketdyne was to start with the best available values for heat of formation of the pure components in HDA, then to calculate or estimate from known data their heats of solution or reaction in the HDA mixture. The heats of formation of pure compounds, used in these calculations, are shown in the following table:

TABLE 2.2-2 HEATS OF FORMATION OF PURE COMPOUNDS AT STANDARD CONDITIONS

Compound	Heat of Formation, Liquid at 25°C (Kcal/g-mole)	Uncertainty (Kcal/g-mole)	Reference
HNO_3	-41.46	±0.09	8
N_2O_4	-4.68	±0.4	8
H_2	-68.32	±0.01 (est.)	9
HF	-71.99	±0.2	9
N_2O_3	+12.02	±2.0 (est.)	9
HNO_2	-27.6	±2.3 (est.)	9

For convenience in making estimates of heats of formation for other mixtures similar to HDA, a special set of heats of formation for the HDA components in solution were derived, combining the pure components heats of formation with the heats of solution and reaction. The heat of formation that was assigned to HNO_3 is the JANNAF value for the pure compound. With this approach, once the special set of heats of formation has been worked out, it is easy to compute the heat of formation of another mixture (as long as the composition is similar to that of HDA). The derivation of these special heats of formation of N_2O_4, H_2O, and HF, which include heats of interaction, are discussed in the following sections.

N_2O_4 is not known to react with HNO_3; i.e., no reaction can be written. A small heat of solution, -1.56 Kcal/g-mole N_2O_4, has been measured (18 and 19). Calorimetric equipment was not used; however, large quantities (~100 g) were involved and temperature rises were in the range of 14 to 16°C. Therefore, heat loss effects should have been minor. The assignment of an uncertainty of ±0.5 Kcal/g-mole to the above value seems exceptionally pessimistic since it corresponds to an error of about 5°C in temperature rise. Combining the above value for the heat of N_2O_4 in HNO_3, -1.56 ±0.5 Kcal/g-mole N_2O_4, with the heat of formation of N_2O_4, -4.68 ±0.4 Kcal/g-mole, leads to the following values for N_2O_4, dissolved in HDA:

Low	Nominal	High
-7.14	-6.24	-5.34 Kcal/g mole

These values, converted to the basis of 100 g HDA, were used in Table 2.2-1.

Although H_2O would exhibit an exothermic heat of solution in HNO_3, it will react with the N_2O_4 in HDA. The reaction of H_2O with excess N_2O_4 has been qualitatively observed to be endothermic. Two overall reactions are possible for H_2O with excess N_2O_4.

	Heat of Reaction, Kcal/g-mole	Reaction
$H_2O + N_2O_4 \longrightarrow HNO_2 + HNO_3$	+ 5.51 ± 3.32	(I)
$H_2O + 2\,N_2O_4 \longrightarrow N_2O_3 + 2\,HNO_3$	+ 9.9 ± 4.0	(II)

Reaction II is preferred, since HNO_2 is rather unstable and since NO is stablized in the form of N_2O_3. Therefore, 9.9 Kcal/g-mole is selected as the nominal heat of solution. The high value is 13.9 (9.9 + 4.0) and the low value is 2.19 (5.51 - 3.32). Combining these values with the heat of formation of H_2O yields the following values for H_2O dissolved in HDA.

Low	Nominal	High
-66.1	-58.4	-54.5 Kcal/g-mole

The heat of solution of HF in HNO_3 was assumed to be between 0 (minimum) and that of HF in H_2O (maximum). The value of -71.99 ±0.2 Kcal/g-mole was taken for the heat of formation of HF from Table 2.2-2 and heat of solution in H_2O was derived from data in Reference 9. Using these data together with the uncertainty of 0.2 Kcal/g-mole for the heat of formation of HF, the following values for HF dissolved in HNO_3 are obtained.

Low	Nominal	High
-76.7	-74.0	-71.8 Kcal/g-mole

The nominal value was selected approximately midway between the high and low values.

The nominal values that were derived for the heats of formation of N_2O_4, H_2O, and HF dissolved in HNO_3, are summarized below.

Compound	H_f, Kcal/mole
N_2O_4	- 6.24
H_2O	-58.4
HF	-74.0

They were used to calculate the heats of formation of the nominal formulation in Table 2.2-1, subject to the restriction that the H_2O and HF concentrations are small; i.e., a few percent or less. Thus from the data just developed, the heat of formation of HDA at 298°K (25°C and 77°F) is given as follows:

$\Delta H_f = -30.698$ Kcal/mole

$\Delta H_f = -779.4$ BTU/lb

2.2.5.2 Melting Point and Heat of Fusion

Rocketdyne (3) reports a melting point of -37.2°C (-35°F) for HDA citing as its source a chemical safety bulletin, Fuming Nitric Acids, by Bell Aerospace (10).

No experimental value for HDA heat of fusion is available. The value for latent heat of fusion depends in part on the crystal form of the solid phase, and attempts to obtain general correlations have been quite unsuccessful (6).

Heat of fusion for the hydrates of HNO_3 can be estimated by summation of the fusion heats (9) of the constituents.

Species	Exp. ΔH_{fusion} (cal/mole)	$\sum \Delta H_{fusion}$	Δ [Calc-Exp.]	Δ%
HNO_3	2503	—	—	—
H_2O	1440	—	—	—
$HNO_3 \cdot H_2O$	4184	3943	-243	-5.7
$HNO_3 \cdot 3H_2O$	6954	6823	-131	-1.9

On this basis, assuming HDA consists mainly of $2HNO_3 \cdot N_2O_4$ (42% N_2O_4) the heat of fusion (9) is:

Species	Exp. ΔH_{fusion} (cal/mole)	$\sum \Delta H_{fusion}$
HNO_3	2503	—
N_2O_4	3602	—
$2HNO_3 \cdot N_2O_4$	—	8608

For the nominal HDA composition, the estimated value is 120.0 cal/gm (216 BTU/lb) based on a molecular weight of 70.897.

2.2.5.3 Critical State Constants

Experimental values for the critical constants of HDA do not exist. It is not possible to obtain reliable values because of the decomposition of nitric acid at elevated temperatures. Consequently, pseudocritical properties are estimated for the nominal HDA composition. The technique and procedure used in obtaining these values are reported by Rocketdyne (3).

Pseudocritical temperature and pressure were estimated by Kay's Rule (11), and the pseudocritical compressibility factor was estimated by the analogous Leland-Mueller rule (12). Pseudocritical volume was calculated from the other constants.

In applying Kay's Rule to HDA, there is uncertainty as to the most appropriate value to use for the molecular weight of N_2O_4 (46, 92, or some intermediate value). Thus, the rule was applied using the extreme values. Pseudocritical pressure and compressibility were surprisingly insensitive to the molecular weight of N_2O_4 and even the temperatures were close (ΔT = 31°K). Values are summarized in Table 2.2-3. There is no good reason to select either extreme; therefore, they were averaged to obtain the recommended values given in Table 2.2-3.

2.2.5.4 Heat Capacity of Liquid HDA

Experimental values of heat capacity (Cp) for HDA has not been determined. Lockeed (1) has estimated Cp values based on the following observations in the literature of the physical and chemical behavior of the constituents that make up HDA. An examination of the literature (3, 5, 13, 14) indicates that while C_p for pure HNO_3 does not vary appreciably with temperature, there is a significant shift in C_p for N_2O_4 over the same temperature range. It is therefore reasonable to assume that HDA would exhibit a similar shift in C_p, and further, that the shift would mimic the N_2O_4 data slope which has a very pronounced upward trend.

Reference 13 describes the mechanism by which NO_2 is ionized in HNO_3 to produce an equilibrium quantity of the associated molecule $NO_3^{-}(HNO_3)_2$ accounting for the increased density of the solution. Since heat capacity, like density, is an additive property, it is possible to estimate the C_p values for HDA as a function of temperature, if a correction is made for the abnormal density change. Taking the summed contribution of heat capacities for the respective mole fractions of the solution ingredients and multiplying the value by the ratio of actual HDA density to the computed additive densities for the ingredients, provides an estimate of what the C_p value for HDA might reasonably be.

TABLE 2.2-3 PSEUDOCRITICAL CONSTANTS OF HDA

	Assumption		
Constant	**N_2O_4 present as NO_2 (MW = 46.005)**	**N_2O_4 present as N_2O_4 (MW = 92.001)**	**Recommended Values**
P_c, atm	97.4	97.1	97.2 (1428 psia)
T_c, °K	524	556	540 (972°R)
Z_c	0.235	0.235	0.235
V_c, (cc/g)	1.4215	1.5036	1.4625 (.0234 ft/lb)
ρ_c, g/cc	0.7035	0.6651	0.6837 (42.68 lb/ft^3)

The estimated values of heat capacity for liquid HDA are given in Table 2.2-4.

TABLE 2.2-4 ESTIMATED C_p VALUES OF LIQUID HDA

Temperature			Heat Capacity, C_p
°R	°F	°K	BTU/lb$_m$-°F or cal/g-°K
459.67	0	255.37	0.4263
469.67	10	260.93	0.4313
479.67	20	266.48	0.4323
491.67	32	273.15	0.4360
499.67	40	277.59	0.4380
509.67	50	283.15	0.4398
519.67	60	288.71	0.4415
536.67	77	298.15	0.4435
549.67	90	305.37	0.4446
559.67	100	310.93	0.4455
579.67	120	322.04	0.4486
599.67	140	333.15	0.4516
619.67	160	344.26	0.4576

Using a least-squares curve-fit computer program, the estimated values of C_p for liquid HDA as a function of temperature may be expressed as:

$$C_p\ (\text{Cal/g-°K}) = -1.764 + 0.02146\ (T, °K) - 7.010 \times 10^{-5}\ (T, °K)^2 + 7.704 \times 10^{-8}\ (T, °K)^3 \tag{2.2-15}$$

$$C_p\ (\text{BTU/lb-°R}) = -1.764 + 1.192 \times 10^{-2}\ (T, °R) - 2.163 \times 10^{-5}\ (T, °R)^2 + 1.321 \times 10^{-8}\ (T, °R)^3 \tag{2.2-15a}$$

The standard deviation computed for equations 2.2-15 and 2.2-15a are 5.624×10^{-4} cal/g-°K and 5.617×10^{-4} BTU/lb°R respectively. The estimated values for C_p of liquid HDA are graphically shown in Figures 2.2-10 and 2.2-10a.

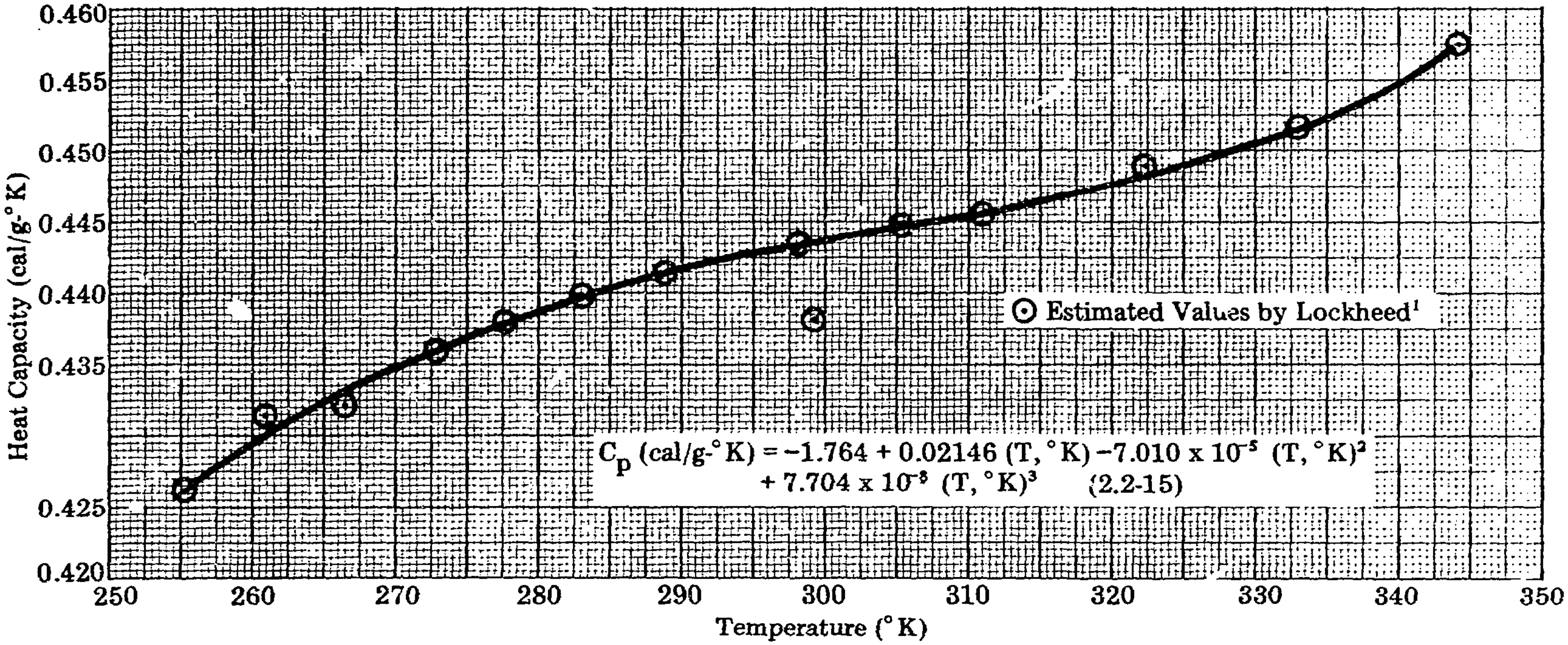


Figure 2.2-10. Heat Capacity of Liquid HDA versus Temperature

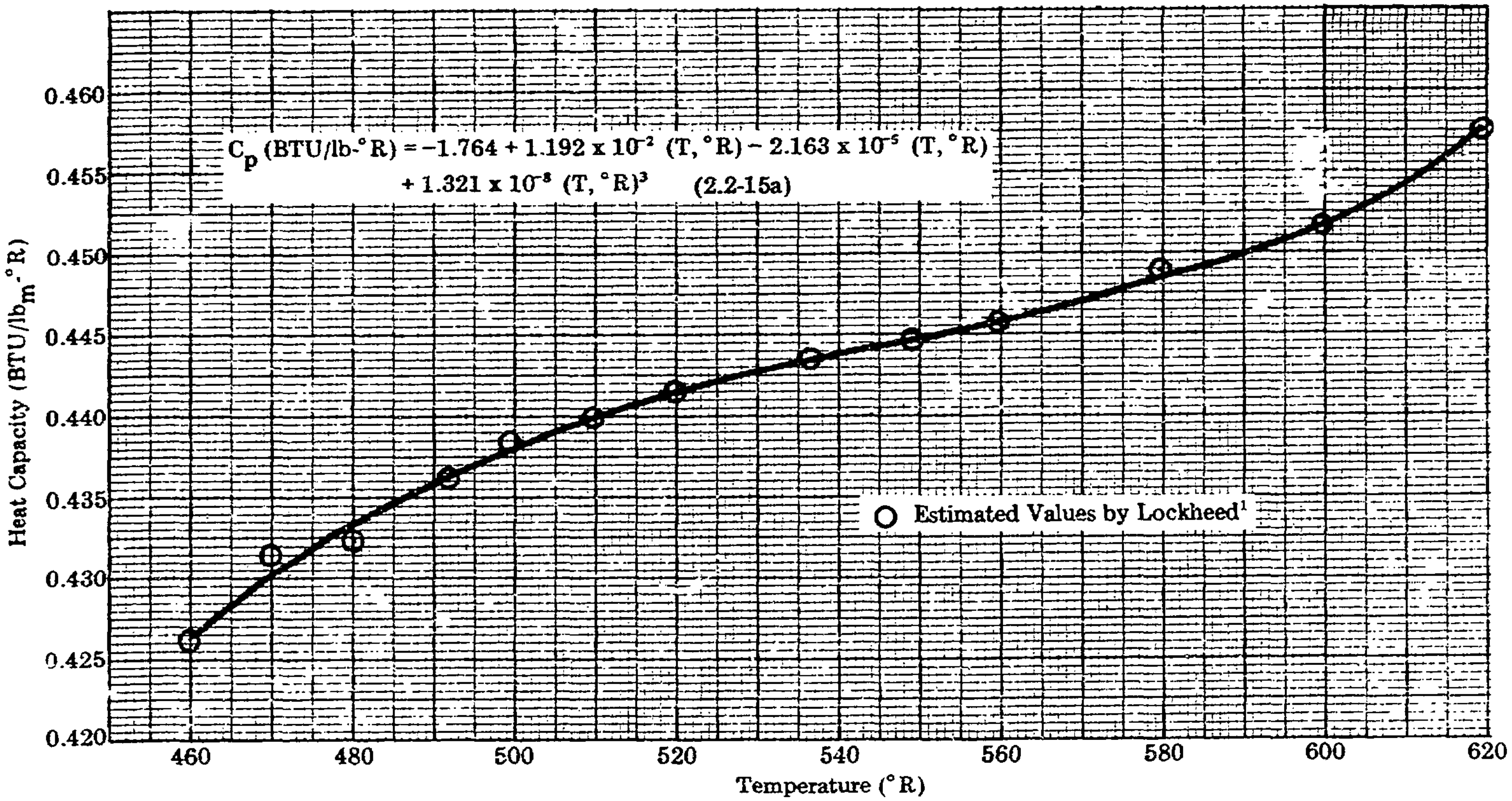


Figure 2.2·10a. Heat Capacity of Liquid HDA versus Temperature

2.2.5.5 Latent Heat of Vaporization of HDA

An equation for the latent heat of vaporization of HDA was derived from the vapor pressure equation, using the Clapeyron equation (3):

$$\frac{d\,\ell n(P_{vp})}{d\,\ell n(\frac{1}{T})} = -\frac{\Delta H_v}{R(Z_v - Z_\ell)} \tag{2.2-16}$$

The term, Z_ℓ (the compressibility factor of the liquid) may be neglected since it is very small, about 0.004. The value for Z_v (the compressibility factor of the vapor) was obtained by assuming the vapor to be entirely NO_2. A value of 0.9888 for Z_v was obtained from the generalized tables of Lydersen, Greenhorn and Hougen (15). Combining these components generated the following equations for the heat of vaporization of HDA:

$$\Delta H_v \begin{pmatrix}\text{Kcal/g mole}\\ \text{vapor}\end{pmatrix} = 21.251 - 0.12882\,N_{(w/o)} - \frac{2557.2}{(T, {}^\circ K)} \tag{2.2-17}$$

$$\Delta H_v \begin{pmatrix}\text{BTU/lb mole}\\ \text{vapor}\end{pmatrix} = 38{,}252 - 231.88N_{(w/o)} - \frac{8{,}285{,}300.}{(T, {}^\circ R)} \tag{2.2-17a}$$

which are valid for 43.2 to 45.6 w/o N_2O_4 and 256 to 397°K (461 to 714°R).

These equations were evaluated for the nominal composition (54.8 w/o HNO_3, 44.0 w/o N_2O_4, 0.5 w/o H_2O, 0.7 w/o HF) at the normal boiling point, 24.7°C (76.5°F), to give the following values: 7.00 Kcal/g-mole vapor or 12,600 BTU/lb mole vapor.

In order to put the heat of vaporization on a weight basis it is necessary to know the molecular weight and thus the composition of the vapor phase. This has not been determined for HDA. Attempts to estimate the composition, assuming ideal behavior, produced a poor estimate of the total pressure at the boiling point, 0.47 atm. Therefore, this assumption was discarded. Subsequently, molecular weight was estimated by two methods which represent extreme assumptions: (1) the vapor is pure NO_2, therefore MW = 46.005 (minimum); and (2) the partial pressure of HNO_3 is equal to the vapor pressure of pure nitric acid, therefore MW = 47.43 (maximum). Fortunately, the range of values is small. Using these values, the following range is obtained for heat vaporization of HDA on a weight basis: 148 to 152 cal/g (266 to 274 BTU/lb).

2.2.6 LOGISTICS OF NITRIC ACID, TYPE IV (HDA)

2.2.6.1 Manufacture

The oxidizer, HDA, is a blend of nitric acid (Type IIILS) and nitrogen tetroxide (MON-1). The blend is defined in MIL-P-7254F (30 April 1970), Amendment 2, (18 January 1972). The details of the process for manufacturing nitric acid is described in Section 2.1.6.1 and for nitrogen tetroxide is described in Section 2.3.6.1.

2.2.6.2 Analysis

The analysis of HDA is covered in Section 2.1.6.2 on nitric acid. The same techniques are used for this oxidizer.

2.2.6.3 Cost and Availability

HDA is readily available in large quantities for aerospace usage. The only known usage is the Agena vehicle. The oxidizer is supplied to the government by Allied Chemical Company of Buffalo, New York. The unit price in 1976 was \$0.22/pound from the government. The government procured 30,000 pounds in 1976 (20).

2.2.6.4. Shipping and Transportation

The requirements for shipping and transportation of HDA are basically the same as those for the nitric acids. See Section 2.1.6.4. HDA, per Reference 16, has been assigned Federal Stock Number 91354334963 and is commercially available from Industrial Chemicals.

2.2.7 REFERENCES

1. Lockheed Missiles and Space Company, *High Density Acid (HDA) Physical Properties Handbook,* (Third Edition), LMSC/D538660, Sunnyvale, California (22 July 1976).
2. Bell Aerospace Company, *Model 8096 Maximum Density Acid Engine Definition Program,* Final Report, Propellant Characterization Program, Volume II, Basic Issue, Report 8096-910082 (1 September 1970).
3. Rocketdyne Division, Rockwell International, *Engineering Properties of Rocket Propellants,* Final Report. AFRPL-TR-73-105, Canoga Park, California (November 1973).
4. Elverum. G.W., Jet Propulsion Laboratory, CIT-JPL-PR 20-224, (24 May 1954).
5. Constantine, M.T., *Engineering Property Determinations on Rocket Propellants,* Rocketdyne Division, Rockwell International, Final Report, AFRPL-TR-70-147, Canoga Park, California (November 1970).
6. Reid, R.C. and Sherwood, T.K., *The Properties of Gases and Liquids,* McGraw-Hill Book Co., 1st Ed., p 257 (1958).
7. Chang, E.T., Goken, N.A., and Poston, T.M., *Solubilities of Gases in Simple and Complex Propellants,* J. Spacecraft and Rockets 6, 1177 (1969).
8. Dow Chemical Company, *The Heat of Formation of Propellant Ingredients,* Special Report, AFRPL-TR-67-311, Midland, Michigan (1967).
9. Rossini, F.D., et al, *Selected Values of Chemical Thermodynamic Properties,* NBS Circular 500, USGPO, Washington, D.C. (1952).
10. Bell Aerospace Company, *Fuming Nitric Acids,* Chemical Safety Bulletin No. 6, Buffalo, New York, (19 June 1970).
11. Kay, W.B., Ind. Eng. Chem, 28, 1014 (1936).
12. Leland, T.W., Jr., and Mueller, W.H., Ind. Eng. Chem., 51, 597 (1959).
13. Stern, S.A., Mulhaupt, J.T., and Kay, W.B., *The Physiochemical Properties of Pure Nitric Acid,* Chemical Reviews, 60, 185-207 (1960).
14. Mason, D.M., Petker, I., and Vango, S.P., *Viscosity and Density of the Nitric Acid–Nitrogen Dioxide–Water System,* J. Phys. Chem., 59, 511-519, (June 1955).
15. Lydersen, A.L., Greenhorn, R.A., and Hougen, O.A., *Generalized Thermodynamic Properties of Pure Liquids,* Engineering Experiment Station Report No. 4, University of Wisconsin, Madison, Wisconsin (October 1955).
16. Heubusch, H. Ph., *Material Selection for Use with HDA,* Bell Aerospace Company, Buffalo, New York (1973).
17. Heubusch, H. Ph., *Use of a New Inhibitor to Improve the Compatibility of HDA,* Bell Aerospace Company, Buffalo, New York, 27 November 1972.
18. Bell Aerospace Company, Interoffice Memo, 914:70:0311-1:GJ, Buffalo, New York, March 1970.
19. Bell Aerospace Company, Interoffice Memo, 914:70:0424-1:GJ, Buffalo, New York, April 1970.
20. Personal Communication with Mr. W. Watje, Kelly AFB, San Antonio, Texas.

2.3 N_2O_4

2.3.1 PROPERTY SUMMARY SHEET

Chemical Name: Nitrogen Tetroxide **Common Name:** NTO, MON-1, MON-3*

Chemical Formula: N_2O_4 **Formula Weight:** 92.016 (O^{16})

Property	Value	Units	Temp (°K)	Reference	Figure
Melting Point	261.95 -11.2 471.47 11.8	°K °C °R °F		6, 9, 10, 23	
Heat of Fusion	38 68.5	cal/g BTU/lb	261.95	6, 10, 24	
Normal Boiling Point	294.35 21.2 529.77 70.1	°K °C °R °F		6, 7, 10, 23	
Heat of Vaporization	99 178.2	cal/g BTU/lb	294.35	6, 23, 24	
Heat of Disassociation (Liquid)	17.82	kcal/mole	298.1	6	
Critical State Constants Temperature	431.35 158.2 776.47 316.8	°K °C °R °F		6, 24	
Pressure	98.0 1440.2	atm psia		9	
Density	0.5504 34.3641	g/cc lb/ft^3		9	
Vapor Pressure of Liquid	898.57 17.38	mm Hg psia	298.15	9	2.3-2
Density of Liquid	1.433 89.52	g/cc lb/ft^3	298.15	1, 10	2.3-5
Sonic Velocity (Liquid)	977 3204	m/sec ft/sec	298.15	9	2.3-8
Compressibility of Liquid Adiabatic	7.44×10^{-5} 5.006×10^{-6}	atm^{-1} psi^{-1}	298.15	1, 9, 10	2.3-9
Isothermal	9.34×10^{-5} 6.4×10^{-6}	atm^{-1} psi^{-1}	298.15	6	2.3-10
Viscosity of Liquid	0.396 2.67×10^{-4}	cp lb/ft-sec	298.15	6	2.3-11
Heat Capacity of Liquid	.378 .378	cal/gm-°C BTU/lb-°F	298.15	9, 23	2.3-15
Thermal Conductivity of Liquid	3.13×10^{-4} 2.11×10^{-5}	cal/cm-sec-°K BTU/ft-sec-°K	298.15	6	2.3-13
Surface Tension	25.1 .00172	dynes/cm lb/ft	298.15	7, 9	2.3-12
Parachor	144.0		298.15	Calc	
Refractive Index	1.40 1.0046		293.15 298.15	6	
Dielectric Constant	2.42		291.15 1000 cycles/sec	6, 18	
Entropy (Gas)	72.724 .7904	cal/mole-°K BTU/lb-°R	298.15	6, 9, 10	
Entropy (Liquid)	50.007 0.5435	cal/mole-°K BTU/lb-°R	298	9	
Heat of Formation (Liquid)	-4676 -91.476	cal/mole BTU/lb	298.15	20	

*See Section 2.3.2.1.

2.3.2 GENERAL

2.3.2.1 Introduction

Nitrogen tetroxide (also known as dinitrogen tetroxide, NTO, and nitrogen peroxide) is a volatile, heavy, reddish-brown liquid which boils at 71°F and melts at 12°F. It is highly regarded as a propellant oxidizer because it is highly reactive chemically, thermally stable and insensitive to all types of mechanical shock and impact. Although nonflammable, it will support combustion and upon contact with high energy fuels such as hydrazine, will react hypergolically.

At ordinary temperatures N_2O_4 exists in equilibrium with nitrogen dioxide (NO_2), $N_2O_4 \rightleftharpoons 2NO_2$, with the degree of dissociation varying directly with the temperature and inversely with the pressure. At atmospheric pressure, the equilibrium mixture contains approximately 15 percent NO_2 at its boiling point (70.1°F), increasing to about 90 percent at 212°F (100°C) and dissociation is practically complete at 302°F (150°C).

In the solid state, N_2O_4 is colorless; in the liquid state the equilibrium is yellow to red-brown, varying with temperature and pressure; in the gaseous state it is red-brown. The addition of 0.45 to 0.85 percent nitric oxide (NO) gives a "green" N_2O_4 mixture. The low percentage addition of NO is specified to minimize stress-corrosion cracking of titanium tanks (12).

The specific impulses of N_2O_4 with amine-type fuels such as Unsymmetrical Dimethylhydrazine (UDMH), hydrazine (N_2H_4), and aniline are five percent higher than that of red fuming nitric acid (RFNA). RFNA has a lower freezing point and a higher density than N_2O_4, but in many propulsion systems, especially those not subjected to temperature extremes, the oxidizer of higher performance is preferred when it provides greater mission capability than the more dense oxidizer.

Nitrogen tetroxide when mixed with nitric oxide forms MON-type acids. The performance of MON-type acids is slightly higher with amine-type fuels than that of N_2O_4. MON-type acids have lower freezing points. See Figures 2.3-1 and 2.3-1a for the relationship of freezing point versus weight percent of NO. MON's density is lower than the density of N_2O_4 and MON's higher vapor pressure requires the use of larger and heavier pumps.

MON-type acids, Mon-1 and MON-3, are currently being specified for rocket oxidizers because the addition of NO acts as an inhibitor against stress corrosion. MON-1 is specified where stress corrosion of propellant tanks is anticipated. MON-3 is specified for Space Shuttle; to assure that the NO content of the oxidizer will remain above 0.5 percent NO after handling and storage of the oxidizer and ventings of the oxidizer tanks. The slight addition of NO does not change the thermophysical properties of N_2O_4 significantly. Therefore, the listed properties for N_2O_4 are applicable for MON-1 and MON-3.

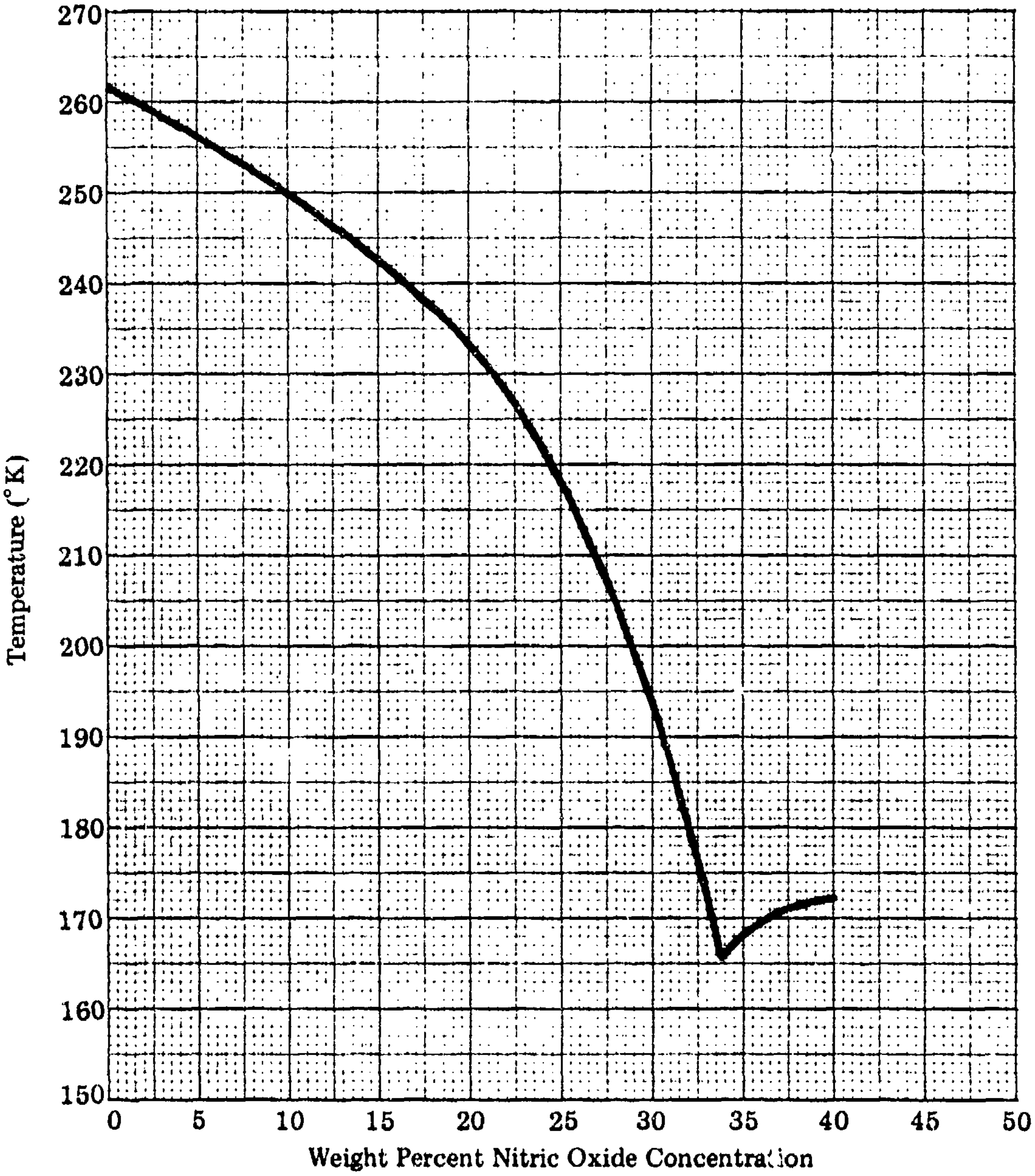


Figure 2.3-1. Freezing Point of the Nitrogen Tetroxide - Nitric Oxide System

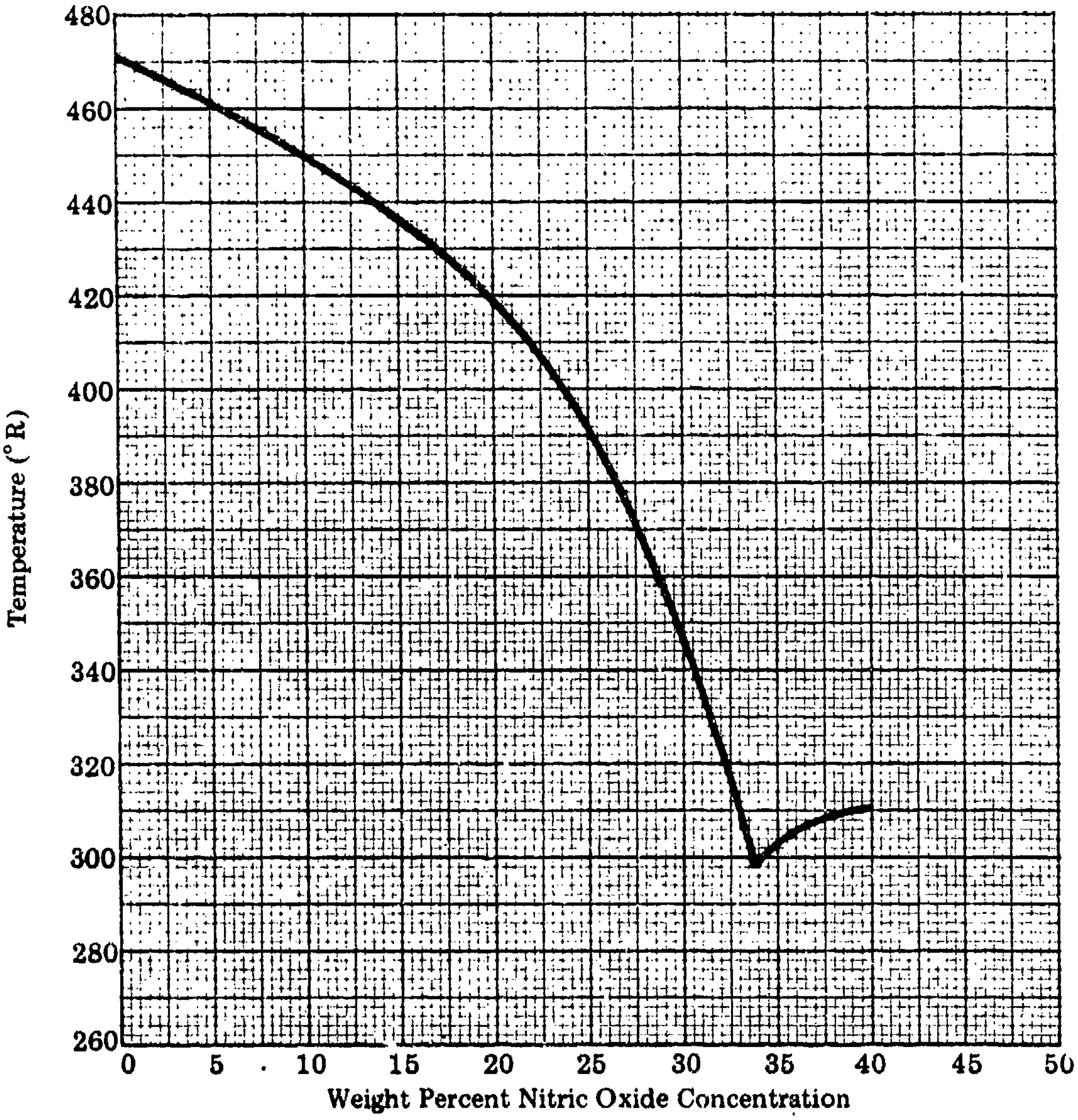
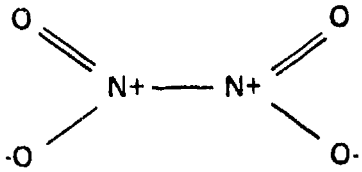


Figure 2.3-1a. Freezing Point of the Nitrogen Tetroxide - Nitric Oxide System

2.3.2.2 Structure of N_2O_4

The structure of the N_2O_4 molecule, controversial for a long time, has been established by electron diffraction data to have in the gaseous state a coplanar structure, and N-N bond distance of 1.75°A, and N-O bond distance of 1.180°A, and an O-N-O angle of 133.7° (13). The pictorial form of the molecular structure is shown at the end of this paragraph. Solid N_2O_4 is similar by x-ray diffraction measurements at -40°C with slightly different distances and angles (14). Infrared spectra of the gas (23°C), liquid (10°C), and solid (-180°C) show no evidence for a different structure in the liquid state (15).



planar form

2.3.2.3 Specification

The chemical requirements for procuring N_2O_4 and MON-1 are documented in Specification MIL-P-26539C, dated 30 March 1970. MON-3 requirements are described in the amendment 2, dated 5 April 1976, to MIL-P-26539C. Bell Aerospace lists their procurement requirements for "Minuteman Grade N_2O_4" in their specification 8477-947041. MIL-P-27408A, dated 15 October 1971, lists the requirements for MON-10 and MON-25.

Table 2.3-1 is a compilation of the chemical composition and physical properties of the N_2O_4 -MON series.

TABLE 2.3-1 CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES

Composition	Limits					
	NTO (Red-Brown)	MINUTEMAN Grade	MON-1 (Green)	MON-3 (Green)	MON-10	MON-25
Nitrogen tetroxide assy (N_2O_4) percent by weight	99.5				88.8 min	73.8 min
Nitric oxide (NO) content-max	1/	0.51	1.0	3.0	11.0	26.0
percent by weight-min		0.11	0.6	1.5	10.0	25.0
N_2O_4 + NO-percent by weight-minimum		99.5	99.5	99.5		
Water equivalent-percent by weight-max	0.17	0.10	0.17	0.17	0.17	0.17
Chloride content-percent by weight-max	0.040	5 ppm	0.040	0.040	0.040 2/	0.040 2/
Iron (Fe)		5 ppm				
Particulate-mg/liter	10	10	10	10	10	10

1/ The NO content shall be limited to that which does not change the specified Red-Brown color of the propellant.

2/ This test need not be performed on propellant manufactured by the ammonia-oxidation process.

2.3.3 PHYSICAL PROPERTIES

2.3.3.1 Vapor Pressure and Normal Boiling Point

Several equations have been determined to calculate the vapor pressure of liquid N_2O_4 (NTO). Hercules (6) used values calculated from the Antoine constants and the Antoine equation, namely

$$\log_{10} P = A - B/(C + t) \qquad (2.3\text{-}1)$$

where:

A,B,C = Antoine constants
t = temperature, °C
P = vapor pressure, mm Hg

Allied Chemical (10) lists a different equation for the vapor pressure of liquid N_2O_4 between -11.3°C and 21.7°C:

$$\log_{10} P = \frac{-1753.000}{(T, °K)} + 9.00436 - 11.8078 \times 10^{-4}\ (T, °K) + 2.0954 \times 10^{-6}\ (T, °K)^2 \qquad (2.3\text{-}2)$$

Rocketdyne took the experimental data as listed by Hercules and Allied Chemical and curve-fitted the data (9). Rocketdyne's equations are:

$$\log P\ (\text{mmHg}) = 9.82372 - \frac{2331.98}{(T, °K)} + \frac{84567}{(T, °K)^2} \qquad (2.3\text{-}3)$$

Temperature range: -11.2 to 158.2°C

$$\log P\ (\text{psia}) = 8.11012 - \frac{4197.55}{(T, °R)} + \frac{273994}{(T, °R)^2} \qquad (2.3\text{-}3a)$$

Temperature range: 11.8 to 316.8°F

Calculated values of Hercules, Allied Chemical, and Rocketdyne are plotted in Figures 2.3-2 and 2.3-2a. The equations of Rocketdyne are considered adequate to determine vapor pressure values of liquid N_2O_4 (NTO, MON-1, MON-3). A normal boiling point value of 21.2°C (70.1°F) is reported by Hercules (6) and Allied Chemical (10).

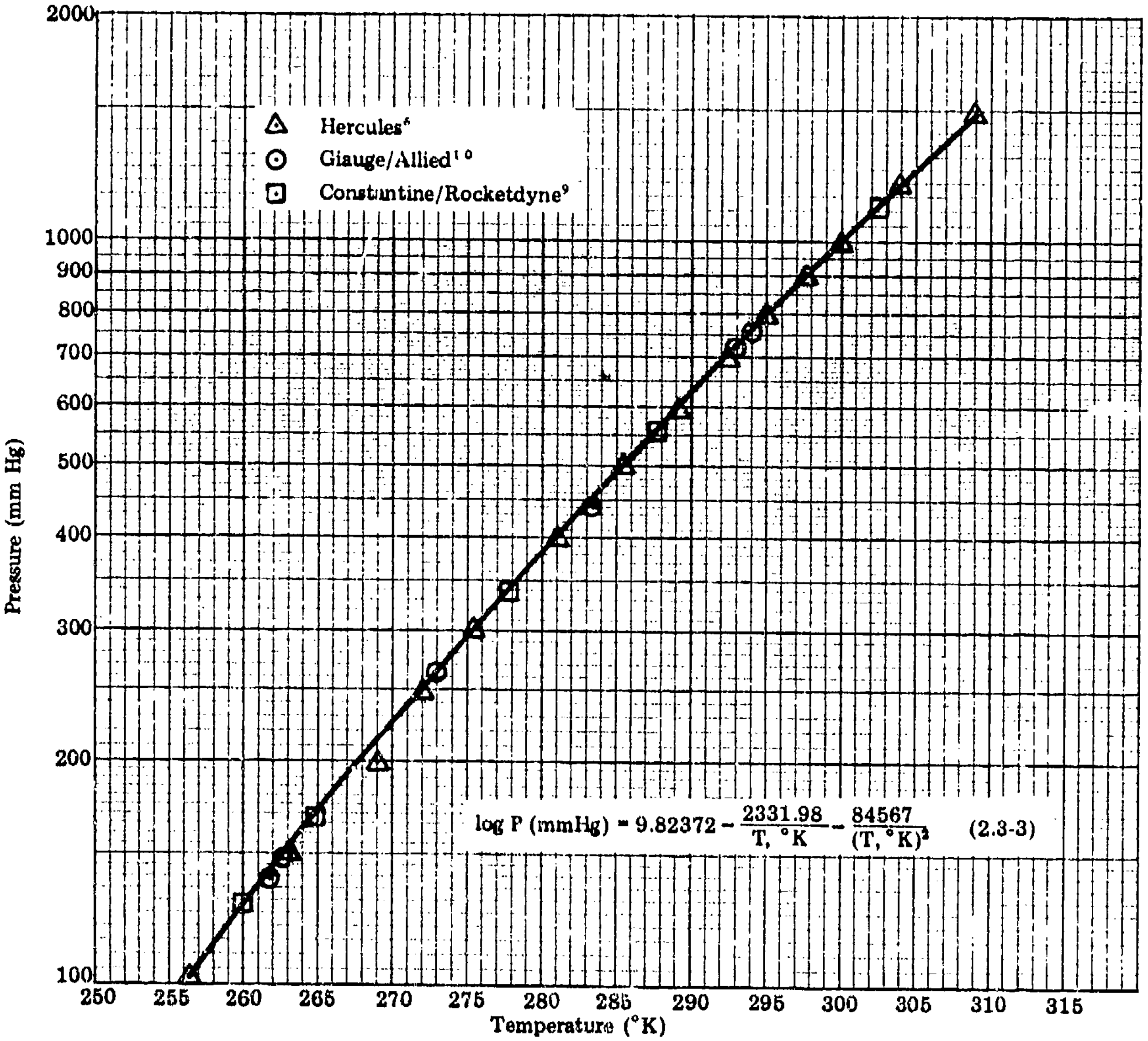
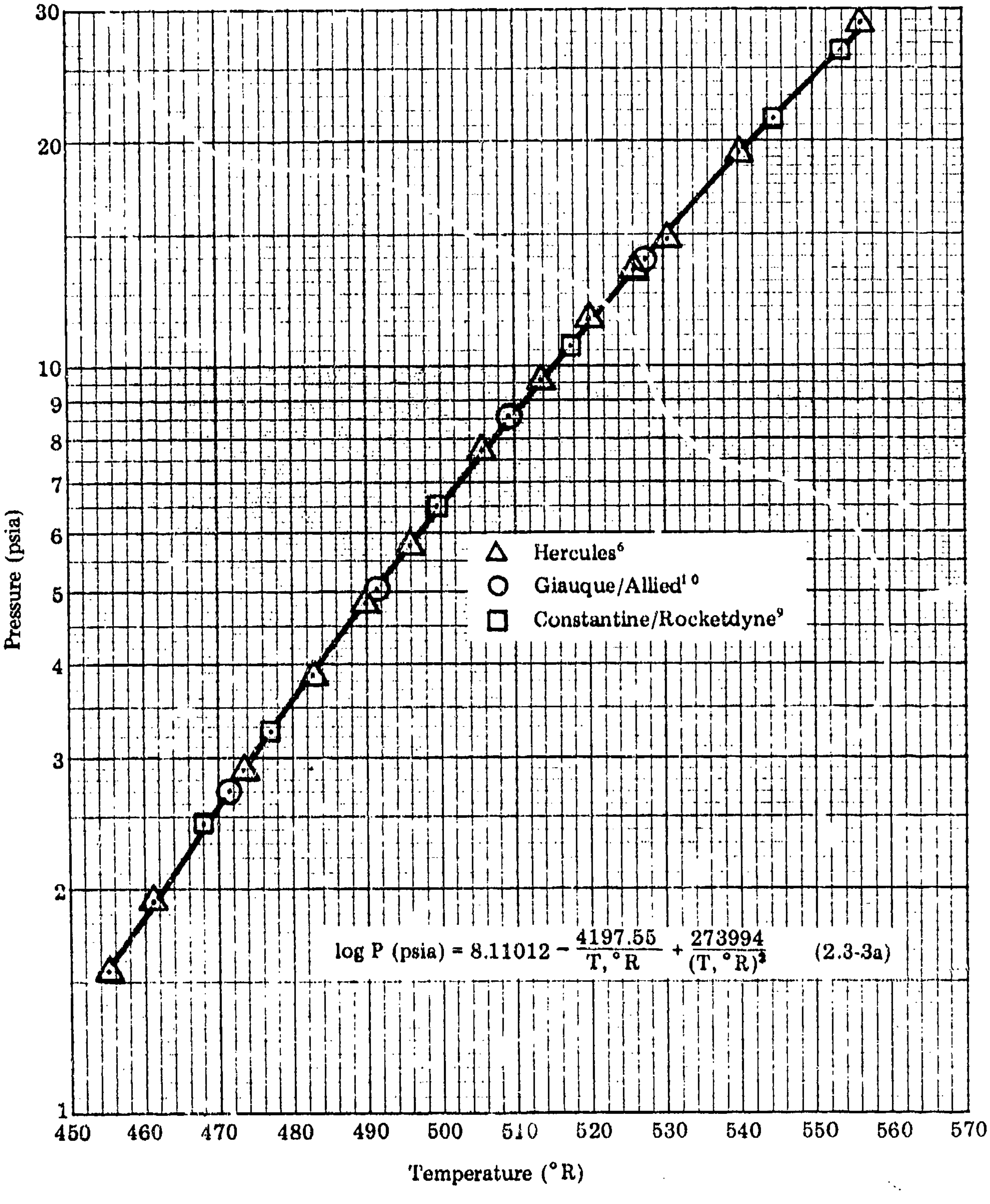


Figure 2.3-2. Vapor Pressure versus Temperature, Liquid Nitrogen Tetroxide



$$\log P\ (\text{psia}) = 8.11012 - \frac{4197.55}{T,\ ^\circ R} + \frac{273994}{(T,\ ^\circ R)^2} \qquad (2.3\text{-}3a)$$

Figure 2.3-2a. Vapor Pressure versus Temperature, Liquid Nitrogen Tetroxide

Rocketdyne (7) also expressed in equation form the vapor pressure values for the MON-10, MON-25, and MON-30 mixtures. The expressions are based on available data; Rocketdyne reports that additional characterization (or confirmation) of the N_2O_4-NO system is recommended. The curve-fit equations for the data in the temperature range of freezing point to 132°C (270°F) are:

MON-10:

$$\log P\ (\text{atm}) = 5.4899 - \frac{1352.4}{(T, °K)} - \frac{56662}{(T, °K)^2} \tag{2.3-4}$$

$$\log P\ (\text{psia}) = 6.6571 - \frac{2434.3}{(T, °R)} - \frac{1.836 \times 10^5}{(T, °R)^2} \tag{2.3-4a}$$

MON-25:

$$\log P\ (\text{atm}) = 5.4899 - \frac{1236.0}{(T, °K)} - \frac{56662}{(T, °K)^2} \tag{2.3-5}$$

$$\log P\ (\text{psia}) = 6.6571 - \frac{2224.7}{(T, °R)} - \frac{1.836 \times 10^5}{(T, °R)^2} \tag{2.3-5a}$$

MON-30:

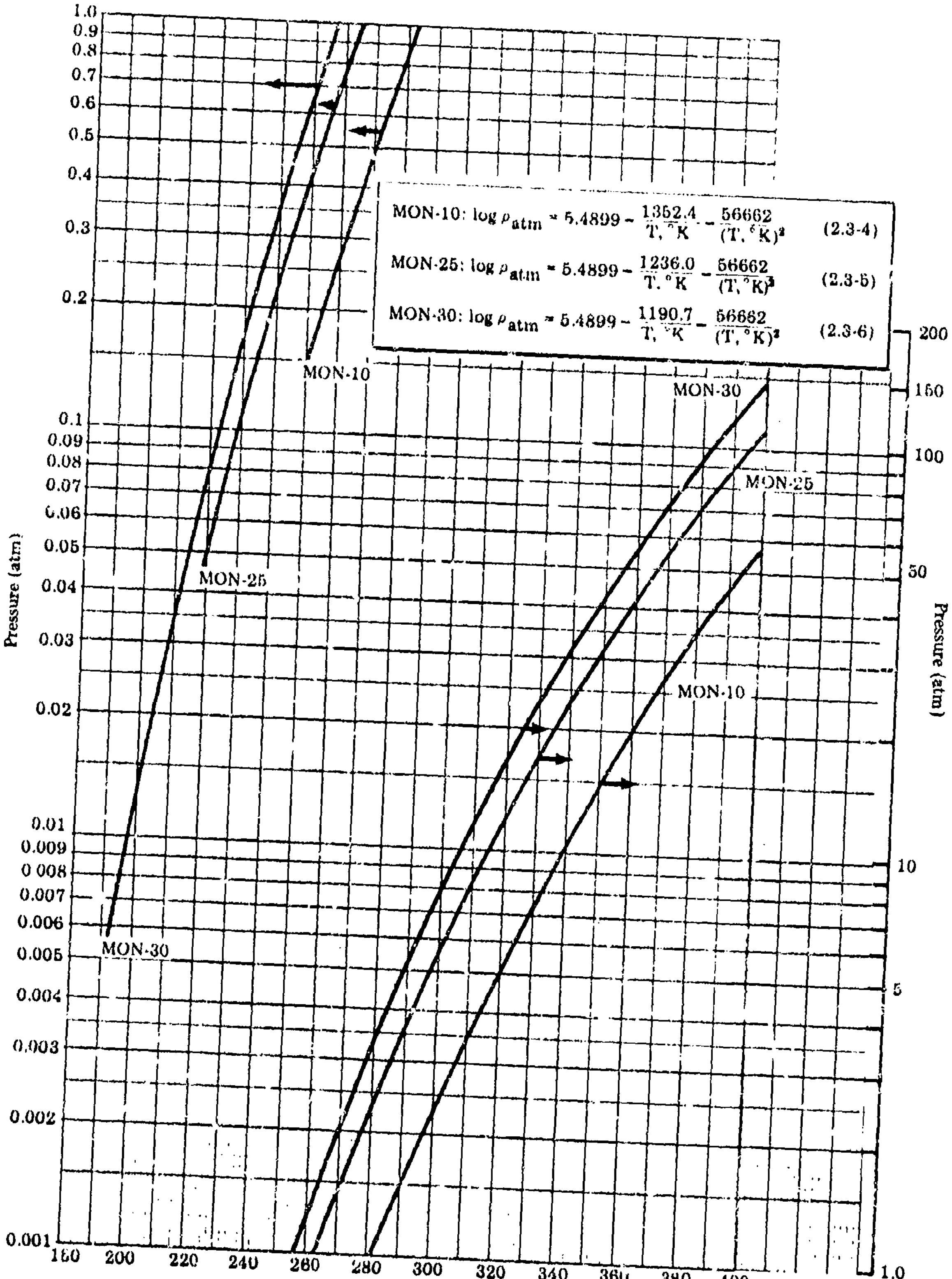
$$\log P\ (\text{atm}) = 5.4899 - \frac{1190.7}{(T, °K)} - \frac{56662}{(T, °K)^2} \tag{2.3-6}$$

$$\log P\ (\text{psia}) = 6.6571 - \frac{2143.2}{(T, °R)} - \frac{1.836 \times 10^5}{(T, °R)^2} \tag{2.3-6a}$$

Figures 2.3-3 and 2.3-3a graphically show the vapor pressure as a function of temperature. The normal boiling points of the three MON mixtures as obtained from the vapor pressure equations by Rocketdyne are as follows:

MON-10	9.7°C (49.4°F)
MON-25	-9.0°C (15.9°F)
MON-30	-16.1°C (3.0°F)

Figure 2.3-4 shows the vapor pressure value of MON solutions as a function of the weight percent of NO in MON at 25°C (298.15°K).

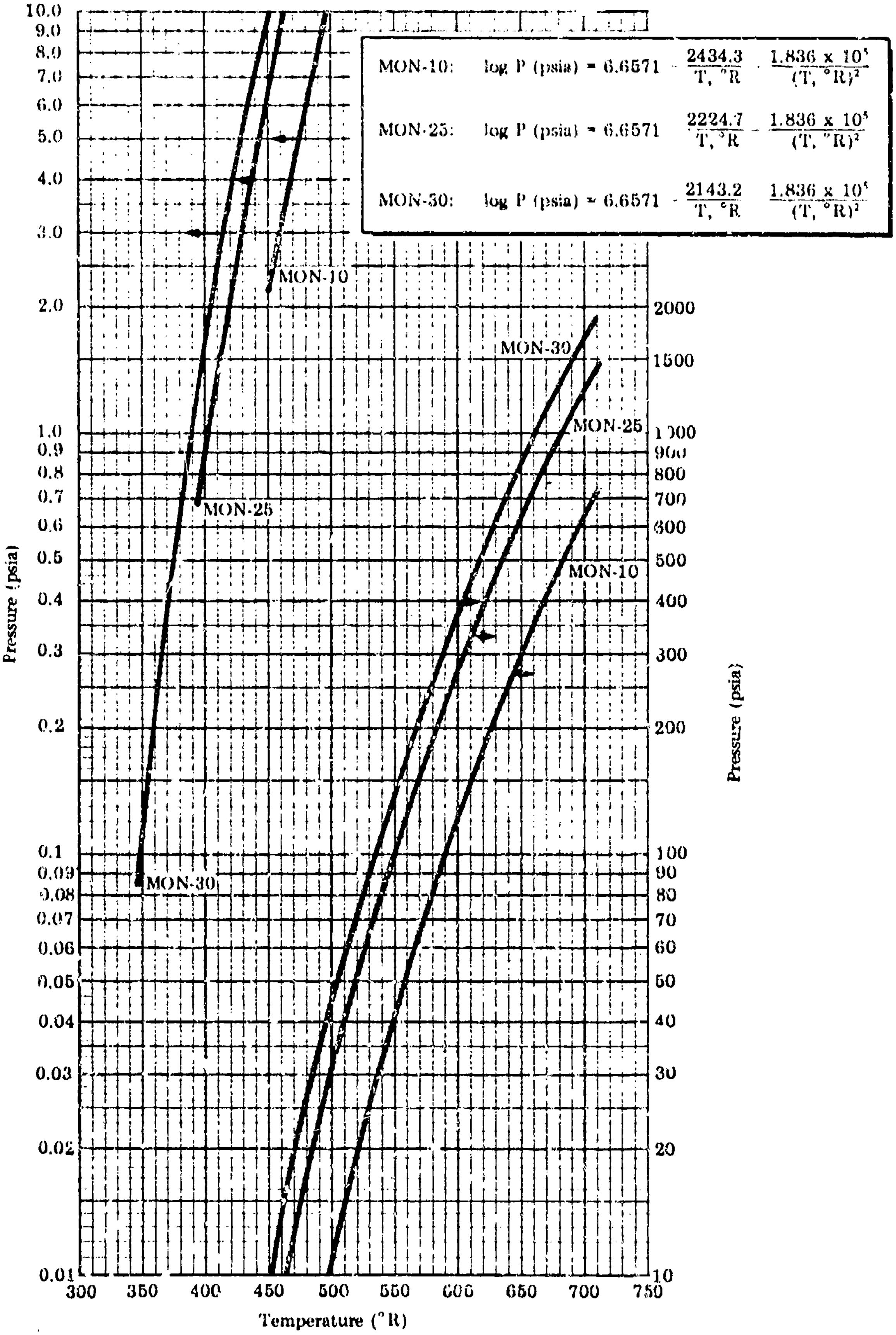


$$\text{MON-10: } \log p_{atm} = 5.4899 - \frac{1352.4}{T, {}^\circ K} - \frac{56662}{(T, {}^\circ K)^2} \qquad (2.3\text{-}4)$$

$$\text{MON-25: } \log p_{atm} = 5.4899 - \frac{1236.0}{T, {}^\circ K} - \frac{56662}{(T, {}^\circ K)^2} \qquad (2.3\text{-}5)$$

$$\text{MON-30: } \log p_{atm} = 5.4899 - \frac{1190.7}{T, {}^\circ K} - \frac{56662}{(T, {}^\circ K)^2} \qquad (2.3\text{-}6)$$

Figure 2.3-3. Vapor Pressure of the Mixed Oxides of Nitrogen



MON-10: $\log P\ (\text{psia}) = 6.6571 - \dfrac{2434.3}{T,\ ^\circ R} - \dfrac{1.836 \times 10^5}{(T,\ ^\circ R)^2}$

MON-25: $\log P\ (\text{psia}) = 6.6571 - \dfrac{2224.7}{T,\ ^\circ R} - \dfrac{1.836 \times 10^5}{(T,\ ^\circ R)^2}$

MON-30: $\log P\ (\text{psia}) = 6.6571 - \dfrac{2143.2}{T,\ ^\circ R} - \dfrac{1.836 \times 10^5}{(T,\ ^\circ R)^2}$

Figure 2.3-3a. Vapor Pressure of the Mixed Oxides of Nitrogen

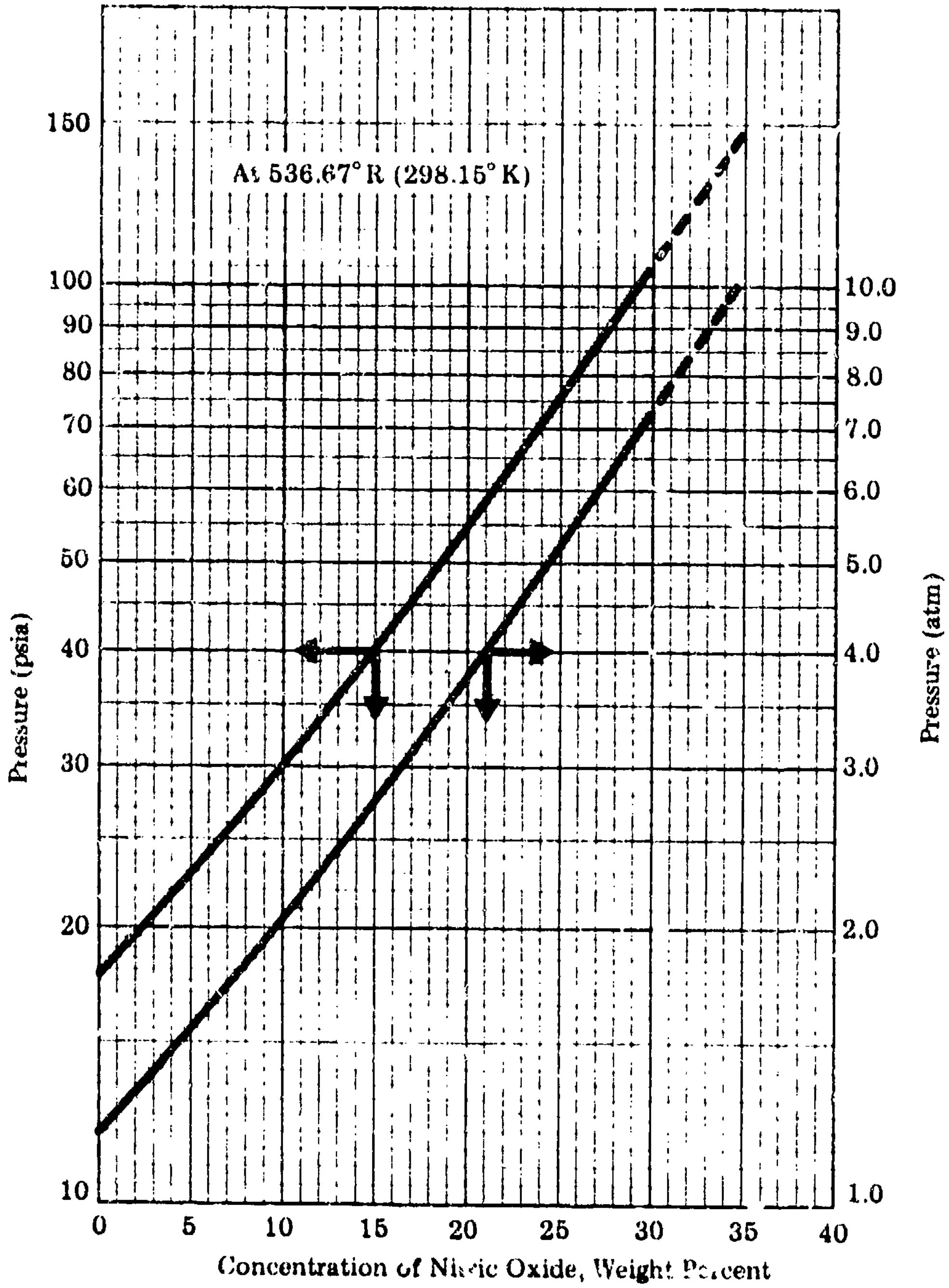


Figure 2.3-4. Vapor Pressure of the Mixed Oxides of Nitrogen at 536.67° R (298.15° K) versus Weight Percent of Nitric Oxide

2.3.3.2 Density of N_2O_4, MON

Density values were taken from the *Nitrogen Tetroxide Product Bulletin* of the Allied Chemical Corporation (10) and Aerojet's tabulation of density values in their report, "Storable Liquid Propellants Nitrogen Tetroxide/Aerozine 50" (1). A curve fitted correlation was obtained as follows:

$$\rho(\text{g/cc}) = 2.066 - 1.979 \times 10^{-3} (T, °K) - 4.826 \times 10^{-7} (T, °K)^2 \qquad (2.3\text{-}7)$$

$$\rho(\text{lb/ft}^3) = 129.850 - 7.175 \times 10^{-2} (T, °R) - 6.3276 \times 10^{-6} (T, °R)^2 \qquad (2.3\text{-}7a)$$

Figures 2.3-5 and 2.3-5a show the density values of N_2O_4 as a function of temperature. These figures may also be used for MON-1 and MON-3.

Rocketdyne (7) evaluated available N_2O_4-NO system data for density and recommended the following curve-fit expressions for MON mixtures (this report converts to °K and °R):

MON-10

$$(\text{g/cc}) = 1.8525 + 1.280 \times 10^{-3} (T, °K) - 6.26 \times 10^{-6} (T, °K)^2 \qquad (2.3\text{-}8)$$

$$(\text{lb/ft}^3) = 98.73 + 4.47 \times 10^{-2} (T, °R) - 1.21 \times 10^{-4} (T, °R)^2 \qquad (2.3\text{-}8a)$$

MON-25

$$(\text{g/cc}) = 1.6679 + 4.622 \times 10^{-4} (T, °K) - 4.80 \times 10^{-6} (T, °K)^2 \qquad (2.3\text{-}9)$$

$$(\text{lb/ft}^3) = 104.21 + 1.56 \times 10^{-2} (T, °R) \; 9.2 \times 10^{-5} (T, °R)^2 \qquad (2.3\text{-}9a)$$

MON-30

$$(\text{g/cc}) = 1.6688 + 2.846 \times 10^{-4} (T, °K) - 4.31 \times 10^{-6} (T, °K)^2 \qquad (2.3\text{-}10)$$

$$(\text{lb/ft}^3) = 104.10 + 0.01 (T, °R) - 8.3 \times 10^{-5} (T, °R)^2 \qquad (2.3\text{-}10a)$$

Figures 2.3-6 and 2.3-6a show the density values of MON solutions as a function of temperature.

Figure 2.3-7 is also presented for estimating density values of MON solutions at 25°C (298.15) as a function of the weight percent of NO in the solution.

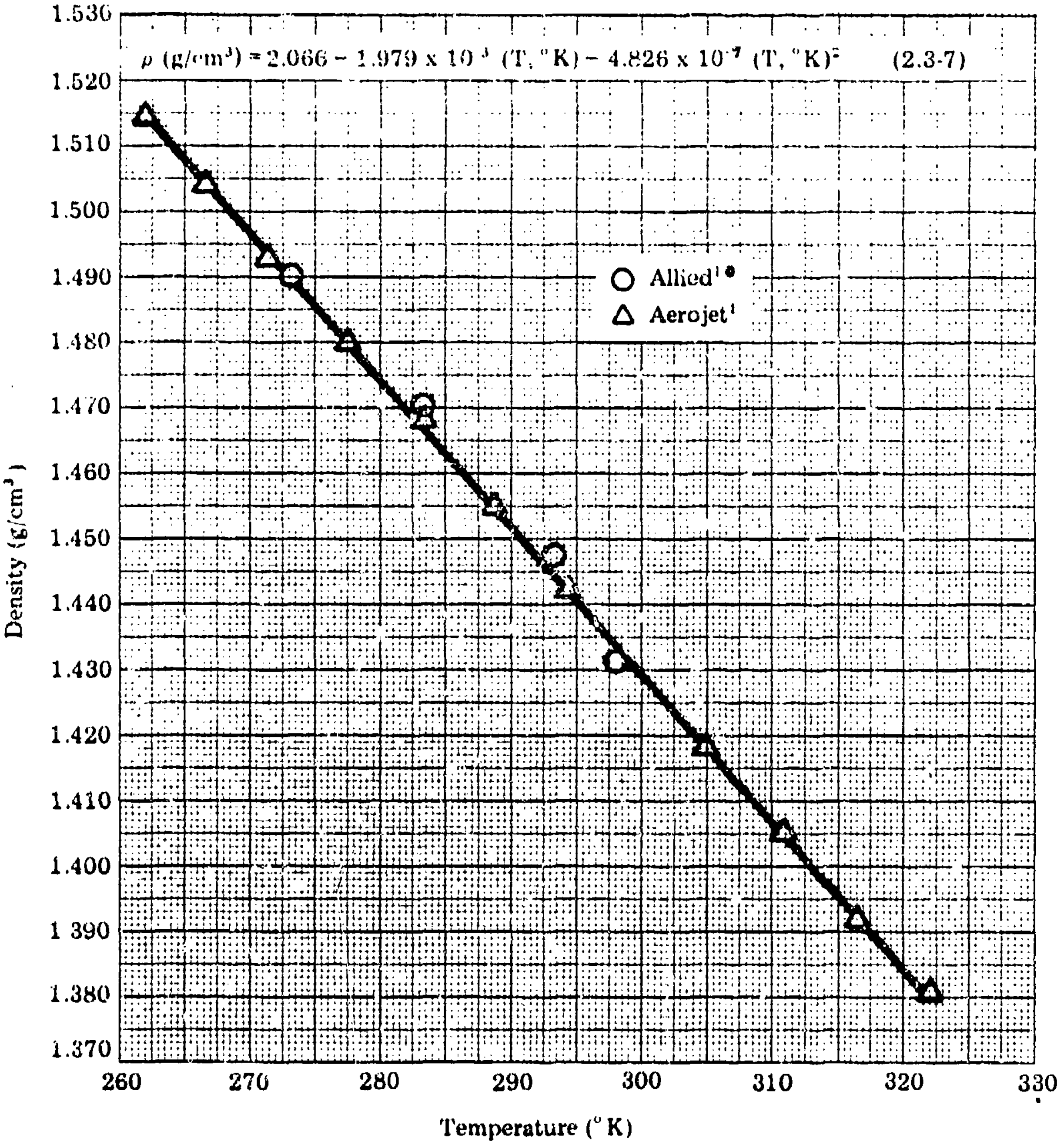


Figure 2.3-5. Density versus Temperature, Liquid Nitrogen Tetroxide

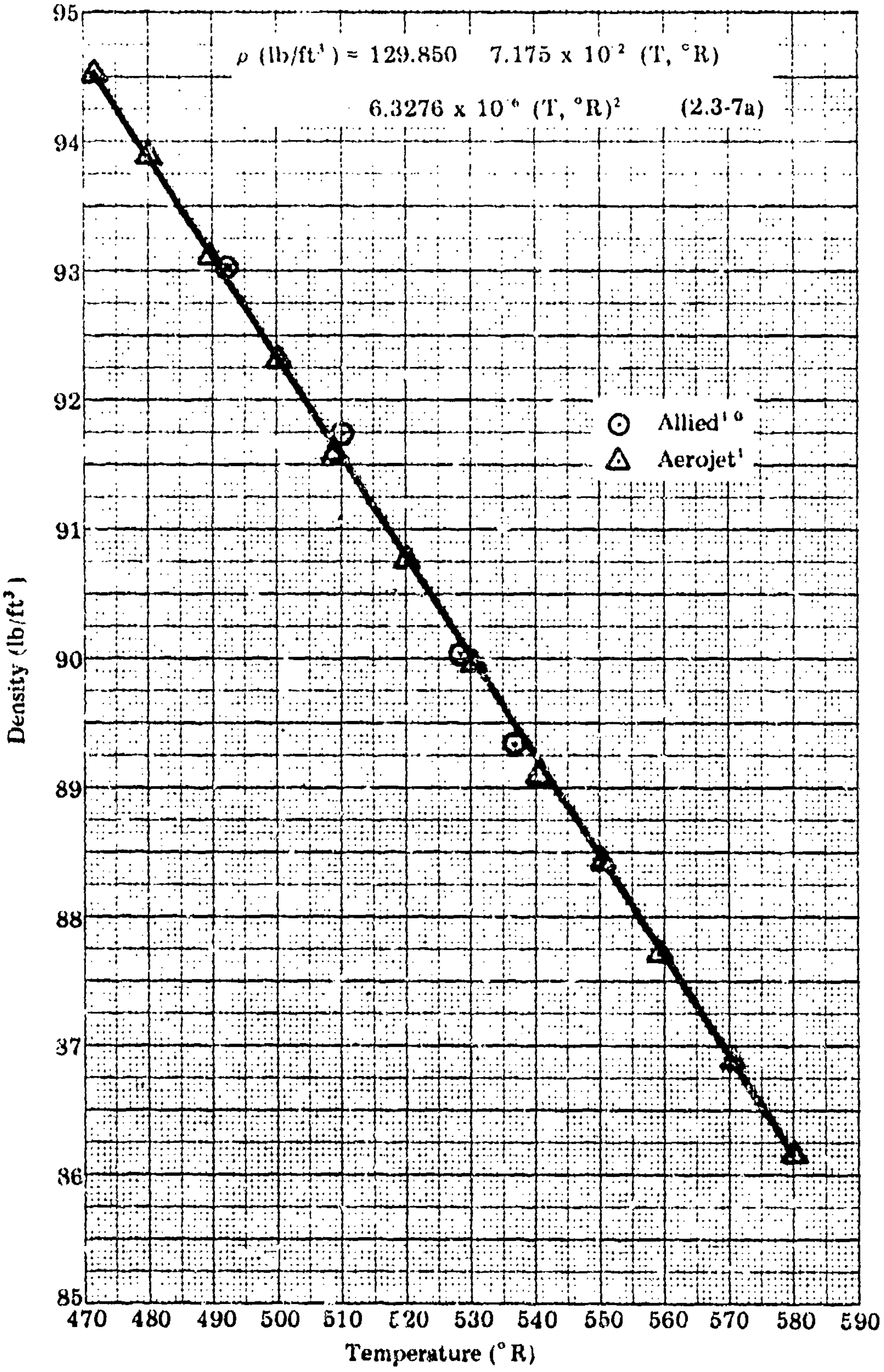


Figure 2.3-5a. Density versus Temperature, Liquid Nitrogen Tetroxide

MON-10: $\rho\ (g/cc) = 1.5825 + 1.280 \times 10^{-3}\ (T, °K) - 6.26 \times 10^{-6}\ (T, °K)^2$ (2.3-8)

MON-25: $\rho\ (g/cc) = 1.6679 + 4.622 \times 10^{-4}\ (T, °K) - 4.80 \times 10^{-6}\ (T, °K)^2$ (2.3-9)

MON-30: $\rho\ (g/cc) = 1.6688 + 2.846 \times 10^{-4}\ (T, °K) - 4.31 \times 10^{-6}\ (T, °K)^2$ (2.3-10)

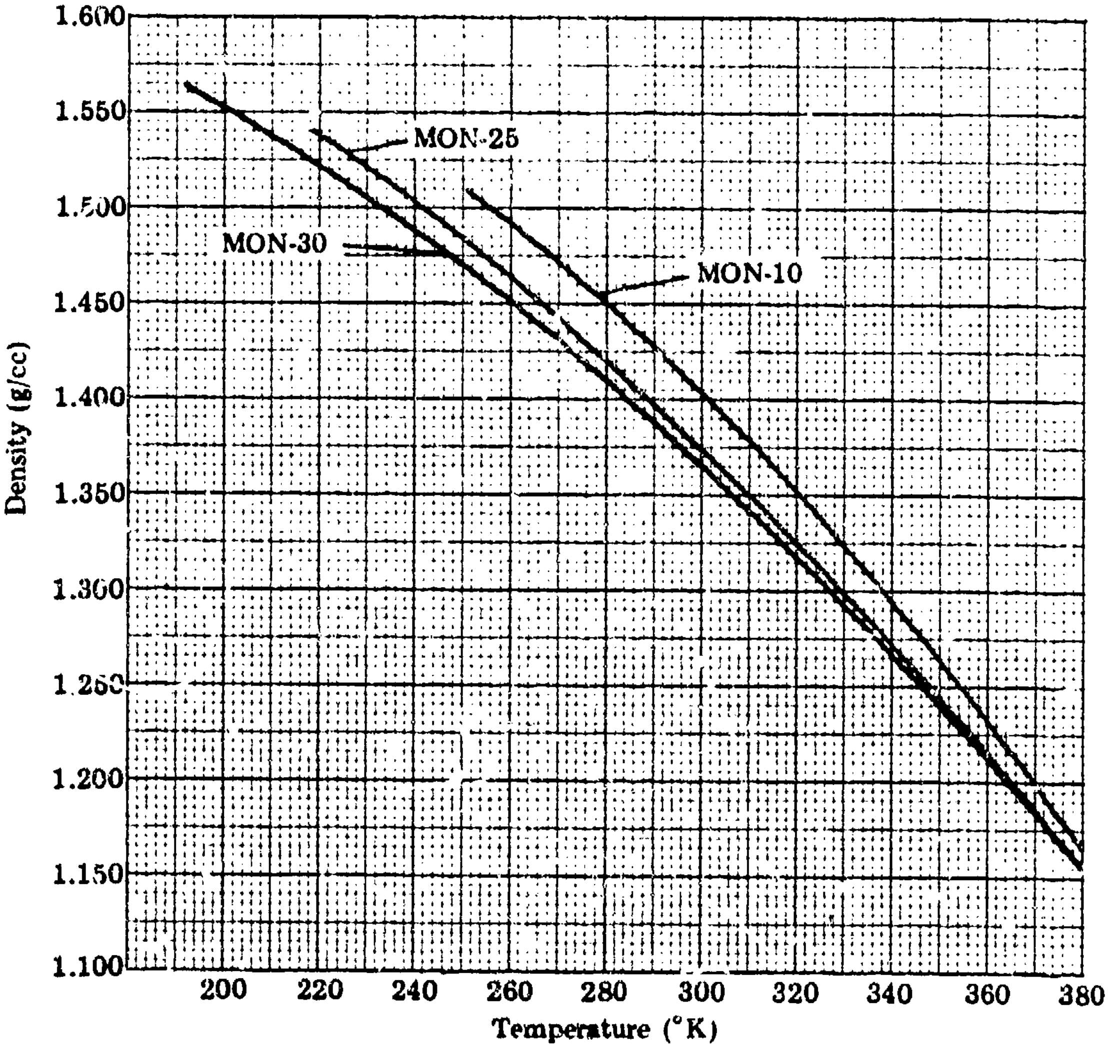
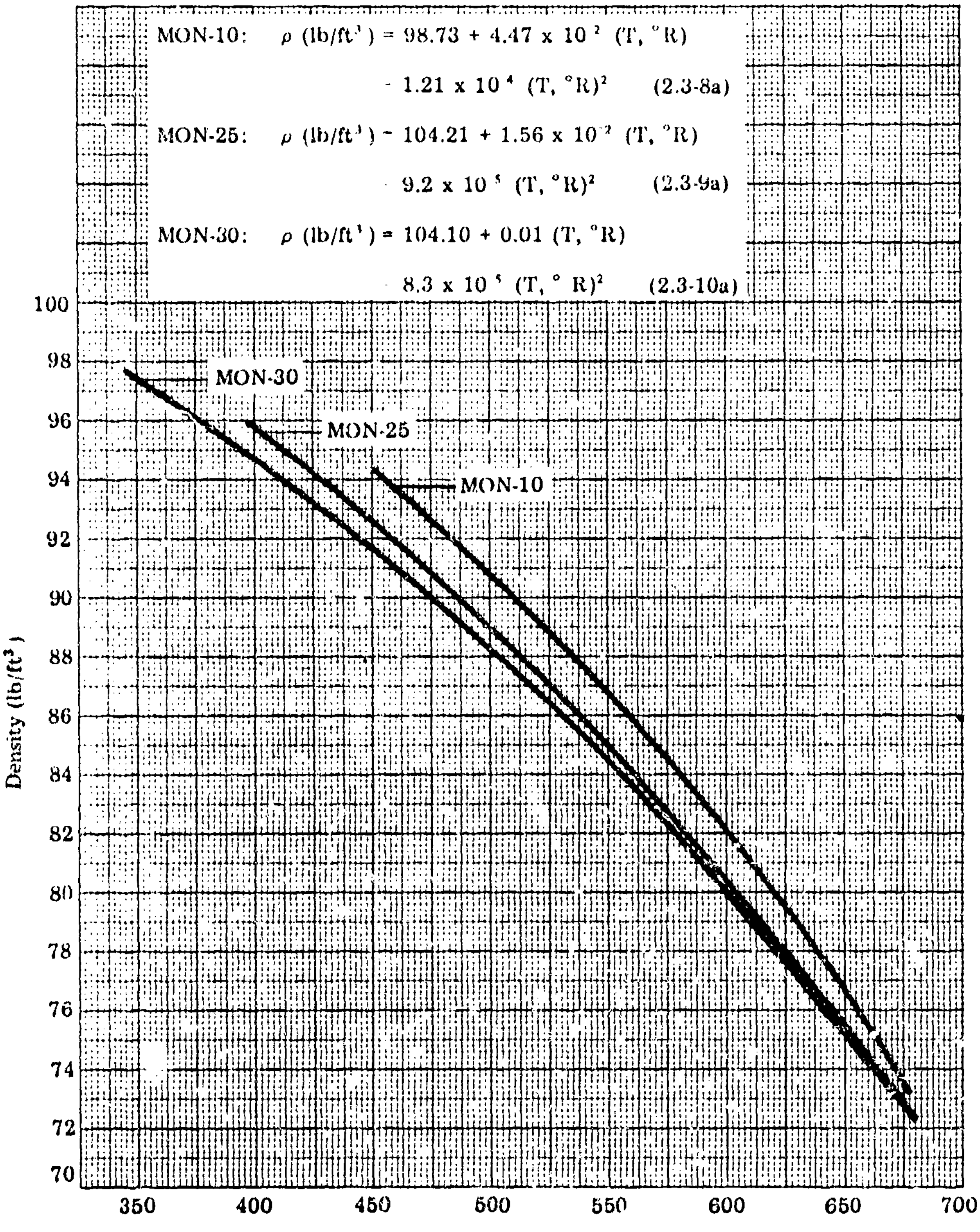


Figure 2.3-6. Density of the Mixed Oxides of Nitrogen versus Temperature (°K)



MON-10: $\rho\ (\mathrm{lb/ft^3}) = 98.73 + 4.47 \times 10^{-2}\ (T, {}^\circ R) - 1.21 \times 10^{-4}\ (T, {}^\circ R)^2$ (2.3-8a)

MON-25: $\rho\ (\mathrm{lb/ft^3}) = 104.21 + 1.56 \times 10^{-2}\ (T, {}^\circ R) - 9.2 \times 10^{-5}\ (T, {}^\circ R)^2$ (2.3-9a)

MON-30: $\rho\ (\mathrm{lb/ft^3}) = 104.10 + 0.01\ (T, {}^\circ R) - 8.3 \times 10^{-5}\ (T, {}^\circ R)^2$ (2.3-10a)

Figure 2.3-6a. Density of the Mixed Oxides of Nitrogen versus Temperature

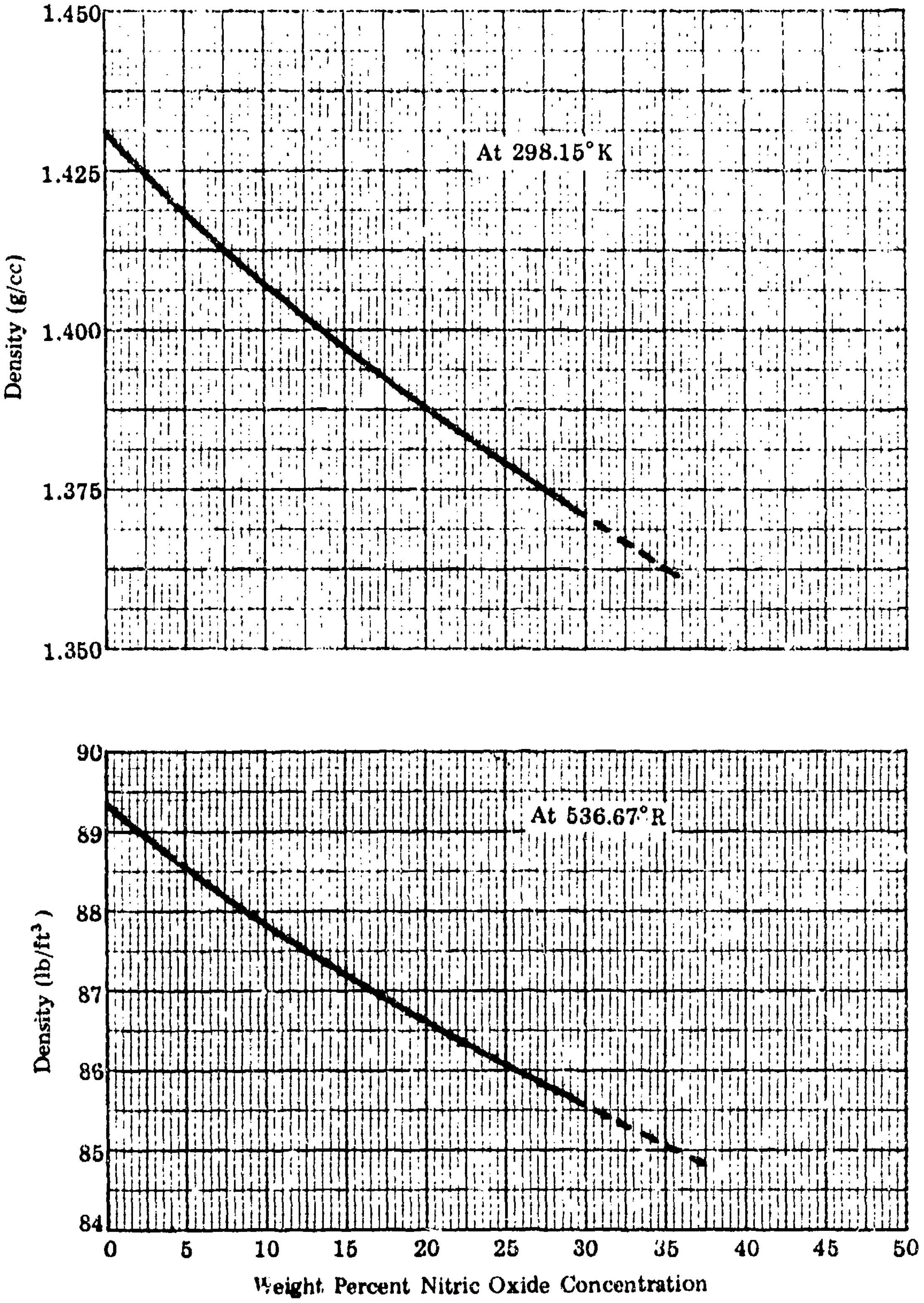


Figure 2.3-7. Density of the Mixed Oxides of Nitrogen

2.3.3.3 Sonic Velocity of N_2O_4

Constantine of Rocketdyne reported their experimental measurements (9) for sonic velocities in the saturated liquid system, N_2O_4-NO_2. The experimental data is not actually presented, but smoothed-value curves are presented in which the sonic velocity is determined as a linear function of temperature by:

$$c(\text{m/sec}) = 2296 - 4.425\ (T, °K) \qquad (2.3\text{-}11)$$

$$c(\text{ft/sec}) = 3825 - 8.065\ (t, °F) \qquad (2.3\text{-}12)$$

The temperature range in which the velocity of sound was measured was from -5°C to 56°C (23°F to 133°F). The condition was from near freezing (f.p. is -11.2°C) to above the normal boiling point (nbp, 21.2°C). Constantine's effort was reported in 1968. Equation 2.3-12 expressed in terms of °R is:

$$c(\text{ft/sec}) = 7532 - 8.065\ (T, °R) \qquad (2.3\text{-}11a)$$

The values of the curve-fitted equation for sonic velocity in saturated N_2O_4-NO_2 are plotted in Figures 2.3-8 and 2.3-8a.

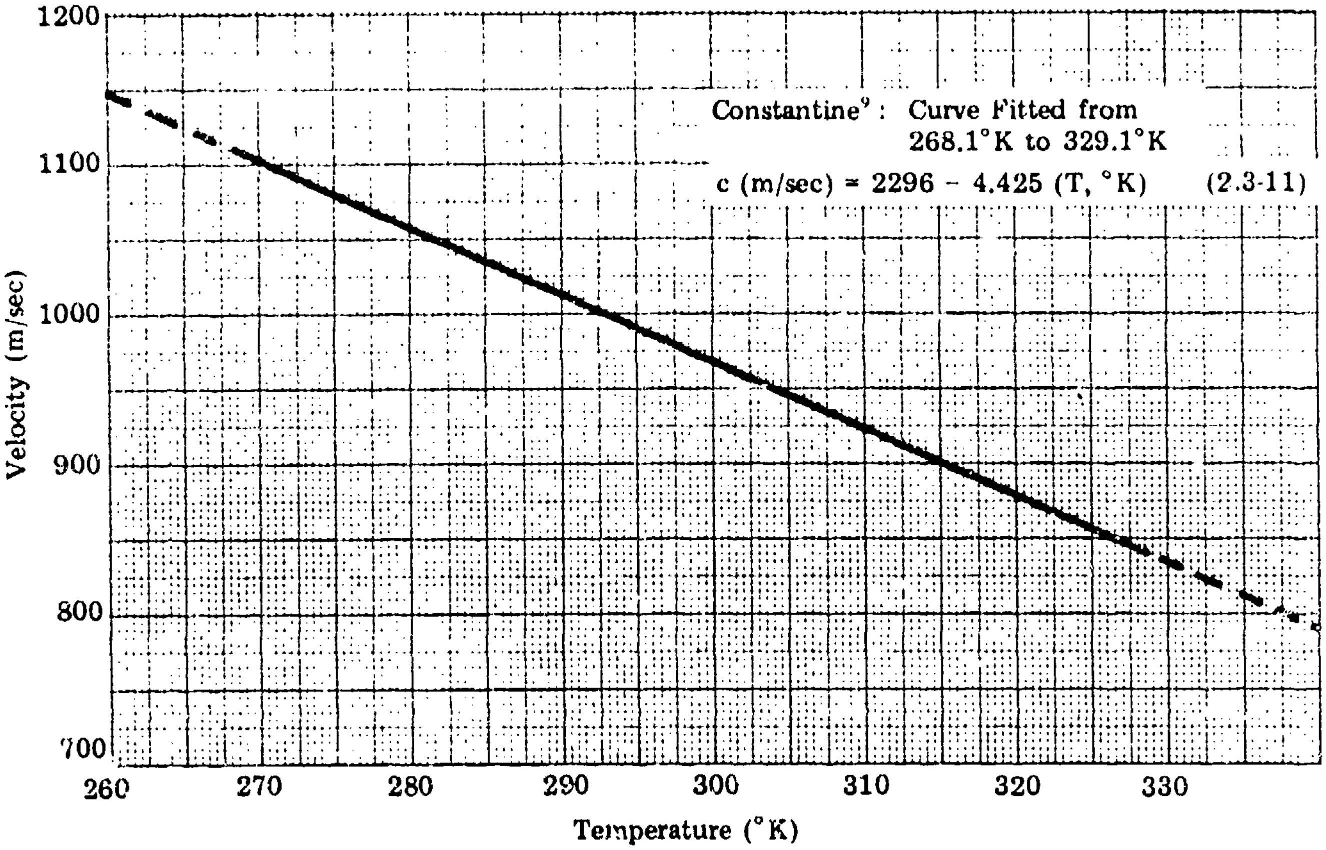


Figure 2.3-8. Sonic Velocity versus Temperature, Saturated N_2O_4 - NO_2

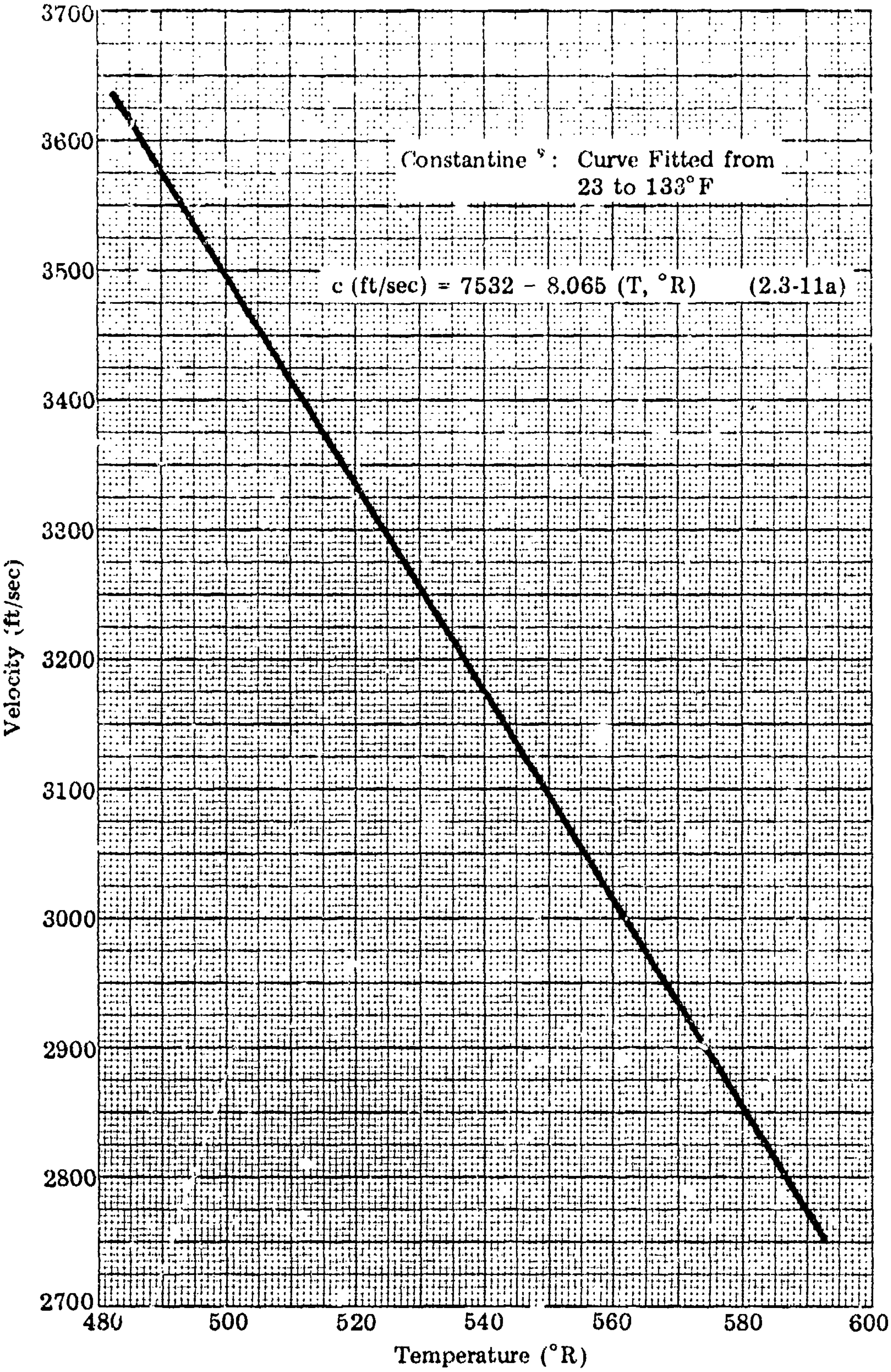


Figure 2.3-8a. Sonic Velocity versus Temperature, Saturated N_2O_4 - NO_2

2.3.3.4 Compressibility of Liquid N_2O_4

The adiabatic compressibility (βa) can be determined using sonic velocity data and the acoustical equation:

$$\beta_a = \frac{1}{\rho c^2} \qquad (2.3\text{-}13)$$

where

ρ = density

c = sonic velocity

The compressibilities were computed using the empirical values of Rocketdyne's correlation of sonic velocity in N_2O_4. The sonic velocity in liquid N_2O_4 has been measured by Constantine of Rocketdyne (9). The results are discussed in Section 2.3.3.3. The density for the comparable temperature was obtained from equations 2.3-7 and 2.3-7a. The calculated compressibility data is shown in Figures 2.3-9 and 2.3-9a. Also plotted are some of Rocketdyne's compressibility values as determined by Constantine (9).

Using the least-square curve fit computer program, the change in compressibility with temperature is described by:

$$\begin{aligned}\beta_a(\text{atm}^{-1}) = {} & 4.021 \times 10^{-4} \\ & - 3.029 \times 10^{-6} (T, °K) \\ & + 6.473 \times 10^{-9} (T, °K)^2\end{aligned} \qquad (2.3\text{-}14)$$

$$\begin{aligned}\beta_a(\text{psi}^{-1}) = {} & 2.748 \times 10^{-5} \\ & - 1.147 \times 10^{-7} (T, °R) \\ & + 1.358 \times 10^{-10} (T, °R)^2\end{aligned} \qquad (2.3\text{-}14a)$$

The temperature range is 268.15°K to 329.15°K (482.67 to 592.67°R). The standard deviation of the empirical values compared to the curve-fit equations 2.3-14 and 2.3-14a respectively are 4.786×10^{-7} atm^{-1} and 3.442×10^{-8} psi^{-1}.

The isothermal compressibility of NO_2 was calculated from the relationship:

$$\beta_i(\text{psi}^{-1}) = \frac{\rho_2 - \rho_1}{(P_2 - P_1)\ \rho_2} \qquad (2.3\text{-}15)$$

where

ρ = density of NO_2, condition 1 (5000 psi), 2 (500 psi)

P = pressure for density reading, condition 1 (5000 psi), 2 (500 psi)

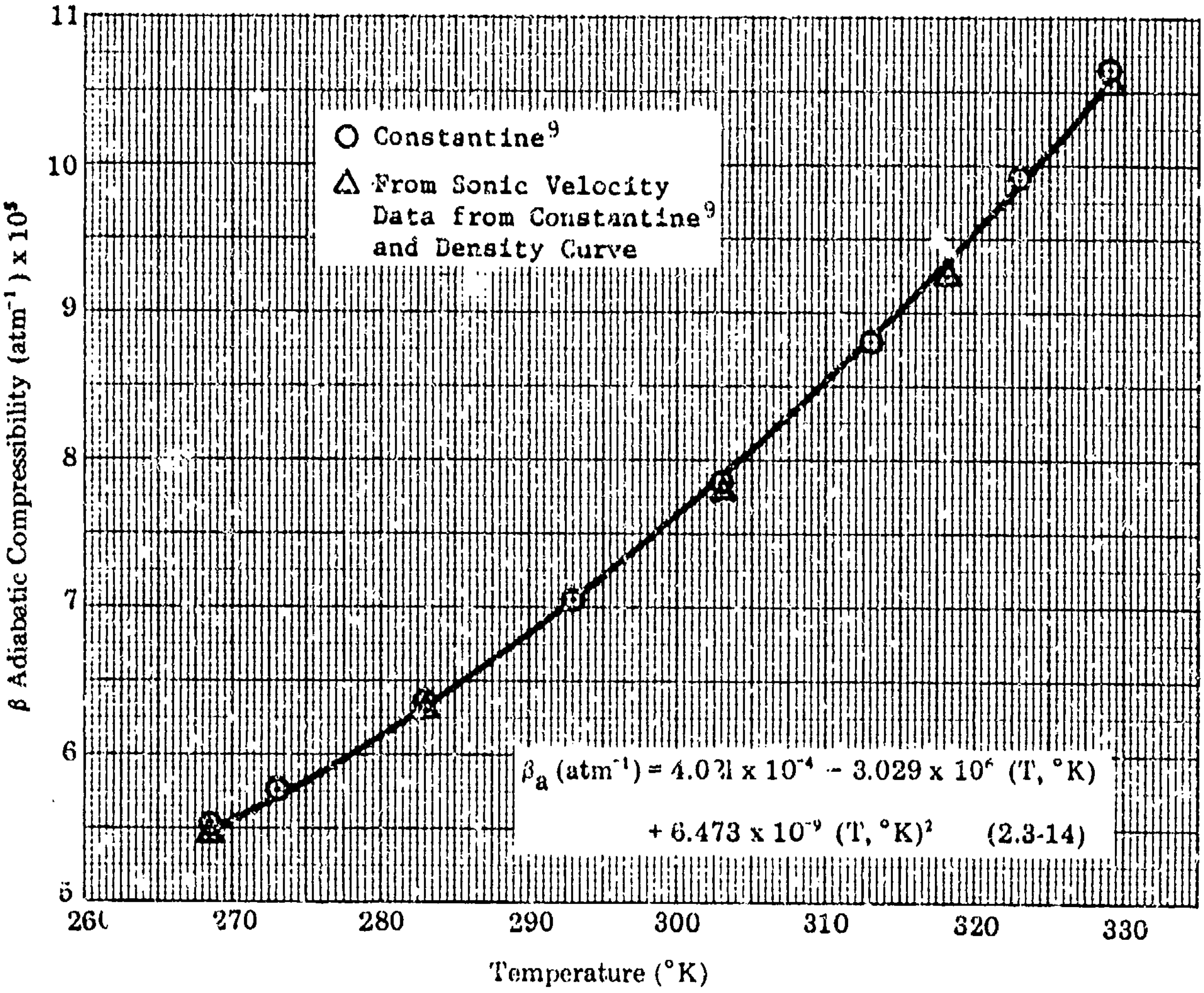
Values of specific volume compiled by Hercules in Table XVII of their publication (6) were used. The calculated isothermal compressibility values are shown in Table 2.3-2 and Figures 2.3-10 and 2.3-10a.

The values as a function of temperature are expressed in the following curve-fit equations:

$$\begin{aligned}\beta_i(\text{atm}^{-1}) = {} & 1.285 \times 10^{-2} \\ & - 1.650 \times 10^{-4} (T, °K) \\ & + 8.022 \times 10^{-7} (T, °K)^2 \\ & - 1.743 \times 10^{-9} (T, °K)^3 \\ & + 1.433 \times 10^{-12} (T, °K)^4\end{aligned} \qquad (2.3\text{-}16)$$

$$\begin{aligned}\beta_i(\text{psi}^{-1}) = {} & 8.6289 \times 10^{-4} \\ & - 6.1682 \times 10^{-6} (T, °R) \\ & + 1.6684 \times 10^{-8} (T, °R)^2 \\ & - 2.0166 \times 10^{-11} (T, °R)^3 \\ & + 9.227 \times 10^{-15} (T, °R)^4\end{aligned} \qquad (2.3\text{-}16a)$$

The standard deviation for equations 2.3-16 and 2.3-16a are 7.09×10^{-6} (atm^{-1}) and 4.831×10^{-7} (psi^{-1}).



$$\beta_a\,(\text{atm}^{-1}) = 4.021 \times 10^{-4} - 3.029 \times 10^{6}\ (\text{T}, ^\circ\text{K}) + 6.473 \times 10^{-9}\ (\text{T}, ^\circ\text{K})^2 \qquad (2.3\text{-}14)$$

Figure 2.3-9. Adiabatic Compressibility versus Temperature

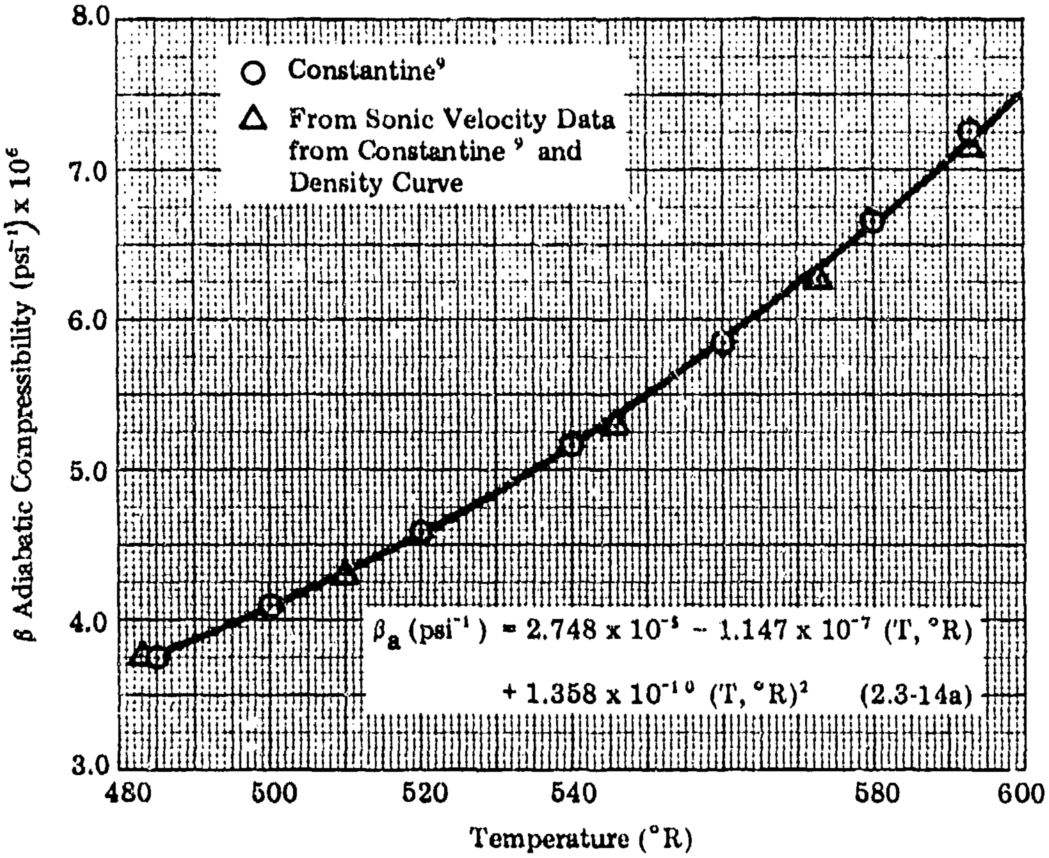
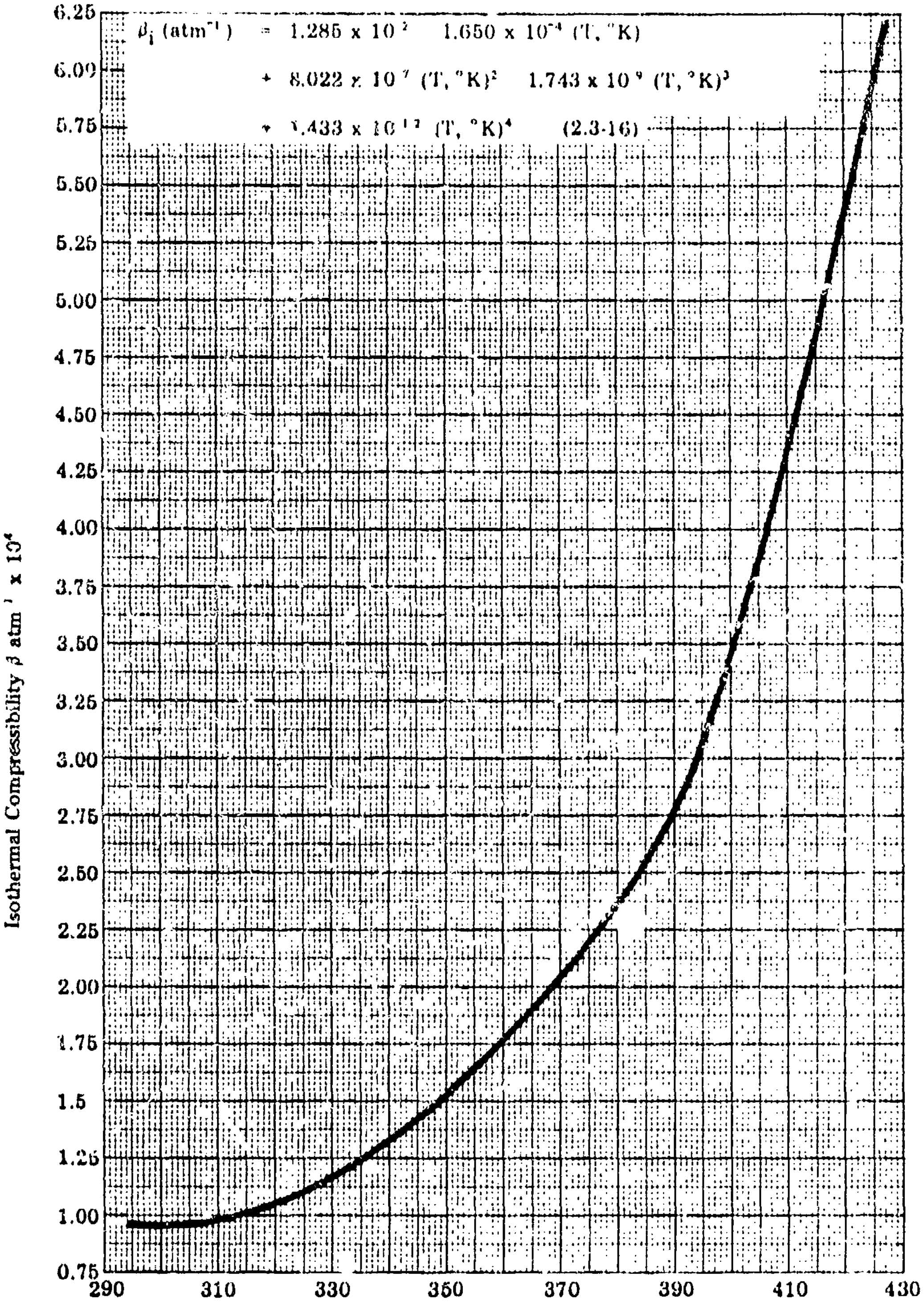


Figure 2.3-9a. Adiabatic Compressibility versus Temperature

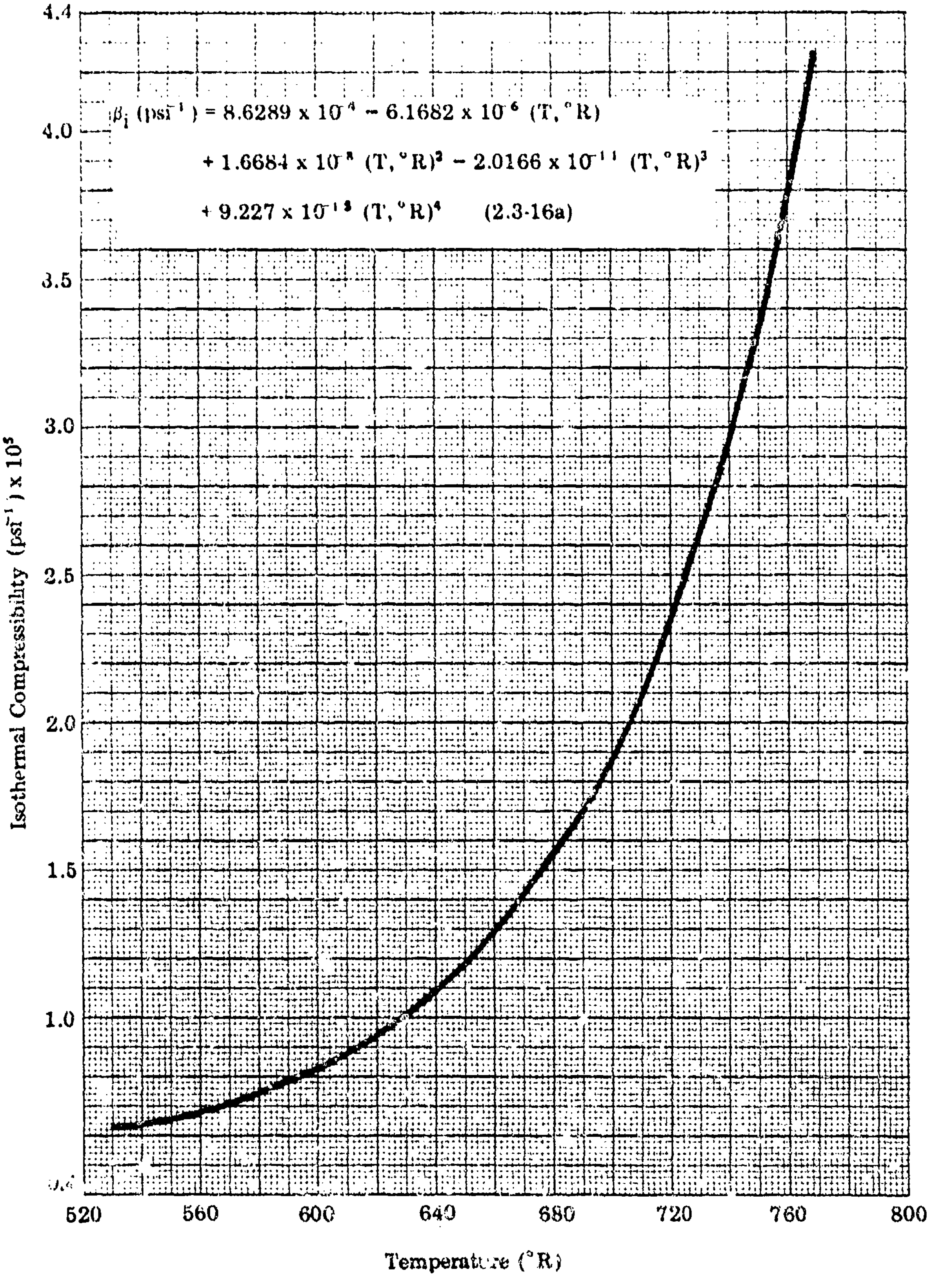
TABLE 2.3-2 CALCULATED ISOTHERMAL COMPRESSIBILITY OF NO_2

Temp °R °K	ρ_1 lb/ft³ g/cc	ρ_2 lb/ft³ g/cc	$\Delta\rho$ lb/ft³ g/cc	P_1 psi atm	P_2 psi atm	ΔP psi atm	β_i $psi^{-1} \times 10^5$	β_i $atm^{-1} \times 10^4$
529.67 294.26	92.8505 1.4873	90.2201 1.4452	2.6304 0.0421	5000 340.23	500 34.02	4500 306.21	0.630	0.926
559.67 310.93	91.2992 1.4625	87.8966 1.9080	3.4026 0.0595	6000 408.28	500 34.02	5500 374.25	0.678	0.996
589.67 327.59	89.2379 1.4295	85.3461 1.2671	3.8918 0.0624	6000 408.28	500 34.02	5500 374.25	0.993	1.165
619.67 344.26	87.0474 1.3944	82.8981 1.3279	4.1492 0.0665	6000 408.28	1000 68.05	5000 340.23	0.953	1.401
649.67 360.92	84.7314 1.3573	79.6686 1.2762	5.0628 0.0811	6000 408.28	1000 68.05	5000 340.23	1.195	1.756
679.67 377.59	82.2166 1.3169	75.8438 1.2149	6.3728 0.1020	6000 408.28	1000 68.05	5000 340.23	1.550	2.278
709.67 394.26	79.2456 1.2694	71.0934 1.1388	8.1521 0.1306	6000 408.28	1000 68.05	5000 340.23	2.057	3.023
739.67 410.93	75.8668 1.2153	64.2674 1.0295	11.5994 0.1858	6000 408.28	1000 68.05	5000 340.23	3.058	4.494
679.67 427.59	71.9528 1.1526	59.7193 0.9566	12.2334 0.1960	6000 408.28	2000 136.09	4000 272.18	4.251	6.247



$$\beta_i\ (\text{atm}^{-1}) = 1.285 \times 10^{2} \quad 1.650 \times 10^{-4}\ (T, {}^\circ K)$$
$$+\ 8.022 \times 10^{7}\ (T, {}^\circ K)^2 \quad 1.743 \times 10^{9}\ (T, {}^\circ K)^3$$
$$+\ 1.433 \times 10^{12}\ (T, {}^\circ K)^4 \qquad (2.3\text{-}16)$$

Figure 2.3-10. Isothermal Compressibility of Nitrogen Dioxide



$$\beta_i \,(\mathrm{psi}^{-1}) = 8.6289 \times 10^{-4} - 6.1682 \times 10^{-6}\,(T, {}^\circ R) + 1.6684 \times 10^{-8}\,(T, {}^\circ R)^2 - 2.0166 \times 10^{-11}\,(T, {}^\circ R)^3 + 9.227 \times 10^{-15}\,(T, {}^\circ R)^4 \qquad (2.3\text{-}16a)$$

Figure 2.3-10a. Isothermal Compressibility of Nitrogen Dioxide

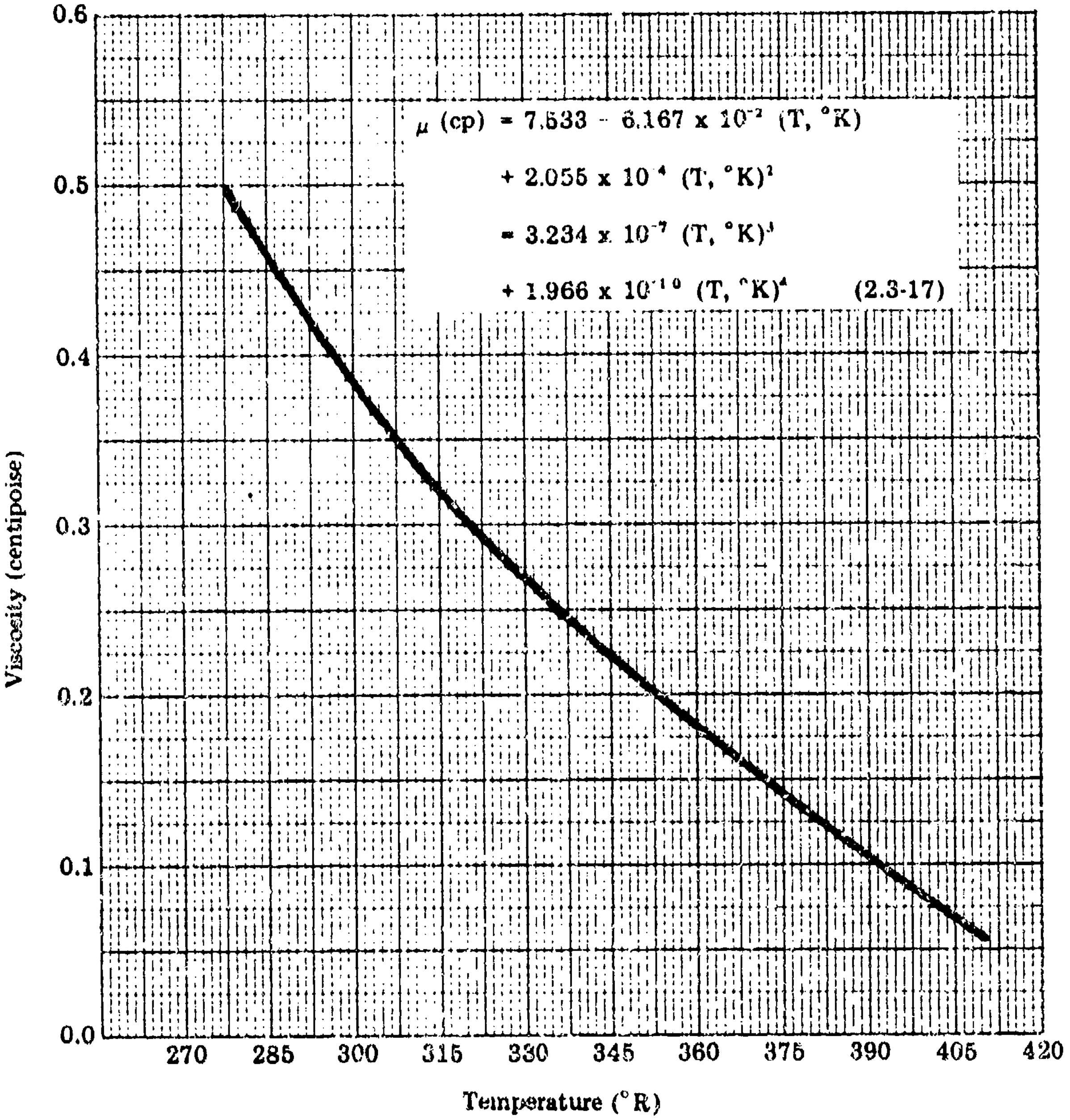
2.3.3.5 Viscosity of Liquid N_2O_4

Hercules (6) tabulated viscosity data of nitrogen dioxide in the liquid phase citing the work of Richter, Reamer, and Sage (16) as their source. Using the least-squares curve fit computer program, the change of viscosity at the bubble point with temperature is described by:

$$\begin{aligned}\mu(\text{cp}) = {} & 7.533 - 6.167 \times 10^{-2}\ (T, °K) \\ & - 2.055 \times 10^{-4}\ (T, °K)^2 \\ & - 3.234 \times 10^{-7}\ (T, °K)^3 \\ & + 1.966 \times 10^{-10}\ (T, °K)^4 \qquad (2.3\text{-}17)\end{aligned}$$

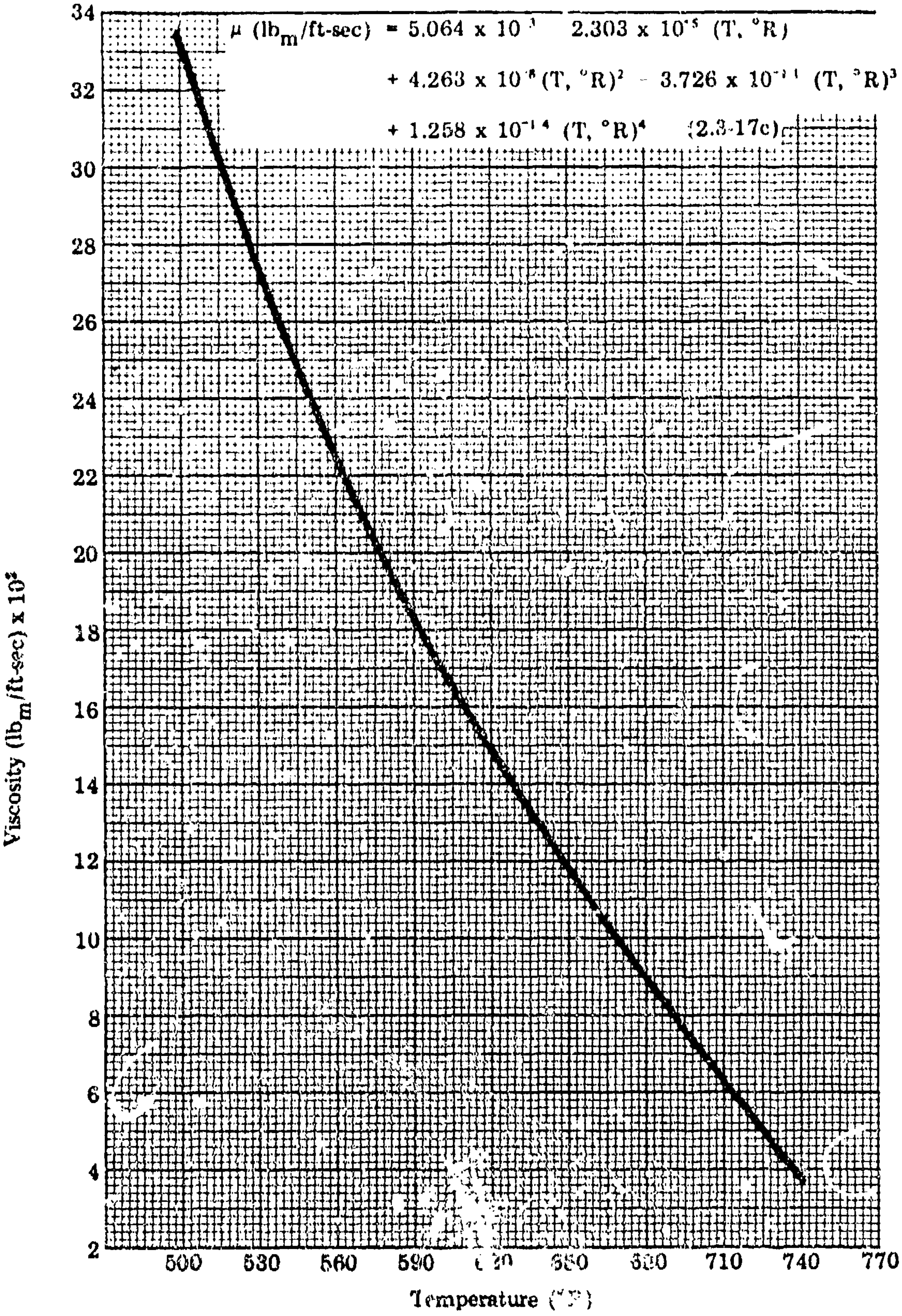
$$\begin{aligned}\mu(\text{lb}_m/\text{ft-sec}) = {} & 5.064 \times 10^{-3} \\ & - 2.303 \times 10^{-5}\ (T, °R) \\ & + 4.263 \times 10^{-8}\ (T, °R)^2 \\ & - 3.726 \times 10^{-11}\ (T, °R)^3 \\ & + 1.258 \times 10^{-14}\ (T, °R)^4 \qquad (2.3\text{-}17a)\end{aligned}$$

Viscosity values are plotted in Figures 2.3-11 and 2.3-11a. The temperature range was from 277.59 to 410.93°K (499.67 to 739.67°R). The standard deviation of equations 2.3-17 and 2.3-17a are 0.00063 cp and 4.207 x 10^{-7} lb_m/ft-sec) respectively.



$$\mu\ (\mathrm{cp}) = 7.533 - 6.167 \times 10^{-2}\ (T, {}^{\circ}K) + 2.055 \times 10^{-4}\ (T, {}^{\circ}K)^2 - 3.234 \times 10^{-7}\ (T, {}^{\circ}K)^3 + 1.966 \times 10^{-10}\ (T, {}^{\circ}K)^4 \qquad (2.3\text{-}17)$$

Figure 2.3-11. Viscosity of Nitrogen Dioxide at the Bubble Point



$$\mu\ (lb_m/\text{ft-sec}) = 5.064 \times 10^{-3} - 2.303 \times 10^{-5}\,(T, {}^\circ R) + 4.263 \times 10^{-8}\,(T, {}^\circ R)^2 - 3.726 \times 10^{-11}\,(T, {}^\circ R)^3 + 1.258 \times 10^{-14}\,(T, {}^\circ R)^4 \qquad (2.3\text{-}17c)$$

Figure 2.3-11a. Viscosity of Nitrogen Dioxide at the Bubble Point

2.3.3.6 Surface Tension and Parachor of Liquid N_2O_4

Rocketdyne (7) measured the surface tension of liquid N_2O_4 over the temperature range from -9.3 to 90.7°C (15.3 to 195.2°F). The surface tension was calculated and curve fit with a least square computer program. Liquid and vapor densities used in the reduction of the experimental data were obtained from their earlier (9) evaluation and correlation of available literature values. The resulting data are represented by the following equations:

$$\gamma(\text{dynes/cm}) = 30.07 - 0.207\,(t, °C) + 3.0 \times 10^{-4}\,(t, °C)^2 \qquad (2.3\text{-}18)$$

$$\gamma(\text{lb}_f/\text{ft}) = 2.319 \times 10^{-3} - 8.29 \times 10^{-6}\,(t, °F) + 6.4 \times 10^{-9}\,(t, °F)^2 \qquad (2.3\text{-}18a)$$

The standard errors of estimate for these equations are 0.30 dynes/cm and 2.0×10^{-6} lb_f/ft, respectively. Graphical presentation of these correlations is presented in Figures 2.3-12 and 2.3-12a.

The equations expressed in temperatures of °K and °R are:

$$\gamma(\text{dynes/cm}) = 109.00 - 0.379\,(T, °K) + 3.0 \times 10^{-4}\,(T, °K)^2 \qquad (2.3\text{-}19)$$

$$\gamma(\text{lb}_f/\text{ft}) = 7.482 \times 10^{-3} \quad 1.4174 \times 10^{-5}\,(T, °R) + 6.4 \times 10^{-9}\,(T, °R)^2 \qquad (2.3\text{-}19a)$$

The parachor at 25°C was found to be 144.0 from the relation:

$$P = \frac{M\gamma^{1/4}}{\rho_l - \rho_v}$$

where

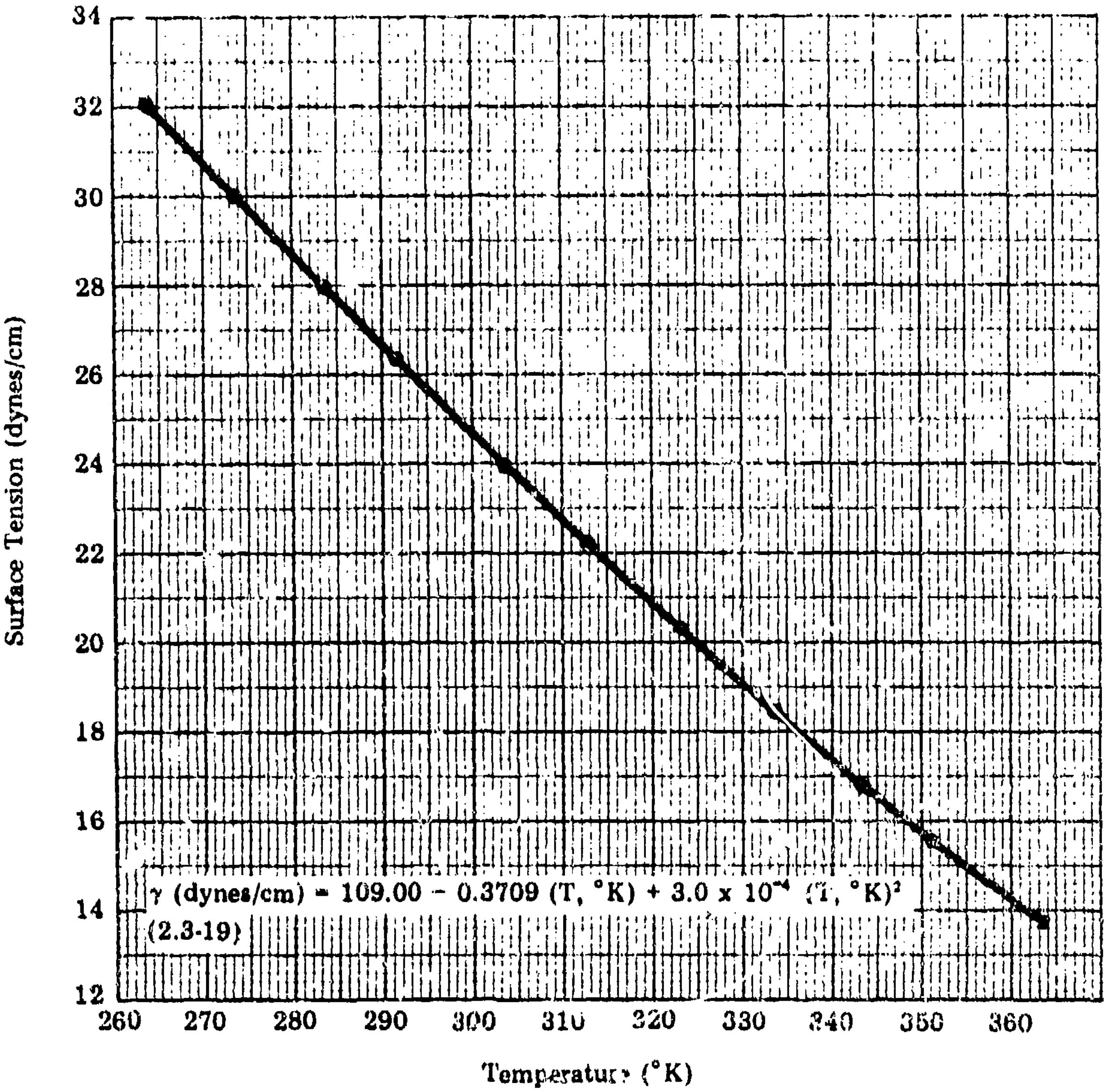
P = parachor

M = molecular weight (92.016)

γ = surface tension (25.1 dyne/cm)

ρ_l = density of liquid (1.433 g/cm³)

ρ_v = density of vapor (3.182×10^{-3} g/cm³)



$$\gamma \text{ (dynes/cm)} = 109.00 - 0.3709 \text{ (T, °K)} + 3.0 \times 10^{-4} \text{ (T, °K)}^2 \quad (2.3\text{-}19)$$

Figure 2.3-12. Surface Tension of Saturated Nitrogen Tetroxide

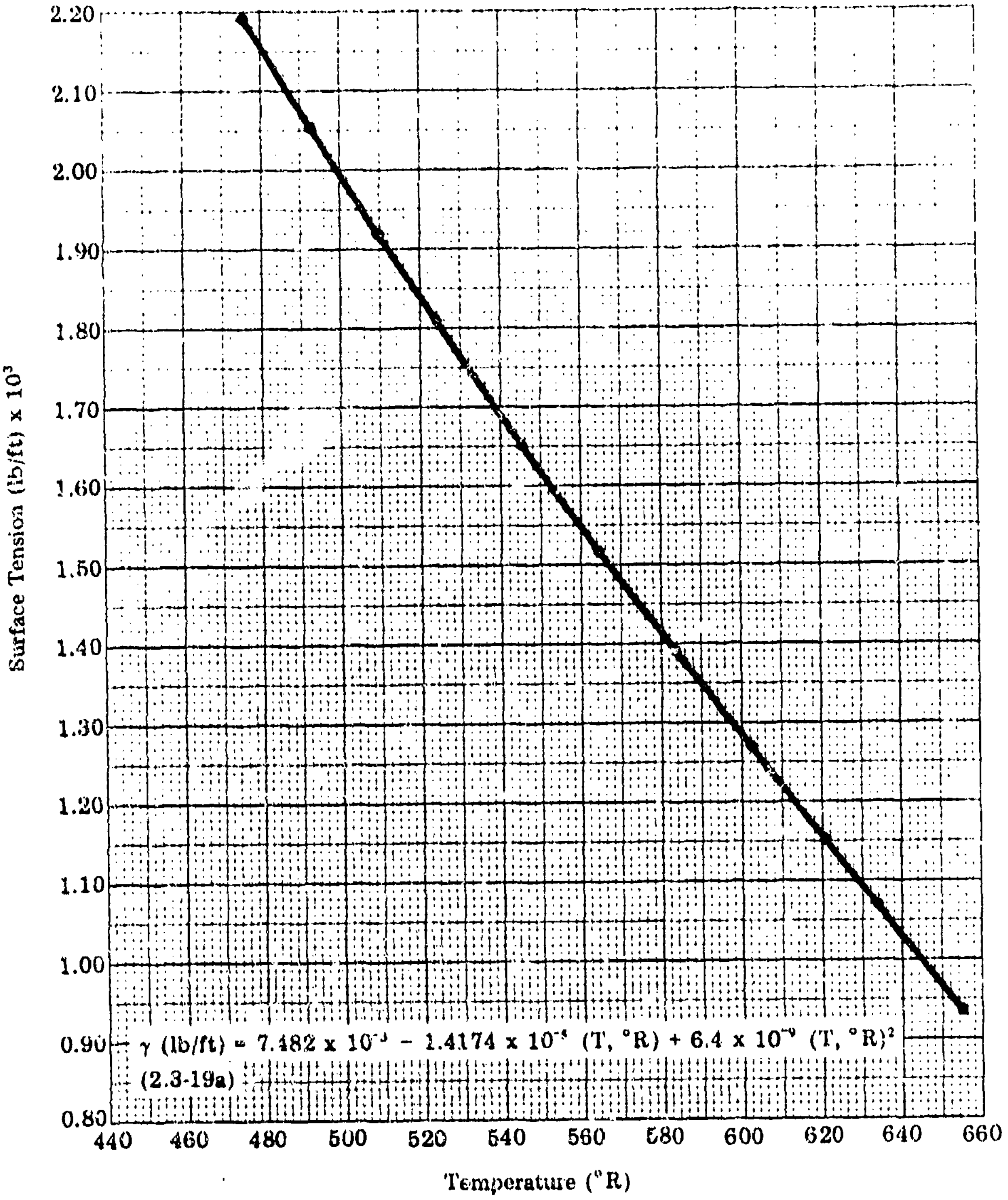


Figure 2.3-12a. Surface Tension of Saturated Nitrogen Tetroxide

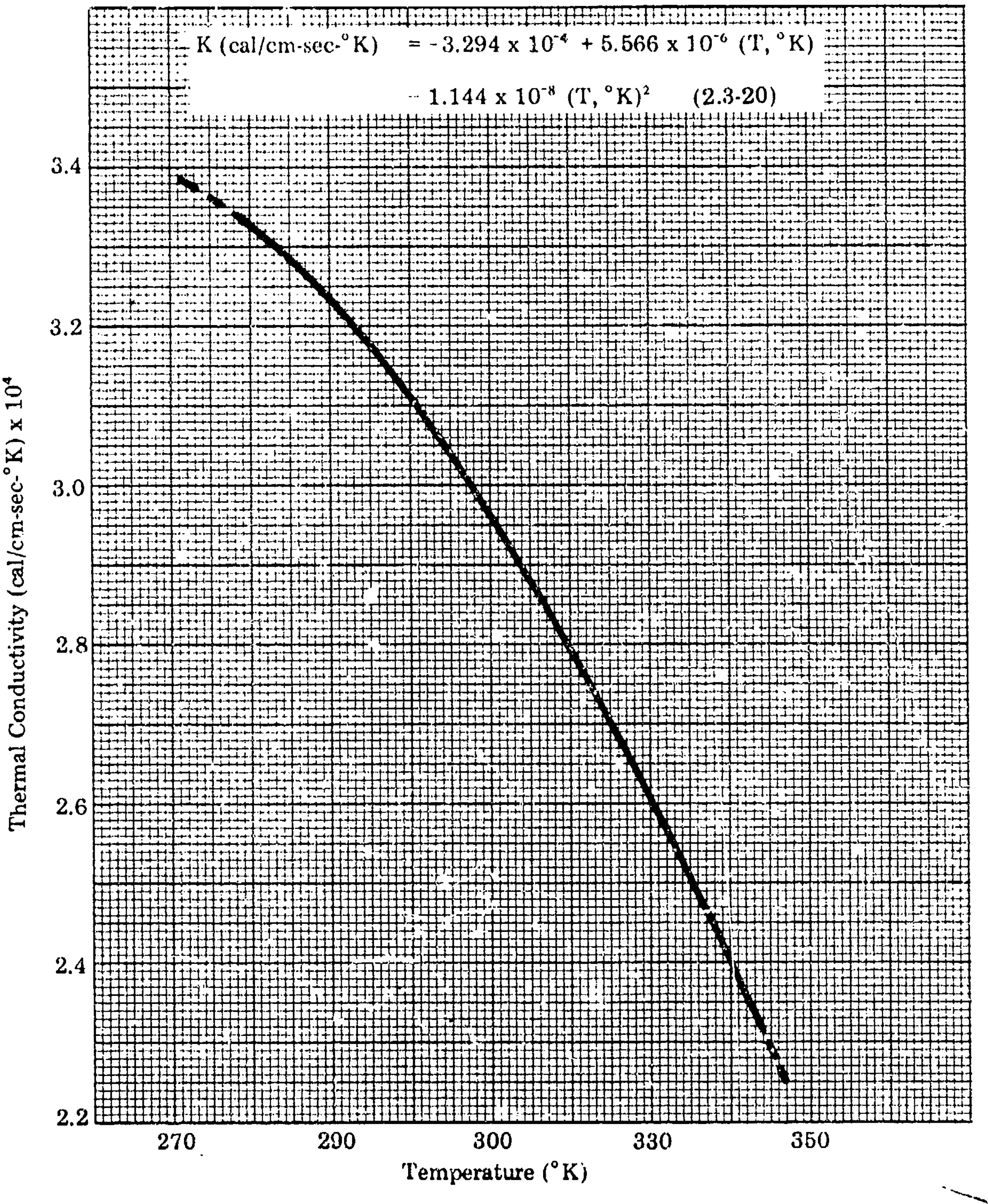
2.3.3.7 Thermal Conductivity of Liquid NO_2

Hercules (6) tabulated thermal conductivity values of NO_2 in the liquid phase citing the work of Richter and Sage (17). Three temperature values for thermal conductivity at the bubble point were listed. A second-order curve-fit for the listed values at 40, 100, and 160°F was determined for this section. The correlations are:

$$K\ (\text{cal/cm-sec}^\circ\text{K}) = -3.294 \times 10^{-4} + 5.566 \times 10^{-6}\ (T, {}^\circ\text{K}) - 1.144 \times 10^{-8}\ (T, {}^\circ\text{K})^2 \quad (2.3\text{-}20)$$

$$K\ (\text{BTU/sec-ft-}^\circ\text{R}) = -2.143 \times 10^{-5} + 2.052 \times 10^{-7}\ (T, {}^\circ\text{R}) - 2.347 \times 10^{-10}\ (T, {}^\circ\text{R})^2 \quad (2.3\text{-}20a)$$

The curves are plotted in Figures 2.3-13 and 2.3-13a.



$$K\ (\text{cal/cm-sec-}^\circ\text{K}) = -3.294 \times 10^{-4} + 5.566 \times 10^{-6}\ (T,\ ^\circ K) - 1.144 \times 10^{-8}\ (T,\ ^\circ K)^2 \qquad (2.3\text{-}20)$$

Figure 2.3-13. Thermal Conductivity of Nitrogen Dioxide

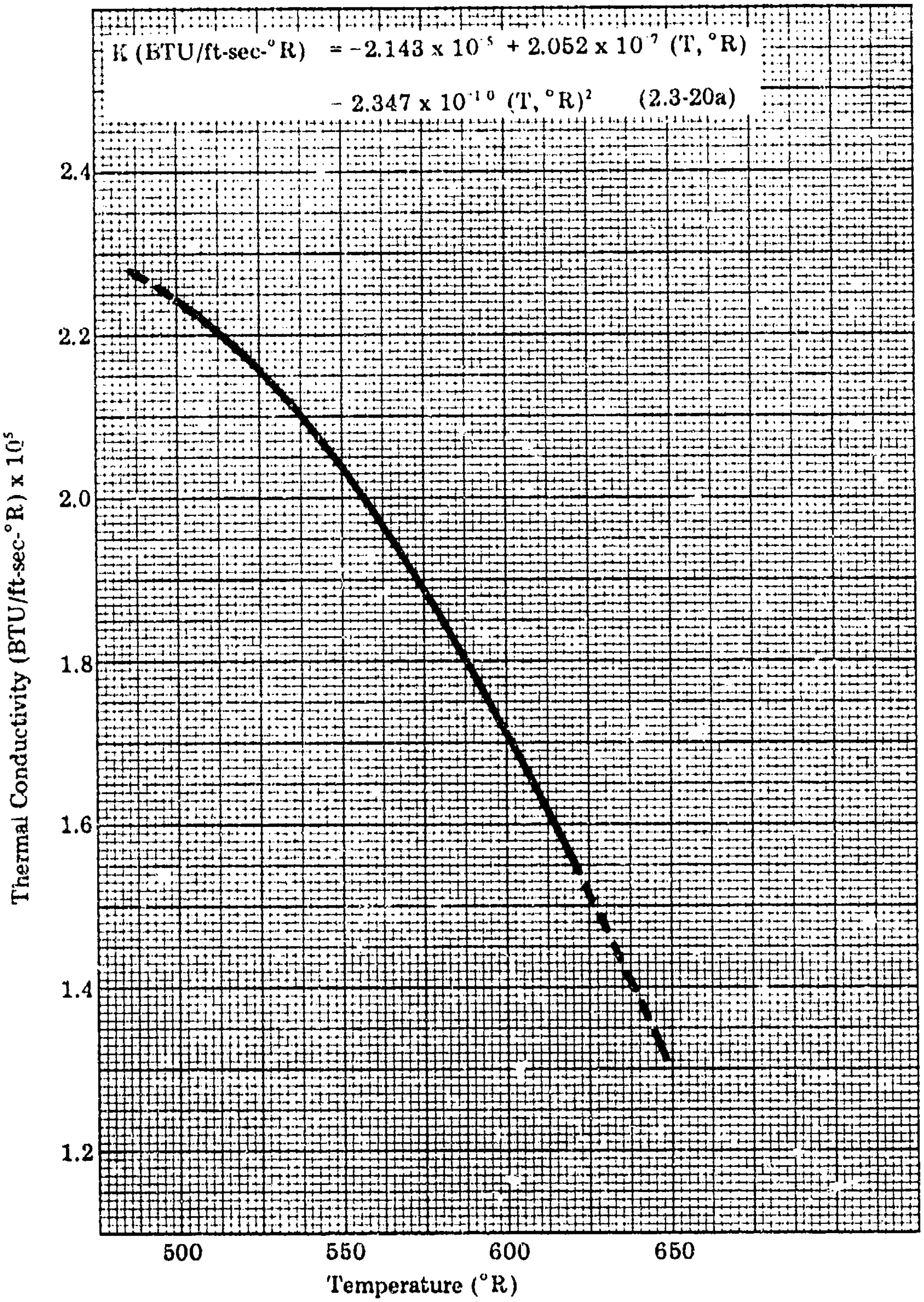


Figure 2.3-13a. Thermal Conductivity of Nitrogen Dioxide at Bubble Point

2.3.3.8 Dielectric Constant

Hercules (6) lists a single point value of 2.42 for the dielectric constant of liquid N_2O_4 at 18°C and 1000 cycle/sec. Its literature source is the work of Addison, Bolton and Lewis (18). Rocketdyne (7) performed an extensive literature survey for all available data on the dielectric constant and electrical loss tangent for N_2O_4 in the temperature range of 32 to 140°F and a frequency range of 1 to 10 Ghz. Their survey indicated none of this data existed for the propellant, although there was some dielectric constant data outside the desired frequency range.

2.3.4 CHEMICAL PROPERTIES OF N_2O_4

2.3.4.1 Chemical Reactions

Nitrogen tetroxide is a powerful oxidizer. It readily undergoes reactions with a variety of both organic and inorganic compounds. Hercules (6) gives a summarized review of the chemical reactions of nitrogen tetroxide with the various substances. Some of the typical reactions are as follows:

Water

Nitrogen tetroxide reacts with water in large excess as follows:

$$N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2$$

The nitrous acid undergoes decomposition:

$$3\ HNO_2 \longrightarrow HNO_3 + 2\ NO + H_2O$$

Over-all, two-thirds of the N_2O_4 goes to form nitric acid; the other third may be oxidized with air or oxygen to re-form NO_2 or N_2O_4.

Metals

A general reaction can be written for all metals that react with N_2O_4 at low temperatures.

$$M + N_2O_4 \longrightarrow MNO_2 + NO$$

If the temperature is maintained low and the metal is sufficiently electropositive, the reaction will end here. With weakly electropositive metals, such as zinc, the reaction may continue with the formation of a complex salt. At higher temperatures, or under conditions of reduced pressure, where the N_2O_4 has dissociated into NO_2, the products of reaction with metals are somewhat different from those in the liquid systems. The products here may be a mixture of nitrite and nitrate.

Ammonia, Hydrazine, and Amines

Ammonia reacts readily and violently with solid N_2O_4 and, if the temperature is not carefully controlled, decomposition is complete. Controlled reaction produces water, nitric oxide, nitrous oxide, nitrogen, ammonium nitrite, and ammonium nitrate. In the gas phase, between the temperatures 22° and 100°C, the reaction is:

$$2NO_2 + 2NH_3 \longrightarrow N_2 + H_2O + NH_4NO_3$$

Hydrazine and N_2O_4 react readily and violently with complete decomposition. The reaction is hypergolic (spontaneous cumbustible upon mixing). Reaction of various amines with N_2O_4 are also hypergolic.

Inorganic Acids

Hydrogen chloride reacts with nitrogen tetroxide in the dark at room temperature to form nitrosyl chloride, water, and chlorine:

$$N_2O_4 + 4\ HCl \longrightarrow 2\ NOCl + 2\ H_2O + Cl_2$$

Allied Chemical (10) reports that the above reaction occurs with excess hydrochloric acid. With an excess of N_2O_4 the reaction with hydrochloric acid is:

$$N_2O_4 + HCl \longrightarrow HNO_3 + NOCl$$

Sulfuric acid rapidly absorbs gaseous N_2O_4 and forms nitrosyl sulfuric acid and nitric acid:

$$H_2SO_4 + N_2O_4 \rightleftharpoons NOHSO_4 + HNO_3$$

The nitric acid reacts further to form more nitrosyl sulfuric acid and the equilibrium is strongly to the right. On heating, NO_2 is evolved and the equilibrium is shifted toward the left.

Hydrogen, Oxygen, Ozone, and Carbon Monoxide

Mixtures of hydrogen and nitrogen dioxide ignite spontaneously with the reaction proceeding only as far as nitric oxide:

$$NO_2 + H_2 \longrightarrow NO + H_2O$$

In the presence of oxygen and water, the following equilibrium reaction occurs:

$$N_2O_4 + H_2O + \tfrac{1}{2}O_2 \longrightarrow 2HNO_3$$

Nitrogen dioxide reacts rapidly and quantitatively with ozone to form dinitrogen pentoxide and oxygen as follows:

$$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$$

Carbon monoxide reacts with nitrogen dioxide to form carbon dioxide and nitric oxide, namely:

$$NO_2 + CO \longrightarrow CO_2 + NO$$

The reaction is slow at room temperature.

Nitration of Aromatic Compounds and Aliphatic Hydrocarbon

Both benzene and toluene show little tendency to interact with nitrogen tetroxide for short periods of contact at ordinary temperature, but on exposure for several months, oxidation and nitration occur. The equation for benzene is:

$$2C_2H_6 + 3NO_2 \longrightarrow 2C_6H_5NO_2 + NO + H_2O$$

Nitration for high yields occurs with the reaction in the vapor phase and use of a catalyst such as silica gel.

Nitroparaffins are commonly prepared by the vapor phase nitration of paraffins with nitric acid or nitrogen dioxide derived from N_2O_4.

Reaction with Organic Compounds

Both Hercules (6) and Allied Chemical (10) cites Riebsomen's work (19) as the most recent comprehensive survey (260 references) of reactions of nitrogen tetroxide with organic compounds.

2.3.4.2 Inert Gas Solubility on Liquid N_2O_4

The solubility of gaseous helium was calculated from test data reported by the Martin Marietta Company (11). Test values were obtained at four temperatures and two pressures. The Oswald coefficient was calculated. Table 2.3-3 lists the test values and the derived values in ppm. Lockheed (8) also listed the solubility of helium in N_2O_4 at one atmosphere as follows:

0°C	3.0 ppm
25°C	4.3 ppm

The solubility of helium thus derived and reported are plotted as Figures 2.3-14 and 2.3-14a.

Lockheed (8) reports the solubility of nitrogen in N_2O_4 at one atmosphere for two temperature points. They are:

0°C	182 ppm
25°C	203 ppm

TABLE 2.3-3 TEST DATA, HELIUM SOLUBILITY IN N_2O_4

Oswald Coefficient β (1)	Temperature (T) °F	Pressure (P) psia	Weight of Helium x 10^5 (2)	Density of N_2O_4 at (3) T & P, g/cc	Wt Helium to Wt N_2O_4 x 10^6
.0260	46	90	2.767	1.472	18.8
.0245	44	190.25	5.533	1.474	37.5
.0285	56	89.75	2.966	1.459	20.3
.0281	57	189.75	6.170	1.458	42.3
.0297	70	90.25	3.026	1.442	21.0
.0294	70	190	6.305	1.442	43.7
.034	80	90	3.231	1.429	22.6
.0320	80	189	6.700	1.429	46.9
.0330	90	90.5	3.248	1.417	22.9
.0338	90	189.75	6.976	1.417	49.2

1. $\beta = \frac{\text{volume of gas dissolved (at the temp and pressure of the liquid)}}{\text{volume of the liquid}}$

2. The weight of helium was calculated as follows: (assume ideal gas law applies for test conditions)

$$W = \frac{(\beta)(P)(M)}{(R)(T)} \qquad (2.3\text{-}21)$$

W = weight of helium, g

= Oswald coefficient

P = pressure, psia

M = Molecular weight of helium, 4.003 g

R = Gas constant, 669.53 $\frac{\text{Psia-cc}}{\text{g-mole-°R}}$

T = Temperature, °R, (T, °F + 459.67°)

3. The weight (g/cc) of the solvent, N_2O_4, was determined from equation 2.3-7 which is:

$$\rho N_2O_4 = 2.066 - 1.979 \times 10^{-3} (T, °K) - 4.826 \times 10^{-7} (T, °K)^2$$

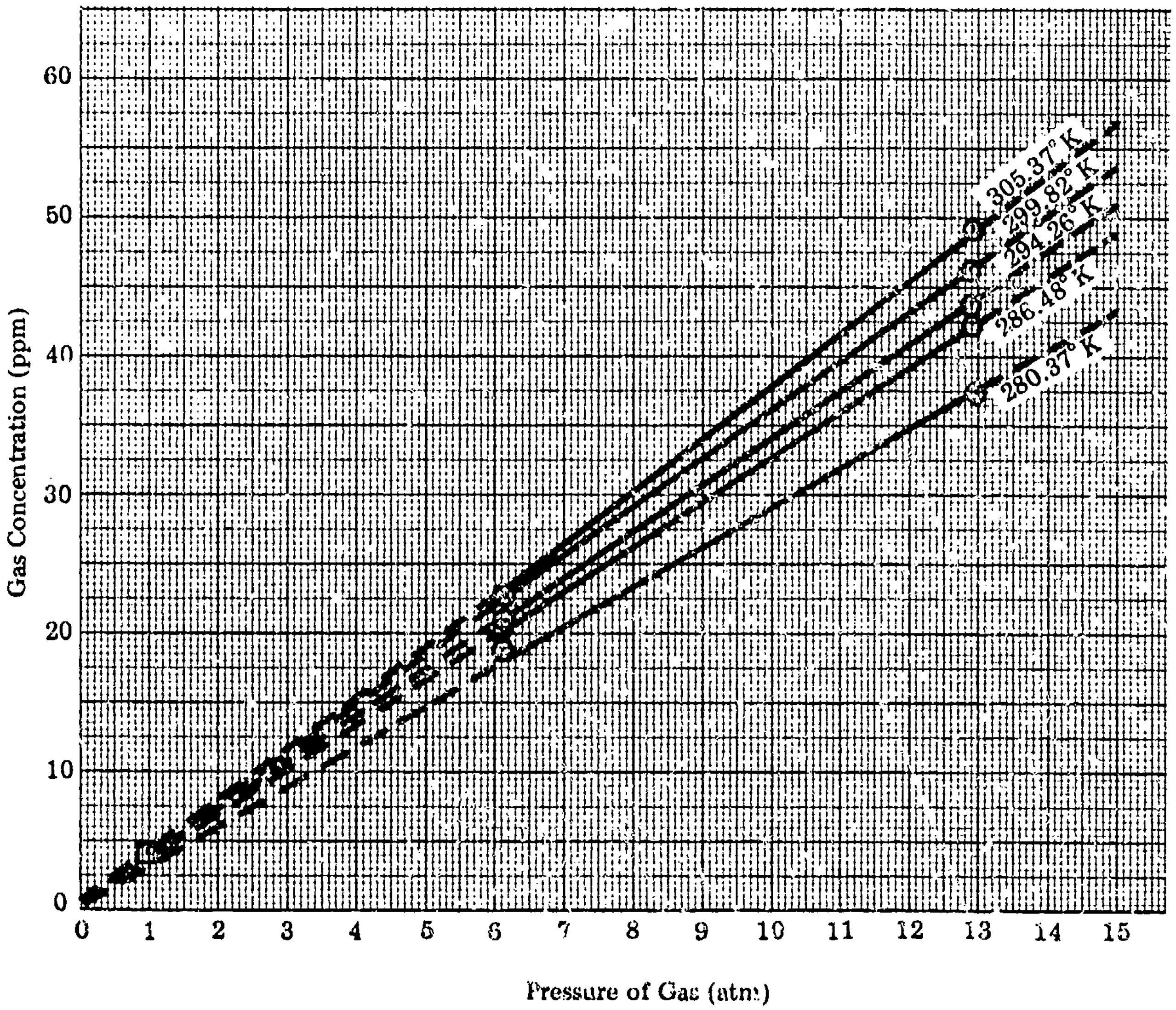


Figure 2.3-14. Helium Gas Solubility in Liquid Nitrogen Tetroxide

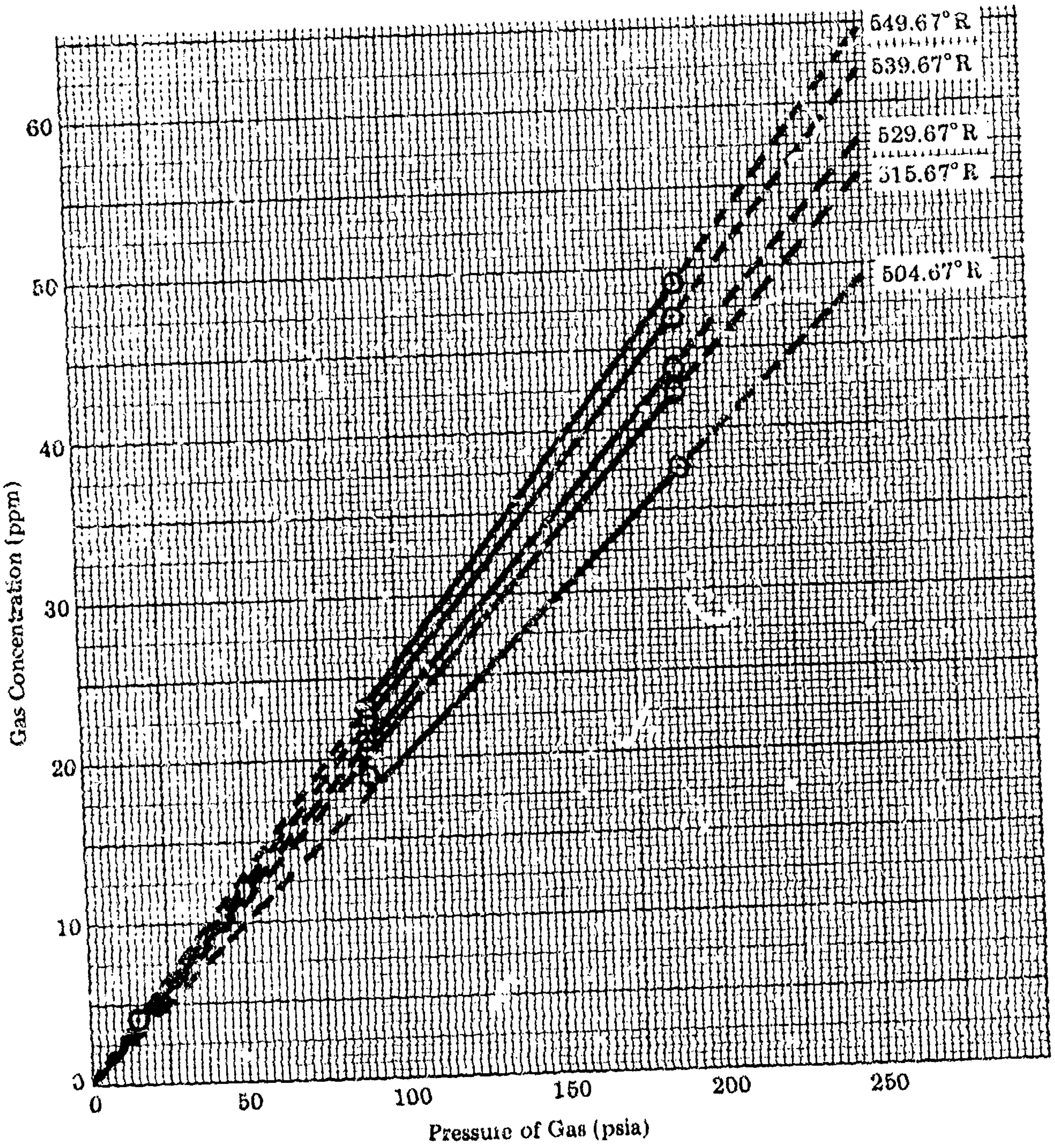


Figure 2.3-14a. Helium Gas Solubility in Liquid Nitrogen Tetroxide

2.3.5 THERMODYNAMIC PROPERTIES OF N_2O_4

2.3.5.1 Heat of Formation

The heat of formation of liquid N_2O_4 at 298.15°K was determined to be -4.676 Kcal/mole or -91.476 BTU/lb. This is the number quoted from the JANNAF (was JANAF) Thermochemical Tables (20) compiled by the Dow Chemical Company. Rocketdyne (21), in using the value, assesses a 0.4 Kcal/mole uncertainty to the heat of formation determination. Bell Aerospace (22) calculated -87.62 BTU/lb for the liquid equilibrium mixture at 298.15°K at an earlier time.

2.3.5.2 Melting Point and Heat of Fusion

The melting point of N_2O_4 is -11.2°C (11.84°F). The work by Giauque and Kemp (23) was cited as the source by Hercules (6), Rocketdyne (9), and Allied Chemical (10). Although the source was not given, others such as CPIA (5), CPIA (2), Autonetics (3), Bell (4), and Aerojet-General (1) quote the same value.

The heat of fusion at the melting point is 3.502 Kcal/mole or 68.51 BTU/lb. Hercules (6) and Allied Chemical (10) cites a symposium-type document, "Selected Values of Properties of Chemical Compounds" (24) as the source.

2.3.5.3 Critical State Constants

The critical temperature (the maximum temperature at which a gas can be liquified; above this temperature it cannot be liquified regardless of the pressure applied) is agreed to be 158.2°C (316.8°F). Hercules (6) cites the "Selected Values of Properties of Chemical Compounds" Project (24) as the reference; Allied Chemical cites both the Project (24) as well as the data of Reamer and Sage (25). Rocketdyne (9) goes back to a 1913 document to list the work of Scheffer and Treub (26).

The pressure required to cause liquification at the critical temperature is known as the critical pressure. Knowing the critical temperature and using the vapor pressure equation, the critical pressure can be calculated. As noted in Section 2.3.3.1, there are some differences between vapor pressure correlations as a function of temperature from the literature sources. Rocketdyne's vapor pressure equation, proposed as adequate to use due to their interpretation of experimental data, results in a value of 98.0 atm. Hercules (6) reports 100 atm; Allied Chemical reports 99.96 atm.

The critical density is 0.5504 g/cc (34.364 lb/ft^3) (9).

2.3.5.4 Heat Capacity of N_2O_4

The critique of the values of the heat capacity of liquid N_2O_4 has been done by Rocketdyne (9). They cited the observations of Giauque and Kemp (23). Both Hercules (6) and Allied Chemical (10) tabulated values taken from smooth curve through observations citing the work of Giauque and Kemp. Rocketdyne proposed the following curve-fit expression based on their interpretation of experimental data:

$$C_p\,(\text{cal/g - °C}) = 0.360 + 8.82 \times 10^{-4}\,(t, °C) - 1.03 \times 10^{-5}\,(t, °C)^2 + 1.77 \times 10^{-7}\,(t, °C)^3 \qquad (2.3\text{-}22)$$

$$C_p\,(\text{BTU/lb °F}) = 0.340 + 7.87 \times 10^{-5}\,(t, °F) - 6.09 \times 10^{-6}\,(t, °F)^2 + 3.03 \times 10^{-8}\,(t, °F)^3 \qquad (2.3\text{-}22a)$$

The temperature ranges of the expressions are -7.9°C to 108.1°C and 17.8°F to 226.6°F respectively. It is noted that Giauque and Kemp's work is performed to the boiling point of N_2O_4 which is 21.2°C (294.35°K); thus values above 21.2°C are extrapolated.

The equations in terms of absolute temperature are:

$$C_p\,(\text{Cal/g-°K}) = -4.257 + 4.6127 \times 10^{-2}\,(T, °K) - 1.5534 \times 10^{-4}\,(T, °K)^2 + 1.77 \times 10^{-7}\,(T, °K)^3 \qquad (2.3\text{-}23)$$

$$C_p\,(\text{BTU/lb-°R}) = -4.252 + 2.5593 \times 10^{-2}\,(T, °R) - 4.7874 \times 10^{-5}\,(T, °R)^2 + 3.03 \times 10^{-8}\,(T, °R)^3 \qquad (2.3\text{-}23a)$$

The smoothed data are plotted in Figures 2.3-15 and 2.3-15a.

Also presented herein are the curve-fit expressions by Rocketdyne (9) of N_2O_4 in the solid phase:

$$C_p\,(\text{cal/g-°C}) = 0.3108 + 1.474 \times 10^{-3}\ (t, °C) + 7.98 \times 10^{-6}\ (t, °C)^2 + 2.60 \times 10^{-8}\ (t, °C)^3 \qquad (2.3\text{-}24)$$

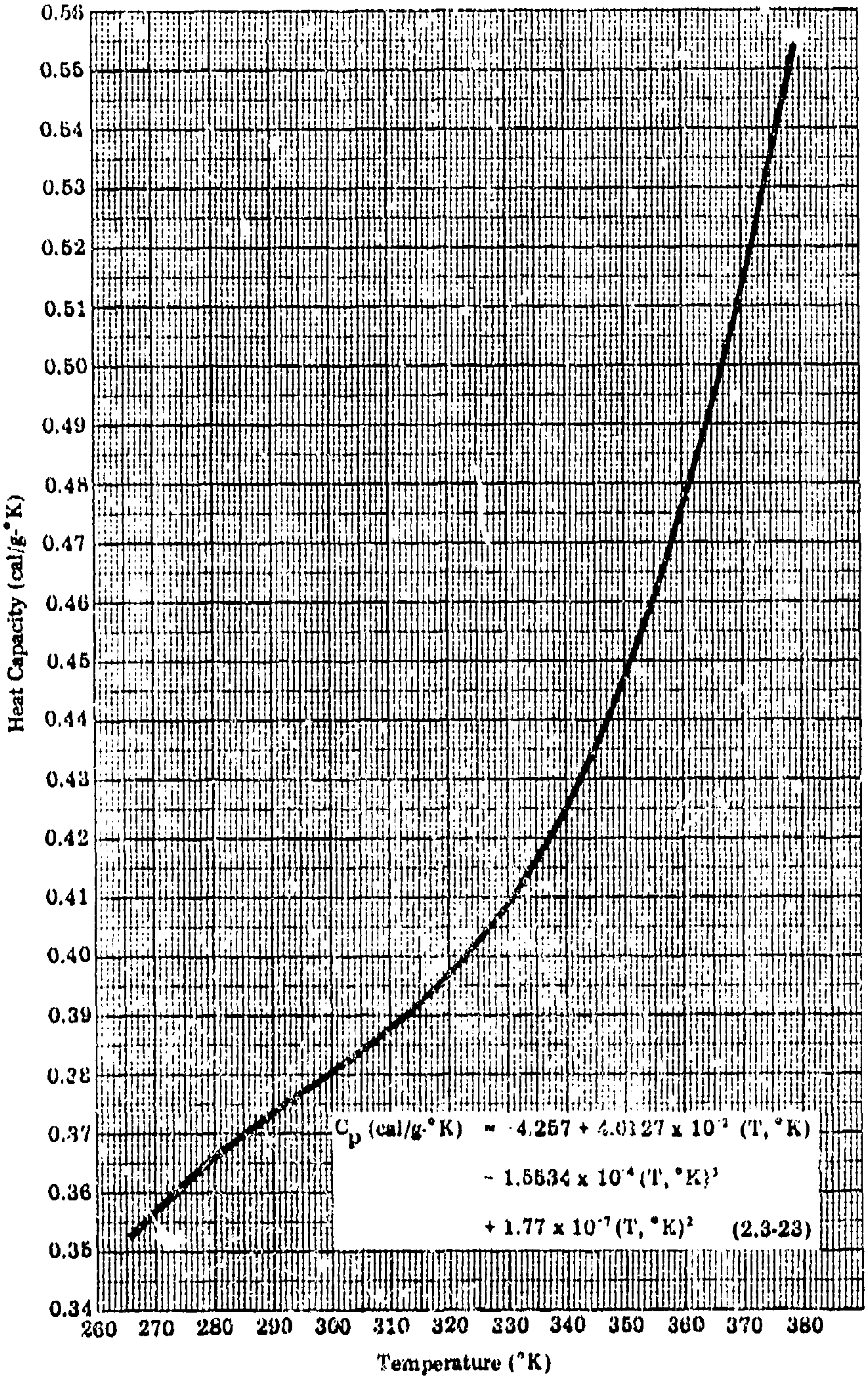
$$C_p\,(\text{BTU/lb-°F}) = 0.2870 + 6.761 \times 10^{-4}\,(t, °F) + 2.032 \times 10^{-6}\ (t, °F)^2 + 4.47 \times 10^{-9}\ (t, °F)^3 \qquad (2.3\text{-}24a)$$

The temperature range is from -256.4 to -14.9°C (-429.5 to 5.2°F). Rocketdyne interpreted the experimental data of Giauque and Kamp (23). Hercules (6) and Allied Chemical (10) also tabulated values from 20 to 260°K referring to Giauque and Kemp. In terms of absolute temperature, the equations become:

$$C_p\,(\text{cal/g-°K}) = -0.02631 + 2.934 \times 10^{-3}\ (T, °K) - 1.3326 \times 10^{-5}\ (T, °K)^2 + 2.60 \times 10^{-8}\ (T, °K)^3 \qquad (2.3\text{-}25)$$

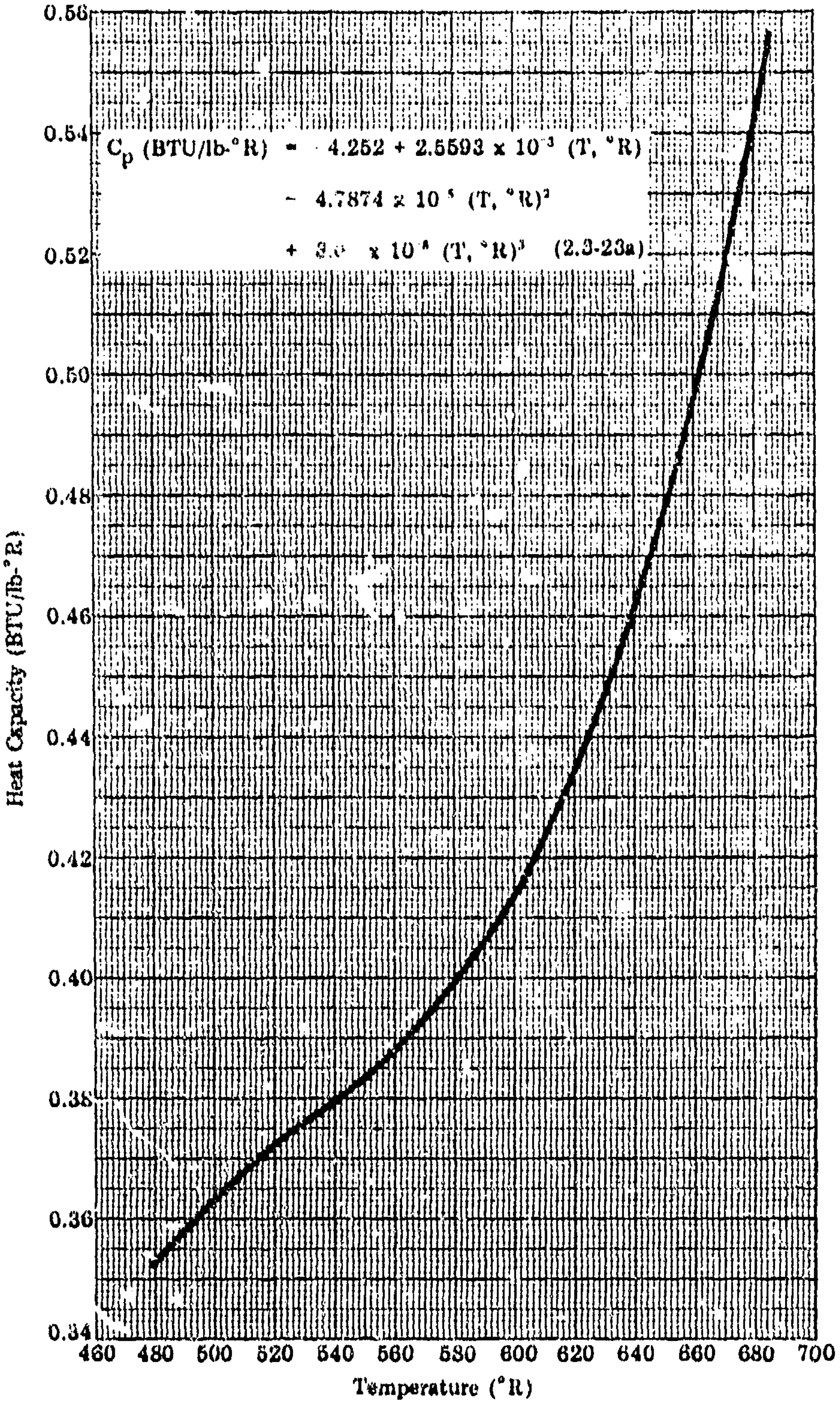
$$C_p\,(\text{BTU/lb-°R}) = -0.02812 + 1.6405 \times 10^{-3}\ (T, °R) - 4.1322 \times 10^{-6}\ (T, °R)^2 + 4.47 \times 10^{-9}\ (T, °R)^3 \qquad (2.3\text{-}25a)$$

The smoothed data are plotted in Figures 2.3-16 and 2.3-16a.



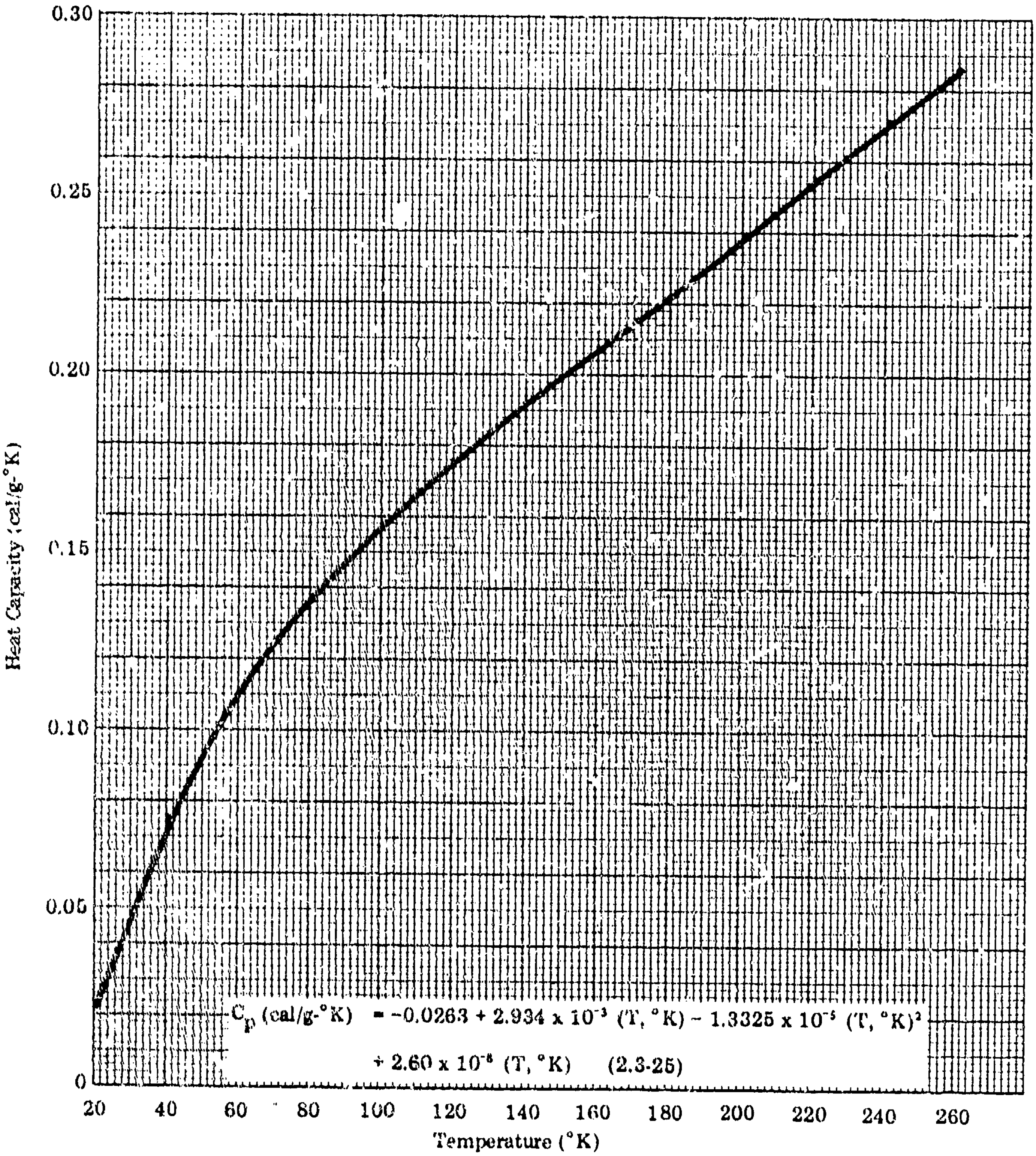
$$C_p\ (\text{cal/g-°K}) = -4.257 + 4.0127 \times 10^{-2}\ (T, °K) - 1.5534 \times 10^{-4}\ (T, °K)^2 + 1.77 \times 10^{-7}\ (T, °K)^3 \qquad (2.3\text{-}23)$$

Figure 2.3-15. Heat Capacity of Liquid Nitrogen Tetroxide



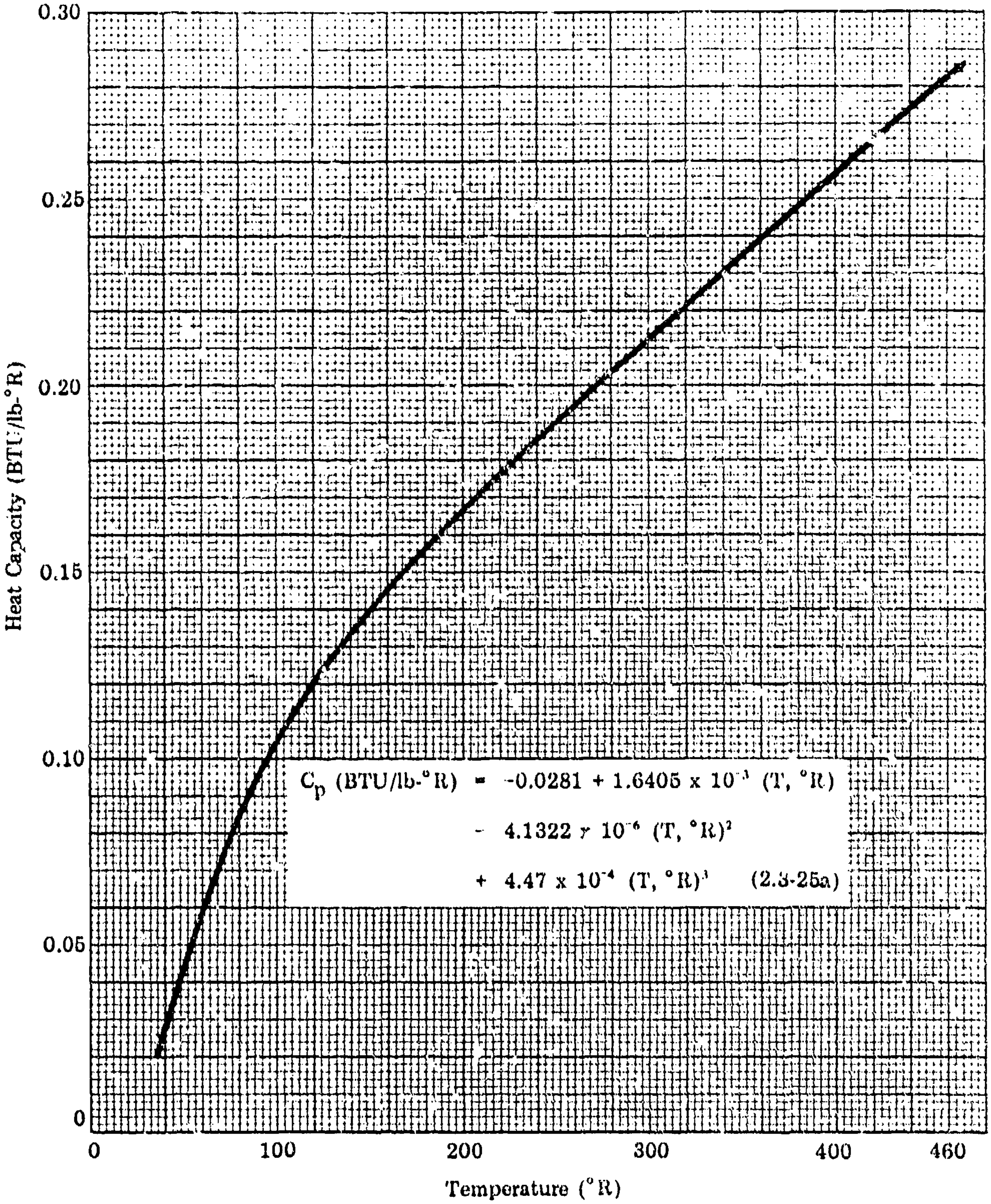
$$C_p\ (\mathrm{BTU/lb\text{-}^\circ R}) = 4.252 + 2.5593 \times 10^{-3}\ (T, {}^\circ R) - 4.7874 \times 10^{5}\ (T, {}^\circ R)^2 + 3.6 \times 10^{8}\ (T, {}^\circ R)^3 \quad (2.3\text{-}23a)$$

Figure 2.3-15a. Heat Capacity of Liquid Nitrogen Tetroxide



$$C_p \text{ (cal/g-°K)} = -0.0263 + 2.934 \times 10^{-3} \text{ (T, °K)} - 1.3325 \times 10^{-5} \text{ (T, °K)}^2 + 2.60 \times 10^{-8} \text{ (T, °K)} \quad (2.3\text{-}25)$$

Figure 2.3-16. Heat Capacity of Solid Nitrogen Tetroxide



$$C_p\ (\mathrm{BTU/lb\text{-}^\circ R}) = -0.0281 + 1.6405 \times 10^{-3}\ (T, {}^\circ R) - 4.1322 \times 10^{-6}\ (T, {}^\circ R)^2 + 4.47 \times 10^{-4}\ (T, {}^\circ R)^3 \qquad (2.3\text{-}25a)$$

Figure 2.3-16a. Heat Capacity of Solid Nitrogen Tetroxide

2.3.5.5 Latent Heat of Vaporization

The heat of vaporization of N_2O_4 at the boiling point (21.2°C) has been established at 99 cal/g (178.2 BTU/lb) by the 1956 project to select properties of chemical compounds (24). Rocketdyne (9) lists the same value citing Giauque and Kemp's work (23). Hercules (6) gives a table of values of heat of vaporization of liquid N_2O_4 calculated according to the Clausius-Chapeyron Equation.

2.3.6 LOGISTICS OF NITROGEN TETROXIDE (NTO, MON-1, MON-3, MM Grade, MON-10 and MON-25)

2.3.6.1 Manufacture

The principal supplier of nitrogen tetroxide for the government is the Vicksburg Chemical Company, Vicksburg, Mississippi. They supply the NTO, MON-1 and MON-3 presently being procured. The Minuteman Grade N_2O_4 is procured from Valley Nitrogen in Fresno, California. Vicksburg Chemical is the manufacturer of MON-10 and MON-25 for the government; none was produced in 1976. Commercial N_2O_4 is available from Air Products and Chemicals, Inc., La Porte, Texas.

Nitrogen tetroxide can be produced by a number of methods. Some of the more important are:

1) By catalytic oxidation of ammonia:

$$4\ NH_3 + 5\ O_2 \longrightarrow 4\ NO + 6\ H_2O$$

$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

$$2\ NO_2 \longrightarrow N_2O_4$$

2) By oxidation of nitrosyl chloride when nitrosyl chloride is formed from a salt and nitric acid and then oxidized with oxygen:

$$3\ NaCl + 4\ HNO_3 \longrightarrow 3\ NaNO_3 + NOCl + 2\ H_2O + Cl_2$$

$$2\ NOCl + O_2 \longrightarrow 2\ NO_2 + Cl_2$$

$$2\ NO_2 \longrightarrow N_2O_4$$

3) By decomposition of metal nitrates with nitric acid. In this method the acid oxidizes the nitrite to a nitrate. This liberates the nitric oxide to form nitrogen dioxide:

$$3\ NaNO_2 + 2\ HNO_3 \longrightarrow 3\ NaNO_3 + 2\ NO + H_2O$$

$$2\ NO + O_2 \longrightarrow 2\ NO_2$$

$$2\ NO_2 \longrightarrow N_2O_4$$

4) The process for manufacture of propellant grade nitrogen tetroxide (28) consists of intercepting a stream of hot mixed oxide gases from the platinum catalyst converter of a nitric acid plant. The hot mixed oxide gases are passed countercurrent to a stream of medium-strength nitric acid in a nitrogen tetroxide converter. This condenses out most of the crude N_2O_4 from the overhead gas stream. Subsequently, the spent gases are allowed to enter the nitric acid oxidation absorption tower. The crude nitrogen tetroxide is distilled to yield a product of at least 99.9% purity.

2.3.6.2 Analysis

The analysis of propellant grade N_2O_4 is covered in MIL-P-26539C, Amendment 2, dated 5 April 1976. This includes NTO, MON-1 and MON-3. The analysis of Minuteman Grade N_2O_4 is controlled by Bell aerospace specification 8477-947041. The analysis of Mixed Oxides of Nitrogen MON-10 and MON-25 are covered in MIL-P-27408A, dated 15 October 1971.

The NO content of the oxidizer shall be determined by allowing O_2 flow into a sample bomb and determining the NO content by the amount of O_2 required to complete the reaction. This is the method specified in MIL-P-26539C. An alternate spectrophotometric method is optional.

The N_2O_4 content is determined by neutralizing a sample of the oxidizer with a solution of 0.5 N NaOH. The percent by weight of N_2O_4 is calculated from the volume of NaOH required to neutralize the sample of a pH of 6.8-7.0.

The water equivalent is determined using a gas chromatograph.

The chloride content using a spectrophotometer and the particulates are measured in accordance with ASTM Designation D-2276-67T, Method A.

2.3.6.3 Cost and Availability

Nitrogen tetroxide is readily available in large quantities for aerospace industrial use. The first large user was the Titan II missile system developed in 1958. Every major space application has used it since, including Titan III, Transtage, Gemini, Apollo, LEM, Mariner Mars '71 and Viking Orbiter. In the near future the Space Shuttle will use vast amounts in its orbit maneuvering and attitude control systems.

At the present time the bulk of the propellant grade N_2O_4 produced in this country is produced by Vicksburg Chemical Company, Vicksburg, Mississippi. The government (27) procured about a million pounds of NTO (red-brown). 300,000 pounds of MON-1 and 75,000 pounds for MON-3 in 1976. The unit price (1976) is $0.23/pound from the government. An unknown quantity of Minuteman grade N_2O_4 was procured from Valley Nitrogen, Fresno, California at a unit price of $1.90/pound.

2.3.6.4 Shipping and Transportation

The requirements for shipping and transportation of nitrogen tetroxide are specified in MIL-P-26539C, Amendment 2, 5 April 1976 for NTO, MON-1, and MON-3. Minuteman grade N_2O_4 is controlled by Reference (29). MON-10 and MON-25 requirements are specified in MIL-P-27408A dated 15 October 1971. Excerpts are included here for information.

> The product furnished under this specification is a hazardous material as defined and regulated by the Department of Transportation (DOT) regulations. All packaging to be shipped commercially by any mode of transportation shall comply with the requirements of DOT regulations 49 CFR 171-190, or DOT special permit obtained in accordance with 49 CFR 170.13 by shipper in conjunction with the Commander, Headquarters Military Traffic Management and Terminal Service, Attn: Safety Division (TES), Washington, D.C. 20315. All packaging to be shipped by military air shall comply with DSAM 4145.3 (AFM 71-4). The product shall be packaged in containers and unit quantities as specified by the procuring activity.
>
> The following listed containers are considered acceptable for military use and unless otherwise noted are approved by DOT regulations and special permits for use with nitrogen tetroxide.
>
> (a) Sample quantities of product may be shipped in Cosmodyne Sampler, Model RPS 500-OX, as specified in special permit number 4483 or on specification DOT 3E1800 cylinders as specified in special permit number 4483. Shipment in sampling cylinder conforming to MIL-83690 (USAF), Type I, Style I, High Pressure, should also be considered even though a special permit does not presently exist.
>
> (b) Product may be shipped in cylinders of specifications DOT 3A480 or 3AA480, or individual cylinders of specification DOT 106A500 or 106A500-X as specified in CFR 173.336: or modified as specified in special permit number 5018.
>
> (c) Product may be shipped in cargo tanks as specified in special permit number 3121.
>
> (d) Product may be shipped in tank cars of specifications DOT 106A500 or 106A500-X, or specification DOT 105A500-W as specified in 49CFR 173.336, or special permit number 2986.

The capacity of common shipping containers used for nitrogen tetroxide or mixed oxides of nitrogen is:

Cylinders — high-pressure seamless steel to the following specifications:

DOT—3D 480—10 lb net and 156 lb. net
DOT—3A 2015—13 lb. net
DOT—3A 2215—30 lb. net (Sp. Permit 5376)
DOT—3A 1800—125 lb. net
DOT—106A 500-X—2000 lb. net

Tank cars—single unit car to specification:

DOT—105A 500-W—10,000 gal.

2.3.7 REFERENCES

1. Aerojet-General Corporation, *Storable Liquid Propellants, Nitrogen Tetroxide/Aerozine 50,* Report No. LRP 198 (Second Edition) June 1962.

2. Chemical Propulsion Information Agency, *Liquid Propellant Manual (U),* The Johns Hopkins University, Applied Physics Laboratory, Contact No. 62-0604-C (December 1966).

3. Autonetics Division, *PBPS Propellant Characteristics Report,* C5-1988/319, North American Aviation, Suc. (1 November 1965).

4. Bell Aerosystems Company, *Titan II Storable Propellant Handbook,* Bell Report No. 8182-933004 Rev. B., Contract Number AF04 (694)-72 Buffalo, New York, March 1963.

5. Chemical Propulsion Information Agency, *Chemical Rocket/Propellant Hazards, Liquid Propellant Handling, Storage and Transportation,* Vol III, CPIA No. 194 Change 1 (1 July 1972).

6. Hercules Incorporated, *Nitrogen Tetroxide,* Wilmington, Delaware 1968.

7. Constantine, M.T., *Engineering Property Determination of Rocket Propellants,* Rocketdyne ,Division of North American Rockwell Corporation, Final Report, AFRPL-TR-70-147 (November 1970).

8. Lockheed Missiles and Space Company, *High Density Acid (HDA) Physical Properties Handbook* (Third Edition), LMSC/D538660, Sunnyvale, California (22 July 1976).

9. Constantine, M.T., *Engineering Property Data On Rocket Propellants (U),* Rocketdyne Division of North American Rockwell Corporation, Final Report AFRPL-TR-68-100. (May 1968).

10. Allied Chemical, *Nitrogen Division, Product Bulletin,* New York (June 1958).

11. Personal communication with Karpis, J., *Solubility of Gaseous Helium in N_2O_4 and in Aerozine-50,* ER 13418, Martin Company. (No date).

12. NASA TN-D-4289.

13. Smith, D.W., and Hedberg, K., J., Chem Phys., 5, 1282 (1956).

14. Broadley, J.S., and Robertson, J.M., Nature 164, 915 (1949); cf. Groth, P., ibid., 198, 1081(1963).

15. Snyder, R.G., and Hisatsune, J. Molec. Spectr., 1, 139 (1957).

16. G.N. Richter, Reamer, H.H., and Sage, B.H., *Viscosity of Nitrogen Dioxide in the Liquid Phase,* Ind Eng. Chem., 45, 2117-19 (1953).

17. G.N. Richter, and Sage, B.H., *Thermal Conductivity of Fluids. Nitrogen Dioxide in the Liquid Phase,* Chemical and Engineering Data Series, 2 (1), 61-6 (1957).

18. Addison, C.C., Bolton, H.C., and Lewis, J., *The Liquid Dinitrogen Tetroxide Solvent System. Part IV. Dielectric Constant, Refractive Index, and Polarization of Liquid Dinitrogen Tetroxide: the Nature of Solutions,* J. Chem. Soc., 1951, 1294-7 (1951).

19. Riebsomer, J.L., *The Reactions of Nitrogen Tetroxide with Organic Compounds,* Chem. Rev., 36, 157-233 (1945).

20. *JANAF Thermochemical Tables,* compiled by the Dow Chemical Company, Thermal Laboratory, Midland, Michigan, Series C, (April 1965).

21. Mitchell, R.C., Melvold, R.W., Quaglino, J., *Engineering Properties of Rocket Propellant,* Final Report AFRPL-TR-73-105, Rocketdyne Division, Rockwell International, Canoga Park, California (November 1973).

22. Bell Aerosystems Company, *Performance Parameters of Liquid Nitrogen and 50/50 Fuel Blend,* Research Report 9105-920001, (27 September 1961).

23. Giauque W.F. & 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 Vapor Pressure. The Equilibria* $N_2O_4 = 2NO_2 = 2NO + O_2$, J. Chem. Phys., 6, 40-52 (1938).

24. Texas A & M University, *Selected Values of Properties of Chemical Compounds,* Thermodynamics Research Center Data Project, Thermodynamics Research Center, College Station, Texas, Tables 18-1 (1956, 1960, 1962). See also Carnegie Institute of Technology, Manufacturing Chemists Association Research Project, *Selected Values of Properties of Chemical Compounds,* Table 18-1m and 18-1-n, (June 30, 1956).

25. Reamer, H.H., and Sage, B.H., *Volumetric Behavior of Nitrogen Dioxide in the Liquid Phase*, Ind. Eng. Chem., 44, 185-7 (1952).

26. Schaeffer, F.E.C., and Treub, J.P., *The Vapor Pressure Curve of Nitrogen Tetroxide,* Z. Physik Chem., 81, 208-332 (1913).

27. Personal Communications with Mr. W. Watje, Kelly AFB, San Antonio, Texas.

28. *Manufacture of Nitrogen Tetroxide and Red Fuming Nitric Acid,* F.E. deVry, Hercules Incorporated, Paper at Nitrogen Tetroxide/Nitric Acid Status Meeting, 4-6 June 1968.

29. Bell Aerosystems Company Specification 8477-974041, *Minuteman Grade Nitrogen Tetroxide.*

3.0 HANDLING, STORAGE AND COMPATIBILITY

3.1 INTRODUCTION

3.1.1 GENERAL

3.1.2 ORGANIZATION

3.1.3 SCOPE

3.1.4 USAGE LIMITATION

3.1 INTRODUCTION

3.1.1 GENERAL

This section presents the recommended procedures for handling and storing of the various oxidizers and blends based on the nitric acids and nitrogen tetroxides. Data on the long term storage requirements and materials compatibility for these oxidizers is also included.

The use of a propellant usually involves a series of operations beginning with procurement and ending with actual usage. Procurement and shipping of the propellants concerned are described separately, by propellant, in Section 2 of this Handbook. Specific uses of the propellants will not be covered individually, however, the storability and compatibility subsections (3.3 and 3.4) will provide for the selection of materials to be used in specific applications.

The generally recommended equipment, procedures, and precautions for transferring propellants between storage, shipping and usage functions are presented in Section 3.2.

3.1.2 ORGANIZATION

This section is divided in three major subsections as described above. These appear in the table of contents at the beginning of this section. The subsections are divided into propellant groupings based on commonality of procedures and similarities in their compatibility and storability characteristics, together with the volume of data available on the propellants.

3.1.3 SCOPE

Subsection 3.2 deals with accepted methods of transferring propellants between storage, shipping, and usage functions as practiced by major manufacturers and users, and is in concurrence with other standard handling manuals concerned with these propellants. Propellants requiring identical procedures and equipment are discussed together as a group.

Subsection 3.3 is concerned only with the storage of the nitric acid and nitrogen tetroxide oxidizers in ground based facilities. This subsection is divided into a brief discussion for each group of propellants. Propellants which show similar behavior are discussed together as groups.

Subsection 3.4, compatibility, deals mainly with the effect of the propellants and their vapors on materials in contact with them.

A compatibility rating scheme is used which is similar to or nearly identical with the rating systems now in use in the various standard manuals dealing with compatibility of materials with the nitric acid and nitrogen tetroxide oxidizers. The various other rating schemes are also briefly discussed.

All of the oxidizers considered, exhibit similar compatibility behavior and no definite additional criteria exist for grouping of propellants along compatibility lines. The propellants are grouped, for convenience, according to usage, availability of data, and commonality of ingredients. This reresults in three groups of oxidizers: nitric acid, HDA and nitrogen tetroxide.

3.1.4 USAGE LIMITATIONS

The data presented herein is considered adequate for use in designing ground-based equipment and facilities. For flight vehicles applications, requirements are sometimes much more stringent, requiring an in-depth study of a particular combination of propellants and materials. For these applications, the data herein can serve only as a preliminary selection guide, it being essential to conduct or consult more detailed studies.

3.2 HANDLING AND TRANSFER

3.2.1 GENERAL

3.2.2 HANDLING AND TRANSFER OF NITRIC ACID AND HDA

3.2.3 HANDLING AND TRANSFER OF NITROGEN TETROXIDE

3.2.4 DISPOSAL AND POLLUTION CONTROL

3.2 HANDLING AND TRANSFER

3.2.1 GENERAL

All of the oxidizers discussed in this Handbook are fuming liquids which, depending upon the amount of dissolved nitrogen oxides, vary from colorless to reddish brown. Therefore, handling, transfer, and storage procedures which apply to one oxidizer, are found generally to apply equally well to all of the oxidizers.

Nitric acid and the blend, high density acid, are covered as a family while the nitrogen tetroxides and mixed oxides of nitrogen are discussed separately.

3.2.2 HANDLING AND TRANSFER OF NITRIC ACID

3.2.2 HANDLING AND TRANSFER OF NITRIC ACID

3.2.2.1 General

The nitric acids and high density acids discussed in this chapter are fuming liquids which, depending upon the amount of dissolved nitrogen oxides, vary from colorless to reddish brown. Vapors from these acids have a characteristic pungent odor. The fuming nitric acids are highly corrosive oxidizing agents and will vigorously attack most metals. They react with many organic materials; spontaneously causing fire. In rare instances, on gross contact with certain materials (e.g., hydrazine) and when spontaneous ignition is delayed because of degraded materials, an explosion may occur. The nitric acids will react with sea water, releasing large quantities of nitrogen oxides which are toxic. These chemicals are hygroscopic.

The nitric acids are soluble in water in all proportions: there is an accompanying evolution of heat and oxides of nitrogen. Unless the acid is added slowly to water, the large amount of heat released when they dissolve may cause spattering.

Nitric acid is stable to all types of mechanical shock and impact.

The most complete and up-to-date sources of detailed handling, storage, and safety procedures include the *Liquid Propellant, Handling Storage and Transportation Manual* (1) and the product bulletin of nitric acid manufacturers.

3.2.2.2 Materials for Transfer Equipment

The following types of metals are approved for use with fuming nitric acids and HDA.

Aluminum	Stainless Steel
1060	347
1100	19-9 DL
3003	19-9 DX
3004	304 ELC
6061	321
5052	303
5154	316
	Durimet 20

All other ferrous and nonferrous metals and their alloys are prohibited because they react with fuming nitric acid, producing toxic oxides of nitrogen as well as failures from corrosion. Titanium metal and alloys of which titanium is a major constituent must be particularly avoided in RFNA, IRFNA systems because of a possible fire and explosion (49) hazard.

The following are nonmetals approved for this service:

a. Kel-F-81, Teflon TFE, Halon TFE or equivalent

b. Resin-X (concrete protective coating) Epoxy, type MIL-P-22808A

Three types of lubricants approved for use with fuming nitric acids are as follows:

a. Nordcoseal-147-S

b. Fluorolube

c. Perfluorocarbons

All storage tanks shall be of welded construction and after fabrication should be properly stress relieved. They shall be of dip-leg design in which the inlet is located about 3 inches above the bottom of a sump. They shall be equipped with pressure-relief valves and lines of adequate size and where venting to the atmosphere is impractical, discharged into a fume-scrubbing system. Tanks shall be equipped with a high- and low-liquid-level alarm system which also controls the pump motor. Because carbide precipitation takes place during the welding of stainless steel, the section of a stainless-steel storage vessel most susceptible to corrosion failure is its welded area. This danger may be materially lessoned by proper heat treatment of the vessel after fabrication. Packings and lubricants should be installed in pumps, valves, etc. after delivery.

The pipes and fittings shall be of approved construction materials and tested at design pressure. Whenever possible, piping and fitting shall be installed by welding.

Gaskets of the following type are acceptable for use with fuming nitric acid:

a. Sheet TFE (Halon TFE, Teflon or equivalent)

b. Kel-F (chlorotrifluoroethylene polymer or equivalent)

c. Aluminum

d. Teflon-sheathed asbestos (envelope)

e. Corrugated aluminum with asbestos-filled depressions

The most satisfactory valve is a plug type. Valves used for acid operations shall be constructed of compatible materials and shall be rebuilt prior to reuse with fuel systems, because the packing material may become contaminated and cause a fire. Gate valves are not recommended for nitric acid service.

Pumps shall be constructed of approved materials and may be of a centrifugal or a positive-displacement type, as suitable. The shaft seal shall be either a mechanical seal constructed of material resistant to fuming nitric acids, or of braided blue asbestos packing impregnated with approved lubricant. Acid hoses shall be made of flexible braided stainless-steel wire with TFE or stainless-steel bellows inner liner.

Acid-storage facilities should be monitored with pressure gages of approved stainless-steel construction and cleaned for oxidizer service. In order to minimize operator reading errors, all pressure gages used for a common purpose should have identical scales.

All acid-storage tanks shall be provided with a venting system and with a vapor-pressure-relief valve of adequate size, set at a safe working pressure which will be determined by the material and construction of the tank.

Further details concerning equipment for transfer and handling of nitric acids can be found in the CIPA Manual (1) on the handling and storage of liquid propellants, or in the manufacturers' literature.

Detailed information on the toxic and fire hazards of nitric acids as well as safety precautions, are presented in Section 4.0 of this Handbook. That section, as well as the safety information in one or more of the referenced publications should be consulted before attempting to handle or work with these oxidizers.

3.2.2.3 Transfer Procedures

In any operation relating to the handling, transfer or storage of fuming nitric acids, there shall never be fewer than two operators present, and ready avenues of retreat for them should be available. In all handling operations, personnel shall wear approved protective clothing and respiratory safety equipment.

Operating procedures with sequencing check list shall be defined by the cognizant authority or by the manufacturer of the nitric acid equipment. All operating personnel shall be completely and thoroughly instructed before operating the equipment. All valves, pumps, switches, etc., shall be identified and tagged. The operators will use the sequencing check list provided. All enclosed spaces should be provided with general ventilation, if there is any danger of any accumulation of vapors.

If there is any evidence, visual or by odor, of nitrogen dioxide in the air, the atmosphere will be checked and monitored for the threshold limit value prior to the start of transfer operations.

Safety showers shall be located in easily accessible places near the transfer and storage equipment.

Drums shall be stored with bung side up to prevent possible leakage at that point. With the exception of containers of IRFNA, drums shall be pressure relieved when received, and once each week thereafter. This is done by slightly loosening the bung cap until all vapor pressure has been relieved and then immediately retightening the caps. To prevent the loss of hydrogen fluoride, drums containing Type IIIA, IRFNA, should not be vented. No excessive internal pressure build-up in such drums is experienced as long as a minimum of 0.3 percent hydrofluoric acid is maintained. Ullage should never be greater than 50 percent; if possible, a 10 percent ullage should be maintained. Drums should be emptied using a self-priming hand or motor driven pump. Pressure transfer should not be used. The empty drums shall be completely filled with water, drained and the bung replaced before being set aside for storage or return to the supplier.

As part of their service, suppliers of nitric acid furnish loading and unloading instructions. The users shall be instructed by the supplier in the proper use of the equipment and shall always follow the procedures prescribed by the manufacturer for operating and maintaining equipment used with nitric acid. Personnel engaged in the transfer of nitric acid from tank car or tank truck must be specifically trained in that operation.

After all filling and transfer connections have been made, all inlet and outlet valves shall be set and checked. After the transfer is completed, the pump shall be shut down before closing the valves and making the necessary disconnections.

3.2.2.4 Personal Protection and Other Precautions

Protective equipment and emergency facilities comprise the following:

Hand, face, head, body, and foot protection.

Respiratory protection.

Safety showers, eye-wash facilities, and other water supply.

The wearing of proper respiratory protection in high concentrations, such as an approved self-contained breathing apparatus, proper protective clothing, and other measures is discussed in Section 4.2.3.1 of this Handbook.

In case of an accident large amounts of water is the most effective means of counteracting nitric acid exposure. First Aid is covered in more detail in Section 4.2.4.

3.2.3 HANDLING AND TRANSFER OF NITROGEN TETROXIDE

3.2.3.1 General

3.2.3.2 Materials for Transfer Equipment

3.2.3.3 Transfer Procedures

3.2.3.4 Personal Protection and Other Precautions

3.2.3 HANDLING AND TRANSFER OF NITROGEN TETROXIDE

3.2.3.1 General

Nitrogen tetroxide is actually an equilibrium mixture of nitrogen tetroxide and nitrogen dioxide ($N_2O_4 \rightleftharpoons 2\ NO_2$). It is sometimes called dinitrogen tetroxide, nitrogen peroxide or liquid nitrogen dioxide.

Mixed oxides of nitrogen consist of various mixtures of N_2O_4 and nitric oxide (NO). The addition of NO to nitrogen tetroxide lowers the freezing point of the propellant.

Nitrogen tetroxide (N_2O_4) is a volatile reddish-brown liquid. It is a powerful oxidizing agent containing about 70% available oxygen. The fumes are yellowish to reddish brown and have a charateristic odor. Propellant mixed oxides of nitrogen, containing 90% N_2O_4 and 10% NO, resembles nitrogen tetroxide in color and odor. Nitric oxide is a volatile blue liquid. The fumes are colorless.

Oxides of nitrogen are corrosive oxidizing agents. In the presence of water the corrosiveness of these oxidizing agents is enhanced. N_2O_4 may react with combustible materials and is hypergolic with UDMH. As NO concentrations are increased, the N_2O_4 mixture shows decreased hypergolicity. Oxides of nitrogen are not sensitive to mechanical shock, heat or detonation. They are nonflammable with air, but can support combustion.

N_2O_4 in water reacts to form nitric and nitrous acids. The nitrous acid decomposes forming additional nitric acid and envolving nitric oxide (NO).

N_2O_4 is very stable at room temperature. At 302°F it begins to dissociate into nitric oxide and free oxygen, but upon cooling it reforms into N_2O_4. Dry N_2O_4 (less than 0.1 percent water equivalent) may be stored in low-pressure carbon-steel containers, since the vapor pressure at 140°F is only 74 psia and the corrosiveness at this water content is negligible for an indefinite period.

NO is stable at room temperature. Mixed oxides of nitrogen (MON-10) has a vapor pressure of 140 psia at 140°F which is moderately higher than that of nitrogen tetroxide, and requires containers rated for this higher pressure.

The most complete and up-to-date sources of detailed handling, storage and safety procedures include the *Liquid Propellant Handling, Storage and Transportation Manual* (1) and the product bulletins of nitrogen tetroxide manufacturers (2 and 3).

3.2.3.2 Materials for Transfer Equipment

Although N_2O_4 and mixed oxides of nitrogen at ordinary temperatures and pressures are not corrosive to most common metals, the selection of metals for this service should be governed by the oxidizer's moisture content. The following metals are suitable for this service:

a. When moisture is 0.1 percent or less
   - Carbon steels
   - Aluminum
   - Stainless steels
   - Nickel
   - Inconel

b. When moisture content is above 0.1 percent
   - Stainless steel (300 series)

NOTE: *Use of silver solder should be avoided in component or system fabrication.*

The following nonmetals may be used:
- Ceramic (acid-resistant)
- Pyrex glass
- Polytetrafluoroethylene (TFE or equivalent)
- Polytrifluorochloroethylene (Kel-F or equivalent)
- Asbestos (cotton-free)
- Polyethylene (limited use)

Since hydrocarbon lubricants react with oxidizers, they must be avoided; the following lubricants, which are resistant to strong oxidizers, may be used:
- Fluorocarbon oils, greases and waxes
- Nordo seal-147 and DC 234S or equivalent
- Polytetrafluoroethylene tape

N_2O_4 and mixed oxides of nitrogen are shipped in cylinders, tank trucks and tank cars, and may be stored in cylinders and tanks (main storage and mobile).

The tanks shall be of welded construction and shall be constructed according to the ASME Boiler and Pressure Vessel Code (4). Since N_2O_4 and mixed oxides of nitrogen do not present a particular corrosion hazard, the tank may be equipped with bottom outlets for transfer and cleaning. The tanks shall be equipped with adequate pressure relief devices. Storage tanks for service in mixed oxides of nitrogen require higher pressure ratings. Storage and mobile tanks must be equipped with both top-fill lines and fume-return (or vent) and pressure-balance lines. This design is necessary to keep the system closed during transfer and filling operations. The tanks shall also be equipped with liquid-level gages and, if practical, a high- and low-level alarm system.

The design and construction of mobile tanks should, insofar as possible, comply with DOT regulations (5). This would avoid the use of low-pressure tanks which may be satisfactory for stationary storage but too light for safe handling in transit.

The pipes and fittings shall be of approved construction materials and shall be tested for the design working pressure. Whenever possible, piping and fittings shall be installed by welding; a thread sealing compound of water glass (disodium silicate) and graphite and polytetrafluoroethylene tape, however, has been used successfully.

Gaskets and "O" rings may be fabricated from any of the recommended nonmetals listed herein.

Leakage cannot be tolerated in valves selected for nitrogen tetroxide or mixed oxides of nitrogen service. Where full flow with minimum pressure drop is required, ball valves may be used; however, seal design is critical. Needle valves can be used for bleed, sampling, and purge systems. Polytetrafluoroethylene chevron packing is recommended for valve stem seals. Valve body construction should be of stainless steel. Valve trim should be polytetrafluoroethylene or polychlorotrifluoroethylene. Gate and butterfly valves should be avoided for nitrogen tetroxide service due to particle migration problems in a soft seated valve of this type.

Transferring nitrogen tetroxide and mixed oxides of nitrogen by pump is preferred because it minimizes the possibility of introducing moisture into the system. The pumps shall be constructed of an approved material and may be of the centrifugal or rotary type. A seal-less pump (such as Chem-pump or equivalent) of stainless steel construction is recommended; as the design includes no exposed shafts. The gear type of rotary pump is widely used for small volume propellant service. This type of pump can use mechanical seals in place of packing, and is quite reliable. The seat material shall not contain carbon or graphite. Hoses shall be fabricated of polytetrafluoroethylene with stainless steel braid and fittings. Flexible metal hoses of stainless steel construction are also satisfactory. The hose must be designed for the service intended.

Standard types of pressure gages made of compatible materials and cleaned for oxidizer service shall be used with N_2O_4 and mixed oxides of nitrogen. In order to minimize operator reading errors, all pressure gages used for a common purpose should have identical scales.

Venting and safety relief equipment shall be constructed of compatible materials and provided as required.

Further details concerning equipment for transfer and handling of nitrogen tetroxide can be found in the CPIA Manual on the handling and storage of liquid propellants (1), or in the manufacturers' literature.

Detailed information on the toxic and fire hazards of nitrogen tetroxide, as well as safety precautions, are presented in Section 4.0 of this Handbook. That section, as well as the safety information in one or more of the referenced publications should be consulted before attempting to handle or work these oxidizers.

3.2.3.3 Transfer Procedures

Operating procedures with a sequencing check list will be defind by the cognizant authority or by the manufacturer of the N_2O_4 or mixed oxides of nitrogen equipment. All operating personnel shall be completely and thoroughly instructed before operating the equipment. All valves, pumps, switches, etc., shall be identified and tagged. The operators will use a provided sequencing check list.

It is desirable that facilities for transferring N_2O_4 or mixed oxides of nitrogen from a shipping container to a storage vessel be located outdoors. Whenever operations are conducted indoors or there is a possibility of contamination indoors, adequate mechanical ventilation shall be provided.

N_2O_4 of commercial purity and mixed oxides of nitrogen are stable at ordinary temperatures. N_2O_4 exhibits a reversible dissociation to NO_2. Refrigeration is not required to keep N_2O_4 or mixed oxides of nitrogen as liquids. Although pure N_2O_4 will freeze when the material is used below 12°F, the addition of nitric oxide to achieve the 90% N_2O_4 - 10% NO mixture lowers the freezing point to -9°F and allows the oxidizer to be handled under more extreme climatic conditions.

Liquid N_2O_4 and mixed oxides of nitrogen can be stored safely at relatively low pressure (less than 30 psig); however, the vessels used for mixed oxides of nitrogen service require a higher pressure rating.

Liquid N_2O_4 may be stored or transported in tank cars or cylinders with capacities up to 1 ton, and it may be stored in bulk tanks. Mixtures containing NO, due to their higher vapor pressure, are restricted to high pressure cylinders. The storage tanks must be of approved design. materials and construction and must be suitably housed.

Normal safety precautions in handling any toxic material should be strictly observed. Storage, transfer and test areas must be kept neat and free from combustibles and must be frequently inspected. Piping systems shall be clearly identified. In general, the precautions taken in handling liquid N_2O_4 and mixed oxides of nitrogen are very similar to those for fuming nitric acid.

If there is any evidence, visual or by odor, of N_2O_4 or mixed oxides of nitrogen leakage, the atmosphere will be checked and monitored for vapor content prior to the start of transfer operations.

At least two men should always be assigned to any operation concerning the handling, transfer and storage of N_2O_4 and mixed oxides of nitrogen. Ready avenues of escape should always be available for them.

Safety showers shall be located in easily accessible places near the transfer and storage equipment.

N_2O_4 and mixed oxides of nitrogen are not shipped or stored in drums, but may be shipped and stored in cylinders. The two types of cylinders which may be used for N_2O_4 are as follows:

a. One type is closed by a screwed plug and protective cap. Before being unloaded the cylinder's contents shall be cooled to below 70°F (21°C). After they have cooled, remove the cap and plug, and install a cylinder valve in the threaded opening. The N_2O_4 may then be withdrawn as a gas when the cylinder is upright, or the cylinder may be inverted to allow the withdrawal of the liquid.

b. Another type is fitted with valves for the withdrawal of either liquid or gaseous N_2O_4. The type equipped with valves are also approved for mixed oxides of nitrogen up to 33.2 percent nitric oxide (NO). A caulking and lubricating compound composed of water glass and powdered graphite or TFE tape will facilitate the operation of making up threaded joints on cylinders. The use of hydrocarbon lubricants should be avoided when they may come into contact with N_2O_4.

A tank car may be unloaded into a storage tank by transfer pump. The suppliers of N_2O_4 will furnish instructions for the proper unloading of tank cars. Before charging any system with N_2O_4 or mixed oxides of nitrogen, it is important that the storage tank and all pipe lines, valves and fittings are free of oil, other organic materials, scale, foreign matter and traces of water. If any part of the system contains moist air, it should be flushed thoroughly with dry compressed air or dry compressed inert gas before charging begins.

After all filling and transfer connections have been properly made, all inlet and outlet valves shall be properly set and checked. After the transfer has been completed, the pump or compressed gas shall be shut down before anyone approaches the installation to close valves and make necessary disconnections. An adequate supply of water shall be available for flushing spills and for safety showers. All valves, pumps, switches, etc., should be clearly identified. Good housekeeping must be maintained at all times.

3.2.3.4 Personal Protection and Other Precautions

Protective equipment and emergency facilities comprise the following:

Hand, face, head, body, and foot protection.
Respiratory protection.
Safety showers, eye-wash facilities, and other water supply.

The wearing of proper respiratory protection in high concentrations, such as an approved self-contained breathing aparatus and protective clothing and other measures is discussed in Section 4.2.3.2 of this Handbook.

In case of an accident large amounts of water is the most effective means of counteracting N_2O_4 exposure. First Aid is covered in more detail in Section 4.2.4.

3.2.4 DISPOSAL AND POLLUTION CONTROL OF ALL NITRIC ACID/NITROGEN TETROXIDE OXIDIZERS

The disposal and pollution control of these oxidizers has been the subject of U.S. Public Laws which dictate increased effort to improve air, land, and water pollution control of toxic propellant vapors, leaks, spills, and disposal during all phases of manufacture, transfer, storage, and transportation operations. The manufacturer and users are enjoined to approach the appropriate pollution control district to mutually resolve all problem areas, and to develop adequate control and disposal methods for situations which are likely to develop in any of the phases.

Disposal of these oxidizers shall be conducted in a manner such that the following requirements can be met:

1. Discarded oxidizers and by products should not be able to collect in areas where they can do harm later.
2. Oxidizers should be disposed of in such a way which will prevent toxic vapors from reaching work or inhabited areas.
3. Oxidizers should be disposed of in a manner which will not create a fire or explosion hazard.
4. Disposal products should not be allowed to enter waterways in any significant concentration.

All personnel engaged in disposal procedures must wear full protective clothing and respiratory equipment. Water is the most easily used and the most readily available decontaminating agent. Laboratory and field tests on reactions at 77°F between fuming nitric acids and aqueous 5 percent NaOH (caustic soda, sodium hydroxide), 5 percent $NaHCO_3$ (bicarbonate of soda), 5 percent Na_2CO_3 (sodium carbonate) and limestone indicate that approximately 50 percent more NO_2 fumes evolve during the treatment with the foregoing alkaline materials than are given off during water dilution. Concrete and asphalt contaminated with fuming nitric acids retain small amounts of acid in surface pores even though flushed with large quantities of water. The most practical decontamination procedures, therefore, are as follows.

When fuming nitric acid is spilled on concrete or other hard surfaces having a proper drainage system and neutralizing pit and an adequate supply of water, complete washing down with water is sufficient. In enclosed areas, flush with large quantities of water, then spray entire working surface with a 5 percent solution of Na_2CO_3 (sodium carbonate).

For spills on concrete, asphalt or other hard surfaces in the field where an adequate supply of water is not available and where drainage is impossible, it is recommended that the surface be sprayed with a 5 percent solution of $NaHCO_3$ (sodium bicarbonate) or Na_2CO_3 (sodium carbonate) until bubbling ceases.

Small quantities of N_2O_4 or mixed oxides of nitrogen can be disposed of by permitting them to evaporate and disperse in the atmosphere. Pit neutralization of N_2O_4 with limestone or soda ash is used but is not very effective.

Large quantities can be burned in a controllable manner with a fuel such as kerosene. The disposal area should be well isolated and the perimeter cleaned of all combustibles. Spray the N_2O_4 or mixed oxides of nitrogen onto the surface of a burning pit partially filled with fuel. Repeat the procedure after burned out area has cooled. Fire-fighting equipment should be nearby during burning and disposal operations, and persons engaged in the operation should wear suitable protective equipment.

3.3 STORABILITY

3.3.1 GENERAL

3.3.2 STORAGE PROCEDURES

3.3.2.1 Nitric Acid and High Density Acid

3.3.2.2 Nitrogen Tetroxide and Mixed Oxides of Nitrogen

3.3.1 GENERAL

This section is concerned with the storage of the nitric acid and nitrogen tetroxide oxidizers in ground based facilities. Flight vehicle applications may require in depth study of a particular oxidizer and tank material.

3.3.2 STORAGE PROCEDURES

3.3.2.1 Nitric Acid and High Density Acid

Nitric acid must be stored in fixed or mobile drums or tanks of approved design, materials and construction. Storage, transfer and test areas must be kept neat and free from combustibles. All leaks and spills must be flushed away at once with large amounts of water. These areas must be frequently inspected. An adequate water supply must be available for firefighting, flushing, decontamination, personnel showers and eye baths. Cold-water eye baths and approved safety-type personnel showers must be properly located for immediate use in an emergency.

The important factors to be considered in site selection for main and ready storage are:

a. Quantity of nitric acid to be stored

b. Type of container

c. Distance to nearest inhabited areas

d. Intraline distance to other propellant storage areas.

The whole system and acid-storage area shall be built on a covered concrete base and shall have an adequate drainage and decontaminating system. The system shall be surrounded by an earthen or concrete dike of sufficient height to contain 110 percent of the maximum amount of acid stored at the installation.

For each storage and transfer installation, a complete drainage system flowing to a decontamination pit containing limestone or similar neutralizing agent shall be provided.

At least two access roads to transfer and storage sites shall be provided. Roads should be wide enough to provide adequate space for turning. Pavement in the vicinity of potential spills should be concrete.

All tanks, containers, and handling areas shall be separated with due regard to the minimum safe distance established by Department of Defense regulations. The total TNT equivalents must be used if the facility design does not include positive measures to prevent mixing of fuel and oxidizer.

All buildings in the main storage area shall be of fireproof construction, using materials not readily affected by nitric acids or their fumes. Shade, ventilation and weather protection shall be provided for storage tanks and transfer systems under open-sided, steel-frame buildings with sloped roofs of corrugated asbestos or aluminum. Because they reflect the sun best, aluminum roofs are preferred. The base of the building shall be of concrete with a resin protective covering. The structural framework of all other buildings in the area shall be steel or masonry, free of wood. The siding shall consist of brick, plaster, tile, corrugated sheet asbestos, aluminum or asbestos shingles. Conventional petroleum-based roofing material is prohibited. Wooden or rubberized floors are prohibited. It is recommended that the floors be made of concrete covered with a resin protective coating (Epoxy, MIL-P-22808A).

All electrical lines and wires shall be installed in rigid metal conduits, and all electrical controls, junction boxes and panels shall be vaporproof and weatherproof. A master switch that will shut off all power in the handling and storage area shall be provided for emergencies. It shall be located in an accessible spot outside the acid area and an appropriate weatherproof sign shall be mounted over it to indicate its function.

Nitric acid shall always be handled in well-ventilated areas to keep excessive concentrations of fumes from accumulating. If natural ventilation is impossible or inadequate, mechanical ventilation should be provided. If the location of the acid storage site does not allow venting the oxides of nitrogen to the atmosphere, then an efficient fume-scrubbing system shall be provided.

An alarm and detection instrument should be provided to warn personnel operating indoors when the concentration of nitrogen dioxide in the air reaches the threshold limit value. All packing gland seals around shafts on pumps, valves, etc., shall be protected by shields to prevent acid from spraying on operators in case of seal failure.

Because fuming nitric acid reacts readily with organic matter, good housekeeping is essential. The acid storage and transfer site shall be kept free of any materials other than those recommended for use with fuming nitric acids.

Local requirements will determine the size and number of containers which can be stored at one site. Approved 11,000-gallon aluminum tank units are most acceptable for permanent storage; acid deliveries by tank car will be approximately 8,000 gallons, and it is mandatory that sufficient space be available to receive the shipment. The horizontal type tank is acceptable for this service.

Nitric acid may be shipped in 55-gallon aluminum drums with a single bung opening on the side, but other containers of convenient size are also used. If proper precautions are taken, drums may be used for storing acid. The drums should be stored, with the bung side up, on a concrete base with a shed-type roof provided to protect them from the direct rays of the sun.

Nitric acid may be transported and stored in specially constructed semitrailers or trucks of various types and capacities. These units shall have transfer equipment, vents and pressure-relief devices, and instrumentation. The trucks should be equipped with a water system for safety showers.

The proposed storage site should be reasonably level. Since one 11,000-gallon tank full of acid weighs approximately 75 tons, soil charateristics must be considered to ensure proper footings for the storage installation. Nitric acid should be stored according to DOD quantity-distance requirements and the requirements of the user.

The design of run tankage will be similar to that of main storage. The requirements for tanks, access roads, building construction, drainage, electrical equipment, and quantity-distance separation are given herein.

Use a written operating procedure with a check list. Use care when connecting or disconnecting transfer lines to avoid body contact. Immediately flush small spills with hand lines (small hose). At all times, the valve for the small hose shall be cracked and a small flow of water visible upon casual observation by the operators of the transfer equipment.

A fire hose station shall be nearby for controlling gross spillage and/or in case of catastrophic tank failure.

3.3.2.2 Nitrogen Tetroxide and Mixed Oxides of Nitrogen

The important factors to be considered in site selection for main and ready storage are:

a. Quantity of nitrogen tetroxide or mixed oxides of nitrogen to be stored
b. Type of container
c. Distance to nearest inhabited areas
d. Intraline distance to other propellant storage areas.

A complete drainage system, with gravity flow to a disposal pit or emergency sump, shall be provided at each storage and transfer facility.

At least two access roads to transfer and storage sites shall be provided. Roads should be wide enough to give adequate space for turning. Pavement in the vicinity of potential spills should be concrete.

In the main and ready storage areas, each tank, or group of tanks, shall be on concrete pads which drain to the disposal area, and are surrounded by a concrete dike high enough to contain 110 percent of the storage capacity.

Local user requirements will determine the size and number of storage vessels.

All tanks, containers, and handling areas shall be separated with due regard to the minimum safe distance established by the Department of Defense regulations. The total TNT equivalents must be used if the facility design does not include positive measures to prevent mixing of propellants and oxidizers.

All buildings for storage or transfer shall be of fireproof construction. They should be the open-side type with steel framework and sloped roofs of corrugated asbestos or aluminum. Because they reflect the sun better, aluminum roofs are preferred. Shade, ventilation and weather protection should be provided by the buildings.

All electrical lines, wires and equipment shall be installed with due regard for the oxidizing and corrosive properties of N_2O_4 and mixed oxides of nitrogen in the presence of moisture.

If natural ventilation is impossible or inadequate, all storage and transfer structures shall be equipped with mechanical ventilating systems.

The normal safety precautions applicable to handling any toxic material should be strictly observed. Storage, transfer and test areas must be kept neat and free from combustibles and must be frequently inspected. In general, the precautions taken in handling liquid N_2O_4 and mixed oxides of nitrogen are very similar to those for fuming nitric acid (paragraph 3.3.2.1).

A detection and alarm instrument (see Section 4.2.3.2) should be provided to warn personnel operating indoors when the concentration of N_2O_4 (NO_2 is the agent detected) or mixed oxides of nitrogen (NO is the agent detected) in the air reaches the threshold limit value. If the location of the storage site does not allow the oxides of nitrogen to be vented to the atmosphere, an efficient fume-scrubbing system shall be provided. All tanks shall be provided with a vapor pressure-relief valve of adequate size set at a safe working pressure which will be determined by the design of the tank.

All packing gland seals around shafts on pumps, valves, etc., should be protected by shields to prevent the product from spraying on operators in case of failure.

Adequate water shall be provided for flushing, showers and eye baths. An adequate water supply must be available for flushing or decontamination of leaks or spills.

The 11,000-gallon aluminum tank units are most acceptable for permanent storage of N_2O_4, since tank cars will deliver approximately 8,000 to 10,000 gallons of N_2O_4. The horizontal-type tank is acceptable for this service. Cylinders of N_2O_4 and mixed oxides of nitrogen shall be stored in facilities constructed in accordance with this Section. There shall be provision for handling the larger cylinders of N_2O_4 mechanically.

When the tanks are so located that it is impossible to vent to the atmosphere, vent lines of adequate size shall be provided on the downstream side of the pressure-relief equipment, discharging into a fume-scrubbing system. Venting of tanks to the atmosphere should be done through a steel vent stack, located away from the working area and discharging at least 50 feet above the highest operating level.

The design of run tankage will be similar to that of main storage. The requirements for tanks, access roads, building construction, drainage, electrical equipment, and quantity-distance separation are given herein.

Use a written operating procedure with a check list. Use care when connecting or disconnecting transfer lines to avoid body contact. Immediately flush small spills with hand lines (small hose). At all times, the valve for the small hose shall be cracked and a small flow of water visible.

A fire hose station shall be nearby for controlling gross spillage and/or in case of catastrophic tank failure.

3.4 COMPATIBILITY OF MATERIALS

3.4 COMPATIBILITY OF MATERIALS

3.4.1 GENFRAL

3.4.1.1 Introduction

The selection of materials for use in contact with nitric acid and nitrogen tetroxide oxidizers is determined both by the effect of the propellant on the materials, and by the effect of the material on the propellant. Determination of the proper materials for use with propellants is based initially on a series of materials compatibility tests. The tests may range from an evaluation of a material sample under a set of general test conditions, to the definition of the specific limitations of various assemblies containing a number of different materials. The compatibility of materials with a propellant is usually based primarily on the material's corrosion rate.

The effect of a propellant on materials has been generally classified as the materials compatibility of the propellant. Because compatibility is often a function of temperature, propellant contamination, prior materials preparation (cleaning, passivation, etc.) surface area, the material's physical state (stressed, unstressed, welded, heat treated, etc.), plus other variables, all of these factors must be considered

3.4.1.2 Caution

The user of this Handbook should be cautioned that the materials compatibility data presented herein should only serve as a basis for selection of materials. Careful consideration should be given to the conditions of testing; the use of the material under a different set of conditions may have an entirely different effect. Materials not suitable for use at high temperatures may be acceptable for uses at low temperatures. Different fabrication procedures and passivation techniques may result in variation in compatibility classification. Even different lots of the same parts fabricated from "compatible" materials by the same manufacturer using the same manufacturing technique have revealed variations in compatibility. Thus, it must be emphasized that any material must be thoroughly tested and qualified under the conditions of its intended use before it is placed in service.

3.4.1.3 Content

This subsection contains tables of compatibility ratings based on the rating schemes shown in Section 3.4.1.4. Also included are tables of compatibility data which were presented in terms other than the standard ratings.

The first set of tables deals with nitric acid.

The next set of tables contain data for high density acid and the third set of tables contain data on the nitrogen tetroxide oxidizers.

This subsection presents reported compatibility ratings, and data on corrosion rates and volume and weight changes for metals and nonmetals. The specific materials, temperature conditions, test duration, and other parameters are presented in a series of tables for the various propellant groupings.

Compatibility of metals is usually reported in terms of corrosion rate in mils/year. The compatibility ratings presented are based primarily on these data.

Some of the tables present weight-loss data. Since it is impossible to convert weight-loss of metal samples to corrosion rates without knowledge of the sample sizes, no ratings are applied. The ratings for non-metals are based on volume swelling and hardness changes. Non-metals are included in the tables, along with the metals.

3.4.1.4 Compatibility Rating Schemes and Criteria

The compatibility classification scheme adopted in this Handbook for materials is based on the rating schemes recommended by the oxidizer users in their reports and handbooks. The several sources which used similar rating schemes were in essential agreement on the metals. There is a greater degree of uncertainty with the non-metals, where some sources classified materials purely on a subjective or qualitative basis, and others, on a semi-quanitative basis. The rating scheme to be used is shown in each table of compatibility data.

3.4 1.5 Usage Limitations and Special Provisions

The oxidizers vary widely in quantity of data available for them. The most extensive testing has been performed on nitrogen tetroxide, so this data is readily available and is included here. Representative data is shown for nitric acid and HDA. In all applications, the reader is advised to test the specific material in the specific oxidizer with the specific inhibitor at the highest design temperatures before determining the suitability of any material. These tables are a guide to screen out unsuitable materials and suggest potentially suitable materials.

3.4.2 MATERIALS COMPATIBILITY OF NITRIC ACID

The corrosion resistance of materials with nitric acids has been investigated extensively. The data compiled in Table 3.4-1 are specifically for red fuming nitric acid (RFNA) and inhibited red fuming nitric acid (IRFNA).

When data was found in more than one reference, the earliest or most original source is cited in the reference list (Section 3.5). In some cases the earliest obtainable source could not be located. In these cases, the earliest obtainable source was cited.

The data cited is for Type III and IIIA nitric acid (6 and 9) but is equally applicable to the Type IIIB and IIILS nitric acids. The Type IIIB has reduced solids to prevent formation of sludges and the IIILS was a further step to reduce the corrosiveness of the oxidizer by reducing the water content. See Reference 10.

A materials compatibility study was performed by the Naval Weapons Center Liquid Gun Program for 90% nitric acid (48). The tests that were conducted are classified as screening tests and are somewhat qualitative. The composition of the nitric acid used in this study is defined in Section 2.1. Data obtained from the test is shown in Table 3.4-2.

TABLE 3.4-1 COMPATIBILITY OF MATERIALS WITH RED FUMING NITRIC ACID AND INHIBITED RED FUMING NITRIC ACID (Reference 11)

	Temperature Limits (°F)							
	RFNA (Type III)				IRFNA (Type IIIA)			
Materials	Class 1	Class 2	Class 3	Class 4	Class 1	Class 2	Class 3	Class 4
Type 301 Stainless Steel	80			122				
Type 302 Stainless Steel	80	125	130	212		130	160	
Type 303 Stainless Steel				130		130	160	
Type 304 Stainless Steel	80		130	160		130	160	
Type 304 ELC Stainless Steel	80		130	160				
Type 309 Stainless Steel	80		122	160				
Type 310 Stainless Steel	80		122	160				
Type 316 Stainless Steel	80			120				
Type 316 ELC Stainless Steel	80							
Type 318 Stainless Steel	80			160				
Type 321 Stainless Steel	80		130	130		130	160	
Type 322 Stainless Steel	80							
Type 347 Stainless Steel	80		130	130		130		
Type 410 Stainless Steel				130			130	
Type 414 Stainless Steel		80		250				
Type 416 Stainless Steel				250				
Type 420 Stainless Steel								
Type 430 Stainless Steel	80	130		160		130		
Type 440 Stainless Steel			130					
Type 446 Stainless Steel		130					130	
Worthite	80	125		250				
Carpenter 20	80	125						
Aloyco 20	80	125						
Durimet 20	80	125		300				
17-7PH Annealed, 1900F			130	130		130		
17-7PH Hardened				130		130		
19-9DL				130	130			

TABLE 3.4-1 (Continued)

Materials	Temperature Limits (°F)							
	RFNA (Type III)				IRFNA (Type IIIA)			
	Class 1	Class 2	Class 3	Class 4	Class 1	Class 2	Class 3	Class 4
19-9DX			130	130		130		
Mild Steel			75					
1020 Steel				120				130
Cast Iron								
Duriron		75	300					
Ni-Resist				75				
4130				130				130
Aluminum:								
1060	80		160					
1100		80	150		130			
2014		100	130	160	130			
2017		100	130	250	130			
2024	80		150	250	130			
3003		80	150					
3004		80						
4043		80	160					
5052		80	160	160				
6061		80	160	160	130			
6063		80	160	160				
7075		80	130	160	130			
43		80		160				
		80						
214			80					
355		80						
356		80	130	160	130			
Inconel			75	130				
Illium G	125	125		175				
Hastelloy B				75				
Hastelloy C	75		75	300				
A. Nickel			130	75			130	
Monel				75				
Invar				75				
Copper								All
Sn Bronze								All
Al Bronze								All
Si Bronze								All
Yellow Brass								All
Red Brass								All
Chromium	80	130		250				
Stellite No. 1	80			250				
Stellite No. 6	80			250				
Haynes 25		160						
Gold	80	250	300					
Platinum	300	300						

Compatibility Classification (Ref. 11)*

---

*The classification of a material is based on the lowest rating of any one of the three properties.

Class 1 materials are those which exhibit a corrosion rate of less than 1 mil/yr. The material does not promote decomposition and is free from impact sensitivity.

Class 2 materials are similar to those in Class 1, except that the corrosion rate may be as great as 5 mils/yr.

Class 3 material shows only fair corrosion resistance. Rates of attack may be of the order of 5 to 50 mils/yr. The materials also may cause a moderate breakdown of the propellant but is not shock-sensitive under conditions likely to be encountered in service.

Class 4 materials that are not considered useable for containing the propellant have corrosion rates greater than 50 mils/yr, cause extensive decomposition of the propellant, cause spontaneous ignition, or react on impact.

Class	Corrosion Resistance		Decomposition of Propellant	Shock Sensitive
	Rating	Penetration Rate, mils/yr		
1	Excellent	<1	No	No
2	Good	<5	No	No
3	Fair	5 to 50	Some	No
4	Poor	>50	Extensive	Yes

TABLE 3.4-2 METAL STRIP/90% NITRIC ACID STORAGE TEST DATA AT 20 ± 5°C (48)

Sample No.	Metal	Storage Time (days)/Corrosion (Mils/year)				Comments
1	Nitronic 60 S.S.	35/0.57	76/0.56	124/0.54	200/0.49	White layer on metal surface. White residue in HNO_3.
2	304 S.S.	35/0.18	76/0.20	124/0.19	200/0.20	Ultra clean surface on immersed section. White residue in liquid.
3	5052-H Al	35/0	76/0	124/<0.1	200/<0.1	Whitish film on surface in liquid phase.
4	7075-0 Al	35/0	76/0	124/<0.1	200/<0.1	Whitish film on surface in liquid phase.
5	6061-T6 Al	10/0	51/0	99/<0.1	175/<0.1	Whitish film on surface in liquid phase.
6	Ti Alloy NA2-7128	10/31				Acid turned deep yellow. Large quantity of white residue in acid.
7	17-4 PH S.S.	27/0.36	75/0.27	151/0.19		Surface in liquid appeared duller than original. White residue in HNO_3.
8	316 S.S.	27/0.26	75/0.18	151/0.18		Surface in liquid appeared duller than original. White residue in HNO_3.
9	1100-0 Al	27/0	75/<0.1	151/<0.1		Surface in liquid had whitish film.
10	Ti Alloy 6 Al 4V	27/31				Large quantity of yellow residue in liquid. Metal surface turned dark gray and appeared spongy.

TABLE 3.4-2 ELASTOMER/90% NITRIC ACID STORAGE TEST DATA AT 25 ± 5°C (48)

Material	% Weight Gain/% Swell						
	22 days	34 days	70 days	75 days	123 days	259 days	312 days
Haskel Viton 9009-75 (O-ring)	32/19^a						
Parker Vitron V747-75 (O-ring)	22/6		27/8			42/11	
DuPont 1050 (strip)		8/3^b		13/6	18/9		41/19
DuPont 1061 (strip)		4/3^c		9/4	14/5		37/16

^{a}Nitric acid turned deep yellow. O-ring became flabby and much weaker.

^{b}No change. Unwetted by nitric acid.

^{c}Wetted by nitric acid. Surface of sample became rough and leathery after several weeks.

3.4.3 MATERIALS COMPATIBILITY OF HIGH DENSITY ACIDS

Bell Aerospace Company (12) in conjunction with the Lockheed Missiles and Space Company, has developed a more energetic oxidizer for the AGENA rocket engine. The new oxidizer is a blend of nitric acid and nitrogen tetroxide in proportions chosen to assure optimum density impulse. The blend is referred to as High Density Acid, or HDA. Because it contains a relatively large amount of (ca. 44 wt%) of nitrogen tetroxide, the blend possesses unique properties. Because the blend contains a relatively large amount (ca. 55 wt%) of nitric acid, it is quite corrosive and requires special care in selection of materials for propulsion system components. Hydrofluoric acid is normally added to reduce the corrosiveness of HDA.

Tables 3.4-3 through 3.4-6 from reference (7) present the results of corrosion tests performed with HDA (Type IV Nitric Acid from MIL-P-7254F).

TABLE 3.4-3 COMPATIBILITY CLASSIFICATION OF MATERIALS WITH ROCKET PROPELLANTS

The classification of a material is based on the lowest rating of any of the properties.

Compatibility Classification of Non-Metals				
Class	I	II	III	IV
Volume Change in Percent	0 to + 25	-10 to +25	-10 to +25	<-10 or >+25
Durometer Reading	± 3	± 10	± 10	<-10 or>+10
Effect on Propellant	None	Slight Change	Moderate Change	Severe
Visual Examination	No Change	Slight Change	Moderate Change	Severely Blistered, Cracked or Dissolved
General Usage	Satisfactory, General Use	Satisfactory for Repeated Short-Term-Use	Satisfactory for Short-Term Use	Unsatisfactory

Compatibility Classification of Metals				
Class	I	II	III	IV
Rating	Excellent	Good	Fair	Poor
Corrosion Rate in Mils/Year	<1	<5	5 to 50	>50
Decomposition of Propellant	No	No	Some	Extensive
Shock Sensitivity	No	No	No	Yes

TABLE 3.4-4 COMPATIBILITY OF VARIOUS NON-METALS WITH HDA

Material	Time	Temp °F	Changes in Acid			Changes in Material				Rating
			Physical Appearance	Composition	Others	Physical Appearance	Wt. %	Vol. %	Hardness	
EP Rubber	1 hour	70	None	–	–	Losing Carbon	–	–	–	II
	16 Hours	70	Discolored	–	Black Particles	Tacky, Inelastic, Deformed	–	–	–	IV
Teflon-TFE	3 Days After Outgas	70	None	-1% NO_2	IR Neg. for Halocarbon	Tan Lt. Tan	1.1 0.3	1.0 0.2	-21 ShoreD -18 Units	IV IV
	7 Days After Outgas	70	None	-2% NO_2	IR Neg. for Halocarbon	Tan Lt. Tan	1.4 0.5	1.5 0.4	-23 -17	IV IV
	3 Days After Outgas	100	None	-3% NO_2	IR Neg. for Halocarbon	Tan Lt. Tan	1.4 0.6	1.7 0.4	-22 -18	IV IV
Kel-F 5500	3 Days After Outgas	70	None	-1% NO_2	IR Neg. for Halocarbon	Tan Lt. Tan	0.1 <0.1	0.1 <0.1	24 19	IV IV
	7 Days After Outgas	70	None	-2% NO_2	IR Neg. for Halocarbon	Tan Lt. Tan	0.1 <0.1	<0.1 <0.1	20 15	IV IV
	3 Days After Outgas	100	None	-3% NO_2	IR Neg. for Halocarbon	Tan Lt. Tan	0.1 <0.1	0.2 0.1	18 15	IV IV
Rulon LD	7 Days	120	OK	–	0.8 mg. Particulate /1.	Color Change Red to Grey	2.9	7.3	-2	II
Rulon 123	7 Days	120	OK	–	0.3 mg. Particulate /1.	Surface Change Smooth to Rough	7.6	9.0	-6	II
Kel-F 81	7 Days	120	OK	–	0.1 mg. Particulate /1.	Color Change White to Amber	1.1	1.5	-0	II

TABLE 3.4-5 COMPATIBILITY OF VARIOUS METALS WITH HDA

Material	Time (Days)	Temp °F	S/V -1 in.	PA Metal		CR-mpy		PA Acid	Rating
				Vap.	Liq.	Vap.	Liq.		
5086	7	120	1.0	NE*	NE	0.1	0.1	OK	I
W5086	7	120	1.0	NE	NE	<0.1	0.2	OK	I
5454-H32	7	120	1.0	NE	NE	<0.1	0.1	Clear	I
W5454-H32	7	120	1.0	NE	NE	<0.1	<0.1	Clear	I
5454-0	7	120	1.0	NE	NE	<0.1	0.3	OK	I
6061-T6	7	120	1.0	Discolored	NE	<0.1	<0.1	Clear	I
W6061	7	120	1.0	Discolored	NE	<0.1	0.2	Clear	I
Nituff on 6061	7	120	1.0	–	Irridescent	–	–	OK	II
C6061-T6	7	120	1.0	Anodize	Anodize	0.1	3.6	Clear	II
(H_2SO_4 Anodize)			(total)	OK Except for wCP in Crevice	OK Except for wCP in Crevice				
304L				NE	NE	0.6	0.5		I
Beryllium	7	120	0.4	–	CP**	–	1.9	OK	II
Hafnium Diboride	7	120	1.0	–	CP	–	59.5	P	IV
Platinum Cobalt Alloy	7	120	10.0	–	Discolored Blue-Black	–	0.8	Clear	I
Tantalum	7	120	1.0	–	Dissolved	–	–	Clear	IV
Tungsten	2	120	1.1	–	Etched	–	647	>P	IV
Tungsten Carbide	7	120	1.0	–	CP	–	1110	P	IV
Cb-1-Zr	6	120	0.8	–	Pits CP	–	98.1	>P	IV
SCb-291	7	120	0.6	–	Pits CP	–	132	Cloudy	IV
Cb 103/A505	7	120	0.7	–	Pits CP	–	72	Clear	IV
SCb 291/R508C	2	120	1.6	–	CP	–	773	>P	IV
Carpenter-20	7	120	0.1	–	Discolored	–	3.4	Clear	II
Nickel	6	120	0.7	–	NE	–	190	Discolored	IV
Haynes Star J	7	120	1.0	–	Severe Etch	–	32.6	Discolored	III
Haynes 25 Bar Stock	7	120	0.6	–	Etched	–	3.3	Discolored	
Haynes 25 Screen	7	120	1.0	–	NE	–	3.8	Clear	II
C Haynes-25/ 304L	7	120	1.0 (total)	– –	NE NE	– –	1.0 2.1	Clear	II II
MP 35N	4	120	0.4	–	NE	–	5.4	Clear	III
Multimet	7	120	1.0	–	CP	–	5.2	>P	III
17-7 PH Torsion Tube	7	120	1.0	–	wCP in capillary	–	4.4	Clear	II
17-7 PH RH 950	7	120	1.0	wCP Etched	wCP Etched	0.7	2.5	Clear	II
17-7 PH RH 1050	7	120	1.0	wCP Etched	wCP Etched	0.7	3.0	Clear	II
A1 on High-Strength Steel	7	120	0.5	–	NE	–	0.5	Clear	I

TABLE 3.4-5 (Cont.)

Material	Time (Days)	Temp °F	S/V -1 in.	PA Metal		CR-mpy		PA Acid	Rating
				Vap.	Liq.	Vap.	Liq.		
356 – Hard Coated	6	120	–	--	NE	–	1.8	Clear	II
C356-T6/ 304	7	120	1.0 (total)	wCP in Crevice	wCP in Crevice	1.9 5.1	3.4 1.9	Clea	II
C356-T6/ 304L	7	120	1.0 (total)	wCP in Crevice	wCP in Crevice	3.4 2.4	2.4 0.6	>P	II
2021	7	120	1.0	–	NE	–	<0.1	Clear	I
W2021	7	120	1.0	–	NE	–	0.1	Clear	I
2219	7	120	1.0	–	NE	–	<0.1	Clear	I
W2219	7	120	1.0	–	NE	–	<0.1	Clear	I
5083	7	120	1.0	–	NE	–	<0.1	Clear	I
W5083	7	120	1.0	–	NE	–	<0.1	Clear	I
SAE-52100 Not Hardened	4	120	0.2	–	Discolored	–	1.7	Clear	II
440C Not Hardened	7	120	0.5	–	CP	--	4.8	Clear	II
440C Rockwell C58	7	120	1.0	Pits CP	Pits CP	1.6	4.3	Clear	III
440C Cr Plated	7	120	1.0	–	Plating Flaking	–	--	Clear	IV
AM350 Bellows	7	120	1.4	–	CP	–	1.8	Clear	II
W347/AM350	7	120	1.0	–	wCP Welds Etched	--	3.1	>P	III
E-Brite 26-1	7	120	1.3	Pits Discolored	NE	4.2	3.1	Clear	III
Armco 21-6-9	7	120	1.0	Lt.gn CP	Lt.gn CP	0.5	2.2	>P	III
W302/304	7	120	1.0	–	302 Etched	--	4.4 (total)	Clear	II
304L	7	120	1.0	– NE	NE –	– 0.6	1.1 –	Clear P	II II
316 ELC	7	120	1.0	Gray Stains	Lt.gn CP	0.6	2.5	Clear	II
347 Sheet	7	120	1.0	Discolored	Pits Discolored	0.5	3.4	P	III
347 Full Hard	7	120	1.0	NE	NE	0.5	2.3	>P	III
W347 Sheet	7	120	1.0	Discolored	Discolored	0.8	3.4	>P	III
W347 Bellows	6	120	1.3	–	Pits Discolored	–	2.4	P	III
Worthite	7	120	0.5	–	Etched	–	2.0	Clear	II
C347/ Cr Plt'd Worthite	7	120	1.0 (total)	–	Etched NE	– –	2.4 <0.1	Clear –	II I

*NE = No Noticeable Effect
**CP = Corrosion Product

TABLE 3.4-6 HDA CORROSION INHIBITOR COMPARISONS (13)

Inhibitors at 0.6-0.8 wt.%

7 Days, 120°F S/V - 1.0 in^{-1}

Material	Rating		
	HF	PF_6	AHP*
440C	III	IV	III
AM350 - Bellows	II	I	I
304L - Condition A	I	I	I
304L - Condition B	II	I	I
316 Stainless Steel	II	I	I
347 Stainless Steel	III	I	I
347 TIG Welded	III	I	I
17.7 PH RH 950 - Torque Tube	II	I	I
17.7 PH RH 1050	II	II	II
Armco 21-6-9	III	I	I
6061 T6 Aluminum	I	I	I
356 - T6 Aluminum	II	II	II
Kel-F 81	II	II	II

* - AHP = Ammonium hexafluorsphosphate

3.4.4 MATERIALS COMPATIBILITY OF NITROGEN TETROXIDE

The compatibility of materials with the nitrogen tetroxide oxidizer family has been studied extensively because of the many applications of this oxidizer in the Aerospace industry. The compatibility results presented here were developed for the nitrogen tetroxides known as NTO (red-brown), MON-1 (green) and Minuteman Grade. Some testing is available on MON-3 (14 and 15). This was included where available. In general, mixed oxides of nitrogen, MON-10 and MON-25, are less corrosive than the NTO/MON-1 series. See section 2.3.2.3 for a definition of the types of N_2O_4.

The compatibility of both metals and non-metals with N_2O_4 is summarized in Table 3.4-7 from Reference 16 as determined by interpreting available compatibility information. Specific references used are listed in the table. Compatibility of a material with N_2O_4 was based primarily on the criteria that the material be essentially unaffected by N_2O_4 exposure (negligible corrosion for metals and negligible loss of physical properties for non-metals). However, also taken into consideration was the potential for formation of clogging agents when exposed to N_2O_4. This was a prime consideration for iron-based metals since the data indicate serious flow decay problems can occur with N_2O_4/ferric metal systems (see Section 3.4.5). In some instances, two compatibility ratings were assigned to the same material due to conflicting data. Also, where compatibility was determined for a specific form of N_2O_4 or for a specific use with N_2O_4, this is indicated in the remarks section of the table.

TABLE 3.4-7 N_2O_4 SUMMARY COMPATIBILITY CHART

Materials	Rating					References	Remarks
	1	2	3	4	5		
Metals							
1) Aluminums							
a. Aluminum alloys, in general		A,B				19,20,21,22,23,24,25,26,27	H_2O content must be limited. Ratings based on dry N_2O_4 (<0.1% H_2O). Also flow decay problems may exist. Use of high temperatures (>160°F) is also not recommended.
b. 1100		A				19,20,23	
c. 2014		A				20,23,24,29,31,32	
d. 2021			A			30	
e. 2024		A				22,29,32	
f. 2219		A				20,23,29,30	
g. 3003	A					19,22,32	
h. 5052	A					19,22,32	
i. 6061		A	A			19,20,23,29,32	Conflicting data
j. 7075		A				19,22,23,29	
k. 356		A				19,23,28	
l. Anodized aluminum alloys	A,B					32	
2) Steels							
a. Steels in general			A,B			20,25,26,28,29,30 32,33,34,35	Practically all steels are incompatible at high temperatures (>200°F). Severe iron adduct problems are usually encountered. H_2O also increases corrosion.
b. Stainless steels in general			A,B				Earlier summaries listed stainless steels as compatible. However, later studies indicate doubtful compatibility due to iron adduct problem, except as noted.
c. 300 series in general			A,B			20,25,26,32,34,35	
d. 301 cryoformed			A,B			20,25,26,33,34,35	
e. 304			A,B			20,25,26,33,34	
f. 316			A,B			20,25,26,35	
g. 321			A,B			20,25,26,35	
h. 347			A,B			20,25,26,33,35	
i. 400 series in general		A,B				21,28,32	
j. 410		A				28,30	
k. 416		A				28	
l. 430		A				28,32	
m. 440C		A	A			28	Conflicting data
n. A-286			A			20,33	
o. AM350 or AM355			B			20,25,35	
p. 17-4PH or 17-7PH			A			20	
q. 1018 or 1020 steels			A,B			25,29,35	
r. 19-9DL		A				28	
s. Maraging steels			A			20	
t. Carpenter 20Cb		A				20	
u. HY-140 steel		A				32	

TABLE 3.4-7 (Cont.)

Materials	Rating					References	Remarks
	1	2	3	4	5		
3) Titaniums							
a. Titanium alloys in general	A,B					19,20,21,23,25,36,37, 31,32	Some shock sensitivity reported
b. 6Al-4V	A					19,20,23,25,31	All titanium alloys subject to stress corrosion in Mil Spec. (NTO) N_2O_4. Ratings based only on NASA Spec. N_2O_4.
c. 5Al-2.5Sn	A					35	
d. 75A	A					19	
e. 65A		A				19	
f. B12OVCA	A					23	
g. Pure	A					20	
h. 8Al-1Mo	A					32	
4) Miscellaneous Metals							
a. Beryllium	A					32	
b. Columbium	A					32	
c. Tantalum	A					19,32	
d. Tungsten	A					32	
e. TZM-alloy			A			32	
f. L-605 Cobalt Alloy			A			32	
g. Nickel (pure)				A		20	
h. Magnesium alloys				A		22,28	
i. Zinc				A		19	
j. Copper				A		19,22	
k. Brass				A		19	
l. Bronze				A		19	
m. Tin		A				19	
n. Inconel		A	B			20,22,32	Conflicting data
o. Pure Molybdenum				A		28	
p. Hastelloy alloys			A			20,28,33	
q. Kovar metal				A		28	
r. Pure lead				A		20	
s. Monel			B			20,32	
t. Gold		A				19	
u. Platinum		A				19	
v. Silver				A		19	
w. Zirconium				A		19	
x. Pure iron				B		20,25,26,32,35	
y. Chromium			A			32	
Non-Metals							
1) Polymerics							Rated for general use (no specific application except as noted).
a. FEP Teflon		A	A			19,20,21,38,39 22,23	Teflon is highly permeable. FEP 9511 probable, FEP 120 doubtful.
b. TFE Teflon		A				19,20,21,22,38,39 23,40	Teflon is highly permeable.
c. Kel-F				A		19,21,22,23,38	
d. Polyethelene				A		19,21,22,23,38	
e. Polypropylene				A		19,22,38	
f. Nylon				A		19,22,38	
g. Mylar				A		19,22,38	
h. Saran		A				19,22,38	
i. Kynar				A		19,22,23,38	
j. Lexan				A		19,22,38	
k. Plexiglas				A		19,22,38	
l. Isobutylene copolymers				A		19,22,38	
m. EPR rubbers				A		19,20,22,23,38	

TABLE 3.4-7 (Cont.)

Materials	Rating					References	Remarks
	1	2	3	4	5		
n. Butyl rubbers				A		19,20,22,23,38	
o. Fluro-rubbers				A		19,22,38	
p. Silicone rubbers				A		19,22,23,38	
q. Buna N				A		19,22,38	
r. Neoprene				A		19,22,38	
s. Natural rubbers				A		19,22,23,38	
t. Polyurethanes				A		19,22,38	
u. Rulon (PTFE)		A				28	
v. Fluon-fluorinated hydrocarbon		A				40	
w. Carboxy nitroso rubber (CNR)		A				41,42	
2) Lubricants							
a. Graphite		A				19,22,38	
b. Fluorolube		A				19,22,38	
c. Halocarbon grease				A		19,22,38	
d. Kel-F grease			A			28	
e. LOX safe		A				19,22,38	
f. Molykote Z		A				19,22,38	
3) Miscellaneous Non-Metals							
a. Epon resins				A		19,22,38	
b. RTV silicones				A		19,22,38	
c. Polyesters				A		19,22,38	
d. Most ceramics				A		19,22,38	
e. Al_2O_3	A					28,32	
f. Beryllium oxide	A					32	
g. Carbon		B				19,22,38	
h. Asbestos		A				19,22,38	

1 - Compatible
2 - Probable Compatibility
3 - Doubtful Compatibility
4 - Incompatible
5 - Unable to Rate

A - Rating based on data on the specific material with the specific propellant.
B - Rating based on data on a similar or sister material with the specific propellant.
C - Rating based on data on the specific material but with a sister propellant.
D - No specific data.

The Bell Aerosystems N_2O_4 compatibility tests (17) were run to determine the reliability of rocket propulsion materials used to store N_2O_4 under the influence of both high temperature and applied stress. Two test phases were conducted: the first phase used Military Specification Grade or "brown" N_2O_4 while the second phase was NO inhibited N_2O_4 similar to NASA Specification Grade (18) or "green" N_2O_4. In each case, the N_2O_4 was dry (H_2O 0.1%).

Only stainless steels were tested in the initial phase. The test specimens consisted of bars constructed of various stainless steels:

A286/A286 Welded with Hastelloy W
A-286 Parent Metal
A-286/347 Welded with Hastelloy W
304L/304L Meltdown Weld
347/304L Meltdown Weld
Cryoformed 301 Stainless Steel
A286/347 Meltdown Weld

Testing was accomplished by immersion in 150°F liquid N_2O_4 while stressed in bending to 25% of yield strength. The containers were constructed of 300-series stainless steel. After two months of testing, discoloration and intergranular corrosion occurred with all of the test bars. In particular, the welded A286 specimens cracked in the weld heat affected zones and the Hastelloy W weldments suffered from severe intergranular corrosion.

After four months of testing, severe blackening and sludging (build up of sludge like material) of the specimens occurred. Although the intergranular attack did not deepen, penetrations became more numerous. Also, the cryoformed 301 samples developed cracks on the tension side. Propellant analysis showed that the dissolved O_2 content had decreased during testing. On the basis of this fact and the other results obtained, Bell came to the following conclusions concerning storage of Military Specification Grade N_2O_4 with stainless steels.

1. MIL-P-26539B (oxygenated) nitrogen tetroxide is not suitable for long term (greater than four months) storage in types 347 and A286 stainless steel thin walled containers (0.030-in. or less);
2. Type A286 stainless steel with a nitric-hydrofloric pickled surface is more susceptible to intergranular corrosive attack by oxygenated nitrogen tetroxide than a nitric acid passivated surface. This attack is accelerated by applied stress and can cause a fracture;
3. The cryoformed 301 stainless steel is susceptible to surface cracking in oxygenated N_2O_4, when stressed;
4. Hastelloy W weldments are more susceptible to corrosion in oxygenated nitrogen tetroxide than meltdown welds.

For the second phase, approximately 0.2 to 0.4% NO inhibitor was added to MIL-P-26539B Specification N_2O_4 to form a green N_2O_4. The test techniques and procedures were identical to those of the earlier phase except that three test temperatures (70°F, 125°F, and 150°F) and three stress levels (0%, 40%, and 90% of yield strength) were used. Also, only A286/A286 (Hastelloy W weld), A286/347 (meltdown weld), and 347/347 (meltdown weld) specimens were used. After six months of testing, the specimens appeared unaffected.

For the Rocketdyne compatibility tests, both stress corrosion and long term storage were assessed (29). For the stress corrosion tests, tensile specimens of three metal alloys stressed to 2/3 of ultimate strength were stored in both brown and inhibited (or green) N_2O_4 at ambient temperatures for up to 45 days. The specimens were notched cylindrical tensile bars of 2219-T6 aluminum, 347 stainless steel and 250 maraging steel. Both the containers used to hold the specimens and N_2O_4 and the frames used to stress the specimens were constructed of the same materials as the specimens. Prior to testing, all the specimens were consecutively cleaned by degreasing in acetone, vacuum annealed at 1400°F for 4 hours, solution treated in air at 1743°F for one hour, and aged in air at 1000°F for 8 hours. None of the samples failed during testing. The ultimate strength of the 2219-T6 aluminum alloy and the 250 maraging steel decreased as a result of exposure to specification grade MIL-P-26539B N_2O_4. There was no change in the 347 stainless steel ultimate strength with either the Military Specification or NASA Specification N_2O_4 (18).

For the long term storage, small discs of ferric and aluminum alloys were immersed in both dry (H_2O 0.1%) and wet (H_2O 0.33%) MIL-P-26539A N_2O_4 (brown). The stainless steel alloys used consisted of 304L, 316, 321, AM 350 and 440C. The aluminum alloys were 6061-T6, 7075-T73, TENS-50, 2014-T6, and 2024. 1018 carbon steel was also tested. Two test temperatures were employed. For tests run at ambient temperature, test duration was 21 months, while for tests run at 158°F, test duration was only one month. Prior to testing, all test samples were cleaned with a soap solution, rinsed with water and acetone, and weighed. Test containers used in the tests were made out of stainless steel for the ferric samples and aluminum for the aluminum alloy samples. From the results, Rocketdyne stated that 304, 316, 321, and AM 350 stainless steels and 2014, 2024, and 7075 aluminum seem to be compatible with either dry or wet Military Specification N_2O_4 at ambient temperature, while 440C and 1018 steel and TENS-50 and 6061 aluminum seem incompatible. Of the materials tested, only 7075 aluminum appeared compatible with dry or wet N_2O_4 at 158°F since all of the other metal specimens showed significant weight losses.

Further stress corrosion testing was conducted by Boeing to determine the fracture toughness and flaw growth characteristics of various metal alloys in N_2O_4 (30). As-welded specimens of 2219-T851 aluminum, including base metal and weldment steel were tested. Only the 2021-T81 samples showed very low threshold intensity of 10 ksi $\sqrt{in}$; the corresponding value for the weldments was 9 ksi $\sqrt{\text{in.}}$ These low values indicated to Boeing that 2021 aluminum might cause functional problems if used as a N_2O_4 storage pressure vessel materials.

As shown by the stress corrosion tests conducted by Bell, stainless steels are subject to stress corrosion in Military Specification N_2O_4 (33). In the same report, Bell also stated that titanium was subject to stress corrosion. In fact, Bell used 6Al-4V titanium sample bars to check out their test apparatus. Three specimens were stressed to 90 ksi (bending stress) while immersed in "brown" N_2O_4 at 150°F. After 135 hours, all three specimens failed, thus verifying to Bell the quality of their test apparatus for the stainless steel testing. TRW, in a report rating materials for use with N_2O_4, also states that titanium is incompatible with Military Specification or "brown" N_2O_4 due to stress corrosion, while NASA specification or "green" N_2O_4 is perfectly compatible with titanium (38). The conclusions were based on N_2O_4 handling experience as of 1967.

In a program to evaluate the effects of sterilization on the materials and components of a propulsion subsystem, Martin Marietta found titanium to be the only material compatible with N_2O_4 at elevated temperatures (20). Prescreening, screening, and long term storage tests were conducted with dry (.03% H_2O) NASA Specification N_2O_4 at sterilization temperatures (275°F). In the prescreening tests, samples of 6061-T6 and 1100-0 aluminum, 321 and 316 stainless steel, 6Al-4V titanium, pure nickel, and pure lead were exposed to N_2O_4 at 275°F for periods up to 120 hours. Before testing, the samples were cleaned and passivated by immersion in HCl followed by immersion in HNO_3/HF. The test containers used to hold the samples and N_2O_4 were fabricated of 304 stainless steel. These tests indicated that the ferric based alloys were incompatible with N_2O_4 at 275°F. Iron based adducts were formed on all of the ferric based metal samples as well as on the test containers. The rate of information of this adduct appeared to be approximately linear with time and seemed to increase as the amount of alloying agents increased. Nickel and molybdenum appeared to contribute to adduct formation. No residual contamination (adduct) formed on the aluminum and titanium samples.

The screening tests exposed metal strips to 275°F NASA Specification N_2O_4 for periods of 300 and 600 hours in glass containers. All samples were cleaned and passivated before testing using the same procedure employed for the prescreening tests. The metals tested were:

Stainless Steel—304,321,347, 17-4 PH,
17-7 PH, Carpenter 20 Cb
A/286
Maraging Steel
Pure Nickel
Titanium—Pure/6Al-4V
Aluminum—1100-0, 2014-T6, 2219-T8,
6061-T6
Hastelloy C
Pure Lead

The results of the 300-hr tests verified those of the precreeening tests. Only the aluminum alloys, Hastelloy C, and the titanium didn't corrode. All the ferric alloys were attacked immediately and formed the tar-like adduct. In the 600-hr tests, only the 6Al-4V and pure titanium didn't corrode. The aluminum alloys showed severe pitting and intergranular corrosion and the tar-like adduct was formed with the stainless steels. The nickel specimen was severely attacked and formed a heavy deposit of nickel nitrate. The maraging steel sample was the only specimen to fracture as well as corrode which indicated the occurrence of stress corrosion. The Carpenter 20 Cb and Hastelloy C specimens exhibited only minor corrosion.

Four 15-in. diameter spherical tanks constructed of 6Al-4V titanium were used in the long term storage tests. A sample of Teflon laminate and a welded titanium specimen were installed in each tank. Prior to filling with N_2O_4, the tanks were cleaned and passivated using the procedure outlined earlier. After filling to 5% ullage, the tanks were subjected to the 275°F sterilization temperature and then stored at ambient temperature for up to one year. Three of the tanks were opened for examination once every four months. The fourth tank was held as a control specimen. During this 12-month storage, no metal corrosion was observed.

Additional 600 hour, 275°F compatibility tests were conducted by Martin Marietta using metal alloys not considered previously (32). Some of the metal alloys tested earlier were also included with protective coatings to evaluate protection potential. Test procedures were the same as those described previously.

The test results are summarized in Table 3.4-8. Bare 2024-T3 aluminum was incompatible; formation of corrosion products plus intergranular attack occurred with this alloy. Other alloys considered as only marginally compatible were: the chrome plated 321, the precipitation hardened AMS 5538, the austenitic 21-6-9 stainless steels, the TZM high temperature alloy, and the L-605 cobalt alloy. The stainless steels suffered from only light attack but formed the gelatinous iron adduct. The TZM alloy suffered from both light surface attack and formation of a smut-like material while the cobalt alloy only corroded slightly forming a white, loosely adherent product. No adduct was formed with either the 430 stainless steel or the HY-140 steel specimens. Since these alloys do not contain large amounts of nickel, this led to the feeling that nickel may be a major contributor in the formation of the adduct. Primary conclusions were:

1. Anodic coating of aluminum alloys can ensure almost 100% protection against N_2O_4;
2. Commercially pure aluminum cladding of structural aluminum alloys provides excellent protection with only a slight amount of corrosion products being formed. The formation of corrosion products was so small the material may be classified as compatible;
3. Tantallum and columbium were unaffected by the propellant;
4. Chromium plating affords excellent protection to stainless steels (only 321 stainless steel was tested). This protection could be afforded to any metallic material.

TABLE 3.4-8 MATERIALS COMPATIBILITY
(EXPOSED TO N_2O_4 at 275°F FOR 600 HOURS) (32)

Material	Results*
1. 2014-T6 Aluminum, Chromic Acid Anodized	C
2. 2014-T6 Aluminum, Sulfuric Acid Anodized	C
3. 6061-T6 Aluminum, Chromic Acid Anodized	C
4. 6061-T6 Aluminum, Sulfuric Acid Anodized	C
5. 2021-T6 Aluminum, Sulfuric Acid Anodized	C
6. 6061 Aluminum Screen, Chromic Acid Anodized	C
7. 2024-T3 Aluminum, Pure Aluminum Clad	C
8. 2024-T3 Aluminum, Clad Stripped	NC
9. 430 Stainless Steel	C
10. 321 Stainless Steel, Chrome Plated	MC
11. AMS 5538 Stainless Steel	MC
12. 21-6-9 Stainless Steel	MC
13. HY-140 Steel	C
14. Titanium 5Al-2.5 Sn	C
15. Titanium 8Al-1 Mo	C
16. Beryllium	C
17. Columbium DP14	C
18. Columbium CB752	C
19. Tantalum, Pure	C
20. Tungsten, Pure	C
21. TZM Titanium-Zirconium-Molybdenum	MC
22. L-605 Cobalt	MC

*C—compatible; MC—marginally compatible; NC—not compatible.

DMIC, Bell Aerosystems, and TRW rated various non-metals for service with N_2O_4 ($H_2O < 0.2\%$) based on available compatibility data for the 1961-1967 time period (19, 22 and 38). These reports are not independent of one another since DMIC referenced the Bell report and TRW referenced both the DMIC and Bell reports. In each case, a non-metal was considered compatible if it had a volume change of less than 25%, a durometer reading change of less than ±3, showed no visual change, and did not affect the N_2O_4. The ratings are presented in Table 3.4-9. As can be seen, only FEP Teflon was rated compatible at 160°F. All elastomers were considered incompatible as well as most ceramics.

The compatibility ratings made by Bell, DMIC, and TRW (presented in Table 3.4-9) were determined, in part, from compatibility tests conducted by both Martin Marietta and Aerojet-General as part of the Titan II program.

TABLE 3.4-9 COMPATIBILITY RATING SUMMARY FOR SELECTED NON-METALS WITH N_2O_4 (19, 23 and 38)

Non-Metal	Compatible for Service Below			Incompatible
	160°F	85°F	60°F	
1) Plastics				
TFE Teflon			X	
FEP Teflon	X			
Teflon-Glass		X		
Teflon-Graphite			X	
Teflon-Asbestos			X	
Armalon 7700			X	
Fluorobestos			X	
Fluorogreen			X	
Kel-F				X
Kel-F 300				X
Genetron GCX-38			X	
Genetron XE-28			X	
Alcar 191			X	
Polyethylene				X
Polypropylene				X
Irradiated Raythenen			X	
Nylon				X
Mylar				X
Saran		X		
Kynar				X
Lexan				X
Tedlar			X	
Plexiglas				X
Teslar 30			X	
Isobutylene-Copolymers				X
Polyethylene+Isobutylene Polymer (Formula 53)		X		
2) Elastomers				
EPR Rubbers				X
Butyl Rubbers				X
Fluoro Rubbers				X
Fluoro-Silicone Rubbers				X
Buna N				X
Neoprene				X
Natural Rubber				X
Polyurethane				X

TABLE 3.4-9 (Cont.)

Non-Metal	Compatible for Service Below			Incompatible
	160°F	85°F	60°F	
3) Lubricants				
XC 150			X	
Molykote Z			X	
Mircroseal 100-1			X	
LOX Safe		X		
Graphite		X		
Graphitar			X	
CCP-72			X	
Fluorolube MG6DO		X		
Fluoroethane G		X		
Krytox 240		X		
Drilube 703			X	
Electrofilm 66-C			X	
Halocarbon Grease				X
4) Sealants and Potting Compounds				
Reddy Lube 100	X			
Reddy Lube 200	X			
Waterglass-Graphite			X	
Oxylube Sealant		X		
Teflon Tape		X		
Crystal M&CF			X	
4-3			X	
Proseal 333			X	
Epon Resins				X
RTV Silicones				X
Polyesters				X
5) Ceramics				
Rock Flux				X
Sauereisen P-1			X	
Temporell 1500				X
Sauereisen 47				X

For the Martin Marietta tests, non-metals were tested with 60°F N_2O_4 having various H_2O contents for periods up to one year (8). Teflon TFE samples, tested in dry N_2O_4, showed no visible changes; close inspection revealed up to a 0.73% increase in elongation, a 2.4% increase in volume, and a 3% increase in weight. The addition of up to 1% H_2O to the N_2O_4 showed no effect on the TFE samples. Teflon FEP samples, after immersion in dry N_2O_4, showed a 2.6% increase in elongation, a 4% increase in volume, and a 5% increase in weight. The addition of water to the N_2O_4 resulted in a 4.8% volume increase of the FEP compared to the 4% increase with dry N_2O_4. Kynar samples were only tested in dry N_2O_4. They showed a definite loss in hardness plus a 0.24% increase in elongation. All other common non-metals tested were totally incompatible. Kel-F samples were attacked immediately and began cracking. All rubbers (natural, butyl, silicone, and EPR) were severely attacked and polyethylene samples oxidized immediately and turned brittle.

For the Aerojet tests, the non-metals were immersed in dry N_2O_4 at test temperatures of approximately 75°F (21). After 70 days of immersion, a 2 to 3% volume increase, a weight gain of 0.5%, a hardness loss of 20%, and 11% increase in elongation, and a loss in strength of 11.5% occurred with TFE Teflon. After 20 days, the FEP Teflon showed a volume increase of 1.6%, a weight gain of 0.4%, a 38% loss in hardness, an increase in elongation of 2.9% and a loss in strength of 20.5%. For both Teflons, the changes in physical properties took place within the first 2 days of immersion; after that time all other changes were nearly zero (the hardness loss of the FEP Teflon was an exception which was linear with time). Other non-metals tested were completely incompatible. Kel-F 300 absorbed the N_2O_4 and became plastic; after 70 days of immersion, it showed a 6% volume increase, a 72% loss in strength, and a hardness loss of 76%. Polyethylene was tested only for short times (hours), since it oxidized immediately and became brittle.

As part of the long term capability testing conducted by JPL (reported earlier), various ceramics, lubricants, and plastics were immersed in N_2O_4 at 110°F (28). The test techniques and procedures for these non-metal tests were the same as those for the JPL testing of metals in N_2O_4. Specific non-metals tested were a sapphire ball (Al_2O_3); Kel-F grease coated on 6061-T6 aluminum, on 6Al-4V titanium, and on a sapphire ball; and a polytetrafluoroethylene (PTFE) named Rulon coated on the 6061-T6, 6Al-4V, and Al_2O_3 materials. After approximately four years of immersion, SRI analyzed the results. The only non-metal analyzed for compatibility with N_2O_4 was the Al_2O_3 ball; the Rulon and Kel-F grease were only evaluated as protective coatings. Al_2O_3 was completely compatible with N_2O_4, while the Rulon and Kel-F grease were ineffective as protective coatings. The Kel-F grease was loosened and was found as heavy, flocculent particles in the N_2O_4. The Rulon coating was removed from the 6Al-4V titanium and Al_2O_3 specimens. It remained intact on the 6061-T6 aluminum, but no benefit was obtained from the coating since corrosion of the specimens occurred.

Further data on the compatibility of fluorinated hydrocarbons with N_2O_4 has recently been reported by SRI (40). Samples of Fluon GP-1 and Teflon TFE-30 films were creased and folded to failure in air and after 20 hours of soaking in N_2O_4. For the Fluon GP-1, an increase in the cycles to failure of 3.3% was found, while for the Teflon TFE-30, a decrease in the cycles to failure of 16% was reported. From these results, SRI concluded that the flex resistance of the Fluon and Teflon films are not affected substantially by exposure to N_2O_4.

From the data presented so far, Teflon seems to be about the best non-metal one can use with N_2O_4. However, problems can exist depending on the application. TRW states that if Teflon is used for bladder service with N_2O_4, the FEP Teflon is probably preferable since TFE has N_2O_4 permeability rates 3 times those of FEP (38). This conclusion seems supported by tests run at JPL (43). In 24-hr tests run at 70°F, TFE had a N_2O_4 permeability rate of 2.4 $mg/in^2/hr$ compared to the FEP rate of 0.66 $mg/in^2/hr$.

Besides permeability problems, JPL has recently found stress-cracking problems with bladders made of Teflon Laminate (39). As discussed in Chapter III, specimens of the standard Teflon laminate bladder material planned for the Mariner Mars 1971 spacecraft were stretched to failure while immersed in various solvents including N_2O_4. Both biaxial and uniaxial tests were performed. It was found that the standard laminate was highly sensitive to N_2O_4 stress cracking. Because of this, JPL also tested a codispersion laminate to determine sensitivity to N_2O_4. The standard laminate consisted of a layer of TFE 30 Teflon covered with a layer of FEP 120 Teflon. The codispersion laminate consisted of a layer of FEP 9511 Teflon sandwiched between layers of a Teflon codispersion of 80% TFE and 20% FEP 9511.

JPL deduced the following results from their teats:

"(1) All solvents including N_2O_4 significantly reduced the ultimate properties of the standard laminate, which indicates that this material is highly sensitive to solvent-stress-cracking.

(2) Codispersion laminate resists solvent-stress-cracking.

(3) A study of the solvent sensitivity of construction materials, FEP 120, FEP 9511, and TFE 30, revealed that only FEP 120 is significantly solvent-sensitive. This material, not used in codispersion laminate is a major component of standard laminate and must therefore be labeled as the dominant contributor to the solvent sensitivity of standard laminate. This is

further substantiated by the experimental observation that surface crazing, which precedes the failure of the standard laminate in solvent, occurs in FEP 120.

(4) The solvent sensitivity of standard laminate is revealed only during immersion testing. Removing the specimens from the test solvent and air-drying them results in a recovery of their initial properties.

(5) Both codispersion and standard laminates experience an immediate reduction in ultimate properties upon exposure to solvents, although the effect is more critical with the standard laminate. With further exposure, both codispersion and standard laminates undergo a recovery in ultimate properties. The codispersion laminate achieves or surpasses its initial properties, while the standard laminate, even with some recovery, displays significantly lowered properties as compared to its initial properties.

(6) Codispersion laminate has superior flex fatigue properties as compared to standard laminate.

(7) Crystallinity variation in the Teflon material did not affect the mechanical performance of either standard or codispersion laminate. It was believed that large increases in crystallinity could lead to brittle failure."

Thiokol-RMD attempted to develop a positive expulsion bladder material resistant to N_2O_4 (42). This material consisted of a laminate of electroformed gold and carboxy nitrosos rubber (CNR). The gold was added to make the laminate as impermeable as possible. In a series of compatibility tests, Thiokol found the gold/CNR laminate to be fairly resistant to N_2O_4.

Further data on CNR with N_2O_4 was obtained by TRW in compounding studies to develop polymetric bladder materials (41). As a result of these studies, TRW chose a HYSTL resin cured TFE Teflon reinforced CNR compound, designated Compound 238-3, as their prime candidate. This new compound exhibited resistance to N_2O_4 attack comparable to similar CNR formulations but had superior permeability characteristics.

At high temperatures, all non-metals are apparently incompatible with N_2O_4. In pre-screening tests to select a bladder material for a sterilizable propulsion system, Martin Marietta immersed different non-metals in dry N_2O_4 (H_2O = .03%) at temperatures of 275° for periods up to 88 hours (20). All rubbers (butyl, EPR, and nitroso rubber) either blistered, ignited or completely dissolved. Both TFE and FEP Teflon showed losses in strength of about 7% and changes in elongation up to 50%. It was also noted that the N_2O_4 washed out particles of Teflon which caused the N_2O_4 to turn milky. Kynar was severely attacked. Although Teflon did fare better than the other non-metals tested, no non-metal was considered compatible with N_2O_4 at the high temperature. Conversely, aluminum oxide and beryllium oxide ceramics were immersed in dry N_2O_4 at 275°F for 600 hours with no sign of chemical attack and no increase in weight (32).

As a result of the work reported in Reference (8), it was concluded that:

a. AF-E-124T elastomer is compatible with dinitrogen tetroxide and has sufficient mechanical strength to provide reliable service as a positive expulsion bladder or diaphragm. Following 159-day storage in propellant, three thousand expulsion cycles were demonstrated with negligible elastomer degradation.

b. AF-E-124T can be used successfully as a seal for dinitrogen tetroxide (and as demonstrated previously for fuels) using special designs which take into consideration the material's creep under compressive stress.

The objectives of a test program in References (14 and 15) were to define the effect of MON-1 nitrogen tetroxide exposure on candidate propellant acquisition system materials for the propellant tankage of the Space Shuttle Aft Propulsion Subsystem (APS), to define the effect of MON-3 nitrogen tetroxide exposure on the candidate materials; and, to evaluate techniques for repairing acquisition screen materials that had devleoped leaks.

One of the screen test specimens which was exposed to MON-1 and later exposed to MON-3 was used to evaluate the compatibility and structural integrity of different materials proposed for use to repair leaks that could develop in the acquisition system screens.

The results of the test conducted with MON-1 showed that there was no degradation in screen bubble point during 90 additional days of exposure to MON-1; that materials of construction of test specimens were compatible with MON-1; and, that Teflon S-100 compound is not an acceptable material for repair of screen leaks.

The results of the test conducted with MON-3 showed that all materials tested were compatible with MON-3; that two of the three screen specimens had no degradation in bubble point during 180 days exposure to MON-3; that screen specimens bubble point with MON-3 is the same as MON-1; and, that both Teflon and Teflon S 200 compounds are acceptable materials for repairing of screen leaks.

TRW Systems performed corrosion testing using engineering materials at elevated temperatures with impure N_2O_4 for NASA (38). It was the intent of the NASA program to enhance corrosion, not suppress it, for purposes of determining the effect of corrosion products on contaminating the N_2O_4. However, this information and test data generated is valuable, since it represents the only known matrix testing done showing the effects of impurities in the propellant on corrosion. The work also included a different rating analysis on reporting corrosion not generally used by investigators. The test specimens were unstressed samples of 6061-T6 Aluminum, 347 Stainless Steel and Ti-6Al-4V Alloy subjected to one and four month durations at 165°F. The specimens measured nominal 0.025" thickness x 3/4" x 4" long and were placed in glass capsules containing the N_2O_4 and sealed. The impurities individually added to the N_2O_4 are listed as follows:

Added Impurity	Pre-Storage Concentration, % (wt)
Chlorine (Cl_2)	0.10
Water (H_2O)	0.91
Oxygen (O_2)	0.04
Nitrosyl Chloride (NOCl)	0.025
Nitrosyl Chloride + O_2 (NOCl + O_2)	0.054 NOCl + 0.050 O_2

Martin Marietta Corporation (44) is conducting tests to demonstrate the feasibility of using Sn96Ag4 solder (96% tin, 4% silver) to repair screen leaks in the Shuttle RCS tank. These repairs have successfully passed all compatibility tests and are serviceable for long term exposure to MON-3 on Shuttle.

The effects of the selected impurities in the corrosivity of N_2O_4, showed no significant increase in dissolved metal content with time. Of all the impurities, water resulted in the greatest increase in corrosivity. Tables 3.4-10, 3.4-11, and 3.4-12, present a visual description of the appearances of the one and four month specimens for aluminum, stainless steel, and titanium.

TABLE 3.4-10 PHYSICAL APPEARANCE OF ONE AND FOUR MONTH ALUMINUM SPECIMENS PRIOR TO AND AFTER REMOVAL OF PROPELLANT (N_2O_4)

Added Contaminant	Appearance of One Month Capsules		Appearance of Four Month Capsules	
	Before Propellant Removal	After Propellant Removal	Before Propellant Removal	After Propellant Removal
None	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.	Some oily substances on bottoms of tubes.
H_2O	Specimens covered with white salts.	Specimens covered with white salts.	White crystals on bottom of tubes. Specimens covered with white salts.	Specimens covered with white salts. Some crystals on walls and bottoms of tubes.
O_2	Slight spotted discoloration of specimens.	Slight spotted discoloration of specimens.	Slight discoloration.	Slight spotted discoloration of specimens. Yellow crystals at tops of the tubes. White powdery coating on the walls of the tubes.
NOCl	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.
NOCl + O_2	Specimens slightly tarnished. One tube contained yellow gelatinous material.	Specimens appeared corroded. One tube had a yellow powdery coating at the top of the tube and a yellowish-brown gelatinous material adhering to the walls.	Slight corrosion of specimens. One tube had yellow-green spots at at the top of the liquid.	Specimens were slightly corroded. One tube had yellow particles at the top and a few on the bottom.
Cl_2	No noticeable corrosion.	No noticeable corrosion of specimens. One tube had a yellow ring at the N_2O_4 liquid vapor interface.	No noticeable corosion.	No noticeable corrosion.

TABLE 3.4-11 PHYSICAL APPEARANCE OF ONE AND FOUR MONTH STAINLESS STEEL SPECIMENS PRIOR TO AND AFTER REMOVAL OF PROPELLANT (N_2O_4)

Added Contaminant	Appearance of One Month Capsules		Appearance of Four Month Capsules	
	Before Propellant Removal	After Propellant Removal	Before Propellant Removal	After Propellant Removal
None	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.	Some gelatinous material on the bottoms of the tubes. One tube had yellow coating on wall.
H_2O	Specimens were black with few black crystals on them. Greenish colored immiscible droplets on sides of tubes.	Specimens were black with few black crystals on them. Greenish colored immiscible droplets on sides of tubes.	Specimens were black with black crystals on them. Greenish colored immiscible droplets on sides of tubes.	Black salt crystals on specimens. Green oily substance on walls and bottom of tubes.
O_2	Specimens were black. Some yellow crystals on specimens and walls of the tubes. One tube had a few immiscible droplets.	Specimens were black and had some yellow crystals on them and on the tube walls. One tube had green immiscible droplets on it.	Specimens were black. Reddish-brown crystals on walls of tubes above the liquid N_2O_4.	Specimens were black. Reddish-brown crystals on the walls of the tubes.
NOCl	No noticeable corrosion.	No noticeable corrosion.	Gelatinous material on the walls of the tubes. No noticeable corrosion of specimens.	Specimens are slightly discolored. Coating on the walls. No sign of gelatinous material.
NOCl + O_2	Specimens were black. Yellow crystals at the top of the liquid. Clear crystals on the bottoms of the tubes.	Specimens were black. Some yellow crystals and coatings on the tops of the tubes.	Specimens were black. One tube had reddish-brown gelatinous material above and 1/2" below the liquid. Some gelatinous material on the tube wall.	Specimens were black and tube walls were coated. One tube had yellow crystals on the wall and the other tube had black spots.
Cl_2	Clear crystals on the tube walls. No noticeable corrosion of the specimens.	Slight discoloration of specimens.	No noticeable corrosion.	Slight discoloration of specimens. Reddish-brown crystals on bottoms of tubes.

TABLE 3.4-12 PHYSICAL APPEARANCE OF ONE AND FOUR MONTH TITANIUM SPECIMENS PRIOR TO AND AFTER REMOVAL OF PROPELLANT (N_2O_4)

Added Contaminant	Appearance of One Month Capsules		Appearance of Four Month Capsules	
	Before Propellant Removal	After Propellant Removal	Before Propellant Removal	After Propellant Removal
None	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.	A few crystals on the walls of the tubes.
H_2O	Specimens slightly spotted.	Specimens slightly spotted.	No noticeable corrosion.	Small amount of oily substance on bottoms of tubes. Clear crystals on walls of tubes.
O_2	No noticeable corrosion of the specimens. Tube walls covered with a yellowish-white material.	No noticeable corrosion of specimens. Tube walls coated with a yellowish-white substance.	No noticeable corrosion of specimens. One tube had reddish-yellow crystals on the wall above the liquid.	No noticeable corrosion. One tube had reddish-brown crystals above the liquid level.
NOCl	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.
NOCl + O_2	A few clear crystals on the walls of the tubes.	No noticeable corrosion.	Clear colorless gelatinous material at the top of the liquid on the tube walls.	No noticeable corrosion Yellowish-green inmiscible droplets at the tops of the tubes and a few crystals on the bottoms.
Cl_2	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.	No noticeable corrosion.

3.4.5 FLOW DECAY PHENOMENA

The phenomenon of flow decay is defined in reference (45) as a spontaneous decrease in the flow rate through a constant flow system. Flow decay in a nitrogen tetroxide system is a function of the in situ formation of solid or gel-like materials that can obstruct the flow through valves, filters, orifices, or any other flow element with a constriction of small size. There are several ferric nitrate derivatives which can be deposited to produce flow decay, such as nitrosyl tetranitratoferrate, $NOFe(N_3)_4$, and partially hydrated or hydrolyzed ferric nitrates, $FE(NO_3)_{3-n}(OH)_n \cdot x\ H_2O$. These materials are soluble in nitrogen tetroxide at levels of the order of a few parts per million (as iron). While there are many factors which can influence the corrosion processses that produce these compounds in solution, the extensive exposure of all nitrogen tetroxide to iron during the manufacturing and shipping processes can be expected to form these materials in approximately equilibrium amounts.

The phenomenon of flow decay has been experienced, identified and studied for the past ten years. A number of basic investigations have been conducted under government and industry funding. Foremost among these are Rocketdyne's, Boeing's, and University of Nottingham's studies for the Air Force Rocket Propulsion Laboratory (AFRPL) (e.g., references 45, 46 and 47). Valuable insights were gained in these studies, which elucidated the physicochemical nature of the phenomenon.

Flow decay is a very complex phenomenon. There are many independent variables that affect the incidence and amount of flow decay. The effects of these parameters are generally not simple or independent of each other; they exhibit many interactions. In addition, there are often threshold effects for flow decay (i.e., an identifiable boundary between a range of variables for which no flow decay occurs and a range for which flow decay occurs in varying amounts). These thresholds are not sharp, and further depend upon the interactions of the independent variables.

A number of major effects of parameters on flow decay are outlined in reference (45), and are listed here. The reader should keep in mind the complex nature of flow decay, and that these are only intended to be interim conclusions. Extreme caution must be taken in extrapolating effects and trends to different flow situations and conditions.

Increasing the filter pore size has a significant effect in preventing or reducing flow decay. It appears that flow decay will not occur, under the conditions tested during this program, with filters with nominal pore size at least as large as 40 microns. There are a few tests that might appear to be exceptions to this generalization, however, they are judged to be outliers. Decreasing the filter pore size, below its threshold, increases the rate of flow decay.

Keeping the temperature drop (from the initial propellent temperature) as small as possible is another important factor in preventing or minimizing flow decay. However, some cases of flow decay were observed with no temperature drop. There is often a non-zero temperature drop threshold below which no flow decay occurs. The amount or rate of flow decay increases as the temperature drop is increased above its threshold value. In some ranges of conditions, there is approximately a linear relationship between the rate of flow decay and the temperature drop.

Decreasing the local velocity through the screen decreases the amount of flow decay, at least over the range tested during this program. The actual velocity-related parameter considered was Q/A, for which the range of values was about 0.7 to 4.7 gal/min-sq in. There appear to be strong interactions between Q/A and many of the other independent variables. Use of a filter Reynolds Number was not particularly advantageous in the data correlation efforts

Comparisons between green and red-brown N_2O_4 were not without complications. There appeared to be a number of sizable differences in the effects of other variables between the two types of propellant, especially in the effects of Q/A, initial temperature, and the history parameter V. However, direct comparisons between sets of test data for matched conditions (i.e., sets for which the only difference in the nine basic independent variables considered was between green or red-brown N_2O_4) indicate that the green N_2O_4 tested exhibited somewhat lower rates of flow decay than did the red-brown N_2O_4 tested.

Rapid temperature drops (during flow) seem to cause somewhat more flow decay than occurs with the same temperature drop imposed slowly over a period of approximately two days.

The effect of initial temperature was less consistent between differing types of N_2O_4 when the propellants were doped with iron pentacarbonyl to ensure saturation. With green N_2O_4, increasing T_o increased flow decay, while the opposite trend was observed with red-brown N_2O_4.

There was some difference between the amount of flow decay for the as-received propellants and for the propellants doped with a small amount (one saturation dose) of iron pentacarbonyl to ensure iron saturation. The differences seem to be regular and more a matter of degree than substantive differences in type of flow decay behavior. Therefore, the data for doped N_2O_4 represent slightly conservative results as applied to the particular nitrogen tetroxide propellants that were used in the testing.

The current status of nitrogen tetroxide flow decay investigations is that it cannot be predicted with confidence when or if any flow decay will occur. However, the most basic common theme with all decay phenomena is the presence of small dimensions in critical elements of the flow system. Filtering or distillation is an effective means for temporary removal of ferric nitrate and chemical additives show promise of relieving the flow decay problem. A complete list of references on this subject is also included in Section 3.5.

3.5 REFERENCES

3.5 REFERENCES

1. *Liquid Propellant Handling, Storage, and Transportation, Volume III*, Chemical Propulsion Information Agency, JANNAF Hazards Working Group, CPIA Publication No. 194, May, 1970.

2. Allied Chemical Corporation, *Nitrogen Tetroxide*, Industrial Chemical Div., Morristown, N.J., Product Bulletin, June, 1953.

3. Hercules, Incorporated, anonymous, *Nitrogen Tetroxide*, published by Hercules, Inc., 910 Market Street, Wilmington, Delaware 19899, 1968.

4. American Society of Mechanical Engineers, *A.S.M.E. Boiler and Pressure Vessel Code* (with addenda). Includes the "A.S.M.E. Unfired Pressure Vessel Code," which is published separately, as well as testing and other specifications.

5. Code of Federal Regulations, Department of Transportation, Title 49, Chapter I, General Services Administration, National Archives and Records Services; Federal Register Division, Parts 171 to 190. (For sale by Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402).

6. *Corrosion Resistance of Metal Alloys and Plastics with Red Fuming Nitric Acid and Chlorine Trifluoride*, OM66-160, Aerojet, April 27, 1966.

7. Heubusch, Henry Ph: *Material Selection for Use with HDA*, Bell Aerospace Company, paper presented at Fourth National SAMPE Technical Conference, October 1972.

8. Martin, J.W., et al: *Elastomers for Liquid Rocket Propellant Containment*, AFML-TR-71-59 Part III, TRW Systems Group, Redondo Beach, California, January 1976.

9. "Agena C Degradation Investigation," Final Report, LMSC-A918454, Lockheed Missiles Space Company, May, 1968.

10. *Propellants, Nitric Acid*, Military Specification, MIL-P-7254F, 30 April 1970, and Amendment 2, 18 January 1972.

11. *Compatibility of Rocket Propellants with Materials of Construction*, DMIC Memorandum 65, Defense Metals Information Center, Battelle Memorial Institute.

12. Bell Aerospace Company, *Model 8096, Maximum Density Acid Engine Definition Program, Final Report*, Volume II Propellant Characterization Program, Report No. 8096-910082, 1 September 1970.

13. Bell Aerospace Company, *Use of New Inhibitor to Improve the Compatibility of HDA*, Compatibility Test Report, 27 November 1972. GIDEP Report No. 563.70.00.00.C4-04.

14. *Supplementary NTO Storage Tests*, Final Report No. 073-070.02.01, McDonnell Aircraft Company, St. Louis, Mo., 22 June 1976.

15. *Screen Specimen Bubble Point, Flow ΔP, Wicking, and Compatibility Tests Using Actual Propellants*, Final Report No. 073-070.02. McDonnell Aircraft Company, St. Louis, Mo., 20 May 1975.

16. Uney, P.E. and Fester, D.A.: *Material Compatibility with Space Storable Propellants*, Design Guidebook MCR-72-26, Martin Marietta Corporation, Denver, Colorado, March 1972.

17. *Minuteman III Post Boost Propulsion System, Phase II A Stress Corrosion Program, One Month through One Year Immersion Tests*, Summary Report 8477-927133, Bell Aerosystems Company, Buffalo, N.Y., October 1969.

18. NASA Specification MSC-PPD-2A or B.

19. White, E.L., Boyd, W.K., and Berry, W.E.: *Compatibility of Materials with Rocket Propellants and Oxidizers*. Memorandum 201, Defense Metals Information Center, Columbus, Ohio, January 1965.

20. Brady, H.F., and DiStefano, D.: *Sterilizable Liquid Propulsion System, Part I.* MCR-68-119, Martin Marietta Corporation, Denver, Colorado, August 1968.

21. Fish, W.R., et al: *Storable Liquid Propellants for Titan II.* LRP 198, Aerojet General Corporation, Sacramento, California, September 1960.

22. Liberto, R.R.: *Titan II Storable Propellant Handbook.* AFFTC-TR-61-32, Bell Aerosystems Company, Buffalo, New York, June 1961.

23. Schaefle, A.L.: *Propellants Compatibility Report.* MCR-64-88, Martin Marietta Corporation, Denver, Colorado. November 1964.

24. Hollywood, L.P., Metz, T.R., and Porter, R.N.: *Storage Tests of Nitrogen Tetroxide and Hydrazine in Aluminum Containers.* Technical Report 32-1039, Jet Propulsion Laboratory, Pasadena, California, January 1967.

25. Salvinski, R.J., et al.: *Investigation of the Formation and Behavior of Clogging Material in Earth and Space Storable Propellants.* 08113-6007-R000, TRW Systems Group, Rodondo Beach, Calfornia, October 1967.

26. Skartvedt, G.: "Propellant Clogging and Flow Decay Problems Encountered in Liquid Rocket Propellant Systems," Paper presented at USAF/Martin Marietta Corporation Technology Review, Denver, Colorado, May 6-7, 1969.

27. Williams, L.: *Crystalline Material Found on Aluminum Exposed to Nitrogen Tetroxide Vapor.* IDC 0441-69-254, Martin Marietta Corporation, Denver, Colorado, May 1969.

28. Muraca, R.F. and Whittick, J.S.: *The Results of Long-Term Storage Tests for Compatibility of Nitrogen Tetroxide with Various Spacecraft Materials.* Special Report No. 2, Stanford Research Institute, Menlo Park, California, May 1967.

29. Axworthy, A.E., et al.: *Research and Engineering Data on Inhibited N_2O_4.* AFRPL-TR-69-4, Rocketdyne, Canoga Park, California, January 1969.

30. Lorenz, P.M.: *Compatibility of Tankage Materials with Liquid Propellants.* AFML-TR-69-99, The Boeing Company, Seattle, Washington, May 1969.

31. Toy, S.M., et al: *Tankage Materials in Liquid Propellants.* DAC-59868-S1, McDonnell Douglas Corporation, Astropower Laboratory, Newport Beach, California, June 1967 to December 1967.

32. Lukens, S.C.: *Sterilizable Liquid Propulsion System, Part II.* MCR-68-119, Martin Marietta Corporation, Denver, California, September 1969.

33. Piccirillo, F.: "Compatibility of Stainless Steels with Monomethylhydrazine and Inhibited Nitrogen Tetroxide." Paper presented at the 23rd Meeting of the ICRPG Liquid Propellent Test Methods Working Group, Naval Postgraduate School, Monterey, California, March 28-29, 1968.

34. Personal Communication with C. L. Caudill, Martin Marietta Corporation, Denver, Colorado, September 1969.

35. Takimoto, H.H., et al.: *Iron Containing Contaminants in N_2O_4.* SAMSO-TR-68–421, Aerospace Corporation, El Segundo, California, September, 1968.

36. Boyd, W.K.: *Summary of Present Information on Impact Sensitivity of Titanium when Exposed to Various Oxidizers.* Memorandum 89, Defense Metals Information Center, Columbus, Ohio, March 1961.

37. Jackson, J.D., Miller, P.D., and Boyd, W.K.: *Reactivity of Titanium with Gaseous N_2O_4 Under Conditions of Tensile Rupture.* Memo 173, Defense Metals Information Center, Columbus, Ohio, August 1963.

38. Salvinski, R.J., et al.: *Advanced Valve Technology, Volume II—Material Compatibility and Liquid Propellant Study.* 06641-6014-R000, TRW Systems Group, Redondo Beach, California, November 1967.

39. Cuddihy, E.F.: *Solvent-Stress-Cracking and Fatigue Properties of Liquid-Propellant Expulsion Teflon Bladders.* Technical Report 32-1535, Jet Propulsion Laboratory, Pasadena, California, August 1971.

40. Muraca, R.F., et al.: *Development of Techniques to Improve Bladder Materials and Test Methods.* Final Technical Report: Addendum One to JPL Contract 951484, Stanford Research Institute, Menlo Park, California, March 1969.

41. Martin, J.W., et al.. *Elastomers for Liquid Rocket Propellant Containment.* AFML-TR-71-59 PT1, TRW Systems Group, Redondo Beach, California, June 1971.

42. Heilman, R.L., et al.: *Propellant Expulsion Bladder for the Saturn V/S-IVB.* RMD 5125-F1, Reaction Motors Division, Thiokol Chemical Corporation, Denville, New Jersey, June 1969.

43. Stanford, H.B. and Porter, R.N.: *Propellant Expulsion in Unmanned Spacecraft.* Technical Report 32-899, Jet Propulsion Laboratory, Pasadena, California, July 1966.

44. Stenereen, A.A.: *Corrosion Resistance of Metal Alloys and Plastics with Red Fuming Nitric Acid and Chlorine Tri Fluoride.* OM 66-160, April 1966.

45. Mitchell, R.C., Lecce, J.V., Fertig, K.W.: *Engineering Parameters Study of Nitrogen Tetroxide Flow Decay—Final Report,* AFRPL-TR-72-38, Rocketdyne, June 1972.

46. Pullen, K.E., Smith, T.L., Stebbins, J.P.: *A Method for the Prevention of N_2O_4 Flow Decay,* AFRPL-TR-72-121, Boeing Company, December 1972.

47. Addison, C.C.: *Flow Decay—Final Scientific Report,* AFRPL-72-84, The University, Nottingham N672RD, June 1972.

48. Personal Communication with Burdette, G.W.: *Compatibility of Various Metals and Elastomers with 90% Nitric Acid,* Naval Weapons Center Memorandum 3244-0006-77, dated 17 October 1976.

"FLOW DECAY" REFERENCE LIST

49. *Investigation of the Formation and Behavior of Clogging Material in Earth and Space Storable Propellants,* by TRW for NASA, October 1968, RL. No. 113046.

50. *N_2O_4/IRFNA Conference,* Abstracts and Slides—Aerospace Corp.; sponsored by AFRPL, June 4-5, 1968 – RL No. 82433 – CPIA Pub. No. 171, July 1968.

51. *Flow Decay: Impaired Flow in Nitrogen Tetroxide Propulsion Systems Caused by Corrosion Product Deposits,* Rocketdyne for AFRPL, Nov. 1968—AFRPL-TR-68-220—RL. NO. 112775.

52. *Iron Containing Contaminants in N_2O_4,* Takimoto, Denault, Marsh for SAMSO—Sept 1968—RL. No. 112672.

53. *Investigation of the Formation and Behavior of Clogging Material in Earth and Space Storable Propellants,* by TRW for NASA, October 1967—RL. No. 112214.

54. *Crystalline Material Found on Aluminum Exposed to Nitrogen Tetroxide Vapor,* L. Williams MMC IDC to R. VandeKoppel, May 1969—0441-69-254.

55. *Properties and Performance of Nitrogen Tetroxide and Unsymmetrical Dimethylhydrazine,* Boeing Report No. P5-14077, Michoud, 1969 Report D6778.

56. *Propellant Clogging and Flow Decay Problems Encountered in Liquid Rocket Propellant Systems,* MMC Report, G. Skartvedt, May 1969.

4.0 SAFETY

4.1 INTRODUCTION

The purpose of the Safety Section of this Handbook is to present and evaluate information concerning hazard characteristics of the nitric acid/nitrogen tetroxide oxidizers, together with procedures and equipment employed for their safe handling.

The reader should be made aware that this section of the Handbook is not a Safety Manual, and it must not be employed as such. Regulations concerning the safe handling, storage, transportation, and disposal of hazardous materials are promulgated by Federal, State, and local agencies charged with responsibility for public health and safety, and such regulations take precedence over any conclusions or recommendations stated or implied in this Handbook. Specific reference to these Regulations is made in the Handbook where known; however, no claim is made for completeness. Interested users are urged to contact their own State and Local regulatory agencies for complete information on safety regulations applying to them.

The reader is further cautioned that, while every reasonable effort has been made to assure the information given in this section is accurate, the authors and Martin Marietta Corporation make no warranty nor do they assume legal responsibility for its correctness.

In order to improve clarity and reduce duplication, the following safety sections are classified first according to type of hazard (toxicity, fire, explosion). Under each hazard category, the primary oxidizers are described.

4.2 TOXICITY

4.2.1 GENERAL INTRODUCTION

The oxidizers considered in this Handbook are all classified as toxic substances and may cause death or permanent injury after very short exposure to small quantities. Tests to determine lethal doses and concentration-time combinations have been conducted on several types of animals, the latest being the dog. Experience with human exposure is very limited; however, exposure limits have been established.

This section is divided into three subsections to provide a separate discussion of the hazards and exposure limits, the preventive measures, and first aid, respectively.

The oxidizers will be discussed as two families: one which is nitric acid and high density acid, and the other is nitrogen tetroxide and mixed oxides of nitrogen. All of these oxidizers have a common vapor component which is nitrogen dioxide.

Exposures are expressed as concentration and exposure duration for exposure to vapors in the air. The concentration of vapors in air is expressed in terms of parts of vapor per million parts of air (PPM) and in milligrams per cubic meter.

4.2.2 HAZARDS AND EXPOSURE LIMITS

4.2.2.1 Nitric Acid and High Density Acid

Red Fuming Nitric Acid (RFNA) is a yellow to red-brown, clear, strongly fuming, very corrosive liquid which evolves toxic nitric acid vapor and yellowish-red vapors of nitrogen oxides.

RFNA, in contact with any surfaces of the body (skin, mucous membranes, eyes), destroys tissue by direct action. It stains the skin and tissue yellow or yellowish brown. More than instantaneous contact will result in a chemical burn. RFNA vapors are highly irritating and toxic to the respiratory tract. Immediately after exposure to dangerous concentrations, there may be coughing, increased respiratory rate, asthmatic-type breathing, nausea, vomiting, and marked fatigue. A fatal pulmonary edema may develop.

RFNA contaminates the surrounding atmosphere with nitric acid vapor, nitric oxide, and nitrogen dioxide (or its dimer nitrogen tetroxide). Consequently, a threshold limit value for RFNA has not been established. However, the atmospheric threshold limit values (1 and 2) for its more toxic components are as follows:

Nitric acid vapor	2 ppm	(5 mg/m^3)
Nitrogen dioxide*	5 ppm	(9 mg/m^3)

4.2.2.2 Nitrogen Tetroxide and Mixed Oxides of Nitrogen

N_2O_4 in liquid form destroys body tissues. It volatilizes readily, giving off yellowish to reddish-brown vapors containing a mixture of N_2O_4 and NO_2. Most discussions of the toxicity of these vapors identify the mixture as one or the other compound; likewise, calculations of atmospheric concentrations are normally made in terms of one compound or the other. In this chapter the same practice will be followed; it should be kept in mind, however, that the two oxides exist together in equilibrium.

Dr. Tamas of the Aerospace Medical Division of WADD has indicated in Reference 2 that, at vapor concentrations of 100 ppm or lower, N_2O_4 does not exist for purposes of practical measurement, but the vapors are primarily NO_2. Even at concentrations as high as 10,000 ppm, only about 0.1% is N_2O_4 at room temperature and one atmosphere. Thus, as mentioned in the section on Detection Devices later in this handbook, instruments that are sensitive to NO_2 vapors are desirable.

Because N_2O_4 liquid is corrosive, severe burns of the skin and eyes can result unless it is immediately removed and first aid is obtained. The inhalation of toxic vapors is normally the most serious hazard of handling N_2O_4. The color of the vapors is not a reliable index of degree of toxic hazard. The initial symptoms of poisoning—irritation of the eyes and throat, cough, tightness of the chest, and nausea—are slight and may not be noticed. Then, hours afterward, severe symptoms begin; their onset may be sudden and precipitated by exertion. Coughing, a feeling of constriction in the chest, and difficult breathing are typical.

---

*National Institute of Occupational Safety and Health (NIOSH) is recommending a ceiling concentration of 1 ppm (1.8 mg/m^3).

Cyanosis (a blue tinge to the mucous membranes of the mouth, eyelids, lips and fingernail beds) may follow. Persons with such symptoms are in great danger. Milder cases may show signs of bronchitis with cyanosis, and others may vomit and suffer nausea and abdominal pain.

The established threshold limit value (also ceiling value) of NO_2 vapors is 5 ppm (9 mg/m^3) as recommended by the American Conference of Industrial Hygenists and 2.5 ppm (9 mg/m^3) for N_2O_4 vapors. This limit is based on an eight-hour, five-day work week. In the case of mixed oxides of nitrogen, nitric oxide is also present and may be detected. The TLV for NO is 25 ppm (30 mg/m^3) but the more toxic NO_2 is usually the agent to be detected. See Reference 1 and 2.

4.2.3 PREVENTIVE MEASURES

4.2.3.1 Nitric Acid and High Density Acid Safety Measures

The following safety precautions have been recommended in Reference 1.

Safety Measures. All operations involving the handling of the nitric acids shall be performed by two persons. There shall be trained supervision for all potentially hazardous activities. An individual properly equipped should be stationed outside the work area. Operations shall be performed using written procedures.

Education of Personnel. The principal hazards for which personnel should be informed are:

a. Hazards
b. Relevant symptoms
c. Emergency procedures
d. Precautions
e. Respiratory protection

Safety Clothing. The hands and feet are always subject to contamination during handling of liquid propellants or propellants equipment. Gloves and boots that do not let nitric acid through to the skin must always be worn. The gloves used should protect against nitric acid and at the same time allow free movement of the fingers. A vinyl-coated glove meets these requirements. Since boots of approved protective construction materials are not commercially available, an overboot, designed to be worn over regular safety footwear and high enough to fit comfortably under the protective trousers, is used. Boots made of natural or reclaimed rubber or GR-S may be used with reasonable safety if any contamination is washed off quickly. Rubber sometimes burns in contact with these chemicals. They must be frequently inspected to detect flaws that might result in personal injury.

Protective body clothing, acid- and fuel-resistant vinyl coated protective suit or polyethylene clothing, should be worn. Fiberglass clothing, impregnated with acid-resisting plastic, such as Teflon TFE and Kel-F-81, Halon TFE, or equivalent, is excellent for protecting handlers of nitric acid. The clothing must cover all parts of the body; it must be adjusted so it will prevent body contamination and keep leaked or spilled liquid acid from draining into boots or gloves. A hood of approved type must be worn to protect the head. Any protective clothing materials should be proven compatible before procurement.

Respiratory Protection. Whenever men are exposed for prolonged periods to nitrogen dioxide (released from fuming nitric acid) at concentrations greater than the threshold limit value, NIOSH* approved respiratory protection equipment shall be worn. NIOSH approved self-contained breathing apparatus will give the most reliable respiratory protection against gases or mists from fuming nitric acid. The canister-type gas mask is not recommended as respiratory protection against concentrations of nitrogen oxides above 1250 ppm. Military protective masks are discussed in References 4, 5, and 6.

Other Safety Equipment. Safety showers and eyewashes should be provided in the immediate vicinity of nitric acid handlers during transfer operation. In all cases a commercial type hose connected to a water line should be "cracked open" so that casual observation may indicate water is available. Enclosed spaces shall have entry equipment, i.e., harnesses and life lines.

4.2.3.2 Nitrogen Tetroxide and Mixed Oxides of Nitrogen Safety Measures

The following safety procedures have been recommended in References 1 and 3.

Safety Measures. All operations involving the handling of N_2O_4 and mixed oxides of nitrogen shall be performed by two persons. There shall be

---

*National Institute of Occupational Safety & Health.

trained supervision for all potentially hazardous activities. An individual properly equipped to enter a confined contaminated area should be stationed outside the work area. Confined spaces must be ventilated to prevent accumulation of vapors. Mechanical exhaust ventilation should also be supplied. An adequate water supply must be available for firefighting and decontamination. Operations should be performed by using written procedures.

Education of Personnel. Because N_2O_4 and mixed oxides of nitrogen are oxidizers (approximately 70 percent oxygen), their mixture with rocket fuels create an explosion hazard. The following subjects should be thoroughly explained to all persons working with the storage, handling and transfer of N_2O_4 or mixed oxides of nitrogen:

a. Nature and properties of N_2O_4 and mixed oxides of nitrogen in both the liquid and vapor states, with emphasis on its high toxicity and relatively high volatility, including symptoms
b. Compatible construction materials
c. Proper equipment and its operation
d. Use and care of personal protective equipment and clothing
e. Safety measures, self aid and first aid instructions (self aid is intended for use when first aid or medical treatment is not immediately available)
f. Locations of safety showers and eyewashes, emergency telephone, safety and rescue equipment, firefighting devices, neutralizing and decontamination agents, and safety areas
g. Emergency procedures to be used in case of spills
h. Hazards to be expected

Personnel Protection. The principal personal hazards associated with the handling of N_2O_4 and mixed oxides of nitrogen are as follows:

a. Inhalation of the vapors
b. Exposure of the skin to the liquid or high vapor concentration
c. Splashing of N_2O_4 or mixed oxides of nitrogen into the eyes

Safety Clothing.

Hand and Foot Protection. During the handling of these oxidizers, the hands and feet are subject to contamination. Gloves and boots that do not let N_2O_4 or mixed oxides of nitrogen through to the skin must be worn. The gloves should protect against N_2O_4 and allow free movement of the fingers. A vinyl-coated glove (7) meets these requirements. Because boots of the approved materials are not commercially available, an overboot, designed to be worn over regular safety footwear and high enough to fit comfortably under protective trousers, must be used. Boots made of polyethylene, polyvinyl chloride rubber or GR-S may be used with reasonable safety if any contamination is washed off quickly. The boots should be inspected frequently to detect flaws that might result in personal injury.

Head, Face and Body Protection. Suitable body-protective-clothing (acid- and fuel-resistant, vinyl coated protective suit) should be worn. Polyethylene clothing may also be worn. Fiberglass clothing impregnated with acid-resisting plastics, such as polytetrafluoroethylene (TFE) and polymonochlorotrifluoroethylene, is excellent for handling N_2O_4 and mixed oxides of nitrogen. Ruber may burn when it comes into contact with N_2O_4 or mixed oxides of nitrogen. The clothing must cover all parts of the body that may be exposed. It must be adjusted so it will prevent leaks or spills from contaminating the body or draining into boots or gloves. An approved type of hood must be worn to protect the head.

Respiratory Protection. Whenever the concentration of oxides of nitrogen fumes exceed the threshold limit value, approved respiratory protection shall be worn. Approved supplied air, self-contained breathing apparatus gives the most reliable respiratory protection against gases or mists of nitrogen tetroxide. The canister-type mask is not recommended for respiratory protection against nitrogen oxides. Breathing equipment shall be NIOSH approved.

Other Safety Equipment. Work areas and storage rooms shall be provided with the equipment listed below, properly located for immediate use in an emergency.

a. Deluge safety showers which are easily accessible, clearly marked, and controlled by quick opening valves so N_2O_4 or mixed oxides of nitrogen can quickly be rinsed from the body if spillage occurs.
b. Fire blankets located near the showers

c. Eyewashes or bubbler drinking fountains, so eyes can be thoroughly irrigated without delay
d. Rescue harnesses and life lines for those entering a tank or enclosed space
e. A facility near the area for the proper storage, repair and decontamination of approved protective clothing and protective equipment
f. An adequate water supply for decontamination purposes
g. Portable or permanently installed life support detection equipment.

Several types of direct reading colorimetric indicators can be used for rapid determination of atmospheric concentrations of NO_2 or NO. Examples of these portable instruments are:

Kitagawa Precision Gas Detector, UNICO Model 400 or equivalent

M-S-A Universal, Tester Model 1, or equivalent

The instruments should be installed or kept readily available.

4.2.4 FIRST AID

4.2.4.1 Nitric Acid and High Density Acid

The following first aid procedures are recommended for the nitric acids.

First Aid and Self Aid. Inhalation of the gases and vapor evolving from RFNA can produce severe respiratory irritation which may prove fatal. Exposed individuals should be kept at rest and placed under the care of a physician.

Skin contamination should be washed off immediately and thoroughly with large quantities of cool fresh water for at least 15 minutes or with copious amounts of saturated bicarbonate of soda solution, whichever can be reached first. Early medical attention is necessary where damage to the skin or deeper tissues has occurred.

If the eyes are contaminated, they should be held open, if necessary, and flushed with copious amounts of water for at least 15 minutes or until a physician arrives. Medical treatment should be obtained as soon as possible.

If nitric acid is swallowed, liberal amounts of lukewarm water should be administered. If the acid is concentrated, it is usually unwise to induce vomiting because of the danger of rupturing the esophagus and stomach. Medical treatment should be obtained as soon as possible.

Individuals should be taught to self-administer the measures outlined above. The importance of speed in flushing the acid off the skin with water, especially from the eyes, and the need to continue the flushing process for at least 15 minutes should be emphasized.

Special Medical Information (5, 8 and 9). Exposure to dangerous atmospheric concentrations of the oxides of nitrogen may cause spasm of the terminal bronchioles and disturbance of reflexes causing respiration. Circulatory collapse may ensue, or the symtoms may subside and reappear several hours later with the onset of pulmonary edema. Complete rest from the moment of exposure is essential even if the initial symptoms are not particularly alarming. The individual should be hospitalized promptly. Certain signs indicating that severe lung damage has occurred may appear within the first few hours. These are an increase in platelets in the venous blood, often as great as 60 to 100 percent, a decrease in blood pressure, and an increase in the hemoglobin content of the blood. Spasmodic cough and dyspnea appearing several hours after exposure are evidence of the development of pulmonary edema. Bronchopneumonia may be a complication.

4.2.4.2 Nitrogen Tetroxide and Mixed Oxides of Nitrogen

The following first aid procedures are recommended for these oxidizers.

First Aid and Self Aid. If liquid N_2O_4 is spilled on skin or in the eyes, it must be removed immediately to avert serious injury. If the liquid is splashed into the eyes, immediately flush them with large amounts of water for at least 15 minutes, with a companion holding the eyes open if necessary. Summon medical assistance. Skin contamination should be immediately and thoroughly washed off with large amounts of water and the injury should be checked by a physician.

Persons exposed to N_2O_4 vapors should be removed at once from the contaminated area. When the vapors can be seen, smelled or sensed by the eyes or throat, there may be imminent danger.

Persons exposed to the vapors should be carried and not allowed to walk; other exertion should also be discouraged. It is difficult to tell soon after exposure how much physical damage has occurred. Despite their protestations of well-being, persons so exposed should be removed to a hospital. Absolute rest is essential; patients should be kept warm but not overheated. Administration of oxygen by properly trained persons is often desirable. Apply artificial respiration whenever breathing stops.

Special Medical Information. (See References 6, 8, and 9). The development of pulmonary edema is the principal danger associated with the inhalation of N_2O_4 vapor. A person may breath an atmosphere containing a dangerous concentration of N_2O_4 vapor without serious discomfort at the time, only to suffer severe effects several hours later. Detailed therapeutic regimen is described in Reference 10.

Repeated exposure to low level concentrations of N_2O_4 vapors may cause ulceration of the nose and mouth, wearing down and decay of teeth and chronic irritation of the entire respiratory tract. Bronchitis, bronchiectasis, and secondary pulmonary edema may develop.

4.2.5 DETECTION OF FUMES

Although a number of devices have been proposed from time to time for the detection of fumes of nitric acid and nitrogen tetroxide and for the monitoring of personnel exposure, none of these devices has experienced general acceptance in the rocket or chemical industry. Reliance is thus placed on the sense of smell. It should be of some concern to those responsible for health and safety to note that the odor threshold is an order of magnitude higher than the recommended TLV for an 8-hour day exposure. Further, vapors are known to cause olfactory fatigue; thus, the detection of fumes by odor can be used only as an initial warning of potential danger. Area fume-monitoring devices are described in section 4.2.7.

4.2.6 LEAK DETECTION

There is no chemical reagent currently available for the specific detection of nitric acid or nitrogen tetroxide or its residues in very small quantities (11). Until one becomes available, the detection of nitric acid by means of a pH-indicating paper must be relied upon. Nitric acid (and nitrous acid) is produced when nitrogen tetroxide is diluted with water, as follows:

$$N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2$$

Hydrion paper is also used for this purpose, except that pH values are less than 7 in solutions of nitric acid. This paper is capable of reliably measuring acidity produced by nitrogen tetroxide concentrations as low as 3×10^{-6}% (0.03 ppm).

Although this is not a specific test, it is 50 times more sensitive than colorimetric spot tests that are specific. The specific tests also have the disadvantage of requiring the use of concentrated sulphuric acid as a solvent for the reagents. This makes the test unusable with samples in water solutions and on filter paper. For detecting acidity caused by N_2O_4 the Hydrion paper is used in the same manner as it is used to detect alkalinity caused by hydrazine and UDMH. The color chart supplied with the paper is consulted to determine the color corresponding to the lowest level of detectable acidity.

Currently there are two development efforts, associated with the Space Shuttle, which may produce acceptable hardware to monitor oxidizer leakage occurrence. These are the NASA/KSC effort, RTOP-909-60-09-Task 63, and the Brooks AFB effort initiated February 12, 1976.

4.2.7 AREA MONITORING

There are several instruments available specifically for detecting the presence of oxides of nitrogen in the air. The Kitagawa Company manufactures a portable detector for air sampling. A dry reagent turns yellowish brown at NO_2 concentrations of approximately 2.5 ppm. This instrument is distributed by the Union Industrial Equipment Corporation, Port Chester, New York (1). Kruger Instrument Company and American Systems Incorporated (11) manufacture a recording device for detecting oxides of nitrogen in the order of 1 ppm.

Another portable device, manufactured by Brothers Chemical Company of Orange, New Jersey, is being used by Aerojet with success. This device uses a precision volumetric pump for air sampling. A color change imparted to detector tubes indicates the presence of oxides of nitrogen in the range of 0.1 to 500 ppm.

American Systems, Incorporated manufactures portable and fixed devices for detecting NO_2. An electrical current is developed by a sensing cell when NO_2 is absorbed by a solution. This current is proportional to the quantity of NO_2 absorbed. The instruments can sense NO_2 concentrations over the range of 0 to 250 ppm.

The General Electric Vapor Detector is a fixed unit sensitive to NO_2 over the range of 0 to 100 ppm. This unit is no longer manufactured.

A unit manufactured by Teledyne Systems, Olfactron Foxie Propellant Vapor Detector—Model 6110 (12), was used by Apollo for detecting the presence of oxides of nitrogen in air.

4.2.8 DOSIMETERS

A prototype dosimeter has been developed and tested by the Bureau of Mines, U. S. Department of the Interior for oxides of nitrogen.

4.3 FIRE AND EXPLOSION HAZARDS

4.3.1 GENERAL

All of the oxidizers covered in this Handbook by themselves will not burn. The fumes liberated support combustion. The type of fire that may occur is governed by the combustible material or fuel involved. These oxidzers are stable to mechanical shock and impact.

A list of the tests conducted to evaluate the hazard potential of liquid rocket propellants is given in Table 4.3-1 from Reference 13.

TABLE 4.3-1 LIST OF SAFETY TESTS USED TO DETERMINE FIRE AND EXPLOSION HAZARDS

TEST	USED TO DETERMINE
Drop Weight Test	Whether propellant detonates. How much energy required.
Card Gap Test	Whether propellant detonates. How much energy required.
Modified Card Gap	Detonation velocity. Energy required to initiate.
1/4 in. Tube Detonation	Whether detonation propagates. Distance of propagation.
Wedge Test and Other Critical Diameter Tests	Detonation velocity. Critical diameters.
Trauzl Block Test	Energy released by detonation. Whether propellant detonates.
Thermal Stability Test	Decomposition Temperature Limits.
Pan Burning Test	Intensity and Duration of fires. Extinguishment and control.
Open Cup Test	Ease of ignition of vapors in air.
Flammability Limit Test	Limits of flammability of vapor in air.
Spontaneous Ignition Test	Temperature of spontaneous ignition.
Gross Spill Test (bipropellants)	TNT Equivalent explosion hazard.

Specific information concerning each of the oxidizers follows.

4.3.2 FIRE HAZARDS

4.3.2.1 Nitric Acid and High Density Acid

Nitric acids by themselves will not burn. The fumes liberated by the acids support combustion. The type of fire that may occur in the presence of nitric acid is governed by the combustible material or fuel involved. Acid spills may ignite materials such as wood or rope, and the fire will be typical of the materials burning. Aniline and other hypergolic fuels quickly ignite on contact with acid. Both hypergolic and nonhypergolic fuels, once ignited, undergo flare burning in contact with the acids. The intensity of this type of fire depends upon the rate at which the fuel and acid mix; if large quantities of fuel and acid are mixed rapidly, there may be a violent reaction.

4.3.2.2 Nitrogen Tetroxide and Mixed Oxides of Nitrogen

N_2O_4 and mixed oxides of nitrogen are normally stored and handled as liquids without refrigeration. Liquid N_2O_4 and mixed oxides of nitrogen will not burn; however, they will support combustion.

The oxygen content of N_2O_4 is about 70 percent by weight. When mixed with a fuel, it readily supports combustion. N_2O_4 is hypergolic with a number of fuels, including UDMH, hydrazine, aniline and furfuryl alcohol. Mixed oxides of nitrogen are less hypergolic with increasing concentrations of NO.

Table 4.3-2 contains the observed results of various materials after exposure to N_2O_4 drippings at room temperature in air; certain materials were soaked in N_2O_4 for 20 seconds (14). In both instances, after exposure to N_2O_4, the materials were allowed to gas off in air for a minimum time of one hour. Of all the materials tested, only 50/50 fuel blend, aniline, four commercially available rubber gloves, and masking tape ignited spontaneously. Methyl and isopropyl alcohol, acetone, and benzene caused temperature rises, but no ignition.

Similar tests are recommended for all materials where information is lacking on the fire hazard potential of the material when used in areas where N_2O_4 spills may occur.

4.3.3 EXPLOSION HAZARDS

4.3.3.1 Nitric Acid and High Density Acid

Although nitric acid is stable to mechanical shock and impact, upon contact with certain fuels (such as aniline or furfuryl alcohol) it will react violently. Nitric acid will form explosive mixtures with nonhypergolic fuels (such as hydrocarbons) and with hypergolic fuels if either the fuels or the nitric acid are not diluted with an excess of water. In rare instances, as on gross contact with certain materials (e.g. H_2) and when spontaneous ignition is delayed because of degraded materials, an explosion may occur. High temperatures in confined spaces may cause containers or other equipment to rupture from pressure build-up.

TABLE 4.3-2 FIRE HAZARD TESTS OF VARIOUS MATERIALS EXPOSED TO N_2O_4

MATERIAL	OBSERVATIONS
Liquids	
Acetone	No ignition, acetone turned green, 80°F rise when N_2O_4 added below surface
Aniline	Ignition preceded by popping and sparking
Benzene	No ignition, 5°F rise when N_2O_4 added below surface
50/50 Fuel Blend	Immediate audible report with ignition
Isopropyl Alcohol	No ignition even when heated to 120°F prior to dripping N_2O_4, 60°F rise when N_2O_4 added below and on surface
Kel-F Fluorocarbon Oil 3	No ignition
Methyl Alcohol	No ignition, 5°F rise when N_2O_4 added below surface
Motor Oil (SAE10)	No ignition, slight foaming
Penetrating Oil	No ignition, discolored
Red Hydraulic Oil (MIL-H-5606A)	No ignition, darkened
Silicone Oil SF77	No ignition
Trichlorethylene	No ignition

TABLE 4.3-2 (Continued)

MATERIAL	OBSERVATIONS	
	SOAK	DRIP
Solids		
Asphalt	No ignition	No ignition
Blotter		No ignition
Cadmium (mossy)		No ignition
Cardboard	No ignition	No ignition
Cotton Cloth		No ignition
Dust		No ignition
Dacron Yarn	No ignition	No ignition, dissolved
Fairprene Cloth (Neoprene 0.01 inch thick)	No ignition	No ignition, hardened
Grass (dry)		No ignition, bleached
Leather	No ignition	No ignition, softened
Leaves		No ignition, bleached
Magnesium (turnings)		No ignition
Mohair		No ignition
Molykote G		No ignition
Mylar	No ignition	No ignition, softened
Nylon Cloth	No ignition	No ignition, dissolved
Nylon Yarn		No ignition, dissolved
Orlon Yarn		No ignition
Paper		No ignition
Rags (oily)		No ignition
Rayon (taffeta)	No ignition	No ignition, dissolved
Rubber Gloves (surgical)		
Latex Seamless Standard (0.008 in.)		No ignition
Amber Plus (0.0137 in.)		No ignition, hardened
National Glove No. 200 (0.018 in.)		No ignition, hardened and became brittle
Latex, Davol (0.008 in.)	Ignition in 75 sec.	Ignition after 160 seconds
Ebonettes (0.013 to 0.015 in.)	Ignition in 90 sec.	No ignition
Rollproof[a] 32894	Ignition	
Neosole[b] SA8-8N-3032	Ignition	
Sawdust		No ignition, darkened
Silk Cloth		No ignition, bleached
Silk Cloth (Hong Kong)		No ignition
Styrene (Styrofoam)	No ignition	No ignition, dissolved
Tape (Masking)	Ignition in 20 sec.	Ignition in 15-20 seconds
Tobacco		No ignition
Vermiculite		No ignition
Wool		No ignition, bleached

[a] Wyle Laboratories Communication

[b] The Martin Marietta Corporation Communication

4.3.3.2 Nitrogen Tetroxide and Mixed Oxides of Nitrogen

N_2O_4 and mixed oxides of nitrogen are oxidizers, but they are not hypergolic with all combustible materials. Such non-hypergolic mixtures, therefore, present an explosion hazard, particularly when subjected to elevated temperatures, pressures or impact. If containers leak, the oxides of nitrogen vapors can form explosive mixtures with fuel vapors, especially in confined spaces. N_2O_4 of commercial purity and mixed oxides of nitrogen are stable at ordinary temperatures. There is a possibility that containers in proximity to a fire may pressure rupture and the released vapors can form explosive mixtures.

Organic materials and partially halogenated solvents shall not be used as flushing or decontamination fluids unless specifically tested previously under the conditions of usage. Mixtures of N_2O_4 and mixed oxides of nitrogen and the following partially halogenated solvents can be initiated by heat and shock, yielding violent explosions:

Methylene chloride
1, 1, 1, Trichlorethane
(Methyl Chloroform)
Trichloroethylene
Perchlorethylene
Chloroform Carbon Tetrachloride
Dichloroethylene
1, 2-Dichloroethane
Asymmetrical Tetrachloroethane
Mixtures of N_2O_4 and ethylene glycol when confined will react explosively.

Martin Marietta (15) and Aerojet (16) performed drop-weight tests with a modified Army Ballistic Missile Agency impact tester. The materials were immersed in N_2O_4 and the plummet was dropped. The results of the tests as shown in Table 4.3-3 indicate that only polydimethylsiloxane and penton 1215 (a chlorinated polyether) detonated on impact. Some of the others exhibited chemical attack.

TABLE 4.3-3 RESULTS OF IMPACT TESTS IN LIQUID N_2O_4

MATERIAL	ENERGY, FT-LB	RESULTS	REFERENCE
Polychloroprene	70	Passed	15
Polydimethylsiloxane	70 60 50	Failed Failed Passed	15 15 15
Polyethylene, Branched	70	Passed	15
Polyethylene, Linear	70	Passed	15
Polypropylene	70	Passed	15,16
Polyvinylidene Fluoride	70	Passed	15
Fluorel (Viton A)	70	Passed	15,16
Alathon 34 (Irradiated)	70	Passed	16
Parco 805-70	70	Passed	16
Linear 7806-70	70	Passed	16
Precision 9257	70	Passed	16
Kel-F 300	70	Passed	16
Penton 1215	70 60 50	Failed Failed Passed	16 16 16
Teflon TFE 1	70	Passed	16
Teflon 100X	70	Passed	16
Resin Cured Butyl (Formula 121)	400/in.^{2}	Passed	17
Ethylene Propylene Rubber (Formula 132)	400/in.^{2}	Passed	17

4.4 REFERENCES

1. *Liquid Propellant Handling, Storage and Transportation,* Volume III, CPIA Publication 194, Chemical Propulsion Information Agency. Change 1, July 1, 1972.

2. American Conference of Government Industrial Hygenists (ACGIH) Standards.

3. *Titan II Storable Propellant Handbook,* AFBSD-TR-62-2, Bell Aerosystems Company, March 1963.

4. AFM-127-100, *Explosive Safety Manual,* (Department of the Air Force), 20 April 1964.

5. AFM 127-201, *Missile Safety Handbook,* Department of Air Force.

6. AFRPL-TR-67-241, AD819289, *Inhibited N_2O_4 Engineering Data,* Department of the Air Force.

7. AFTO 11C-1 6, *General Safety Precautions—Missile Liquid Propellants,* Department of the Air Force, 18 October 1961; rev. 27, November 1961, AFTO 11C-1-6C (Same title) 31 August 1962.

8. AFP 160-6-3, *Health Hazards from Propellant Fuels and Oxidizers,* Department of the Air Force.

9. AFP 161-1-1, *Respiratory Protective Devices,* 29 August 1962

10. Fleming, A. J., M.D., *A Method for Handling Cases Gassed with Nitrous Fumes,* Industrial Medicine, 12 March 1973.

11. Aerojet LRP-198, *Storable Liquid Propellants Nitrogen Tetroxide/Aerozine 50,* Revision B, October 1960.

12. Teledyne Systems Brochure, *Olfactron Toxic Propellant Vapor Detector—Model 6110,* March 1976.

13. *USAF Propellant Handbook, Hydrazine Fuels,* AFRPL-TR-69-149, Volume 1, March 1970.

14. AFBSD *Storable Propellant Data for the Titan II Program,* Bell Aerosystems Company, Second Progress Report, AFBSD-TDR-62-6, March 1962.

15. *Mechanically Initiated Reactions of Organic Materials in Missile Oxidizers,* ASD-TR-61-324, The Martin Company, October 1961.

16. *Conversion of Titan Engine for Use with Storable Non-Cryogenic Propellants,* CCN103, Report No. CRP 166, Aerojet-General Corporation, Liquid Rocket Plant, May 11, 1960 (Confidential).

17. Reaction Motors, Division of Thiokol Chemical Corporation, *Elastomeric and Compliant Materials for Contact with Liquid Rocket Fuels and Oxidizers,* Report RMD2028-P7, September 1962.

5.0 APPENDICES

5.1 INDEX OF PROPELLANTS, ACRONYMS AND COMPOSITIONS

5.2 UNITS AND CONVERSION FACTORS

TABLE 5.1 INDEX OF PROPELLANTS, ACRONYMS AND COMPOSITIONS

OXIDIZER	COMPOSITION OR FORMULA	OTHER NAMES	SECTION (PROPERTIES)
HDA	55.0 HNO_3 · 44.0 NO_2 · 0.5 H_2O · .04 Solids · 0.7 HF	High Density Acid	2.2
IRFNA	83.2 HNO_3 · 14.0 NO_2 · 2.0 H_2O · .04 Solids · 0.7 HF	Inhibited Red Fuming Nitric Acid	2.1
IWFNA	96.8 HNO_3 · 0.5 NO_2 · 2.0 H_2O · .10 Solids · 0.7 HF	Inhibited White Fuming Nitric Acid	2.1
Modified HDA	55.0 HNO_3 · 44.0 NO_2 · 0.5 H_2O · .04 Solids · 0.5 PF_5	HDA · PF_5 Inhibitor	2.2
MON-1	98.5 N_2O_4 · 1.0 NO · 0.17 H_2O · .10 Solids	Mixed Oxides of Nitrogen	2.3
MON-3	96.5 N_2O_4 · 3.0 NO · 0.17 H_2O · .10 Solids	Mixed Oxides of Nitrogen	2.3
MON-10	88.8 N_2O_4 · 10.0 NO · 0.17 H_2O · .10 Solids	Mixed Oxides of Nitrogen	2.3
MON-25	73.8 N_2O_4 · 25.0 NO · 0.17 H_2O · .10 Solids	Mixed Oxides of Nitrogen	2.3
Nitric Acid (Anhydrous)	99.0 HNO_3 · 1.0 H_2O	Nitric Acid	2.1
Nitric Acid (90%)	89.5 HNO_3 · .02 NO_2 · 10.0 H_2O · 0.6 HF	90% Nitric Acid	2.1
Nitric Acid – Type I	97.5 HNO_3 · 0.5 NO_2 · 2.0 H_2O · .10 Solids	WFNA	2.1
Nitric Acid – Type IA	96.8 HNO_3 · 0.5 NO_2 · 2.0 H_2O · .10 Solids	IWFNA	2.1
Nitric Acid – Type II	91.3 HNO_3 · 6.0 NO_2 · 2.0 H_2O · .10 Solids	RFNA	2.1
Nitric Acid – Type III	83.9 HNO_3 · 14.0 NO_2 · 2.0 H_2O · .10 Solids	RFNA	2.1
Nitric Acid – Type IIIA	83.2 HNO_3 · 14.0 NO_2 · 2.0 H_2O · .10 Solids · 0.7 HF	IRFNA	2.1
Nitric Acid – Type IIIB	83.2 HNO_3 · 14.0 NO_2 · 2.0 H_2O · .04 Solids · 0.7 HF	IRFNA	2.1
Nitric Acid – Type III LS	85.4 HNO_3 · 14.0 NO_2 · 0.5 H_2O · .04 Solids · 0.7 HF	IRFNA-Limited Storage	2.1
Nitric Acid – Type IV	55.0 HNO_3 · 44.0 NO_2 · 0.5 H_2O · .04 Solids · 0.7 HF	HDA	2.1
Nitrogen Tetroxide (MM Grade)	99.5 N_2O_4 · 0.5 NO · 0.10 H_2O · .10 Solids	Minuteman Grade NTO	2.3
NTO	99.5 N_2O_4 · 0.1 NO · .17 H_2O · .10 Solids	Red-Brown Nitrogen Tetroxide	2.3
RFNA	83.9 HNO_3 · 14.0 NO_2 · 2.0 H_2O · .10 Solids	Red Fuming Nitric Acid	2.1
WFNA	97.5 HNO_3 · 0.5 NO_2 · 2.0 H_2O · .10 Solids	White Fuming Nitric Acid	2.1

5.2 UNITS AND CONVERSION FACTORS

5.2.1 GENERAL

The preponderance of data reported in the chemical literature for the properties of propellants is given in the c.g.s system: for engineering applications, these have been converted to English units. The hundreds of basic handbooks available to the chemist, physicist and engineer nearly all contain tables on conversion factors. These tables are rarely in exact agreement, since the progress made in laboratory equipment has afforded greater accuracy in determining some of the basic constants of measurements.

In 1963 the National Research Council (U.S.) Committee on Fundamental Constants* recommended a uniform set of fundamental constants to be used in physical chemistry. These constants are divided into three categories:

(a) defined constants (ten exact values by definition)

(b) basic constants (five experimentally determined constants)

(c) derived constants (six constants coupled to basic constants through known physical relations).

5.2.2 DEFINED CONSTANTS

These constants have been accepted by the National Bureau of Standards but as yet have not been adopted by any of the international conventions such as the International Union of Pure and Applied Chemistry or the International Union of Pure and Applied Physics. The 1963 set of constants given below are taken from Rossini* and Somayajula†:

---

*Nat'l. Bureau of Standards (U.S.) Tech. News Bull., 47, No. 10, (1963).

*Rossini, F. D., J. Pure, Appl. Chem. 8, 95 (1964).

†Somayajula, G. R., et al., Annual Review of Phys. Chem., 16 213 (1965).

CONSTANT	SYMBOL	1963 VALUE
Unified atomic mass unit	u	1/12 times the mass of C^{12}
Standard acceleration of gravity (in free fall)	g	980.665 cm/sec^2
Normal atmosphere, pressure	atm	1,013,250 dyne/cm^2
‡Absolute temperature of the triple point of water	T_{tp}	273.16°K
Thermochemical calorie	cal	4.184J (joules)
International steam calorie	cal$_{IT}$	4.1866J (joules)
Inch	in.	2.54 cm (exactly)
Pound, avoirdupois	lb	453.59237 g
Liter	l	1000 cm^3

‡The ice point of water (temperature of equilibrium between solid and liquid saturated with air at one atmosphere) is .01°K less than the triple point temperature of 273.15°K.

The tenth constant defines the Mole (mole) as the amount of a substance of specified chemical formula containing the same number of formula units (atoms, molecules, ions, electrons, or other entities) as there are atoms in 12 grams (exactly) of the pure nuclide C^{12}.

5.2.3 BASIC CONSTANTS

CONSTANTS	SYMBOL	1963 VALUE
Velocity of light (vacuum)	c	2.997925×10^{10} cm/sec
Avogardo number	N	6.02252×10^{23} molecules/mole
Faraday constant	f	96,487 coulombs/mole
Plank's constant	h	6.6256×10^{-27} erg - sec
Pressure-volume product for one mole of gas at O°C and zero pressure	$(PV)^{P=0}_{0°C}$	2271.06 joules/mole 22413.6 cm^3 atm/mole

5.2.4 DERIVED CONSTANTS

CONSTANT	SYMBOL	1963 VALUE
Elementary charge (charge on the electron)	$e = f/N$	4.80298×10^{-10} e.s.u
Gas constant	R	8.31433 joules/deg-mole 1.98717 cal/deg-mole
Boltzman constant	$K = R/N$	1.38054×10^{-16} erg/deg-mole
Second radiation constant	$c_2 = hc/k$	1.43879 cm deg
Einstein constant (relating mass and energy)	$Y = c^2$	8.987554×10^{13} joules/g
Constant relating wave number and energy	$Z = nhc$	11.96255 joules-cm/mole 2.85912 cal-cm/mole

5.2.5 CONVERSION FACTORS

The table of conversion factors presented on the next page are calculated from the defined or derived constants given above. The conversion units are reported to significant figures beyond the requirements of normal engineering application. They are, however, accurate as reported and are the values used for conversions in this handbook.

TABLES OF CONVERSION FACTORS

MULTIPLY	BY	TO OBTAIN
Density		
g/cc	62.42796	lb/ft^3
g/cc	0.0361273	lb/m^3
g/cc	1.0	specific gravity H_2O at 4°C
Force		
dyne	2.248089×10^{-6}	lb weight
Energy		
cal	0.00396567	BTU
cal_{IT}	0.00396832	BTU
joule	0 000947817	BTU
Energy Content		
cal/g	1.798796	BTU/lb
cal/$_{IT}$/g	1.8	BTU/lb
cal/g-°K	0.9993312	BTU/lb-°R
cal_{IT}/g-°K	1 0	BTU/lb°R
cal/g-mole	$\frac{1.798796}{M.W.}$	BTU/lb
cal/g-mole-°K	0.9993312	BTU/lb-mole-°R
cal/g-mole-°K	$\frac{0.9993312}{M.W.}$	BTU/lb-°R
joules/g	0.429922	BTU/lb
joules/g-mole	$\frac{0.429922}{M.W.}$	BTU/lb
joules/g-°K	0.238846	BTU/lb-°R
Pressure		
atmospheres	14.695949	lb/in.^{2}
atmospheres	2116.2166	lb/ft^2
mm Hg	0.019336775	lb/in.^{2}
dyne/cm^2	1.450377×10^{-5}	lb/in.^{2}
Length		
cm	$0.3937008 = (\frac{1}{2.54})$	inches
cm	$0.0328084 = (\frac{1}{30.48})$	feet
Thermal Conductivity		
cal/cm-sec °K	0.06715196	BTU/ft-sec-°R
milliwatt/cm-sec-°K	1.604970×10^{-5}	BTU/ft-sec-°R

TABLES OF CONVERSION FACTORS (Cont.)

MULTIPLY	BY	TO OBTAIN
Viscosity		
poise (g/cm-sec)	0.0671969	lb_m/ft-sec
centipoise	6.71969×10^{-4}	lb_m/ft-sec
stoke (cm^2/sec)	0.0671969 x density (g/cc)	lb_m/ft-sec
stoke	0.00107639	ft^2/sec
stoke	0.00107639 x density (lb/ft^3)	lb_m/ft-sec
Surface Tension		
dyne/cm	6.852177×10^{-5}	lb_f/ft
dyne/cm	5.710146×10^{-6}	lb_f/in.
Standard Acceleration of Gravity (g)		
980.665 cm/sec^2		
32.174049 ft/sec^2		
Gas Constant (R)		
$8.31433 \frac{\text{joule}}{\text{g-mole-°K}}$		
1.98717 cal/g-mole-°K		
$0.0820561 \frac{\text{liter-atm}}{\text{g-mole-°K}}$		
$1545.32 \frac{\text{lb-ft}}{\text{lb-mole-°R}}$		
Temperatures		
°F = (°C x 1.8) + 32	0°C = 273.15°K	25°C = 298.15°K
°F = (°K x 1.8) - 459.67	= 491.67°R	= 536.67°R
°R = (°C x 1.8) + 491.67	= 32°F	= 77°F
°R = °K x 1.8		