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HYDRAZINE FUELS

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VOLUME I

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FOREWORD

This propellant handbook is the product of a program sponsored by the Propellants Branch of the Air Force Rocket Propulsion Laboratory. The objective of this program was to provide a comprehensive and systemized text of the properties, handling procedures, design criteria, catalytic decomposition, cost, and availability of hydrazine fuels and selected blends and ingredients of these fuels.

This program was initiated in August 1968, and was conducted by Bell Aerosystems Company, Propellants and Combustion Technology Section, for the AFRPL, under Contract FO4611-69-C-0005. Lt. Douglas Huxtable served as the Air Force Program Manager. Mr. W. R. Scott was the Bell Program Manager and Mr. W. R. Marsh was the Bell Technical Director.

This report has been assigned Bell Aerosystems identification number D8558-953014.

This technical report has been reviewed and is approved.

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ABSTRACT

The Hydrazine Fuels Handbook is a compilation of engineering information on the physical and chemical properties, storage and handling, production, transportation, safety, and the thermal and catalytic decomposition of the hydrazine family of fuels and their blends. It contains information on the following propellants:

- Ammonia
- Diethylenetriamine
- Hydrazine
- Monomethylhydrazine
- 1,1-Dimethylhydrazine
- 50/50, N_2H_4/UDMH
- MAF-1
- MAF-2
- MAF-3
- MAF-4
- MAF-5
- MHF-1
- MHF-2
- MHF-3
- MHF-4
- MHF-5
- MHF-5B
- MHF-6
- BA-1014
- BAF-1185
- MGGP-1

This 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.

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1.0 INTRODUCTION

TABLE 1.1-1 INDEX OF SUBJECT MATTER

*MHF = Mixed Hydrazine Fuel.

**MAF = Mixed Amine Fuel.

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 hydrazine, its derivatives, related compounds and blends, pertinent to their use as fuels or monopropellants 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 authors and other members of Bell Aerosystem's Company organization have carefully reveiwed and evaluated this information, and have attempted to resolve all disagreements wherever possible, with the aid of their own considerable experience in the use of these propellants.

Since 1945 hydrazine (N_2H_4) and its derivatives have become increasingly important as rocket engine fuels and monopropellants, due to a number of unique physical and chemical properties. First isolated by Lobry de Bruyn in 1894, hydrazine remained an expensive chemical curiosity for almost 50 years. Then during World War II, engineers at Walter Werke in Kiel Germany, developed a rocket engine for the Messerschmidt ME-163B manned interceptor using a hydrazine hydrate-methanol fuel blend with hydrogen peroxide as the oxidizer. In support of this project, the German Government built a plant at Gersthofen to produce 85% hydrazine hydrate by the Raschig process. After the war, details of the rocket engine, the Raschig process, several tank cars of hydrazine hydrate, and a number of key personnel were acquired by this country. These events catalyzed both the introduction of hydrazine and the initiation of exploratory development of hydrazine rocket technology in the United States.

Subsequent to 1945, several agencies undertook development of thrust chambers and rocket engine components utilizing hydrazine as fuel. Concurrently there was a lot of activity in search of fuel blends or derivatives of hydrazine that would overcome some of its shortcomings (i.e., high freezing point and a tendency toward uncontrolled decomposition in the presence of hot surfaces). Finally, improved synthesis methods for hydrazine were actively sought.

In 1950, the Olin Mathieson Chemical Company, under an Army Ordnance contract, developed a continuous Raschig synthesis process for hydrazine, which resulted in a substantial increase in availability and reduction in price. In 1954, the Westvaco Chlor-Alkali Division of FMC Corp., introduced a continuous process for synthesis of unsymmetrical dimethylhydrazine (UDMH) from ammonia and methanol. This development made an important hydrazine derivative available at a low price, and led rapidly to increased utilization of hydrazine fuels in the rocket industry. Aerojet General adopted JP-X (a blend of JP-4 jet engine fuel and UDMH) as the fuel for the Bomarc and Nike-Ajax rocket engines. Bell Aircraft adopted eutectic hydrazine as the starting fluid for the Rascal and Hustler engines, and in 1958 Bell converted the LR-81 Agena rocket engines to UDMH and IRFNA (inhibited red fuming nitric acid). Also in 1958, the Titan II rocket engine development began at Aerojet General. This engine, using a 50/50 UDMH/hydrazine fuel blend with N_2O_4 oxidizer, created for the first time a large tonnage demand for both hydrazine and UDMH, and resulted in expansion of production facilities at both Olin and FMC.

Today a large variety of possible blends incorporating hydrazine and its derivatives are known. Early development of blends began in an effort to provide fuels which will freeze at -65F or lower, be free flowing at these temperatures, and have better thermal stability than hydrazine, for use as a regenerative coolant.

Although a number of hydrazine fuel blends have been investigated since 1945, those which have survived and which appear in this Handbook have their origins in 1955 or later. Blends of hydrazine with methanol, hydrogen sulfide, hydrogen cyanide, methylamine, lithium borohydride, and others have been investigated, but most were abandoned for various deficiencies. Water, ammonia, hydrazinium nitrate, and the methyl-substituted hydrazines have survived, along with diethylenetriamine and acetonitrile, as the components for all hydrazine fuel blends in use today. Investigation of new and improved blend is still continuing, and components such as hydrazinium azide, hydrazinium pechlorate, and methoxylamine have shown promise.

As discussed in Section 3.0, all of the blends described in this Handbook can be considered as members of seven families of ternary mixtures, the properties of which vary regularly and predictably with composition. With the help of the ternary diagrams presented herein, the investigator can select compositions having the most satisfactory combination of properties to suit his needs.

The use of hydrazine as a monopropellant for attitude control thrusters and as a gas generator for propellant tank pressurization has been under investigation since the late 1940's. JPL developed a monopropellant hydrazine orbit adjust system for the Ranger and Mariner space vehicles using an N_2O_4 "slug" start in conjunction with a cobalt-alumina thermal reactor which would sustain decomposition of the hydrazine, or restart spontaneously, if its temperature was above 400F.

A significant breakthrough in monopropellant hydrazine technology was the development of Shell 405 catalyst. This catalyst, which will spontaneously decompose hydrazine and some of the fuel blends at room temperature, consists of iridium metal deposited on a high surface area alumina substrate. The availability of Shell 405 since 1965 has triggered a number of development programs in the small thrust chamber and gas generator field using monopropellant hydrazine. The high cost and scarcity of iridium limits its operational use; hence a search for a low-cost spontaneous catalyst for hydrazine is still under way at this writing. More about monopropellant catalytic decomposition can be found in Section 6.

1.2 SCOPE AND CONTENT

This handbook is a comprehensive compilation of all available data pertaining to propellants composed of hydrazine, ammonia, hydrazine derivatives, diethylenetriamine and water. An extensive treatment of the physical, chemical, thermodynamic, and electrical properties of the propellants is combined here, in a single volume, with a survey of the available information on storage, handling, safety, materials compatibility, cost, and availability. Also included are sections describing the variation of properties with composition of blends, and the catalytic and thermal decomposition behavior of some of the propellants.

1.3 USER INSTRUCTIONS

1.3.1 Format

This Handbook is divided into seven major sections (1.0-7.0). 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 under that section tab. Each major subsection has a seperator (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 on the Section 7.0 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 2.4.3.3 denote the following information:

> The first numeral, 2, denotes major section 2, properties. The second numeral, .4, denotes the propellant, MMH. 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 will 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. For example, section 2.19 (MHF-6) contains subsection 2.19.3.2 (density) followed by subsection 2.19.3.5 (viscosity). This indicates that no data were available for the indicated properties, "sonic velocity" and "compressibility".

1.3.2 Use of Index and References

Each section divider contains an index to the contents of that section. The major section dividers (tabbed) list 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 Section 7 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 back of 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, 4.0, 5.0, and 6.0) 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 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 AMMONIA

2.1.1 PROPERTY SUMMARY SHEET

Chemical Name: Ammonia
Common Name: Ammonia
Chemical Formula: NH_3
Formula Weight: 17.032 (O^{16}), 17.0306 (C^{12})

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	195.40	°K	-	(2)	
	−77.75	°C			
	351.72	°R			
	−107.95	°F			
HEAT OF FUSION	1351.6	cal/mole	MP	(2)	
	142.75	BTU/lb	(195.40)		
NORMAL BOILING POINT	239.80	°K	-	*	
	−33.35	°C			
	431.64	°R			
	−28.03	°F			
HEAT OF VAPORIZATION	5.569	kcal/mole	NBP	(10)	2.1-17
	588.16	BTU/lb			
TROUTON CONSTANT	23.2	-	NBP		
CRITICAL STATE CONSTANTS					
Temperature	405.6	°K		*	
	132.4	°C			
	730.1	°R			
	270.4	°F			
Pressure	112.2	atms		*	
	1647.5	psia			
Density	0.235	g/cc		*	
	14.671	lb/ft^3			
VAPOR PRESSURE OF LIQUID	9.897	atm	298.15	(3) (1)	2.1-1, 2.1-2
	145.45	psia			2.1-3
DENSITY OF LIQUID	0.6819	g/cc	NBP	(4) (31)	2.1-4, 2.1-5
	42.570	lb/ft^3			2.1-6
SONIC VELOCITY	1731	m/sec	NBP	(8) (28)	2.1-7
	5679	ft/sec			
COMPRESSIBILITY OF LIQUID					
ADIABATIC	4.960×10^{-5}	atm^{-1}	NBP	(8) (28)	2.1-8
	3.375×10^{-6}	psi^{-1}			
ISOTHERMAL	7.664×10^{-5}	atm^{-1}		(51)	
	5.215×10^{-6}	psi^{-1}			2.1-9
VISCOSITY OF LIQUID	0.2527	centipoise	NBP	(12) (13) (14) (17)	2.1-10
HEAT CAPACITY OF LIQUID	1.698×10^{-4}	lb_m/ft-sec		(22) (23) (24) (21)	
	1.066	cal/g-°K	NBP	(2) (9)	2.1-15, 2.1-16
	1.065	BTU/lb-°R			
THERMAL CONDUCTIVITY OF LIQUID	1.355×10^{-3}	cal/cm-sec-°K	NBP	(36) (52) (24)	
	9.105×10^{-5}	BTU/ft-sec-°R			2.1-12
SURFACE TENSION	34.05	dynes/cm	NBP	(15) (16)	2.1-11
	2.33×10^{-3}	lb/ft			
PARACHOR	60.5	-		*	
DIELECTRIC CONSTANT	21.29	-	NBP	59, 60, 61, 63, 64, 67	2.1-13
ENTROPY (GAS)	40.73	cal/mole-°K	298.15		
	2.390	BTU/lb-°R		34	
ENTROPY (LIQUID)	24.80	cal/mole-°K	298.15	34	
	1.455	BTU/lb°R			
HEAT OF FORMATION (LIQUID)	−17.104	kcal/mole	NBP		
	−1806.4	BTU/lb			
REFRACTIVE INDEX	1.3298	-	298.5	73	

* [illegible]

2.1.2 GENERAL

2.1.2.1 Introduction

Ammonia is one of the most widely used chemicals produced in this country. As a fuel, it is mildly cryogenic and gives high performance with most oxidizers. It was used in the NAA X-15 rocket-powered research aircraft.

Ammonia is a colorless gas at room temperature and is easily detected by its strong odor. It is miscible in all proportions with the hydrazines, and water, both separately and in multi-component combinations. Thus, it offers some potential as an ingredient of propellant blends. Ammonia acts as a freeing-point depressant on hydrazine and water. It forms two solid hydrates, NH_3-H_2O and 2 NH_3-H_2O at low temperatures.

The history of ammonia goes back to the Egyptians who, in the fourth century B.C., reportedly used ammonium chloride prepared by the distillation of camel dung. Ammonia was produced commercially for many years as a byproduct in the manufacture of coke and gas from coal. The present day manufacture of ammonia is largely based on modifications of the Haber-Bosch systems; direct synthesis from nitrogen and hydrogen in the presence of a catalyst.

2.1.2.2 Structure of Ammonia

The ammonia molecule is nearly tetrahedral in shape, with a wide equilateral triangle base with nitrogen at the apex. The height of the molecule is 0.360 Å; it has an N-H bond distance of 1.016 Å, an H-H bond distance of 1.645 Å. The H-N-H bond angle is variously reported as 107 and 109 degrees. The dipole moment is 1.46 x 10^{-18} esu. Considerable hydrogen bonding between molecules results in freezing and boiling points higher than expected.

A more complete and current description of the ammonia structure can be obtained from Reference 69.

2.1.2.3 Specification

Procurement, analysis, and use of anhydrous propellant grade ammonia is covered by MIL-P-27406 (USAF) which calls for a purity of at least 99.5% NH_3. This specification is dated 2 May 1966. Further details are noted in Section 2.1.6.

2.1.3 PHYSICAL PROPERTIES OF AMMONIA AND NORMAL BOILING POINT

2.1.3.1 Vapor Pressure

The vapor pressure of liquid ammonia has been so would constitute a major task. Fortunately, several reviews of the literature have been made. In 1913, Goodenough and Mosher(32) prepared thermodynamics tables for ammonia making extensive use of the early (1847) work of Regnault. Cragoe, Meyers and Taylor(3) of the National Bureau of Standards made a critical review of the earlier literature in their paper on vapor pressure. Armstrong(5) in 1953, Davis(34) in 1956 and Edwards(35) in 1964 are the most recent reviews.

In general, all the studies prior to the work of Cragoe and his co-workers in 1918 are of historical interest only. Since this study, the works of Overstreet and Giauque(2), Beattie and Lawrence(1), Keyes and Brownlee(7), and Henning and Stock(30), are of importance for liquid pressures.

The vapor pressure of the solid has been reported by Karwat(42), Postma(29) and Overstreet(2). The latter work is undoubtedly superior but all three studies are in essential agreement and cover a temperature range from -111 C (-79 F) to the melting point. The experimental data are presented in Figures 2.1-1 and 2.1-1a. The combined data were found to be represented best by the classical Kirchoff equation

$$\log P\ (\text{mm Hg}) = 1.00094 - \frac{1631.54}{T,\ ^{\circ}K} \qquad (2.1\text{-}1)$$

$$\log P\ (\text{psia}) = 8.29576 - \frac{2936.77}{T,\ ^{\circ}R} \qquad (2.1\text{-}1a)$$

The triple-point pressure from equation 2.1-1 is found to be 45.67 mm Hg at 195.40K.

The vapor pressure of liquid ammonia is reported here in two separate temperature ranges. The experimental data for the range from the melting point to -13 C (11 F) were taken from the studies of Overstreet(2), Cragoe(3) and Henning(30). The work of Cragoe is most heavily weighted simply because of the greater number of experimental values. All temperatures were corrected to the presently accepted ice point. As many of the experimental data points as could be conveniently plotted are shown in Figures 2.1-2 and 2.1-2a.

Several different equations were used in an attempt to express the combined data. A third-degree polynomial with the inverse of absolute temperature gave an average deviation of 0.124% and a standard deviation of 0.727 mm Hg. The coefficients found by the least-squares method are:

$$\log P\ (\text{mm Hg}) = 8.48827 - \frac{1671.722}{(T.\ ^{\circ}K} + \frac{1.34466.8}{(T,\ ^{\circ}K)^2} - \frac{1.34390\text{x}10^7}{(T,\ ^{\circ}K)^3} \qquad (2.1\text{-}2)$$

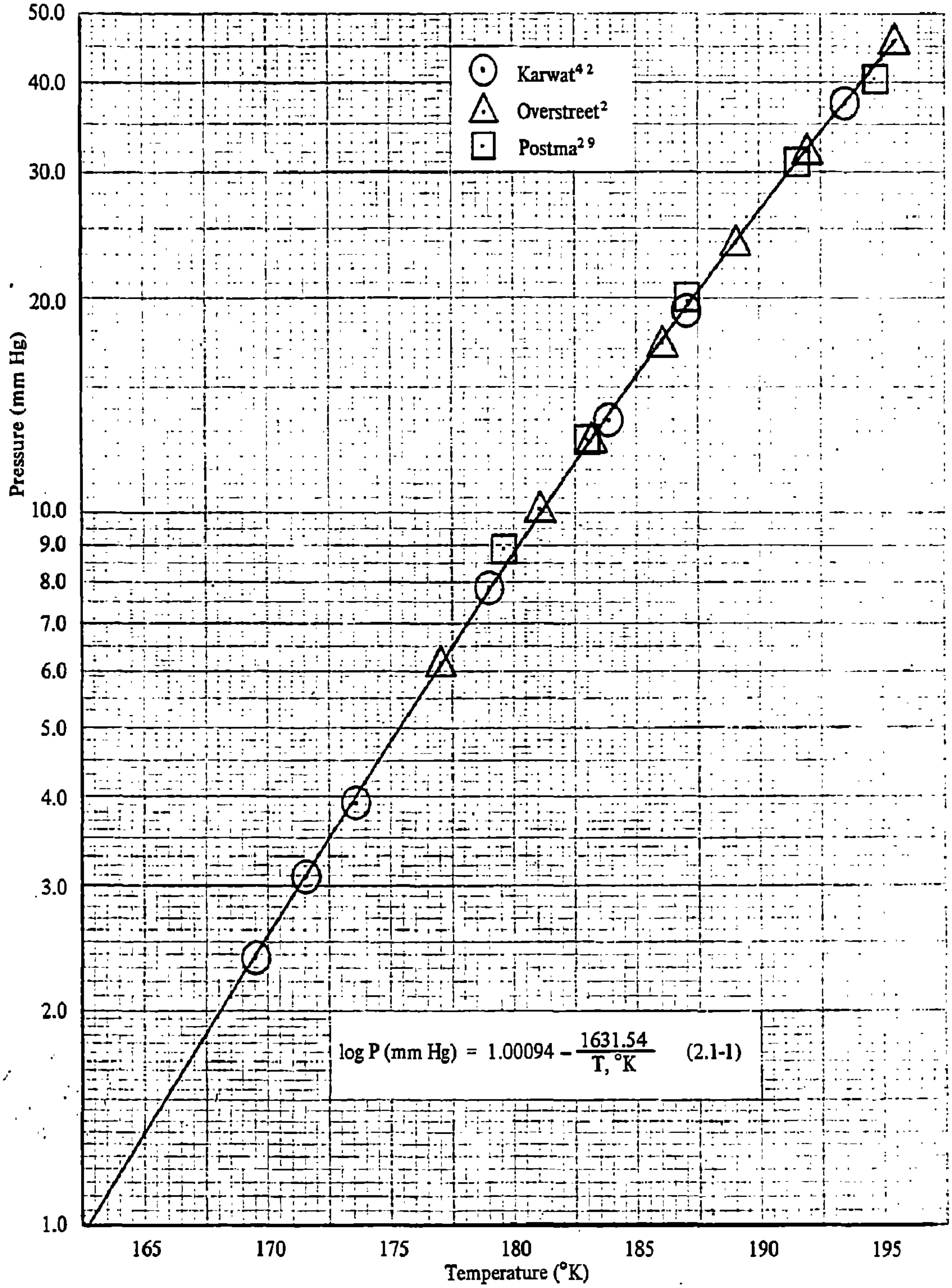


Figure 2.1-1. Vapor Pressure versus Temperature, Solid Ammonia

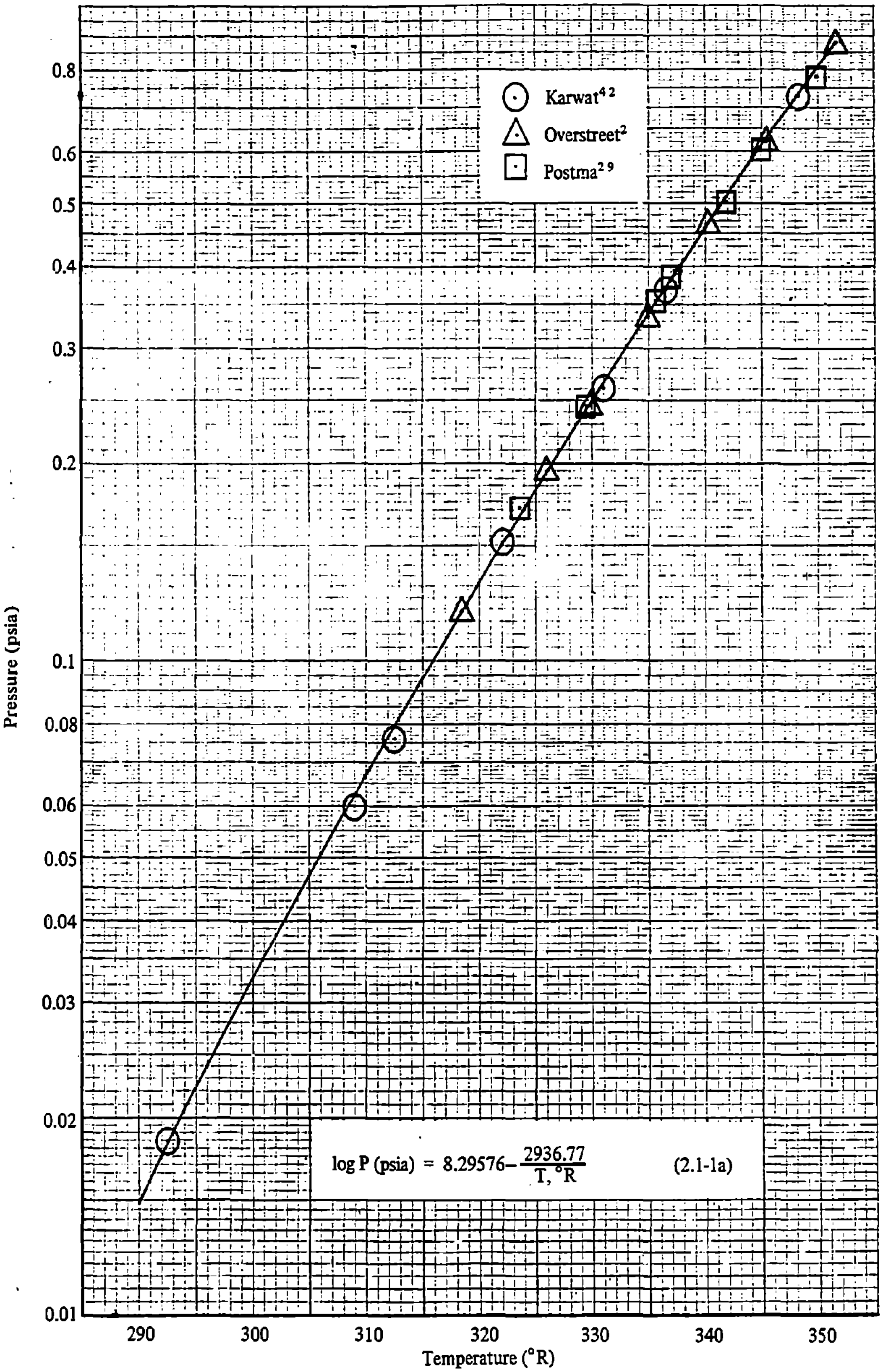
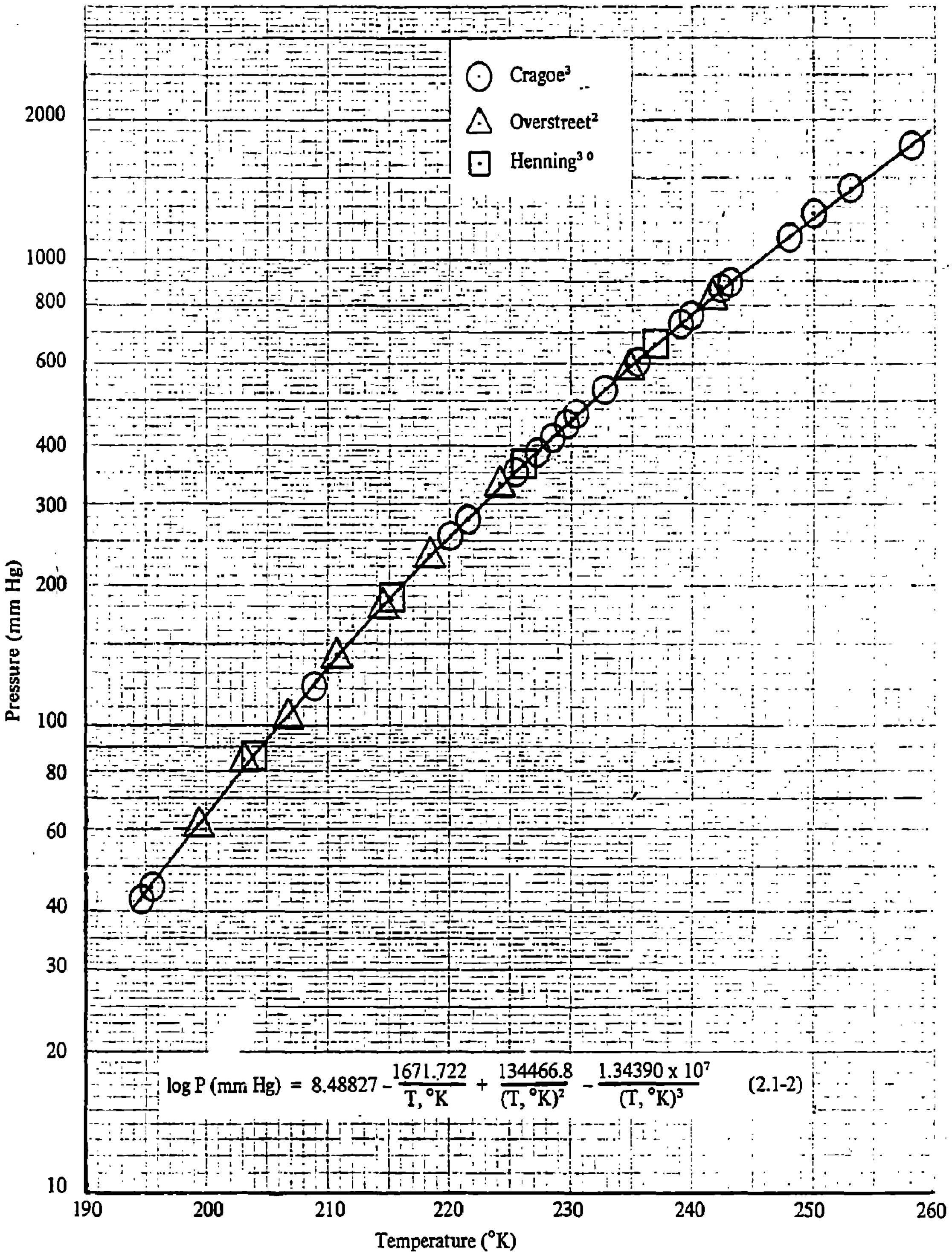
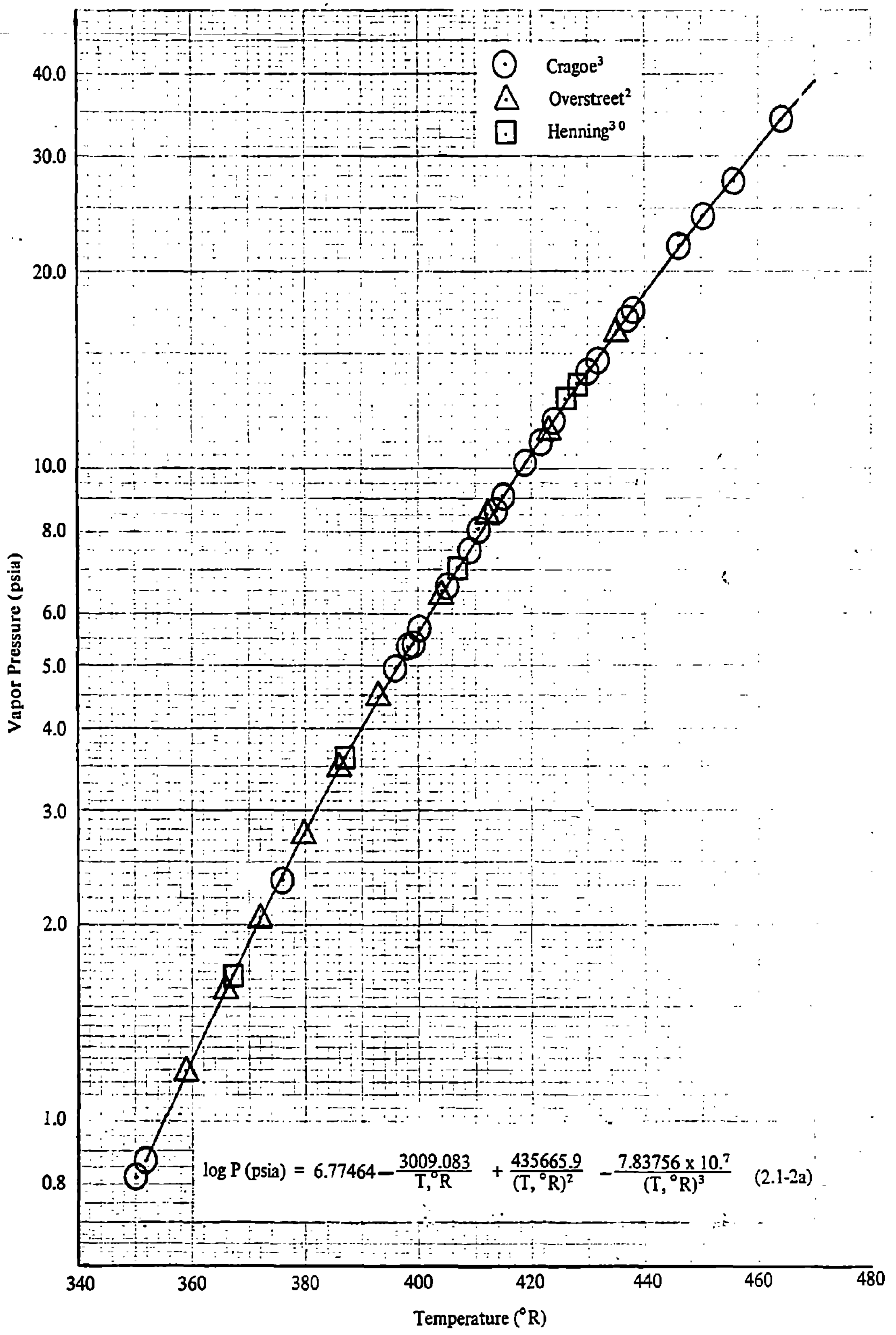


Figure 2.1-1a. Vapor Pressure versus Temperature, Solid Ammonia



$$\log P\,(\text{mm Hg}) = 8.48827 - \frac{1671.722}{T,\,°K} + \frac{134466.8}{(T,\,°K)^2} - \frac{1.34390 \times 10^7}{(T,\,°K)^3} \qquad (2.1\text{-}2)$$

Figure 2.1-2. Vapor Pressure versus Temperature, Liquid Ammonia



$$\log P\,(\text{psia}) = 6.77464 - \frac{3009.083}{T,°R} + \frac{435665.9}{(T,°R)^2} - \frac{7.83756 \times 10.^{7}}{(T,°R)^3} \qquad (2.1\text{-}2a)$$

Figure 2.1-2a. Vapor Pressure versus Temperature, Liquid Ammonia

$$\log P\ (\text{psia}) = 6.77464 - \frac{3009.083}{T,\ {}^\circ R} + \frac{435665.9}{(T,\ {}^\circ R)^2} - \frac{7.83756\text{x}10^7}{(T,\ {}^\circ R)^3} \qquad (2.1\text{-}2a)$$

The normal boiling point obtained from equation 2.1-2 is 239.80 K or 431.64 R. This value is accepted in this work and discussed in detail later.

For the temperature range from −13C (11F) to the critical point, the experimental data of Cragoe(3) and Beattie and Lawrence(1) were chosen. The work of Keyes and Brownlee(7) has been reviewed by Davis(34), Armstrong(5) and Edwards(35) and found to be approximately 1% high. In a later paper, Keyes(44) redetermined the vapor pressure and stated that the earlier study was in slight error. In the later work, only a few smoothed values were given to compare with the work of Cragoe(3). Since the experimental data were not given, this study could not be used. The experimental data for the temperature range under discussion are plotted in Figures 2.1-3 and 2.1-3a.

The experimental data were found to be best represented by

$$\log P\ (\text{atm}) = 8.42347 - \frac{1565.85}{T,\ {}^\circ K} - 0.01036\ (T,\ {}^\circ K) + 1.0269 \times 10^{-5}\,(T,\ {}^\circ K)^2 \qquad (2.1\text{-}3)$$

$$\log P\ (\text{psia}) = 9.59079 - \frac{2818.55}{T,\ {}^\circ R} - 5.7559\text{x}10^{-3}(T,{}^\circ R) + 3.1696 \times 10^{-6}\ (T,{}^\circ R)^2 \qquad (2.1\text{-}3a)$$

The average deviation from the experimental and determined from equation (2.1-3) is 0.029%. The standard deviation is 0.0329 atmospheres or 0.48 psia.

At the selected critical temperature of 405.6 K, a critical pressure of 112.2 atmospheres was obtained from equation 2.1-3. A discussion of the critical state properties can be found later in this section.

The normal boiling point of ammonia has been reported by numerous authors. Both Davis(34) and Armstrong(5) have summarized the reported values back to 1839. Armstrong reported an average value of 239.78 K (-33.38 C) based on an average of the work of Cragoe(3), Overstreet(2), Henning(30) and Taylor(48) and for an ice point equal to 273.16 K. A value of 239.77 K would then be consistent with the presently accepted ice point. Davis(34) accepts a value of 239.76 K from the survey of Rossini(49) at the National Bureau of Standards. Actually, Rossini reports 239.73 K or 239.72 K at the present ice point.

Cragoe(3) made 17 direct observations of the normal boiling point and obtained an average of −33.354 C. A value of −33.341 C was obtained from the vapor pressure work and the average of −33.35 C (239.80 K) was reported. Overstreet and Giauque(2) reported a value of 239.68 K from their vapor pressure data at an ice point of 273.16 K which is corrected to 239.73 K. Henning(30) reported a value of -33.36 C (239.79 K). Bergstrom(47) reports a value 0.1 C below that of Cragoe(3) or 239.70 K.

Keyes and Brownlee(7) gave a value of −33.21 C (239.94 K) from a series of direct measurements and a value of −33.25 C (239.90 K) from manometric measurements. In a later reference, Keyes(44) notes that the vapor pressure data of Keyes and Brownlee(7) were in slight error but new estimates of the normal boiling point were not given.

From equation 2.1-2 for the vapor pressure of the liquid between the melting point (194.4 K) and 258 K, based on the experimental work of Cragoe(3), Overstreet(2) and Henning(30) a value of 239.80 K was obtained. This agrees with the average value accepted by Cragoe(3) and is retained in this work as the accepted normal boiling point.

This value is open to criticism since it is based on the heavily weighted vapor pressure work of Cragoe(3), whereas most of the other authors give slightly lower values. It is, however, internally consistent with the accepted vapor pressure data and will certainly be very close to any untimately selected value.

2.1.3.2 Density of Anhydrous Ammonia

The most reliable values for the specific volume of saturated liquid ammonia are given by Cragoe and Harper(4) of the National Bureau of Standards in 1922. The study covered a temperature range from the melting point to 100 C (212 F) and the authors report an accuracy of about one part in 10,000.

Davis(34) has reviewed other studies and found most of them to be of historical interest only. Goodenough(32) in 1913 reviewed and reported the experimental work of many of the early investigations.

The only data found for the density of the solid appear to be those given by McKelvy(6). At -79 C, a value of 0.817 g/cm^3 was reported while the density at -185 C was found to be 0.836 g/cm^3.

The density of the liquid is shown for three separate temperature ranges in this work. The first range includes the data between the melting point and 0 C (32 F). The data of Cragoe(4) and Timmermans(31) was selected. The experimental values for density are shown in Figures 2.1-4 and 2.1-4a although Cragoe actually reported specific volume. A second-order equation was found to best describe the data.

$$\rho(\text{g/cc}) = 0.88824 - 4.7742 \times 10^{-4}\ (T, °K) - 1.5977 \times 10^{-6}\ (T, °K) \quad (2.1\text{-}4)$$

$$\rho(\text{lb/ft}^3) = 55.4510 - 0.016558\ (T, °R) - 3.0784 \times 10^{-5}\ (T, °R)^2 \quad (2.1\text{-}4a)$$

The average deviation of the experimental data from the smoothed data obtained from equation 2.1-4 is 0.013% and the standard deviation is 1.2×10^{-4} g/cc.

The second temperature range covers the region from 0 to 100 C (32 to 212 F). Again, the excellent work of Cragoe was chosen. Plank(14) also reported a few values in this region which agree well with the National Bureau of Standards study. The experimental data are plotted in Figures 2.1-5 and 2.1-5a. The data can accurately be described by

$$\rho(\text{g/cc}) = 0.54529 + 1.89323 \times 10^{-3}\ (T, °K) - 5.69427 \times 10^{-6}\ (T, °K)^2 \quad (2.1\text{-}5)$$

$$\rho(\text{lb/ft}^3) = 34.0414 + 0.65661\ (T, °R) - 1.0972 \times 10^{-4}\ (T, °R)^2 \quad (2.1\text{-}5a)$$

The average deviation of the experimental data from the data obtained from equation 2.1-5 is 0.087% and the standard deviation is 6.83×10^{-4} g/cc.

The third temperature range from 80 C (176 F) to the critical point is shown in Figures 2.1-6 and 2.1-6a; both the saturated liquid and vapor densities are shown. The saturated liquid densities were taken from the work of Cragoe(4), and Berthard(16) while the saturated vapor data from Berthard(16) and Dietrici as reported by Goodenough(32) were used.

2.1.3.3 Sonic Velocity

The speed of sound in saturated liquid ammonia has been measured by Bowen(8) and Blagoi(28). The paper by Bowen notes data previously given in a doctoral thesis at Boston University by R. H. Maybury. This reference was not obtainable but, according to Bowen, the data agreed fairly well with his work but had a good deal of scatter.

Bowen covered a temperature range from near the melting point to -33 C (-27 F) while Blagoi also covered this range and extended it to -3 C (27 F). The experimental data are plotted in Figures 2.1-7 and 2.1-7a. The agreement in the temperature range common to both studies is fair with the data from the more recent Russian study being about 1.4% higher near the melting point. Agreement at the higher temperature is better. The sonic velocity is adequately represented as a linear function of temperature by

$$c\ (\text{m/sec}) = 3202.49 - 6.1366\ (T, °K) \quad (2.1\text{-}6)$$

$$c\ (\text{ft/sec}) = 10506.85 - 11.1851\ (T, °R) \quad (2.1\text{-}6a)$$

The average deviation of the experimental data from the data calculated from equation 2.1-6 is 0.26% and the standard deviation is 7.051 m/sec.

2.1.3.4 Compressibility of Liquid Ammonia

The adiabatic compressibility of saturated liquid ammonia can be calculated from the measurement of sonic velocity using the relation

$$\beta_a = \frac{1}{\rho c^2}$$

where

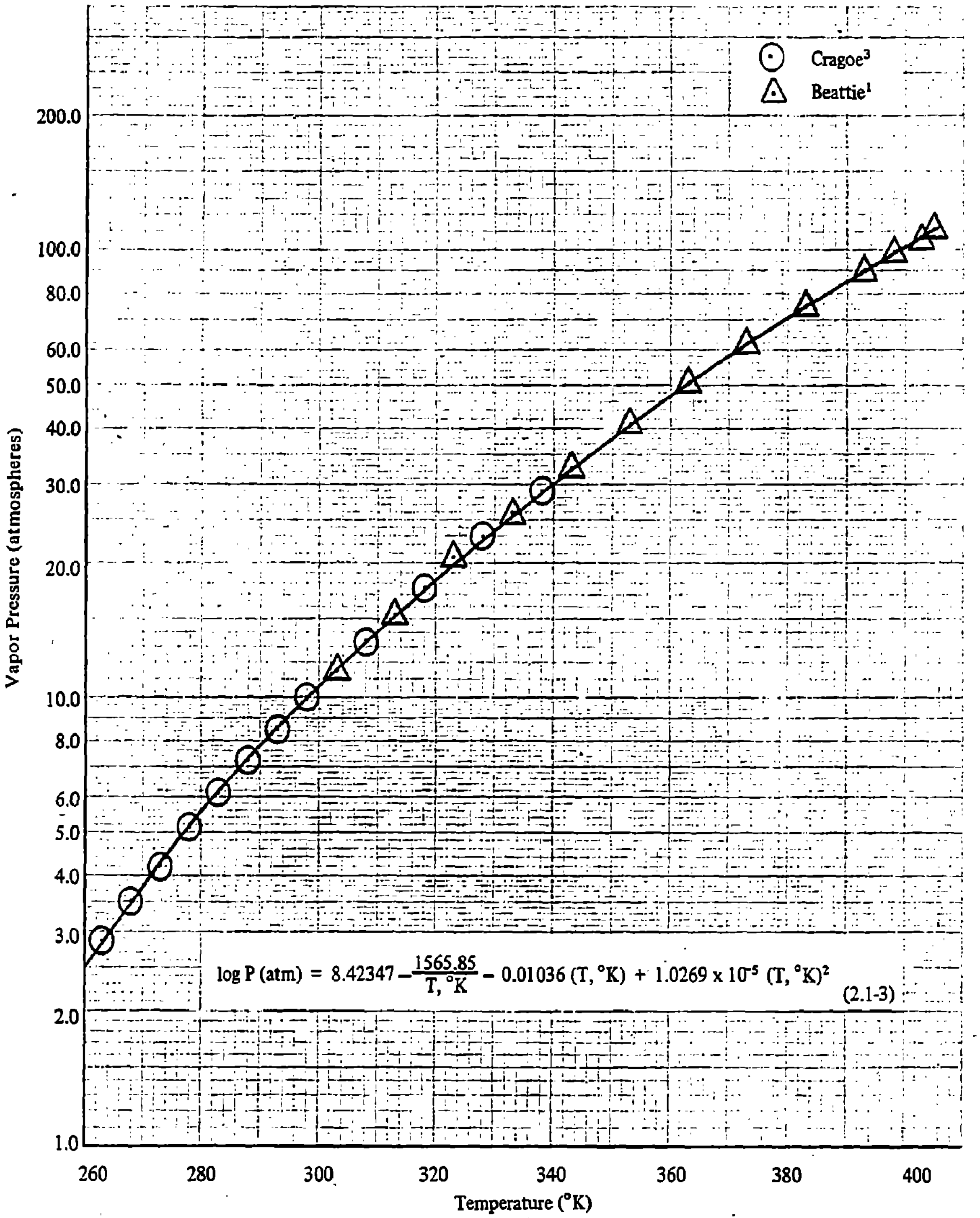
β_a = adiabatic compressibility
ρ = saturated liquid density
c = velocity of sound

In the previous section, the ultrasonic propagation of sound through the saturated liquid was reported from the work of Bowen(8) and Blagoi(28). A temperature range from the melting point to -3 C (27 F) was studied. At each of the experimentally determined sonic velocity measurements, the corresponding adiabatic compressibility was calculated using the density values obtained from equation 2.1-4. The calculated compressibilities are shown in Figures 2.1-8 and 2.1-8a.

The adiabatic compressibility change with temperature is adequately described by

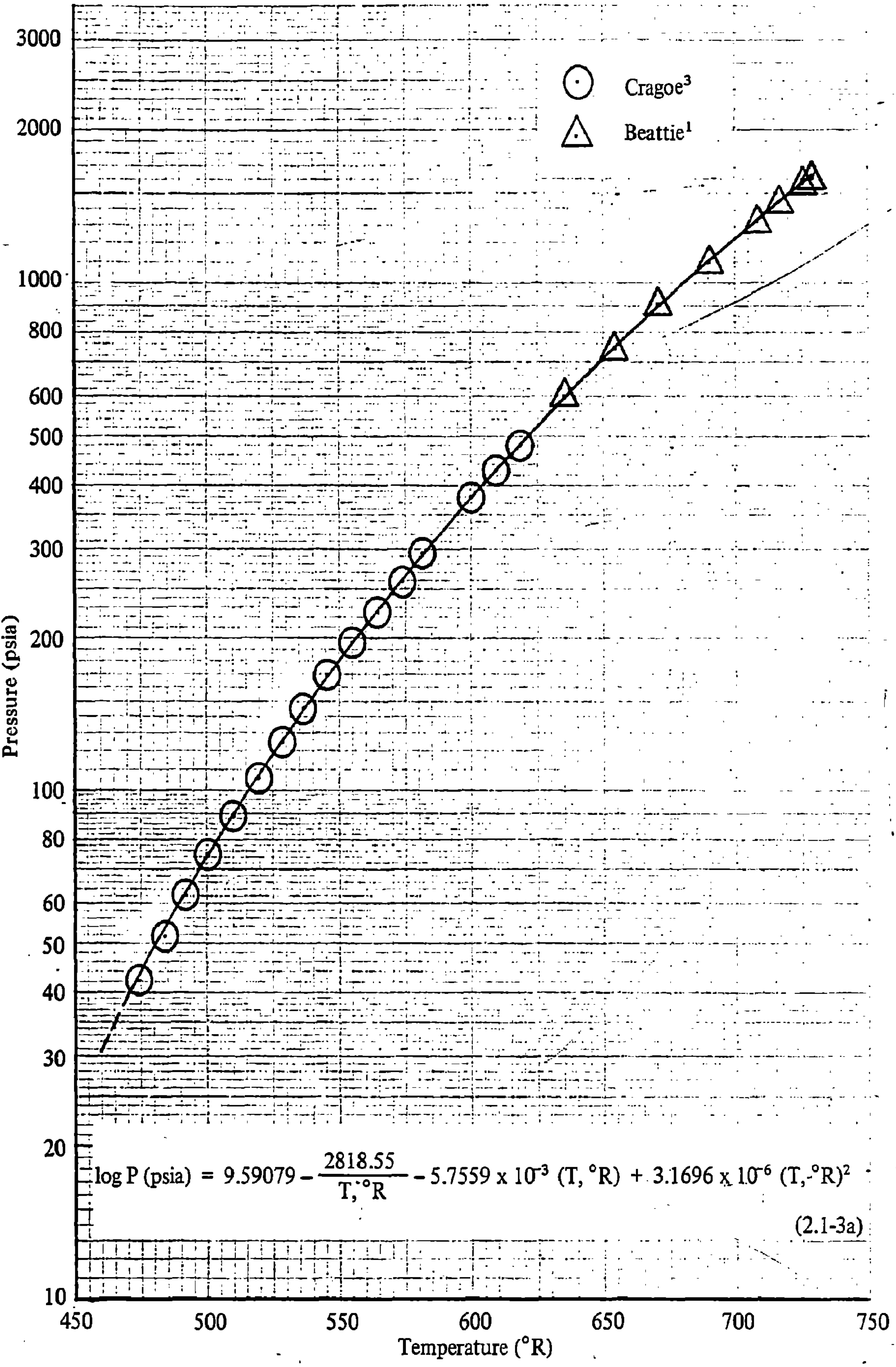
$$\beta_a\ (\text{atm}^{-1}) = 1.0098 \times 10^{-4} + 1.68095 \times 10^{-6}\ (T, °K) - 8.0004 \times 10^{-9}\ (T, °K)^2 + 1.5051 \times 10^{-11}\ (T, °K)^3 \quad (2.1\text{-}7)$$

$$\beta_a\ (\text{psi}^{-1}) = -0.68713 + 6.3545 \times 10^{-3}\ (T, °R) - 1.6802 \times 10^{-5}\ (T, °R)^2 + 1.7561 \times 10^{-8}\ (T, °R)^3 \quad (2.1\text{-}7a)$$



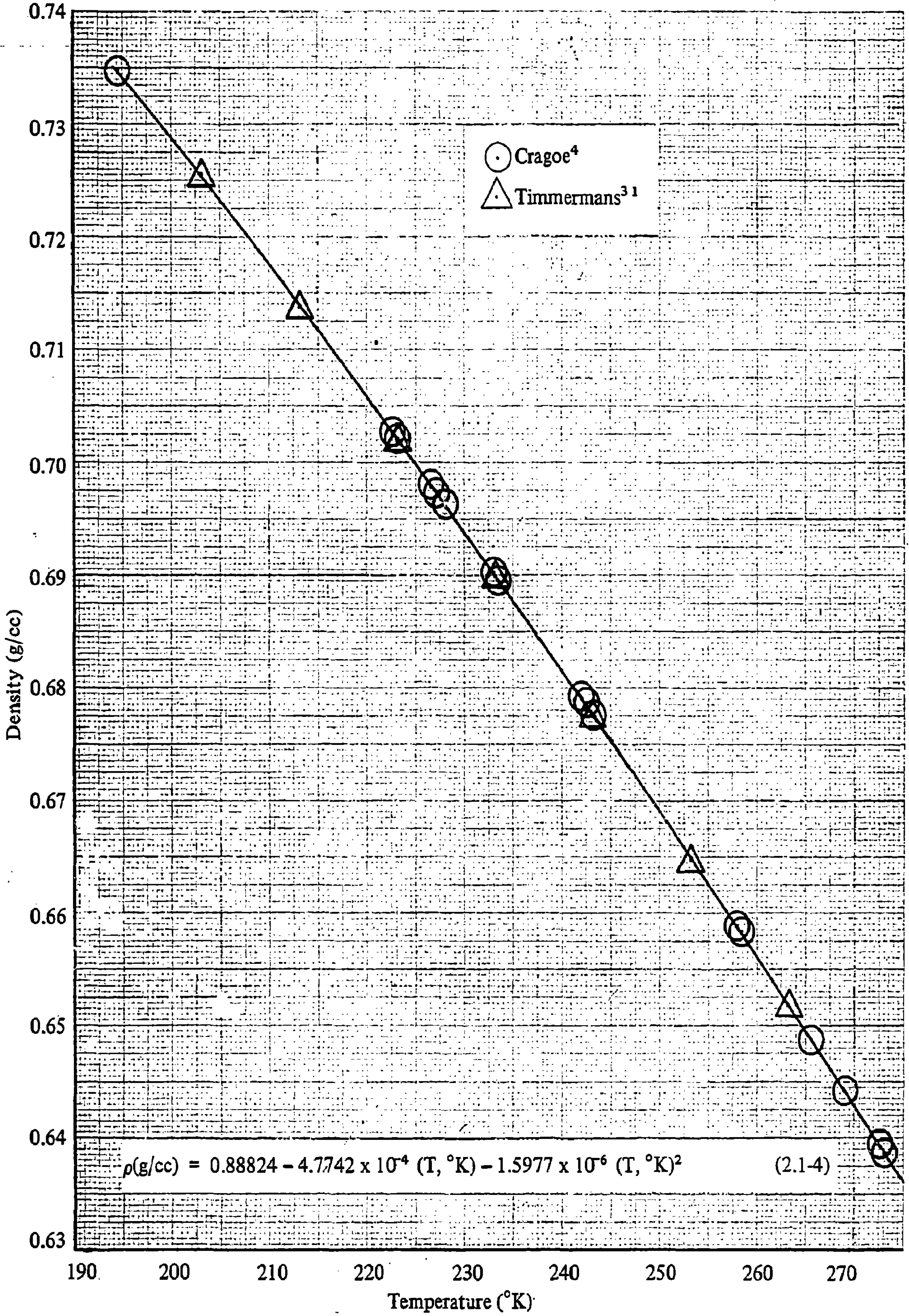
$$\log P\,(\text{atm}) = 8.42347 - \frac{1565.85}{T,\,^{\circ}K} - 0.01036\,(T,\,^{\circ}K) + 1.0269 \times 10^{-5}\,(T,\,^{\circ}K)^2 \qquad (2.1\text{-}3)$$

Figure 2.1-3. Vapor Pressure versus Temperature, Liquid Ammonia



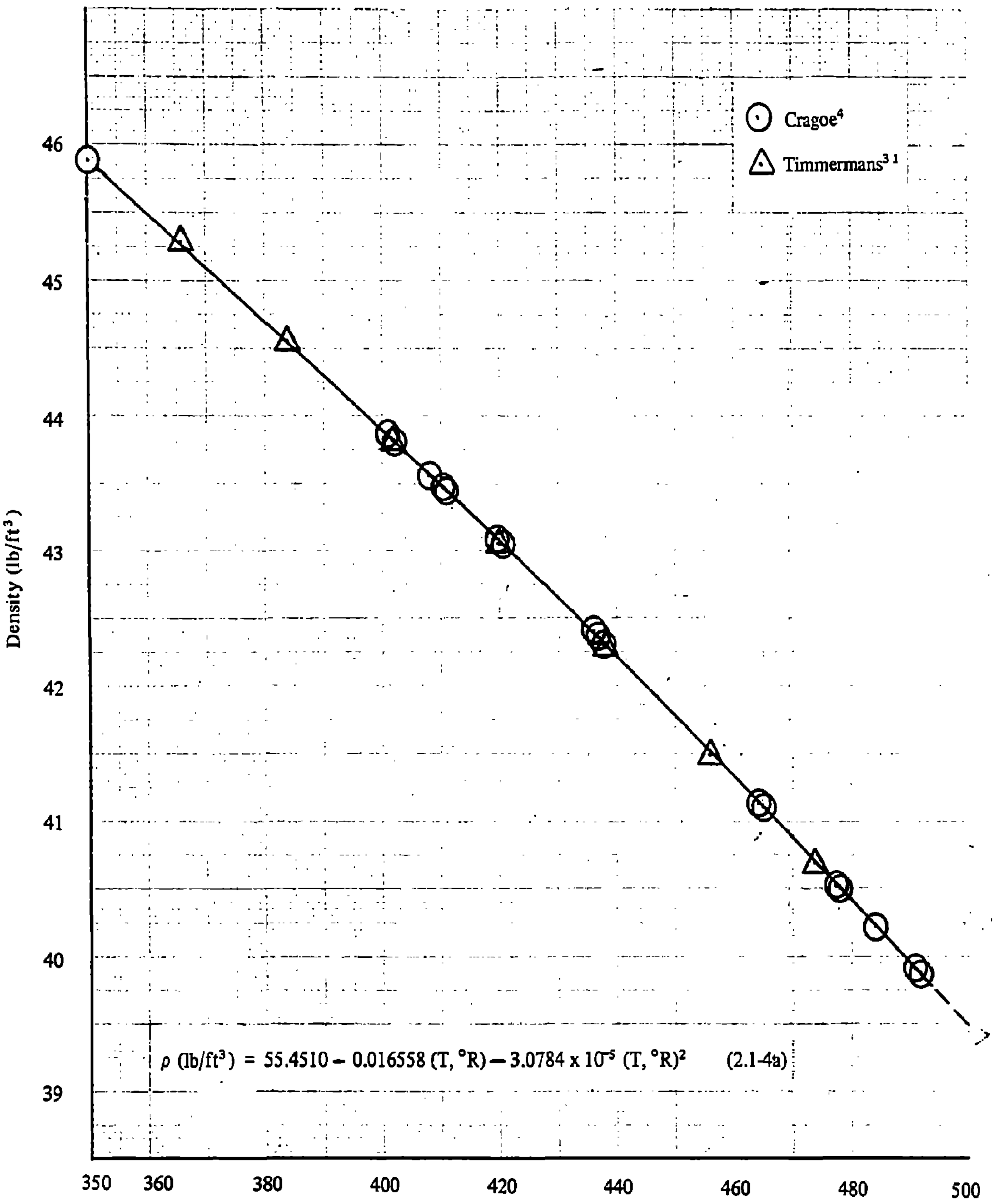
$$\log P \text{ (psia)} = 9.59079 - \frac{2818.55}{T, {}^\circ R} - 5.7559 \times 10^{-3} \,(T, {}^\circ R) + 3.1696 \times 10^{-6} \,(T, {}^\circ R)^2 \qquad (2.1\text{-}3a)$$

Figure 2.1-3a. Vapor Pressure versus Temperature, Liquid Ammonia



$$\rho(\text{g/cc}) = 0.88824 - 4.7742 \times 10^{-4}\ (T, {}^\circ K) - 1.5977 \times 10^{-6}\ (T, {}^\circ K)^2 \qquad (2.1\text{-}4)$$

Figure 2.1-4. Density versus Temperature, Liquid Ammonia



$$\rho\ (\mathrm{lb/ft^3}) = 55.4510 - 0.016558\ (T, {}^\circ R) - 3.0784 \times 10^{-5}\ (T, {}^\circ R)^2 \qquad (2.1\text{-}4a)$$

Figure 2.1-4a. Density versus Temperature, Liquid Ammonia

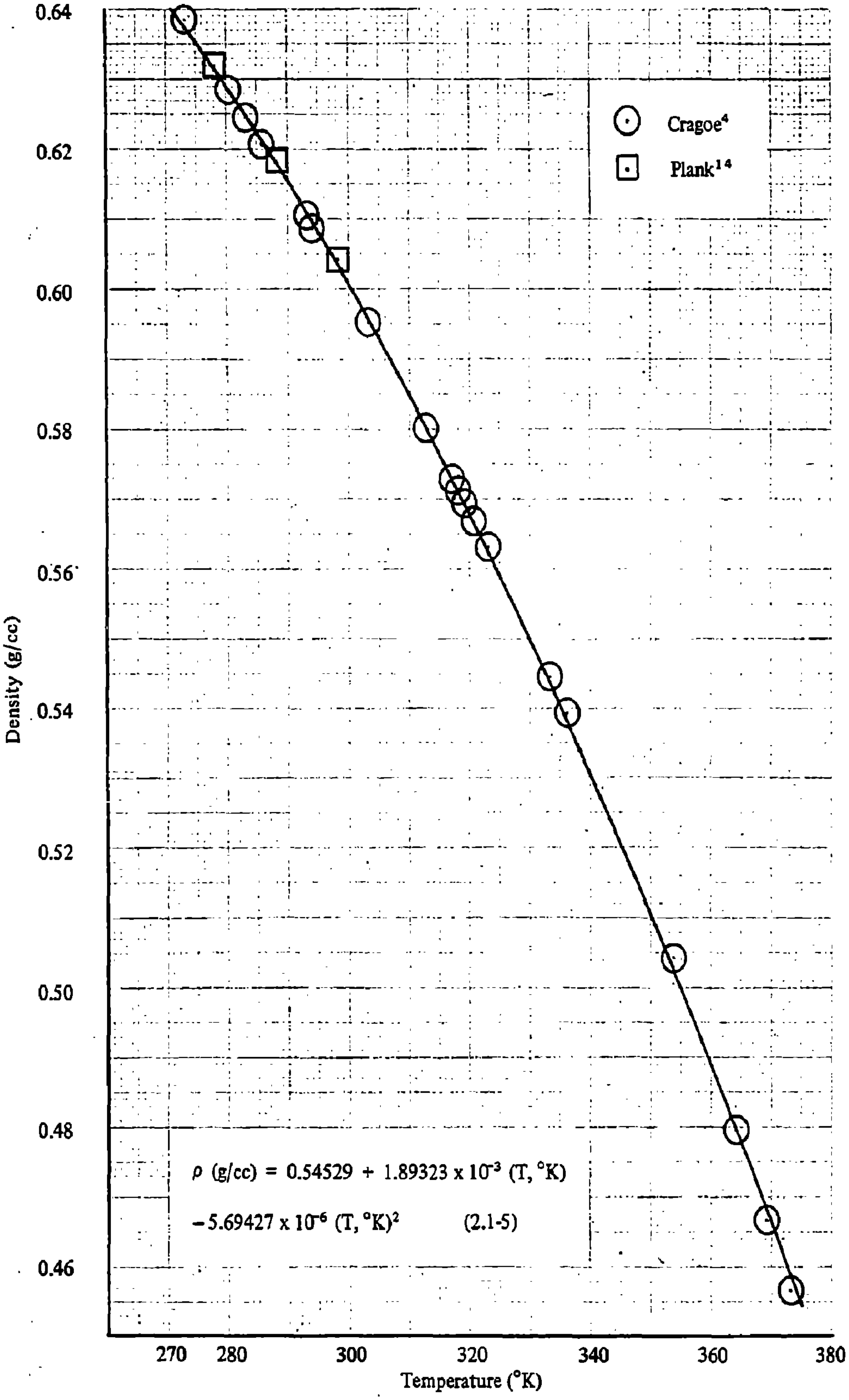


Figure 2.1-5. Density versus Temperature, Liquid Ammonia

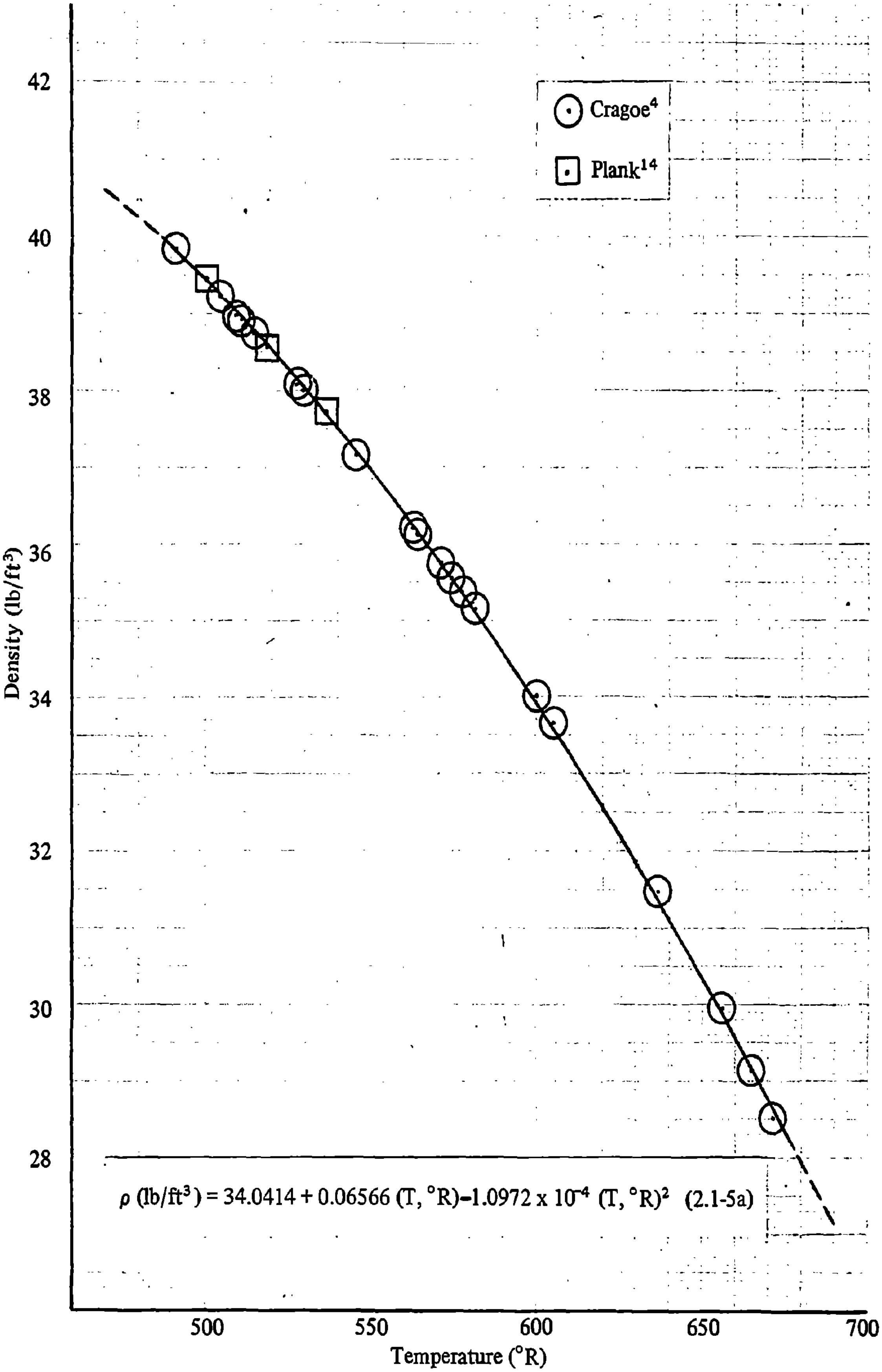


Figure 2.1-5a. Density versus Temperature, Liquid Ammonia

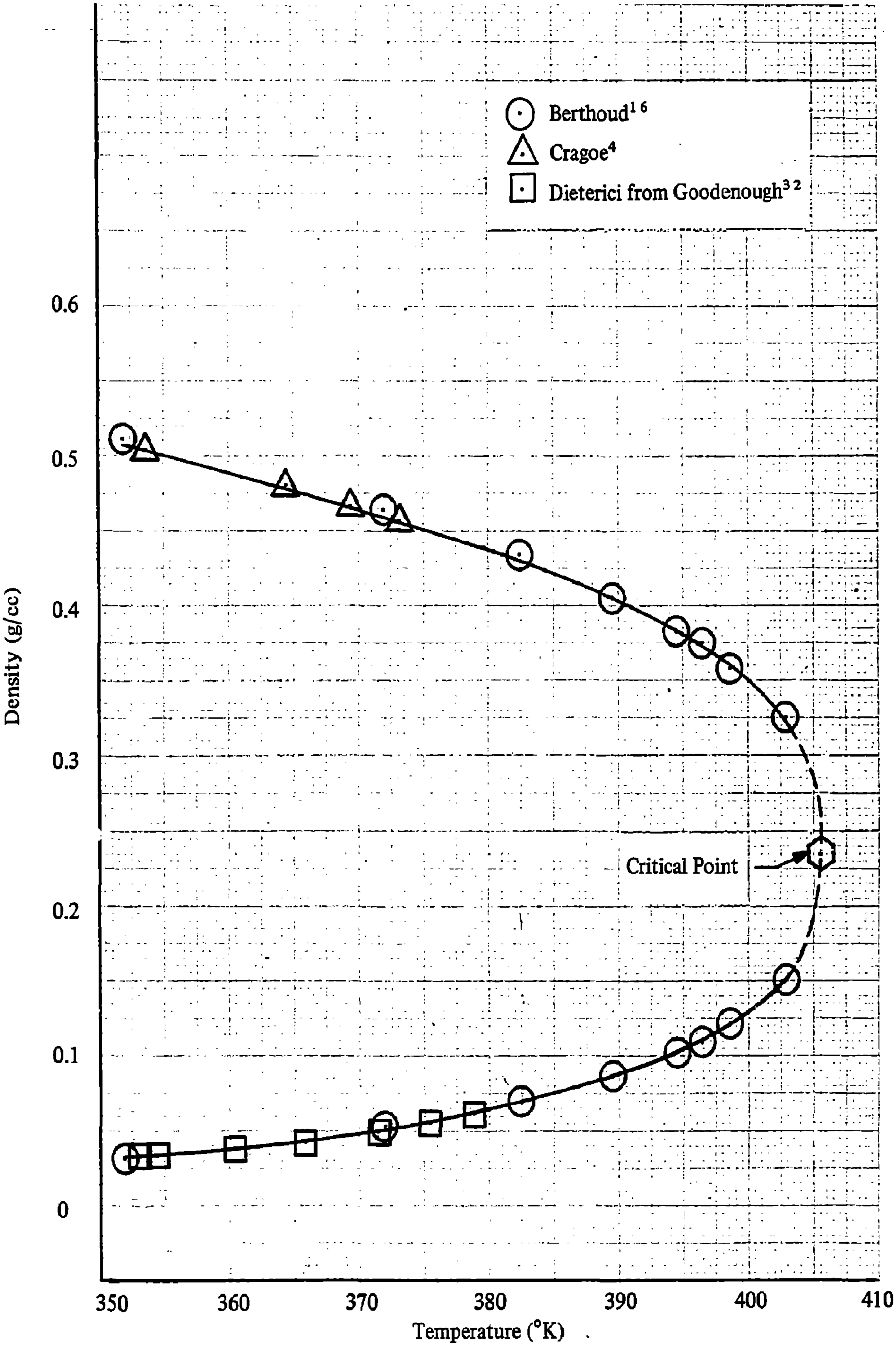


Figure 2.1-6. Density versus Temperature, Saturated Liquid and Vapor Ammonia

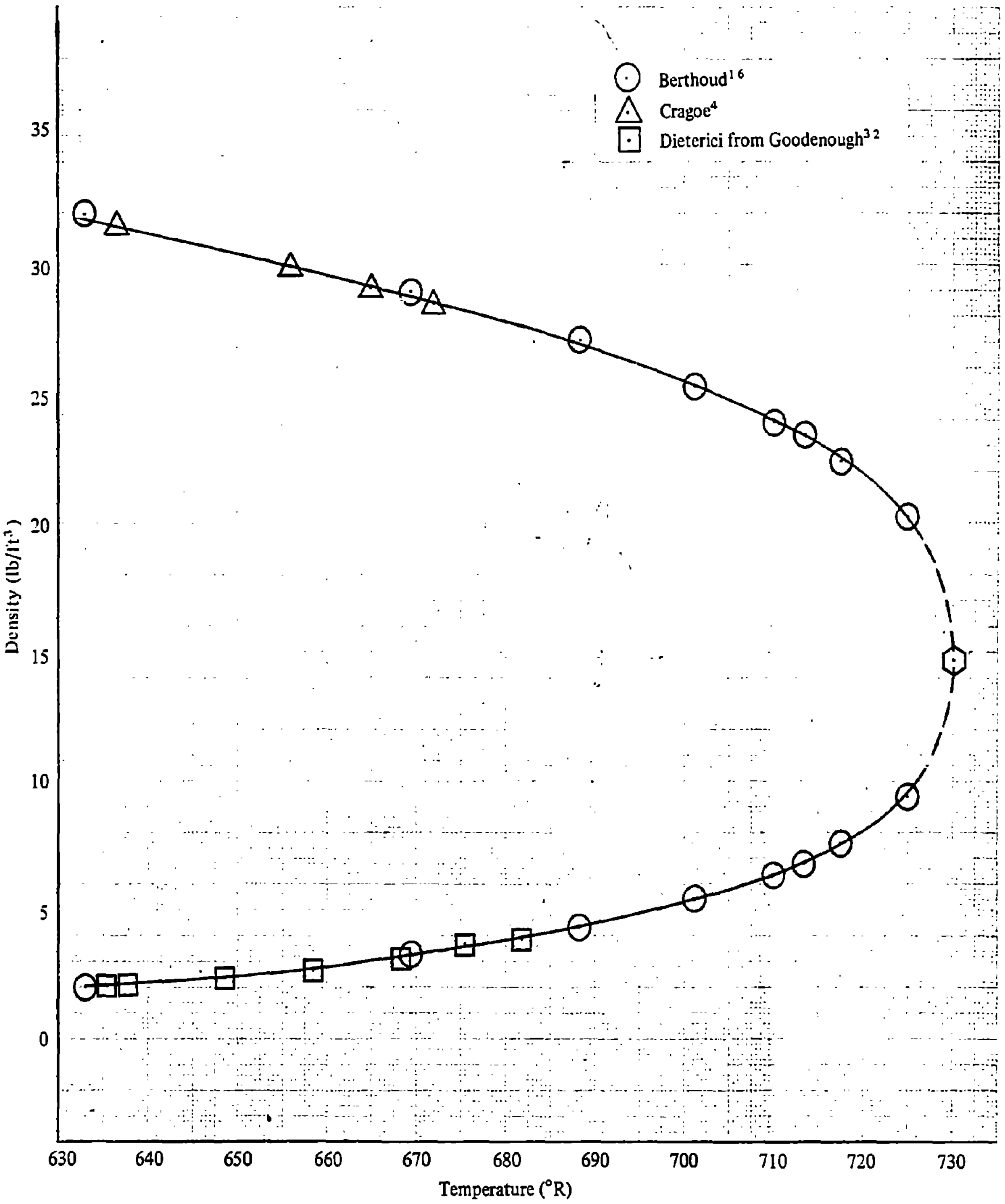
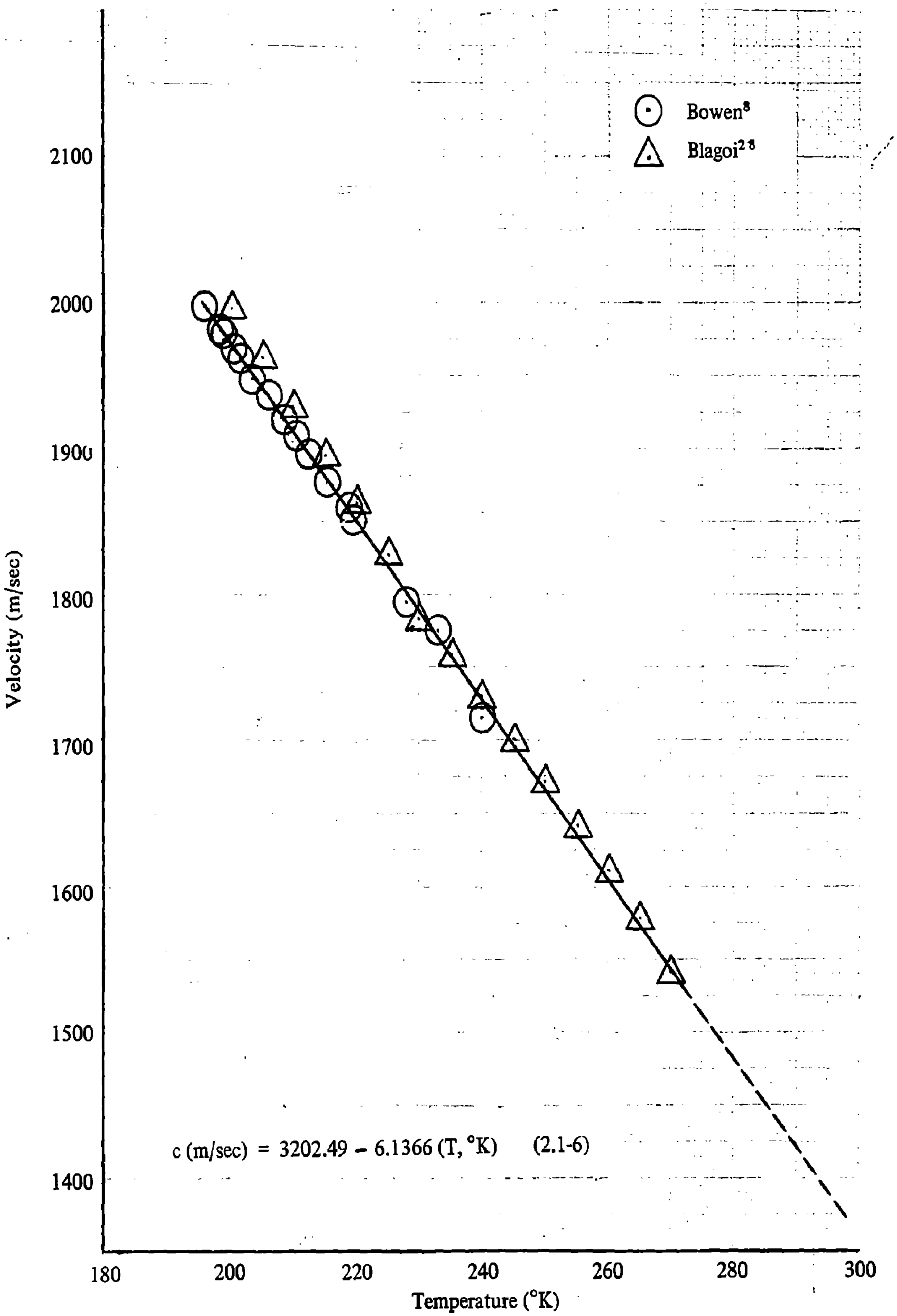
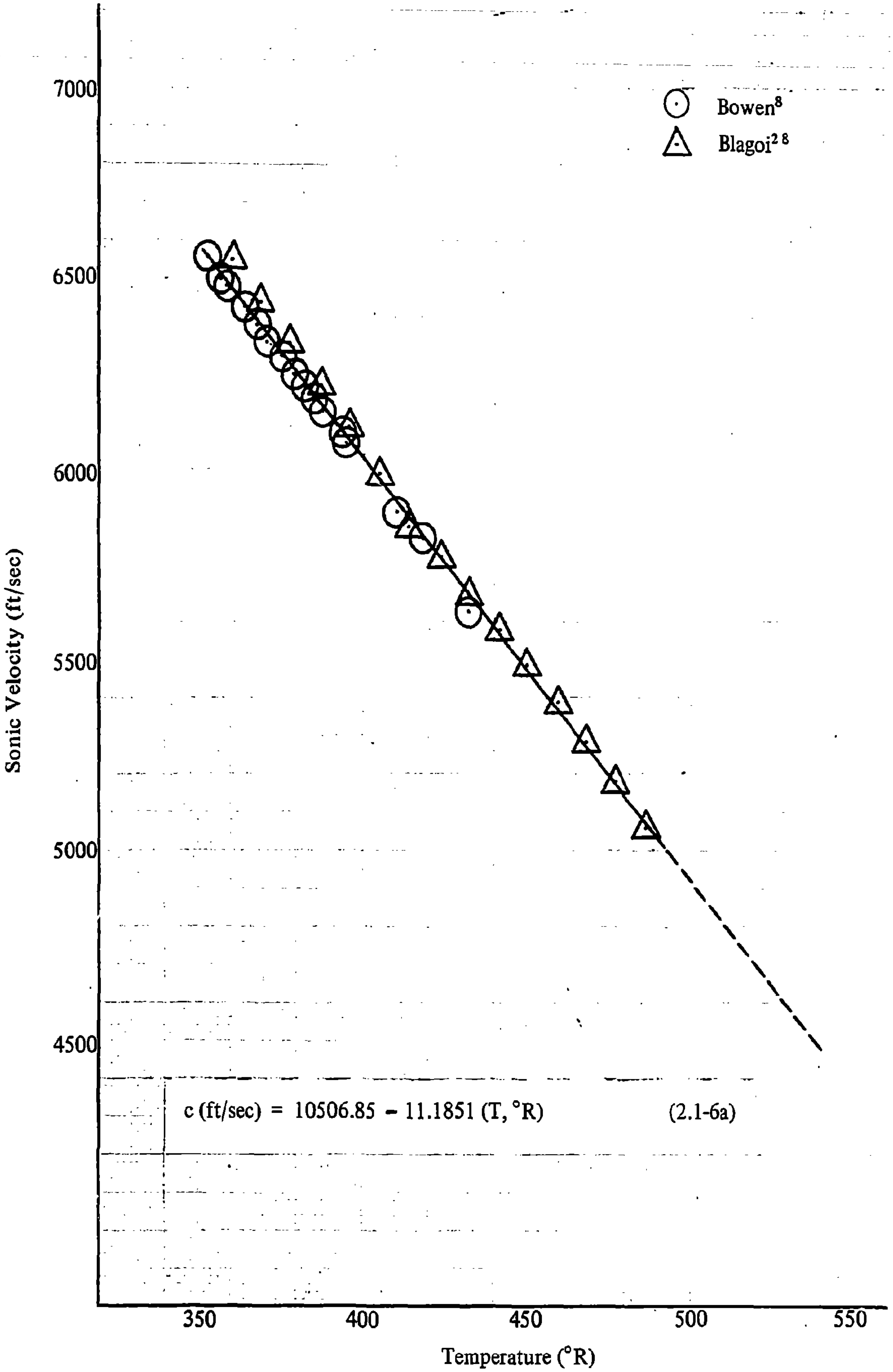


Figure 2.1-6a. Density versus Temperature, Saturated Liquid and Vapor Ammonia



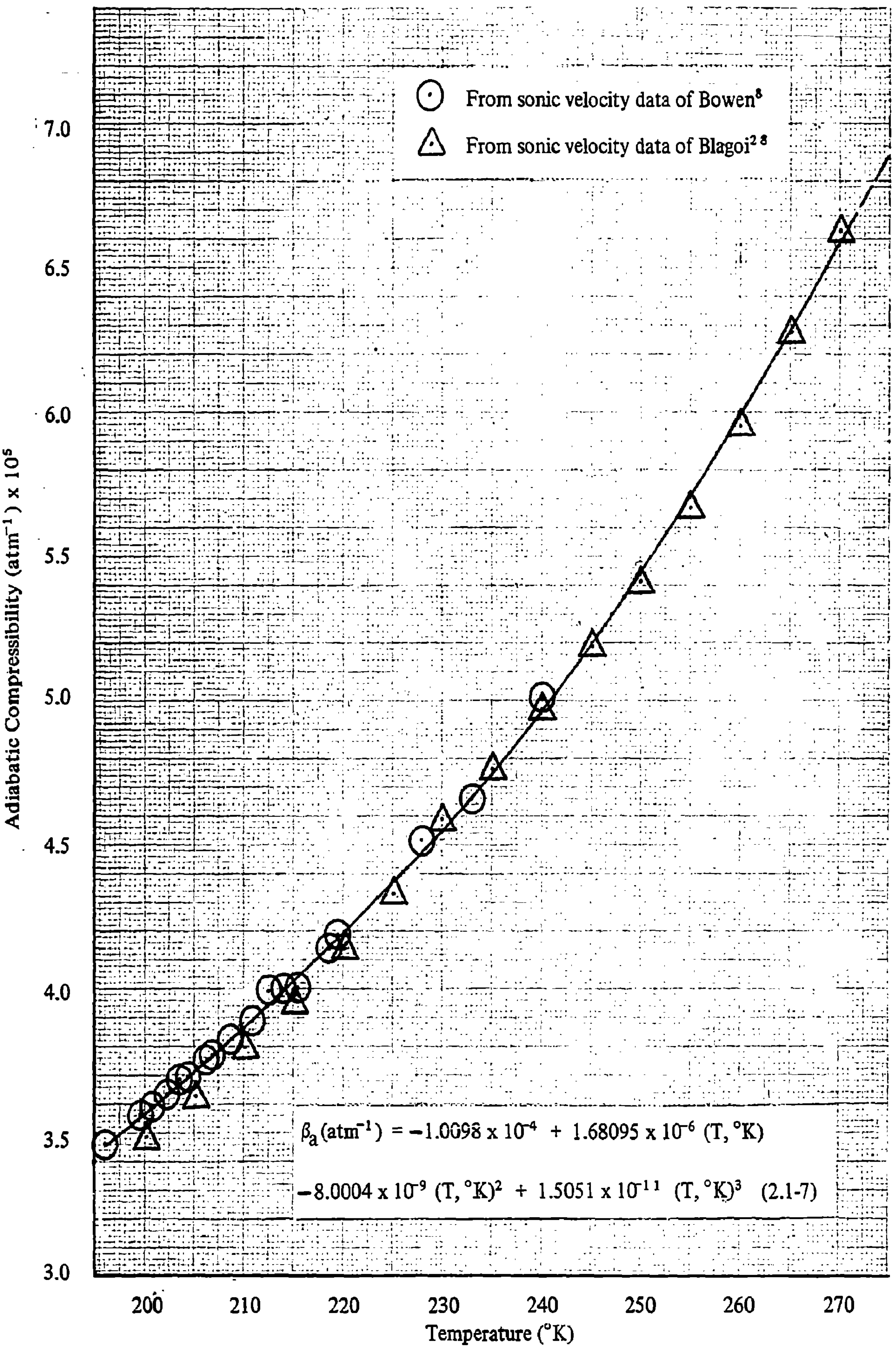
$$c\ (\mathrm{m/sec}) = 3202.49 - 6.1366\ (T, {}^\circ\mathrm{K}) \qquad (2.1\text{-}6)$$

Figure 2.1-7. Sonic Velocity versus Temperature, Liquid Ammonia



$$c\,(\text{ft/sec}) = 10506.85 - 11.1851\,(T, {}^{\circ}R) \qquad (2.1\text{-}6a)$$

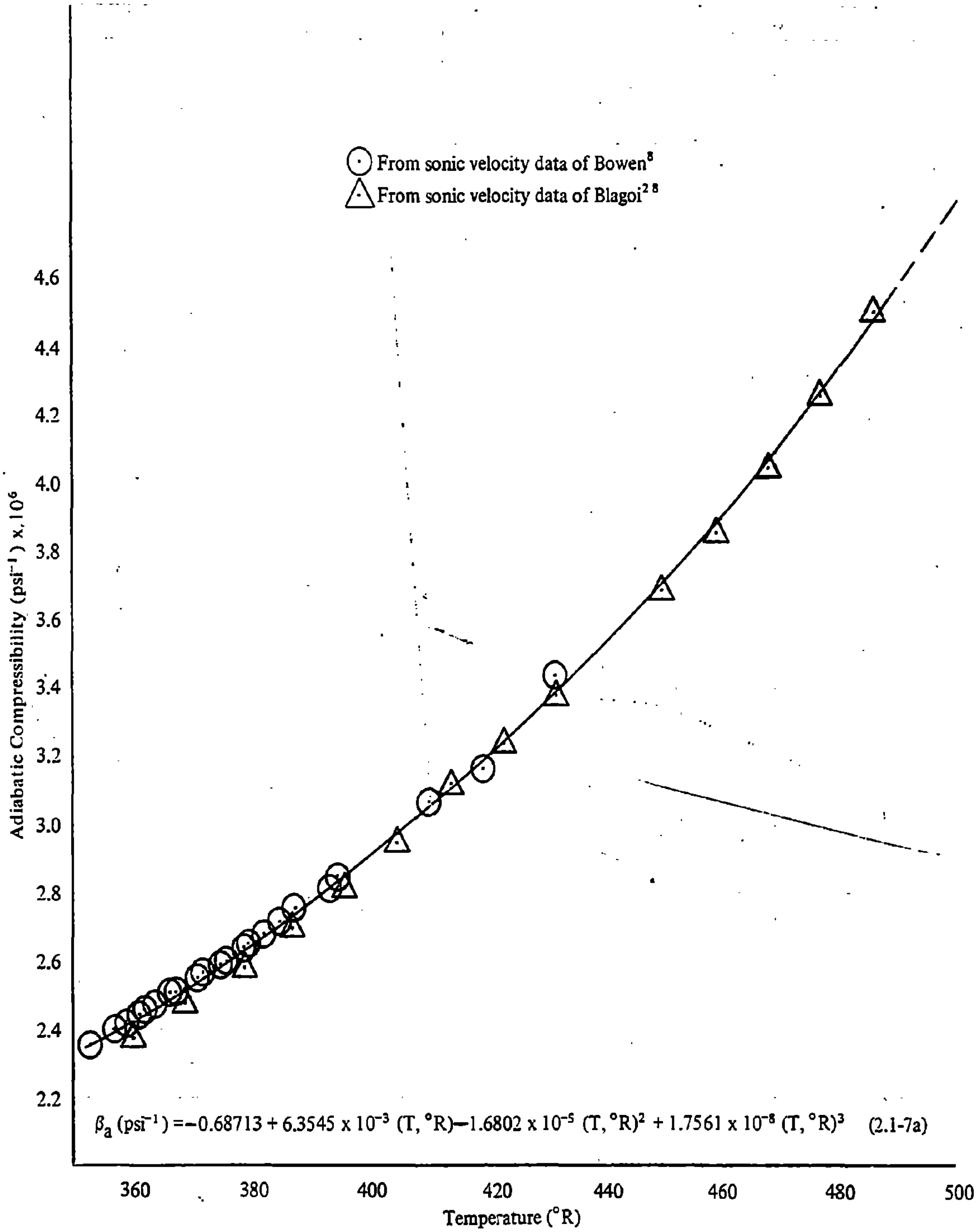
Figure 2.1-7a. Sonic Velocity versus Temperature, Liquid Ammonia



$$\beta_a(\text{atm}^{-1}) = -1.0098 \times 10^{-4} + 1.68095 \times 10^{-6} (T, °K)$$

$$-8.0004 \times 10^{-9} (T, °K)^2 + 1.5051 \times 10^{-11} (T, °K)^3 \quad (2.1\text{-}7)$$

Figure 2.1-8. Adiabatic Compressibility versus Temperature, Liquid Ammonia



$$\beta_a\,(\text{psi}^{-1}) = -0.68713 + 6.3545 \times 10^{-3}\,(T, {}^\circ R) - 1.6802 \times 10^{-5}\,(T, {}^\circ R)^2 + 1.7561 \times 10^{-8}\,(T, {}^\circ R)^3 \quad (2.1\text{-}7a)$$

Figure 2.1-8a. Adiabatic Compressibility versus Temperature, Saturated Liquid Ammonia

The average deviation of the data from equation 2.1-7 is 0.52% and the standard deviation is 3.22 x 10^{-7} atm^{-1}.

The isothermal compressibility is defined as

$$\beta_i = -\frac{1}{v}\left[\frac{\partial V}{\partial P}\right]_T$$

Keys(43) has reported the volume change with respect to pressure changes at constant temperature. The actual experimental data were not given, but rather he listed two tables of smoothed data. The first table gives the pressure-volume product for experimental temperatures at various volumes. The second table gives the pressure-volume product at a series of even temperatures for various isobars.

The isothermal compressibility appears on the surface to be easily obtained. The natural log of volume is fitted by the least-squares method with pressure as the independent variable for the given isotherms. The derivative of the resulting equation gives the function, $-1/V\ [\partial V/\partial P]_T$ which, by definition, is the compressibility.

The data reported by Keyes was taken at pressures from 100 to 1100 atmospheres. A liquid is somewhat easily compressed with an initial low pressure since the molecular spacing affords some compression. As the pressure is increased, the change in volume is quite restricted. In other words, the compressibility is much less at higher pressure than at lower pressures.

Since Keyes(43) reported the volumes at rather large (100 atmospheres) intervals, it was possible to obtain a good fit of his data but insufficient data was given to adequately define the change in volume with pressure near the saturation line. Therefore, the compressibility values could not be directly obtained from the data supplied by Keyes(43).

The isothermal compressibilities have been reported in the National Bureau of Standards Thermodynamic Tables(51). The smoothed values are plotted in Figures 2.1-9 and 2.1-9a. The data were found to be adequately expressed by:

$$\begin{aligned}\beta_i\,(\text{atm}^{-1}) = &-2.8773 \times 10^{-3} + 3.5420 \times 10^{-5}\,(T, {}^\circ K) \\ &-1.4428 \times 10^{-7}\,(T, {}^\circ K)^2 \\ &+ 1.9992 \times 10^{-10}\,(T, {}^\circ K)^3 \qquad (2.1\text{-}8)\end{aligned}$$

$$\begin{aligned}\beta_i\,(\text{psi}^{-1}) = &-1.9579 \times 10^{-4} + 1.3390 \times 10^{-6}\,(T, {}^\circ R) \\ &-3.0301 \times 10^{-9}\,(T, {}^\circ R)^2 \\ &+2.3326 \times 10^{-12}\,(T, {}^\circ R)^3 \qquad (2.1\text{-}8a)\end{aligned}$$

2.1.3.5 Viscosity of Saturated Liquid Ammonia

The viscosity of saturated liquid anhydrous ammonia has been reported by a number of investigators. The experimental data are plotted in Figures 2.1-10 and 2.1-10a and, as can be noted, there is general disagreement. The various studies are discussed in chronological order.

In 1912, Fitzgerald(13) reported a single value at -33.4 C (-28.3 F) which is close to the normal boiling point. The value of 0.2662 centipoise reported is an average of four readings from two modified Atwald viscometers. A density value of 0.6823 g/cc was used which is very close to the presently accepted value of 0.6819. Fitzgerald noted that the repeatability of the values was not as good as he anticipated and believed that eddies were formed below the foot of capillary.

In 1920, Elsey(12) also made a single-point determination at -33.5 C with a double capillary viscometer calibrated with water. The reported value of 0.2543 centipoise is nearly 5% lower than the value given by Fitzgerald(13).

Fredenhagen(17) in 1930 reported viscosity measurements at -69.0 and -33.5 C. At the lower temperature, a value of 0.475 centipoise was reported based on a density value of 0.7182 obtained by extrapolation. This density value is only slightly lower than the presently accepted value. A value of 0.26475 centipoise was reported at -33.5 C using the density value of Fitzgerald(13) previously mentioned. The difference in significant figures for the two readings was apparently based on the density confidence. The value at -33.5 C is in good agreement with that obtained by Fitzgerald(13).

Stakelbeck(11) in 1933 reported five readings from -20 to +20 C and by extrapolation found that the value obtained at -33.5 C fell between the previously reported data of Fitzgerald(13) and Elsey(12). This apparent agreement was only fortuitous, as shown in Figure 2.1-10, since the slope of the Stakelbeck data only gives agreement with the other investigators at this particular temperature. Plank(14), in a later study, noted that the data of Stakelbeck would agree with his own if multiplied by density. This is merely a coincidence since the values reported are definitely absolute and the density values used from a German handbook were not considered important compared with the density of the falling steel ball used by the author. The units of kg-sec/m(2) reported are somewhat confusing since force is generally reported in newtons rather than grams.

In the same paper, Stakelbeck reported the viscosity of methyl chloride and this writer found the value to be approximately 11% higher than the value reported in the Mathieson Gas Data Book(57) at 20 C. The work of Stakelbeck is only shown for the sake of completeness.

In 1931, Monosson(23) reported three values at −50, −40 and −33.5 C. The latter value is in good agreement with the Elsey(12) value but disagrees with the values of Fitzgerald(13) and Fredenhagen(17). The low temperature values would appear by extrapolation to contradict the value at -69 C reported by Fredenhagen(17).

The first viscosity values above 0 C since the study of Stakelbeck were reported by Plank(14) in 1939. Values at 5, 15 and 25 C were reported. Two viscometers calibrated with carbon disulfide and carbon tetrachloride were used. The data at low temperatures obtained from previous investigations could be reasonably joined with this data.

In 1948, Pinnevich(22) studied the viscosity over a fairly large temperature range from -26 to 50 C. The lower temperature data fall into the general trend of the earlier studies. The data at higher temperatures can only be compared with the work of Plank(14) and are somewhat higher.

In 1949, Shatenshtein(72) gave viscosity measurements over a narrow temperature range from 15 to 25 C. These data show a high degree of internal scatter but the average readings fall within the general trend.

Carmichael(18) extended the observed temperature range in 1952 out to 100 C. At the lower temperatures, where comparison with the other studies was possible, the agreement with the work of Pinnevich was fair, but near 0 C the data reported was over 10% higher. In a later study, Carmichael(21) reported data significantly different and, generally, he repudiates his earlier work on the basis of a turbulence effect on the rolling ball.

For this study, all the data except the studies of Stakelbeck(11) and Carmichael(18) were considered. The combined data are represented by

$$\log \mu \text{ (centipoise)} = 5.7757 - 0.05837 \, (T, ^\circ K) + 1.7980 \times 10^{-4} \, (T, ^\circ K)^2 - 1.9689 \times 10^{-7} \, (T, ^\circ K)^3 \qquad (2.1\text{-}9)$$

$$\log \mu \, (lb_m/\text{ft-sec}) = 2.6030 - 0.03243 \, (T, ^\circ R) + 5.5492 \times 10^{-5} \, (T, ^\circ R)^2 - 3.3760 \times 10^{-8} \, (T, ^\circ R)^3 \qquad (2.1\text{-}9a)$$

The average deviation from equation 2.1-9 is slightly over 3%.

2.1.3.6 Surface Tension and Parachor of Ammonia

The surface tension of liquid ammonia has been studied by Berthoud(16) and Durrant(15). Berthoud used a single capillary tube and measured the height rise. Three measurements were taken at approximately 11, 34, and 59 C. Durrant(15) reported five values for the surface tension for a temperature range from −33 to −56 C and also stated that the prior work of Berthoud was verified. Since the temperature range of the two studies was not common, Durrant must have made his conclusions on the basis of extrapolation. The method employed by Durrant was not reported.

The experimental data from both studies are shown in Figures 2.1-11 and 2.1-11a. The separate studies are smoothly joined by the linear relationship:

$$\gamma \text{ (dynes/cm)} = 89.8093 - 0.23252 \, (T, ^\circ K) \qquad (2.1\text{-}10)$$

$$\gamma \, (lb_f/ft) = 6.1539 \times 10^{-3} - 8.8517 \times 10^{-6} \, (T, ^\circ R) \qquad (2.1\text{-}10a)$$

The parachor (P) can be calculated from the relation

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

where

M = molecular weight (17.032)
γ = surface tension (dynes/cm)
ρ_l = density of liquid
ρ_v = density of vapor

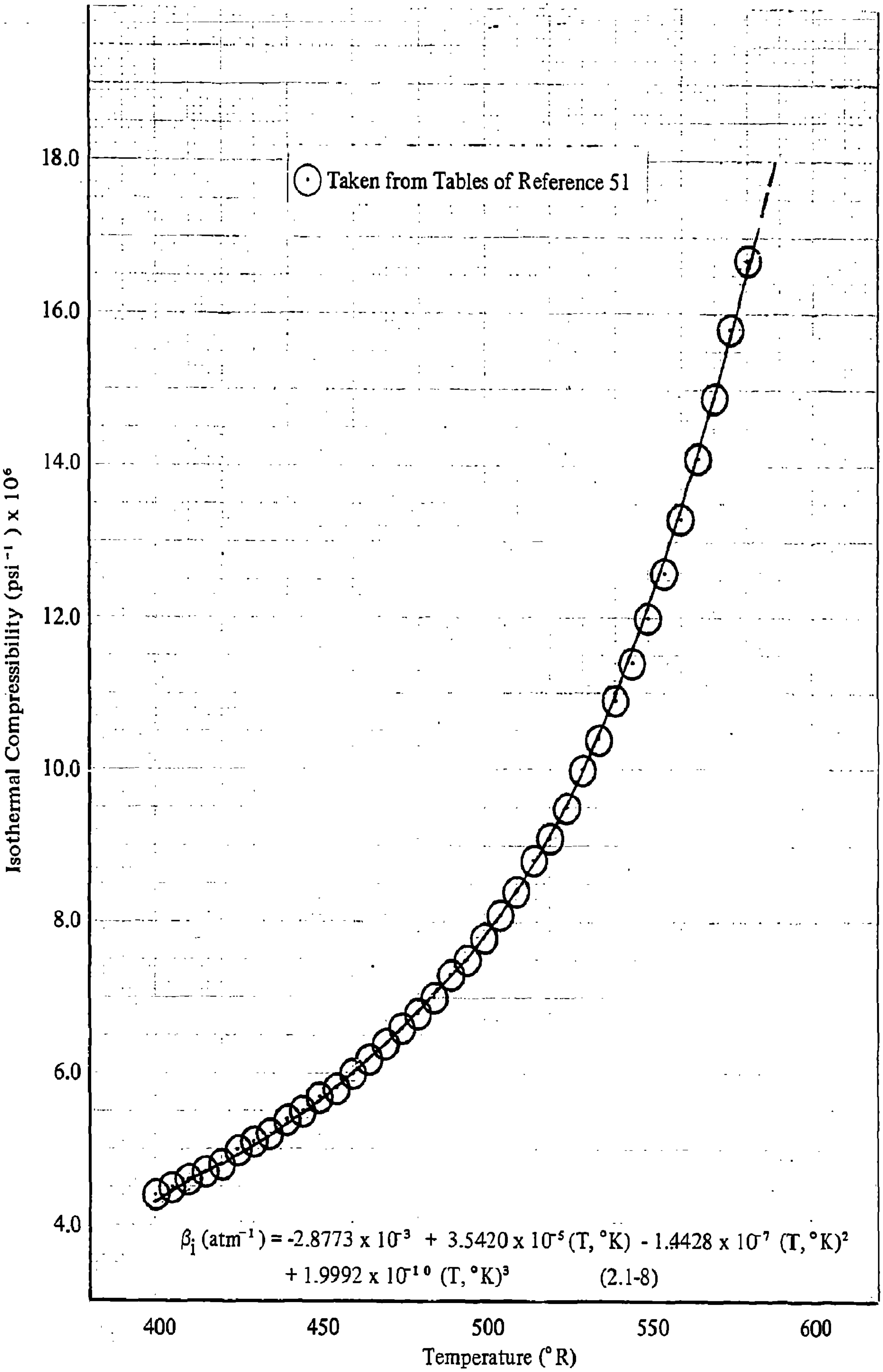
At the normal boiling point (239.8 K) a parachor value of 60.42 was obtained and at 298.15 K the calculated value was found to be 60.46. Daniels(53) gives the value of the atomic parachors for H as 17.1 and for N 12.5; from these parachors, a value of 63.8 is obtained.

2.1.3.7 Thermal Conductivity of Liquid Ammonia

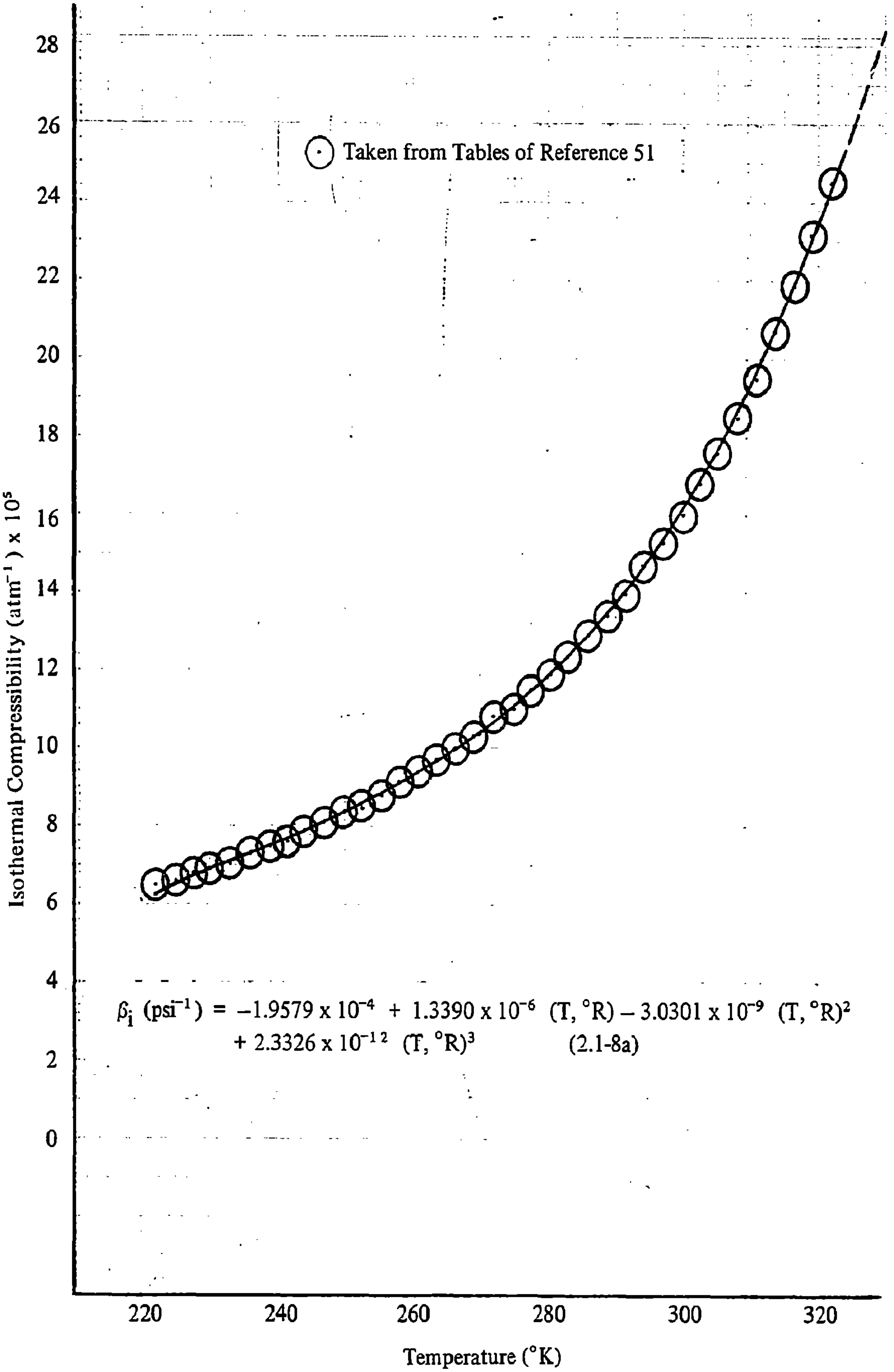
Experimental thermal conductivity data for liquid ammonia have been reported by Kardos(37)(38)(39), Selleshop(25) and more recently by Richter and Sage(24), Needham and Ziebland(36) and Golubev(52).

The early work of Kardos in 1934 is of historical interest only. A temperature range from −10 to +20 C was studied, but experimental difficulties due to the high electrical conductivity of ammonia prevented accurate values. Kardos was unable to define the change in conductivity with temperature and reported on a single nominal value of 12.0 x 10^{-4} cal/g-sec-C for the temperature range of his work.

Sellschopp(25) studied the conductivity of the saturated liquid over a temperature range from 30 to 100 C. A coaxial-cylinder apparatus was used with the inner cylinder constructed of silver and the outer of copper. Sellschopp found that some of the copper plated out on the silver. For this reason, he considered the work to be only provisional.



$$\beta_i\,(\text{atm}^{-1}) = -2.8773 \times 10^{-3} + 3.5420 \times 10^{-5}(T, ^\circ K) - 1.4428 \times 10^{-7}(T, ^\circ K)^2 + 1.9992 \times 10^{-10}(T, ^\circ K)^3 \qquad (2.1\text{-}8)$$



$$\beta_i\ (\text{psi}^{-1}) = -1.9579 \times 10^{-4} + 1.3390 \times 10^{-6}\ (T, {}^\circ R) - 3.0301 \times 10^{-9}\ (T, {}^\circ R)^2 + 2.3326 \times 10^{-12}\ (T, {}^\circ R)^3 \qquad (2.1\text{-}8a)$$

Figure 2.1-9a. Isothermal Compressibility versus Temperature, Saturated Liquid Ammonia

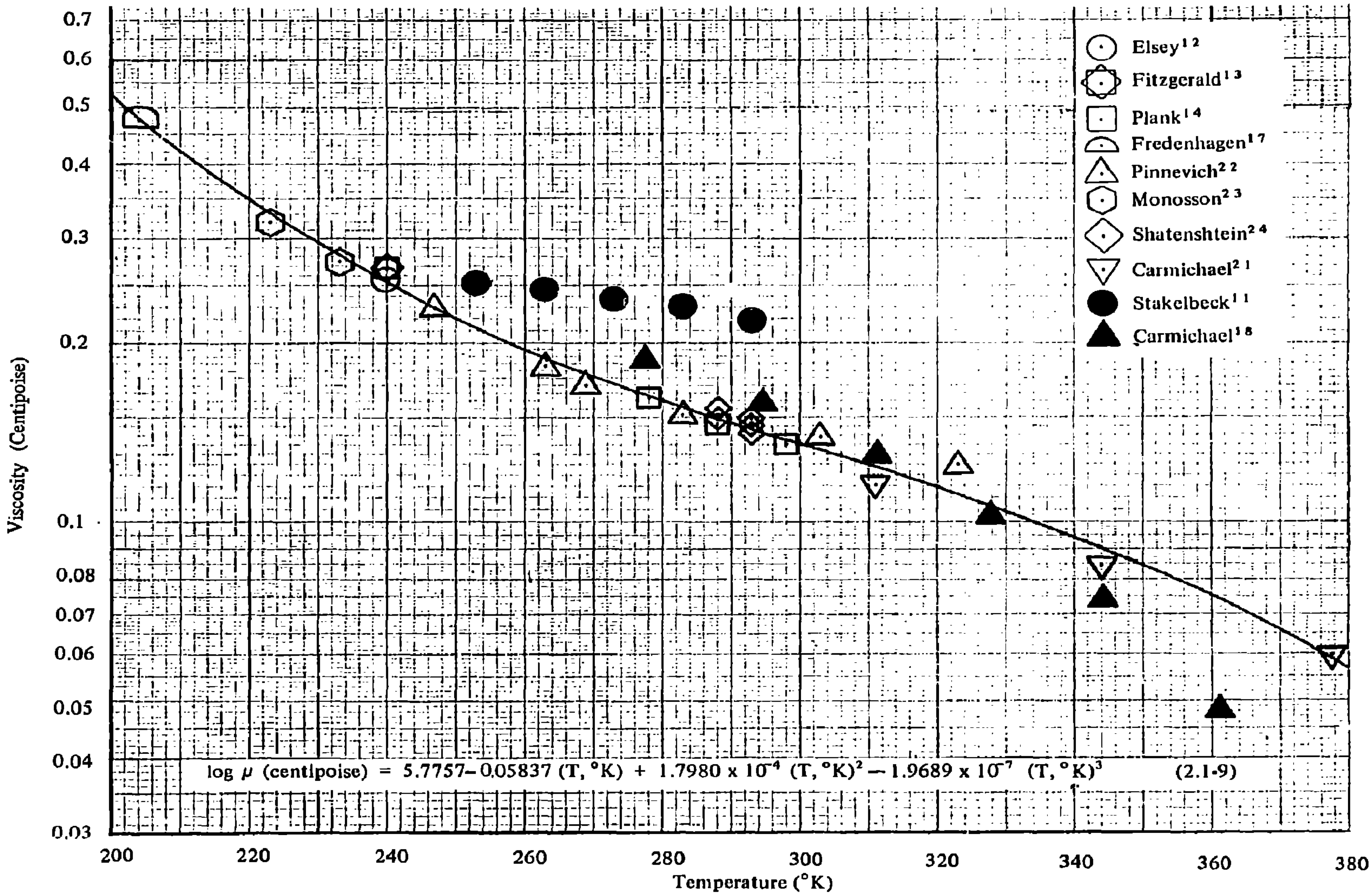
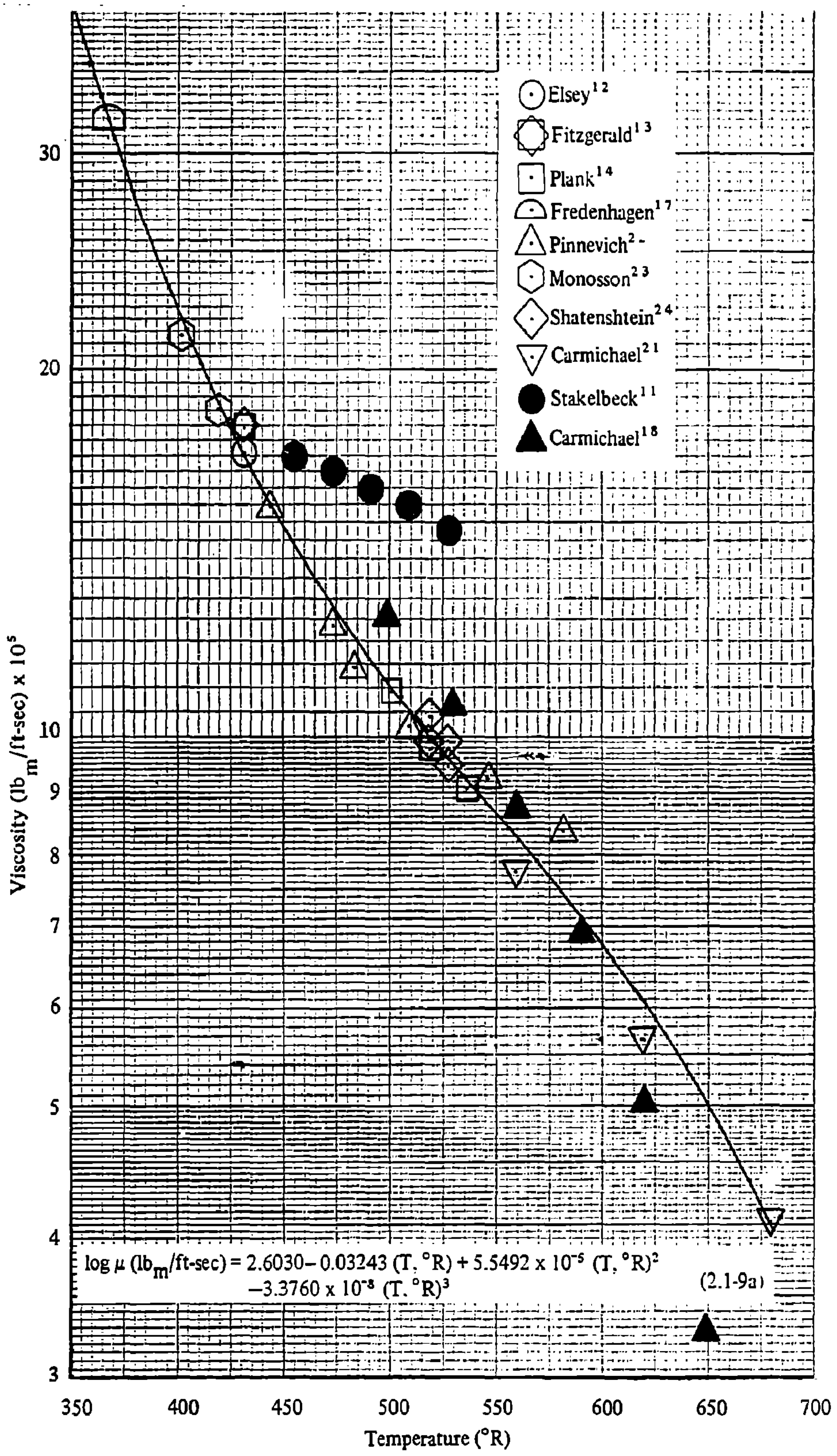


Figure 2.1-10. Viscosity versus Temperature, Liquid Ammonia



$$\log \mu \,(\mathrm{lb_m/ft\text{-}sec}) = 2.6030 - 0.03243\,(T,\,^{\circ}R) + 5.5492 \times 10^{-5}\,(T,\,^{\circ}R)^2 - 3.3760 \times 10^{-8}\,(T,\,^{\circ}R)^3 \qquad (2.1\text{-}9a)$$

Figure 2.1-10a. Viscosity versus Temperature, Liquid Ammonia

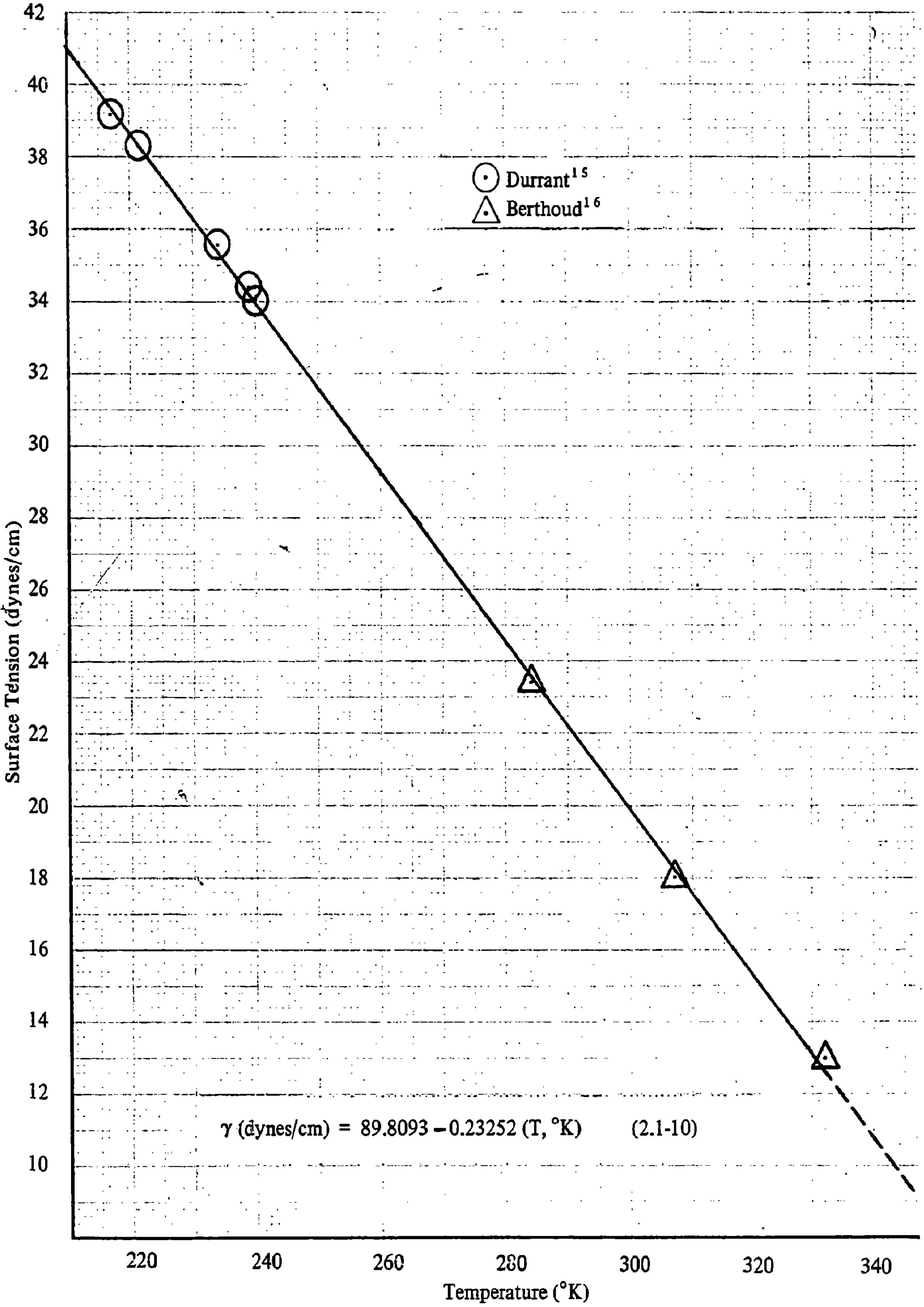
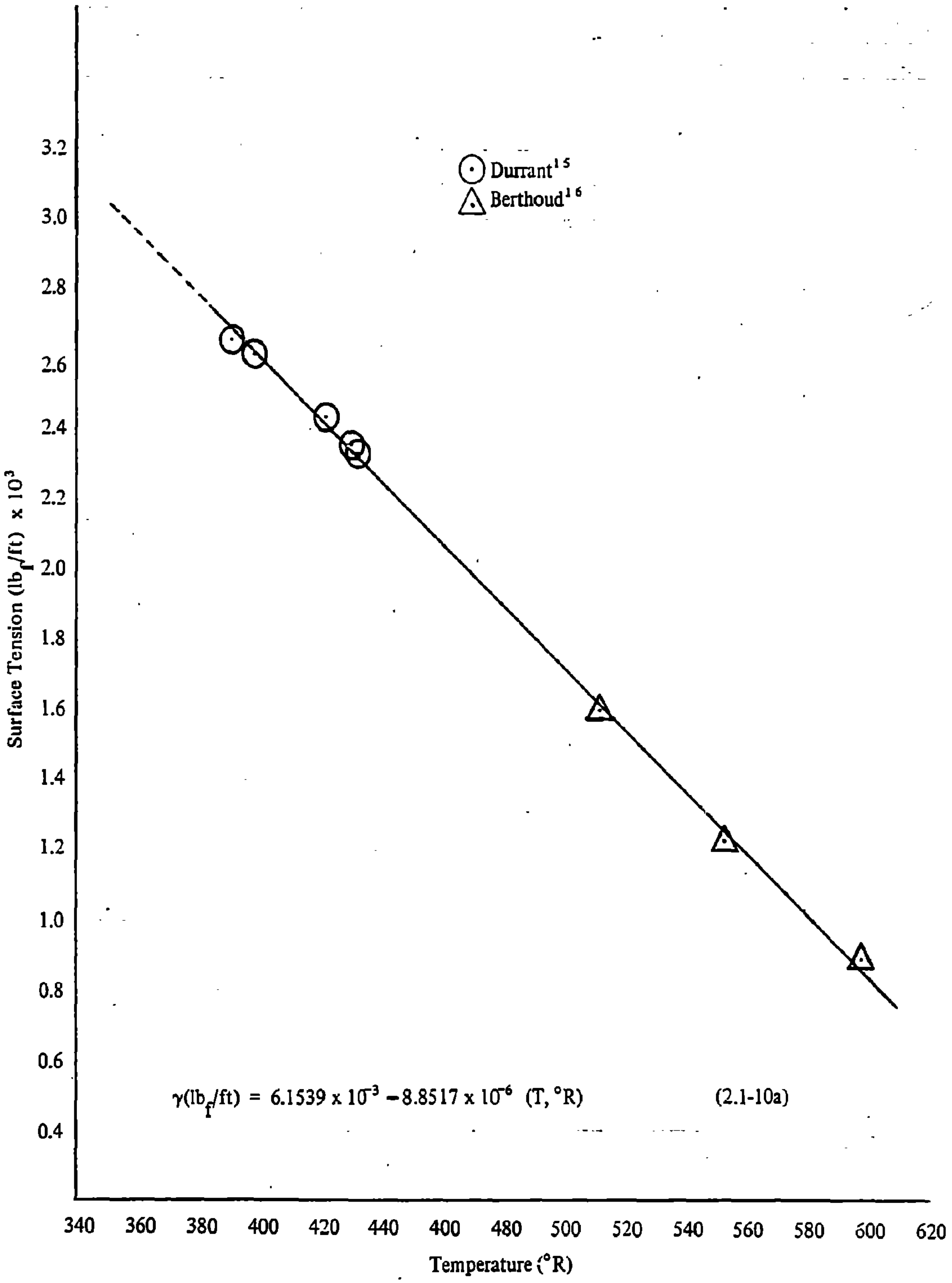


Figure 2.1-11. Surface Tension versus Temperature, Liquid Ammonia



$$\gamma(lb_f/ft) = 6.1539 \times 10^{-3} - 8.8517 \times 10^{-6}\ (T, {}^\circ R) \qquad (2.1\text{-}10a)$$

Figure 2.1-11a. Surface Tension versus Temperature, Liquid Ammonia

The experimental data were not reported and the following equation was given to represent the smoothed data:

$$K(\text{cal/m-hr-}^\circ\text{C}) = 0.464\ [1 - 0.0042\ (T, ^\circ C)] \qquad (2.1\text{-}11)$$

or alternately, in terms of centimeters and absolute temperature, equation 2.1-11 can be written

$$K(\text{cal/cm-sec-}^\circ\text{K}) = 1.288 \times 10^{-4}\ [2.1472 - 0.0042\ (T, ^\circ K)] \qquad (2.1\text{-}12)$$

Since the experimental data were not given by Sellschopp, his study was not considered in this work, but his smoothed data are shown in Figures 2.1-12 and 2.1-12a for the sake of completeness.

Richter and Sage(24) in 1964 and Needham and Ziebland(36) in 1965 reported data for the liquid and gas above 0 C and at pressures above saturation. In 1964, Golubev and Sokolova(52) also reported experimental data at elevated pressures and over a temperature range from approximately –64 to +23 C.

Richter studied the conductivity for four isotherms below the critical temperature and for three isotherms above the critical point. Pressures up to 360 atmospheres were obtained. Needham and Ziebland(36) published their final results in 1965, although some preliminary work(26) was published in 1962. Six isotherms below and three above the critical temperature were studied. Pressures up to 500 atmospheres were obtained. Golubev(52) reported data for four isotherms up to 400 atmospheres pressure.

This writer plotted the thermal conductivity as a function of pressure for all the isotherms given in the three separate studies. In general, the conductivity was found to be a linear function of pressure. Richter(24) reported the data for the saturated liquid as found by extrapolation to the saturation pressure. From the previously mentioned plots, the saturated liquid values from the data of Needham and Golubev were also found by extrapolation.

The extrapolated data from the three separate studies are shown in Figures 2.1-12 and 2.1-12a. The data from three sources would appear to be in good agreement. The thermal conductivity as a function of temperature for the saturated liquid from approximately –64 to +105 C is represented by

$$K(\text{cal/cm-sec-}^\circ\text{K}) = 1.4790 \times 10^{-3} + 2.2947 \times 10^{-6}(T, ^\circ K) - 1.1726 \times 10^{-8}(T, ^\circ K)^2 \qquad (2.1\text{-}13)$$

$$K(\text{BTU/lb-sec-}^\circ\text{R}) = 9.9144 + 8.6230 \times 10^{-8}(T, ^\circ R) - 2.4353 \times 10^{-10}(T, ^\circ R)^2 \qquad (2.1\text{-}13a)$$

Needham chose to represent the thermal conductivity with density as the independent variable. This somewhat unusual variable has an advantage in being able to represent both the effect of pressure and temperature with a single variable. The equation given by Needham is

$$K(\text{cal/cm-sec-}^\circ\text{K}) \times 10^4 = 8.695 - 27.015\,\rho + 52.591\,\rho^2 \qquad (2.1\text{-}14)$$

where ρ is the density in g/cm^3. The authors used this equation to report conductivity values down to the melting point. The reported value was 1.720×10^{-3} cal/cm-sec/°K. The value obtained in this study from equation 2.1-13 was found to be 1.480, which would indicate that the use of equation 2.1-14 given by Needham is not valid for extrapolation to temperatures below 0 C.

The smoothed data obtained from equation 2.1-11 and reported by Sellschopp gives values approximately 3 to 5% higher than obtained from equation 2.1-13. The effect of pressure on the thermal conductivity of liquid ammonia is not severe. At a pressure of 100 atmospheres (1470 psia), the conductivity increases by approximately 4.5%.

2.1.3.8 Dielectric Constant of Anhydrous Liquid Ammonia

The dielectric constant of liquid ammonia has been studied by a number of separate investigations dating back to 1899. A temperature range from –77 to +35 C has been studied but, unfortunately, the data are not in good agreement. The experimental data are shown in Figure 2.1-13 and 2.1-13a. The early data of Palmer(59) Coolidge(60) and Godwin(61) were taken from the International Critical Tables(62). The data from Franklin(63) and Mellor(64) were taken from Battelle(65). Smyth(66) reported a single-point value for the liquid at the melting point in his study on the solid.

The most accurate values are probably those published by Grubb(67). Unfortunately, Grubb only covered a narrow temperature range from 5 to 35 C. In this range, the values reported in the International Critical Tables are some 12% lower.

As provisional data, the results of all the investigations were combined and the dielectric constant as a linear function of temperature is expressed by

$$\epsilon = 42.79 - 0.08966\ (T, ^\circ K) \qquad (2.1\text{-}15)$$

$$\epsilon = 42.79 - 0.04981\ (T, ^\circ R) \qquad (2.1\text{-}15a)$$

The experimental data expressed by equation 2.1-15 have an average deviation of 4.2%. Additional experimental work is required to resolve the discrepancies in the existing data.

> NOTE: Hosted. J. B.. and Tirmazi. S. H., (J. Chem. Phys. 50, 1969) have recently reported values for the dielectric properties of liquid ammonia which could not be included in this work. This study appears to repudiate the data of Grubb(67) while showing fair agreement with the other sources.

2.1.3.9 Index of Refraction

The refractive index of liquid ammonia has been measured by Francis(13) for three temperatures from 9 to 35 C. The values are given for the usual sodium D line frequency.

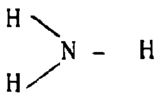
t, °C	Refractive Index N_D
9	1.3365
14.5	1.3345
35	1.3248

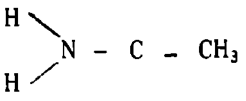
From the above data, Francis gives a value of 1.3327 and 1.3298 at 20 and 25 C, respectively.

2.1.4 CHEMICAL PROPERTIES

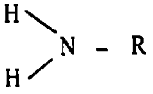
2.1.4.1 General

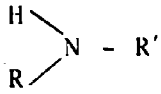
Two important compound groups that are derivatives are the amides and amines. The amides represent ammonia with one or more of its hydrogen atoms replaced by acyl groups:

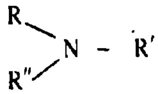

(Ammonia)


(Amide)

The amines are carbon, hydrogen, and nitrogen compounds obtained from ammonia through the replacement of one, two, or three of its hydrogen atoms by alkyl groups. Ammonia can therefore be considered as the "mother substance" for the amines as follows:


Primary Amine


Secondary Amine


Tertiary Amine

Section 2.1.2.2 gives details of the bond lengths and angles.

2.1.4.2 Inert Gas Solubility in Liquid Ammonia

The solubility of both Gaseous helium and gaseous nitrogen in liquid ammonia has recently been reported by Cannon(74). The solubility for both gases was measured at total pressures of 300 and 700 psia.

A temperature range for nitrogen from −100 to +50 F (-45 to +10 C) was studied. The same temperature range for helium was also planned to be covered but the solubility of helium at −100 F was so low that reliable measurements could not be obtained. The helium measurements started at -50 F.

The equilibrium constants for both helium and nitrogen were calculated for both pressures. These constants were found to be in fair agreement for both gases at the two pressures studied indicating Henry's law was obeyed or that the solubility is proportional to the partial pressure of the gas.

The calculated equilibrium constants as a function of temperature are shown in Figures 2.1-14 and 2.1-14a. The quantity of dissolved gas can be determined from the relationship

$$X = Kp$$

where

X = mole fraction of dissolved gas
p = partial pressure of the gas (psia)
K = equilibrium constant

In order to determine the solubility of dissolved gas in pressurized tankage, the vapor pressure of ammonia for the temperature recorded should be subtracted from the total pressure measured.

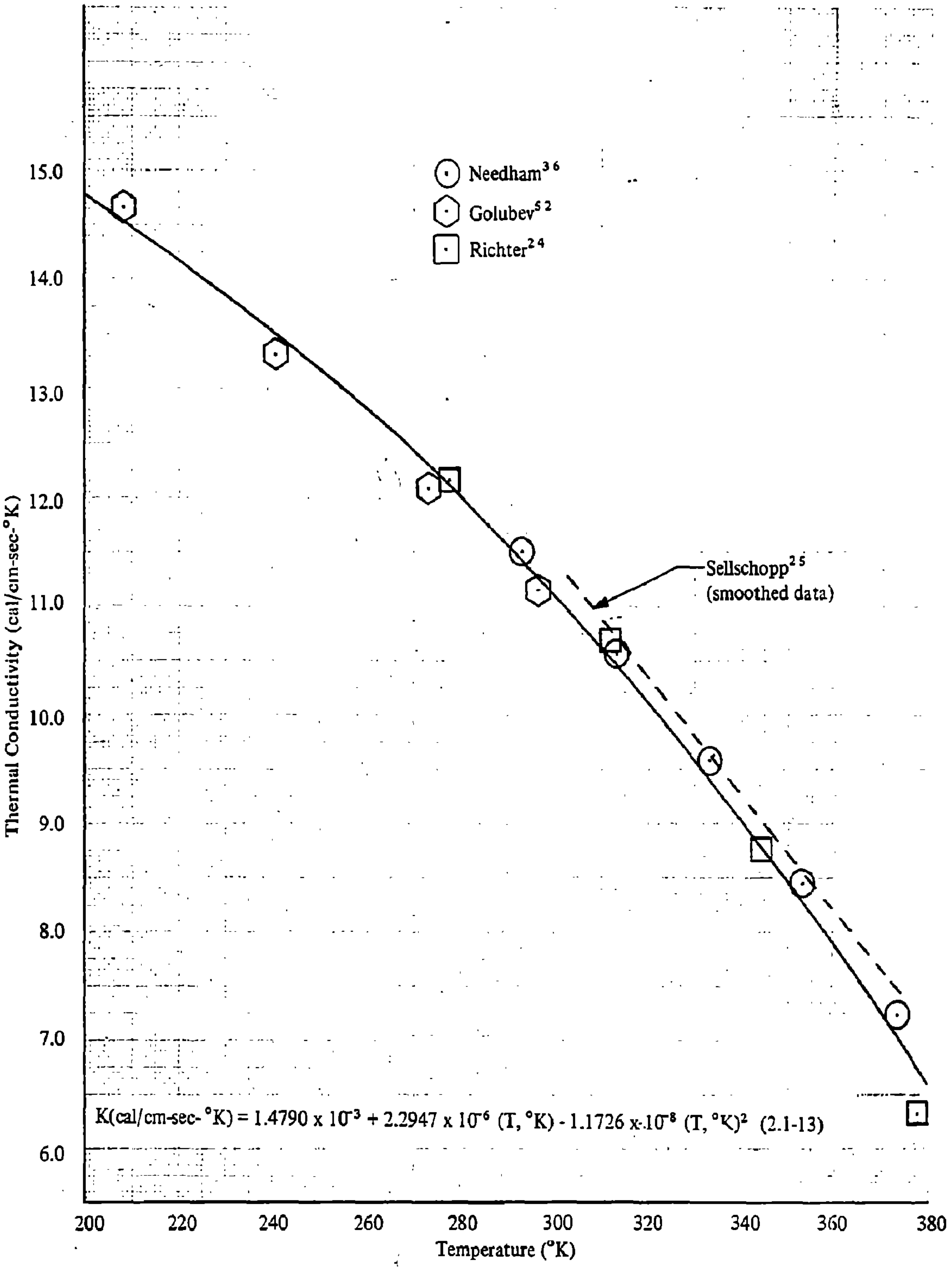
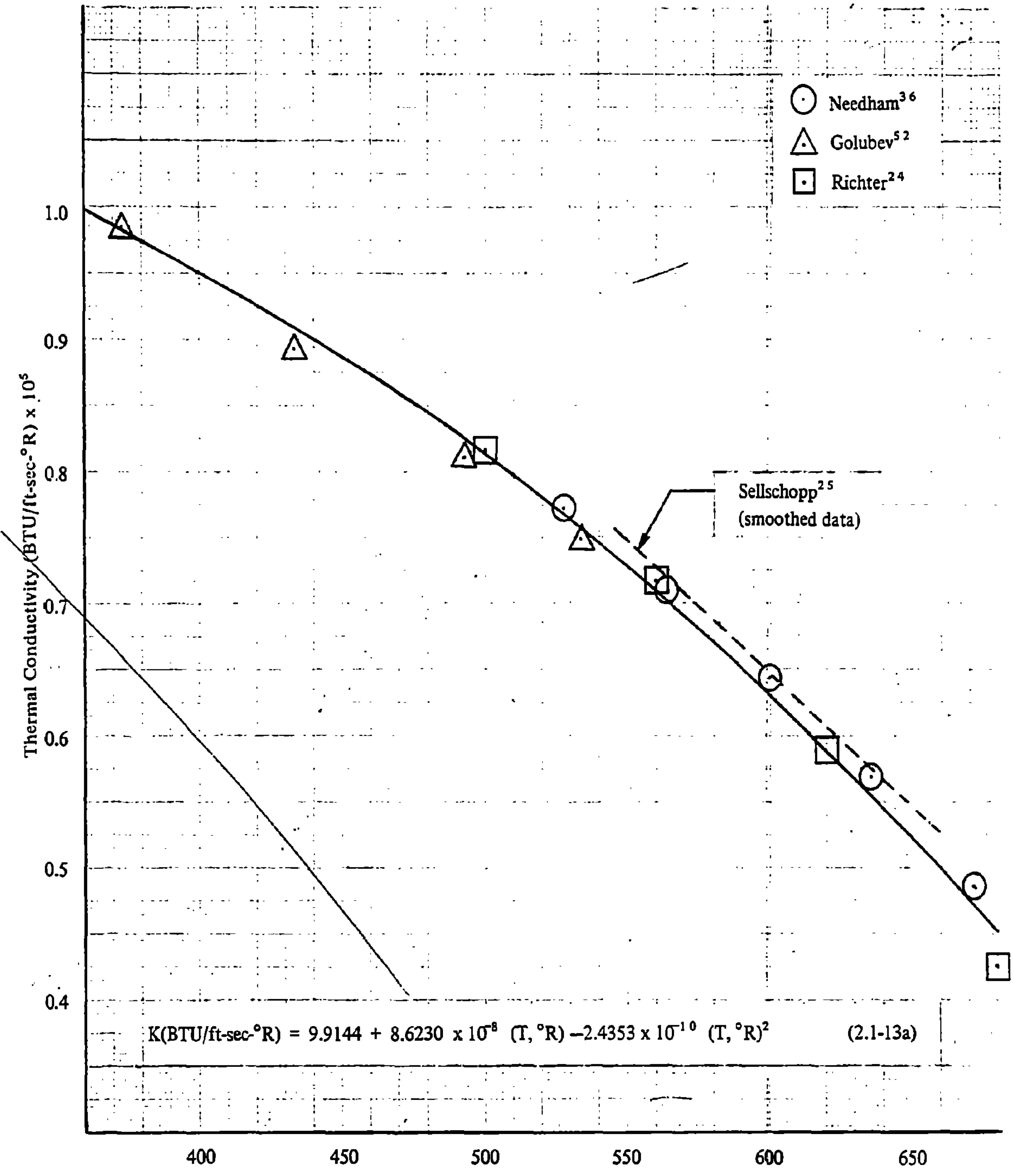


Figure 2.1-12. Thermal Conductivity versus Temperature, Saturated Liquid Ammonia



$$K(BTU/ft\text{-}sec\text{-}°R) = 9.9144 + 8.6230 \times 10^{-8} (T, °R) - 2.4353 \times 10^{-10} (T, °R)^2 \qquad (2.1\text{-}13a)$$

Figure 2.1-12a. Thermal Conductivity versus Temperature, Saturated Liquid Ammonia

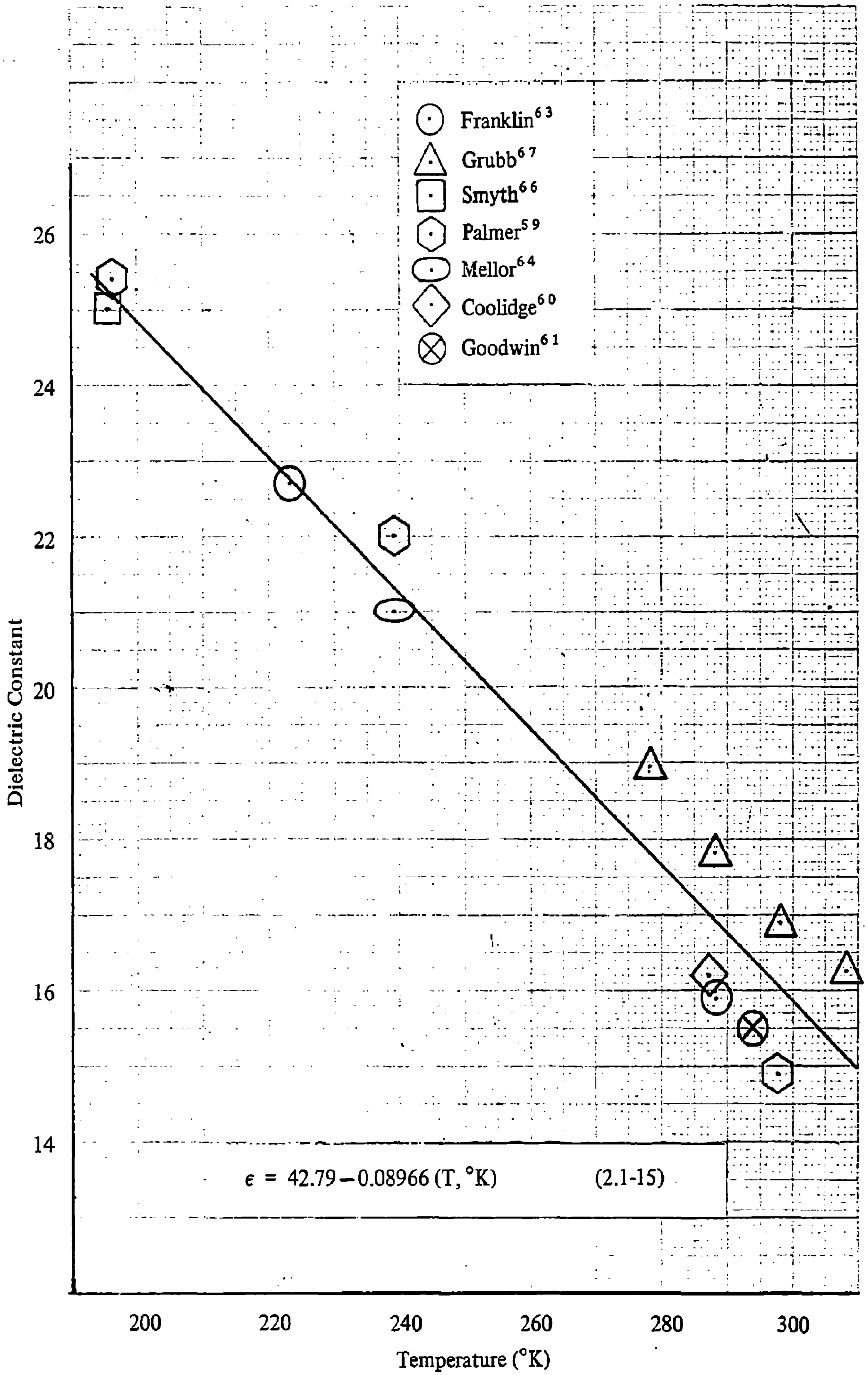


Figure 2.1-13. Dielectric Constant versus Temperature, Liquid Anhydrous Ammonia

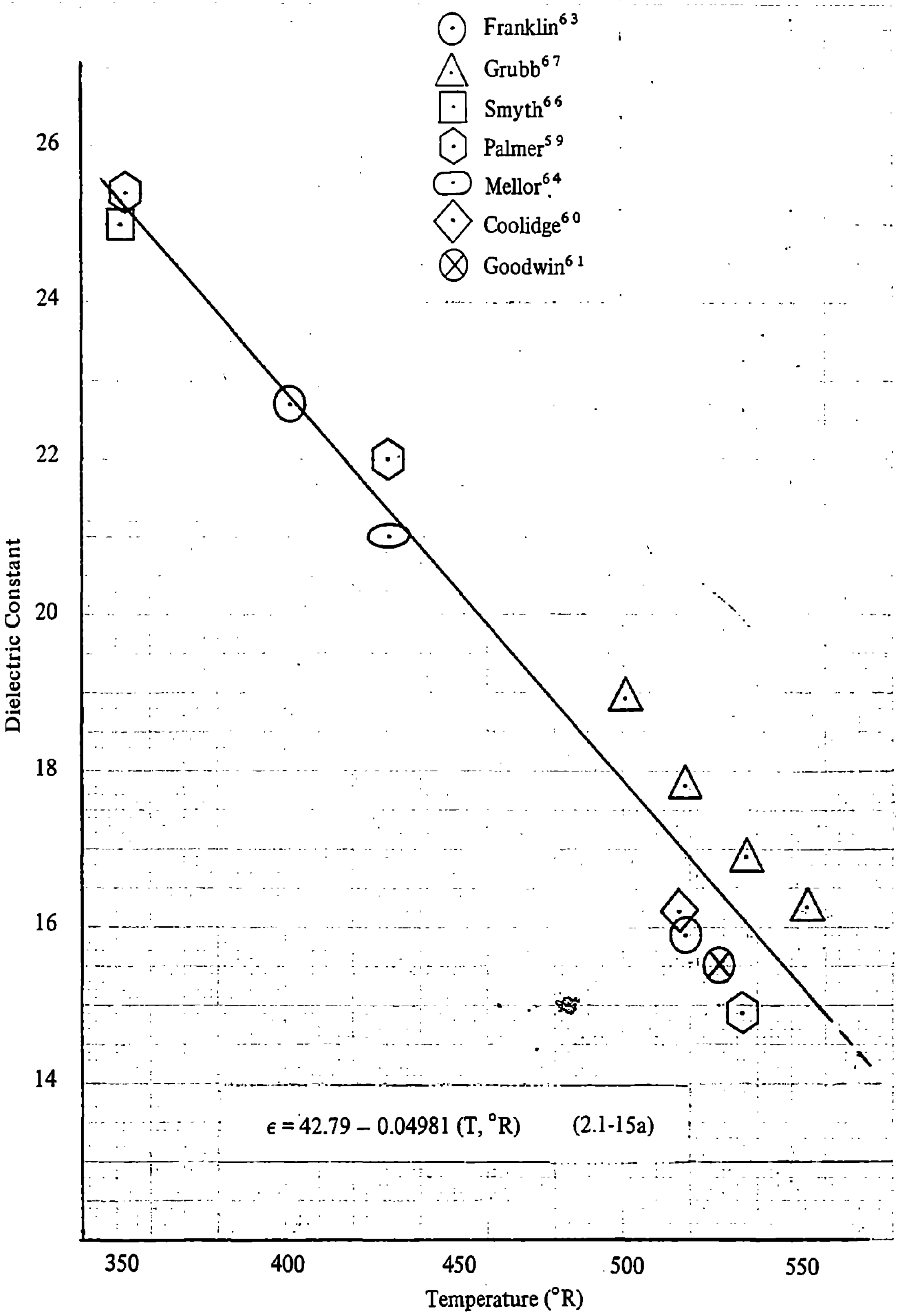


Figure 2.1-13a. Dielectric Constant versus Temperature, Liquid Anydrous Ammonia

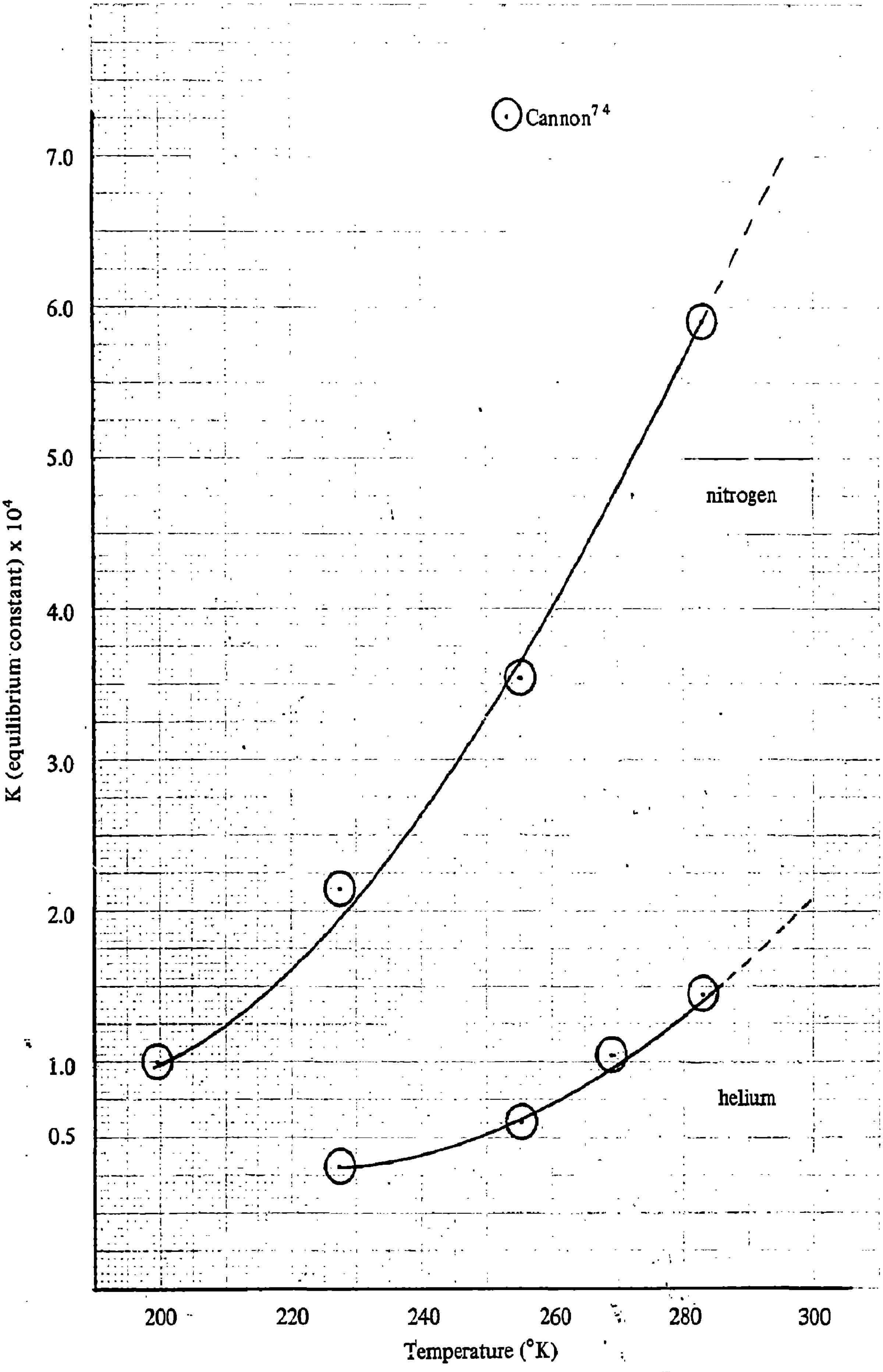


Figure 2.1-14. Gas Solubility in Liquid Ammonia versus Temperature

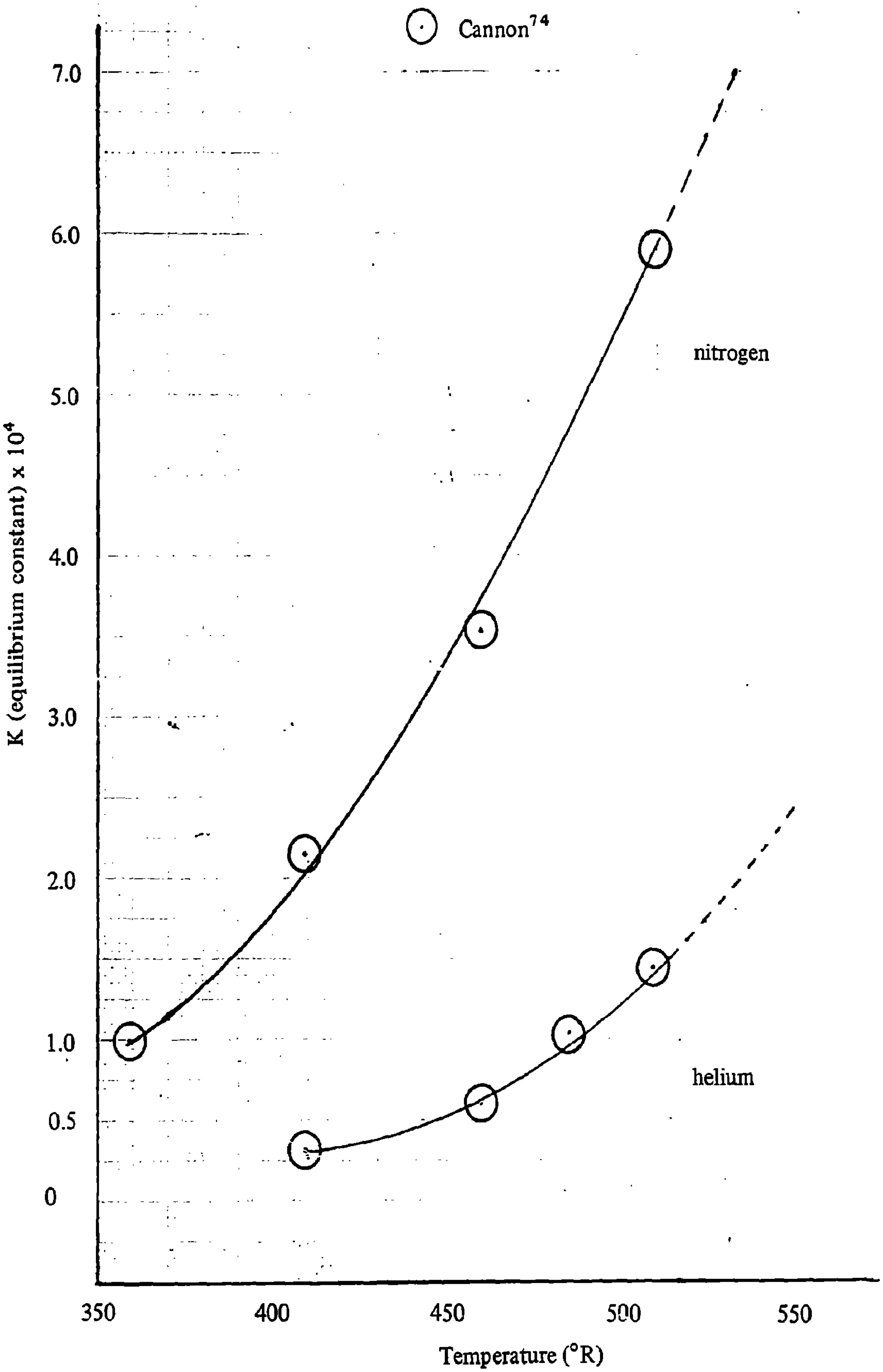


Figure 2.1.14. Gas Solubility in Liquid Ammonia versus Temperature

2.1.5 THERMODYNAMIC PROPERTIES

2.1.5.1 Heat of Formation of Liquid Ammonia

The heat of formation of gaseous ammonia at 298.15 K is reported as 10.97 +0.1 kcal/mole in the JANAF(58) thermochemical tables. This value is a weighted average of several calorimetric and equilibrium studies. The heat of formation of the liquid at the normal boiling point is found by addition of the heat of vaporization at the normal boiling point, the enthalpy change of the real gas from 298.15 K to the normal boiling point and correcting for the enthalpy difference between the real and ideal gas.

		ΔH (kcal/mole)
$1/2\ N_2 + 3/2\ H_2$ (g. 298)	$\rightarrow NH_3$ (ideal gas, 298)	-10.97
NH_3 (ideal gas, 298)	$\rightarrow NH_3$ (ideal gas, 239.72)	-0.488
NH_3 (ideal gas, 239.72)	$\rightarrow NH_3$ (real gas, 239.72)	-0.053
NH_3 (real gas, 239.72	$\rightarrow NH_3$ (liq. 239.72)	-5.581
$1/2\ N_2 + 3/2\ H_2$ (g,298)	$\rightarrow NH_3$ (liq. 239)	-17.092

The value of 239.72 K selected by JANAF is only slightly different than the value of 239.80 K selected in this work and any corrections would not be warranted. The value for the heat of vaporization (5.581 kcal/mole) is taken from the excellent work of Giauque and Overstreet(2). It is difficult to dispute this value, but the work of Osborne(10) at the National Bureau of Standards must also be considered. Osborne studied the heat of vaporization over a temperature range of-42 to +50 C. A curve fit of all of Osborne's data gives a smoothed value of 5.569 kcal/mole at the normal boiling point or 12 cal/mole less than that of Giauque(2).

Using the selected value in the work for the heat of vaporization at the normal boiling point, the heat of formation of liquid ammonia at 239.80 K becomes -17.104, and is selected in this work to maintain internal consistency. In the calculation of rocket engine performance, the choice is academic since either value will give the same performance numbers since the enthalpy difference is less than 0.1%.

2.1.5.2 Melting Point and Heat of Fusion

The melting point of ammonia has been experimentally determined by a number of investigators. Armstrong(5) lists 12 separate studies and selects a value of -77.70 C incorrectly attributed to Cragoe(3); this value was actually determined by McKelvy and Taylor(6). Armstrong selected this value based on the internal consistency of four separate readings. At the ice point value of 273.10 K used by McKelvy, the value becomes 195.40 K; when corrected to 273.15 K by ratio, the value is 195.44 K.

Davis(34) also reviewed the various literature pertaining to the melting point and selected the value given by Overstreet and Giauque(2). The value reported was 195.36 K based on six separate determinations. The ice point used by Overstreet was also 273.10 K and, by correction, the melting point value becomes 195.45 K.

Bergstrom(47) reports a value of -77.9 C from the determination of the melting point pressure and his vapor pressure equation. The corrected value is 195.2 K. Eucken and Karwat(55) report a value of 195.5 K and, when corrected to the presently accepted value for the ice point, becomes 195.54 K.

The value accepted in this work is 195.40 K which is the corrected value given by Overstreet and Giauque(2). The melting point pressure reported by Overstreet is 45.58 mm Hg. Thode(46) reports 45.61 while Cragoe(3) gives 44.9. In a later study, Kirshenbaum(19) reports 45.47. A value of 45.67 mm Hg was obtained at 195.40 K using equation 2.1-2 for the vapor pressure and is accepted in this work.

The heat of fusion at the melting point has been reported as 1426 cal/mole by Eucken and Karwat in 1924 and in 1926 Eucken and Donath(56) reported 1380 cal/mole. Overstreet and Giauque reported an average from three separate determinations as 1351.6 cal/mole or 588.16 BTU/lb and this value is selected here.

2.1.5.3 Critical State Constants

The critical state constants for ammonia have been reviewed by Kobe(20) and the reported values given by various authors are given in tabular form. For the critical temperature, Kobe gave equal weight to all values since 1900 and selects a value of 132.3 C (405.45 K). The most recent value is 132 C (405.65 K) reported by Kopper(50) and was not considered by Kobe. Postma(29) reported a value equal to the selected value given by Kobe.

Davis(34) and Armstrong(5) both accept a value of 405.6 K which appears to be a good compromise between the older studies and the more recent value of Kopper(50) and this value is retained in this work.

The critical pressure selected by Kobe(20) in a review of all the data from 1900 to 1923 is 111.3 atmospheres. Davis(34) selected a value of 111.5 atmospheres which is in agreement with the value reported by Myers(54). Using the critical temperature value of 405.6 K, a value of 112.2 atmospheres is obtained from the vapor pressure equation accepted in this work (equation 2.1-3) and this is in good agreement with the value of 112.4 atmospheres selected by Armstrong(5).

The critical density selected by Kobe(20) in his review was 0.235 g/cc based mainly on the work of Berthoud(16) who selected 0.2364 g/cc at a critical temperature of 405.65 K. In the early review by Goodenough, 0.236 g/cc was selected. Davis (34) selected 0.235 g/cc, which is the value accepted in this work. The critical density is shown in Figure 2.1-6 with the data of the saturated liquid and vapor at elevated temperatures.

2.1.5.4 Heat Capacity of Ammonia

The heat capacity of solid ammonia has been studied by Eucken and Karwat(55). Clusius(74) and more recently by Overstreet and Giauque(2). Davis(34) has reviewed these studies and concluded that only the work of Overstreet should be considered. Although the separate German studies are in good agreement with each other, they are consistently higher than the American data over most of the temperature range from 20 K to the melting point. The experimental data reported by Overstreet are shown in Figures 2.1-15 and 2.1-15a.

Using the least-squares method, the data was fitted using third and fourth degree polynomials. Although most of the data could be smoothly joined at the low temperatures, they could not be smoothly fitted and extrapolation did not give a zero value at absolute zero temperature. It was found that a linear expression would adequately describe the data for most applications. Extrapolation below 15 K will, of course, give erroneous values.

$$C_p\ (\mathrm{cal/g\text{-}^{\circ}K}) = -0.040675 + 3.9238 \times 10^{-3}\ (\mathrm{T,^{\circ}K}) \qquad (2.1\text{-}16)$$

$$C_p\ (\mathrm{BTU/lb\text{-}^{\circ}R}) = 0.040675 + 2.1799 \times 10^{-3}\ (\mathrm{T,^{\circ}R}) \qquad (2.1\text{-}16a)$$

The average deviation of the data is quite high (13.7%) when compared to the smoothed data obtained from equation 2.1-16; however, the standard deviation is only 0.013 cal/g-K.

The heat capacity of saturated liquid ammonia has been studied by a number of investigators. The exhaustive studies at the National Bureau of Standards by Osborne and Van Dusen(9) and the excellent work of Overstreet and Giauque(2) were selected by Davis(34) as the best. Earlier studies reviewed by Davis showed a high degree of scatter and generally poor agreement with the Osborne and Overstreet studies. The experimental data are plotted in Figures 2.1-16 and 2.1-16a.

Overstreet(2) covered a somewhat limited temperature range from the melting point to 239 K. Osborne included a temperature range from 227 to 319 K. Although the data reported by Overstreet is given as C_p (constant pressure), Davis points out that it is actually C_{sat} (saturated liquid), and further points out that differences for the temperature range covered would be very small. The combined data of C_{sat} or, for all practical purposes, C_p, can be expressed.

$$\begin{aligned} C_p(\mathrm{cal/g\text{-}^{\circ}K}) = {} & 0.62839 + 0.011328\ (\mathrm{T,^{\circ}K}) \\ & - 4.5591 \times 10^{-5}\ (\mathrm{T,^{\circ}K})^2 \\ & + 6.5877 \times 10^{-8}\ (\mathrm{T,^{\circ}K})^3 \qquad (2.1\text{-}17) \end{aligned}$$

$$\begin{aligned} C_p(\mathrm{BTU/lb\text{-}^{\circ}R}) = {} & 0.62839 + 6.2936 \times 10^{-3}\ (\mathrm{T,^{\circ}R}) \\ & - 1.4071 \times 10^{-5}\ (\mathrm{T,^{\circ}R}) \\ & + 1.1296 \times 10^{-8}\ (\mathrm{T,^{\circ}R})^3 \qquad (2.1\text{-}17a) \end{aligned}$$

The average deviation obtained from equation 2.1-17 is 0.069%.

2.1.5.5 Latent Heat of Vaporization

The latent heat of vaporization was accurately determined over a temperature range from −42 to +52 C by Osborne and Van Dusen(10) of the National Bureau of Standards in 1918. Measurements made prior to this time are summarized by Goodenough(32) but are generally of historical interest only.

The experimental work of Osborne is shown in Figures 2.1-17 and 2.1-17a. The experimental data can accurately be expressed by

$$H_V(\mathrm{kcal/mole}) = 5.3115 + 0.013307\ (\mathrm{T,^{\circ}K}) - 5.1012 \times 10^{-5}\ (\mathrm{T,^{\circ}K})^2 \qquad (2.1\text{-}18)$$

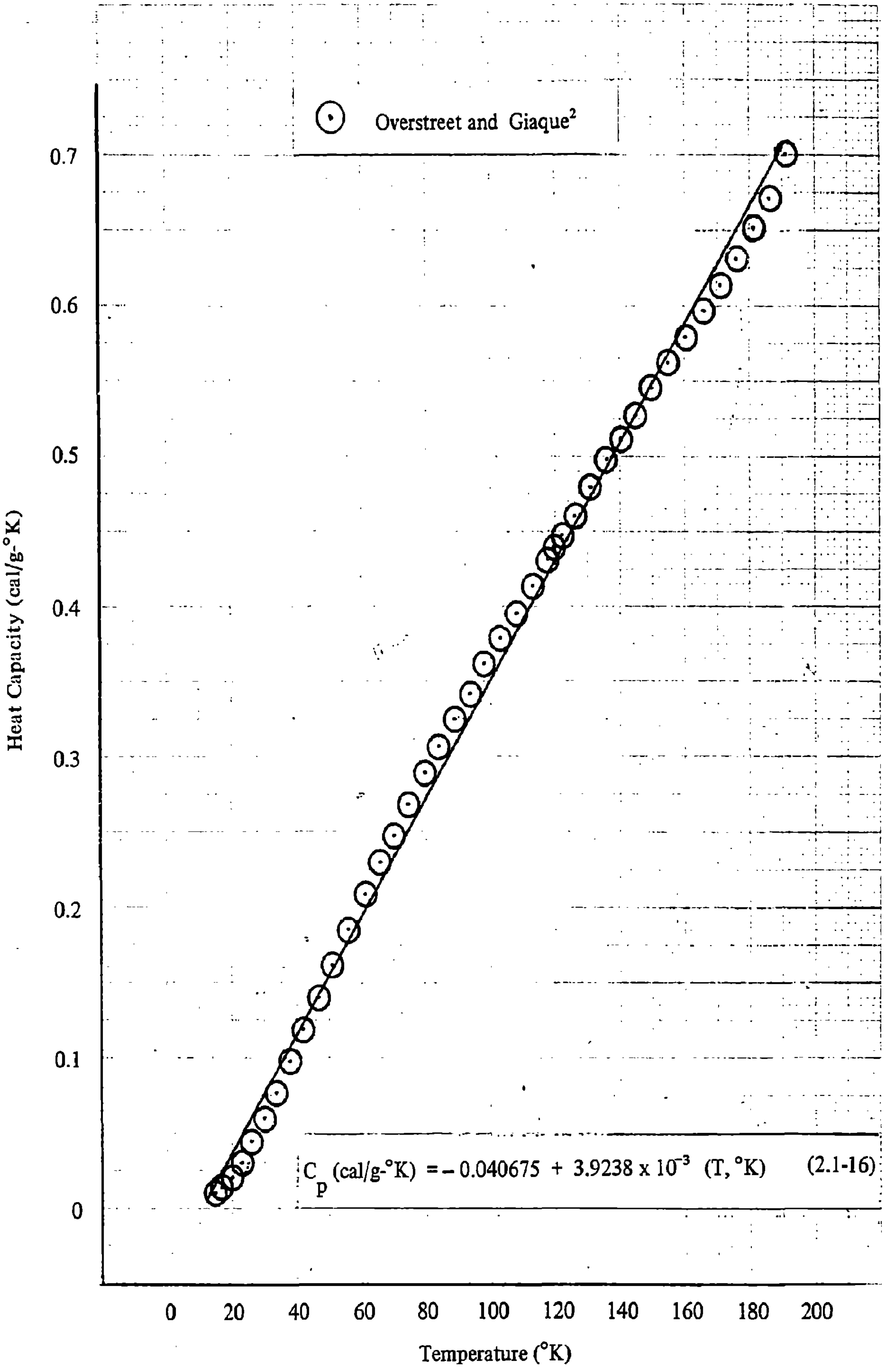
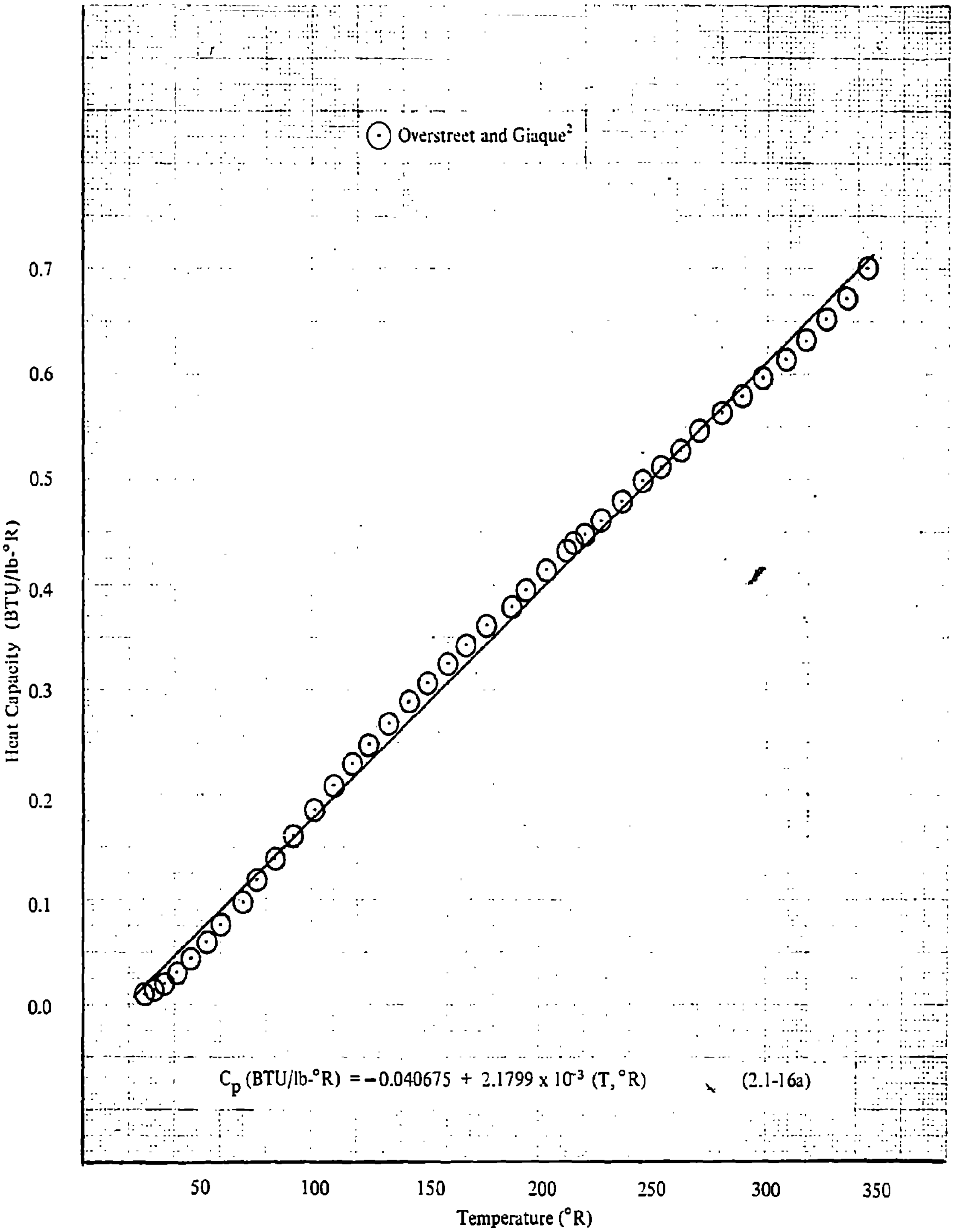
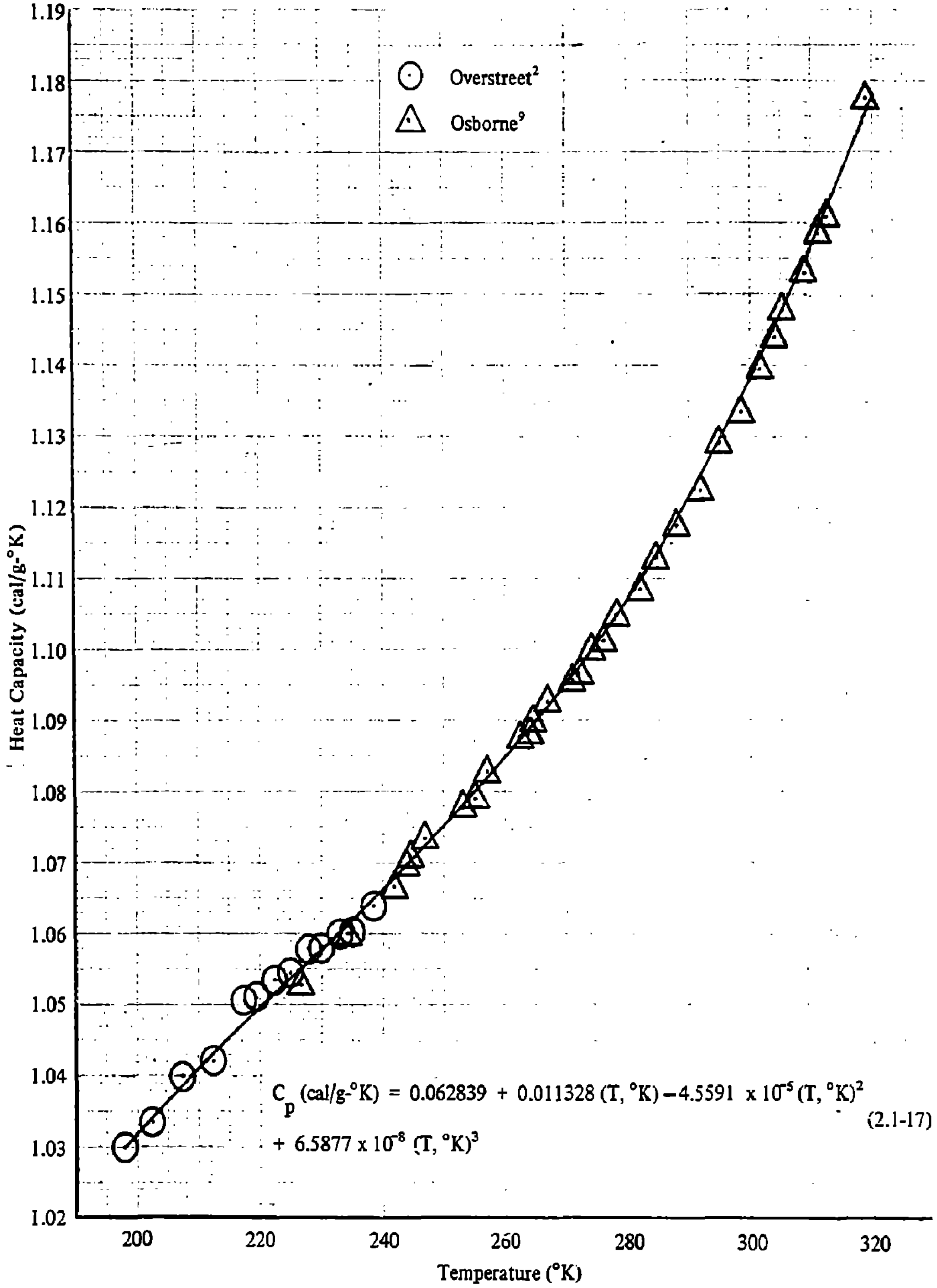


Figure 2.1-15. Heat Capacity versus Temperature, Solid Ammonia



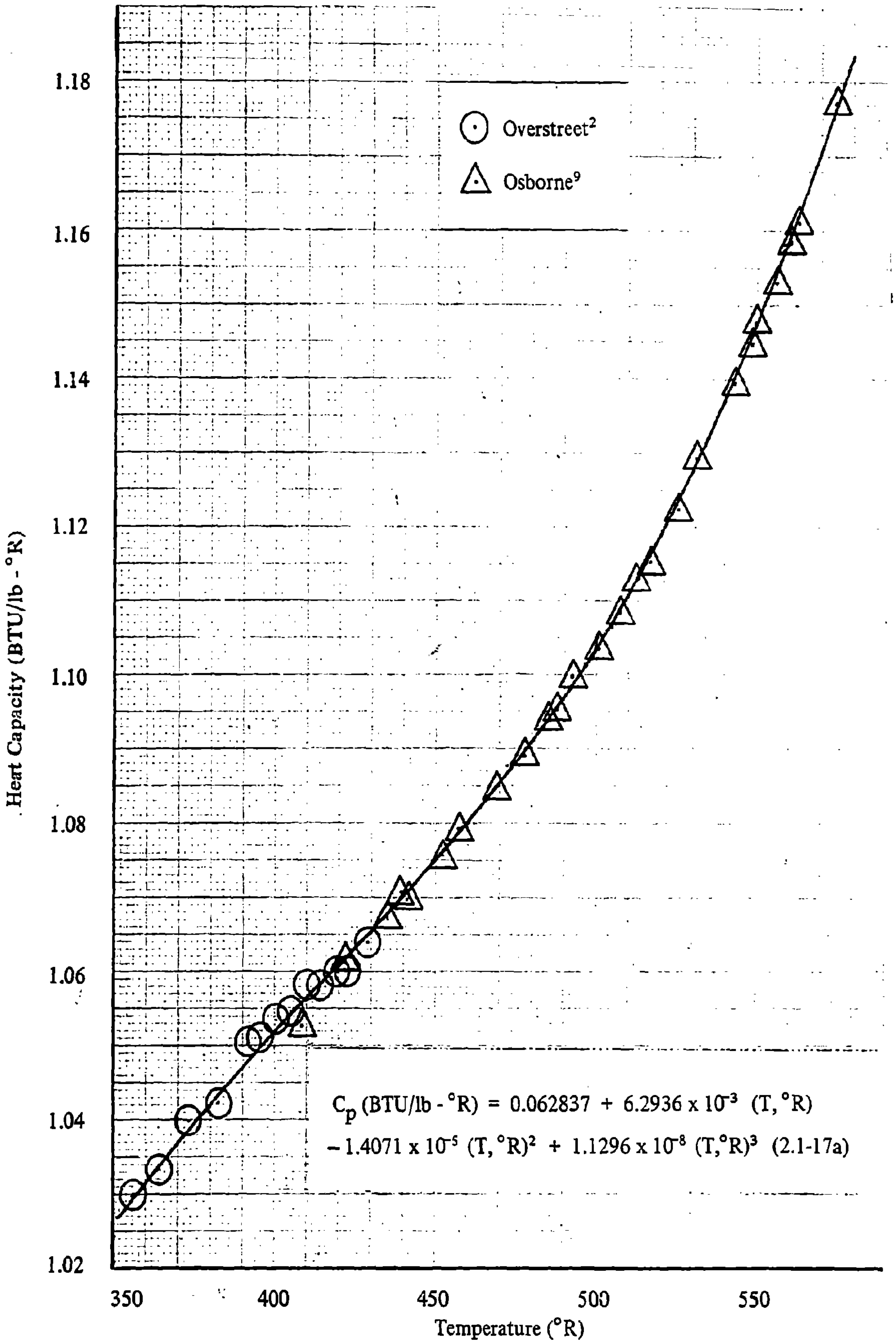
$$C_p\ (\mathrm{BTU/lb\text{-}^\circ R}) = -0.040675 + 2.1799 \times 10^{-3}\ (T, {}^\circ\mathrm{R}) \qquad (2.1\text{-}16a)$$

Figure 2.1-15a. Heat Capacity versus Temperature, Solid Ammonia



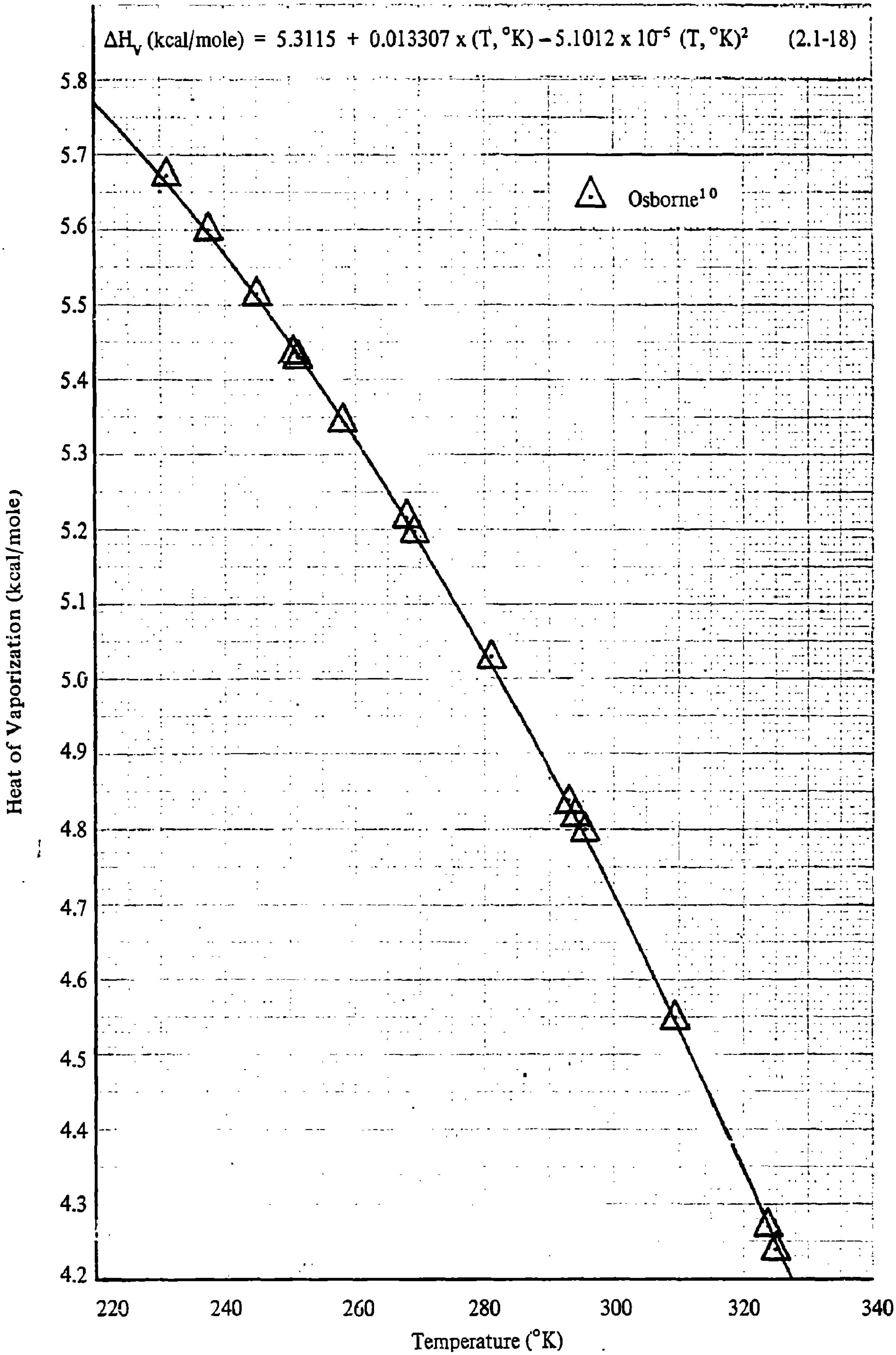
$$C_p\ (\text{cal/g-}^\circ\text{K}) = 0.062839 + 0.011328\ (T, ^\circ\text{K}) - 4.5591 \times 10^{-5}\ (T, ^\circ\text{K})^2 + 6.5877 \times 10^{-8}\ (T, ^\circ\text{K})^3 \qquad (2.1\text{-}17)$$

Figure 2.1-16. Heat Capacity versus Temperature, Liquid Ammonia



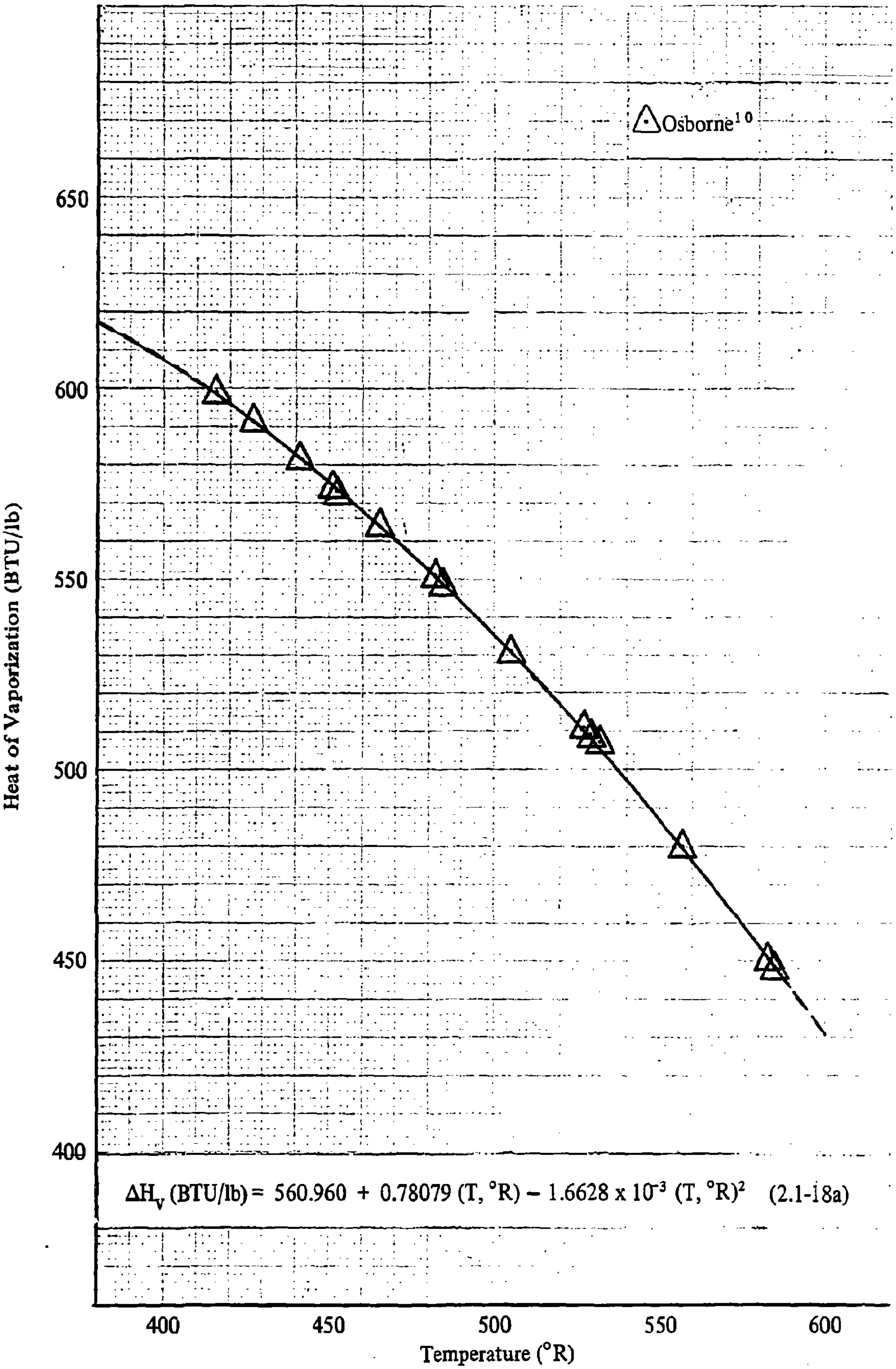
$$C_p\,(\text{BTU/lb}-{}^\circ\text{R}) = 0.062837 + 6.2936 \times 10^{-3}\,(T, {}^\circ\text{R}) - 1.4071 \times 10^{-5}\,(T, {}^\circ\text{R})^2 + 1.1296 \times 10^{-8}\,(T, {}^\circ\text{R})^3 \quad (2.1\text{-}17a)$$

Figure 2.1-16a. Heat Capacity versus Temperature, Liquid Ammonia



$$\Delta H_v \text{ (kcal/mole)} = 5.3115 + 0.013307 \times (T, {}^\circ K) - 5.1012 \times 10^{-5} (T, {}^\circ K)^2 \qquad (2.1\text{-}18)$$

Figure 2.1-17. Latent Heat of Vaporization versus Temperature, Liquid Ammonia



$$\Delta H_V \text{ (BTU/lb)} = 560.960 + 0.78079 \text{ (T, °R)} - 1.6628 \times 10^{-3} \text{ (T, °R)}^2 \qquad (2.1\text{-}18a)$$

Figure 2.1-17a. Latent Heat of Vaporization versus Temperature, Liquid Ammonia

$$H_V(\text{BTU/lb} = 560.960 + 0.78079\,(\text{T},^\circ\text{R})$$

$$-1.6628 \text{ x } 10^{-3}\,(\text{T},^\circ\text{R})^2 \qquad (2.1\text{-}18a)$$

and the average deviation is 0.095%. Extrapolation of equation 2.1-18 to the critical point does not, however, give a value of zero. Osborne expressed his data in terms of the critical temperature by

$$H_V(\text{Joules/g}) = 137.91\ (133\ \ \text{T},^\circ\text{C})^{1/2} - 2.466\ (133.\text{T},^\circ\text{C}) \qquad (2.1\text{-}19)$$

$$H_V(\text{kcal/mole}) = 0.56140\,(406.15\ \text{T},^\circ\text{K})^{1/2}$$

$$-1.00385 \text{ x } 10^{-2}\,(406.15\ \text{T},^\circ\text{K}) \qquad (2.1\text{-}19a)$$

Since the critical temperature chosen by Osborne is slightly different than the value of 405.6 K selected here, the data was fitted to the same form chosen by Osborne and the corrected equation becomes

$$H_V(\text{kcal/mole}) = 0.56433\,(405.6\text{-T},\ ^\circ\text{K})^{1/2}$$

$$-\ 0.01023\,(405.6\text{-T},^\circ) \qquad (2.1\text{-}20)$$

At the normal boiling point (239.80 K), a value of 5.569 kcal/mole is obtained from both equations 2.1-16 and 2.1-20. Overstreet and Giauque(2) made seven experimental determinations at the normal boiling point and obtained an average value of 5.581 kcal/mole. Postma(29) reports a value of 5.864 kcal/mole which appears to be too high. From the Clapeyron equation, using equation 2.1-16 for the vapor pressure, a value of 5.560 kcal/mole was obtained.

The data reported by Osborne(10) is accepted in this work and at the normal boiling point (239.80 K) the value is 5.569 kcal/mole. The calculated Trouton constant is 23.22.

2.1.6 LOGISTICS OF AMMONIA

2.1.6.1 Manufacture

Ammonia was produced commercially for many years as a by-product in the manufacture of coke and gas from coal. The most important method is the direct synthesis of nitrogen and hydrogen in the presence of a catalyst.

In 1823, Dobereiner published a paper on the direct synthesis of ammonia. In 1908, Haber and his co-workers started work on finding an improved catalyst. After several years, a catalyst consisting of iron promoted with metallic oxide was perfected. Using Haber's groundwork, Bosch and Mittasch developed a large-scale ammonia plant. The present day manufacture of ammonia is largely based on modification of the Haber-Bosch system.

The source of the hydrogen and nitrogen is largely dependent upon local raw materials. Generally, hydrogen is obtained from the thermal reforming of natural gas with steam. Other sources include the decomposition of steam over coke, partial oxidation of hydrocarbons, hydrogen byproducts from the refining of petroleum naphtha for gasoline and the electrolysis of water.

Nitrogen for the direct element process is generally obtained from burning hydrogen or hydrocarbons in air in sufficient amounts to produce the desired 3:1 hydrogen-nitrogen ratio, mixing producer gas with water gas and the liquefication of air.

Quite briefly, the Haber-Bosch process first produces water gas by passing steam over an incandescent coke bed. Some of the products of combustion are then diverted to furnish the required nitrogen. The mixed gases are then passed through a scrubber to remove dust particles and water. The gas is then mixed with steam and passed through a catalyst where the carbon monoxide is converted to carbon dioxide.

The gas is then compressed to 25 atmospheres and passed through a carbon dioxide purifier. The gas is then compressed to 200 atmospheres and any residual carbon monoxide is removed. The remaining gas mixture is three parts hydrogen and one part nitrogen. For the direct synthesis of ammonia, the gas enters an ammonia converter containing the catalyst. The unconverted gas is returned to join the incoming makeup gas while the ammonia gas is condensed out. Several other processes are given in Reference 69 and 70.

2.1.6.2 Analysis

The purity of ammonia produced in the United States is consistently high. Federal Specification O-A445a for refrigeration grade ammonia was previously used as the procurement document for propellant grade ammonia(71). This document did not control oil content but did control pyridine, napthalene and hydrogen sulfide which would not affect engine performance.

MIL-P-27406 (USAF), dated May 1966, now covers the procurement and use of anhydrous ammonia as a propellant, calling out a minimum purity of 99.5% by weight. The impurity limitations are maximums of 0.5 weight % water and 5.0 parts per million of oil.

Water content of the ammonia is determined by the Karl Fisher method. A 100 ml sample of ammonia is placed in a centrifuge tube. The ammonia is then boiled off in a water bath with the aid of boiling chips washed with carbon tetrachloride. The residue after boiling is mixed with 25 ml of anhydrous methanol and then titrated to the dead-end stop with sulfiodine as the reagent. The water content is then calculated from the quantity of reagent used, water equivalent of the reagent and the evaporation factor based on the temperature of the sample lot. (See MIL-P-27406 (USAF) for complete details.)

The oil content is checked by drawing a 1000 ml sample in a round-bottomed flask. The ammonia is boiled off with the aid of boiling chips and the residue is then rinsed out with carbon tetrachloride and filtered into a weighed evaporating dish. After the carbon tetrachloride has evaporated, the weight of the oil is carefully determined on an analytical balance. (See MIL-P-27406 (USAF) for complete details.)

2.1.6.3 Cost and Availability

The Kirk-Othmer Encyclopedia(69) gives the annual capacity of United States plants for the manufacture of synthetic ammonia at nearly five million tons for 1962. The principal suppliers are: Allied Chemical Corp., Commercial Solvents Corp., DuPont, Monsanto Chemical Co., Phillips Petroleum Co., Solar Nitrogen Chemicals. Spencer Chemical and Tennessee Corp. These companies can all produce over 100,000 tons annually. Other companies producing lesser amounts are too numerous to mention.

Nearly 70% of the ammonia produced in the United States is for agriculture, largely as fertilizer. Other applications include use as a refrigerant, water purifier, household ammonia, explosives, inorganic chemical manufacture, pulp and paper and rubber manufacture. As a rocket propellant, ammonia has found little use to this date.

If a major missile system were to employ ammonia as its fuel, it would be readily available in large quantities in most areas of the United States. In 1966, the stock price of ammonia was listed as five cents per pound or about twenty cents a gallon. This puts ammonia very close to water in cost.

2.1.6.4 Shipping and Transportation

For complete and detailed laws concerning the shipment of anhydrous ammonia the Code of Federal Regulations, Title 49 parts 71 to 90 should be considered. Anhydrous ammonia is shipped as a compressed gas and marked with a green label marked "Nonflammable Compressed Gas." Tank cars and cargo tanks should be marked in accordance with the Code of Federal Regulations 49-CFR77-823(d).

Anhydrous ammonia may be packaged and shipped in the following types of containers in accordance with the ICC specifications listed:

Cylinders

Anhydrous ammonia may be shipped in cylinders not to exceed 300 pounds of ammonia per cylinder. The following ICC regulations are applicable: ICC-3, 3A480, 3AA480, 3A480X, 3E1800 and 4AA480.

Cargo Tanks

Anhydrous ammonia shipped in tanks designed to be permanently attached to motor vehicles such as tank trucks and trailers must comply with ICC Specification MC-330. Tanks must be designed to withhold at least 264 psig.

Portable Bulk Tanks

Anhydrous ammonia may be shipped in portable tanks having a minimum design pressure of 265 psig. ICC Specification 51 is applicable.

Tank Cars

Anhydrous ammonia can be shipped in 11,000 gallon steel insulated tanks. Applicable ICC Specifications are 105A300-W, 106A500, 106A500-X, 112A400-F and 112A400-W, 106A500, 106A500-X, 112A400-F and 112A400-W. The safety vent is set to open at 225 psig which is approximately the vapor pressure at 108 F.

2.1.7 REFERENCES

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2.2.1 PROPERTY SUMMARY SHEET

Chemical Name: Diethylenetriamine **Common Name:** DETA

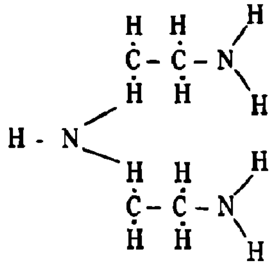
Chemical Formula: $(NH_2CH_2CH_2)_2NH$ **Formula Weight:** 103.172 (O^{16})

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	238.15 -35.0 428.67 -31.0	°K °C °R °F		4,6	
HEAT OF FUSION	-	kcal/mole BTU/lb			
NORMAL BOILING POINT	480.6 207.45 865.08 405.41	°K °C °R °F		calc.	
HEAT OF VAPORIZATION	12.068 210.54	kcal/mole BTU/lb	NBP	calc.	
TROUTON CONSTANT	25.11	-	NBP	calc.	
DENSITY OF LIQUID	.9488 59.231	g/cc lb/ft^3	298	2,3	2.2-2
VAPOR PRESSURE OF LIQUID	.320 .0062	mm Hg psia	298	1	2.2-1
VISCOSITY OF LIQUID	5.58 3.75×10^{-3}	centipoise lb$_m$/ft-sec	298	2	2.2-3
HEAT CAPACITY OF LIQUID		cal/g-°K BTU/lb-°R			
DIPOLE MOMENT	2.22	Debyes	298	5	
HEAT OF FORMATION	-18.5 -322.76	kcal/mole BTU/lb	298	2	
REFRACTIVE INDEX	1.4815	-	298	3	

2.2.2 GENERAL

2.2.2.1 Structure and Description

Diethylenetriamine falls in the general category of polyamines and is available in quantity as an industrial chemical. Its structural formula is:



As seen, it may be considered as the dimer of ethylene diamine.

DETA is water-white to light amber in color, is relatively viscous, and is a caustic liquid (1). It is hygroscopic and will absorb moisture upon exposure to a humid atmosphere. It has been used mainly as a propellant ingredient, specifically in MAF-1, MAF-3, and MAF-4, in order to obtain improved physical properties in these fuels.

2.2.2.2 Specification and Purity

Commercial DETA, at the time of consideration as a propellant, had a purity of at least 91% by weight, with the major impurity being aminoethylpiperazine. It was formerly covered by MIL-D-50025B(MU). DETA is currently covered by Federal Specification O-D-1271, dated Nov. 20, 1967. This specification requires a purity of at least 97.0% by weight.

2.2.3 PHYSICAL PROPERTIES

2.2.3.1 Vapor Pressure and Normal Boiling Point of Liquid DETA

The vapor pressure of diethylenetriamine (DETA) has been reported by Sarner (1) and referenced to a product bulletin of Carbide and Carbon Chemicals Company. The data in Figures 2.2-1 and 2.2-1a appear to be smoothed and of minimal precision and can be described by:

$$\log P\,(\text{nm Hg}) = 8.3982 - \frac{2651.50}{T,\,^{\circ}K} \qquad (2.2\text{-}1)$$

$$\log P\,(\text{psia}) = 6.6846 - \frac{4772.69}{T,\,^{\circ}R} \qquad (2.2\text{-}1a)$$

Equation 2.2-1 is applicable for a temperature range from 20 to 210 C (68 to 410 F). The extrapolated normal boiling point from Equation 2.2-1 is 480.6 K or 207.4 C (405.3 F). This value is in good agreement with the 207.1 C value reported in the LPIA manual (4).

The vapor pressure presented here should be considered as provisional data since the original data source was not available.

2.2.3.2 Density of Liquid Diethylenetriamine (DETA)

A single-point density determination at 25 C (77 F) for high purity DETA has been reported by Rouleau (3). RMD (2) has supplied this contractor with density data from 0 to 60 C (32 to 140 F). The exact source is unknown but it is believed that Carbide and Carbon Chemicals Company obtained the experimental data. At 25 C the density is in excellent agreement with the published value of Rouleau.

The experimental work is plotted in Figures 2.2-2 and 2.2-2a. The density for the temperature range from 0 to 60 C is a linear function of temperature:

$$\rho\,(\text{g/cc}) = 1.1955 - 8.2751 \times 10^{-4}\,(T,\,^{\circ}K) \qquad (2.2\text{-}2)$$

$$\rho\,(\text{lb/ft}^3) = 74.6339 - 0.02870\,(T,\,^{\circ}R) \qquad (2.2\text{-}2a)$$

Equation 2.2-2 was derived by the least-squares method and the single-point determination of Rouleau (3) was given triple weight. This equation describes the experimental data with a standard deviation of 0.0006g/cc and the average deviation is 0.04%.

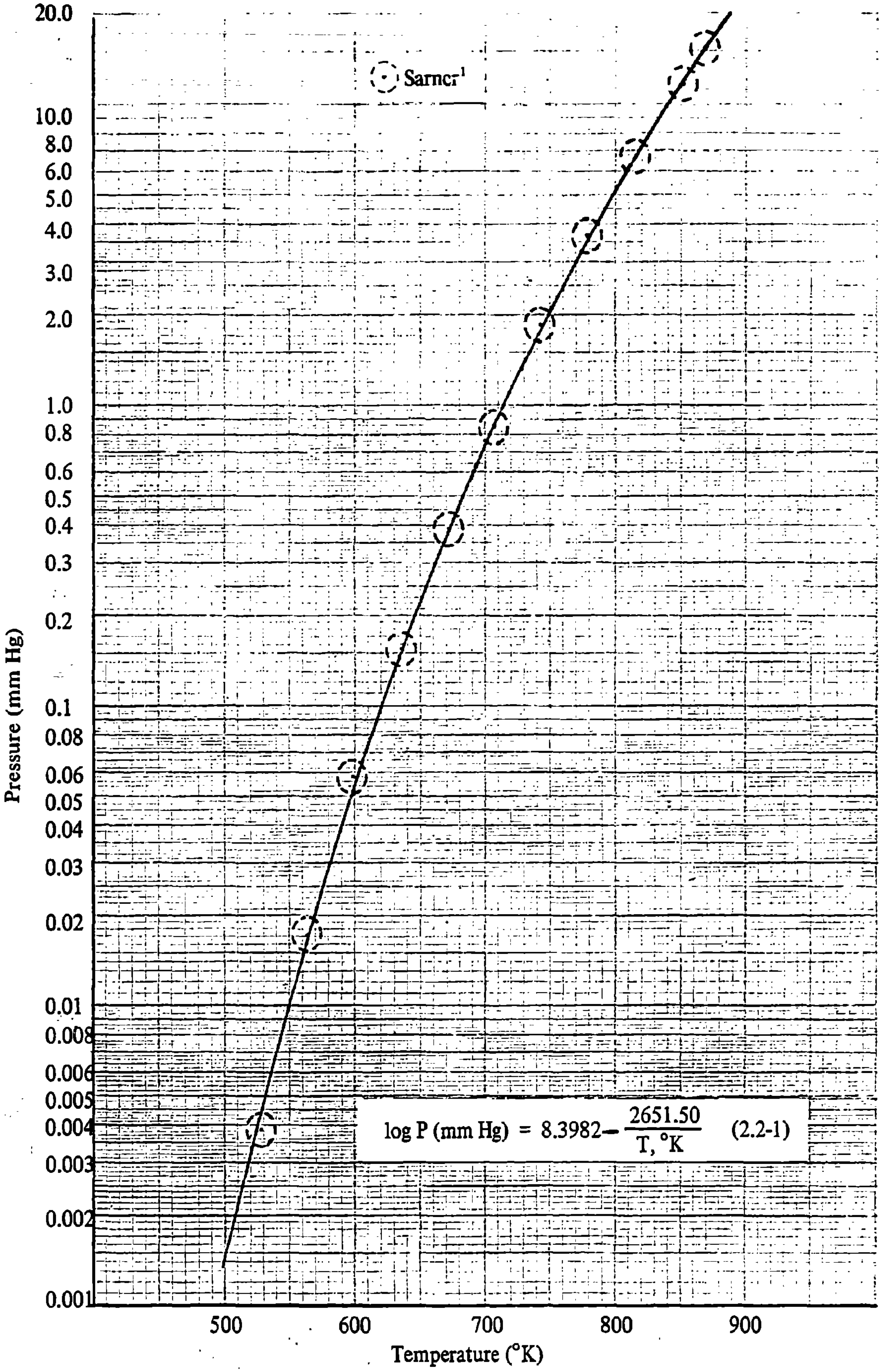
2.2.3.4 Viscosity of Liquid Diethylenetriamine (DETA)

The absolute viscosity of liquid DETA for a temperature range from -20 to +30 C (-4 to +86 F) has been obtained from RMD (2). It is believed that these data originated at Carbide and Carbon Chemicals Company. No details of this work were made available.

The data are plotted in Figures 2.2-3 and 2.2-3a and are well defined by:

$$\log \mu\,(\text{centipoise}) = 18.3037 - \frac{1.1384 \times 10^{4}}{T,\,^{\circ}K} + \frac{1.833 \times 10^{6}}{(T,\,^{\circ}K)^2} \qquad (2.2\text{-}3)$$

$$\log \mu\,(\text{lb}_m/\text{ft-sec}) = 15.1311 - \frac{2.0491 \times 10^{4}}{T,\,^{\circ}R} + \frac{5.9399 \times 10^{6}}{(T,\,^{\circ}R)^2} \qquad (2.2\text{-}3a)$$



$$\log P\ (\text{mm Hg}) = 8.3982 - \frac{2651.50}{T,\ {}^{\circ}K} \qquad (2.2\text{-}1)$$

Figure 2.2-1. Vapor Pressure versus Temperature, Liquid DETA

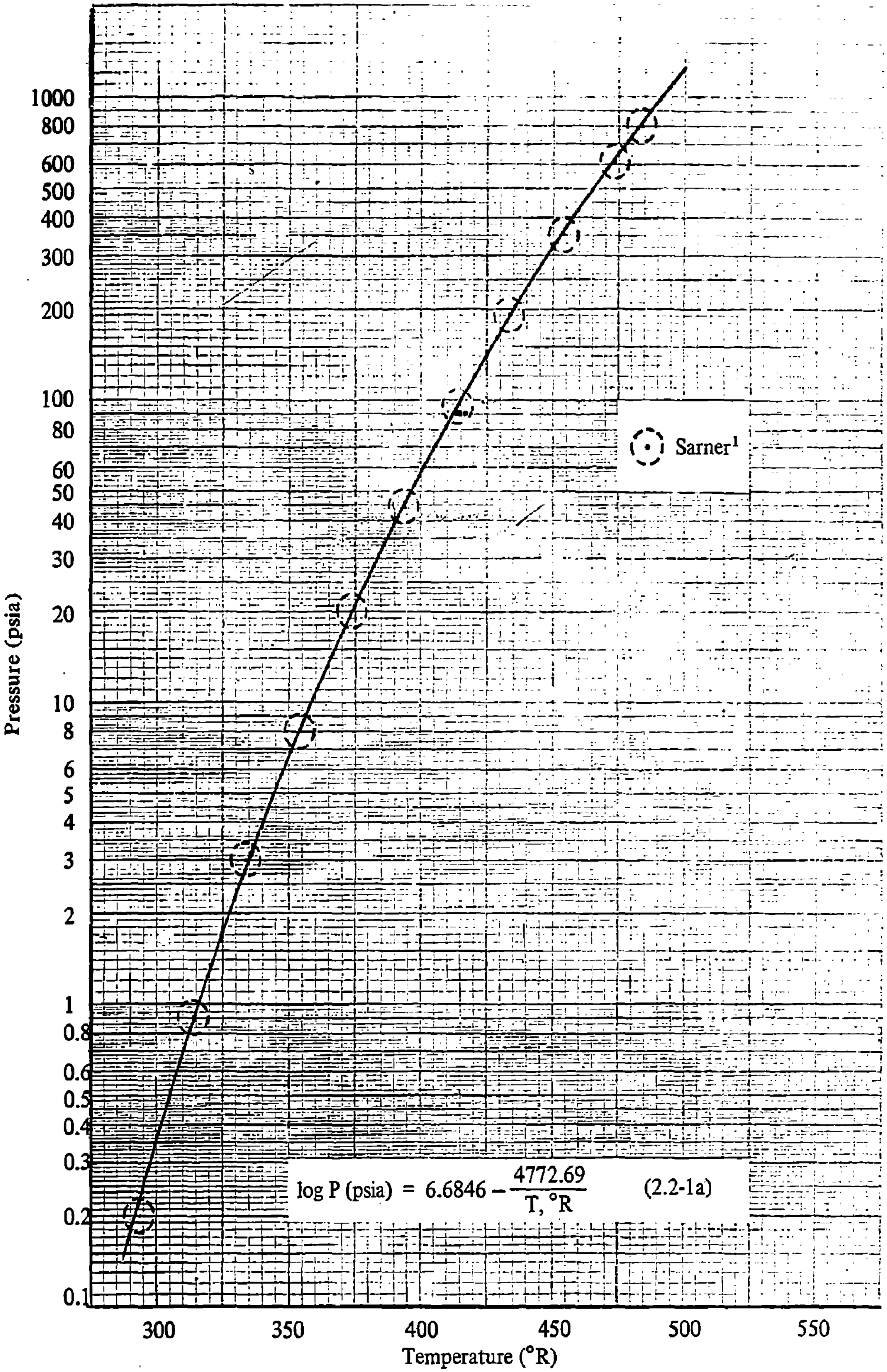


Figure 2.2-1a. Vapor Pressure versus Temperature Liquid DETA

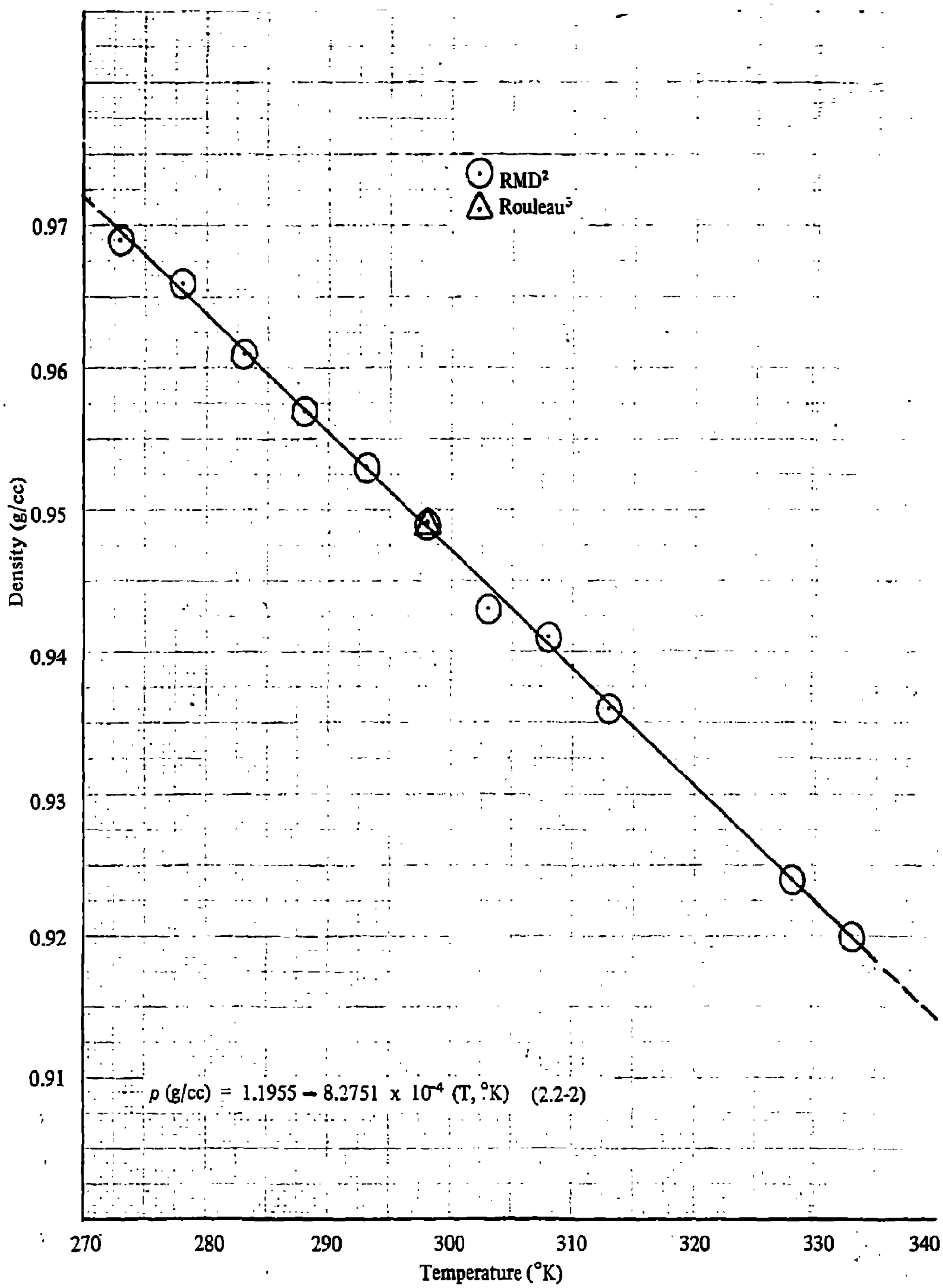
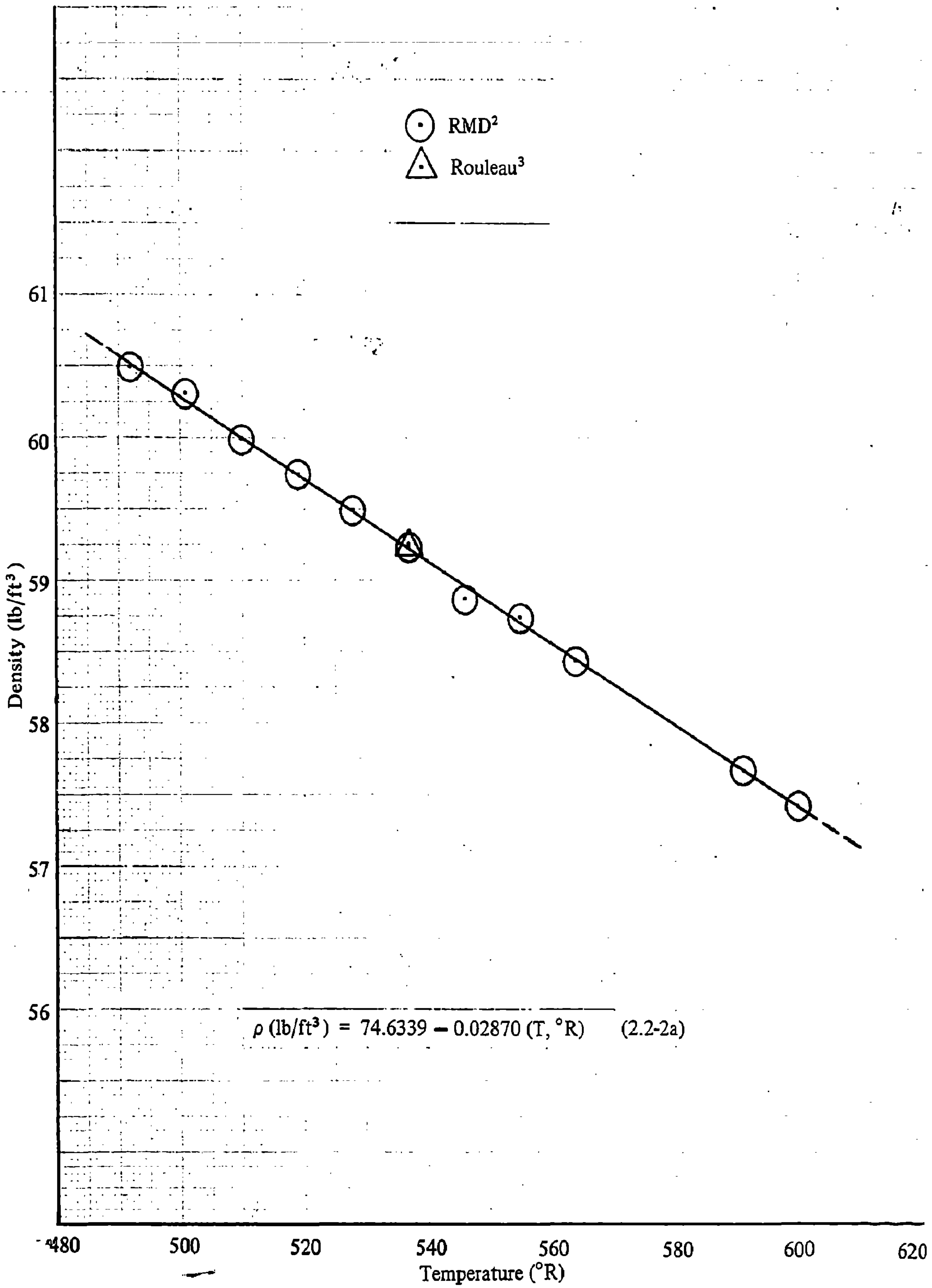
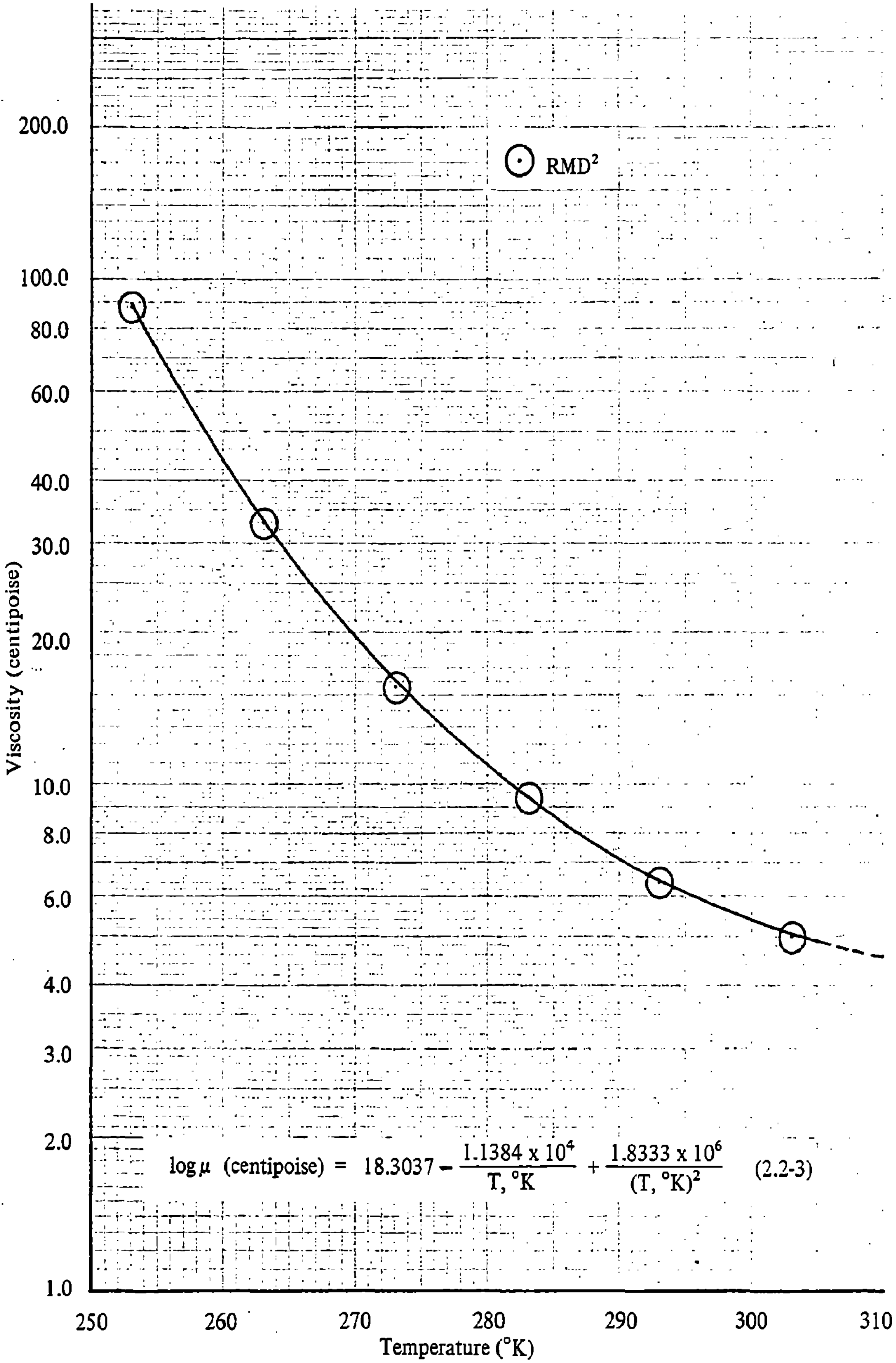


Figure 2.2-2. Density versus Temperature, Liquid DETA



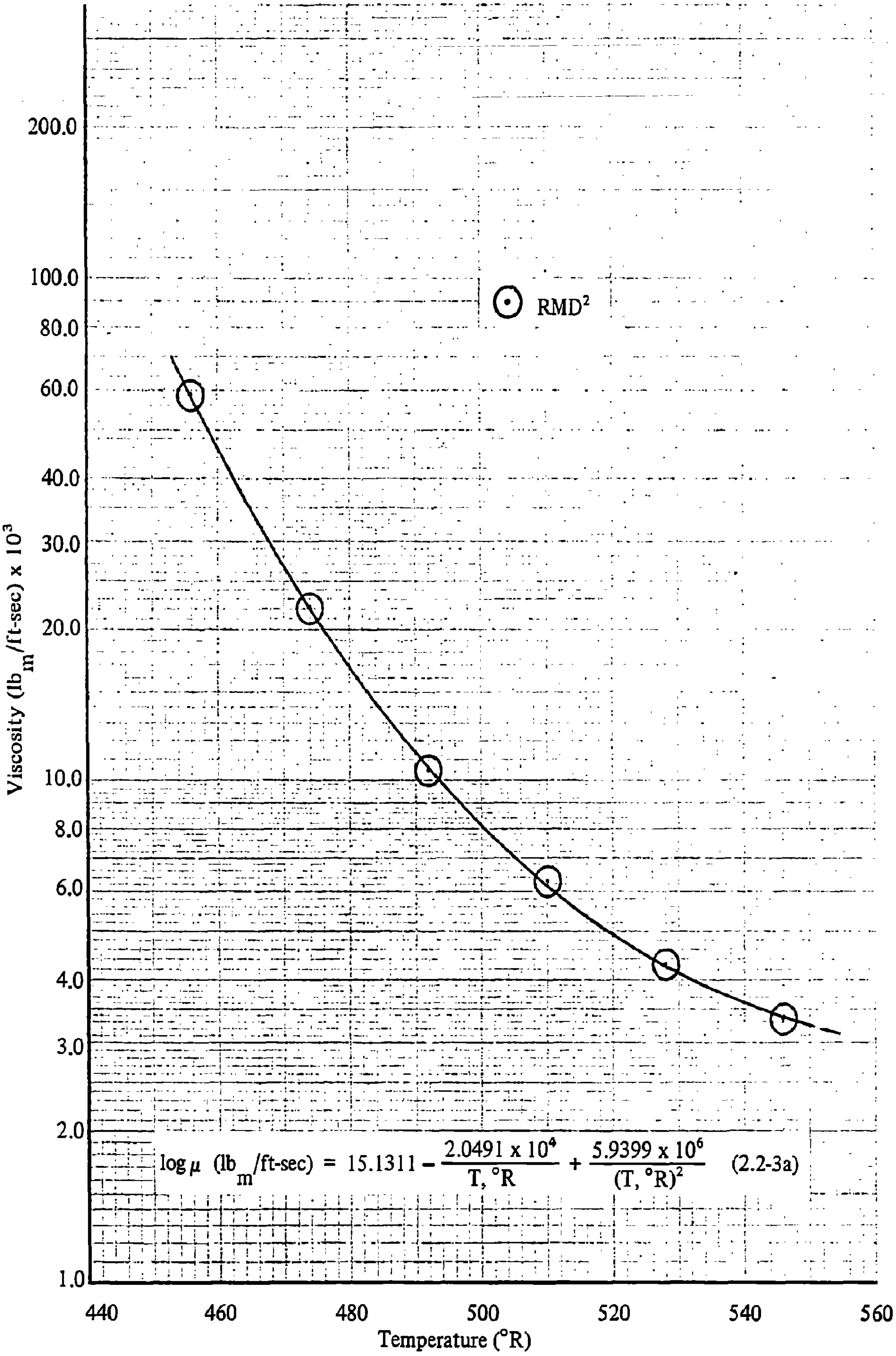
ρ (lb/ft³) = 74.6339 − 0.02870 (T, °R) (2.2-2a)

Figure 2.2-2a. Density versus Temperature, Liquid DETA



$$\log \mu \text{ (centipoise)} = 18.3037 - \frac{1.1384 \times 10^{4}}{T, {}^{\circ}K} + \frac{1.8333 \times 10^{6}}{(T, {}^{\circ}K)^{2}} \qquad (2.2\text{-}3)$$

Figure 2.2-3. Absolute Viscosity versus Temperature, Liquid DETA



$$\log \mu \; (lb_m/\text{ft-sec}) = 15.1311 - \frac{2.0491 \times 10^4}{T, {}^\circ R} + \frac{5.9399 \times 10^6}{(T, {}^\circ R)^2} \quad (2.2\text{-}3a)$$

Figure 2.2-3a. Absolute Viscosity versus Temperature, Liquid DETA

The standard deviation of the data as computed by equation 2.2-3 is 0.23 centipoise and the average deviation is 0.73%.

The LPIA Liquid Propellant Manual (4) gives a value of 21 centipoise at 25 C and lists a 1956 JPL report as the reference.

From equation 2.2-1 a value of 5.58 centipoise is obtained at 25 C. This disagreement, plus the lack of detail concerning the data from RMD (2), would seem to dictate that this data be considered provisional.

2.2.4 CHEMICAL PROPERTIES

2.2.4.1 Reactions

The most prominent reaction of DETA from a storage viewpoint is its reaction with carbon dioxide to form a salt. DETA is highly reducing in character and reacts spontaneously with most rocket oxidizers. A more complete discussion of chemical reactions can be found in Reference 6.

2.2.5 THERMODYNAMIC PROPERTIES

2.2.5.1 Heat of Formation

The only information appears to be a value of -18.5 kcal/mole for the liquid at 298 K from Reference 2.

2.2.6 LOGISTICS OF DETA

2.2.6.1 Manufacture

Diethylenetriamine is prepared commercially by treating ethylene dichloride with ammonia. Reaction conditions vary, but in all cases a mixture is obtained. At low temperatures and pressures, predominately ethylenediamine is produced in low yield. At higher temperatures and pressures, the yield is higher and a larger proportion of diethylenetriamine and other polyethylene polyamines are produced. Dow Chemical Company and Carbide and Carbon Chemicals Company currently manufacture DETA.

2.2.6.2 Analysis

Diethylenetriamine is assayed by titration of a one gram sample with hydrochloric acid in the presence of methyl red indicator. The boiling range is determined by distillation of a 100 ml sample in a flask fitted with a condenser and a calibrated thermometer. The temperature is recorded at periodic points in the collection of the distillate. A pycnometer is used to determine the specific gravity. The acceptable limits as prescribed by specification O-D-1271 are:

Characteristic	Requirements
Diethylenetriamine, % by weight	97.0 min.
Water, % by weight	0.5 max.
Specific Gravity at 20°/20°C	0.950 - 0.958
Initial boiling point, °C	185.0
Dry point, °C	215.0

2.2.6.3 Cost and Availability

Diethylenetriamine is presently being produced by Dow Chemical Company and Carbide and Carbon Chemicals Company with total production of approximately 10 million lb/year. DETA is available in tank car (or truck) lots at approximately $0.40/lb and in 55 gallon drums at approximately $0.45/lb.

2.2.6.4 Shipping and Transportation

Diethylenetriamine is shipped in aluminum or steel tank cars and trucks and in tin-lined or steel drums. No special precautions are required for shipment other than a precautionary marking as prescribed in O-D-1271 describing treatment if exposed to the liquid or vapors.

2.2.7 REFERENCES

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2.3 N_2H_4

2.3.1 PROPERTY SUMMARY SHEET

Chemical Name: **Hydrazine**
Chemical Formula: N_2H_4

Common Name: N_2H_4
Formula Weight: 32.048 (O^{16}), 32.0453 (C^{12})

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	274.68	°K	-	1	2.3-12
	1.53	°C			
	494.42	°R			
	34.75	°F			
HEAT OF FUSION	3.025	kcal/mole	274.68	1	
	169.9	BTU/lb			
NORMAL BOILING POINT	387.4	°K		calc.	
	114.2	°C			
	697.3	°R			
	237.6	°F			
HEAT OF VAPORIZATION	10.38	kcal/mole	298.15	*	
	583.0	BTU/lb			
TROUTON CONSTANT	24.1		NBP	*	
CRITICAL STATE CONSTANTS					
Temperature	653.	°K	-		
	380.	°C		10, 22	
	1175.	°R			
	716.	°F			
Pressure	145	atms	-	10, 22	
	2131	psia			
Density	.231	g/cc		23	
	14.42	lb/ft^3			
VAPOR PRESSURE OF LIQUID	14.19	mm Hg	298.15	1, 2, 3, 9	2.3-1
	0.274	psia			2.3-2
DENSITY OF LIQUID	1.0037	g/cc	298.15	4, 5, 6, 7, 8	2.3-3
	62.659	lb/ft^3			
SONIC VELOCITY	2074	m/sec	298.15	31, 39, 45	2.3-4
	6804	ft/sec			
COMPRESSIBILITY OF LIQUID					
ADIABATIC	2.35×10^{-5}	atm^{-1}	298.15	31, 39, 45	2.3-5
	1.60×10^{-6}	psi^{-1}			
ISOTHERMAL	2.54×10^{-5}	atm^{-1}	298.15	31	-
	1.73×10^{-6}	psi^{-1}			
VISCOSITY OF LIQUID	0.913	centipoise	298.15	4, 5, 8, 11	2.3-6
	6.135×10^{-4}	lb$_m$/ft-sec			
HEAT CAPACITY OF LIQUID	.7356	cal/g-°K	298.15		2.3-1
	.7351	BTU/lb-°R		1, 12	2.3-14
THERMAL CONDUCTIVITY OF LIQUID	7.86×10^{-5}	cal/cm-sec°K	298.15	(33)	2.3-8
		BTU/ft-sec°R			
SURFACE TENSION OF LIQUID	66.45	dynes/cm	298.15	13, 35	2.3-7
	4.553×10^{-3}	lb$_f$/ft			
PARACHOR	91.2	-	298.15	*	
DIPOLE MOMENT	1.84	Debye units	298.15	44	
DIELECTRIC CONSTANT	51.7	-	298.15	25, 28	2.3-9
ENTROPY (LIQUID)	28.97	cal/mole-°K	298.15	1	
	0.904	BTU/lb-°R			
ENTROPY (IDEAL GAS)	56.97	cal/mole-°K	298.15	1	
	1.778	BTU/lb-°R			
HEAT OF COMBUSTION	148.635	kcal/mole	298.15	27	
HEAT OF FORMATION	12.054	kcal/mole	298.15	26, 27	
	676.57	BTU/lb			
INDEX OF REFRACTION	1.4686		298.15	3, 7, 42, 43	2.3-10

* Calculated or Selected Best Value

2.3.2 GENERAL

2.3.2.1 Introduction

Chemically, hydrazine (diamide) is a saturated hydronitrogen like ammonia having the type formula $N_n + H_{n+2}$. Hydrazine salts and the monohydrate were first isolated by Curtius(49) in 1887. In 1894, Lobry deBruyn(50) successfully prepared anhydrous hydrazine.

Anhydrous hydrazine is a clear colorless liquid at ordinary temperatures. It is quite hygroscopic and tends to absorb carbon dioxide and oxygen from the atmosphere. Chemically, hydrazine is highly reactive and extreme care must be exercised in handling. The vapors of hydrazine may ignite spontaneously with air or oxygen. It is the analog of hydrogen peroxide if ammonia may be considered to correspond to water.

Hydrazine, as a rocket fuel, is very attractive from a performance standpoint. Its major drawback is its relatively high melting point (34.75 F). To date, hydrazine as a rocket propellant has been generally restricted to use as a constituent of mixtures with MMH or UDMH which give much lower melting points.

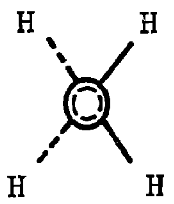
2.3.2.2 Structure of Hydrazine

From the study of both Raman and infrared spectra of hydrazine, the stable configuration form of C_2 symmetry is indicated. The coincidences of the two spectra preclude the trans configuration of rotation about the N-N single bond. The cis configuration, although consistent with the spectroscopic data, requires the hydrogen atoms to have an opposed rather than staggered configuration.

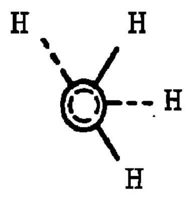
For the calculation of the moments of inertia, Scott(1) used bond distances of N-N, 1.47 Å and N-H, 104 Å. The bond angles were assumed to be tetrahedral and the two NH_2 groups rotated 60 degrees from the cis configuration. The moments of inertia as calculated by Scott are:

$$6.18 \times 10^{-40}, 35.33 \times 10^{-40} \text{ and } 36.98 \times 10^{-40} \text{ g cm}^2$$

The structure for both the trans and cis (gauche) forms are:



(Trans)



(Cis or Gauche)

2.3.2.3 Specification and Purity

Procurement and purity of propellant grade hydrazine is controlled by Military Specification MIL-P-26536C dated 23 May, 1969. The limits on purity, impurities, and density given by this specification are:

N_2H_4 assay	98.0% by weight, min.
Water	1.5% by weight, max.
Particulate matter	10 mg/l, max.
Density (Rev. B)	1.004 ±0.002 g/cc

2.3.3 PHYSICAL PROPERTIES

2.3.3.1 Vapor Pressure, Normal Boiling Point, and Heat of Vaporization of Anhydrous Hydrazine

The vapor pressure of hydrazine has been studied by Scott(1), Hieber(2), Chang(3), and Cragoe(9). The latter study was conducted at elevated temperatures only. Hieber's observations were made over a temperature range from 20 to 114 C (68 to 237 F). Scott reported vapor pressure data for the liquid from 15 to 70 C (59 to 158 F) and single point measurements at 0 C for both the solid and supercooled liquid. Chang measured the vapor pressure over the narrow temperature range from 3 to 51 C (37 to 124 F).

Scott actually reported three series of measurements; the first set after 20% of the original sample had been pumped off and the second series after 80% had been removed. The third series was conducted after pumping off 20% of original sample and then distilling the remainder under its own vapor pressure. The results of the three separate readings showed a slight increase in pressure for each succeeding measurement. Scott suspected that some water was present in the first sample used and the increase in vapor pressure after distillation seems to verify this. Hydrazine and water form a maximum-boiling azeotrope so that water as an impurity in hydrazine gives a lower vapor pressure than for the pure liquid. Only the third set of measurements was considered in this study.

Scott(1) compared his vapor pressure data with the previously published data of Hieber(2) and concluded, since the pressures of the earlier investigation were consistently lower, that water was present in the sample of hydrazine used by Hieber.

Chang(3) compared his recent work with both that of Scott(1) and Hieber(2) and concluded that the hydrazine used in both these investigations contained some water since his vapor pressure readings were higher and he used a double-distilled sample. The actual difference in data is quite small and, since Chang covered only the low temperature range, his comparison of work at higher temperatures required extrapolation and his conclusions do not appear to be valid. The experimental data are shown in Figures 2.3-1 and 2.3-1a.

The data from the three separate studies were combined by the least-squares method and several equations were obtained. The data were found to be best represented by the equation

$$\log P\ (\text{mm Hg}) = -6.50603 - \frac{653.880}{T,{}^\circ K} + 0.047914(T,{}^\circ K) - 4.9886 \times 10^{-5}\ (T,{}^\circ K)^2 \qquad (2.3\text{-}1)$$

$$\log P\ (\text{psia}) = -8.21964 - \frac{1176.98}{T,{}^\circ R} + 0.026619(T,{}^\circ R) - 1.5397 \times 10^{-5}\ (T,{}^\circ R)^2 \qquad (2.3\text{-}1a)$$

The standard deviation of the experimental data from the values obtained from 2.3-1 is 1.71 mm Hg with the average deviation being 2.3%. The normal boiling point obtained from equation 2.3-1 is 387.37 K (697.27 R). Hieber did not report a value for the normal boiling point but a value of 387.27 K is obtained from his vapor pressure equation

$$\log P = 8.339 - \frac{2113.8}{T} \qquad (2.3\text{-}2)$$

Scott(1) represented his data by

$$\log P\ (\text{mm Hg}) = 7.80687 - \frac{1680.745}{T,{}^\circ C + 227.74} \qquad (2.3\text{-}3)$$

From Equation 2.3-3, a normal boiling point value of 386.50 K is obtained.

The only vapor pressure data reported in the literature above one atmosphere is that of Cragoe(9) in the International Critical Tables. The data is taken from the early work of Lobry deBruyn(10). The data is plotted in Figures 2.3-2 and 2.3-2a. The normal boiling temperature (one atmosphere) was given as 113.5 C or 386.65 K, but was taken to be 114.22 C or 387.37 K to be consistent with the normal boiling point accepted in this study.

The vapor pressure at elevated temperatures is best defined by

$$\log P\ (\text{atm}) = 4.73294 - \frac{1457.79}{T,{}^\circ K} - \frac{145452.1}{(T,{}^\circ K)^2} \qquad (2.3\text{-}4)$$

$$\log P\ (\text{psia}) = 5.90014 - \frac{2624.01}{T,{}^\circ R} - \frac{471264.7}{(T,{}^\circ R)^2} \qquad (2.3\text{-}4a)$$

2.3.3.2 Density of Anhydrous Hydrazine

The density of anhydrous hydrazine has been reported by numerous investigations. The studies of Ahlert(4), Semishin(5), Pannetier(6), Barrick(7) and Walden(8) are considered here to be the most reliable. The results of these investigations are in essential agreement. The more recent study of Ahlert(4) is the most conclusive and includes data over a large temperature range.

Ahlert(4) used a double-distilled sample which was carefully weighed and sealed in a precision bored glass pycnometer. A carefully regulated constant temperature bath was used and the temperatures were recorded with certified platinum resistance thermometers. The liquid level of the hydrazine in the pycnometer was measured to 0.001 mm with a cathetometer. The densities were obtained from the known sample weight and the volume of the pycnometer obtained from water and mercury calibrations.

The experimental density values are shown in Figures 2.3-3 and 2.3-3a and cover a temperature range from 0 to 177 C. The density variation with temperature is adequately expressed by

$$\rho(\text{g/cc}) = 1.23078 - 6.2668 \times 10^{-4}(T,\ {}^\circ K) - 4.5284 \times 10^{-7}(T,\ {}^\circ K)^2 \qquad (2.3\text{-}5)$$

$$\rho(\text{lb/ft}^3) = 76.8353 - 0.021735\ (T,\ {}^\circ R) - 8.7254 \times 10^{-6}(T,\ {}^\circ R)^2 \qquad (2.3\text{-}5a)$$

The standard deviation of the experimental data compared to the smoothed results from equation 2.3-5 is 0.0011 g/cc. The average deviation is 0.089%.

2.3.3.3 Sonic Velocity in Liquid Hydrazine

The sonic velocity in liquid hydrazine has been measured by Kretschmar(31, 34, 39), Aerojet(40) and recently by Rocketdyne(45). In Reference 34, Kretchmar reported a sonic velocity value of 2059 ±6 m/sec at 25 C for 96% hydrazine. In Reference 31, two samples of anhydrous hydrazine gave identical velocity values of 2090 m/sec also at 25 C. In a later report, Kretschmar(39) reported sonic velocity measurements of various hydrazine-water mixtures at 25 C. A Debye-Sears ultrasonic interferometer was used in the later study and the author fitted his experimental data closely by

$$c(\text{m/sec}) = 1497.40 + 745.460\ H + 382.353\ H^2 - 556.3361\ H^3 \qquad (2.3\text{-}6)$$

where H is the fractional weight of hydrazine.

The author reports a value of 2074 m/sec at 25 C for pure hydrazine while a value of 2069 m/sec is consistent

2.3.2 GENERAL

2.3.2.1 Introduction

Chemically, hydrazine (diamide) is a saturated hydronitrogen like ammonia having the type formula $N_n + H_{n+2}$. Hydrazine salts and the monohydrate were first isolated by Curtius(49) in 1887. In 1894, Lobry deBruyn(50) successfully prepared anhydrous hydrazine.

Anhydrous hydrazine is a clear colorless liquid at ordinary temperatures. It is quite hygroscopic and tends to absorb carbon dioxide and oxygen from the atmosphere. Chemically, hydrazine is highly reactive and extreme care must be exercised in handling. The vapors of hydrazine may ignite spontaneously with air or oxygen. It is the analog of hydrogen peroxide if ammonia may be considered to correspond to water.

Hydrazine, as a rocket fuel, is very attractive from a performance standpoint. Its major drawback is its relatively high melting point (34.75 F). To date, hydrazine as a rocket propellant has been generally restricted to use as a constituent of mixtures with MMH or UDMH which give much lower melting points.

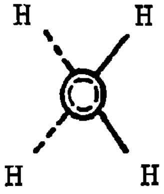
2.3.2.2 Structure of Hydrazine

From the study of both Raman and infrared spectra of hydrazine, the stable configuration form of C_2 symmetry is indicated. The coincidences of the two spectra preclude the trans configuration of rotation about the N-N single bond. The cis configuration, although consistent with the spectroscopic data, requires the hydrogen atoms to have an opposed rather than staggered configuration.

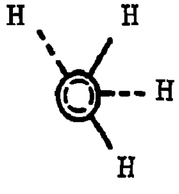
For the calculation of the moments of inertia, Scott(1) used bond distances of N-N, 1.47 Å and N-H, 104 Å. The bond angles were assumed to be tetrahedral and the two NH_2 groups rotated 60 degrees from the cis configuration. The moments of inertia as calculated by Scott are:

$$6.18 \times 10^{-40}, 35.33 \times 10^{-40} \text{ and } 36.98 \times 10^{-40} \text{ g cm}^2$$

The structure for both the trans and cis (gauche) forms are:



(Trans)



(Cis or Gauche)

2.3.2.3 Specification and Purity

Procurement and purity of propellant grade hydrazine is controlled by Military Specification MIL-P-26536C dated 23 May, 1969. The limits on purity, impurities, and density given by this specification are:

N_2H_4 assay	98.0% by weight, min.
Water	1.5% by weight, max.
Particulate matter	10 mg/l, max.
Density (Rev. B)	1.004 ±0.002 g/cc

2.3.3 PHYSICAL PROPERTIES

2.3.3.1 Vapor Pressure, Normal Boiling Point, and Heat of Vaporization of Anhydrous Hydrazine

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The standard deviation of the experimental data compared to the smoothed results from equation 2.3-5 is 0.0011 g/cc. The average deviation is 0.089%.

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where H is the fractional weight of hydrazine.

The author reports a value of 2074 m/sec at 25 C for pure hydrazine while a value of 2069 m/sec is consistent with the reported equation. Either value is only slightly below the 2090 m/sec value reported in Reference 31.

Aerojet(40) measured the sonic velocity in a hydrazine-water mixture containing 91.9% N_2H_4. Values were obtained at 83 F (28.3 C) for pressures between 500 and 1000 psig. The sonic velocity values ranged between 1994 and 2005 m/sec with the average of six readings at different pressures being 2000 m/sec. From equation 2-6, a value of 2073 m/sec is obtained for 91.1% N_2H_4.

The recent Rocketdyne study was conducted over a temperature range of 6.1 to 96.5 C (43 to 206 F) using propellant grade hydrazine. The experimental data are plotted in Figures 2.3-4 and 2.3-4a. The values reported by Kretschmar(31, 34) are also shown and are in good agreement with the Rocketdyne study. The data are adequately described as a linear function of temperature by

$$c(\text{m/sec}) = 3224.9 - 3.8611\ (\text{T},{}^\circ\text{K}) \qquad 2.3\text{-}7$$

$$c(\text{ft/sec}) = 10580.4 - 7.0375\ (\text{T},{}^\circ\text{R}) \qquad 2.3\text{-}7\text{a}$$

The standard deviation of the data from equation 2.3-7 is 8.6 m/sec and the average deviation is 0.3%.

2.3.3.4 Compressibility of Liquid Hydrazine

The adiabatic compressibility (β_a) can be calculated from sonic velocity data

$$\beta_a = \frac{1}{\rho c^2}$$

The sonic velocity in liquid hydrazine has been reported by Rocketdyne(45) and by Kretschmar(31, 39). This data is given in Section 2.3.3.3. The adiabatic compressibility was calculated at the experimental temperature for the sonic velocity. The density at these temperatures was obtained from equation 2.3-5.

The calculated adiabatic compressibilities are shown in Figures 2.3-5 and 2.3-5a. Using the least-squares method, the variation of compressibility with temperature was expressed by

$$\beta_a(\text{atm}^{-1}) = 1.2742 \times 10^{-5} - 4.5295 \times 10^{-8}(\text{T}, {}^\circ\text{K}) + 2.7274 \times 10^{-10}(\text{T}, {}^\circ\text{K})^2 \qquad (2.3\text{-}8)$$

$$\beta_a(\text{psi}^{-1}) = 8.6704 \times 10^{-7} - 1.7123 \times 10^{-9}(\text{T, K}) + 5.7280 \times 10^{-12}(\text{T, R})^2 \qquad (2.3\text{-}8\text{a})$$

The standard deviation from equation 2.3-8 was calculated to be 2.0 x 10^{-7} atm^{-1} while the average deviation was 0.51%.

The isothermal compressibility (β_i) was determined by Kretschmar(31) by what may be described as a "Cartesian diver principle". A thin-walled glass capsule containing the hydrazine sample is immersed in mercury contained within a steel cylinder. The mercury is pressurized and from the known density and compressibility of mercury, the isothermal compressibility of hydrazine at 25 C was found to be 24.83 and 24.38 cm^2/kg for two different samples. The average isothermal compressibility is found to be 1.73 x 10^{-6} psi^{-1}.

2.3.3.5 Viscosity of Liquid Hydrazine

The absolute viscosity of liquid anhydrous hydrazine has been studied by Walden(8), Mason(11), Semishin(5) and Ahlert(4). The experimental data from the four investigations are in essential agreement as shown in Figures 2.3-6 and 2.3-6a. A temperature range from the melting point to 177 C (351 F) is covered; one point reported by Walden(8) is below the melting point, indicating the sample was supercooled.

The data reported by Mason(11) are smoothed data and the experimental values were not given. These data are slightly higher than those of the other investigators at the lower temperatures. The work of Ahlert is probably superior and is the only study reporting data at the higher temperatures.

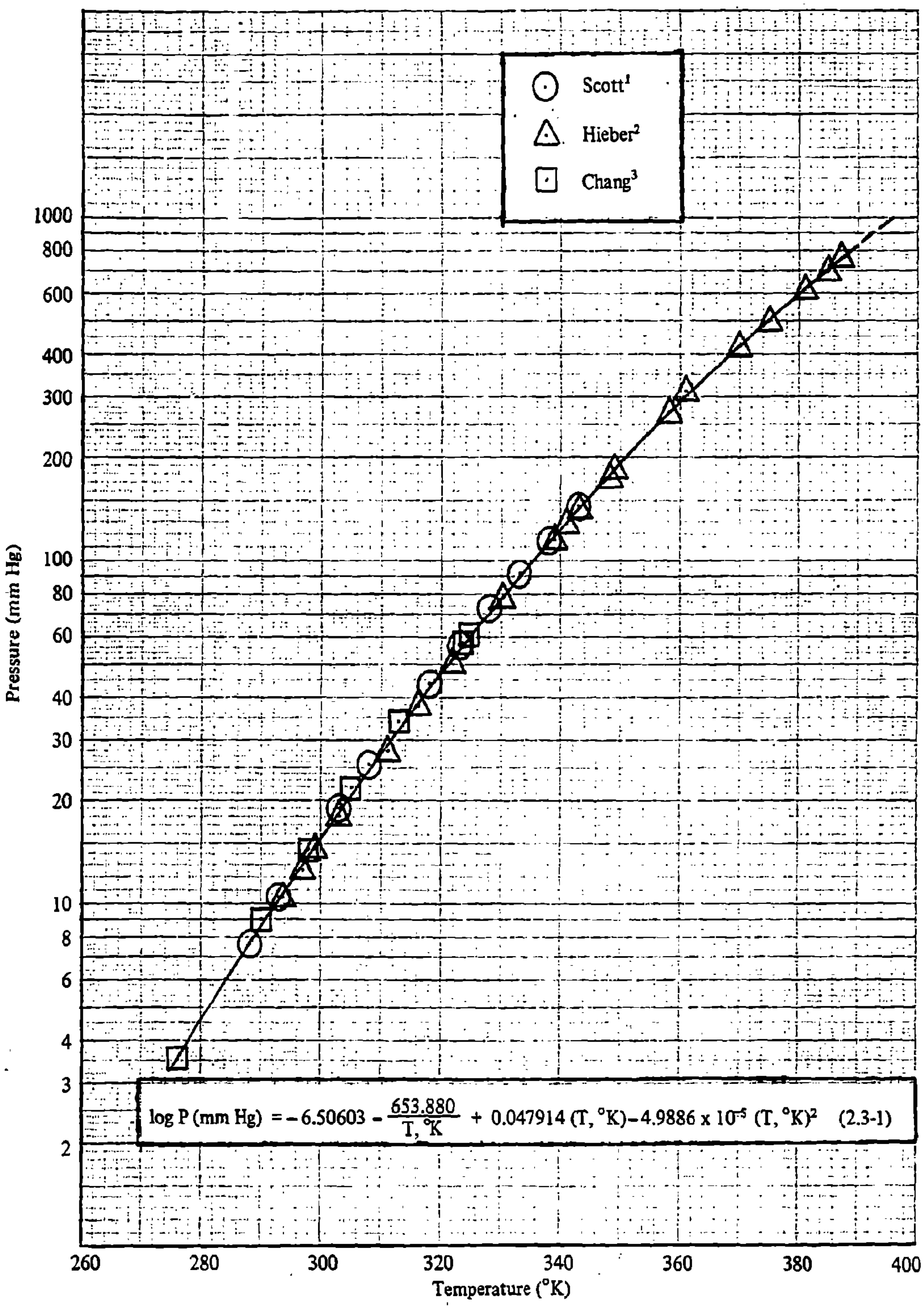
The precision of the data does not warrant corrections for ice point or for density interpretations made here. The smoothed data from the four separate studies have a probable accuracy of ±3.0%.

The variation of absolute viscosity with temperature is described by equation 2.3-9. The standard deviation of the 25 data points is 0.032 centipoise and the average deviation is 2.48%.

$$\log_{10}\mu(\text{cp}) = 3.1788 - 0.015384\ (\text{T},{}^\circ\text{K}) + 1.5395 \times 10^{-5}(\text{T},{}^\circ\text{K})^2 \qquad (2.3\text{-}9)$$

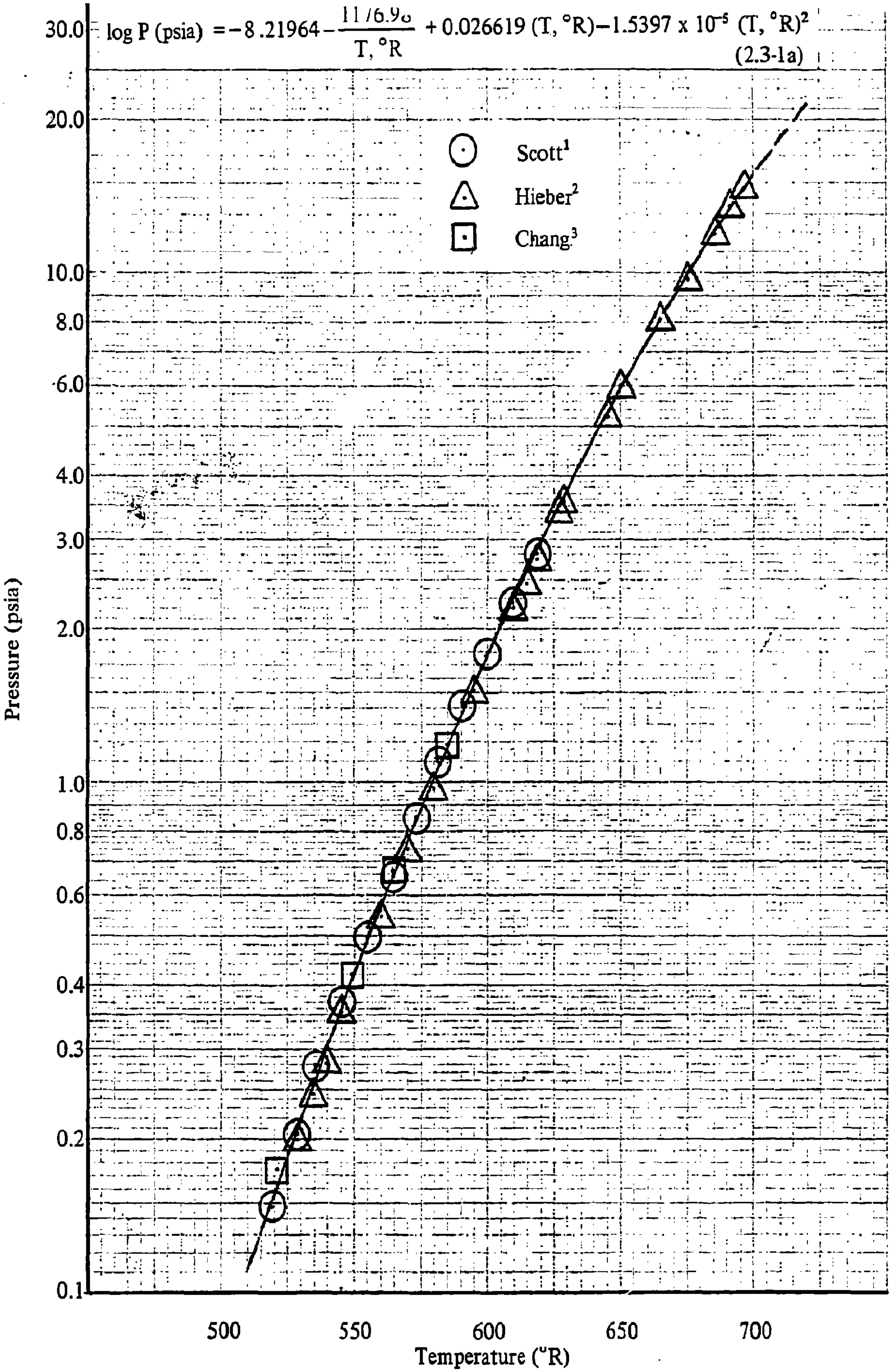
$$\log_{10}\mu(\text{lb}_m/\text{ft-sec}) = 6.1448 \times 10^{-3} - 8.5469 \times 10^{-3}(\text{T},{}^\circ\text{R}) + 4.7516 \times 10^{-6}(\text{T},{}^\circ\text{R})^2 \qquad (2.3\text{-}9\text{a})$$

Mason(11) also reported viscosity data of various pressures up to 250 atmospheres (3675 psia) over a temperature range from 10 to 80 C (50 to 176 F). The smoothed data at 250 atmospheres are shown in Figures 2.3-6 and 2.3-6a for comparison with the saturated liquid data. At the lower temperatures, the increase in viscosity is approximately 3% while the increase due to pressure at 80 C is nearly 10%. At lower pressures, the effect will of course be less. At 50 atmospheres (735 psia), the change in viscosity due to pressure increases by only 0.5% at 10 C and is 2.3% higher at 80 C.



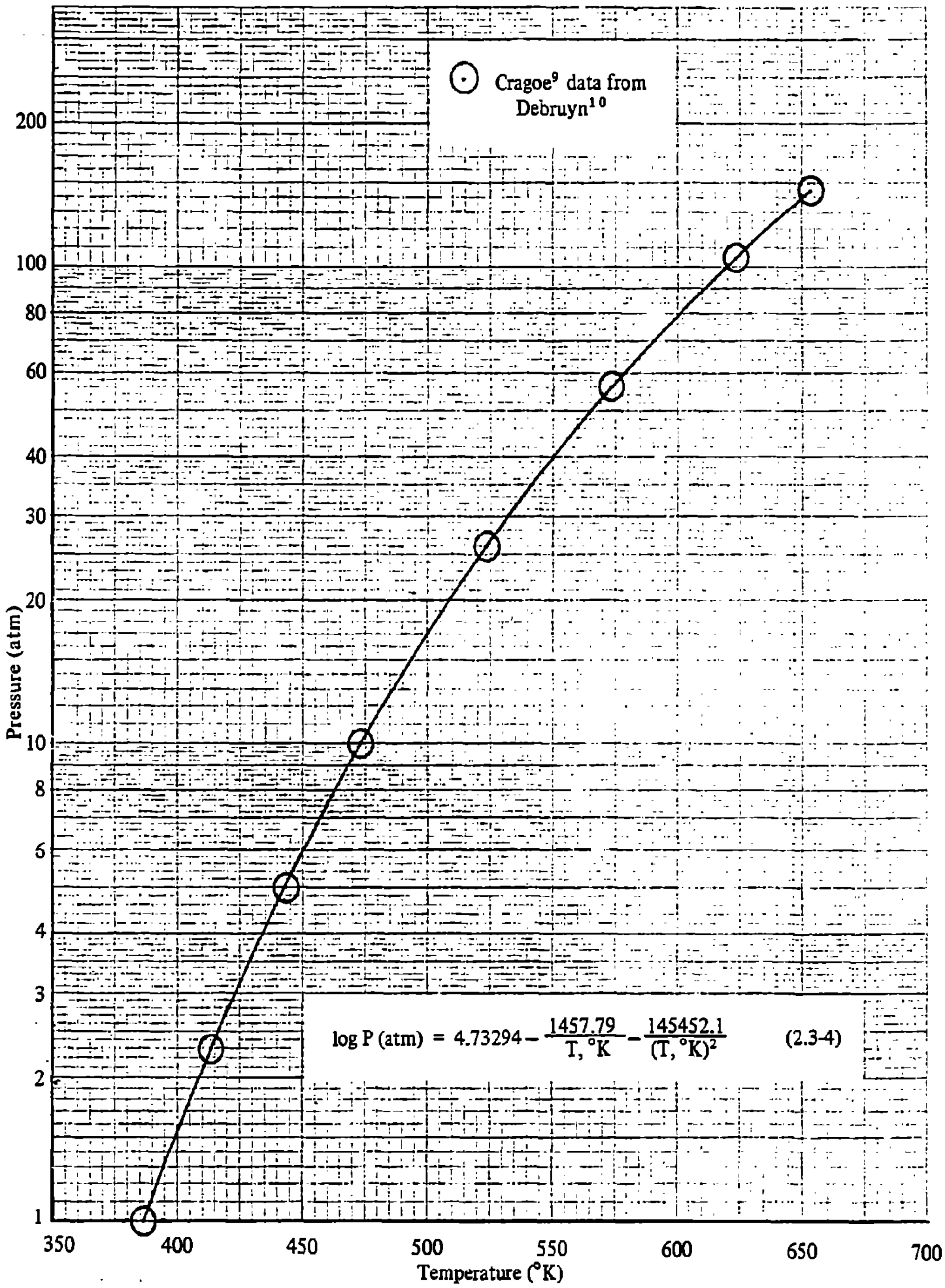
$$\log P\,(\text{mm Hg}) = -6.50603 - \frac{653.880}{T,\,^{\circ}K} + 0.047914\,(T,\,^{\circ}K) - 4.9886 \times 10^{-5}\,(T,\,^{\circ}K)^2 \quad (2.3\text{-}1)$$

Figure 2.3-1. Vapor Pressure versus Temperature, Liquid Anhydrous Hydrazine



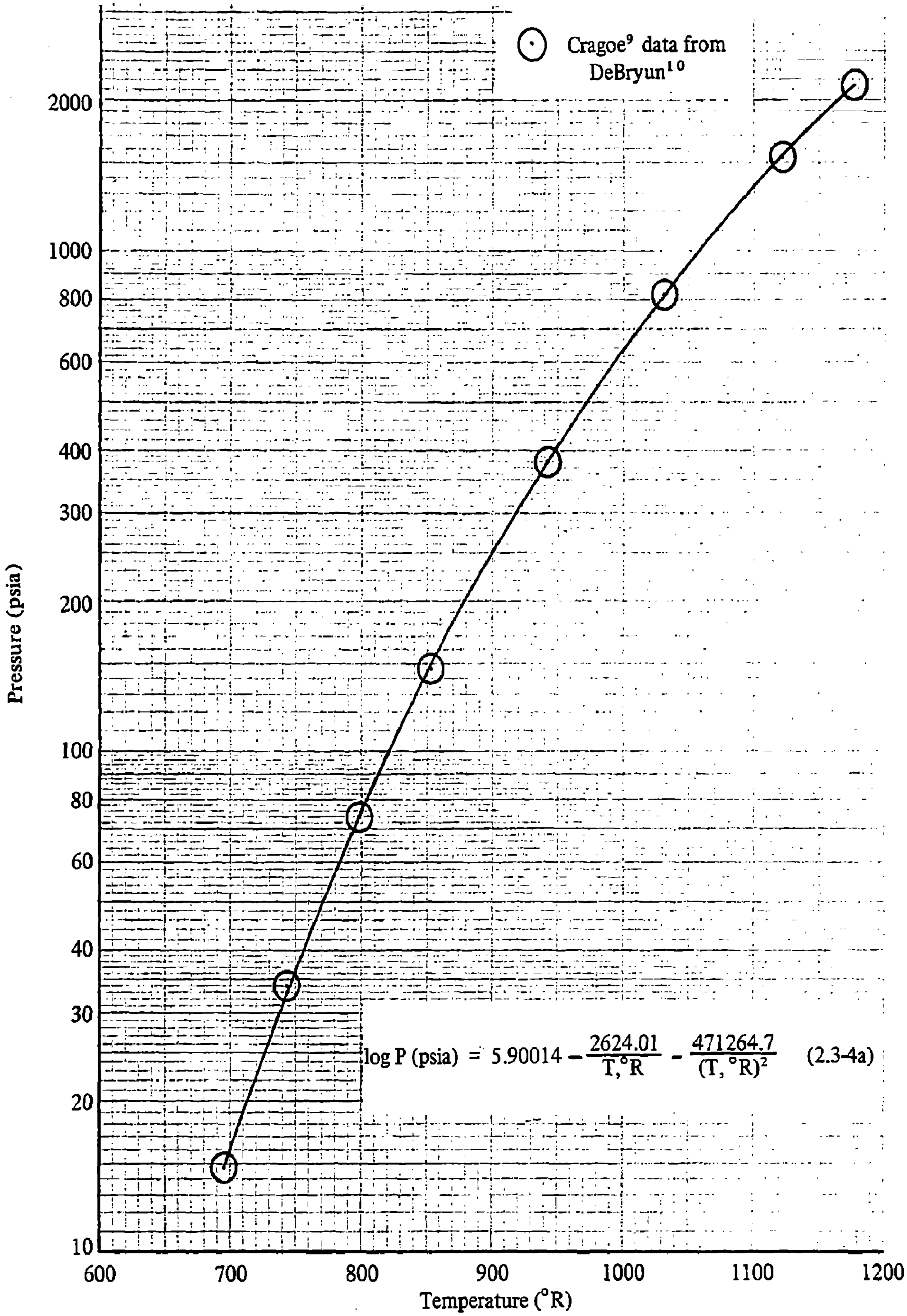
$$\log P\,(\text{psia}) = -8.21964 - \frac{1176.96}{T,\,^{\circ}R} + 0.026619\,(T,\,^{\circ}R) - 1.5397 \times 10^{-5}\,(T,\,^{\circ}R)^2 \qquad (2.3\text{-}1a)$$

Figure 2.3-1a. Vapor Pressure versus Temperature, Liquid Anhydrous Hydrazine



$$\log P\,(\text{atm}) = 4.73294 - \frac{1457.79}{T,\ ^\circ K} - \frac{145452.1}{(T,\ ^\circ K)^2} \qquad (2.3\text{-}4)$$

Figure 2.3-2. Vapor Pressure versus Temperature, Liquid Anhydrous Hydrazine



$$\log P\ (\text{psia}) = 5.90014 - \frac{2624.01}{T, ^\circ R} - \frac{471264.7}{(T, ^\circ R)^2} \qquad (2.3\text{-}4a)$$

Figure 2.3-2a. Vapor Pressure versus Temperature, Liquid Anhydrous Hydrazine

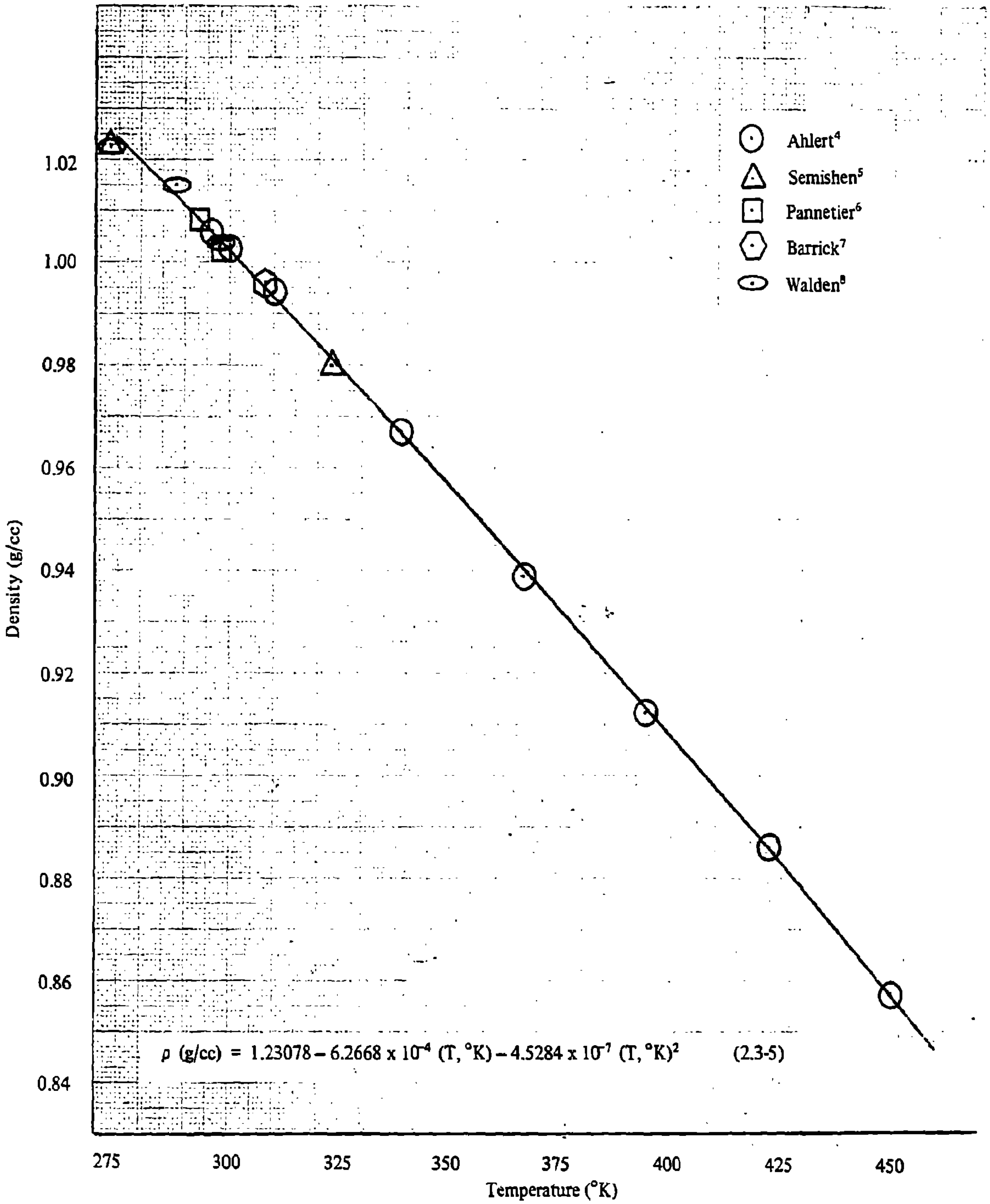


Figure 2.3-3. Density versus Temperature, Liquid Anhydrous Hydrazine

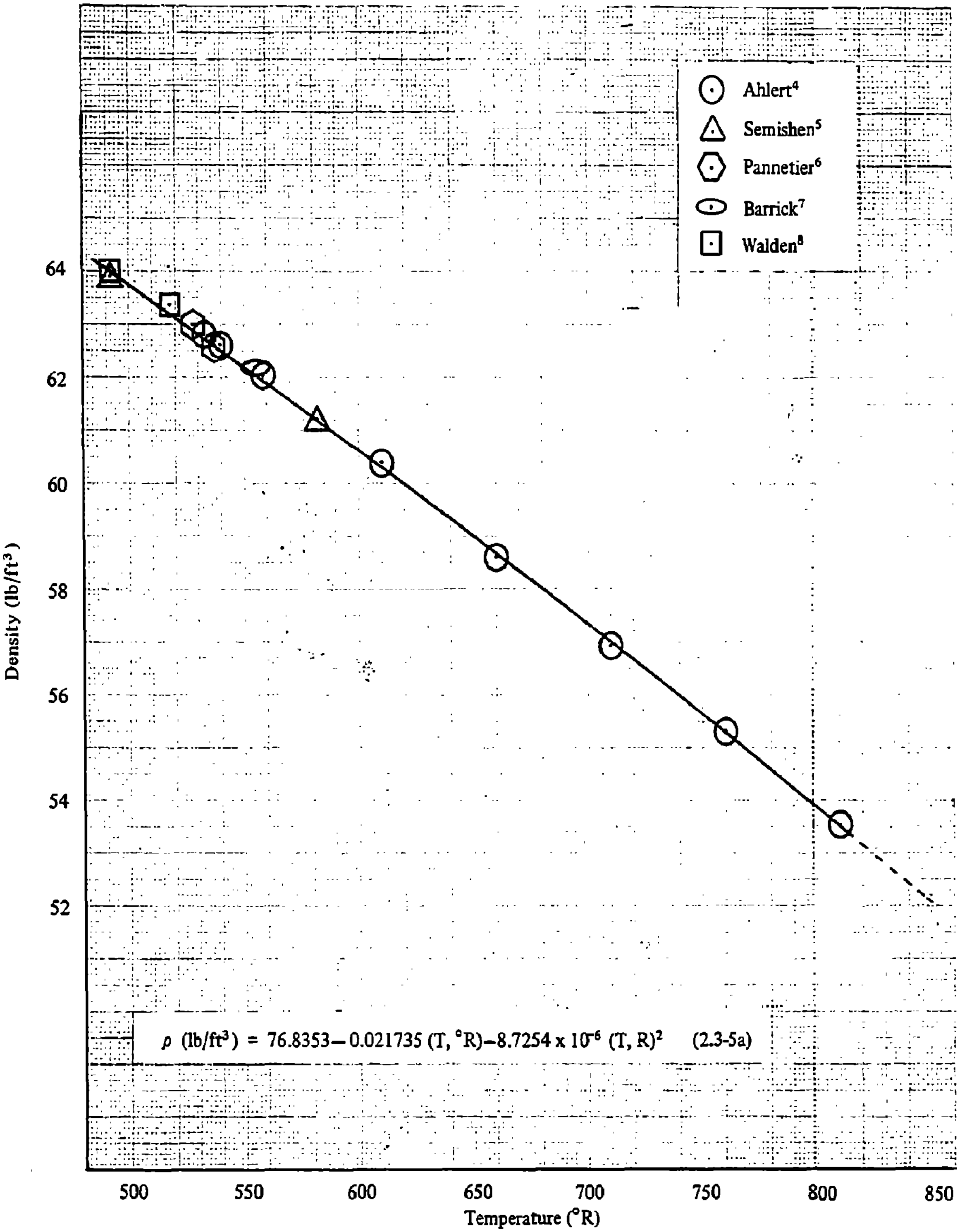
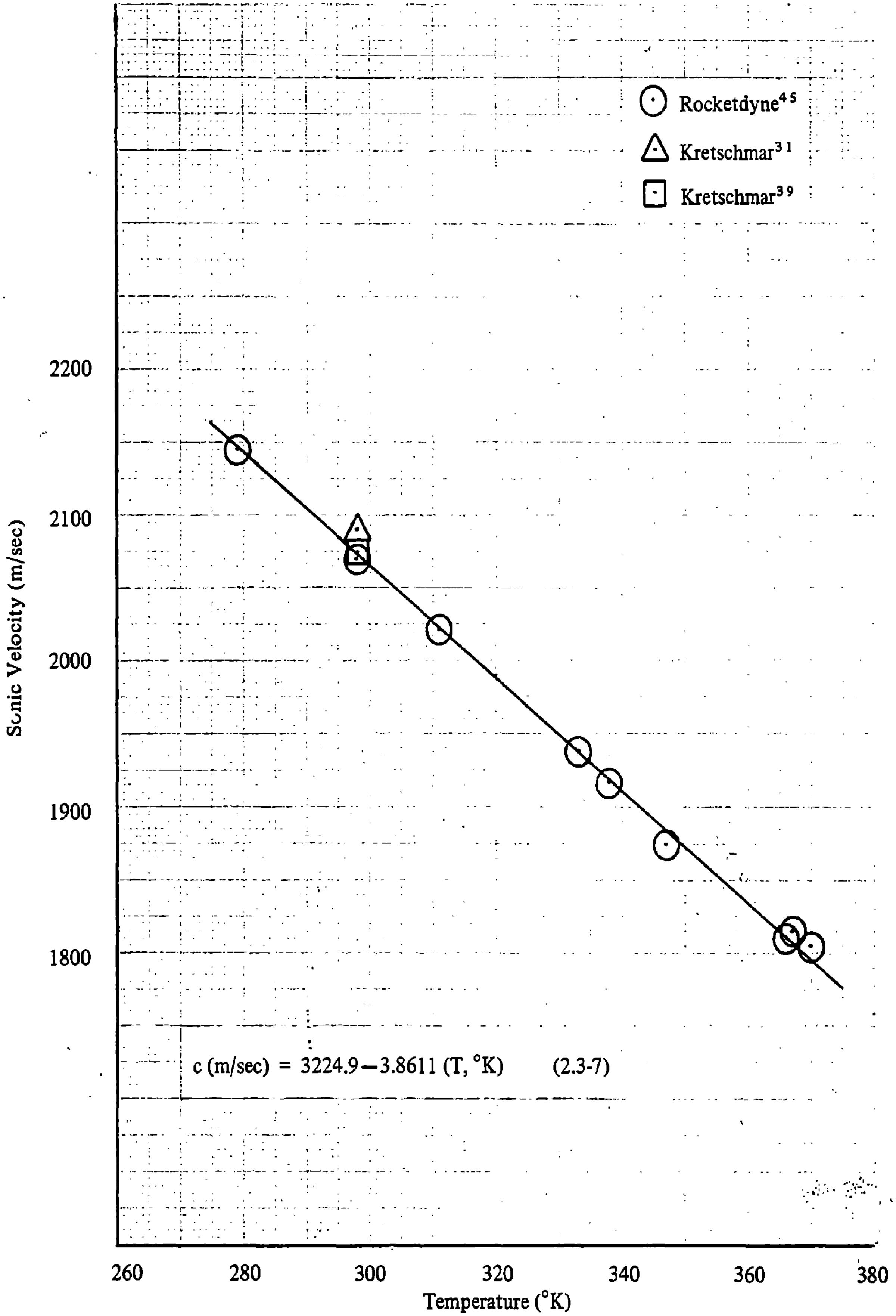


Figure 2.3-3a. Density versus Temperature, Liquid Anhydrous Hydrazine



$$c\ (\text{m/sec}) = 3224.9 - 3.8611\ (T, °K) \qquad (2.3\text{-}7)$$

Figure 2.3-4. Sonic Velocity versus Temperature, Liquid Hydrazine

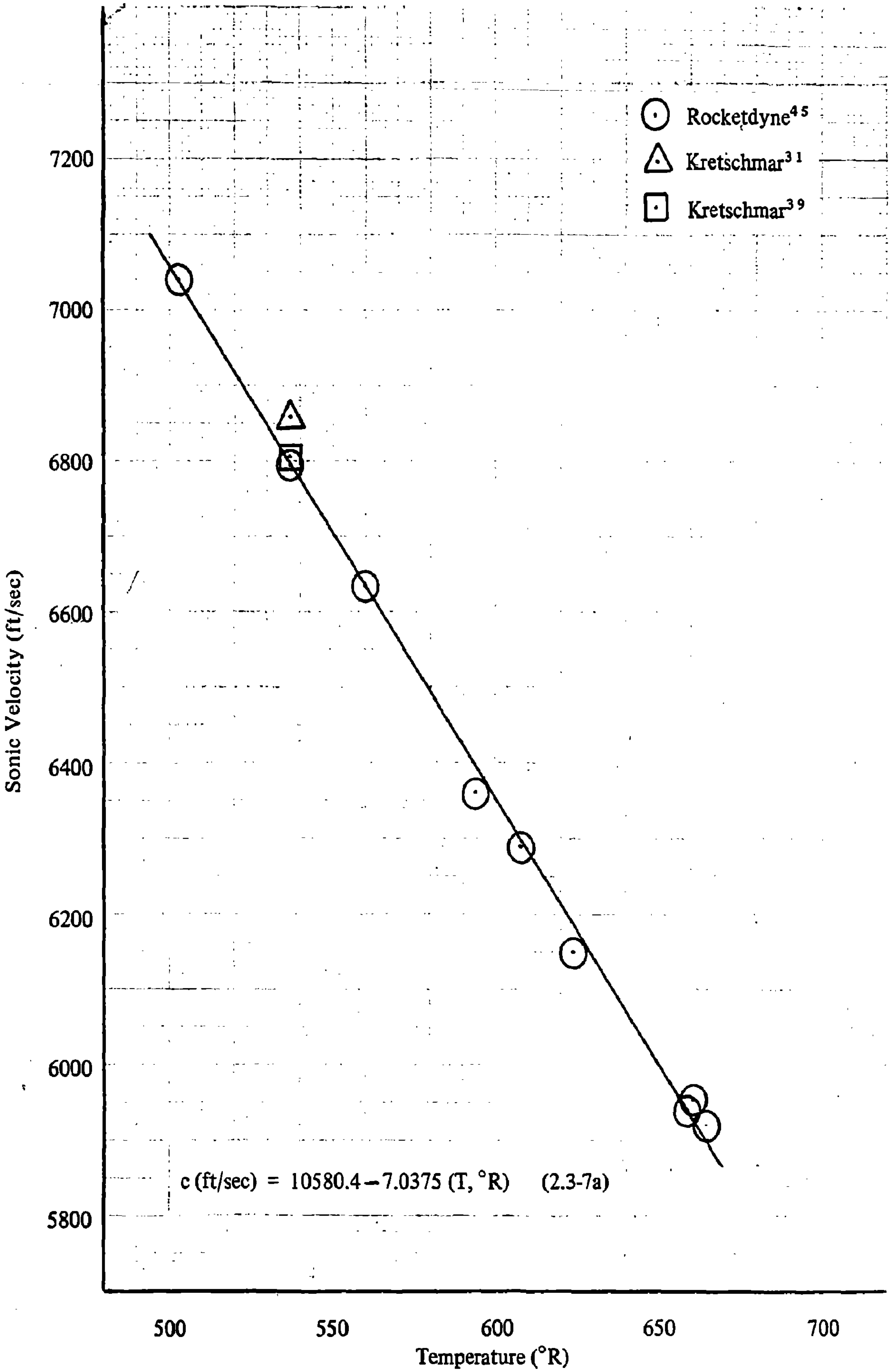
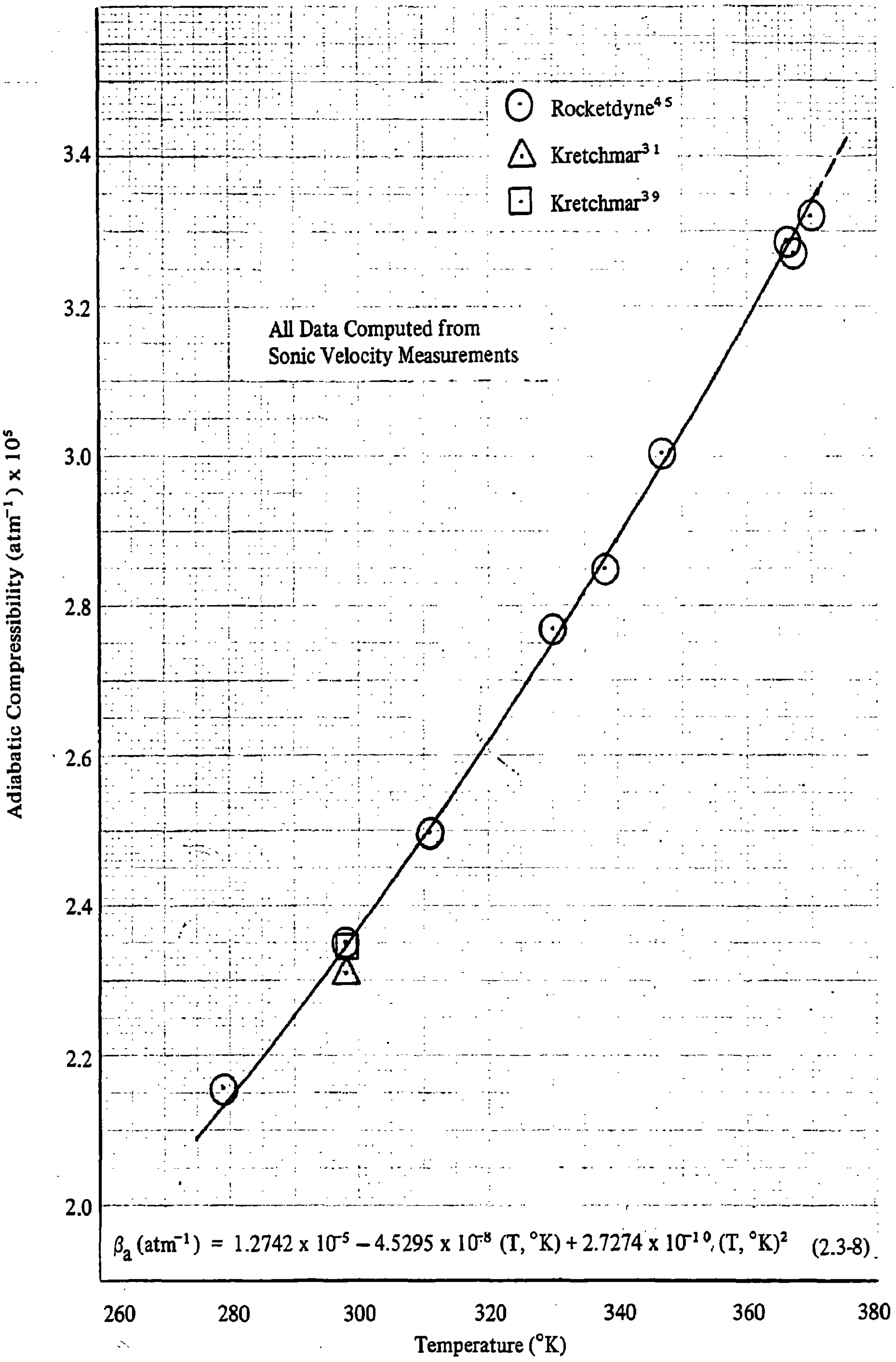
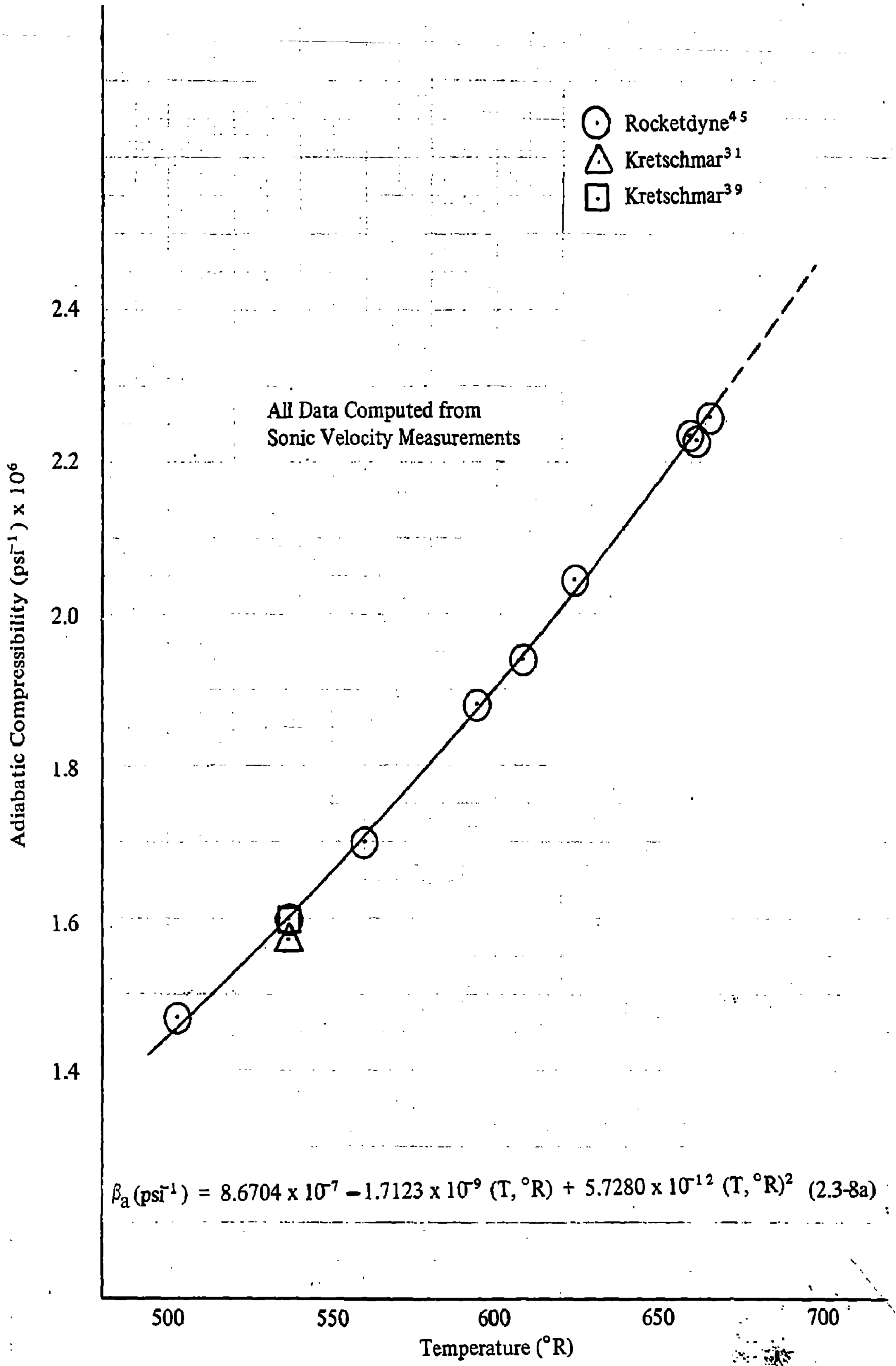


Figure 2.3-4a. Sonic Velocity versus Temperature, Liquid Hydrazine



$$\beta_a\,(\mathrm{atm}^{-1}) = 1.2742 \times 10^{-5} - 4.5295 \times 10^{-8}\,(T, {}^\circ K) + 2.7274 \times 10^{-10}\,(T, {}^\circ K)^2 \qquad (2.3\text{-}8)$$

Figure 2.3-5. Adiabatic Compressibility versus Temperature, Liquid Hydrazine



$$\beta_a\,(\text{psi}^{-1}) = 8.6704 \times 10^{-7} - 1.7123 \times 10^{-9}\,(T, {}^\circ R) + 5.7280 \times 10^{-12}\,(T, {}^\circ R)^2 \quad (2.3\text{-}8a)$$

Figure 2.3-5a. Adiabatic Compressibility versus Temperature, Liquid Hydrazine

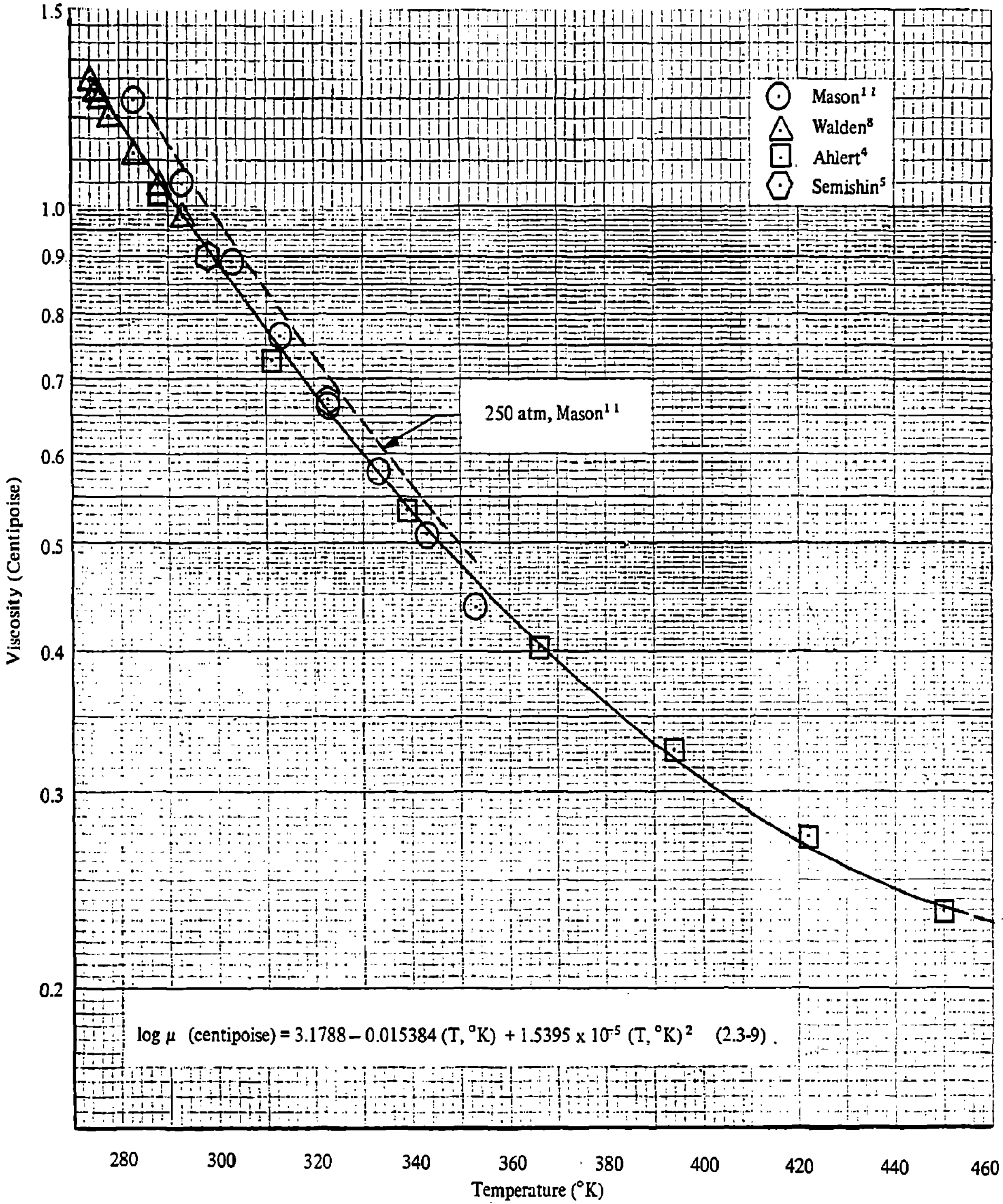
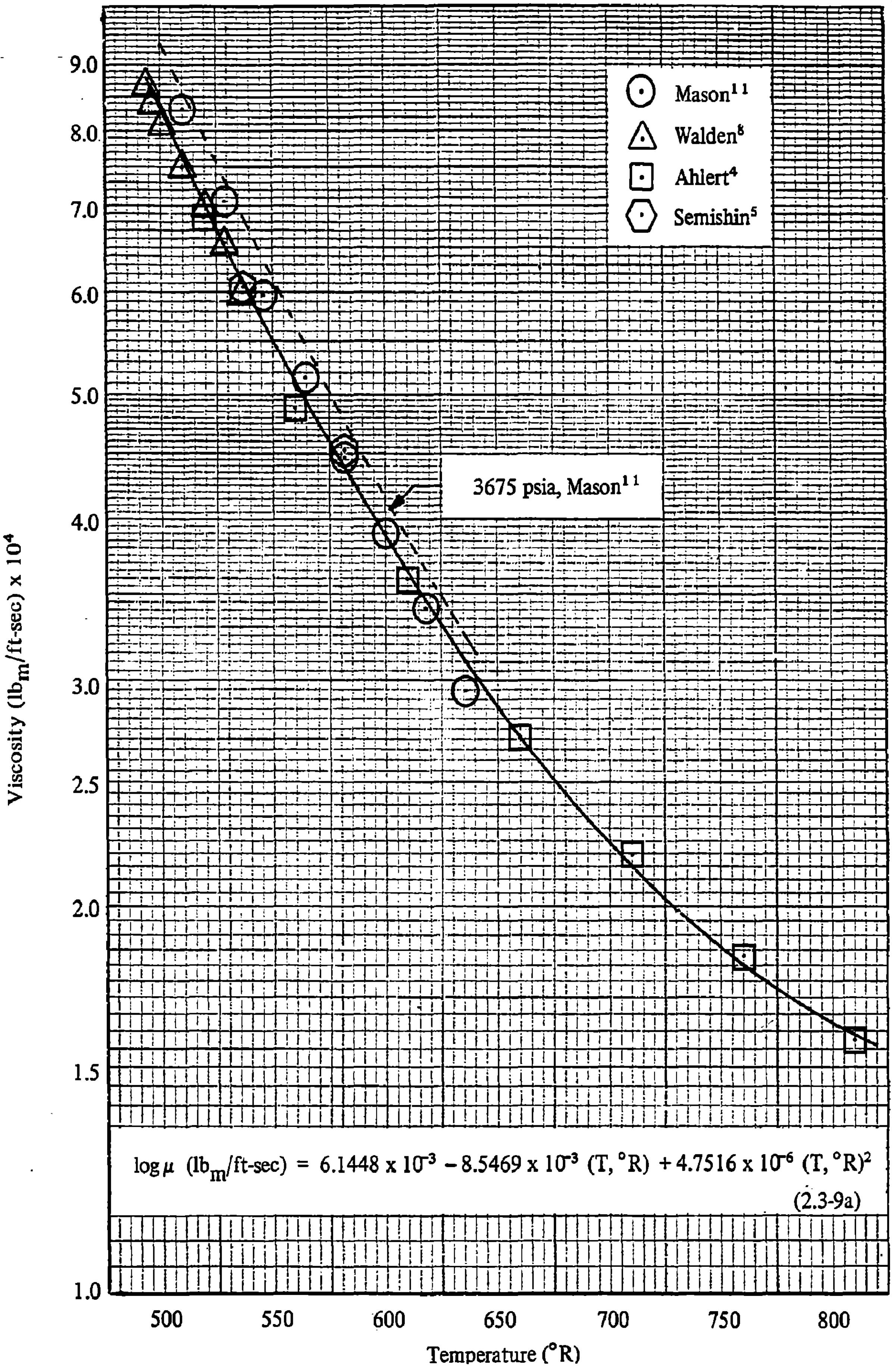


Figure 2.3-6. Viscosity versus Temperature, Liquid Anhydrous Hydrazine



$$\log \mu \ (\mathrm{lb_m/ft\text{-}sec}) = 6.1448 \times 10^{-3} - 8.5469 \times 10^{-3} \ (T, {}^\circ R) + 4.7516 \times 10^{-6} \ (T, {}^\circ R)^2 \quad (2.3\text{-}9a)$$

Figure 2.3-6a. Viscosity versus Temperature, Liquid Anhydrous Hydrazine

The viscosity of anhydrous hydrazine is defined over most of its liquidous range with sufficient accuracy for most engineering applications. The effect of external pressures has been shown to be small for normal propulsion systems applications.

2.3.3.6 Surface Tension and Parachor of Liquid Hydrazine

The surface tension of anhydrous hydrazine under its own vapor pressure has been studied by Barrick(7), Lyerly(37) and Bernard(35). The first two investigators reported single-point determinations while Bernard studied a narrow temperature range from 21 to 40 C (70 to 104 F). Baker(13) has measured the surface tension of hydrazine--water mixtures and also reported a value for 100% hydrazine. The experimental data from the four separate studies are shown in Figures 2.3-7 and 2.3-7a. The single-point determination at 25 C given by Baker is in good agreement with the data reported by Bernard while the single-point determinations by both Lyerly and Barrick are considerably lower.

The surface tension can be expressed as a linear function of temperature using only the data of Bernard and Baker by:

$$\gamma(\text{dynes/cm}) = 139.903 - 0.24637\,(\text{T},^\circ\text{K}) \qquad (2.3\text{-}10)$$

$$\gamma(\text{lb}_f/\text{ft}) = 9.5864 \times 10^{-3} - 9.3786 \times 10^{-6}(\text{T},^\circ\text{R}) \qquad (2.3\text{-}10a)$$

The standard deviation obtained from equation 2.3-16 is 0.9 dynes/cm while the average deviation of the data is only 0.07%.

The surface tension of anhydrous hydrazine appears to be adequately defined but only for a narrow temperature band.

The parachor at 25 C was calculated to be 91.2 from the relation

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

where

P = parachor
M = molecular weight (32.048)
γ = surface tension (66.45 dynes/cm)
ρ_v = 0.00077 g/cc (ideal gas)
ρ_l = 1.0037 g/cc

Daniels(41) gives the atomic parachor of N to be 12.5 and 17.1 for H. A parachor value of 93.4 is calculated from these atomic parachors.

2.3.3.7 Thermal Conductivity

Experimental data for the thermal conductivity of liquid anhydrous hydrazine do not appear in the open literature. Experimental data for the vapor phase are reported by Gray(32).

Recently, Rocketdyne(33) has published thermal conductivity data for liquid hydrazine. The data are given in graphical form and expressed as a function of temperature by

$$\text{K (BTU/ft-hr}\,^\circ\text{F)} = 0.2793 + 1.134 \times 10^{-4}(\text{T},^\circ\text{F}) - 8.341 \times 10^{-7}(\text{T},^\circ\text{F})^2 \qquad (2.3\text{-}11)$$

The work is referenced to a Rocketdyne research memo, but no explanation of the data is given. It is quite conceivable that these data were obtained from a theoretical empirical equation. Tsenberg(30) has shown that empirical equations used to calculate thermal conductivity often give poor correlation to experimentally determined data.

Equation 2.3-11 can be written

$$\text{K(cal/cm-sec-}^\circ\text{K)} = 2.1067 \times 10^{-4} + 6.5541 \times 10^{-6}(\text{T},^\circ\text{K}) - 1.1179 \times 10^{-8}(\text{T},^\circ\text{K})^2 \qquad (2.3\text{-}12)$$

$$\text{K(BTU/ft-sec-}^\circ\text{R)} = 1.4147 \times 10^{-5} + 2.4451 \times 10^{-7}(\text{T},^\circ\text{R}) - 2.3169 \times 10^{-10}(\text{T},^\circ\text{R})^2 \qquad (2.3\text{-}12a)$$

The data obtained from equation 2.3-12 and 2.3-12a are shown in Figures 2.3-8 and 2.3-8a, respectively, and are applicable for a temperature range from 25 to 127 C (77 to 266 F). These curves should be considered as provisional data until the source of the Rocketdyne data has been ascertained.

2.3.3.8 Dielectric Constant of Anhydrous Hydrazine

The dielectric constant of hydrazine is given by Audrieth(22) from the experimental work of Ulich(25) and Drude(38) who studied a temperature range from 9 to 25 C (20 to 77 F). Audrieth reports the following equation to represent the change in dielectric constant as a function of temperature

$$\epsilon = 58.5 - 0.3253(\text{T},^\circ\text{C}) + 0.0028(\text{T},^\circ\text{C})^2 - 0.0000267(\text{T},^\circ\text{C})^3 \qquad (2.3\text{-}13)$$

The experimental data of Ulich and Nespital are plotted in Figures 2.3-9 and 2.3-9a.

It was found that a second-degree polynomial equation represented the data with an average deviation of only 0.07%.

$$\epsilon = 265.82 - 1.2155(T, K) + 1.6565 \times 10^{-3}(T, K)^2 \quad (2.3\text{-}14)$$

$$\epsilon = 266.82 - 0.6715(T, °R) + 5.1127 \times 10^{-4}(T, °R)^2 \quad (2.3\text{-}14a)$$

Audrieth notes that, from these data, hydrazine should be an excellent electrolytic solvent.

2.3.3.9 Index of Refraction of Liquid Anhydrous Hydrazine

The refractive index of liquid anhydrous hydrazine has been reported by a number of investigators, but only over a narrow temperature range. Barrick(7) reported values at 35 C for three separate wavelengths and also gives values obtained by Bruhl(47). Battelle(42) reports values at the sodium wavelength (5893 Å) at 20 and 25 C from Dreisback(48). Chang(3) and Pannetier(43) have reported the refractive index at 25 C for mixtures of hydrazine and UDMH including values for the pure substances.

The experimental data are given in Table 2.3-1. The data at the sodium wavelength are plotted as a function of temperature in Figure 2.3-10. The refractive index values from the various investigators would appear to be in good agreement and for the sodium D-line appears to be a linear function of temperature.

TABLE 2.3-1 INDEX OF REFRACTION

TEMP. °C	n_D (5893 Å)	n_C (6563 Å)	n_F (4861 Å)	REF.
20	1.47074	-	-	48
22.3	1.46979	1.46624	1.47715	47
25	1.4683	-	-	3
25	1.4679	-	-	4
25	1.46867	-	-	48
35	1.46444	1.46207	1.47108	7

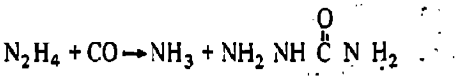
2.3.4 CHEMICAL PROPERTIES OF HYDRAZINE

2.3.4.1 Chemical Reactions

Hydrazine is a powerful reducing agent and reactions with strong oxidizing agents cause violent uncontrolled deflagration. It is possible, however, to oxidize hydrazine or hydrazine salts that are in aqueous solution without explosions. For example, hydrazine sulfate is oxidized to hydrozoic acid:

$$2H_2O_2 + (N_2H_5)_2SO_4 \rightarrow HN_3 + NH_4HSO_4 + 4H_2O$$

Generally, the reactions of hydrazine are similar to those of ammonia and amines but, being a diamine, further reactions often take place. The reaction of hydrazine with carbon monoxide forms semicarbazide at room temperature and under high pressures:

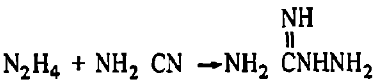


$$N_2H_4 + CO \rightarrow NH_3 + NH_2NH\overset{\overset{\displaystyle O}{\|}}{C}NH_2$$

The reaction of aqueous hydrazine with carbon dioxide gives hydrazine carboxylic acid:

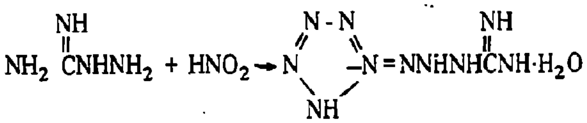
$$N_2H_4 + CO_2 \rightarrow NH_2NHCOOH$$

With cyanamide, hydrazine forms aminoguanidine:

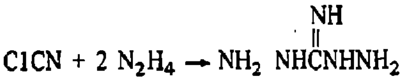


$$N_2H_4 + NH_2CN \rightarrow NH_2\overset{\overset{\displaystyle NH}{\|}}{C}NHNH_2$$

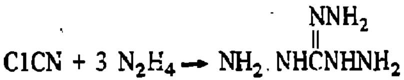
and, when reacted with nitrous acid, forms the primary explosive tetracene



The reaction of cyanogen chloride with two moles of hydrazine forms N, N′- diaminoguanidine and with an excess of hydrazine N, N′, N″- triaminoguanidine is formed.

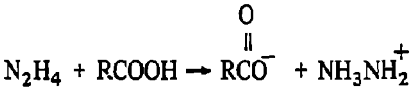


$$ClCN + 2N_2H_4 \rightarrow NH_2NH\overset{\overset{\displaystyle NH}{\|}}{C}NHNH_2$$



$$ClCN + 3N_2H_4 \rightarrow NH_2NH\overset{\overset{\displaystyle NNH_2}{\|}}{C}NHNH_2$$

Carboxylic acids are neutralized by hydrazine to form the hydrazine salt:



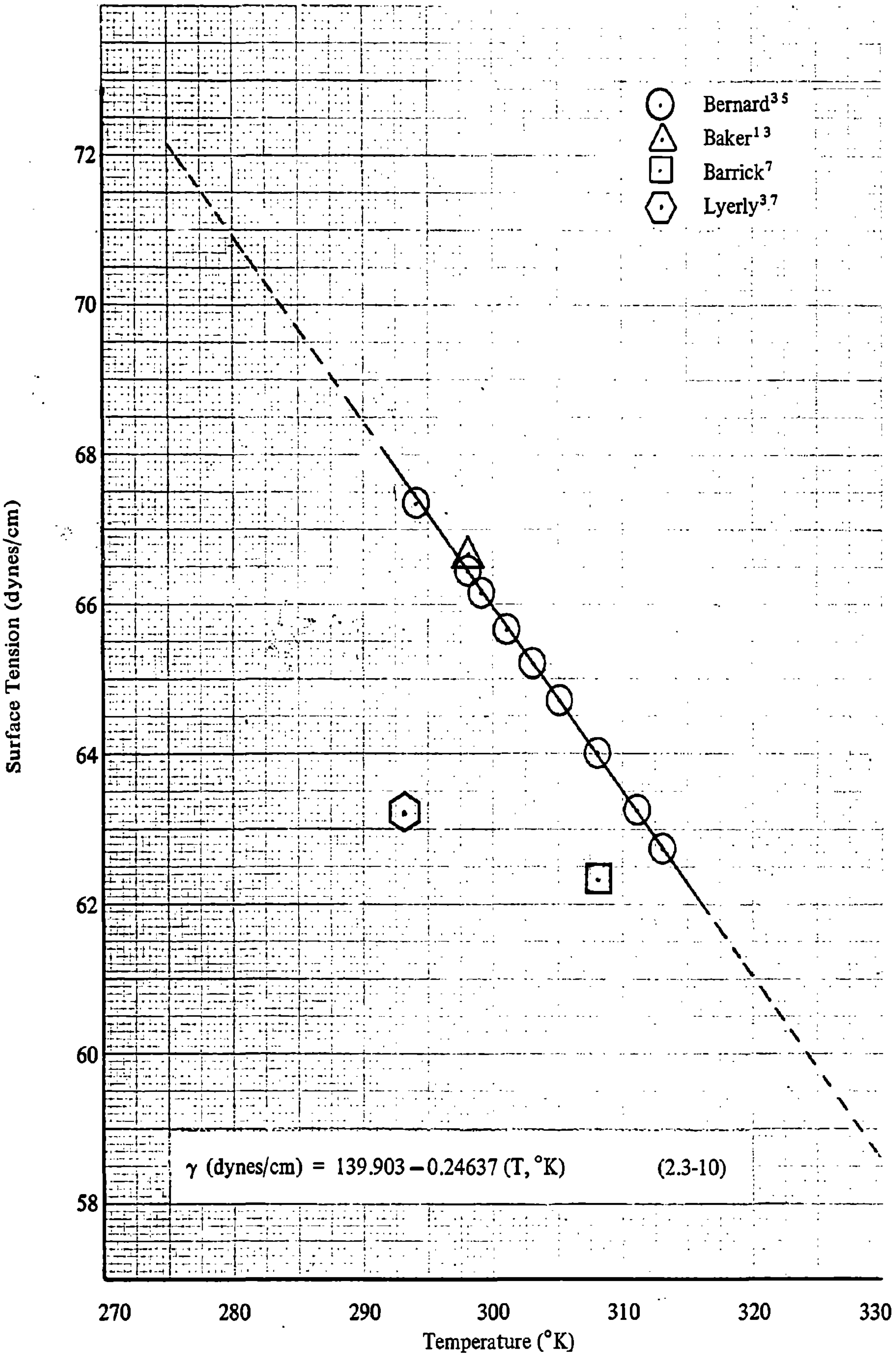
$$N_2H_4 + RCOOH \rightarrow R\overset{\overset{\displaystyle O}{\|}}{C}O^- + NH_3NH_2^+$$

Hydrazine reacts with monobasic acids such as hydrochloric acid to form either monoacid or diacid salt:

$$N_2H_4 + HCl \rightarrow N_2H_4 \cdot HCl + HCl \rightarrow N_2H_4 \cdot 2HCl$$

The monohydrochloride is stable in solution but the dihydrochloride dissociates to the monohydrochloride and hydrocloric acid.

The dibasic acids such as sulfuric acid react with hydrazine to form dihydrazine sulfate, monohydrazine sulfate or hydrazine disulfate:



$$\gamma \text{ (dynes/cm)} = 139.903 - 0.24637 \text{ (T, °K)} \qquad (2.3\text{-}10)$$

Figure 2.3-7. Surface Tension versus Temperature, Liquid Anhydrous Hydrazine

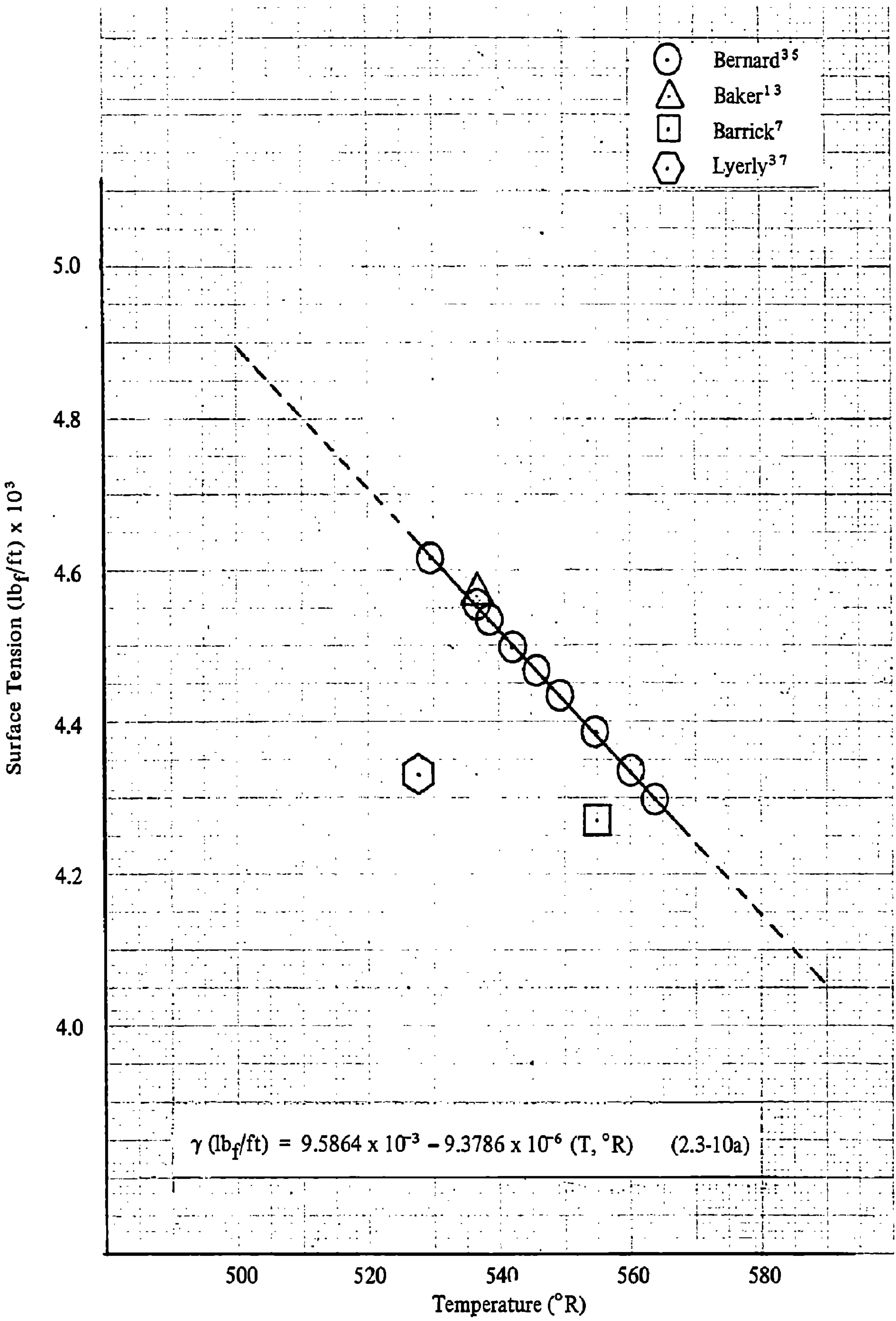
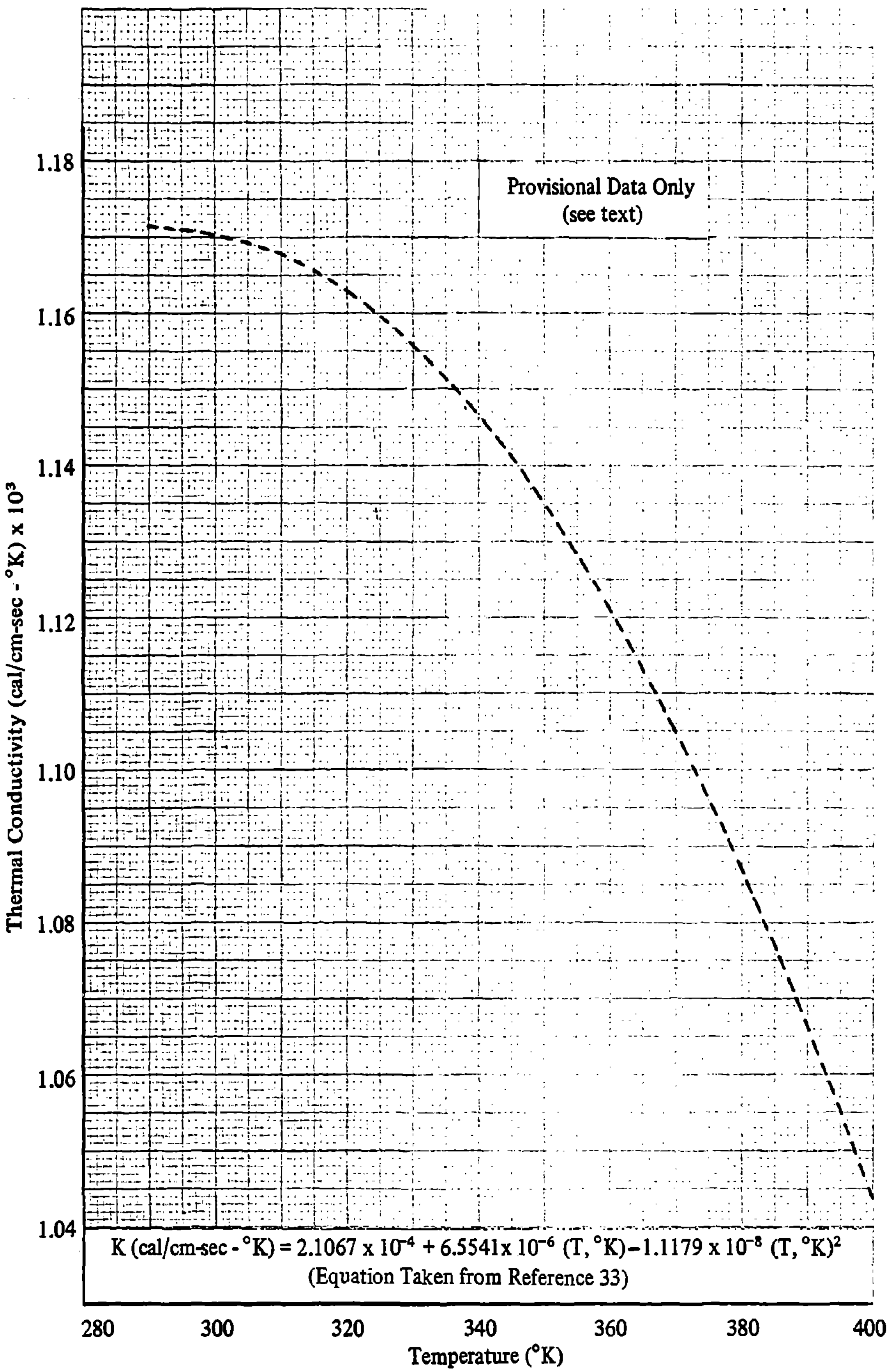


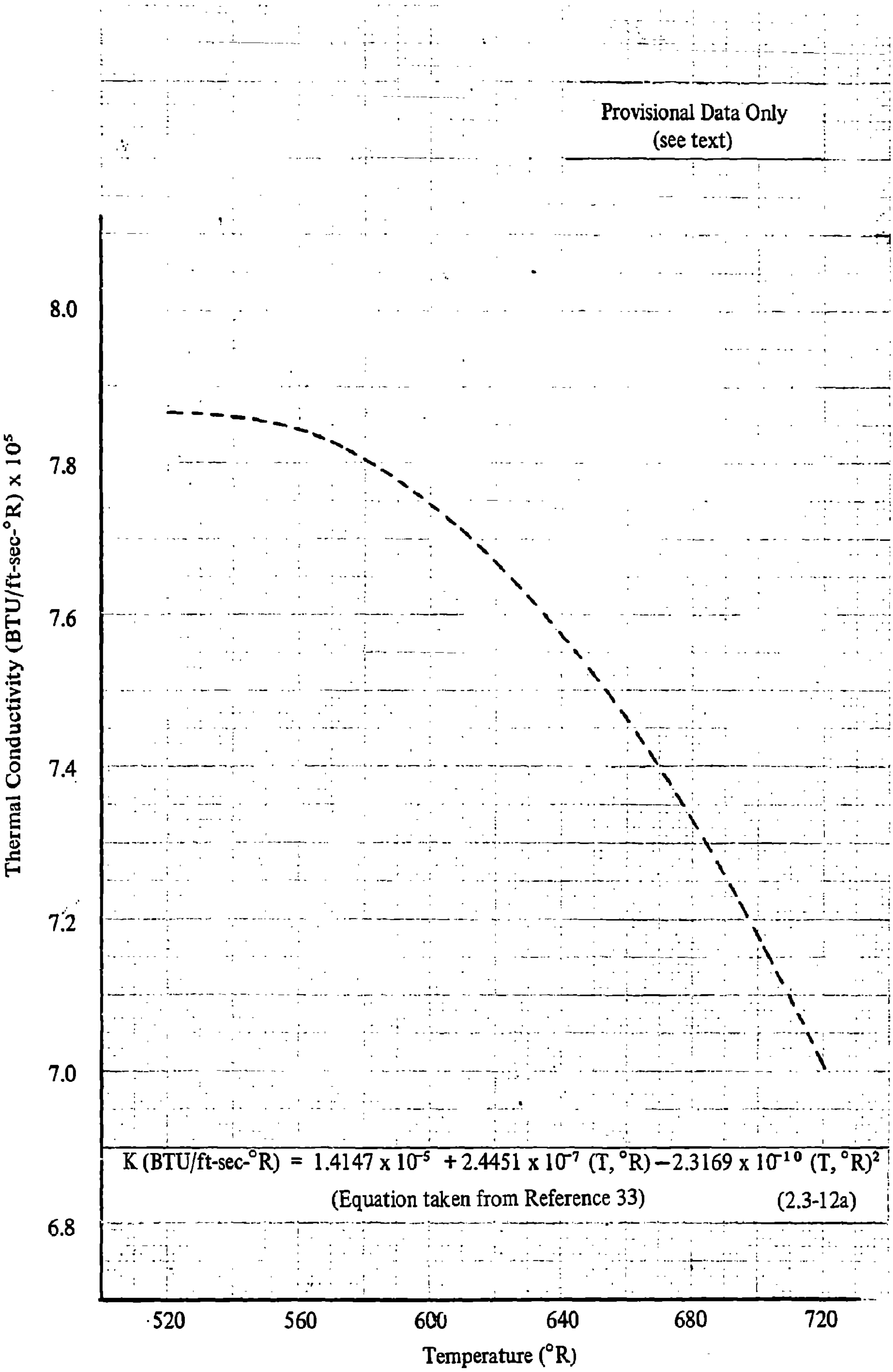
Figure 2.3-7a. Surface Tension versus Temperature, Liquid Anhydrous Hydrazine



Provisional Data Only
(see text)

K (cal/cm-sec - °K) = $2.1067 \times 10^{-4} + 6.5541 \times 10^{-6}$ (T, °K) $- 1.1179 \times 10^{-8}$ (T, °K)^2
(Equation Taken from Reference 33)

Figure 2.3-8. Thermal Conductivity versus Temperature, Liquid Anhydrous Hydrazine

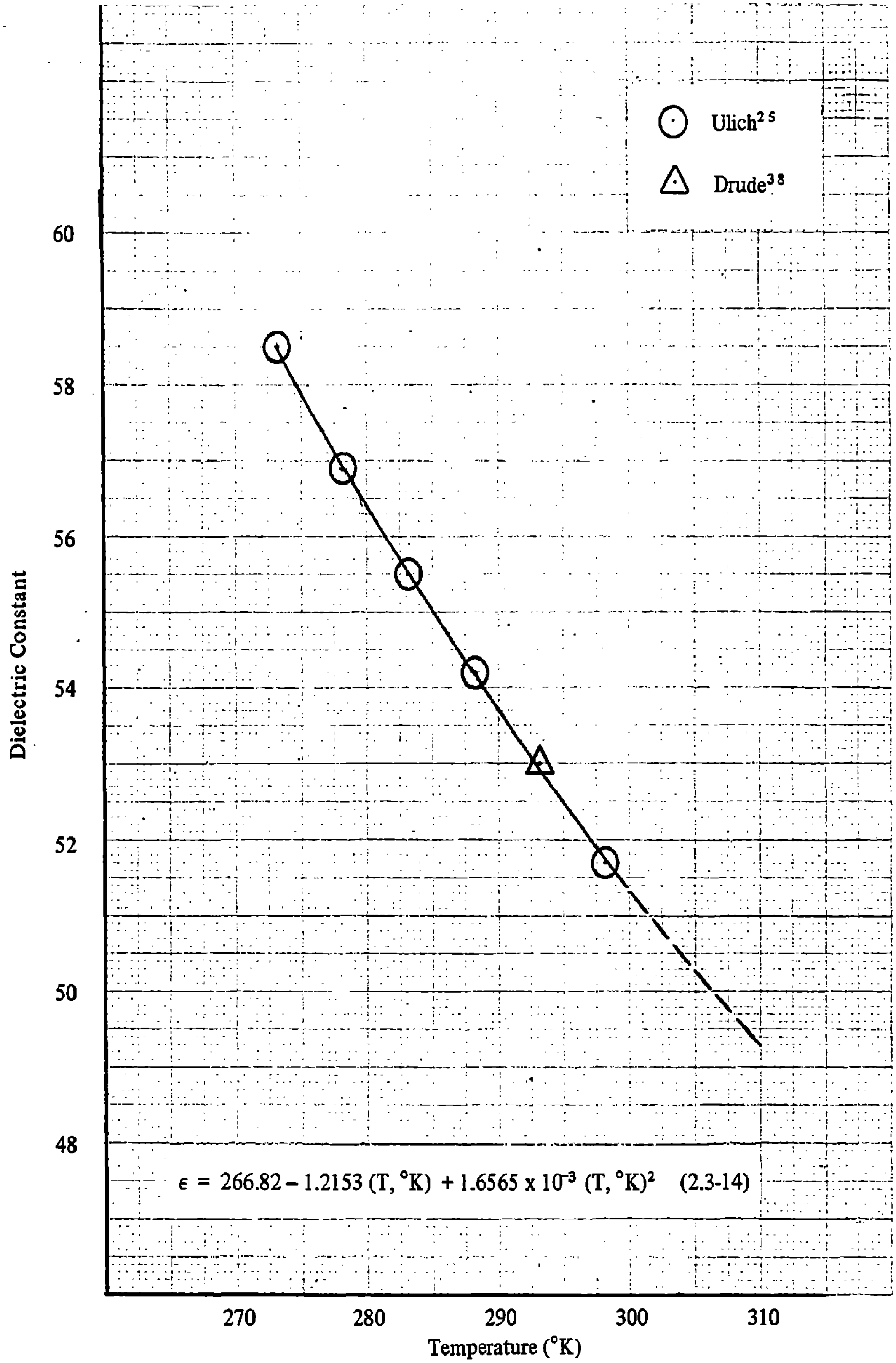


Provisional Data Only
(see text)

$$K\,(\mathrm{BTU/ft\text{-}sec\text{-}^{\circ}R}) = 1.4147 \times 10^{-5} + 2.4451 \times 10^{-7}\,(T, {}^{\circ}R) - 2.3169 \times 10^{-10}\,(T, {}^{\circ}R)^2 \qquad (2.3\text{-}12a)$$

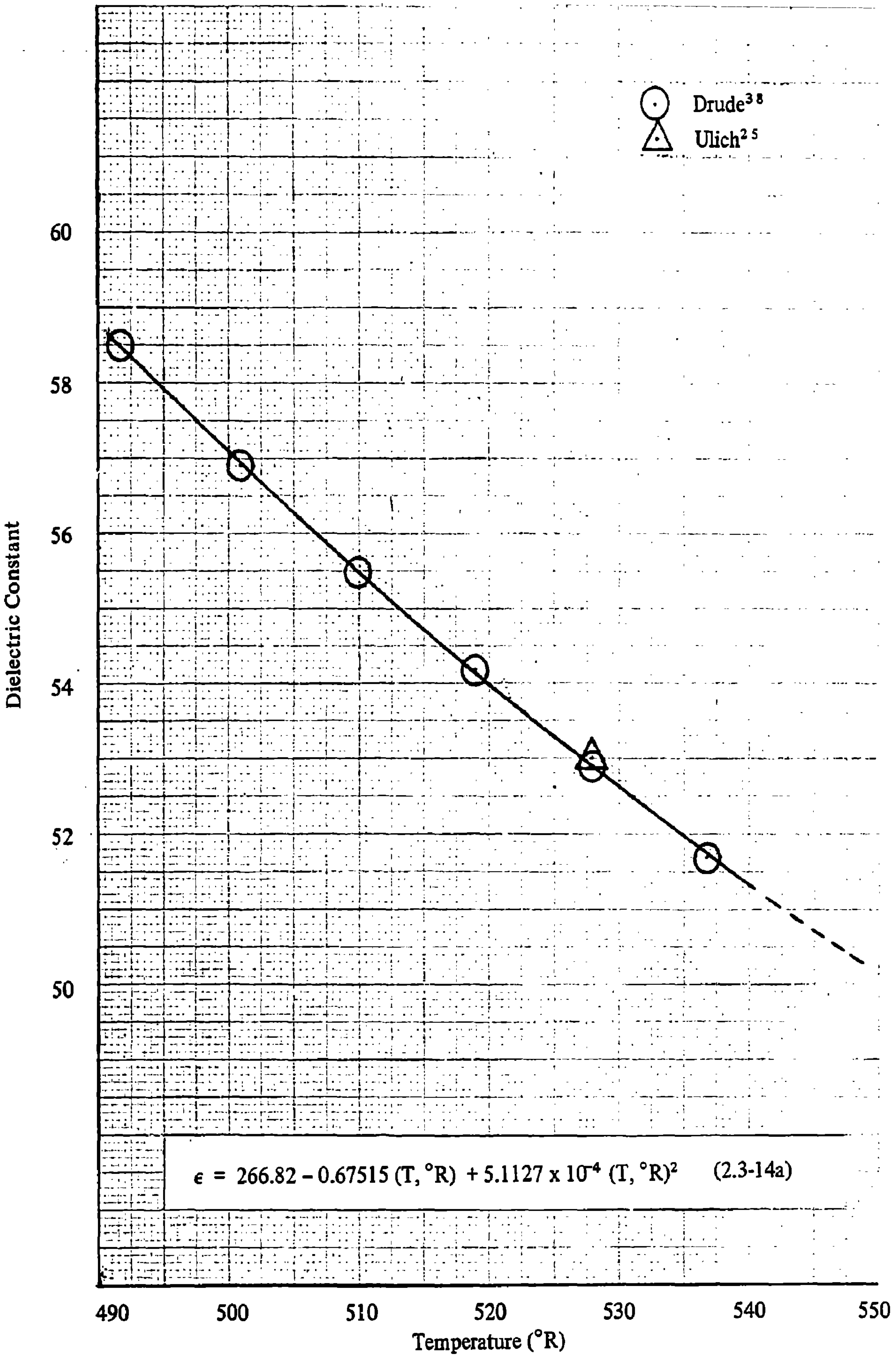
(Equation taken from Reference 33)

Figure 2.3-8a. Thermal Conductivity versus Temperature, Liquid Anhydrous Hydrazine



$$\epsilon = 266.82 - 1.2153\,(T, °K) + 1.6565 \times 10^{-3}\,(T, °K)^2 \qquad (2.3\text{-}14)$$

Figure 2.3-9. Dielectric Constant versus Temperature, Liquid Anhydrous Hydrazine



$$\epsilon = 266.82 - 0.67515\,(T, {}^{\circ}R) + 5.1127 \times 10^{-4}\,(T, {}^{\circ}R)^2 \qquad (2.3\text{-}14a)$$

Figure 2.3-9a. Dielectric Constant versus Temperature, Liquid Anhydrous Hydrazine

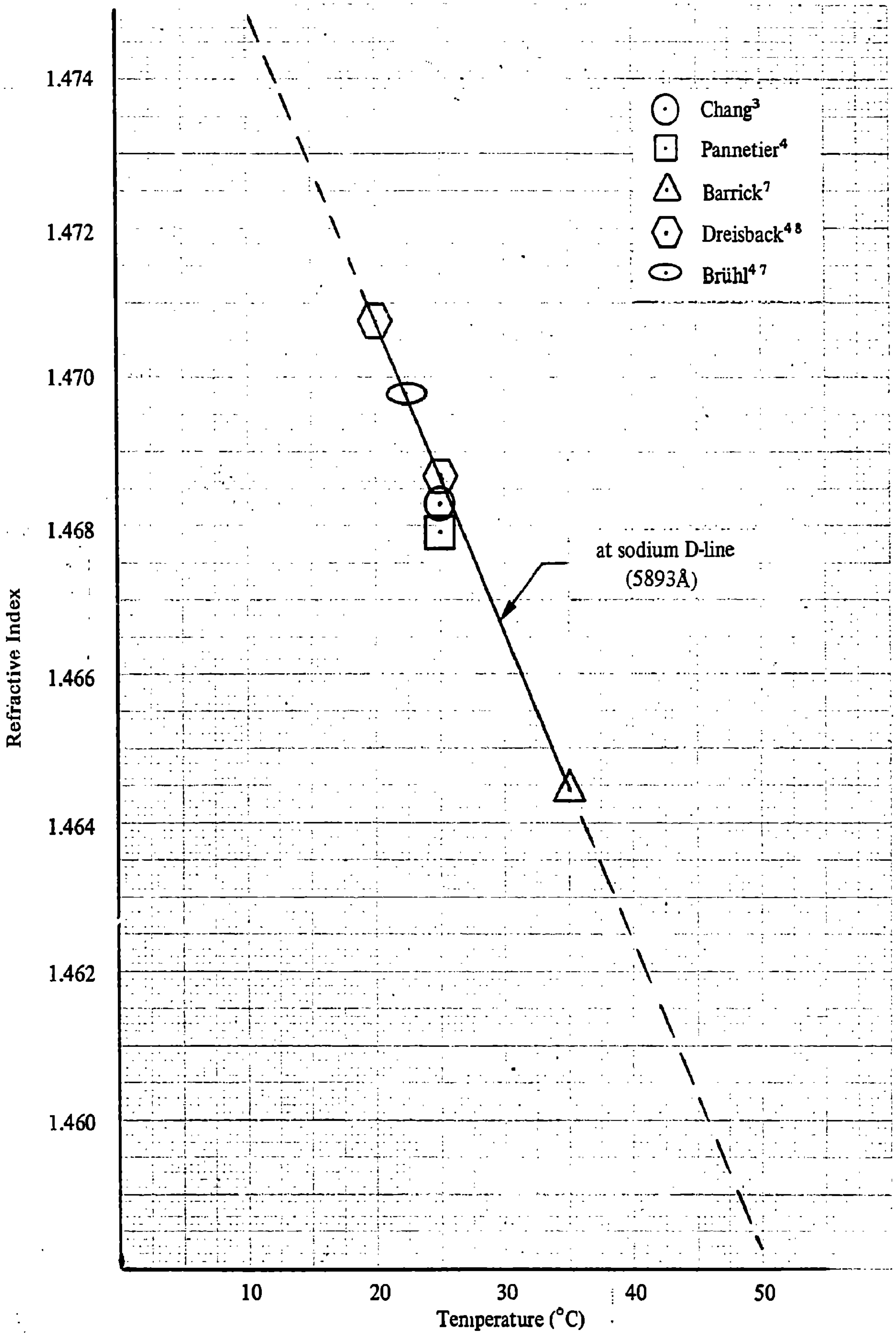


Figure 2.3-10. Refractive Index versus Temperature, Liquid Anhydrous Hydrazine

$N_2H_4 + H_2SO_4 \rightarrow (N_2H_4)_2 \cdot H_2SO_4$

$(N_2H_4)_2 \cdot H_2SO_4 \rightarrow 2(N_2H_4 \cdot H_2SO_4)$

$2(N_2H_4 \cdot H_2SO_4) + H_2SO_4 \rightarrow 2(N_2H_4 \cdot 2H_2SO_4)$

Alkali metals react with hydrazine to form corresponding alkali hydrazide:

$Na + N_2H_4 \rightarrow NaNHNH_2 + 1/2H_2$

The sodium hydrazide explodes violently in the presence of oxygen and this reaction is typical of the alkali hydrazides.

Hydrazine is a very promising monopropellant. The catalytic and thermal decomposition proceed in two steps according to:

$3\ N_2H_4 \rightarrow 4NH_3 + N_2$ (+144,300 BTU/lb)

$4\ NH_3 \rightarrow 2N_2 + 6H_2$ (-79,200 BTU/lb)

Since these reactions proceed at different rates, the overall decomposition reaction may be written as a function of the fraction (X) of ammonia dissociated:

$3\ N_2H_4 = 4(1-X)NH_3 + (1+2X)N_2 + 6\ H_2$

(144,300 - 79,200 BTU/lb)

2.3.5 THERMODYNAMIC PROPERTIES OF HYDRAZINE

2.3.5.1 Heat of Formation

Bushnell(26) has determined the heat of solution of hydrazine hydrate $N_2H_4 . H_2O$ and Hughes(27) has reported the heat of combustion of hydrazine hydrate as well as hydrazine.

Bushnell(26) reports the heat of solution of hydrazine hydrate to be -1.797 kcal/mole. Using the heat of combustion of the hydrate (146.936 kcal/mole) given by Hughes(27) and the heat of formation of water given by Wagman(28), a value for the heat of formation of 12.103 kcal/mole is obtained. (See Table (a) below)

Using the heat of combustion of hydrazine (148.635 kcal/-mole) reported by Hughes(27) and Wagman's(28) value for the heat of formation of water, a value for the heat of formation of liquid hydrazine of 12.005 at 25 C (77 F) is obtained. (See Table (b) below)

The methods and experimental data used to obtain the two heats of formation given both appear to be without serious error. The average of the two values is 12.054 kcal/-mole, which is the value accepted in this work.

2.3.5.2 Melting Point and Heat of Fusion

Scott(1) has calculated the melting point of pure hydrazine from a study of melting point as a function of

Table (a)	ΔH(kcal)	Ref.
$N_2H_4 \cdot H_2O(\ell,298) \rightarrow N_2H_4(\ell,298) + H_2O(\ell,298)$	1.797	(23)
$N_2(g,298) + 3H_2O(\ell,298) \rightarrow N_2H_4 \cdot H_2O(\ell,298) + O_2(g,298)$	146.936	(27)
$2H_2(g,298) + O_2(g,298) \rightarrow 2H_2O(\ell,298)$	2(-68.315)	(28)
$N_2(g,298) + 2H_2(g,298) \rightarrow N_2H_4(\ell,298)$	12.103	

Table (b)	ΔH(kcal)	Ref.
$N_2(g,298) + 2H_2O(\ell,298) \rightarrow N_2H_4(\ell,298) + O_2(g,298)$	148.635	(27)
$2H_2(g,298) + O_2(g,298) \rightarrow 2H_2O(\ell,298)$	2(-68.315)	(28)
$N_2(g,298) + 2H_2(g,298) \rightarrow N_2H_4(\ell,298)$	12.005	

the fraction melted. The hydrazine sample used was estimated to have a purity of 99.75 mole %. Its melting point was found to be 274.56 K and the calculated data for pure hydrazine was 274.69 K. Correcting for the presently accepted ice point, the value is 274.68 K or 1.53 C (34.75 F).

Mohr(21) determined the melting point of various hydrazine-water mixtures and by extrapolation of the melting point diagram reports a value of 2 C (35.6 F) for the melting point of pure hydrazine.

The corrected melting point obtained by Scott is accepted in this work (274.68 K).

It should be noted that even the addition of small quantities of water to hydrazine lowers the melting point. Water forms hydrazine monohydrate ($N_2H_4.H_2O$) and the eutectic composition is 69 weight % of N_2H_4 and its melting point is -54 C as reported by Mohr(21). The melting point of hydrazine-water mixtures is given in Figures 2.3-12 and 2.3-12a.

Scott(1) measured the heat of fusion at the melting point and reported a value of 3.025 kcal/mole (169.90 BTU/lb). The value given by Scott includes corrections for premelting and for the heat required to melt the eutectic mixture since the sample contained a small amount of water. The correction for premelting required an estimate of the heat capacity below the melting point and, for this reason, Scott reported that the heat of fusion value has a large absolute uncertainty.

2.3.5.3 Critical State Constants of Hydrazine

There are no recent determinations for the critical state constants of hydrazine. Audrieth(22) reports the critical temperature to be 380 C from the work of Lobry deBruyn(10) published in 1896. The critical pressure based on the vapor pressure work of deBruyn is given by Audrieth as 145 atmospheres (2131 psia). Audrieth notes that these values may be of doubtful accuracy because of the tendency of hydrazine to undergo decomposition at higher temperature. The critical pressure obtained from the selected vapor pressure equation 2.3-2 is 144.6 atm (2124 psia), which is in good agreement with the value reported by Audrieth.

The critical density is reported in the Liquid Propellant Manual(23) to be 0.231 g/cc.

2.3.5.4 Heat Capacity of Liquid Hydrazine

The heat capacity of hydrazine has been reported by both Scott(1) and Hough(12). Scott reported data for both the solid and liquid phase. The values are actually for the turation conditior [illegible] temperature were held constant. The values of C_{sat} should be nearly equal to values at constant pressure (C_p) and the data of Scott is assumed to be C_p for this work. From a study of the melting point as a function of the fraction melted, the purity of the sample was estimated to be 99.75 mole %.

Scott estimated the precision of the calorimetric measurements to be approximately 0.1% but, because of the sample impurity and difficulties encountered in the measurements, the absolute uncertainty was believed to be 0.3%. Scott did not report his experimental data because of this uncertainty, but rather gave smoothed results at integral temperatures between the melting point and 67 C.

Hough(12) studied the isobaric heat capacities of hydrazine-water mixtures including data for pure hydrazine. From chemical analysis, the hydrazine was found to contain less than 0.001 mole fraction of impurities. A stainless steel bomb calorimeter having a volume of one liter was used. The calorimeter was calibrated with water and temperatures were measured with a platinum resistance thermometer. Energy measurements were made in watt-seconds and converted to gram-calories. Five readings were made between 40 to 80 C (104 to 176 F). Hough estimated the heat capacity data had a maximum uncertainty of 1% with a majority of the values having an uncertainty of less than 0.5%. The experimental data are plotted in Figures 2.3-13 and 2.3-13a with the nine smoothed values given by Scott.

A comparison of the experimental data shows a maximum difference at 40 C where the data reported by Scott(1) are about 1% higher than those of Hough(12). At the higher temperatures, the agreement becomes much better. Extrapolation of Hough's work to lower temperatures would give values much lower than obtained by Scott.

There does not appear to be a clear choice between the two studies. For this work, the data of the two studies were combined by the least squares method and the change in heat capacity with temperature is

$$C_p(\text{cal/g-°K}) = 0.88415 - 1.3949 \times 10^{-3}(T, °K) + 3.0074 \times 10^{-6}(T, °K)^2 \qquad (2.3\text{-}15)$$

$$C_p(\text{BTU/lb-°R}) = 0.88354 - 7.436 \times 10^{-4}(T, °R) + 9.2750 \times 10^{-7}(T, °R)^2 \qquad (2.3\text{-}15a)$$

The standard deviation is 0.0024 cal/g-K. The least squares method weighs the data of Scott(1) more heavily because of the greater number of points used. This is not justified because smoothed data were used and the actual number of experimental data points taken is not known. Partial justification may be warranted because Scott reports a higher [illegible]

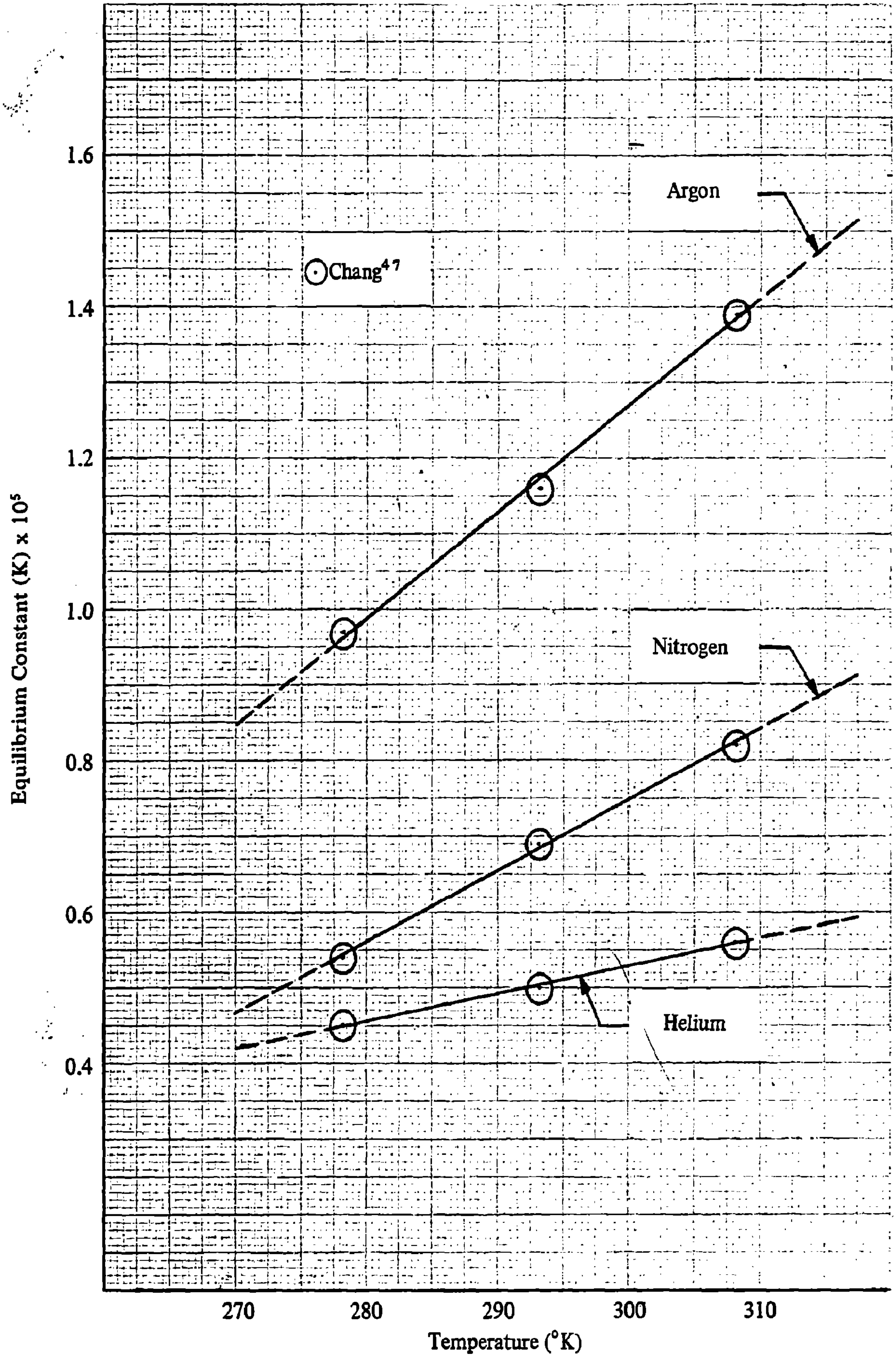


Figure 2.3-11. Gas Solubility in Liquid N_2H_4 versus Temperature

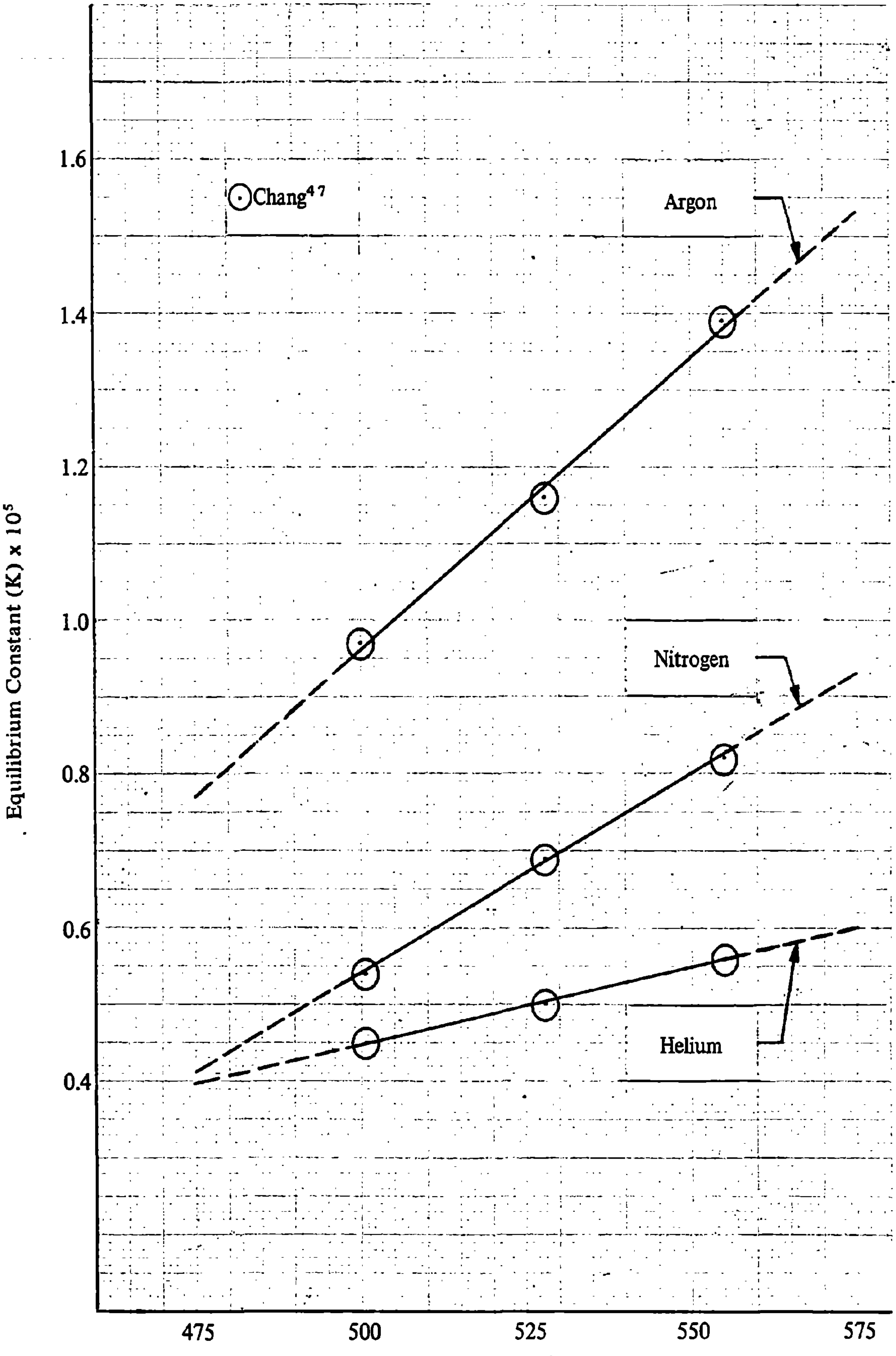


Figure 2.3-11a. Gas Solubility in Liquid N_2H_4 versus Temperature

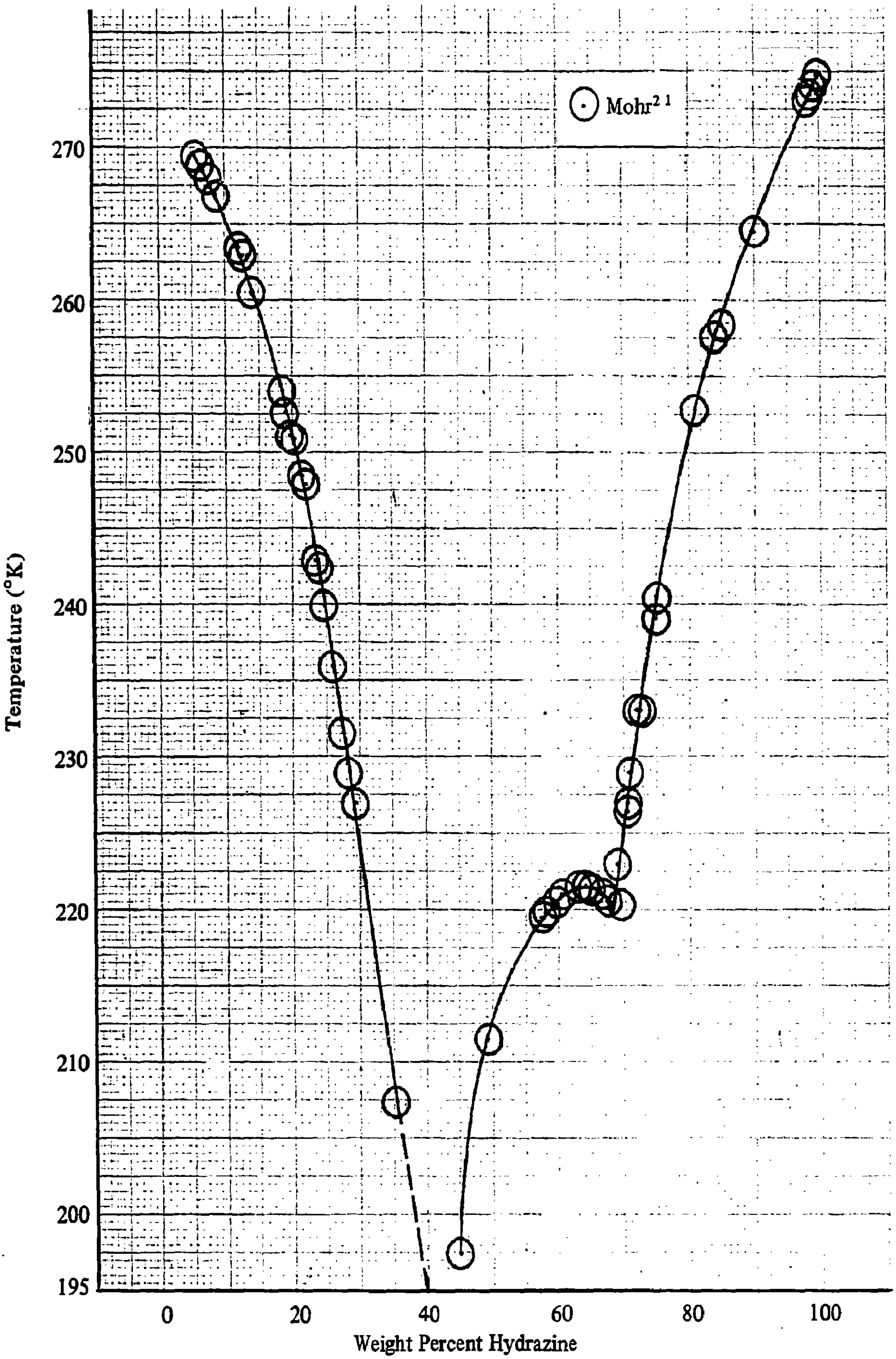


Figure 2.3-12. Freezing Point of Hydrazine - Water Mixtures

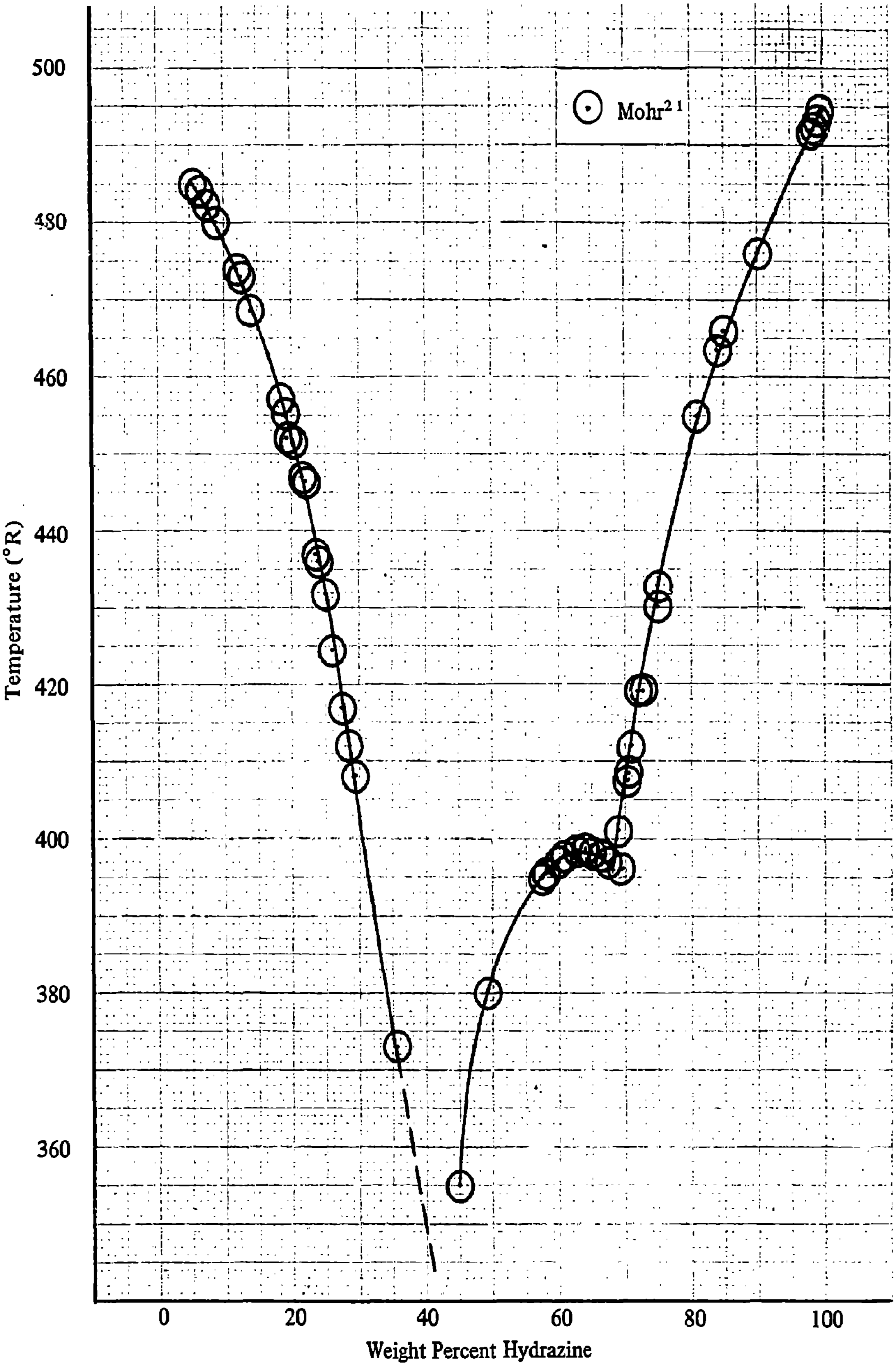
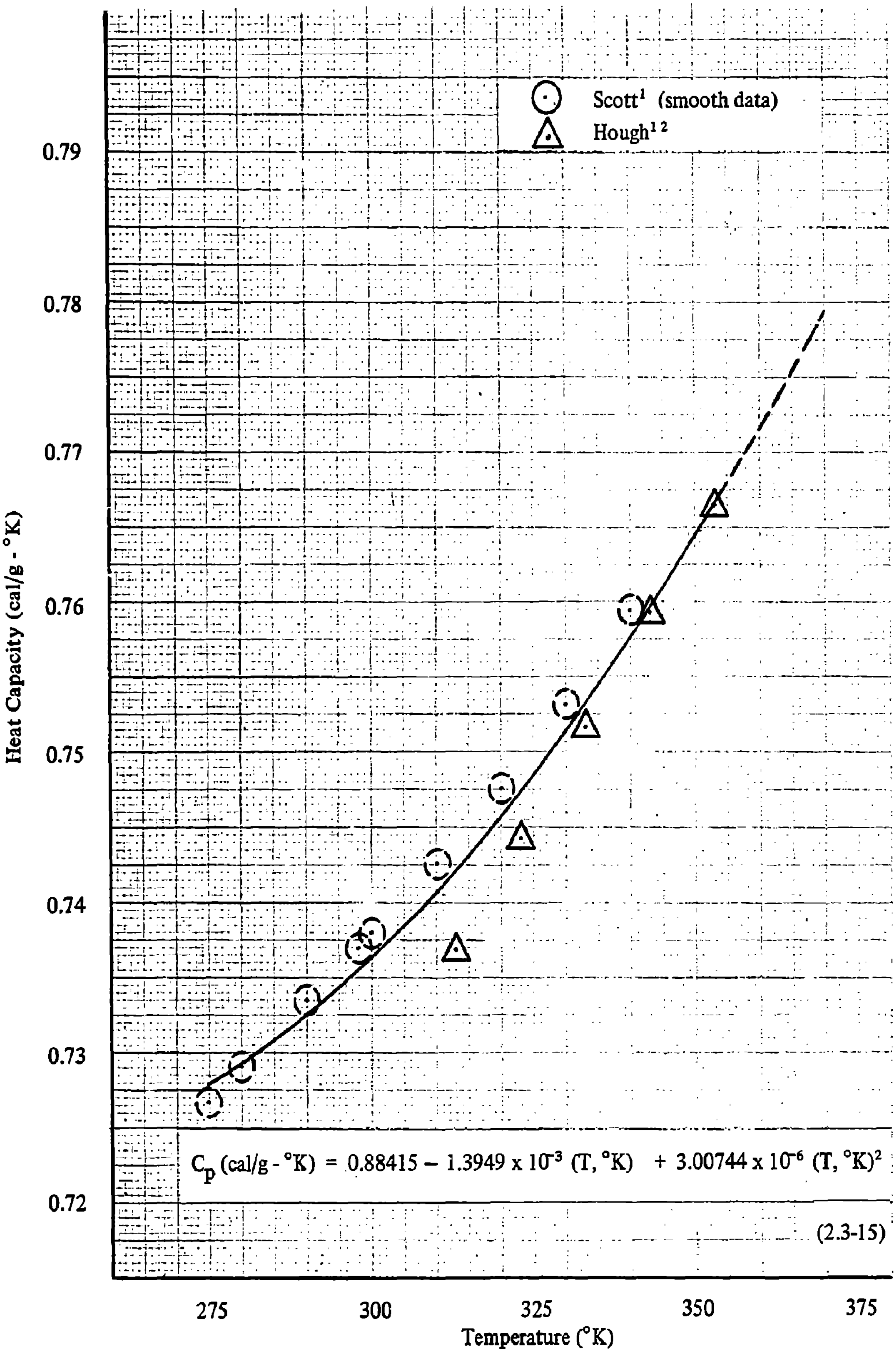


Figure 2.3-12a. Freezing Point of Hydrazine - Water Mixtures



$$C_p\ (\text{cal/g}-°\text{K}) = 0.88415 - 1.3949 \times 10^{-3}\ (T, °\text{K}) + 3.00744 \times 10^{-6}\ (T, °\text{K})^2 \quad (2.3\text{-}15)$$

Figure 2.3-13. Heat Capacity versus Temperature, Liquid Anhydrous Hydrazine

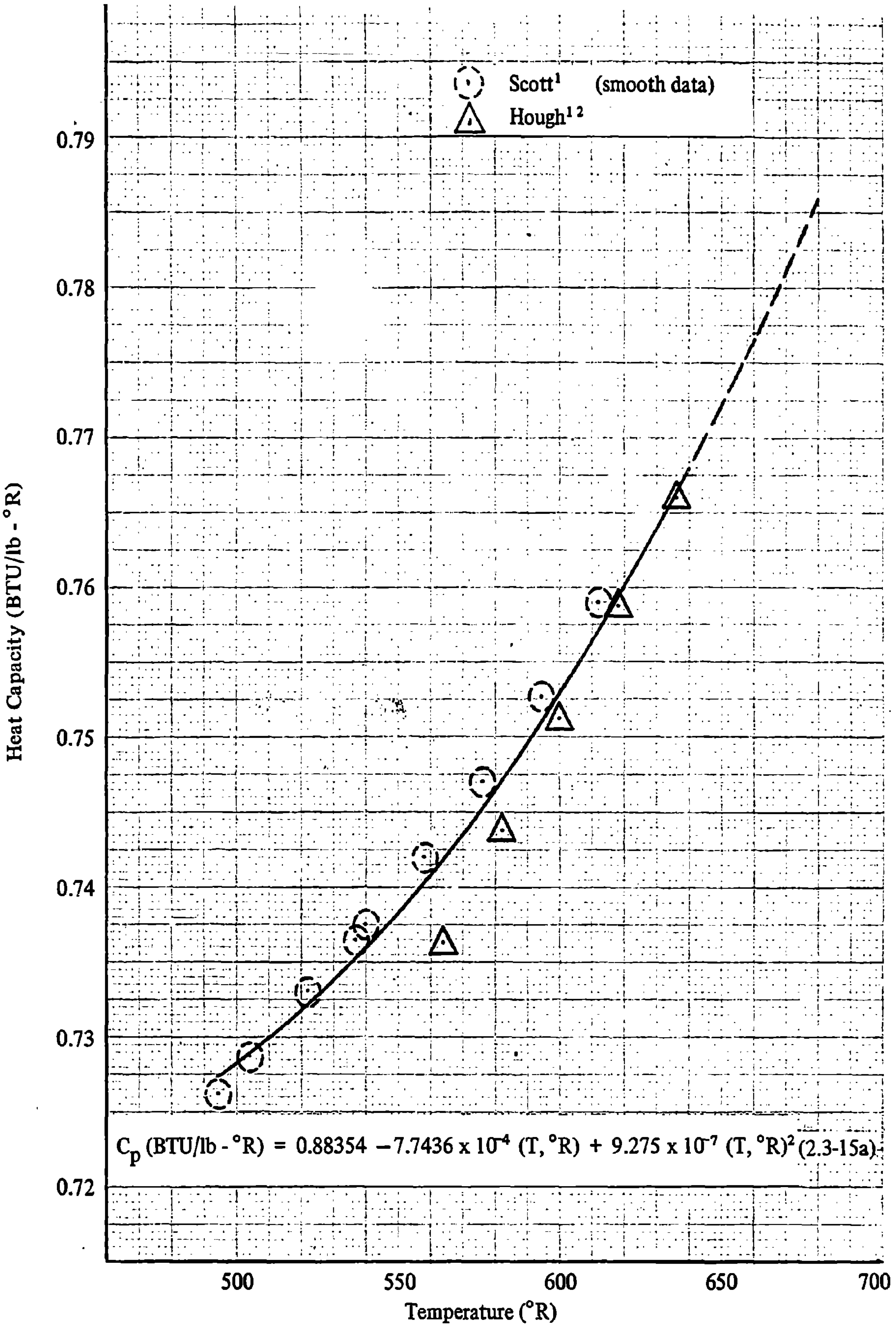
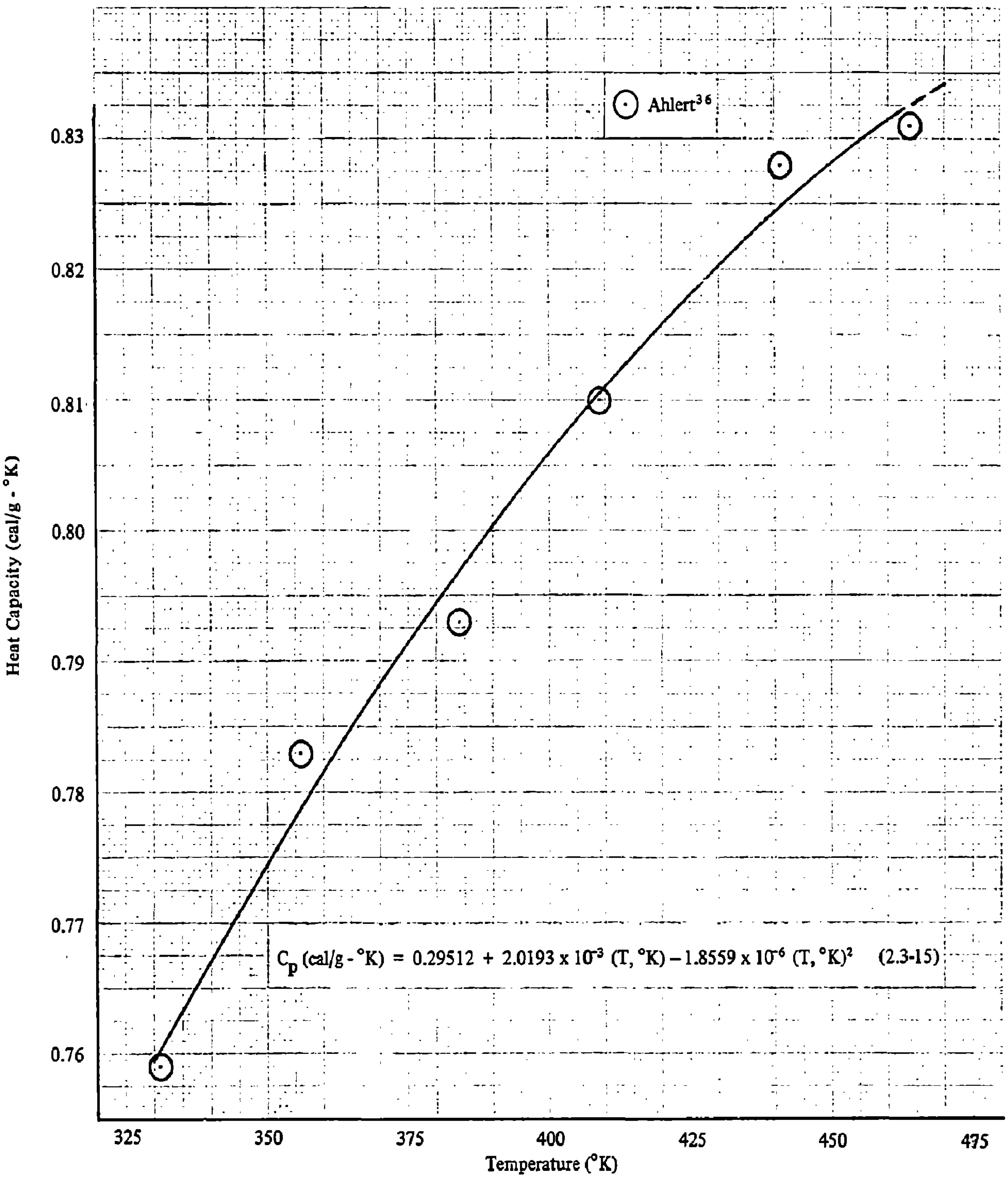
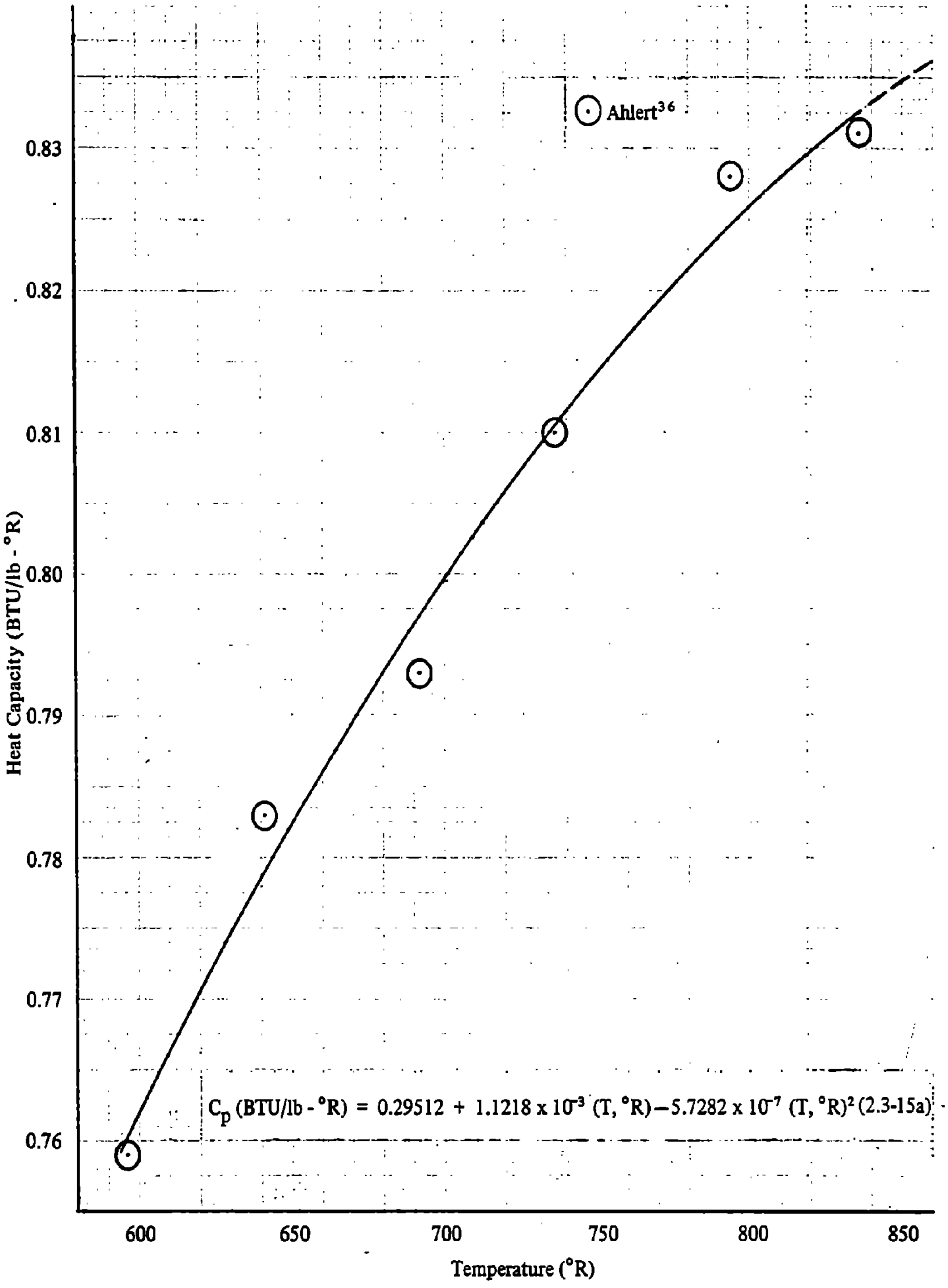


Figure 2.3-13a. Heat Capacity versus Temperature, Liquid Anhydrous Hydrazine



$$C_p\,(\text{cal/g}-°K) = 0.29512 + 2.0193 \times 10^{-3}\,(T, °K) - 1.8559 \times 10^{-6}\,(T, °K)^2 \quad (2.3\text{-}15)$$

Figure 2.3-14. Heat Capacity versus Temperature, Liquid Propellant Grade Hydrazine



C_p (BTU/lb - °R) = 0.29512 + 1.1218 x 10^{-3} (T, °R)−5.7282 x 10^{-7} (T, °R)^2 (2.3-15a)

Figure 2.3-14a. Heat Capacity versus Temperature, Liquid Propellant Grade Hydrazine

The heat capacity of anhydrous hydrazine appears to be well defined from its melting point to approximately 640 R. Extrapolation above this temperature is not advised.

Recently, Ahlert(36) published heat capacity data for commercial grade hydrazine over a temperature range from 58 to 191 C (136 to 376 F). The hydrazine sample contained 2.5% H_2O, 0.5% NH_3 and traces of aniline and heptane. This mixture is slightly above the limits imposed by specification MIL-P-26536C for propellant grade hydrazine.

The experimental data are shown in Figures 2.3-14 and 2.3-14a and are adequately defined by

$$C_p(\text{cal/g-}^\circ\text{K}) = 0.29512 + 2.0193\text{x}10^{-3}(\text{T},^\circ\text{K}) - 1.8559\text{x}10^{-6}(\text{T},^\circ\text{K})^2 \qquad (2.3\text{-}16)$$

$$C_p(\text{BTU/lb-}^\circ\text{R}) = 0.29512 + 1.1218\text{x}10^{-3}(\text{T},^\circ\text{R}) - 5.7282\text{x}10^{-7}(\text{T},^\circ\text{R})^2 \qquad (2.3\text{-}16a)$$

The standard deviation from equation 2.3-16 is 0.004 cal/g-K and the average deviation is 0.31%.

The specific heat of propellant grade hydrazine is higher than for anhydrous hydrazine. At 350 K, the propellant grade hydrazine heat capacity is 1.3% higher.

2.3.5.5 Heat of Vaporization and Trouton Constant

Experimental determination of the heat of vaporization does not appear in the literature. Scott(1) reported a value of 10.7 kcal/mole at 298 K using equation 2.3-3, and the Berthelot equation of state to correct for the non-ideality of the gas. Hieber(2) reported a calculated value of 10.2 kcal/mole at 23 C. A value of 10.38 kcal/mole was obtained at 298 K using equation 2.3-1 and the Clapeyron equation

$$\Delta H_v = T, ^\circ K(V_g - V_\ell)\frac{dp}{dt}$$

and at the NBP (387.37 K) a value of 9.34 kcal/mole is obtained which gives a Trouton constant of 24.1.

2.3.6 LOGISTICS OF HYDRAZINE

2.3.6.1 Manufacture

Quantity manufacture of hydrazine is accomplished by the modified Raschig process. This is essentially a two-step process where initially an excess of ammonia is reacted with sodium hypochlorite to form chloramine:

$$NH_3 + NaO\,Cl \rightarrow + NaOH$$

The chloramine reacts with excess ammonia to form hydrazine.

$$NH_2Cl + NH_3 + NaOH \rightarrow N_2H_4 + Na\,Cl + H_2O$$

The second reaction is slow compared to the first and is run at about 130 C to increase the conversion of chloramine to hydrazine. With a large excess of ammonia (20:1 to 30:1) to react with any chloramine the oxidation of hydrazine by chloramine is minimized.

The reaction liquor is passed into ammonia recovery columns and the ammonia separated by distillation and liquified for reuse. The hydrazine solution is further evaporated to remove sodium chloride and sodium hydroxide. A three-stage fractionation column is used to remove the water and give a yield of 98% or better anhydrous hydrazine.

2.3.6.2 Analysis

Hydrazine assay can be determined by direct titration with potassium iodate (KI_3) in the presence of concentrated hydrochloric acid. The procedure is straightforward. The sample is placed in a glass stoppered flask and concentrated HCl (12N) is added to 20% more than the equal volume of hydrazine. A small quantity of carbon tetrachloride (5 ml) is added before titration with a standard potassium iodate solution. The iodate is added until the dark brown color changes to a light yellow. At this point, drop by drop titration with vigorous shaking is done until the end point is reached. The solution will be a light yellow at the end point. If a potentiometer is used, the end point occurs in the range of 0.67 to 0.70 volt where the potential increases very sharply at the exact end point.

The water content and other soluable impurities would be found by volume differences. The most accurate method of determining water content would be by gas chromatography. According to revision B of the specification, the maximum allowable water and soluble impurities is 2.5 weight %. The density of liquid propellant hydrazine at 25 C (77 F) shall be 1.004 ±0.002 g/cc. Revision C of the military specification dated May 1969 calls out the use of gas Chromatography for analysis. The maximum impurity was changed to 2.0% and density is no longer a requirement.

2.3.6.3 Cost and Availability

The principal supplier of anhydrous hydrazine in this country is Olin Mathieson Chemical Corporation with the hydrazine plant located at Lake Charles. Louisiana. The raw materials for the manufacture of hydrazine are readily available in large quantities. The quantity of hydrazine is then dependent upon manufacturing facilities. The Lake Charles plant has a nominal capacity of two million pounds per year. A government-owned plant in Virginia has a potential capacity of approximately 16 million pounds per year(52).

In a recent communication(53) from Olin Mathieson, the price of propellant grade anhydrous hydrazine was quoted at $2.95/pound in quantities over five 55-gallon drums. Other prices are shown in the table below. In large quantities, the potential cost of hydrazine has been estimated(52) to be as low as $0.50 per pound.

Container	Quantity	Price*
1-lb bottle	Any	$10.00/lb
5-lb bottle	Any	$5.00/lb
30-gal (240 lb) s.s. drum	Any	$3.25/lb + $100 deposit/drum
55-gal (440 lb) s.s. drum	1 to 4	$3.15/lb + $100 deposit/drum
	5-113	$2.95/lb + $100 deposit/drum

*F.O.B. Lake Charles, La.

Although hydrazine has a number of uses (silver plating, fluxes, boiler scale prevention, etc.), the principal use is as a rocket fuel.

2.3.6.4 Shipping and Transportation

For complete and detailed laws concerning the shipment of anhydrous hydrazine the government Code of Federal Regulations should be consulted:

> General Services Administration National Archives and Records Service, Federal Register Div., "Code of Federal Regulations", Title 49 Parts 71 to 90.

Hydrazine is classified by the ICC as a corrosive liquid and requires a white label during shipment.

Hydrazine must be packed in containers covered by the following ICC specifications:

(1) ICC1D: boxed glass carboys.
(2) ICC15A, 15B or 15C: wooden boxes with inside containers of glass bottles not exceeding one gallon each. The glass should be cushioned with vermiculite and covered with tightly closed tin cans.
(3) ICC5, 5A, 5C and 17E: metal drums constructed of 304 or 347 stainless steel.
(4) ICC 103-W: tank cars constructed of 304 or 347 stainless steel with molybdenum content not to exceed 1/2%. Vapor space in tank must be filled with nitrogen gas at atmospheric pressure.
(5) ICC 103A-A1-W: tank cars (aluminum) vapor space to be padded with nitrogen gas at atmospheric pressure.

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2.4 MMH

2.4.1 PROPERTY SUMMARY SHEET

Chemical Name: Methylhydrazine **Common Name:** MMH (Monomethylhydrazine)

Chemical Formula: $CH_3N_2H_3$ **Formula Weight:** 46.0724 (C^{12}), 46.075 (O^{16})

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	220.78	°K			
	-52.37	°C			
	397.40	°R			
	-62.27	°F			
HEAT OF FUSION	2.4905	kcal/mole	220.78	4	
	97.231	BTU/lb	(MP)		
NORMAL BOILING POINT	360.80	°K			
	87.65	°C			
	649.44	°R			
	189.77	°F			
HEAT OF VAPORIZATION	9.648	kcal/mole	298.15	4	
	376.9	BTU/lb			
TROUTON CONSTANT	24.6	-		calc.	
CRITICAL STATE CONSTANTS					
Temperature	585	°K		3	
	312	°C			
	1053	°R			
	593	°F			
Pressure	81.3	atms		3	
	1195	psia			
Density	0.29	g/cc			
	18.10	lb/ft^3		3	
VAPOR PRESSURE OF LIQUID	49.47	mm Hg	298	3, 4	2.4-1
	0.957	psia			2.4-2
DENSITY OF LIQUID	.8702	g/cc	298	1, 2, 3, 20, 21	2.4-3
	54.325	lb/ft^3			2.4-4
SONIC VELOCITY	1548	m/sec	298	24	2.4-5
	5079	ft/sec			
COMPRESSIBILITY OF LIQUID					
ADIABATIC	4.88×10^{-5}	atm^{-1}	298	24	2.4-6
	3.32×10^{-6}	psi^{-1}			
ISOTHERMAL	5.89×10^{-5}	atm^{-1}	348	3	2.4-7
	4.01×10^{-6}	psi^{-1}			
VISCOSITY OF LIQUID	.775	centipoise	298	2, 3	2.4-8
	5.21×10^{-3}	$lb_m/ft\text{-}sec$			
HEAT CAPACITY OF LIQUID	.7002	cal/g-°K	298	4, 19	2.4-12
	.6998	BTU/lb-°R			
THERMAL CONDUCTIVITY OF LIQUID	5.92×10^{-4}	cal/cm-sec°K	298	19	2.4-10
	3.98×10^{-5}	BTU/ft-sec-°R			
SURFACE TENSION	33.83	dynes/cm	298	3	2.4-9
	2.318×10^{-3}	lb_f/ft			
PARACHOR	127.7	-	298	calc.	
DIPOLE MOMENT	1.68 ±.14	Debyes	288	23	
DIELECTRIC CONSTANT	19.2	-	289.8		
	17.3	-	325.4	25	
ENTHALPY OF LIQUID	39.66	cal/mole-°K			
	0.861	BTU/lb-°R	298	4	
ENTROPY OF REAL GAS	72.02	cal/mole-°K	298	4	
	1.563	BTU/lb-°R			
HEAT OF FORMATION	13.106	kcal/mole	298	4	
	511.67	BTU/lb			

2.4.2 GENERAL

2.4.2.1 Introduction

Monomethylhydrazine (MMH) is one of the many hydrazine derivatives: it can be synthesized in the laboratory by direct methylation of hydrazine with dimethyl sulfate, or by methylation of the neutral salt hydrazine sulfate with dimethyl sulfate. It is a clear, colorless, hygroscopic liquid with the ammoniacal odor generally characteristic of amines (6), (8).

The use of MMH as a fuel for rocket engines is very promising. Its performance is slightly below that of hydrazine, but it is much superior to hydrazine with respect to freezing point, stability, storage and as a coolant.

MMH is an excellent fuel for use with both oxygen and fluorine-containing oxidizers. Optimum performance can be achieved by oxidation of the carbon to CO or CO_2; this also eliminates the formation of undesirable solid carbon in the products of combustion. With fluorine oxidizers it is desirable to add a sufficient quantity of oxygen to the system in order to oxidize the carbon.

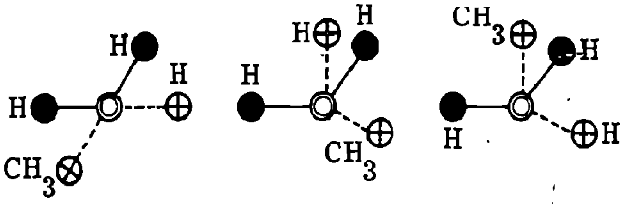
MMH has a positive heat of formation and is an interesting candidate for use as a monopropellant. Its use with present catalysts is, however, not promising since its decomposition can lead to the formation of carbon and polymeric materials which would poison or mask a catalytic surface.

The procurement of MMH as a propellant is covered by MIL-P-27404A, dated May 1969.

2.4.2.2 Structure of Methylhydrazine

The methylhydrazine molecule has three possible theroretical configurations as a result of rotational isomerisms. A single trans and two skew forms are hypothesized. The trans form appears to be unfavorable by anology with the hydrazine molecule. The skew configuration with the methyl group farthest from the hydrogens of the amine group is called the "outer". Conversely, the other skew form is called the "inner". From a steric consideration, the "outer" form is more stable and hence is predominant.

The angles of the molecule are assumed to be tetrahedral by Aston (13). The bond distances are: N-N, 1.45 Å; N-C, 1.47 Å; N-H, 1.04 Å; C-H, 1.09 Å. The product of the principal moments of inertia is 1.803 x 10^{-115} g cm^2 and the reduced moments are 4.32 x 10^{-40} and 2.85 x 10^{-40} g cm^2, respectively, for the methyl and amine groups. Janz (26) has depicted the three theoretical configurations of MMH as:



I. (Trans) II. Outer Skew III. Inner Skew

2.4.3 PHYSICAL PROPERTIES OF MMH

2.4.3.1 Vapor Pressure and Normal Boiling Point.

Precise vapor pressure measurements of liquid MMH were made in 1951 by Aston (4) but only a few determinations were made over a narrow temperature range up to 25 C (77 F) where the vapor pressure is less than 1 psia. Aerojet (3) extended this temperature range to near the normal boiling point. A few additional pressures were also obtained by Aerojet at elevated temperatures.

The experimental data from both investigations are plotted in Figures 2.4-1 and 2.4-1a. The data are smoothly joined by the least-squares method and equation 2.4-1 was found to best describe the data.

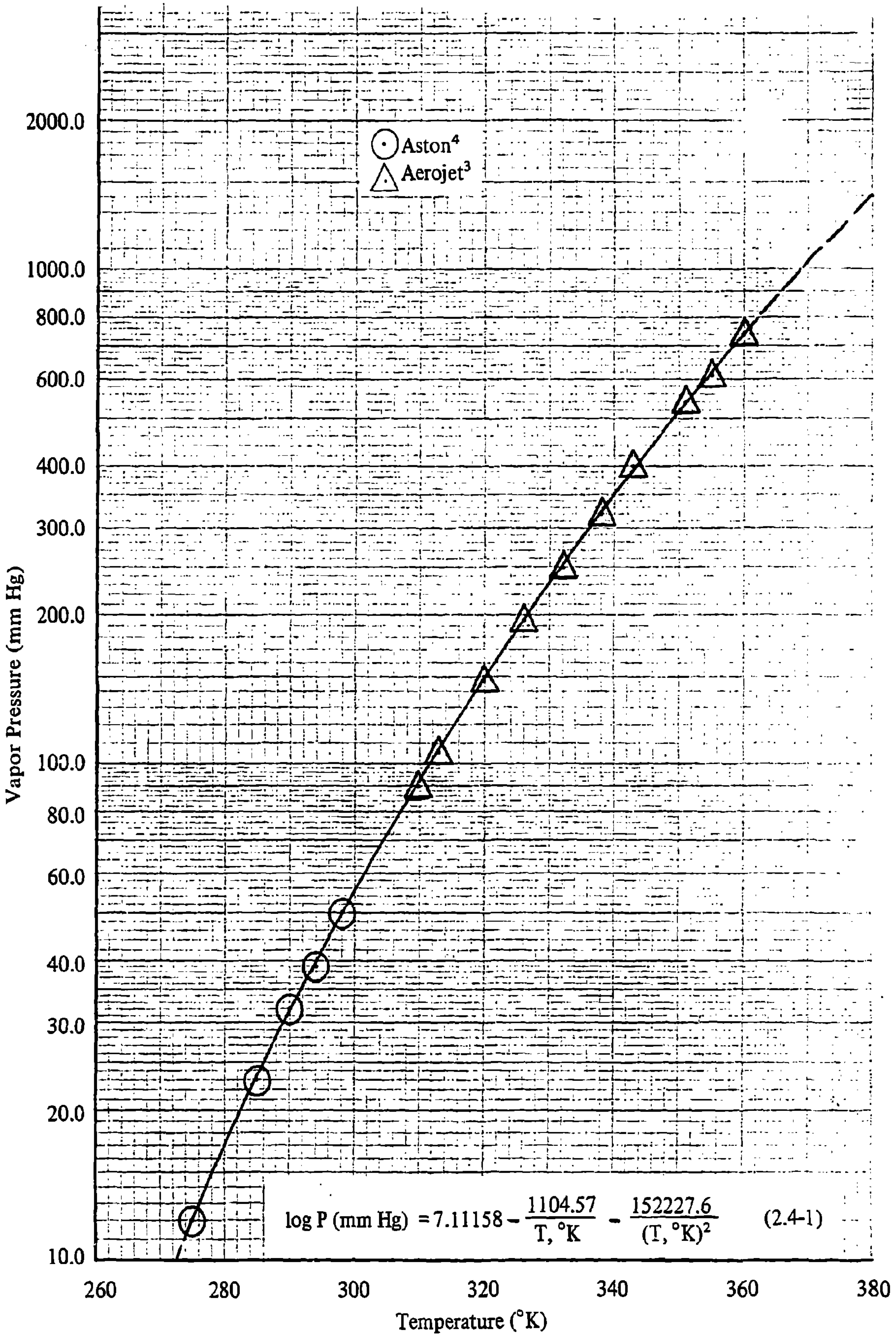
$$\log_{10} P(\text{mmHg}) = 7.11158 - \frac{1104.571}{(T, K)} - \frac{152227.6}{(T,K)^2} \qquad (2.4\text{-}1)$$

$$\log_{10} P(\text{psia}) = 5.39797 - \frac{1988.229}{(T, R)} - \frac{493216.9}{(T, R)^2} \qquad (2.4\text{-}1a)$$

The standard deviation calculated from equation 2.4-1 is 1.28 mm Hg and the average deviation is 0.40%.

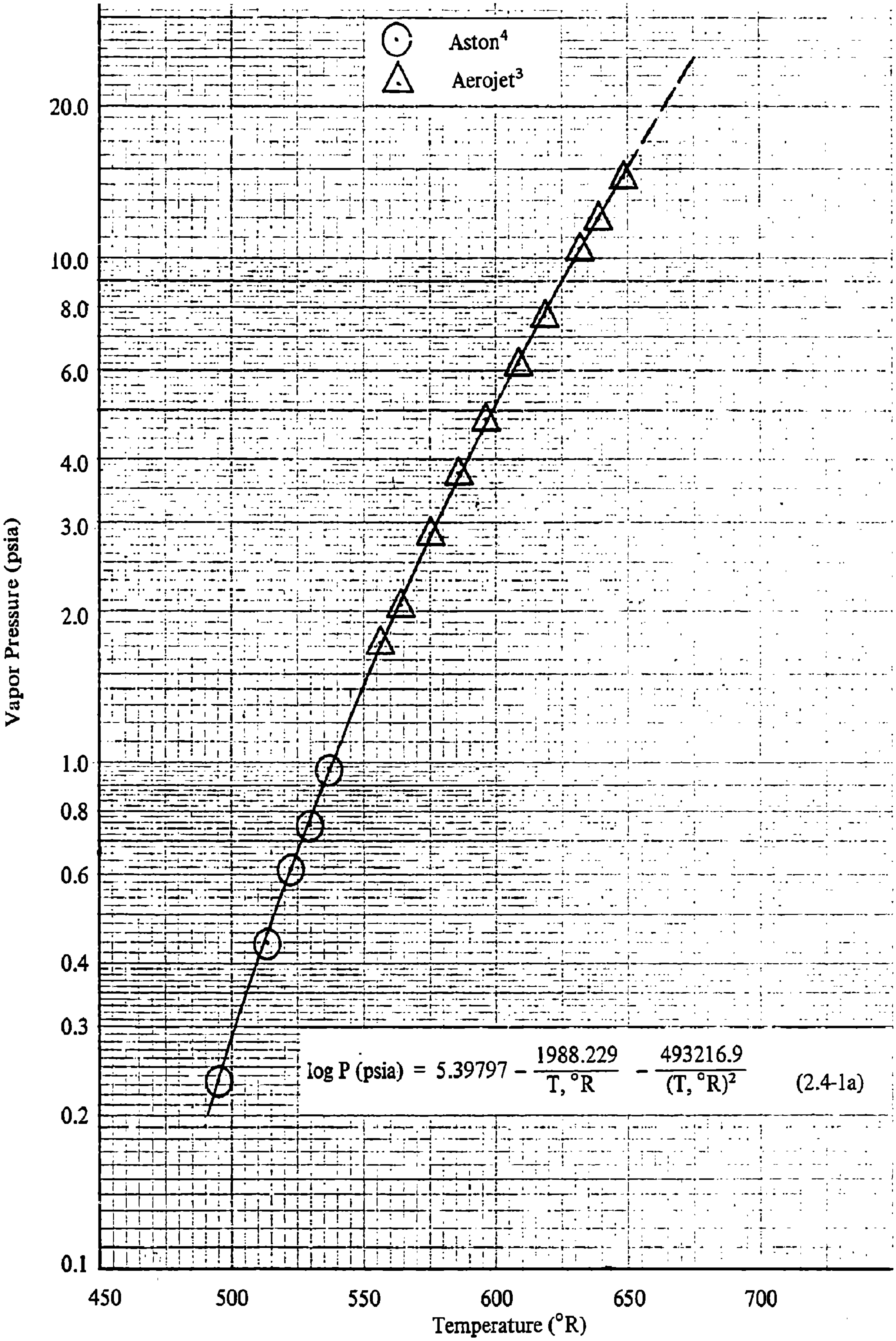
From equation 2.4-1 a normal boiling point value of 360.80 K (87.65 C or 189.78 F) is obtained. Aerojet (3) reports values of 89.5 C and 192.5 F (which are not equal) and Aston (4) is given as the reference. The Liquid Propellant Manual (6) reports the same temperatures given by Aerojet and also uses Aston as the reference. Aston, however, does not report a boiling point and the vapor pressure equation reported is only applicable for a range between 12 and 50 mm Hg. Harshman (5) reports an unreferenced value of 87.5 (189.5 F) which compares favorably to the value selected here.

The Aerojet (3) study also included a few vapor pressure readings above one atmosphere pressure. These points are shown in Figures 2.4-2 and 2.4-2a. Equation 2.4-2 was



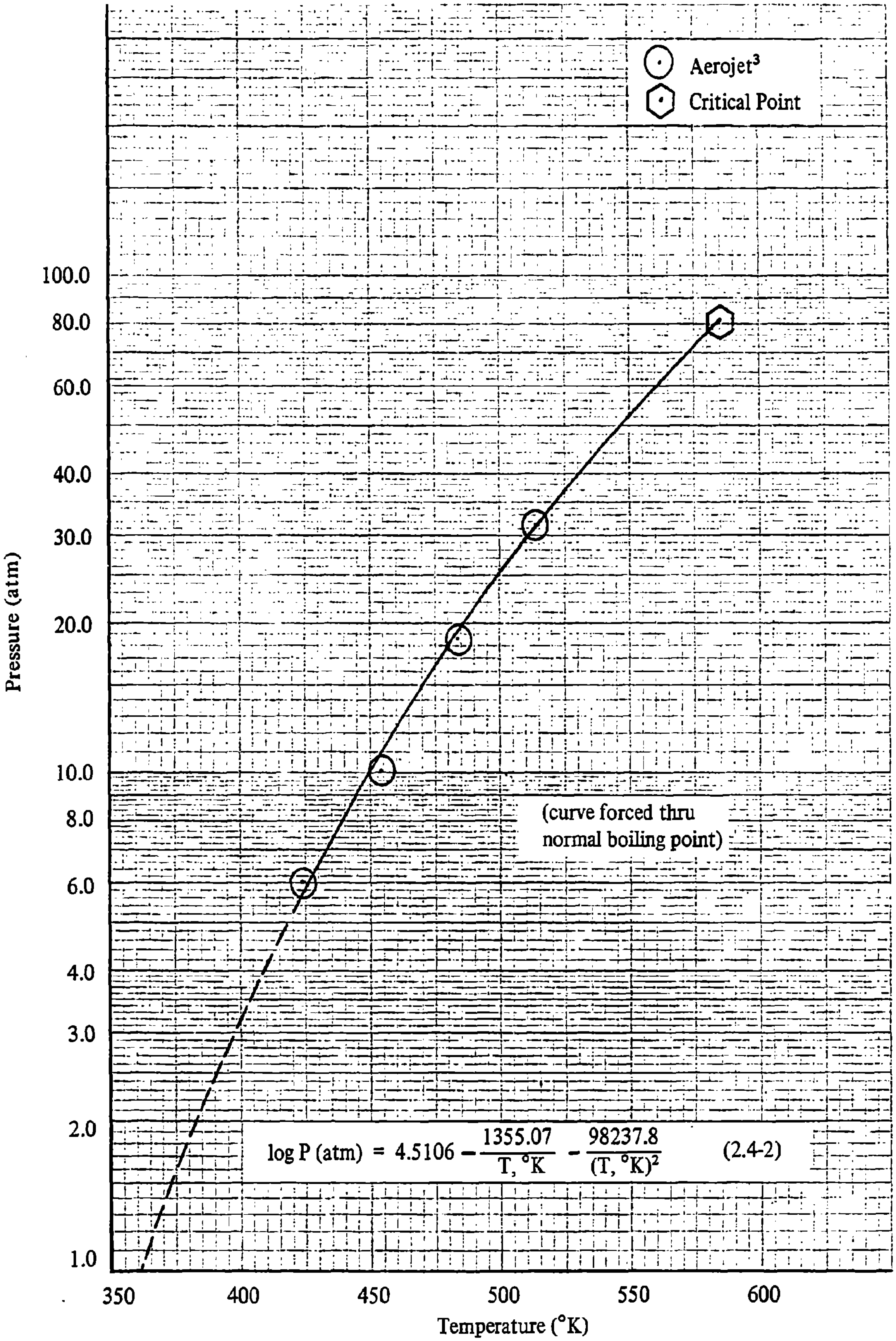
$$\log P\ (\text{mm Hg}) = 7.11158 - \frac{1104.57}{T,\ ^{\circ}K} - \frac{152227.6}{(T,\ ^{\circ}K)^2} \qquad (2.4\text{-}1)$$

Figure 2.4-1. Vapor Pressure versus Temperature, Liquid MMH



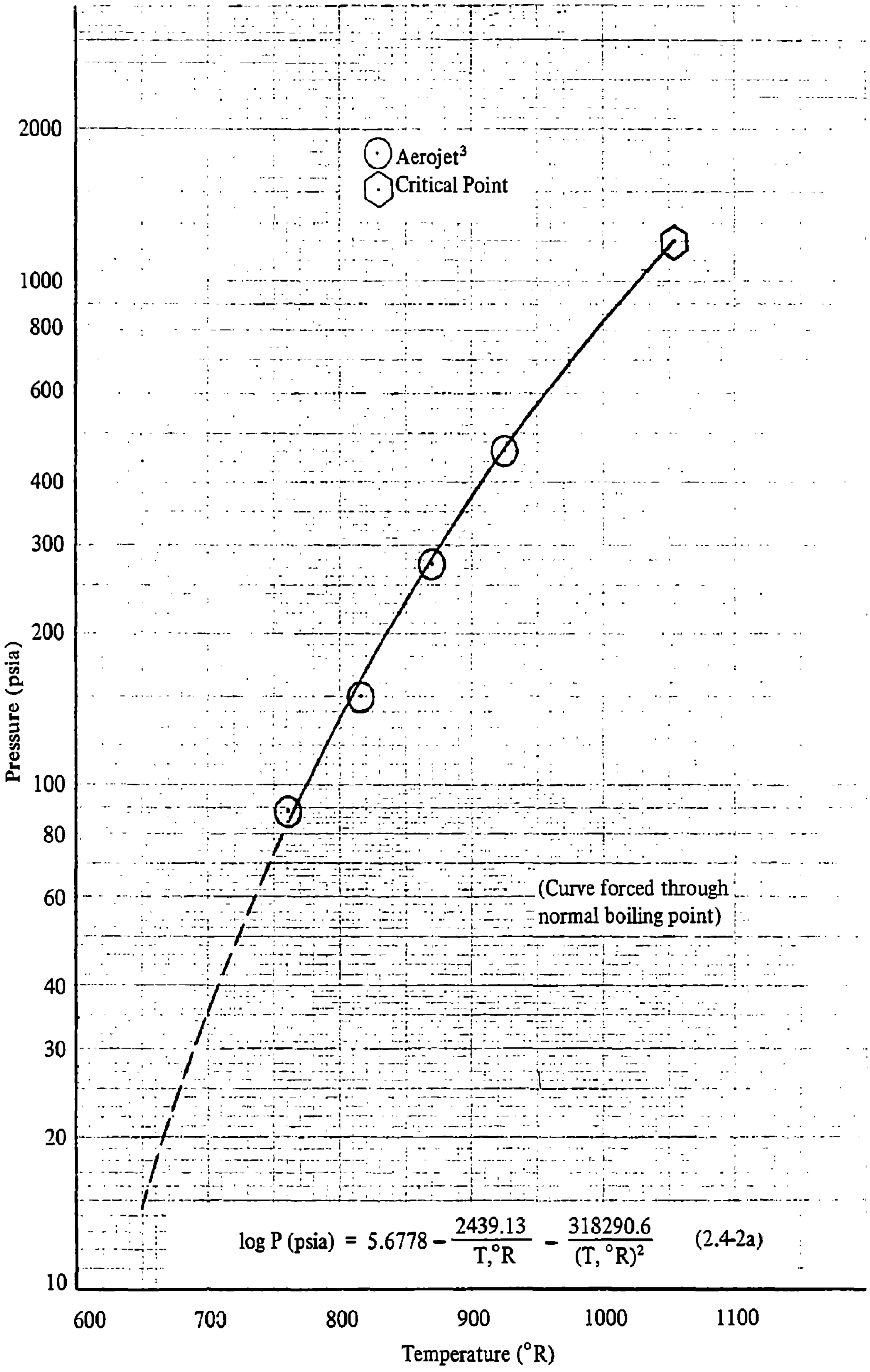
$$\log P\ (\text{psia}) = 5.39797 - \frac{1988.229}{T,\ ^\circ R} - \frac{493216.9}{(T,\ ^\circ R)^2} \qquad (2.4\text{-}1a)$$

Figure 2.4-1a. Vapor Pressure versus Temperature, Liquid MMH



$$\log P\,(\text{atm}) = 4.5106 - \frac{1355.07}{T,\,{}^\circ K} - \frac{98237.8}{(T,\,{}^\circ K)^2} \qquad (2.4\text{-}2)$$

Figure 2.4-2. Vapor Pressure versus Temperature, Liquid MMH (Elevated Temperature)



$$\log P\,(\text{psia}) = 5.6778 - \frac{2439.13}{T,{}^{\circ}R} - \frac{318290.6}{(T,{}^{\circ}R)^2} \qquad (2.4\text{-}2a)$$

Figure 2.4-2a. Vapor Pressure versus Temperature, Liquid MMH (Elevated Temperatures) derived from these points plus the critical point and by forcing the curve through the normal boiling point in order to provide continuity with the lower temperature range data given in Figure 2.4-1.

$$\log_{10} P(\text{atm}) = 4.5106 - \frac{1355.07}{T, {}^{\circ}K} - \frac{98237.8}{(T, {}^{\circ}K)^2} \qquad (2.4\text{-}2)$$

$$\log_{10} P(\text{psia}) = 5.6778 - \frac{2439.13}{T, {}^{\circ}R} - \frac{318290.6}{(T, {}^{\circ}R)^2} \qquad (2.4\text{-}2a)$$

2.4.3.2 Density of Liquid MMH

The density of saturated liquid MMH has been studied by Aerojet (1, 3), Metalectro (2), Rocketdyne (20) and Ahlert (21). A temperature range from near the melting point (-52.4 C) to 84 C was covered by these investigations. In general, the agreement between the various studies is only fair as shown in Figures 2.4-3 and 2.4-3a.

The Aerojet (1) study covered a temperature range from -51 to +14 C (-59.8 to +57.2 F) and a single pycnometer constructed from a capillary tube of known diameter was used. The purity of the MMH sample was not given. Two additional measurements at higher temperatures were reported by Aerojet (3) in a separate study. There is some question as to whether these measurements were made at the saturation pressure. The Metalectro study covered a temperature range from the melting point to 25 C. The sample was reported to have a high purity but the exact compositions were not given. A dilatometer calibrated with methanol was used.

The recent work reported by Rocketdyne (20) covered a wide temperature range from the melting point to 84 C. Propellant grade MMH was used with the analysis showing 0.5 weight % water. A Poole-Nyberg densimeter was used. The recent study of Ahlert and Shimalla (21) reported in the open literature covered a temperature range from 30 to 70 C (86 to 158 F). A minimum purity of 99.5 weight % was reported. The data were obtained using pycnometers calibrated with distilled water. It is not clear how many pycnometers were used but the plural terminology was used. The authors estimate the total error to be one part in ten thousand.

The variation of density with temperature from -52 to +84°C was found to be well described by the linear expression

$$\rho\,(\text{g/cc}) = 1.15034 - 9.3949 \times 10^{-4}\,(T, {}^{\circ}K) \qquad (2.4\text{-}3)$$

$$\rho\,(\text{lb/ft}^3) = 71.8132 - .032584\,(T, {}^{\circ}R) \qquad (2.4\text{-}3a)$$

The standard deviation of the data calculated from the linear fit is 0.0026 g/cc and the average deviation is 0.27% with the maximum of slightly over 0.4%.

The density of the saturated liquid has not been studied at elevated temperatures, but Aerojet (3) has reported the densities at random pressures up to a temperature of 270 C. These densities were corrected to the saturation pressure by estimating the isothermal compressibility from the densities at two different pressures for the same temperature and are shown in Figures 2.4-4 and 2.4-4a. The critical density value of 0.29 g/cc at 312 C given by Aerojet is also shown in Figure 2.4-4 and the estimated saturated densities were smoothly joined to the critical point. The data shown in Figures 2.4-4 and 2.4-4a should be treated as provisional work, but should be a good estimate for use in many engineering applications.

Aerojet (3) also reported densities for the vapor at various pressures. The attempt to correlate the data to saturation pressures gave inconclusive results because of the very high scatter.

2.4.3.3 Sonic Velocity in Liquid MMH

Rocketdyne (24) has recently measured the velocity of sound in liquid propellant grade MMH over a temperature range from -32 to 96 C (-26 to 204 F). The experimental data are plotted in Figures 2.4-5 and 2.4-5a. The variation of sonic velocity with temperature is adequately described by the linear relationship

$$c\,(\text{m/sec}) = 2711.6 - 3.903\,(T, K) \qquad (2.4\text{-}4)$$

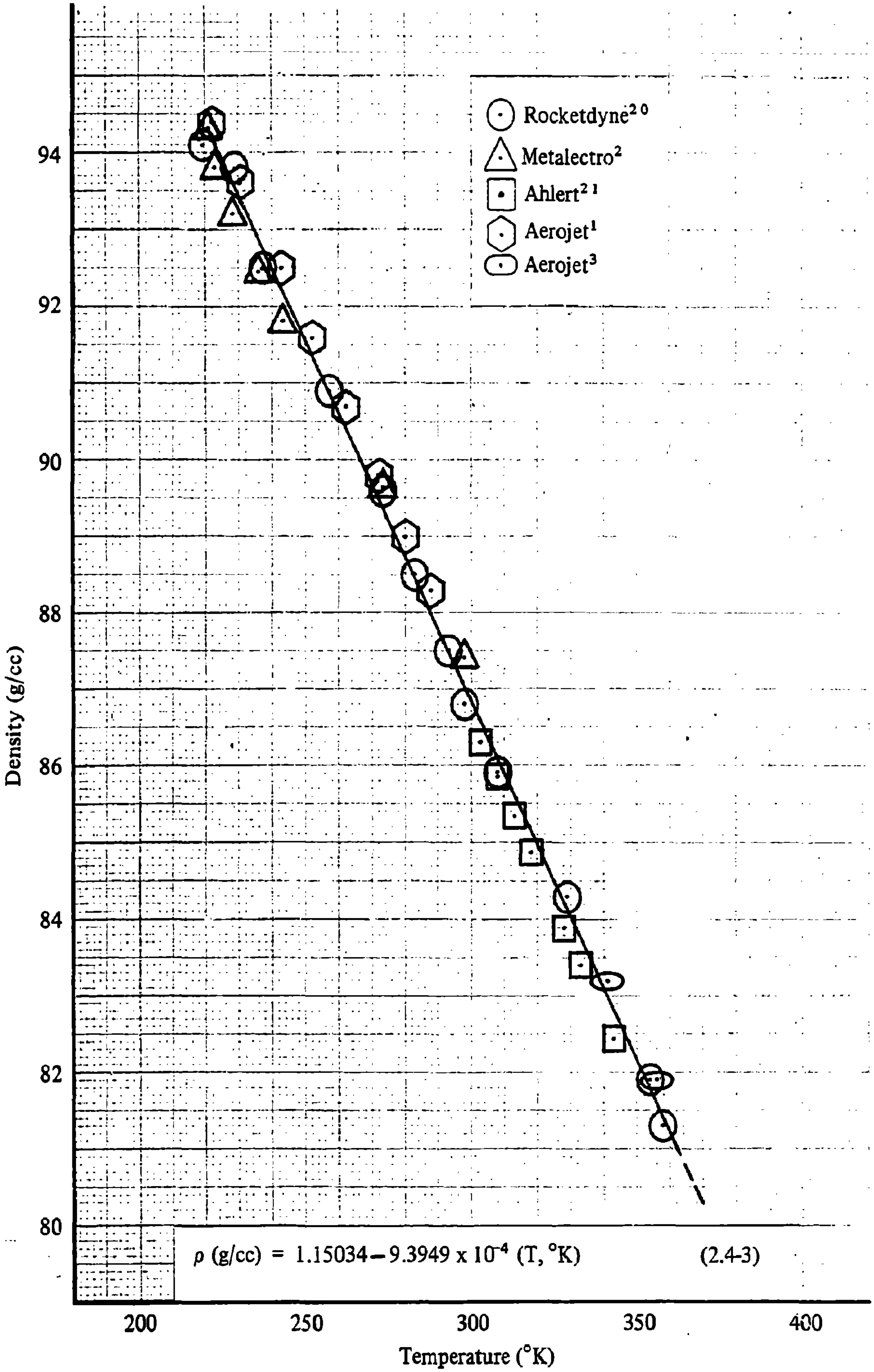
$$c\,(\text{ft/sec}) = 8896.4 - 7.114\,(T, R) \qquad (2.4\text{-}4a)$$

The standard deviation of the experimental from the smoothed data is 4.1 m/sec and the average deviation is 0.2%. The apparatus and methods used by Rocketdyne are briefly discussed in Section 2.6.3.3.

2.4.3.4 Compressibility of Liquid MMH

The sonic velocity in liquid MMH has recently been measured by Rocketdyne (24) and the data are given in section 2.4.3.3 above. The adiabatic compressibility (β_a) can be determined using sonic velocity data and the acoustical equation

$$\beta_a = \frac{1}{\rho c^2}$$



ρ (g/cc) = 1.15034 − 9.3949 x 10^{-4} (T, °K) (2.4-3)

Figure 2.4-3. Density versus Temperature, Saturated Liquid MMH

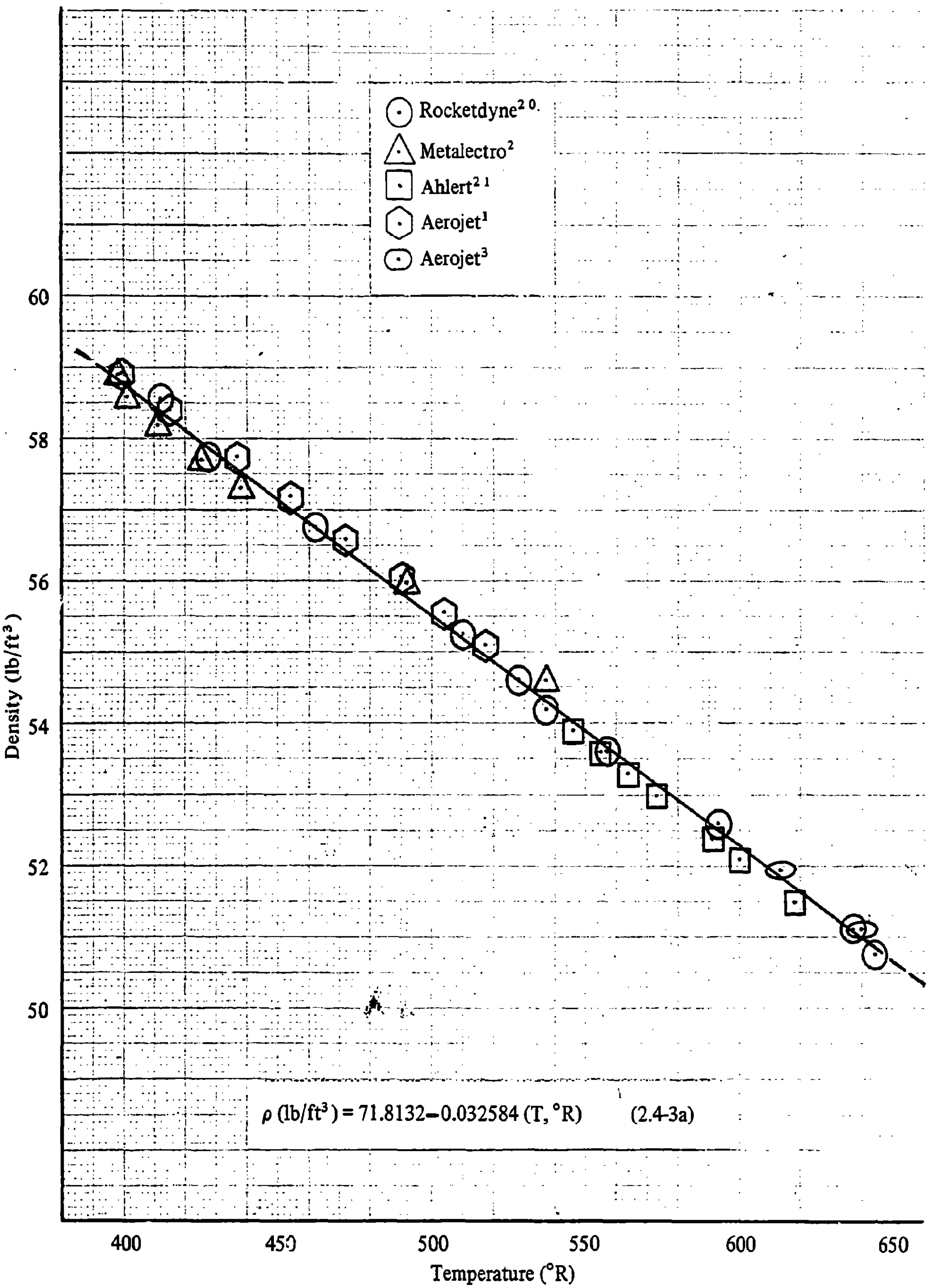


Figure 2.4-3a. Density versus Temperature, Saturated Liquid MMH

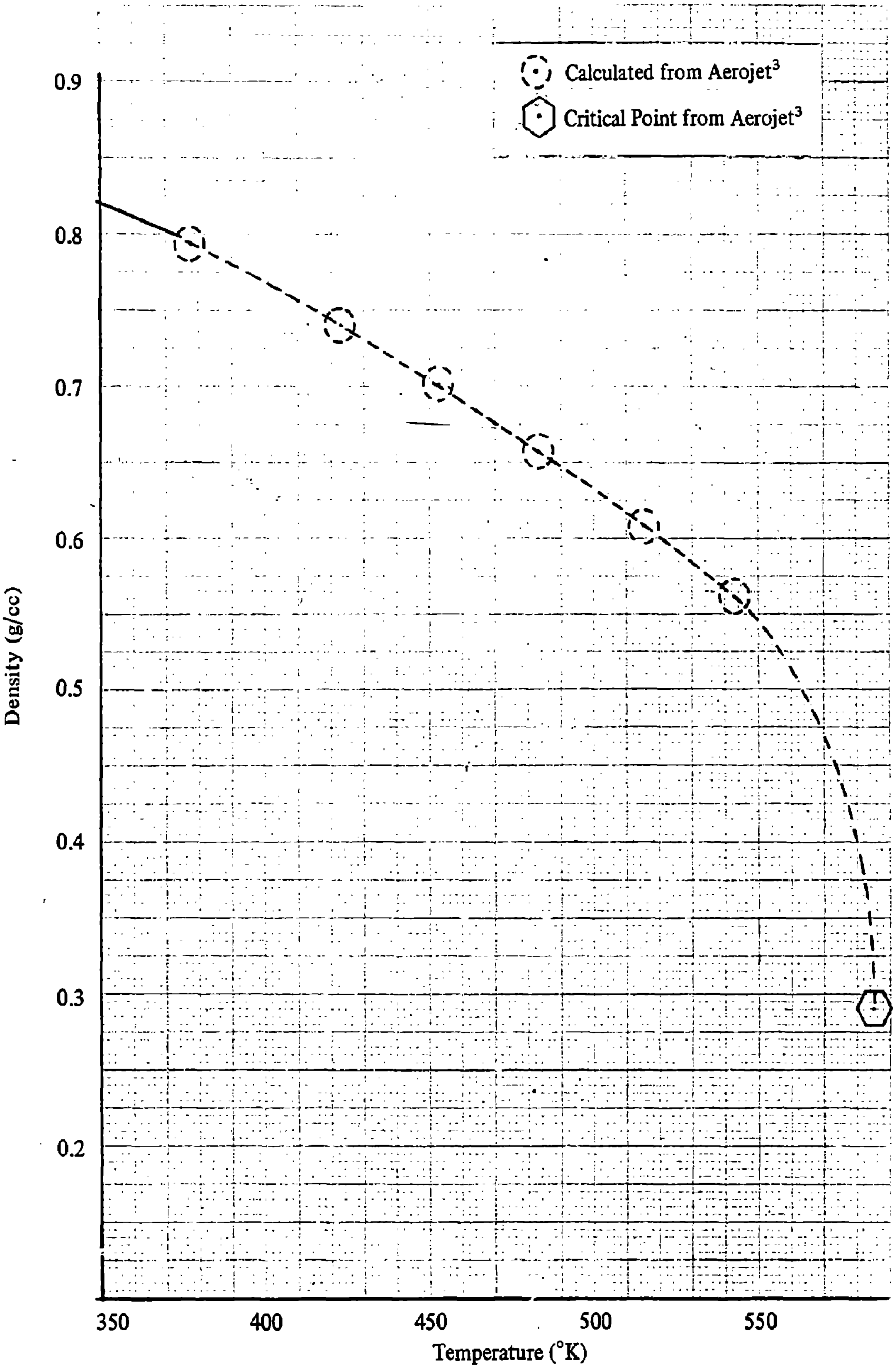


Figure 2.4-4. Density versus Temperature, Saturated Liquid MMH (Elevated Temperatures)

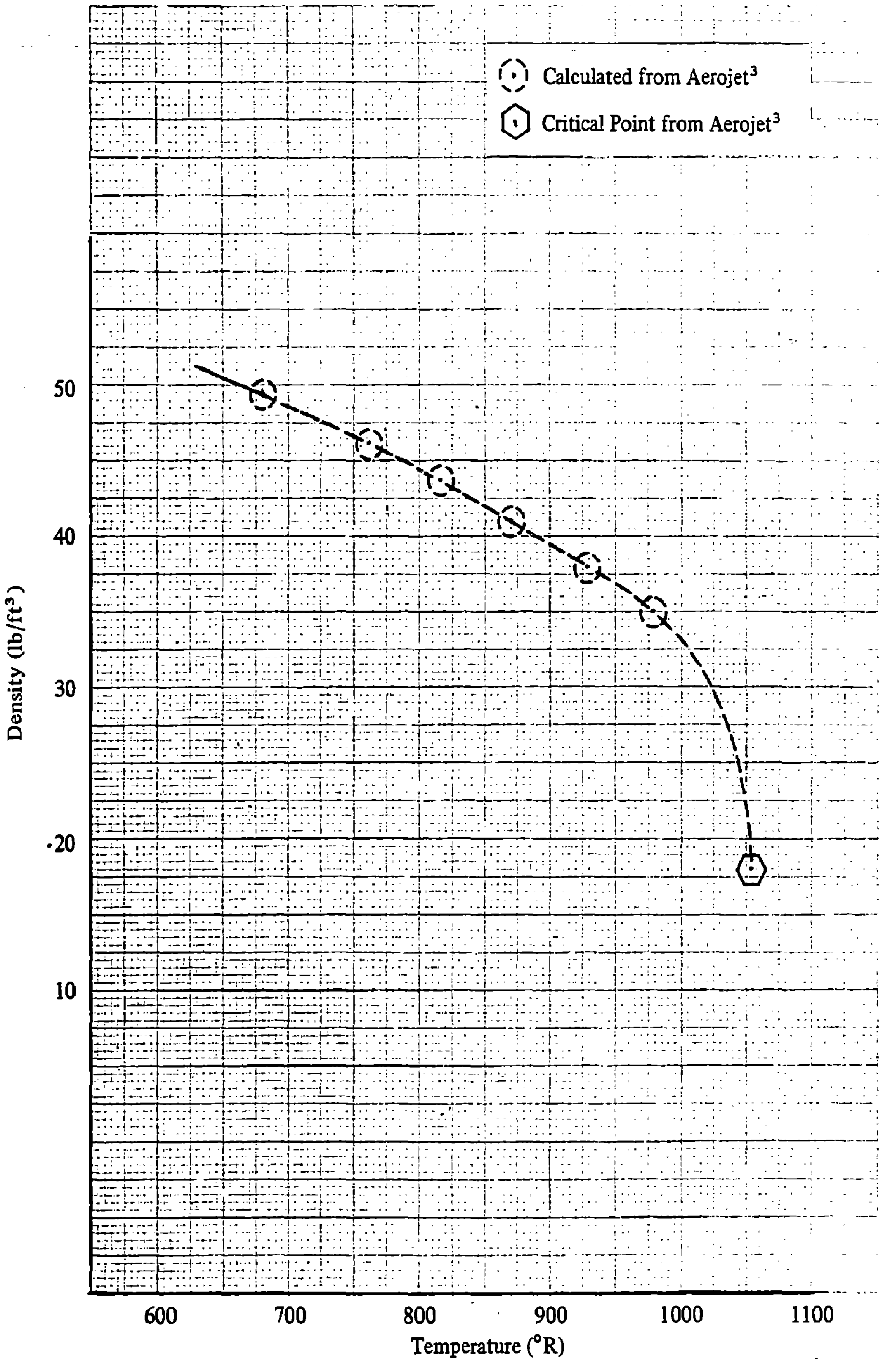


Figure 2.4-4a. Density versus Temperature, Saturated Liquid MMH (Elevated Temperatures)

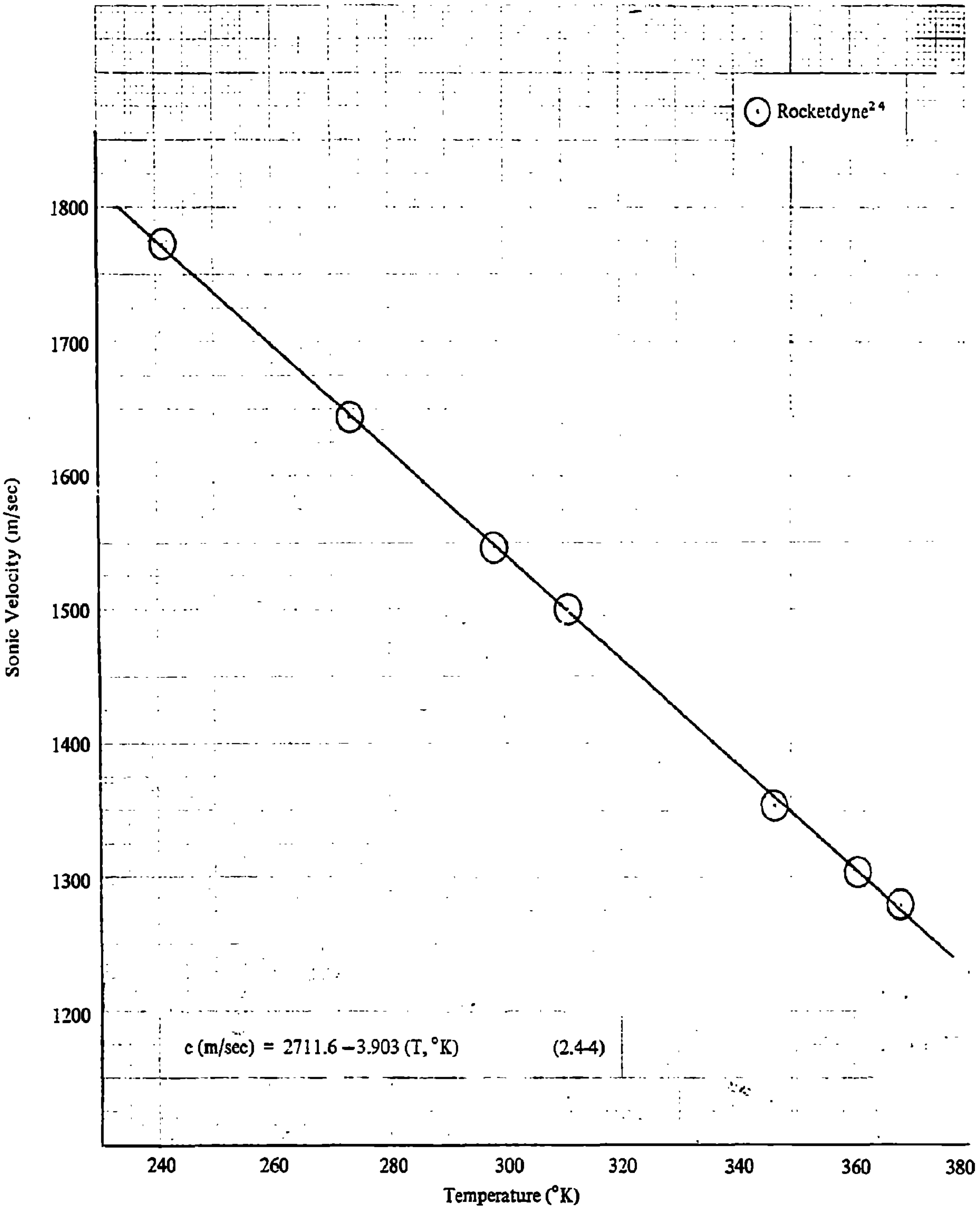
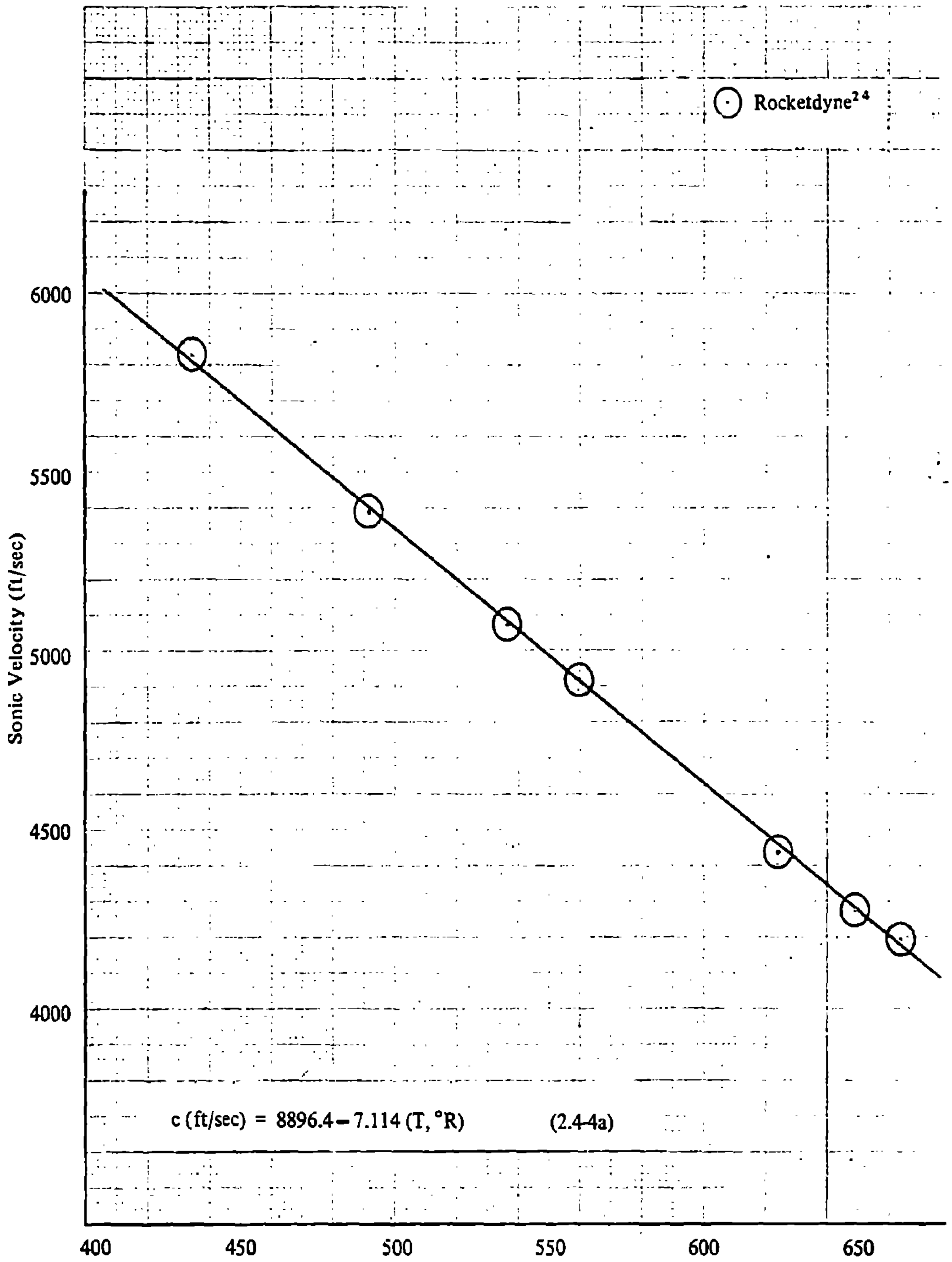


Figure 2.4-5. Sonic Velocity in Liquid MMH versus Temperature



$$c\ (\text{ft/sec}) = 8896.4 - 7.114\ (T, {}^\circ R) \qquad (2.4\text{-}4a)$$

Figure 2.4-5a. Sonic Velocity in Liquid MMH versus Temperature where

ρ = density
c = sonic velocity

The compressibilities were computed at the experimental temperatures for sonic velocity. The density for each temperature was obtained for equation 2.4-3. The calculated compressibility data is shown in Figures 2.4-6 and 2.4-6a.

The change in compressibility with temperature is described by

$$\beta_a\ (\text{atm}^{-1}) = 3.0413 \times 10^{-5} - 2.1258 \times 10^{-7}\ (\text{T}, {}^\circ\text{K}) + 9.194 \times 10^{-10}\ (\text{T}, {}^\circ\text{K})^2 \qquad (2.4\text{-}5)$$

$$\beta_a\ (\text{psi}^{-1}) = 2.0695 \times 10^{-6} - 8.0361 \times 10^{-9}\ (\text{T}, {}^\circ\text{R}) + 1.9310 \times 10^{-11}\ (\text{T}, {}^\circ\text{R})^2 \qquad (2.4\text{-}5a)$$

The standard deviation of the experimental data compared to the least-squares curve fit is 6.76×10^{-7} atm^{-1} and the average deviation is 0.83%.

Aerojet (3) has reported density values over a temperature range from 67.5 to 270°C (154 to 518°F). At each selected temperature the density was obtained for at least two different pressures. The isothermal compressibility β_i is calculated from the relation:

$$\beta_i = -\frac{1}{V}\left[\frac{dV}{dP}\right]$$

The calculated compressibilities are plotted in Figures 2.4-7 and 2.4-7a. The calculated values probably have large errors since the absolute density change is quite small and any small errors in density are magnified in computing the isothermal compressibility. The derived data can best be represented as a linear function of temperature by

$$\beta_i\ (\text{atm}^{-1}) = 2.133 \times 10^{-6}\ (\text{T}, {}^\circ\text{K}) - 6.727 \times 10^{-4} \qquad (2.4\text{-}6)$$

$$\beta_i\ (\text{psi}^{-1}) = 8.063 \times 10^{-8}\ (\text{T}, {}^\circ\text{R}) - 4.577 \times 10^{-5} \qquad (2.4\text{-}6a)$$

The above equations as well as the plotted data should be considered as provisional data only.

2.4.3.5 Viscosity of Liquid MMH

Experimental viscosities for liquid MMH have been reported by both Metalectro (2) and Aerojet (3). Metalectro used carefully purified MMH and employed a Fenske type viscometer modified to prevent air contact. Readings were taken over the temperature range from near the melting point to 25 C. Aerojet reports data from 20 to 80 C (68 to 176 F) using an Ostwald-Fenske viscometer. The purity of the MMH used by Aerojet was not described.

The experimental data is plotted in Figures 2.4-8 and 2.4-8a. The experimental data from the two separate studies can be smoothly joined. At 25 C where the range of two studies overlap the agreement is good. Using the least-squares method, various equations were used to smoothly represent the data. It was found that a cubic equation was required to pass through the points at the extremities of the temperature scale.

$$\log \mu\ (\text{centipoise}) = -7.9944 + \frac{6123.96}{(\text{T}, {}^\circ\text{K})} - \frac{1.7458 \times 10^6}{(\text{T}, {}^\circ\text{K})^2} + \frac{1.8509 \times 10^8}{(\text{T}, {}^\circ\text{K})^3} \qquad (2.4\text{-}7)$$

$$\log \mu\ (\text{lb}_m/\text{ft-sec}) = -11.167 + \frac{11023.1}{(\text{T}, {}^\circ\text{R})} - \frac{5.6565 \times 10^6}{(\text{T}, {}^\circ\text{R})^2} + \frac{1.0794 \times 10^9}{(\text{T}, {}^\circ\text{R})^2} \qquad (2.4\text{-}7a)$$

The standard deviation of the experimental data as determined from equation 2.4-7 was 0.22 centipoise with the average deviation being 1.84%.

2.4.3.6 Surface Tension and Parachor of MMH

The surface tension of liquid MMH has been measured by Aerojet (3) over a temperature range from -40 to 60 C (-40 to 140 F). A capillary rise method was used but the experimental technique and sample purity were not given. The experimental data are plotted in Figures 2.4-9 and 2.4-9a.

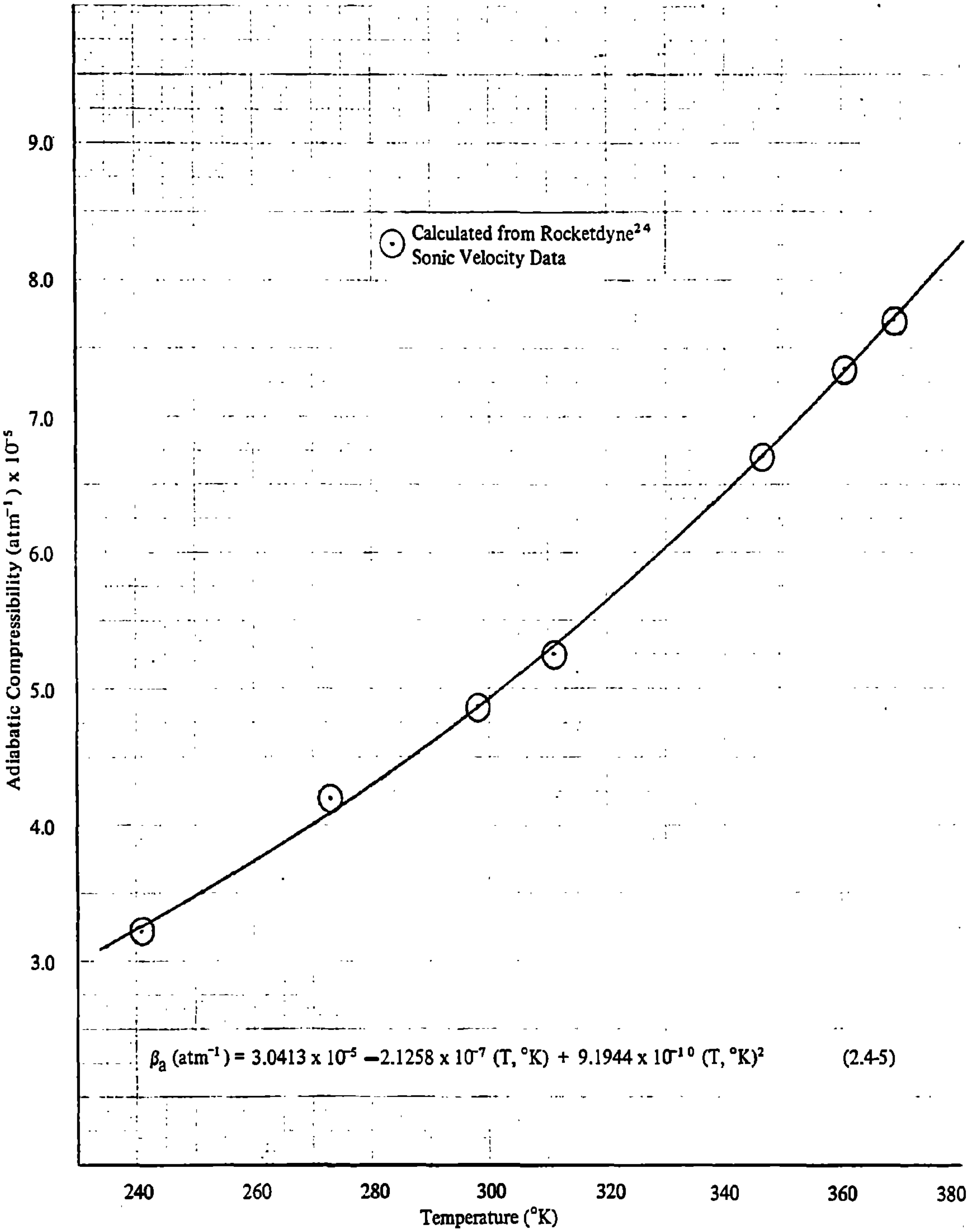
The change in surface tension with temperature is linear and is expressed by

$$\gamma\ (\text{dynes/cm}) = 63.480 - .09944\ (\text{T}, {}^\circ\text{K}) \qquad (2.4\text{-}8)$$

$$\gamma\ (\text{lb}_f/\text{ft}) = 4.3450 \times 10^{-3} - 3.7856 \times 10^{-6}\ (\text{T}, {}^\circ\text{R}) \qquad (2.4\text{-}8a)$$

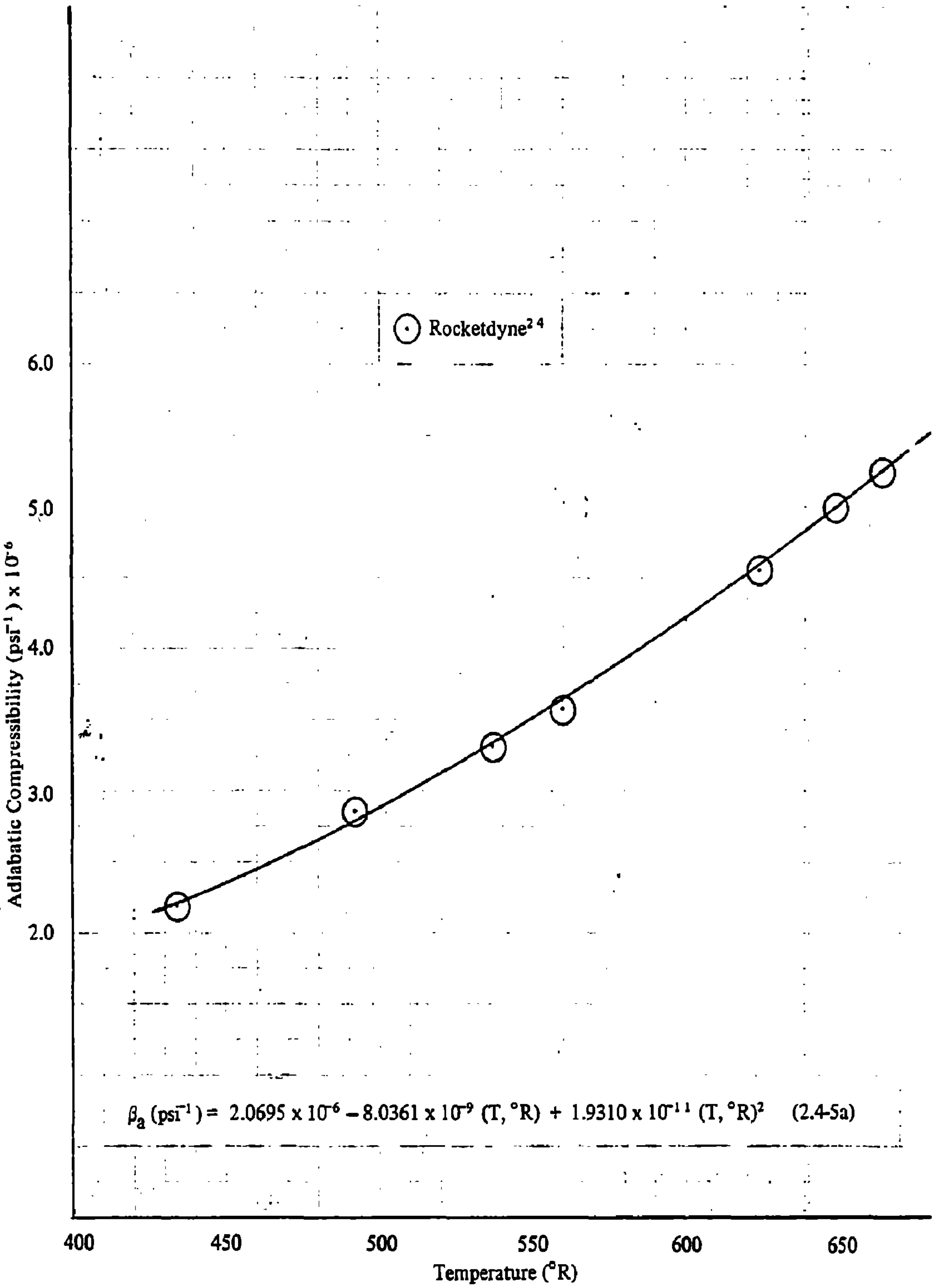
The standard deviation obtained from equation 2.4-8 is 0.16 dynes/cm and the average deviation was calculated to be 0.27%.

The parachor at 25 C was found to be 127.7 from the relation:



$$\beta_a\ (\text{atm}^{-1}) = 3.0413 \times 10^{-5} - 2.1258 \times 10^{-7}\ (T, {}^\circ K) + 9.1944 \times 10^{-10}\ (T, {}^\circ K)^2 \qquad (2.4\text{-}5)$$

Figure 2.4-6. Adiabatic Compressibility versus Temperature, Liquid MMH



$$\beta_a\,(\mathrm{psi}^{-1}) = 2.0695 \times 10^{-6} - 8.0361 \times 10^{-9}\,(T, {}^\circ R) + 1.9310 \times 10^{-11}\,(T, {}^\circ R)^2 \qquad (2.4\text{-}5a)$$

Figure 2.4-6a. Adiabatic Compressibility versus Temperature, Liquid MMH

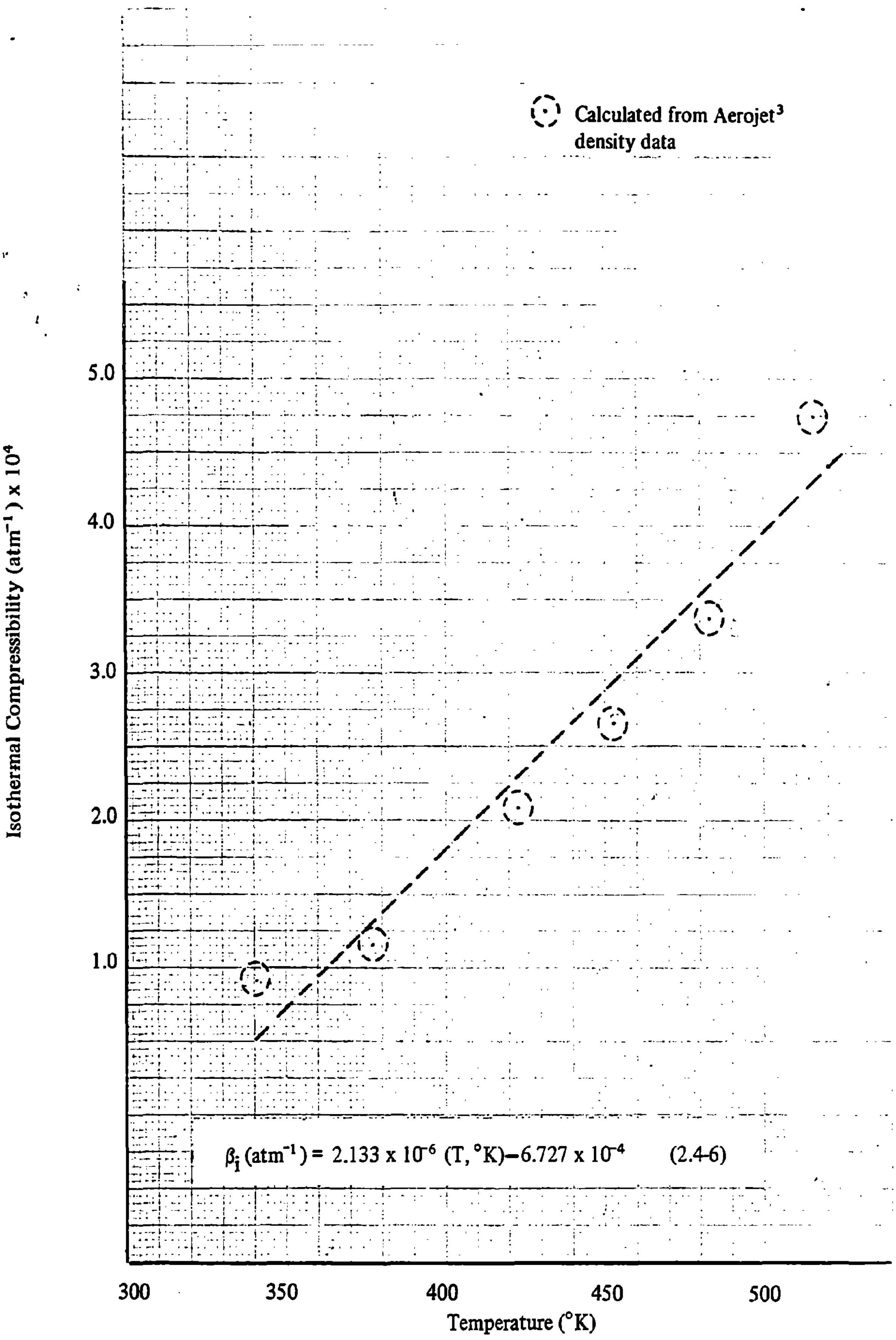


Figure 2.4-7. Isothermal Compressibility versus Temperature, Liquid MMH

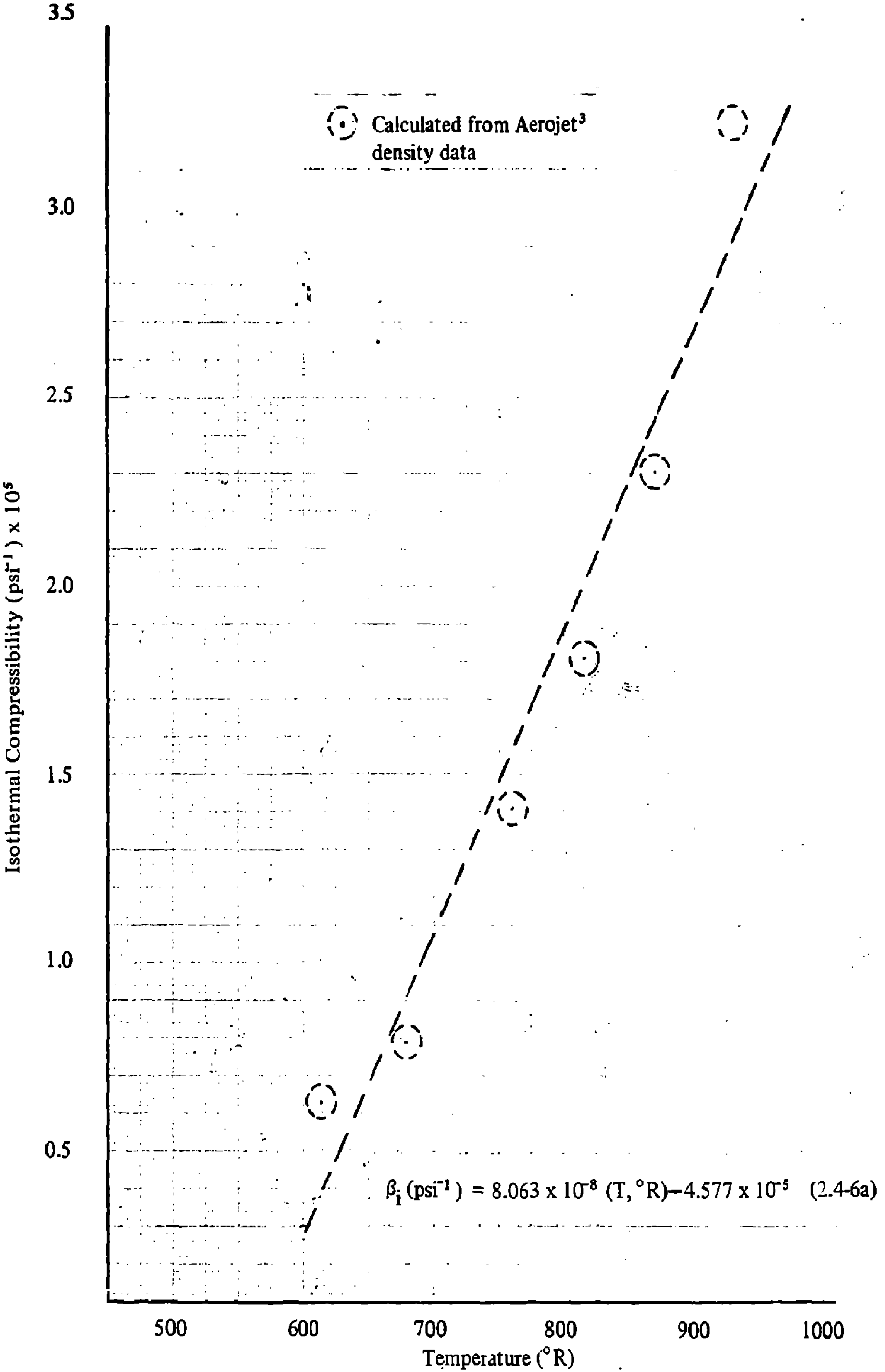
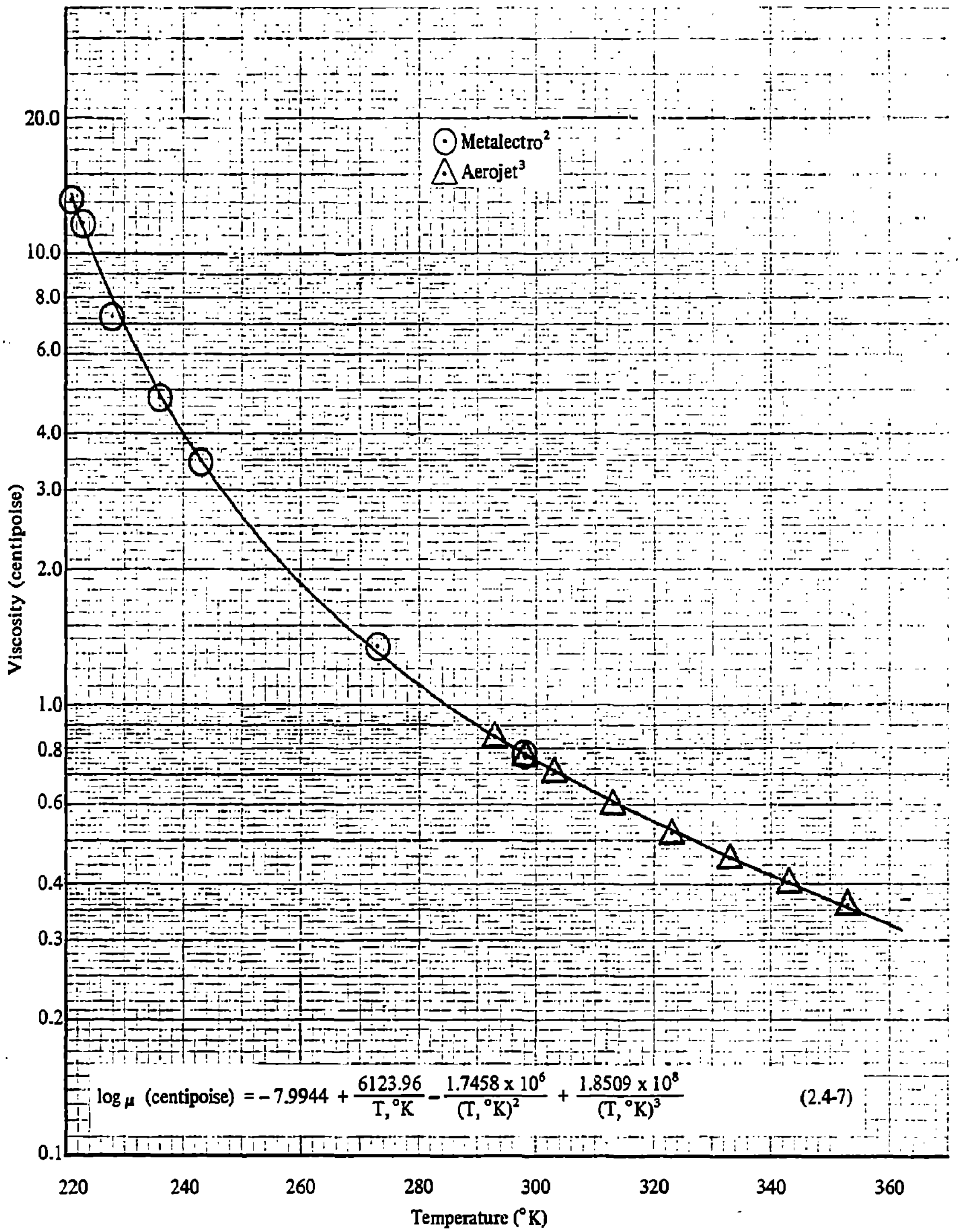
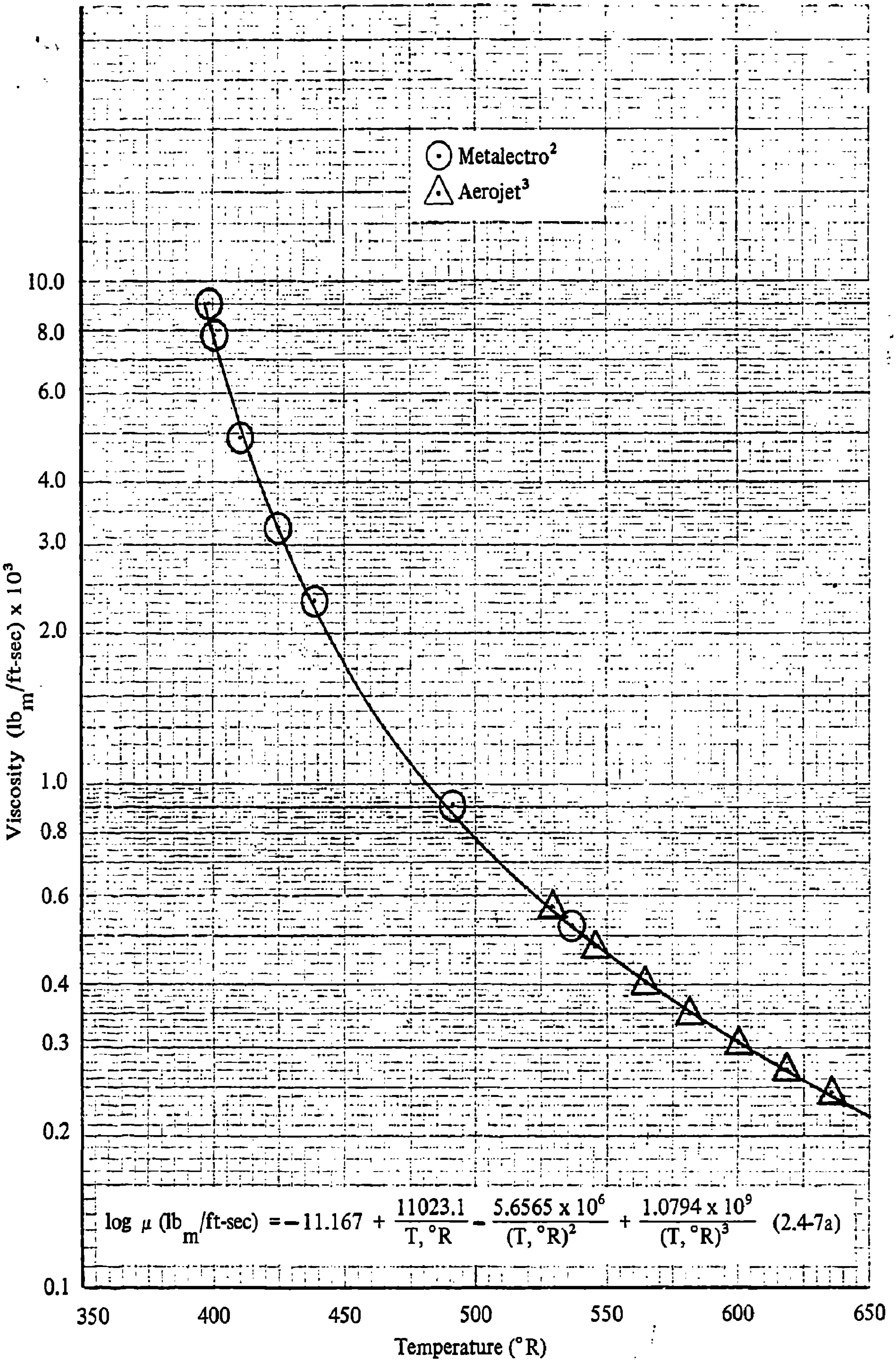


Figure 2.4-7a. Isothermal Compressibility versus Temperature, Liquid MMH



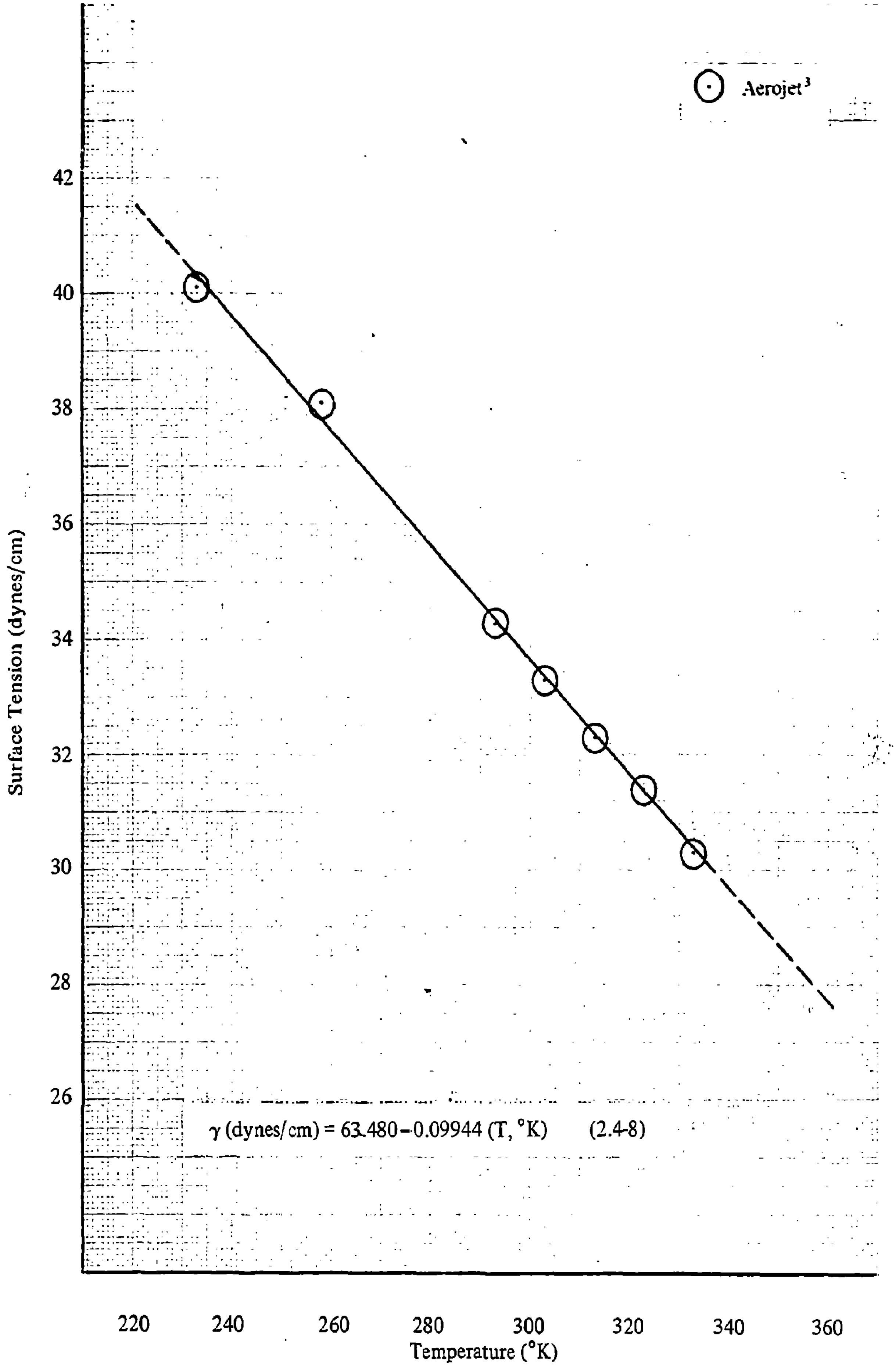
$$\log \mu \text{ (centipoise)} = -7.9944 + \frac{6123.96}{T, {}^\circ K} - \frac{1.7458 \times 10^6}{(T, {}^\circ K)^2} + \frac{1.8509 \times 10^8}{(T, {}^\circ K)^3} \qquad (2.4\text{-}7)$$

Figure 2.4-8. Viscosity versus Temperature, Liquid MMH



$$\log \mu\,(\mathrm{lb_m/ft\text{-}sec}) = -11.167 + \frac{11023.1}{T,\,^\circ R} - \frac{5.6565 \times 10^6}{(T,\,^\circ R)^2} + \frac{1.0794 \times 10^9}{(T,\,^\circ R)^3} \quad (2.4\text{-}7a)$$

Figure 2.4-8a. Viscosity versus Temperature, Liquid MMH



γ (dynes/cm) = 63.480 − 0.09944 (T, °K) (2.4-8)

[illegible]

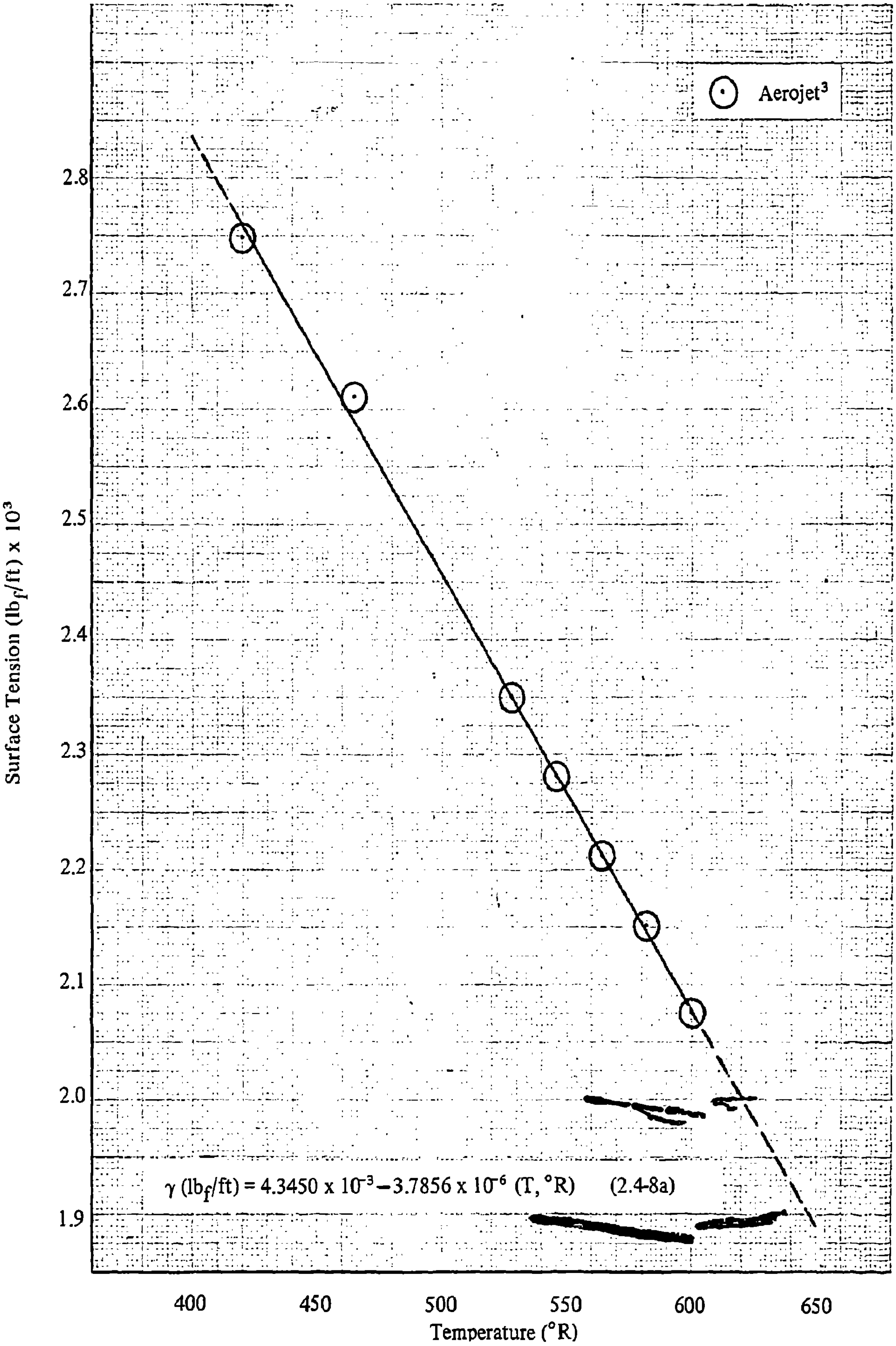


Figure 2.4-9a. Surface Tension versus Temperature Liquid MMH

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

P = parachor
M = molecular weight (46.075)
γ = surface tension (33.83)
ρ_l = density of liquid (0.8702 g/cc)
ρ_v = density of vapor (0.016 g/cc, ideal gas)

Using the atomic parachors given by Daniel (17), a value of 132.4 is obtained.

2.4.3.7 Thermal Conductivity of Liquid MMH

The thermal conductivity of liquid MMH was recently studied by Rocketdyne (19) and appears to be the only data available for this property. A total of 24 determinations were made over a temperature range from -17 to 152 C (1.4 to 306 F). Propellant grade MMH was used which had a purity of 99.2% by weight, the main impurity being 0.7% water. This composition is well within the limits of MIL-P-27404.

The conductivity apparatus consisted of two concentric aluminum alloy cylinders. The test fluid was contained in a thin annular passage between the two cylinders. The ends of the annulus were sealed with two Teflon O-rings to minimize heat conduction and to hold the cylinders concentric. Six pairs of copper-constantin thermocouples were embedded at various locations in both cylinders. Two thermal barriers made of teflon were fitted over the ends of the cylinders, and the cell was held together by two stainless steel end plates which fit over the thermal barriers. An electrical resistance heater in the inner cylinder supplied the heat energy for the temperature gradients across the sample liquid.

The experimental data are plotted in Figures 2.4-10 and 2.4-10a. The data show a somewhat large degree of scatter which is not unusual for this inherently difficult to measure property. The quadratic equation chosen to represent the data has an average deviation of 1.51%. The maximum deviation is 4.0%

$$K\,(\text{cal/cm-sec/}^\circ\text{K}) = 3.4025 \times 10^{-4} + 2.200 \times 10^{-6}\,(T, {}^\circ\text{K}) - 4.545 \times 10^{-9}\,(T, {}^\circ\text{K})^2 \tag{2.4-9}$$

$$K\,(\text{BTU/ft-sec-}^\circ\text{R}) = 2.2848 \times 10^{-5} + 8.207 \times 10^{-8}\,(T, {}^\circ\text{R}) - 9.419 \times 10^{-11}\,(T, {}^\circ\text{R})^2 \tag{2.4-9a}$$

The standard deviation of the experimental data from the smoothed data obtained from equation 2.4-9 is 1.13×10^{-5} cal/cm-sec-K.

2.1.3.8 Dielectric Constant

The dielectric constant has been reported by Olin Mathieson (25) to be 19.2 at 15.6 C and 17.3 at 32.2 C. A value of 19.0 at 25.0 C has been given by Aerojet (29). The single-point determination by Aerojet was made on propellant grade MMH using a Sargent Oscillometer. The data from the two sources would appear to be in slight disagreement. Additional measurements over a larger temperature range are required to adequately define this property.

2.4.4 CHEMICAL PROPERTIES OF MMH

2.4.4.1 Chemical Reactions

Methylhydrazine is considered to be less reactive than hydrazine but it readily undergoes reactions with a variety of both organic and inorganic compounds. Like hydrazine, MMH is a strong reducing agent, weakly alkaline and very hygroscopic. It reacts with carbon dioxide and oxygen in air.

Rocketdyne (27) has given the following chemical reactions as typical examples:

$CH_3NHNH_2 + RX \rightarrow CH_3HNRNH_2\,X$

$CH_3NHNH_2 + HNO_2 \rightarrow CH_3HNNHONO \rightarrow CH_3NH_2$

$CH_3NHNH_2 + CO_2 \rightarrow CH_3HNNHCOOH$

$CH_3NHNH_2 + RCOR^1 \rightarrow CH_3HNNCRR^1$

$CH_3NHNH_2 + RCOOR^1 \rightarrow CH_3HNNHCOR^1$

$CH_3NHNH_2 + CS_2 \rightarrow CH_3HNNHCSSH$

$CH_3NHNH_2 + (RO)_2\,PCl \rightarrow (RO)_2\,PNHNHCH_3$

$CH_3NHNH_2 + HCOOH \rightarrow CH_3\,NHNHCHO$

$CH_3NHNH_2 + HNO_3 \rightarrow CH_3H_2\,NNH_2ONO_2$

2.4.4.2 Inert Gas Solubility in Liquid MMH

The solubility of gaseous helium, nitrogen and argon in liquid MMH has been studied by Chang (22). The MMH (solvent) was weighed and placed in a container with a glass enclosed magnetic bar for stirring. The volume of the solvent was determined from the measured weight and known density. The pressures were measured with a monometer equipped with a microslide cathetometer. The apparatus had three calibrated volumes for the measurements of the admitted gases.

Solubility measurements for each of the three gases were taken at three separate temperatures. At each temperature, data was obtained at two different gas pressures. Chang reports that the three different dissolved gases obey ed Henry's law (that the solubility is proportional to the partial pressure of the gas).

The amount of dissolved gas can be determined from the relationship

$$X = KP$$

where

X = mole fraction dissolved gas
P = partial pressure of the gas (atmospheres)
K = equilibrium constant

The values of K as reported by Chang are plotted in Figures 2.4-11 and 2.4-11a. To determine the amount of dissolved gas in a pressurized tank, the vapor pressure of the MMH should be subtracted from the measured total pressure.

2.4.5 THERMODYNAMIC PROPERTIES OF MMH

2.4.5.1 Heat of Formation

The heat of formation of the liquid at 298 K was determined to be 13.106 kcal/mole.

The heat of formation of liquid MMH was calculated from its heat of combustion. Aston (13) gives the heat of combustion at constant volume for 30 C as -311.711 kcal/mole. The heat of combustion at constant pressure was calculated by using the following equation:

$$\Delta H = \Delta E + \Delta n\,RT$$

where

ΔH = the heat of combustion at constant pressure
ΔE = the heat of combustion at constant volume
Δn = the difference in the number of moles of gas between the reactants and products.

For the combustion of MMH at 30 C

$$\left[CH_3N_2H_3\,(\ell,30^\circ C) + 5/2\,O_2\,(g,30^\circ C) \rightarrow CO_2\,(g,30^\circ C) + N_2\,(g,30^\circ C) + 3H_2O\,(\ell,30^\circ C)\right]$$

$\Delta n = -1/2$ and

$\Delta H_{30^\circ C} = -311.711 + (-1/2)(1.98717 \times 10^{-3})(273.15 + 30)$

-312.01222 kcal/mole

Converting temperatures to K, the heat of combustion at 298 K may be determined in the following manner: (4, 11, 12)

	ΔH (kcal)
$CH_3N_2H_3\,(\ell,303) + 5/2\,O_2\,(g,303) \rightarrow CO_2\,(g,303) + N_2\,(g,303) + 3\,H_2O\,(\ell,303)$	-312.0122
$CO_2\,(g,303) \rightarrow CO_2\,(g,298)$	-0.04484
$N_2\,(g,303) \rightarrow N_2\,(g,298)$	-0.03486
$3\,H_2O\,(\ell,303) \rightarrow 3\,H_2O\,(\ell,298)$	3(-0.08991)
$CH_3N_2H_3\,(\ell,298) \rightarrow CH_3N_2H_3\,(\ell,303)$	0.16134
$5/2\,O_2\,(g,298) \rightarrow 5/2\,O_2\,(g,303)$	5/2(0.03518)
$CH_3N_2H_3\,(\ell,298) + 5/2\,O_2\,(g,298) \rightarrow CO_2\,(g,298) + N_2\,(g,298) + 3\,(H_2O\,(\ell,298)$	-312.1123

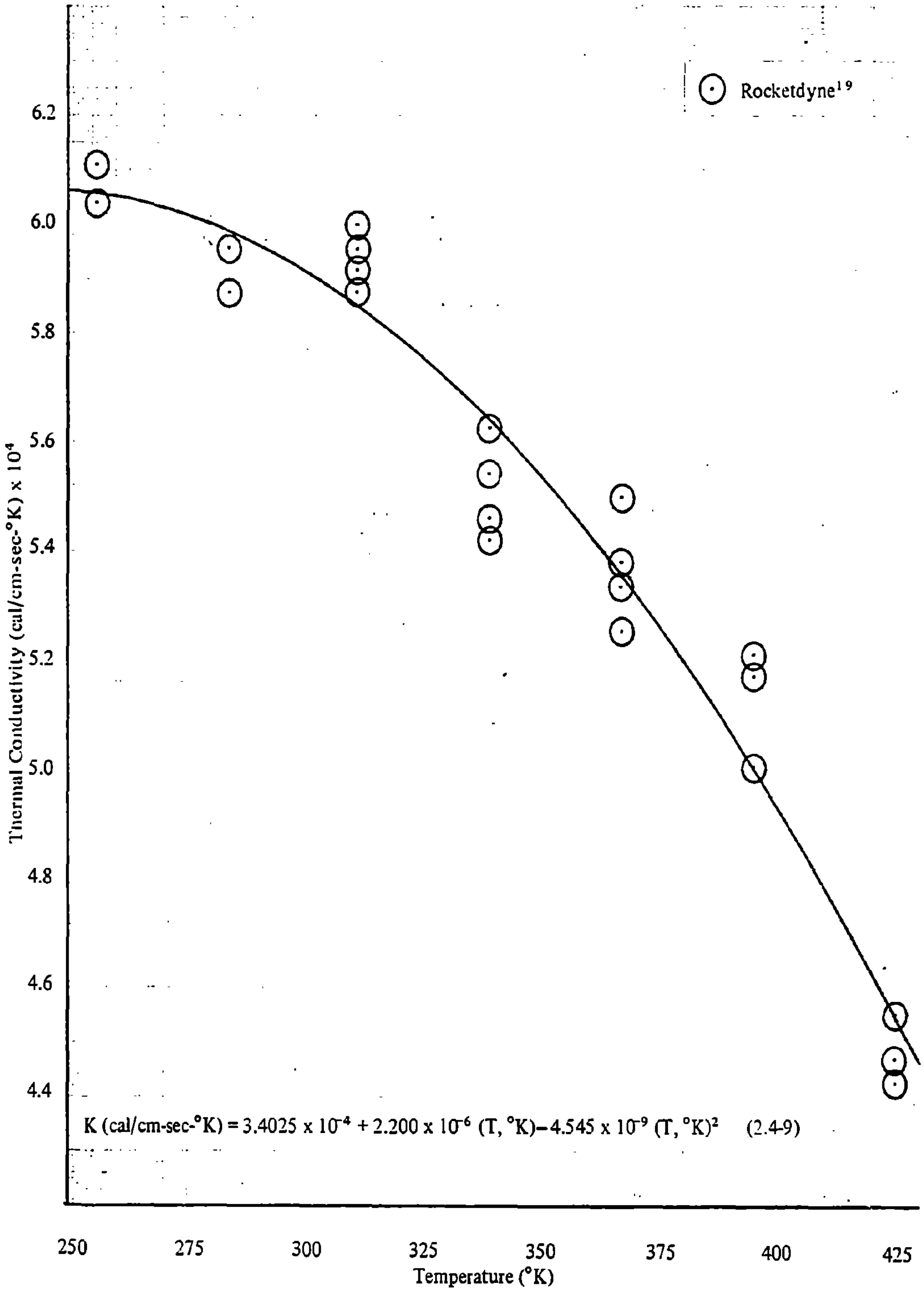
Combining this heat of combustion with the heats of formation of gaseous carbon dioxide and liquid water yields the heat of formation of MMH. (11, 12)

	ΔH (kcal)
$CO_2\,(g,298) + N_2\,(g,298) + 3\,H_2O\,(\ell,298) \rightarrow CH_3N_2H_3\,(\ell,298) + 5/2\,O_2\,(g,298)$	312.1123
$C\,(s,298) + O_2\,(g,298) \rightarrow CO_2\,(g,298)$	-94.054
$3\,H_2\,(g,298) + 3/2\,O_2\,(g,298) \rightarrow 3\,H_2O\,(\ell,298)$	3(-68.3174)
$C\,(s,298) + 3\,H_2\,(g,298) + N_2\,(g,298) \rightarrow CH_3N_2H_3\,(\ell,298)$	13.106

2.4.5.2 Melting Point and Heat of Fusion

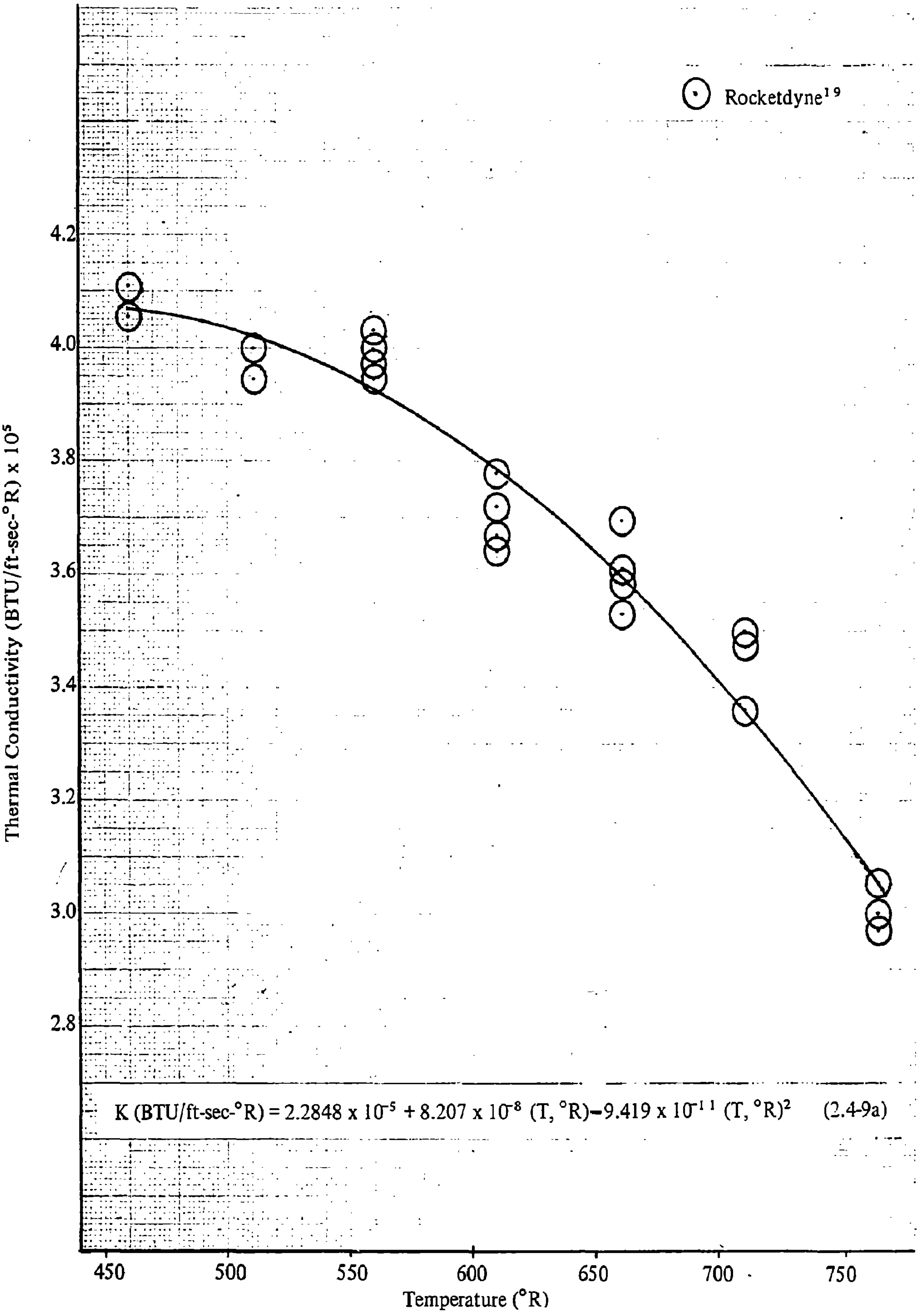
The melting point and heat of fusion at the melting point have been determined by Aston (4). The equilibrium temperatures of solid and liquid MMH were observed with increasing fractions of the sample melted. The solid-insoluble impurity was determined to be 0.25 mole %. The melting point of the pure compound after corrections for the impurity was found to be 220.79 K with the ice point taken to be 273.16 K. The precision of the value may warrant the correction to the presently accepted ice point. and the corrected value is 220.78 K (-52.37 C or -62.27 F).

Two measurements were obtained for the heat of fusion. Corrections for premelting and heating of the solid and liquid were made based on the heat capacity data taken previously. The reported average value was 2.4905 ± 0.0003 kcal/mole (97.231 BTU/lb).



$$K\ (\text{cal/cm-sec-}^\circ\text{K}) = 3.4025 \times 10^{-4} + 2.200 \times 10^{-6}\ (T,\ ^\circ\text{K}) - 4.545 \times 10^{-9}\ (T,\ ^\circ\text{K})^2 \qquad (2.4\text{-}9)$$

Figure 2.4-10. Thermal Conductivity versus Temperature Liquid MMH



$$K\ (\mathrm{BTU/ft\text{-}sec\text{-}^{\circ}R}) = 2.2848 \times 10^{-5} + 8.207 \times 10^{-8}\ (T, {}^{\circ}R) - 9.419 \times 10^{-11}\ (T, {}^{\circ}R)^2 \qquad (2.4\text{-}9a)$$

Figure 2.4-10a. Thermal Conductivity versus Temperature Liquid MMH

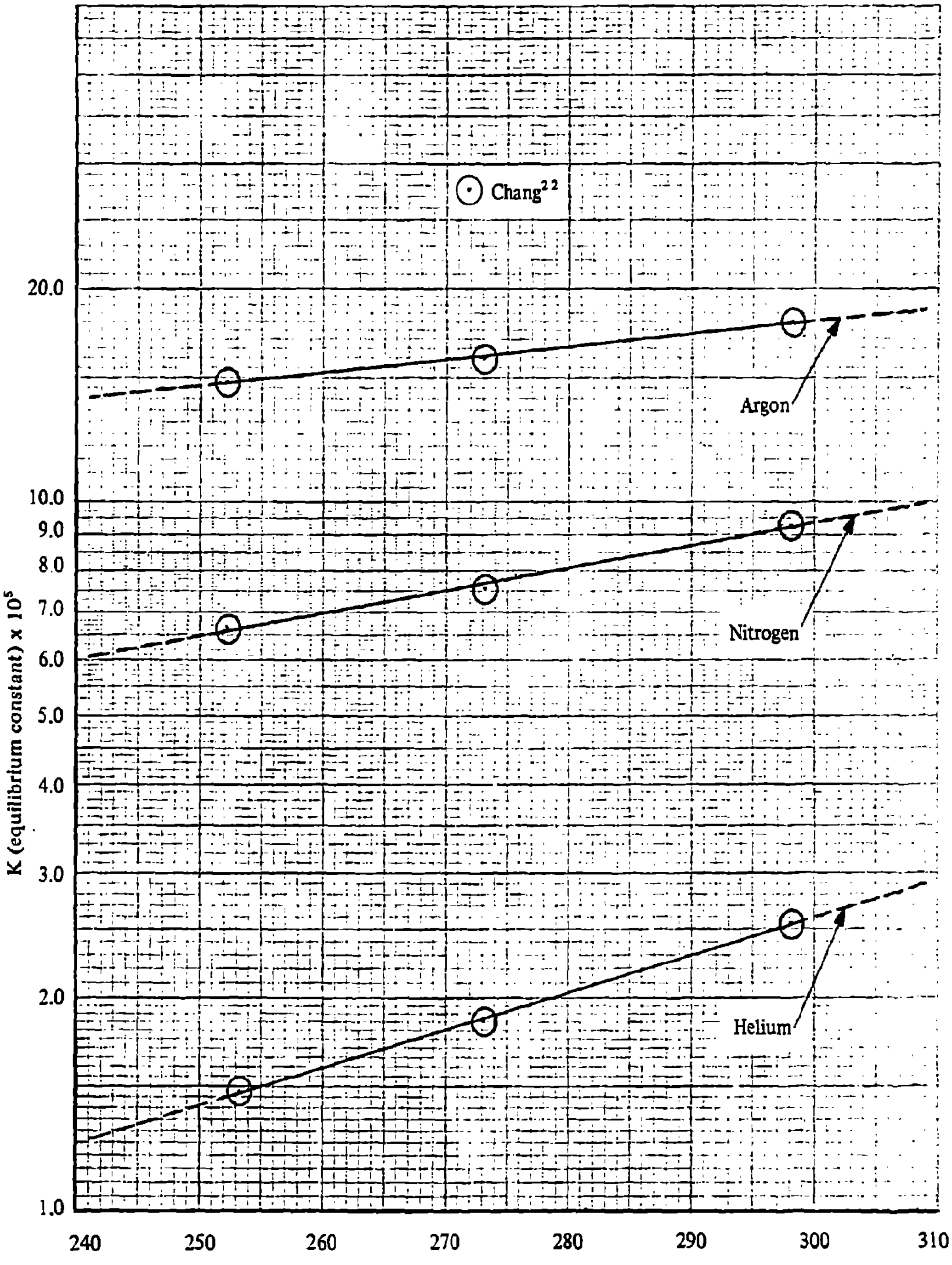


Figure 2.4-11. Gas Solubility in Liquid MMH versus Temperature

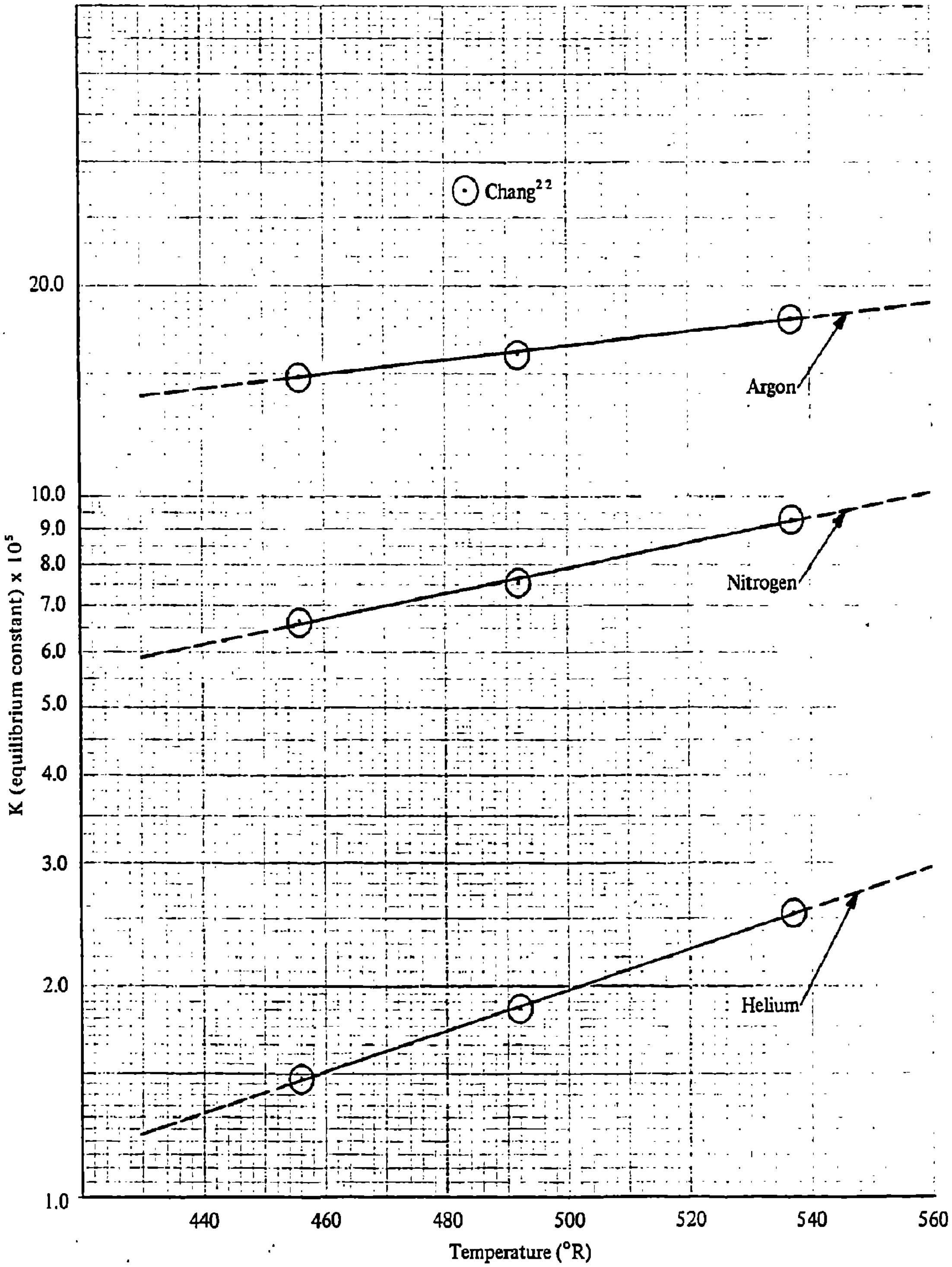


Figure 2.4-11a. Gas Solubility in Liquid MMH versus Temperature

2.4.5.3 Critical State Constants

The critical temperature and pressure of MMH have been experimentally determined by Aerojet (3). A heavy walled calibrated capillary tube, to which pressure could be applied hydraulically using mercury, was used. It was found during the initial measurements that non-condensible gases were formed and erroneous and non-reproducible values of temperature and pressure were obtained.

The method was modified slightly and the MMH sample was maintained at 310 C (590 F). Pressure was applied to maintain a liquid state. When temperature equilibrium was assured, the temperature was raised rapidly and the pressure adjusted to maintain both the liquid and vapor phase. The temperature and pressure at which the liquid-vapor boundary could no longer be maintained was recorded.

The reported values were 312 C (594 F) and 81.3 atmospheres (1195 psia). The critical density was estimated by Aerojet (3) to be 0.29 g/cc from a constructed phase diagram. Aston (4) estimated the critical temperature to be 257°C and the pressure to be 75 atmospheres.

The values obtained by Aerojet (3) are accepted but only as reasonably good estimates due to the experimental difficulties encountered from decomposition.

2.4.5.4 Heat Capacity of Liquid MMH

The heat capacity of liquid MMH has been studied by Aston (4) from near the melting point to 17 C (63 F). The values reported by Aston are smoothed values and neither the experimental data nor the equation used to smooth the data were given. The MMH sample had only 0.25 mole % impurities and the data had a reported precision of ±0.2%.

Recently, Rocketdyne (19) experimentally determined the heat capacity up to 124 C (255 F). The MMH sample used had a purity of 99.6 by weight %. The accuracy of data was given as ±3.0% with the precision being much better.

The smoothed data of Aston as well as the Rocketdyne experimental data are plotted in Figures 2.4-12 and 2.4-12a. The Rocketdyne data appear to have a large degree of scatter because of the expanded scale used; the percent spread is actually small. The combined heat capacities are expressed as a function of temperature by equation 2.4-10. The standard deviation is 3.63×10^{-3} cal/g-K.

$$Cp\,(\text{cal/g-}^\circ\text{K}) = 0.6528 - 1.7284 \times 10^{-5}\,(T, ^\circ\text{K}) + 3.9142 \times 10^{-7}\,(T, ^\circ\text{K})^2 \qquad (2.4\text{-}10)$$

$$Cp\,(\text{Btu/lb-}^\circ\text{R}) = 0.6534 - 1.2801 \times 10^{-5}\,(T, ^\circ\text{R}) + 1.8487 \times 10^{-7}\,(T, ^\circ\text{R})^2 \qquad (2.4\text{-}10a)$$

The heat capacity of liquid MMH is well defined from its melting point to 124°C. Extrapolation to temperatures much above this temperature is not recommended.

2.4.5.5 Latent Heat of Vaporization and Trouton Constant

Aston (4) measured the heat of vaporization of MMH at 298 K and an average of five determinations was reported to be 9.648 kcal/mole. Using the Clapeyron relation and the vapor pressure equation, a value of 9.726 kcal/mole is calculated here. No corrections were made for gas non--ideality. This is in good agreement with the precise measured value and is an indication of the thermodynamic validity of equation 2.4-1. At the normal boiling point (360.8 K), the calculated heat of vaporization is 8.894 kcal/mole and the Trouton constant is 24.6. Aerojet (3) estimated the heat of vaporization from a constructed enthalpy diagram to be 8.601 kcal/mole at the normal boiling point. For vapor pressure data, refer to Section 2.4.3.1.

2.4.6 LOGISTICS OF MMH

2.4.6.1 Manufacture

Methylhydrazine is manufactured by the Olin Mathieson Chemical Corporation using a modified Raschig process. Sodium hypochlorite (NaOCl) is combined with a slight excess of ammonium hydroxide (NH_4OH) to initially form chloramine (NH_2Cl)

$$NaOCl + NH_4OH \rightarrow NH_2Cl + NaOH + H_2O$$

The chloramine (NH_2Cl) is then reacted with anhydrous methylamine (CH_3NH_2) to form the MMH ($CH_3N_2H_3$).

$$NH_2Cl + NaOH + CH_3NH_2 \rightarrow CH_3N_2H_3 + NaCl + H_2O$$

The effluents from the reactor contain a very dilute aqueous solution of MMH. The impurities (NH_3, CH_3NH_2 and N_2) are removed in a recovery column. Additional impurities in the recovery columns are NaCl and H_2O. The NaCl is crystallized in an evaporator and removed by centrifuge. The remaining aqueous MMH is distilled in a three-column distillation system to obtain anhydrous MMH.

2.4.6.2 Analysis

The following volumetric analysis method is quoted directly from the Olin Mathieson product data sheet:

> This is a volumetric procedure utilizing a potentiometric end point with the classical

iodate reaction for hydrazine and related products. The analysis is based on the following reaction:

$$CH_3N_2H_3 + KIO_3 + 2HCl \rightarrow$$

$$KCl + ICl + CH_3OH + 2H_2O + N_2$$

Reagents

Hydrochloric Acid - 12N
Potassium iodate solution - N/10 - Standardized according to Method of Bradstreet "Standardization of Volumetric Solutions", p. 69.
Dry Ice
Acetone
Distilled Water

Calculation

$$\% \text{MMH} = \frac{\text{ml } KIO_3 \times N \times 38.3950}{\text{wt. of sample}}$$

The procedure is then as follows:

Transfer two ml of MMH into a tared weighing bottle containing 15 ml. of distilled water. Replace the stopper and swirl gently to mix: allow to reach room temperature. Reweigh the bottle and determine sample weight by difference. Carefully transfer the contents to a 250 ml volumetric flask, rinsing the bottle into the flask several times with distilled water. Dilute to volume with distilled water, stopper and mix thoroughly by inverting the flask six or seven times. All precautions to prevent atmospheric contamination should be taken.) Transfer a 5.0 ml aliquot into a 400 ml beaker containing 15 ml of distilled water and 60 ml of concentrated HCl. (Acidity should be not less than 6N at the titration end point). Place the beaker in a dry ice-acetone bath atop a magnetic stirrer and place so that the electrodes will be well immersed in the solution and not be damaged by the rotating magnetic rod. Agitation should be sufficient for uniform mixing of titrant. Reduce the temperature of the solution to 10 C by adding small pieces of dry ice to the acetone bath. Carry out the titration with $N/10KIO_3$ as rapidly as possible while maintaining the temperature below 0 C. As the end point is approached, maintain the solution temperature as constant at -10 C as possible. The end point is taken at the greatest emf deflection for the smallest volume of titrant added."

In all probability, the best method to determine water content is by gas chromatography. It is anticipated by Forbes (28) that this method would be included in any future revisions of the governing specification (MIL P-27404)

The density at 25 C (77 F) must be 0.872 ± 0.002 g/cc according to the specification. This criterion seems quite stringent and the minimum allowable density of 0.870 g/cc is almost exactly equal to the density value of 0.8702 g/cc reported in the physical property section of this handbook.

The melting point must be -67.9 F (391.8 R) or less. This requirement is questionable since the melting point of the pure substance is -62.3 F (397.4 R) (see Section 2.4.5.2).

The transmittancy of light must be 90% that of distilled water when measured with a colorimeter.

NOTE: MIL-P-27404 dated April 1962 has been superceded by revision A dated May 1969. This revision calls out the use of gas chromatogrophy for analysis. The density, melting point and light transmittacy requirements have been deleted.

2.4.6.3 Cost and Availability

The principal supplier of methylhydrazine is the Olin Mathieson Chemical Corporation. The production plant is located at Lake Charles, Louisiana. The raw materials for the manufacture of MMH are readily available and the availability of MMH therefore depends upon the manufacturing capabilities. To date, MMH has not been produced on a large scale.

At the present time the cost of MMH is $3.20 per pound in 55 gallon drums F.O.B. Lake Charles, La. If large quantities were being produced, the price could be reduced to close to $1.00 per pound. The following table depicts the cost of MMH in other sizes of containers:

CONTAINER		COST
1 - lb	Bottle	$10.00/lb
4 - lb	Bottle	6.25/lb
30 - gal	(215 lb) S.S. drum	3.50/lb plus $80.00 deposit per drum.
55 - gal	(375 lb) S.S. drum	3.20/lb plus $100.00 deposit per drum.

2.4.6.4 Shipping and Transportation

For complete and detailed laws concerning the shipment of monomethylhydrazine the Code of Federal Regulations, Title 49, parts 71 to 90 should be consulted. Monomethylhydrazine is classified as a flammable liquid by the ICC and containers must be marked with a red label "Flammable Liquids". Containers are covered by the following ICC specifications:

(1) ICC-ID: boxed glass carboys
(2) ICC-15A, 15B and 15C: Wooden boxes, with inside containers of glass bottles not exceeding

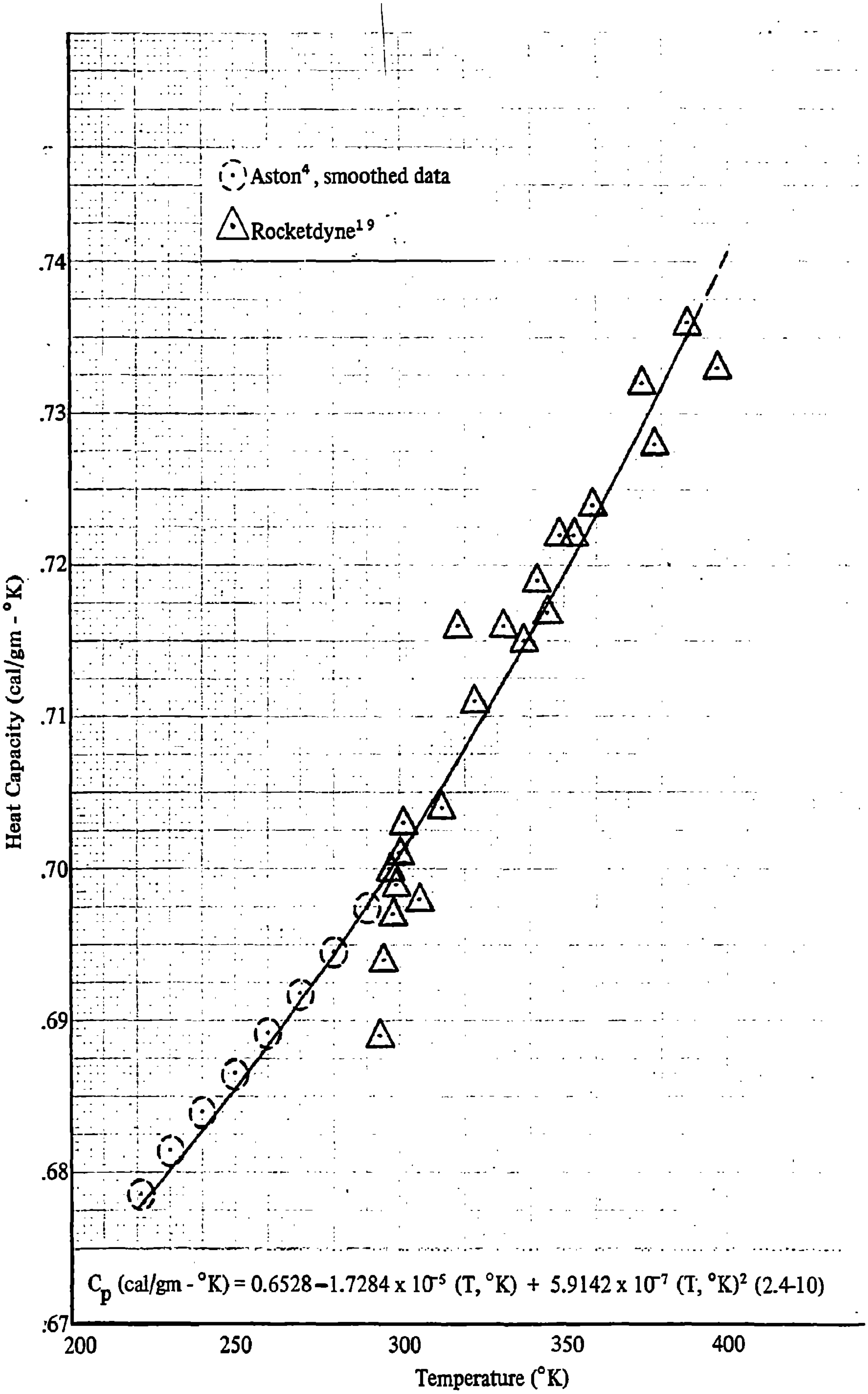


Figure 2.4-12. Heat Capacity versus Temperature, Liquid MMH

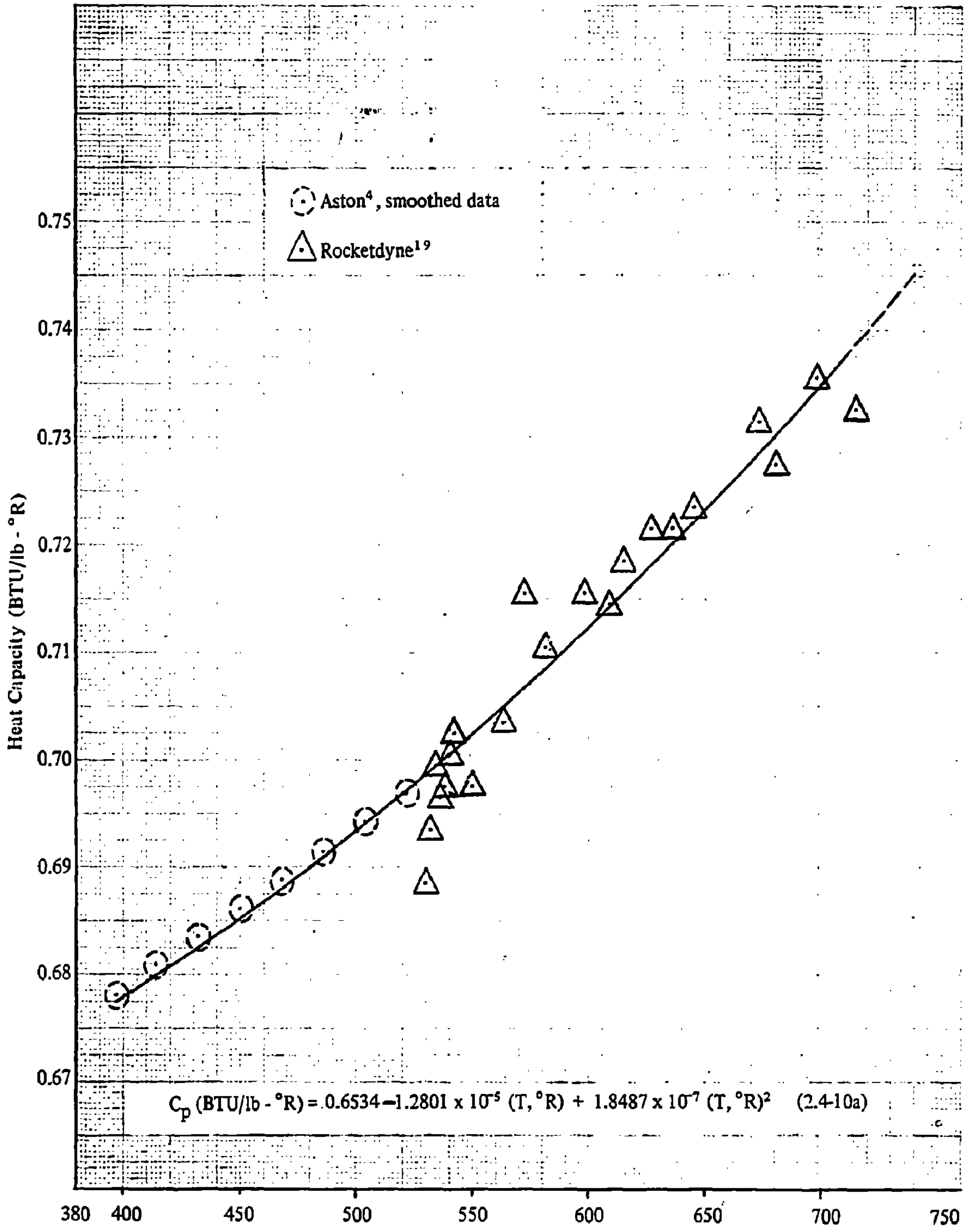


Figure 2.4-12a. Heat Capacity versus Temperature, Liquid MMH

1 gallon each. The glass should be packed with verimiculite and tightly closed with tin cans. Containers made of aluminum not less than 0.04 inch thick whose capacity may not exceed two quarts.

(3) LCC-5, 5A, 5C and 17E: Metal drums constructed of 304 or 347 stainless steel with openings not exceeding 2.3 inches in diameter.

(4) ICC 103-W: Tank cars constructed of 304 or 347 stainless steel with molybdenum content not to exceed 0.5%. Vapor space in tank must be filled with nitrogen gas at atmospheric pressure.

(5) ICC 103A-Al-W: Tank cars (aluminum) vapor space to be padded with nitrogen gas at atmospheric pressure.

2.4.7 REFERENCES

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2.5 UDMH

2.5.1 PROPERTY SUMMARY SHEET

Chemical Name: I, I Dimethylhydrazine   Common Name: UDMH

Chemical Formula: $(CH_3)_2 N_2H_2$ Formula Weight: 60.102 (O^{16})

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	215.94	°K		7	
	−57.21	°C			
	388.70	°R			
	−70.94	°F			
HEAT OF FUSION	2.4074	kcal/mole	215.94	7	
	72.099	BTU/lb			
NORMAL BOILING POINT	335.47	°K			
	62.32	°C			
	603.84	°R			
	144.18	°F			
HEAT OF VAPORIZATION	7.797	kcal/mole	NBP	calc.	
	233.51	BTU/lb	(215.94)		
TROUTON CONSTANT	23.2	-	NBP		
CRITICAL STATE CONSTANTS					
Temperature	523	°K			
	250	°C			
	941	°R			
	482	°F			
Pressure	59	atms			
	867	psia			
Density	.275	g/cc			
	17.16	lb/ft^3			
VAPOR PRESSURE OF LIQUID	167.1	mm Hg	298	2, 3, 7	2.5-1
	3.23	psia			2.5-2
DENSITY OF LIQUID	.7861	g/cc	298	1, 2, 5, 6	2.5-3
	49.073	lb/ft^3			2.5-4
SONIC VELOCITY	1247	m/sec	298	35	2.5-5
	4091	ft/sec			
COMPRESSIBILITY OF LIQUID					
ADIABATIC	8.23×10^{-5}	atm^{-1}	298	35	2.5-6
	5.60×10^{-6}	psi^{-1}			
ISOTHERMAL	2.049×10^{-4}	atm^{-1}	373	2	2.5-7
	1.394×10^{-5}	psi^{-1}			
VISCOSITY OF LIQUID	.492	centipoise	298	1, 2	2.5-8
	3.309×10^{-4}	lb$_m$/ft-sec			
HEAT CAPACITY OF LIQUID	.704	cal/g-°K	298	7, 8, 9	2.5-12
	.704	BTU/lb-°R			
THERMAL CONDUCTIVITY OF LIQUID	3.76×10^{-4}	cal/cm-sec-°K	298	9	2.5-10
	2.27×10^{-5}	BTU/ft-sec-°R			
SURFACE TENSION	24.09	dynes/cm	298	2	2.5-9
	1.650×10^{-3}	lb$_f$/ft			
PARACHOR	171	-	298	calc.	
ENTROPY	72.83	cal/mole-°K	298	7	
	1.212	BTU/lb-°R			
HEAT OF FORMATION	12.339	kcal/mole	298	4, 11	
	369.54	BTU/lb			
HEAT OF COMBUSTION	437.7	kcal/mole	298	4, 11	
	13108.7	BTU/lb			
INDEX OF REFRACTION	1.4053	-	298	3, 36	

2.5.2 GENERAL

2.5.2.1 Introduction

Unsymmetrical dimethylhydrazine (1, 1 dimethylhydrazine) is a clear, colorless hygroscopic liquid at normal room temperature and has a distinctively ammoniacal odor. As a rocket engine fuel, UDMH is not quite as energetic as hydrazine, but still must be considered a high energy fuel. Its relatively low freezing point (-71 F) makes it an excellent candidate as a space storable fuel.

UDMH is completely miscible with water, enthanol and various amine fuels including hydrazine. It is not sensitive to shock and is thermally stable. UDMH is compatible with most metals and can be stored for extended periods of time.

To date, UDMH is one of the leading rocket fuels in terms of annual use. As a neat propellant it has had unqualified success as the fuel for the Agena engine. It has also been used extensively in equal weight proportions with hydrazine in the Titan and Apollo spacecraft engines.

The physical properties of UDMH are generally well defined, although in some cases not at elevated temperatures.

2.5.2.2 Structure of UDMH (1,1 Dimethylhydrazine)

The rotation of the NH_2 group about the single N-N bond in 1, 1 dimethylhydrazine would permit trans and gauche configurations. Aston (7) has studied the configuration using Raman spectrum data to compare with calculated entropy data. The entropy was calculated for both forms assuming all angles tetrahedral and the following bond distances: N-N, 1.45, Å; C-N, 1.47 Å; C-H, 1.09 Å; N-H, 1.04 Å. An angle of 110 degrees was assumed for both the C - N - C and C - N - N bond.

The calculated principal moment of interia for the trans was 1.519×10^{-114} g cm^2 and 1.495×10^{-114} g cm^2 for the gauche. For the trans form, the reduced moment for each of the methyl groups is 5.03×10^{-40} g cm^2 and the amino group is 3.04×10^{-40} g cm^2. The gauche form gives 5.02×10^{-40} g cm^2 for the methyl groups and 3.03×10^{-40} for the amino group.

From the assumed internal rotation of the methyl groups the calculated entropies when compared to the Raman spectrum indicated that the gauche form was the most likely. A calculated entropy based on 75% trans and 25% gauche also gave entropies in agreement with the experimental spectrum data but Aston concluded this configuration to be highly unlikely. The trans form in hydrazine, methylhydrazine and sym-dimethylhydrazine has a higher energy than the gauche or skew form and therefore exists in negligible quantities.

2.5.2.3 Specification and Purity

Procurement and analysis of propellant grade UDMH is controlled by Military Specification MIL-P-25604-C dated May, 1963, including attachment S/N 9135-687-4293 dated June, 1967. The specification requires a purity of at least 98.0% UDMH and a density range from 0.783 to 0.786 g/cc. at 25 C (77 F). The water content must be no greater than 0.3% by weight. The remainder of the allowable impurities are assumed to be amines.

2.5.3 PHYSICAL PROPERTIES

2.5.3.1 Vapor Pressure, and Normal Boiling Point of UDMH

The vapor pressure of UDMH has not been extensively studied. Aston (7) and Chang (3) have both reported data over a limited range at lower temperatures. Barger (2) reported data for two separate ranges, one from 25 C (77 F) to near the normal boiling point and a second series from 130 C (265 F) to the critical point.

The low temperature data of the three separate investigations are shown in Figures 2.5-1 and 2.5-1a. Where the data reported by Chang (3) and Barger (2) overlap, there is good agreement. The work of Chang was reported with some reservations because the manometer used allowed contact of the mercury with the UDMH vapors and it was speculated by the author that this could possibly have caused catalytic decomposition.

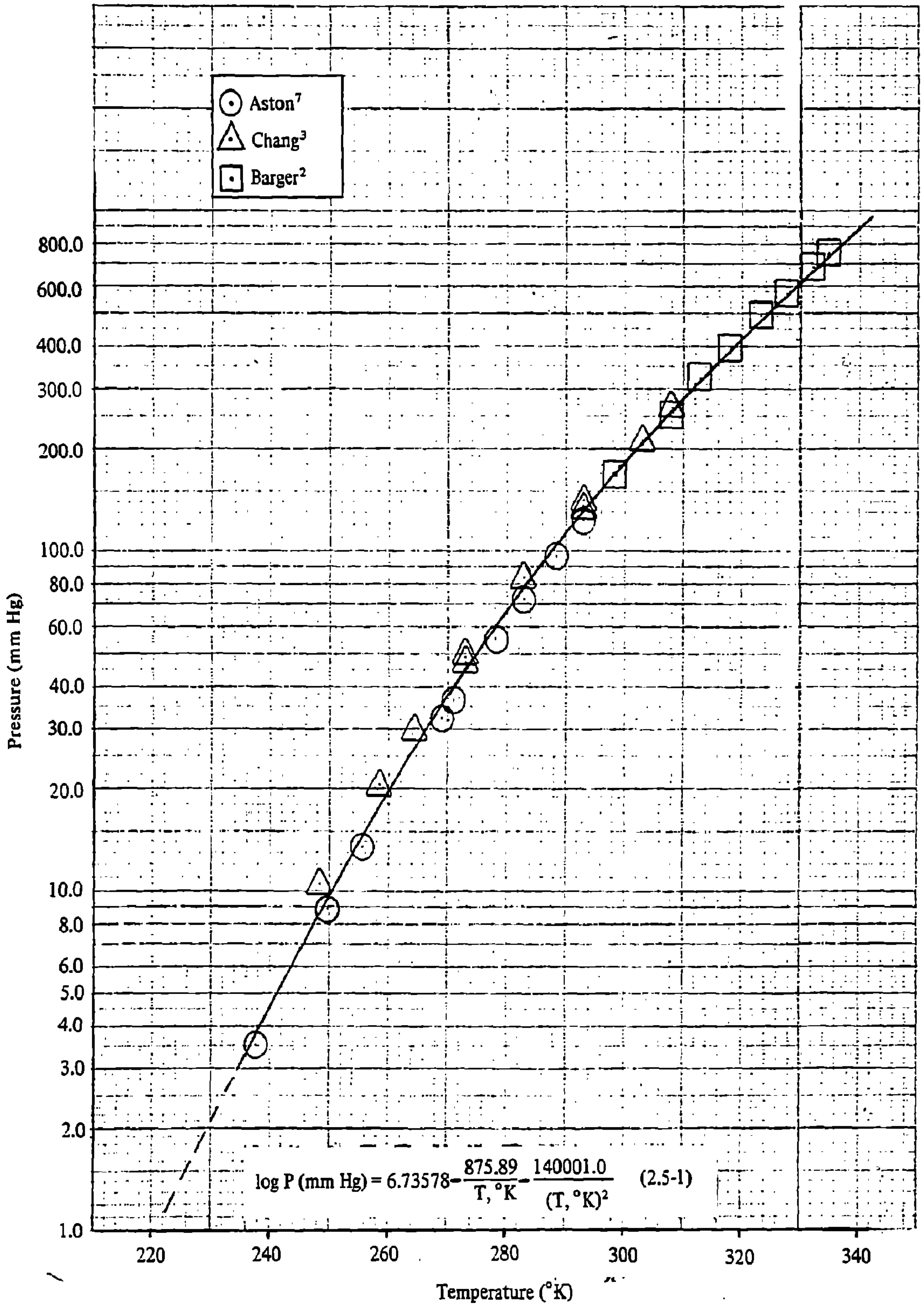
For this study, the combined data of the three investigations are used to describe the vapor pressure of UDMH from -35 C (-31 F) to the normal boiling point. The variation of pressure with temperature can be defined by

$$\log \text{P(mmHg)} = 6.73578 - \frac{875.89}{\text{T, °K}} - \frac{140001.0}{(\text{T, °K})^2} \qquad (2.5\text{-}1)$$

$$\log \text{P(psia)} = 5.02218 - \frac{1576.61}{\text{T, °R}} - \frac{453602.6}{(\text{T, °R})^2} \qquad (2.5\text{-}1a)$$

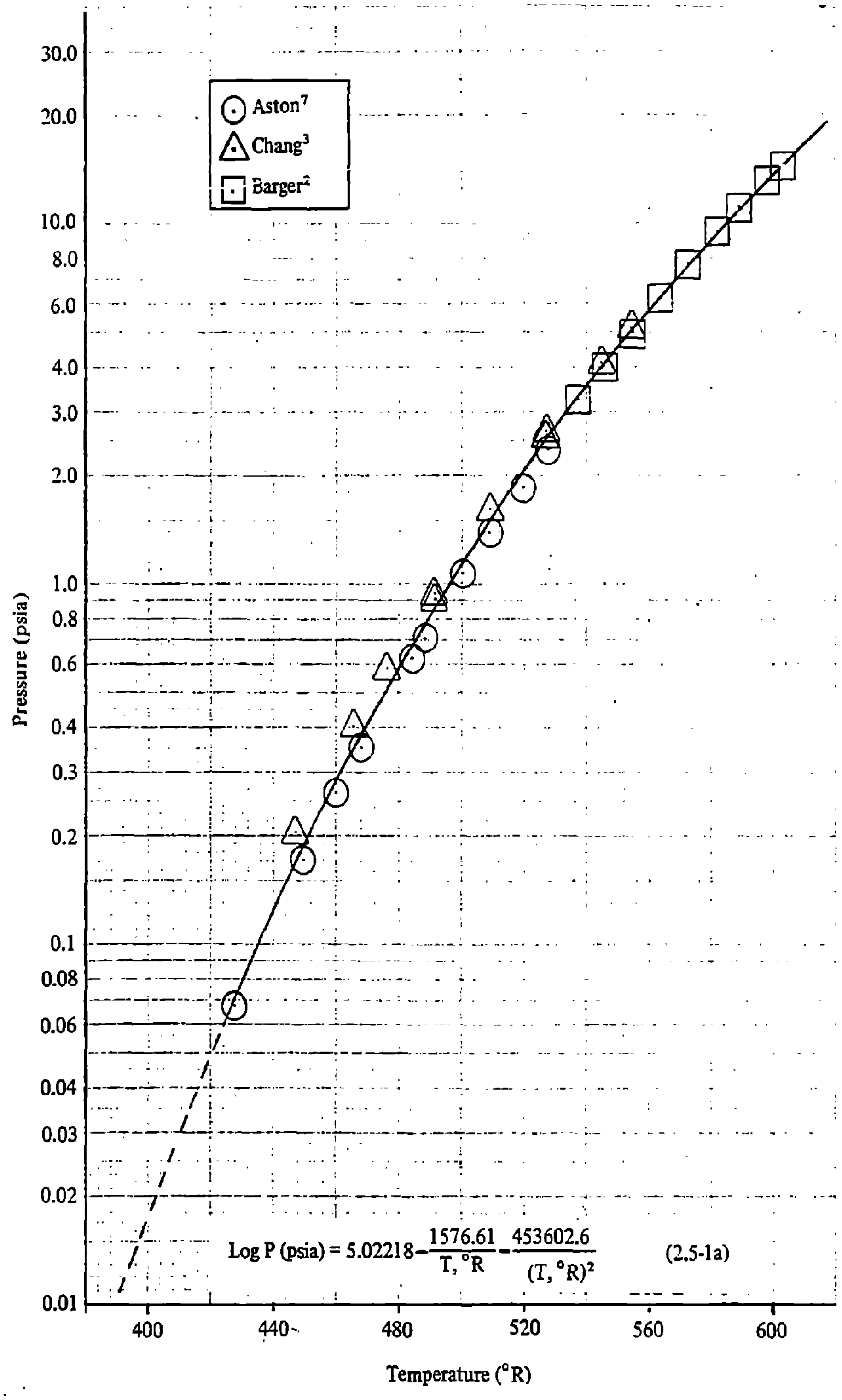
The standard deviation of the experimental data from the smoothed data obtained from equation 2.5-1 is 4.54 mm Hg while the average deviation is 5.4 %.

The normal boiling point obtained from equation 2.5-1 is 335.47 K (62.32 C or 144.17 F) which is somewhat less than the generally accepted value of 63 C reported by Washburn (10) in the International Critical Tables.



$$\log P\,(\text{mm Hg}) = 6.73578 - \frac{875.89}{T,\,^{\circ}\mathrm{K}} - \frac{140001.0}{(T,\,^{\circ}\mathrm{K})^2} \qquad (2.5\text{-}1)$$

Figure 2.5-1. Vapor Pressure versus Temperature, Liquid UDMH



$$\text{Log P (psia)} = 5.02218 - \frac{1576.61}{T, ^{\circ}R} - \frac{453602.6}{(T, ^{\circ}R)^2} \qquad (2.5\text{-}1a)$$

Figure 2.5-1a. Vapor Pressure versus Temperature, Liquid UDMH

The vapor pressure data from Barger (2) at elevated pressures are shown in Figures 2.5-2 and 2.5-2a. The vapor pressure from the normal boiling point to the critical temperature is expressed by:

$$\log P(\text{atm}) = 4.9439 - \frac{1659.84}{T, {}^\circ K} \qquad (2.5\text{-}2)$$

$$\log P(\text{psia}) = 6.1111 - \frac{2987.71}{T, {}^\circ R} \qquad (2.5\text{-}2a)$$

The above equations were obtained using the experimental data of Barger (2) and forcing the curve to go through the normal boiling point obtained from equation 2.5-1.

2.5.3.2 Density of Liquid UDMH

The density of saturated liquid UDMH has been measured by Horvitz (1), Barger (2), Aerojet General (5) and Bell Aerosystems (6). The four separate investigations covered a temperature range from -61 to 60 C (-77 to 140 F). The single-point determination by Aerojet (5) at -60.7 C is below the melting point, indicating the liquid was super-cooled.

The results of these four separate studies are in essential agreement although the data reported by Barger (2) are generally higher. The experimental data points are shown in Figures 2.5-3 and 2.5-3a. Using the least-squares method, the combined density data of Horvitz (1), Aerojet (5) and Bell (6) are nearly a linear function of temperature. The second-order equations given below afford a slightly better fit:

$$\rho(\text{g/cc}) = 1.06041 - 7.7507 \times 10^{-4}\ (T, {}^\circ K) - 4.8648 \times 10^{-7}\ (T, {}^\circ K)^2 \qquad (2.5\text{-}3)$$

$$\rho(\text{lb/ft}^3) = 66.1991 - 2.6881 \times 10^{-2}\ (T, {}^\circ R) - 9.3735 \times 10^{-6}\ (T, {}^\circ R)^2 \qquad (2.5\text{-}3a)$$

Alternately, the linear expressions are

$$\rho(\text{g/cc}) = 1.09450 - 1.0343 \times 10^{-3}\ (T, {}^\circ K) \qquad (2.5\text{-}4)$$

$$\rho(\text{lb/ft}^3) = 68.3277 - 3.5874 \times 10^{-2}\ (T, {}^\circ R) \qquad (2.5\text{-}4a)$$

With the exception of the data given by Bell (6) which is published here for the first time, the experimental details are sketchy. Bell employed two orthobaric pycnometers which had a precision bored capillary section. The pycnometers were calibrated with mercury and each one was vacuum loaded with approximately five grams of propellant grade UDMH. The sample mass was determined from the difference of weight between the empty and charged water constant temperature bath was used. Below the freezing point of water, an acetone-liquid nitrogen bath was employed. At each temperature, five readings were taken on each pycnometer so that the data were an average of 10 separate readings. The meniscus and reference level were measured with a cathetometer and temperatures were recorded using a mercury in glass thermometer immersed in the bath. The thermometer had a readout precision of ±0.1 C.

The propellant grade UDMH analysis showed the sample purity to be 98.33% by weight. The main impurity was dimethylamine with 0.2% water and a trace of ammonia.

The density of UDMH at elevated temperatures has been reported by Barger (2). The measurements were made at various pressures. In order to show the density at saturated conditions, only those points were used where the pressure was close to the liquid vapor pressure. These points are shown in Figures 2.5-4 and 2.5-4a. Three additional points are shown as dashed circles. These points were originally reported at pressures 12 to 18 atmospheres above the saturation pressure. The points as shown were corrected using the compressibility data given in Section 2.5.3.4. Barger (2) also reported a number of vapor density determinations at various pressures. Three of these determinations were made at pressures close enough to the vapor pressure to be considered saturated vapor densities. The critical density shown in Figures 2.5-4 and 2.5-4a is also taken from Barger. The curve, drawn through all the data shown, should be a good approximation of the saturated liquid and vapor densities at elevated temperatures.

The density of liquid UDMH is well defined from its melting point to 60 C (140 F) and is defined for most engineering applications up to the critical point.

2.5.3.3 Sonic Velocity in Liquid UDMH

Rocketdyne (35) has recently measured the velocity of sound in liquid propellant grade UDMH over a temperature range from -32 to 96 C (-26 to 204 F). The experimental data are plotted in Figures 2.5-5 and 2.5-5a. The variation of sonic velocity with temperature is adequately described by the linear relationship:

$$c(\text{m/sec}) = 2582.1 - 4.4781\ (T, {}^\circ K) \qquad (2.5\text{-}5)$$

$$c(\text{ft/sec}) = 8471.4 - 8.1622\ (T, {}^\circ R) \qquad (2.5\text{-}5a)$$

The standard deviation of the experimental from the smoothed data is 3.6 m/sec and the average deviation is 0.23%.

The apparatus and methods used by Rocketdyne are

2.5.3.4 Compressibility of Liquid UDMH

The sonic velocity in liquid UDMH has been measured by Rocketdyne (35). Adiabatic compressibility is related to the sonic velocity by the accoustical equation.

$$\beta_a = \frac{1}{\rho c^2}$$

where

ρ = density

c = sonic velocity

The compressibilities were computed at the experimental points for sonic velocity. The computed values are shown in Figures 2.5-6 and 2.5-6a. The data are adequately expressed by

$$\beta_a(\text{atm}^{-1}) = 3.9348 \times 10^{-4} - 2.8074 \times 10^{-6}\,(T, {}^\circ K) + 5.9151 \times 10^{-9}\,(T, {}^\circ K)^2 \qquad (2.5\text{-}6)$$

$$\beta_a(\text{psi}^{-1}) = 2.6775 \times 10^{-5} - 1.0613 \times 10^{-7}\,(T, {}^\circ K) + 1.2423 \times 10^{-10}\,(T, {}^\circ K)^2 \qquad (2.5\text{-}6a)$$

The standard deviation from equation 2.5-6 is 2.0×10^{-6} atm^{-1} and the average deviation is 1.1%.

Barger (2) has obtained some density values above 210 F at different pressures. The isothermal compressibility can be calculated from change in density at different pressures from the relation:

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

This method is subject to errors because of the small differences in liquid densities. The calculated isothermal compressibilities are shown in Table 2.5-1 and Figures 2.5-7 and 2.5-7a. Only four data points were available and, therefore, a least-squares curve fit was not warranted.

The isothermal compressibility data should be considered as provisional data and only used for preliminary design work. Extrapolation to lower temperatures is not advisable.

2.5.3.5 Viscosity of Liquid UDMH

The absolute viscosity of liquid UDMH has been studied by Horvitz (1) and Barger (2). Horvitz covered a temperature range from -55 to 25 C (-67 to 77 F). Barger extended this temperature range to 60 C and the data from the two studies can be smoothly joined.

The experimental data are shown in Figures 2.5-8 and 2.5-8a. Combining the data of the two studies, the viscosity as a function of temperature is adequately described by:

$$\mu(\text{centipoise}) = -0.25411 - \frac{623.532}{T, {}^\circ K} + \frac{181151.8}{(T, {}^\circ K)^2} \qquad (2.5\text{-}7)$$

$$\mu(\text{lb}_m/\text{ft-sec}) = 3.4268 - \frac{1122.36}{T, {}^\circ R} + \frac{586932}{(T, {}^\circ R)^2} \qquad (2.5\text{-}7a)$$

TABLE 2.5-1 ISOTHERMAL COMPRESSIBILITY OF LIQUID UDMH

TEMP. (°R)	DENSITY (g/cc)			PRESSURE (psia)			β_i
	ρ_1	ρ_2	$\Delta\rho$	P_1	P_2	ΔP	(psi^{-1}) x 10^5
671.67	0.717	0.710	0.007	1015	315	700	1.394
725.67	0.681	0.672	0.009	1015	315	700	1.888
779.67	0.642	0.631	0.011	1015	365	650	2.636
833.67	0.599	0.582	0.017	1015	368	647	4.387
TEMP. (°K)							β_i (atm^{-1}) x 10^4
373.15							2.049
403.15							2.776
433.15							3.874
463.15							6.447

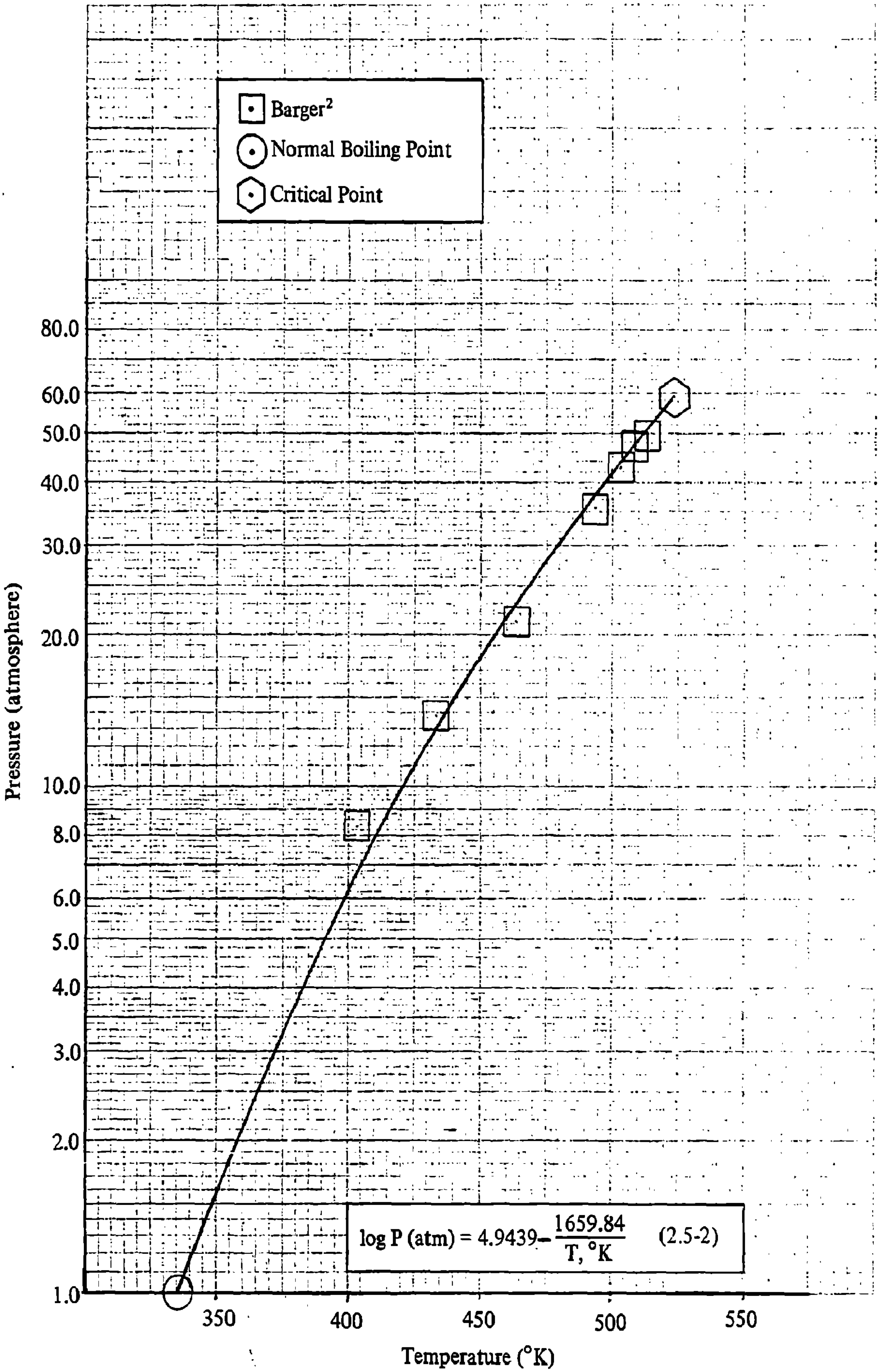


Figure 2.5-2. Vapor Pressure versus Temperature, Liquid UDMH

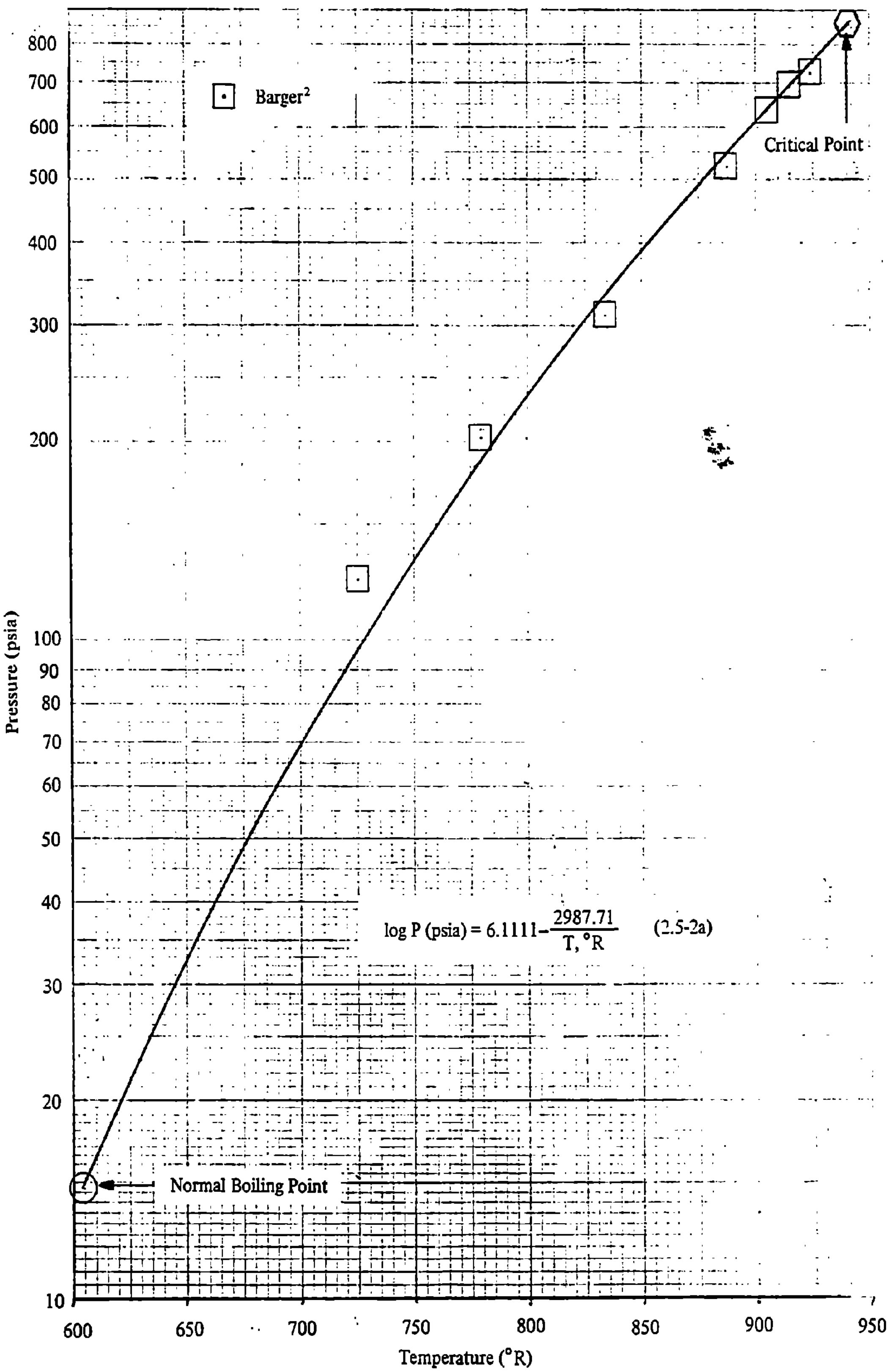


Figure 2.5-2a. Vapor Pressure versus Temperature, Liquid UDMH

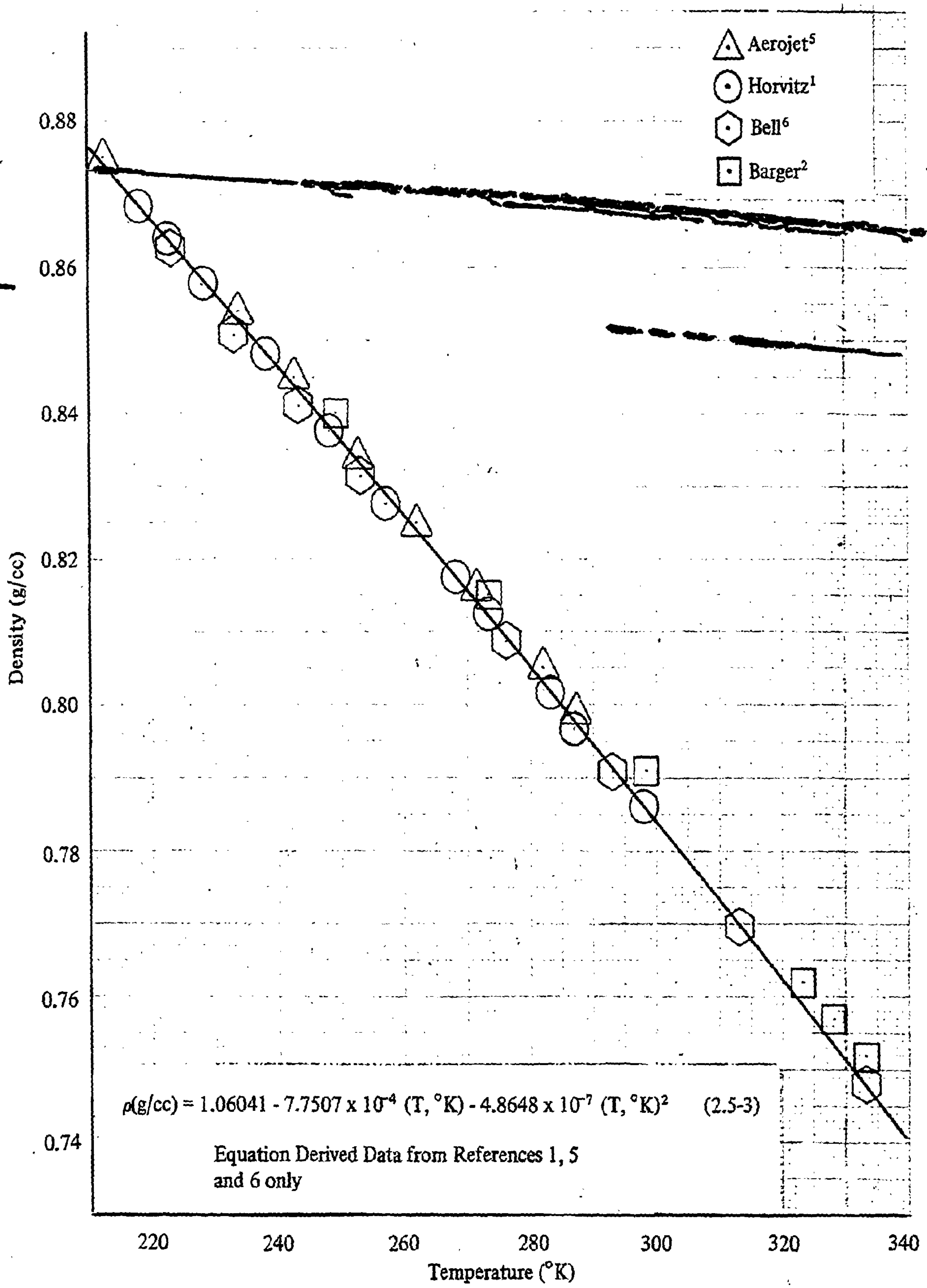


Figure 2.5-3 Density versus Temperature, Liquid UDMH

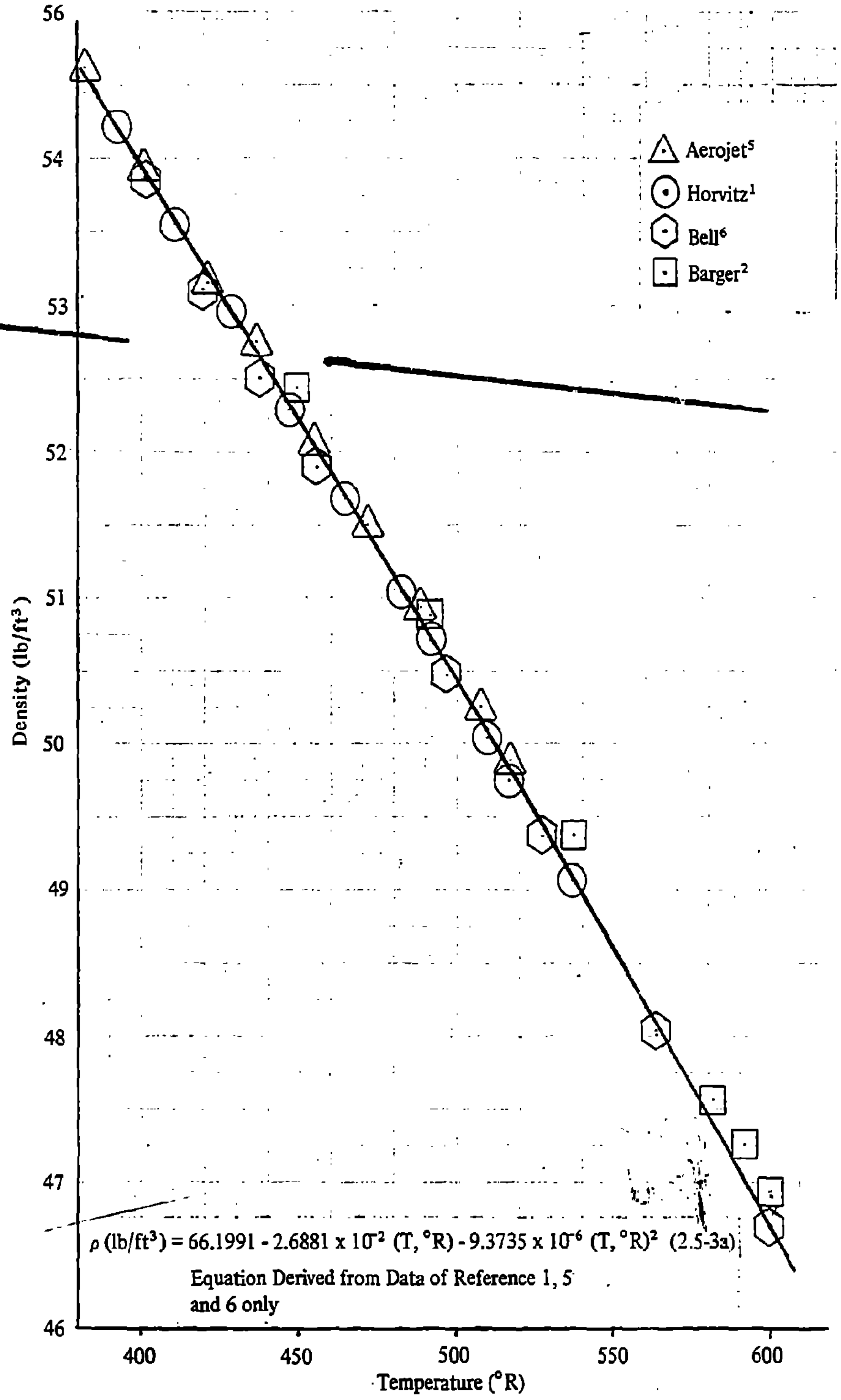


Figure 2.5-3a. Density versus Temperature, Liquid UDMH

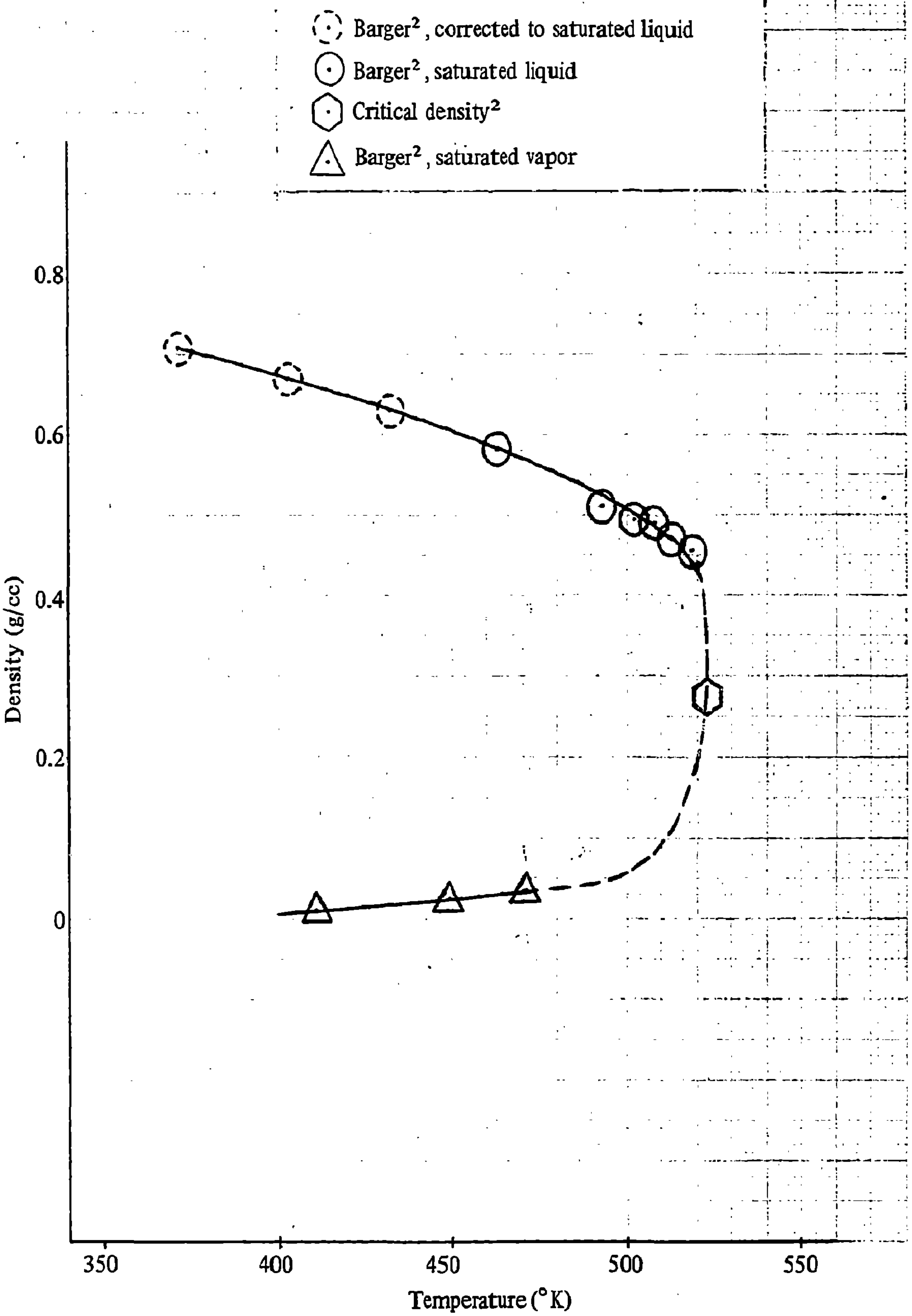


Figure 2.5-4. Density versus Temperature, Saturated Liquid and Vapor UDMH

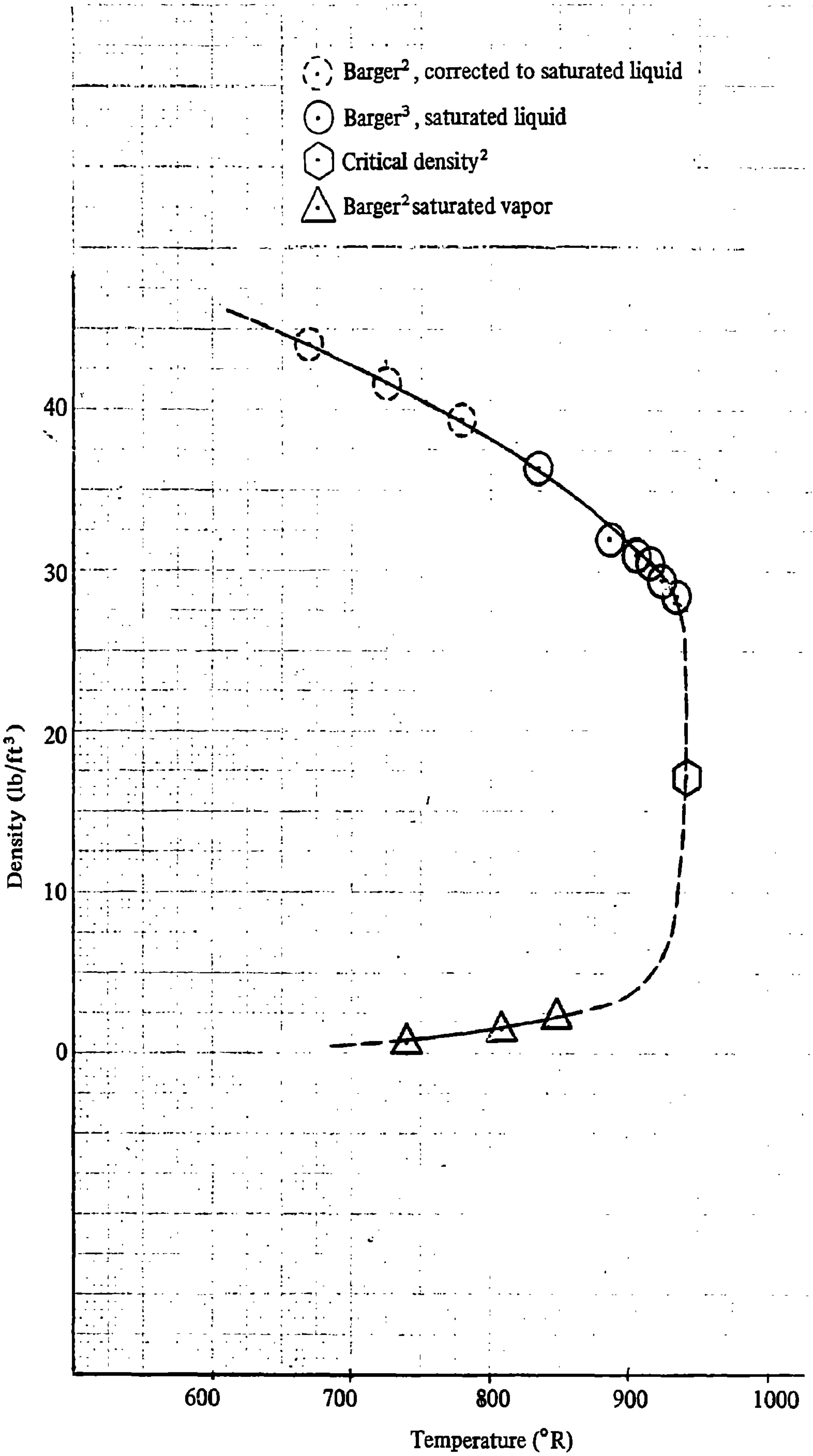
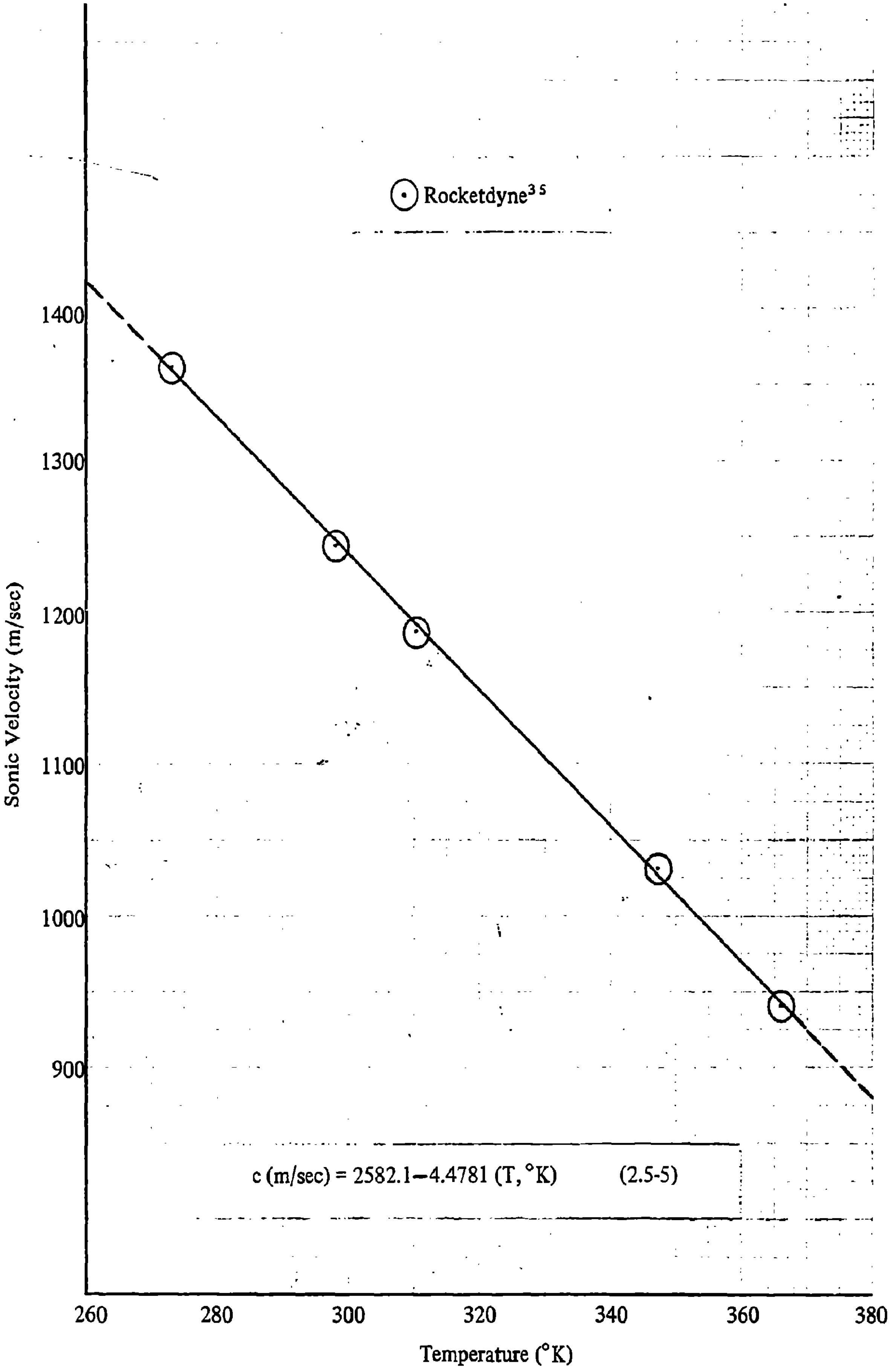


Figure 2.5-4a. Density versus Temperature, Saturated Liquid and Vapor UDMH



$$c\,(\mathrm{m/sec}) = 2582.1 - 4.4781\,(T, {}^{\circ}\mathrm{K}) \qquad (2.5\text{-}5)$$

Figure 2.5-5. Sonic Velocity in Liquid UDMH, versus Temperature

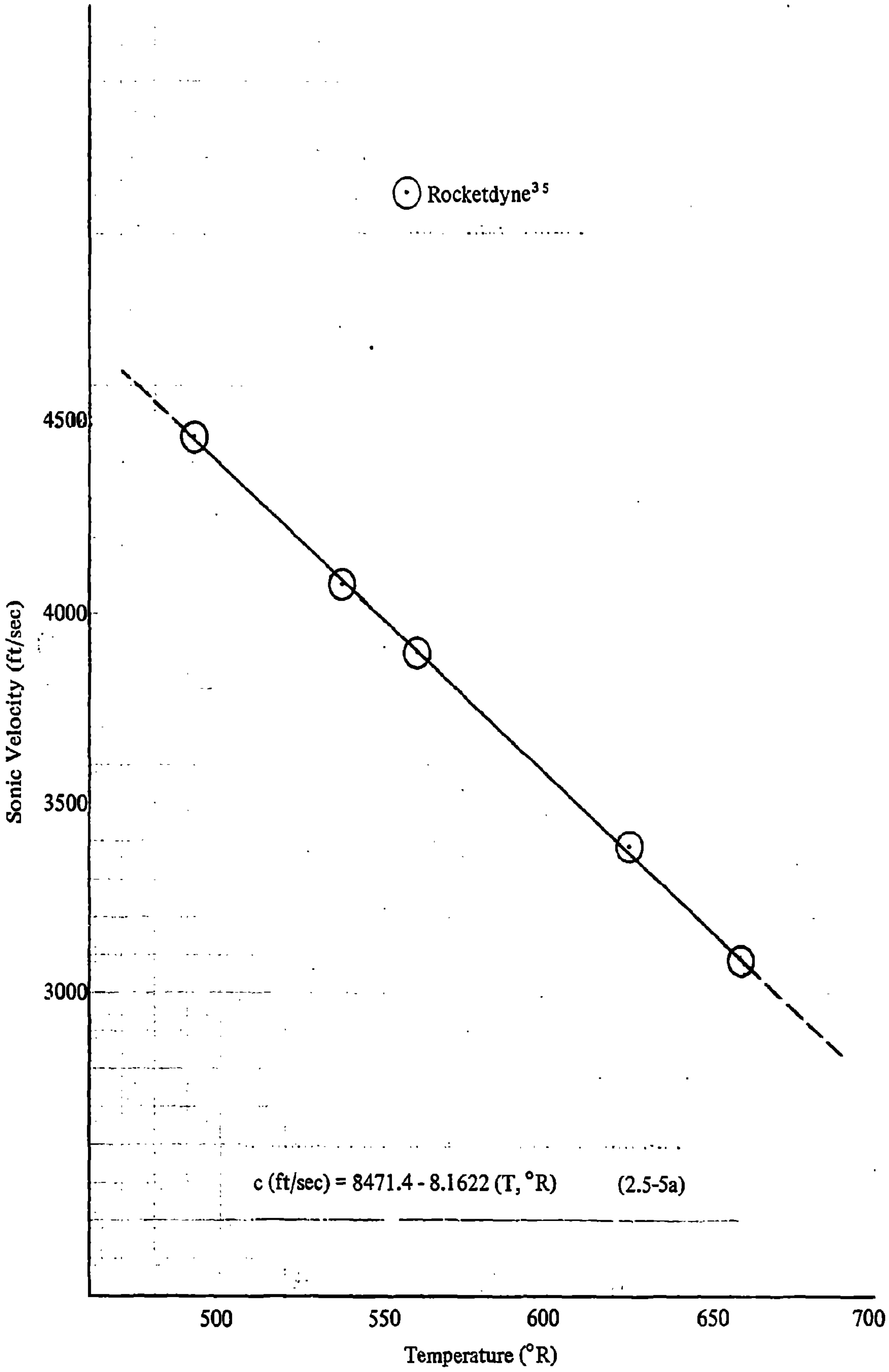
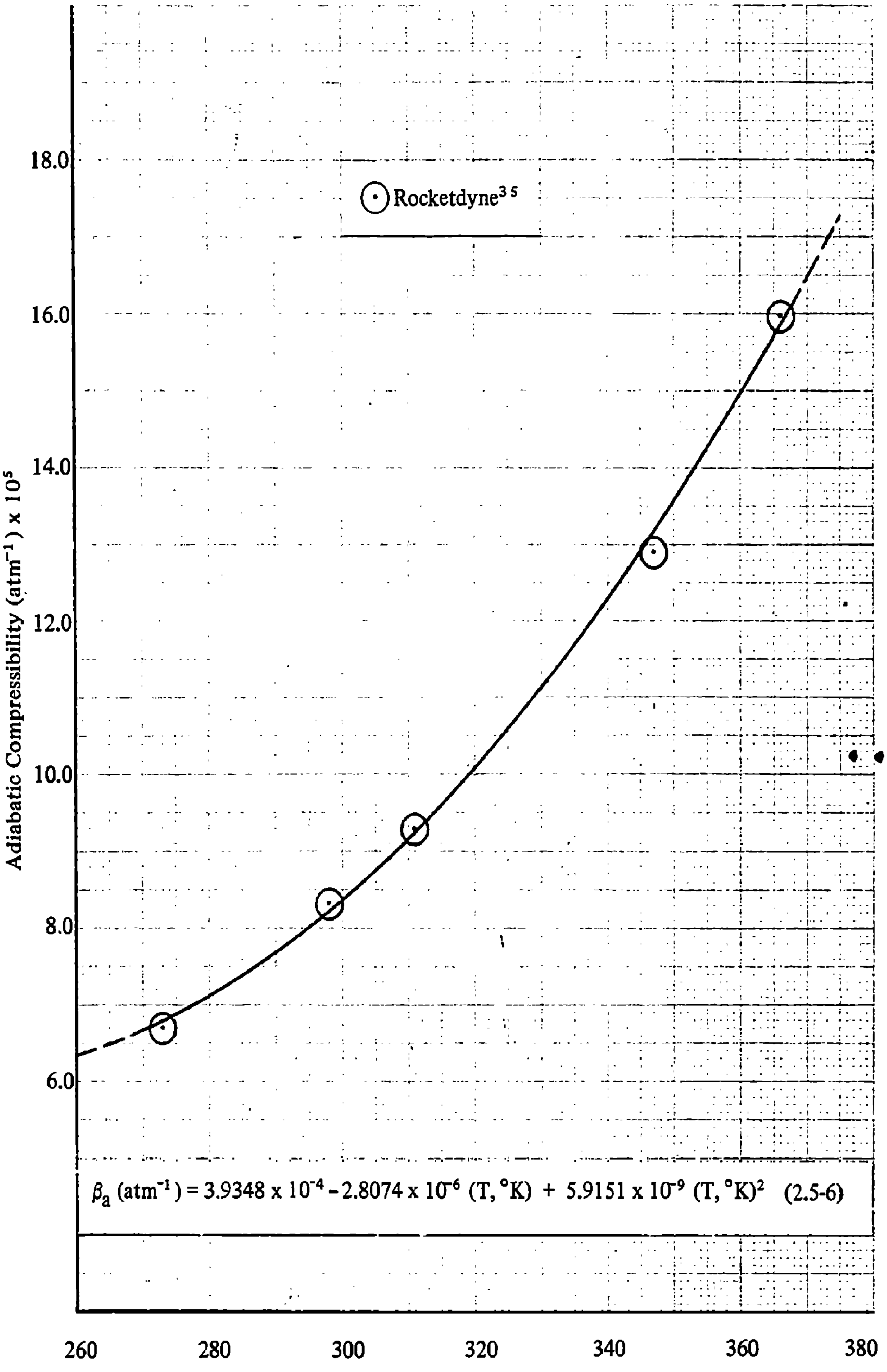
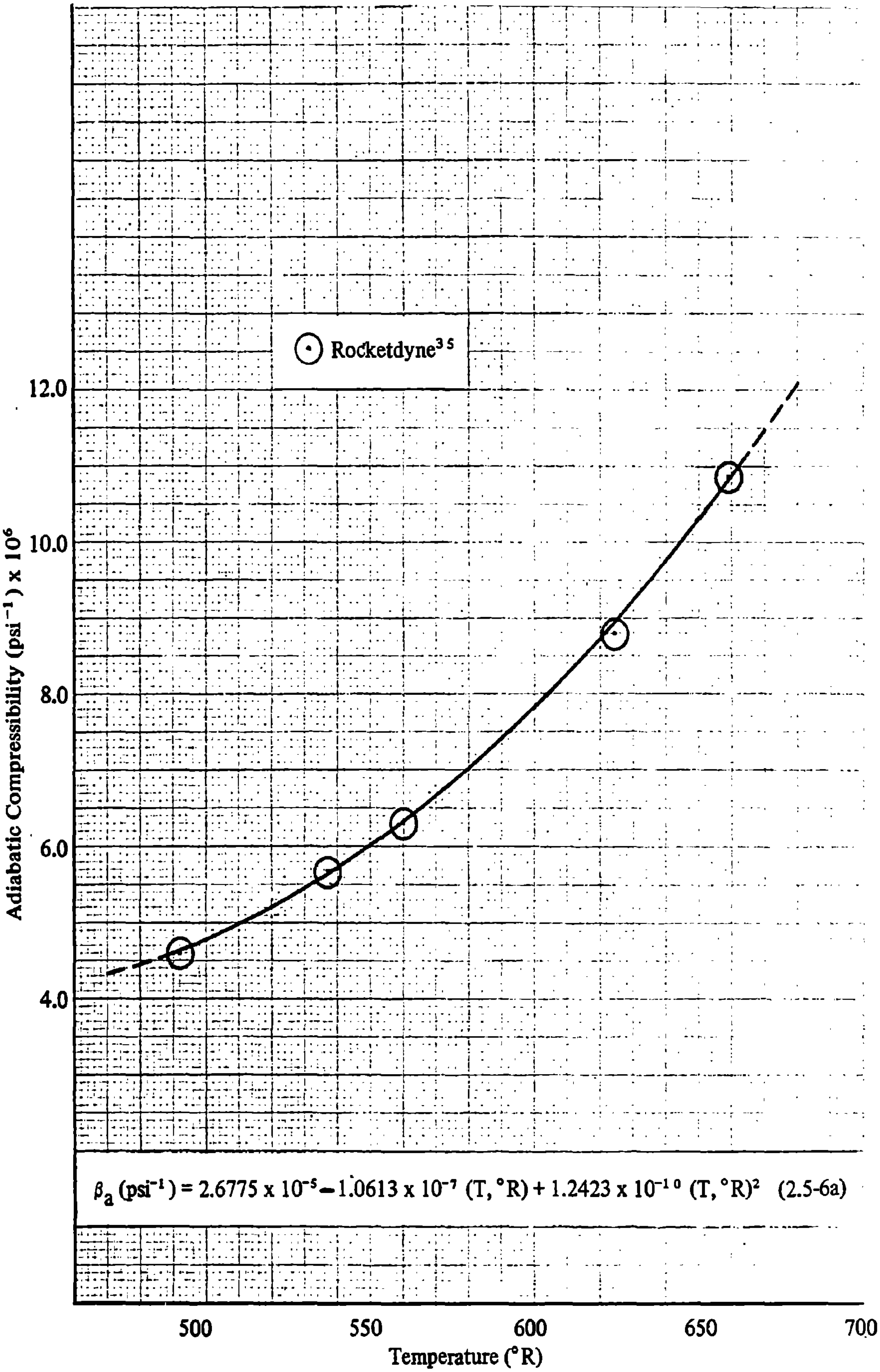


Figure 2.5-5a. Sonic Velocity in Liquid UDMH versus Temperature



$$\beta_a\ (\text{atm}^{-1}) = 3.9348 \times 10^{-4} - 2.8074 \times 10^{-6}\ (T, {}^\circ K) + 5.9151 \times 10^{-9}\ (T, {}^\circ K)^2 \quad (2.5\text{-}6)$$

Figure 2.5-6. Adiabatic Compressibility versus Temperature, Liquid UDMH



$$\beta_a\,(\mathrm{psi}^{-1}) = 2.6775 \times 10^{-5} - 1.0613 \times 10^{-7}\,(T, {}^\circ R) + 1.2423 \times 10^{-10}\,(T, {}^\circ R)^2 \qquad (2.5\text{-}6a)$$

Figure 2.5-6a. Adiabatic Compressibility versus Temperature, Liquid UDMH

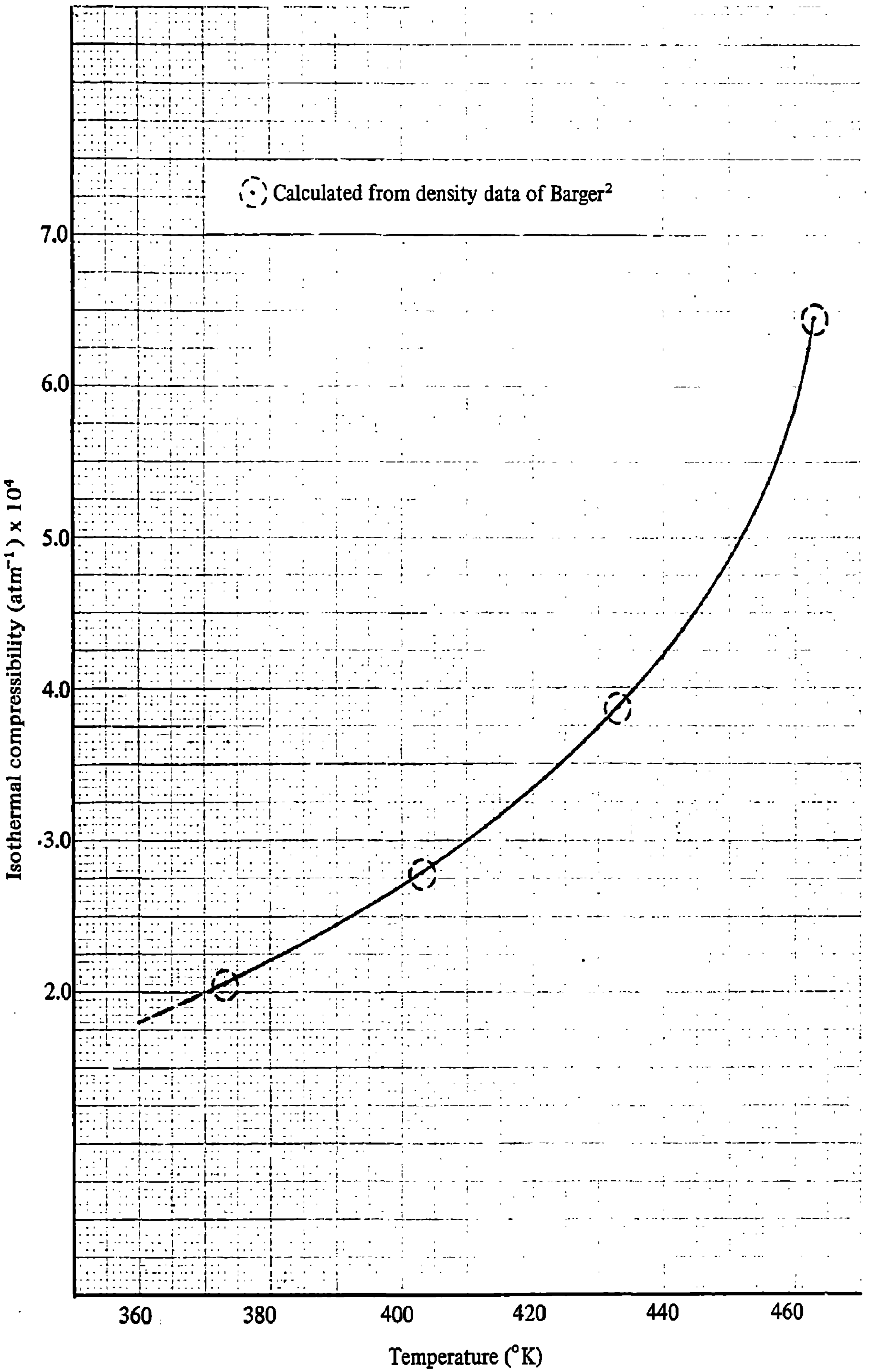


Figure 2.5-7. Isothermal Compressibility versus Temperature, Liquid UDMH

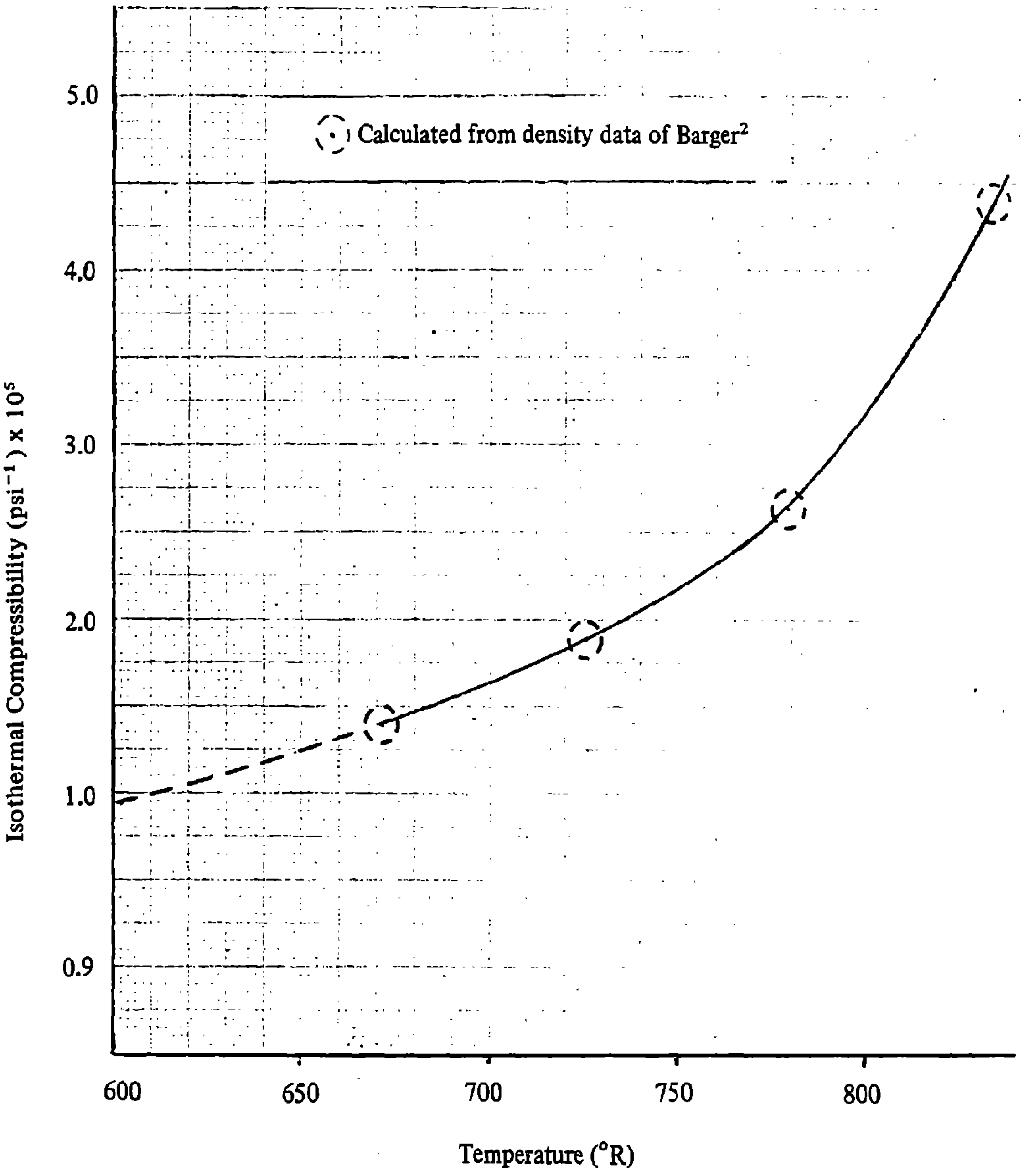
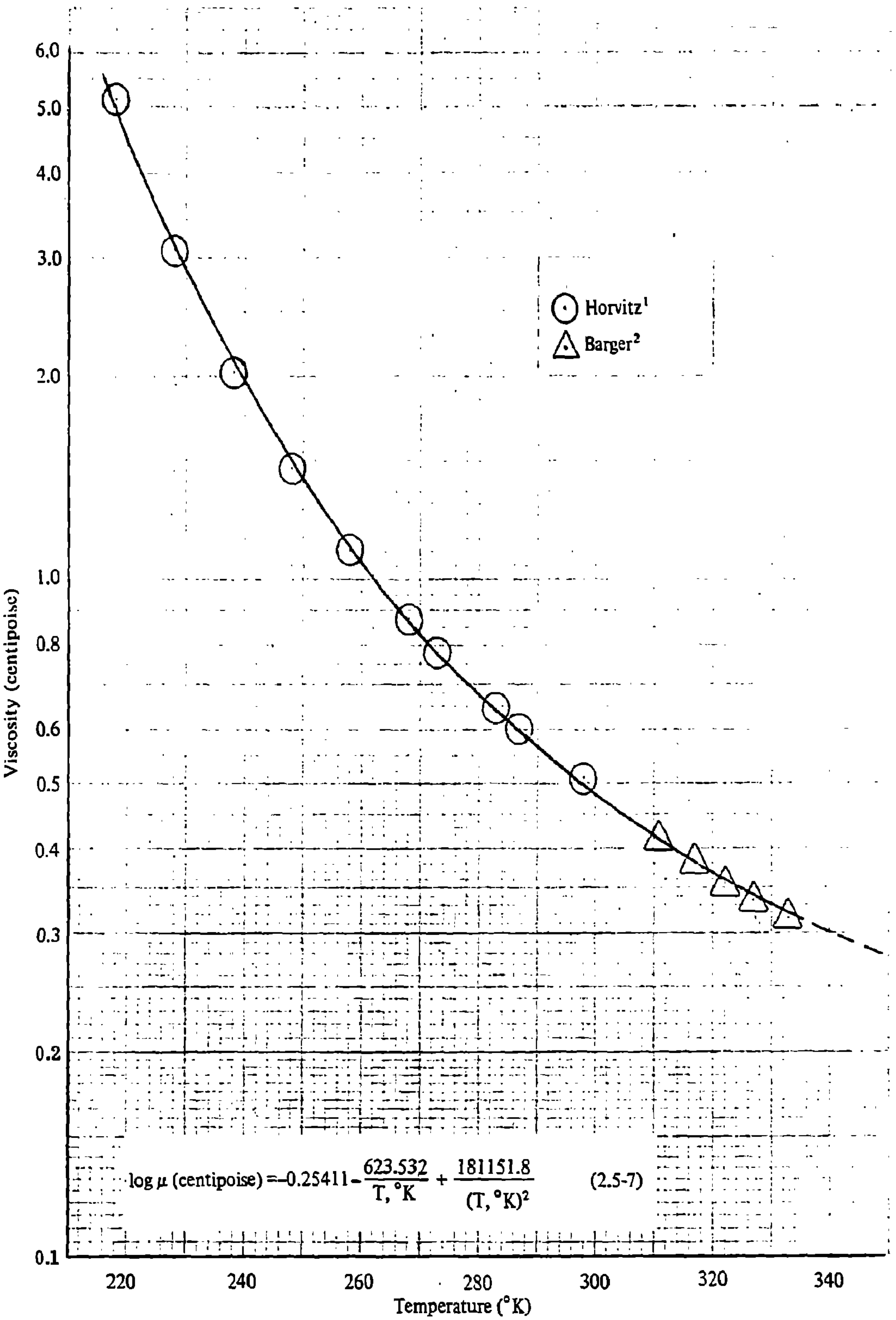
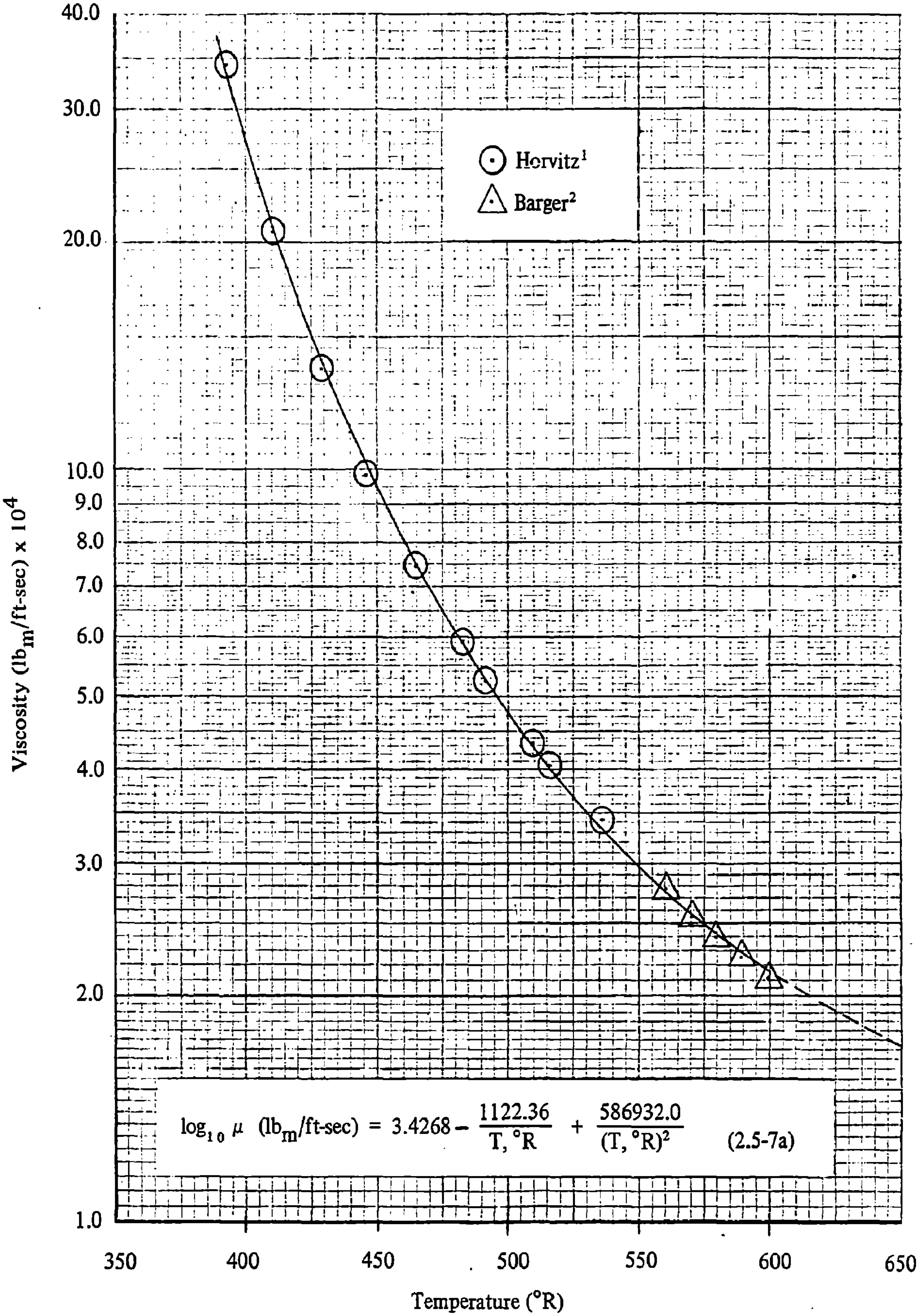


Figure 2.5-7a. Isothermal Compressibility versus Temperature
Liquid UDMH



$$\log \mu \text{ (centipoise)} = -0.25411 - \frac{623.532}{T, {}^\circ K} + \frac{181151.8}{(T, {}^\circ K)^2} \qquad (2.5\text{-}7)$$

Figure 2.5-8. Viscosity versus Temperature, Liquid UDMH



$$\log_{10} \mu \ (\mathrm{lb_m/ft\text{-}sec}) = 3.4268 - \frac{1122.36}{T,\ ^\circ R} + \frac{586932.0}{(T,\ ^\circ R)^2} \qquad (2.5\text{-}7a)$$

Figure 2.5-8a. Viscosity versus Temperature, Liquid UDMH

The viscosity at room temperature (77 F) is 3.309 x 10^{-4} lb_m/ft-sec or at 25 C, 0.4925 centipoise. The standard deviation of the experimental data from the smoothed values of equation 2.5-7 is 0.055 centipoise and the average percent deviation is 1.6%. Additional experimental work is required to define the viscosity at higher temperatures.

2.5.3.6 Surface Tension and Parachor of Liquid UDMH

The only experimental surface tension data for liquid UDMH appears to be in the work of Barger (2). A capillary-rise method was used but details were not given. The temperature range from -54 to 50 C (-65 to 121 F) was covered. The experimental data are shown in Figures 2.5-9 and 2.5-9a.

The variation of surface tension with temperature is nearly linear for the temperature range covered and equation 2.5-8 adequately describes this variation.

$$\gamma(\text{dynes/cm}) = 56.705 - 0.1094\ (T, {}^\circ K) \qquad (2.5\text{-}8)$$

$$\gamma(lb_f/ft) = 3.8855 \times 10^{-3} - 4.1646 \times 10^{-6}\ (T, {}^\circ R) \qquad (2.5\text{-}8a)$$

A parachor value of 171.3 at 298.15 K was determined from the relation:

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

where

P = parachor
M = molecular weight (60.102)
γ = surface tension (24.087 dynes/cm)
ρ_l = 0.7861 g/cc
ρ_v = 0.0089 g/cc (ideal gas)

From the atomic parachors given by Daniels (34) (C=4.8, H=17.1, N=12.5), a value of 171.4 is obtained without considering bonding energies.

2.5.3.7 Thermal Conductivity of Liquid UDMH

The only thermal conductivity data on liquid UDMH appears to be the study recently made by Rocketdyne (9). Conductivity measurements were made over a temperature range from 0 to 251 F (-18 to 122 C).

The conductivity apparatus consisted of two concentric aluminum alloy cylinders. The test fluid was contained in a thin annular passage between the two cylinders. The ends of the annulars were sealed with Teflon O-rings to minimize heat conduction and to hold the cylinders concentric. Six pairs of copper-constantin thermocouples were embedded at various locations in both cylinders. An electrical resistance heater in the inner cylinder supplied the heat energy for the temperature gradient across the sample liquid.

The experimental data are plotted in Figures 2.5-10 and 2.5-10a. Two or more readings were taken at each of the six temperatures studied. The data scatter is somewhat severe, which is not unusual for this property which is inherently difficult to measure.

Using the least-squares method, the data as a linear function of temperature are expressed by:

$$K(\text{cal/cm-sec-}{}^\circ K) = 6.7975 \times 10^{-4} - 1.0187 \times 10^{-6}\ (T, {}^\circ K) \qquad (2.5\text{-}9)$$

$$K(\text{BTU/ft-sec-}{}^\circ R) = 4.5648 \times 10^{-5} - 3.8007 \times 10^{-8}\ (T, {}^\circ R) \qquad (2.5\text{-}9a)$$

The average deviation of the data was calculated to be 1.6%. The sample purity was given as 99.8% by weight.

2.5.3.9 Index of Refraction

The refractive index of hydrazine-UDMH mixtures has been reported by both Chang (3) and Pannetier (36). The experimental data were obtained at the sodium-D wavelength and only at the single temperature of 25 C (77 F). Chang reports a value for pure UDMH of 1.4051, while Pannetier gives 1.4055. The average index is then 1.4053. Additional studies are required to define this property as a function of temperature.

2.5.4 CHEMICAL PROPERTIES

2.5.4.1 Chemical Reactions.

UDMH is somewhat unique in that it is completely miscible in both polar and nonpolar solvents. It can generally be classified as a weak organic base and a strong reductant having antioxidant properties.

FMC (28) suggests many possible uses for UDMH and gives several chemical reactions. Some of the chemical reactions which are significant to propellant fuel applications are listed.

Salt Formation

Acids form two series of salts with UDMH in the general reaction:

$$(CH_3)_2N_2H_2 + HX \rightarrow (CH_3)_2N_2H_2 \cdot HX$$

$$(CH_3)_2N_2H_2 + HX \rightarrow (CH_3)_2N_2H_2 \cdot 2HX$$

Salts formed from hydrochloric, sulfuric, nitric, phosphoric, oxalic and picric acid have been synthesized.

Hydrazine Formation

Aldehydes and ketones react with UDMH to form dimethylhydrazones:

$(CH_3)_2\,N_2H_2 + RCHO \rightarrow (CH_3)_2\,N_2 = CHR$

$(CH_3)_2\,N_2H_2 + RRCO \rightarrow (CH_3)_2\,N_2 = CRR'$

Reduction of dimethylhydrazones may form trisubstituted hydrazines:

$(CH_3)_2N_2H_2 = CHR \rightarrow (CH_3)_2NNHCH_2R$

Carbon Dioxide Reaction

CO_2 reacts with UDMH to form dimethylcarbozate:

$(CH_3)\,N_2H_2 + CO_2 \rightarrow (CH_3)_2\,NNHCOOH$

and further reaction leads to the formation of a salt complex:

$$(CH_3)_2\,N_2H_2 + (CH_3)_2\,NNHCOOH$$
$$\rightarrow \left[(CH_3)_2\,NNHCOO\right]^-(CH_3)_2\,NNH_3^+$$

Boron Compound Reactions

With some Boron compounds UDMH forms well defined compounds:

$(CH_3)_2\,N_2H_2 + BF_3 \rightarrow (CH_3)_2\,N_2H_2 \cdot BF_3$

$(CH_3)_2\,N_2H_2 + Et_3B \rightarrow (CH_3)_2\,N_2H_2 \cdot Et_3B$

Oxidation of UDMH

Gray (31) has investigated the oxidation of UDMH vapors and has defined four distinct regimes depending on mixture, pressure and temperature; slow reaction, chemiluminescent oxidation, weak ignition and strong explosion.

The complete oxidation is very exothermic:

$$(CH_3)_2\,N_2H_2 + 4O_2 \rightarrow 2CO_2 + 4H_2O + N_2$$

(+472.6 kcal/mole)

At 514 C, strong explosions occurred for mixtures of 20 to 40% UDMH. The minimum total pressure for a strong explosion was found to be at composition close to UDMH + 2 O_2. At compositions above 40% ODMH, the ignition was weak.

Chemiluminesience reactions (cool flame) occurred at temperatures from 300 to 400 C for a UDMH + 2 O_2 mixture.

Slow oxidation occurs at a fuel rich mixture of approximately 40 UDMH + O_2 at 420 C. The reaction occurs without light emission.

2.5.4.2 Inert Gas Solubility in Liquid UDMH

The solubility of gaseous helium, nitrogen and argon in liquid UDMH has been studied by Chang (23). The UDMH (solvent) was weighed and placed in a container with a glass enclosed magnetic bar for stirring. The volume of the solvent was determined from the measured weight and known density. The pressures were measured with a manometer equipped with a microslide cathetometer. The apparatus had three calibrated volumes for the measurements of the admitted gases.

The amount of dissolved gas can be determined from the relationship

$$X = KP$$

where,

X = mole fraction dissolved gas
P = partial pressure of the gas (atmospheres)
K = equilibrium constant

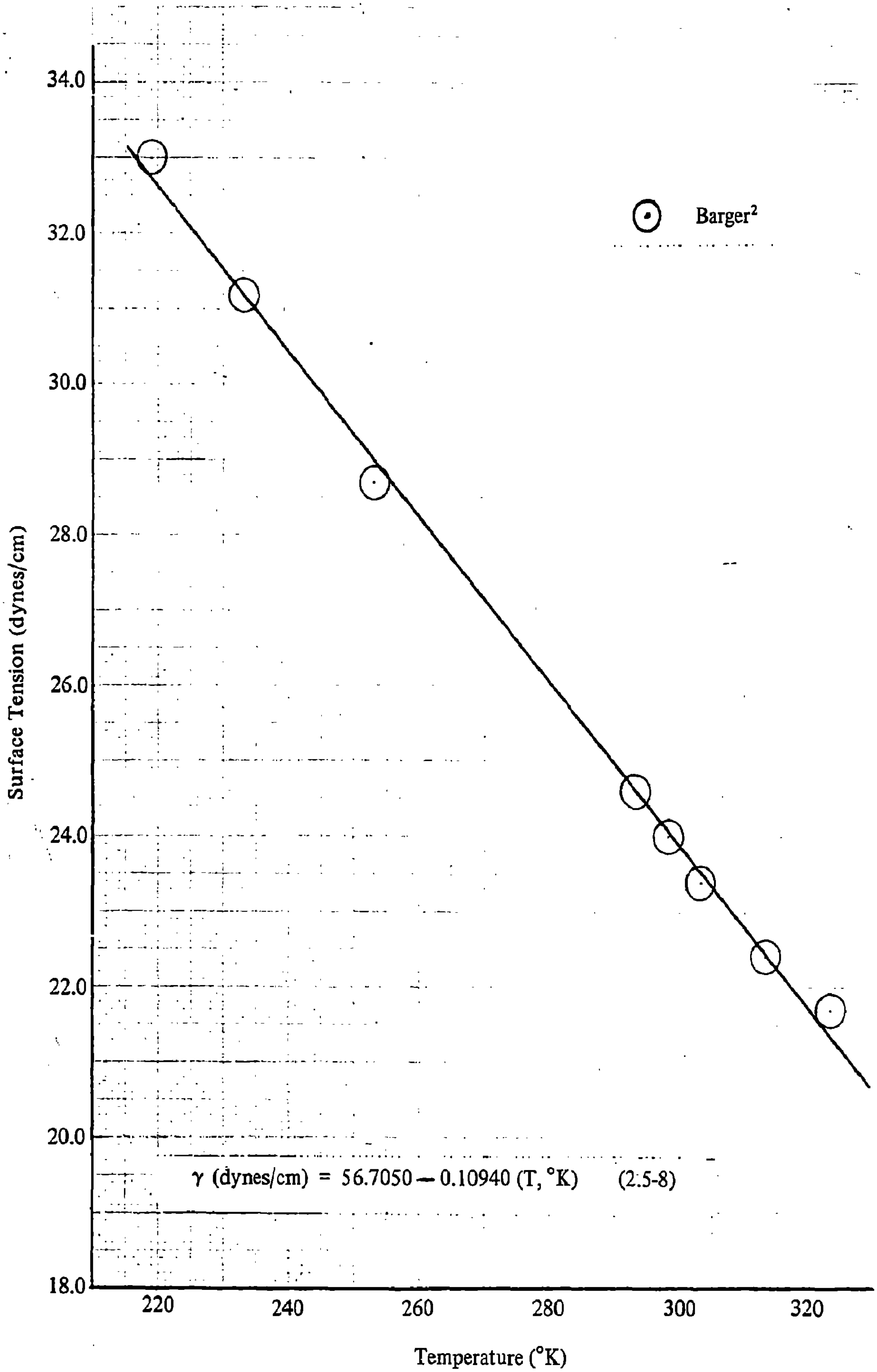
The values of K as reported by Chang are plotted in Figures 2.5-11 and 2.5-11a. To determine the amount of dissolved gas in a pressurized tank, the vapor pressure of the UDMH should be subtracted from the measured total pressure.

2.5.5 THERMODYNAMIC PROPERTIES

2.5.5.1 Heat of Formation and Combustion of UDMH

The heat of combustion of UDMH has been determined in separate investigations by Aston(4) and Donovan (11). The heat of combustion given by Donovan is 473.28 kcal/mole. The value obtained from Aston's work after corrections to constant pressure and to 25 C is 474.122. The agreement between the two studies is good and the average heat of combustion becomes 473.701 kcal/mole at 25 C.

Combining this heat of combustion at 298 K with the heats of formation of gaseous carbon dioxide and liquid water reported by Wagman (12) yields a heat of formation of 12.339 kcal/mole for the liquid at 298 K.



γ (dynes/cm) = 56.7050 − 0.10940 (T, °K) (2.5-8)

Figure 2.5-9. Surface Tension versus Temperature Liquid UDMH

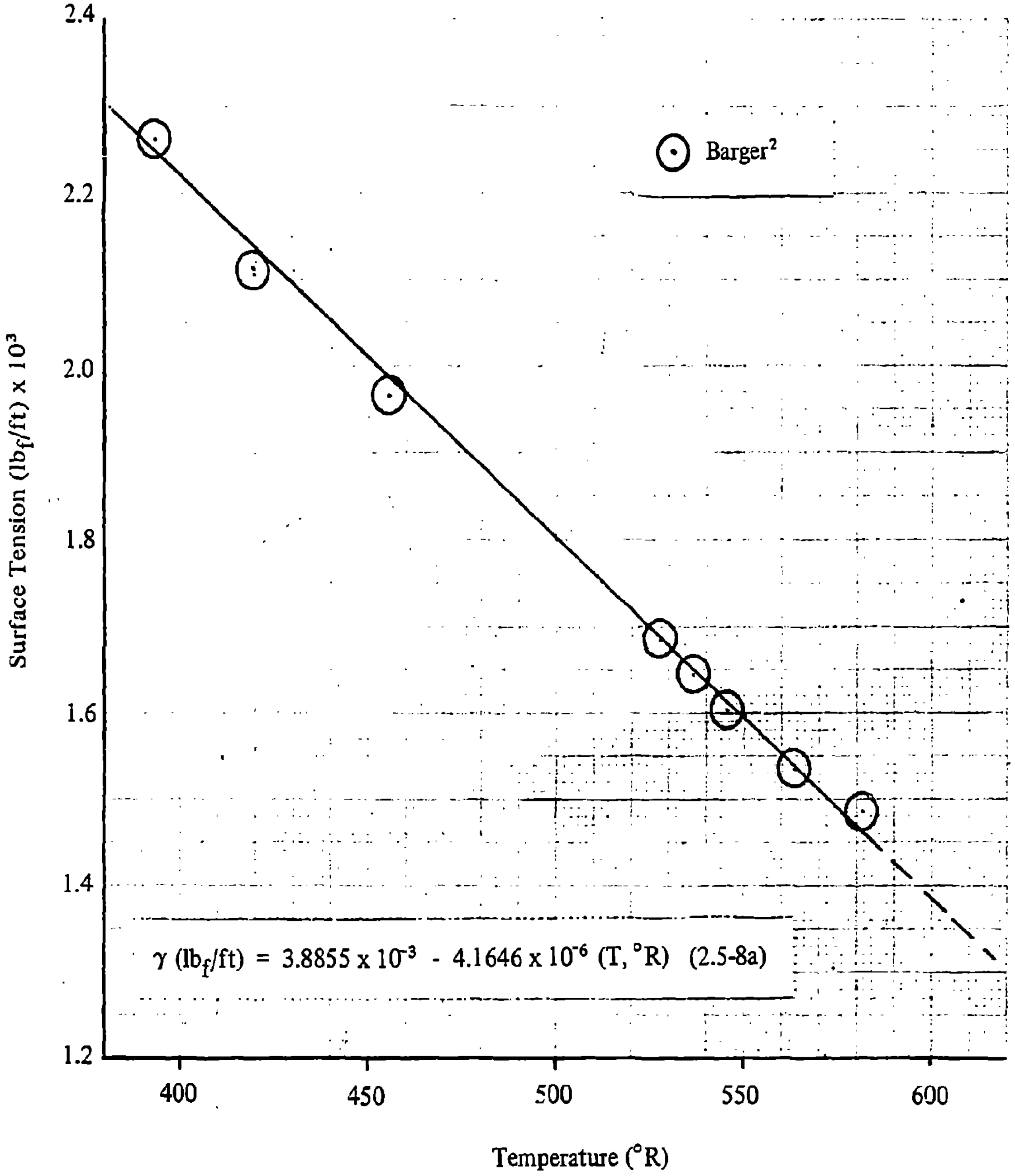


Figure 2.5-9a. Surface Tension versus Temperature, Liquid UDMH

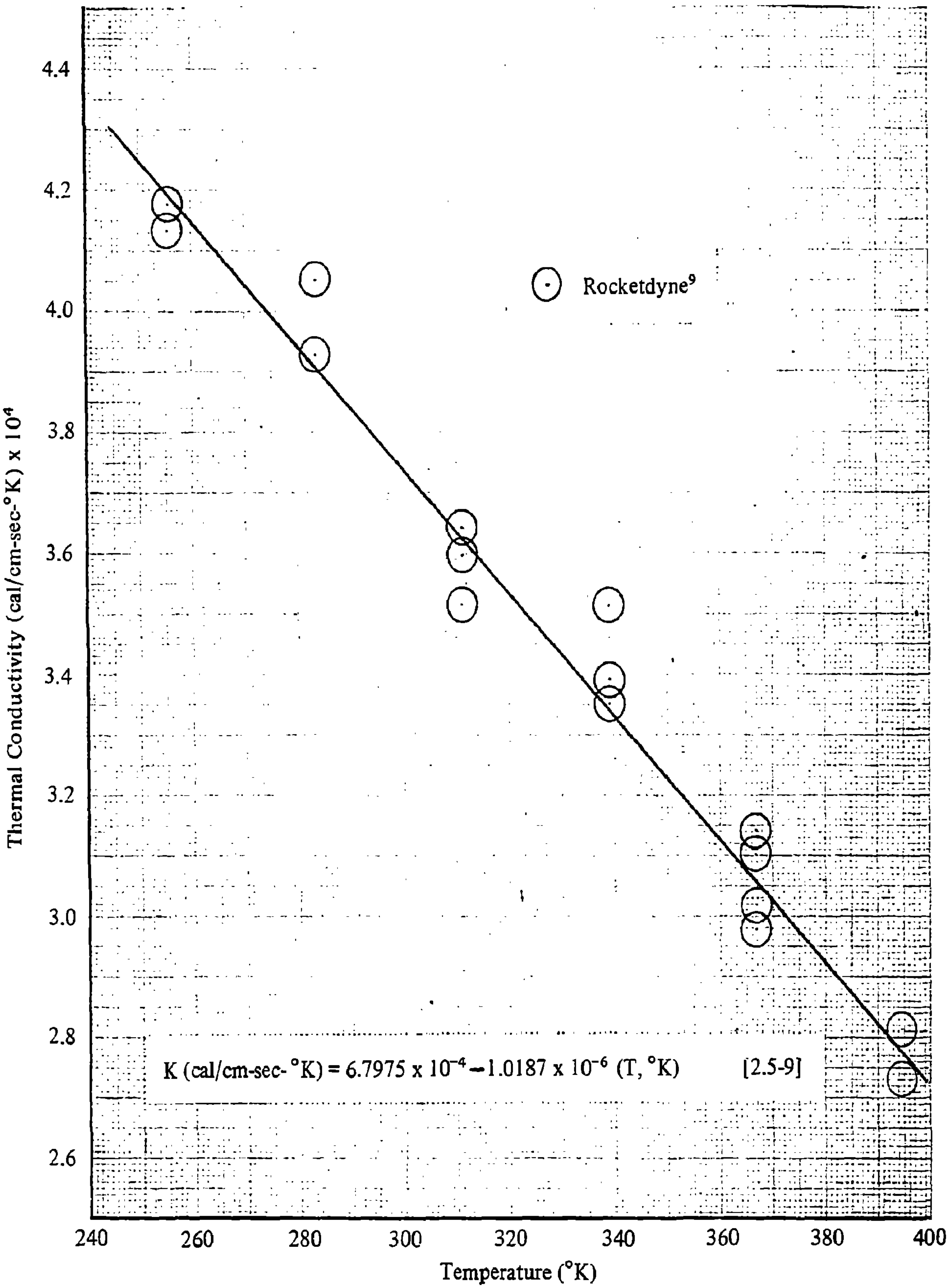
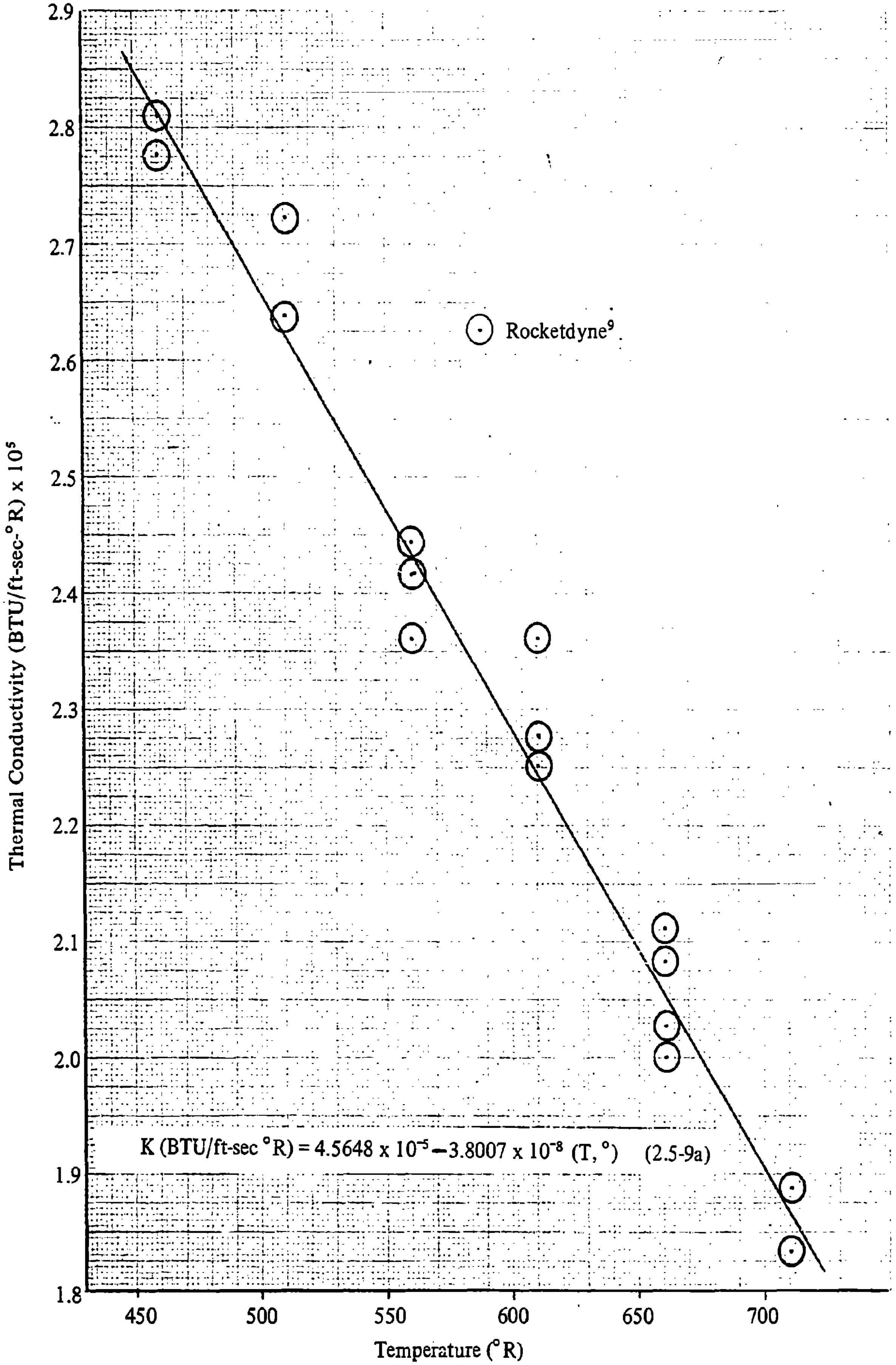


Figure 2.5-10. Thermal Conductivity versus Temperature,Liquid UDMH



K (BTU/ft-sec °R) = $4.5648 \times 10^{-5} - 3.8007 \times 10^{-8}$ (T, °) (2.5-9a)

Figure 2.5-10a. Thermal Conductivity versus Temperature of Liquid UDMH

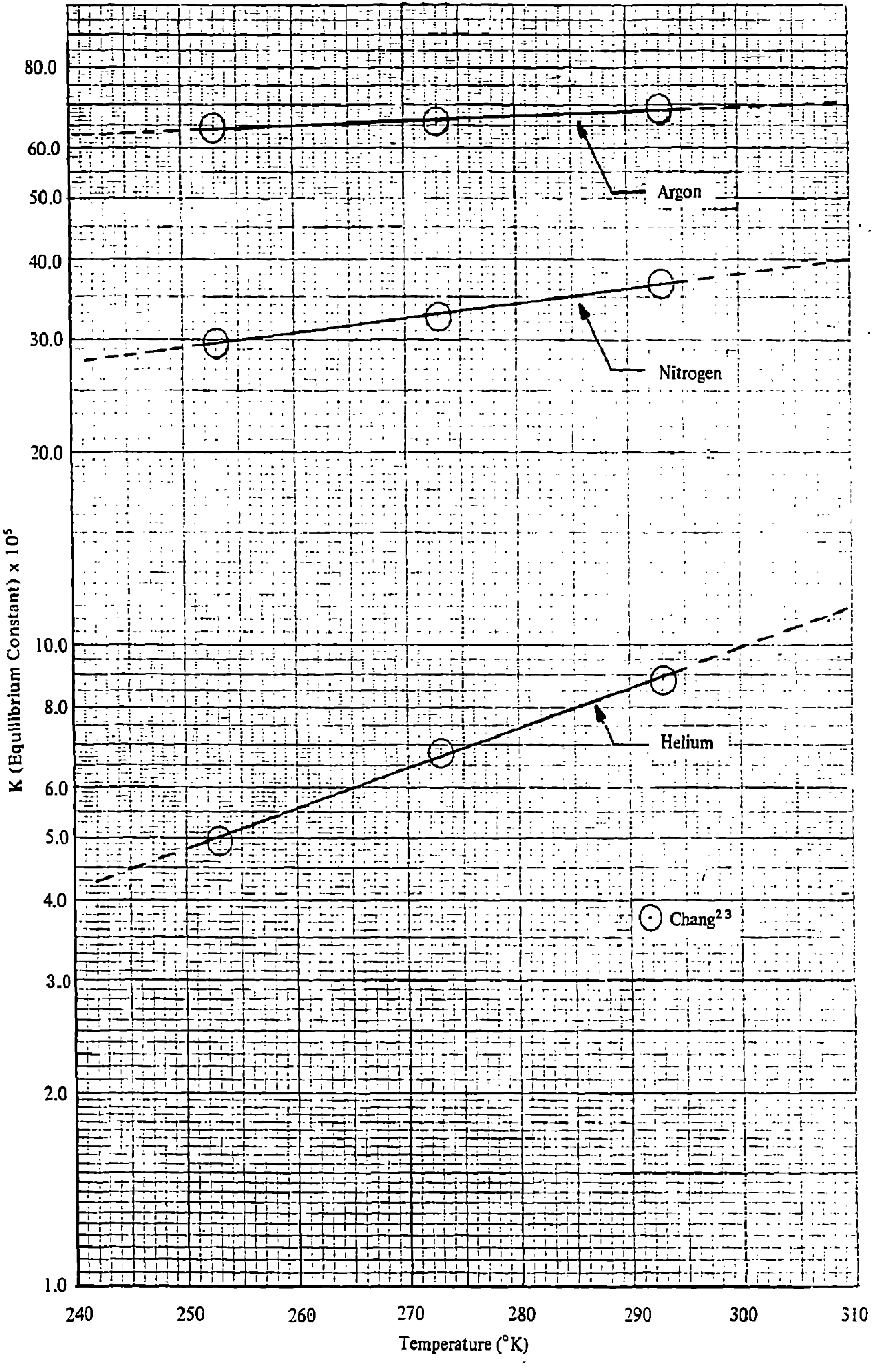


Figure 2.5-11. Gas Solubility in Liquid UDMH

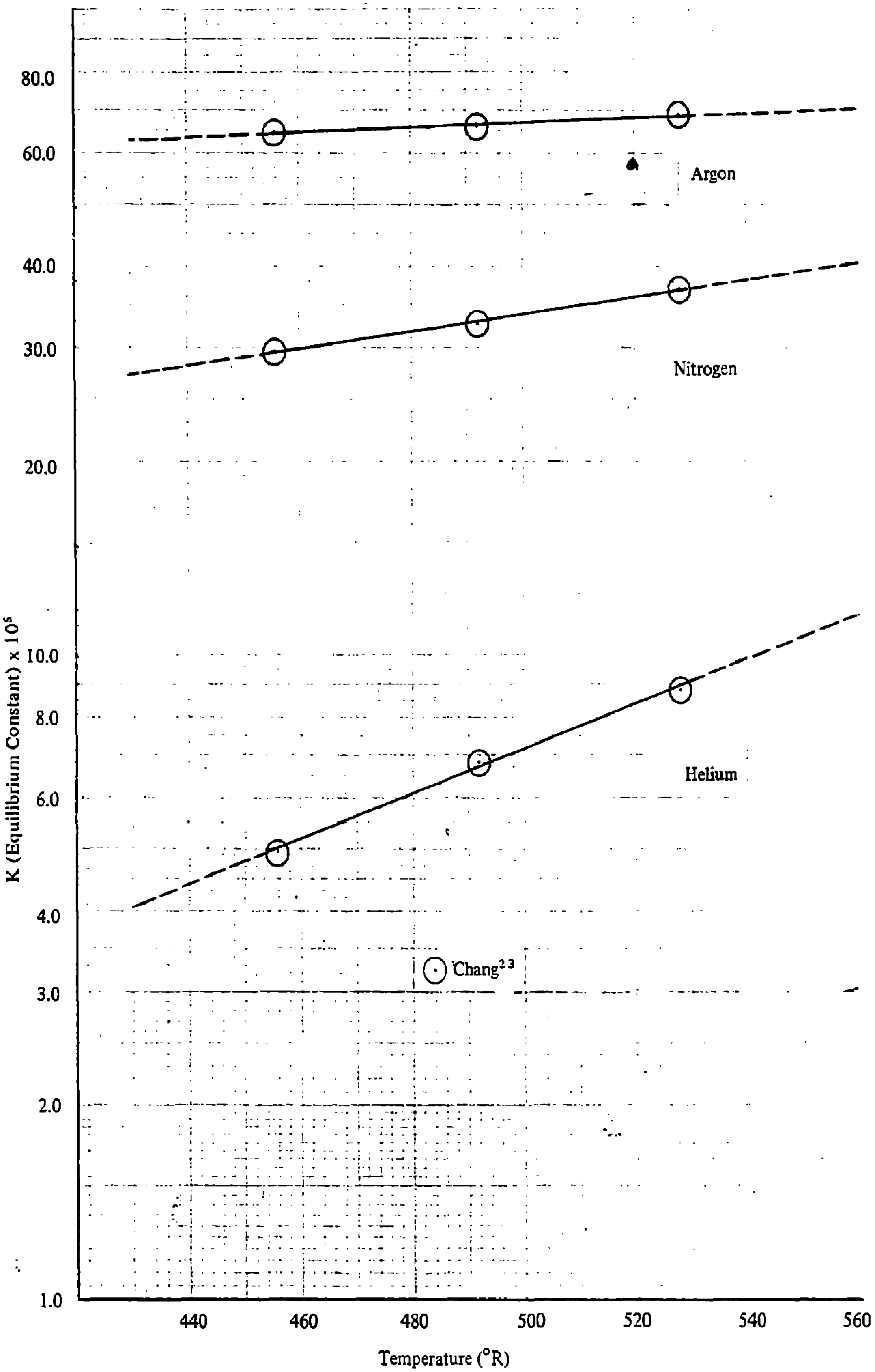


Figure 2.5-11a. Gas Solubility in Liquid UDMH

	ΔH(kcal)
$2CO_2 (g, 298) + N_2 (g, 298)$ $\rightarrow C_2H_8N_2 (\ell, 298) + 4 O_2 (g, 298)$ $+ 4 H_2O (\ell, 298)$	473.701
$2C (s, 298) + 2 O_2 (g, 298) \rightarrow 2 CO_2 (g, 298)$	2(-94.051)
$4H_2 (g, 298) + 2 O_2 (g, 298) \rightarrow 4 H_2O (\ell, 298)$	4(-68.315)
$2C (s, 298) + 4 H_2 (g, 298)$ $\rightarrow C_2H_8N_2 (\ell, 298) + N_2 (g, 298)$	12.339

Aston reported a mean value of 32948.3 ±48.7 international joules per gram at 30 degrees for the heat of combustion from four separate determinations. Using a conversion factor of one calorie equal to 4.1833 international joules and a molecular weight of 60.102, the heat of combustion becomes 473.3724 kcal/mole at constant volume at 30 C.

The heat of combustion at constant pressure is calculated from

$$\Delta H = \Delta E + \Delta n RT$$

where,

ΔH = heat of combustion at constant pressure
ΔE = heat of combustion at constant volume
Δn = difference in the number of moles of gas between the reactants and products

For the combustion of UDMH at 30 C then

$$\left[C_2H_8N_2 (\ell\, 30^\circ C) + 4 O_2 (g, 30^\circ C) \rightarrow 2CO_2 (g, 30^\circ C) + N_2 (g, 30^\circ C) + 4 H_2O (\ell\, 30^\circ C)\right]$$

Δn = −1 and

$$\Delta H_{30^\circ C} = -473.3724 + (-1)(1.98717 \times 10^{-3})(273.15 + 30.0)$$

$$\Delta H_{30^\circ C} = -473.9748$$

Using the following equation the heat of combustion can be changed from 30 C to the standard reference temperature of 298.15 K (25 C).

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \, dT$$

Since the limits of the above integral are very small for this case, the change in heat capacity was assumed to be constant over the limited temperature range and the equation above is then

$$\Delta H_{303^\circ K} - \Delta H_{298^\circ K} = \Delta Cp (303\text{-}298)$$

Using the heat capacities of the gaseous products CO_2, N_2 and O_2 from Hilsenrath (13), the heat capacity of liquid UDMH from Aston(7) and the heat capacity of liquid water from Rossinni (14) the heat of combustion at 298 K is calculated as follows:

$$\Delta H_{298^\circ K} = \Delta H_{303^\circ K} - \Delta Cp (303\text{-}298)$$

$$\Delta H_{298^\circ K} = -473.9748 - [2 (0.00896) + (0.00697) + 4 (0.01798) - (0.03928) - 4 (0.00703)] (303\text{-}298)$$

$$\Delta H_{298^\circ K} = -473.9748 - [0.01792 + 0.00697 + 0.07192 - 0.03928 - 0.02812] [5]$$

$$\Delta H_{298^\circ K} = -473.9748 - [0.14705]$$

$$\Delta H_{298^\circ K} = -474.122 \text{ kcal/mole}$$

2.5.5.2 Melting Point and Heat of Fusion

The melting point (triple point) of liquid UDMH has been experimentally measured by Aston(7). The equilibrium temperature of high purity UDMH was observed with increasing fractions of the sample method. At the reported ice point of 273.16 K, the melting point given by Aston was 215.951 K. At the presently accepted ice point, this value becomes 215.943 K (−57.21 C) or 388.70 R (−70.97 F).

Heat of fusion was also determined by Aston(7). Three separate determinations were made and after correcting for premelting, the average reported was 2.4074 ± 0.0015 kcal/mole or 72.099 BTU/lb.

2.5.5.3 Critical State Constants

Aston (7) estimated the critical temperature of UDMH to be 522 K (939.6 R) and the critical pressure to be 60 atmospheres (882 psia). The only experimental work is that reported by Barger (2). Originally, Barger attempted to measure the disappearance of the meniscus by gradually increasing the pressure. This method proved inconclusive because of the decomposition of the UDMH which resulted in a non-condensible gas at the temperature conditions.

The experimental method was modified and the sample was maintained at 240 C (432 F) and sufficient pressure applied to maintain the sample in the liquid state. After thermal equilibrium was achieved, the temperature was rapidly raised and the pressure adjusted so that both liquid and vapor were present. The temperature and pressure at which the two-phase condition could no longer be maintained were recorded as the critical constants. The reported values for temperature and pressure respectively were: 250 C (482 F) and 53.5 atmospheres (786 psia).

Barger states that the method used precluded absolute accuracy, but feels that the values are a good estimate. It would appear that the critical temperature is more valid than the pressure reading. Using the vapor pressure equation for elevated temperatures (equation 2.5-2), a critical pressure of 59 atmospheres (867 psia) was obtained at the critical temperature and is accepted in this work.

The critical density is reported by Barger (2) to be 0.275 g/cc and was taken from a constructed phase diagram.

2.5.5.4 Heat Capacity of Liquid UDMH

The heat capacity of liquid and solid UDMH has been measured, by Aston(7) from -260 to 25 C -436 to 77 F using a platinum calorimeter. Fifty-four separate readings were obtained over this temperature range. A platinum resistance thermometer was used to record the sample temperatures.

Aston did not report the experimental data points, but rather the smoothed data at integral temperature increments. The liquid heat capacity measurements had a reported mean deviation of only 0.01% from the best curve. The fractional distilled sample had an estimated purity of 99.99 mole % based on the melting point data.

Additional heat capacity data have been reported by Rocketdyne (8), (9) from 1.7 to 71 C (35 to 160 F). The data were originally reported in Reference (9) and later in Reference (8). The data reported in the later reference are approximately 0.6% lower.

The experimental data given in the Rocketdyne study are plotted in Figures 2.5-12 and 2.5-12a along with the smoothed values given by Aston. The scatter of the Rocketdyne data appears to be excessive. A comparison of the data near 500 R where the temperature range of the two studies overlap, shows the Rocketdyne data to be 0.7 to 4.5 % higher. At this temperature range, Rocketdyne used a copper sample container. At the higher temperatures, an aluminum container was used.

The experimental heat capacity as a function of tem- [illegible]

The trend of the Rocketdyne data would indicate the slope increases with temperature. This trend is generally true of liquids but is usually pronounced at temperatures closer to the critical point.

Rocketdyne (8) also measured the heat capacity of water in the same equipment and obtained results higher than the literature values. The apparent discrepancies are presently being investigated by Rocketdyne. Until the results of this investigation are published, the heat capacity of UDMH reported here should be considered provisional.

Since the experimental data are conflicting, the type of least-squares curve fit is somewhat academic. It was found that the linear expression gave the smallest standard deviation:

$$C_p\ (\text{cal/g - }^\circ\text{K}) = 0.4071 + 8.838 \times 10^{-4}\ (T, {}^\circ\text{K}) \quad (2.5\text{-}8)$$

$$C_p\ (\text{BTU/lb -}^\circ\text{R}) = 0.4071 + 4.909 \times 10^{-4} (T, {}^\circ\text{R}) \quad (2.5\text{-}8a)$$

The maximum deviation of the Aston data from the linear fit is 2.9% while the maximum deviation of the Rocketdyne data is 3.8%. The average deviation is 1.3%.

2.5.5.5 Latent Heat of Vaporization and Trouton's Constant

The heat of vaporization at 25 C (77 F) has been experimentally determined by Aston (7) to be 8.366 ±0.016 kcal/mole or 250.55 BTU/lb. Chang (3) reports a calculated value of 7.844 kcal/mole from his vapor pressure work. The measured value obtained by Aston is retained in this manual. From equation 2.5-1, a value of 7.797 kcal/mole (233.51 BTU/lb is obtained at the normal boiling point from the Clapeyron equation (see Section 2.5.3.1).

$$H_V = T, {}^\circ K\ (V_v - V_\ell)\ \frac{dP}{dt}$$

The Trouton constant is calculated to be 23.2 using the calculated heat of vaporization value (7.797 kcal/mole).

2.5.6 LOGISTICS OF UDMH

2.5.6.1 Manufacture

The principal supplier of UDMH in this country is the Food Machinery and Chemical Corporation with the manufacturing plant in Baltimore, Md. The synthesis of UDMH is accomplished by FMC through the nitrosation of dimethylamine (DMA) to N-nitrosodimethylamine, followed by the reduction of this intermediate to $(CH_3)_2\ N_2H_2$ (UDMH):

$$(CH_3)_2\ NH + HNO_2 \rightarrow (CH_3)_2\ NNO + H_2O$$

$$(CH_3)_2\ NNO + NH_3 \rightarrow (CH_3)_2\ NNH_2 + H_2O$$

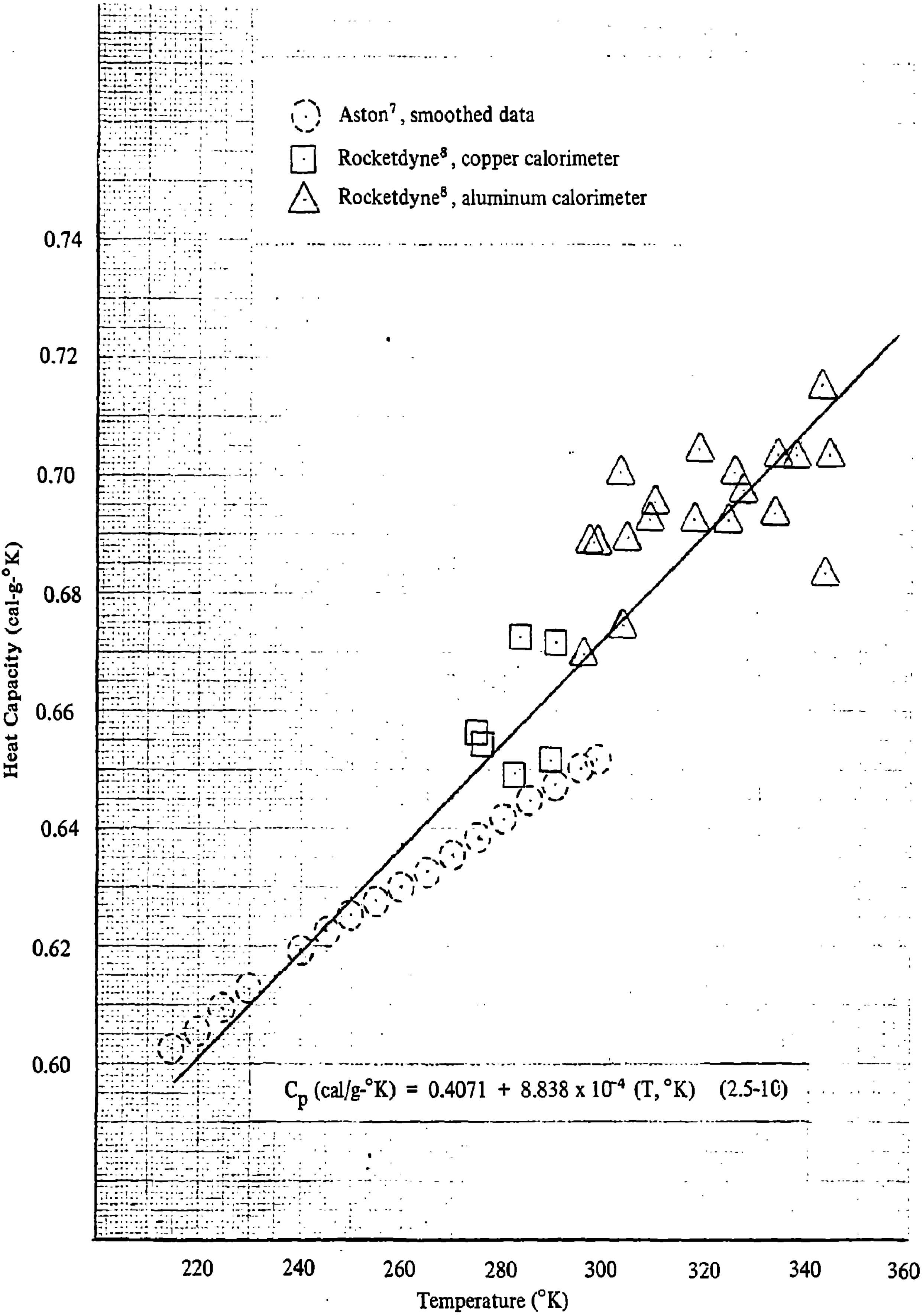


Figure 2.5-12. Heat Capacity versus Temperature
Liquid UDMH

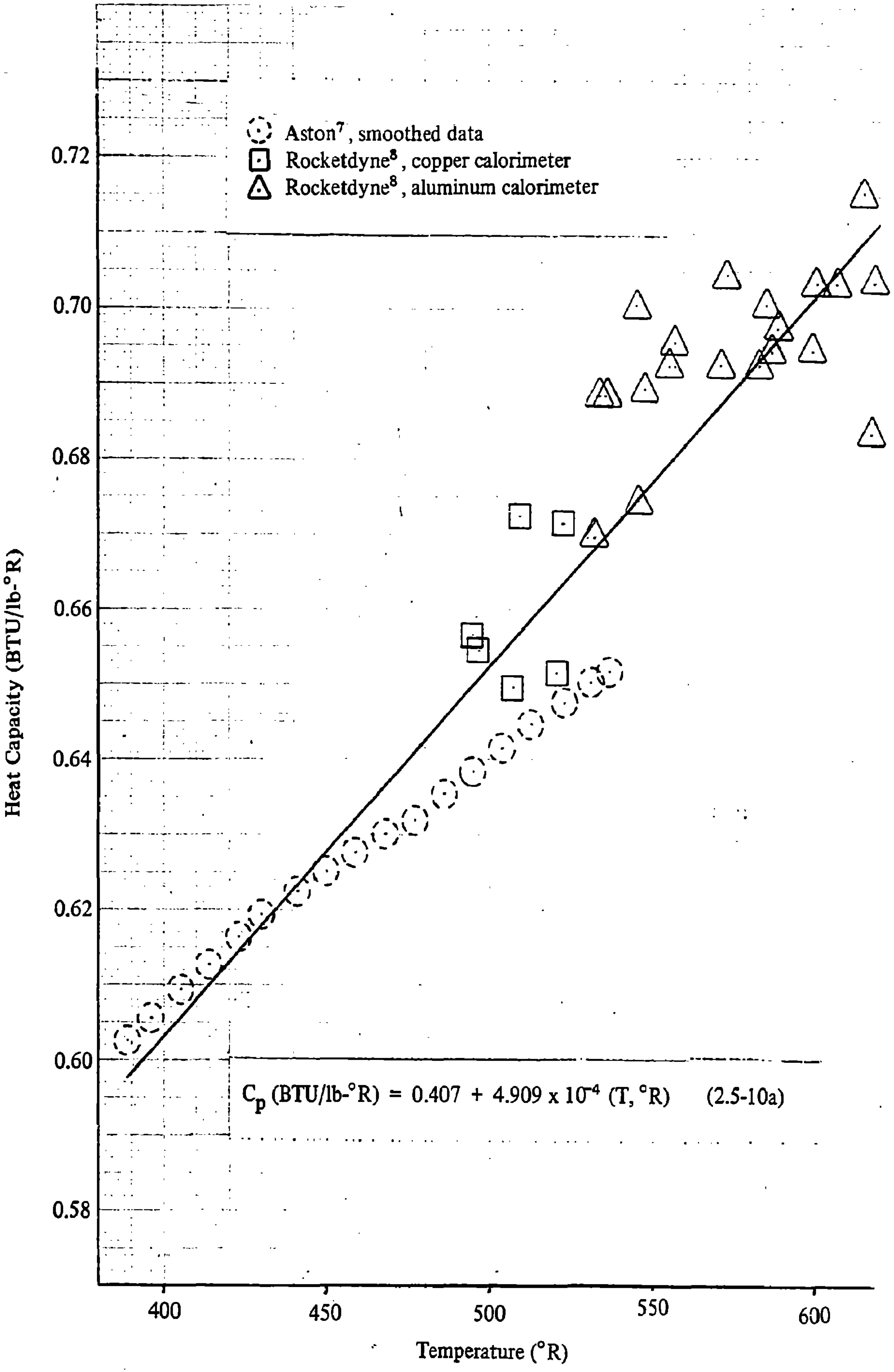


Figure 2.5-12a. Heat Capacity versus Temperature Liquid UDMH

The dilute aqueous solution is then purified and distilled to obtain a nearly anhydrous UDMH.

Another method of manufacture is the Raschig process used in the manufacture of hydrazine and methylhydrazine. For UDMH the process is modified by the substitution of dimethylamine for ammonia in the second step reaction with chloramine.

2.5.6.2 Analysis

The analysis of propellant grade UDMH is covered in MIL-P-25604C (May 1963) including attachment S/N 9135-687-4293 dated June 1967.

UDMH assay can be determined by direct titration with potassium iodate (KIO_3) in the presence of concentrated hydrochloric acid. The procedure is essentially the same as given for hydrazine and methylhydrazine. The detailed procedures are given in MIL-P-25604C.

The water content of UDMH is determined by gas chromotography according to procedures found in attachment S/N 9135-687-4293 to the specification. Since gas chromotography offers an accurate determination of water content, it could also afford an accurate means of determining assay.

The density at 25 C (77 F) must have a minimum of 0.783 and a maximum of 0.786 g/cc. The melting point must be -70 F (390 R) or less. The light transmittancy must be at least 90% that of distilled water as measured by colorimeter. A 100 ml sample shall be distilled at a rate of 4 to 5 ml per minute. The temperature recorded after 10% distillation must be greater than 143.0 F and after 90% distillation the temperature must be 148.0 F or less. The distillation flask should then be cooled to assure that distillation losses were not over 3.0%.

2.5.6.3 Cost and Availability

UDMH is readily available in large quantities for the aerospace industries which had a yearly consumption of approximately 19 million pounds in 1964. The principal use of UDMH is the neat fuel for the Agena engine and as a 50-50 blend with hydrazine for the Titan II program.

At the present time, the sole supplier of large scale quantities is the Food Machinery and Chemical Corporation, Baltimore, Md. UDMH is being procured on a long time commitment basis by the government. The unit price is $0.59/pound from the government in drum lots.

2.5.6.4 Shipping and Transportation

tank cars are constructed of mild steel and the drums are nonreturnable.

Container		Net Lading
1-gallon glass bottle		6 lb
5-gallon drum, ICC-17C		30 lb
55-gallon drum, ICC-17C		335 lb
Tank car, ICC-103W -	4,000-gal	26,500 lb
	6,000-gal	39,750 lb
	8,000-gal	53,000 lb

UDMH has also been handled by tank truck, and this service can be arranged if desired. Railway express shipments are limited to five pints per case, and up to this amount may be shipped by air, but only on all-cargo flights.

UDMH is classified by the ICC as a flammable liquid and requires a red label during shipment. It must be packed in containers covered by the following ICC specifications:

1D: Boxed glass carboys

15A, B or C: Wooden boxes with inside containers; these must consist of (1) glass bottles not holding over one gallon each and cushioned by vermiculite within tin cans, which shall be tightly closed or (2) containers not holding over two quarts each and made of aluminum no less than 0.104 inch thick; closures and gaskets must be of material that will not react dangerously with, or be decomposed by contact with UDMH.

5A, 5C, 17E: (Single Trip): Metal barrels or drums of type 304 or 347 stainless steel, with openings not exceeding 2.3 inches in diameter.

17C: Mild-steel barrels or ICC-42B aluminum drums (Single-trip), with openings not exceeding 2.3 inches in diameter.

The ICC has recently approved the following specifications for transporting UDMH:

Tank cars - 103W, 103c-W, 105A100-W, 105A200-W, 105A400-W, 105A500-W, 105A600-W or 111A100-W4.
Tank motor vehicles - MC-300, MC-301, MC-302, MC-303, MC-310, or MC-311.

Complete information is contained in the Code of Federal Regulations, Title 49, Parts 71 to 90.

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2.6 50-50 BLEND

2.6.1 PROPERTY SUMMARY SHEET

Chemical Name:	50% 1, 1 Dimethyhydrazine +50% Hydrazine	Common Name:	50-50
Empirical Formula:	$C_{0.6956}H_{5.3911}N_{2.0}$	Formula Weight:	41.805
Composition: % b.w.:	50.0 $C_2H_8N_2$ + 50.0 N_2H_4		

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	267.6	°K		5	2.6-13
	-5.6	°C			
	481.7	°R			
	22.0	°F			
NORMAL BOILING POINT	343	°K		1, 2	
	70	°C			
	618	°R			
	158	°F			
HEAT OF VAPORIZATION	8.048	kcal/mole	NBP	calc.	
	346.3	BTU/lb			
TROUTON CONSTANT	23.5		NBP	calc.	
CRITICAL STATE CONSTANTS					
	607	°K		1, 3	
	334	°C			
	1093	°R			
	633	°F			
Pressure	117.5	atms		calc.	
	1731	psia			
Density	Not Avail	g/cc			
		lb/ft^3			
VAPOR PRESSURE OF LIQUID	138.4	mm Hg	298	1, 2, 3	2.6-1, 2.6-2
	2.68	psia			
DENSITY OF LIQUID	0.8987	g/cc	298	1, 4, 7	2.6-3
	56.103	lb/ft^3			
SONIC VELOCITY	1612	m/sec	298	27, 28	2.6-4, 2.6-5
	5287	ft/sec			
COMPRESSIBILITY OF LIQUID					
ADIABATIC	4.36×10^{-5}	atm^{-1}	298	calc.	2.6-6
	2.97×10^{-6}	psi^{-1}			
ISOTHERMAL	Not Avail	atm^{-1}			
		psi^{-1}			
VISCOSITY OF LIQUID	0.809	centipoise	298	1, 4	2.6-7
	5.43×10^{-4}	lb$_m$/ft-sec			
HEAT CAPACITY OF LIQUID	0.732	cal/g-°K	298	9, 20	2.6-14
	0.732	BTU/lb-°R			
THERMAL CONDUCTIVITY OF LIQUID	6.83×10^{-4}	cal/cm-sec-°K	298	8	2.6-9
	4.58×10^{-5}	BTU/ft-sec-°R			
SURFACE TENSION	29.10	dynes/cm	298	6	2.6-8
	1.994×10^{-3}	lb$_f$/ft			
HEAT OF FORMATION	12.153	cal/mole	298		
	522.9	BTU/lb			
HEAT OF COMBUSTION	312.112	kcal/mole	298	4	
	12,185.	BTU/lb			
Index of Refraction	1.4393	—	298	22, 23	2.6-10

2.6.2 GENERAL

2.6.2.1 Introduction

Hydrazine is one of the more energetic fuels but, due to its relatively high freezing point (+34 F) and tendency to detonate in the vapor phase when heated, it has not been extensively used. Hydrazine has been mixed with many other fuels in order to obtain a lower freezing point, reduce the tendency of vapors to detonate, and still retain the high impulse characteristics of hydrazine.

The fuel mixture that has been most often utilized in rocket propulsion is the blend of 50% by weight of hydrazine mixed with 50% by weight of unsymmetrical dimethylhydrazine (UDMH). This propellant was utilized in the Titan II missile and the Titan II - SLV, as well as in the NASA Gemini flight program. Because of its extensive usage and "man-rated" status, it was also chosen for the Apollo Primary Propulsion System and the LM Ascent and Descent stages.

As are other members of the hydrazine family, this fuel mixture is a strong reducing agent; it reacts violently with oxidizing agents, and is hypergolic with many rocket oxidizers. It retains the major characteristics of N_2H_4 and UDMH which are discussed in Sections 2.3.2.1 and 2.5.2.1, respectively.

2.6.2.2. Structure

The structures of the components of 50-50 are discussed in Section 2.3.2.2 for hydrazine and Section 2.5.2.2 for UDMH. The blend exhibits weak hydrogen bonding between the hydrazine and the UDMH at low temperatures.

2.6.2.3 Specification

The manufacture, procurement and analysis of 50-50 blend are controlled under Military Specification MIL-P-27402, revision A, dated 24 February 1967. This specification requires a minimum purity of 98.2% by weight N_2H_4 + UDMH (see Section 2.6.6.2).

2.6.3 PHYSICAL PROPERTIES OF 50-50 BLEND

2.6.3.1 Vapor Pressure and Normal Boiling Point

The vapor pressure of a mixture will vary with the composition of the mixture. However, if the 50-50 blend is kept within specification limits, the slight variation in composition would not significantly affect its vapor pressure. The ullage above the liquid will, however, have a noticeable effect. The vapor pressure of an ideal mixture is the sum of the partial pressures of each of the component gases. If a large volume space above the liquid occurs, the more volatile component vaporizes from the liquid and the composition of the liquid phase is altered. Since the more volatile component appears in a greater proportion in the gas, its lower partial pressure is dominant and the vapor pressure decreases as the ullage volume is increased. Conversely, as the volume is decreased, the vapor pressure increases. The true vapor pressure of a mixture occurs when the gas and liquid compositions are identical, as is the case at zero ullage. This difference in pressure was demonstrated by measurements at Bell Aerosystems (2). At a temperature of 26.7 C (80 F), a pressure of 3.96 psia was recorded at a 25% ullage. When the ullage was increased to 75%, the pressure decreased to 3.06 psia.

The vapor pressure of 50-50 blend has been measured by Aerojet (1) Bell (2) and Rocketdyne (3). The first two studies were conducted with a 46% ullage and at pressures below one atmosphere. The Rocketdyne study was made with a small ullage space and over a wide temperature range.

Aerojet (1) reported readings for a blend having a composition of 51.0 N_2H_4, 48.2 UDMH and 0.5 H_2O by weight. The type of equipment used was not given, but it is assumed that a mercury manometer was employed. Ten readings were reported over a temperature range from - 10 to 71 C (14 to 160 F). Bell reported three measurements within the temperature range covered by Aerojet. An isoteniscope was used and pressures were measured with a mercury manometer. The exact composition of the blend was not reported but was within the specification limits. The data from these two investigations are presented in Figures 2.6-1, and 2.6-1a. Using the least-squares method, equation 2.6-1 was obtained to describe the pressure change as a function of temperature.

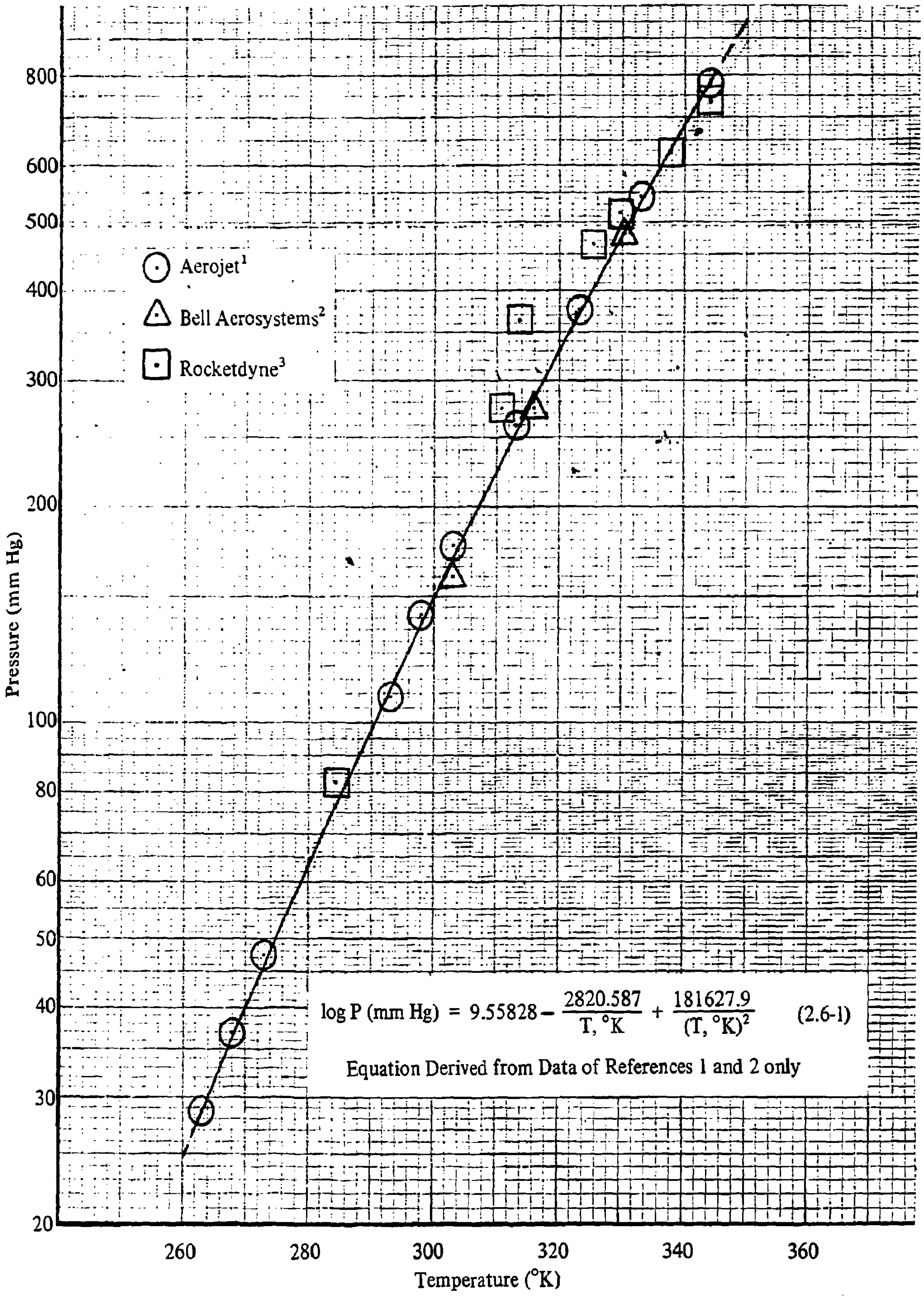
$$\log P\,(\text{mmHg}) = 9.55828 - \frac{2820.587}{(T, {}^{\circ}K)} + \frac{181627.9}{(T, {}^{\circ}K)^2} \qquad (2.6\text{-}1)$$

$$\log P(\text{psia}) = 7.84466 - \frac{5077.049}{(T, {}^{\circ}R)} + \frac{588473.7}{(T, {}^{\circ}R)^2} \qquad (2.6\text{-}1a)$$

The experimental data obtained by Rocketdyne (3) in this temperature range is shown in Figure 2.6-1 for comparison purposes. The pressure readings were obtained with pressure pickups; interpreted here to mean strain gage transducers. This instrument is not recommended for high precision pressure measurements.

The vapor pressures obtained at elevated temperatures by Rocketdyne (3) are presented in Figures 2.6-2 and 2.6-2a. Using the least-squares method, the coefficients were obtained for equation 2.6-2.

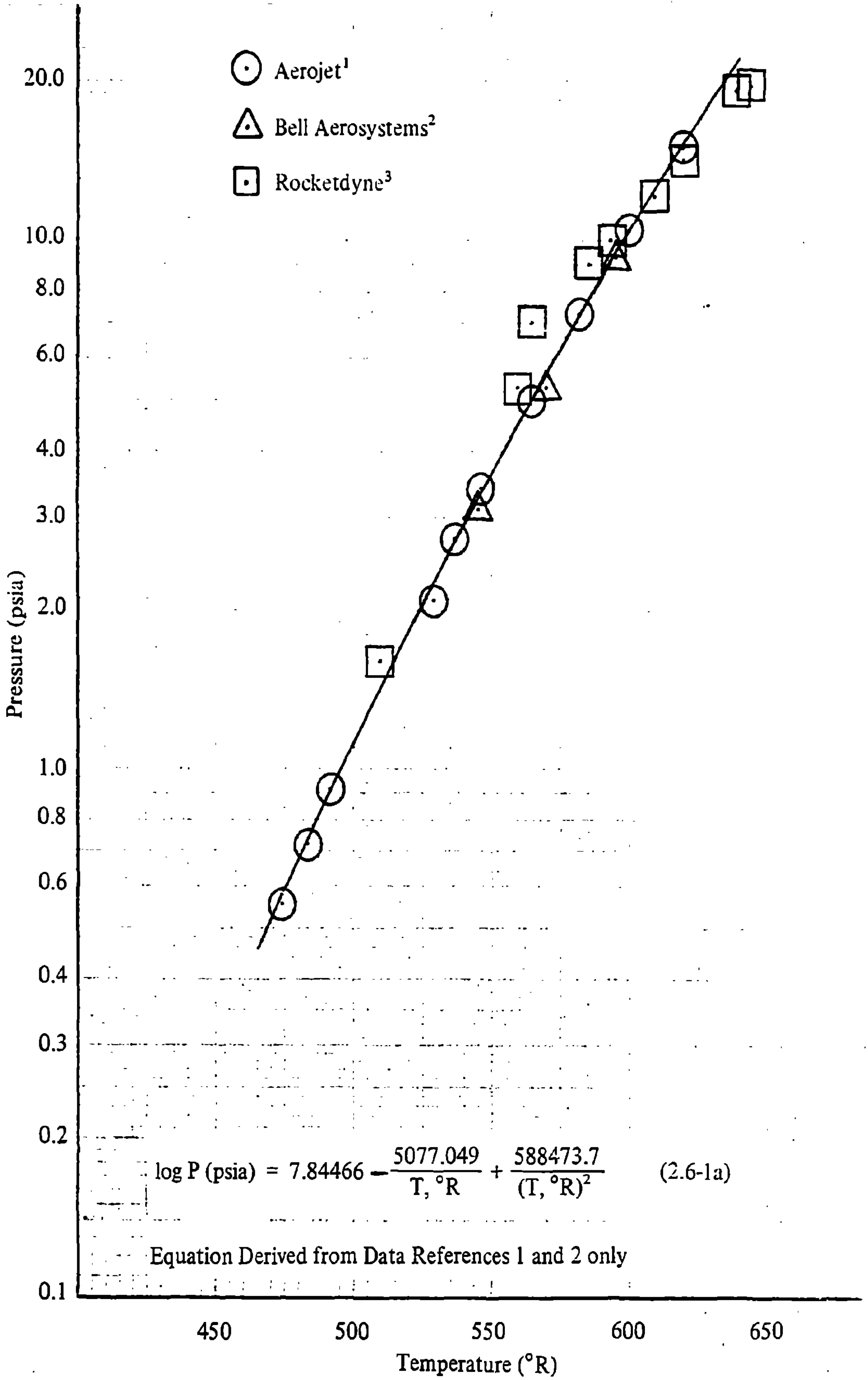
$$\log P(\text{atm}) = 5.2379 - \frac{2086.62}{T, {}^{\circ}K} + \frac{99387.3}{(T, {}^{\circ}K)^2} \qquad (2.6\text{-}2)$$



$$\log P\ (\text{mm Hg}) = 9.55828 - \frac{2820.587}{T,\ ^{\circ}K} + \frac{181627.9}{(T,\ ^{\circ}K)^2} \qquad (2.6\text{-}1)$$

Equation Derived from Data of References 1 and 2 only

Figure 2.6-1. Vapor Pressure versus Temperature, Liquid 50-50 Fuel Blend



$$\log P\ (\text{psia}) = 7.84466 - \frac{5077.049}{T,\ ^\circ R} + \frac{588473.7}{(T,\ ^\circ R)^2} \qquad (2.6\text{-}1a)$$

Equation Derived from Data References 1 and 2 only

Figure 2.6-1a. Vapor Pressure versus Temperature Liquid 50-50 Fuel Blend

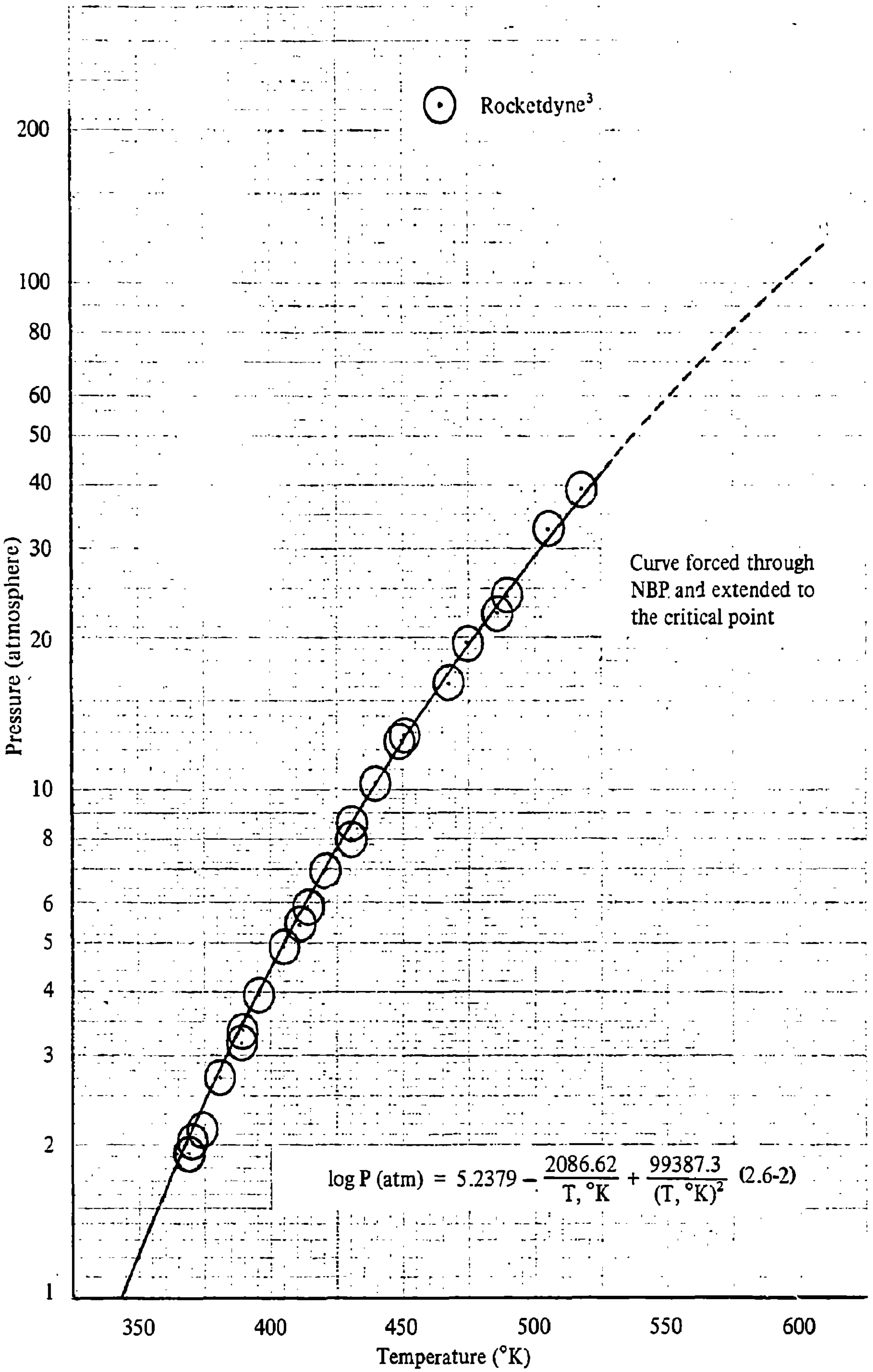
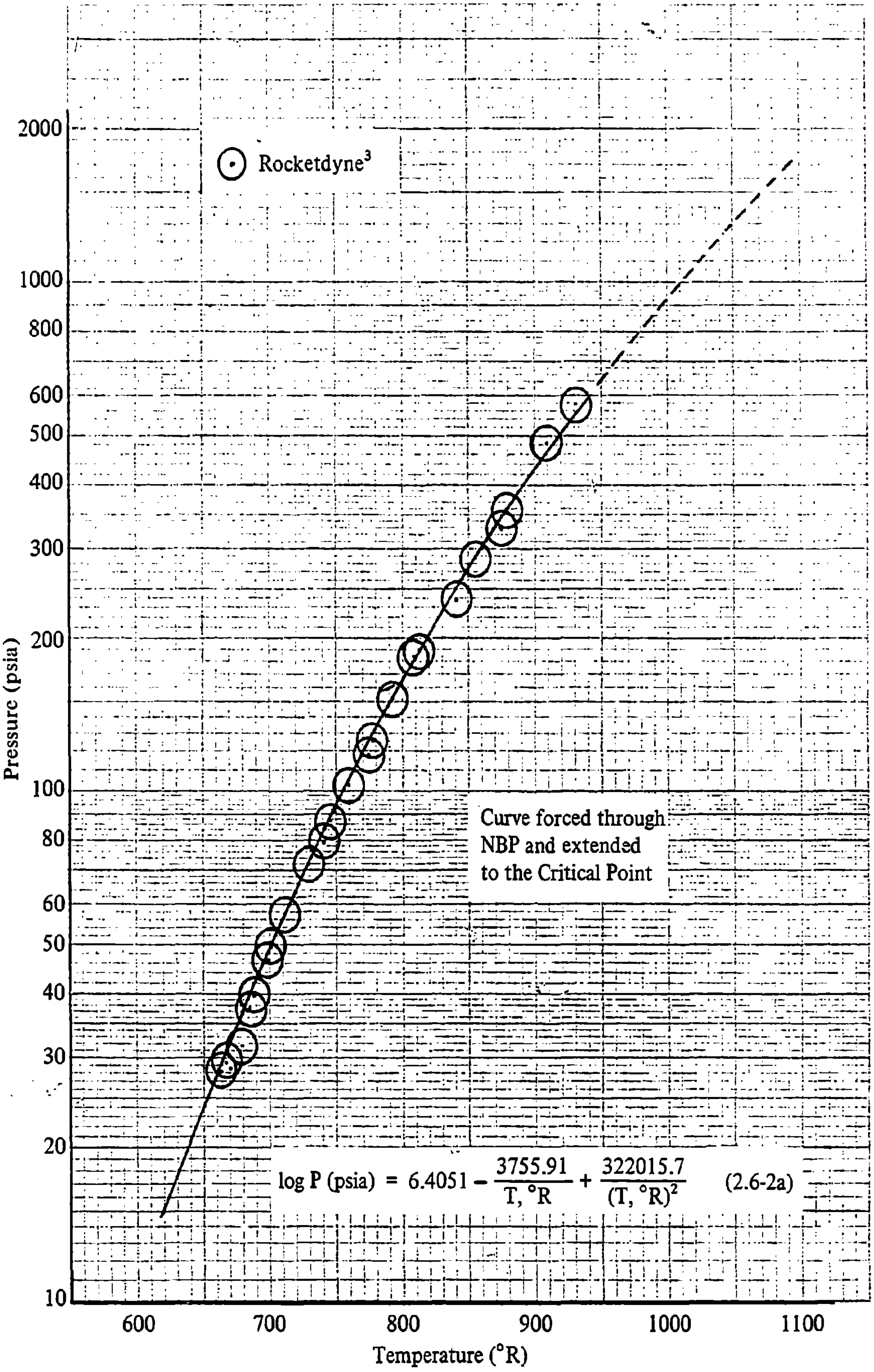


Figure 2.6-2. Vapor Pressure versus Temperature Liquid 50-50 Fuel Blend (High Temperature Region)



$$\log P\ (\text{psia}) = 6.4051 - \frac{3755.91}{T,\ ^\circ R} + \frac{322015.7}{(T,\ ^\circ R)^2} \qquad (2.6\text{-}2a)$$

Figure 2.6-2a. Vapor Pressure versus Temperature Liquid 50-50 Fuel Blend (High Temperature Region)

$$\log P(\text{psia}) = 6.4051 - \frac{3755.91}{T, {}^\circ R} + \frac{322015.7}{(T, {}^\circ R)^2} \qquad (2.6\text{-}2a)$$

The high temperature data of Rocketdyne (3) was forced to smoothly join the lower temperature data from Aerojet (1) and Bell (2).

The normal boiling point obtained from equation 2.6-1 is 343.13 K (617.64 R). This accuracy is obviously not warranted and a nominal value of 70 C (158 F) is selected here. The boiling point of a mixture will depend upon the composition as well as the ullage above the liquid. The vapors of this blend are largely UDMH.

2.6.3.2 Density of Liquid 50-50 Blend

The density of liquid 50-50 blend has been studied by Aerojet (1) and Schluter and Smith (4). Pannetier (7) has studied the density of various hydrazine and UDMH mixtures.

Details of the Aerojet study are lacking. Seventeen readings are given at even integers of temperatures from 0 to 70 C (32-158 F) but these data may be smoothed rather than actual experimental data. Pannetier reported experimental densities for various UDMH-hydrazine mixtures at 20 and 25 C. From a carefully constructed plot of density versus UDMH concentration, the density for an exact 50-50 weight composition was obtained.

Schluter (4) used glass pycnometers with a volume of approximately 50 ml. The exact volume was obtained from several calibrations of each pycnometer with water over a temperature range from 5 to 45 C (41 to 113 F). The density of benzene was obtained and agreement with the literature was within 0.02%. On this basis, the author estimated the density accuracy of the 50-50 blend to also be 0.02%. A temperature range from 0 to 25 C was studied. The blend composition by weight percent was given as follows:

UDMH	47.5 ± 0.03
N_2H_4	51.0 ± 0.03
H_2O	1.2 ± 0.3

It would appear that great care was taken to obtain high precision data, but the report suffers from lack of detail. The experimental data were not given, nor was the number of experimental points taken, but a large number is inferred. The number of different pycnometers used was also omitted. The smoothed values obtained from a least-squares fit were reported at even integers of temperature. These data, along with data reported by Aerojet (1) and Pannetier (7), are shown in Figures 2.6-3 and 2.6-3a. The agreement of the three studies is excellent. In deference to reported accuracy of the Schluter study the six smoothed data points were given double weighted values.

The density as a linear function of temperature is given by

$$\rho\,(\text{g/cc}) = 1.17423 - 9.2417 \times 10^{-4}\,(T, {}^\circ K) \qquad (2.6\text{-}3)$$

$$\rho\,(\text{lb/ft}^3) = 73.3048 - 0.032052\,(T, {}^\circ R) \qquad (2.6\text{-}3a)$$

The standard deviation of the data is 0.0003 g/cc with an average deviation of 0.023%. The density above 70 C does not appear to have been studied.

2.6.3.3 Sonic Velocity in 50-50 Blend

The velocity of sound in liquid 50-50 blend has been determined by Aerojet (27) over a temperature range from 16 to 93 C (61 to 200 F) and at pressures from 400 to 1500 psia. The experimental velocity measurements for the five isotherms studied are plotted as a function of pressure in Figure 2.6-4. There is some scatter, especially at the highest temperature isotherm, but the data for each isotherm appear to be reasonably well expressed as a linear function of pressure. The coefficients of the linear expression were obtained at each isotherm and the sonic velocity was then obtained for the saturated liquid vapor pressure.

Rocketdyne (28) recently measured the sonic velocity in saturated liquid 50-50. A temperature range from 0 to 94.5 C (32 to 202 F) was studied. Propellant grade 50-50 was used but the exact composition was not reported.

The Rocketdyne data is shown in Figures 2.6-5 and 2.6-5a along with the calculated values from the Aerojet study. The agreement between the two studies is remarkably good considering the scatter of the original Aerojet data. The temperature effect on sonic velocity can be adequately expressed as a linear function of temperature by

$$c\,(\text{m/sec}) = 2765.3 - 3.8695\,(T, {}^\circ K) \qquad (2.6\text{-}4)$$

$$c\,(\text{ft/sec}) = 9072.4 - 7.05297\,(T, {}^\circ R) \qquad (2.6\text{-}4a)$$

The standard deviation obtained by the use of equation 2.6-4 is 8.5 m/sec while the average deviation was 0.45%.

The Aerojet study was conducted using a stainless steel 1-1/2 inch diameter pipe approximately 20 feet long. The pipe was fitted with a Teflon diaphram in order to impart a shock wave. Pressure transducers were located at either end of the pipe and were connected electronically to an oscillograph running at 400 inches per second. The total time required for the shock wave to travel the known length of pipe was obtained from the separate transducer signals on the oscillograph paper. The unit was checked out with water and the results compared with the literature values. A system correction factor was applied to the measured values to obtain good agreement with the accepted values for water.

Rocketdyne (28) employed a sonic velocity cell constructed of 6061 aluminum alloy. A 5 mHz radio frequency signal was fed simultaneously to a quartz crystal in the velocity cell and to an oscilloscope. The sound waves reflected from the crystal pass through the test fluid and then to the oscilloscope. From the known distance traveled through the test fluid and from the time differential of the two signals displayed on the oscilloscope, the sonic velocity was calculated. The apparatus was calibrated with both water and methanol.

2.6.3.4 Compressibility of Liquid 50-50 Blend

The isothermal compressibility of liquid 50-50 does not appear in the literature. The sonic velocity in the liquid has been reported by both Aerojet (27) and Rocketdyne (28) and is reported in section 2.6.3.3. The adiabatic compressibility from sonic velocity is found from the relation

$$\beta_a = \frac{1}{\rho c^2}$$

where

β_a = adiabatic compressibility
ρ = density
c = sonic velocity

The calculated compressibility data is plotted in Figures 2.6-6 and 2.6-6a. The compressibility as a function of temperature can be expressed satisfactorily by the linear relation

$$\beta_a(\text{atm}^{-1}) = 5.3196 \times 10^{-5} + 3.245 \times 10^{-7}\ (\text{T,°K}) \quad (2.6\text{-}5)$$

$$\beta_a(\text{psi}^{-1}) = 3.6198 \times 10^{-6} + 1.2270 \times 10^{-8}\ (\text{T,°K}) \quad (2.6\text{-}5a)$$

The standard deviation obtained from equation 2.6-5 is 1.37×10^{-6} atm^{-1} and the average deviation is 1.98%.

2.6.3.5 Viscosity of Liquid 50-50 Blend

The viscosity of the 50-50 fuel blend has been studied by Aerojet (1) and by Schluter (4). The results of the two studies are in excellent agreement and a temperature range from 0 to 70 C (32 to 158 F) was covered.

The Aerojet study was made on a sample having a composition by weight % of 51.0 N_2H_4, 48.2 UDMH and 0.5 H_2O. No other details were given. A total of 14 kinematic viscosity determinations were given and were converted to absolute viscosity using densities obtained from equation 2.6-3.

Schluter (4) employed an Ubhelhode capillary tube viscometer which was calibrated with water. Experimental points were determined over a temperature range from 0 to 25 C (32 to 77 F). The experimental points were not given nor was the number of points, although a large number of individual readings was indicated. The sample had a composition by weight % of 47.7 UDMH + 51.0 N_2H_4 + 1.2 H_2O. The smoothed absolute viscosity values reported in this study along with the Aerojet data, are shown in Figures 2.6-7 and 2.6-7a. The variation of viscosity with temperature can be described by

$$\log \mu\ (\text{cp}) = -0.28445 - \frac{501.489}{\text{T, K}} + \frac{166602.5}{(\text{T, K})^2} \quad (2.6\text{-}6)$$

$$\log \mu\ (\text{lb}_m/\text{ft-sec}) = -3.4572 - \frac{902.540}{\text{T, R}} + \frac{539754.2}{(\text{T, R})^2} \quad (2.6\text{-}6a)$$

Equation 2.6-6 was derived from the combined Aerojet experimental data and the six smoothed values from Schluter which were given double weight. The standard deviation of the experimental data from the smoothed data of equation 2.6-6 is 0.009 centipoise. The average deviation was 0.7%.

2.6.3.6 Surface Tension of Liquid 50-50 Blend

The surface tension of liquid 50-50 fuel blend has been determined by Aerojet (2), Lyerly (18) (single point only) and by Bell Aerosystems (6). The Bell data is published here for the first time and the methods employed are briefly discussed.

The surface tension was measured under its own vapor pressure over a temperature range from 1.5 to 58 C (35 to 136 F) employing a capillary rise method. As Sugden (19) has suggested, the best method is to employ a double capillary system and measure the change in height for two capillaries of different size.

Precision bored capillary tubes having a manufacturer's precision diameter of ±0.001 cm were obtained. Two capillaries approximately 60 cm long were selected. The true diameters were calculated from the height and weight of a mercury thread. Sixteen readings were made on each capillary and the average calculated diameters were 0.4558 and 0.1021 cm. Nearly all of the calculated diameters fell within 0.25% of the average

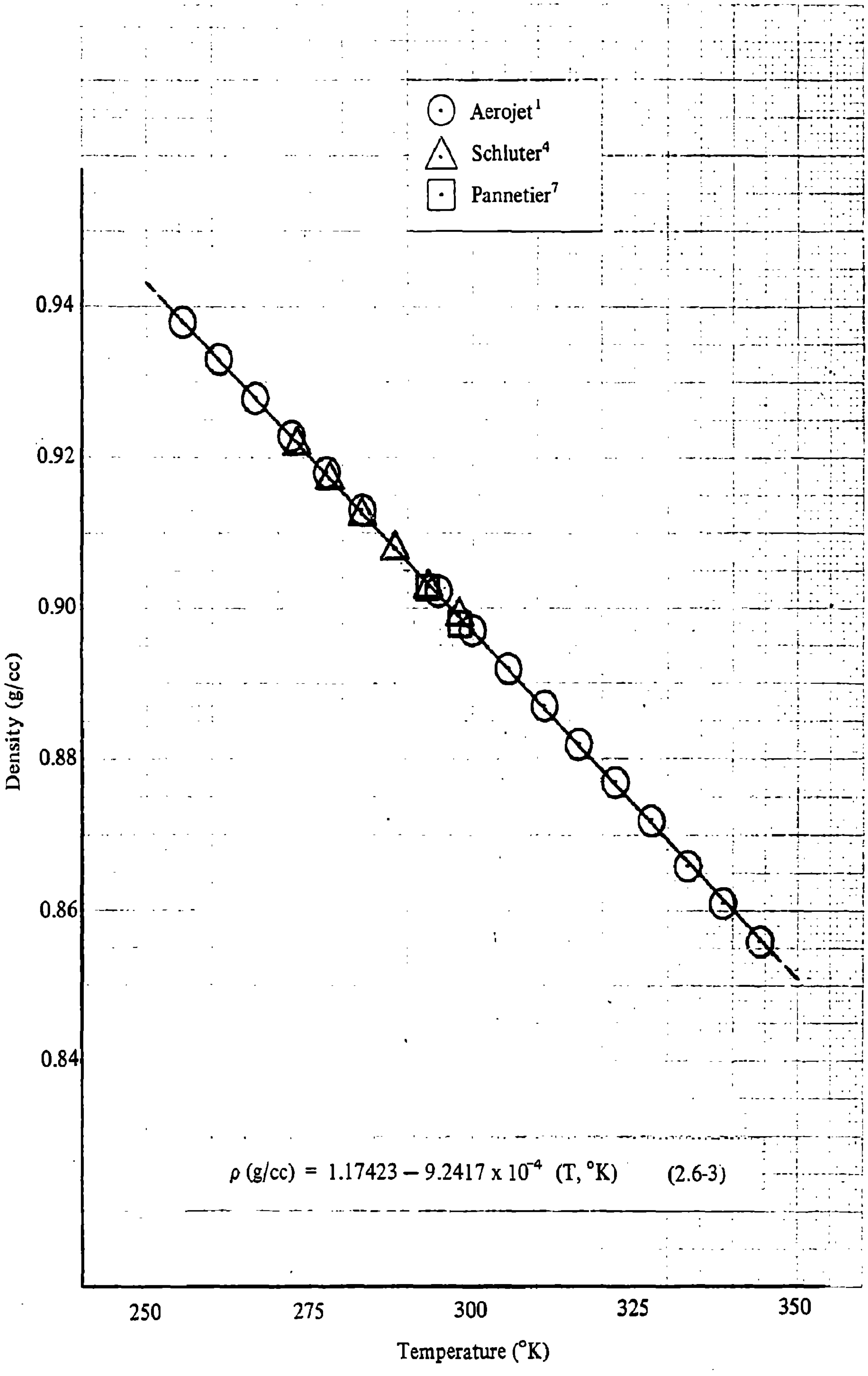


Figure 2.6-3 Density versus Temperature, Liquid 50-50 Fuel Blend

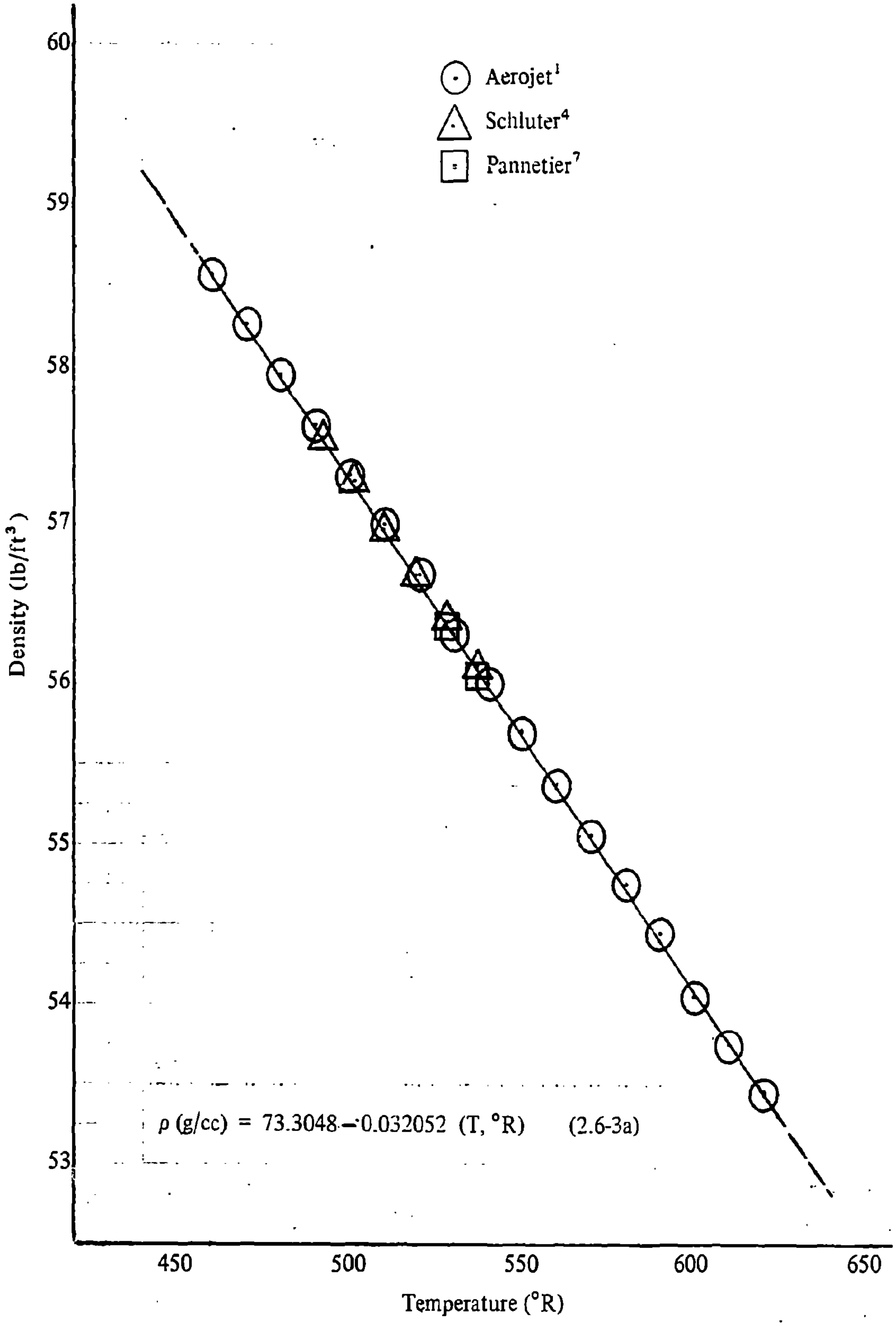


Figure 2.6-3a. Density versus Temperature, Liquid 50-50 Fuel Blend

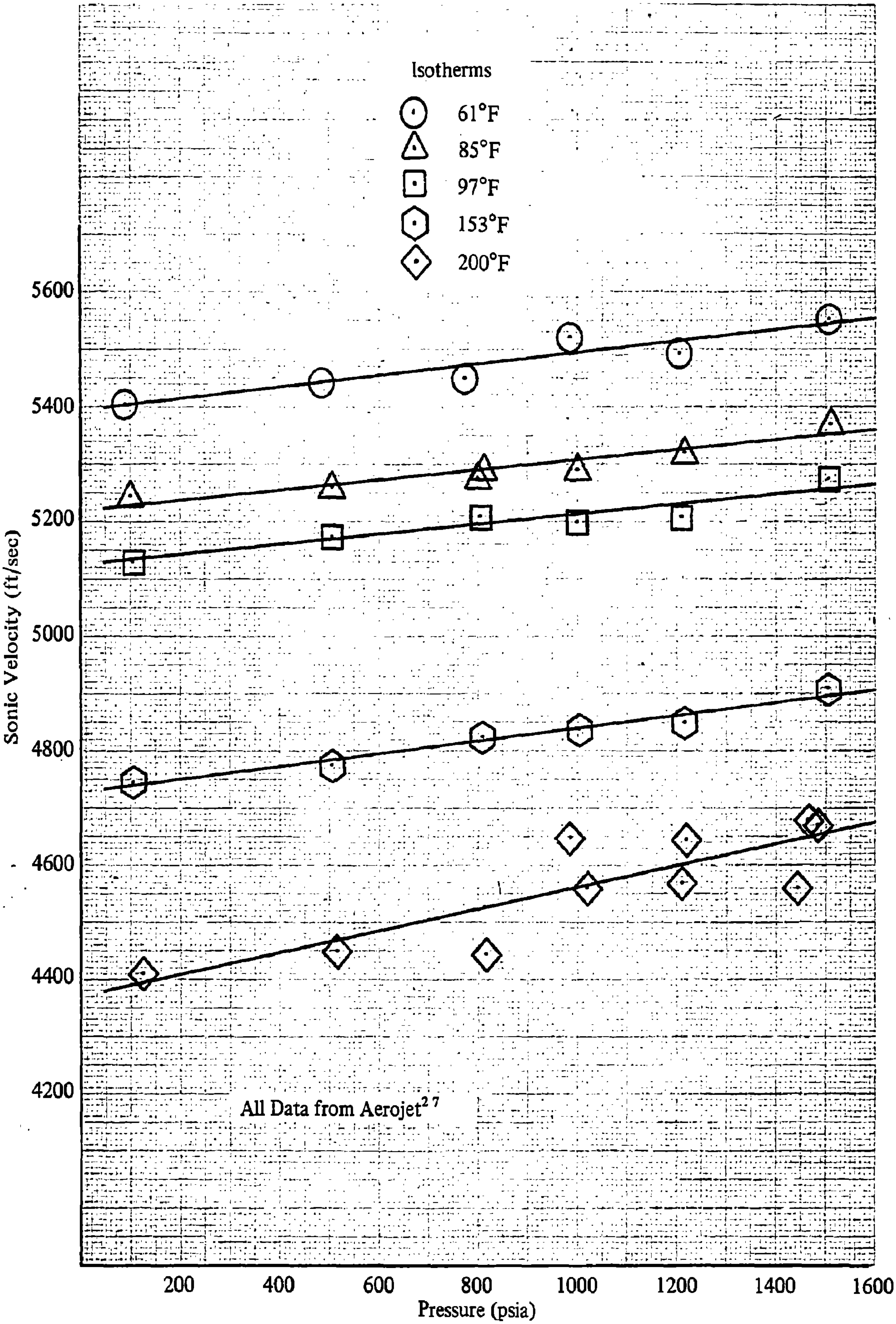


Figure 2.6-4. Experimental Sonic Velocity versus Pressure for Liquid 50-50 Blend

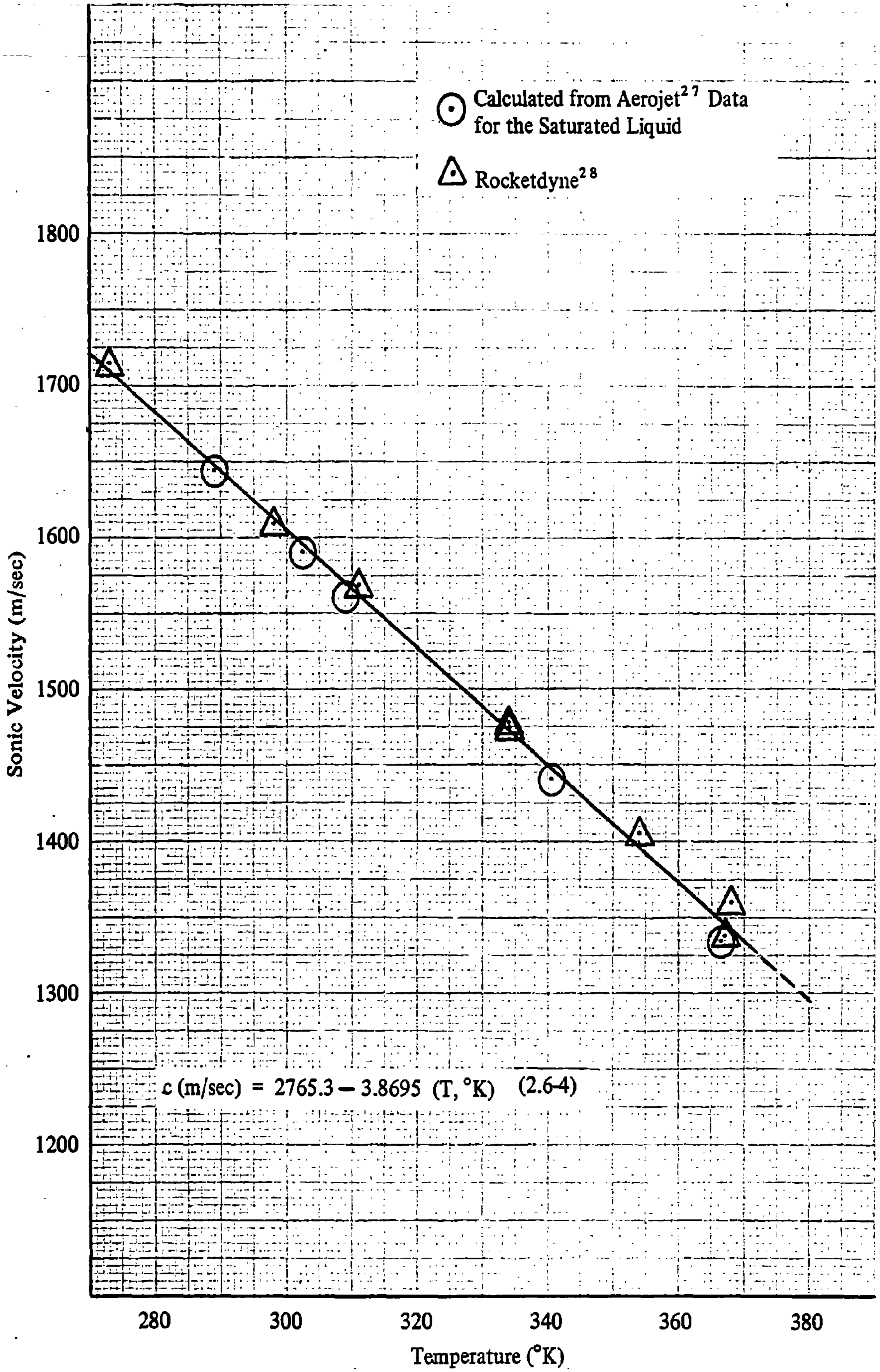


Figure 2.6-5. Sonic Velocity versus Temperature in Liquid 50-50 Fuel Blend

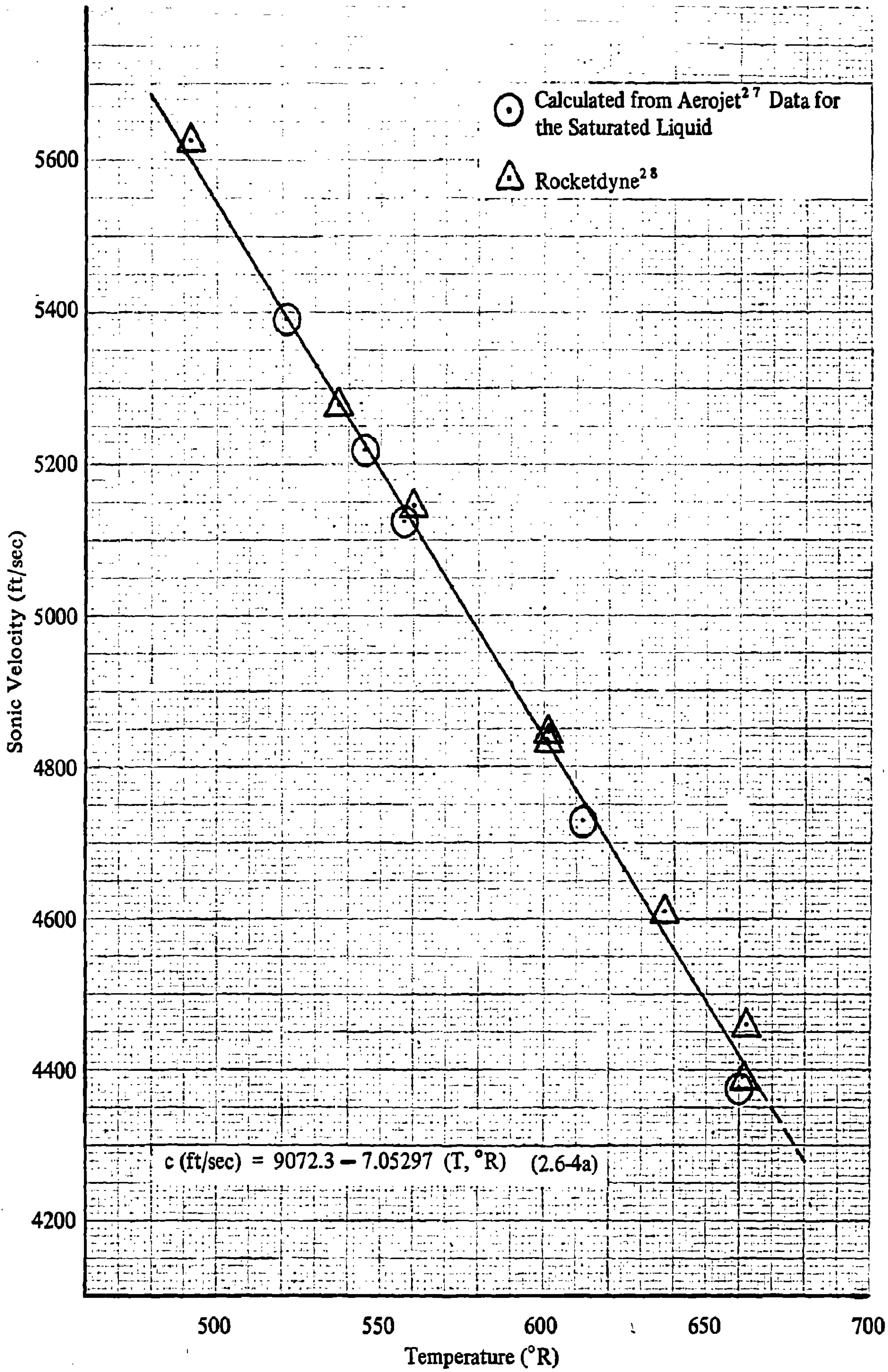
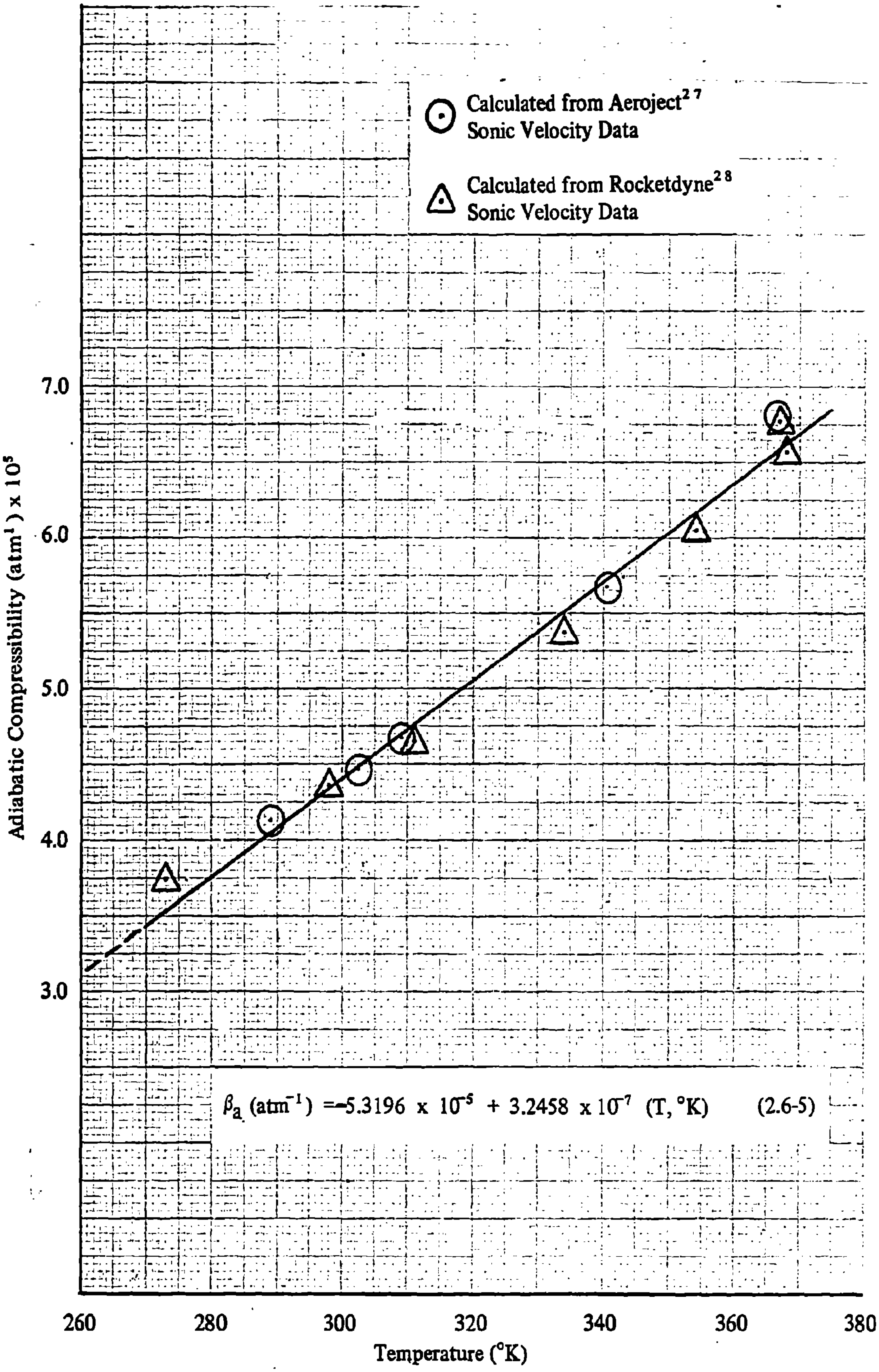


Figure 2.6-5a. Sonic Velocity versus Temperature in Liquid 50-50 Fuel Blend



$$\beta_a\ (\text{atm}^{-1}) = -5.3196 \times 10^{-5} + 3.2458 \times 10^{-7}\ (T, ^\circ K) \qquad (2.6\text{-}5)$$

Figure 2.6-6. Adiabatic Compressibility versus Temperature, Liquid 50-50 Blend

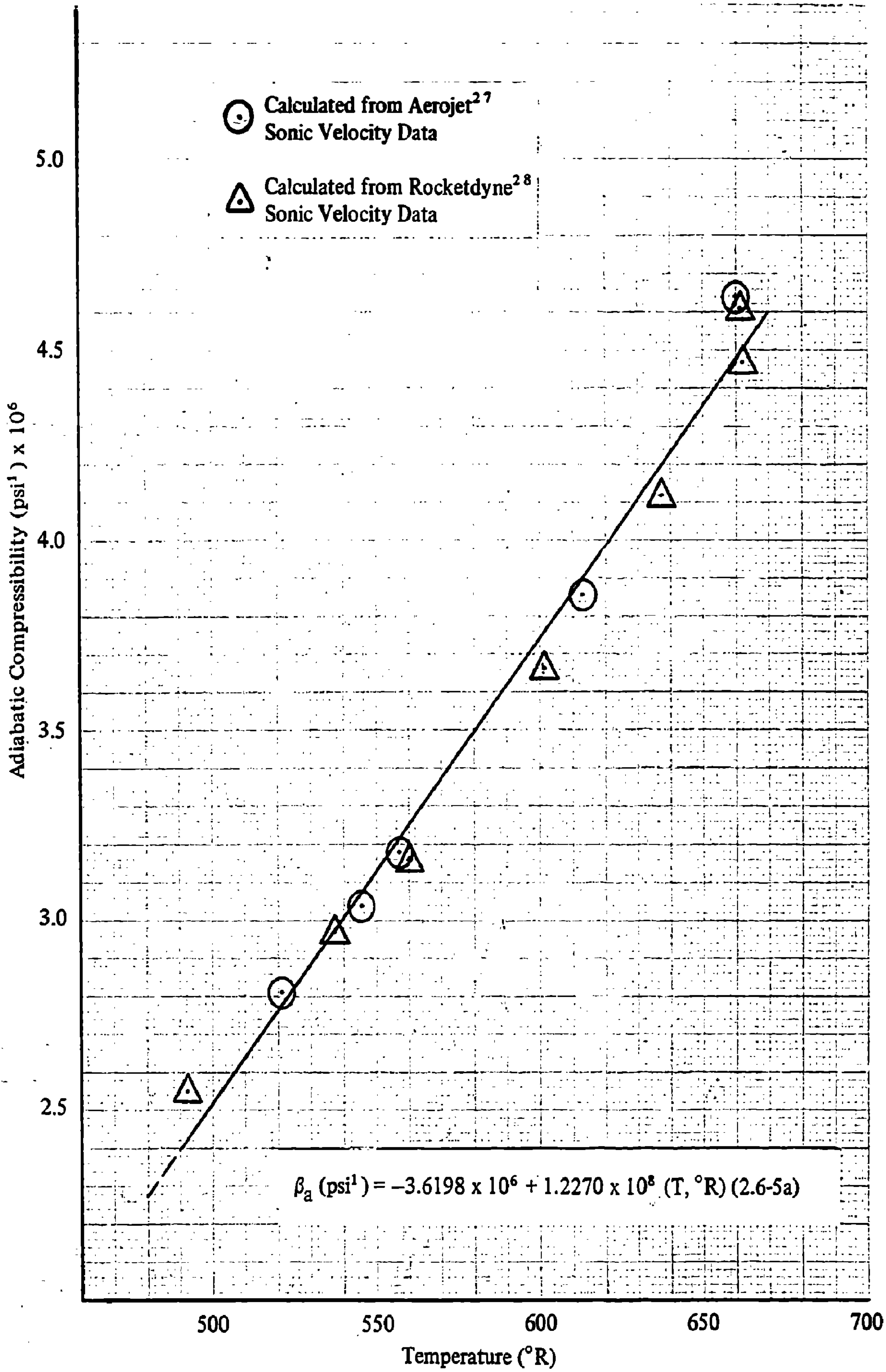
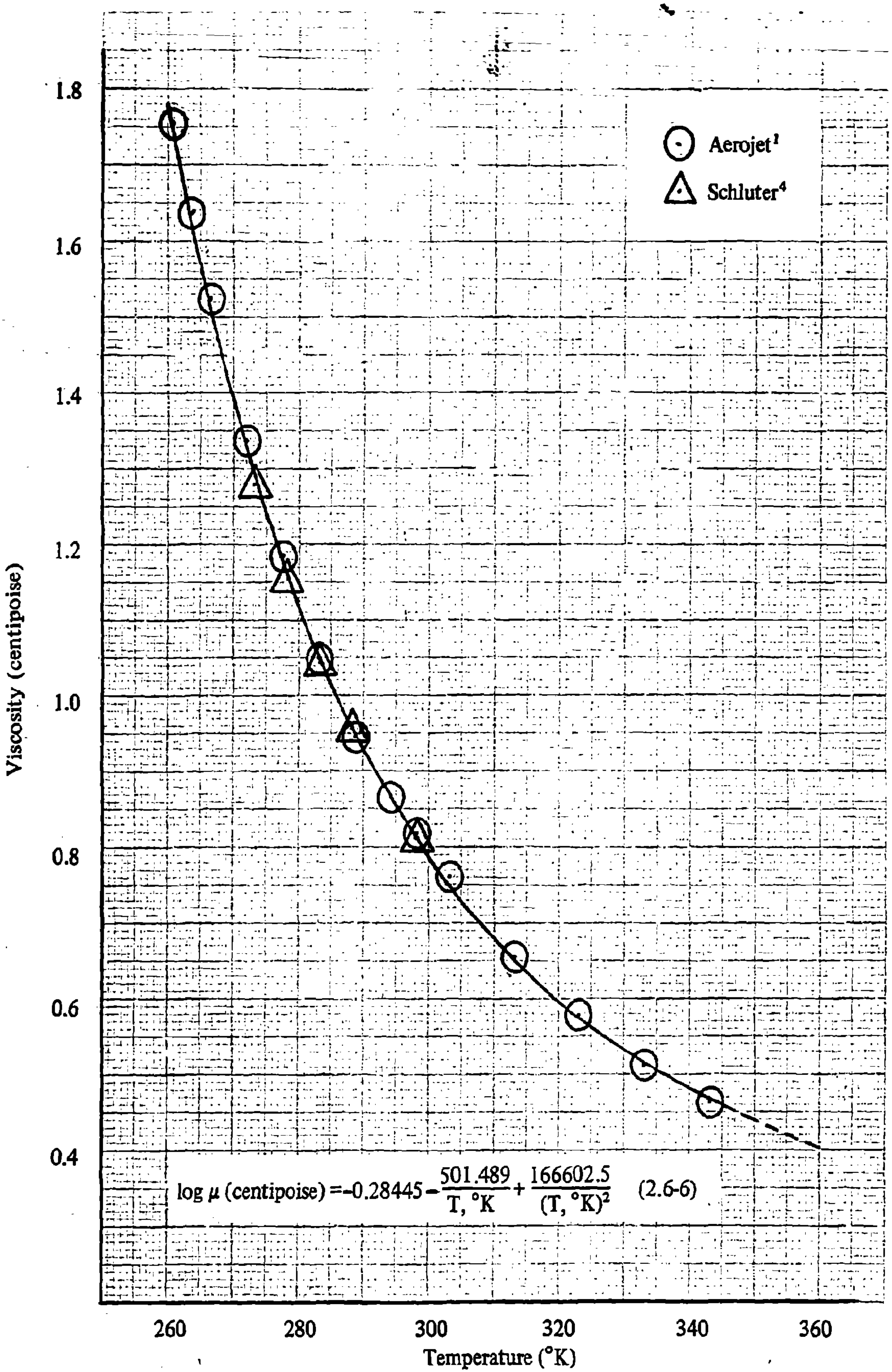


Figure 2.6-6a. Adiabatic Compressibility versus Temperature, Liquid 50-50 Blend



$$\log \mu \text{ (centipoise)} = -0.28445 - \frac{501.489}{T,\ ^\circ K} + \frac{166602.5}{(T,\ ^\circ K)^2} \qquad (2.6\text{-}6)$$

Figure 2.6-7. Viscosity versus Temperature, Liquid 50-50 Fuel Blend

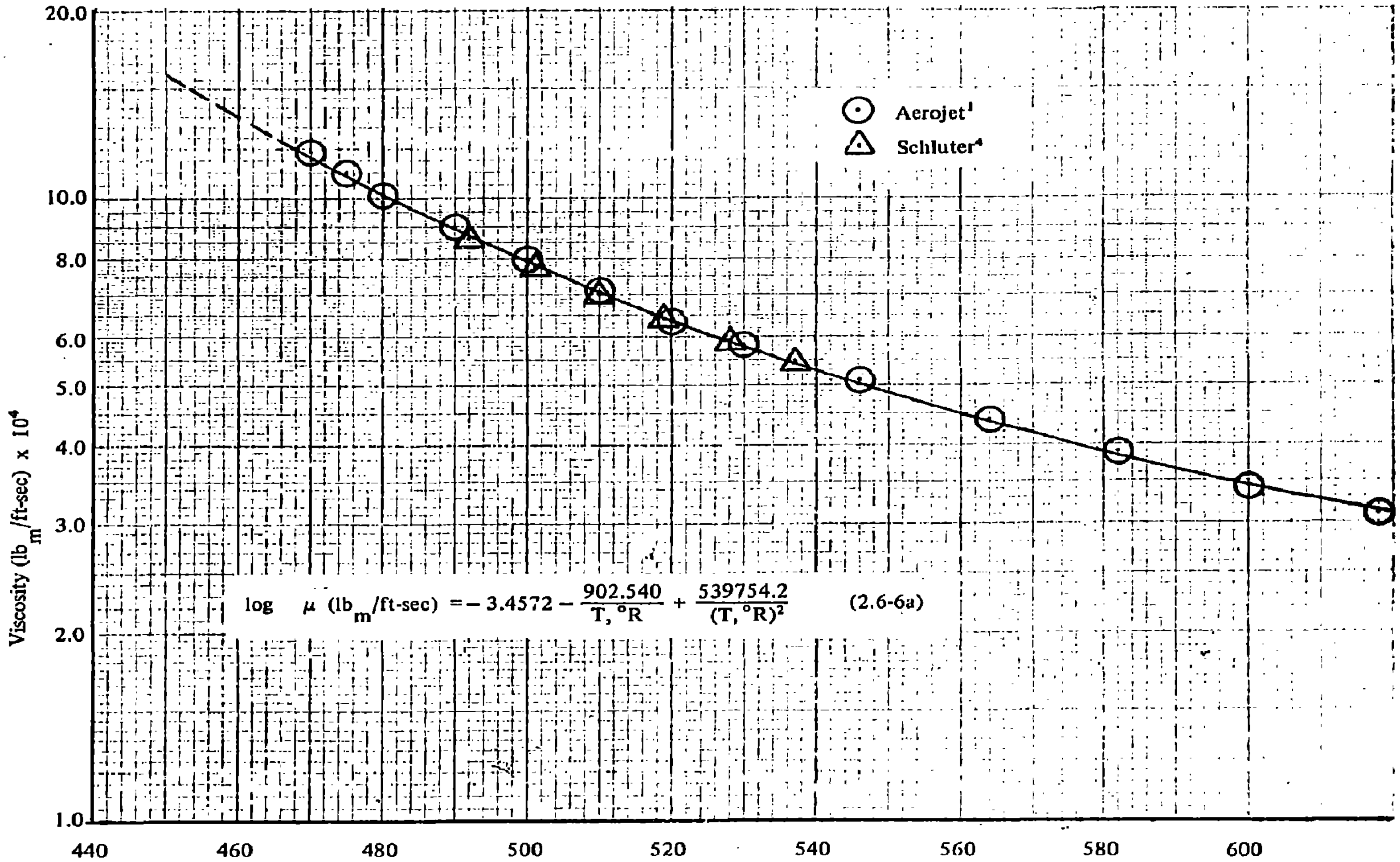


Figure 2.6-7a. Viscosity versus Temperature, Liquid 50-50 Blend

diameter, indicating good uniformity of bore. The ends of the tubes were photographed under high magnification with a Ziess II photographic microscope. When the photographs were examined for ellipiticity, both tubes were found to be almost perfectly circular.

The calibrated capillary tubes were cut to approximately 30 cm and welded inside a glass tube with an approximate 6 cm diameter. The large tube was sealed and provided with a glass stop-cock. The assembled surface tension apparatus was carefully cleaned with chromic-sulfuric acid, flushed with distilled water and dried in an electric oven.

Propellant grade 50-50 blend having a composition by weight % of 47.5 UDMH, 51.4 N_2H_4 and 1.1 H_2O was vacuum loaded into the apparatus which was then immersed in a constant temperature water bath. The bath temperature was measured with a precision mercury-in-glass thermometer which could easily be read to 0.1 C. After bath equilibrium had been obtained, one hour was allowed to insure bath and sample temperature equilibrium.

Four or five readings were taken at 15-minute intervals at each temperature. The height of the meniscus in each capillary was measured with a cathetometer. Thirty-four separate experimental data points were taken. The surface tension was calculated from the relation

$$\gamma\,(\text{dynes/cm}) = \frac{1/2\,(g\Delta h\rho)}{(1/b_1 - 1/b_2)} \qquad (2.6\text{-}7)$$

where

g = gravitational correction (980.665 dynes/cm^2)

ρ = density (g/cc)

Δh = difference in meniscus height (cm)

b_1, b_2 = radii of capillary tubes corrected for curvature of meniscus

The corrections for the deviation of the meniscus from a hemispherical form were made according to the tables given by Sugden (19).

The calculated surface tension values are shown in Figures 2.6-8 and 2.6-8a. The surface tension as a function of temperature is given by

$$\gamma\,(\text{dynes/cm}) = 105.960 - 0.41606\,(T, {}^\circ K) + 5.3088 \times 10^{-4}\,(T, {}^\circ K)^2 \qquad (2.6\text{-}8)$$

$$\gamma\,(lb_f/ft) = 7.2606 \times 10^{-3} - 1.5838 \times 10^{-5}\,(T, {}^\circ R) + 1.1228 \times 10^{-8}\,(T, {}^\circ R)^2 \qquad (2.6\text{-}8a)$$

From equation 2.6-8 a standard deviation of 0.089 dynes/cm is obtained. The maximum deviation is 0.62% with the average % deviation being 0.23%.

A check of the surface tension of methanol at 25 C using this apparatus gave a value of 0.2% above the literature value. Additional measurements on methanol at different temperatures as well as on other fluids such as methanol will be made. These calibrations should define the accuracy limits of the apparatus. It is felt that the data should be accurate to within ± 1.0%.

The single-point determination made by Lyerly (18) at 20 C (68 F) is approximately 0.74% above the smoothed data shown here. The agreement may be fortuitious since Lyerly used a platinum ring with a duNouy tensiometer, and his value for pure N_2H_4 is in serious error with the literature value. The data obtained by Aerojet are also shown in Figures 2.6-8 and 2.6-8a. Near 0 C, the Aerojet data is approximately 2.2% below the smoothed Bell data and near 44 C, the Aerojet data is approximately 3.5% higher.

The Bell data are selected in this work since the apparatus used also gave good agreement with the published data for MHF-3, and because the method used in the Aerojet study was not released with the experimental data.

2.6.3.7 Thermal Conductivity of Liquid 50-50 Blend

The thermal conductivity of 50-50 blend has recently been reported by Rocketdyne (8) and appears to be the only available work. The conductivity apparatus consisted of two concentric aluminum alloy cylinders with the test fluid contained in a thin annular passage between the two cylinders. The ends of the annulus were sealed with two Teflon O-rings to minimize heat conduction and to hold the cylinders concentric. Six pairs of copper-constantin thermocouples were embedded at various locations in both cylincers, and the cell was held together by two stainless steel endplates which fit over the thermal barriers. An electrical resistance heater in the inner cylinder supplied the heat energy for the temperature gradients across the sample liquid.

The test sample had a reported composition by weight % of 51.2 N_2H_4, 48.3 UDMH and 0.5 H_2O and other solubles. Two or more measurements were made at six different temperatures over a range from 10 to 152 C (50 to 306 F). The experimental data are presented in Figures 2.6-9 and 2.6-9a. The thermal conductivity as a function of temperature is given by equation 2.6-9.

$$K\,(\text{cal/cm-sec-}{}^\circ K) = 7.1983 \times 10^{-4} + 3.7467 \times 10^{-7}\,(T, {}^\circ K) - 1.6736 \times 10^{-9}\,(T, {}^\circ K)^2 \qquad (2.6\text{-}9)$$

$$K(\text{BTU/ft-sec}^\circ\text{R})4.8338 \times 10^{-5} + 1.3978 \times 10^{-8}\ (T, {}^\circ\text{R}) - 3.4686 \times 10^{-11}(T, {}^\circ\text{R})^2 \qquad (2.6\text{-}9a)$$

The average deviation of the experimental data from the smoothed values is 0.78%.

2.6.3.8 Dielectric Constant of 50-50 Blend.

The dielectric constant has not been reported.

2.6.3.9 Index of Refraction

The refractive index of various UDMH-hydrazine mixtures has been studied by both Chang (22) and Pannetier (23). Chang presented a table of mole fraction of UDMH versus refractive index for both his and Pannetier's work. The agreement between the two studies is very good. The data were obtained at 25 C (77 F) and at the sodium-D wavelength.

The refractive index at 25 C is shown as a function of percent UDMH in Figure 2.6-10. The data points shown are the average of the two separate studies. From this plot a value of 1.4393 is obtained for a mixture of exactly 50-50 by weight. Chang also expressed the refractive index as a function of UDMH in the mixture as

$$\eta = 1.4683 - 0.09806x + 0.04685x^2 - 0.0119x^3 \qquad (2.6\text{-}10)$$

where

x = mole fraction of UDMH

2.6.3.10 Distillation Range of the Fuel Blend

The distillation range was reported by Bell Aerosystems (2) on the following blend composition (by weight %).

UDMH	48.7
H_2H_4	50.4
H_2O + impurities	0.9

The results are given in the following table:

TEMPERATURE °F	VOLUME % DISTILLED	ANALYSES
149.0	Initial Boiling Point	-
158.0	10	86.0% UDMH, 8.0% N_2H_4
161.6	20	85.0% UDMH, 9.0% N_2H_4
167.0	30	-
170.6	40	-
194.0	50	79.0% UDMH, 16.0% N_2H_4
233.6	60	-
235.4	70	-
235.4	80	100% N_2H_4-
239.0	90	95% N_2H_4

The fuel fractions were analyzed spectrally employing calibration curves covering the UDMH and N_2H_4 concentration range of 45 to 55% by weight. The analytical results in this table were obtained by extrapolating the calibration curves and therefore are considered approximate. N_2H_4 at the 90% fraction probably contains hydrazine hydrate.

2.6.4 CHEMICAL PROPERTIES OF 50-50 BLEND

2.6.4.1 Chemical Reactions

The chemical reactions with 50-50 blend are those which its constituents will undergo. The reactions of hydrazine are discussed in Section 2.3.4.1 and the reactions of UDMH in Section 2.5.4.1. Additionally, UDMH and hydrazine mixtures appear to exhibit weak hydrogen bonding between the components from the fact that some volume contraction occurs upon mixing.

2.6.4.2 Inert Gas Solubility in 50-50 Fuel Blend

The solubility of both helium and nitrogen gas in 50-50 fuel blend has been measured by Chang (22) and by Aerojet (24) while North American Aviation (25) has reported data for just helium. Aerojet reported solubility values over a temperature range from -4 to 80 C (25 to 176 F) for total pressures of 300 and 700 psia for both helium and nitrogen. The North American study covered a temperature range from 0 to 71 C (32 to 160 F) at partial helium pressures of approximately 100, 200 and 250 psia for each temperature studied.

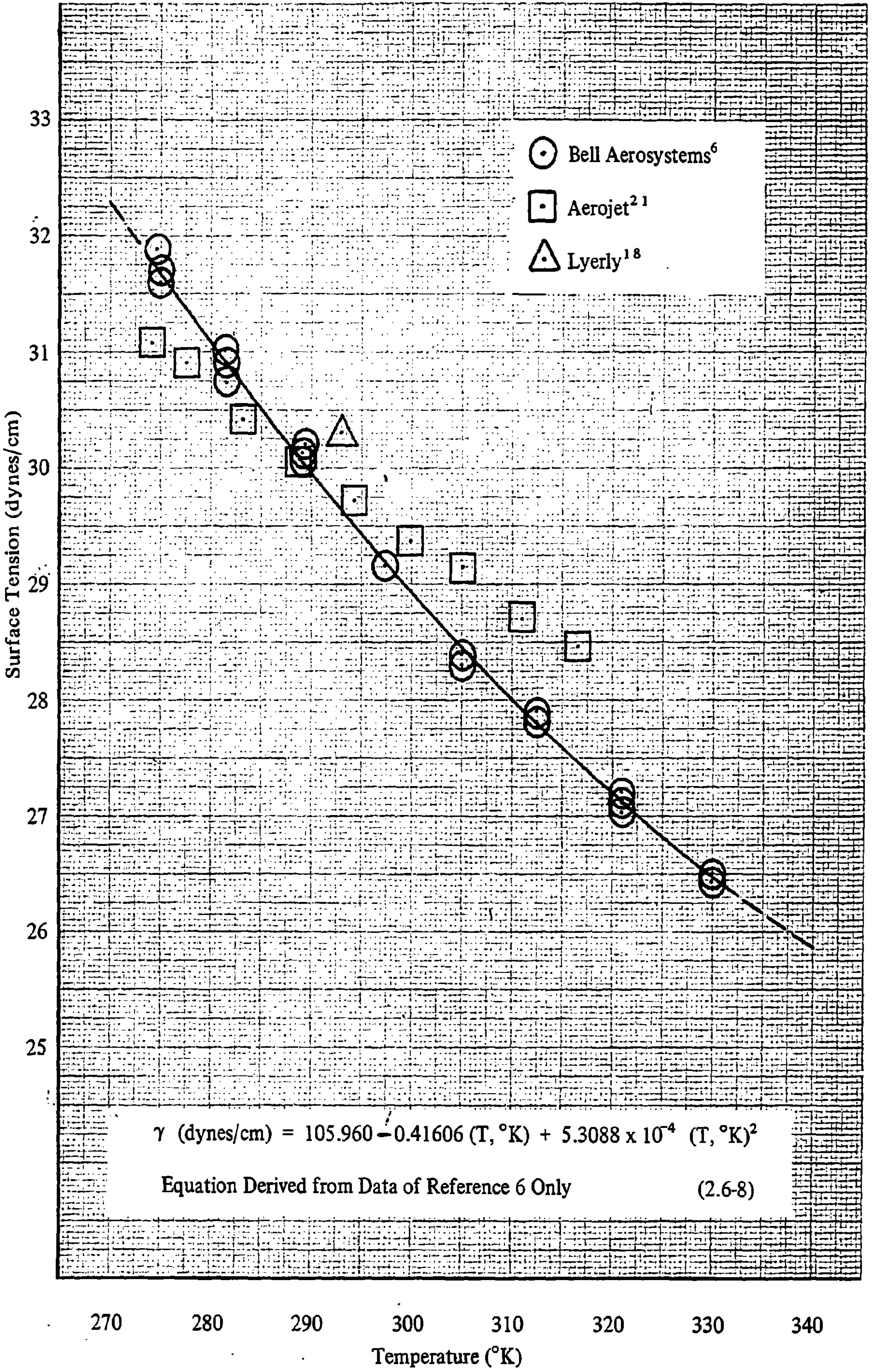
The equilibrium constants were obtained from both studies by dividing the weight % of the inert gas dissolved by the total pressure. The calculated constants are shown in Figure 2.6-11 for helium and in Figure 2.6-12 for nitrogen. The data show some scatter and the North American constants are generally lower than the Aerojet data but the straight line used to join the data should allow for good approximations of the solubility. The weight % can be calculated from the product of the equilibrium constant (K), and the total pressure in psia.

Chang (22) studied the solubility of both helium and nitrogen for temperatures of 0, 15 and 30 C. The maximum pressure was only 2.5 atmospheres and the author did not tabluate his data, but rather presented a curve. Because of the low pressure range and lack of experimental values this study was not used.

2.6.5 THERMODYNAMIC PROPERTIES OF 50-50 BLEND

2.6.5.1 Heat of Formation of Liquid

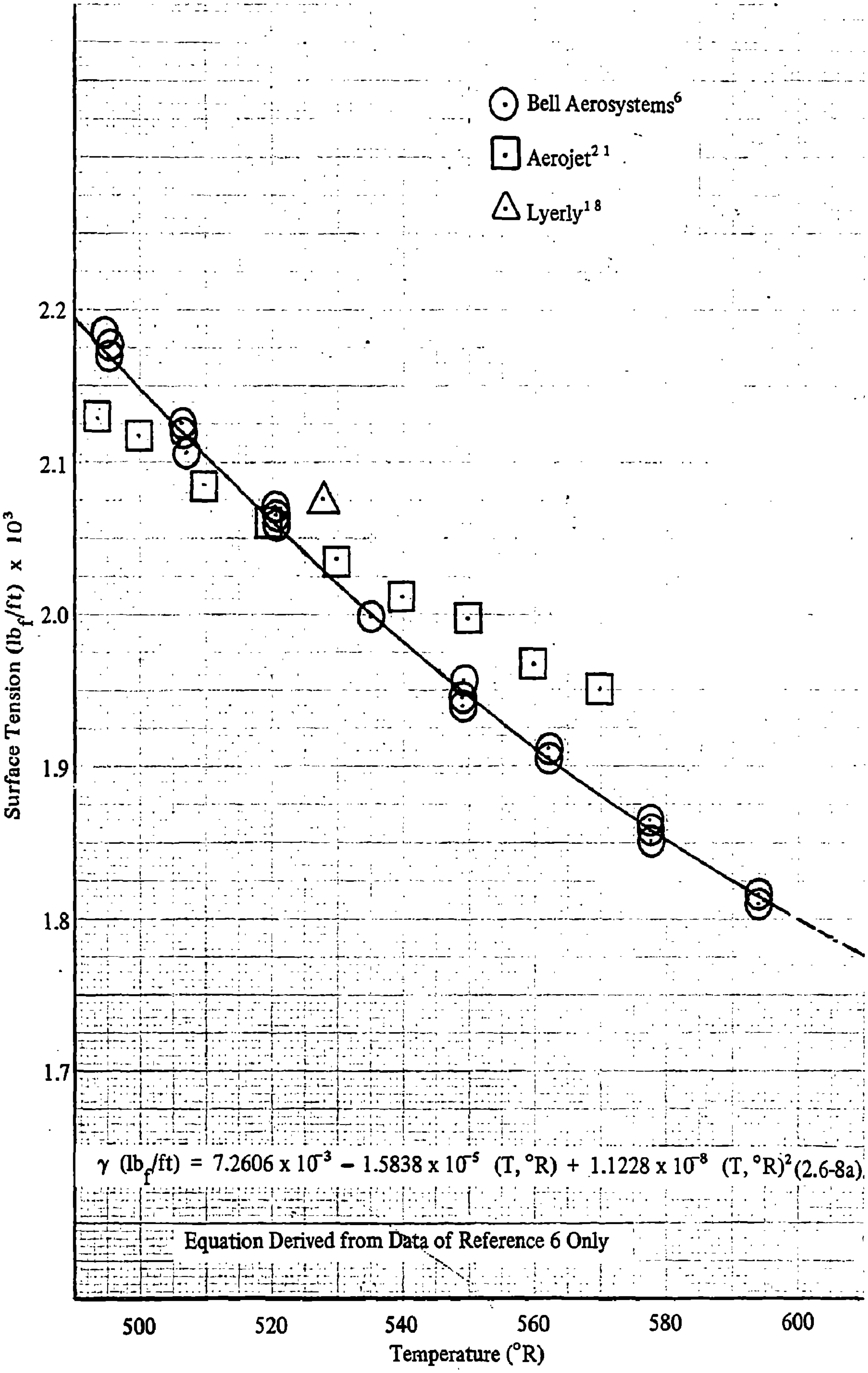
The heat of formation of the 50-50 blend can, for the purposes of determining performance calculations, be



$$\gamma \text{ (dynes/cm)} = 105.960 - 0.41606 \, (T, {}^\circ K) + 5.3088 \times 10^{-4} \, (T, {}^\circ K)^2$$

Equation Derived from Data of Reference 6 Only (2.6-8)

Figure 2.6-8 Surface Tension versus Temperature Liquid 50-50 Fuel Blend



γ (lb_f/ft) = $7.2606 \times 10^{-3} - 1.5838 \times 10^{-5}$ (T, °R) + 1.1228×10^{-8} $(T, °R)^2$ (2.6-8a)

Equation Derived from Data of Reference 6 Only

Figure 2.6-8a. Surface Tension versus Temperature Liquid 50-50 Fuel Blend

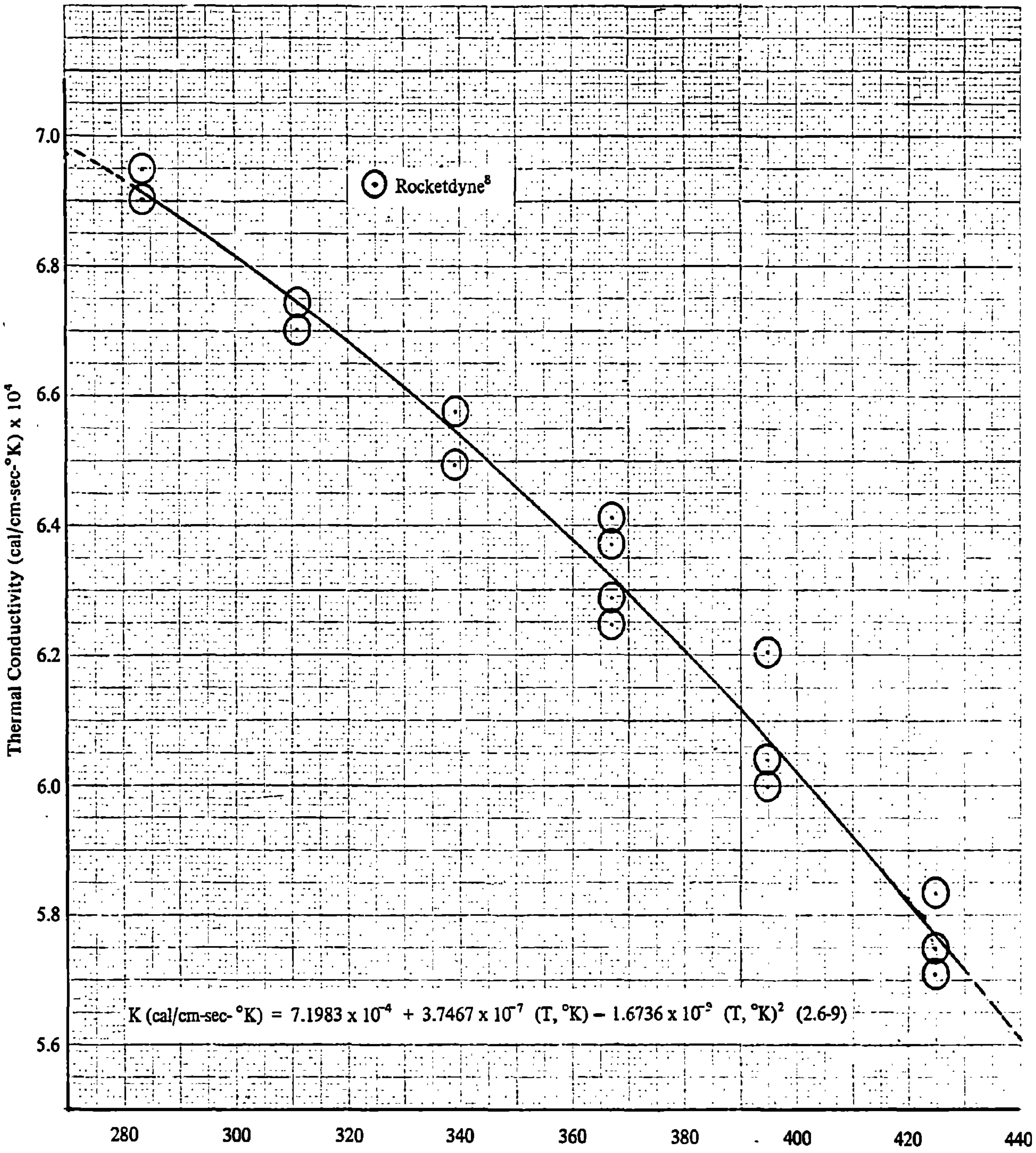


Figure 2.6-9. Thermal Conductivity versus Temperature, Liquid 50-50 Fuel Blend

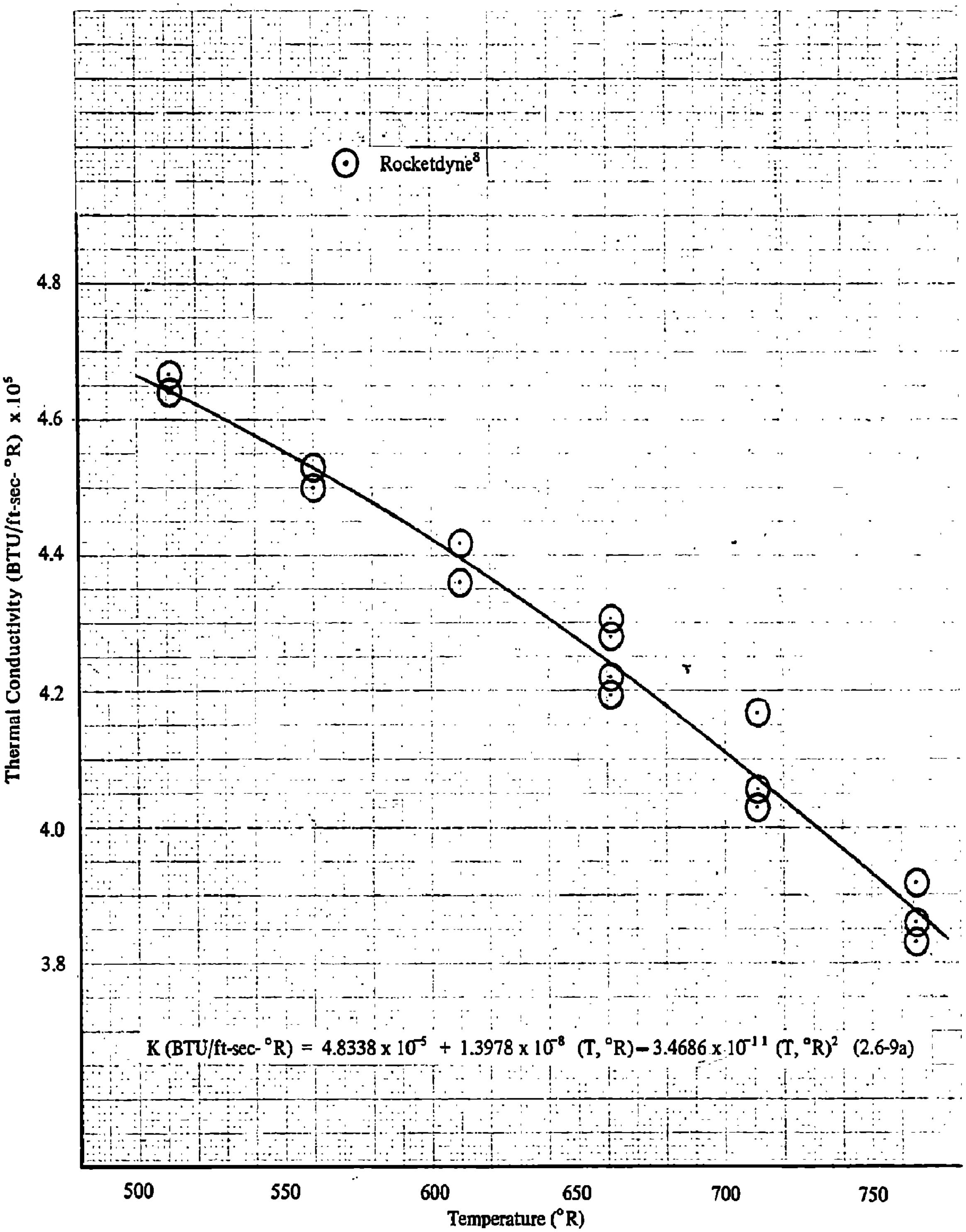


Figure 2.6-9a. Thermal Conductivity versus Temperature Liquid 50-50 Fuel Blend

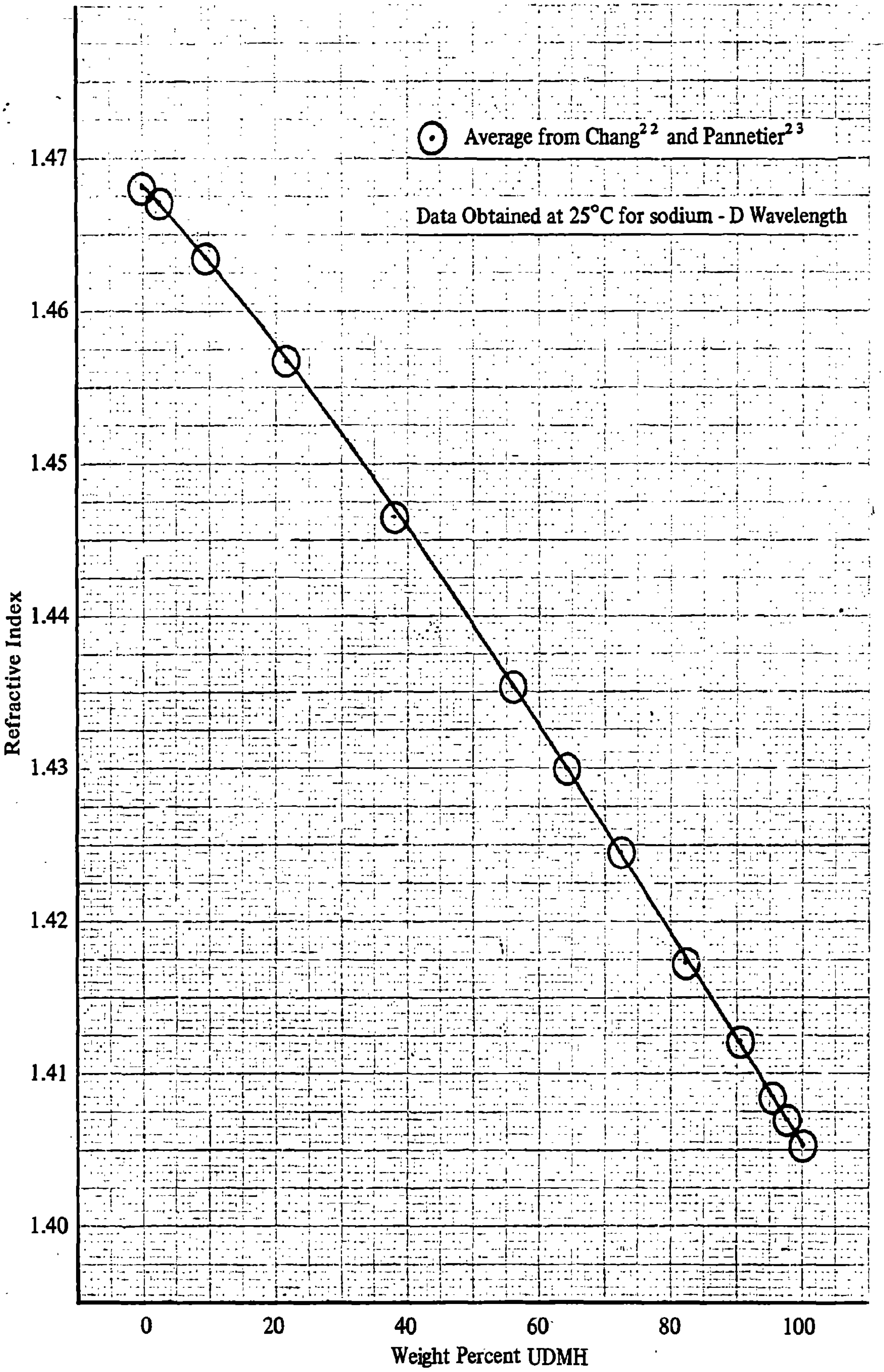


Figure 2.6-10. Refractive Index versus Weight Percent UDMH for UDMH + N_2H_4 Mixtures

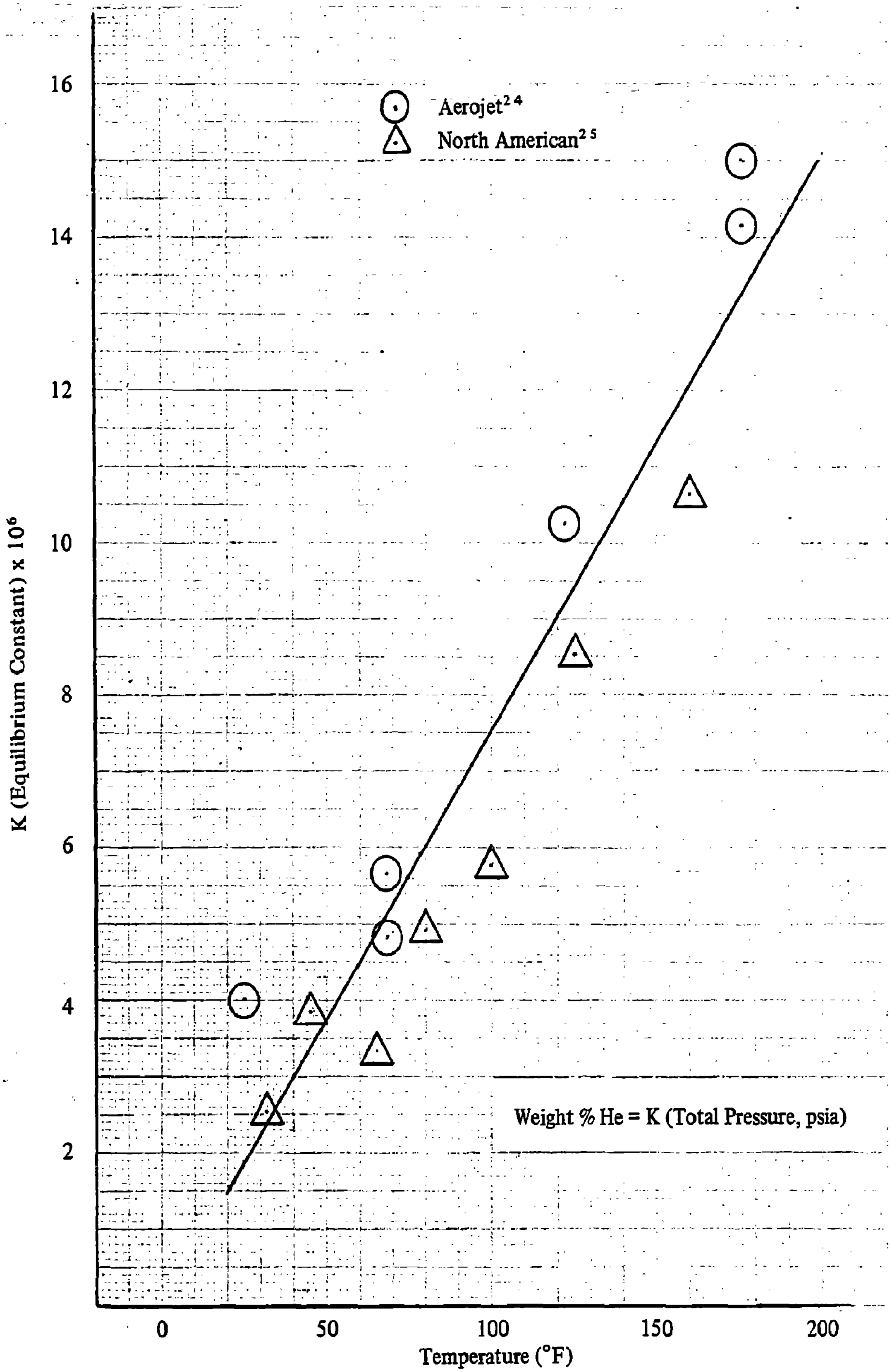


Figure 2.6-11. Helium Solubility in Liquid 50 - 50 versus Temperatures

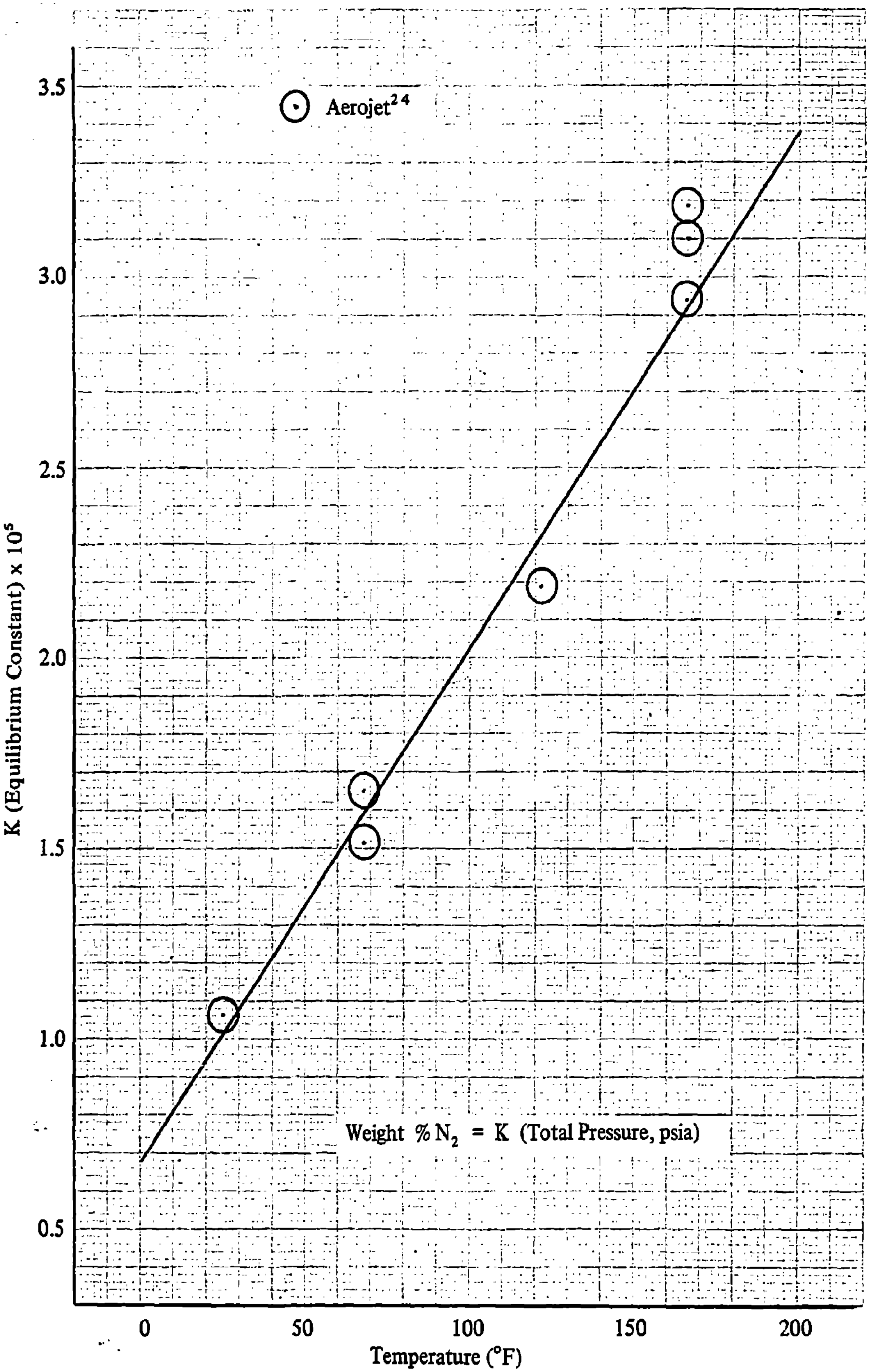


Figure 2.6-12. Nitrogen Solubility in Liquid 50-50 versus Temperature

obtained by the molar additions of the heats of formation of hydrazine and UDMH plus the heat of mixing. The heats of formation of N_2H_4 and UDMH are given in Sections 2.3.5.1 and 2.5.5.1.

Assuming a composition of exactly 50-50 by weight without impurities a value for the heat of formation of the liquid at 25 C is 12.310 kcal/mole, where a mole is defined as 41.805 grams from the empirical formula $C_{0.6956} H_{5.3911} N_{2.0}$

Compound	Weight %	Mole Fraction (1 mole blend)	ΔH_{f298} kcal/mole
N_2H_4	50	0.652219	12.054
$(CH_3)_2N_2N_2$	50	0.347781	12.339

for one mole of the 50-50 then

$$\Delta Hf_{298} = 0.652219(12.054)+0.347781(12.399)+\Delta H_{mix}$$

$$\Delta Hf_{298} = 12.153 + \Delta H_{mix}$$

$$\Delta Hf_{298} = 12.153 + 0.257$$

$$\Delta Hf_{298} = 12.310 \text{ kcal/mole, mole} = 41.805 \text{ grams}$$

or

$$\Delta Hf_{298} = 294.5 \text{ cal/gram}$$

The heat of mixing of various N_2H_4 UDMH mixtures has been reported by Pannetier (26). The endothermic heats of mixing were given at 25, 35, and 50 C. The data at 35 C were obtained for mole fractions between 0.12 and 0.91. The data at 25 C covered a small mixture range and did not include a mole fraction of 0.6522 N_2H_4 (50% by weight). The heat of mixing at 35 C was plotted as a function of mole fractions of N_2H_4 and a value of 3.80 cal/g was obtained for the 50-50 blend. A slight correction of 0.05 cal/g was estimated for the difference between 35 and 25 C and the value is 3.75 cal/g or 0.157 cal/mole at 25 C.

2.6.5.2 Melting Point of 50-50 Blend

The melting point of various mole fractions of UDMH and hydrazine has been reported by McMillan (5). The author found the eutectic melting point to be -59 C (-74.5 F) and the composition to be 94 mole % or 96.7 weight % of UDMH.

The experimental melting points as a function of UDMH weight % are shown in Figures 2.6-13 and 2.6-13a. At a binary mixture of exactly 50-50, the melting point determined from the smoothed curve is -5.6 C (22 F).

Aerojet (1) has estimated that the melting point may range from 18 to 21 F depending upon the exact composition of the blend.

2.6.5.3 Critical State Constants of 50-50 Blend

The critical temperature of a pure liquid may be defined as that temperature above which the substance cannot exist as a liquid regardless of the pressure applied. (The critical point lies on the vapor pressure curve of a pure substance. The critical pressure is then the liquid vapor pressure at the critical temperature.) For a mixture such as the 50-50 fuel blend, the critical point is not as easily defined. In place of the vapor pressure line the bubble and dew point lines are used. At higher temperatures, those curves bend over and meet forming a loop. The top of this loop corresponds to the critical point of a single pure substance. The maximum temperature and maximum pressure at which a distinct vapor and liquid phase still exists are not at the same point for a mixture.

The analogous critical point of a mixture to a pure substance is called the pseudocritical point by Kay (29) since it has no real existance and therefore cannot be measured. Kay (29) suggests that the pseudocritical temperature of a mixture may be calculated from the mole fractions and critical temperatures of the individual constituents. The validity of this mixture rule is probably questionable.

Aerojet (1) has reported a critical temperature for 50-50 of 334 C (633F). It appears that this value was calculated by the mixture rule. The individual critical temperatures of UDMH and N_2H_4 (250 and 380 C) are in themselves doubtful because of decomposition at elevated temperatures. The critical temperature reported by Aerojet is therefore rather dubious but is retained here for lack of a better value. Its use, for instance, in an equation of state for 50-50 could lead to large errors in computing thermodynamic data.

A critical pressure value of 117.5 atmospheres (1731 psia) is obtained when the critical temperature is substituted in equation 2.6-2. This value retains the uncertainty of the critical temperatures. No estimate of the critical density has been found in the literature.

2.6.5.4 Heat Capacity of Liquid 50-50 Blend

The heat capacity of liquid 50-50 blend has been experimentally determined by Rocketdyne (9, 20). In the earlier report (9) the calorimeter had a gold plated copper sample holder. The data reported in Reference 20 were obtained with the same calorimeter but with a different sample holder which was constructed of copper but not gold plated. A temperature range from 2.2 to 49.2 C (36 to 121 F) was studied. The experimental data are shown in Figures 2.6-14 and 2.6-14a.

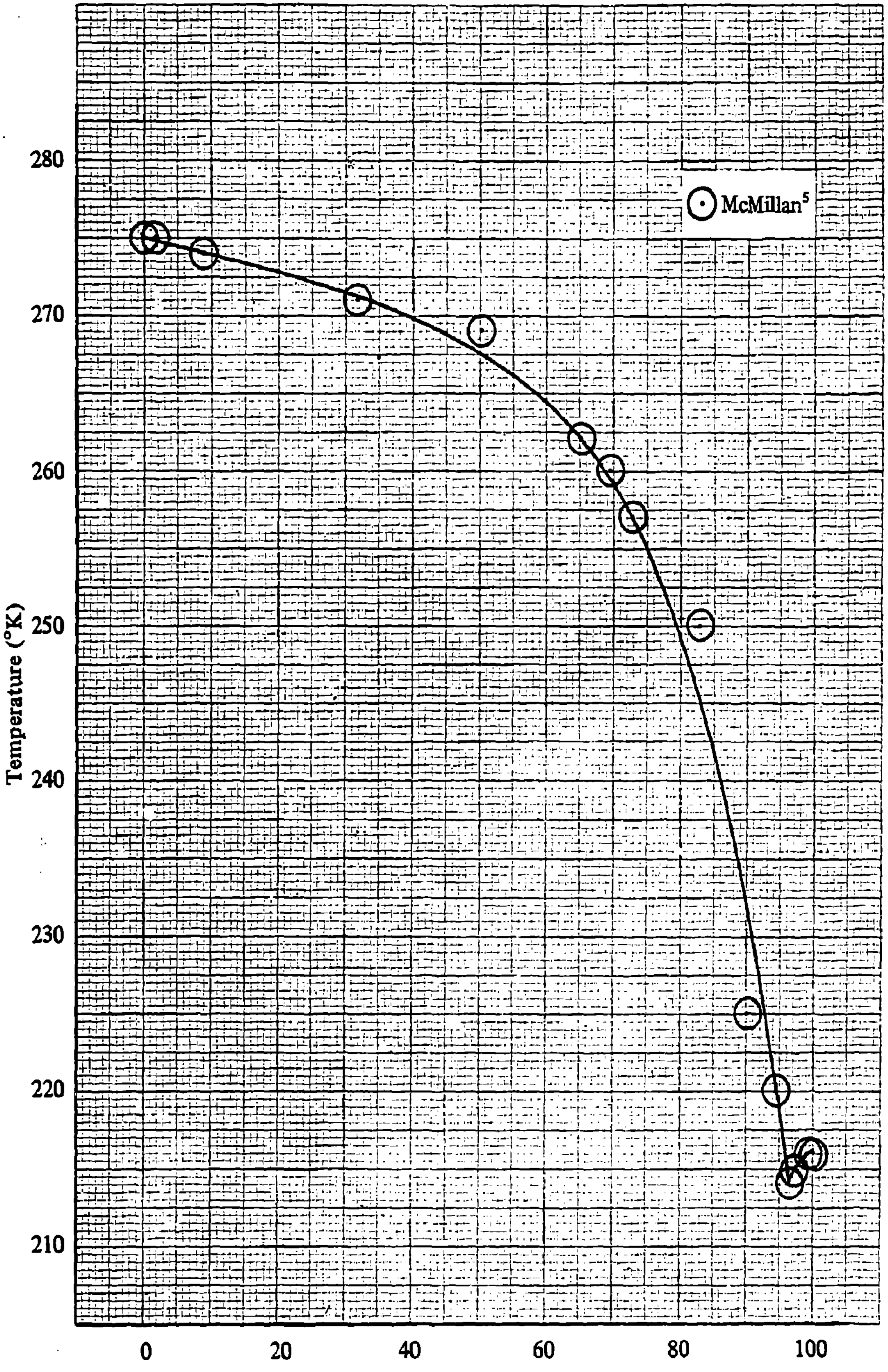


Figure 2.6-13. Melting Temperatures for UDMH + Hydrazine Mixtures

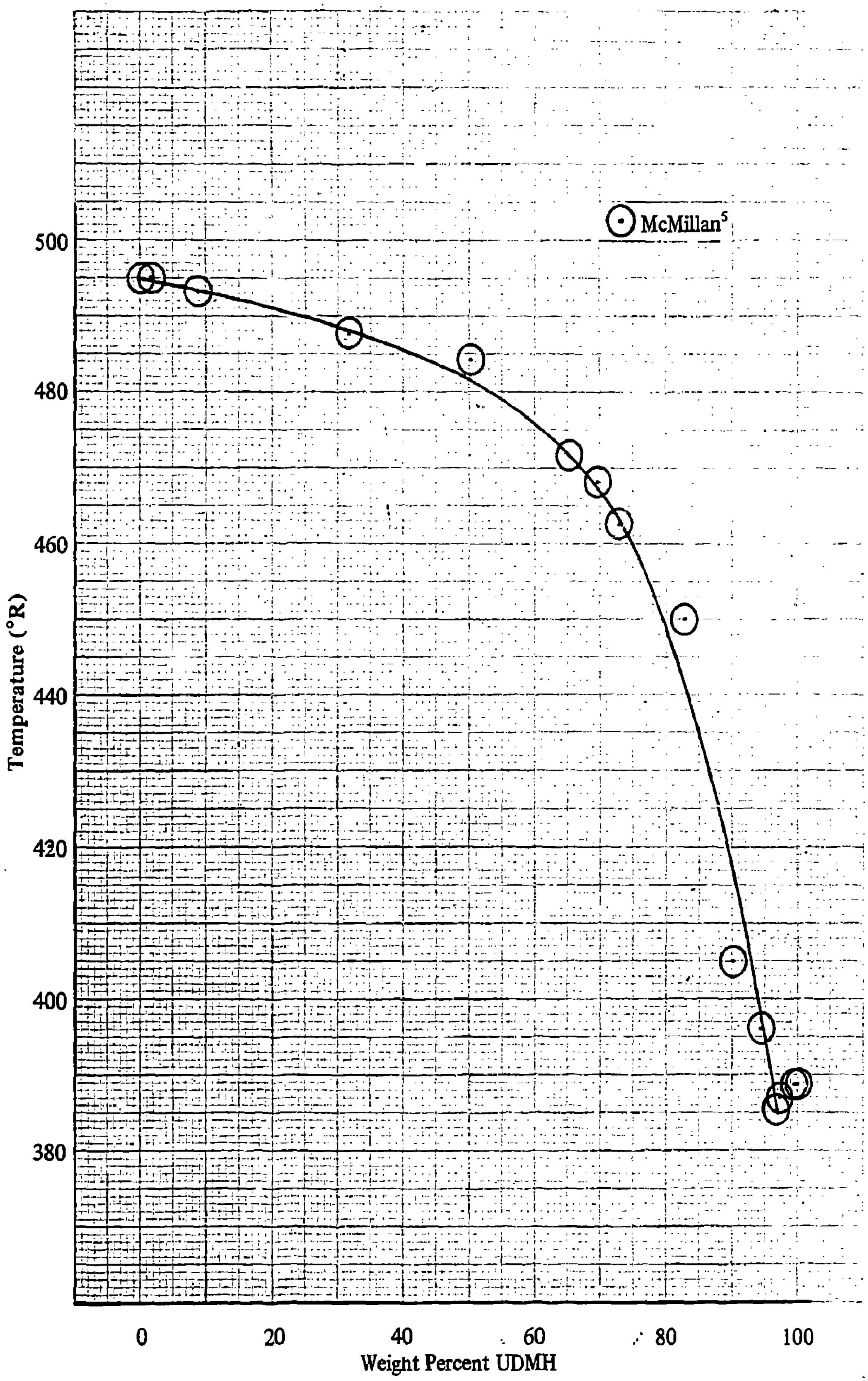


Figure 2.6-13a. Melting Temperatures for UDMH + Hydrazine Mixtures

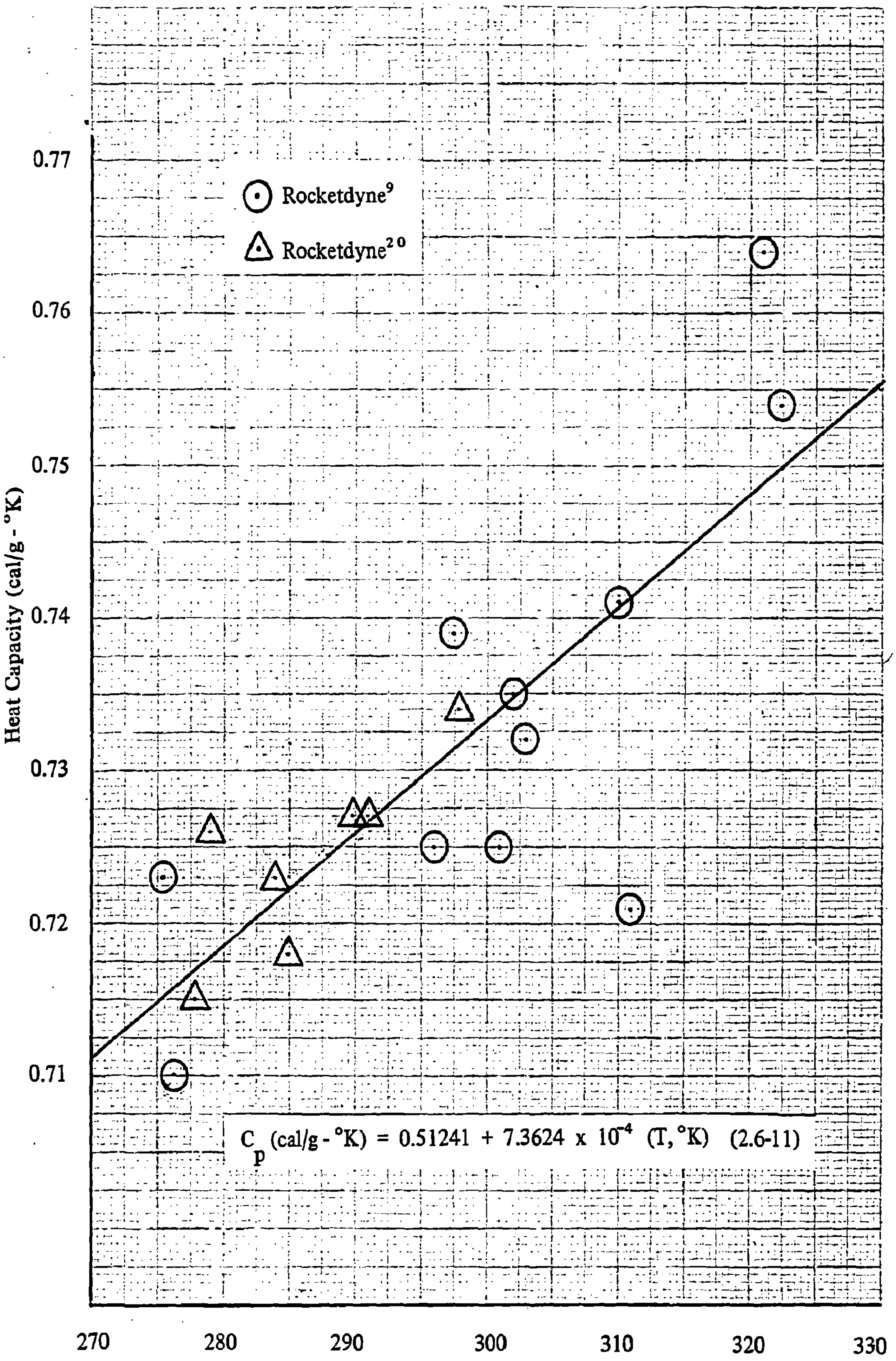
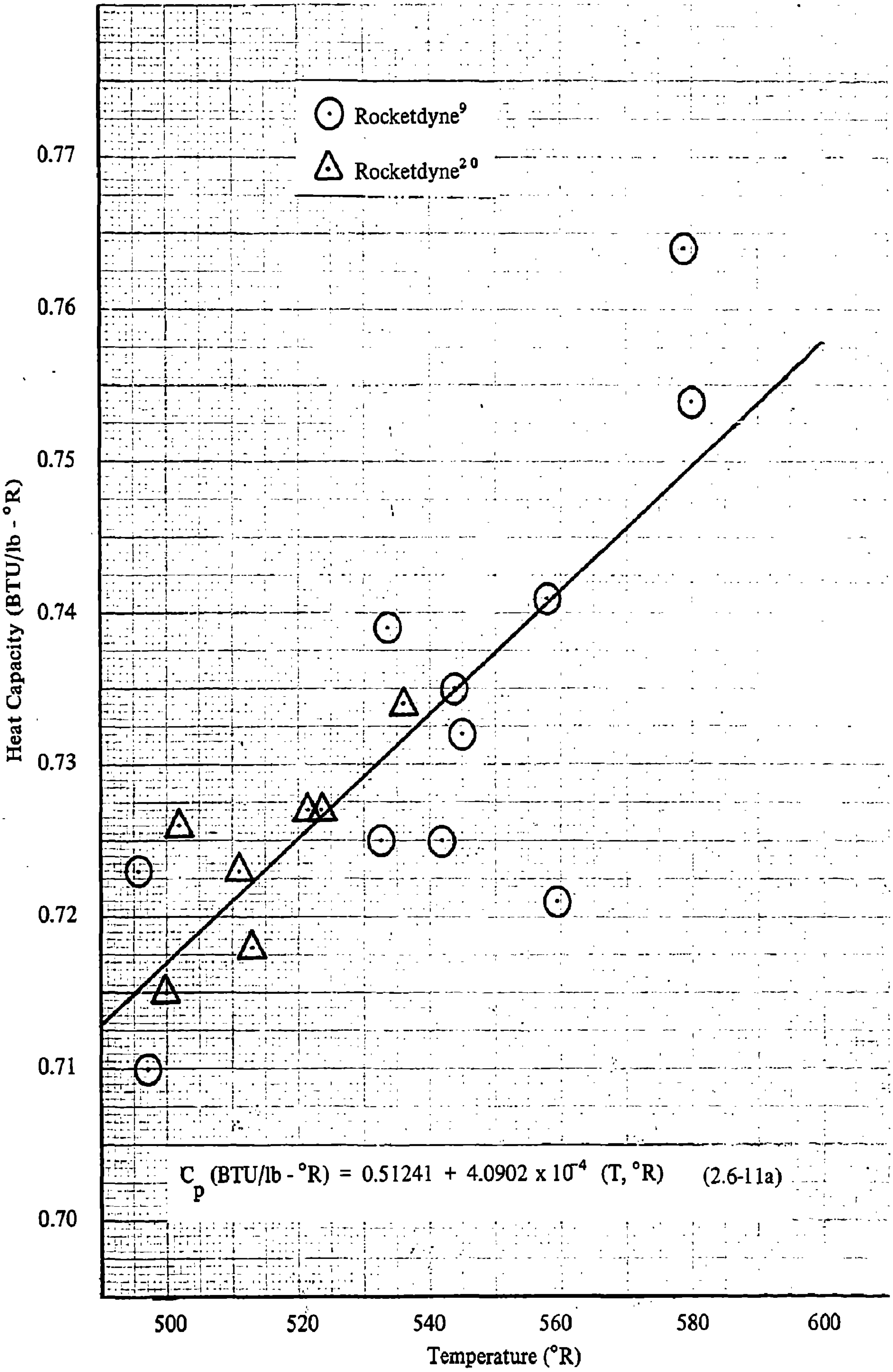


Figure 2.6-14. Heat Capacity versus Temperature Liquid 50-50 Fuel Blend



$$C_p \text{ (BTU/lb - °R)} = 0.51241 + 4.0902 \times 10^{-4} \text{ (T, °R)} \qquad (2.6\text{-}11a)$$

Figure 2.6-14a. Heat Capacity versus Temperature Liquid 50-50 Fuel Blend

The scatter of the data appears to be excessive, but the data are plotted on an expanded scale. The data actually fall within a ± 2.8% band with the average deviation of the linear fit being 0.76%. The heat capacity can be expressed by:

$$Cp\,(cal/g\text{-}^\circ K) = 0.51241 + 7.3624 \times 10^{-4}\,(T, ^\circ K) \qquad (2.6\text{-}11)$$

$$Cp\,(BTU/lb\text{-}^\circ R) = 0.51241 + 4.0902 \times 10^{-4}\,(T, ^\circ R) \qquad (2.6\text{-}11a)$$

The test sample had a composition by weight % of 51.3 N_2H_4, 48.3 UDMH and 0.4 H_2O.

2.6.5.5 Latent Heat of Vaporization

The heat of vaporization at the normal boiling point is calculated to be 8.048 kcal/mole (346.5 BTU/lb) from the Clapeyron equation. The vapor pressure data used for this calculation are discussed in Section 2.6.3.1.

2.6.6 LOGISTICS OF 50-50 BLEND

2.6.6.1 Manufacture

The successful manufacture of 50-50 blend simply involves complete mixing of correct proportions of each component. UDMH and hydrazine are miscible in all proportions, but because their densities differ, they are easily stratified, UDMH above the hydrazine. With sufficient agitation, they are readily mixed and show no tendency to separate as long as the more volatile UDMH is not allowed to evaporate or the mixture allowed to freeze. The following paragraphs discuss some of the various methods employed to mix 50-50 fuel blend.

The most successful method for mixing 50-50 blend is through impingement or swirling. This involves impinging separate streams of each fuel as in a rocket injector, or using a concentric nozzle (swirler). Mixing is complete in either case and is feasible for large volume production. UDMH and hydrazine, in the correct proportions, are passed through the nozzle and then to the fuel blend storage tank. This is the method employed by Aerojet-General in blending Aerozine-50 fuel.

Other methods include mixing by mechanical stirring, N_2 gas bubbling, and by diffusion. Each has drawbacks which make it less attractive for large-scale use.

When UDMH and hydrazine are mixed, small bubbles of dissolved gas are formed and there is a temperature decrease. The volume of the mixture is less than the total volume of the two separate fuels indicating some molecular bonding (probably hydrogen bonding) occurs.

The synthesis of UDMH is accomplished by FMC through the nitrosation of dimethylamine (DMA) to N-nitrosodimethylamine, followed by reduction of this intermediate to UDMH and subsequent purification (12), (16).

$$(CH_3)_2NH + HNO_3 \rightarrow (CH_3)_2NNO + H_2O$$

Reference 17

$$(CH_3)_2NNO + 2H_2 \rightarrow (CH_3)_2NNH_2 + H_2O$$

Hydrazine is generally produced by a modified Rashig process involving the oxidation of ammonia with hypochlorite or by the reaction of urea with hypochlorate.

2.6.6.2 Analysis of 50-50 Blend

The 50-50 fuel blend is procured under Military Specification MIL-P-27402A. The composition limits in % by weight are:

N_2H_4	51.0 ± 0.8
UDMH and Amines	47.0 (min.)
H_2O + Soluble Impurities	1.8 (max.)
N_2H_4 + UDMH	98.2 (min.)

The specification requires a determination of the amount of hydrazine and UDMH through direct titration methods. The water content is determined through gas chromatography which is very accurate for the small quantity present. The specification also calls for a determination of the particulate matter present in the fuel which is defined as the undissolved solids left on a 10 micron filter membrane after passing 500 ml of propellant through it. The acceptable density range for 50-50 is 0.894 to 0.903 g/cc at 25 C (77 F). The UDMH and hydrazine used in manufacturing 50-50 blend must conform to their particular specifications.

UDMH is procured under Military Specification MIL-D-25604C, dated May 1963 and updated in June 1967. The composition limits are:

UDMH	98.0% (min.)
H_2O	0.3% (max.)
Amines and Other Insolubles	1.7% (max.)
	100.0%

The procurement of hydrazine as a propellant is covered by Military Specification MIL-P-26536C dated May 1969. The hydrazine may contain up to 1.5% by weight of water. The minimum hydrazine assay is 98% by weight. The 0.5 % difference is assumed to be other soluble impurities.

2.6.6.3 Cost and Availability of 50-50 Blend

Both UDMH and hydrazine are available in large quantities for rocket industry use. The sole supplier of UDMH in large quantities is Food Machinery and Chemical Corp., Baltimore, Md., while Olin Mathieson Chemical Corp., New York, New York is the principal supplier of N_2H_4.

The cost of UDMH and N_2H_4 are covered in Sections 2.5.6.3 and 2.3.6.3, respectively. Mixing of the blend is generally accomplished at the facility where it is to be used. The cost of mixing would depend upon quantities, labor costs and the method used, but this cost should be small in comparison to the cost of the individual propellants.

2.6.6.4 Shipping and Transportation of 50-50 Blend

Normally, UDMH and hydrazine are shipped to the facility separately and the 50-50 blend is mixed there. Reference to the shipment of individual fuels is covered in Sections 2.3.6.4 and 2.5.6.4. If the fuel is to be shipped as a blend, it shall be packaged in ICC 5, 5A or 5C type 304 or 347 stainless steel drums, tank trucks, and tank cars conforming to Interstate Commerce Commission regulations contained in Code of Federal Regulations 49 CFR 71-90. The space above the liquid shall be filled with nitrogen gas at atmospheric pressure. All containers shall be marked in accordance with ICC Regulation 49 CFR 71-90, MIL-STD-129 and MIL-STD-172.

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2.7 MHF-3

2.7.1 PROPERTY SUMMARY SHEET

Chemical Name:	**Mixed Hydrazine Fuel No. 3**	Common Name:	MHF-3
Empirical Formula:	$C_{0.810345}H_{5.62073}N_{2.0}$	Formula Weight:	43.4148
Composition; % b.w.:	86 $N_2H_2CH_3$ + 14 N_2H_4		

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	219.26	°K			
	−53.9	°C			
	394.67	°R			
	−65.0	°F			
HEAT OF FUSION	Not Avail	kcal/mole			
		BTU/lb			
NORMAL BOILING POINT	362.8	°K	-	2	
	89.65	°C			
	653.04	°R			
	193.37	°F			
HEAT OF VAPORIZATION	8.93	kcal/mole	362.8	calc.	
	370.2	BTU/lb			
TROUTON CONSTANT	24.6	-	362.8	calc.	
VAPOR PRESSURE OF LIQUID	51.44	mm Hg	298	2	2.7-1
	0.995	psia			
DENSITY OF LIQUID	0.8889	g/cc	298	1, 3, 12	2.7-2
	55.490	lb/ft^3			
SONIC VELOCITY	1603	m/sec	298	8	2.7-3
	5260	ft/sec			
COMPRESSIBILITY OF LIQUID					
ADIABATIC	4.42×10^{-5}	atm^{-1}	298	8	2.7-4
	3.00×10^{-6}	psi^{-1}			
ISOTHERMAL	Not Avail	atm^{-1}	-		
		psi^{-1}			
VISCOSITY OF LIQUID	0.810	centipoise	298	4, 10, 12	2.7-5
	5.44×10^{-4}	$lb_m/ft\text{-}sec$			
HEAT CAPACITY OF LIQUID	0.7196	cal/g-°K	298	6	2.7-8
	0.7196	BTU/lb-°R			
THERMAL CONDUCTIVITY OF LIQUID	6.60×10^{-4}	cal/cm-sec-°K	298	9	2.7-7
	4.43×10^{-5}	BTU/ft-sec-°R			
SURFACE TENSION	35.76	dynes/cm		1, 5	2.7-6
	2.45×10^{-3}	lb_f/ft			
HEAT OF FORMATION	12.907	kcal/mole	298	calc.	see page 2.7-18
	535.1	BTU/lb			

2.7.2 GENERAL

2.7.2.1 Introduction to MHF-3

(C) MHF-3 is nominally a blend of 86% by weight methylhydrazine and 14% by weight hydrazine, developed as a prepackagable fuel which would meet a -65 F freezing point requirement, and still retain as much of the performance and density of neat hydrazine as possible. This blend was studied extensively by Rocketdyne, Thiokol-RMD, and Bell Aerosystems for various potential applications. It was selected as the fuel for the Condor Missile propulsion units before that program was discontinued.

(U) MHF-3 is a clear, colorless, hydroscopic liquid having a characteristic ammoniacal odor. It is also toxic and flammable, both as liquid and vapor. Most aspects of the nature of MHF-3 are dominated by the methylhydrazine content.

2.7.2.2 Structure

(U) MHF-3 is a solution of hydrazine and methylhydrazine whose structures are discussed in Sections 2.3.2.2 and 2.4.2.2, respectively. Little or no hydrogen bonding takes place between the components.

2.7.2.3 Specification and Purity

(U) Specification MIL-P-81342 (WP), dated December 1965, requires a minimum purity of 98% N_2H_4 + MMH. Additional details are found in Section 2.7.6.2.

2.7.3 PHYSICAL PROPERTIES OF MHF-3

2.7.3.1 Vapor Pressure and Normal Boiling Point

(U) The vapor pressure of liquid MHF-3 has been measured by RMD (2) over a temperature range from 0 to 90 C (32 to 194 F). Details of the experimental techniques are lacking. A Sickle gauge was employed and is described as a glass apparatus having a glass diaphragm with a needle attached. A back pressure is applied to the diaphragm to maintain the needle at the null reading. It is assumed that a mercury manometer was employed.

(U) The experimental data are shown in Figures 2.7-1 and 2.7-1a. The variation of vapor pressure with temperature was found by the least-squares method to be best represented by the classical relation

$$\log P\,(\text{mmHg}) = 8.2748 - \frac{1956.91}{T,\,^\circ K} \qquad (2.7\text{-}1)$$

$$\log P\,(\text{psia}) = 6.5612 - \frac{3522.43}{T,\,^\circ K} \qquad (2.7\text{-}1a)$$

The standard deviation of the experimental data from equation 2.7-1 is 4.05 mm Hg and the average deviation is 0.77%.

(U) The normal boiling point found from equation 2.7-1 is 362.8 K or 89.6 C (193.4 F). The boiling point range of this mixture does not appear in the literature.

2.7.3.2 Density of Liquid MHF-3

(U) Experimental density values of saturated liquid MHF-3 have been reported by Bell Aerosystems (1), RMD (3), and Rocketdyne (10). The data are plotted in Figures 2.7-2 and 2.7-2a. The agreement among the three studies is good. The density from -54 to 94 C (-65 to 201 F)) can be expressed as a linear function of temperature

$$\rho\,(\text{g/cc}) = 1.1716 - 9.4836 \times 10^{-4}\,(T,\,^\circ K) \qquad (2.7\text{-}2)$$

$$\rho\,(\text{lb/ft}^3) = 73.1416 - 0.032891\,(T,\,^\circ R) \qquad (2.7\text{-}2a)$$

(U) The RMD study was conducted using a glass pycnometer which consisted of a small bulb attached to a calibrated precision bore capillary tube. No other details were reported and the composition of the sample was not given.

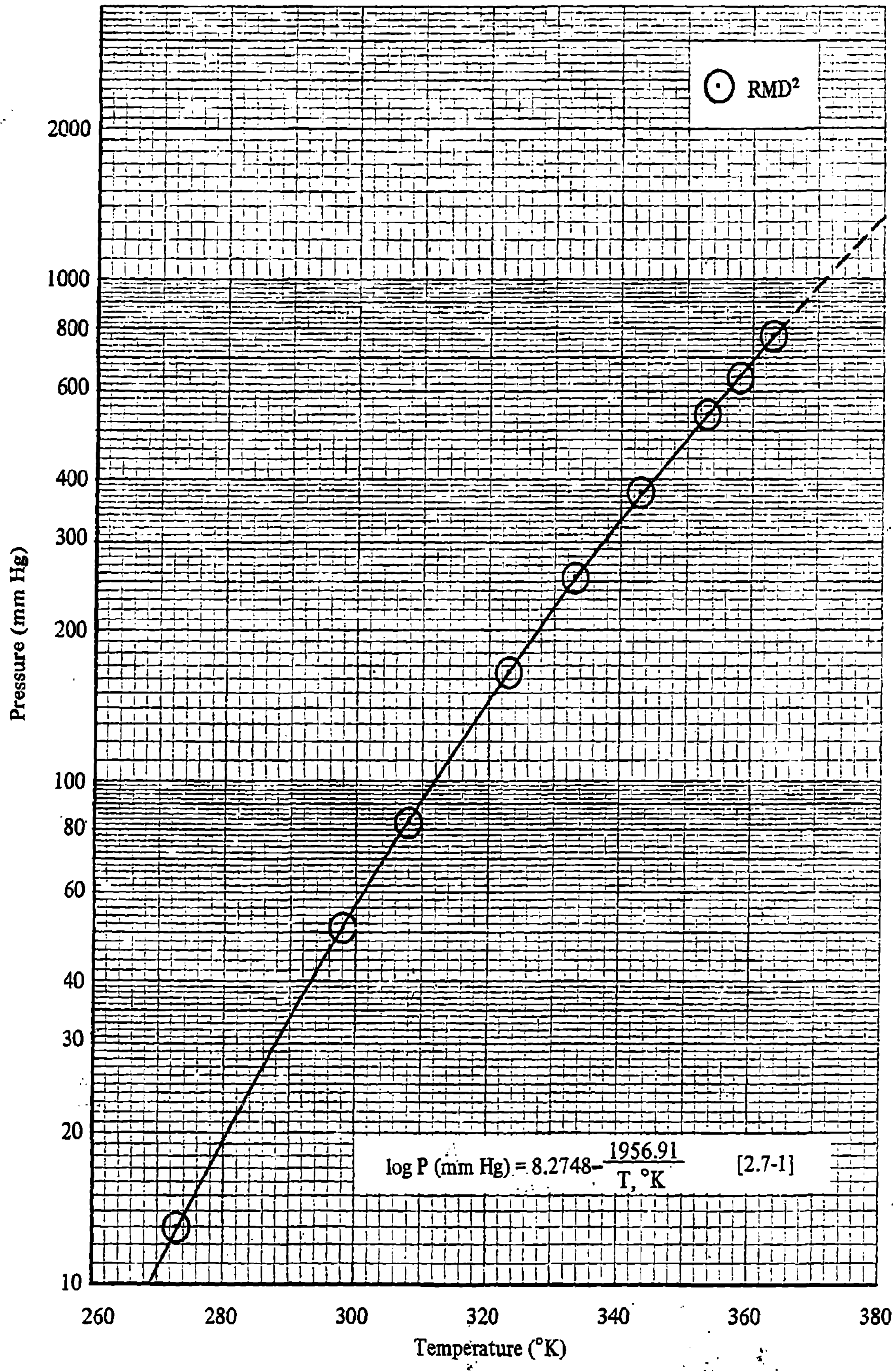
(C) Bell used three glass pycnometers having reservoir bulbs of different volumes welded to precision bore capillary tubes. The volumes to a scribe mark on the capillaries were determined with mercury. The liquid height above the reference marks was measured with a cathetometer. The densities were calculated from the volumes, weight of the sample and differences of mass volume product between two pycnometers. Therefore, at each temperature three density values were obtained. The agreement was considered excellent and the data shown in Figure 2.7-2 are the averages. The composition (weight %) as determined by gas chromatography was 85.6 MMH, 13.4 N_2H_4 and 1.0 as impurities (mostly water).

(C) Rocketdyne employed a 25 ml flask type pycnometer to which a precision bore capillary tube was fuzed. A cathetometer was used to measure the liquid height above or below an etch mark on the capillary. An analytical balance was used to weigh the samples. The apparatus was calibrated with water and acetone at lower temperatures. The MHF-3 sample composition (weight %) was 85.6 MMH. 13.9 N_2H_4, 0.3 H_2O, and 0.2 other soluble impurities.

(C) Rocketdyne also measured the density of three other MHF-3 related blends and gave an equation which has the composition as well as temperature for the independent variable:

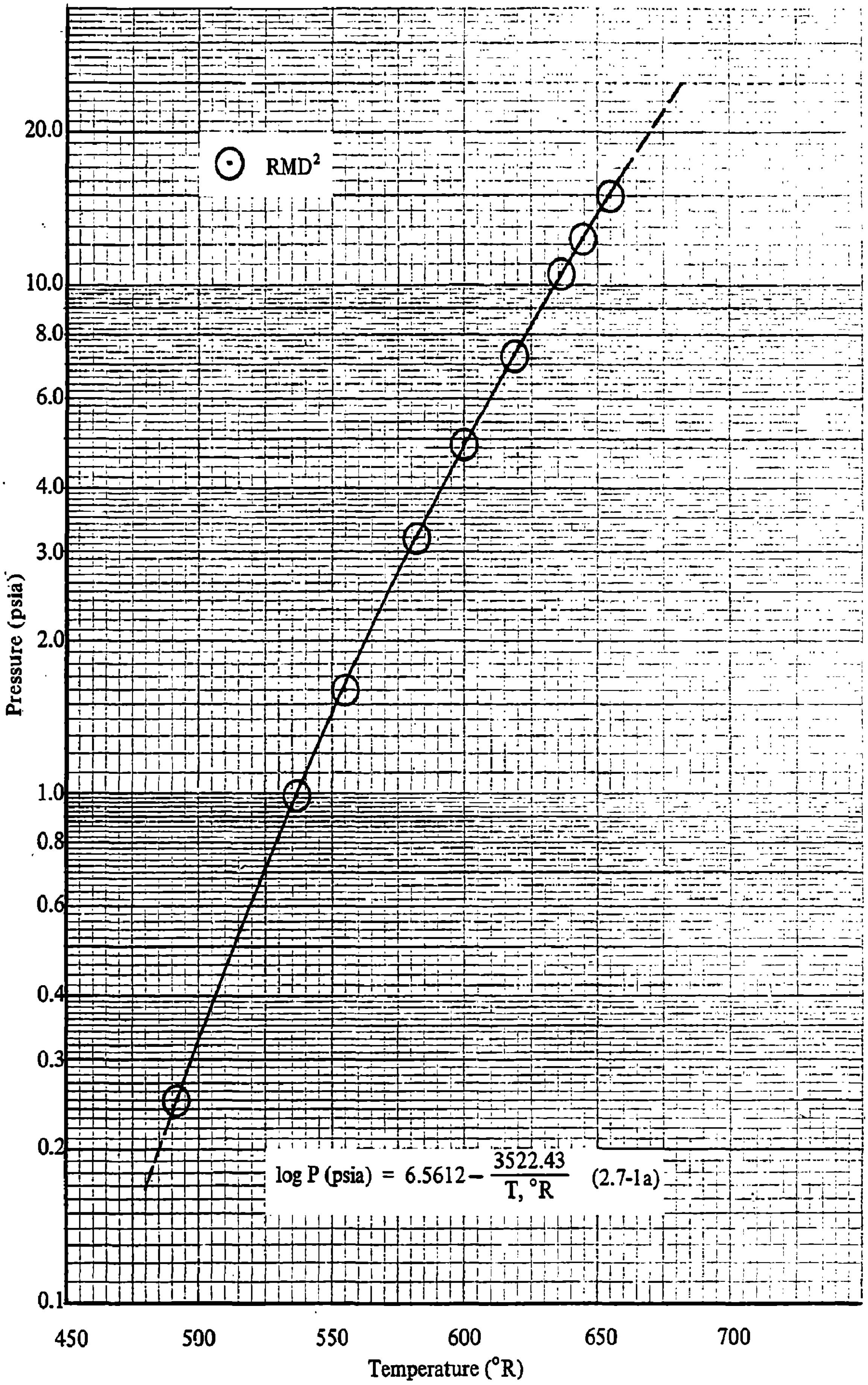
$$\rho\,(\text{g/cc}) = 0.894 - 9.55 \times 10^{-4}\,(T,\,^\circ C) - 2.214 \times 10^{-7}\,(T,\,^\circ C)^2 + 1.34 \times 10^{-3} H + 3.040 \times 10^{-3} W \qquad (2.7\text{-}3)$$

(This page is Unclassified)



$$\log P\ (\text{mm Hg}) = 8.2748 - \frac{1956.91}{T,\ ^\circ K} \qquad [2.7\text{-}1]$$

Figure 2.7-1. Vapor Pressure versus Temperature, Liquid MHF-3



$$\log P\ (\text{psia}) = 6.5612 - \frac{3522.43}{T,\ ^{\circ}R} \qquad (2.7\text{-}1a)$$

Figure 2.7-1a. Vapor Pressure versus Temperature, Liquid MHF-3

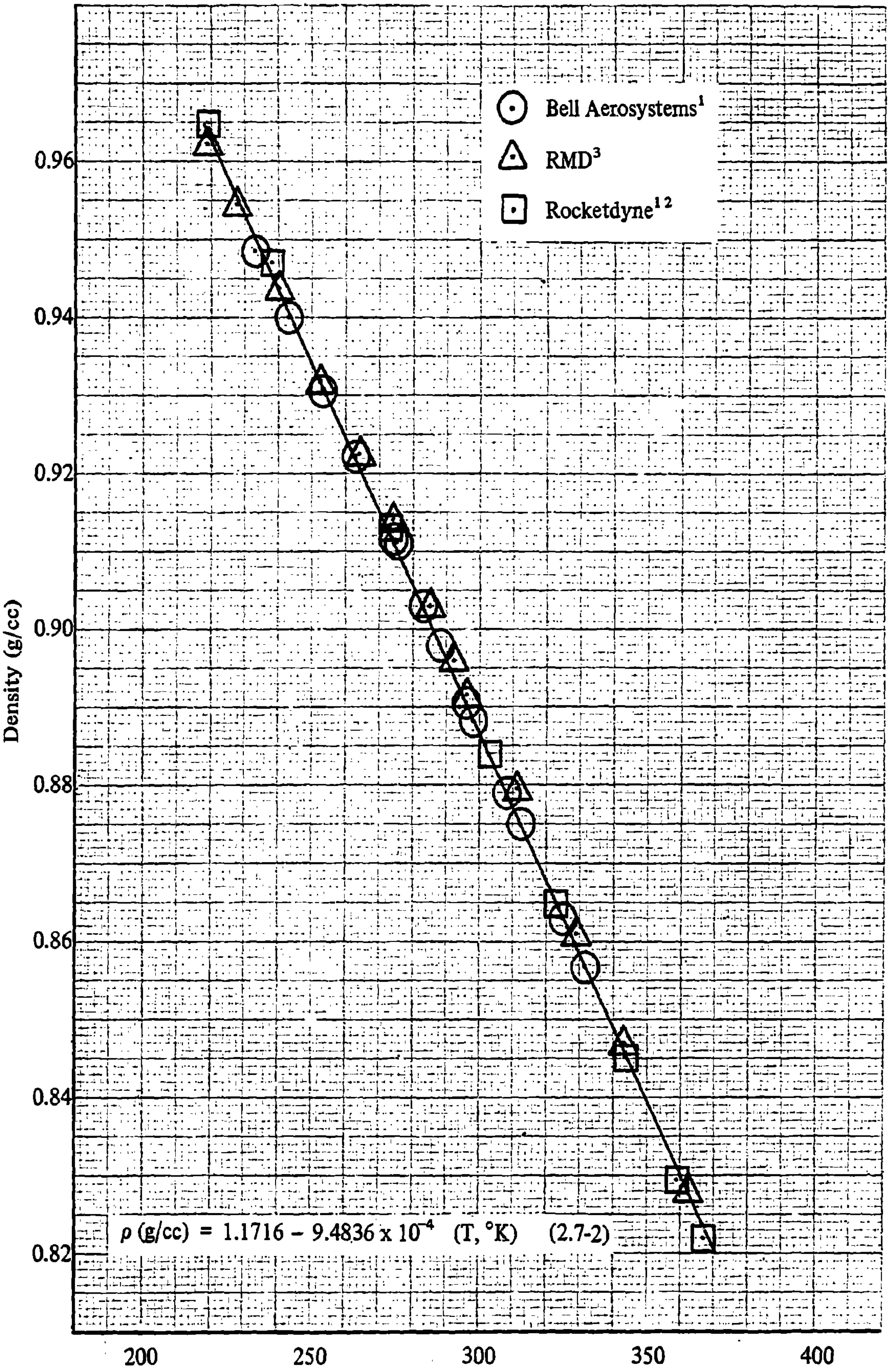


Figure 2.7-2. Density versus Temperature, Liquid MHF-3

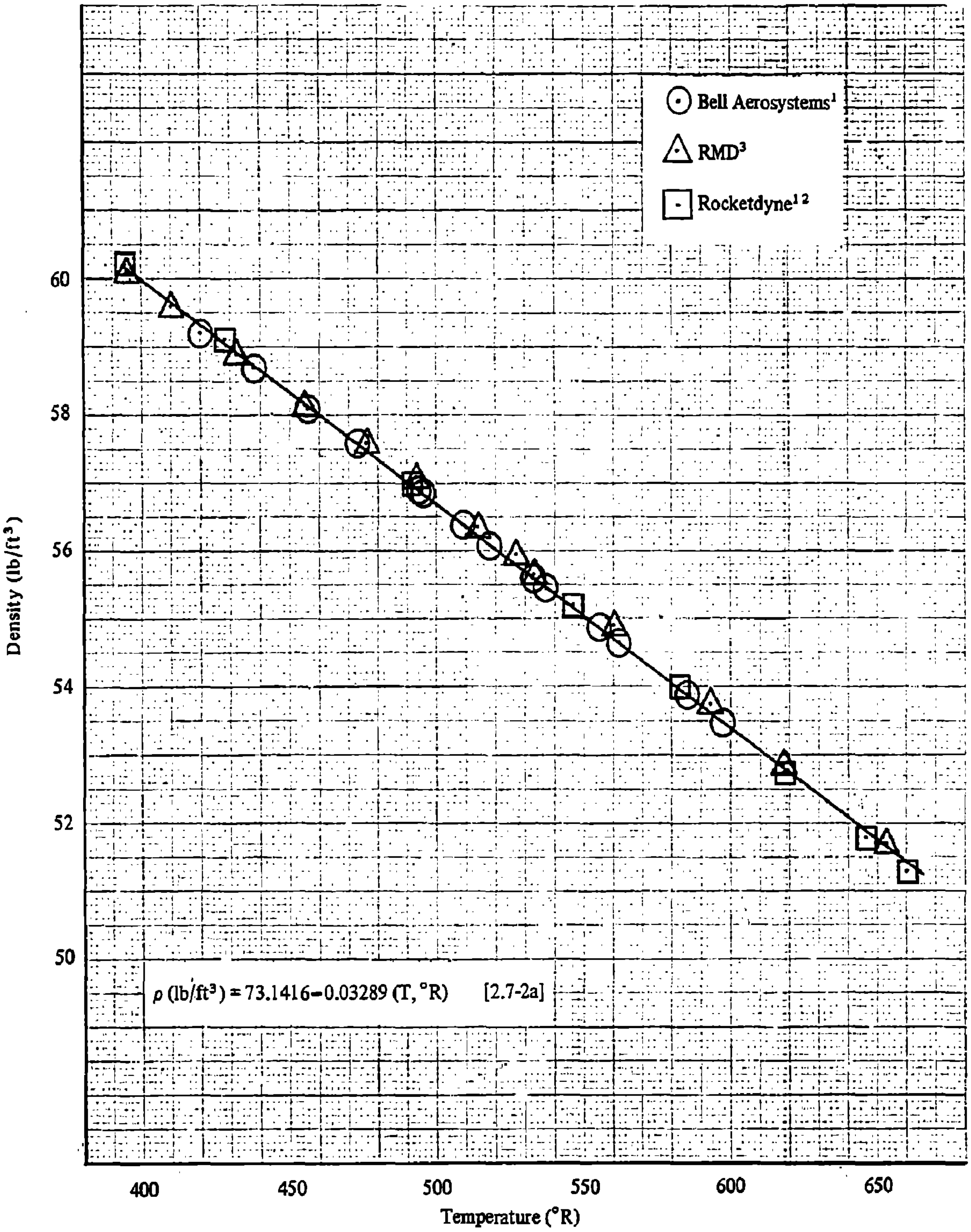


Figure 2.7-2a. Density versus Temperature, Liquid MHF-3

(C) where

H = weight % N_2H_4
W = weight % H_2O

equation 2.7-3 may be of value if a particular MHF-3 blend was found to vary significantly from the nominal.

(C) Ahlert (13) has recently reported density values for some mixtures of N_2H_4 and MMH. The lowest N_2H_4 value studied was 30% whereas MHF-3 has only 14%. The measured densities were compared to those calculated by mass average densities of the two pure compounds. The average deviation between measured and calculated was only 0.18% and the largest deviation was 0.25%.

2.7.3.3 Sonic Velocity in Liquid MHF-3

(U) The sonic velocity in liquid MHF-3 has been reported by Rocketdyne (5, 7, 8). Reference 8 stated that the data reported previously in References 5 and 7 were in error. Therefore, only the data reported in Reference 8 were considered. The experimental points are plotted in Figures 2.7-3 and 2.7-3a.

(U) The sonic velocity is a linear function of temperature over the experimental temperature range of -36 to 95 C (-33 to 203 F)

$$c(\text{m/sec}) = 2808.5 - 4.0427(\text{T, °K}) \qquad (2.7\text{-}4)$$

$$c(\text{ft/sec}) = 9214.3 - 7.3686(\text{T, °R}) \qquad (2.7\text{-}4a)$$

The standard deviation of the experimental points from those calculated by equation 2.7-4 is 4.34 m/sec and the average deviation is 0.24%.

2.7.3.4 Compressibility of Liquid MHF-3

(U) The isothermal compressibility of MHF-3 has not been studied. The adiabatic compressibility can be found from sonic velocity

$$\beta_a = \frac{1}{\rho c^2}$$

where

ρ = density
c = sonic velocity

The sonic velocity in liquid MHF-3 has been measured by Rocketdyne (8). At each experimental sonic velocity point, the adiabatic compressibility was calculated using densities obtained from equation 2.7-2.

(U) The computed values for a temperature range from -36 to 95 C (-33 to 203 F) are shown in Figures 2.7-4 and 2.7-4a. The adiabatic compressibility is adequately described by

$$\beta_a\,(\text{atm}^{-1}) = 1.6201 \times 10^{-4} + 1.9278 \times 10^{-6}\,(\text{T,°K})$$
$$-6.8281 \times 10^{-9}\,(\text{T,°K})^2 + 8.9935 \times 10^{-12}\,(\text{T,°K})^3 \qquad (2.7\text{-}5)$$

$$\beta_a\,(\text{psi}^{-1}) = 1.1024 \times 10^{-5} + 7.2879 \times 10^{-8}\,(\text{T,°R})$$
$$-1.4340 \times 10^{-10}\,(\text{T,°R})^2 + 1.0493 \times 10^{-13}\,(\text{T,°R})^3 \qquad (2.7\text{-}5a)$$

The average deviation of the data from equation 2.7-5 is 0.41%.

2.7.3.5 Viscosity of Liquid MHF-3

(U) The viscosity of liquid MHF-3 has been studied by both RMD (4) and Rocketdyne (10, 12). The early study by RMD covered a temperature range from -54 to 21 C (-65 to 69 F) and utilized a modified Cannon-Zhukov viscometer. Rocketdyne used capillary viscometers and covered a temperature range from -40 to 93 C (-40 to 195 F). Four different compositions were studied by Rocketdyne and the effect of small changes in composition on viscosity was insignificant. The composition (weight %) of the MHF-3 sample was 85.6 MMH, 13.9 N_2H_4, 0.3 H_2O and 0.2 other soluble impurities.

(U) The kinematic viscosity values from the two studies were converted to absolute values using density values obtained from equation 2.7-2. The absolute values are plotted in Figures 2.7-5 and 2.7-5a. The agreement between the two studies is only fair. The combined data over the temperature range from -54 to 93 C (-65 to 195 F) were curve fitted by the least squares method.

$$\log \mu\,(\text{centipoise}) = -11.179 + \frac{9291.8}{(\text{T,°K})} - \frac{2.7687 \times 10^6}{(\text{T,°K})^2}$$
$$+ \frac{2.9336 \times 10^8}{(\text{T,°K})^3} \qquad (2.7\text{-}6)$$

$$\log \mu\,(\text{lbm/ft-sec}) = -14.351 + \frac{16725.2}{(\text{T,°K})} - \frac{8.9706 \times 10^6}{(\text{T,°R})^2}$$
$$+ \frac{1.7109 \times 10^9}{(\text{T,°R})^3} \qquad (2.7\text{-}6a)$$

The standard deviation of the experimental data from equation 2.7-6 is 0.72 centipoise and the average deviation is a relatively high 8.3%. The disagreement between the two studies warrants additional experimental work in order to resolve the discrepancy.

2.7.3.6 Surface Tension of Liquid MHF-3

(U) The surface tension of liquid MHF-3 has been measured by both Bell Aerosystems (1) and Rocketdyne (5). The two studies covered a temperature range from -44 to 94 C (-47 to 201 F). The data from the two studies are in good agreement. Generally, the surface tension of liquids is a linear function of temperature. The MHF-3 blend tended to be linear above 0 C but both studies seem to show a change in slope below this temperature. Although probably coincidental, this is approximately at the freezing point of N_2H_4.

(U) The combined data of the two studies are plotted in Figures 2.7-6 and 2.7-6a. The data are adequately described by the following equations:

$$\gamma\,(\text{dynes/cm}) = 37.4305 + 0.09252\,(T,{}^\circ K) - 3.2915 \times 10^{-4}\,(T,{}^\circ K)^2 \qquad (2.7\text{-}7)$$

$$\gamma\,(\text{lbf/ft}) = 2.5648 \times 10^{-3} + 3.5219 \times 10^{-6}\,(T,{}^\circ R) - 6.9610 \times 10^{-9}\,(T,{}^\circ R)^2 \qquad (2.7\text{-}7a)$$

The standard deviation of experimental data from equation 2.7-7 is 0.49 dynes/cm and the average deviation is 1.1% which is rather high.

(U) Both studies were conducted using a double capillary rise system with the liquid under its own vapor pressure. The difference in height rise of two capillaries of different diameters is measured. The surface tension is then calculated from the relation

where

g = gravitational constant
ρ = density of liquid
Δh = height difference
$r_1 r_2$ = radii of capillaries

(C) Rocketdyne substracted the vapor density (calculated from the ideal gas law) from the liquid density. Bell made corrections for the radius of the capillary tubes according to tables given by Sugden (11). Either correction is nearly negligible. The sample compositions (weight %) from the two studies are:

	Bell^1	Rocketdyne^5
MMH	85.6	85.6
N_2H_4	13.4	13.9
H_2O	0.4	0.3
Other soluble Impurities	0.6	0.2

2.7.3.7 Thermal Conductivity of Liquid MHF-3

(U) The thermal conductivity of liquid MHF-3 has been experimentally determined by Rocketdyne (9) over a temperature range from -18 to 122 C (0 to 251 F). The experimental data are plotted in Figures 2.7-7 and 2.7-7a. The data can be adequately described by

$$K(\text{cal/cm-sec-}{}^\circ K) = 7.3524 \times 10^{-4} + 5.0303 \times 10^{-7}\,(T,{}^\circ K) - 2.5343 \times 10^{-9}\,(T,{}^\circ K)^2 \qquad (2.7\text{-}8)$$

$$K(\text{BTU/ft-sec-}{}^\circ R) = 4.9373 \times 10^{-5} + 1.8766 \times 10^{-8}\,(T,{}^\circ K) - 5.2526 \times 10^{-11}\,(T,{}^\circ R)^2 \qquad (2.7\text{-}8a)$$

The standard deviation of the experimental data from equation 2.7-8 is 1.09 x 10^{-5} cal/cm-sec-K while the average deviation is 1.39%. The maximum deviation was -3.0%.

(C) The sample composition (weight %) was reported to be 85.1 MMH, 13.9 N_2H_4, 0.8 H_2O, 0.1 NH_3 and 0.1 other soluble impurities. The thermal conductivity cell was also used for 50 UDMH + 50 N_2H_4 fuel blend and is briefly described in Section 2.6.3.7.

2.7.3.8 Dielectric Constant of MHF-3

(U) Aerojet (14) reported a single value of the dielectric constant at 25 C (77 F) of 23.5. No other data are available.

2.7.3.9 Index of Refraction of MHF-3

(U) No data are available.

2.7.4 CHEMICAL PROPERTIES OF MHF-3

2.7.4.1 Reactions

(C) Since MHF-3 is a mixture of hydrazine and methylhydrazine (MMH), the fuel is capable of any reactions particular to either component. Rocketdyne (10) indicates that the preponderance of MMH (86% by weight) will mask the effect of the hydrazine and that the chemical behavior of MHF-3 will be similar to that of MMH.

(U) MMH is discussed in Section 2.4.4.1 and hydrazine is discussed in Section 2.3.4.1.

2.7.4.2 Inert Gas Solubility

(U) Although no data on the solubility of inert gases in MHF-3 are available, RMD (3) developed tank pressure versus temperature curves for MHF-3 loaded with argon over a temperature range of -80 to +195 F.

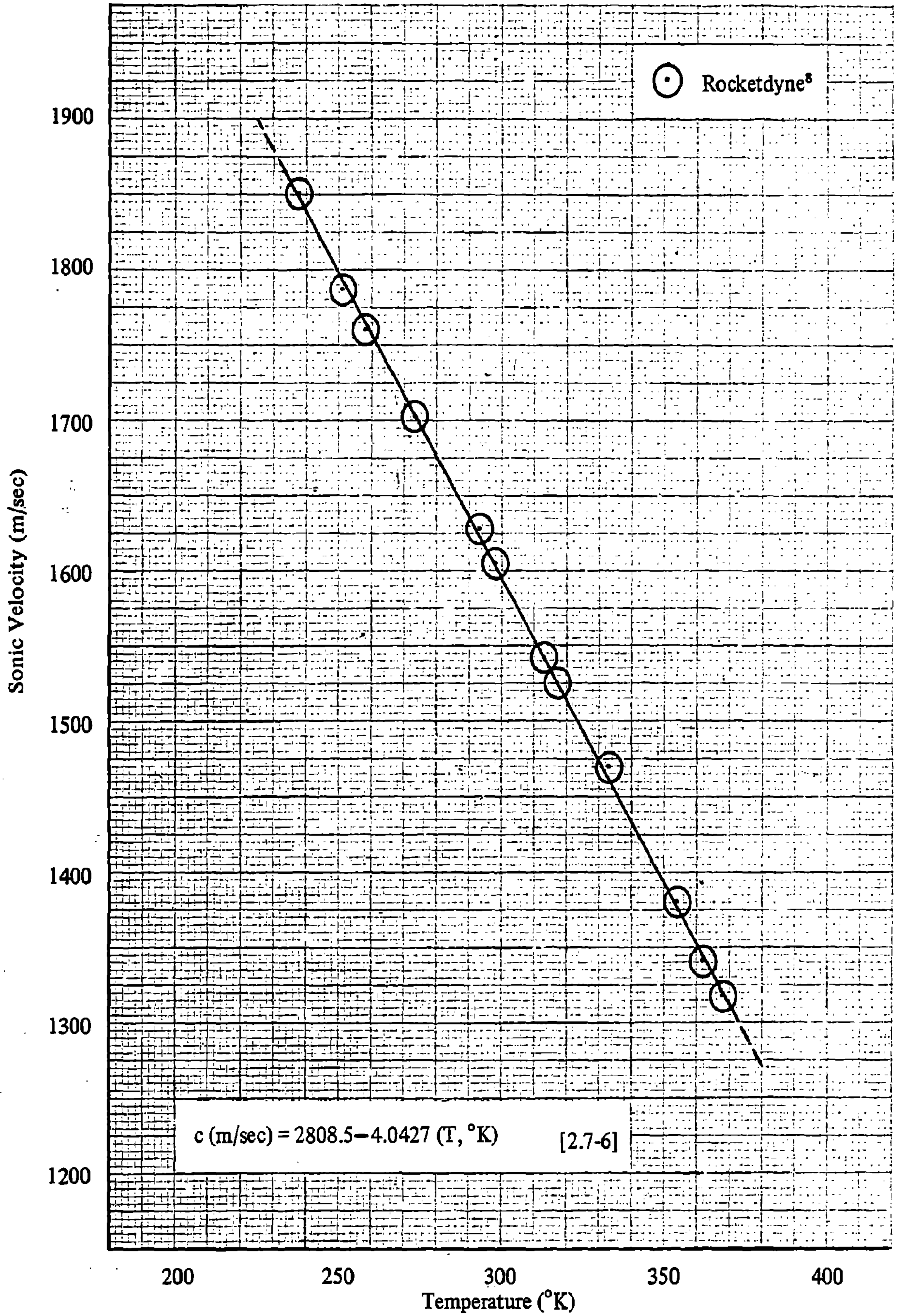


Figure 2.7-3. Sonic Velocity in Liquid MHF-3 versus Temperature

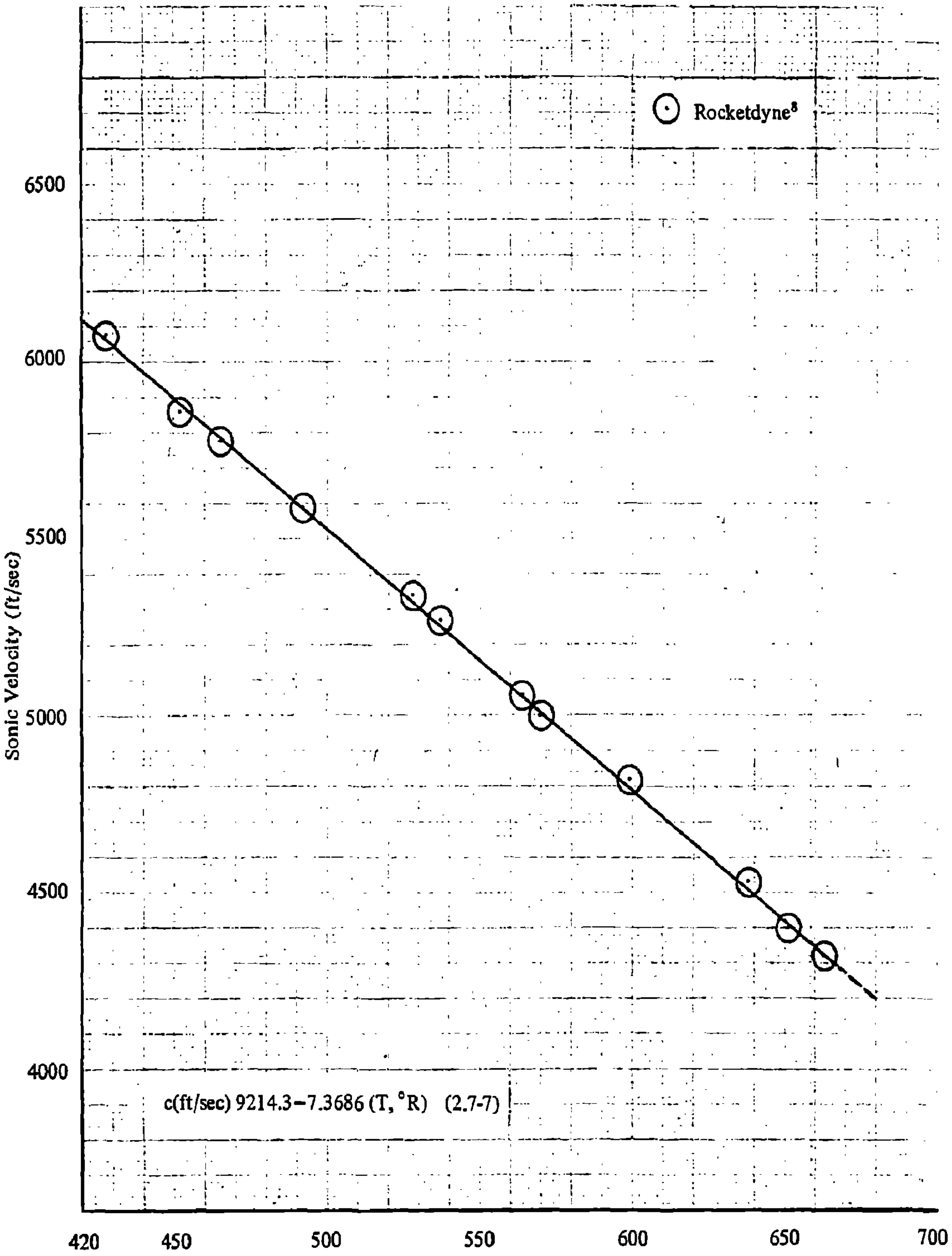
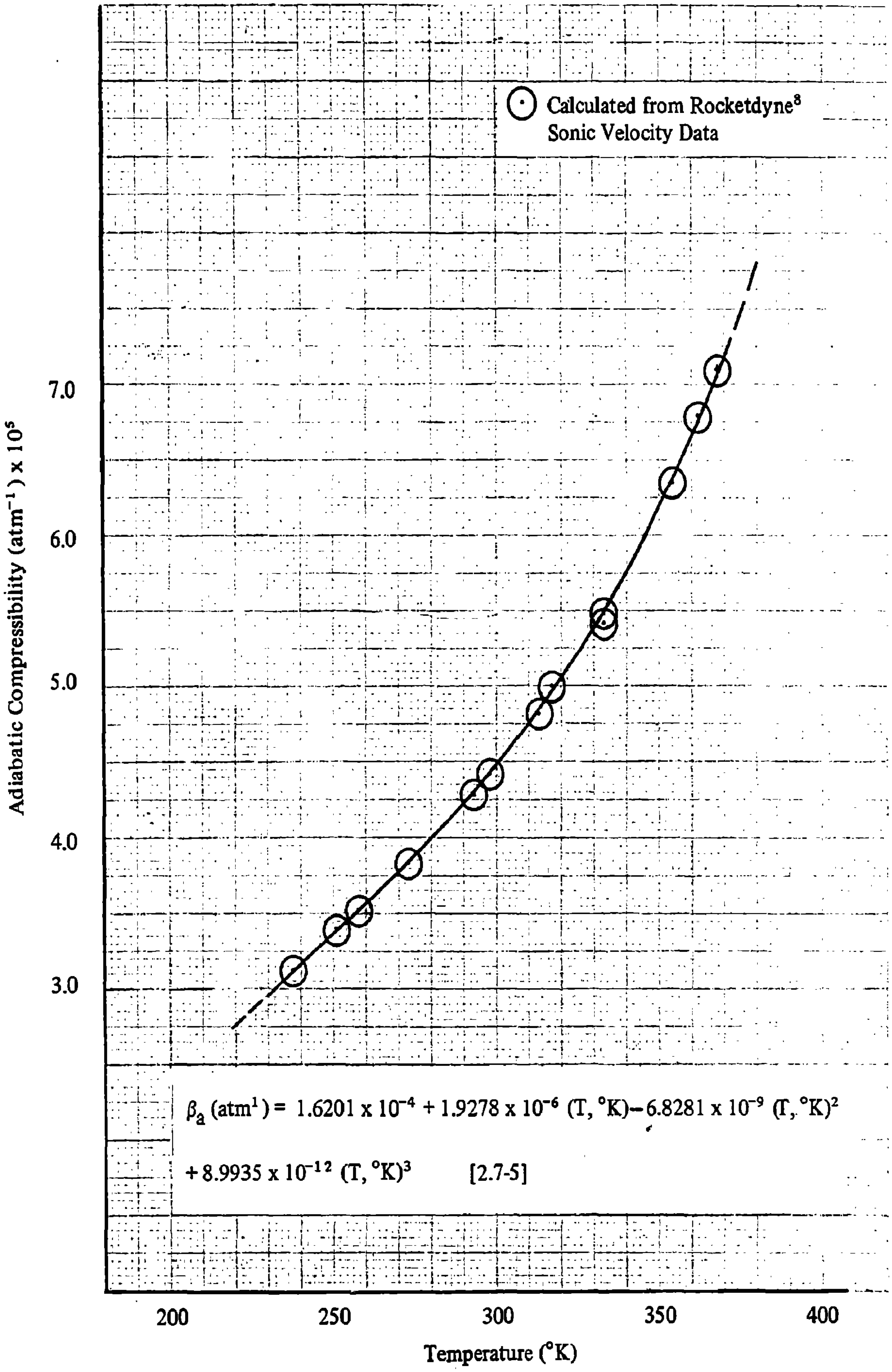
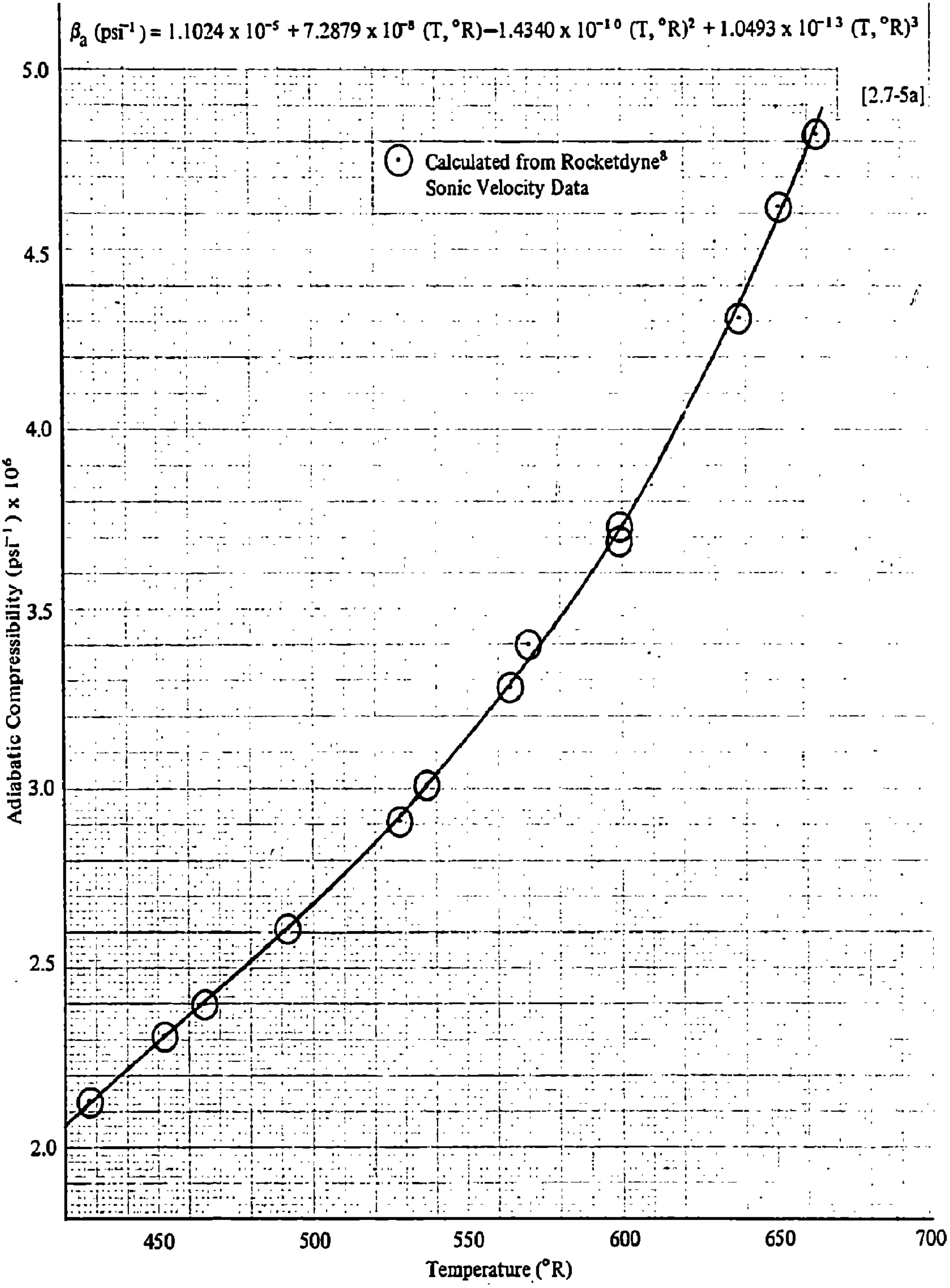


Figure 2.7-3a. Sonic Velocity versus Temperature, Liquid MHF-3



$$\beta_a\,(\text{atm}^1) = 1.6201 \times 10^{-4} + 1.9278 \times 10^{-6}\,(T, {}^\circ K) - 6.8281 \times 10^{-9}\,(T, {}^\circ K)^2 + 8.9935 \times 10^{-12}\,(T, {}^\circ K)^3 \qquad [2.7\text{-}5]$$

Figure 2.7-4. Adiabatic Compressibility versus Temperature, Liquid MHF-3



$$\beta_a\,(\mathrm{psi}^{-1}) = 1.1024 \times 10^{-5} + 7.2879 \times 10^{-8}\,(T, {}^{\circ}R) - 1.4340 \times 10^{-10}\,(T, {}^{\circ}R)^2 + 1.0493 \times 10^{-13}\,(T, {}^{\circ}R)^3 \quad [2.7\text{-}5a]$$

Figure 2.7-4a. Adiabatic Compressibility versus Temperature Liquid MHF-3

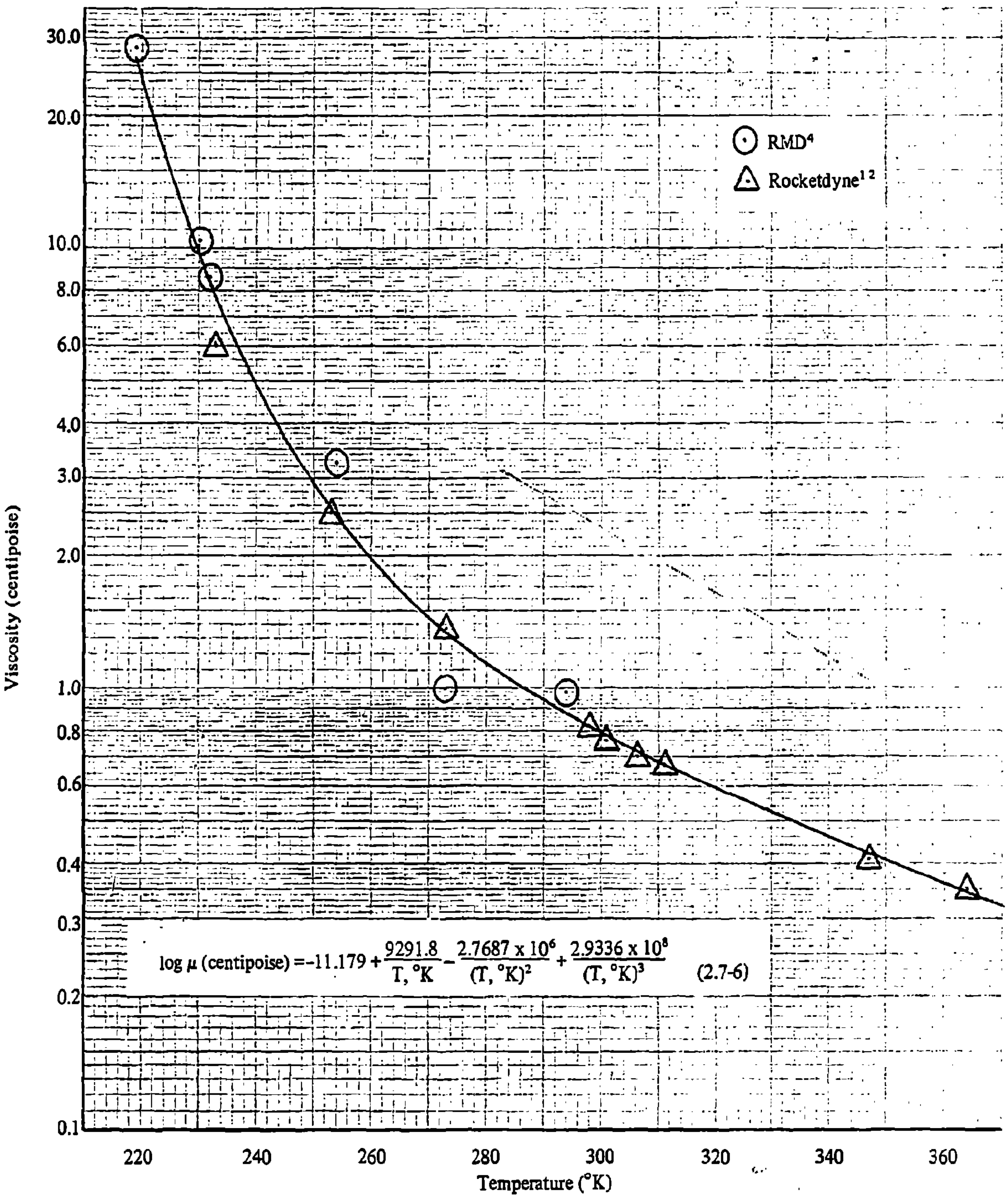
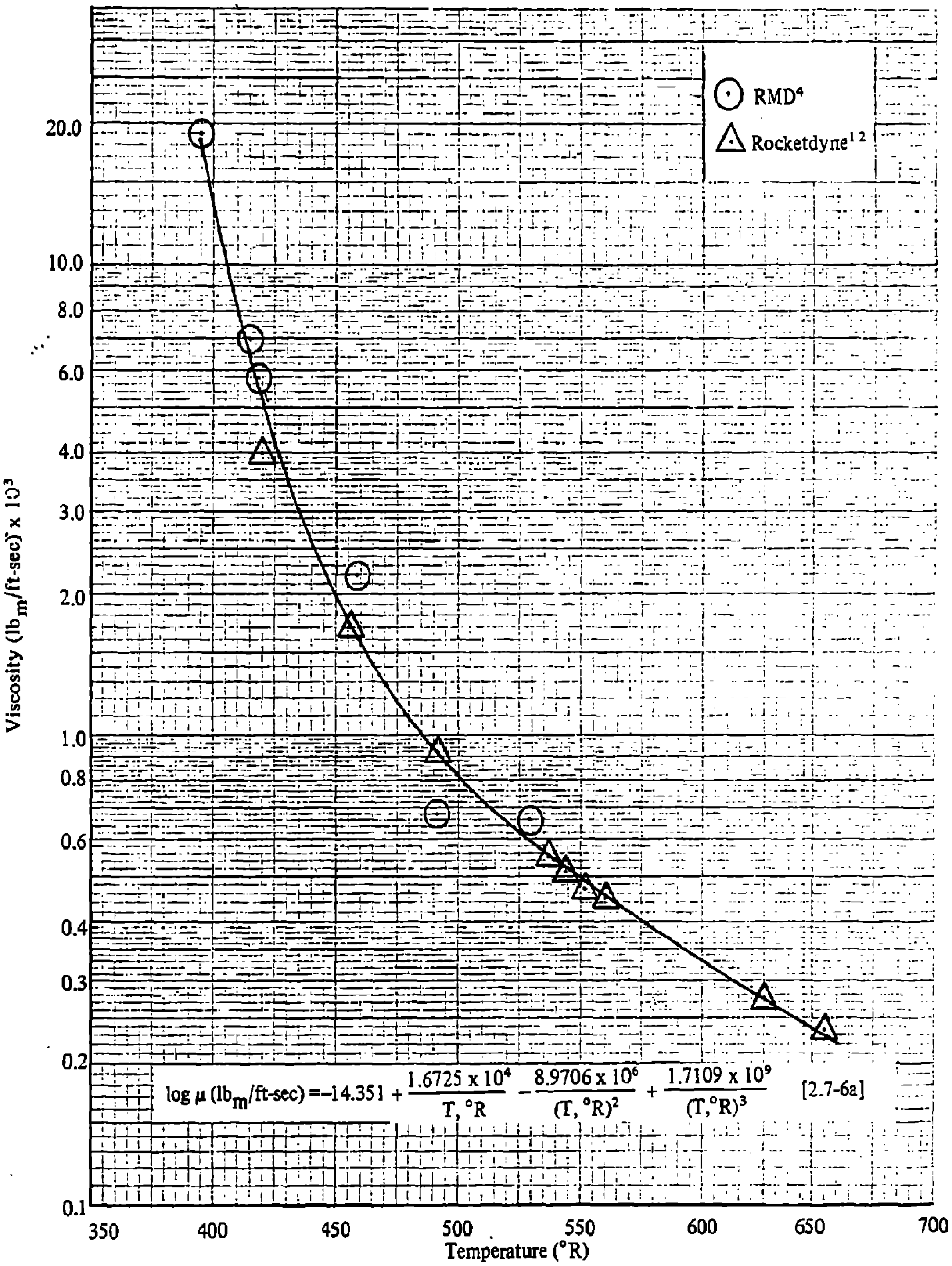
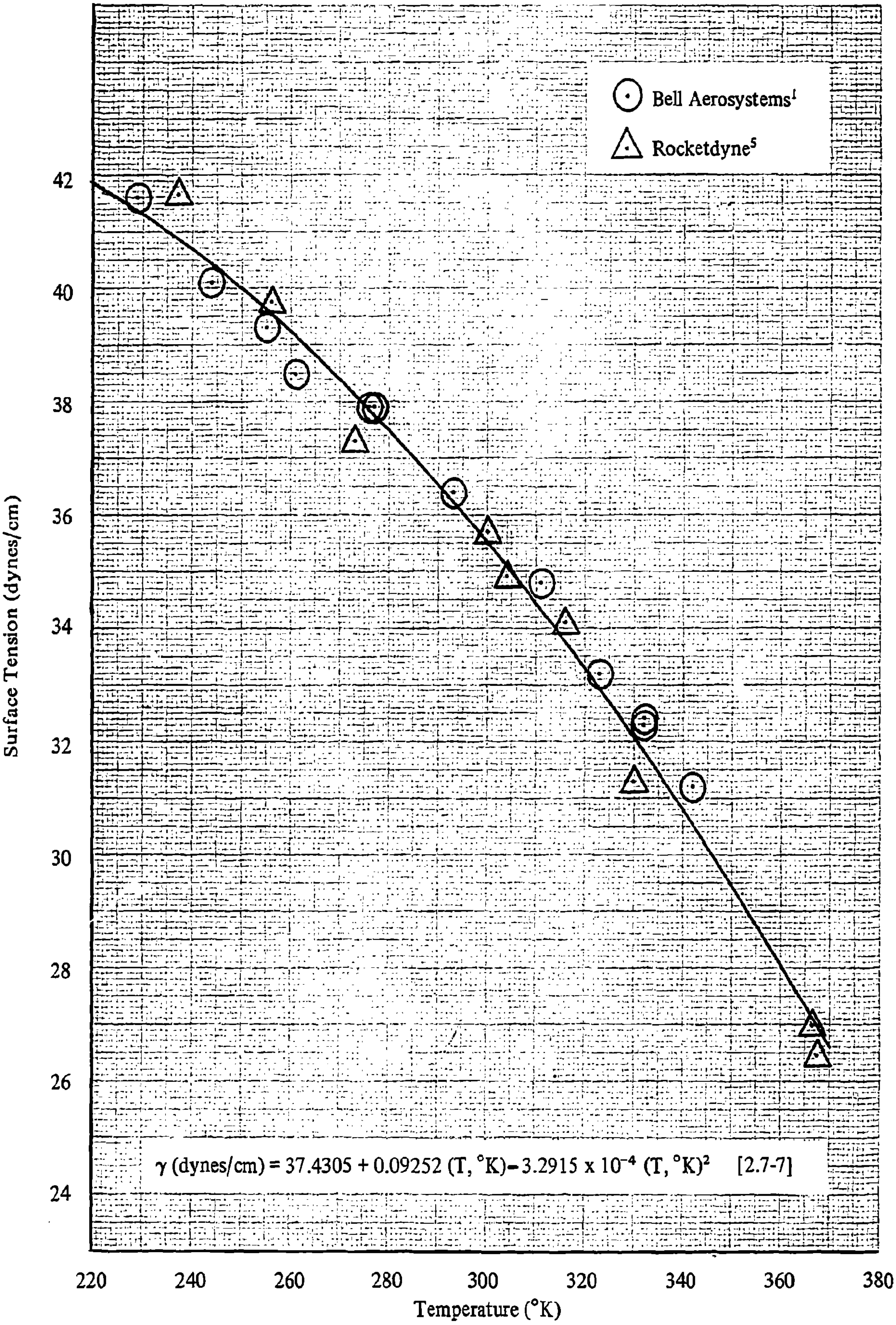


Figure 2.7-5. Absolute Viscosity versus Temperature, Liquid MHF-3



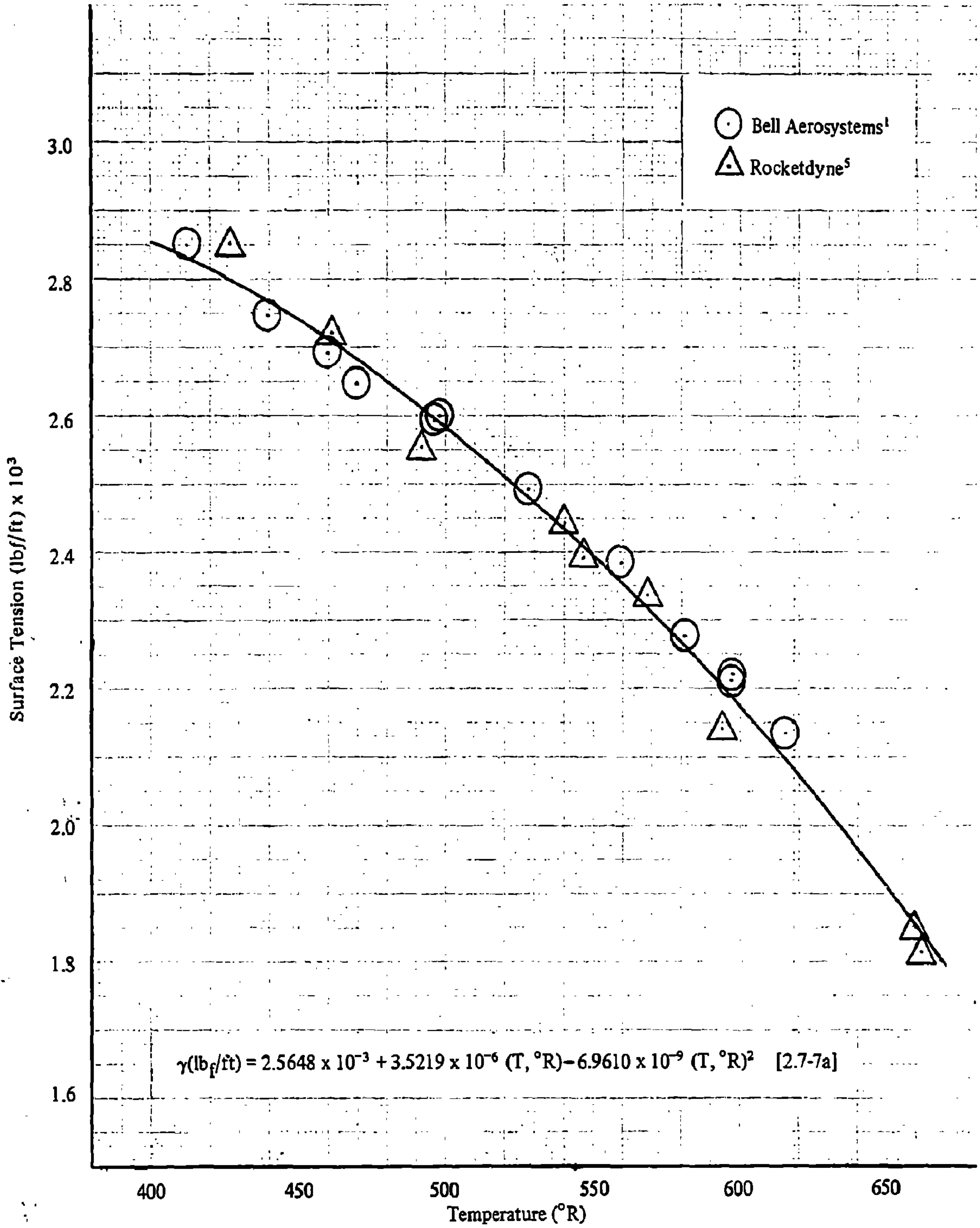
$$\log \mu\,(lb_m/ft\text{-}sec) = -14.351 + \frac{1.6725 \times 10^4}{T, °R} - \frac{8.9706 \times 10^6}{(T, °R)^2} + \frac{1.7109 \times 10^9}{(T, °R)^3} \quad [2.7\text{-}6a]$$

Figure 2.7-5a. Absolute Viscosity versus Temperature, Liquid MHF-3



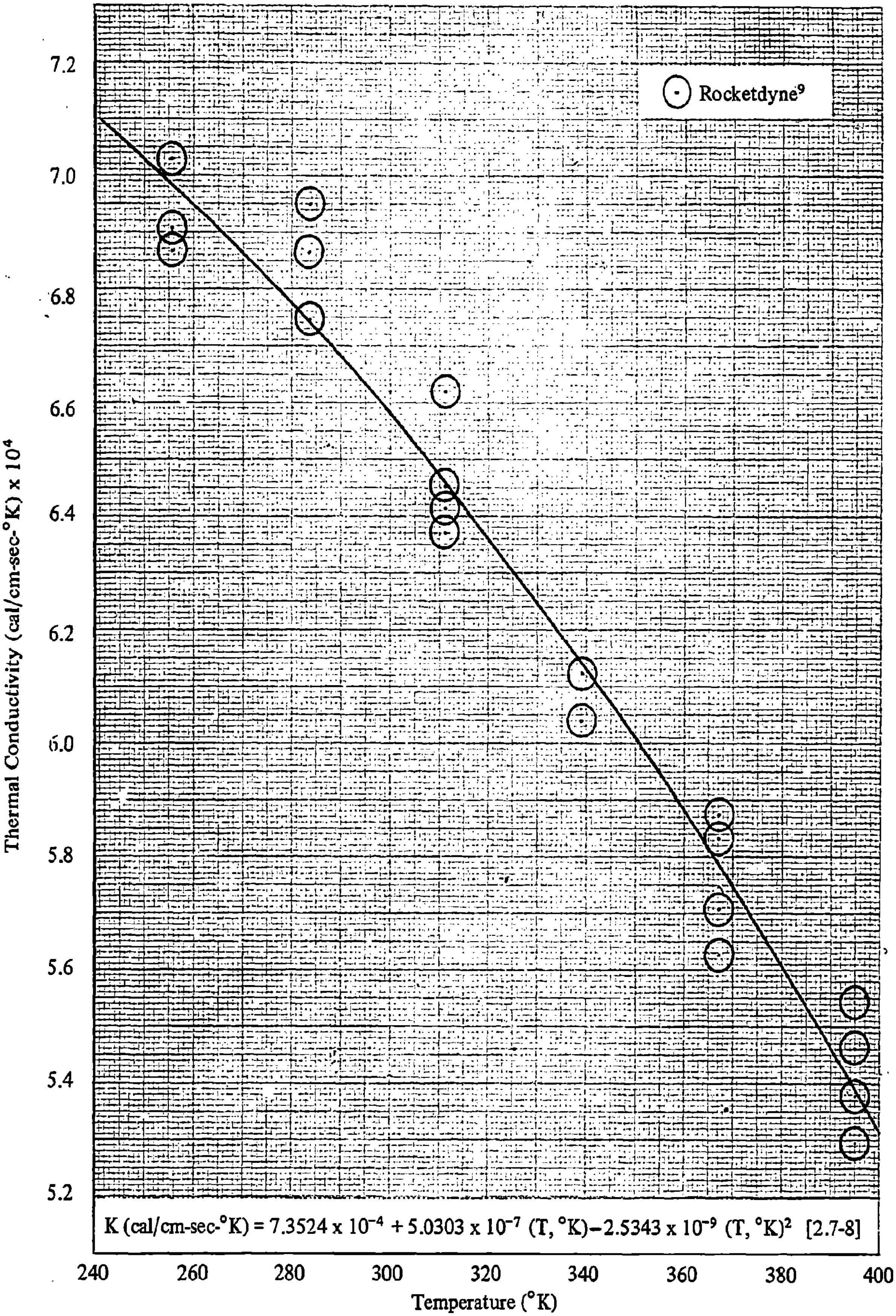
$$\gamma \text{ (dynes/cm)} = 37.4305 + 0.09252 \text{ (T, °K)} - 3.2915 \times 10^{-4} \text{ (T, °K)}^2 \quad [2.7\text{-}7]$$

Figure 2.7-6. Surface Tension versus Temperature Liquid MHF-3



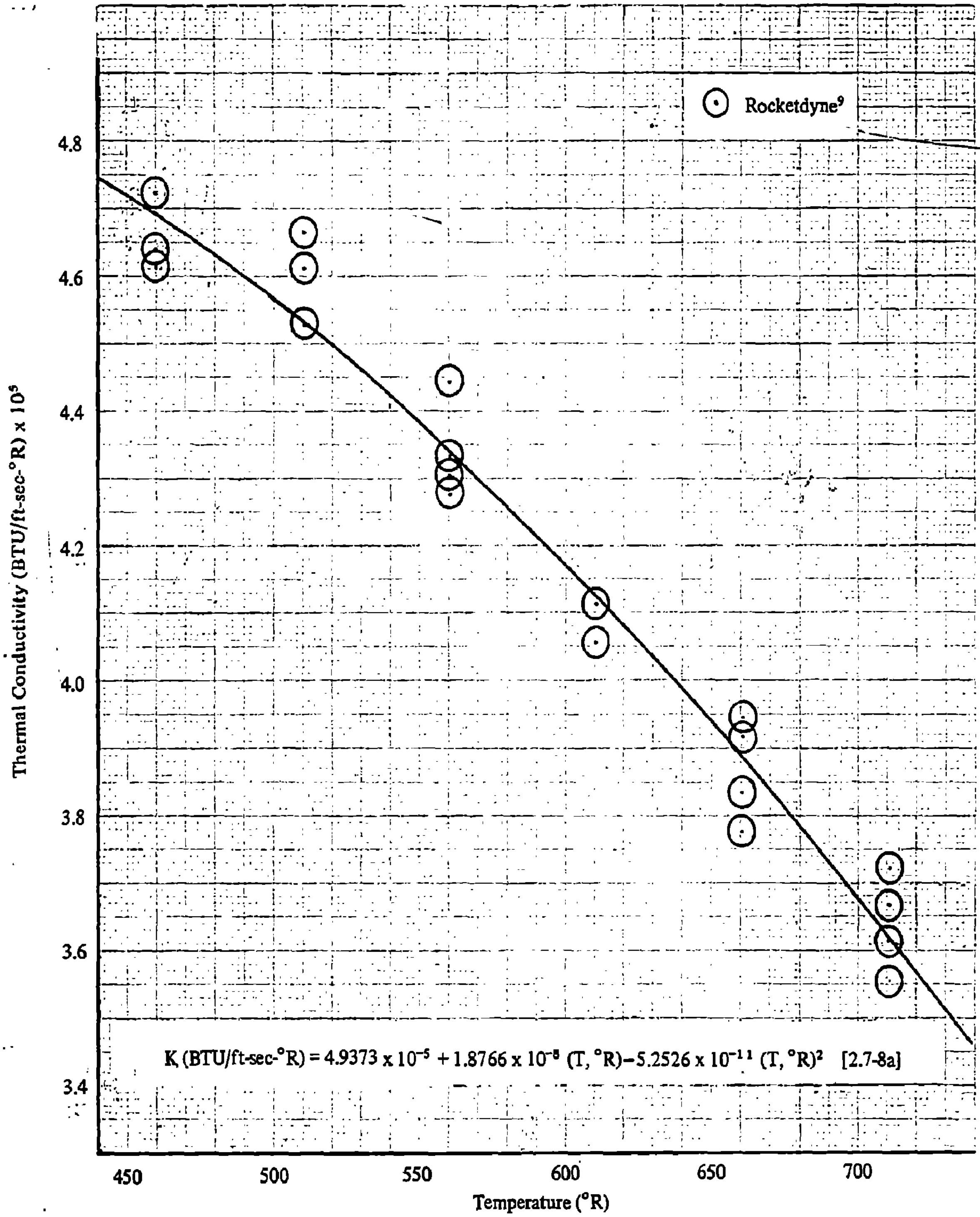
$$\gamma(\mathrm{lb_f/ft}) = 2.5648 \times 10^{-3} + 3.5219 \times 10^{-6}\,(T, {}^\circ R) - 6.9610 \times 10^{-9}\,(T, {}^\circ R)^2 \quad [2.7\text{-}7a]$$

Figure 2.7-6a. Surface Tension versus Temperature Liquid MHF-3



$K\ (\text{cal/cm-sec-}^\circ\text{K}) = 7.3524 \times 10^{-4} + 5.0303 \times 10^{-7}\ (T, {}^\circ\text{K}) - 2.5343 \times 10^{-9}\ (T, {}^\circ\text{K})^2$ [2.7-8]

Figure 2.7-7 Thermal Conductivity versus Temperature, Liquid MHF-3



$$K\,(\mathrm{BTU/ft\text{-}sec\text{-}^\circ R}) = 4.9373 \times 10^{-5} + 1.8766 \times 10^{-8}\,(T, {}^\circ R) - 5.2526 \times 10^{-11}\,(T, {}^\circ R)^2 \quad [2.7\text{-}8a]$$

Figure 2.7-7a. Thermal Conductivity versus Temperature, Liquid MHF-3

(U) Nonequilibrium data were obtained for a one-gallon stainless steel tank which had 5% ullage at 195 F. Details may be obtained from Reference 3.

2.7.5 THERMODYNAMIC PROPERTIES OF MHF-3

2.7.5.1 Heat of Formation of Liquid

(C) The heat of formation of this liquid mixture can be calculated from the molar addition of the individual heats of formation. The heat of mixing is not known and is assumed to be negligible. Assuming a composition of 86% MMH and 14% N_2H_4 with no impurities, the heat of formation at 298.15 K is 12.907 kcal/mole. The mole is defined as 43.4148 grams with the empirical formula of $C_{0.810345}H_{5.62073}N_{2.0}$.

Compound	Weight %	Mole Fraction (1 mole blend)	ΔH_{f298} kcal/mole
$CH_3N_2H_3$	86	0.810345	13.106
N_2H_4	14	0.189665	12.054

for one mole of MHF-3 then:

$$\Delta H_{f298} = 0.810345\ (13.106) + 0.189665\ (12.054)$$

$$\Delta H_{f298} = +12.907 \text{ kcal/mole, mole} = 43.4148 \text{ g}$$

or

$$\Delta H_{f298} = 297.3 \text{ cal/g}$$

The heats of formation used for N_2H_4 and MMH are discussed in Sections 2.3.5.1 and 2.4.5.1, respectively.

2.7.5.2 Melting Point and Heat of Fusion of MHF-3

(C) The accepted melting point of MHF-3 is (-53.8 C) -65 F over the allowable composition range. From the freezing point diagram (15) of binary N_2H_4-MMH mixtures a eutectic is indicated at -60 C (-76 F) at a composition of 88% by weight of MMH. No data were reported on the heat of fusion.

2.7.5.3 Critical State Constants

(C) No experimental or calculated data are available on the critical properties. Since MHF-3 is a mixture of N_2H_4 and MMH, there is also no well-defined critical point.

2.7.5.4 Heat Capacity of Liquid MHF-3

(U) The heat capacity of saturated liquid MHF-3 has been experimentally determined by Rocketdyne (6) over a temperature range from -46 to 47 C (-51 to 117 F). An adiabatic calorimeter was used and the usual precautions taken to minimize heat losses. The experimental data are plotted in Figures 2.7-8 and 2.7-8a. The data appears to have a large scatter but it is plotted on a large scale. A linear type fit was found to give an average deviation of 0.46%. The maximum deviation was 1.4%.

$$C_p(\text{cal/g-}^\circ\text{K}) = 0.6073 + 3.766 \times 10^{-4}(T,^\circ\text{K}) \quad (2.7\text{-}9)$$

$$C_p(\text{BTU/lb-}^\circ\text{R}) = 0.6073 + 2.0923 \times 10^{-4}(T,^\circ\text{R}) \quad (2.7\text{-}9a)$$

The composition (weight %) of the MHF-3 sample was 84.7 MMH, 14.0 N_2H_4, 1.0 H_2O, 0.1 NH_3 and 2.0 other soluble impurities.

2.7.5.5 Latent Heat of Vaporization of MHF-3

The heat of vaporization is estimated to be 8.93 kcal/mole at the normal boiling point from the Clapeyron equation. The calculated Trouton constant is 24.6.

2.7.6 LOGISTICS OF MHF-3

2.7.6.1 Manufacture

(C) Since MHF-3 is a mixture of 86% MMH and 14% N_2H_4 by weight it is manufactured by proper mixing. The manufacturing methods for both constituents can be found in Section 2.3.6.1 for hydrazine, and in section 2.4.6.1 for MMH.

(C) MMH and N_2H_4 are completely miscible in all proportions. In order to insure proper blending complete mixing is necessary to prevent stratification. When properly agitated a homogeneous blend will be obtained.

(U) The individual components should be carefully weighed prior to mixing. The most common methods of mixing are by diffusion, agitation, and stirring. Diffusion (self-mixing) requires a long period of time. For small quantities (drum lots), a mechanical shaker or mechanical stirrer can be used. Care must be taken in all methods to prevent contact of the liquids with air. Inert gas bubbling has been used, but it is not recommended.

(U) Regardless of the mixing method used, the batch should be checked for complete mixing by analysis of samples taken from different heights in the container or tank.

2.7.6.2 Analysis of MHF-3

(C) The MHF-3 fuel blend should be procured under MIL-P-81342 (WP) dated December 1965. The chemical requirements are:

(C) Component	Weight Percent
Hydrazine (N_2H_4)	14.0 ±2.0
MMH ($CH_3N_2H_3$)	86.0 ±2.0
Water plus soluble Impurities	2.0 Maximum

(U) The assay of the fuel blend can be determined by gas chromatography. Rocketdyne (10) has published the following guidelines which can serve as a general procedure:

Chromatograph:	Perkin - Elmer, 154-D
Recorder:	Leeds and Northrup Model G
Column:	12 foot x 1/4 inch O.D. stainless steel, filled with 4 percent Qudrol on Chromosorb-T, 4/60 mesh.
Temperature:	Approximately 111°C at injection port.
Carrier Gas:	Helium, at a flowrate of 55 cc/min.
Sample Size:	1 to 2 microleters, injected with a 0 to 10 microleter syringe.

Known constituents are evaluated in the following order:

Constituent	Retention Time, Minutes
Fixed Gases, N_2, etc.	0.6
Ammonia, NH_3	0.9
Methylamine, CH_3NH_2	1.4
Water	4.7
MMH, $CH_3N_2H_3$	7.8
Hydrazine, N_2H_4	12.2

(C) The gas chromatograph is calibrated with mixtures using titrimetrically assayed MMH and N_2H_4. The water content is determined directly from a calibration curve prepared using water free pyridine as the matrix fluid. Other soluble impurities are determined by difference of 100% and the total assay including water.

(U) MIL-P-81342 (WP) also gives a procedure for chemical analysis quite similar to the Rocketdyne guidelines. The density requirement is 0.892 to 0.896 g/cc at 25 C (77 F). In this handbook the density at 25 C is given a value of 0.8889 (See Section 2.7.3.2).

(U) The freezing point requirement is not higher than -65 F. Particulate matter (undissolved solids retained on a 10-micron filter paper) must not exceed 10 mg/1.

2.7.6.3 Cost and Availability of MHF-3

(C) The unit price and availability of a mixture is, of course, dependent upon the cost and availability of the constituents. The only large scale manufacturer of MMH and hydrazine is the Olin Mathieson Corporation, Chemicals Division, with manufacturing facilities in Lake Charles, Lousiana. The unit price of hydrazine and MMH in ton quantities is $2.95/pound and $3.20/pound, respectively. The unit cost of MHF-3 would then be slightly above the cost of MMH and would include the cost of mixing and analysis. Production of either component on a very large scale would decrease the unit price.

(C) Both N_2H_4 and MMH are available from stock at the Lake Charles facility in nominal tonnage orders. Availability of this fuel blend in million pound orders would require a certain amount of lead time.

2.7.6.4 Shipping and Transportation of MHF-3

(U) The following information on shipping and transportation was abstracted from Rocketdyne (10). Shipment of MHF-3 by common carrier is authorized by the Interstate Commerce Commission (ICC) and it is classified as "Hydrazine Solution, Corrosive Liquid", and requires a white label. The following containers have been approved by the ICC according to the specifications listed:

(1) Boxed glass carboys (ICC-ID)
(2) Glass bottles not exceeding one-gallon capacity, cushioned with vermiculite, covered with tightly sealed tin cans and packaged in wooden boxes (ICC-15A, 15B or 15C).
(3) Metal barrels or drums constructed of 304 or 347 stainless steel with openings not to exceed 2.3 inches in diameter. (ICC-5, 5A, 5C, and for single trip, ICC-17E.)
(4) Tank cars (ICC-103C-W or 111A100-W-6) and tank motor vehicles (ICC-MC310, MC311 or MC312). Tanks must be constructed of 304L or 347 stainless steel with a maximum molybdenum content of 0.5%. Vapor space must be filled with nitrogen gas at atmospheric pressure.

(U) Tank truck shipments are only authorized by ICC special permit. A maximum of five pints of MHF-3 may be shipped by air in cargo aircraft only and packaged according to ICC-15A or 15B specification. (See "Official Air Transportation Restricted Articles", Tariff No. 6-D-Note No. 135, August 1966.)

(U) The shipment of MHF-3 on waterways is allowable on decks of cargo vessels only (U.S. Coast Guard Regulations, NAV-CG-108). ICC Specification ID covers cargos not to exceed 6.5 gallons. Stainless steel drums under 55 gallon

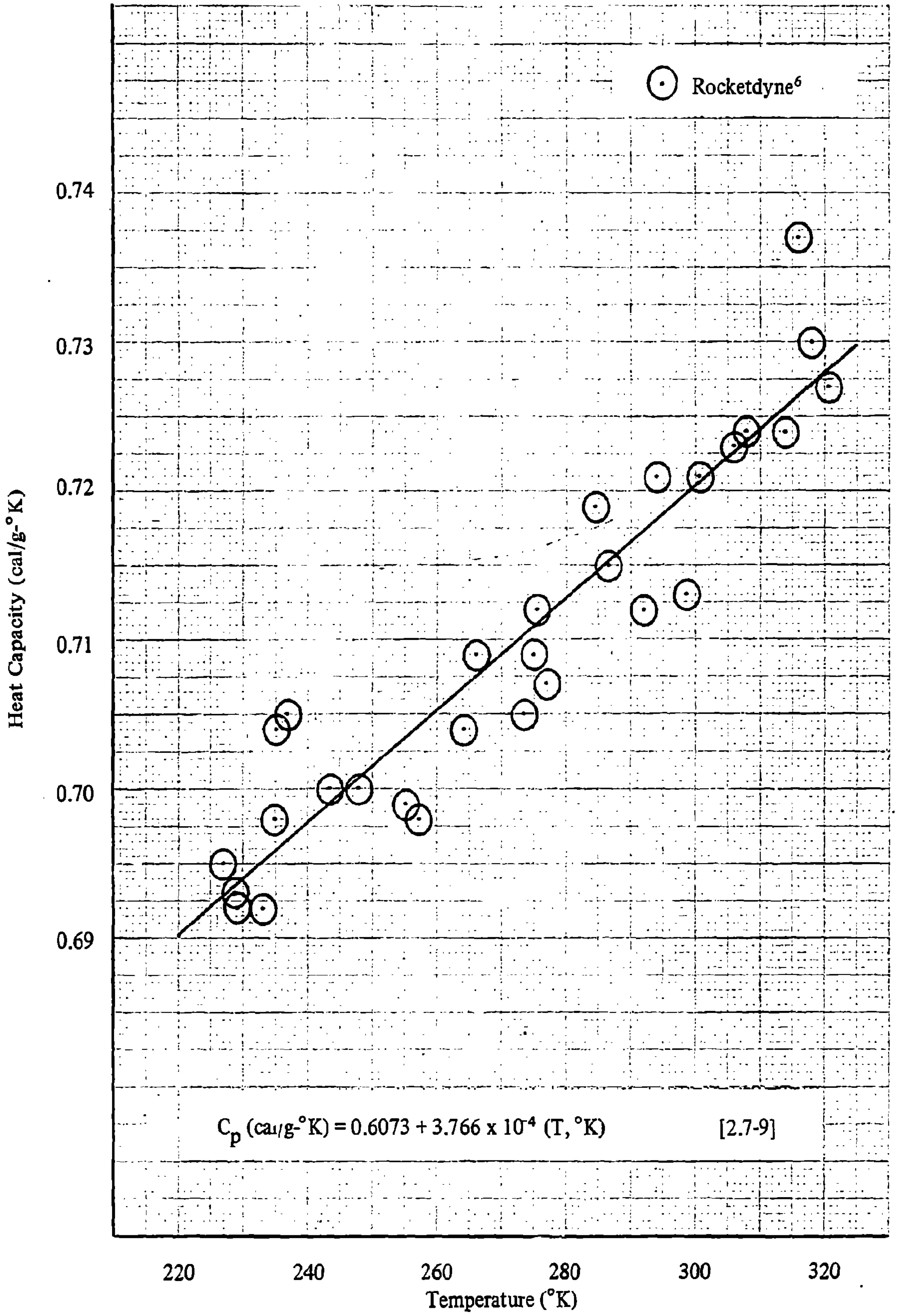
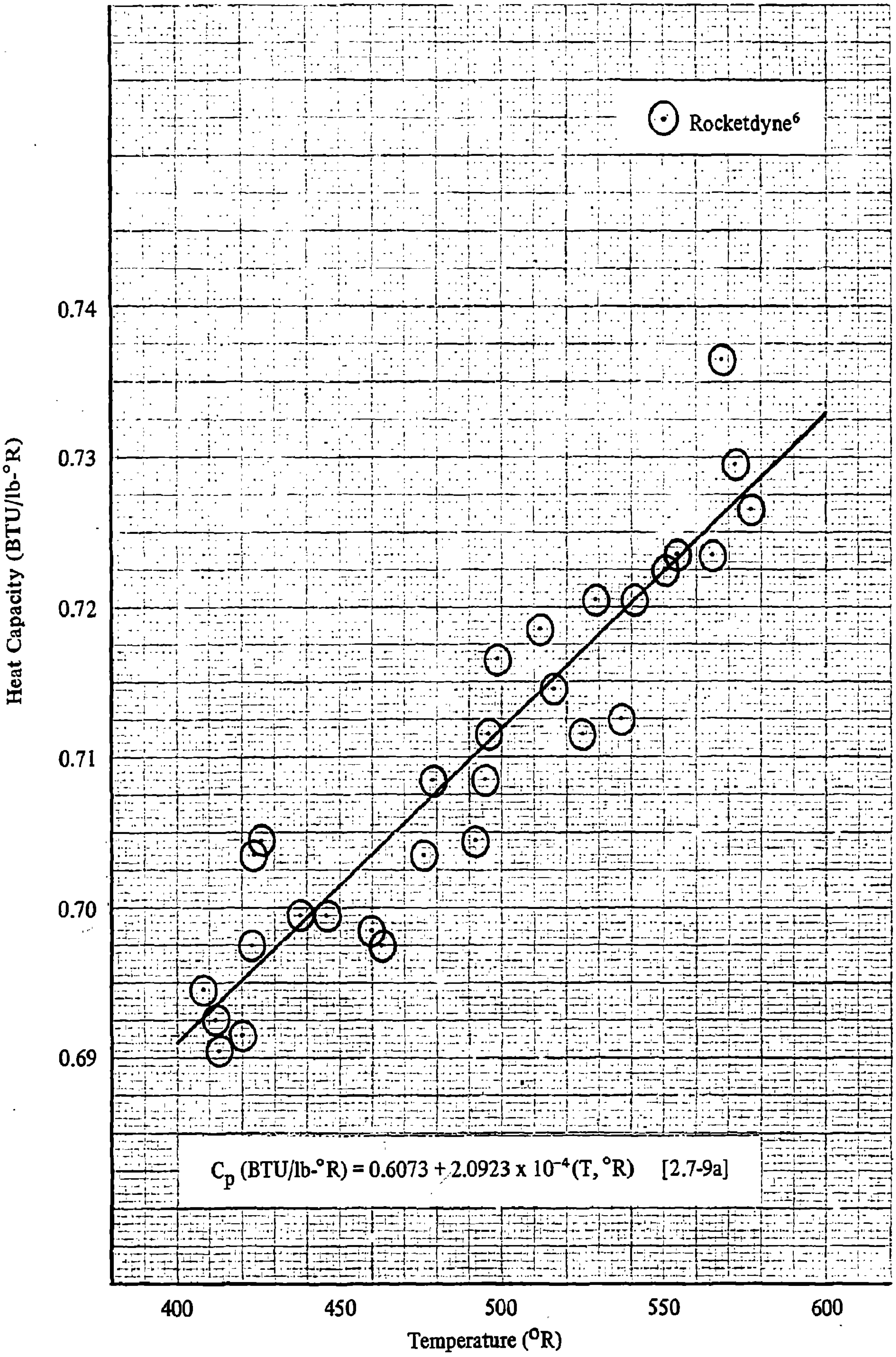


Figure 2.7-8. Heat Capacity versus Temperature Liquid MHF-3



C_p (BTU/lb-°R) = 0.6073 + 2.0923 x 10^{-4}(T, °R) [2.7-9a]

Figure 2.7-8a. Heat Capacity versus Temperature Liquid MHF-3 capacity are covered under ICC-5, 5A, 5C, 5G or 17E. Wooden boxes not over 200 pounds gross weight are covered by ICC Specifications 15A, 15B and 15C.

2.7.7 REFERENCES

1. Bell Aerosystems Co., Physical Chemistry Section, unpublished data.
2. Reaction Motors Div. of Thiokol Chemical Corp. "Advanced Propellants Investigation for Prepackaged Liquid Engines." Report No. RMD [illegible]46-F, Denville, New Jersey, June 1965 (CONFIDENTIAL).
3. Ibid, "Advanced Propellants for Prepackaged Liquid Engines," Report No. RMD 5073-F, Denville, New Jersey, June 1967 (CONFIDENTIAL).
4. Ibid, "High Performance Packageable Liquid Propellants," Report No. RMD 2004-F, Denville, New Jersey, December 1960. (CONFIDENTIAL).
5. Rocketdyne, Division of North American Rockwell Corp., "Engineering Property Data on Rocket Propellants," Final Report No. AFRPL-TR-68-100 (Rocketdyne R-7437), Canoga Park, California, May 1968 (CONFIDENTIAL).
6. Ibid, "Engineering Property Data on Rocket Propellants," Fifth Quarterly Report, AFRPL-TR-67-274 (Rocketdyne R-6638-5), Canoga Park, California, October 1967 (CONFIDENTIAL).
7. Ibid, unpublished data, USAF Contract FO4611-68-C-0087.
8. Rocketdyne, Canoga Park, California, Personal Communication with Mr. Weber, March, 1969.
9. Rocketdyne, Division of North American Aviation, "Engineering Property Data on Rocket Propellants." Third Quarterly Report, AFRPL-TR-67-26 (Rocketdyne R-6638-3), Canoga Park, California, January 1967 (CONFIDENTIAL).
10. Rocketdyne, Division of North American Rockwell Corp., "Condor Propellant Handbook," Vol. II-MHF-3, Report No. R-7556, Contract NOw 66-0728-i (CONFIDENTIAL) (to be published).
11. Sugden, S., J. Chem. Soc. (London) 119 1483 (1921).
12. Rocketdyne, Division of North American Rockwell Corp., "Condor Propulsion System, Quarterly Technical Progress Report for Period Ending 31 July 1968," Report No. R-7275-4, Contract NOw 66-0728-i (CONFIDENTIAL).
13. Ahlert, R.C. and Shimalla, C.J., J. Chem. and Eng. Data 13 108 (1968).
14. Aerojet General Corp., Personal Communication with Mr. S.D. Rosenberg, December 20, 1968.
15. Metallectro Corp., Bladensburg, Md. "Improved Liquid Propellants," Report No. M-52-1-ONR, March (1953) (CONFIDENTIAL).

2.8 MAF-3

2.8.1 PROPERTY SUMMARY SHEET

Chemical Name:	Mixed Amine Fuel No. 3	Common Name:	MAF-3
Empirical Formula:	$C_{3.3994}H_{11.4986}N_{2.6997}$	Formula Weight:	90.239
Composition; % b.w.:	20 UDMH, 80 DETA		

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	*	°K °C °R °F			
DENSITY OF LIQUID	0.9167	g/cc	298	1	2.8-1
	57.227	lb/ft^3			
VISCOSITY OF LIQUID	3.387	centipoise	298	1	2.8-2
	2.276×10^{-3}	lb_m/ft-sec			
HEAT CAPACITY OF LIQUID	0.688	cal/g-°K	298	1	2.8-3
	0.688	BTU/lb-°R			
HEAT OF FORMATION	−9.240	cal/mole	298		
	−184.3	BTU/lb			
INDEX OF AFFRACTION	1.4722 - 1.4729		260	3	

*No data available, Viscosity limits practical application.

2.8.2 GENERAL

2.8.2.1 Introduction

Mixed Amine Fuel No. 3 or MAF-3 was developed by Thiokol Chemical Corp. (RMD) as a high-density packageable fuel. Experimental data on MAF-3 were obtained by RMD, circa 1958. The only properties for which sufficient data are available for curve fitting are density and viscosity. Additional data (estimated) are included on the property summary sheet.

MAF-3 is no longer known to be used operationally in any application, although it was once the fuel in the Sparrow III, a prepackaged missile.

Due to the uncertainty in the (unreported) purity of the components used in the MAF-3 samples, the data presented herein should be considered as provisional.

2.8.2.2 Specification

Procurement and sampling of MAF-3 is controlled under MIL-P-23686A, dated 15 April 1964, and Amendment 1, dated 15 March 1965(2). The composition of MAF-3, as determined by the specification is:

UDMH (MIL-L-25604)	20.0± 1.0% by weight
DETA (FED-O-D-1271)	80.0± 1.0% by weight
Water (H_2O)	1.0 maximum % by weight

2.8.3 PHYSICAL PROPERTIES OF MAF-3

2.8.3.1 Vapor Pressure and Normal Boiling Point

No data were reported on vapor pressure. A provisional estimate can be made by adding the partial pressures of DETA (80%) and UDMH (20%). Data on the vapor pressure of DETA and UDMH are found in Sections 2.2.3.1 and 2.5.3.1, respectively. At 25 C (77 F) the calculated vapor pressure is approximately 39. mm. Hg. (0.754 psia).

2.8.3.2 Density of MAF-3

The density of liquid MAF-3 as a function of temperature was determined by RMD (1). Although the experimental scatter was low, the exact composition and purity were not reported. Therefore, the data are considered provisional. Figures 2.8-1 and 2.8-1a show the plotted results. The equations for density versus temperature are:

$$\rho\ (\text{g/cc}) = 1.1709 - 8.5269 \times 10^{-4}\ (\text{T, °K}) \qquad (2.8\text{-}1)$$

$$\rho\ (\text{lb/ft}^3) = 73.0982 - 0.02957\ (\text{T, °R}) \qquad (2.8\text{-}1\text{a})$$

The calculated density at 298.15 K (77 F) is 0.9167 g/cc, compared with the specification range of 0.909 to 0.920 g/ml. In the absence of any additional information, no corrections were made to the original data.

2.8.3.3 Viscosity of MAF-3

The viscosity of liquid MAF-3 as a function of temperature was reported in unpublished data by RMD (1). The purity of the MAF-3 sample was not reported; therefore, the data are considered provisional. Figures 2.8-2 and 2.8-2a illustrate the plotted data. The equations, derived from a least-square fit, for absolute viscosity versus temperature are:

$$\log \mu(\text{centipoise}) = -3.3444 + \frac{2828.6}{\text{T, °K}} - \frac{1.0403\text{x}10^6}{(\text{T, °K})^2} + \frac{1.6141\text{x}10^8}{(\text{T, °K})^3} \qquad (2.8\text{-}2)$$

$$\log \mu(\text{lbm/ft-sec}) = -6.5171 + \frac{5091.5}{\text{T, °R}} - \frac{3.3706\text{x}10^6}{(\text{T, °R})^2} + \frac{9.4133\text{x}10^8}{(\text{T, °R})^3} \qquad (2.8\text{-}2\text{a})$$

At -65 F, the viscosity is approximately 1690 centipoise.

2.8.3.4 Refractive Index of MAF-3

A single point determination was reported by the U.S. Bureau of Mines (3). The value was expressed as a range from 1.4722 to 1.4729 at 13 C.

2.8.4 CHEMICAL PROPERTIES OF MAF-3

2.8.4.1 Chemical Reactions

No data have been reported on chemical reactions; however, MAF-3 is expected to undergo the reactions common to UDMH and DETA. In general, MAF-3 is a hygroscopic, flammable liquid, and is soluble in all proportions with UDMH, DETA, acetonitrile (CH_3CN), water, and hydrazine. MAF-3 is basic in nature.

2.8.5. THERMODYNAMIC PROPERTIES OF MAF-3

2.8.5.1 Heat of Formation

The heat of formation of this liquid mixture can be calculated from the molar addition of the individual heats of formation. The heat of mixing is not known and is

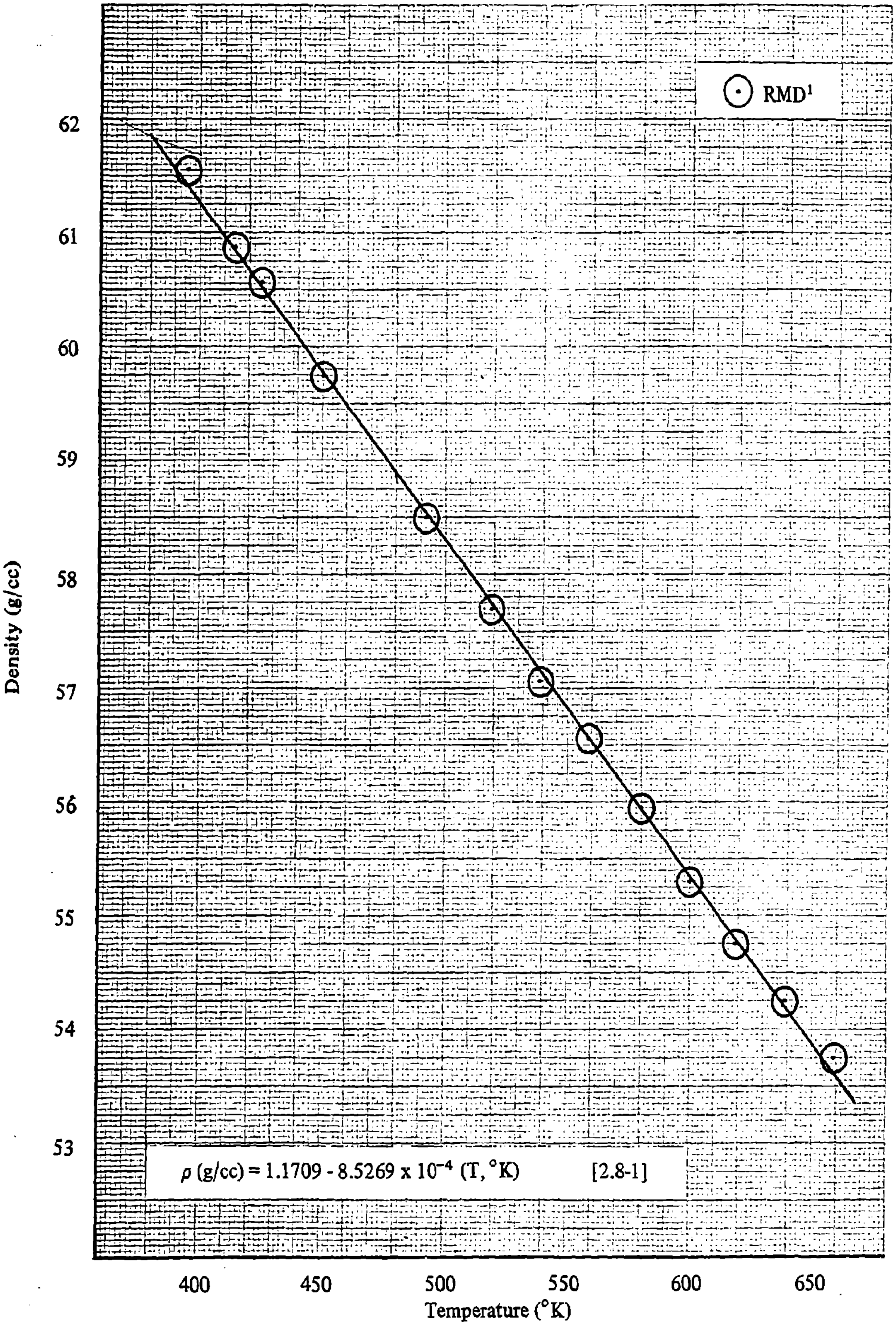


Figure 2.8-1. Density versus Temperature, Liquid MAF-3

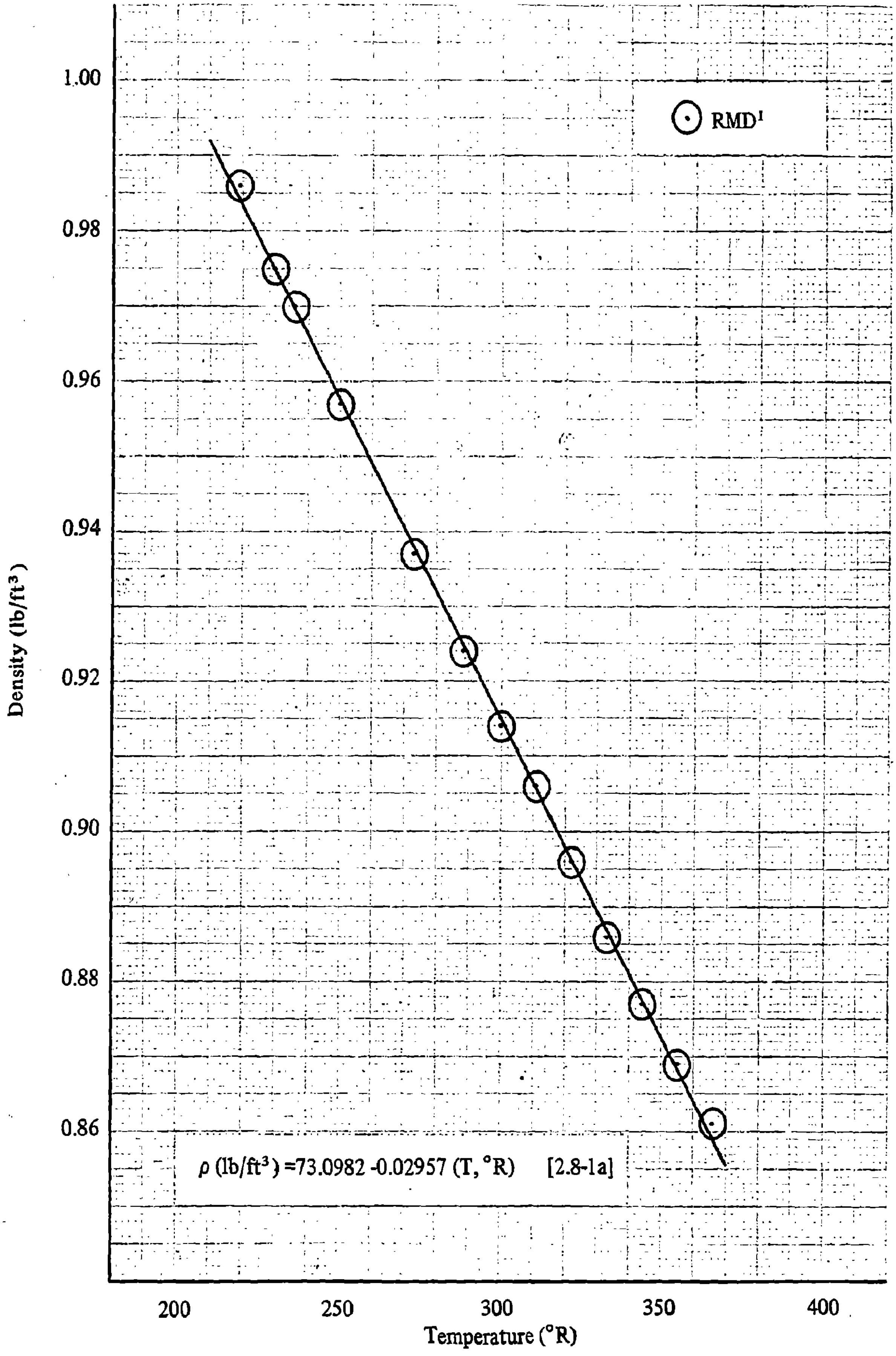
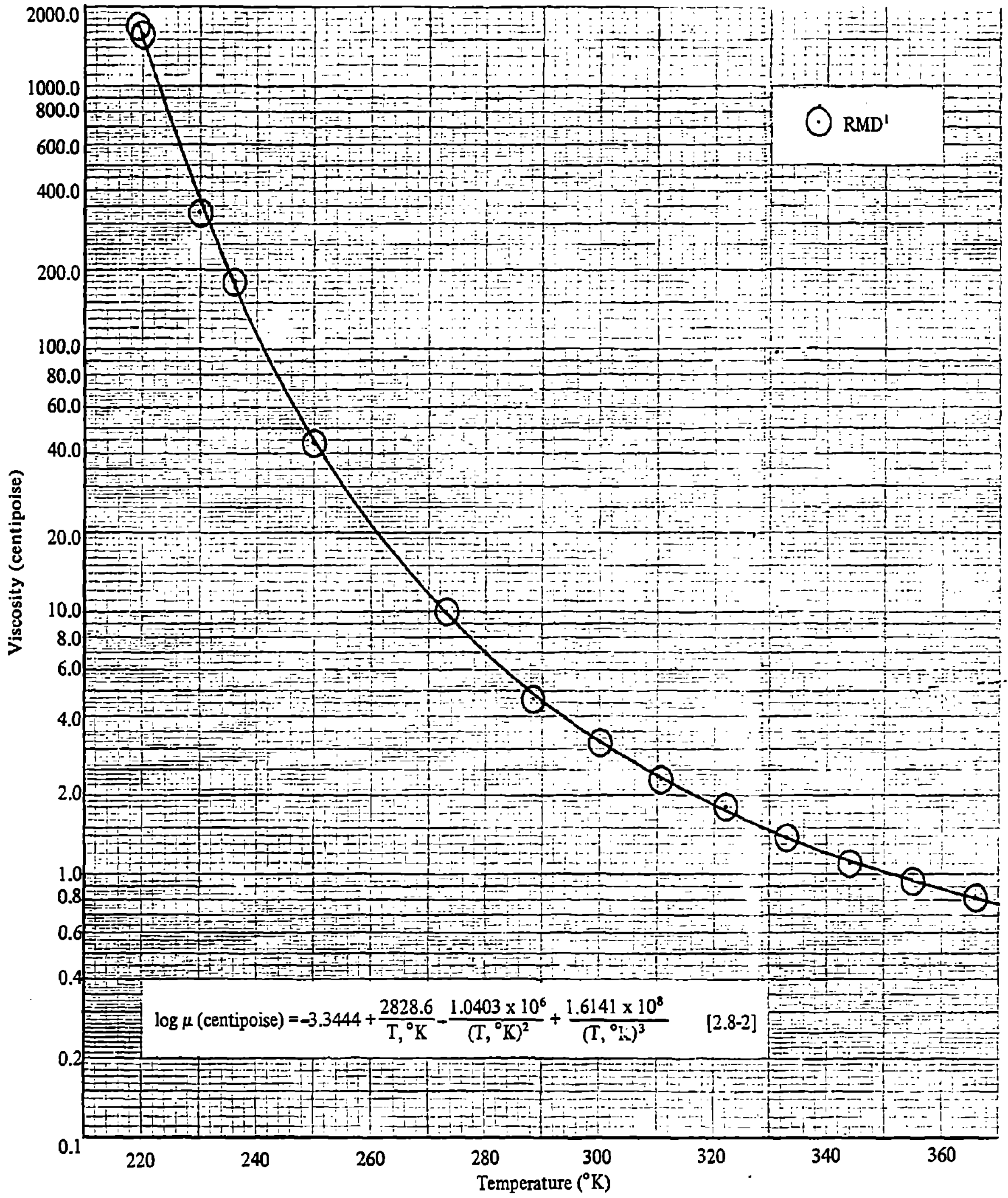
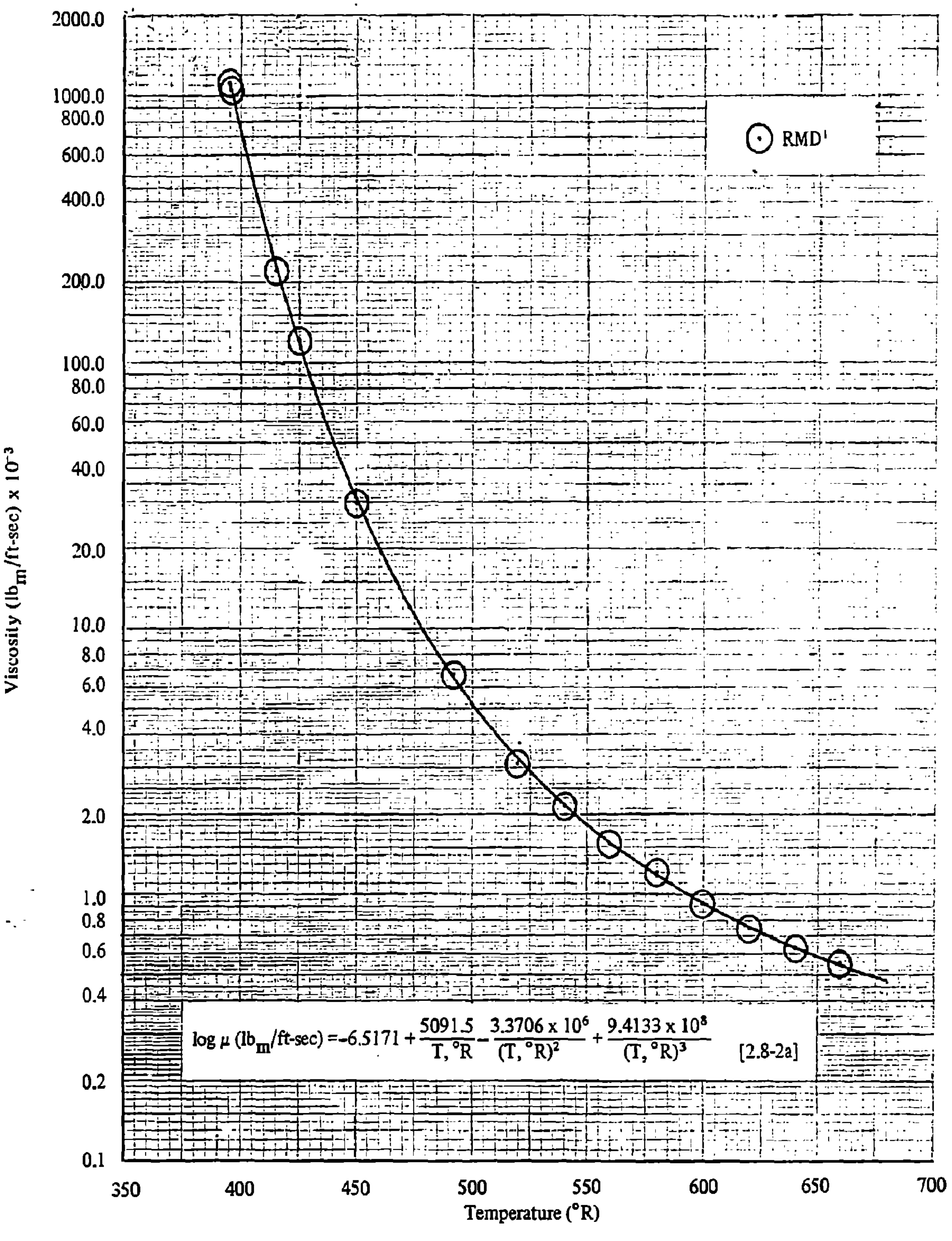


Figure 2.8-1a. Density versus Temperature, Liquid MAF-3



$$\log \mu \text{ (centipoise)} = -3.3444 + \frac{2828.6}{T, ^\circ K} - \frac{1.0403 \times 10^6}{(T, ^\circ K)^2} + \frac{1.6141 \times 10^8}{(T, ^\circ K)^3} \qquad [2.8\text{-}2]$$

Figure 2.8-2. Absolute Viscosity versus Temperature Liquid MAF-3



$$\log \mu\ (lb_m/ft\text{-}sec) = -6.5171 + \frac{5091.5}{T,\ ^\circ R} - \frac{3.3706 \times 10^6}{(T,\ ^\circ R)^2} + \frac{9.4133 \times 10^8}{(T,\ ^\circ R)^3} \qquad [2.8\text{-}2a]$$

Figure 2.8-2a. Absolute Viscosity versus Temperature, Liquid MAF-3

assumed to be negligible for this calculation. Taking an exact composition (weight %) of 80 diethylenetriamine (DETA) and 20 UDMH, the heat of formation for the liquid at 298.15 K is -9.240 kcal/mole. The mole is defined as 90.2387 grams with the emperical formula

$C_{3.3994}H_{11.4986}N_{2.6997}$

Compound	Weight %	Mole Fraction (1 mole blend)	ΔH_{f298} kcal/mole
$C_4H_3N_3$	80	0.6997147	-18.5
$C_2H_8N_2$	20	0.3002852	+12.339

For one mole of MAF-3 then:

$$\Delta H_{f298} = 0.6997147\ (-18.5) + 0.3002852\ (12.339)$$

$$\Delta H_{f298} = -9.240 \text{ kcal/mole, mole} = 90.2387 \text{ grams or}$$

$$\Delta H_{f298} = 102.39 \text{ cal/gram}$$

The heats of formation used for DETA and UDMH are discussed in Sections 2.2.5.1 and 2.5.5.1, respectively.

2.8.5.2 Specific Heat Capacity

The specific heat capacity was reported twice by RMD (1, 4). Reference 1 contained estimated data and Reference 4 contained experimental data. The two sources are in reasonable agreement. Figure 2.8-3 shows the data which were considered too sparse for a least-squares fit.

2.8.6 LOGISTICS OF MAF-3

2.8.6.1 Manufacture

MAF-3 is no longer available as an off-the-shelf item. Blending of MAF-3 can be accomplished by simple mixing of UDMH and DETA in a suitable container under a dry atmosphere or nitrogen padding.

2.8.6.2 Analysis

Procurement and analysis of MAF-3 is controlled under MIL-P-23686A, and Amendment 1 (2).

2.8.6.3 Cost and Availability

The cost of MAF-3 can be determined from the cost of the ingredients, plus blending costs. The ingredients, UDMH and DETA, are discussed under sections 2.5.6.3 and 2.2.6.3 of this handbook.

2.8.6.4 Shipping and Transportation

The shipping and transportation of MAF-3 should be dominated by the DETA content. Regulations for DETA and UDMH are described in Sections 2.2.6.4 and 2.5.6.4, respectively.

2.8.7 REFERENCES

1. Thiokol Chemical Corp., RMD; Unpublished data, dated October 1958 supplied to Bell Aerosystems Company by Dr. A. Beardell, 2/27/69.

2. Military Specification MIL-P-23686A, 15 April 1964, and Amendment 1 thereto, 15 March 1965.

3. U.S. Dept. of Interior, bureau of Mines, "Research on the Fire and Explosion Hazards Associated with New Liquid Propellants," Annual Report, April 24, 1959 to April 30, 1960.

4. Thiokol Chemical Corp. RMD, Direct Communication with Dr. A. Beardell, December, 1968.

2.9.1 PROPERTY SUMMARY SHEET

Chemical Name:	Mixed Amine Fuel No. 4	Common Name:	MAF-4, (HYDYNE), (U-DETA)
Empirical Formula:	$C_{2.5595}H_{9.3986}N_{2.2797}$	Formula Weight:	72.1498
Composition; % b.w.:	60 UDMH, 40 DETA		

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	188.76	°K		4	
	-84.4	°C			
	339.67	°R			
	-120.	°F			
HEAT OF FUSION	Not Available	kcal/mole			
		BTU/lb			
NORMAL BOILING POINT	342.7	°K		1, 2	
	69.6	°C			
	617.0	°R			
	157.33	°F			
CRITICAL STATE CONSTANTS					
Temperature	558.15	°K		2	
	285.	°C			
	1004.67	°R			
	545.	°F			
Pressure	53.3	atms		2	
	784.	psia			
Density	Not Available	g/cc			
		lb/ft^3			
DENSITY OF LIQUID	0.8459	g/cc	298	1, 3, 5	2.9-2
	52.807	lb/ft^3			
VAPOR PRESSURE OF LIQUID	118	mm Hg	298		2.9-1
	2.29	psia			
VISCOSITY OF LIQUID	1.40	centipoise		1, 2, 3	2.9-3
	0.941×10^{-3}	lb_m/ft-sec			
HEAT CAPACITY OF LIQUID	0.65	cal/g-°K			
HEAT OF FORMATION	54.455	cal/gram	298		
	98.02	BTU/lb			
INDEX OF REFRACTION	1.438		298	9	

2.9.2 GENERAL

2.9.2.1 Introduction

Mixed Amine Fuel No. 4, alternately known as "U-DETA" and "Hydyne", was used in the North American/Rocketdyne LR-64-NA-4 target drone engine and in the Army Jupiter-C launch vehicle.

No military or other government specification has been generated for MAF-4, although its ingredients are covered by specifications. The nominal composition (weight %) of MAF-4 is 60% 1, -1, dimethylhydrazine (UDMH) (MIL-P-25604C) and 40% diethylenetriamine (DETA) (Fed. Spec. O-D-1271).

MAF-4 is a clear hygroscopic liquid at room temperature having a characteristic fishy odor. Its properties are similar to those of its components and the other mixed amine fuels.

MAF-4 is miscible in all proportions with water, UDMH, acetonitrile, DETA, hydrazine, ethanol and MMH. It is only partially miscible with gasoline, JP-4 or RP-1. The available physical property data are sparse and inconsistent, and the values reported here should be considered as provisional. The purity of the MAF-4 samples used was not reported.

2.9.3 PHYSICAL PROPERTIES OF MAF-4

2.9.3.1 Vapor Pressure and Normal Boiling Point.

The vapor pressure of MAF-4 was measured and reported by FMC (1), and Rocketdyne (2). Purity and compositional data were lacking, however, and relatively few data points with considerable scatter were obtained. Based on the available data, the vapor pressure can be described by

$$\log_{10} P\,(\text{mm Hg}) = 8.2762 - \frac{1849.4}{T,\,^{\circ}K} \qquad (2.9\text{-}1)$$

$$\log_{10} P\,(\text{psia}) = 6.5626 - \frac{3329.0}{T,\,^{\circ}R} \qquad (2.9\text{-}1a)$$

Plots of the data appear in Figures 2.9-1 and 2.9-1a. The above equations should be considered provisional in light of the scatter and a lack of information on purity and composition. The normal boiling point was reported by FMC Corp (9) and Rocketdyne (2) as 64.4 C (147.9 F) and 71.7 C (161.1 F), respectively. The least-squares curve fit of vapor pressure yielded a value of 69.57 C (157.23 F) which is within the range quoted by the two sources, and which is accepted for this work.

2.9.3.2 Density of Liquid MAF-4

The density of MAF-4 was measured by FMC Corp. and RMD (3). Additional data from Grant (5) (original source unknown) were included. The three sets of data are somewhat inconsistent, indicating measurement errors or compositional variations. The actual composition and purity of the samples used was not reported. It is known that in the late 1950's when these measurements were made, commercial DETA contained up to 9% impurities.

Since little is known about the conditions or methods used in the measurements, no attempt has been made to correct any of the data. All of the available data, with the exception of one point obviously in disagreement with the rest, were used in deriving the following density equations:

$$\rho\,(\text{g/cc}) = 1.1697 - 0.001086\,(T,\,^{\circ}K) \qquad (2.9\text{-}2)$$

$$\rho\,(\text{lb}_m/\text{ft}^3) = 73.020 - 0.03766\,(T,\,^{\circ}R) \qquad (2.9\text{-}2a)$$

The data points and curves are presented in Figures 2.9-2 and 2.9-2a. When using these data, the relatively poor consistency should be kept in mind.

2.9.3.5 Viscosity of Liquid MAF-4

The viscosity of MAF-4 was measured by FMC (1), Rocketdyne (2), and RMD (3). The data from FMC was accompanied by actual readings from a Bendix "Ultra-Viscoson" apparatus, enabling the viscosity to be recomputed from the density data. The measurement methods used by RMD and Rocketdyne were not reported. Furthermore, the RMD data were obtained in the form of a plot from which the values were taken.

There is reasonable agreement between the data of FMC and of Rocketdyne. RMD's data are, however, consistently lower. The lack of information about purity and exact composition further reduces the validity of all of the data, since the diethylenetriamine may have contained up to 9% impurities.

The available data have been fitted and plotted, and are shown in Figures 2.9-3 and 2.9-3a. The data of FMC and Rocketdyne have been doubly weighted in the curve fit due to their agreement, and the fact that the RMD data were taken from a plot. The viscosity of MAF-4 as a function of temperature can be tentatively described by the following equations

$$\log \mu\,(\text{centipoise}) = -13.063 + \frac{1.1095 \times 10^4}{(T,\,^{\circ}K)} - \frac{3.2894 \times 10^6}{(T,\,^{\circ}K)^2} + \frac{3.4457 \times 10^8}{(T,\,^{\circ}K)^3} \qquad (2.9\text{-}3)$$

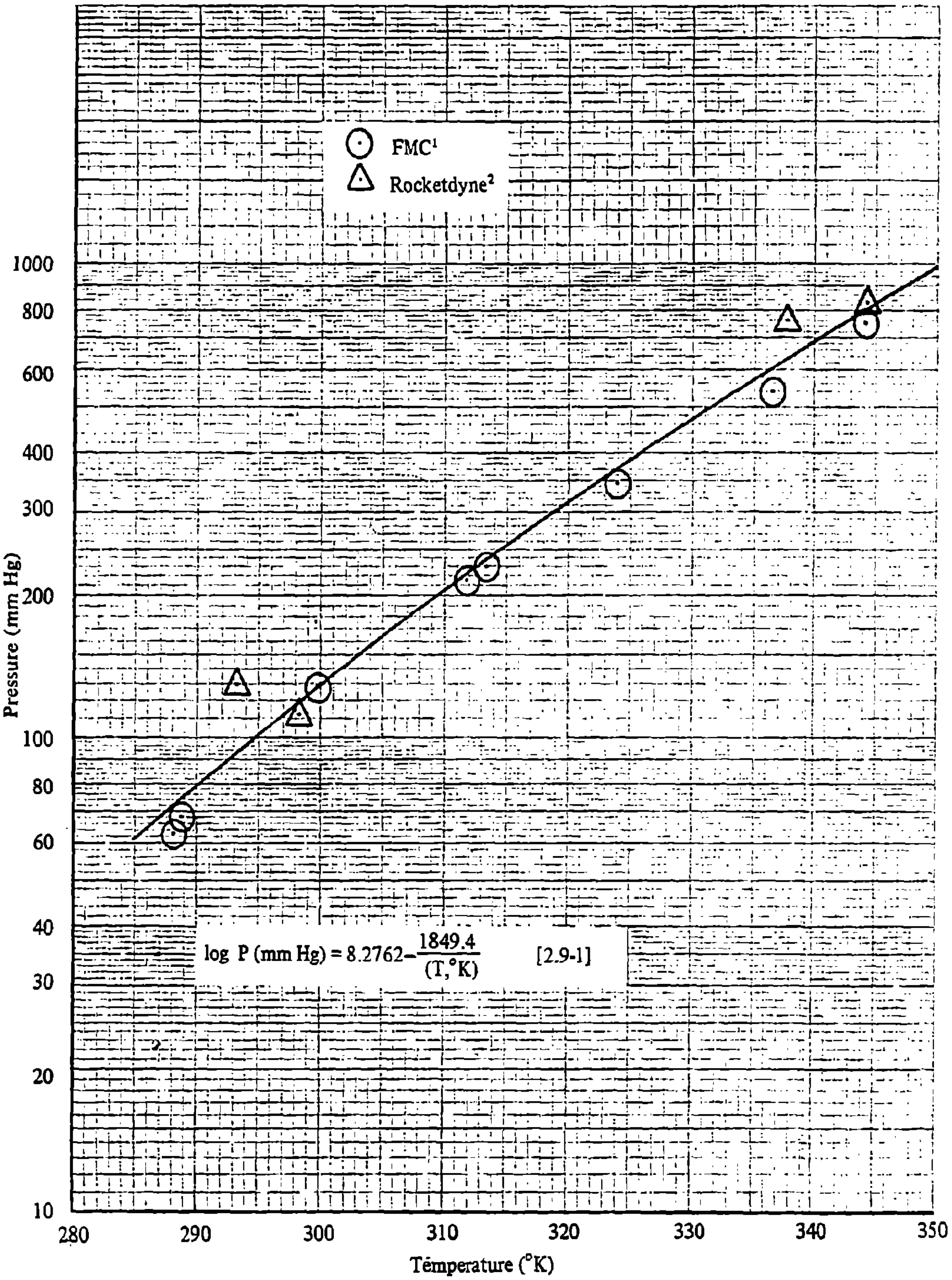


Figure 2.9-1. Vapor Pressure versus Temperature, Saturated Liquid MAF-4

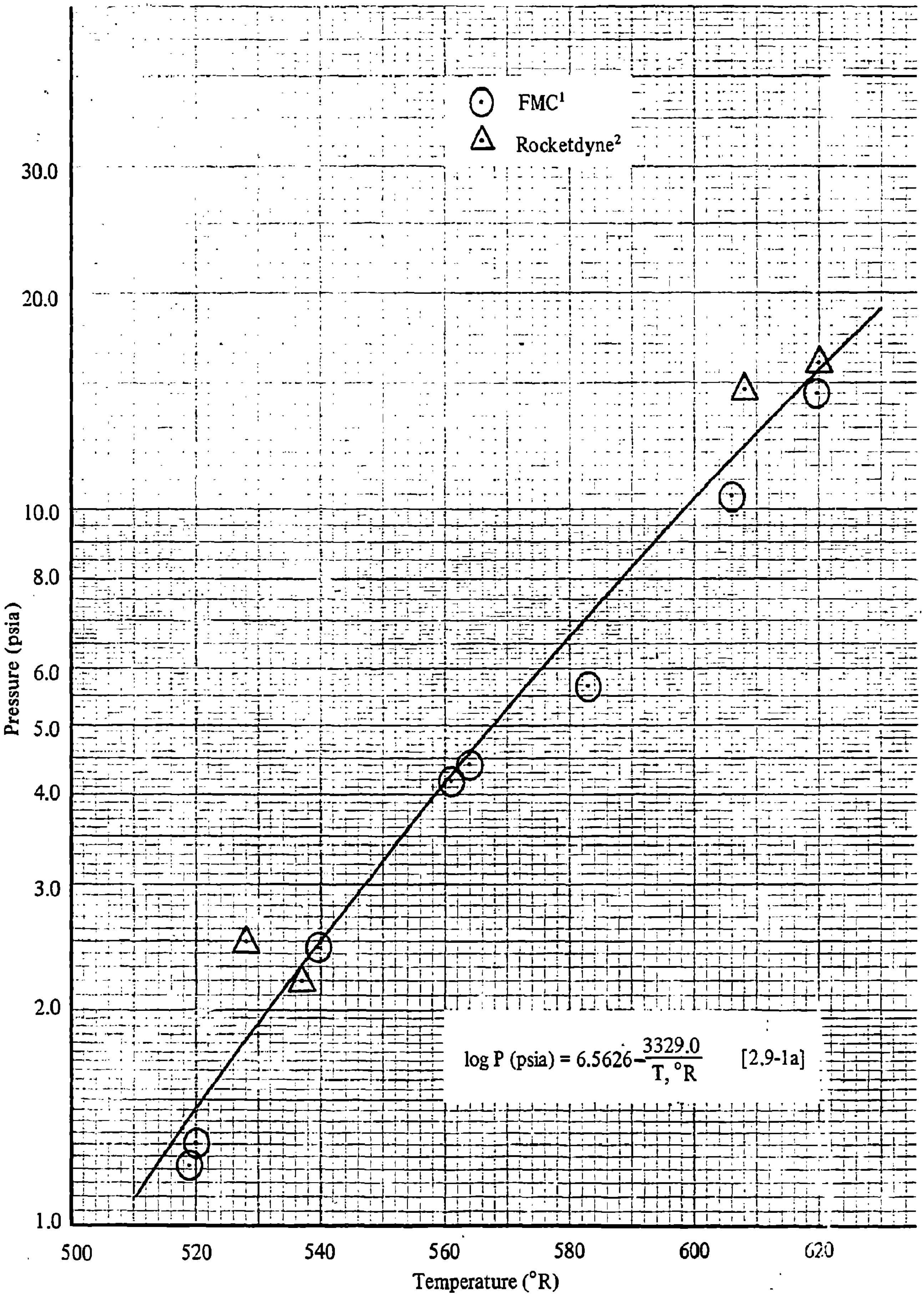
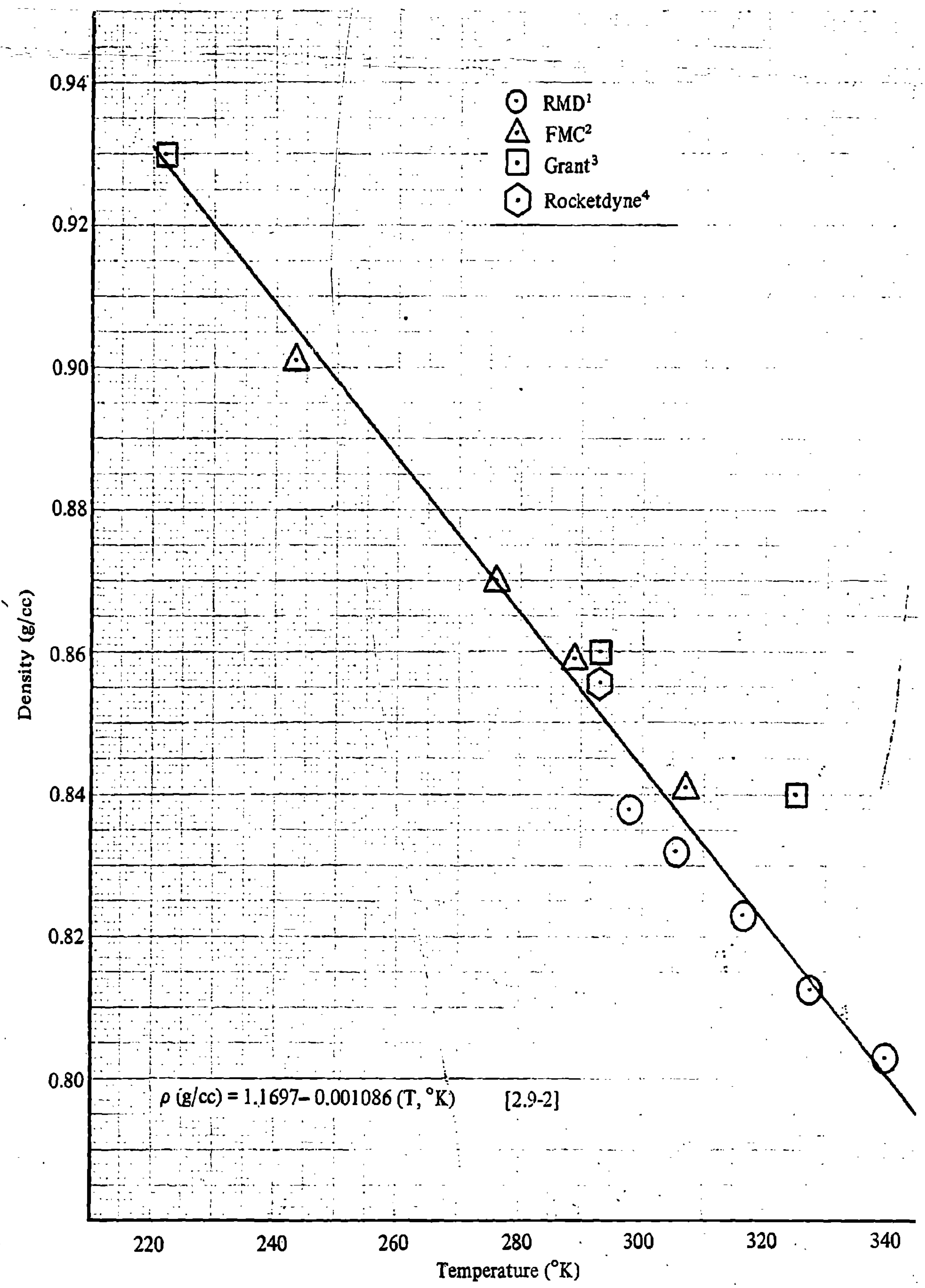


Figure 2.9-1a. Vapor Pressure versus Temperature, Saturated Liquid MAF-4



ρ (g/cc) = 1.1697 – 0.001086 (T, °K) [2.9-2]

Figure 2.9-2. Density versus Temperature Liquid MAF-4

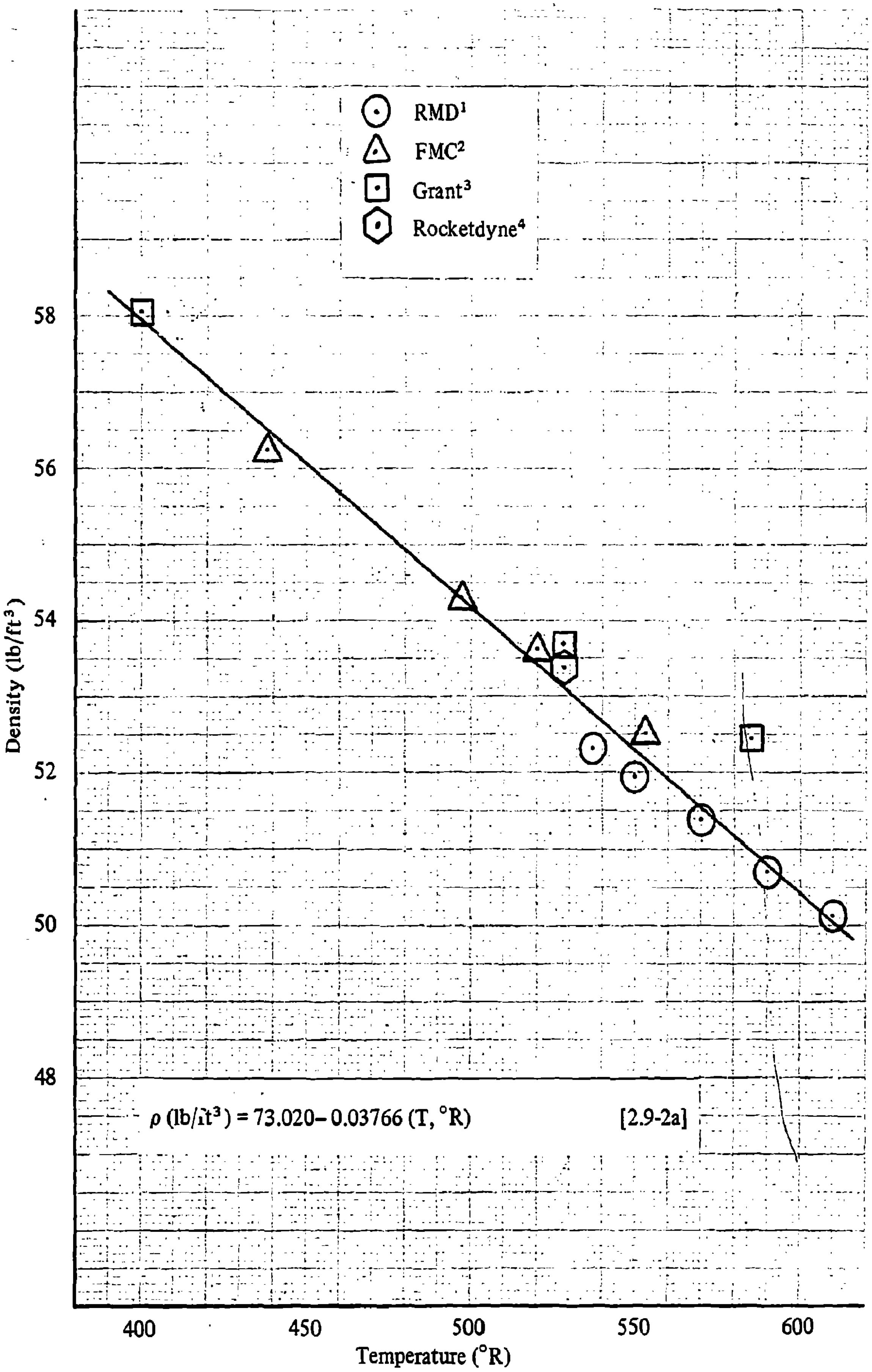
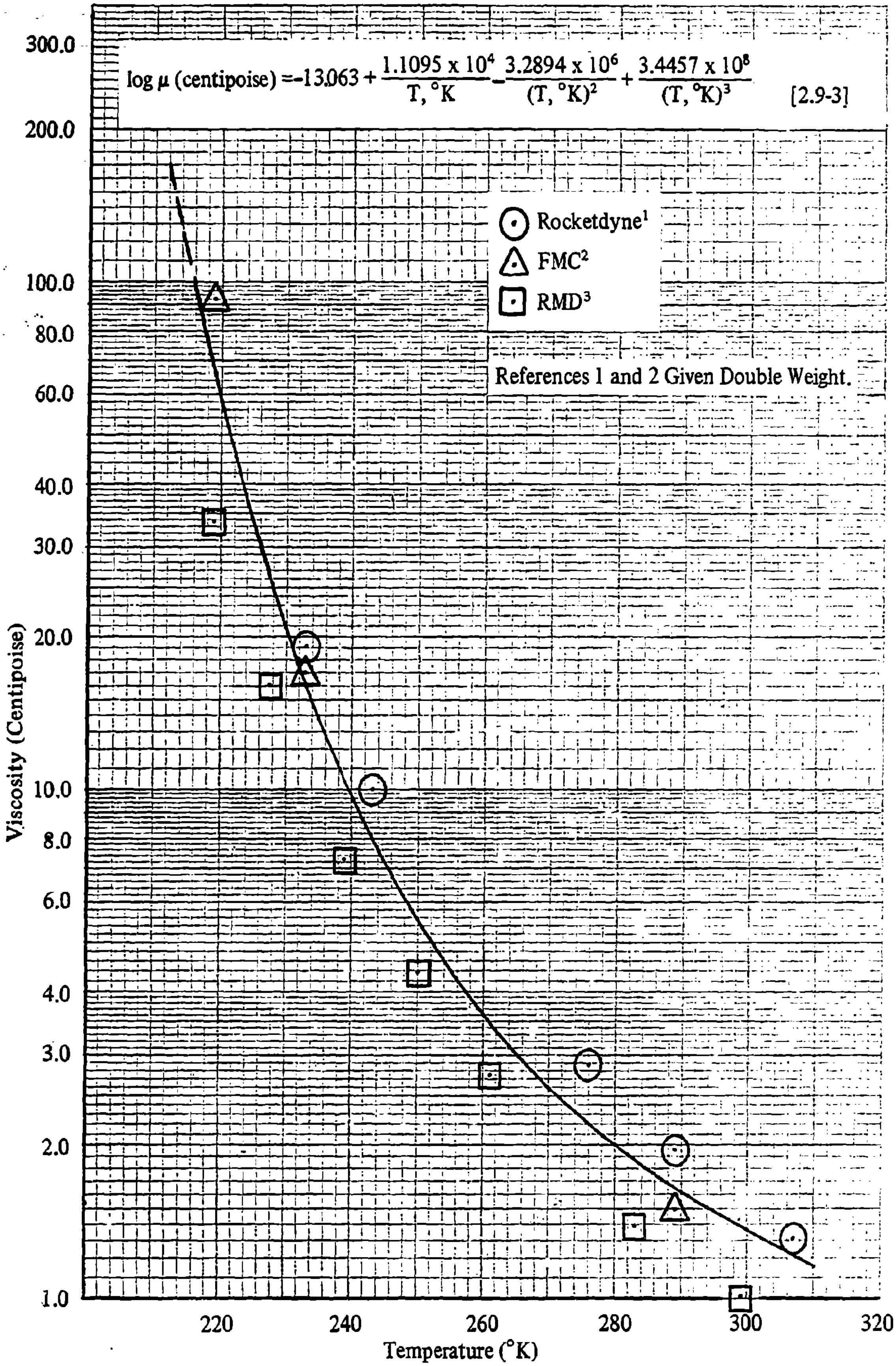
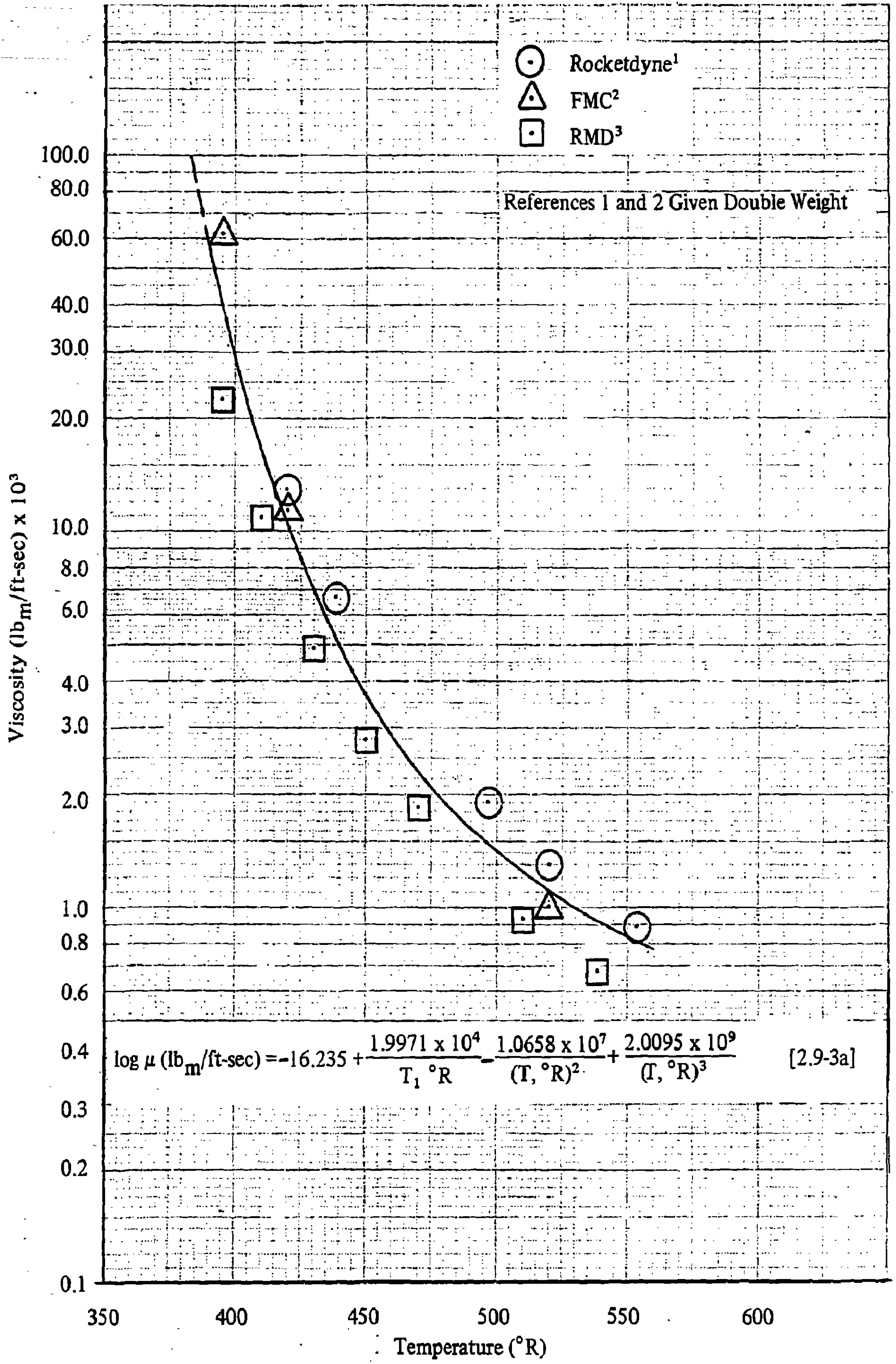


Figure 2.9-2a. Density versus Temperature Liquid MAF-4



$$\log \mu \text{ (centipoise)} = -13.063 + \frac{1.1095 \times 10^4}{T, {}^\circ K} - \frac{3.2894 \times 10^6}{(T, {}^\circ K)^2} + \frac{3.4457 \times 10^8}{(T, {}^\circ K)^3} \qquad [2.9\text{-}3]$$

Figure 2.9-3. Absolute Viscosity versus Temperature Liquid MAF-4



$$\log \mu\ (\mathrm{lb_m/ft\text{-}sec}) = -16.235 + \frac{1.9971 \times 10^4}{T_1\ ^\circ R} - \frac{1.0658 \times 10^7}{(T, ^\circ R)^2} + \frac{2.0095 \times 10^9}{(T, ^\circ R)^3} \qquad [2.9\text{-}3a]$$

Figure 2.9-3a. Absolute Viscosity versus Temperature Liquid MAF-4

$$\log \mu \text{ (lb/ft-sec)} = -16.235 + \frac{1.9971 \times 10^4}{(T, {}^\circ R)} - \frac{1.0658 \times 10^7}{(T, {}^\circ R)^2} + \frac{2.0095 \times 10^9}{(T, {}^\circ R)^3} \qquad (2.9\text{-}3a)$$

The user is warned that the above data should be regarded as highly provisional until such time as it may be verified by the acquisition of additional data.

2.9.3.9 Index of Refraction

Two determinations of the refractive index of MAF-4 were reported. The U.S. Bureau of Mines (6) reported a range of 1.443 to 1.446 at 13 C and Grant (5) reported a value of 1.438 at 25 C. Insufficient data has been reported to determine any relationship with temperature.

2.9.4 CHEMICAL PROPERTIES OF MAF-4

2.9.4.1 Chemical Reactions

The chemical behavior of MAF-4 is determined by its components. UDMH and DETA. It is a basic substance, and can be slowly oxidized by CO_2 in the atmosphere. It will attack copper and brass in the same way as UDMH. Although no specific data on chemical reactions of MAF-4 were reported. it can be assumed to behave like UDMH for which chemical properties are discussed in Section 2.5.4.

2.9.5 THERMODYNAMIC PROPERTIES OF MAF-4

2.9.5.1 Heat of Formation of Liquid

The heat of formation of this liquid mixture can be calculated from the molar addition of the individual heats of formation. The heat of mixing is not known and is assumed to be negligible for this calculation. Taking an exact composition by weight % of 40 diethylenetriamine (DETA) and 60 UDMH. the heat of formation for the liquid at 298.15 K is +3.7125 kcal/mole. The mole is defined as 72.1498 grams with the emperical formula.

$$C_{2.5595}H_{9.3986}N_{2.2797}$$

Compound	Weight %	Mole Fraction (1 mole blend)	ΔHf_{298} kcal/mole
$C_4H_{13}N_3$	40	0.2797263	-18.5
$C_2H_8N_2$	60	0.7202736	+12.339

for one mole of MAF-4. then:

$$\Delta H_{f298} = 0.2797263\,(-18.5) + 0.7202736\,(12.339)$$

$$\Delta H_{f298} = +3.7125 \text{ kcal/mole, mole} = 72.1498 \text{ grams}$$

or

$$\Delta H_{f298} = 51.455 \text{ cal/gram}$$

The heats of formation used for DETA and UDMH are discussed in Sections 2.2.5.1 and 2.5.5.1. respectively.

2.9.5.2 Melting Point and Heat of Fusion

Rocketdyne (8) reported a melting point of -84.4 C (-119.9 F). The melting point is subject to considerable uncertainty because the liquid becomes highly viscous and glassy at these temperatues.

2.9.5.3 Critical State Constants

Rocketdyne (2) reported values for the critical temperature and pressure as 558.15 K (545 F) and 784 psia, respectively. The methods used to arrive at these data are not known, since the original source of data was not available. Also, since MAF-4 is a mixture, the data most likely refer to a "pseudocritical" point. These values should therefore be regarded as provisional.

2.9.6 LOGISTICS OF MAF-4

2.9.6.1 Manufacture

MAF-4 is produced by the blending of 60% by weight UDMH with 40% by weight DETA. Blending should be conducted under nitrogen padding. The manufacture of UDMH and DETA is covered in Section 2.5.6.1 and 2.2.6.1, respectively.

2.9.6.2 Analysis

Analysis of MAF-4 can be conducted by chemical titrimetry for UDMH and DETA and by gas chromatography for water content. The procedures are described in detail in MIL-P-23686A.

2.9.6.3 Cost and Availability

MAF-4 is not commercially available as such, but its constituents are available. The cost and availability of MAF-4 is therefore determined from the constituents, plus blending costs. Blending of MAF-4 is accomplished by mixing 60% by weight UDMH and 40% by weight DETA under a nitrogen blanket.

2.9.6.4 Shipping and Transportation

No regulations for shipping of MAF-4 are available, however, the regulations and procedures for UDMH, its major constituent, should apply. Refer to Section 2.5.6.4.

2.9.7 REFERENCES

1. Strunk, W. C., "U-Deta Vapor Pressure and Viscosity," Memo to P. F. Derr, dated 2 May 1956. Food Machinery and Chemical Corp., Westvaco Chlor-Alkali Division.
2. Rocketdyne, Division of North American Aviation, "Storable Propellants Briefing Charts," (Quoted in Goodman, "A Survey of Rocket Engine Liquid Chemical Propellant Data," ABMA DSP-TR-2-59 (6), 25-26 September 1958 (Confidential).
3. Thiokol Chemical Corp., Reaction Motors Division; Unpublished Data Supplied to Bell Aerosystems, November 1968.
4. Liquid Propellant Information Agency, "Liquid Propellant Manual," Vol. 1, Unit 10 ("MAF-4"). (Confidential)
5. Grant, A. F., Jr.; "Storable Propellants For Use in Transportable Prefueled Missiles," ARDC/Industry Symposium on Storable Liquid Propulsion Systems, WADC-TR-59-110, 12-13 January 1959. (Confidential)
6. U. S. Dept. of Interior, Bureau of Mines, "Research on the Fire and Explosion Hazards Associated with New Liquid Propellants," Annual Report, Apr. 1959 to Apr. 1960.
7. Aerojet General Corp. "Performance and Properties of Liquid Propellants," Report 8160-6S Rev. A, June 1961.
8. Evans, R. C. and Voorhees, G. A. "Propellant Properties Manual," Rocketdyne, Report RR-59-48, February 1960.
9. Anon., "Preliminary Data on U-DETA Blend (60 weight % UDMH, 40 weight % DETA)," FMC Corp., June 1956.

2.10 MAF-1

2.10.1 PROPERTY SUMMARY SHEET

Chemical Name:	Mixed Amine Fuel No. 1	Common Name:	MAF-1
Empirical Formula:	$C_{3.705}H_{12.397}N_{3.006}O_{0.0555}$	Formula Weight:	100 grams/mole
Composition; % b.w.:	50.0 DETA; 39.0 UDMH; 10.0 CH_3CN; 1.0 H_2O		

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	<173	°K		1, 6	
	<-100	°C			
		°R			
		°F			
NORMAL BOILING POINT	350.35	°K		6	
	77.19	°C			
	630.63	°R			
	170.96	°F			
HEAT OF VAPORIZATION*	99-174	cal/gram			
	178-313	BTU/lb	**	6	
DENSITY OF LIQUID	0.8701	g/cc	298	1, 4, 5	2.10-2
	54.319	lb/ft^3			
VAPOR PRESSURE OF LIQUID	0.132	atm	298	1, 6	2.10-1
	100.3	mm Hg			
	1.94	psia			
VISCOSITY OF LIQUID	1.145	centipoise	298		
	7.7×10^{-4}	lb_m/ft-sec		1, 4	2.10-3
HEAT CAPACITY OF LIQUID	0.67	cal/g-°K	298		
	0.67	BTU/lb-°R		6	
HEAT OF FORMATION	−1.8646	kcal/100 gms.	298	1	
	−33.56	BTU/lb			

* Depends on vapor-liquid ratio. Range shown is range for ingredients.

** Not specified.

2.10.2 GENERAL

2.10.2.1 Introduction

Mixed Amine Fuel No. 1 is a liquid blend of diethylenetriamine, unsymmetrical dimethylhydrazine and acetonitrile (methyl cyanide). It is a clear, yellowish hygroscopic liquid giving off a slightly ammoniacal and fishy odor.

The only operational use of MAF-1 as a propellant has been as the fuel in the ASM-N7A and B (GAM-83) Bullpup missiles. Both the fuel and the missile propulsion unit were produced as a prepackaged entity, including the IRFNA oxidizer, by the Reaction Motors Division of Thiokol Chemical Corp. The fuel and the missiles were produced in large quantities for the Air Force and Navy.

MAF-1 is miscible in all proportions with water. (6) From its composition, and the nature of its constituents, it can be assumed to be miscible in all proportions with any of its constituents or with hydrazine. It is also believed to be soluble in methyl alcohol by virtue of the solubility of its ingredients. The solubility in other compounds was not reported.

2.10.2.2 Specification and Composition.

Procurement of MAF-1 is covered by MIL-P-23741A (3) dated 15 April 1964, including Revision 1, dated 15 March 1965. The effect of Revision 1 was to relax the lower limit on density at 25 C from 0.863 g/ml to 0.861 g/ml

The composition of MAF-1 has been reported as two variations (1, 2, 3). The following table indicates the composition as reported by RMD and as contained in MIL-P-23741A.

Ingredient	RMD Data	MIL-P-23741A
DETA (MIL-D-50025)	50.5%	49.7 ±0.7%
UDMH (MIL-D-25604)	40.5%	39.0 ±1.5%
CH_3CN	9.0%	10.0 ±1.0%
Water	-	1.0% Max.

The nominal data given by RMD appear to be at one extreme of the specification tolerance range. In addition, it should be noted in using the data presented herein, that commercial DETA contained up to 9% impurities during the 1957-1959 time period. Presently available DETA is described in Section 2.2 of this handbook.

2.10.3 PHYSICAL PROPERTIES of MAF-1

2.10.3.1 Vapor Pressure and Normal Boiling Point.

Vapor pressure data for MAF-1 was reported by RMD (1) in 1957 and in 1959 (6).The two sets of data showed a consistent discrepancy of about 50 to 100% in vapor pressure. Only the more recent data (6) which showed less scatter and also gave the highest vapor pressure was considered in this work. The 1957 data did have one point which was actually higher than the curve adopted in this work. The 1959 data were apparently adopted by RMD (6).

The data from both studies are shown in Figures 2.10-1 and 2.10-1a. The equations which best fit the data of Reference 6 as determined by the least-squares method are:

$$\log P\,(\text{mm Hg}) = 12.9134 - \frac{5008.6}{T,\,^\circ K} + \frac{5.2332 \times 10^5}{(T,\,^\circ K)^2} \quad (2.10\text{-}1)$$

$$\log P\,(\text{psia}) = 11.1998 - \frac{9015.6}{T,\,^\circ R} + \frac{1.6956 \times 10^6}{(T,\,^\circ R)^2} \quad (2.10\text{-}1a)$$

The normal boiling point, as determined from the curve fit, is 350.35 K (630.63 R). RMD (6) reported a value of 171 F which converts to 350.38 K, verifying complete agreement. Reference 5 reported the bubble point to be 144 F according to ASTM distillation.

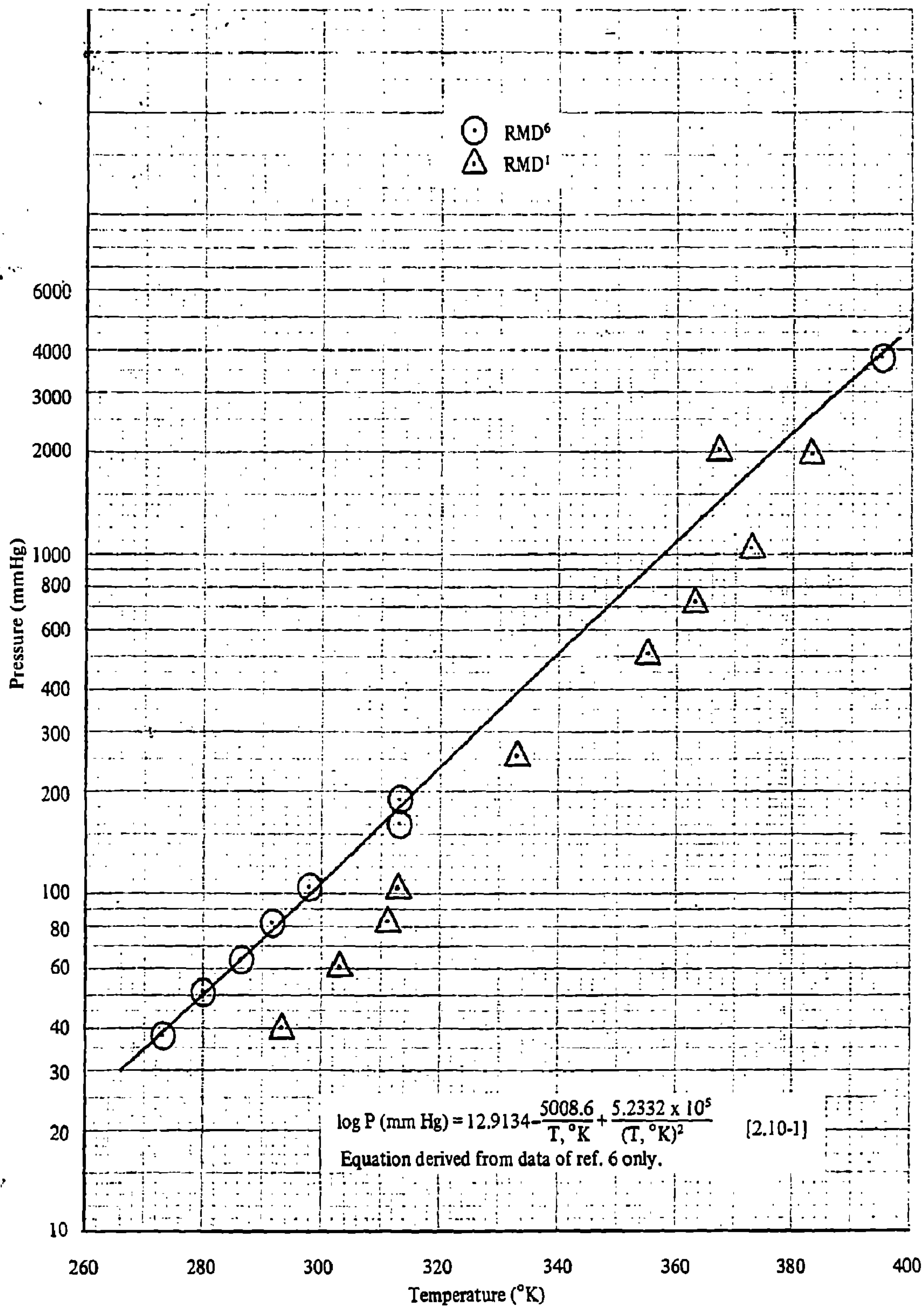
2.10.3.2 Density of Liquid MAF-1

Density data for MAF-1 was obtained from three RMD sources(1, 4, 5). These sources are in essential agreement within reasonable experimental scatter. It should be noted that the MAF-1 used in these measurements was not controlled by a military specification at that time. RMD requirements limited water content to 2% by weight, maximum, but the quantity of other impurities, mainly from the DETA, is unknown.

The density as a function of temperature is presented in Figures 2.10-2 and 2.10-2a. The equations which best fit the data are:

$$\rho\,(\text{g/cc}) = 1.1391 - 9.0228 \times 10^{-4}\,(T,\,^\circ K) \quad (2.10\text{-}2)$$

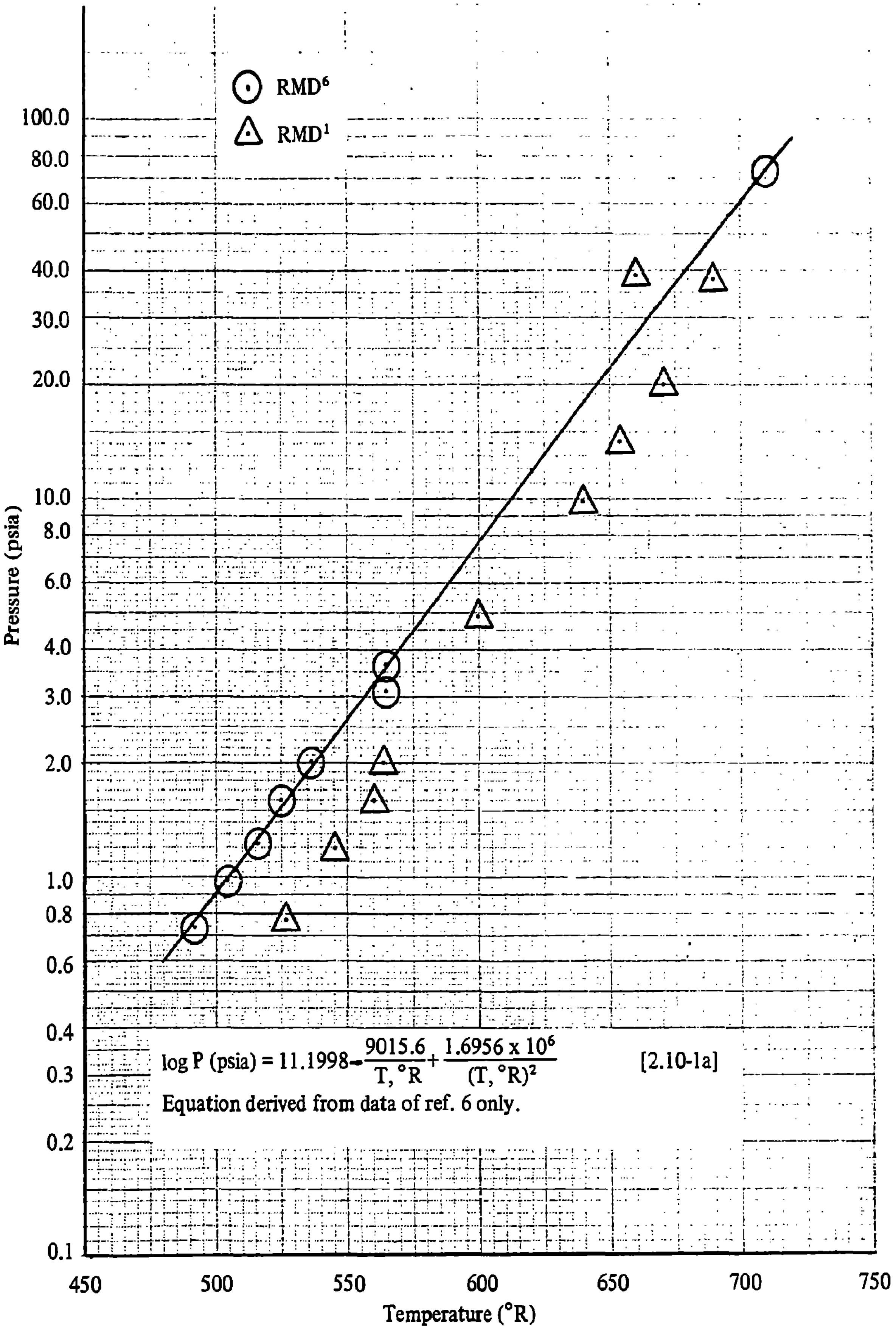
$$\rho\,(\text{lb/ft}^3) = 71.111 - 0.03129\,(T,\,^\circ R) \quad (2.10\text{-}2a)$$



$$\log P\ (\text{mm Hg}) = 12.9134 - \frac{5008.6}{T,\ ^\circ K} + \frac{5.2332 \times 10^5}{(T,\ ^\circ K)^2} \qquad [2.10\text{-}1]$$

Equation derived from data of ref. 6 only.

Figure 2.10-1. Vapor Pressure versus Temperature, Liquid MAF-1



$$\log P\ (\text{psia}) = 11.1998 - \frac{9015.6}{T, {}^{\circ}R} + \frac{1.6956 \times 10^{6}}{(T, {}^{\circ}R)^{2}} \qquad [2.10\text{-}1a]$$

Equation derived from data of ref. 6 only.

Figure 2.10-1a. Vapor Pressure versus Temperature, Liquid MAF-1

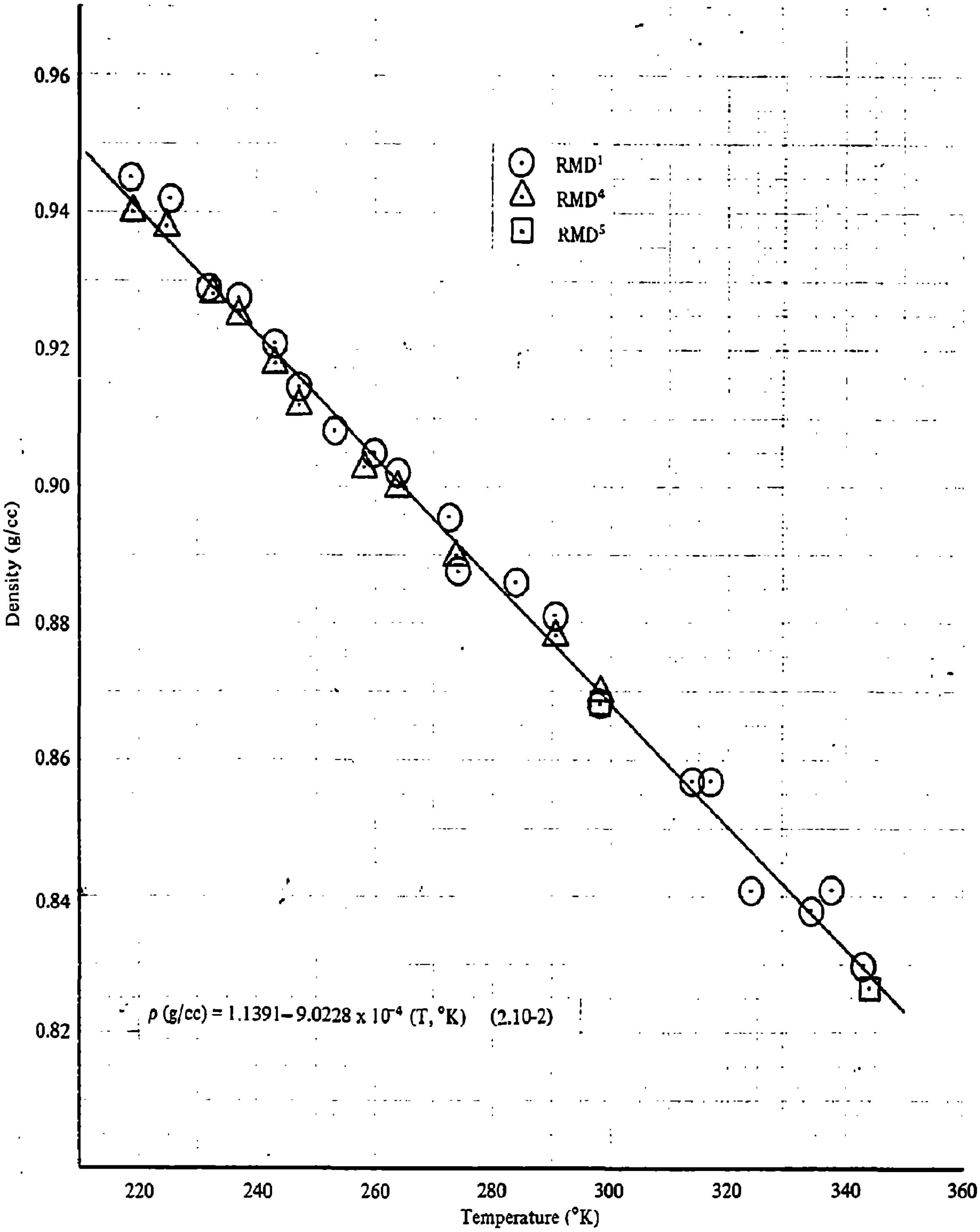


Figure 2.10-2. Density versus Temperature, Liquid MAF-1

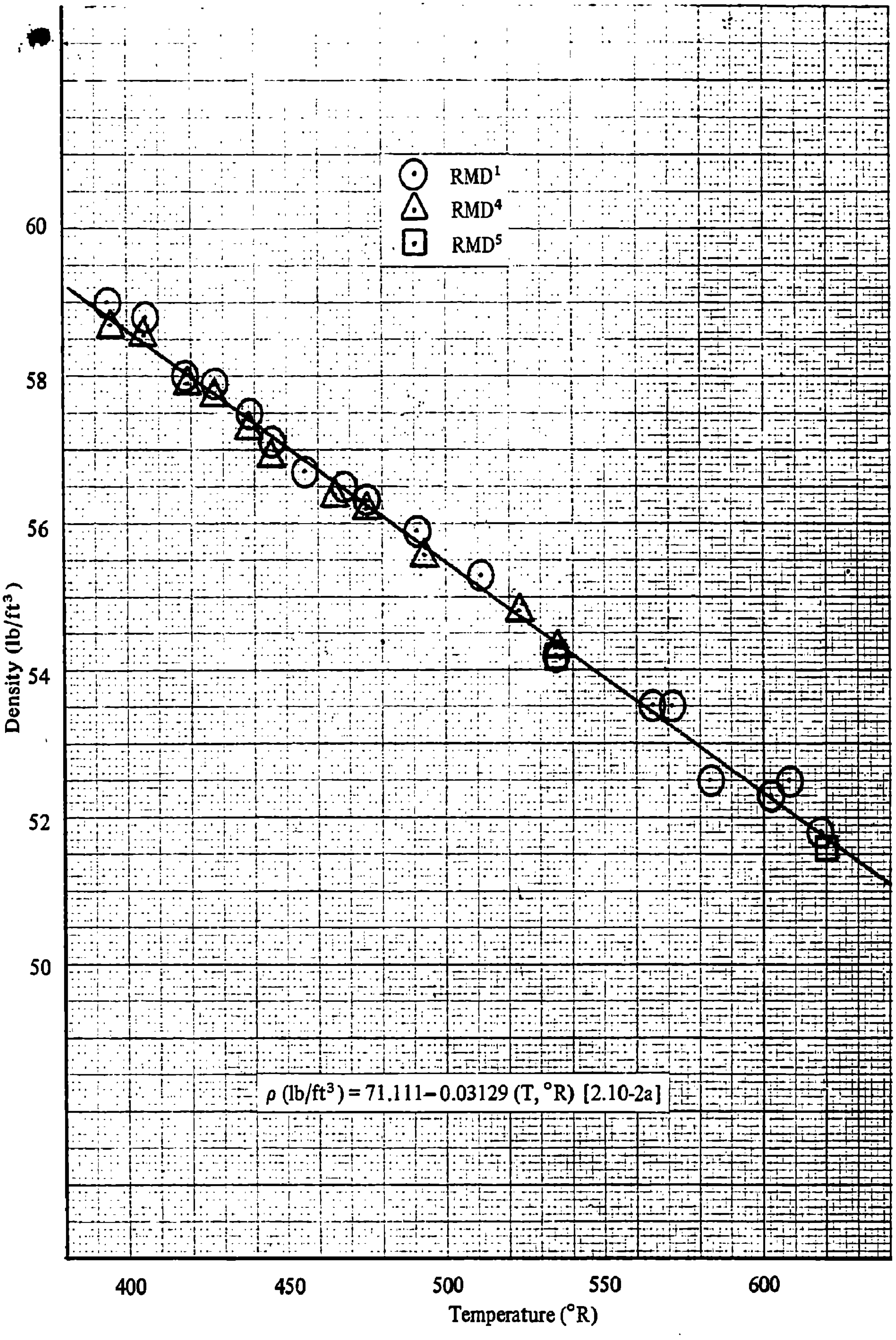


Figure 2.10-2a. Density versus Temperature, Liquid MAF-1

2.10.3.5 Viscosity of Liquid MAF-1

Two sets of viscosity determinations were apparently conducted by RMD (1, 4) in the late 1950's. The two determinations were in essential agreement. When using these data, it should be kept in mind that the purity of the MAF-1 samples was not controlled by any military specification at that time, and the actual purity was not published with the data.

The data and fitted curves are presented in Figures 2.10-3 and 2.10-3a. The equations which best fit the data are:

$$\log \mu\,(\text{centipoise}) = 1.9815 - \frac{2000.1}{T,\,^{\circ}K} + \frac{4.2543 \times 10^5}{(T,\,^{\circ}K)^2} \quad (2.10\text{-}3)$$

$$\log \mu\,(\text{lbm/ft-sec}) = 1.1911 - \frac{3600.2}{T,\,^{\circ}R} + \frac{1.3784 \times 10^6}{(T,\,^{\circ}R)^2} \quad (2.10\text{-}3a)$$

It should be kept in mind that the viscosity measurements and the corresponding curve at low temperatures where the curve is steep, may not be very accurate. Earlier estimates of the viscosity at -65 F for example, range from 40 cp to more than 100 cp.

2.10.4 CHEMICAL PROPERTIES OF MAF-1

Since MAF-1 is a mixture of UDMH, DETA, and acetonitrile, its chemical behavior is determined by these components. RMD (6) reports that MAF-1 is hygroscopic and a strong reducing agent. MAF-1 exhibits the strong reactivity of UDMH with carbon dioxide, and it is also known to be hypergolic with a wide variety of rocket propellant oxidizers. In solution with other materials, especially water, intermediate compounds are formed with the ingredients via hydrogen bonding.

2.10.5 THERMODYNAMIC PROPERTIES OF MAF-1

2.10.5.1 Heat of Formation

The heat of formation, calculated from the components, and based on the empirical formula $C_{3.705} H_{12.397} N_{3.006} O_{0.0555}$ was given as -1.8646 kcal/mole (1). The formula was derived for an arbitrary molecular weight of 100 grams giving a heat of formation of -18,646 cal/g.

2.10.5.2 Melting Point

No definite melting or freezing point has been reported for MAF-1. Instead, it is described as becoming very viscous below -70 C and becoming hard below -100 C This viscosity at low temperatures is the limiting factor for practical applications. At -65 F the viscosity is approximately 55 centipoise.

2.10.5.4 Specific Heat Capacity

The specific heat was estimated by RMD (6) to be 0.67 BTU/lb- R (cal/g- R) at 25 C. No experimental data were reported.

2.10.6 LOGISTICS OF MAF-1

Procurement requirements for MAF-1 are covered in MIL-P-23741A dated 15 April, 1964 (3). Since the only use of MAF-1 was in the Bullpup A and B missiles, and since production has been discontinued, MAF-1 is not readily available in large quantities. It can, however, be obtained by blending the ingredients, all of which are available. The cost of MAF-1 can be derived from the cost of its ingredients plus blending costs.

Analysis of MAF-1 for UDMH and DETA content is accomplished by titration as described in MIL-P-23741A. Acetonitrile content is determined by infrared spectroscopy and water content by gas chromatography, also described in MIL-P-23741A (3).

In blending specification grade MAF-1, careful attention should be paid to keeping the water content to 1% by weight or less. No limit has been set on the dimethylamine content in MAF-1, whereas specification grade UDMH is governed by such a limit.

2.10.7 REFERENCES

1. Thiokol Chemical Corp. RMD., Unpublished data dated May 1957, on MAF-1 supplied to Bell Aerosystems by Dr. A. Beardell, 2/27/69.
2. Applied Physics Laboratory, John Hopkins University, LPIA; Liquid Propellant Manual.
3. Military Specification MIL-P-23741A, April 15, 1964, and Amendment 1 dated March 15, 1965.
4. Thiokol Chemical Corp. RMD, Report TR 4293 (1959).
5. Thiokol Chemical Corp. RMD, Memo-Gordon to Strang, dated 1/8/59.
6. Thiokol Chemical Corp. RMD, "Safety and Special Regulations for Guided Missile Propellants," (Properties Section on MAF-1) unpublished document (1959).

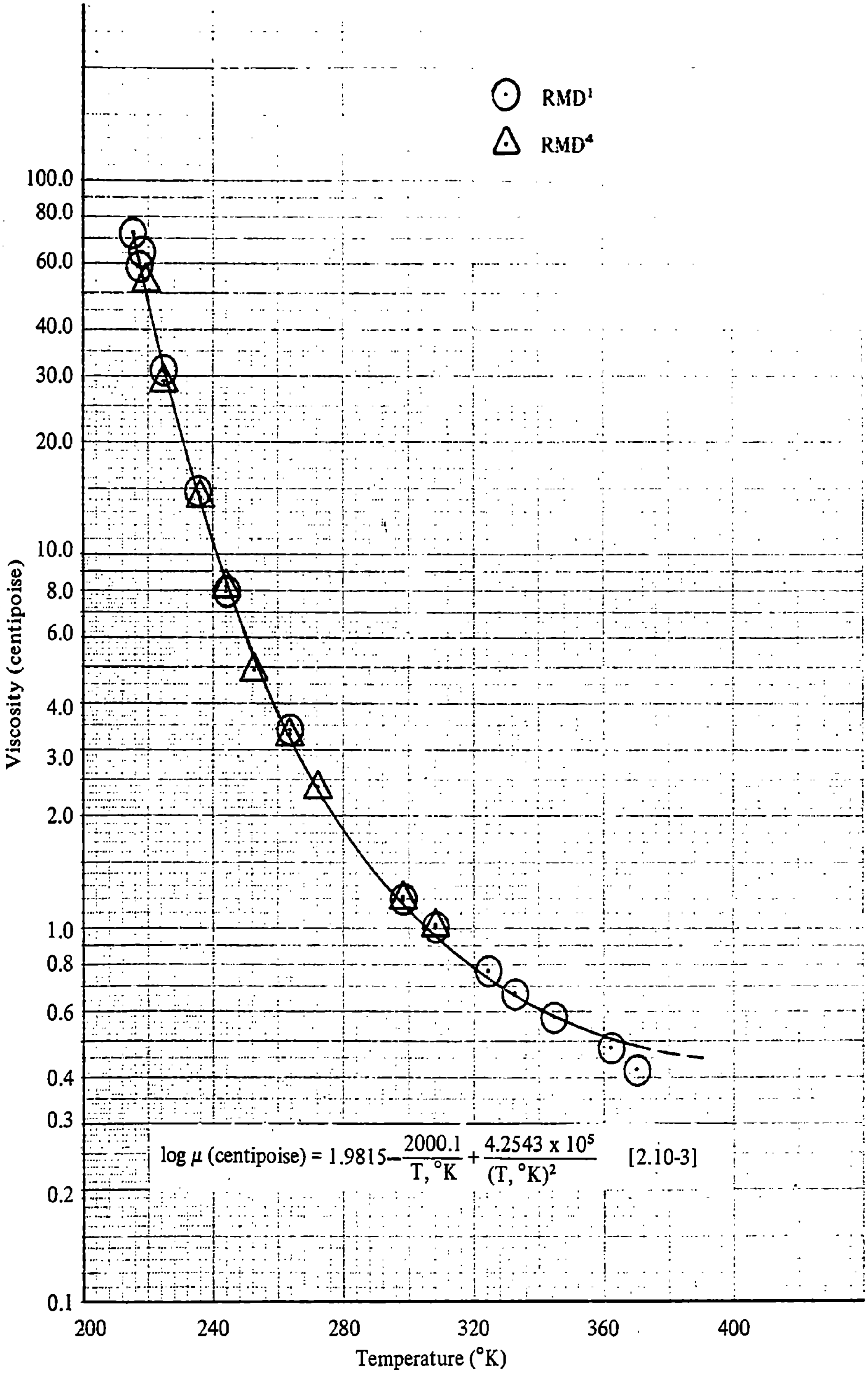


Figure 2.10-3. Absolute Viscosity versus Temperature, Liquid MAF-1

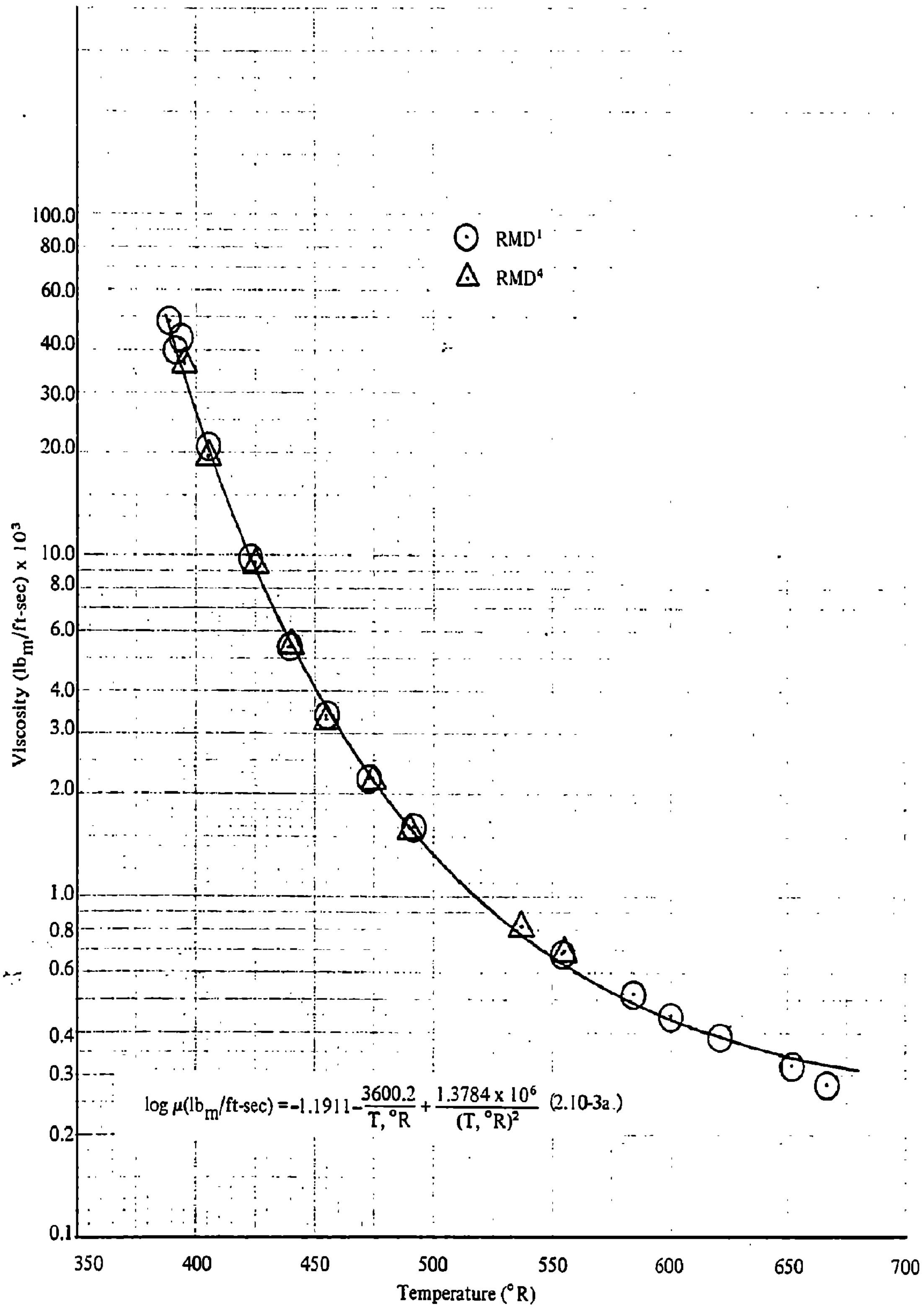


Figure 2.10-3a. Absolute Viscosity versus Temperature, Liquid MAF-1

2.11 MAF-2

2.11.1 PROPERTY SUMMARY SHEET

Chemical Name: **Mixed Propargyl-Glycidyl Amines** Common Name: **MAF-2**

Empirical Formula: $C_{9.0000}H_{11.5723}O_{1.2862}N_{1.0000}$ Formula Weight: **154.35**

Composition; % b.w.: 42.6% $C_9H_{13}NO_2$ + 48.3% $C_9H_{11}NO$ + 9.1% C_9H_9N

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	203	°K		(7)	
	-70	°C		Est.	
	366	°R			
	-94	°F			
HEAT OF FUSION		kcal/mole			
		BTU/lb			
NORMAL BOILING POINT	723	°K			
	450	°C		(7)	
	1301	°R			
	842	°F			
DENSITY OF LIQUID	1.024	g/cc	298	(7)	2.11-1
	63.95	lb/ft^3			
VAPOR PRESSURE OF LIQUID	1.3	mm Hg	313	(7)	
	.025	psia	301	(7)	
VISCOSITY OF LIQUID	23.5	centipoise	298	(7)	2.11-2
	0.0016	lb_m/ft-sec			
HEAT OF FORMATION	+83.47	kcal/mole			
	+973.4	BTU/lb	298	calc.	

2.11.2 GENERAL

Mixed Amine Fuel No. 2 or MIGA as it is sometimes referred to, is a little-known, little-characterized fuel developed by the Reaction Motors Division of Thiokol about 1957. As a propellant candidate, it was abondoned in the late 1950's due to deficiencies in its properties (1). These deficiencies were probably high viscosity, and poor ignition characteristics when tested with IRFNA (2).

The nominal composition of MAF-2, according to the best available knowledge, (3) is:

42.6% Propargyldiglycidylamine (PRODGA), $N(H_2C_2CH)(CH_2OCHCH_2)_2$

48.3% Dipropargylglycidylamine (DIPGA), $N(H_2C_2CH)_2CH_2OCHCH_2$

9.1% Tripropargylamine (TRIPRAM), $N(H_2C_2CH)_3$

MAF-2 is believed to be a pale yellowish liquid having an acrid odor characteristic of the propargyl substituted amines. It is one of several compositions having the acronym MIGA, which were studied by Thiokol-RMD (7). Table 2.11-1 summarizes the compositions and some of the properties reported for the MIGA series. The ingredients are included for comparison. The data are abstracted from References 4, 5, 6 and 7. Additional properties are listed in the property summary sheet. The chemical formula and formula weight were calculated based on the nominal composition and assuming pure ingredients.

TABLE 2.11-1 MIGA SERIES COMPOSITION

FUEL COMPOSITION*	PRODGA	DIPGA	TRIPRAM	MAF-2	MIGA-1	MIGA-2	MIGA-3	MIGA-4	MIGA-5
% PRODGA	100*			42.6	10.13	20.21	29.95	19.97	19.99
% DIPGA		100*		48.3	44.92	39.87	34.98	49.88	30.08
% TRIPRAM			100*	9.1	44.95	39.96	35.08	30.15	49.93
Molecular Weight	167.2	149.2	131.2	154.35	-	-	-	-	-
Melting Point °C	**	−39.0	+16.5	−70.0	-	-	-	-	-
Boiling Point °C	81	61	300	40.0	-	-	-	-	-
at P (mm Hg)	(0.5)	(0.05)	(760)	(1.3)					
		75	88						
		(13)	(3.0)						
Density g/ml at	1.059	1.054	0.9216	1.024	0.968	0.973	0.987	0.984	0.968
(T °C)	(25)	(25)	(20)	(25)	(25)	(25)	(25)	(25)	(25)
	1.113								
	(-35)								
Viscosity at 25°C (Centistokes)	14.5	10.7	4.7	22-23	8.2	8.9	9.7	9.4	8.2

* The ingredients investigated were probably impure.

** Becomes viscous, then glassy. No detectable breaks in cooling curve.

2.11.3 PHYSICAL PROPERTIES OF MAF-2

2.11.3.1 Vapor Pressure of MAF-2

Only two values of the vapor pressure of MAF-2 were reported by RMD (7). Measurements were made on the sample numbered L-197-72, the composition and purity of which is uncertain. The method used to measure the vapor pressure was not reported.

The vapor pressure was reported to be 1.3 mm Hg (0.025 psia) at 313 K (564 R) and 3.0 mm Hg (0.058 psia) at 361 K (650 R). This would imply a very high normal boiling point, probably above the auto-decomposition temperature. The data are insufficient to generate a reliable equation for vapor pressure.

2.11.3.2 Density

RMD (7) conducted density measurements on five different samples of MIGA which were reportedly representative of MAF-2. The samples were impure, and their exact compositions are unknown, therefore, the original uncorrected data are presented in Figures 2.11-1 and 2.11-1a, for the five samples.

Samples numbered L-197-74, L-197-75, MIGA II, and 232-5B were measured using pycrometers. Sample L-197-72 was measured using a Westphal balance. Only the points for sample L-197-74 have been used to generate the equations. The best fit yields the following dependence of density on temperature. The discrepancies between samples must be attributed to differences in composition.

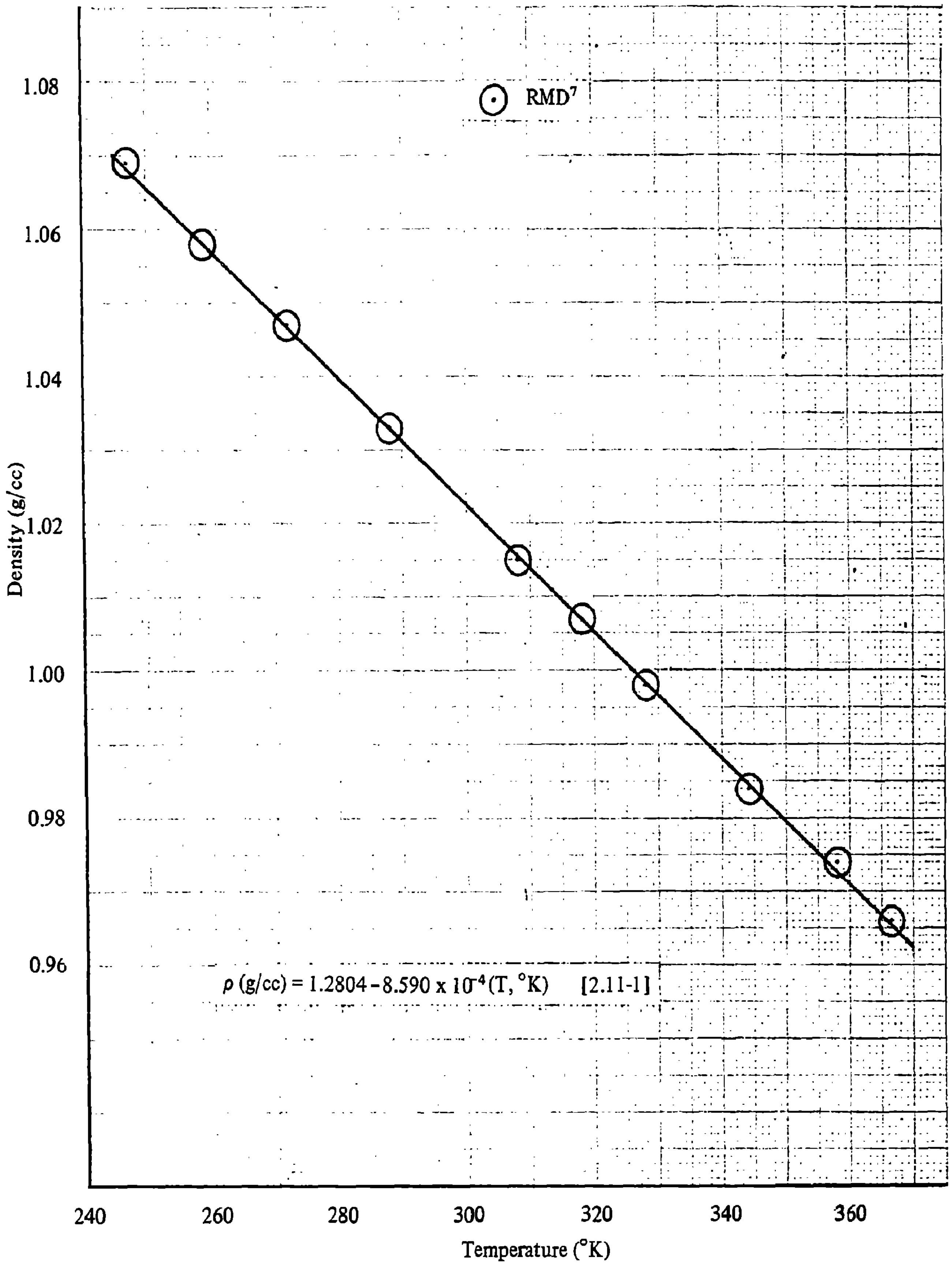


Figure 2.11-1. Density versus Temperature, Liquid MAF-2

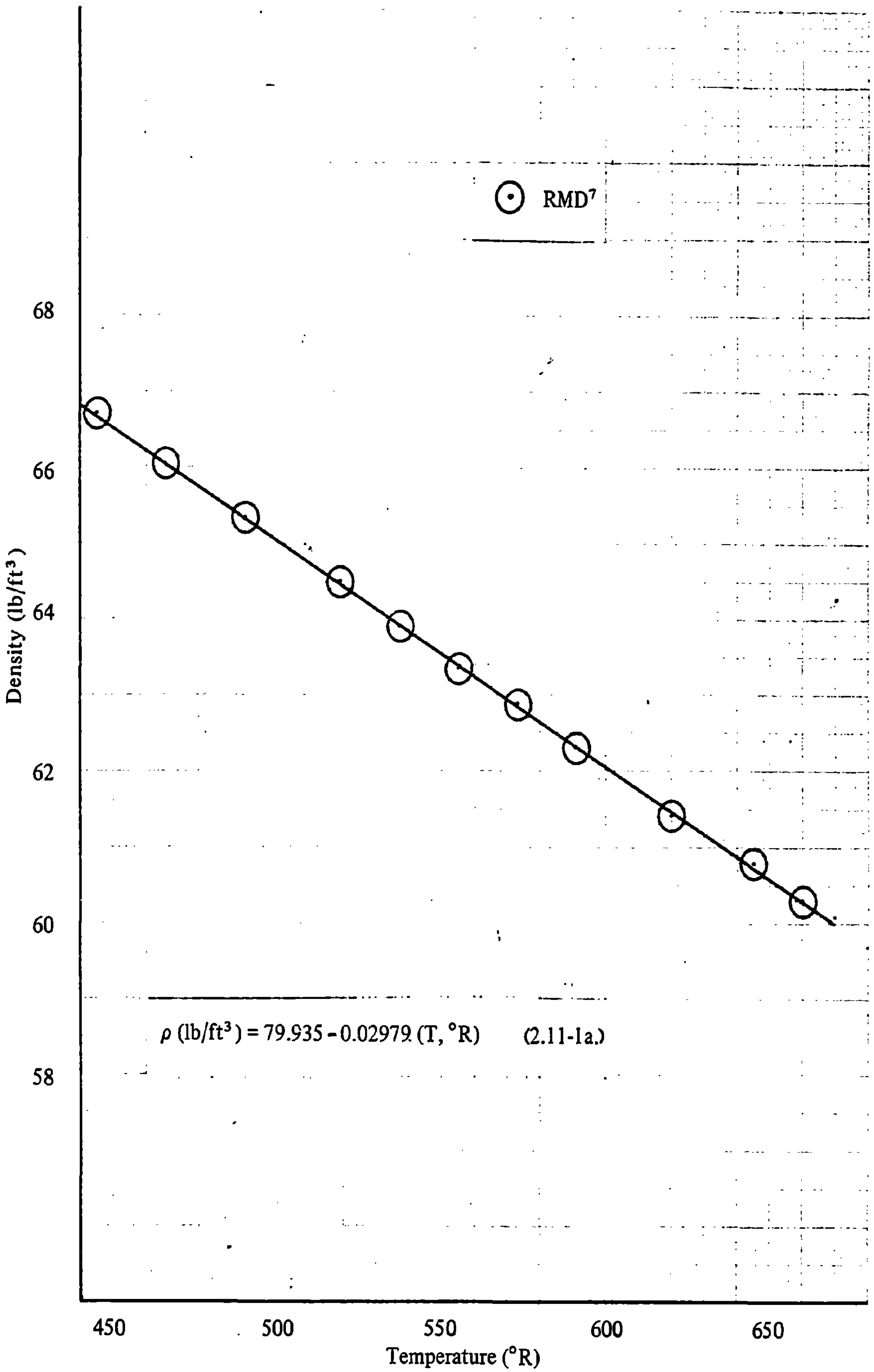


Figure 2.11-1a. Density versus Temperature, Liquid MAF-2

$$\rho\,(\text{g/cm}^3) = 1.2804 - 0.000859\ (\text{T}, {}^\circ\text{K}) \qquad (2.11\text{-}1)$$

$$\rho\,(\text{lb/ft}^3) = 79.935 - 0.02979\ (\text{T}, {}^\circ\text{R}) \qquad (2.11\text{-}1a)$$

2.11.3.5 Viscosity of MAF-2

The viscosity of three samples of MIGA representative of MAF-2 was measured by RMD (7). Since the composition of the samples and their purity are unknown, the data for the sample known as L-197-74 are presented, without corrections, in Figure 2.11-2 and 2.11-2a.

The equations for viscosity as a function of temperature, based on sample L-197-74, are:

$$\log\mu\,(\text{cp}) = 8.6632 - \frac{6714.4}{\text{T}, {}^\circ\text{K}} + \frac{1.3537 \times 10^6}{(\text{T}, {}^\circ\text{R})^2} \qquad (2.11\text{-}2)$$

$$\log\mu\,(\text{lbm/ft-sec}) = 5.4790 - \frac{1207.2}{\text{T}, {}^\circ\text{R}} + \frac{4.3822 \times 10^6}{(\text{T}, {}^\circ\text{R})^2} \qquad (2.11\text{-}2a)$$

The method used to measure viscosity was not reported.

A large discrepancy exists between sample L-197-74 and MIGA II and can be tentatively attributed to differences in composition, since the scatter for a single sample is small. Sample L-197-74 had the largest quantity of available data.

2.11.4 CHEMICAL PROPERTIES OF MAF-2

The molecular weight of MAF-2 has been calculated as a mean molecular weight of the ingredients. The ingredients, their structural formulas, estimated heats of formation, and their fractions are:

Ingredient	Mol. Wt.	Wt. Fraction	Mol. Fraction	ΔH_f, Kcal/gram	Ref.
$N(H_2C_2 = CH)_3$	131.179	0.091	0.1071	1.200	5
$N(H_2C_2 = CH)_2$ CH_2CHOCH_2	149.194	0.483	0.4997		8
$N(H_2C_2 = CH)$ $(CH_2CHOCH_2)_2$	167.209	0.426	0.3932		8

From these fractions, an empirical formula and molecular weight were calculated as:

$$C_{9.0000}H_{11.5723}O_{1.2862}N_{1.0000}$$

Formula Weight = 154.35

These compounds are believed to decompose exothermically to methane, ammonia, carbon, and lesser quantities of CO, nitrogen, and water.

Evidence of possible polymerization of the blend was found by RMD (2) when gummy residues were found on test hardware components.

2.11.5 THERMODYNAMIC PROPERTIES

2.11.5.2 Melting Point of MAF-2

No melting point data were reported for MAF-2. An estimate made for this work is -70 C however, the viscosity of these blends is so high that the melting point is not a useful guideline for establishing the practicality of this fuel in a cold environment.

2.11.6 LOGISTICS OF MAF-2

MAF-2 and its ingredients were produced in laboratory quantities by RMD (7). Procedures for preparation were not given.

MAF-2 is not available and no cost data are available. The only ingredient reported in the literature was tripropargylamine. Should new interest arise in any of the propargyl or glycidyl-substituted amines, chemical manufacturers may be of help in synthesizing these chemicals.

2.11.7 REFERENCES

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2. Gere, R.A., "Motor Tests, MIGA or MAF-2," Thiokol-RMD, unpublished memorandum to Dr. S. Tannenbaum, 12/18/57. Released to Bell Aerosystems 2/28/69.

3. Beardell, Dr. A., Thiokol Chemical Corp., Reaction Motors Division; personal contact with W. Marsh, Bell Aerosystems, 1/20/69.

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5. Winternitz, P.F. and Markowitz, M.M., "A Monopropellant Review," New York University College of Engineering, Research Division, Report No. 333-3, April 15, 1956 (CONFIDENTIAL).

6. Charyk, J.V. et al., "Final Summary Report on Research for Acetylenic Materials," Air Reduction Company, Inc., New York, December 15, 1954 (CONFIDENTIAL, AD-73-619).

7. Thiokol Chemical Corp., Reaction Motors Division; unpublished data released to Bell Aerosystems, 2/28/69.

8. Marsh, W.R., "Estimates of the Density, Heats of Formation, Viscosity, Normal Boiling Points, and Melting Points of Acetylenic Amines," Bell Aerosystems, Internal Memorandum, 4/11/69.

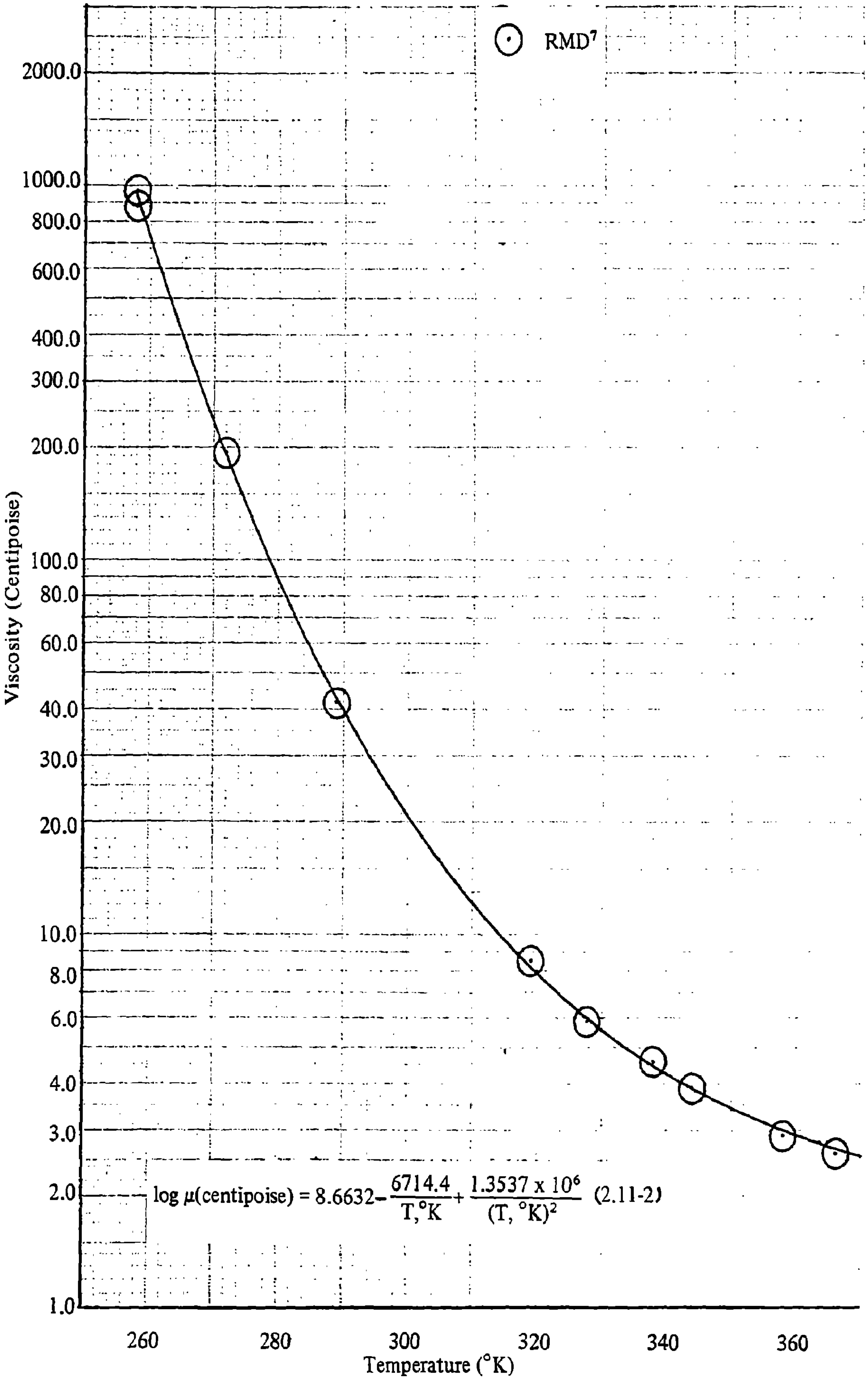
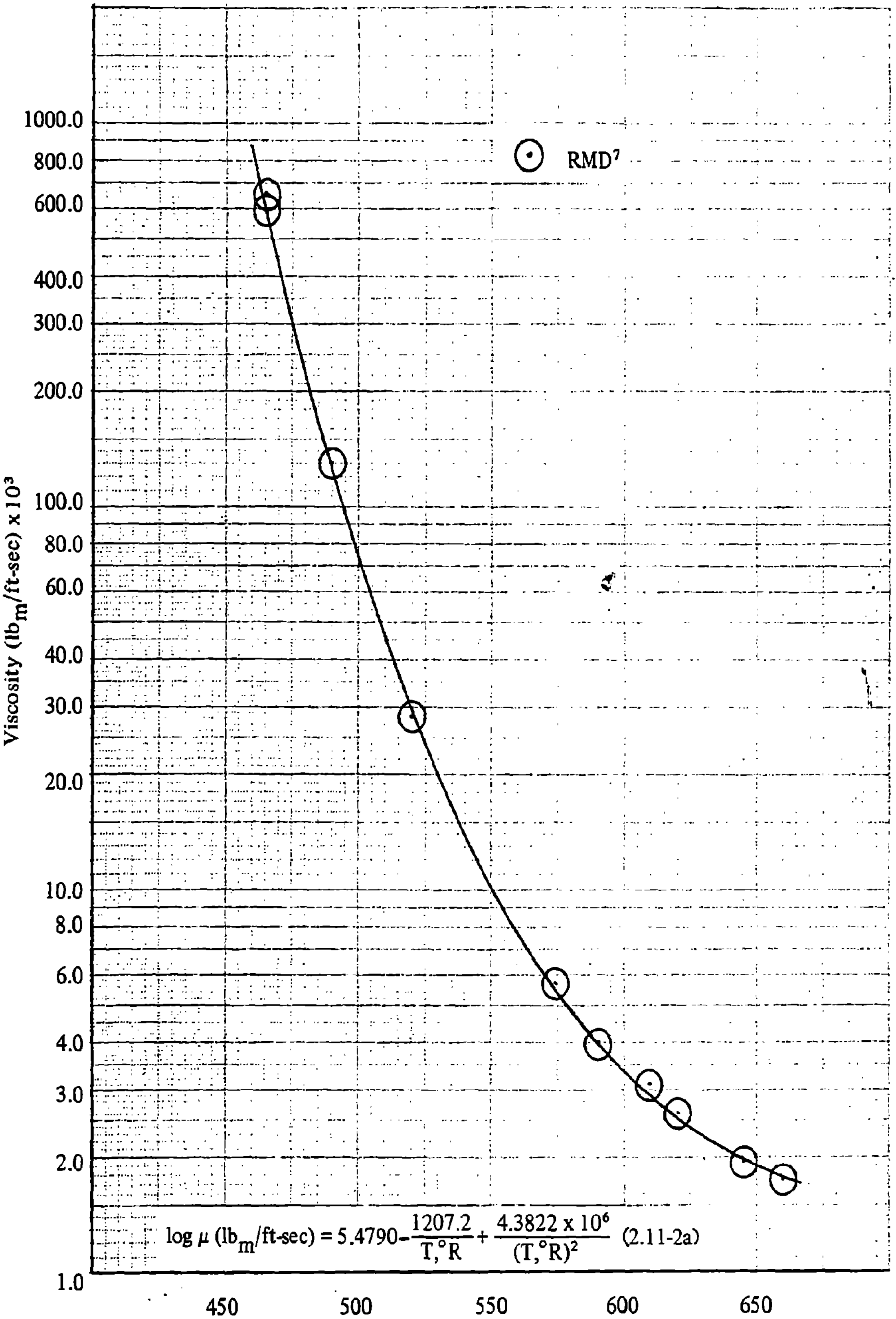


Figure 2.11-2. Absolute Viscosity versus Temperature, Liquid MAF-2



$$\log \mu \,(\text{lb}_m/\text{ft-sec}) = 5.4790 - \frac{1207.2}{T,{}^\circ R} + \frac{4.3822 \times 10^6}{(T,{}^\circ R)^2} \quad (2.11\text{-}2a)$$

Figure 2.11-2a. Absolute Viscosity versus Temperature, Liquid MAF-2

2.12 MAF-5

2.12.1 PROPERTY SUMMARY SHEET

Chemical Name: **Mixed Amine Fuel No. 5** Common Name: **MAF-5**
Empirical Formula: $C_{3.9139}H_{11.5713}N_{2.9372}$ Formula Weight: 100.0
Composition; % b.w.: $50.5\ C_4N_3H_{13}$, $29.5\ N_2H_2(CH_3)_2$, $20.0\ CH_3CN$

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	<219.3	°K			
	<-53.9	°C			
	<394.7	°R			
	<-65.0	°F			
DENSITY OF LIQUID	0.868 ±0.003	g/cc	298	2	3.7-1
	54.2 ±0.19	lb/ft^3			
VISCOSITY OF LIQUID	63 ±7	Centipoise	219.3	2	3.7-2
	0.0423 ±0.0047	lb_m/ft-sec			

2.12.2 GENERAL

Mixed Amine Fuel No. 5 (MAF-5) is believed to have been the designation for a blend containing 50.5% by weight DETA, 29.5% by weight UDMH, and 20.0% by weight acetonitrile (1). This and several related blends (including MAF-1) were either proposed and/or investigated as prepackaged missile fuels. No reported data were found for MAF-5, although a number of density determinations were reported for related blends (2). The two blends most closely approaching the composition of MAF-5 are discussed below.

In general, MAF-5 will resemble MAF-1 in its appearance and behavior. except for the higher acetonitrile concentration. It was probably proposed as a refinement of MAF-1 with a reduced viscosity. Performance and density of MAF-5 would be essentially the same as for MAF-1.

There is no military or other specification covering MAF-5. It is not known whether the blend was ever made or characterized.

2.12.3 PHYSICAL PROPERTIES OF MAF-5

2.12.3.1 Vapor Pressure and Normal Boiling Point.

No data are available. Based on UDMH content, the vapor pressure would be slightly lower than for MAF-1, and the normal boiling point slightly higher.

2.12.3.2 Density of Liquid

The only reported information which may be applicable to MAF-5 consists of two single-point density determinations by RMD (2) on two closely-related compositions at 25 C (77 F). The compositions and density values reported are:

45.0% DETA; 36.8% UDMH; 18.2% CH_3CN: $\rho = 0.856$ g/ml
58.5% DETA; 23.5% UDMH; 18.0% CH_3CN: $\rho = 0.878$ g/ml

Inspection of the ternary density plot generated from all available data on UDMH-DETA-CH_3CN blends (Section 3.7) suggests that the density of MAF-5 is approximately the mean of the above two blends, or approximately equal to that of MAF-1. A provisional value of 0.868 ±0.003 g/cc at 25 C is adopted for this work based on averaging of the density reported for the above two blends with the adopted value for MAF-1 (see Section 2.10).

2.12.3.3 Viscosity of Liquid MAF-5

No experimental data were reported. A highly provisional value of absolute viscosity at -65 F (-54 C) of 60 ±10. Centipoise has been adopted from inspection of the ternary plot in Section 3.7. The viscosity of MAF-5 is expected to be similar to MAF-4.

2.12.4 CHEMICAL PROPERTIES OF MAF-5

No data are available. As in the case of MAF-1, the constituents will be the determining factor in chemical behavior.

2.12.5 THERMODYNAMIC PROPERTIES OF MAF-5

No data are available.

2.12.6 LOGISTICS OF MAF-5

MAF-5 is not available as such. and no specifications exist covering its procurement. Cost and availability may be determined from its constituents, plus blending. Blending may be accomplished by simple mixing of the ingredients under a nitrogen atmosphere. The proportions of ingredients, by weight, are:

Diethylenetriamine:	50.5%
1,-dimethylhydrazine:	29.5%
Acetonitrile (CH_3CN):	20.0%

2.12.7 REFERENCES

1. Thiokol Chemical Corporation, Reaction Motors Division. Unpublished personal notes supplied to Bell Aerosystems by W. R. Marsh.

2. Thiokol Chemical Corporation, Reaction Motors Division. Unpublished data supplied to Bell Aerosystems Company by Dr. A. Beardell, 2/27/69.

2.13.1 PROPERTY SUMMARY SHEET

Chemical Name: **Monopropellant Gas Generator Propellant No. 1.** Common Name: **MGGP-1**

Empirical Formula: $N_{1.1898}H_{3.1898}O_{0.50824}$ Formula Weight: **28.014**

Composition; % b.w.: **63. N_2H_4 + 27. H_2O + 10. $N_2H_5NO_3$**

PROPERTY	VALUE	UNITS	TEMP ($^\circ$K)	REFERENCE	FIGURE
MELTING POINT	219.3 −53.9 394.67 −65	$^\circ$K $^\circ$C $^\circ$R $^\circ$F			
NORMAL BOILING POINT	387.1 114.0 696.8 237.1	$^\circ$K $^\circ$C $^\circ$R $^\circ$F		calc.	
VAPOR PRESSURE OF LIQUID	7.39 0.143	mm Hg psia	298	1	20-2
DENSITY OF LIQUID	1.063 66.37	g/cc lb/ft^3	298	1	20-2
VISCOSITY OF LIQUID	2.04 1.367×10^{-3}	centipoise $lb_m/ft\text{-}sec$	298	1	20-3
HEAT OF FORMATION	−867.1 −1560.8	cal/gram BTU/lb			

2.13.2 GENERAL

MGGP-1 was developed by NOTS (1) as a result of studies of the hydrazine-water-hydrazinium nitrate system directed toward developing a gas generator propellant with a low melting point. moderately low flame temperature and good gas generation capability.

The propellant having the designation MGGP-1 is a blend consisting nominally of 63% by weight hydrazine (N_2H_4) 27% by weight water, and 10% by weight hydrazinium nitrate ($N_2H_5NO_3$). It is a clear, hydroscopic liquid at room temperature having the characteristic odor of hydrazine. No government specification has been generated for this monopropellant, since it is believed to be mainly in the experimental stage. The only data available on MGGP-1 pertain to its vapor pressure, boiling point, melting point, density, viscosity, and heat of formation.

2.13.3 PHYSICAL PROPERTIES OF MGGP-1

2.13.3.1 Vapor Pressure and Normal Boiling Point.

The vapor pressure of liquid MGGP-1 has been experimentally determined by the Reaction Motors Division of Thiokol. and reported by NOTS (1). The experimental data were obtained over a temperature range from 10 to 93 C (50 to 200 F). The data points are plotted in Figures 2.13-1 and 2.13-1a. The experimental data are adequately defined as a function of temperature for the range of the study by the classical relation.

$$\log P\,(\text{mm Hg}) = 9.6250 - \frac{2610.67}{T,{}^\circ K} \qquad (2.13\text{-}1)$$

$$\log P\,(\text{psia}) = 7.91131 - \frac{4.699.20}{T,{}^\circ R} \qquad (2.13\text{-}1a)$$

The standard deviation of the experimental data from the calculated smoothed data is 7.8 mm Hg while the average deviation was 3.3%.

RMD used an all glass isoteniscope with a double-armed mercury manometer. The mercury level was read with a cathetometer. The constant temperature bath was controllable to ±0.05 C. The composition of the blend as determined by gas chromatography was given as 62.8 N_2H_4 + 10.3 $N_2H_5NO_3$ + 26.8 H_2O by weight %.

From equation 2.13-1, an extrapolated value of 387.1 K or 114 C (237.1 F) was obtained for the normal boiling point of the blend. The boiling point range does not appear in the literature.

2.13.3.2 Density of Liquid MGGP-1

The density of liquid MGGP-1 has been experimentally determined by Reaction Motors Div. of Thiokol over a temperature range from -54 to 93 C (-65 to 199 F). The experimental data are plotted in Figures 2.13-2 and 2.13-2a. The data are a linear function of temperature

$$\rho\,(\text{g/cc}) = 1.2779 - 7.2032 \times 10^{-4}\,(T,{}^\circ K) \qquad (2.13\text{-}2)$$

$$\rho\,(\text{lb/ft}^3) = 79.778 - 0.024982\,(T,{}^\circ R) \qquad (2.13\text{-}2a)$$

The standard deviation of the experimental data as expressed by equation 2.13-2 is 0.0011 g/cc while the average deviation is 0.075%.

A glass pycnometer consisting of a 20 cc reservoir attached to a one millimeter ID graduated capillary tube was used by RMD. The measurements had a reported accuracy of ±0.001 g/cc. The MGGP-1 sample had a weight % composition of 62.8 N_2H_4 + 10.3 $N_2H_5NO_3$ + 26.8 H_2O as determined by gas chromatography.

2.13.3.5 Viscosity of Liquid MGGP-1

The absolute viscosity of liquid MGGP-1 has been studied by Reaction Motors Div. of Thiokol over a temperature range from -54 to 93 C (-65 to 199 F). The experimental data have been reported by NOTS (1) and are plotted in Figures 2.13-3 and 2.13-3a. The change in viscosity due to its temperature dependence can be expressed by:

$$\log \mu\,(\text{centipoise}) = -12.4093 + \frac{1.0069 \times 10^4}{T,{}^\circ K} - \frac{2.8520 \times 10^6}{(T,{}^\circ K)^2} + \frac{2.9235 \times 10^8}{(T,{}^\circ K)^3} \qquad (2.13\text{-}3)$$

$$\log \mu\,(\text{lb}_m/\text{ft-sec}) = -15.5820 + \frac{1.8123 \times 10^4}{T,{}^\circ R} - \frac{9.2404 \times 10^6}{(T,{}^\circ R)^2} + \frac{1.7050 \times 10^9}{(T,{}^\circ R)^3} \qquad (2.13\text{-}3a)$$

Equation 2.13-3 fits the data quite well with the exception of the data point at the freezing point. Even a fourth-order polynomial did not significantly improve the deviation.

RMD used standard Cannon-Zhukov viscometers. Three separate viscometers were employed depending upon the temperature range. By changing viscometers. the efflux time was kept between 100 and 300 seconds to insure the highest accuracy.

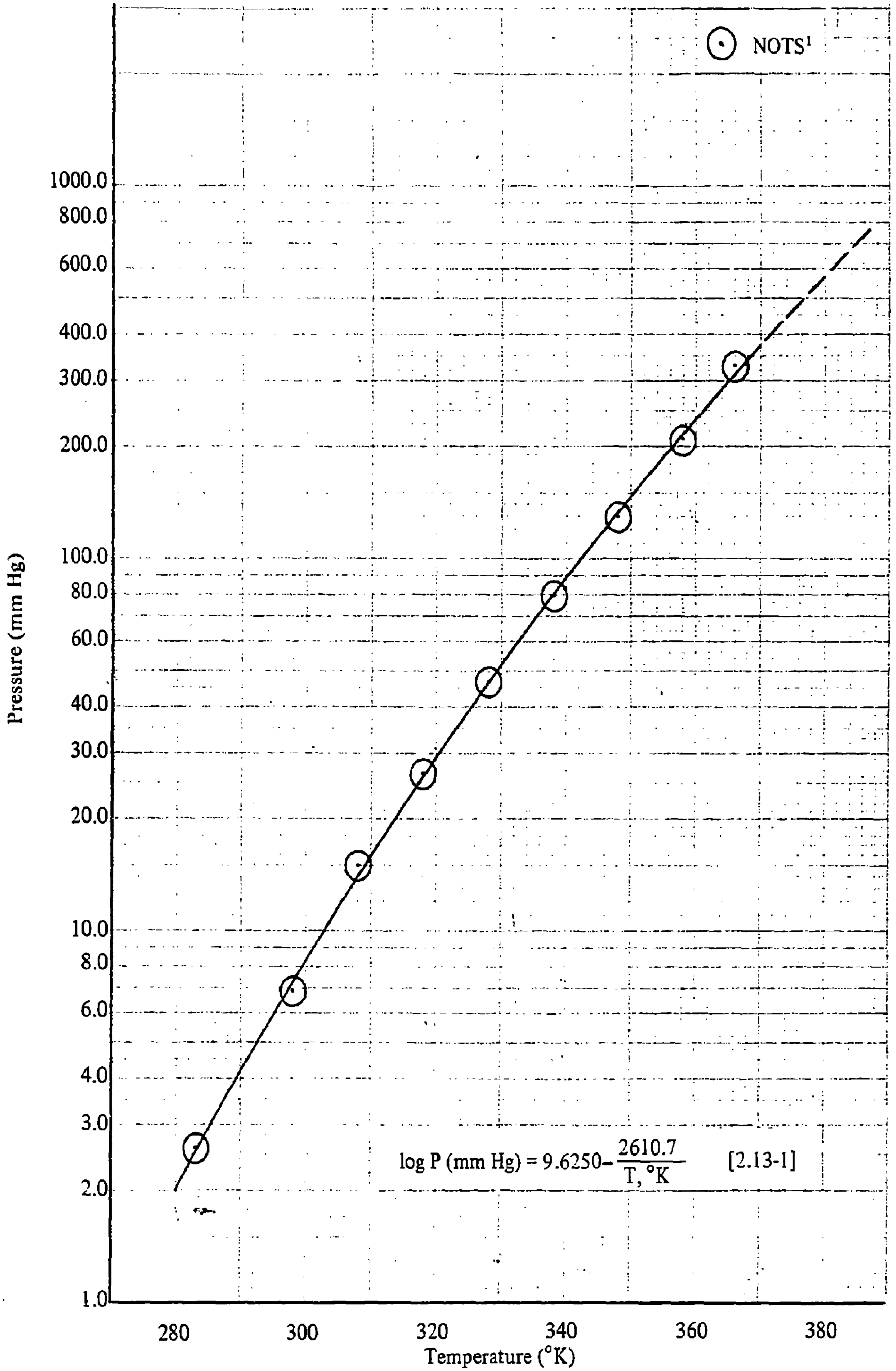


Figure 2.13-1. Vapor Pressure versus Temperature, Liquid MGGP-1

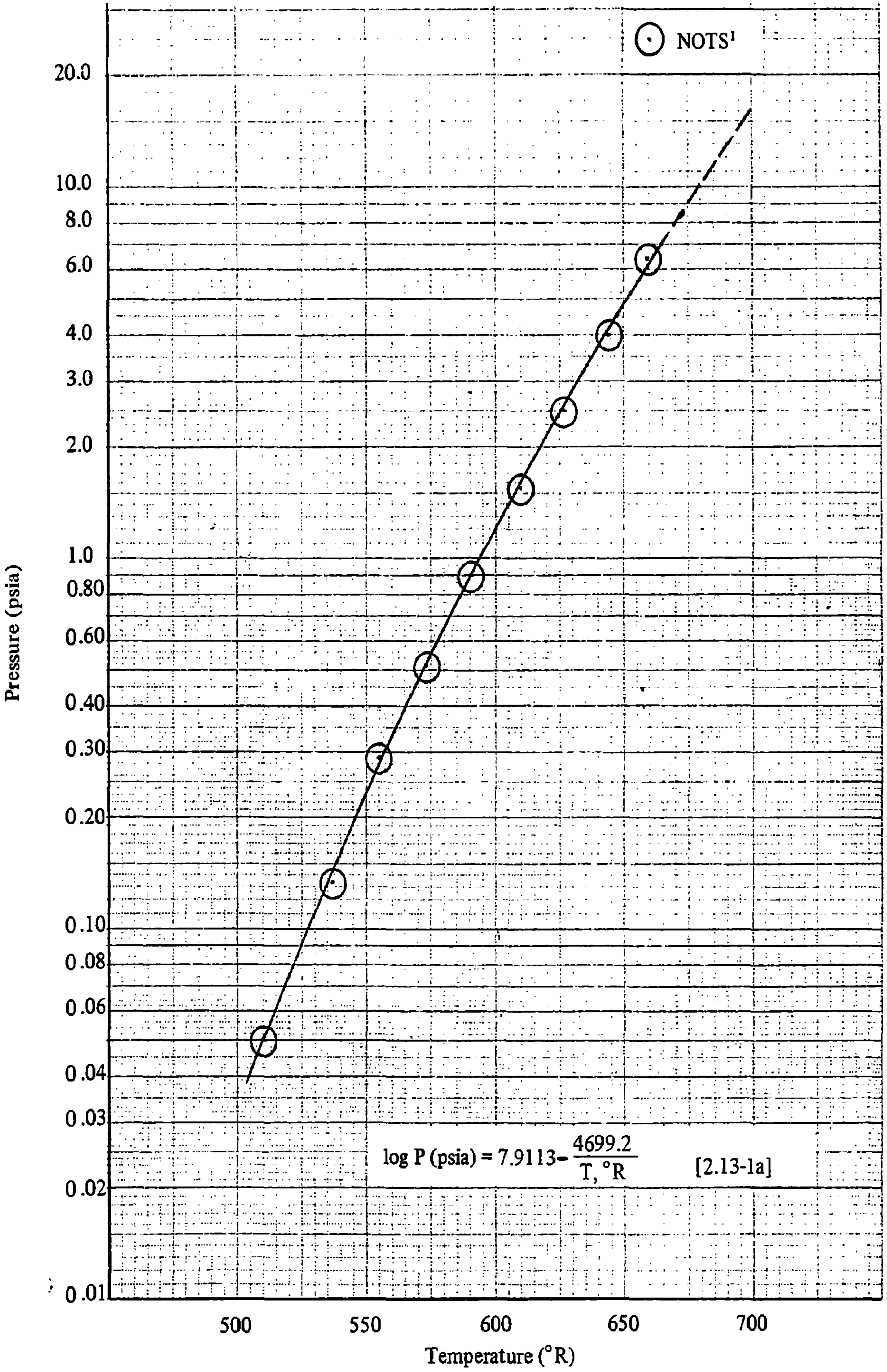


Figure 2.13-1a. Vapor Pressure versus Temperature, Liquid MGGP-1

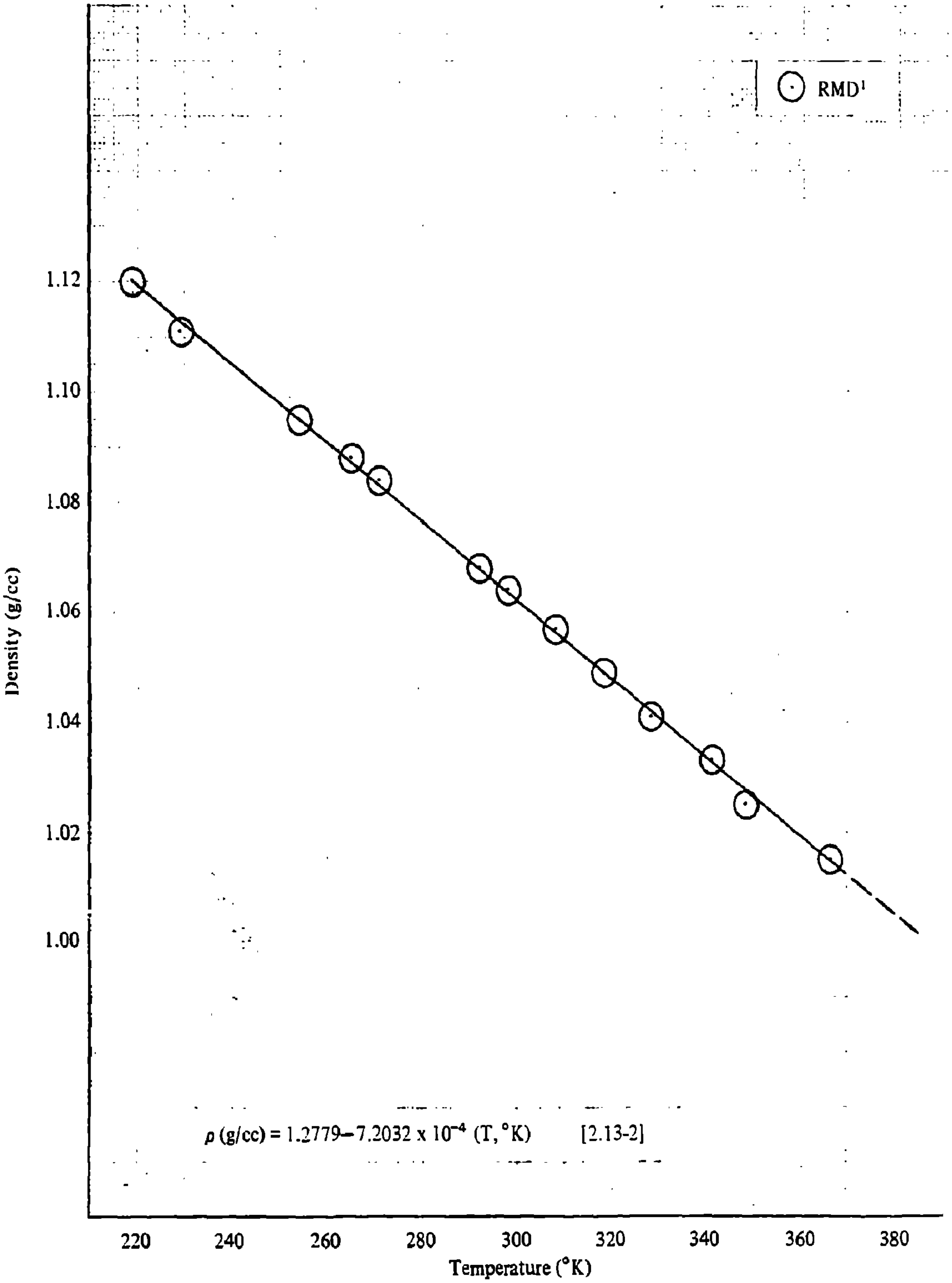


Figure 2.13-2. Density versus Temperature, Liquid MGGP-1

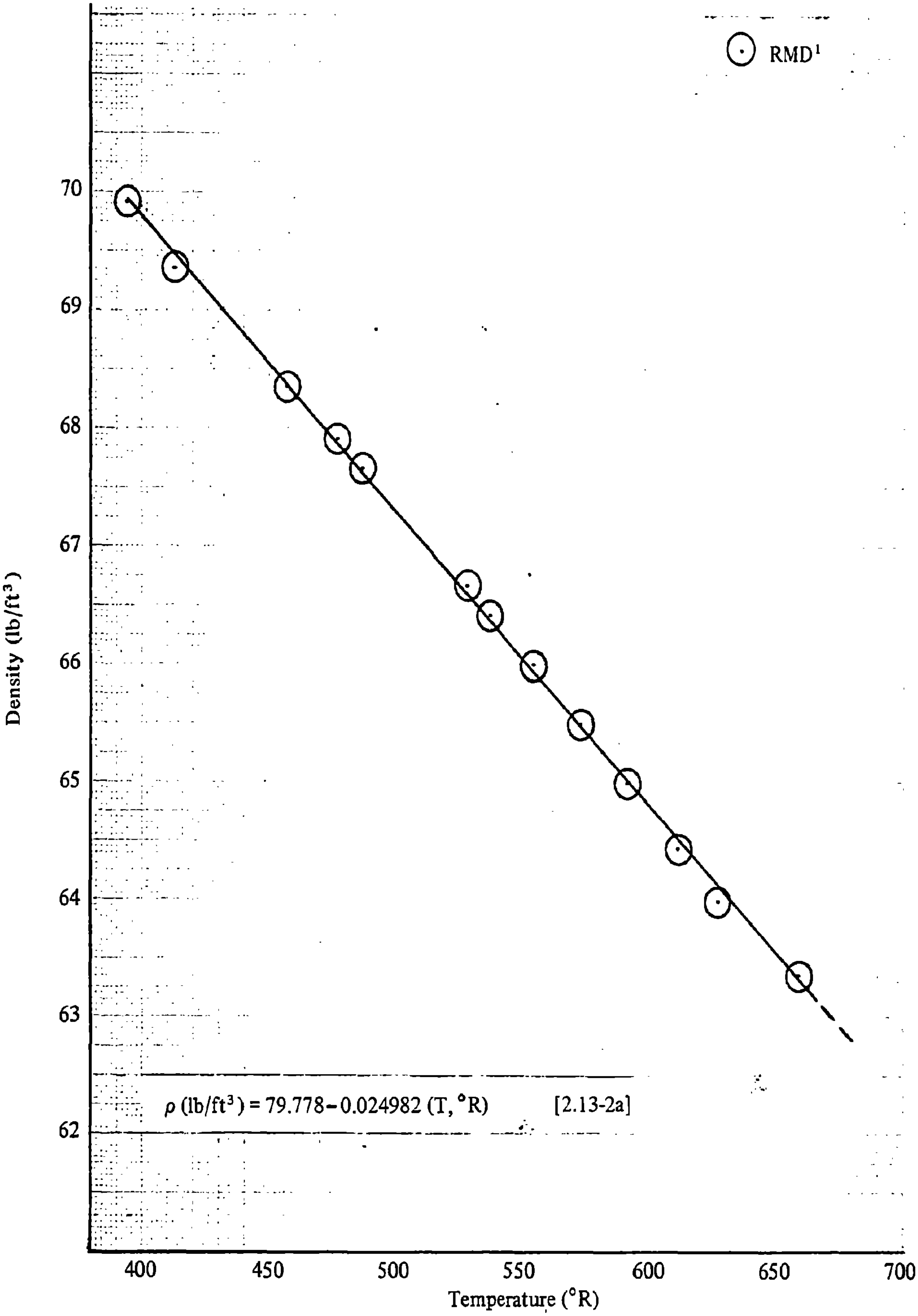
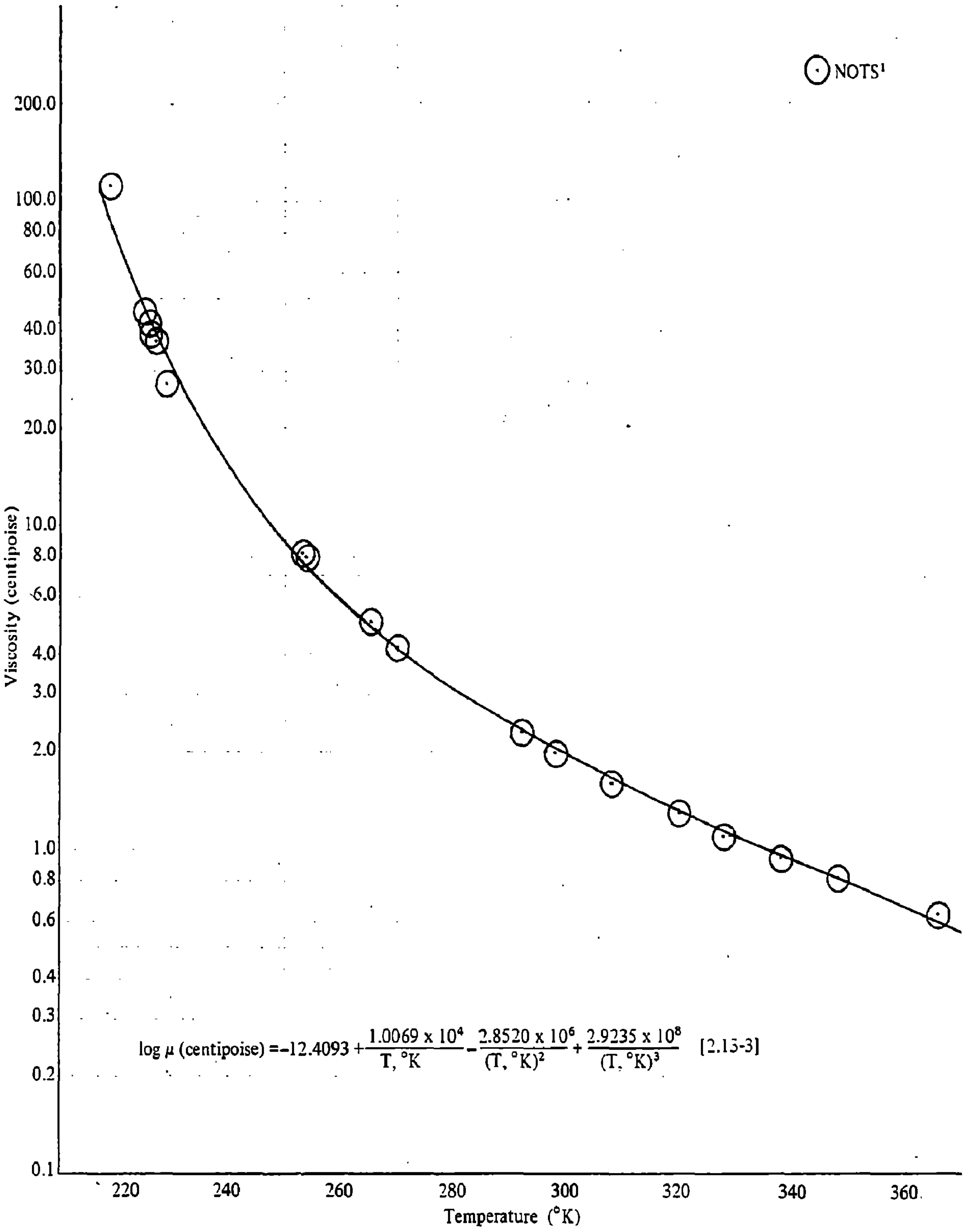
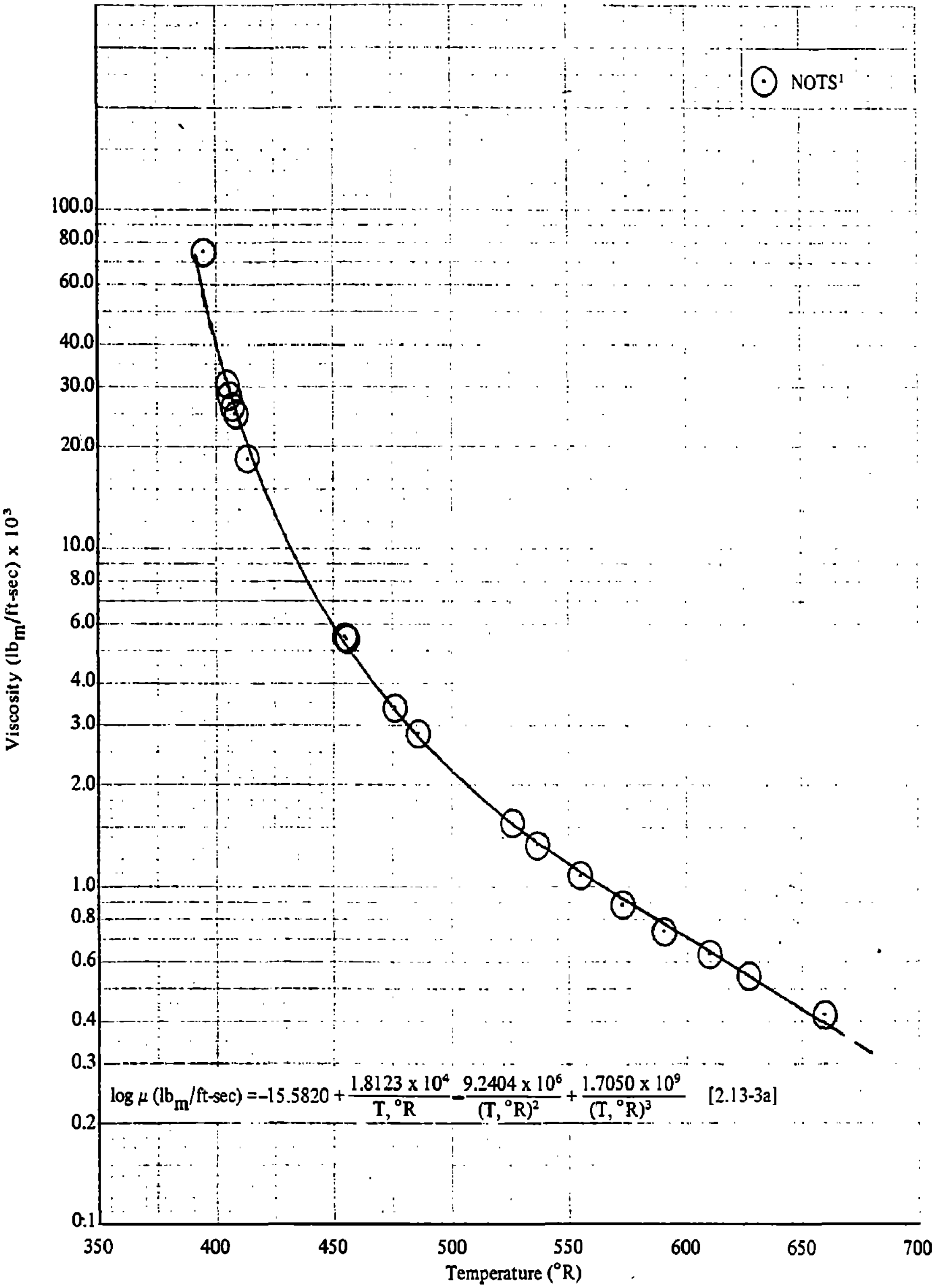


Figure 2.13-2a. Density versus Temperature, Liquid MGGP-1



$$\log \mu \text{ (centipoise)} = -12.4093 + \frac{1.0069 \times 10^{4}}{T, {}^{\circ}K} - \frac{2.8520 \times 10^{6}}{(T, {}^{\circ}K)^{2}} + \frac{2.9235 \times 10^{8}}{(T, {}^{\circ}K)^{3}} \qquad [2.13\text{-}3]$$

Figure 2.13-3. Absolute Viscosity versus Temperature, Liquid MGGP-1



$$\log \mu\ (lb_m/\text{ft-sec}) = -15.5820 + \frac{1.8123 \times 10^4}{T, {}^\circ R} - \frac{9.2404 \times 10^6}{(T, {}^\circ R)^2} + \frac{1.7050 \times 10^9}{(T, {}^\circ R)^3} \qquad [2.13\text{-}3a]$$

Figure 2.13-3a. Absolute Viscosity versus Temperature Liquid MGGP-1

2.13.5 THERMODYNAMIC PROPERTIES OF MGGP-1

2.13.5.1 Heat of Formation of the Liquid

The heat of formation of this mixture has not been experimentally studied. For the purposes of determining theoretical performance data, the heat of formation can be estimated by the molar addition of the individual heats of formation. It was assumed that the available water would form hydrazine hydrate and that the heat of mixing (except for the $N_2H_4.H_2O$) would be negligible.

The calculated value is -24.2922 kcal/mole where a mole is defined as having the empirical formula:

$$N_{1.1898}H_{3.1898}O_{0.50824}$$

with a formula weight of 28.014 grams. The heat of formation of the liquid at 298.15 K (25 C) per gram of propellant is -867.1 cal/g. The derivation is given below and is based on nominal composition (weight %) of 63 N_2H_4, 27 H_2O, and 10 $N_2H_5NO_3$.

Starting with exactly 100 grams of the ternary mixture, the following mole fractions are calculated:

Compound	Wt. (grams)	Mole Weight	Moles	Mole Fraction
N_2H_4	63	32.048	1.965801	0.550697
H_2O	27	18.016	1.498668	0.419835
$N_2H_5 \cdot NO_3$	10	95.064	0.105192	0.029468
			3.569661	1.000000

Combining the available H_2O with the hydrazine we have:

Compound	Mole Fraction	ΔH_{f298} (kcal/mole)
N_2H_4	0.130862	12.054
$N_2H_4 \cdot H_2O$	0.419835	-58.01
$N_2H_5NO_3$	0.029468	-51.41

ΔH_{f298} = 0.130862 (12.054) + 0.419835 (-58.01) + 0.029468 (-51.41)

ΔH_{f298} = -24.2922 kcal/mole, mole = 28.014 grams

ΔH_{f298} = 867.1 cal/gram

The heat of formation of N_2H_4 is discussed in Section 2.3.5.1 and the values for the hydrate and nitrate were taken from Wagman (2).

2.13.7 REFERENCES

1. Dake, J.O., "Catalytic Monopropellant Decomposition of Hydrazine Blend Fuels at -65 F, NOTS report TP 4141, U.S. Naval Ordnance Test Station, China Lake, California, October 1966.

2. Wagman, D. D. et al., "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-1, U.S. Dept. of Commerce, Washington, D.C., October 1965.

2.14 MHF-1

Chemical Name: Mixed Hydrazine Fuel No. 1
Common Name: MHF-1
Empirical Formula: $C_{0.48183}H_{5.12553}N_{2.16187}O_{0.48562}$
Formula Weight: 49.007
Composition; % b.w.: 45.3 MMH + 31.4 $N_2H_5NO_3$ + 23.3 N_2H_4

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	219.26	°K			
	-54	°C			
	394.67	°R			
	-65	°F			
NORMAL BOILING POINT	364.15	°K			
	91.0	°C		4	
	655.47	°R			
	195.8	°F			
DENSITY OF LIQUID	1.083	g/cc	298	1	9-2
	67.61	lb/ft^3			
VAPOR PRESSURE OF LIQUID	27.98	mm Hg	298	1	9-1
	0.54	psia			
VISCOSITY OF LIQUID	3.92	centipoise	298	1	9-3
	2.64×10^{-3}	lb_m/ft-sec			
HEAT OF FORMATION	46.683	cal/g	298		
	84.029	BTU/lb			

2.14.2 GENERAL

MHF-1 or mixed hydrazine fuel No. 1 is the most energetic fuel blend in the mixed hydrazine family due to the high percentage of hydrazinium nitrate ($N_2H_5NO_3$).

The nominal composition of this blend is as follows:

Compound	Formula	Weight %
Monomethylhydrazine (MMH)	$N_2H_3CH_3$	45.3
Hydrazinium Nitrate (HN)	$N_2H_5NO_3$	31.4
Hydrazine	N_2H_4	23.3

The composition of this blend was arrived at by RMD(1) from a desire to maintain an equimolar balance between carbon from the MMH and oxygen from the HN, and to provide as much hydrazine as possible in a blend with a–65 F melting point.

MHF-1, along with the other hydrazinium nitrate containing blends, has been proposed both as a fuel and as a monopropellant gas generant in prepackaged liquid propulsion systems. It was dropped from consideration due to its high rate of pressure buildup during hermetic storage and also due to its high viscosity, and its tendency to explode in open-cup burning tests.

MHF-1 is a clear, colorless, hygroscopic liquid at room temperature. It gives off an ammoniacal odor characteristic of the hydrazines.

2.14.3 PHYSICAL PROPERTIES OF MHF-1

2.14.3.1 Vapor Pressure

The vapor pressure of liquid MHF-1 has been reported by RMD(1) over a temperature range from–44.5 to 70 C (-48.1 to 158 F). Additional measurements were also given by RMD(2) over a temperature range from 25 to 70 C (77 to 158 F). The experimental data from the two references shows considerable scatter as shown by Figure 2.14-1 and 2.14-1a. Because of this scatter conventional vapor pressure equations represented the data poorly. The logarithm of pressure as a linear expression of temperature gave the best results.

$$\log P\,(\text{mmHg}) = -4.7576 + 0.02081\,(T, {}^\circ K) \qquad (2.14\text{-}1)$$

$$\log P\,(\text{psia}) = -6.4713 + 0.01156\,(T, {}^\circ R) \qquad (2.14\text{-}1a)$$

The vapor pressure of liquid MHF-1 reported here should be treated as provisional data.

2.14.3.2 Density of Liquid MHF-1

The density of liquid MHF-1 has been reported by RMD(1) over a temperature range from–55 to 70 C (-67 to 158 F). The experimental data is shown in Figures 2.14-2 and 2.14-2a. The density is well described as a linear function of temperature

$$\rho\,(\text{g/cc}) = 1.3196 - 7.9341 \times 10^{-4}\,(T, {}^\circ K) \qquad (2.14\text{-}2)$$

$$\rho\,(\text{lb/ft}^3) = 82.381 - 0.02752\,(T, {}^\circ R) \qquad (2.14\text{-}2a)$$

The standard deviation of the experimental data from that described by equation 2.14-2 is 0.0014 g/cc with the average percent deviation being 0.1 percent.

RMD used a graduated precision bore capillary tube attached to a 10 ml bulb. The sample composition by weight was 45.7% MMH, 31.0% $N_2H_5NO_3$ and 23.3% N_2H_4 which is very close to the nominal composition.

2.14.3.5 Viscosity of Liquid MHF-1

The kinematic viscosity of liquid MHF-1 has been studied by RMD(1) over a temperature range from–55 to 70 C (-67 to 158 F). At each temperature the density was also measured and is shown in Figure 2.14-2. Using these density values, the absolute viscosities were calculated and are shown in Figures 2.14-3 and 2.14-3a.

The variation of viscosity with temperature is adequately described by

$$\log \mu\,(\text{centipoise}) = -14.113 + \frac{1.1492 \times 10^4}{T, {}^\circ K} - \frac{3.2505 \times 10^6}{(T, {}^\circ K)^2} + \frac{3.3736 \times 10^8}{(T, {}^\circ K)^3} \qquad (2.14\text{-}3)$$

$$\log \mu\,(\text{lb}_m/\text{ft-sec}) = -17.286 + \frac{2.0686 \times 10^4}{T, {}^\circ R} - \frac{1.0532 \times 10^7}{(T, {}^\circ R)^2} + \frac{1.9675 \times 10^9}{(T, {}^\circ R)^3} \qquad (2.14\text{-}3a)$$

RMD used a modified capillary viscometer and an accuracy of ±1% was obtained. The composition by weight of the fuel blend sample was 45.7% MMH, 31.0% $N_2H_5NO_3$ and 23.3% N_2H_4 which is very close to the nominal composition.

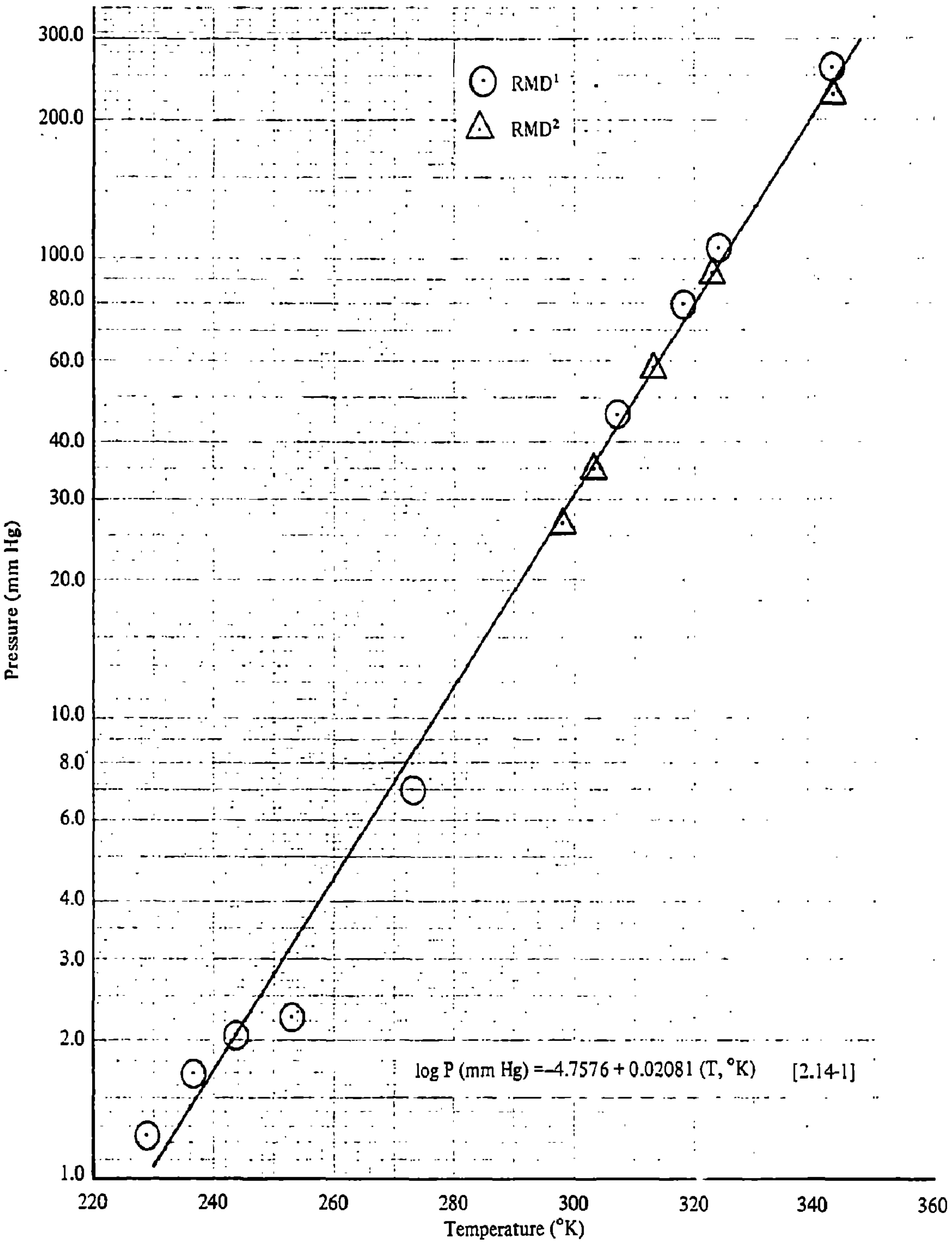
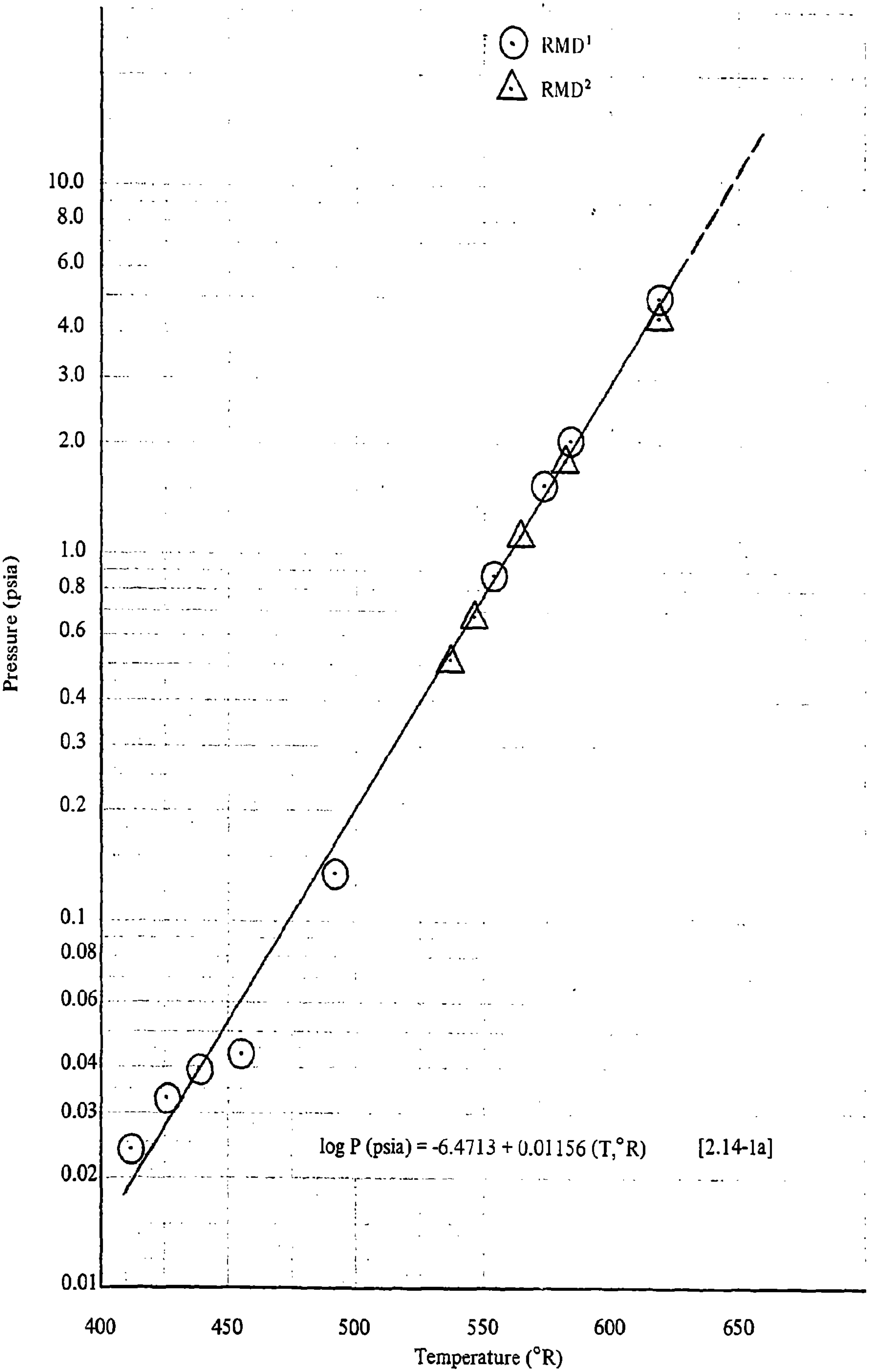


Figure 2.14-1. Vapor Pressure versus Temperature, Liquid MHF-1



$$\log P \text{ (psia)} = -6.4713 + 0.01156 \, (T, {}^\circ R) \qquad [2.14\text{-}1a]$$

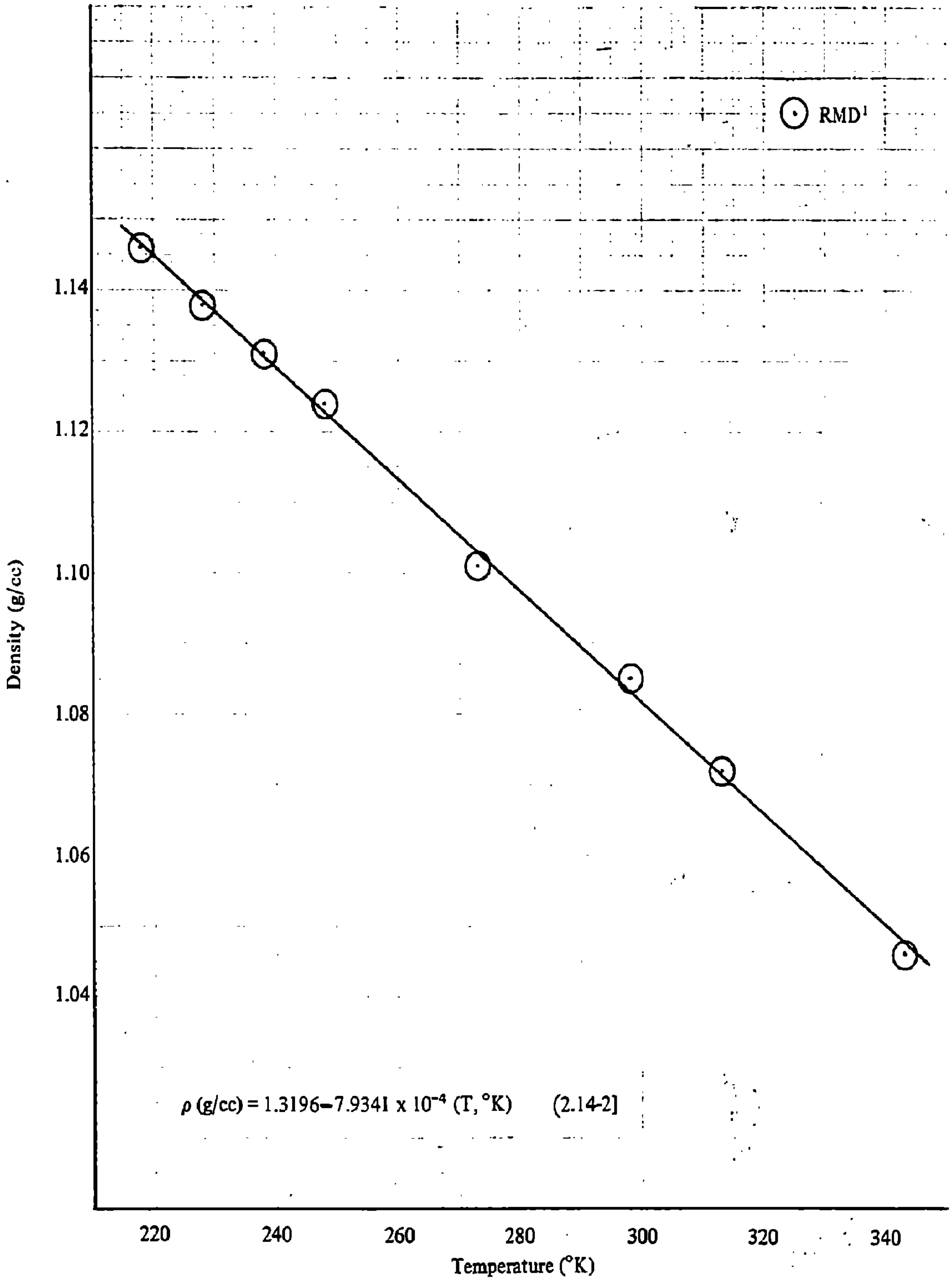


Figure 2.14-2. Density versus Temperature, Liquid MHF-1

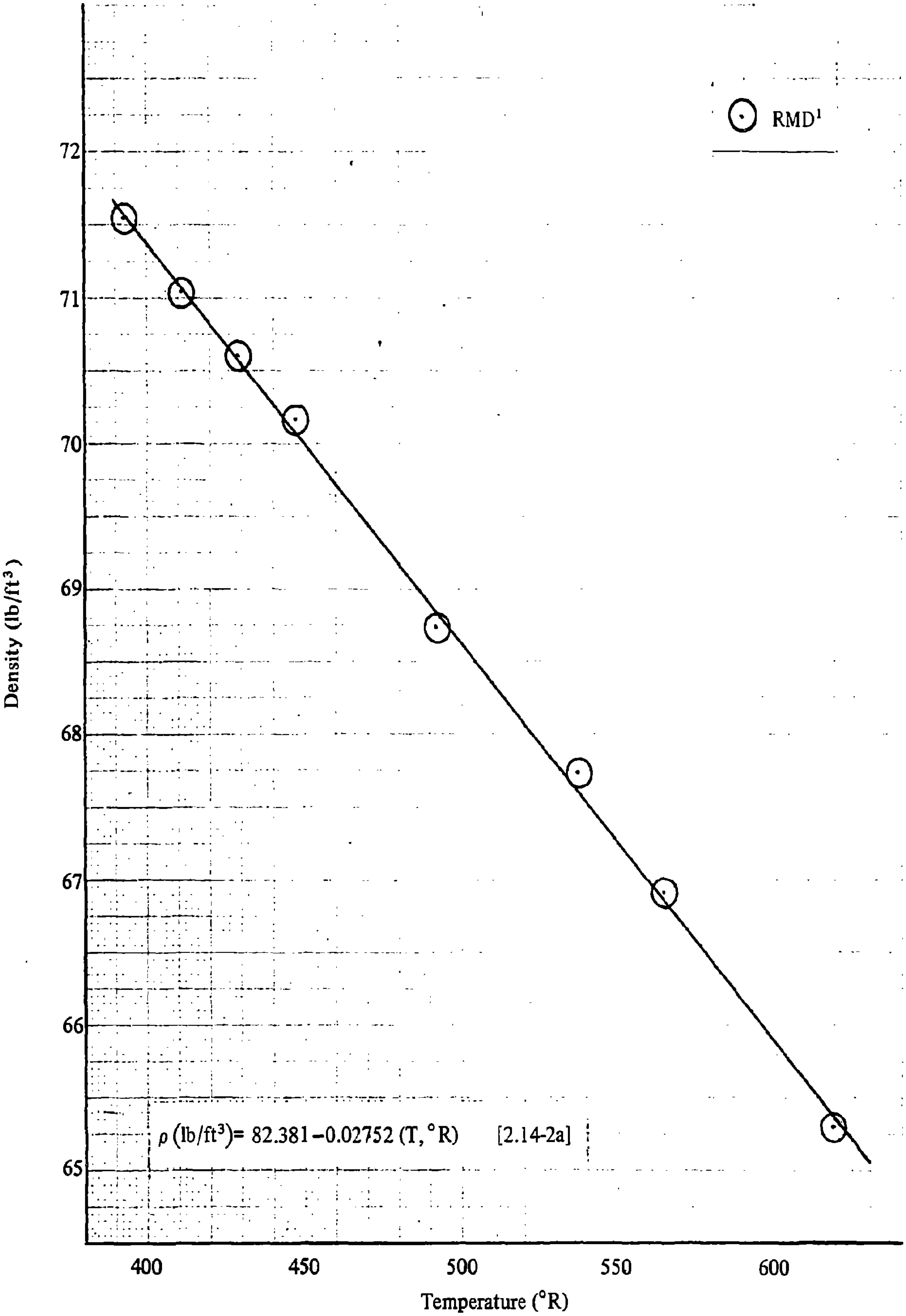


Figure 2.14-2a. Density versus Temperature; Liquid MHF-1

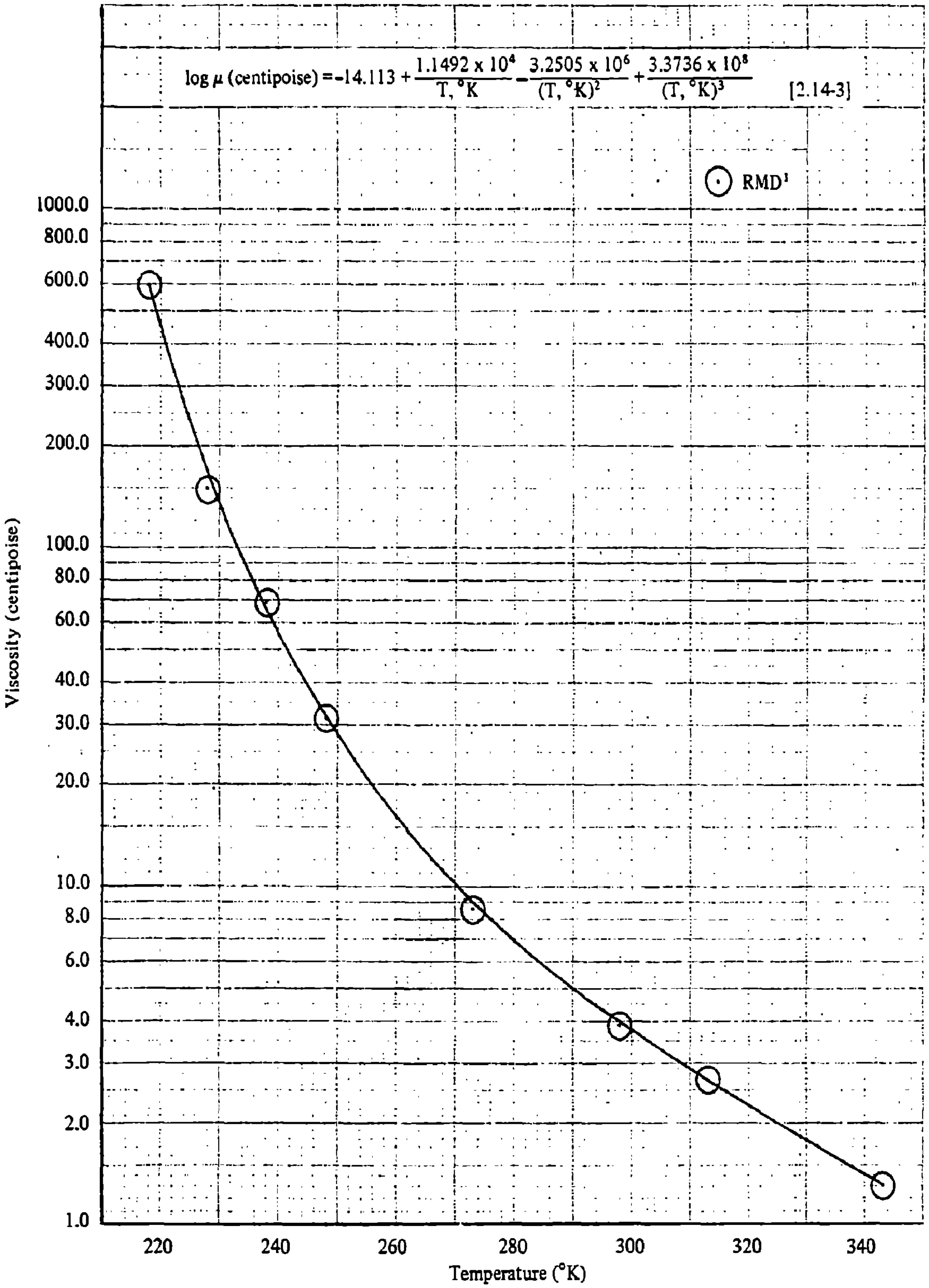
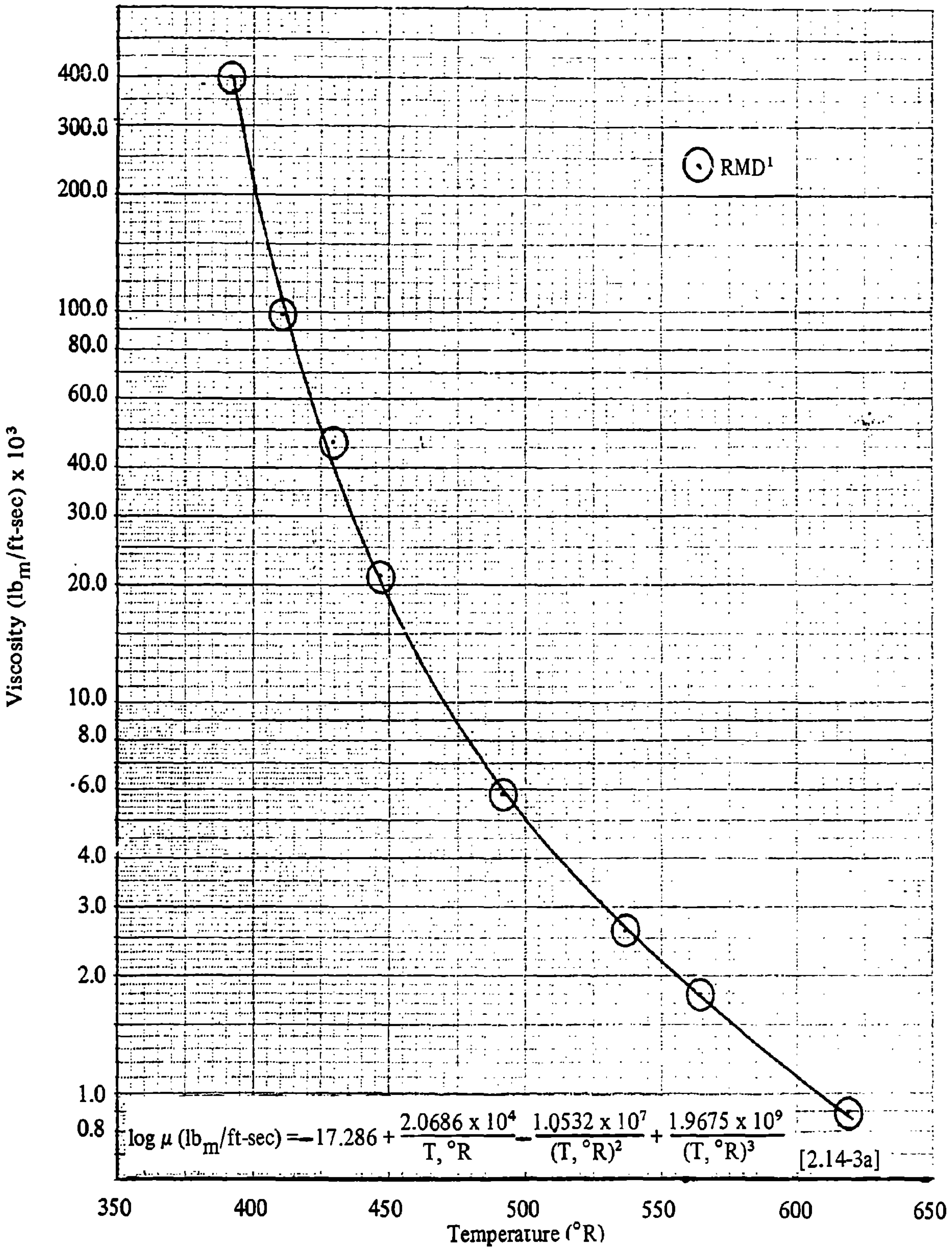


Figure 2.14-3. Absolute Viscosity versus Temperature, Liquid MHF-1



$$\log \mu \ (\mathrm{lb_m/ft\text{-}sec}) = -17.286 + \frac{2.0686 \times 10^4}{T, {}^\circ R} - \frac{1.0532 \times 10^7}{(T, {}^\circ R)^2} + \frac{1.9675 \times 10^9}{(T, {}^\circ R)^3} \qquad [2.14\text{-}3a]$$

Figure 2.14-3a. Absolute Viscosity versus Temperature, Liquid MHF-1

2.14.4 CHEMICAL PROPERTIES OF MHF-1

2.14.4.1 Chemical Reactions

In addition to the reactions common to hydrazine and methylhydrazine (see sections 2.3.4.1 and 2.4.4.1), MHF-1 is also capable of reactions involving the hydrazinium nitrate component. When hydrazinium nitrate is added to MMH, an equilibrium reaction occurs in the solution in which methylhydrazine nitrate is formed. Much of the hydrazinium nitrate is ionized in solution according to:

$$N_2H_5NO_3 \overset{N_2H_4}{\rightleftharpoons} N_2H_5^+ + NO_3^-$$

The hydrazinium nitrate solutions are very reactive with some metals, particularly zinc and copper. These solutions will also react with oxidizing agents such as permanganates, chromates and peroxides more readily than hydrazine alone.

2.14.4.2 Inert Gas Solubility

No data have been reported on solubility of inert gases in MHF-1.

2.14.5 THERMODYNAMIC PROPERTIES OF MHF-1

2.14.5.1 Heat of Formation of Liquid

The heat of formation of this fuel blend can be calculated for the liquid by the molar addition of the individual heats of formation. The heat of mixing is not known and is assumed to be negligible. Taking the nominal composition to be 45.3% $CH_3N_2H_3$ 23.3% N_2H_4 and 31.4% $N_2H_5NO_3$, the heat of formation at 298.15 K (25 C) is 2.2878 kcal/-mole. The mole is defined as 49.007 grams with the empirical formula

$$C_{0.48183}H_{5.12553}N_{2.16187}O_{0.485619}$$

Compound	Weight %	Mole Fraction (1 Mole Blend)	ΔH_{f298} (kcal/mole)
$CH_3N_2H_3$	45.3	0.481828	13.106
N_2H_4	23.3	0.356299	12.054
$N_2H_5NO_3$	31.4	0.161873	-51.41

For one mole of MHF-1 then,

$$\Delta H_{f298} = 0.481828\,(13.106) + 0.356299\,(12.054) + 0.161873\,(-51.41)$$

ΔH_{f298} = 2.2878 kcal/mole, (mole = 49.007 grams)

or 46.683 cal/gram.

The heats of formation used for N_2H_4 and MMH are described in sections 2.3.5.1 and 2.4.5.1, respectively. The value for $N_2H_5NO_3$ was taken from Wagman, et al(3).

2.14.6 LOGISTICS OF MHF-1

Reaction Motors Division of Thiokol Chemical Corp. developed this fuel blend in 1958. It was found to detonate in open cup burning tests and generally has been disregarded as a possible fuel. It has never been produced except on a laboratory scale and therefore no manufacturing, analysis, cost, availability or shipping information is available.

This fuel blend is analogous to the MHF-5 fuel blend in that the same ingredients are used and the data from section 2.17.6 could be used for approximating logistical information.

2.14.7 REFERENCES

1. Reaction Motors Div. of Thiokol Chem. Corp., "High Performance Storable Liquid Propellants." Report No. 239-F, Denville, N.J., May 1959. (CONFIDENTIAL)

2. Reaction Motors Div. of Thiokol Chem. Corp., "High Performance Packageable Liquid Propellants." Report No. RMD 2004-1, Denville, N.J., December 1960. (CONFIDENTIAL)

3. Wagman, D.D. et al., "Selected Values of Chemical Thermodynamic Properties," NBS Technical Note 270-1, U.S. Dept. of Commerce, Washington, D.C., October 1965.

4. Liquid Propellants Manual, Liquid Propellant Information Agency, Applied Physics Laboratory, John Hopkins University, Silver Springs Maryland, 1967 (CONFIDENTIAL).

2.15 MHF-2

2.15.1 PROPERTY SUMMARY SHEET

Chemical Name:	**Mixed Hydrazine Fuel No. 2**	Common Name:	**MHF-2**
Empirical Formula:	$C_{0.7011} H_{5.6364} N_{2.2341} O_{0.7024}$	Formula Weight:	**56.637**

Composition; % b.w.: $37.2\ (CH_3)_2 N_2H_4 + 39.3\ N_2H_5NO_3 + 23.5\ N_2H_4$

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	219.3 –59.9 394.7 –65	°K °C °R °F			
DENSITY OF LIQUID	1.095 68.355	g/cc lb/ft^3	298	1	2.15-1
VISCOSITY OF LIQUID	6.467 4.35×10^{3}	centipoise lb_m/ft-sec	298	1	2.15-2
HEAT OF FORMATION	–47.771 –85.988	cal/g BTU/lb	298	calc.	

2.15.2 GENERAL

MHF-2 is a blend of UDMH, Hydrazine and hydrazinium nitrate first formulated by Thiokol Chemical Corp., RMD, in 1958. It was intended as a low melting point storable fuel but was found to have a higher viscosity and poor thermal stability when compared to MHF-1 and MHF-5, the corresponding MMH containing fuels. It was therefore abandoned in favor of the MMH containing counterparts. The composition, in percent by weight, is:

N_2H_4	23.3%
$N_2H_2(CH_3)_2$	36.5%
$N_2H_5NO_3$	40.2%

The physical property data available on MHF-2 is meager. Only density and viscosity were reported by RMD(1). The data should be regarded as provisional if MHF-2 is ever considered for use as a propellant.

2.15.3 PHYSICAL PROPERTIES OF MHF-2

2.15.3.1 Vapor Pressure and Normal Boiling Point

No data are available.

2.15.3.2 Density of Liquid MHF-2

The density of liquid MHF-2 has been reported by RMD(1) over a temperature range from–55 to 60 C (-67 to 140 F). The experimental data which was obtained using a precision bored capillary pycnometer is plotted in Figures 2.15-1 and 2.15-1a.

The experimental data is adequately described as a linear function of temperature:

$$\rho\,(\text{g/cc}) = 1.3201 - 7.552 \times 10^{-4}\,(\text{T, °K}) \qquad (2.15\text{-}1)$$

$$\rho\,(\text{lb/ft}^3 = 82.4119 - 0.02619\,(\text{T, °R}) \qquad (2.15\text{-}1a)$$

The standard deviation of the data as defined by equation 2.15-1 is 0.0014 g/cc with the average percent deviation being 0.085%. RMD stated that the measured densitied had an accuracy of ±0.002 g/cc. The composition was reported to be 37.2 UDMH, 39.3 $N_2H_5NO_3$ and 23.5 N_2H_4 by weight percent.

2.15.3.5 Viscosity of Liquid MHF-2

The viscosity of liquid MHF-2 has been measured by RMD(1) over a temperature range from–55 to 60 C (-67 to 140 F). A modified capillary viscometer was used and an accuracy of ±1% was claimed. The experimental data was given in kinematic units and were converted to absolute units using the density data also obtained by RMD at the same experimental temperatures. The data is shown in Figures 2.15-2 and 2.15-2a. The data can be described by:

$$\log \mu\,(\text{centipoise}) = -16.4232 + \frac{1.4392 \times 10^4}{\text{T, °K}} - \frac{4.3522 \times 10^6}{(\text{T; °K})^2} + \frac{4.7592 \times 10^8}{(\text{T, °K})^3} \qquad (2.15\text{-}2)$$

$$\log \mu\,(\text{lb}_\text{m}/\text{ft-sec}) = -19.5958 + \frac{25906 \times 10^4}{\text{T, °R}} \; \frac{-1.4111 \times 10^7}{(\text{T, °R})^2} + \frac{2.7755 \times 10^9}{(\text{T, °R})^3} \qquad (2.15\text{-}2a)$$

The average percent deviation as determined by equation 2.15-2 is 2.8%.

2.15.4 CHEMICAL PROPERTIES OF MHF-2

2.15.4.1 Chemical Reactions

In addition to the reactions common to hydrazine and UDMH (see sections 2.3.4.1 and 2.5.4.1), MHF-2 is also capable of reactions involving the hydrazinium nitrate component. When hydrazinium nitrate is added to UDMH, an equilibrium reaction occurs in the solution in which dimethylhydrazine nitrate is formed. Much of the hydrazinium nitrate is ionized in solution according to:

$$N_2H_5NO_3 \overset{N_2H_4}{\rightleftarrows} N_2H_5^+ + NO_3^-$$

The hydrazinium nitrate solutions are very reactive with some metals, particularly zinc and copper. These solutions will also react with oxidizing agents such as permanganates, chromates, and peroxides more readily than hydrazine alone.

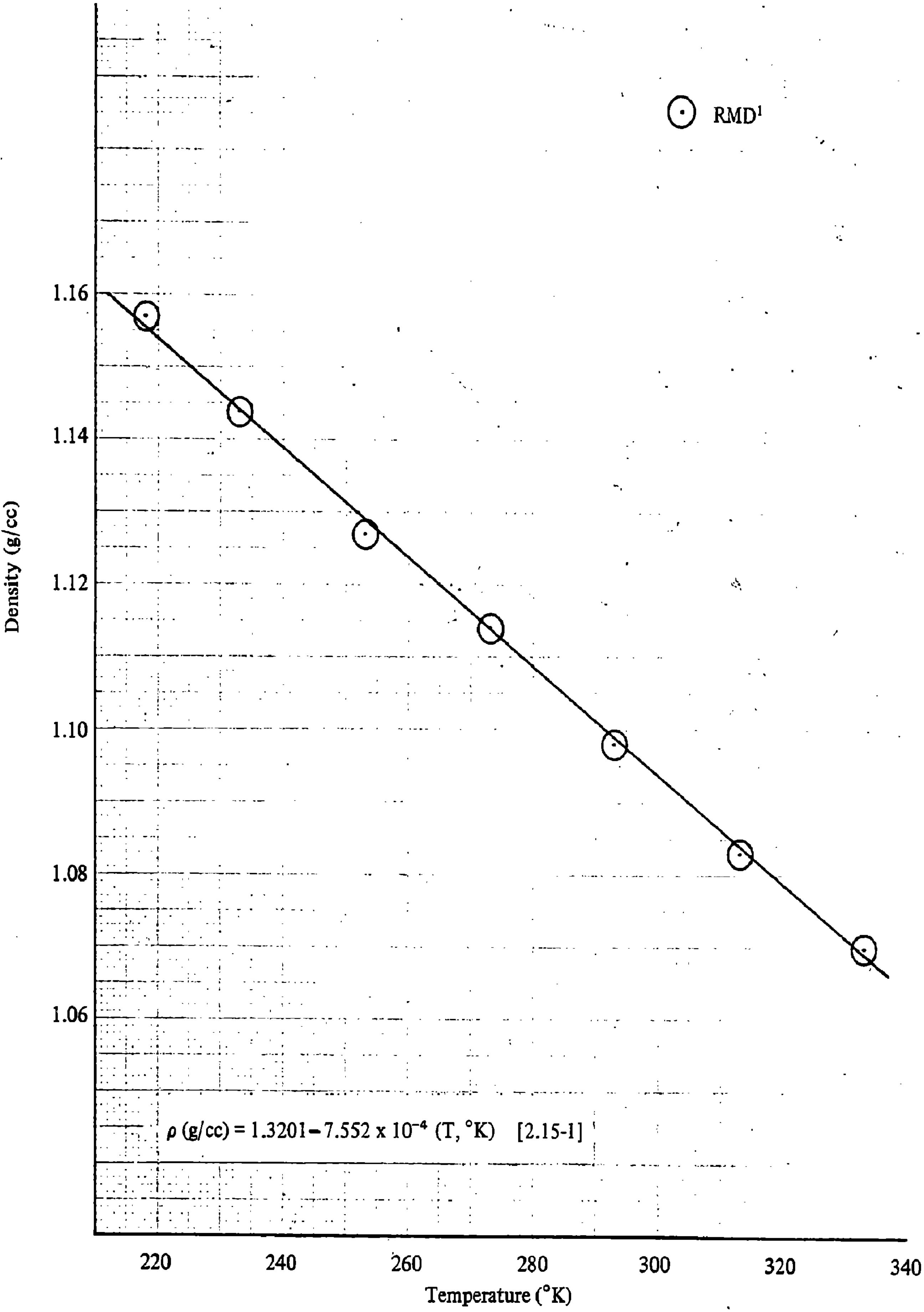
2.15.4.2 Inert Gas Solubility

No data have been reported on solubility of inert gases in MHF-2.

2.15.5 THERMODYNAMIC PROPERTIES OF MHF-2

2.15.5.1 Heat of Formation of Liquid

The heat of formation of MHF-2 fuel blend can be calculated for the liquid by the molar addition of the individual heats of formation. The heat of mixing is not known and is assumed to be negligible. Taking the nominal composition of 37.2% UDMH, 23.5% N_2H_4 and 39.3% $N_2H_5NO_3$, the heat of formation at 298.15 K (25 C) is



ρ (g/cc) = 1.3201 − 7.552 x 10^{-4} (T, °K) [2.15-1]

Figure 2.15-1. Density versus Temperature, Liquid MHF-2

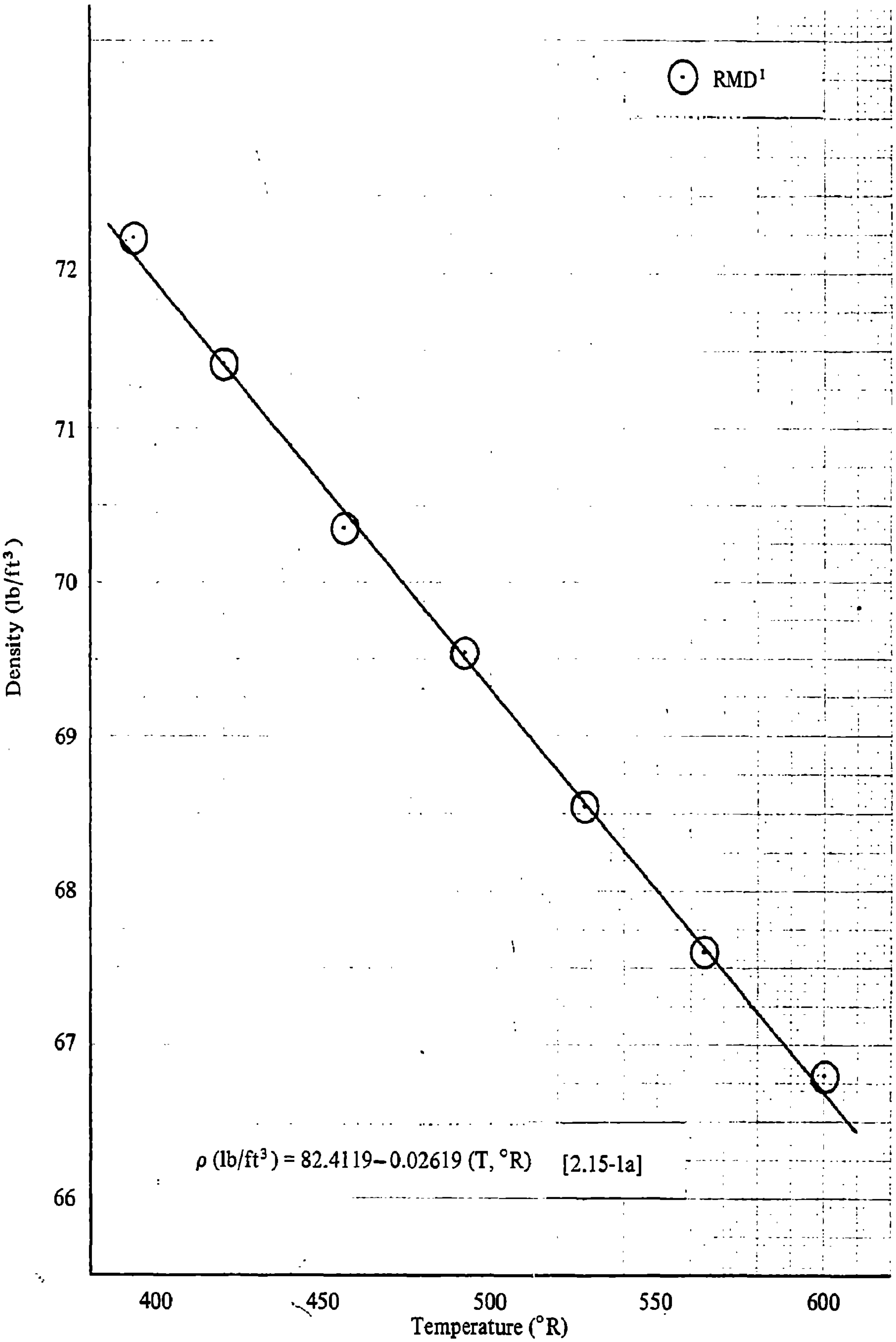


Figure 2.15-1a. Density versus Temperature, Liquid MHF-2

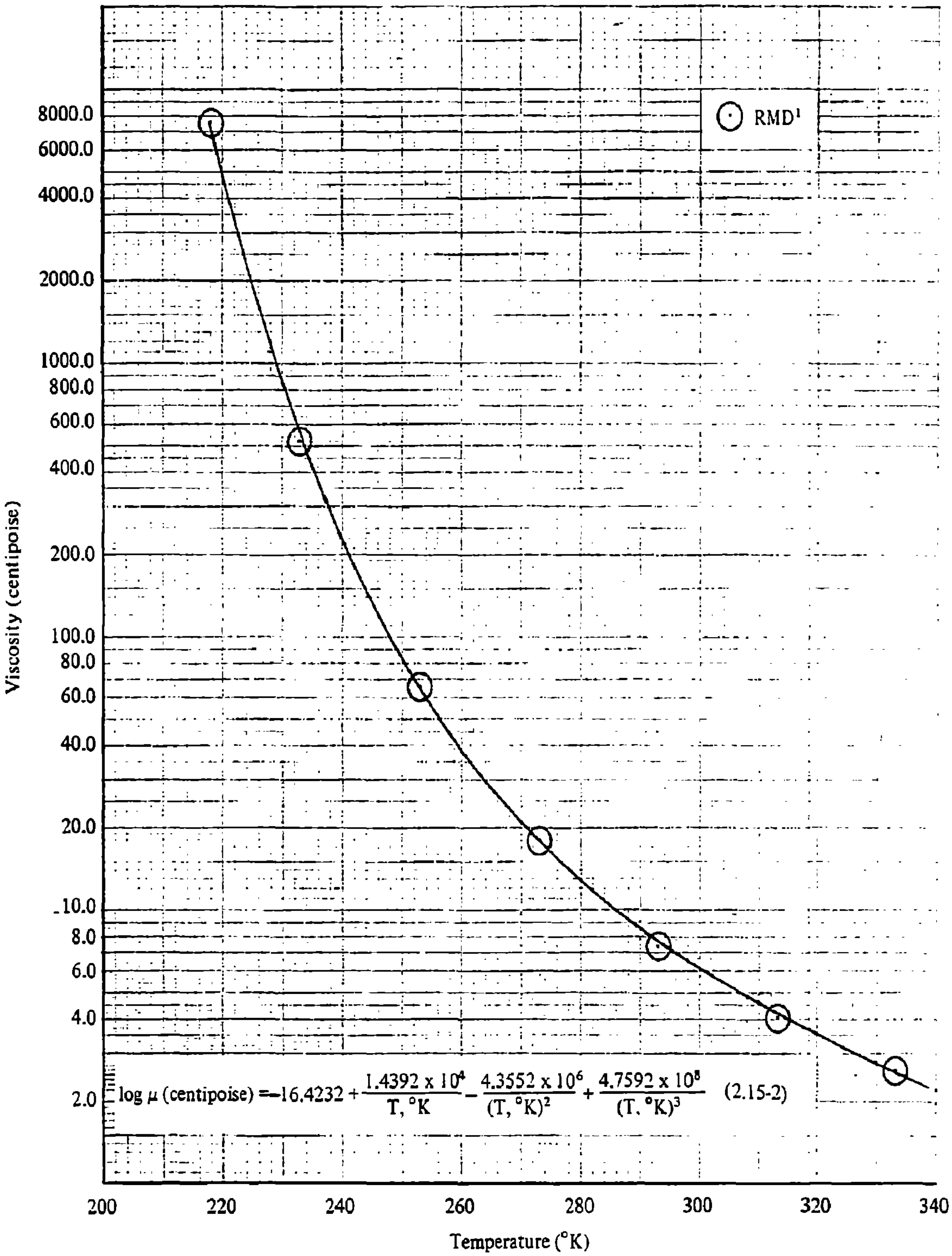


Figure 2.15-2. Absolute Viscosity versus Temperature, Liquid MHF-2

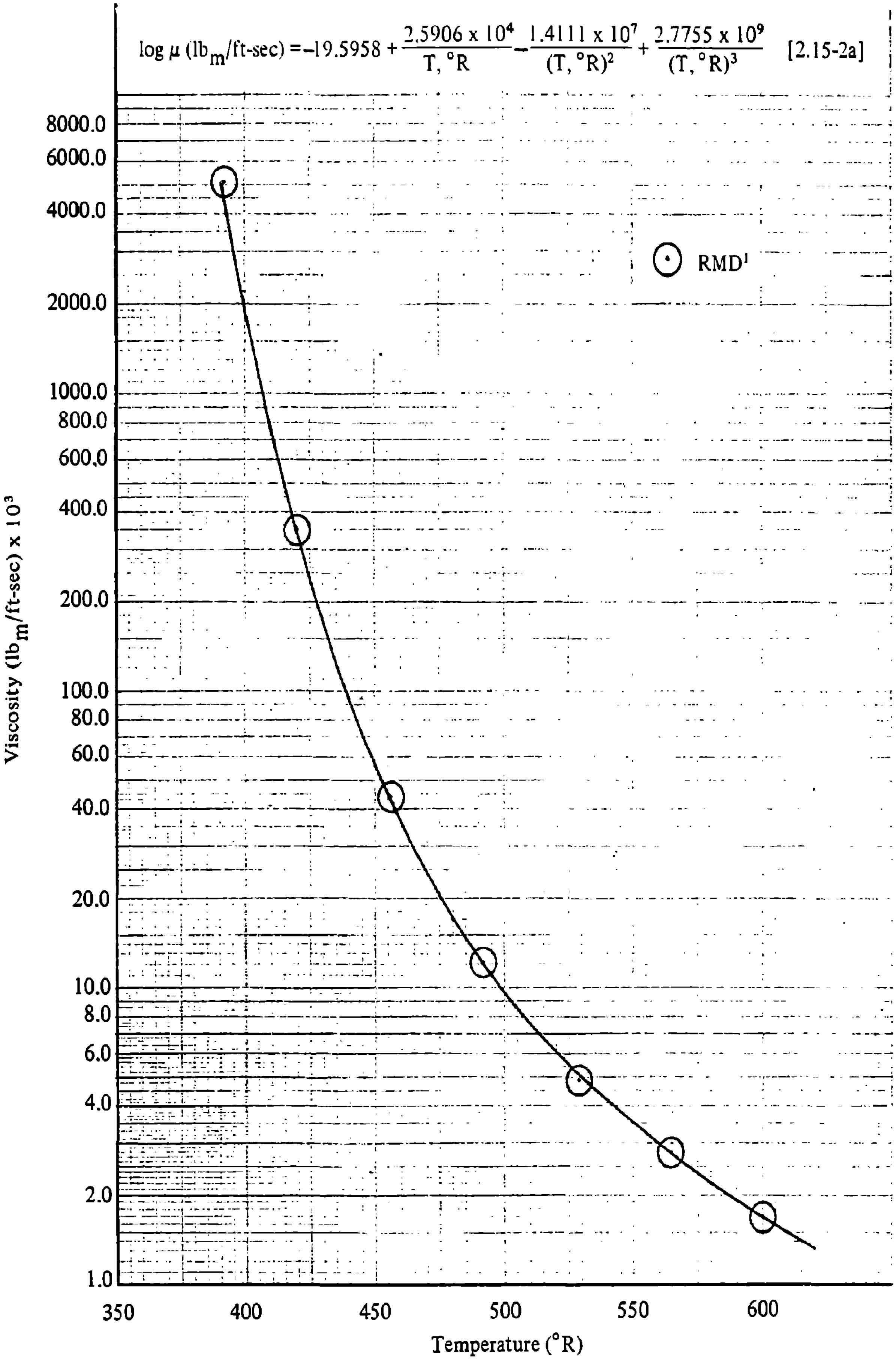


Figure 2.15-2a. Absolute Viscosity versus Temperature, Liquid MHF-2

calculated to be -2.7056 kcal/mole. The mole is defined as 56.637 grams with the empirical formula

$$C_{0.70111}H_{5.63635}N_{2.23414}O_{0.70242}$$

Compound	Weight %	Mole Fraction (1 mole blend)	ΔH_{f298} (kcal/mole)
$C_2H_8N_2$	37.2	0.350554	12.339
N_2H_4	23.5	0.415305	12.054
$N_2H_5NO_3$	39.3	0.234141	-51.41

For one mole of MHF-2 then;

$$\Delta H_{f298} = 0.350554\,(12.339) + 0.415305\,(12.054) + 0.234141\,(-51.41)$$

$$\Delta H_{f298} = -2.7056 \text{ kcal/mole, mole} = 56.637 \text{ grams or } -47.771 \text{ cal/grams}$$

The heats of formation used for N_2H_4 and UDMH are discussed in sections 2.3.5 and 2.5.5, respectively. The value for $N_2H_5NO_3$ was taken from Wagman, et al(2).

2.15.6 LOGISTICS OF MHF-2

Thiokol Chemical Company produced and evaluated MHF-2 blend in 1958 in laboratory quantity only. It was found to have a higher viscosity and lower performance than corresponding MMH containing MHF fuels and was dropped from further consideration. Therefore, no manufacturing, analysis, cost, availability, or shipping information is available or warranted for MHF-2.

2.15.7 REFERENCES

1. Reaction Motors Div., Thiokol Chem. Corp., "High Performance Storable Liquid Propellants." Report No. RMD 239-F, Denville, N.J., May 1959. (CONFIDENTIAL)

2. Wagman, D.D. et al., "Selected Values of Chemical Thermodynamic Properties," NBS Tech. Note 270-1, U.S. Dept. of Commerce, Washington, D.C., October 1965.

2.16 MHF-4

2.16.1 PROPERTY SUMMARY SHEET

Chemical Name: **Mixed Hydrazine Fuel No. 4**
Common Name: **MHF-4**
Empirical Formula: $C_{0.4788}H_{5.0358}N_{2.0781}O_{0.2344}$
Formula Weight: **43.688**
Composition; % b.w.: **50.5 MMH, 32.5 N_2H_4, 17.0 N_2H_5 NO_3**

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	236.8	°K		2	
	−36.4	°C			
	426.2	°R			
	−38	°F			
DENSITY OF LIQUID	1.007	g/cc	298	1	
	62.86	lb/ft^3			
VISCOSITY OF LIQUID	4.3	centipoise	270	1	
	2.9×10^{-3}	lb_m/ft-sec			
HEAT OF FORMATION	173.95	cal/g	298	calc.	
	313.1	BTU/lb			

2.16.2 GENERAL

MHF-4 fuel blend was first reported by RMD in Report 2004-F dated 1960(1). The nominal composition was given as 50.5% MMH, 32.5% N_2H_4 and 17% $N_2H_5NO_3$. It was thought to have a freezing point of -65 F with a low viscosity of 70 centistokes at that point. Further studies were reported in RMD Report 5005-F, dated 1962(2) where the freezing point was redetermined to be -38 F. At this point, interest in the MHF series was concentrated on MHF-5 and work on MHF-4 was discontinued.

2.16.3 PHYSICAL PROPERTIES

The only available physical property data appears to be the freezing point (-38 F), a single point determination of the density at 77 F of 1.077 g/cc, and four kinematic viscosity points.

°F	μ (centistokes)
-65	70 (supercooled)
-35	17
-4	6.8
26	4.3

The viscosity data are insufficient to warrant a curve fit.

The experimental density point is believed to be in error. A more realistic value, obtained from the ternary plot, Section 3.4.1, would be 1.007 g/cc at 25 C (77 F).

2.16.4 CHEMICAL PROPERTIES

No information on the chemical properties of MHF-4 is available. The proximity of its composition to that of MHF-5 suggests that the chemical behavior will be essentially the same as for MHF-5 which is discussed in section 2.17.4.1.

2.16.5 THERMODYNAMIC PROPERTIES

No data have been reported. The computation of heat of formation would be conducted in the same manner as for MHF-5 (Section 2.17.5.1).

2.16.6 LOGISTICS

Thiokol Chemical Corporation (RMD) produced and evaluated MHF-4 blend in laboratory quantity in 1959. Tests revealed it to have a much higher freezing point than MHF-5 and it was dropped from further consideration. Therefore, no manufacturing, analysis, cost, availability, or shipping data is available or warranted for MHF-4.

2.16.7 REFERENCES

1. Thiokol Chemical Corp., Reaction Motors Div., "High Performance Packageable Liquid Propellants," RMD Report 2004-F, Contract No. NOW 60-0106-C, 1960 (CONFIDENTIAL).
2. Thiokol Chemical Corporation, Reaction Motors Div., "Packaged Liquid Propellants (U)," RMD Report 5005-F, Contract NOw 62-0785-C, September 30, 1962 (CONFIDENTIAL).

2.17 MHF-5

CONFIDENTIAL

2.17.1 PROPERTY SUMMARY SHEET

Chemical Name:	**Mixed Hydrazine Fuel No. 5**	Common Name:	**MHF-5**
Empirical Formula:	$C_{0.54140}H_{5.1734}N_{2.0906}O_{0.2719}$	Formula Weight:	**45.354**
Composition; % b.w.:	$55.N_2H_3CH_3 + 26.N_2H_4 + 19.N_2H_5NO_3$		

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	231.15 -42 416.07 -43.6	°K °C °R °F		8	
HEAT OF FUSION	Not Available	kcal/mole BTU/lb			
NORMAL BOILING POINT	369.7 96.6 665.5 205.8	°K °C °R °F			
HEAT OF VAPORIZATION	8.17 324.2	kcal/mole BTU/lb	NBP	calc.	
TROUTON CONSTANT	22.1		NBP	calc.	
CRITICAL STATE CONSTANTS					
TEMPERATURE	636 363 1145 685	°K °C °R °F		7	
PRESSURE	100 1470	atms psia		7	
DENSITY	0.316 19.73	g/cc lb/ft^3		7	
VAPOR PRESSURE OF LIQUID	40.41 0.78	mm Hg psia	298	1,3	2.17-1
DENSITY OF LIQUID	1.011 63.102	g/cc lb/ft^3	298	1,8	2.17-2
SONIC VELOCITY	1791 5875	m/sec ft/sec	298	6	2.17-3
COMPRESSIBILITY OF LIQUID					
ADIABATIC	3.13×10^{-5} 2.13×10^{-6}	atm^{-1} psi^{-1}	298	5	2.17-4
ISOTHERMAL	Not Available	atm^{-1} psi^{-1}			
VISCOSITY OF LIQUID	1.97 1.32×10^{-3}	centipoise lb_m/ft-sec	298	1,3,7,8	2.17-5
HEAT CAPACITY OF LIQUID	0.667 0.667	cal/g-°K BTU/lb-°R	298	2,3,4,6	2.17-8
THERMAL CONDUCTIVITY OF LIQUID	7.52×10^{-4} 5.05×10^{-5}	cal/cm-sec-°K BTU/ft-sec-°R	298	9	2.17-7
SURFACE TENSION	42.53 2.914×10^{-3}	dynes/cm lb_f/ft	298	6	2.17-6
DIELECTRIC CONSTANT	>108		298	13	
HEAT OF FORMATION OF LIQUID	6.872 272.7	kcal/mole BTU/lb	298		

2.17.2 GENERAL

2.17.2.1 Description of MHF-5

(C) The mixed hydrazine fuel – MHF-5 is one of the most energetic blends in the hydrazine – MMH family due to the additions of $N_2H_5NO_3$. The nominal composition of this blend is:

N_2H_4	-	26% by weight ±2.0
$N_2H_3CH_3$	-	55% by weight ±2.0
$N_2H_5NO_3$	-	19% by weight ±2.0
H_2O	-	2% Max.

(U) This propellant has been utilized as both a fuel for rocket propulsion and as a monopropellant for gas generation. It was utilized in the Condor program and is the progenitor of MHF-5A and MHF-5B.

2.17.2.2 Structure

(U) As MHF-5 is a blend of three compounds, it will exhibit the characteristics of its constituents. Density measurements indicate a lower density than that predicted by the theory of additive volumes. The molecular structures of hydrazine and MMH are discussed elsewhere in this handbook. The hydrazinium nitrate is dissociated into $N_2H_5^+$ and NO_3^- ions.

2.17.2.3 Government Specification

(U) Manufacture and procurement of MHF-5 is covered by MIL. Spec. MIL-P-81507(AS). The compositional limits are indicated in Section 2.17.2.1, above.

2.17.3 PHYSICAL PROPERTIES OF MHF-5

2.17.3.1 Vapor Pressure and Normal Boiling Point

(U) The vapor pressure of liquid MHF-5 has been reported by RMD(1, 3). The experimental data in Reference 1 covered a temperature range from 17 to 65 C (62 to 149 F). In reference 3, the temperature range studied was extended from 0 to 95 C (32 to 203 F). The experimental data is plotted in Figures 2.17-1 and 2.17-1a.

(U) Using the method of least squares, the data was fitted and is best described by:

$$\log P\,(\text{mmHg}) = -61.243 + \frac{5725.80}{T,\ ^\circ K} + 0.20818\,(T,\ ^\circ K) - 2.0727 \times 10^{-4}\,(T,\ ^\circ K)^2 \qquad (2.17\text{-}1)$$

$$\log P\,(\text{psia}) = -62.956 + \frac{10306.4}{T,\ ^\circ R} + 0.11566\,(T,\ ^\circ R) - 6.3972 \times 10^{-5}\,(T,\ ^\circ R)^2 \qquad (2.17\text{-}1a)$$

The standard deviation of the experimental data from equation 2.17-1 is 2.83 mmHg and the average percent deviation is 2.2 percent.

(U) The normal boiling point calculated from equation 2.17-1 is 269.7 K, or 96.5 C (205.8 F). Rocketdyne(10) reports a calculated value of 97.3 C based on the same vapor pressure data. They chose the classical relationship that the logarithm of pressure is a linear function of the reciprocal of absolute temperature. It was found in this study that this equation gave a large standard deviation. The boiling point range of the mixture has not been studied.

2.17.3.2 Density of Liquid MHF-5

(U) The density of saturated liquid MHF-5 has been experimentally determined by RMD(1, 3) and Rocketdyne(8). The two studies covered a temperature range from -54 to 94 C (-65 to 201 F). The first study made by RMD(1) in 1962 covered a range from -54 to 71 C (-65 to 160 F). The second study by RMD(3) in 1965 covered a range from 25 to 93 C (77 to 200 F) but the experimental data was not given and this work was not considered here. Rocketdyne(8) recently published data for the range of -54 to 94 C (-65 to 201 F).

(U) The experimental data from the two studies are shown in Figures 2.17-2 and 2.17-2a and are in good agreement. Over the temperature range studied, the density is a linear function of temperature.

$$\rho\,(\text{g/cc}) = 1.2558 - 8.2178 \times 10^{-4}\,(T,\ ^\circ K) \qquad (2.17\text{-}2)$$

$$\rho\,(\text{lb/ft}^3) = 78.3975 - 0.028501\,(T,\ ^\circ R) \qquad (2.17\text{-}2a)$$

The standard deviation of the experimental data from equation 2.17-2 is 0.00086 g/cc and the average percent deviation was found to be 0.07%.

(C) Details of the RMD study are lacking and the composition of the blend was not given. Rocketdyne reported a composition by weight percent of:

MMH = 54.3%

N_2H_4 = 25.4%

$N_2H_5NO_3$ = 19.7%

H_2O = 0.6%

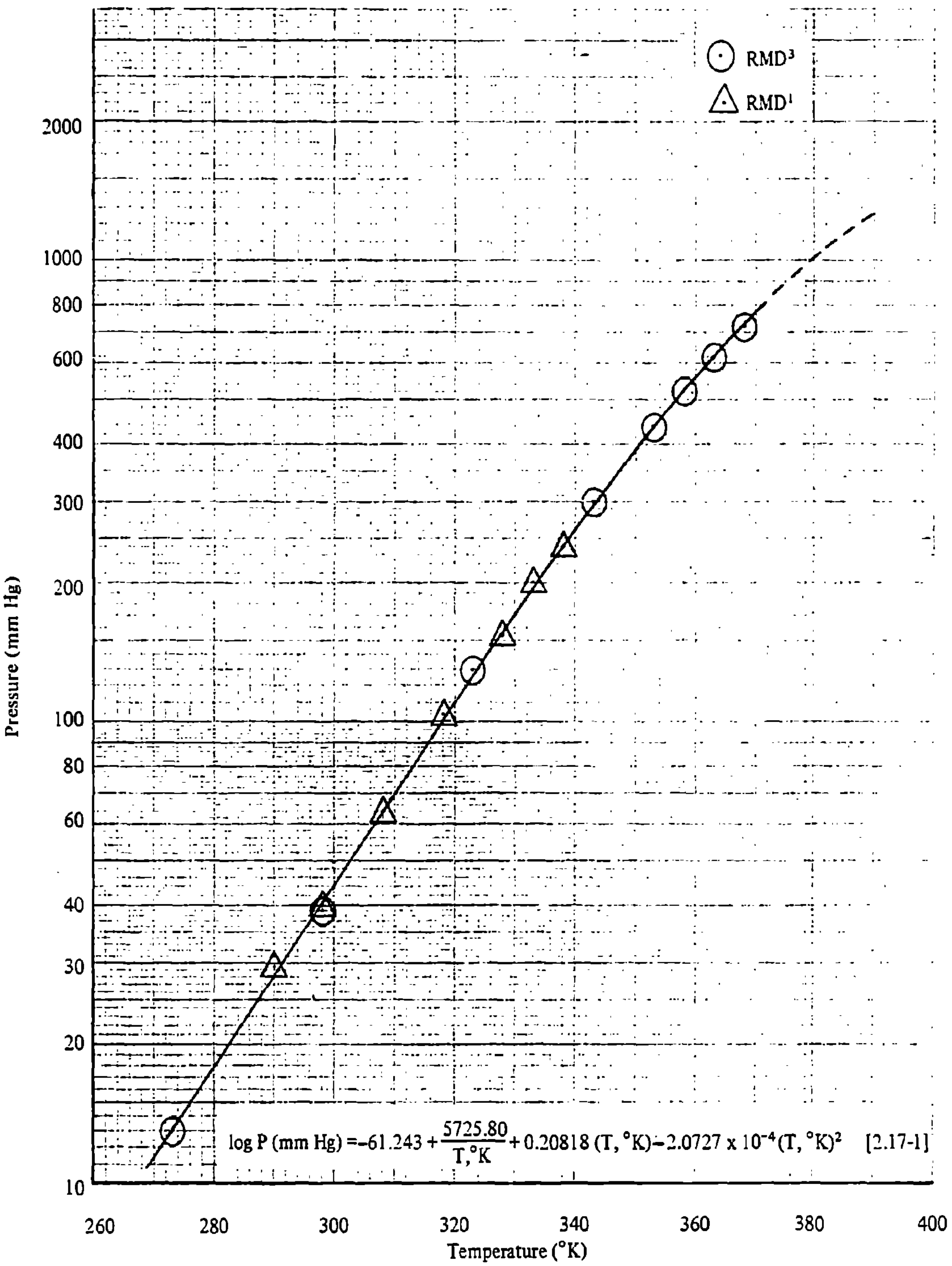
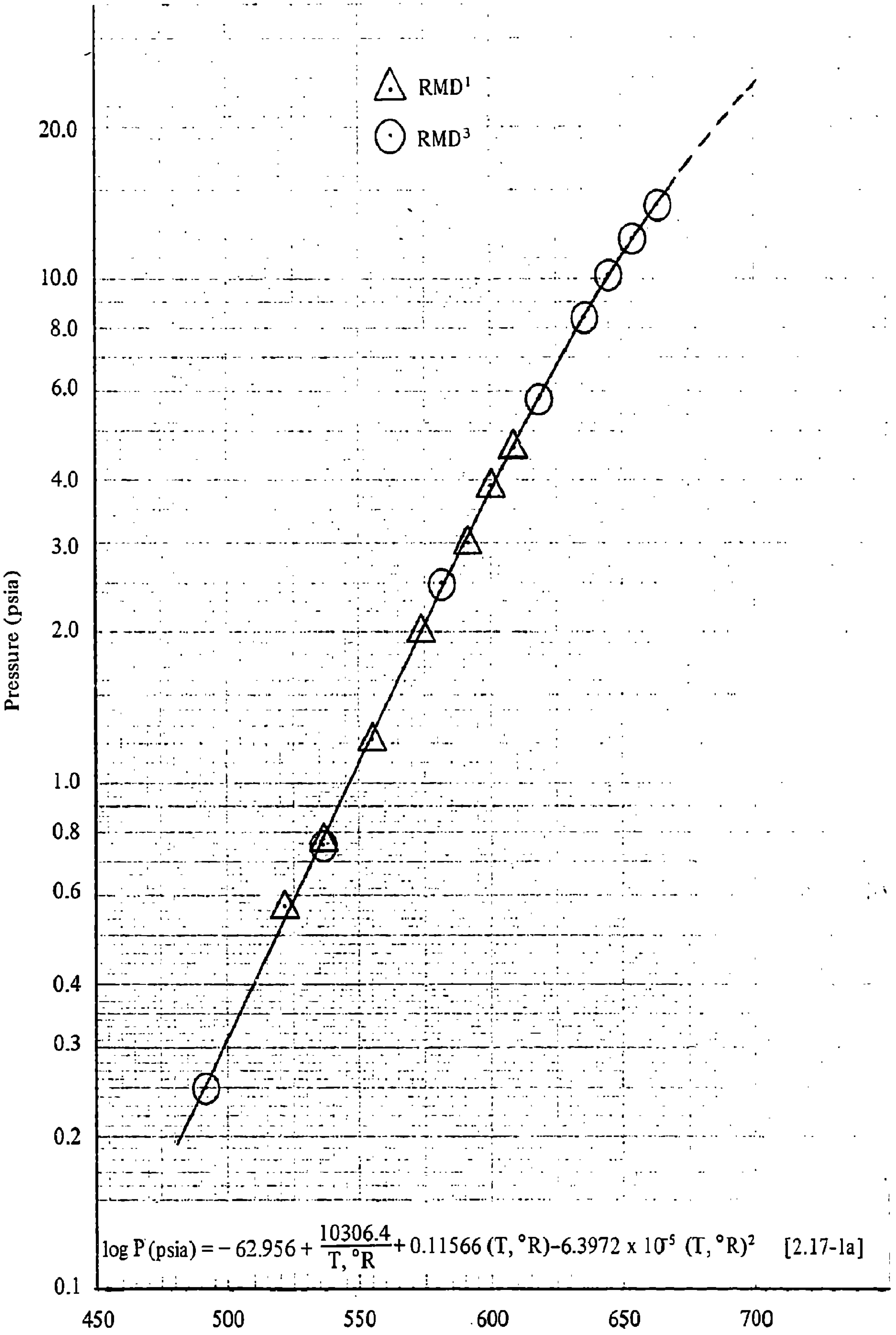
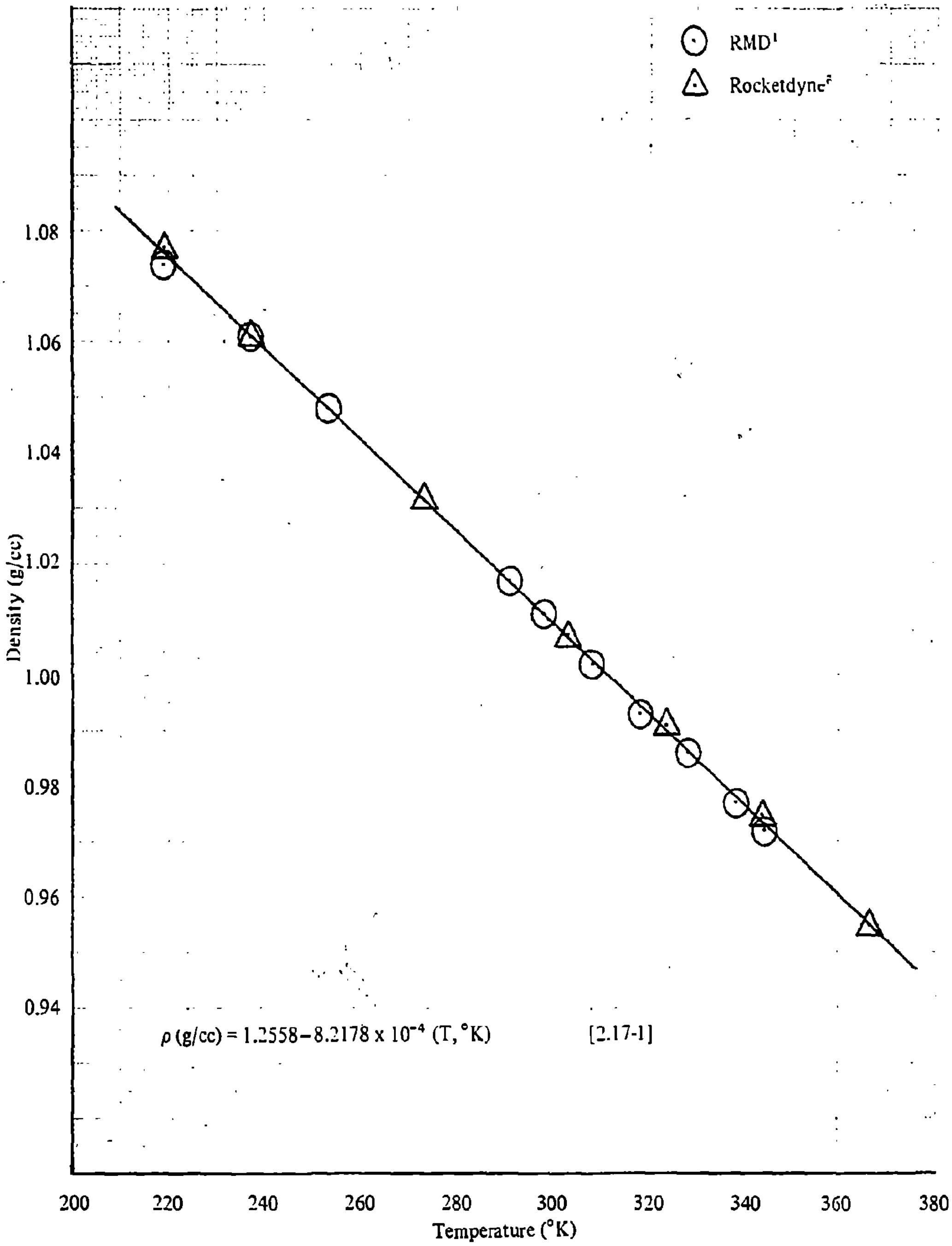


Figure 2.17-1. Vapor Pressure versus Temperature. Liquid MHF-5



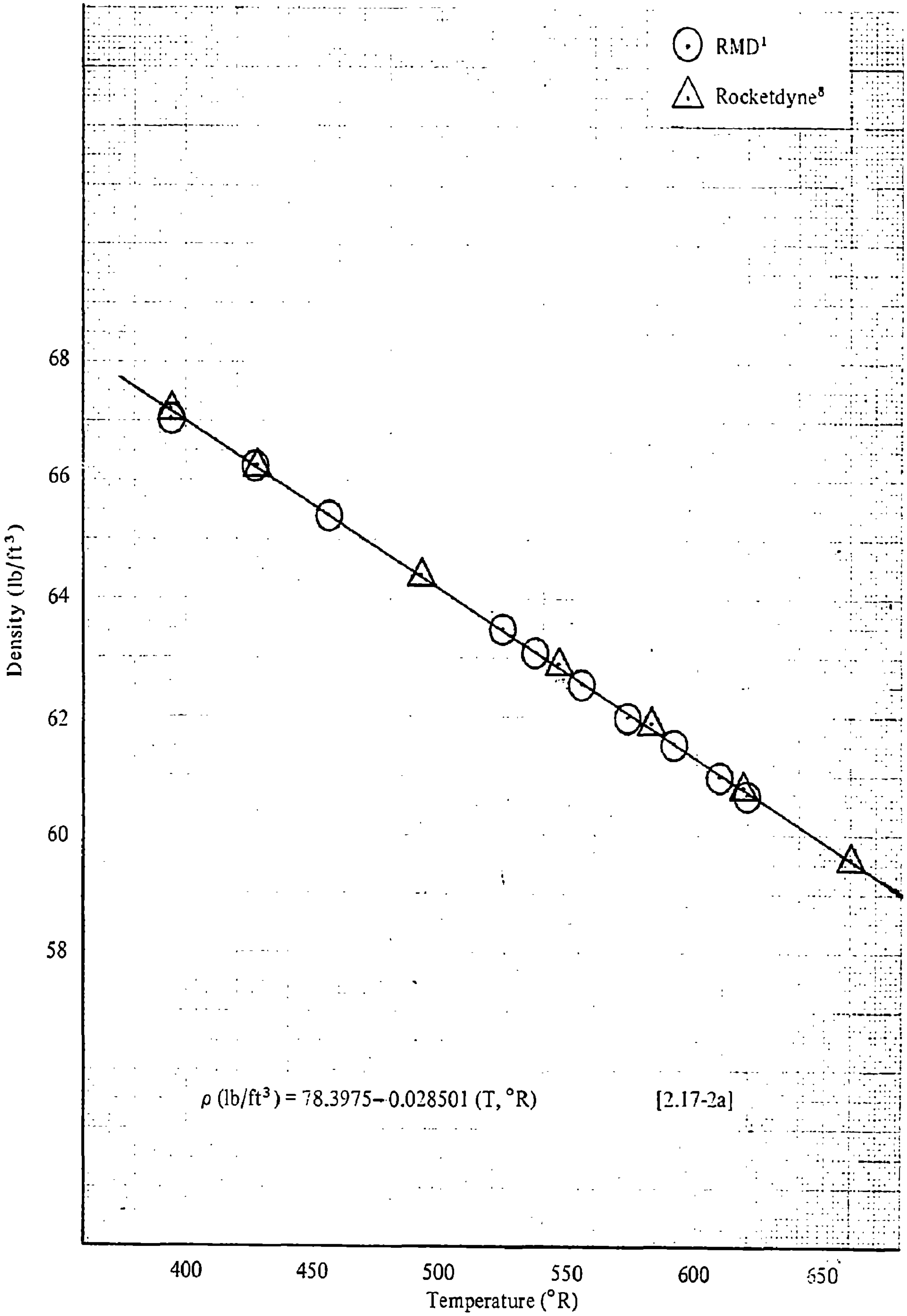
$$\log P\,(\text{psia}) = -62.956 + \frac{10306.4}{T,\,^{\circ}R} + 0.11566\,(T,\,^{\circ}R) - 6.3972 \times 10^{-5}\,(T,\,^{\circ}R)^2 \qquad [2.17\text{-}1a]$$

Figure 2.17-1a. Vapor Pressure versus Temperature, Liquid MHF-5



$$\rho\,(g/cc) = 1.2558 - 8.2178 \times 10^{-4}\,(T, °K) \qquad [2.17\text{-}1]$$

Figure 2.17-2. Density versus Temperature, Liquid MHF-5



$$\rho\ (lb/ft^3) = 78.3975 - 0.028501\ (T, {}^\circ R) \qquad [2.17\text{-}2a]$$

Figure 2.17-2a. Density versus Temperature, Liquid MHF-5

(U) A glass pycnometer was constructed from a 25 ml flask to which a 2 ml precision bore capillary tube was attached. A cathetometer was used to measure the height above or below an etch mark on the capillary tube. The sample was weighed on an analytical balance to ±0.1 milligram. The apparatus was calibrated with distilled water and, at lower temperatures with acetone.

(C) Rocketdyne(10) reported the density of four various MHF-5 related blends and gave the following equation where composition is a variable.

$$\rho\,(\text{g/cc}) = 1.028 - 8.232 \times 10^{-4}\,(T,{}^\circ C) - 5.199 \times 10^{-8}\,(T,{}^\circ C)^2 - 1.512 \times 10^{-3}\,M + 4.42 \times 10^{-3}\,N \qquad (2.17\text{-}3)$$

or by conversion

$$\rho\,(\text{g/cc}) = 1.2490 - 7.948 \times 10^{-4}\,(T,{}^\circ K) - 5.199 \times 10^{-8}\,(T,{}^\circ K) - 1.512 \times 10^{-3}\,M + 4.42 \times 10^{-3}\,N \qquad (2.17\text{-}3a)$$

Where

M = weight percent MMH
N = weight percent $N_2H_5NO_3$

Using a nominal MHF-5 composition, the results obtained from equation 2.17-3 were found to be in excellent agreement with the density values obtained from equation 2.17-2. Equation 2.17-3 would appear to be of value if the blend in question deviated significantly from the nominal.

2.17.3.3 Sonic Velocity in Liquid MHF-5

(U) The sonic velocity in liquid MHF-5 has been experimentally determined by Rocketdyne(5) over a temperature range from -39 to 95 C (-38 to 203 F). The experimental data is plotted in Figures 2.17-3 and 2.17-3a.

(U) The variation of sonic velocity with temperature is a linear function:

$$c(\text{m/sec}) = 2776.1 - 3.3054\,(T,{}^\circ K) \qquad (2.17\text{-}4)$$

$$c(\text{ft/sec}) = 9108.0 - 6.0247\,(T,{}^\circ R) \qquad (2.17\text{-}4a)$$

The standard deviation of the data as expressed by Equation 2.17-3 is 5.1 meters/sec with an average percent deviation 0.21 percent.

(C) Propellant grade MHF-5 was used with a nominal composition of 55 MMH, 26 N_2H_4 and 19 $N_2H_5NO_3$ by weight percent. The apparatus employed is briefly discussed in Section 2.6.3.3 on the 50-50 fuel blend.

2.17.3.4 Compressibility of Liquid MHF-5

(U) The isothermal compressibility of MHF-5 has not been studied. The sonic velocity in liquid MHF-5 has been studied by Rocketdyne(5). The adiabatic compressibility (β_a) can be calculated from the acoustical equation

$$\beta_a = \frac{1}{\rho c^2}$$

Where

ρ = saturated liquid density c
c = sonic velocity

(U) The adiabatic compressibility was calculated here at each experimental sonic velocity point. The values are shown in Figures 2.17-4 and 2.17-4a.

(U) The adiabatic compressibility is adequately described over a temperature range from -39 to 95C (-38 to 203F) by

$$\beta_a\,(\text{atm}^{-1}) = 3.0498 \times 10^{-5} - 1.4018 \times 10^{-7}\,(T,{}^\circ K) + 4.7885 \times 10^{-10}\,(T,{}^\circ K)^2 \qquad (2\text{-}17\text{-}5)$$

$$\beta_a\,(\text{psi}^{-1}) = 2.0752 \times 10^{-6} - 5.2992 \times 10^{-9}\,(T,{}^\circ R) + 1.0057 \times 10^{-11}\,(T,{}^\circ R)^2 \qquad (2\text{-}17\text{-}5a)$$

(U) The average percent deviation of the data as described by equation 2.17-5 is 0.59%.

2.17.3.5 Viscosity of Liquid MHF-5

(C) The viscosity of liquid MHF-5 has been experimentally determined by RMD(1.3) with a Cannon-Zukov viscometer. over a temperature range from -54 to 71 C (-65 to 160 F). Aerojet(7) reported twoexperimental points at -40 and 77 F without giving any details. Rocketdyne(8) used a capillary viscometer and gave data from (-40 to 195.1 F). The composition of the blend used by Rocketdyne in weight percent was:

MMH	54.3
N_2H_4	25.4
$N_2H_5NO_3$	19.7
H_2O	0.6

(C) The experimental data from the various studies was given in kinematic units. The absolute viscosities were de-

(U) termined from density data using equation 2.17-2 and are plotted in Figures 2.17-5 and 2.17-5a. The agreement is generally good. The combined data covering a temperature range from -54 to 91 C (-65 to 195 F) is defined by:

$$\log \mu \text{ (centipoise)} = -3.6683 + \frac{2834.40}{T, {}^\circ K} - \frac{8.9456 \times 10^5}{(T, {}^\circ K)^2} + \frac{1.1976 \times 10^8}{(T, {}^\circ K)^3} \qquad (2.17\text{-}6)$$

$$\log \mu \text{ (lb}_m\text{/ft-sec)} = -6.8409 + \frac{5101.91}{T, {}^\circ R} - \frac{2.8984 \times 10^6}{(T, {}^\circ R)^2} + \frac{6.9843 \times 10^8}{(T, {}^\circ R)^3} \qquad (2.17\text{-}6a)$$

The standard deviation of the experimental data from equation 2.17-6 is 2.19 centipoise with an average percent deviation of 3.4 %.

2.17.3.6 Surface Tension of Liquid MHF-5

(U) The surface tension of liquid MHF-5 has been experimentally determined by Rocketdyne(6) over a temperature range from -36 to 93 C (-32 to 200 F). Only five determinations were made and they are plotted in Figures 2.17-6 and 2.17-6a.

(U) The surface tension is adequately defined as linear function of temperature by

$$\gamma \text{ (dynes/cm)} = 78.4745 - 0.12056 \text{ (T, } {}^\circ\text{K)} \qquad (2.17\text{-}7)$$

$$\gamma \text{ (lb}_f\text{/ft)} = 5.3772 \times 10^{-3} - 4.5894 \times 10^{-6} \text{ (T, } {}^\circ\text{R)} \qquad (2.17\text{-}7a)$$

The standard deviation of the experimental data from Equation 2.17-7 is 0.87 dynes/cm and the average percent deviation is 1.48%.

(C) The MHF-5 sample used had the following composition by weight percent: MMH = 54.3; N_2H_4 = 25.4; $N_2H_5NO_3$ = 19.7 and H_2O = 0.6. A double capillary rise method was employed. Precision bored capillary tubes of different bore diameters are used. The difference in height rise of the liquid in the capillaries is measured with a cathetometer. The surface tension is then calculated from

$$\gamma = \frac{\frac{1}{2} \Delta hg \left[\rho_l - \rho_v\right]}{\frac{1}{r_1} - \frac{1}{r_2}}$$

where

g = gravitational constant (980.665 cm/sec^2)
ρ_l = density of liquid
ρ_v = density of vapor
Δh = difference in height rise
r_1 r_2 = radii of capillaries

2.17.3.7 Thermal Conductivity of Liquid MHF-5

(U) The thermal conductivity of saturated liquid MHF-5 has been experimentally determined by Rocketdyne(9) over a temperature range from -18 to 93 C (0 to 200 F). The experimental data is plotted in Figures 2.17-7 and 2.17-7a. The data is a linear function of temperature for the range studied.

$$K(\text{cal/cm-sec - } {}^\circ K) = 9.4074 \times 10^{-4} - 6.3264 \times 10^{-7} \text{ (T, } {}^\circ\text{K)} \qquad (2.17\text{-}8)$$

$$K(\text{BTU/ft-sec } {}^\circ R) = 6.1355 \times 10^{-5} - 2.3602 \times 10^{8} \text{ (T, } {}^\circ\text{R)} \qquad (2.17\text{-}8a)$$

(C) The standard deviation of the experimental data from equation 2.17-8 is 4.3 x 10^{-6} cal/cm-sec-K while the average percent deviation was 0.43% with the maximum percent deviation being 1.2%. The sample composition had the following weight percentages; 54.9 MMH, 25.4 N_2H_4, 18.9 $N_2H_5NO_3$, 0.2 NH_3 and 0.6 H_2O.

(U) The thermal conductivity cell employed is briefly described in Section 2.6.3.7 on 50-50 blend.

2.17.3.8 Dielectric Constant of MHF-5

(C) Aerojet(13) has recently reported a single value of dielectric constant "greater than 108". They used a Sargent Oscillometer on a sample of nominal composition. The high dielectric constant resulting from the hydrazinium nitrate content probably caused the instrument to saturate or go off scale. The measurement was attempted at 25 C (77 F).

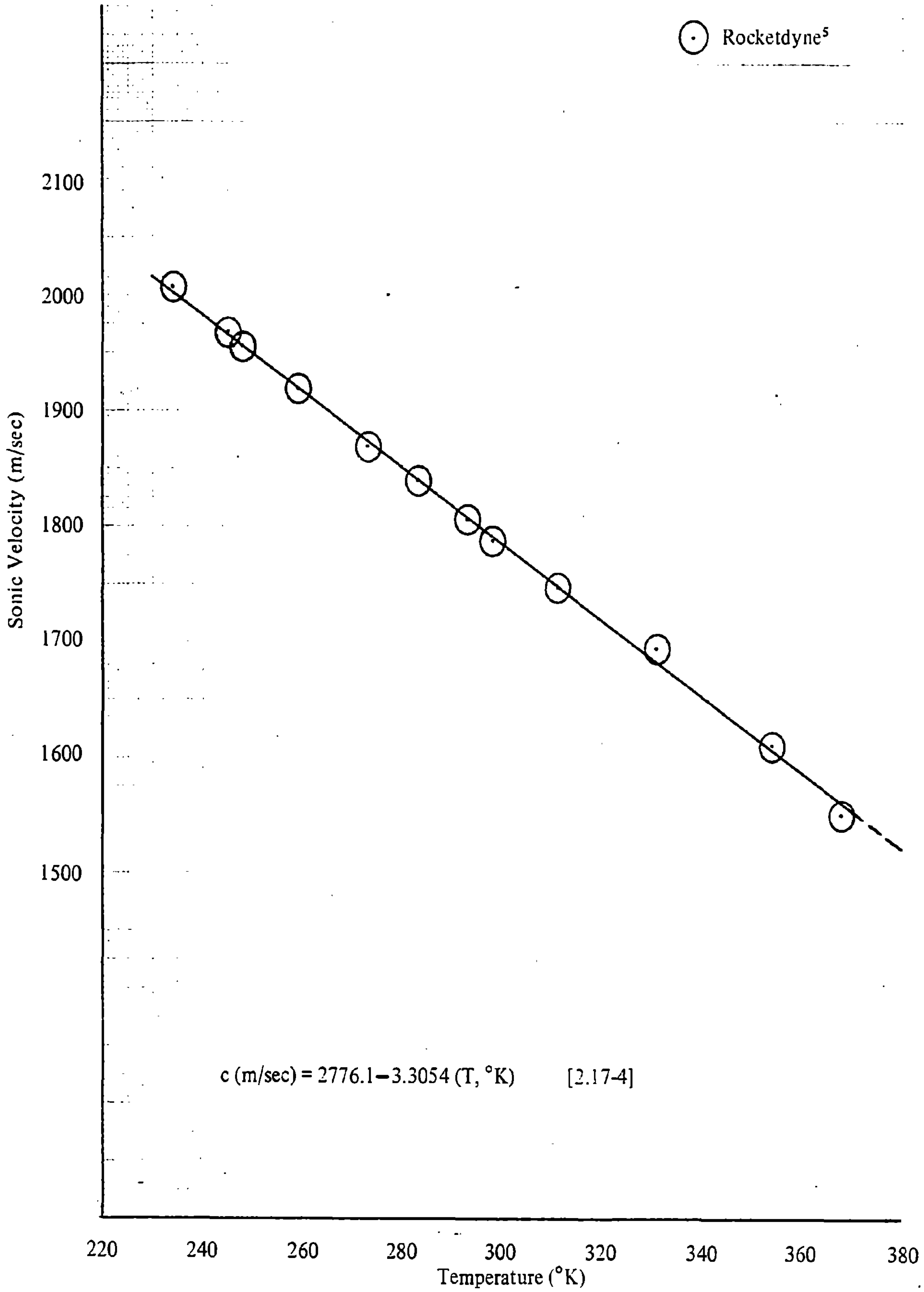
2.17.3.9 Index of Refraction

(U) No data have been reported.

2.17.4 CHEMICAL PROPERTIES OF MHF-5

2.17.4.1 Chemical Reactions

(C) In addition to the reactions common to hydrazine and methylhydrazine (see sections 2.3.4.1 and 2.4.4.1), MHF-5 is also capable of reactions involving the hydrazinium nitrate component. When hydrazinium nitrate is added to MMH, an equilibrium reaction occurs in the solution in



c (m/sec) = 2776.1−3.3054 (T, °K) [2.17-4]

Figure 2.17-3. Sonic Velocity versus Temperature Liquid MHF-5

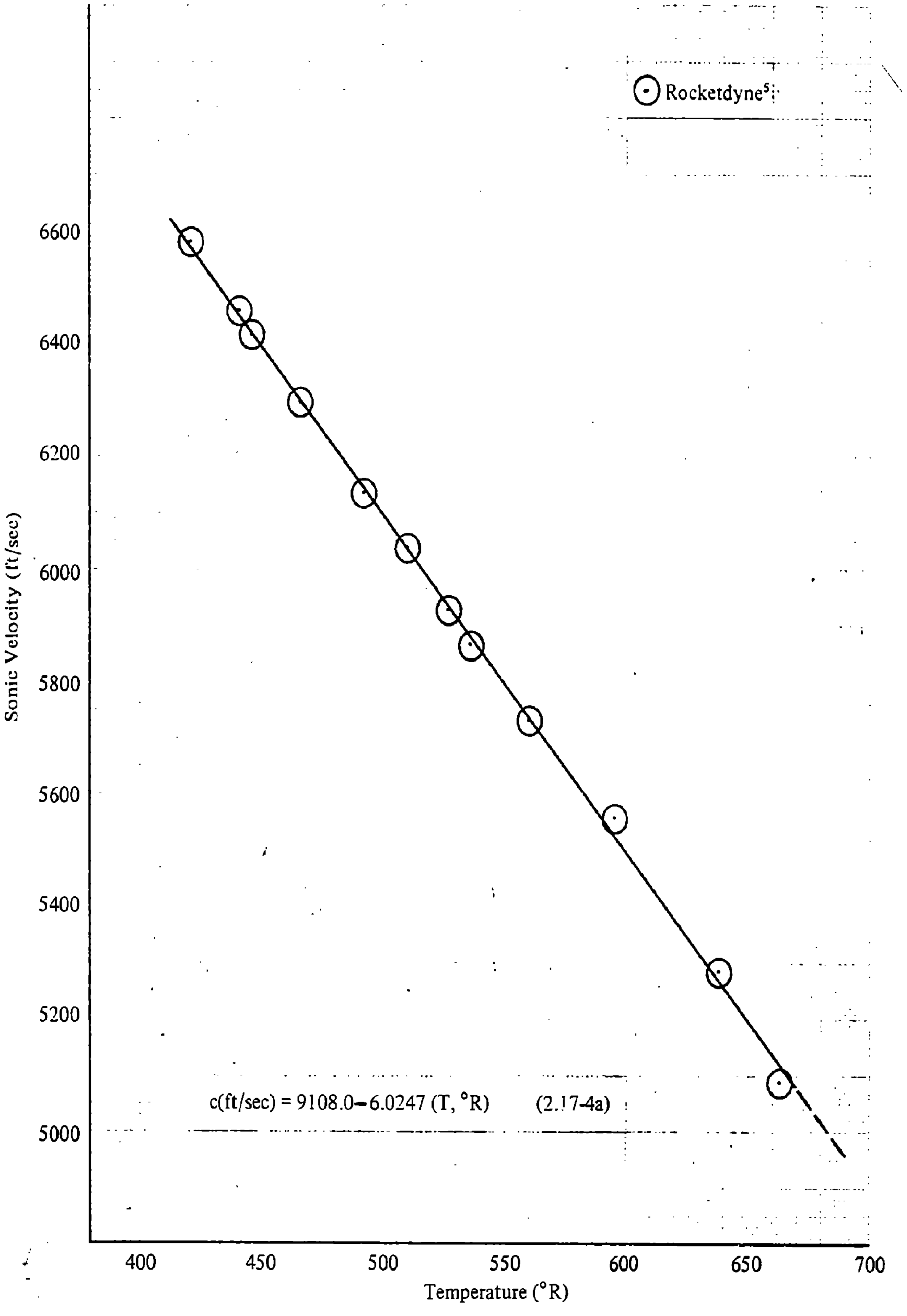
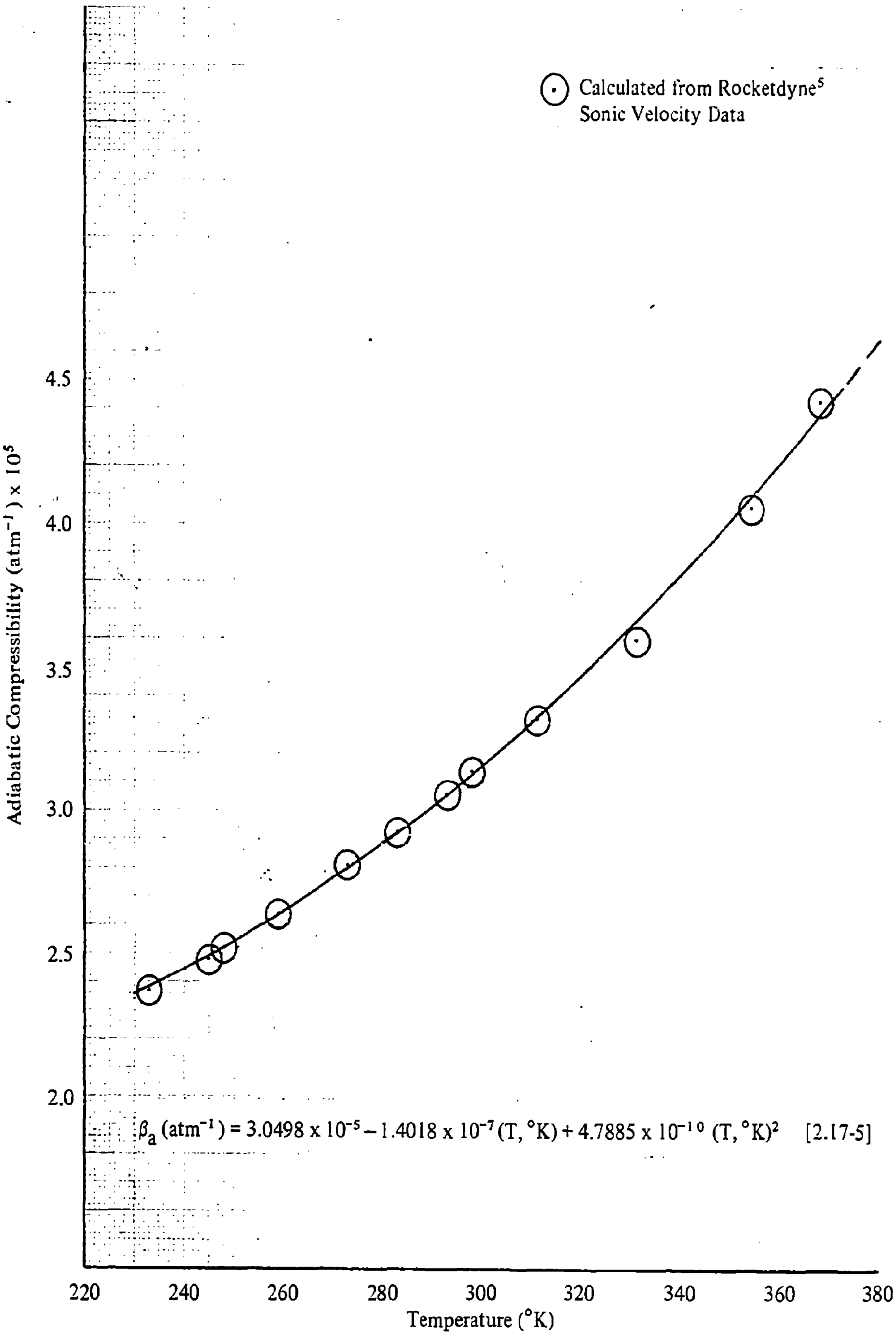
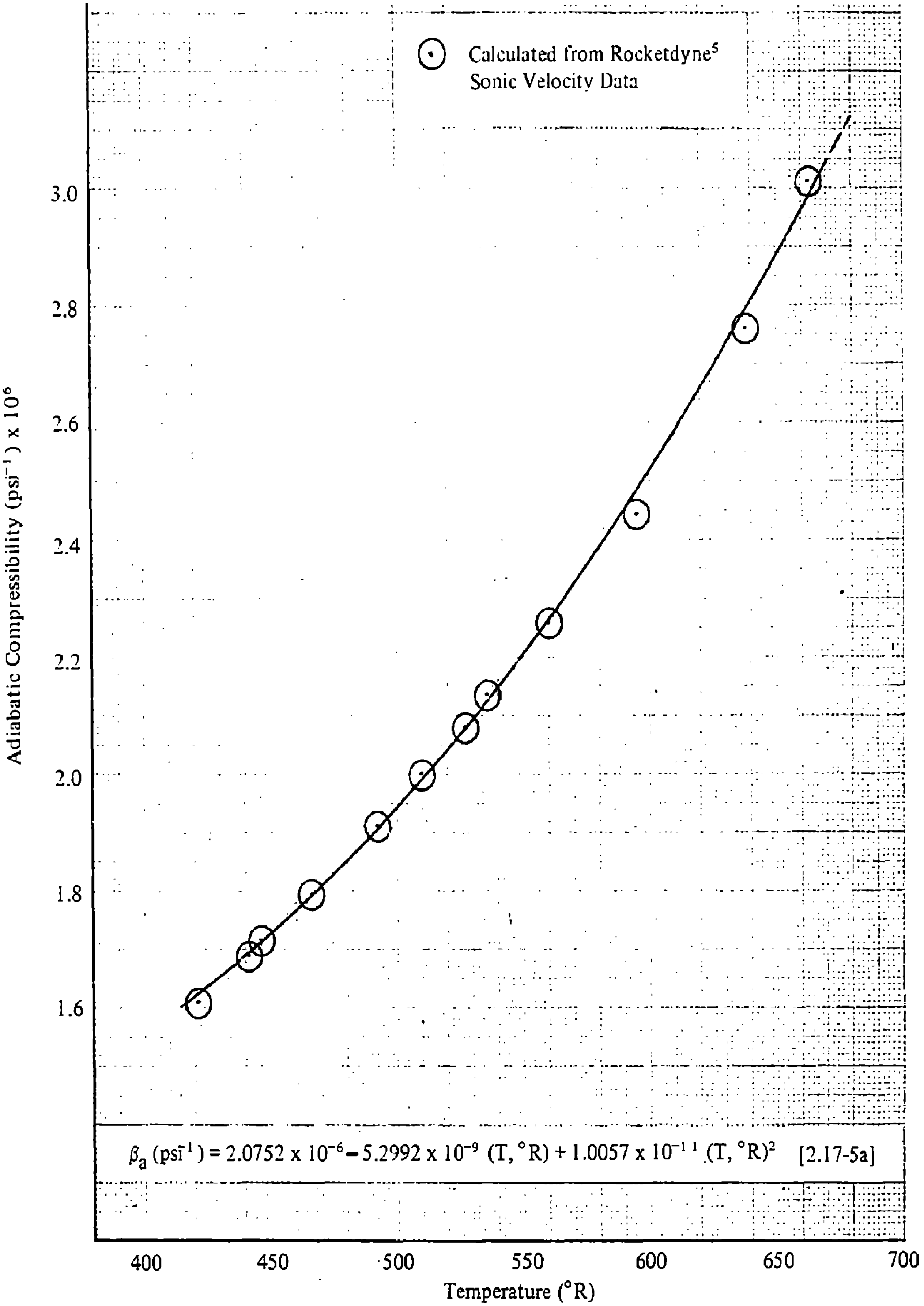


Figure 2.17-3a. Sonic Velocity versus Temperature, Liquid MHF-5



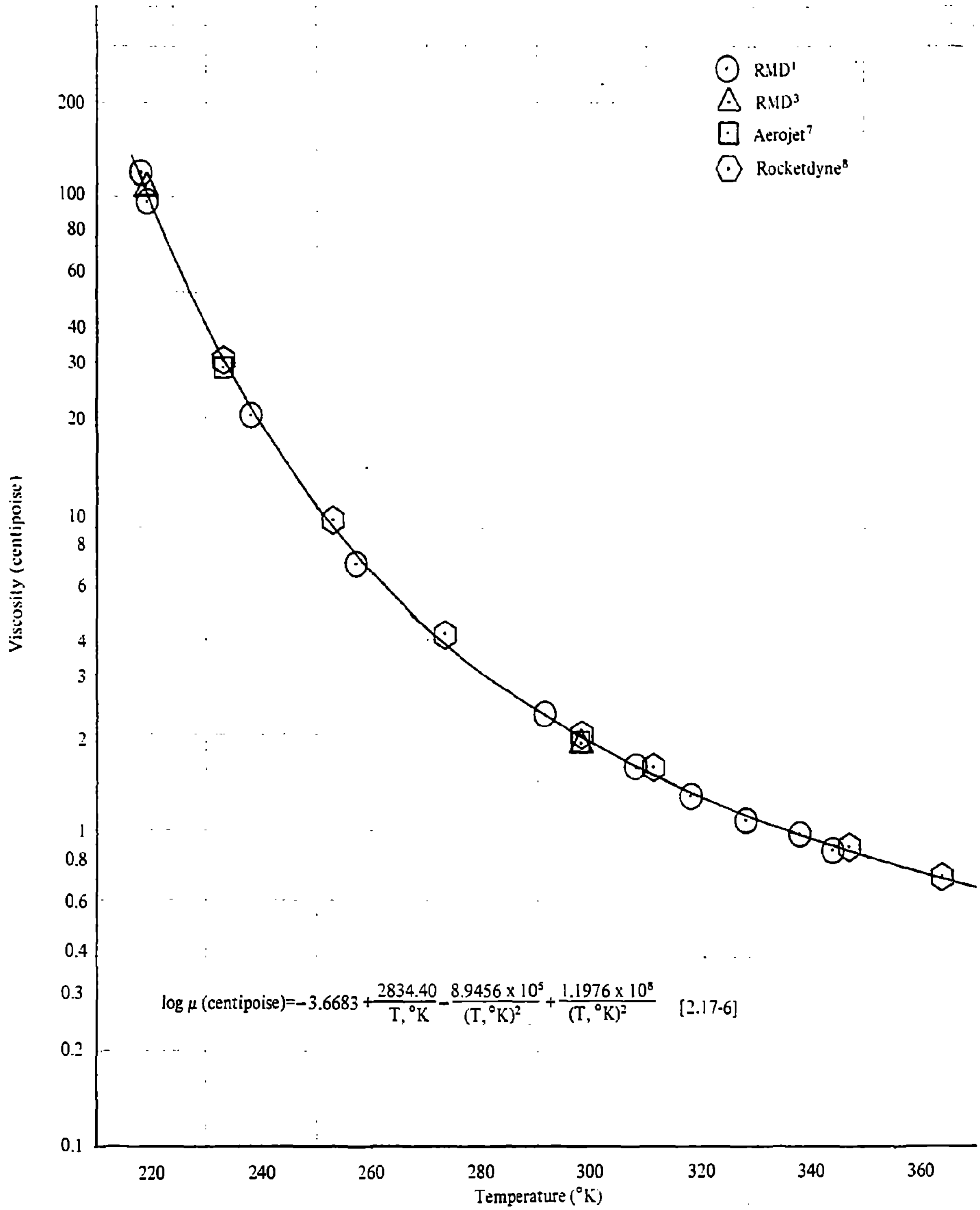
$$\beta_a\,(\text{atm}^{-1}) = 3.0498 \times 10^{-5} - 1.4018 \times 10^{-7}\,(T, {}^{\circ}K) + 4.7885 \times 10^{-10}\,(T, {}^{\circ}K)^2 \qquad [2.17\text{-}5]$$

Figure 2.17-4. Adiabatic Compressibility versus Temperature, Liquid MHF-5



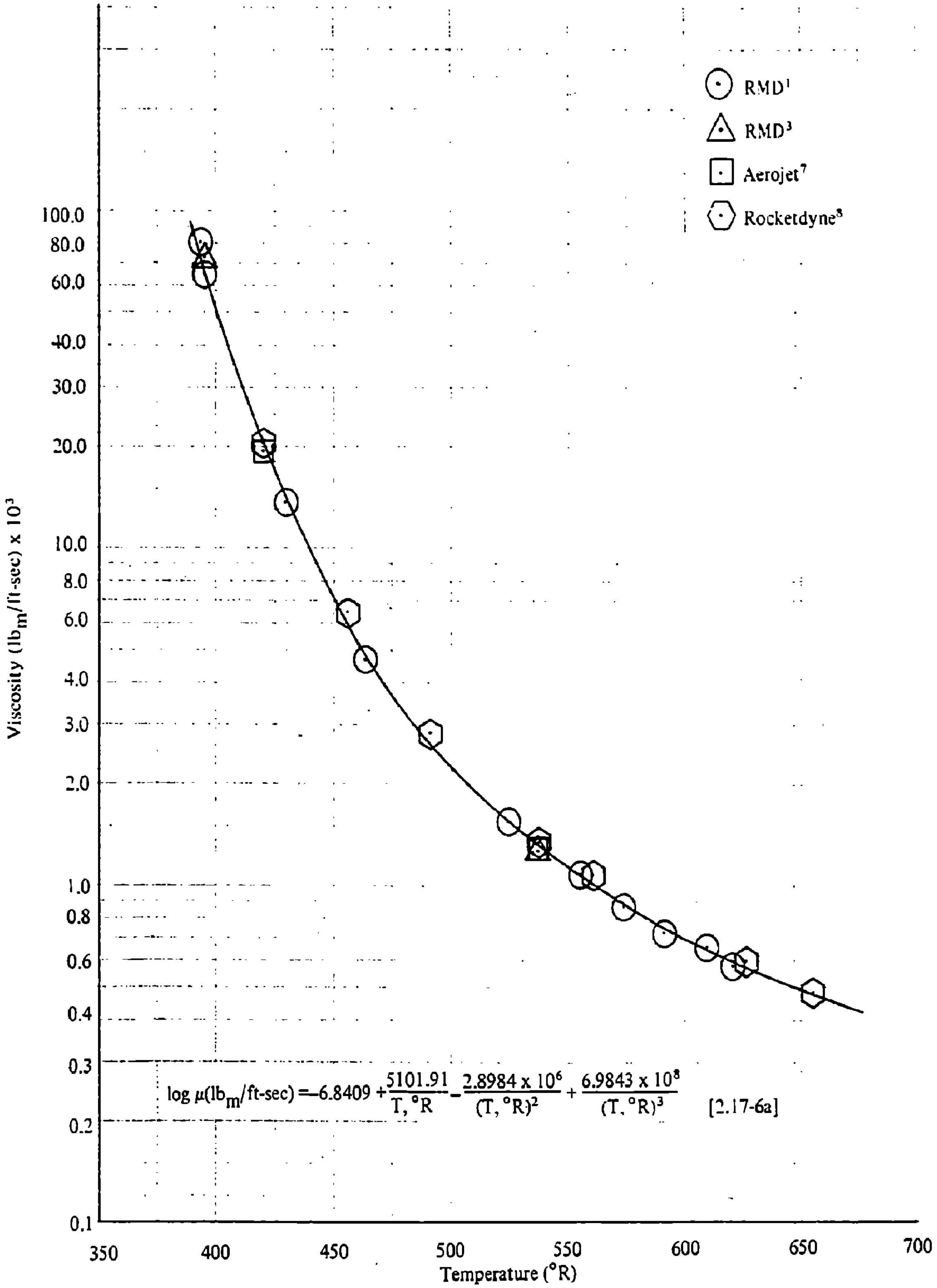
$$\beta_a\ (\mathrm{psi}^{-1}) = 2.0752 \times 10^{-6} - 5.2992 \times 10^{-9}\ (T, {}^\circ R) + 1.0057 \times 10^{-11}\ (T, {}^\circ R)^2 \qquad [2.17\text{-}5a]$$

Figure 2.17-4a. Adiabatic Compressibility versus Temperature, Liquid MHF-5



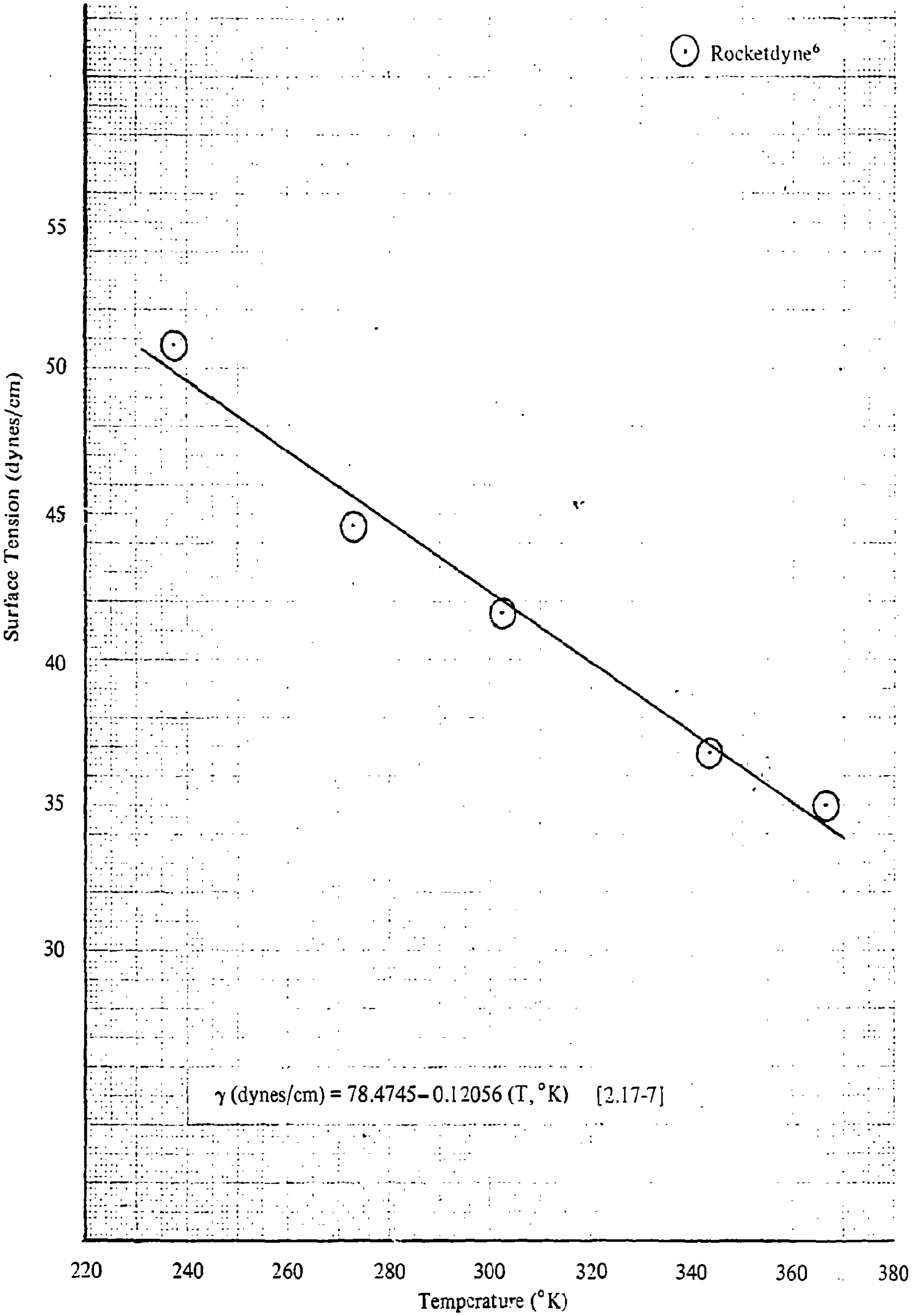
$$\log \mu \text{ (centipoise)} = -3.6683 + \frac{2834.40}{T, °K} - \frac{8.9456 \times 10^5}{(T, °K)^2} + \frac{1.1976 \times 10^8}{(T, °K)^3} \qquad [2.17\text{-}6]$$

Figure 2.17-5. Viscosity versus Temperature, Liquid MHF-5



$$\log \mu(\mathrm{lb_m/ft\text{-}sec}) = -6.8409 + \frac{5101.91}{T,\,^\circ R} - \frac{2.8984 \times 10^6}{(T,\,^\circ R)^2} + \frac{6.9843 \times 10^8}{(T,\,^\circ R)^3} \qquad [2.17\text{-}6a]$$

Figure 2.17-5a. Viscosity versus Temperature, Liquid MHF-5



γ (dynes/cm) = 78.4745 − 0.12056 (T, °K) [2.17-7]

Figure 2.17-6. Surface Tension versus Temperature, Liquid MHF-5

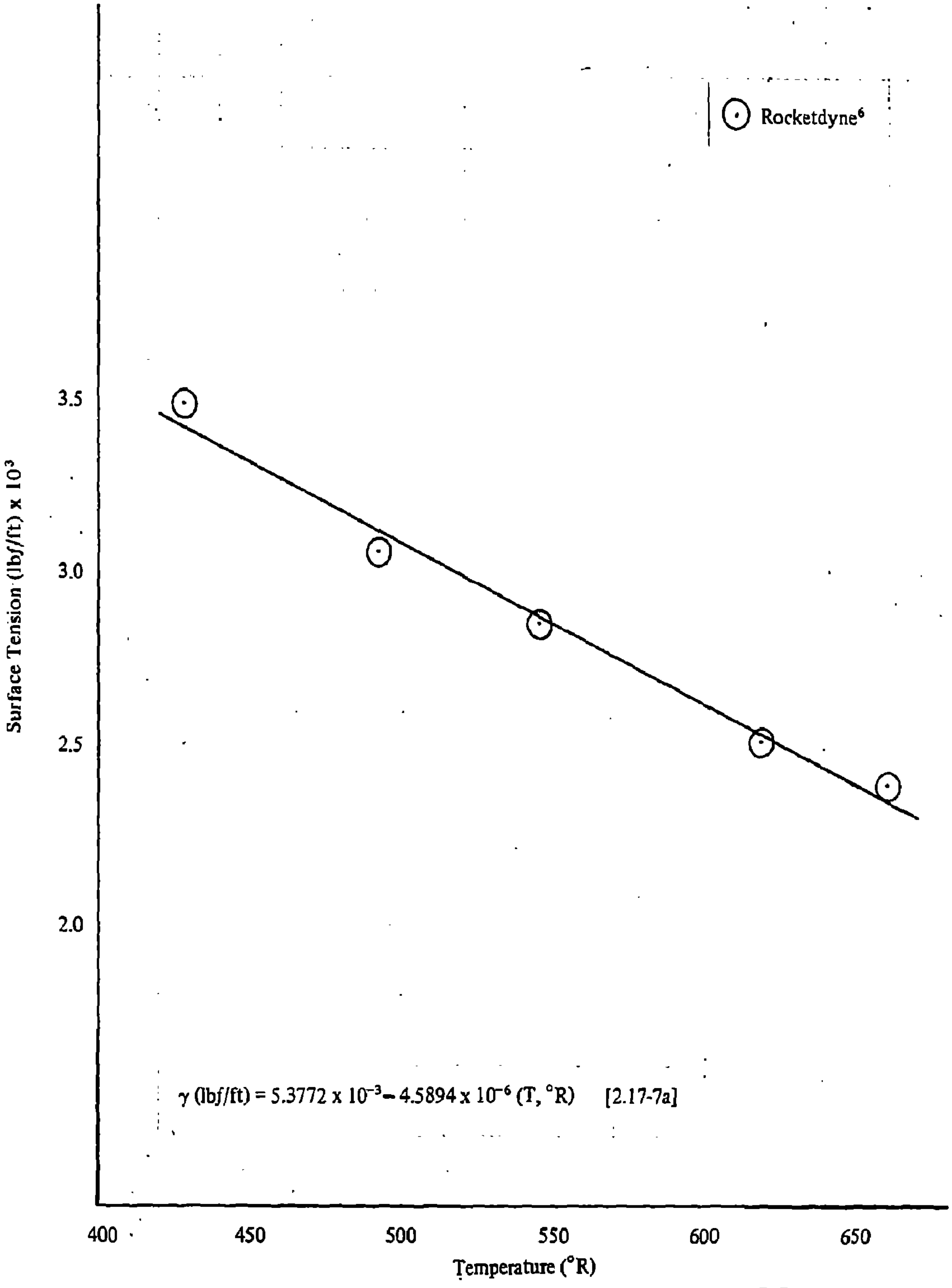


Figure 2.17-6a. Surface Tension versus Temperature, Liquid MHF-5

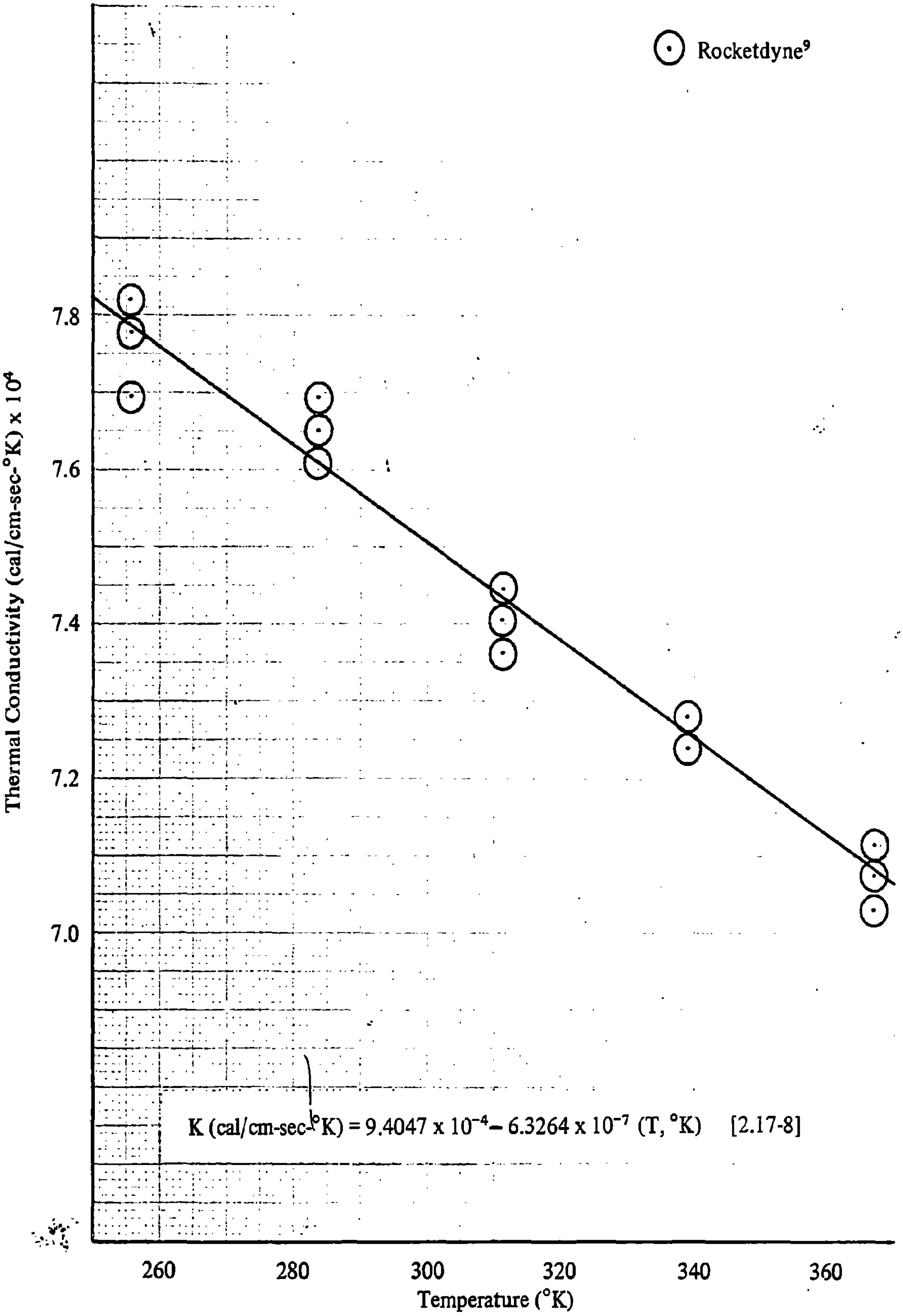
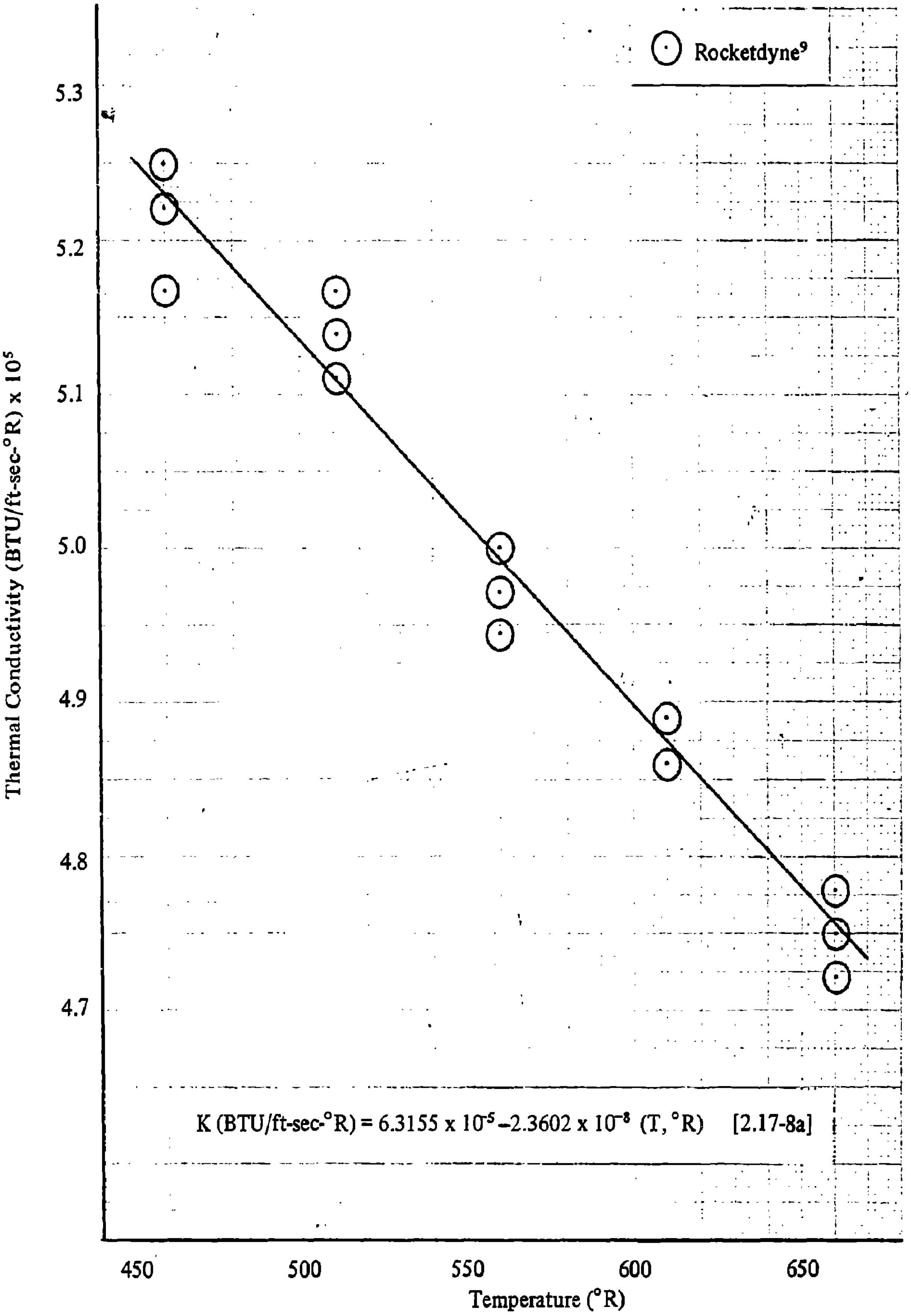


Figure 2.17-7. Thermal Conductivity versus Temperature, Liquid MHF-5



$$K\,(\mathrm{BTU/ft\text{-}sec\text{-}^\circ R}) = 6.3155 \times 10^{-5} - 2.3602 \times 10^{-8}\ (T, {}^\circ R) \qquad [2.17\text{-}8a]$$

Figure 2.17-7a. Thermal Conductivity versus Temperature, Liquid MHF-5

(C) which methylhydrazine nitrate is formed. Much of the hydrazinium nitrate is ionized in solution according to:

$$N_2H_5NO_3 \overset{N_2H_4}{\rightleftharpoons} N_2H_5^+ + NO_3^-$$

The hydrazinium nitrate solutions are very reactive with some metals, particularly zinc and copper. These solutions will also react with oxidizing agents such as permanganates, chromates and peroxides more readily than hydrazine alone.

2.17.4.2 Inert Gas Solubility

(U) No data have been reported on solubility of inert gases in MHF-5.

2.17.5 THERMODYNAMIC PROPERTIES OF MHF-5

2.17.5.1 Heat of Formation of Liquid

(C) The heat of formation of this mixture can be calculated for the liquid by the molar addition of the individual heats of formation. The heat of mixing is not known and is assumed to be negligible. Taking the nominal composition to be 55% $CH_3N_2H_3$, 26% N_2H_4 and 19% $N_2H_5NO_3$, the heat of formation at 298.15 K is 6.872 kcal/mole. The mole is defined as 45.354 grams with the empirical formula

$$C_{0.5414}H_{5.1734}N_{2.0906}O_{0.2719}$$

Compound	Weight %	Mole Fraction (1 Mole Blend)	ΔH_{f298} kcal/mole
$CH_3N_2H_3$	55	0.541399	13.106
N_2H_4	26	0.367953	12.054
$N_2H_5NO_3$	19	0.090647	-51.4

For one mole of MHF-5 then:

$$\Delta H_{f298} = 0.541399\,(13.106) + 0.367953\,(12.054) + 0.090647\ (-51.4)$$

$$\Delta H_{f298} = 6.872 \text{ kcal/mole, mole} = 45.354 \text{ grams or } 151.5 \text{ cal/g}$$

(U) The heats of formation used for N_2H_4 and MMH are discussed in units 2.3.5.1 and 2.4.5.1, respectively. The value for $N_2H_5NO_3$ was taken from Wagman, et al.(11) for an aqueous solution where the hydrazine was assumed to act as the electrolytic for $N_2H_5NO_3$.

2.17.5.2 Melting Point and Heat of Fusion

(C) The melting point was reported as -71 F (-57 C) by RMD(1) but a more recent study by Rocketdyne(8) indicate a value in the order of -43 F (-42 C) for MHF-5 containing nominally 1.2% water. Studies of the melting points of the N_2H_4-MMH-$N_2H_5NO_3$ system in this work indicate that the actual melting point of MHF-5 is equal to or slightly lower than the value reported by Rocketdyne, depending on water content. This system is discussed further in Section 3.4.2 of this handbook.

The heat of fusion has not been reported.

2.17.5.3 Critical State Constants of MHF-5

(U) The critical state constants of MHF-5 have not been experimentally determined but have been estimated by Aerojet(7). There are many methods for estimating critical constants, but often these estimates are in serious error even for a pure substance. Since a mixture does not have a true critical point Kay(12) has called it a pseudocritical point.

(C) Estimating the pseudocritical constants of MHF-5 is further complicated because of the uncertainty of the critical state constants of MMH and hydrazine because of decomposition. The critical constants of hydrazinium nitrate are not known and these in turn must be estimated.

(U) The values given by Aerojet are 1145 R for temperature, 1470 psia for pressure and 0.316 g/cc for density.

(U) It should be pointed out that these values have little justification.

2.17.5.4 Heat Capacity of Liquid MHF-5

The heat capacity of liquid MHF-5 fuel blend has been experimentally determined by Rocketdyne(4, 6) over a temperature range from -47 to 7 C (-53 to 45 F) and by RMD(2, 3) from 4 to 68 C (39 to 154 F). The data from the two separate studies are plotted in Figures 2.17-8 and 2.17-8a. The two studies generally fall in a straight line. The linear fit describes the data with an average percent deviation of 0.54%. The maximum percent deviation was 2.0%.

$$C_p(\text{cal/g-}^\circ\text{K}) = 0.63119 + 1.2162 \times 10^{-4}\ (T, {}^\circ\text{K}) \qquad (2.17\text{-}9)$$

$$C_p(\text{BTU/lb-}^\circ\text{R}) = 0.63119 + 6.7566 \times 10^{-5}\ (T, {}^\circ\text{R}) \qquad (2.17\text{-}9a)$$

(C) The sample used by Rocketdyne(4, 6) had a composition by weight percent of 54.9 MMH, 25.4 N_2H_4, 18.9 $N_2H_5NO_3$, 0.2 NH_3 and 0.6 H_2O. The composition of the test fluid used by RMD(2) was not given.

2.17.5.5 Latent Heat of Vaporization

(C) The heat of vaporization was calculated from the Clapeyron equation to be 8.17 kcal/mole at the normal boiling point (369.7 K). Using a nominal composition of 55% MMH, 26% N_2H_4 and 19% $N_2H_5NO_3$, an average molecular weight of 45.354 grams was calculated and the empirical formula is:

$$C_{0.5414}H_{5.1734}N_{2.0906}O_{0.2719}$$

This gives a value for the heat of vaporization of 180.1 cal/gram or 324.2 BTU/lb.

(U) The trouton constant is calculated to be 22.1.

2.17.6 LOGISTICS OF MHF-5

2.17.6.1 Manufacture

(C) The MHF-5 fuel blend has a nominal composition by weight percent of 55 MMH, 26 hydrazine and 19 hydrazinium nitrate (55 $CH_3N_2H_3$, 26 N_2H_4 and 19 $N_2H_5NO_3$). The actual manufacture of MHF-5 involves only the proper mixing of the ingredients. Although hydrazinium nitrate ($N_2H_5NO_3$) is specified as an ingredient Rocketdyne has shown that the nitrate ion (NO_3^-) is actually dissociated from the N_2H_5 + ion after mixing with MMH and N_2H_4. It is therefore not necessary to actually add the NO_3 in the form of hydrazinium nitrate. It can be added as nitric acid (HNO_3), ammonium nitrate (NH_4NO_3), etc., as long as the amounts of the final ingredients are properly controlled.

(C) Since hydrazinium nitrate is quite shock sensitive and somewhat costly, Rocketdyne(10) has successfully used ammonium nitrate as the source of the NO_3-. This compound is much less susceptible to explosive decomposition and considerably less expensive than the hydrazinium nitrate. In actual practice, the Rocketdyne formulation is based on the addition of solid ammonium nitrate (NH_4NO_3) to a large excess of MMH ($CH_3N_2H_3$). The ammonia produced is removed by sparging with dry nitrogen. Some of the $CH_3N_2H_3$ vapor is also removed by this process. The final step is the addition of the proper amount of N_2H_4 and whatever MMH was lost during sparging. The final ingredients are then mechanically stirred for a sufficient time to insure a homogeneous blend.

$$NH_4NO_3 + CH_3N_2H_3 \Rightarrow CH_3N_2H_4^+ + NO_3^- + NH_3$$

(C) The hydrogen ion exchange shown above is the same as results from the addition of hydrazinium nitrate.

$$N_2H_5^+ + NO_3^- + CH_3N_2H_3 \rightleftarrows N_2H_4 + CH_2N_2H_4^+ + NO_3^-$$

(U) The final ingredients are then mechanically stirred for a sufficient time to insure a homogeneous blend.

2.17.6.2 Analysis

(C) The chemical analysis of MHF-5 fuel blend is accomplished by Rocketdyne using a combination of gas chromatography and titration. The nitrate (defined as hydrazinium nitrate) is determined by gravimetric analysis. See either Rocketdyne (Reference 10), or MIL Specification (MIL-P-81507 (AS)). The hydrazine, MMH and water content are determined directly by gas chromatography. According to MIL-P-81507 (AS) the following analysis limits are given:

Component	Limit
Hydrazine (N_2H_4)	26.0 ±2.0 wt. %
MMH ($CH_3N_2H_3$)	55.0 ±2.0 wt. %
Hydrazine Nitrate ($N_2H_5NO_3$)	19.0 ±2.0 wt. %
H_2O + Other Soluble Impurities	2.0 wt. % Max.
Particulate	10.0 Milligrams/liter
Density at 25°C (77°F)	1.00 to 1.02 g/cc
Freezing Point	-71 ±5°F

(U) The density limits would appear to be too stringent for the composition limits given. The freezing point limits (-71.0 ±5.0F) were obviously based on earlier melting point estimates. The accepted melting point for MHF-5 is -43 F and the present MIL Spec. will require changing. The particulate level of 10.0 milligrams per liter is defined as undissolved solids retained on a 10 micron filter paper.

2.17.6.3 Cost and Availability

(U) At the present time firm cost estimates for MHF-5 are not available. This fuel blend can be mixed by individual users from commercially available materials or purchased from Rocketdyne, a division of North American Rockwell Corp., 6633 Canoga Avenue, Canoga Park, California, 91304. The current production facility at Rocketdyne can produce approximately 40,000 pounds per year but could be increased if firm requirements for larger quantities and sufficient lead time were given.

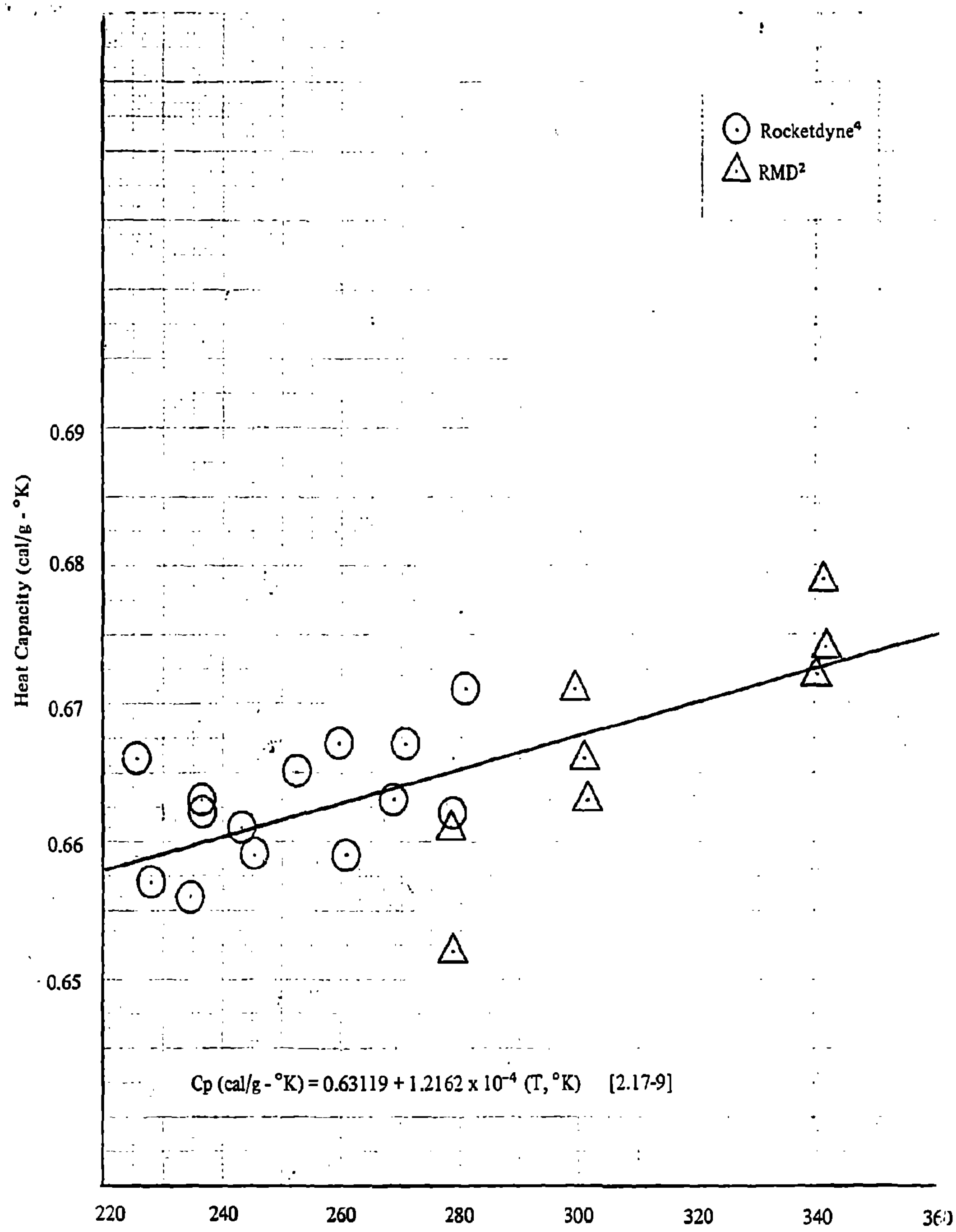


Figure 2.17-8. Heat Capacity versus Temperature, Liquid MHF-5

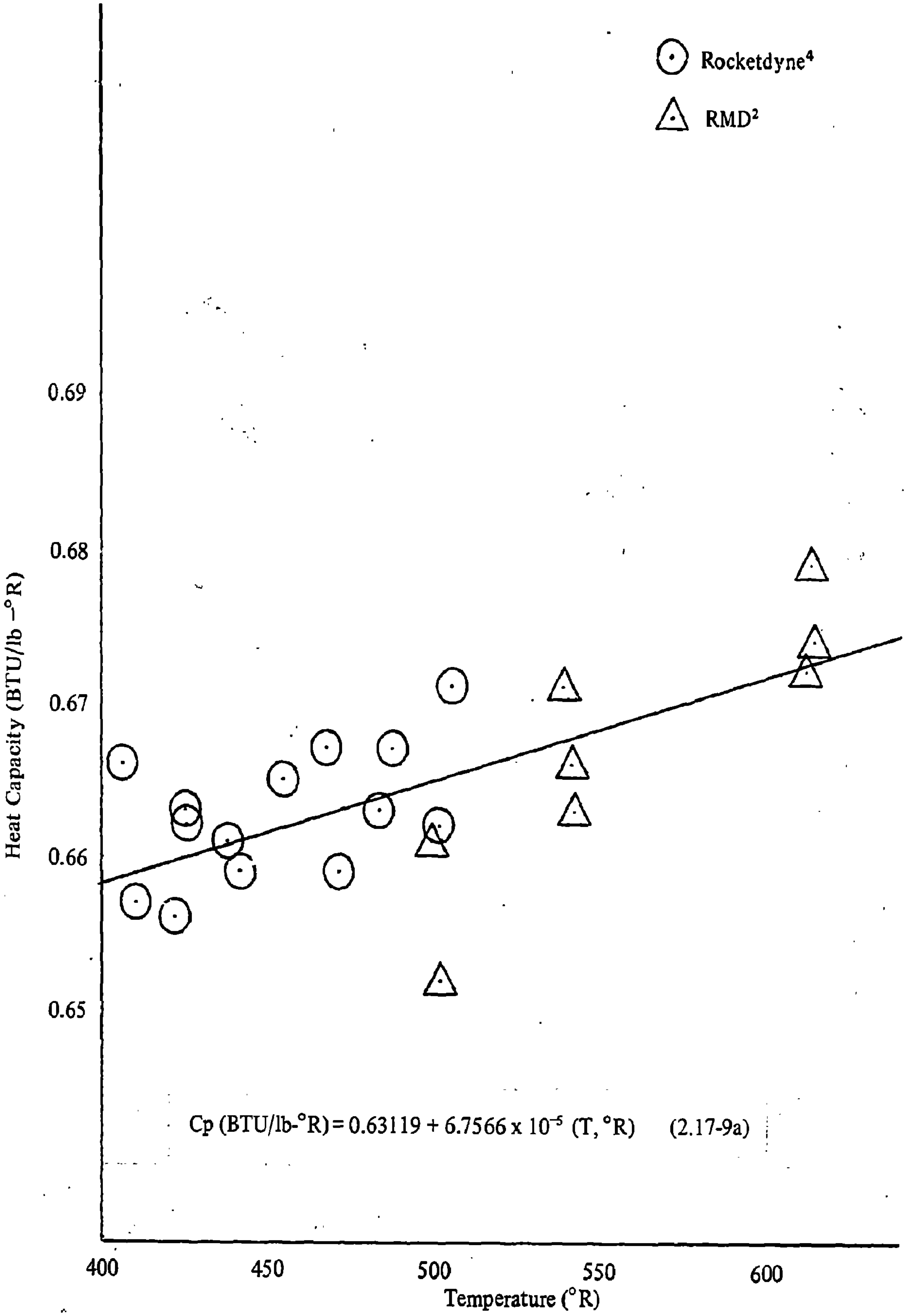


Figure 2.17-8a. Heat Capacity versus Temperature, Liquid MHF-5

(C) Hydrazine and MMH are available in large quantities at $2.95/lb and $3.20/lb, respectively. Ammonium nitrate is readily available in large quantities at $0.41 per pound. Hydrazinium nitrate, if used, is only available in small quantities at a minimum of $10.00 per pound.

2.17.6.4 Shipping and Transportation

(U) The following information on shipping and transportation was abstracted from Rocketdyne(10).

(U) Shipment of MHF-5 by common carrier is authorized by the Interstate Commerce Commission (ICC) and it is classified as "Hydrazine Solution, Corrosive Liquid", and requires a white label. The following containers have been approved by the ICC according to the specifications listed:

1. Boxed glass carboys (ICC - 1D)
2. Glass bottles not exceeding 1 gallon capacity cushioned with vermiculite covered with tightly sealed tin cans and packaged in wooden boxes (ICC-15A, 15B or 15C).
3. Metal barrels or drums constructed of 304 or 347 stainless steel with openings not to exceed 2.3 inches in diameter. (ICC-5, 5A, 5C and for single trip ICC-17E).
4. Tank cars (ICC-103C-W or 111A100-W-6) and tank motor vehicles (ICC-MC310, MC311 or MC312). Tanks must be constructed of 304L or 347 stainless steel with a maximum molybdenum content of 1/2%. Vapor space must be filled with nitrogen gas at atmospheric pressure.

Tank-truck shipments are only authorized by ICC special permit. A maximum of 5 pints of MHF-5 may be shipped by air in cargo aircraft only and packaged according to ICC-15A or 15B specification. (See "Official Air Transportation Restricted Articles", Tariff No. 6-D- Note No. 135, August 1966.)

The shipment of MHF-5 on waterways is allowable on decks of cargo vessels only. (U.S. Coast Guard regulations, NAV-CG-108) ICC Specification 1D covers carboys not to exceed 6-1/2 gallons. Stainless steel drums under 55 gallon capacity under ICC-5, 5A, 5C, 5G or 17E. Wooden boxes not over 200 pounds gross weight covered by ICC Specification 15A, 15B and 15C.

2.17.7 REFERENCES MHF-5

(U) 1. Reaction Motors Div. of Thiokol Chemical Corp., "Packaged Liquid Propellants," Report No. RMD 5005-F, Denville, New Jersey, September 1962. (CONFIDENTIAL)

2. Reaction Motors Div. of Thiokol Chemical Corp., "Advanced Propellants Investigation for Prepackaged Liquid Engines," Report No. RMD 5046-Q2, Denville, New Jersey, November 1964. (CONFIDENTIAL)

3. ibid Final Report No. RMD 5046-F, Denville, New Jersey, June 1965. (CONFIDENTIAL)

4. Rocketdyne, Div. North American Rockwell Corp., "Engineering Property Data on Rocket Propellants," AFRPL-TR-67-274 (Rocketdyne R-6638-5) Canoga Park, California, October, 1967. (CONFIDENTIAL)

5. Personal Communication, Mr. John Weber, Rocketdyne, Canoga Park, California, October 1967. (CONFIDENTIAL)

6. Rocketdyne, Div. North American Rockwell Corp., "Engineering Property Data on Rocket Propellants," Final Report No. AFRPL RT-68-100 (Rocketdyne R-7437), Canoga Park, California, May 1968. (CONFIDENTIAL)

7. Aerojet-General Corp., "Heat Transfer Study of MHF-5 and MMH," AFRPL-TR-67-208, Part II, Edwards, California, August 1967. (CONFIDENTIAL)

8. Rocketdyne, Div. North American Rockwell Corp., "Condor Propulsion System," Quarterly Technical Progress Report for Period Ending 31 July 1968, Report No. R-7275-4 Contract Now 66-0728-i. (CONFIDENTIAL)

9. Rocketdyne, Div. North American Rockwell Corp., "Engineering Property Data on Rocket Propellants," Fourth Quarterly Report, AFRPL-TR-67-199 (Rocketdyne R-6638-4), Canoga Park, California, July 1967. (CONFIDENTIAL)

10. Rocketdyne, Div. North American Rockwell Corp., "Condor Propellant Handbook Vol. III-MHF-5B, Report No. R-7556, Contract Now 66-0728-i. (to be published)

11. Wagman, D.D., et al., "Selected Values of Chemical Thermodynamic Properties," NBS Tech. Note 270-1, National Bureau of Standards, Washington, D.C., October 1965.

12. Kay, W.B., J. Ind. & Eng. Chem. 28, 1014 (1936).

13. Aerojet-General Corp., Personal Communications with S.D. Rosenberg, December 20, 1968.

2.18 MHF-5B

2.18.1 PROPERTY SUMMARY SHEET

Chemical Name: Mixed Hydrazine Fuel No. 5-B
Common Name: MHF-5B
Empirical Formula: $C_{0.5784}H_{5.2486}N_{2.0918}O_{0.2755}$
Formula Weight: 45.948
Composition; % b.w.: 58.0 MMH, 23.0 N_2H_4, 19.0 N_2H_5 NO_3

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	230.4 -42.8 414.7 -45.0	°K °C °R °F		2	
NORMAL BOILING POINT	369 96 665 205	°K °C °R °F	Approx.	See text and Section 2.17	
HEAT OF VAPORIZATION	See Section 2.17	kcal/mole BTU/lb			
TROUTON CONSTANT	See Section 2.17				
CRITICAL STATE CONSTANTS	See Section 2.17				
DENSITY OF LIQUID	1.0039 62.669	g/cc lb/ft^3	298	1	2.18-1
SONIC VELOCITY	See text and Section 2.17				
COMPRESSIBILITY OF LIQUID					
Adiabatic	See text and Section 2.17				
Isothermal	See text and Section 2.17				
VAPOR PRESSURE OF LIQUID	See text and Section 2.17				
VISCOSITY OF LIQUID	1.994 1.340 x 10^{-3}	centipoise lb$_m$/ft-sec	298	1	2.18-2
HEAT CAPACITY OF LIQUID	See text and Section 2.17				
THERMAL CONDUCTIVITY OF LIQUID	See text and Section 2.17				
SURFACE TENSION	See text and Section 2.17				
HEAT OF FORMATION	6.834 267.7	kcal/mole BTU/lb	298	See Section 2.18.5.1	

2.18.2 GENERAL INTRODUCTION TO MHF-5B

(C) The MHF-5B fuel blend was specifically formulated to meet the–45 F freezing point requirement of the Condor propulsion system. The fuel blend MHF-5 originally designated for Condor was previously thought to have a freezing point of–71 F but later investigations showed the freezing point to be–43 F. An additional blend, MHF-5A, was also formulated to meet a–65 F requirement, but due to relaxed melting point requirements, was later abandoned in favor of MHF-5B. The nominal compositions of the blends are given below:

	Nominal Weight Percent		
Compound	MHF-5	MHF-5A	MHF-5B
MMH ($CH_3N_2H_3$)	55	68	58
Hydrazine (N_2H_4)	26	13	23
Hydrazinium Nitrate ($N_2H_5NO_3$)	19	19	19

(C) The compositions of the two blends MHF-5 and MHF-5B are nearly identical, the only difference being a 3% shift toward higher MMH content. The physical properties of the MHF-5 blend have generally been well defined, while only the density, viscosity and melting point of MHF-5B have been investigated separately.

(U) For many engineering applications, the other properties as defined for MHF-5 can provisionally be used for the MHF-5B blend as well. These properties are given in Section 2.17.3.

2.18.3 PHYSICAL PROPERTIES OF MHF-5B

2.18.3.1 Vapor Pressure

(U) No measurements have been made of the vapor pressure of MHF-5B, however, the proximity in the composition to MHF-5 and the dominance of MMH indicate that the vapor pressure should be equal to or slightly higher than that for MHF-5. MMH is the highest vapor pressure component in MHF-5B. See Sections 2.17.3.1 and 2.4.3.1 for MHF-5 and MMH, respectively.

2.18.3.2 Density of MHF-5B

(C) The density of saturated liquid MHF-5B has been experimentally determined by Rocketdyne(1) over a temperature range from -58 to 71 C (-72 to 160 F). Since the temperature of–58 C is below the reported melting point of -42.8 C, it is assumed that the liquid was supercooled. The composition of the blend used by Rocketdyne was given as;

Compound	Weight Percent
MMH ($CH_3N_2H_3$)	58.3
Hydrazine (N_2H_4)	21.6
Hydrazinium Nitrate ($N_2H_5NO_3$)	19.0
Water (H_2O)	1.1

(U) The five experimental points given by Rocketdyne were obtained using a glass pycnometer and the details are given in Section 2.17.3 (MHF-5). The points are shown in Figures 2.18-1 and in 2.18-1a. Using the method of least-squares, the density is expressed as a linear function of temperature by;

$$\rho\,(\mathrm{g/cc}) = 1.2492 - 8.2274 \times 10^{-4}(\mathrm{T, K}) \qquad (2.18\text{-}1)$$

$$\rho\,(\mathrm{lb/ft^3}) = 77.9827 - 0.028534(\mathrm{T, R}) \qquad (2.18\text{-}1a)$$

The standard deviation of the experimental data described by equation 2.18-1 is 4.04 x 10^{-4} g/cc and the average percent deviation is 0.022 percent.

(C) Rocketdyne(2) has studied the density of four various MHF-5 related blends and reported the following equation for density where composition is a variable.

$$\rho\,(\mathrm{g/cc}) = 1.028 - 8.232 \times 10^{-4}(\mathrm{t, C}) - 5.199 \times 10^{-8}(\mathrm{t, C})^2 - 1.512 \times 10^{-3}\,\mathrm{M} + 4.42 \times 10^{-3}\,\mathrm{N} \qquad (2.18\text{-}2)$$

or by conversion

$$\rho\,(\mathrm{g/cc}) = 1.2490 - 7.948 \times 10^{-4}(\mathrm{T, K}) - 5.199 \times 10^{-8}(\mathrm{T, K})^2 - 1.512 \times 10^{-3}\,\mathrm{M} + 4.42 \times 10^{-3}\,\mathrm{N} \qquad (2.18\text{-}2a)$$

where

M = weight percent MMH
N = weight percent $N_2H_5NO_3$

(U) Using the nominal composition of MHF-5B, the density values obtained from equations 2.18-2a are in excellent agreement with those obtained from equation 2.18-1. Equation 2.18-2a would appear to be of value, if the particular blend under consideration deviated significantly from the nominal composition.

2.18.3.3 Viscosity of Liquid MHF-5B

(C) The viscosity of liquid MHF-5B has been experimentally determined by Rocketdyne(1) over a temperature

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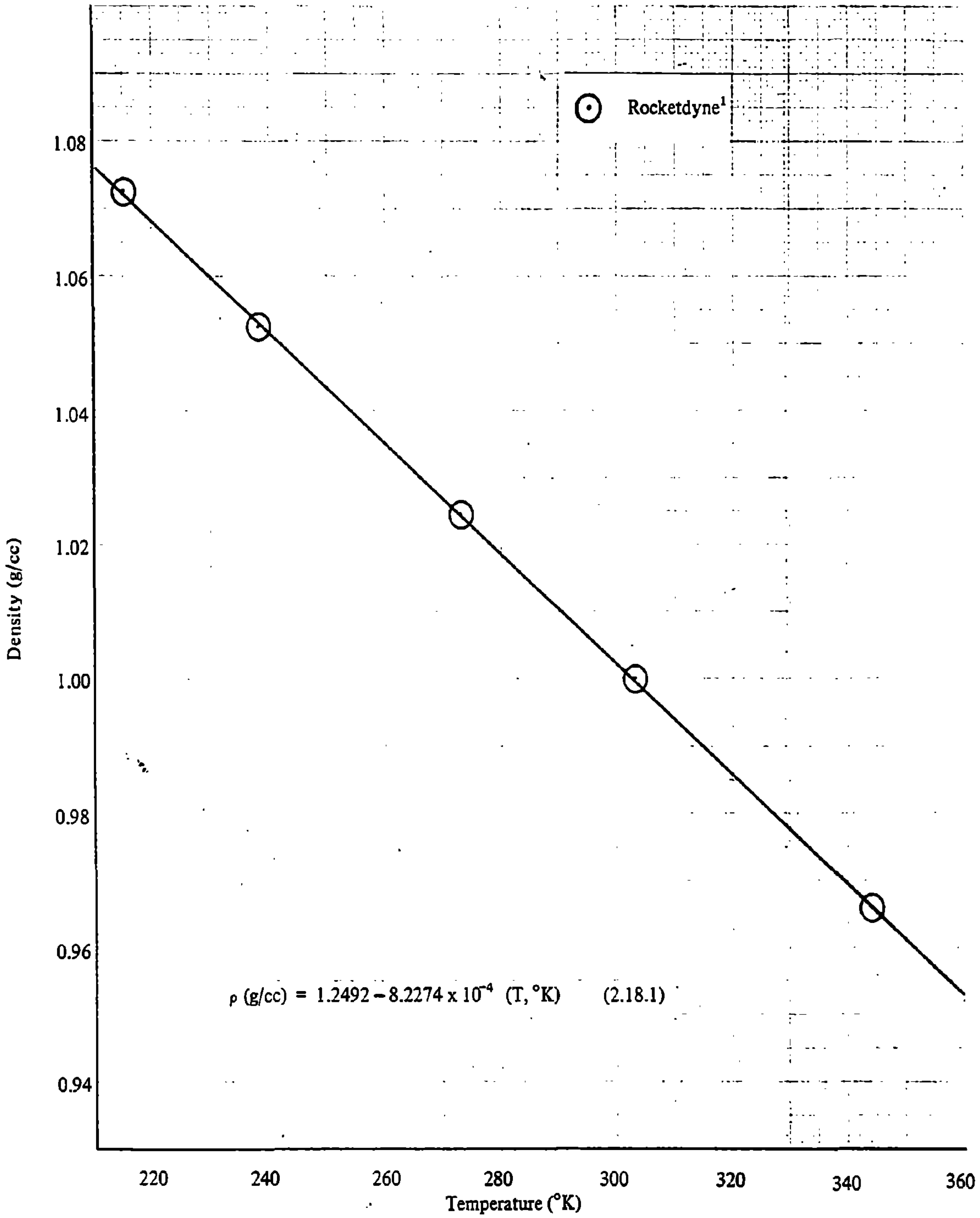


Figure 2.18-1. Density versus Temperature, Liquid MHF-5B

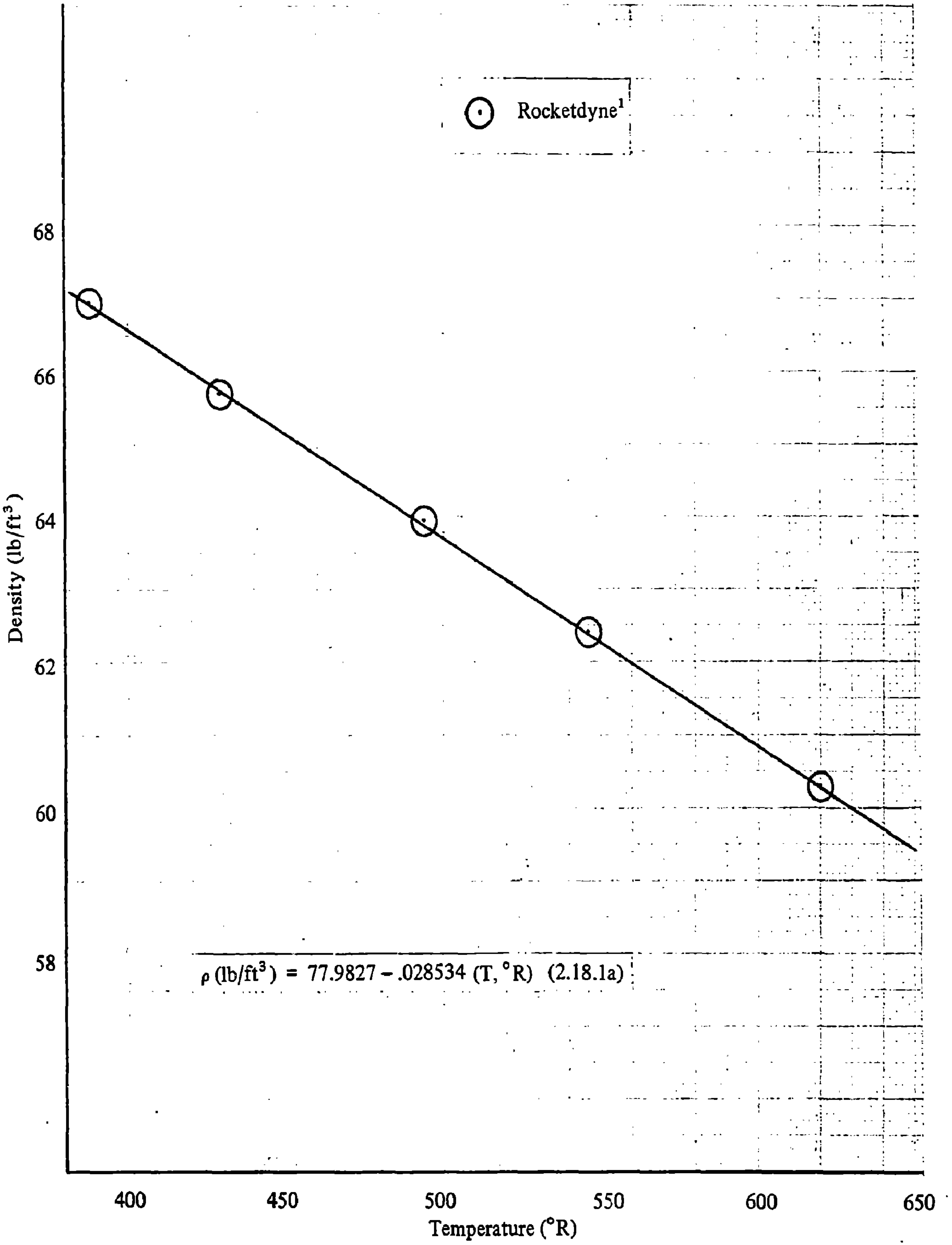


Figure 2.18-1a. Density versus Temperature, Liquid MHF-5B

(C) range from -40 to 93.3 C (-40 to 200 F). A capillary viscometer was employed and the blend composition was given as:

Compound	Weight Percent
MMH ($CH_3N_2H_3$)	58.3
Hydrazine (N_2H_4)	21.6
Hydrazinium Nitrate ($N_2H_5NO_3$)	19.0
Water (H_2O)	1.1

(U) The kinematic viscosities reported where converted to absolute units using density values obtained from equation 2.18-1 and are shown in Figures 2.18-2 and 2.18-2a. The absolute viscosity as a function of temperature was found by a least squares fit to be best represented by.

$$\log \mu\,(\mathrm{cp}) = -3.9625 + \frac{3087.40}{T,K} - \frac{-9.7161\mathrm{x}10^5}{(T,K)^2} + \frac{1.2820\mathrm{x}10^8}{(T,K)^3} \qquad (2.18\text{-}3)$$

and in engineering units,

$$\log \mu\,(\mathrm{lb_m/ft\text{-}sec}) = -7.1352 + \frac{5557.32}{T,R} - \frac{3.1480\mathrm{x}10^6}{(T,R)^2} + \frac{7.4766\mathrm{x}10^8}{(T,R)^3} \qquad (2.18\text{-}3a)$$

The standard deviation of the six experimental points as described by equation 2.18-3 is 2.36×10^{-3} centipoise with the average percent deviation being 0.058 percent.

Note: Other Physical Properties

(U) The proximity of MHF-5B to the composition of MHF-5 indicates that little deviation should occur in the values of the physical properties. Comparison with MMH will also be helpful in determining engineering estimates. Specific measurements of the other physical properties of MHF-5B were not reported.

2.18.4 CHEMICAL PROPERTIES OF MHF-5B

(U) Due to the similarity with MHF-5, the chemical properties of MHF-5B will be essentially the same as those for MHF-5. See Section 2.17.

2.18.5 THERMODYNAMIC PROPERTIES OF MHF-5B

2.18.5.1 Heat of Formation of Liquid

(C) The heat of formation of this fuel blend can be calculated for the liquid at 298 K (25 C) by the molar addition of the individual heats of formation. The heat of mixing is not known and is assumed to be negligible. Taking the nominal composition to be 58.0% $CH_3N_2H_3$, 23.0% N_2H_4 and 19.0% $N_2H_5NO_3$ the heat of formation at 298 K is calculated to be 6.834 kcal/mole. The mole is defined as 45.948 grams having the empirical formula;

$$C_{0.57841}\ H_{5.24865}\ N_{2.09183}\ O_{0.27550}$$

Compound	Weight%	Mole Fraction (1 mole blend)	ΔH_{f298} kcal/mole
$CH_3N_2H_3$	58.0	0.578406	13.106
N_2H_4	23.0	0.329759	12.054
$N_2H_5NO_3$	19.0	0.091835	-51.41

For one mole of MHF-5B then;

$$\Delta H_{f298} = 0.578406\,(13.106) + 0.329759\,(12.054) + 0.091835\,(-51.41)$$

$$\Delta H_{f298} = 6.834 \text{ kcal/mole, mole} = 45.948 \text{ grams}$$

or 148.7 cal/gram

(U) The heat of formation used for N_2H_4 and MMH are discussed in the appropriate sections of this handbook. The value used for $N_2H_5NO_3$ was taken from Wagman et al(3) for an aqueous solution assuming hydrazine to be the electrolyte.

2.18.5.2 Specific Heat, Heat of Vaporization and Heat of Fusion

(U) The use of values of the above quantities for MHF-5 will suffice provisionally for MHF-5B. For engineering estimates, the differences in these properties between MMH, N_2H_4, and MHF-5 can be used as bases for making small corrections for the composition difference.

2.18.6 LOGISTICS OF MHF-5B

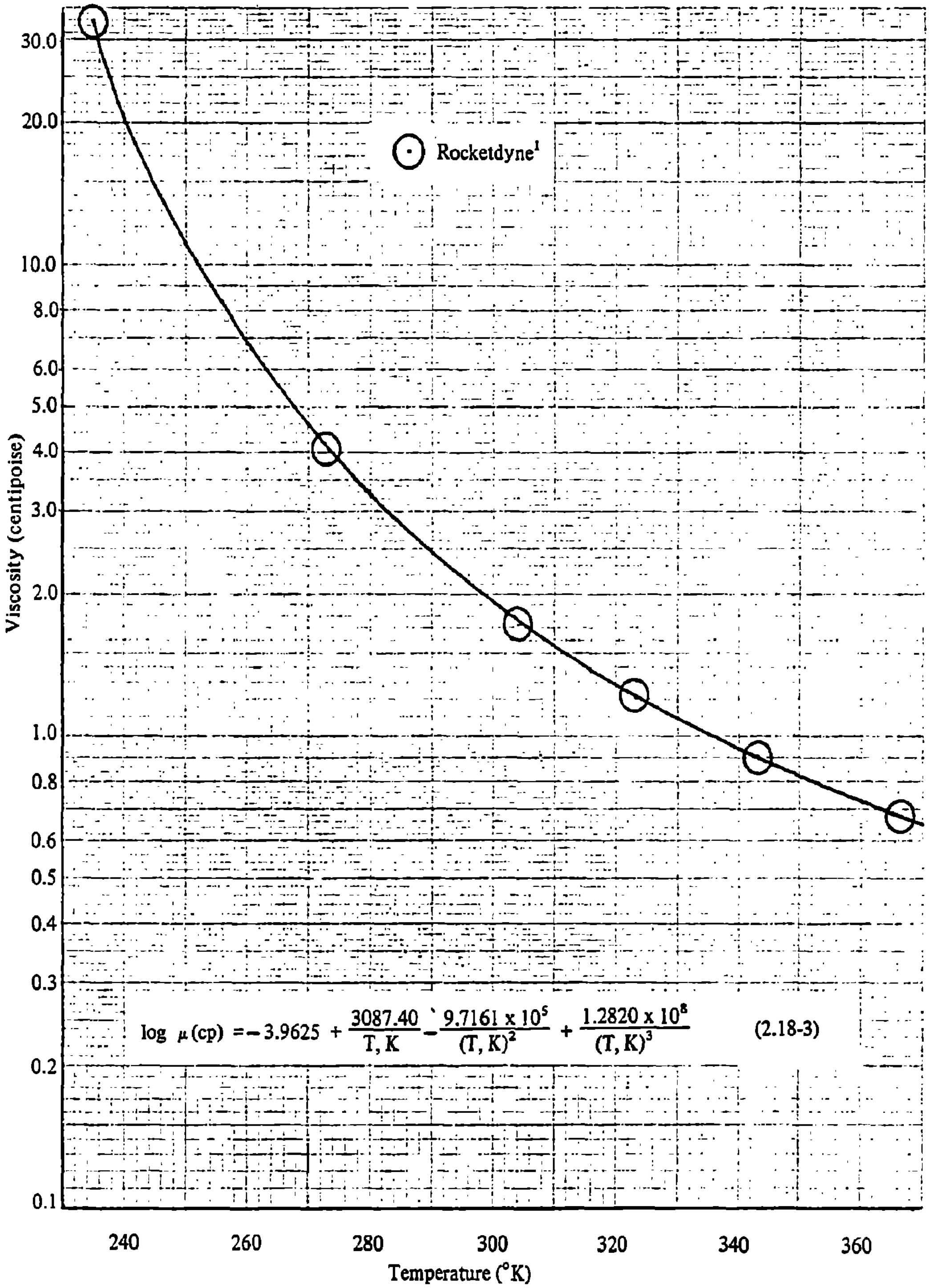
(U) Due to the similar compositions, the logistics data for MHF-5 apply equally to MHF-5B. See Section 2.17.

2.18.7 REFERENCES

1. Rocketdyne, Div. N. Am. Rockwell Corp., "Condor Propulsion System", Quarterly Tech. Progress Report for period Ending 31 July 1968. Report No. R-7275-4 Contract No. 66-0728-i (Confidential).

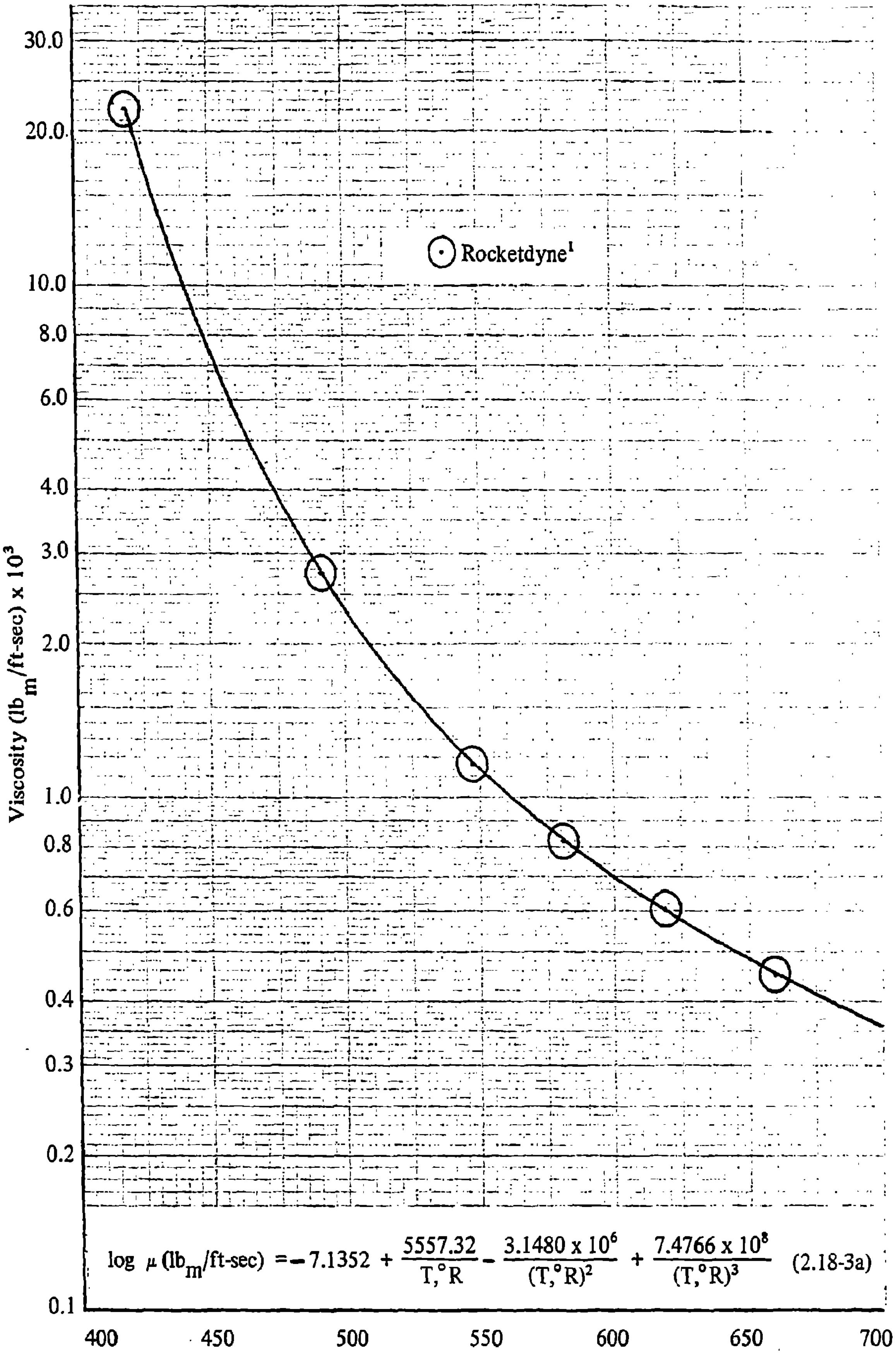
2. Rocketdyne, Div. N. Am. Rockwell Corp., "Condor Propellant Handbook Vol. III-MHF-5B, Report No. R-7556 Contract No. 66-0728-i (to be published). (Confidential).

3. Wagman, D.D., et al, "Selected Values of Chemical Thermodynamic Properties", NBS Tech. Note 070-1, National Bureau of Standards, Washington, D.C., October 1965.



$$\log \mu(\mathrm{cp}) = -3.9625 + \frac{3087.40}{T,K} - \frac{9.7161 \times 10^5}{(T,K)^2} + \frac{1.2820 \times 10^8}{(T,K)^3} \qquad (2.18\text{-}3)$$

Figure 2.18-2. Viscosity versus Temperature, Liquid MHF-5B



$$\log \mu\,(\mathrm{lb_m/ft\text{-}sec}) = -7.1352 + \frac{5557.32}{T,^\circ R} - \frac{3.1480 \times 10^6}{(T,^\circ R)^2} + \frac{7.4766 \times 10^8}{(T,^\circ R)^3} \quad (2.18\text{-}3a)$$

Figure 2.18-2a. Viscosity versus Temperature, Liquid MHF-5B

2.19 MHF-6

2.19.1 PROPERTY SUMMARY SHEET

Chemical Name: **Mixed Hydrazine Fuel No. 6**
Common Name: **MHF-6**
Empirical Formula: $C_{1.5844}H_{12.7313}N_{4.1984}O_{0.5828}$
Formula Weight: **100.0**
Composition; % b.w.: **73.0 MMH, 16.5 N_2H_4, 10.5 H_2O**

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	219.3 –53.9 394.7 –65	°K °C °R °F		1	
NORMAL BOILING POINT	367.2 94.0 661.0 201.3	°K °C °R °F		1	
VAPOR PRESSURE OF LIQUID	45.6 0.88	mm Hg psia	298	1	2.19-1
DENSITY OF LIQUID	0.9223 57.577	g/cc lb/ft^3	298	1	2.19-2
VISCOSITY OF LIQUID	1.17 7.86×10^{-4}	centipoise lb_m/ft-sec	298	1	2.19-3
HEAT OF FORMATION (liquid)	–137.45 –247.41	cal/g BTU/lb	298	calc.	

2.19.2 GENERAL

(C) MHF-6 is a blend of methylhydrazine (MMH), hydrazine and water developed as a low melting-point prepackageable fuel which could be used as a monopropellant, or as a rocket fuel in conjunction with halogen oxidizers. The addition of water to the blend provides oxygen for the combustion of undesirable carbon to CO or CO_2.

(U) MHF-6 and similar blends have been investigated on a laboratory scale by the Navy and RMD. It is roughly midway between MHF-3 and BAF-1185 in composition and many of its properties are similar to those of the latter fuels.

(C) MHF-6 is a clear, colorless, hygroscopic liquid at room temperature and gives off an ammoniacal odor characteristic of the hydrazines. Its nominal composition in weight percent is as follows:

Monomethylhydrazine (MMH)	73.0%
Hydrazine	16.5%
Water	10.5%

(U) No military or other specification exists covering this fuel. The data contained herein is considered provisional.

2.19.3 PHYSICAL PROPERTIES OF MHF-6

2.19.3.1 Vapor Pressure and Normal Boiling Point

(U) The vapor pressure of liquid MHF-6 does not appear in the literature. Some preliminary unpublished values have been furnished by RMD(1). Only five experimental points were obtained and details were not furnished. The data is plotted in Figures 2.19-1 and 2.19-1a and cover a temperature range from 45 to 93 C (113 to 200 F). The data can be expressed in the classical form

$$\log P\,(\text{mm Hg}) = 8.1579 - \frac{1937.63}{T,K} \qquad (2.19\text{-}1)$$

$$\log P\,(\text{psia}) = 6.4442 - \frac{3487.74}{T,R} \qquad (2.19\text{-}1a)$$

(U) The vapor pressure data shown here should be treated as preliminary work, until further verification is obtained.

(U) The normal boiling point obtained from equation 2.19-1 is 367.2 K or 94 C (201 F).

2.19.3.2 Density of Liquid MHF-6

(U) The density of saturated MHF-6 does not appear in the literature. Preliminary unpublished data has been made available by RMD(1). The data, which covers a temperature range from −54 to 74 C (−65 to 165 F) is shown in Figures 2.19-2 and 2.19-2a. The density is a linear function of temperature

$$\rho\,(\text{g/cc}) = 1.1951 - 9.1500 \times 10^{-4}\,(T,K) \qquad (2.19\text{-}2)$$

$$\rho\,(\text{lb/ft})^3 = 74.6081 - 0.03173\,(T,R) \qquad (2.19\text{-}2a)$$

(U) The standard deviation of the experimental data from equation 2.19-2 is 0.0017 g/cc, while the average percent deviation is 0.14 percent.

(U) In all probability this density information is valid but it must be considered preliminary until such time as published data becomes available.

2.19.3.5 Viscosity of Liquid MHF-6

(U) The viscosity of liquid MHF-6 does not appear in the literature. RMD(1) has made available some preliminary data. Only three experimental points at -54, -12 and 22C were given. The points are shown in Figures 2.19-3 and 2.19-3a. Since only three points exist, a curve fit was not warranted.

(U) The viscosity of MHF-6 should be treated as preliminary and used for only the most basic engineering estimates.

2.19.4 CHEMICAL PROPERTIES OF MHF-6

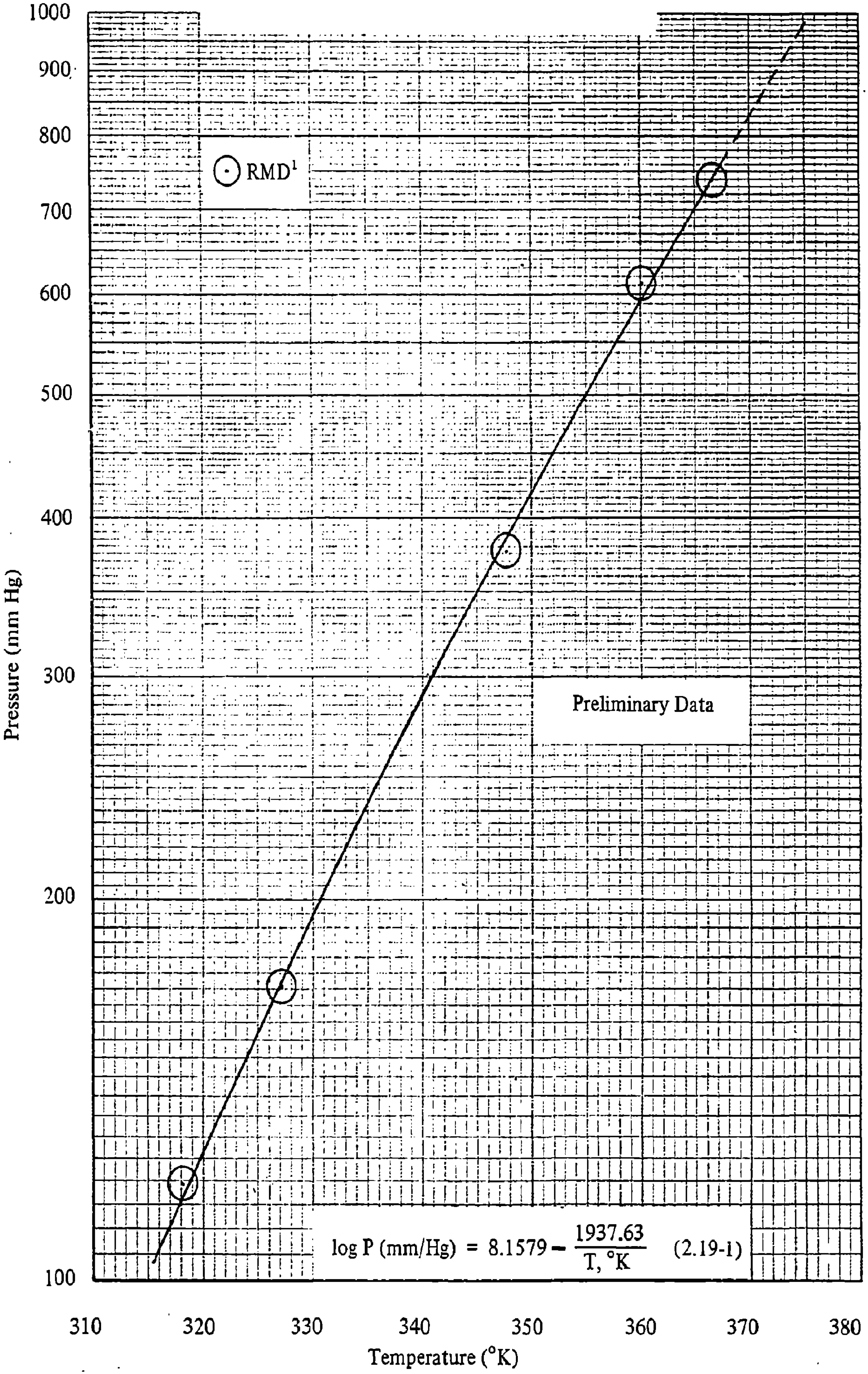
(C) The chemical reactions of which MHF-6 is capable will be dominated by the high methylhydrazine concentration. In general, the fuel will undergo all the reactions of MMH and N_2H_4. The effect of water on the reactions has not been studied.

(U) The reactions of MMH and N_2H_4 are discussed in detail in Sections 2.4.4.1 and 2.3.4.1, respectively.

2.19.5 THERMODYNAMIC PROPERTIES OF MHF-6

2.19.5.1 Heat of Formation of Liquid

(C) The heat of formation of liquid MHF-6 at 298.15 K (25 C) can be calculated from the molar addition of the individual heats of formation. The heat of mixing is not known but is assumed to be negligible. It was assumed that the water would bond with the hydrazine to form hydrazine hydrate. The calculated value is -137.45 cal/gram based on 100 grams of the mixture.



$$\log P\ (\mathrm{mm/Hg}) = 8.1579 - \frac{1937.63}{T,\ ^{\circ}K} \qquad (2.19\text{-}1)$$

Figure 2.19-1. Vapor Pressure versus Temperature, Liquid MHF-6

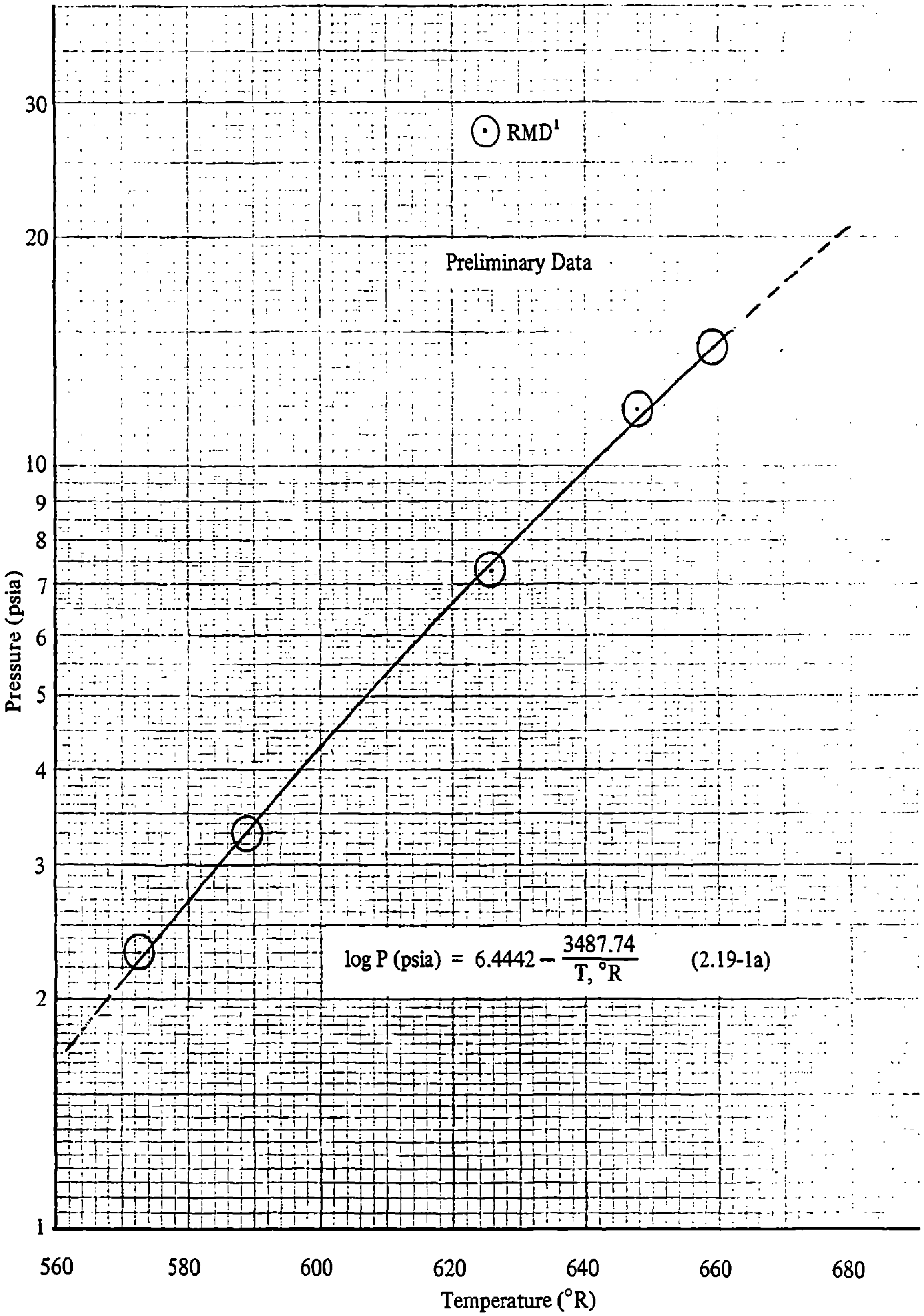
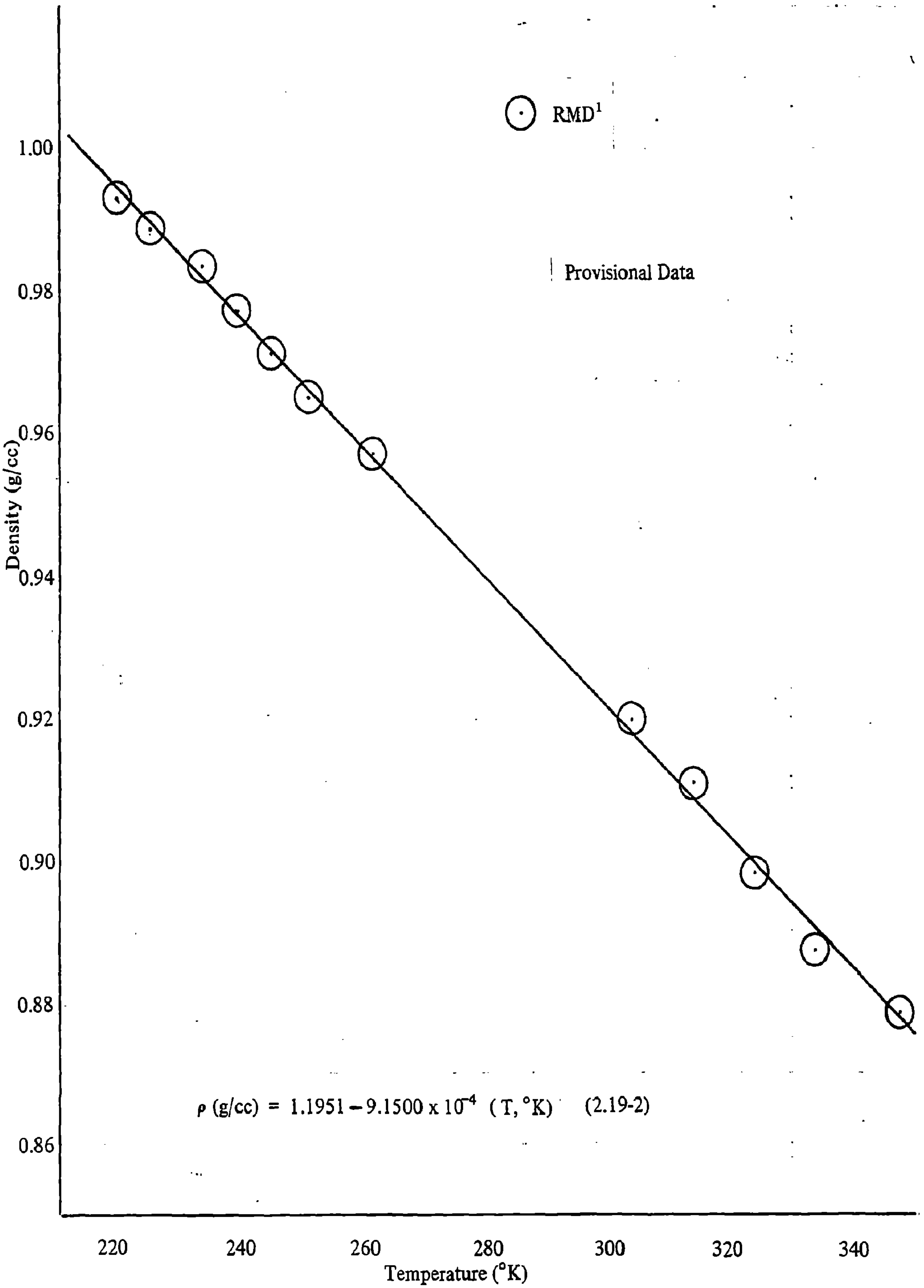


Figure 2.19-1a. Vapor Pressure versus Temperature, Liquid MHF-6



$$\rho\ (\text{g/cc}) = 1.1951 - 9.1500 \times 10^{-4}\ (T, {}^{\circ}\text{K}) \qquad (2.19\text{-}2)$$

Figure 2.19-2. Density versus Temperature, Liquid MHF-6

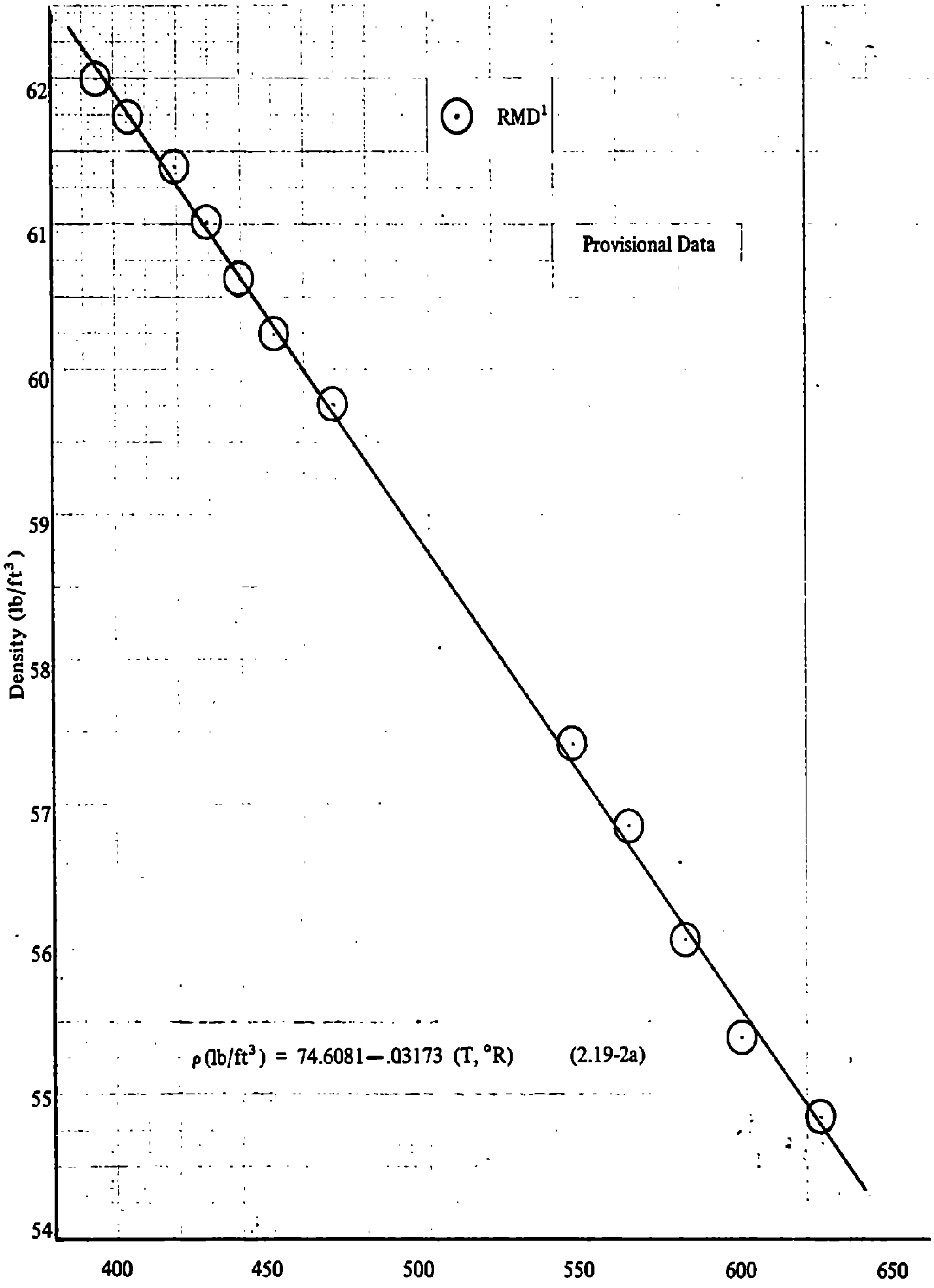


Figure 2.19-2a. Density versus Temperature, Liquid MHF-6

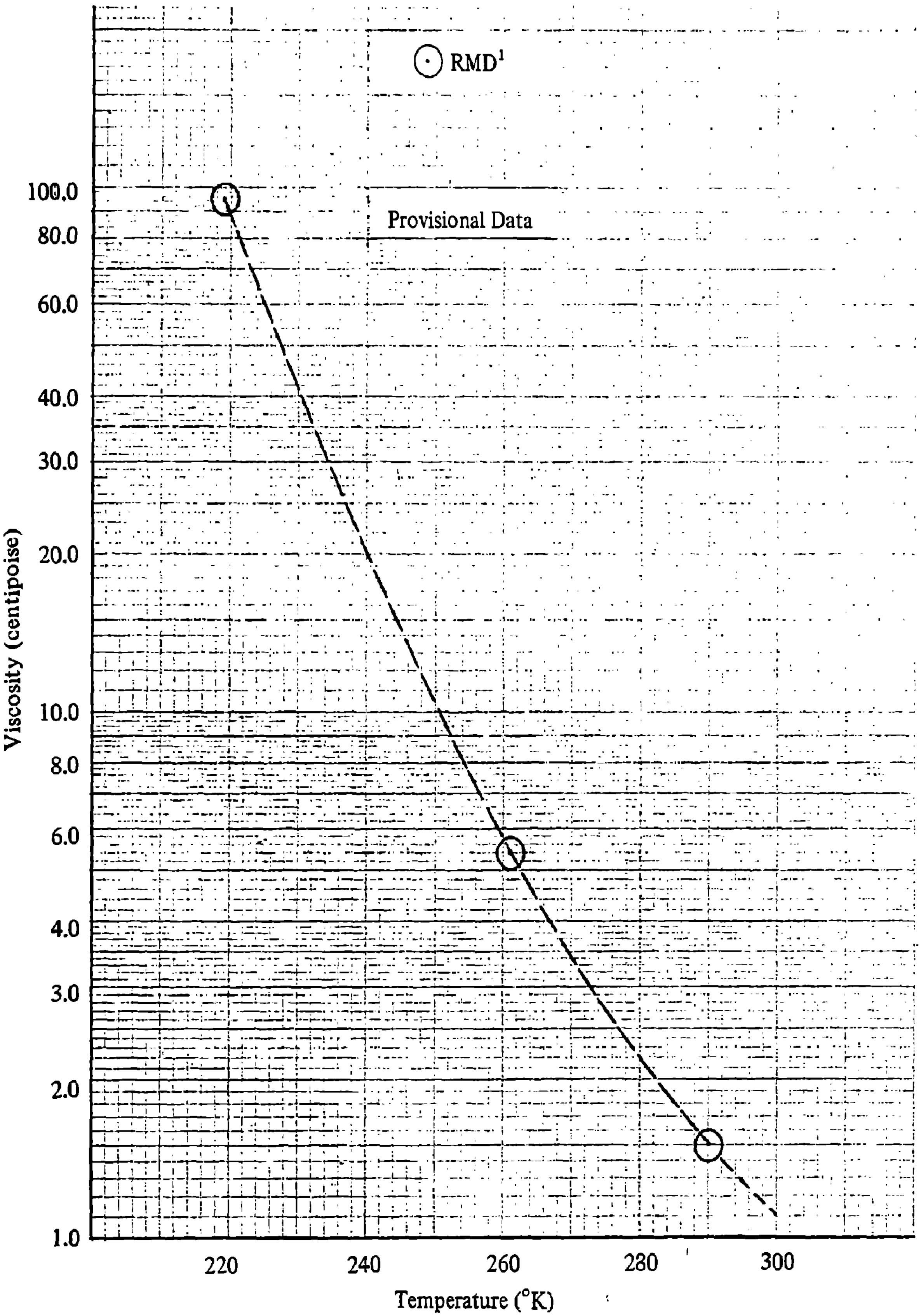


Figure 2.19-3. Absolute Viscosity versus Temperature, Liquid MHF-6

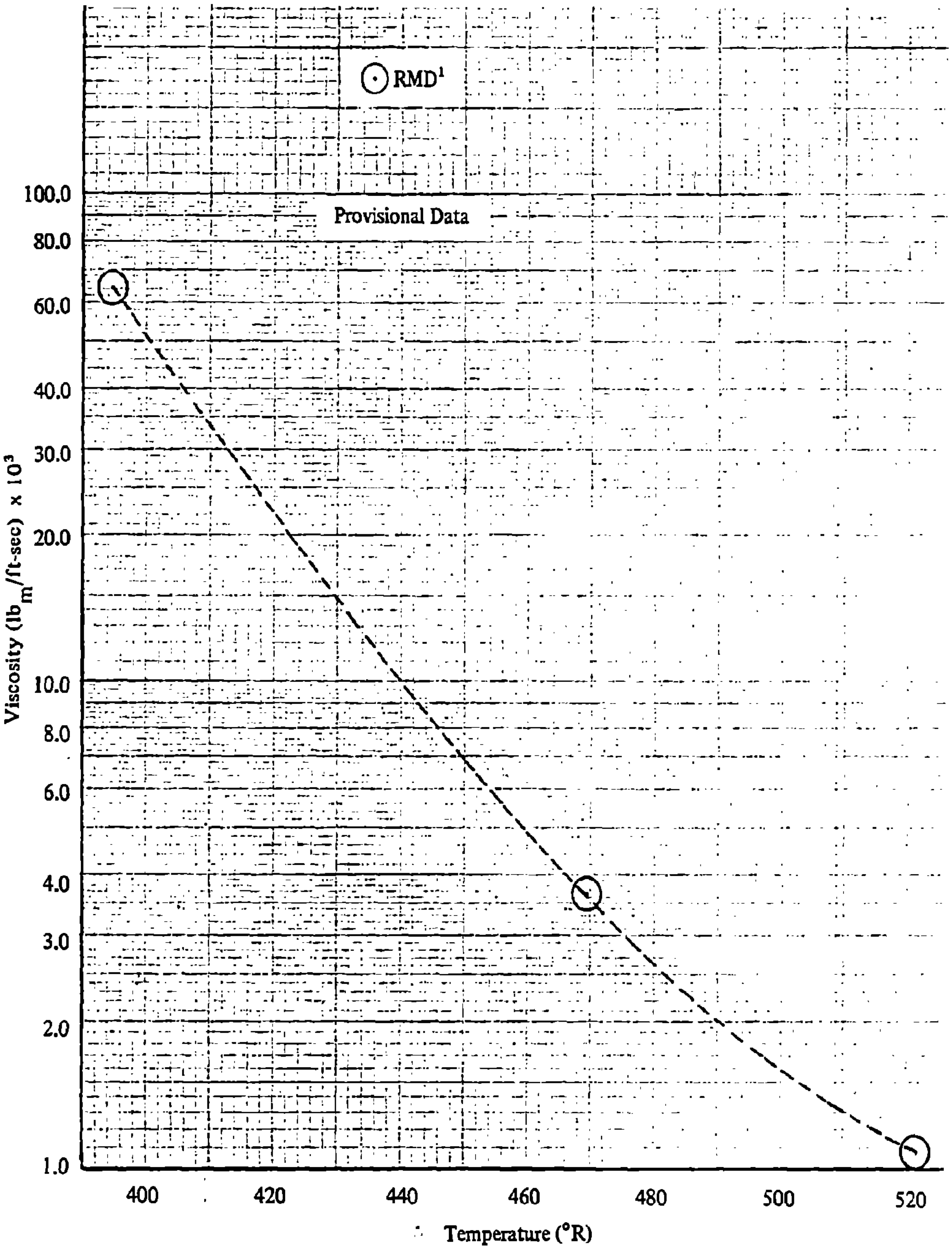


Figure 2.19-3a. Absolute Viscosity versus Temperature, Liquid MHF-6

(C) Compound	Weight (grams)	Molecular Weight	Moles	ΔH_{f298} (kcal/mole)
CH_6N_2	73.0	46.075	1.584373	13.106
N_2H_4	16.5	32.048	0.514853	12.054
H_2O	10.5	18.016	0.582815	-68.315

The mixture then empirically for 100 grams is

$$C_{1.58437}H_{12.73128}N_{4.19845}O_{0.582815}$$

Combining all the hydrazine to its hydrate the heat of formation is

$$\Delta H_{f298} = 1.58427\,(13.106) + 0.514853\,(-58.01) + 0.0679626\,(-68.315)$$

$$\Delta H_{f298} = -13.745 \text{ kcal/mole}$$

$$\Delta H_{f298} = -137.45 \text{ cal/gram}$$

(U) The heats of formation of hydrazine hydrate (-58.01) and water (-68.315) were taken from Wagman(2). The value of 13.106 for MMH is discussed in Section 2.4.5.1.

2.19.5.2 Melting Point

(U) The melting point has been tentatively established as -54 C (-65 F). Although experimental data are lacking, a well-established melting point isotherm at -65 F generated from study of other compositions, passes within 1% of the composition of MHF-6, when plotted on a ternary compositional diagram. This system is discussed, and a diagram presented, in Section 3.3.2. In all likelyhood, the composition was originally selected to lie on the -65 F isotherm.

2.19.6 LOGISTICS OF MHF-6

2.19.6.1 Manfacture

(C) MHF-6 fuel blend is manufactured by the mixing of methylhydrazine, water and hydrazine. The weight % composition is:

Compound	Formula	Weight Percent
Methylhydrazine	$CH_3N_2H_2$	73.0
Water	H_2O	10.5
Hydrazine	H_2H_4	16.5

The manufacture of MMH and N_2H_4 is discussed elsewhere in this handbook. The manufacutre of MHF-6 blend is then simply proper blending of the miscible components. In order to insure proper blending, complete mixing is necessary to prevent stratification.

(U) The individual components should be carefully weighed prior to mixing. The water content of both the MMH and hydrazine should be determined. Distilled water in the proper amount should then be added.

(U) The most common methods of mixing are by diffusion, agitation, stirring and inert gas bubbling. Diffusion (self mixing) requires a long period of time. For small quantities (drum lots), a mechanical shaker or vibrator is recommended. Mechanical stirring is effective but requires special precautions to prevent air contact. Inert gas bubbling can be used but the time required is much longer than for mechanical mixing.

(U) Regardless of the mixing method used, the batch should be checked for complete mixing by analysis of samples taken from different heights in the container or tank.

2.19.6.2 Analysis

(C) At the present time, there is no MIL Specification for the procurement of MHF-6. In the chemical analysis, gas chromatography has been used by Minor (3) for a similar blend and would appear to be the best overall method available. In lieu of a present procurement specification, the following limits are suggested:

Component	Weight Percent
Hydrazine (N_2H_4)	14.5 to 18.5
Monomethylhydrazine - $CH_3N_2H_3$	71.0 to 75.0
Water	10.5 (nominal)
$N_2H_4 + CH_3N_2H_3$	87.5 (minimum)

2.19.6.3 Cost and Availability

(U) The unit price and availability of a mixture is of course, dependent upon the cost and availability of the constituents. The only large scale manufacturer of MMH and hydrazine is the Olin Mathieson Corporation Chemicals Division with manufacturing facilities in Lake Charles, Louisiana. The unit price of hydrazine and MMH in ton quantities is \$2.95/pound and \$3.20/pound, respectively. The unit cost of MHF-6 may approximate the cost of MMH including the cost of mixing and analysis. Production of either component on a very large scale would decrease the unit price.

Both N_2H_4 and MMH are available from stock at the Lake Charles facility in nominal tonnage orders. Availability of this fuel blend in million pound orders would require a certain amount of lead time.

2.19.6.4 Shipping and Transportation

The shipment of MHF-6 fuel blend is not covered by any government regulations at the present time. The shipping regulations for both MMH and hydrazine are included in this handbook. It would be poor economics to ship large quantities of MHF-6 fuel blend since approximately ten percent of its weight is water.

2.19.7 REFERENCES - MHF-6

1. Thiokol Chemical Corp., Reaction Motors Div., Denville, N.J., unpublished preliminary physical chemistry data. (Confidential).

2. Wagman, D.D., et al., "Selected Values of Chemical Thermodynamic Properties", NBS Tech. Note 070-1, National Bureau of Standards, Washington, D.C., October, 1965.

3. Minor, C.O., "Some Physical Properties of 1014 Fuel Blend", Space Systems Div. 6593d Test Group, Edwards, California, January 1962.

2.20 BA-1014

2.20.1 PROPERTY SUMMARY SHEET

Chemical Name:

Common Name: BA-1014

Empirical Formula: $CH_{24}ON_{10}$

Formula Weight: 192.283

Composition; % b.w.: 66.7 N_2H_4, 24MMH, 9.3 H_2O

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	253.98	°K		1	
	−19.2	°C			
	457.17	°R			
	−2.5	°F			
HEAT OF FUSION		kcal/mole			
		BTU/lb			
NORMAL BOILING POINT	380	°K			
	107	°C			
	684	°R			
	224	°F			
DENSITY OF LIQUID	.984	g/cc	298	1	2.20-2
	61.41	lb/ft^3			
VAPOR PRESSURE OF LIQUID	33.9	mm Hg	298	2,3	2.20-1
	0.65	psia			
VISCOSITY OF LIQUID	0.97	centipoise	298	1	2.20-3
	6.51×10^{-4}	lb_m/ft-sec			
HEAT OF FORMATION (liquid)	−45.47	cal/g	298	calc.	
	−81.65	BTU/lb			

2.20.2 GENERAL

BA-1014 fuel blend is a mixture of hydrazine, monomethylhydrazine and water in a molar ratio of 4 moles hydrazine to one mole each of MMH and water. This blend was developed by Bell Aerosystems(1) and further studied by Minor(2) as a fuel for use with interhalogen oxidizers or fluorine. It was intended to eliminate free carbon or CF_4 formation in the exhaust by providing equal moles of oxygen (in the form of water) and carbon. The blend also exhibits a lower melting point than pure hydrazine.

The BA-1014 blend is a clear, colorless, hygroscopic liquid at room temperature and gives off an ammoniacal odor characteristic of hydrazine.

The nominal composition of BA-1014 is as follows:

Monomethylhydrazine	$CH_3N_2H_3$	24.0% b.w.
Hydrazine	N_2H_4	66.7% b.w.
Water	H_2O	9.3% b.w.

BA-1014 is not covered by any military or other specification.

2.20.3 PHYSICAL PROPERTIES OF BA-1014

2.20.3.1 Vapor Pressure and Normal Boiling Point.

The vapor pressure of liquid BA-1014 fuel blend has been determined by Bell Aerosystems(3) and by Minor(2). The results of the two separate studies are in essential agreement as shown in Figures 2.20-1 and 2.20-1a. The experimental data covered a temperature range from -5 to 92 C (23 to 198 F). Using the method of least-squares, it was found that the data could best be represented by the classical relation;

$$\log P\,(\text{mm Hg}) = 7.7766 - \frac{1862.50}{T,K} \qquad (2.20\text{-}1)$$

$$\log P\,(\text{psia}) = 6.0629 - \frac{3352.50}{T,R} \qquad (2.20\text{-}1a)$$

The standard deviation and average percent deviation obtained from equation 2.20-1 were found to be 10.5 mm Hg and 6.6 percent, respectively.

Minor used a 316 stainless steel bomb loaded with 600 ml of BA-1014. The blend had been boiled and some of the vapor removed by a water aspirator in order to eliminate dissolved [illegible]. The pressures were obtained with a Statham pressure transducer (0 to 25 psi). The output of the temperature compensated transducer was read on a potentiometer. The vapor pressure of both water and hydrazine were also made to check out the apparatus. Agreement with the literature values for these liquids was found to be good.

Bell used an isoteniscope and the sample liquid was frozen with liquid nitrogen and then evacuated to remove dissolved gases. The nitrogen gas pressure required to balance the vapor pressure was measured with a manometer. The sample used by Bell was prepared by careful weighing of the individual components. The nominal composition by weight percent was 66.7 N_2H_4, 23.9% MMH and 9.4 H_2O. The uncertainty of the composition is largely dependent upon the impurities present in the individual components. Minor determined the composition of the blend by gas chromatography and reported that it was 65.6% N_2H_4, 23.9% MMH and 10.1% H_2O by weight.

A mixture will have a boiling point range as it is distilled. Minor(2) noted that the first drop distilled at 95 C (203 F) and then the temperature gradually rose until it reached 115 C (239 F) and leveled off. This temperature was reached after approximately 60 percent by volume was boiled off and it would indicate only hydrazine was left. Bell Aerosystems performed the same experiment and noted the first distillation occurred at 99 C (210 F) and then leveled off at 116 C (241 F).

The normal boiling point of the mixture, defined as the temperature where the enclosed liquid exerts a pressure of exactly one atmosphere (760 mm Hg) was found to be 380.43 K from equation 2.20-1. The data does not warrant this precision and the normal boiling point was taken to be 380 K or 107 C (224 F) for this study.

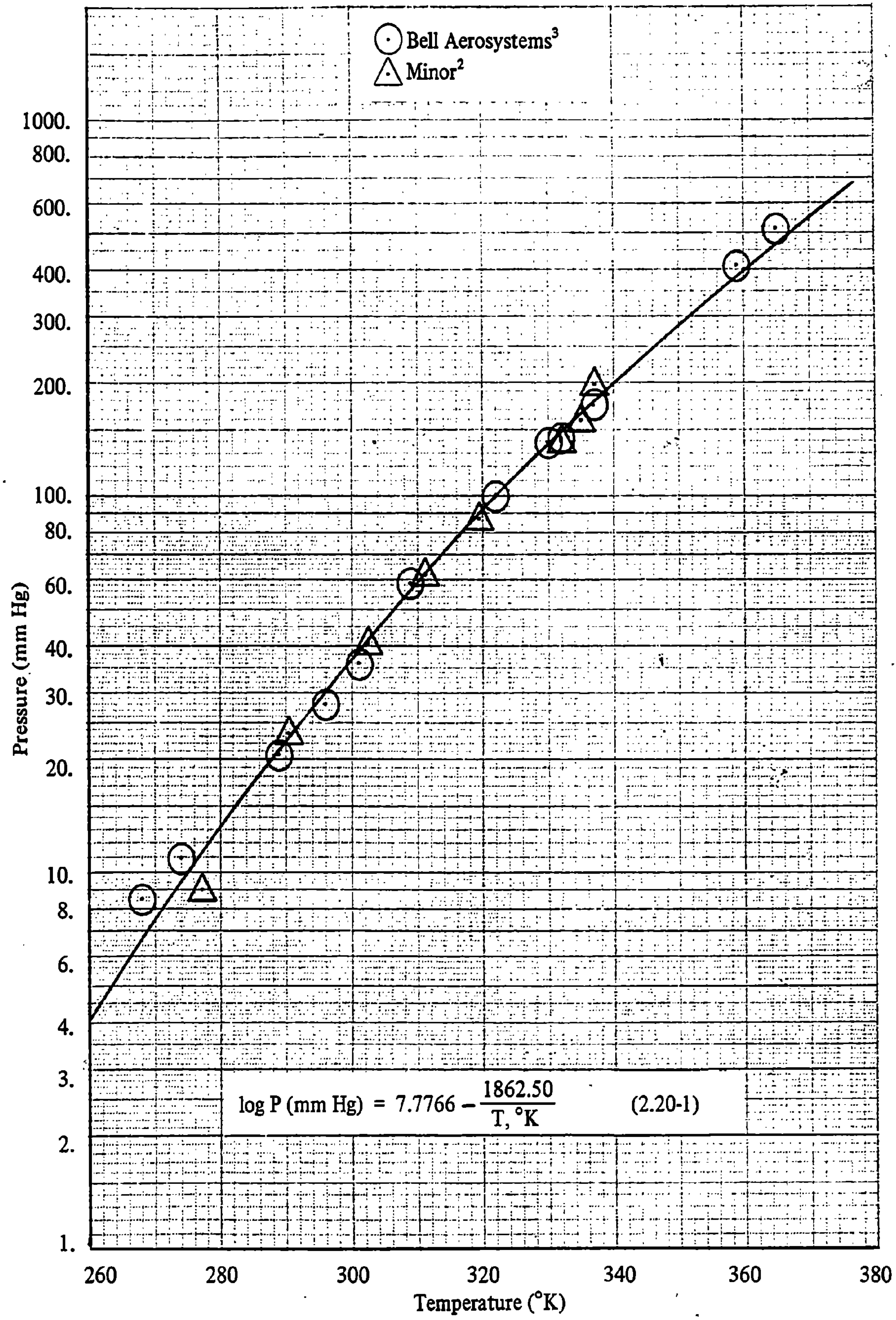
2.20.3.2 Density of Liquid BA-1014 Fuel Blend

The density of liquid BA-1014 does not appear in the literature. Bell Aerosystems(1) has reported smoothed data obtained using a Westphal balance with the liquid at an external pressure of one atmosphere. The data was obtained over a temperature range from -15 to 25 C (5 to 77 F) and can be represented by the linear expression

$$\rho\,(\text{g/cc}) = 1.2422 - 8.673 \times 10^{-4}(T,K) \qquad (2.20\text{-}2)$$

$$\rho\,(\text{lb/ft}^3) = 77.550 - 0.03008\,(T,R) \qquad (2.20\text{-}2a)$$

This data must be considered as provisional only since the Westphal balance is not a precision type instrument and the data is not for the saturated liquid. Additional studies using pycnometers are required to define the density of this



$$\log P\ (\text{mm Hg}) = 7.7766 - \frac{1862.50}{T,\ ^\circ K} \qquad (2.20\text{-}1)$$

Figure 2.20-1. Vapor Pressure versus Temperature, Liquid BA-1014

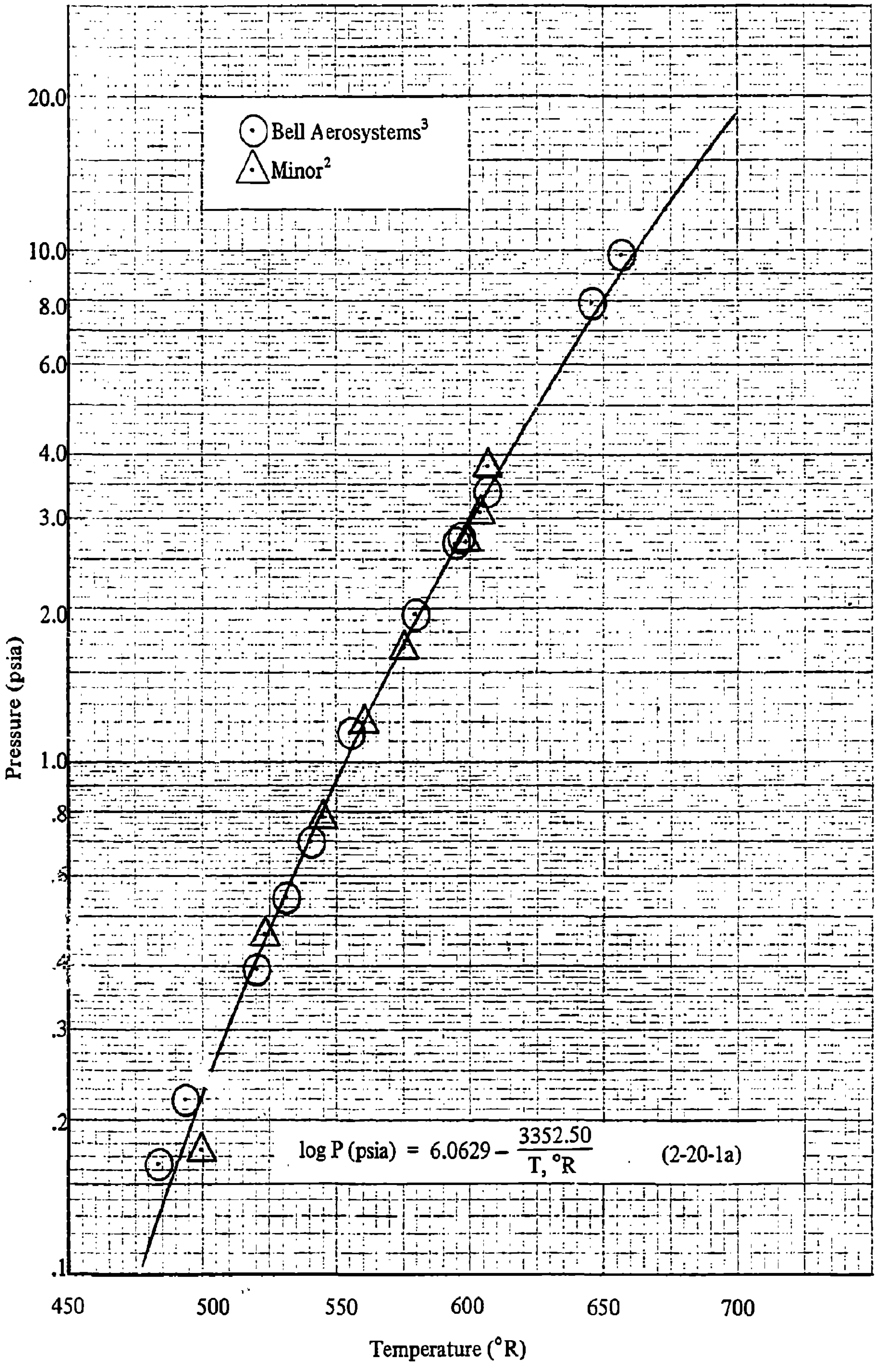


Figure 2.20-1a. Vapor Pressure versus Temperature, Liquid BA-1014

fuel blend. The provisional data is shown as a function of temperature in Figures 2.20-2 and 2.20-2a.

2.20.3.3 Viscosity of Liquid BA-1014 Fuel Blend

The viscosity of liquid BA-1014 has been measured by Bell Aerosystems(1) over a temperature range from -15 to 25 C (5 to 77 F). An Ostwald viscometer was used and the viscosity was measured with the liquid exposed to the normal atmosphere. The experimental data was given as smoothed data at even temperature intervals. Using the smoothed data and employing the least-squares curve fit technique, the absolute viscosity as a function of temperature can be described by;

$$\log \mu(\text{centipoise}) \qquad 2.0297 - \frac{1972.8}{T, K} + \frac{4.0654 \times 10^5}{(T, K)^2} \tag{2.20-3}$$

$$\log \mu(\text{lb}_m/\text{ft-sec}) = -1.1429 - \frac{3551.0}{T, R} + \frac{1.3172 \times 10^6}{(T, R)^2} \tag{2.20-3a}$$

The data points are shown in Figures 2.20-3 and 2.20-3a.

This data should be considered as provisional because of the equipment used and the uncertainty of the density required to obtain the absolute values. Additionally, the viscosity is not for the saturated liquid.

2.20.4 CHEMICAL PROPERTIES OF BA-1014

The chemical reactions which BA-1014 can undergo will be dominated by its high hydrazine concentration. The methylhydrazine, however, can also be expected to undergo reactions peculiar to it.

Specific data on the reactions of BA-1014 blend have not been reported. The water in this blend occurs as the hydrate of hydrazine at ordinary temperatures. The user should consult Sections 2.3.4.1 and 2.4.4.1 for hydrazine and methylhydrazine reactions, respectively.

2.20.5 THERMODYNAMIC PROPERTIES OF BA-1014

2.20.5.1 Heat of Formation of Liquid.

The heat of formation of the BA-1014 fuel blend has not been experimentally studied. Its heat of formation can be closely approximated by the molar addition of the heats of formation of its components. This fuel blend is composed of (by moles) 1 MMH + 4 N_2H_4 + 1 H_2O. It is assumed that the mole of water would combine with one mole of hydrazine to form hydrazine hydrate ($N_2H_4 \cdot H_2O$). Heat of mixing was assumed to be negligible.

$$\Delta Hf_{298} = \Delta H_f CH_3N_2H_3 + 3\,(\Delta H_f N_2H_4) + \Delta H_f N_2H_4 \cdot H_2O$$

$$\Delta Hf_{298} = 13.106 + 3\,(12.054) - 58.01$$

$$\Delta Hf_{298} = 8.742 \text{ kcal/mole}$$

The empirical formula is $CH_{24}ON_{10}$ which has a formula weight of 192.283. The heat of formation is then –45.47 cal/g or –81.85 BTU/lb at 298 K.

The heat of formation of N_2H_4 and MMH are taken from Sections 2.3.5 and 2.4.5 of this work. The heat of formation of $N_2H_4 \cdot H_2O$ was taken from Wagman, et al(4).

2.20.6 LOGISTICS OF BA-1014

2.20.6.1 Manufacture

BA-1014 fuel blend is manufactured by the mixing of 1 mole methylhydrazine, 1 mole water and 4 moles of hydrazine. The weight composition is:

Compound	Formula	Weight Percent	Moles
Methylhydrazine	$CH_3N_2H_3$	24.0	1.0
Water	H_2O	9.3	1.0
Hydrazine	N_2H_4	66.7	4.0

The manufacture of N_2H_4 and MMH are discussed in Sections 2.3.6 and 2.4.6 of this handbook.

The manufacture of BA-1014 blend is then simply proper blending.

The three components are completely miscible in the proportions given above. In order to insure proper blending, complete mixing is necessary to prevent stratification. The individual components should be carefully weighed prior to mixing. The water content of both the MMH and hydrazine should be determined. Distilled water in the proper amount should then be added.

The most common method of mixing are by diffusion, agitation, stirring and inert gas bubbling. Diffusion (self mixing) requires a long period of time. For small quantities (drum lots), a mechanical shaker or vibrator is recommended. Mechanical stirring is effective but requires special precautions to prevent air contact. Inert gas bubbling can be used but the time required is much longer than for mechanical mixing.

Regardless of the mixing method used, the batch should be checked for complete mixing by analysis of samples taken from different heights in the container or tank.

2.20.6.2 Analysis

At the present time, there is no MIL Specification for the procurement of BA-1014. For the chemical analysis, gas Chromatography has been used by Minor and would appear to be the best overall method available. In lieu of a present procurement specification, the following limits are suggested:

Component	Weight Percent
Hydrazine (N_2H_4)	64.7 to 68.7
Monomethylhydrazine $CH_2N_2H_3$	22.0 to 26.0
Water	9.3 (Nominal)
$N_2H_4 + CH_3N_2H_3$	88.7 Minimum

2.20.6.3 Cost and Availability

The unit price and availability of a mixture is of course dependent upon the cost and availability of the constituents. The only large scale manufacturer of MMH and Hydrazine is the Olin Mathieson Corporation Chemical Division with manufacturing facilities in Lake Charles, Louisiana. The unit price of hydrazine and MMH. in ton quantities is $2.95/pound and $3.20/pound, respectively. The unit price of BA-1014 would then be close to the cost of MMH and would include the cost of mixing and analysis. Production of either component on a very large scale would decrease the unit price.

Both N_2H_4 and MMH are available from stock at the Lake Charles facility in nominal tonnage orders. Availability of this fuel blend in million pound orders would require a certain amount of lead time.

2.20.6.4 Shipping and Transportation

The shipment of BA-1014 fuel blend is not covered by any government regulations at the present time. The shipping regulations for both MMH and hydrazine are included in this manual. It would be poor economics to ship large quantities of blended fuel, since approximately ten percent of its weight is water.

2.20.7 REFERENCES - BA-1014

1. Bell Aerosystems Company, "Physical Chemistry Report No. BLR-6-33 (c)", Buffalo 1, New York, December 1961.
2. Minor, C.O., "Some Physical Properties of 1014 Fuel Blend", Space Systems Div. 6593d Test Group, Edwards, California, January 1962.
3. Bell Aerosystems Company, unpublished physical chemistry data.
4. Wagman, D.D., et al, "Selected Values of Chemical Thermodynamic Properties", NBS Tech. Note 270-1 U.S. Dept. of Commerce, Washington, D.C., October 1965.

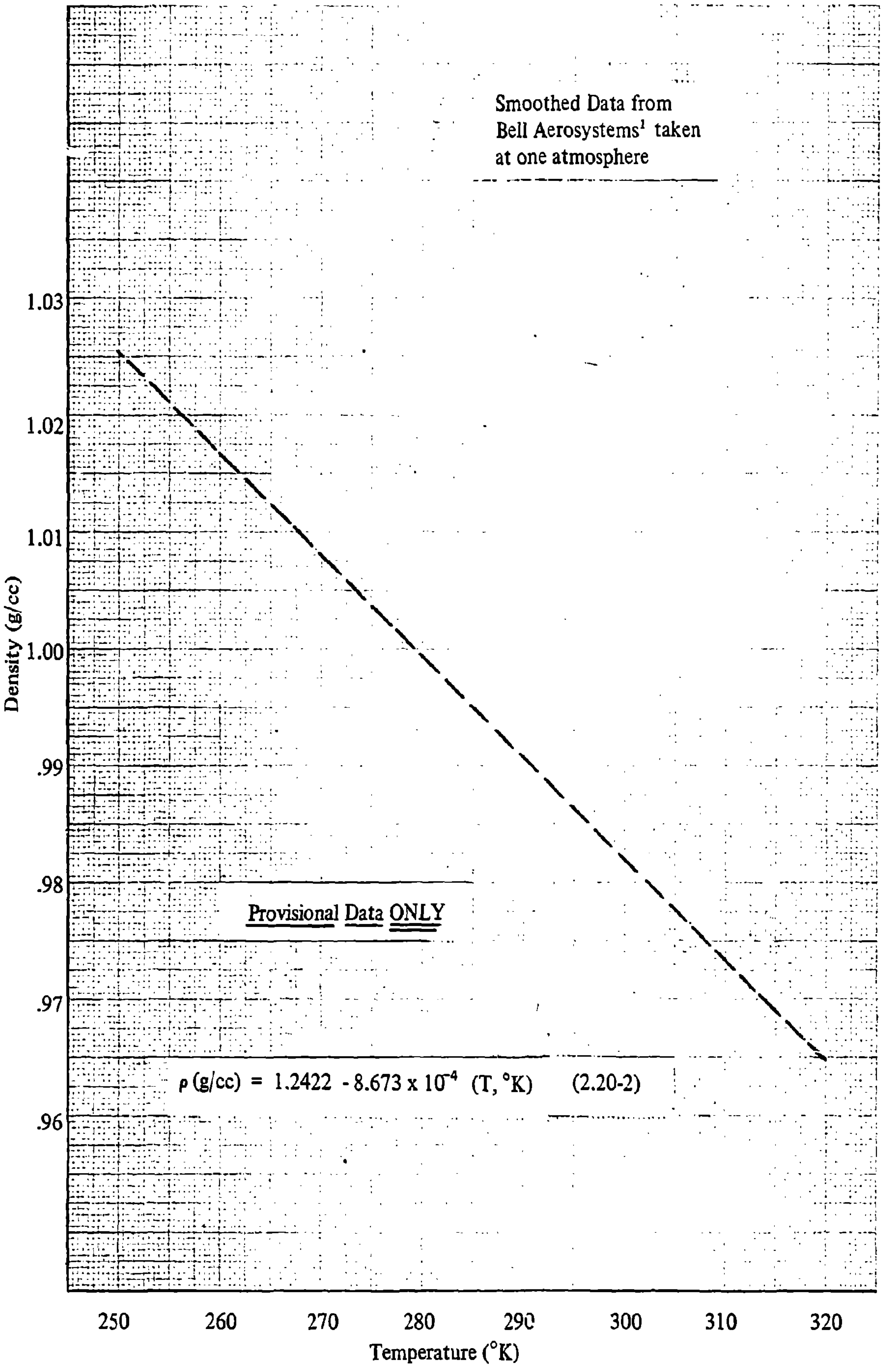


Figure 2.20-2. Density versus Temperature, Liquid BA-1014

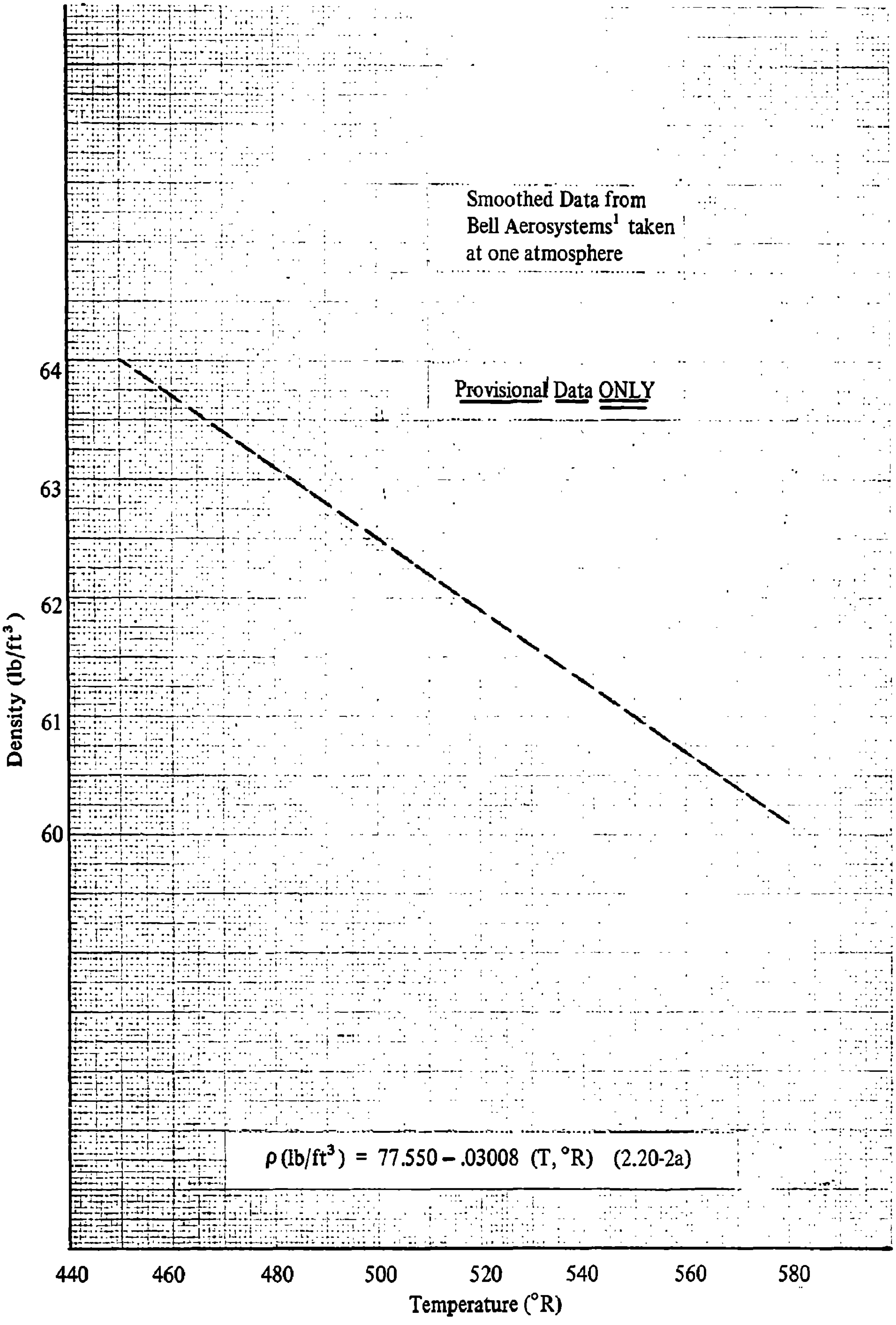
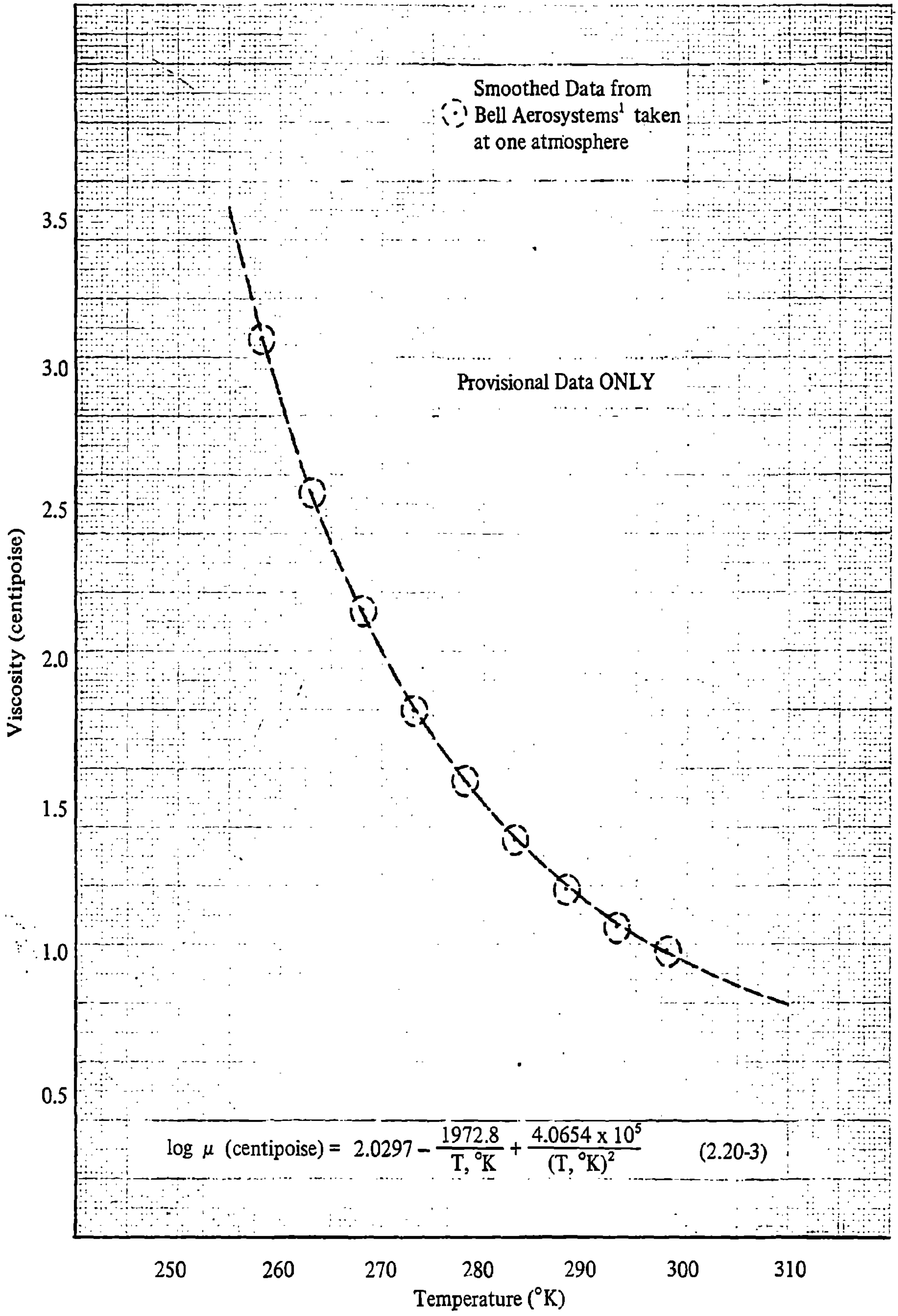
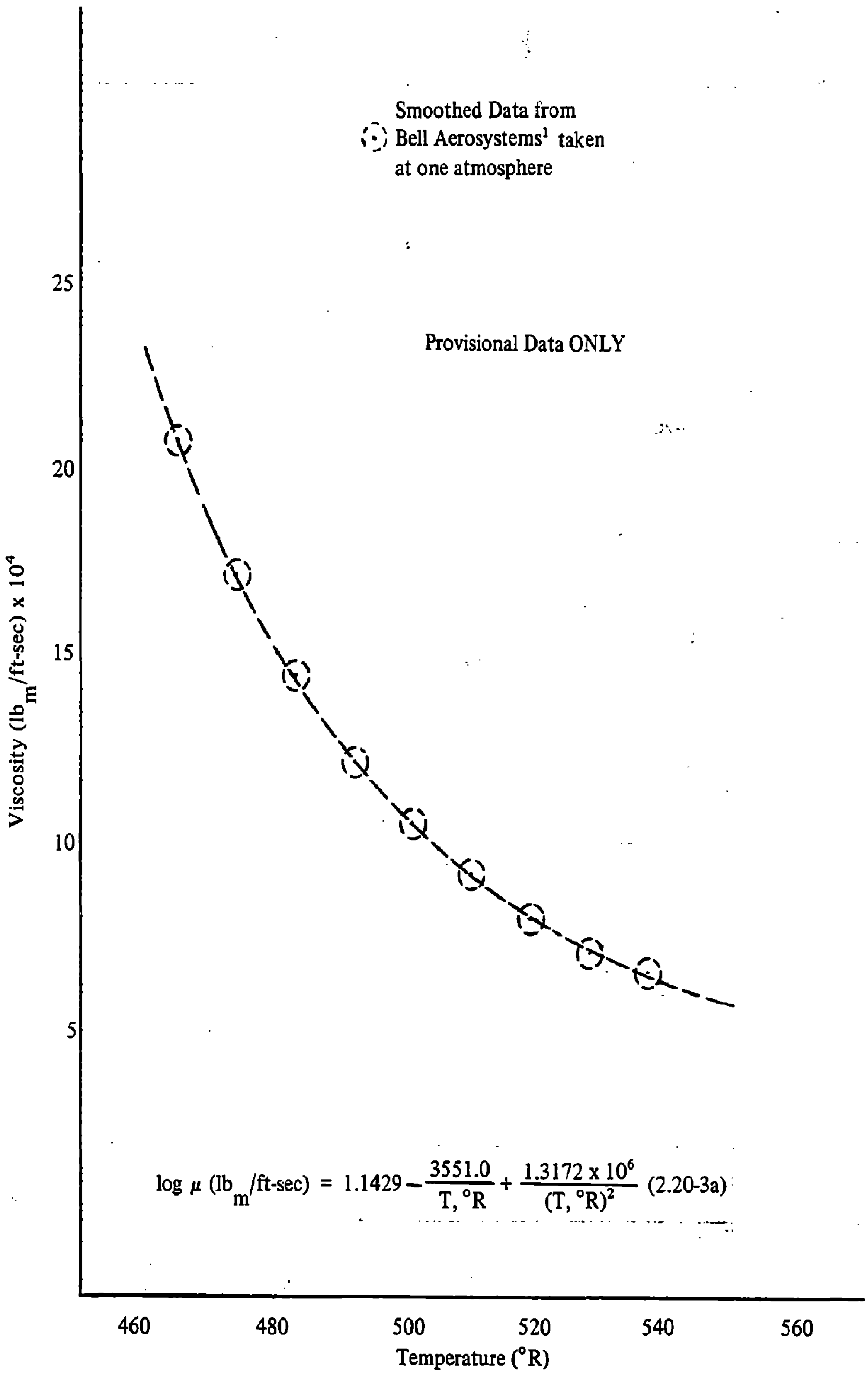


Figure 2.20-2a. Density versus Temperature, Liquid BA-1014



$$\log \mu \text{ (centipoise)} = 2.0297 - \frac{1972.8}{T, °K} + \frac{4.0654 \times 10^5}{(T, °K)^2} \qquad (2.20\text{-}3)$$

Figure 2.20-3. Absolute Viscosity versus Temperature, Liquid BA-1014



$$\log \mu \,(\mathrm{lb_m/ft\text{-}sec}) = 1.1429 - \frac{3551.0}{T,\,°R} + \frac{1.3172 \times 10^{6}}{(T,\,°R)^{2}} \quad (2.20\text{-}3a)$$

Figure 2.20-3a. Absolute Viscosity versus Temperature, Liquid BAF-1014

2.21 BAF-1185

2.21.1 PROPERTY SUMMARY SHEET

Chemical Name:		Common Name:	**BAF-1185**
Empirical Formula:	$CH_{11.4}ON_{3.7}$	Formula Weight:	**91-3318**
Composition; % b.w.:	**50.5 MMH, 29.8 N_2H_4, 19.7 H_2O**		

PROPERTY	VALUE	UNITS	TEMP (°K)	REFERENCE	FIGURE
MELTING POINT	219.2 -53.9 394.7 -65	°K °C °R °F		1	2.21-5
NORMAL BOILING POINT	370.9 97.8 667.7 208	°K °C °R °F		calc.	
HEAT OF VAPORIZATION		kcal/mole BTU/lb			
VAPOR PRESSURE OF LIQUID	30.1 0.58	mm Hg psia	298	calc.	2.21-1
DENSITY OF LIQUID	0.9539 59.552	g/cc lb/ft^3	298	1	2.21-2
VISCOSITY OF LIQUID	1.815 1.219×10^{3}	centipoise lb/ft-sec	298	1	2.21-3
SURFACE TENSION	43.64 2.99×10^{3}	dynes/cm	298	2	2.21-4
HEAT OF FORMATION	-508.6 -915.5	cal/grams BTU/lb	298	See Section 2.21.5.1	

2.21.2 GENERAL

BAF-1185 fuel blend is a mixture of 1.0 mole of MMH, with 1.0 mole of water and 0.85 mole of hydrazine. Its composition was designed to comply with the requirements of a propellant having equal mole fractions of carbon and oxygen for combustion with fluorine oxidizers and a melting point of -65 F.

BAF-1185 and similar blends have been investigated on a laboratory scale by Bell Aerosystems for potential Navy and Air Force application. Picatinny Arsenal also investigated this class of propellants under the acronym "Hydrazoid - W."

In general, BAF-1185 (or Hydrazoid - W) is similar to MHF-6. It is a clear, colorless, hydroscopic liquid having an ammonical odor characteristic of the hydrazines.

The nominal composition of BAF-1185 in weight percent is

Compound	Formula	Weight %
Methylhydrazine	$N_2H_3CH_3$	50.5
Hydrazine	N_2H_4	29.8
Water	H_2O	19.7

No military specification exists for this propellant.

2.21.3 PHYSICAL PROPERTIES OF BAF-1185

2.21.3.1 Vapor Pressure and Normal Boiling Point

The vapor pressure of liquid BAF-1185 has not been experimentally determined. The vapor pressure of a mixture can be reasonably estimated from the molar addition of its partial pressures. The vapor pressure of both MMH and N_2H_4 are discussed in Sections 2.4.3.1 and 2.3.3.1, respectively. The vapor pressure of water is well defined and can be found in most chemical handbooks.

The theoretical vapor pressure of the ternary mixture is shown as a function of temperature in Figures 2.21-1 and 2.21-1a. Since the vapor pressures of the individual constituents are quite low, the resulting ternary blend is of low volatility. At a temperature of 240F, the vapor pressure is estimated to be only about 25 psia. The calculated normal boiling point is approximately 208F.

2.21.3.2 Density of Liquid BAF-1185

The density of liquid BAF-1185 has been measured by Bell Aerosystems(1) over a temperature range from -48 to 72.4C (-54 to 162F). Two orthobaric pycnometers with precision bored capillary sections were used. The pycnometers were calibrated with mercury to determine the volumes up to and also above a scribe mark on the capillaries. The pycnometers were vacuum loaded and carefully weighed. At a temperature range above 0 C, a Forma-model constant temperature water bath was used. Below the freezing point of water, an acetone bath cooled with liquid nitrogen was employed. Temperatures were recorded with mercury in glass thermometers which could easily be read to 0.1 C. The liquid level and reference level were measured with a cathetometer. Several readings were taken at each temperature on each pycnometer.

The average of all the readings at each temperature are plotted in Figures 2.21-2 and 2.21-2a. The density is a linear function of temperature over the range studied.

$$\rho\ (\text{g/cc}) = 1.2066 - 8.4742 \times 10^{-4}\ (\text{T, }^\circ\text{K}) \qquad (2.21\text{-}1)$$

$$\rho\ (\text{lb/ft}^3) = 75.3253 - 0.02939\ (\text{T, }^\circ\text{R}) \qquad (2.21\text{-}1\text{a})$$

The standard deviation of the experimental data from the linear fit is 0.00056 g/cc and the average percent deviation is 0.04 percent.

2.21.3.5 Viscosity of Liquid BAF-1185

The kinematic viscosity of liquid BAF-1185 has been determined by Bell Aerosystems(1) over a temperature range from -54 to 72.5C (-65 to 163F). A commercial Cannon-Fenkse viscometer was used. The manufacturer's calibration constants were verified with NBS oils. The absolute viscosity was determined from the density at the experimental temperatures as determined from equation 2.21-1.

The absolute viscosity values are plotted in Figures 2.21-3 and 2.21-3a.

The experimental data is adequately described by

$$\log \mu\ (\text{cp}) = 1.4997 - \frac{1797.00}{\text{T, }^\circ\text{K}} + \frac{4.2547 \times 10^5}{(\text{T, }^\circ\text{K})^2} \qquad (2.21\text{-}2)$$

$$\log \mu\ (\text{lb}_\text{m}/\text{ft-sec}) = -1.6730 - \frac{3234.61}{\text{T, }^\circ\text{R}} + \frac{1.3785 \times 10^6}{(\text{T, }^\circ\text{R})^2} \qquad (2.21\text{-}2\text{a})$$

The standard deviation and average percent deviation obtained from equation 2.21-2 are quite high; 4.7 centipoise and 5.8 percent, respectively.

The composition determined from gas chromatography was 50.7 MMH, 19.0 H_2O + 30.3 N_2H_4 by weight percent.

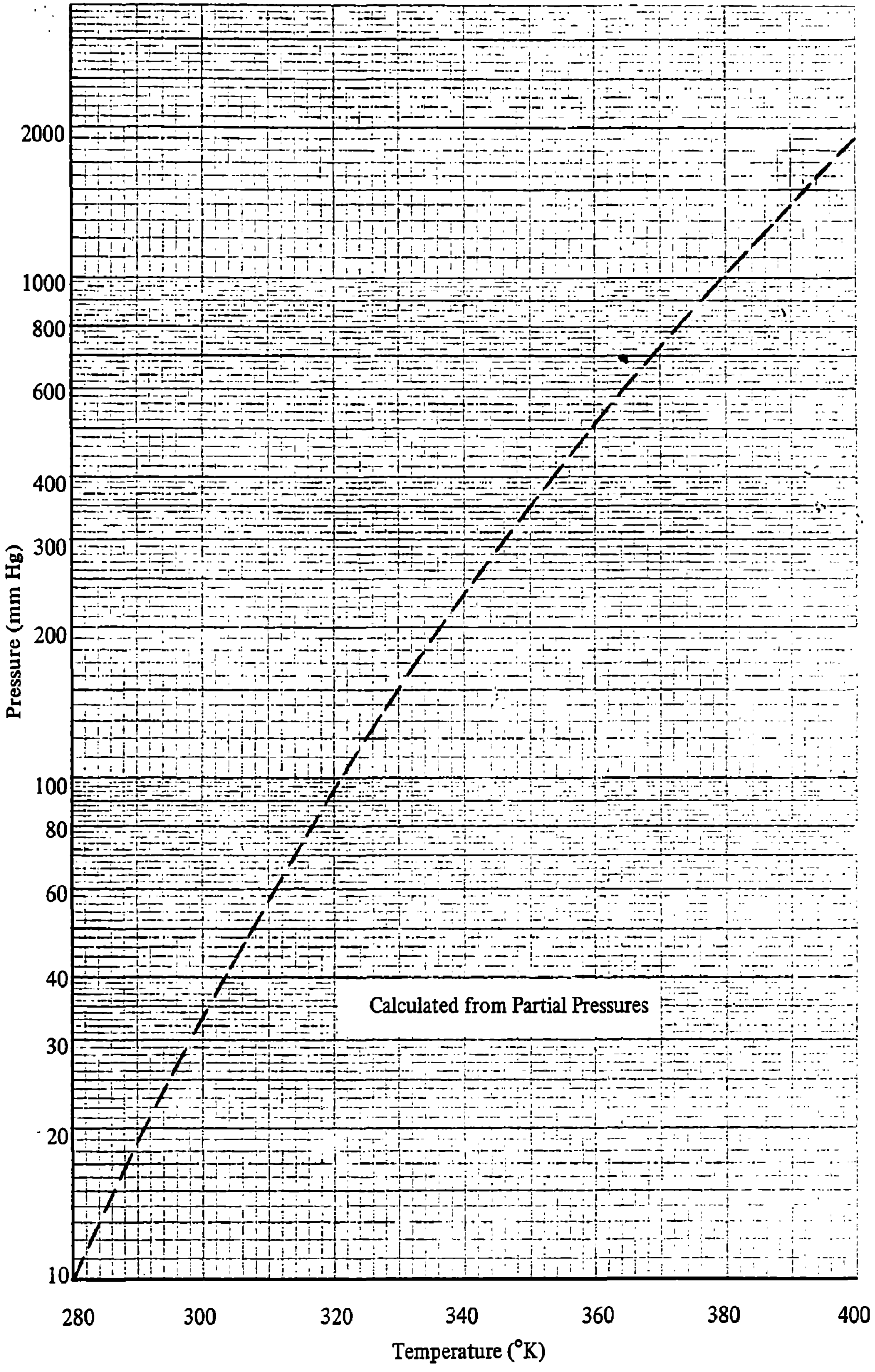


Figure 2.21-1. Vapor Pressure versus Temperature, Liquid BAF-1185

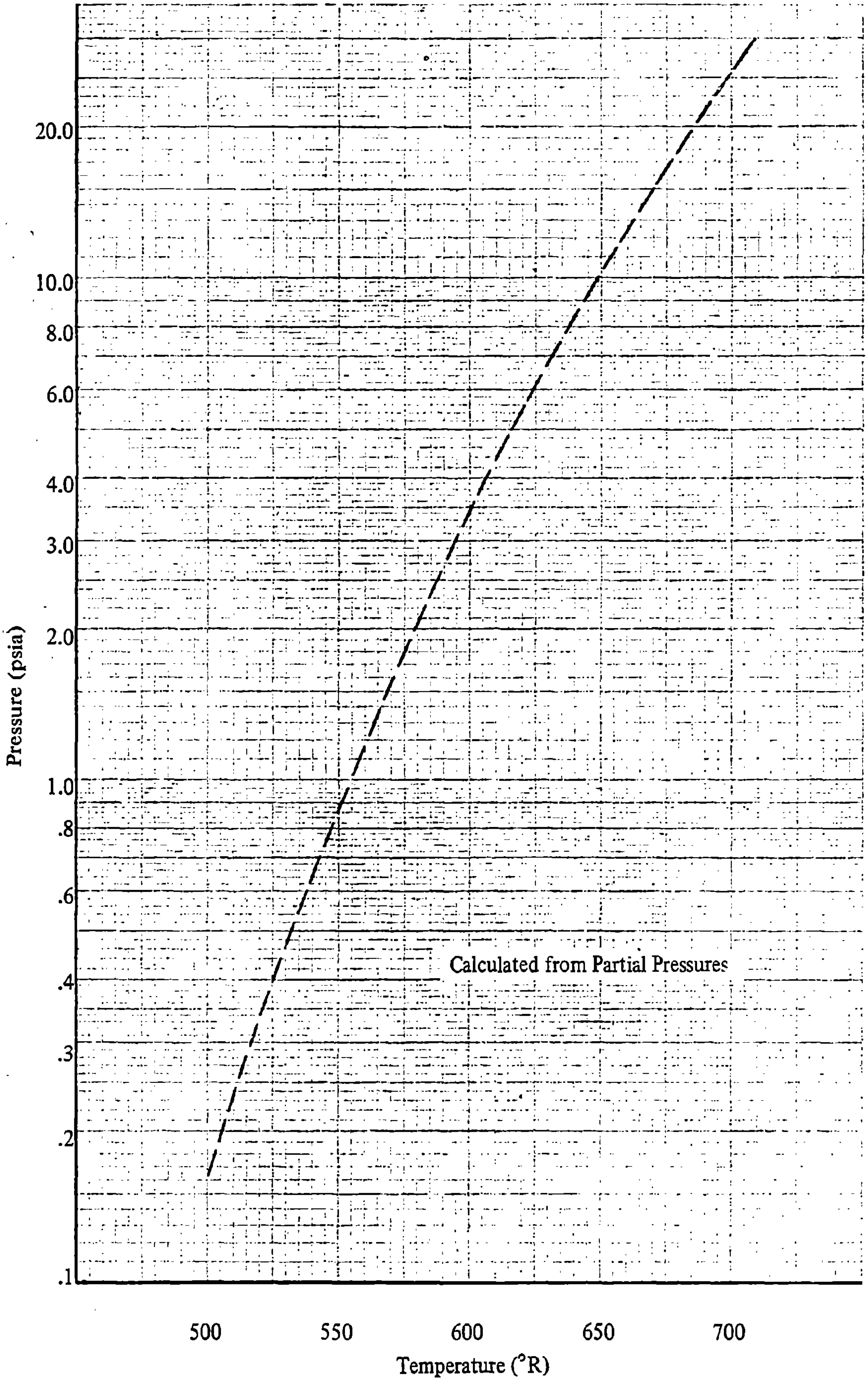


Figure 2.21-1a Vapor Pressure versus Temperature, Liquid BAF-1185

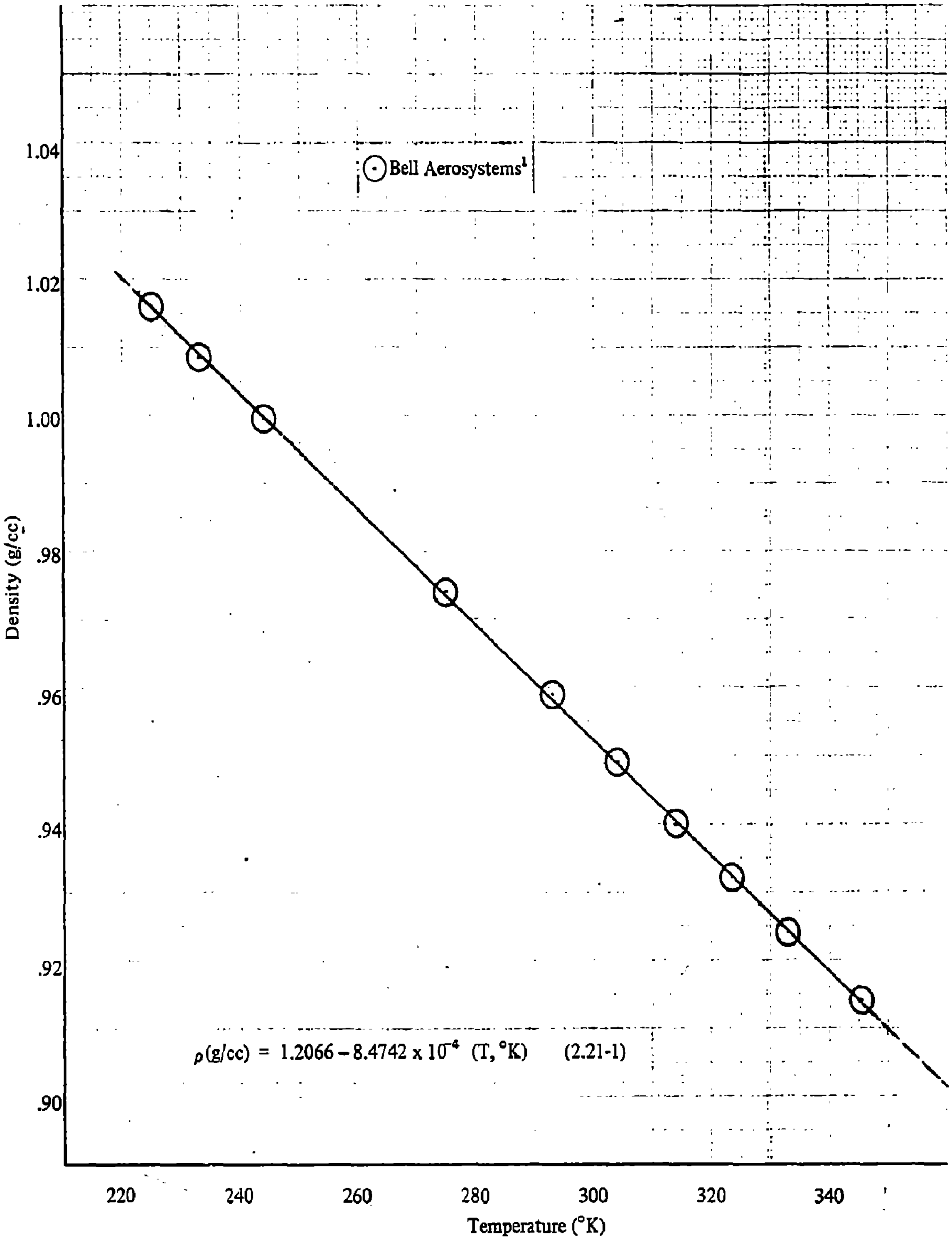


Figure 2.21-2. Density versus Temperature, Liquid BAF-1185 Fuel Blend

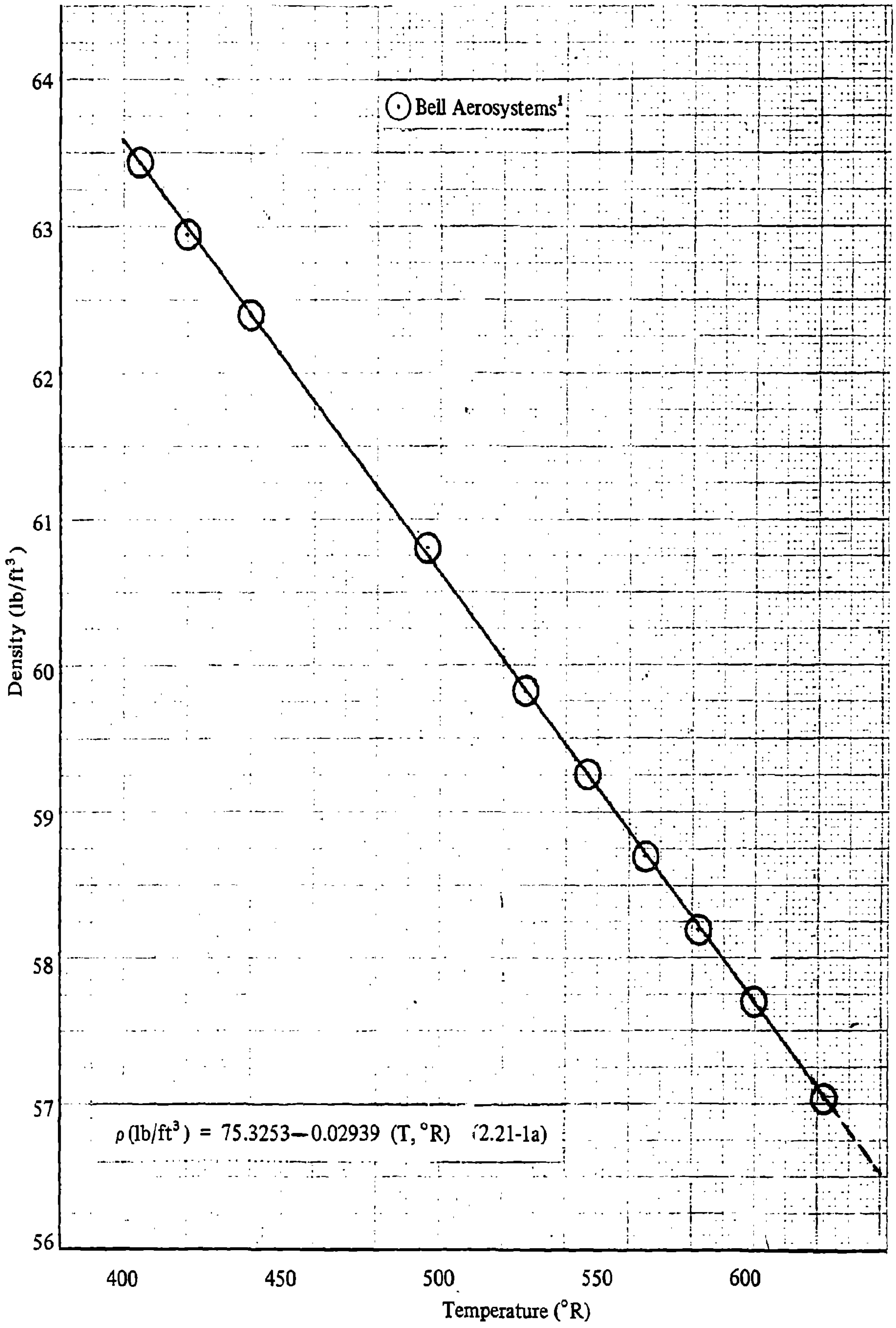
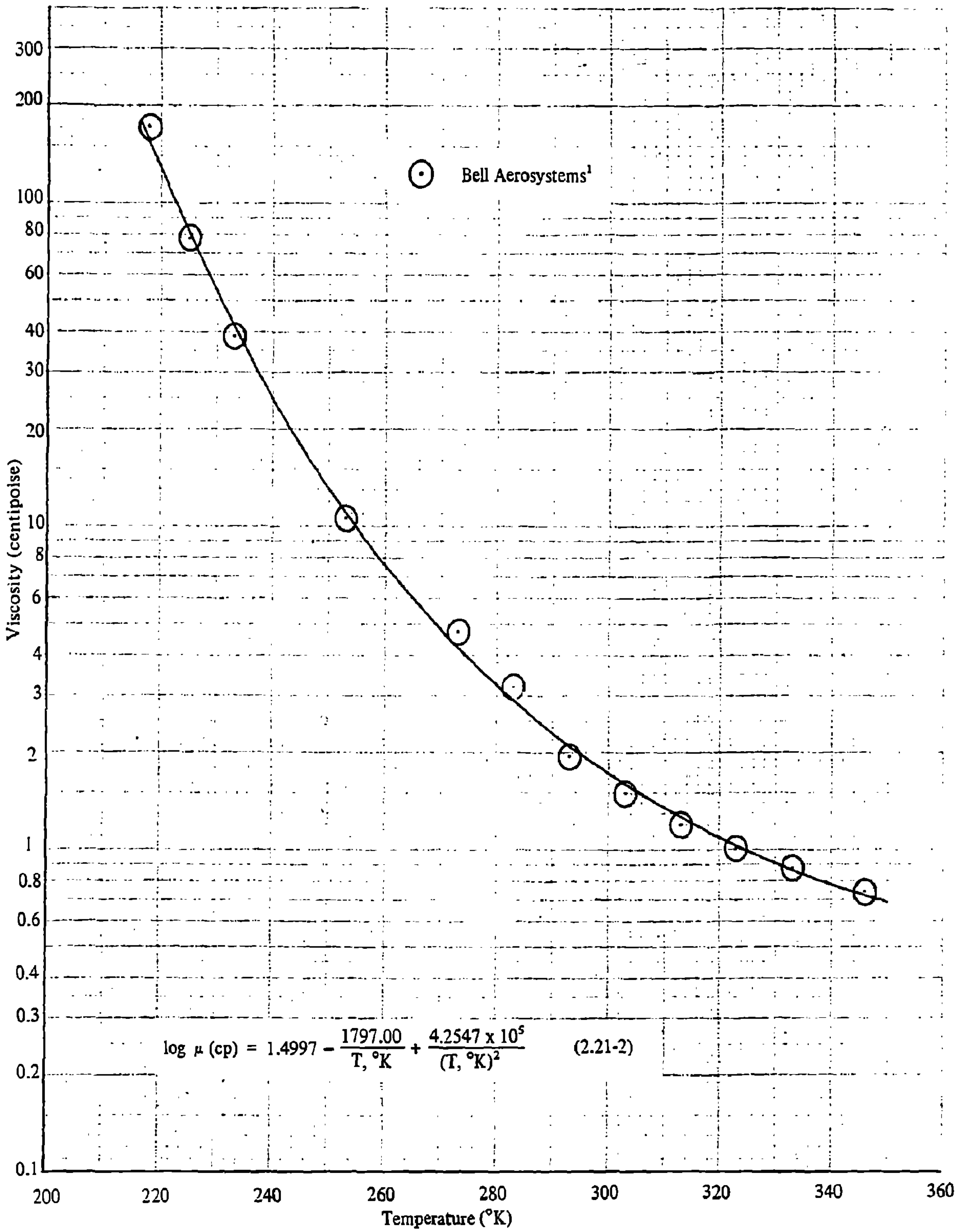
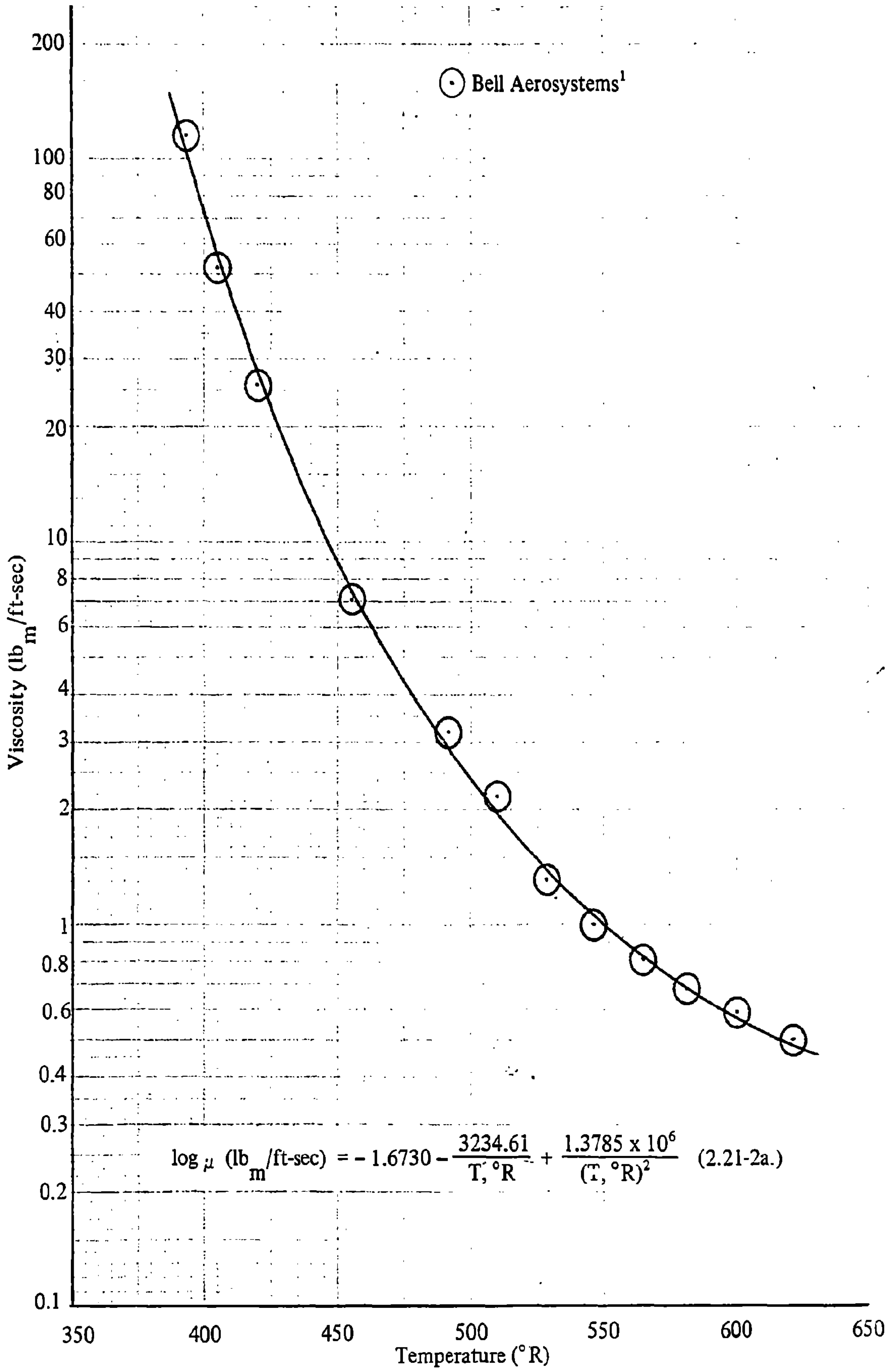


Figure 2.21-2a. Density versus Temperature, Liquid BAF-1185 Fuel Blend



$$\log \mu \text{ (cp)} = 1.4997 - \frac{1797.00}{T, °K} + \frac{4.2547 \times 10^5}{(T, °K)^2} \qquad (2.21\text{-}2)$$

Figure 2.21-3. Viscosity versus Temperature, Liquid BAF-1185 Fuel Blend



$$\log \mu \; (\mathrm{lb_m/ft\text{-}sec}) = -1.6730 - \frac{3234.61}{T,\ ^\circ R} + \frac{1.3785 \times 10^6}{(T,\ ^\circ R)^2} \qquad (2.21\text{-}2a.)$$

Figure 2.21-3a. Viscosity versus Temperature, Liquid BAF-1185 Fuel Blend

2.21.3.6 Surface Tension of Liquid BAF-1185

The surface tension of liquid BAF-1185 has been measured under its own vapor pressure by Bell Aerosystems(2). A double capillary rise system was employed. The same system was used for 50-50 blend and is described in some detail in Section 2.6.3.6.

A temperature range from -40 to 58C (-40 to 137F) was studied. The experimental data is plotted in Figures 2.21-4 and 2.21-4a. The surface tension is adequately described as a linear function of temperature.

$$\gamma\,(\text{dynes/cm}) = 69.006 - 0.085078\,(T, {}^\circ K) \qquad (2.21\text{-}3)$$

$$\gamma\,(\text{lb}_f/\text{ft}) = 4.7284 \times 10^{-3} - 3.2387 \times 10^{-6}\,(T, {}^\circ R) \qquad (2.21\text{-}3a)$$

The standard deviation of the data as expressed by equation 2.21-3 is 0.18 dynes/cm and the average percent deviation is 0.3 percent.

The BAF-1185 sample was determined by gas chromatography to have the following composition:

	Weight Percent
N_2H_4	29.5
$C_2H_6N_2$	49.8
H_2O	20.0
Soluable Impurities	0.7

2.21.4 CHEMICAL PROPERTIES

Since BAF-1185 is a blend of hydrazine, methylhydrazine, and water, its chemical reactions will be those of the constituents. The reactions of MMH (Section 2.4.4) will dominate, since it is the major component. The water exists as the hydrates of N_2H_4 and MMH.

2.21.5 THERMODYNAMIC PROPERTIES

2.21.5.1 Heat of Formation of BAF-1185

The heat of formation of liquid BAF-1185 at 298.15K (25C) has been calculated to be -46.45 kcal/mole. A mole is defined as 91.332 grams with the empirical formula of $CH_{11.4}O_{3.7}$. The heat of formation is then -508.6 calories per gram.

The above value was calculated from the molar addition of the individual heats of formation. It was assumed that the heat of mixing is negligible and that the water forms hydrazine hydrate.

Compound	No. of Moles	ΔH_{f298} (kcal/mole)
CH_6N_2 (MMH)	1.0	13.106
$N_2H_4 \cdot H_2O$	0.85	-58.01
H_2O	0.15	-68.315

The heat of formation of the hydrate and water were taken from Wagman(5). The heat of formation of MMH is given in Section 2.4.5.1 of this handbook.

2.21.5.2 Melting Point of BAF-1185

The melting point (actually freezing point) of a series of BAF-11 fuels has been experimentally determined by Bell Aerosystems(1,3). The BAF-11 series of fuels contain one mole of MMH, one mole of H_2O plus a variable quantity of hydrazine.

The freezing points of several different blends are shown in Figures 2.21-5. The freezing point was defined as the temperature where the formation of crystals was first observed. The observed freezing points plotted as a function of mole percent N_2H_4 in $MMH.H_2O$ (considered one mole) form a straight line including the melting point of pure hydrazine.

A plot of the initial blends showed that at a freezing point of -65F the blend should contain 0.85 mole of N_2H_4.

Two sample blends were mixed with 0.85 mole of N_2H_4 or 29.8 weight percent. The freezing points of the two samples were found to be very close to the anticipated temperature of -65 F and are shown in Figure 2.21-5.

2.21.6 LOGISTICS OF BAF-1185

2.21.6.1 Manufacture

BAF-1185 fuel blend is manufactured by the mixing of 1 mole methylhydrazine, 1 mole water and 0.85 mole of hydrazine. The weight composition is:

Compound	Formula	Weight Percent	Moles
Methylhydrazine	$CH_3N_2H_2$	50.5	1.0
Water	H_2O	19.7	1.0
Hydrazine	N_2H_4	29.8	0.85

The manufacture of MMH and N_2H_4 are discussed elsewhere in this handbook. The manufacture of BAF-1185 blend is then simply proper blending.

The three components are completely miscible in the proportions given above. In order to insure proper blending, complete mixing is necessary to prevent stratification. The individual components should be carefully weighed prior to mixing. The water content of both the MMH and hydrazine should be determined. Distilled water in the proper amount should then be added.

The most common method of mixing are by diffusion, agitation, stirring and inert gas bubbling. Diffusion (self mixing) requires a long period of time. For small quantities (drum lots), a mechanical shaker or vibrator is recommended. Mechanical stirring is effective but requires special precautions to prevent air contact. Inert gas bubbling can be used but the time required is much longer than for mechanical mixing.

Regardless of the mixing method used, the batch should be checked for complete mixing by analysis of samples taken from different levels in the container or tank.

2.21.6.2 Analysis

At the present time there is no MIL Specification for the procurement of BAF-1185. For the chemical analysis, gas chromatography has been used by Minor and would appear to be the best overall method available. In lieu of a present procurement specification, the following limits are suggested:

Component	Weight Percent
Hydrazine (N_2H_4)	27.8 to 31.8
Monomethylhydrazine $CH_3N_2H_3$	48.5 to 52.5
Water	19.7 (Nominal
$N_2H_4 + CH_3N_2H_3$	78.3 Minimum

2.21.6.3 Shipping and Transportation

The shipment of BAF-1185 fuel blend is not covered by any government regulations at the present time. The shipping regulations for both MMH and hydrazine are included in this manual. It would be poor economics to ship large quantities of BAF-1185 fuel blend, since approximately twenty percent of its weight is water.

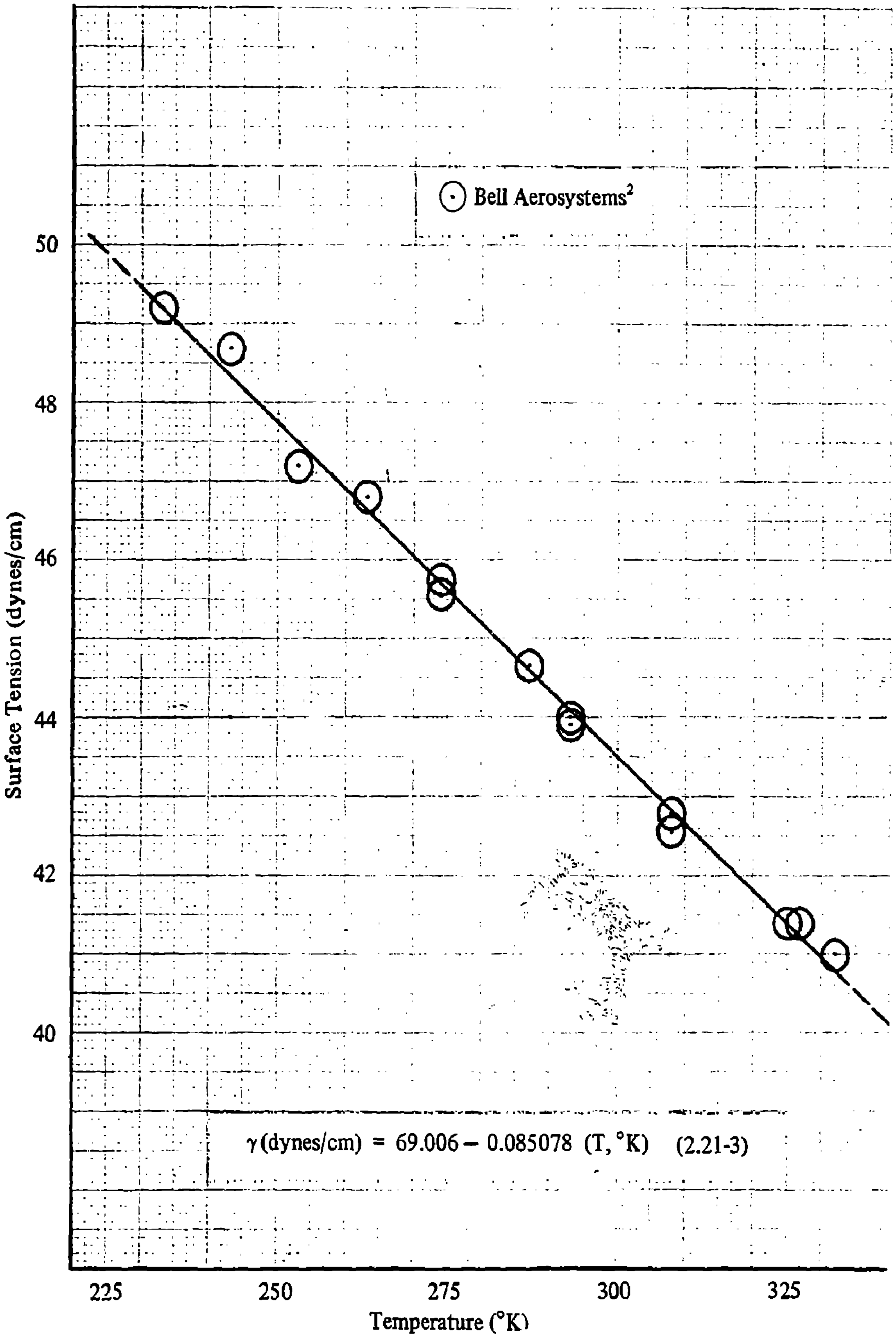
2.21.6.4 Cost and Availability

The unit price and availability of a mixture is of course dependent upon the cost and availability of the constituents. The only large scale manufacturer of MMH and hydrazine is the Olin Mathieson Corporation Chemicals Division in Lake Charles, Louisiana. The unit price of hydrazine and MMH in ton quantities is $2.95/pound and $3.20/pound, respectively. The unit cost of BAF-1185 would then be close to the cost of MMH and would include the cost of mixing and analysis. Production of either component in a very large scale would decrease the unit price.

Both N_2H_4 and MMH are available from stock at the Lake Charles facility in nominal tonnage orders. Availability of this fuel blend in million pound orders would require a certain amount of lead time.

2.21.7 REFERENCES

1. Bell Aerosystems, Physical Chemistry Group. 1966 (unpublished data).
2. Misercola, A.B., and Knox, B.P., "Surface Tension Measurements of Selected Rocket Propellants", Bell Aerosystems Co., (to be published).
3. Misercola, A.B., Engineering and Research Laboratory Report No. BLR-61-33, Bell Aerosystems Company, December 1961.
4. Gaubatz, W.A., Rockets Engineering Report 9500-920023, Bell Aerosystems Company, April 1965.
5. Wagman, D.D., et al, "Selected Values of Chemical Thermodynamic Properties", NBS Tech. Note 270-1, October 1965.



γ(dynes/cm) = 69.006 − 0.085078 (T, °K) (2.21-3)

Figure 2.21-4. Surface Tension versus Temperature, Liquid BAF-1185 Fuel Blend

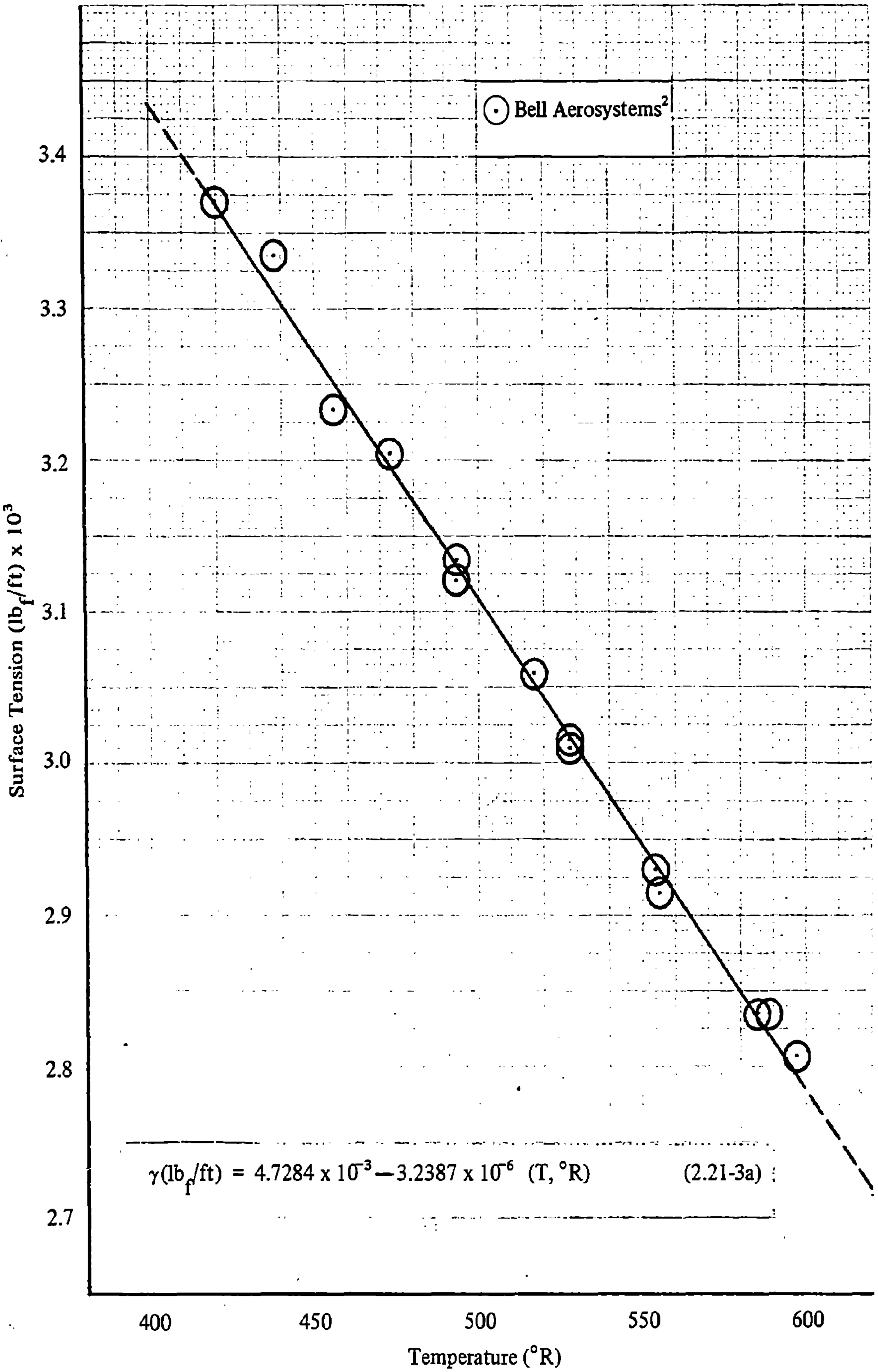


Figure 2.21-4a Surface Tension versus Temperature, Liquid B : F-1185 Fuel Blend

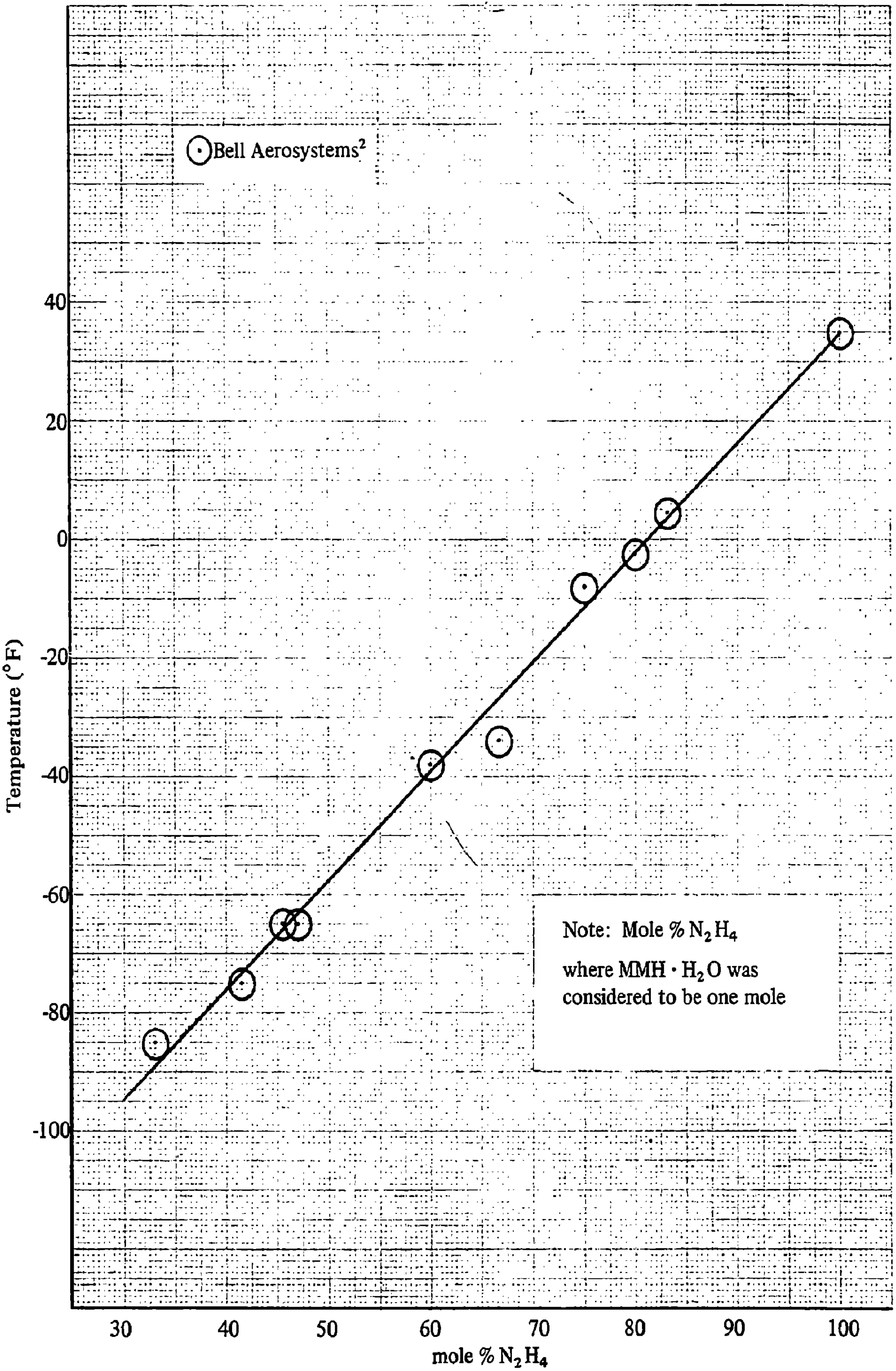


Figure 2.21-5. Freezing Point versus mole percent N_2H_4 for BAF-11 Fuels

3.0 TERNARY BLEND SYSTEM CHARACTERISTICS

3.0 TERNARY BLEND SYSTEM
CHARACTERISTICS

3.1 INTRODUCTION

3.1.1 GENERAL

3.1.2 SCOPE

3.1.3 ADVANTAGES AND LIMITATIONS OF USE

3.1.4 READING TERNARY PLOTS

3.1 INTRODUCTION

3.1.1 General

(U) This section contains a graphical presentation of certain properties of mixtures as they vary with composition. The properties are shown as constant value contours which are superimposed on ternary composition maps. Plots are included for those three-component systems which include specific hydrazine or amine-blend fuels, and for which sufficient data was available.

Considering the number of neat propellant ingredients available, the relation

$$N = \frac{n!}{r!\,(n\text{-}r)!} \qquad \left(\begin{array}{l} n = \text{No. of ingredients} \\ r = \text{No. of components per system} \end{array} \right)$$

shows that for the eight major ingredients (MAF-2 excluded), a total of 56 ternary blend systems are possible. Although several interesting possibilities are brought to mind, the number of systems necessarily had to be limited to the most well-known systems which have already been characterized.

3.1.2 Scope

(C) The eight ingredients from which the selected ternary systems or "families" are composed are the following:

1. Hydrazine, N_2H_4
2. MMH, $N_2H_3CH_3$
3. UDMH, $N_2H_2(CH_3)_2$
4. Ammonia, NH_3
5. Water, H_2O
6. Hydrazinium nitrate $N_2H_5NO_3$
7. DETA, $(C_2H_4)_2(NH_2)_2NH$
8. Acetonitrile, CH_3CN

(C) From the above eight neat ingredients, the following ternary systems have been identified as those for which the most data have been obtained and which have commanded the greatest interest in the industry.

3.2 Hydrazine
UDMH
Water

3.3 Hydrazine
MMH
Water

3.4 Hydrazine
MMH
Hydrazinium Nitrate

3.5 Hydrazine
Water
Hydrazinium Nitrate

3.6 Hydrazine
Ammonia
Water

3.7 UDMH
DETA
Acetonitrile

3.8 Hydrazine
UDMH
Hydrazinium Nitrate

(U) Each of the following subsections is devoted to one of the three-component systems listed above. Within the subsection are a discussion and ternary plots pertaining to the relevant properties. Not all properties have been illustrated in this section because of insufficient data. The specific properties shown for each system appear in the index on the divider tab at the beginning of this section. Some of the plots are not completely covered by contours, again for lack of data in these areas.

(U) The various blended propellants are assigned to these ternary systems based on their principal ingredients. Neat and binary propellants, which appear on some of the corners or edges of these ternary systems are common to more than one system. In these cases, the system to which a propellant is assigned is either determined by the major impurity or by its relationship to other blends.

(U) For example, the 50/50 blend is assigned to the N_2H_4 - UDMH - Water System for the following reasons:

1. The three propellants, N_2H_4, 50/50, and UDMH, all of major importance, appear on the same plot.
2. A major impurity in all three propellants is water, and its effect on the properties, especially in the case of 50/50, is of major importance.

The properties which are considered, if sufficient data exists, are:

Density
Melting Point
Viscosity
Vapor Pressure
Detonable Composition Range

3.1.3 Advantages and Limitations of Use

(U) This section has been compiled in order to provide a logical framework for relating one propellant blend to another, and to provide a visual and graphical picture of the variations which can be expected in various properties as the composition changes. Thus, the effect of out-of-specification blends, or of modifications to propellants can be estimated for preliminary design, planning, or trouble-shooting purposes. Conversely, it is possible to determine what changes in composition are required to effect a given change in property.

(U) The user is cautioned that the plots presented herein vary in their accuracy from one system and property to

(U) another, depending on the quantity and quality of the data and the degree of smoothing which was necessary. The discussions for the individual subsections describe in more detail how the data was interpreted and smoothed, and give a qualitative assessment of the accuracy, precision, and confidence levels thereof. The most critical parameter is probably the detonability of the hydrazinium nitrate containing systems.

(C) The most limiting test for safety was the card gap test, conducted at zero cards on a go, no-go basis. Actual points are plotted for the N_2H_4-$N_2H_5NO_3$-MMH system, exactly as reported by the two sources, for this test. The data for the N_2H_4-$N_2H_5NO_3$-water system is shown as a plot, exactly as reported. In interpreting the data, the user should also consult Section 5.3 on the safety of propellants such as MHF-1, MHF-5 and MGGP-1. No detonability data was available on the N_2H_4-$N_2H_5NO_3$-UDMH system, also discussed in Section 5.3.

3.1.4 Reading Ternary Plots

(U) The ternary plot is a geometrical map of three variables whose sum is always constant. In this case, the variables are the concentrations, in percent by weight, of the three components comprising a mixture, and the sum is always 100 percent.

(U) Any corner of the plot corresponds to 100 percent of the component for which it is labelled. The concentration of the other components is zero. As one proceeds away from the corner in a straight line toward the opposite edge, the concentration of the component drops linearly to zero. The same is true for any other corner. The edges of the plot involve only the two components denoted by the two adjoining corners. For example, a point midway along an edge of the plot corresponds to a composition of 50 percent by weight of each of the two components of the adjoining corners, and zero percent of the component denoted by the corner opposite to the edge.

(U) The percentage of components at any point in the diagram can be found by traversing a line joining the point, the component, and its opposite edge; from the edge to the point. The fraction of the distance to the corner which is covered, denotes the percentage of that component. This is done for two of the components and the third component can be found by the difference required to obtain 100 percent.

(U) The properties are presented in the form of constant value contours, forming a contour map of the property. In regions where these contours are nearly parallel, and nearly equally spaced, a linear interpolation is usually sufficient to determine the property of a composition not falling on one of the curves.

(U) The plot is covered with grids at each 5 percent interval to facilitate determination of compositions. Thus, the composition of a blend can be found by counting the number of grids passed and multiplying by 5. The concentration of a particular component always increases linearly, as the corner so labelled, is approached.

(U) Propellants containing the three principal ingredients are represented as small hexagonal regions centered on the location of their nominal composition.

3.2 THE N_2H_4-UDMH-H_2O SYSTEM

3.2.1 DENSITY

3.2.2 MELTING POINTS

3.2 THE N_2H_4- UDMH - H_2O SYSTEM

3.2.1 Density

The ternary plot, Figure 3.2-1, illustrates the variations of density (g/cc at 25C (77F)) with composition in the N_2H_4-UDMH-H_2O system. Data for the plot was taken principally from Pannetier(27), Aerojet(20), Houston Research Institute(28), Battelle Memorial Institute(26), and Bell Aerosystems(18). Data were smoothed for this plot whithin the constraints of the accepted values for hydrazine, 50/50, UDMH, water and hydrazine hydrate. The only data for ternary mixtures consisted of three points along the line corresponding to a 2 to 1 molar ratio of water to UDMH. Therefore, all of the plot, except near the edges, is somewhat provisional. The dashed lines indicate the region having the lowest confidence level. It should be noted, that although the exact position of the lines is only approximate, the values of density obtained will be sufficiently accurate for engineering and preliminary design purposes. Due to the importance of the 50/50 blend (hexagonal point), additional detailed studies should be conducted of the effect of compositional variations on density near this point.

3.2.2 Melting Points

The ternary plot, Figure 3.2-2, illustrates the approximate variation of melting point in degrees celsius with composition derived from measured data and as smoothed for this handbook. Measured data from RMD(19) and Bell Aerosystems(18) fall along a line through the center of the plot corresponding to a 2 to 1 molar balance of water to UDMH, respectively. The remainder of the data pertain to the edges of the plot (binary mixtures) and some are also common to other systems, as in the case of the hydrazine-water system. All of the measured data were found to be of a high confidence level, with close agreement between the different sources.

The regions of the plot where data was available are therefore covered by solid lines denoting a high confidence level. The regions where data does not exist, however, have been estimated within the constraints of the edges and are covered by dashed lines denoting a low confidence level. The eutectic valleys are shown as dotted lines.

The position of the propellant 50-50 (N_2H_4-UDMH) is indicated by the hexagonal point. Its melting point lies between -6 and -8 C, depending on the precise composition. The positions of three intermediate compounds are shown as circled points. It is believed, as in other systems, that the compositions of low melting points behave as viscous glassy substances without a definite melting or freezing point.

Except near the edges, and along the UDMH-2 H_2O line between hydrazine and the center of the plot, the data should be treated as highly provisional and used for preliminary purposes only.

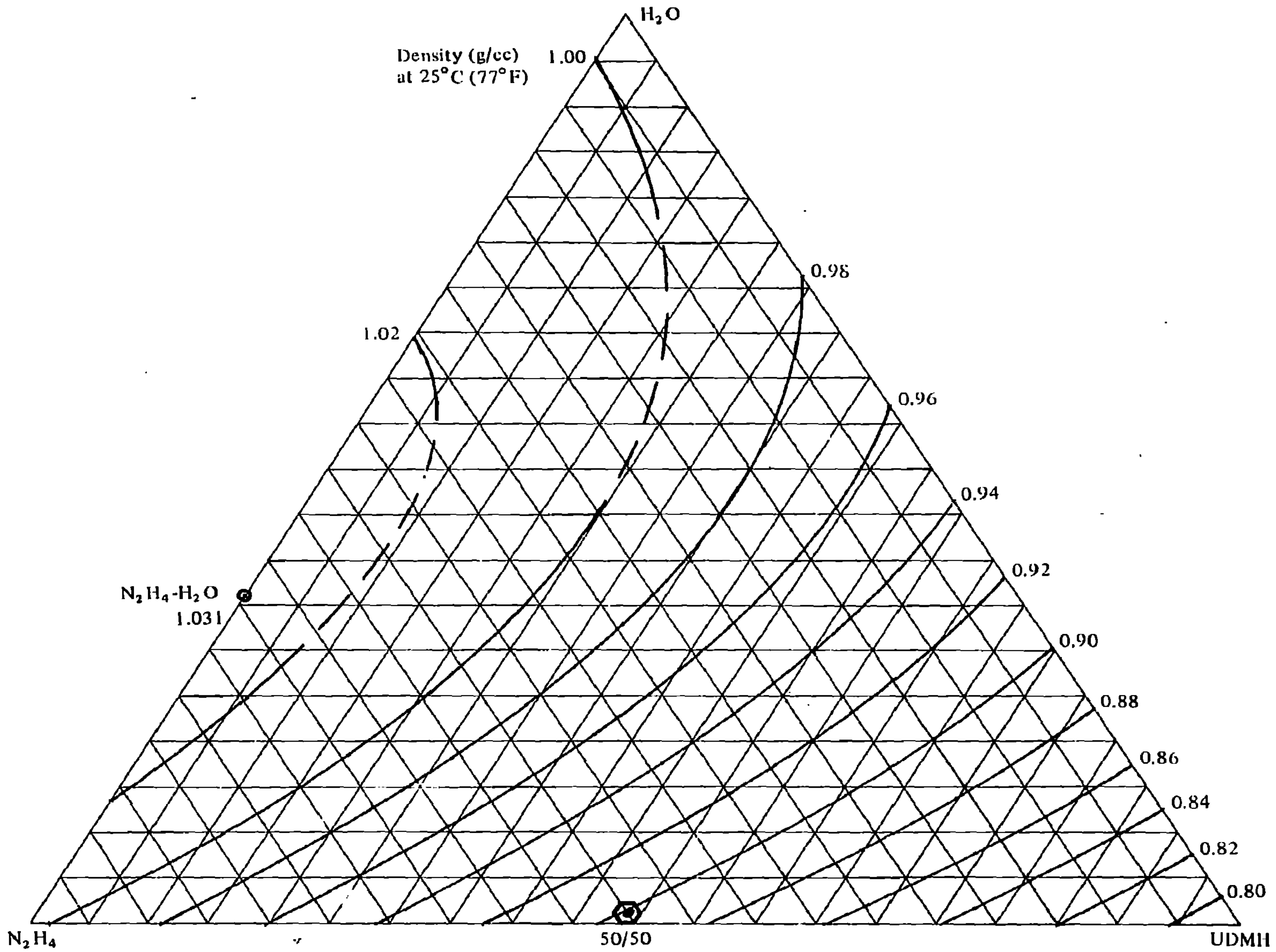


Figure 3.2-1. Density of the N_2H_4-UDMH-H_2O System (g/cc at 25°C (77°F))
Smoothed Data from Pannetier[27], Aerojet[20], HRI[28], Battelle[26] and Bell Aerosystems[18]

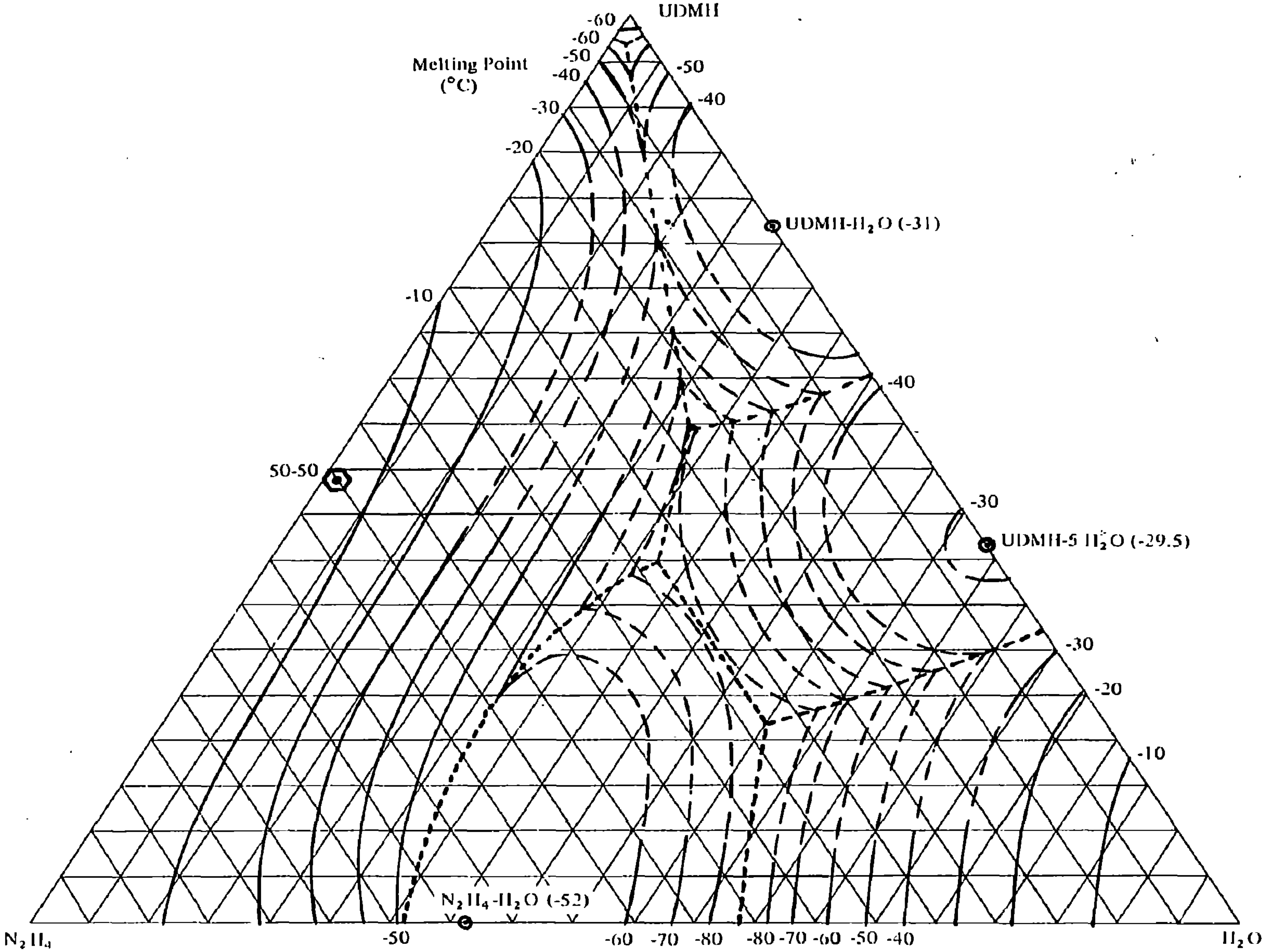


Figure 3.2-2. Melting Point Isotherms in the N_2H_4-UDMH-H_2O System Data from RMD[19], Bell Aerosystems[18], Aerojet[20], Scott[12], Mohr[15], Poole[10], and Horvitz[9]

3.3 THE N_2H_4- MMH-H_2O SYSTEM

3.3.1 DENSITY

3.3.2 MELTING POINT ISOTHERMS

3.3 THE N_2H_4-MMH-H_2O SYSTEM

3.3.1 Density

(C) The ternary plot in Figure 3.3-1 shows the variation of density in g/cc at 25 C (77 F) with composition for mixtures of hydrazine, MMH and water. The plot is based on the data of Wrobel(16), Bell Aerosystems(18), Battelle Memorial Institute(26) and RMD(19), and is constrained by accepted values established in this handbook for hydrazine, MMH, MHF-3, MHF-6, BAF-1185 and BA-1014.

(U) Extensive data for blends along the line of equal moles of MMH and water have been generated by Bell Aerosystems(18), and the majority of data for MMH-water mixtures comes from a paper by Wrobel and Grelecki(16).

(U) It will be noted that mixtures involving water show a considerable positive deviation in density from the additive volumes value. This is due to the formation of the monohydrates of N_2H_4 and MMH (circled points).

(U) Data from different sources were in fairly good agreement, and the resulting smoothed curves of constant density are considered reasonably accurate for the purposes of preliminary design and engineering estimates. The only region with a low confidence level is denoted by the dashed curves at the low MMH concentrations.

(U) The hexagonal points show the position of specific propellants contained in this system. It should be noted that many other mixtures have been considered for use as propellants, particularly along the line connecting MMH-H_2O, BAF-1185, BAF-1014 and hydrazine. MMH-H_2O was, in fact, used as the fuel in the surveyor spacecraft vernier propulsion system. These blends were considered due to certain advantages such as carbon-oxygen balance, and freezing point depression.

3.3.2 Melting Point Isotherms

(C) Figure 3.3-2 illustrates the variation of melting point with composition for the MMH-water binary mixture was reported by Wrobel and Grelecki(16). The N_2H_4-MMH data, including MHF-3 has been reported by RMD(4), Aerojet(20), and Horvitz(9). The N_2H_4-water data was reported by Scott(12), Mohr(15), and Poole(10). In addition, studies of the mixtures of hydrazine with an equimolar mixture of MMH and water, along with some of the above mentioned binery mixtures, were reported by Bell Aerosystems (18), JPL(17), and RMD(19). RMD also reported a value for MHF-6. The data have been smoothed and interpolated for this work to cover the plot, according to the known behavior of eutectic valleys. The broken lines indicate regions where some uncertainty exists as to the exact position of the melting point isotherms. It should be kept in mind that data of this type may be unreliable, especially at the low temperatures, due to glassing and supercooling.

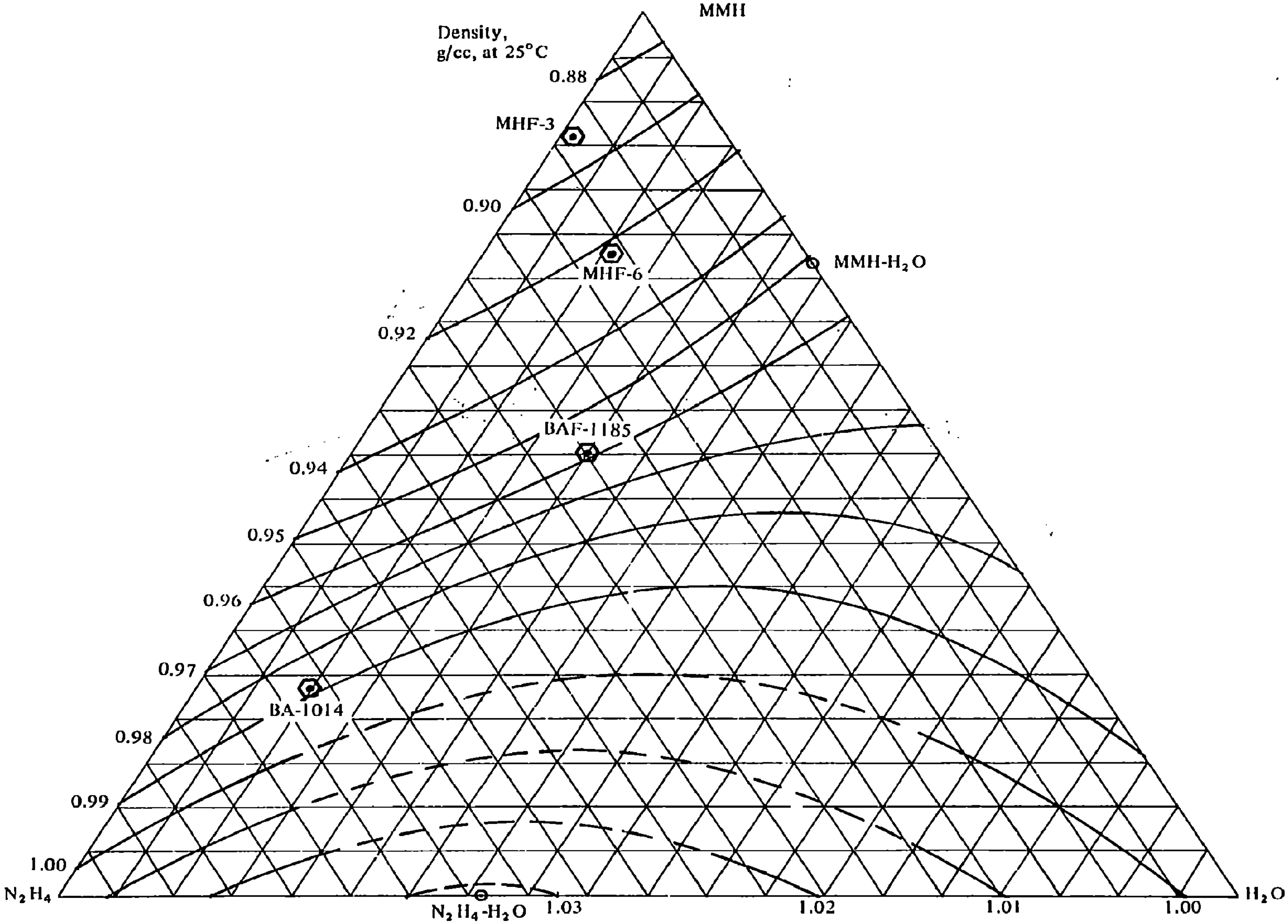
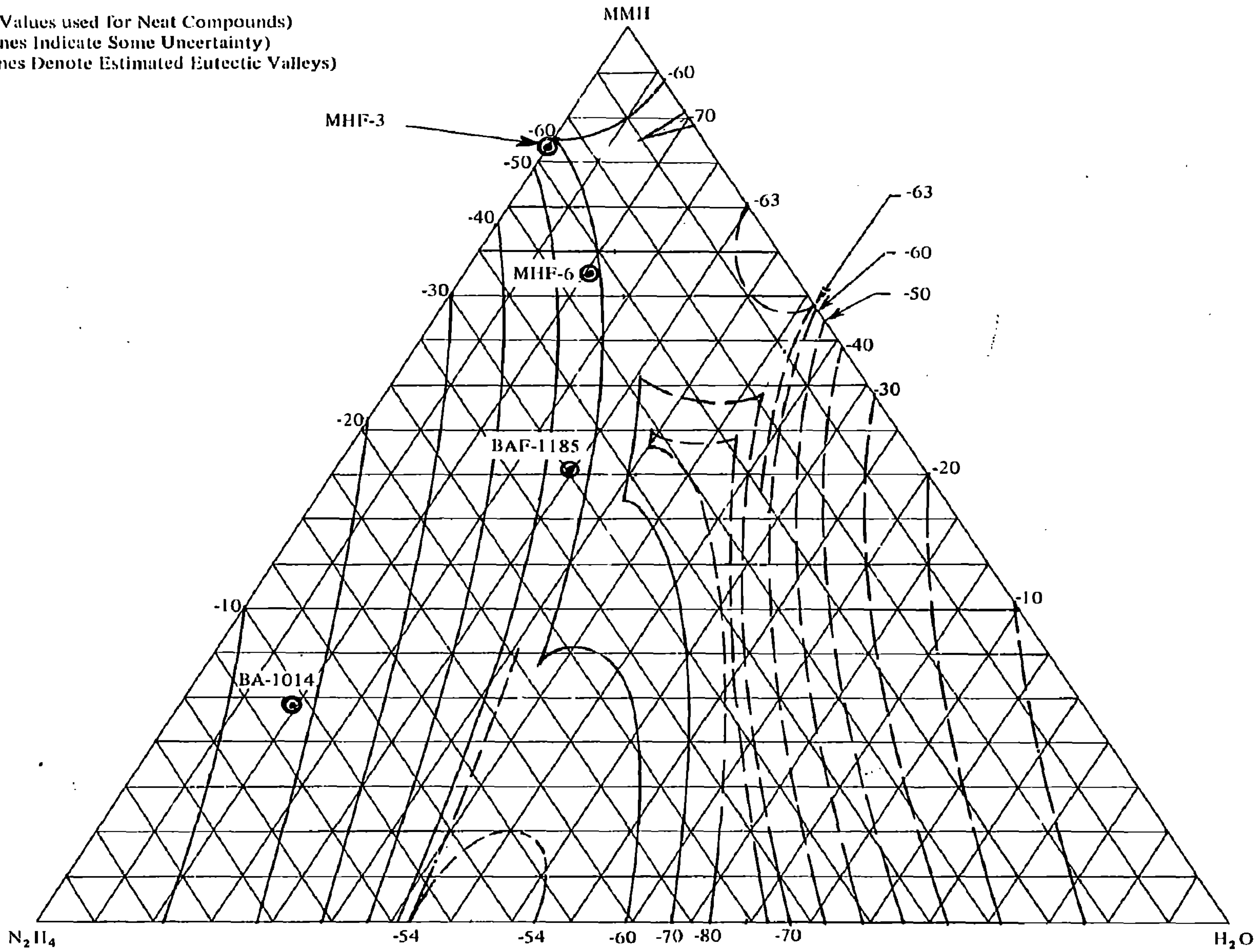


Figure 3.3-1. Density of the N_2H_4-MMH-H_2O System (g/cc at 25°C (77°F))
Data from Wrobel[16], Bell Aerosystems[18], Battelle[26], RMD[19], and Accepted Points



(Accepted Values used for Neat Compounds)
(Broken Lines Indicate Some Uncertainty)
(Dotted Lines Denote Estimated Eutectic Valleys)

Figure 3.3-2. Melting Points of the N_2H_4 -$N_2H_3CH_3$ -H_2O System Smoothed Data from Wrobel[16], JPL[17], Bell Aerosystems[18], RMD[19,4], Scott[12], Mohr[15], Poole[10], Aerojet[20], and Horvitz[9]

3.4 THE HYDRAZINE-MMH-$N_2H_5NO_3$ SYSTEM

3.4.1 DENSITY
3.4.2 MELTING POINT ISOTHERMS
3.4.3 VISCOSITY OF THE MHF COMPOSITIONS
3.4.4 DETONABILITY OF MHF COMPOSITIONS

3.4 THE HYDRAZINE-MMH-$N_2H_5NO_3$ SYSTEM

3.4.1 Density

(C) The density of mixtures of N_2H_4, $N_2H_3CH_3$ and $N_2H_5NO_3$ ($N_2H_5^+ + NO_3^-$) has been measured and reported by RMD(4,5,6), and Rocketdyne(7). The density of neat hydrazinium nitrate (solid) has also been reported by Von Doehren(8) of the AFRPL. The densities of N_2H_4-MMH Mixtures and of neat N_2H_4 and neat MMH have been obtained from the values accepted for this work in the properties section.

(C) The accepted values for N_2H_4, MMH, MHF-3 and MHF-5 have a high confidence level and have been used as constraining boundary values in the smoothing of data for the plot of constant-density contours in Figure 3.4-1.

(U) Figure 3.4-1 shows the plot of constant density lines for the N_2H_4-MMH-hydrazinium nitrate system. These lines have been derived for this work by smoothing the available data within the constraints of the accepted values. The accuracy and reliability of the data is considered to be reasonably good. The values of density for compositions not lying on one of the isoclines can be obtained by linear interpolation.

(U) A density value reported for MHF-4 by RMD(5) was obviously in error, and the value obtained from the plot (1.007 g/cc) has been adopted in the physical properties section.

3.4.2 Melting Point Isotherms

(U) As a group, the MHF propellants containing hydrazinium nitrate have been the subject of several reassessments and modifications, due in large to uncertainty as to their true melting points. For example, MHF-5 was first reported to have a melting point of -71F, and it has since been continually revised upwards to approximately -43F.

(C) As a result, other compositions, MHF-5A and MHF-5B, were investigated as substitutes to meet the melting point requirements of specific applications.

(U) The majority of the data found, and the most recent on this system was that of Rocketdyne(7). Other extensive data from RMD(4,5,6), and some from UARL(22), and Von Doehren(8) have also been utilized to form the isotherms shown in Figure 3.4-2. The difficulty of measuring melting points at low temperatures with supercooling tendencies, and the highly complex equilibria between

(C) It should also be noted that the plot presented herein does not agree exactly with similar plots prepared by Rocketdyne in Reference 7. The Rocketdyne plot is based solely on their data and follows it more precisely. It shows a more complex system of eutectic valleys which are difficult to justify from theoretical reasoning. The complex eutectic valleys on the Rocketdyne plot in the region near MHF-5 may be due to data scatter or may possibly exist and be due to the complex nature of the system. Extensive glassing was observed in the region near MHF-5A.

(U) The position of the isotherms is well established along the N_2H_4-MMH edge of the plot. Elsewhere the position is accurate to within 2 percent in composition. The estimated positions of the eutectic troughs are denoted by the dotted lines. The broken portions of the isothermals are regions where more uncertainty exists.

3.4.3 Viscosity of the MHF Compositions

(C) The viscosity in the N_2H_4-$N_2H_3CH_3$-$N_2H_5NO_3$ system has been studied at several compositions indicated by the circular and hexagonal points on Figure 3.4-3. The viscosity plot is based on data for N_2H_4, MMH, MHF-3, MHF-1, MHF-4, MHF-5, and MHF-5B (hexagonal points) from Sections 2.3.3.5, 2.4.3.5, 2.14.4.5, 2.16.4.5, 2.17.4.5, and 2.18.4.5, respectively. In addition, data from Rockenfeller(22) for compositions denoted by the circular points were used. The viscosity for each composition was well established as a function of temperature. The different compositions, furthermore, remained in the same relative positions in order of viscosity at both low and high temperatures (from -40 to +25 C). The plot in Figure 3.4.3 shows absolute viscosity contours (centipoises) at 0 C. The broken lines denote the region of lesser confidence level. Due to the spread of compositions, the position of the contours is only approximate, and may vary by 2 percent in composition, or by up to 20 percent in viscosity at a given composition.

3.4.4 Detonability of MHF Compositions

(U) Figures 3.4-4, 3.4-5 and 3.4-6 illustrate the detonable composition range for the N_2H_4-MMH-Hydrazinium nitrate blends measured by RMD(4) and the U.S. Bureau of Mines(24). The results of the three types of tests utilized are shown to emphasize the differneces in the results which arise due to the different conditions. In this system, the card gap test at zero cards was the overriding criterion since it gave positive results at the lowest hydrazinium nitrate

(U) Since there is a slight difference between the data of RMD and that of the Bureau of Mines, the largest detonable envelope defined by the lowest curves would give the most conservative limits of safe compositions.

(C) According to the data, any composition lying below the lowest curve should be nondetonable. A reasonable safety margin is also recommended. All of the propellants, MHF-1, 3, 4, 5 and 5B are in the nondetonable range.

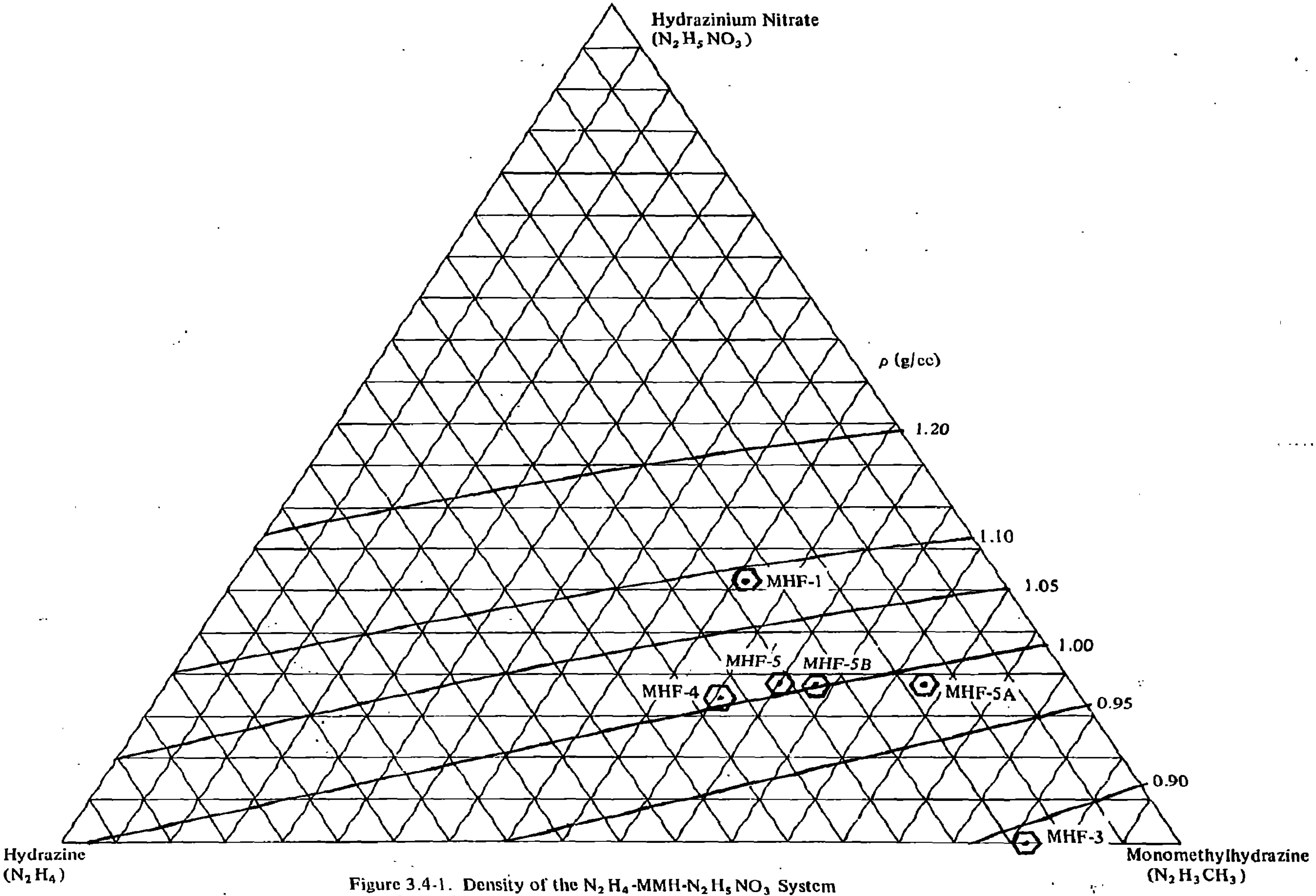


Figure 3.4-1. Density of the N_2H_4-MMH-$N_2H_5NO_3$ System (g/cc at 25°C (77°F)) Smoothed Data from RMD[4,5,6], Rocketdyne[7], and Von Doehren[8]

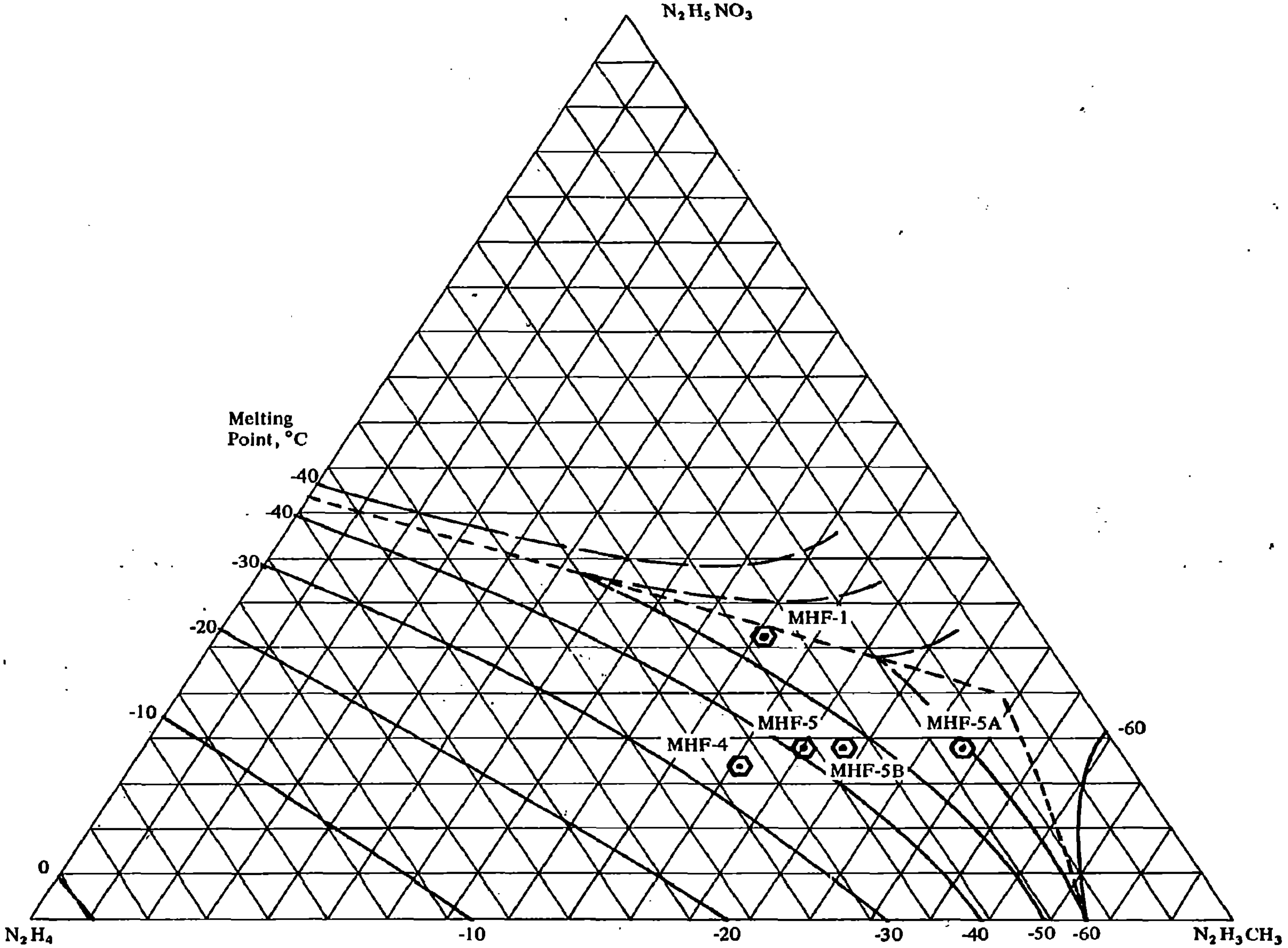


Figure 3.4-2. Melting-Point Isotherms: Hydrazine-Hydrazinium Nitrate-Methylhydrazine System (Smoothed Data of RMD[4 5 6], Rocketdyne[7], and U.A.R.L.[22])

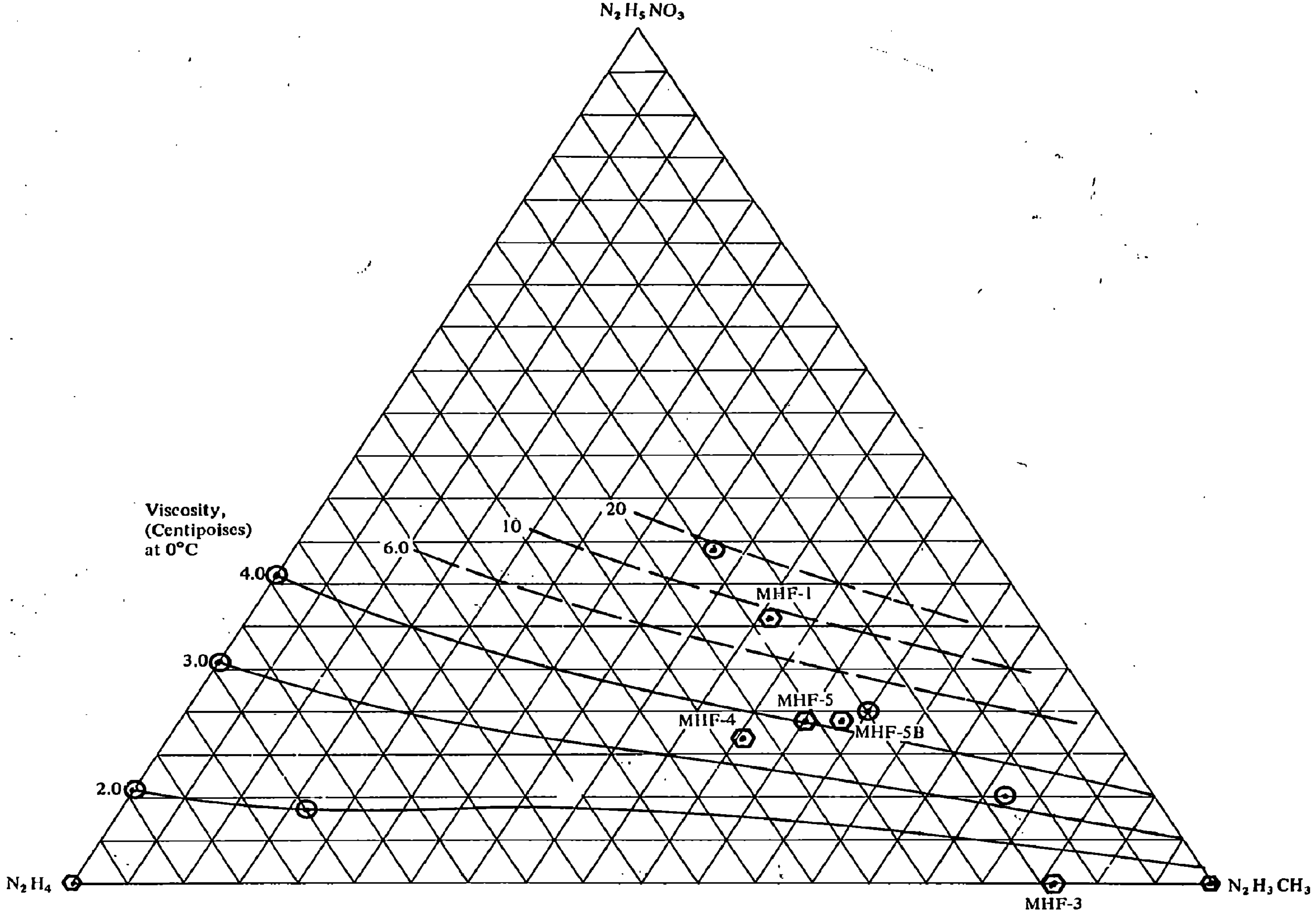


Figure 3.4-3. Absolute Viscosity Contours for the N_2H_4-MMH-$N_2H_5NO_3$ System (Centipoises) at 0°C. Data from Rockenfeller[22] and from sections indicated in text.

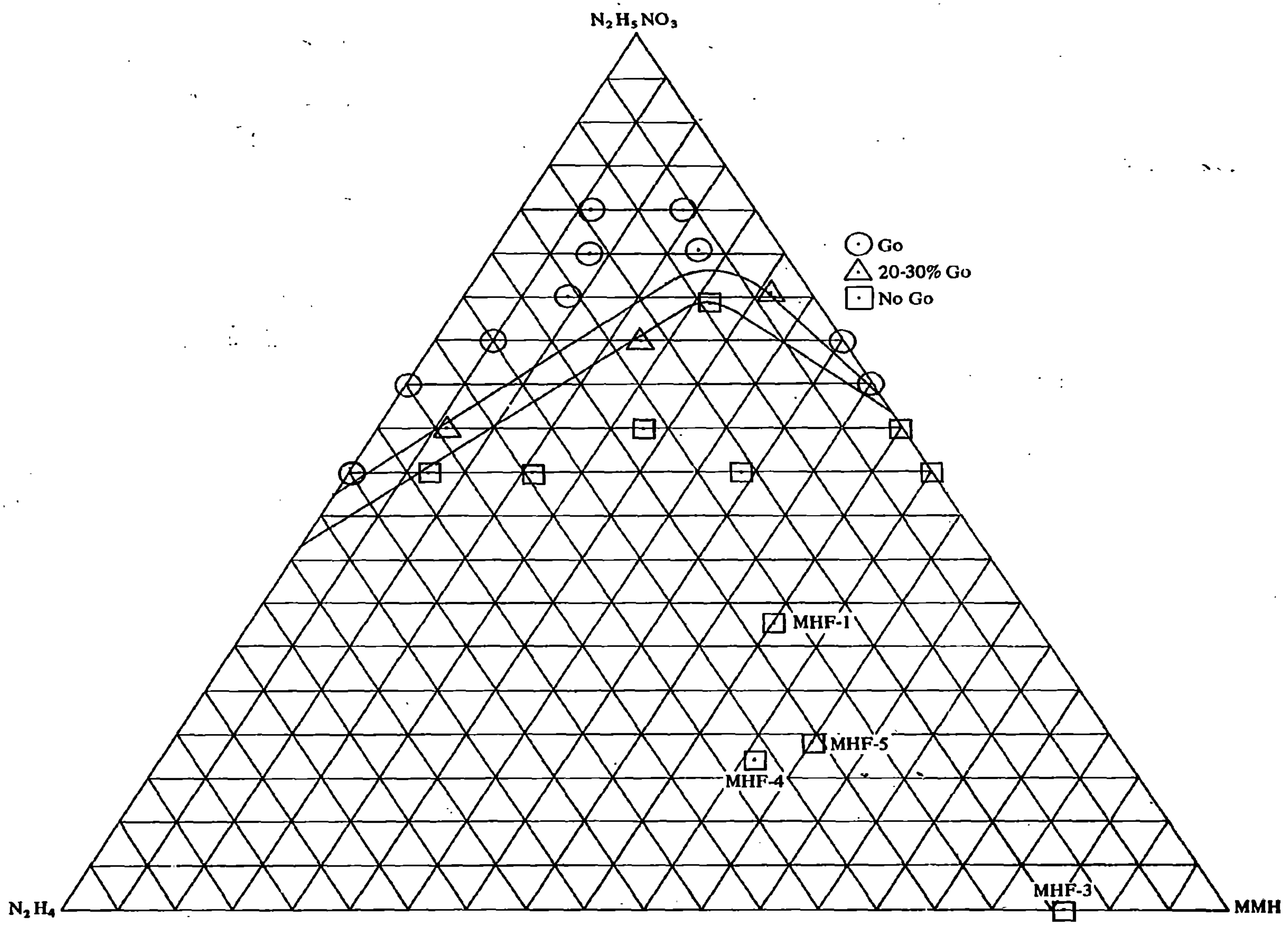


Figure 3.4-4. Drop-Weight Impact Sensitivity of the N_2H_4-MMH-$N_2H_5NO_3$ System, as Reported by RMD[4]

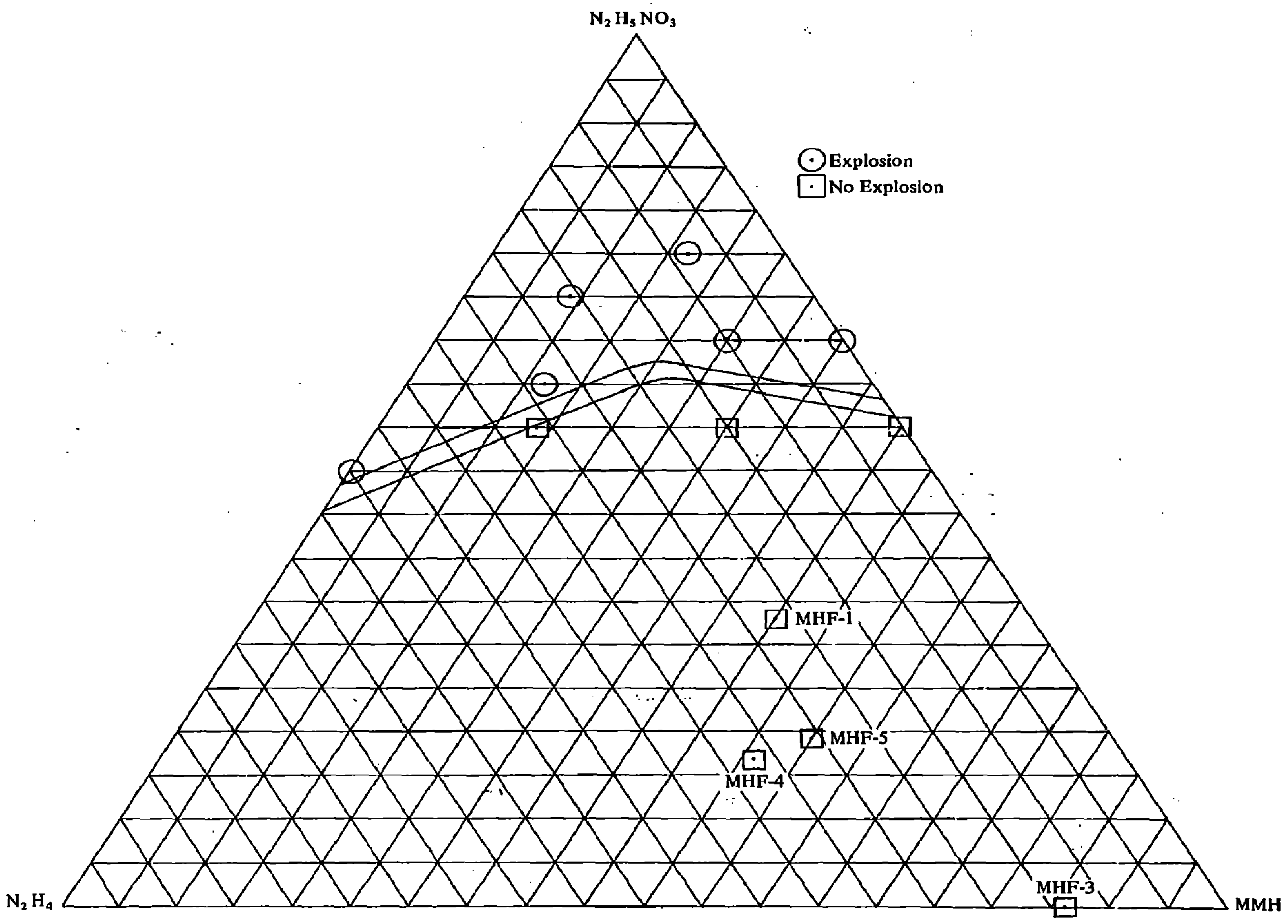


Figure 3.4-5. Trauzl-Block Sensitivity of the N_2H_4-MMH-$N_2H_5NO_3$ System as Reported by RMD[4]

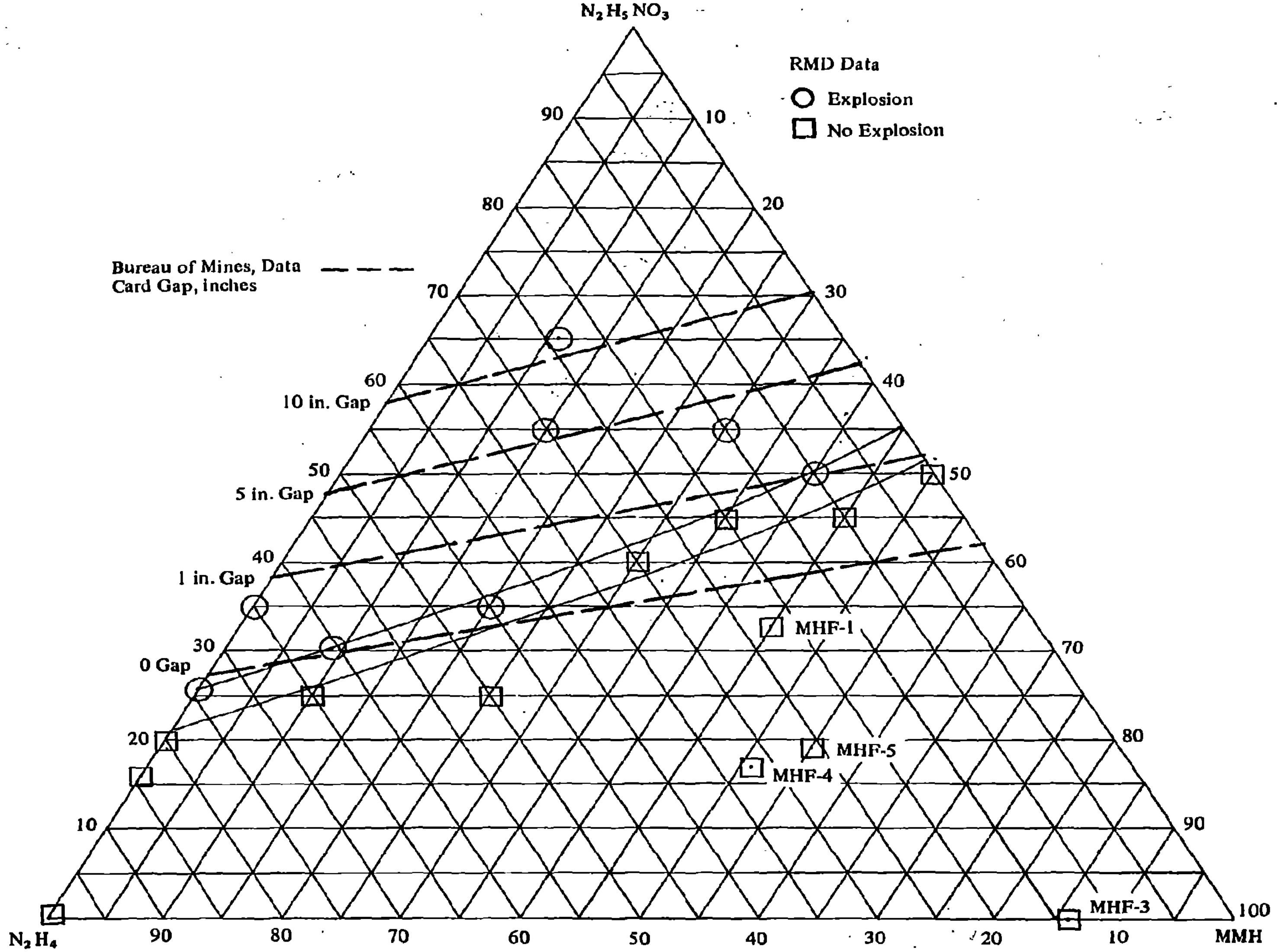


Figure 3.4-6. Card-Gap Sensitivity of the $N_2H_5NO_3$ System as Reported by RMD and the U.S. Bureau of Mines

3.5.1 DENSITY

3.5.2 MELTING POINTS

3.5 THE N_2H_4-$N_2H_5NO_3$-H_2O SYSTEM

3.5.1 Density

Figure 3.5-1 shows the density contours at 25 C (77 F) in the N_2H_4-$N_2H_5NO_3$-H_2O system. The data are mainly from Rockenfeller(22), with additional verification of the hydrazine-water system from data reported in References (26) and (30). The hexagonal point, corresponding to MGGP-1, agrees with the accepted density value from Section 2.13.3.2. The accuracy of the plot is considered reasonably good, owing to the apparant accuracy of the Rockenfeller data and the good agreement with other sources for MGGP-1 and the hydrazine-water blends. One would expect the confidence level to be very high at low $N_2H_5NO_3$ concentrations and to diminish as one approaches the void region. The void region reflects the fact that there has been no interest in the highly viscous, and detonable, high HN concentrations.

3.5.2 Melting Points

The tenary plot in Figure 3.5-2 presents melting point isotherms for the hydrazine-hydrazinium nitrate water system based on data of RMD(25), NOTS(29), Poole(10), Rockenfeller(22), Scott(12), Mohr(15) and Horvitz(9).

Due to increased interest in low-freezing monopropellants, this system has been extensively studied by several of the investigators. Their data, combined with established data for the edges of the plot, forms a plot of reasonably high confidence level. In some cases, data have been smoothed or estimated, and these areas are indicated by dashed lines. The eutectic troughs are indicated by dotted lines. The plot shows the positions of two intermediate compounds; hydrazinium nitrate hydrazinate, and hydrazine hydrate (circled points), and of MGGP-1 (hexagonal point). MGGP-1 has a melting point of approximately -54 C.

The regions of high hydrazine concentration, and the two edges joined by hydrazine have a high confidence level of accuracy. The remainder of the plot should be regarded as provisional. The region of high $N_2H_5NO_3$ concentration has been partially omitted, due to the high freezing points and detonability in this area.

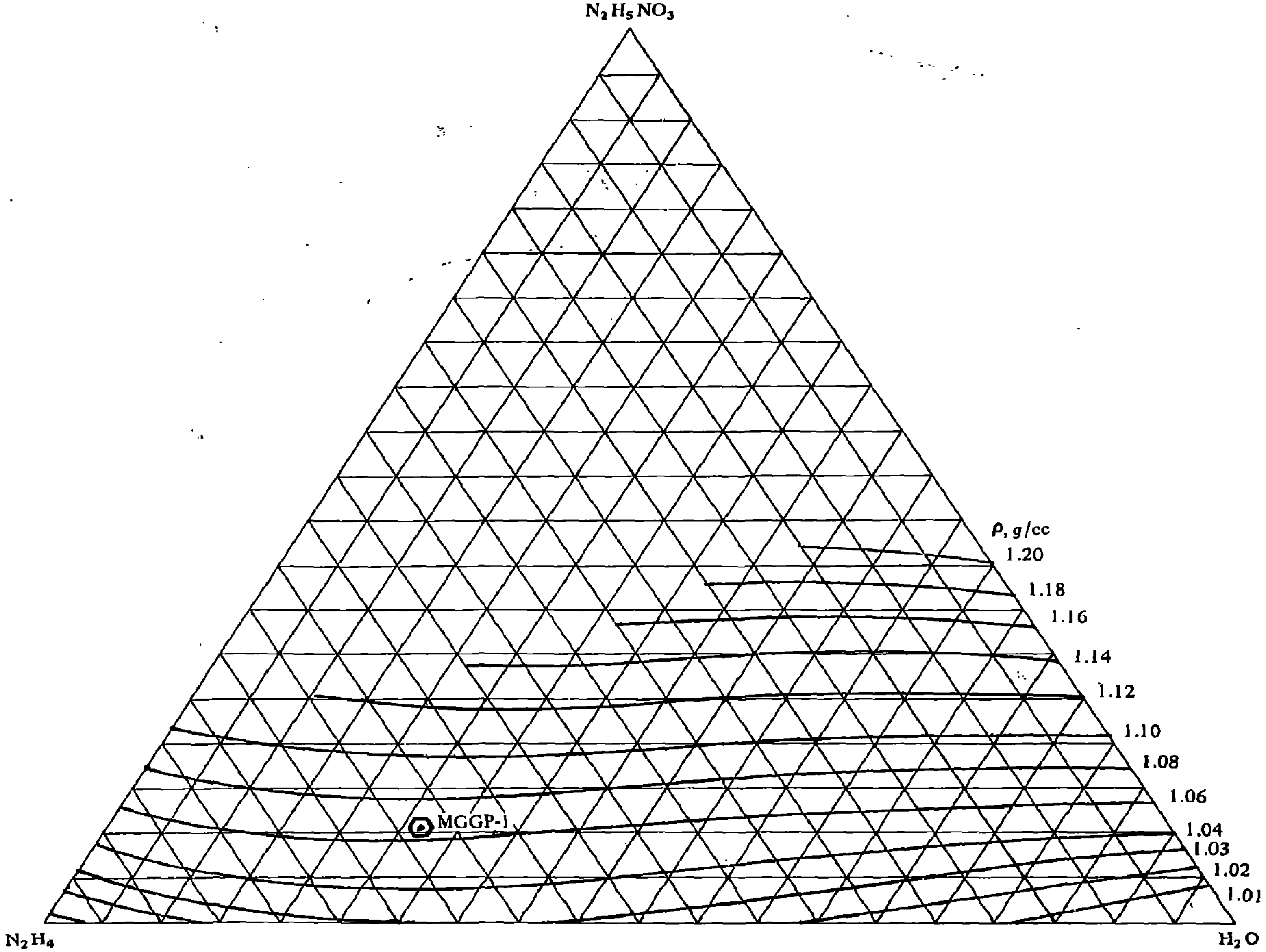


Figure 3.5-1. Density in the Hydrazine-Hydrazinium Nitrate-Water System g/cc at 25°C (77°F). Data from Rockenfeller[22]

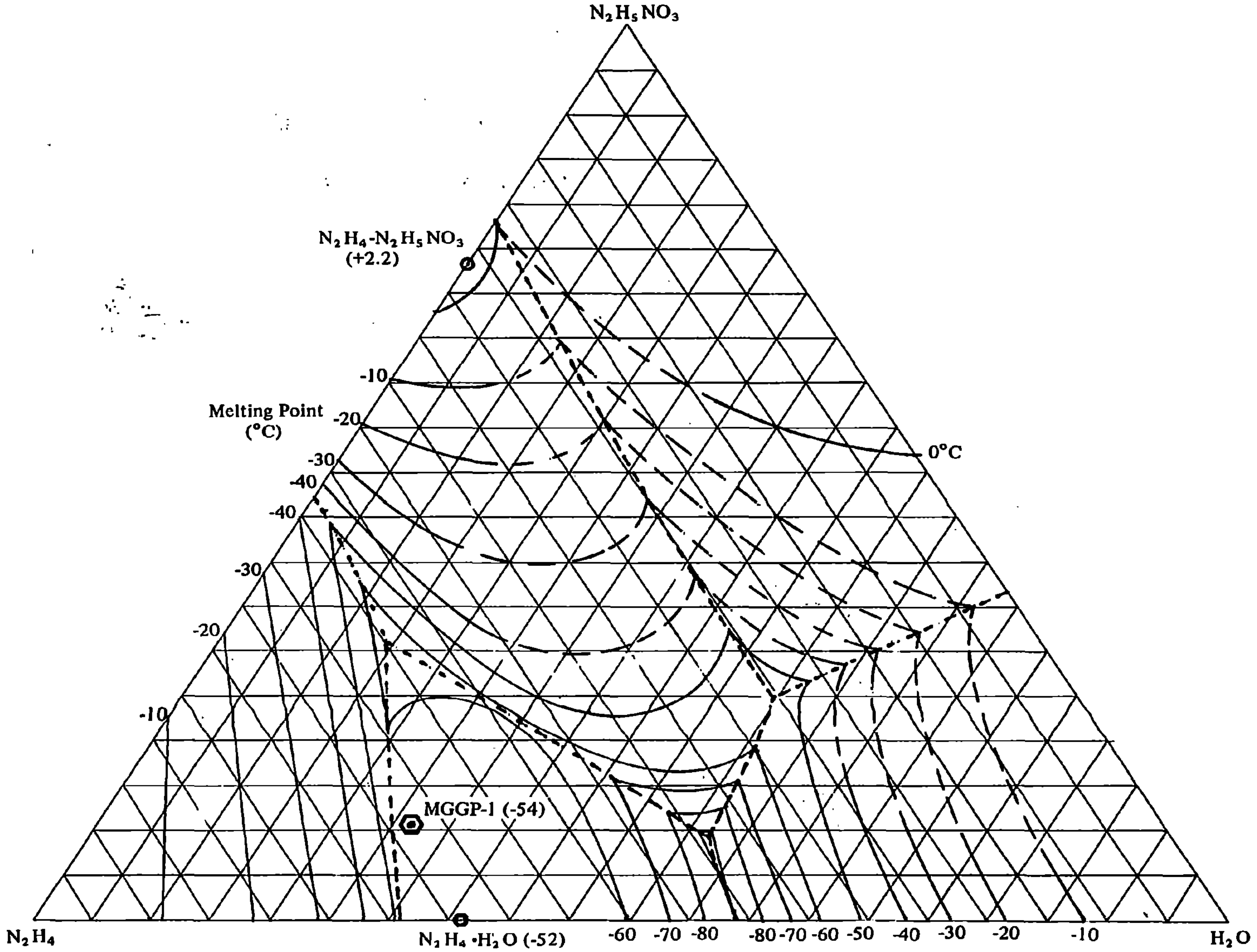


Figure 3.5-2. Melting Point Isotherms for the N_2H_4-$N_2H_5NO_3$-H_2O System. Data from RMD[25], NOTS[26], Poole[10], Rockenfeller[22], Scott[12], Mohr[15], and Horvitz[9].

3.6 THE HYDRAZINE-AMMONIA-WATER SYSTEM

3.6.1 DENSITY

3.6.2 MELTING POINTS

3.6.3 VAPOR PRESSURE

3.6 THE HYDRAZINE-AMMONIA-WATER SYSTEM

3.6.1 Density

Figure 3.6-1 shows a partial plot of constant density contours based on established data for the hydrazine-water system plus data reported by Poole(10) for mixtures containing ammonia. The number of compositions for which data exists are relatively few, and therefore the plot is only partially complete. Data is shown for density in g/cc at 25 C (77 F). The confidence level and accuracy are only fair and the data should be treated as provisional, until additional work is conducted on specific blends.

3.6.2 Melting Points

Figure 3.6-2 shows melting point isotherms for blends of N_2H_4-NH_3, and H_2O in degrees C. Data, as reported by Horvitz(9), Poole(10), Friedricks(11), Scott(12), Redstone Arsenal(13), The Int. Critical Tables(14), and Mohr(15) have been combined and smoothed for this plot. It should be noted that some regions of low N_2H_4 content did not exhibit any definite melting point, but rather became highly viscous, and then glassy with decreasing temperature. The confidence level is considered good, although the rapid change of melting point with changes in composition make the data somewhat approximate near the "glassy" region. The agreement between the several sources was excellent.

3.6.3 Vapor Pressure

Figure 3.6-3 is a plot of constant vapor pressure contours in mm. Hg. at 18.33 C (65.0 F). The data of the Int. Critical Tables(14), Comer(21) and Poole(10) have been combined and smoothed to form the curves.

Relatively few data points were available, and since these were reported at different temperatures, the vapor pressure of some compositions had to first be determined as a function of temperature, then values taken for the different compositions at the same temperature. The temperature chosen was the highest value at which data existed for all reported compositions.

The data must be considered provisional due to the small number of compositions considered.

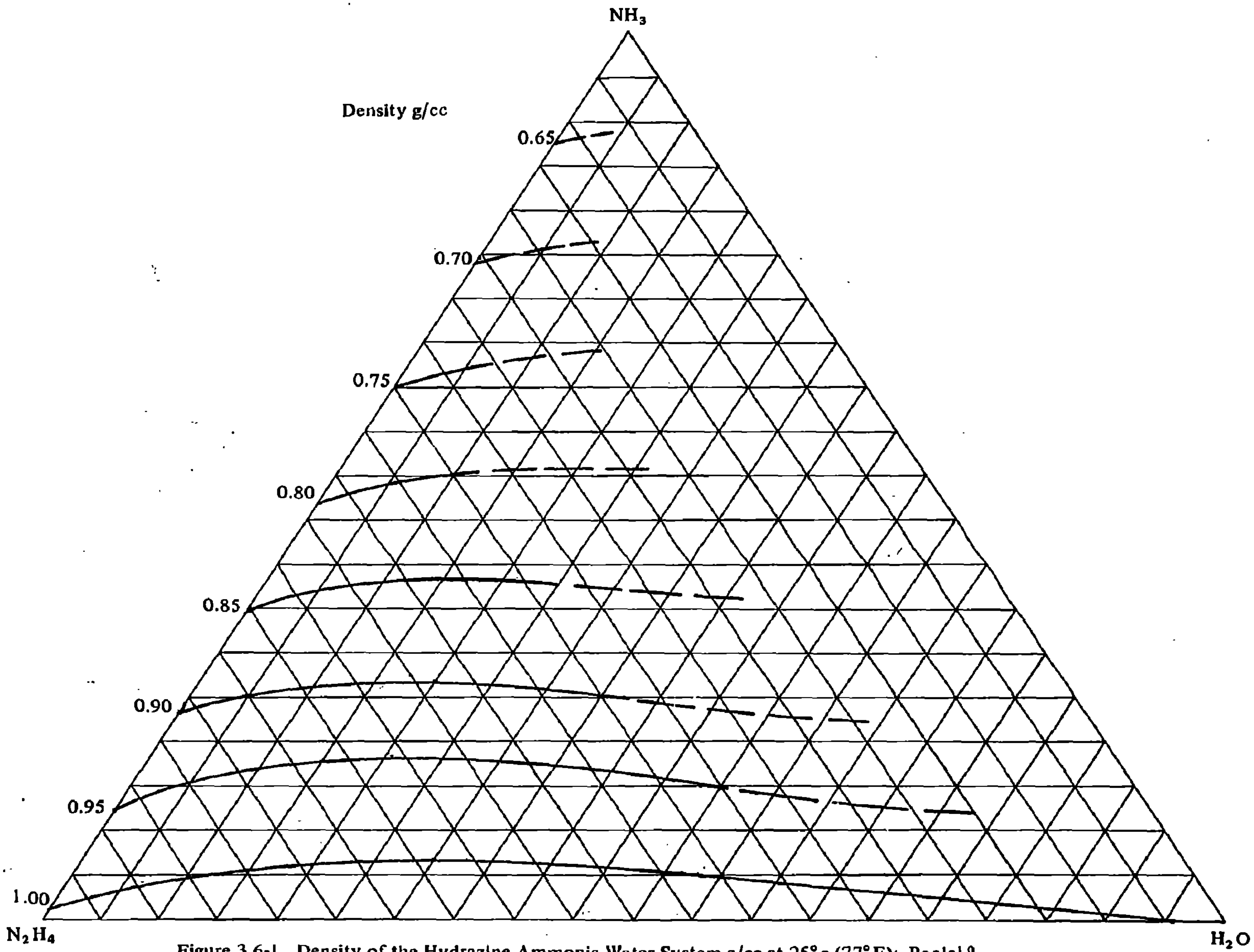


Figure 3.6-1. Density of the Hydrazine-Ammonia-Water System g/cc at 25°c (77°F); Poole[10]

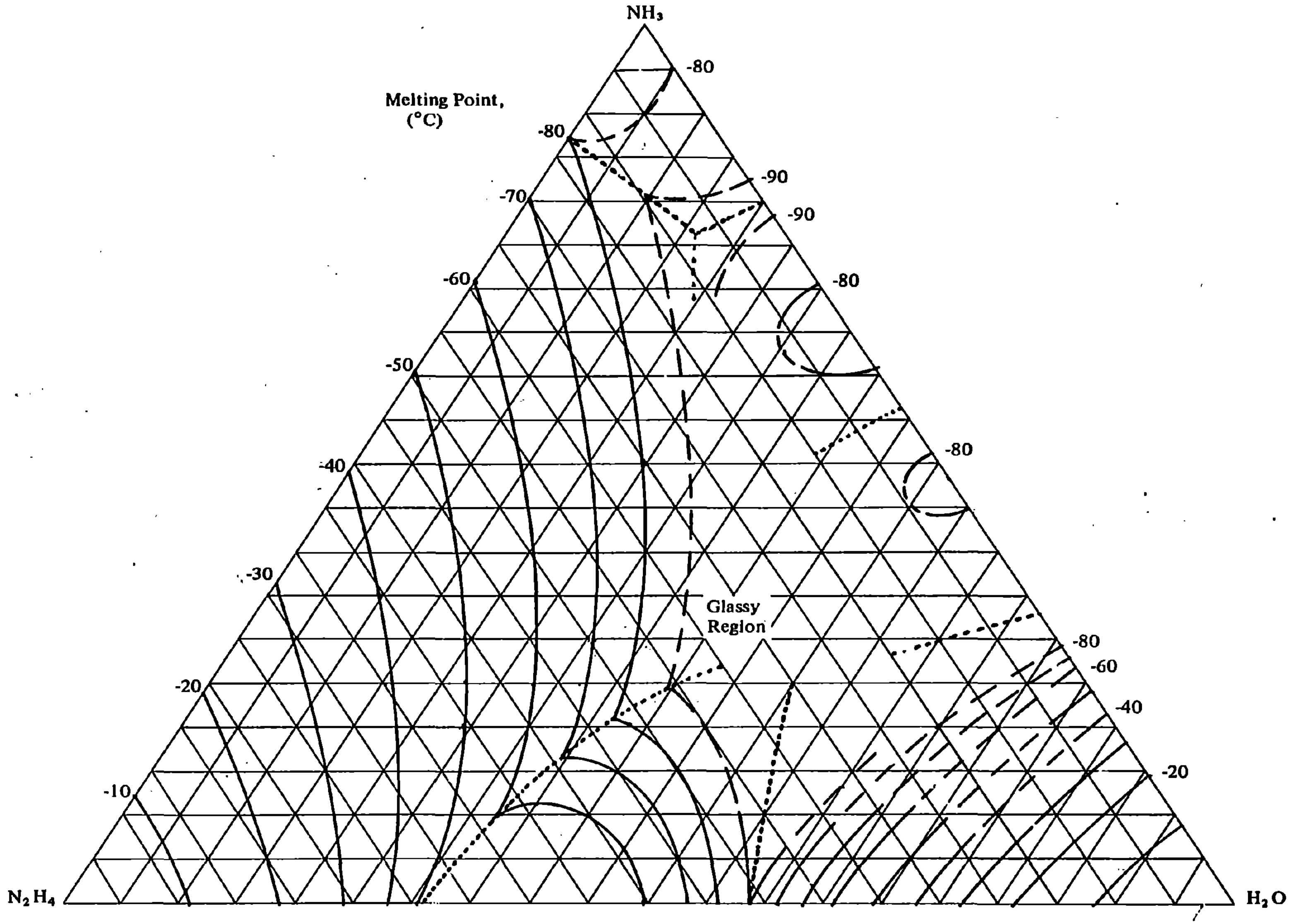


Figure 3.6-2. Melting Points in the N_2H_4-NH_3-H_2O System Smoothed Data from Horvitz[9], Poole[10], Friedrichs[11], Scott[12], Redstone[13], Int. Crit. Tables[14], and Mohr[15]

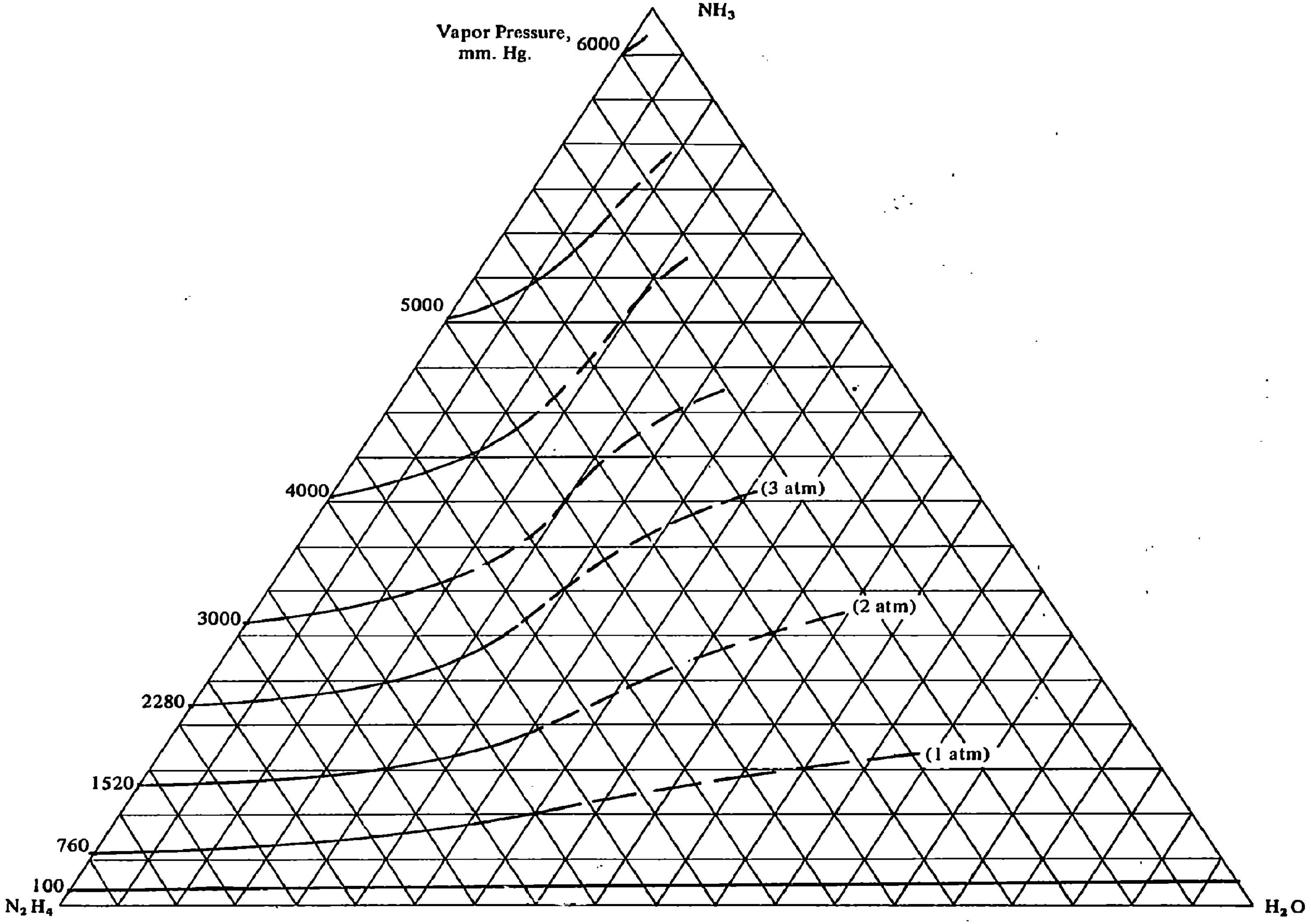


Figure 3.6-3. Vapor Pressure of the N_2H_4-NH_3-H_2O System (mm. Hg.) at 18.33°C (65.0°F) Smoothed Data from Int. Crit. Tables[14], Comer[21], and Poole[10]

3.7 THE UDMH-DETA-CH_3CN SYSTEM

3.7.1 DENSITY

3.7.2 KINEMATIC VISCOSITY

3.7 THE UDMH-DETA-CH_3CN SYSTEM

3.7.1 Density

The density of blends of $N_2H_2(CH_3)_2$, DETA, and CH_3CN has been studied and reported by RMD(1), FMC Corp.(2), and Rocketdyne(3). These data, along with established values for UDMH, DETA, and CH_3CN have been combined and smoothed to form the plot shown in Figure 3.7-1.

Most of the data indicate that the density in this system agrees well with that obtained theoretically by the additive volume method. Due to the small number of compositions studied, however, the exact position of the contours is subject to some uncertainty.

The density is shown in grams/cc at 25 C (77 F). The accuracy for any given composition is within 1/2 of one percent, below 50% b.w. CH_3CN, and within one percent above 50% CH_3CN.

3.7.2 Kinematic Viscosity

The kinematic viscosity of blends of UDMH, DETA, and CH_3CN has been studied by RMD(1), FMC Corp.(2), and Rocketdyne(3). These data, along with established values for neat UDMH and neat DETA have been combined and smoothed to form the plot shown in Figure 3.7-2.

Due to the small number of individual compositions studied, the position of the constant viscosity contours is only approximate. The values were taken at -54 C (-65 F) from smoothed viscosity versus temperature data. The accuracy and confidence level are reasonably good near the propellants UDMH, MAF-1, 3, 4, 5, and DETA. Elsewhere, the curves should be considered highly provisional.

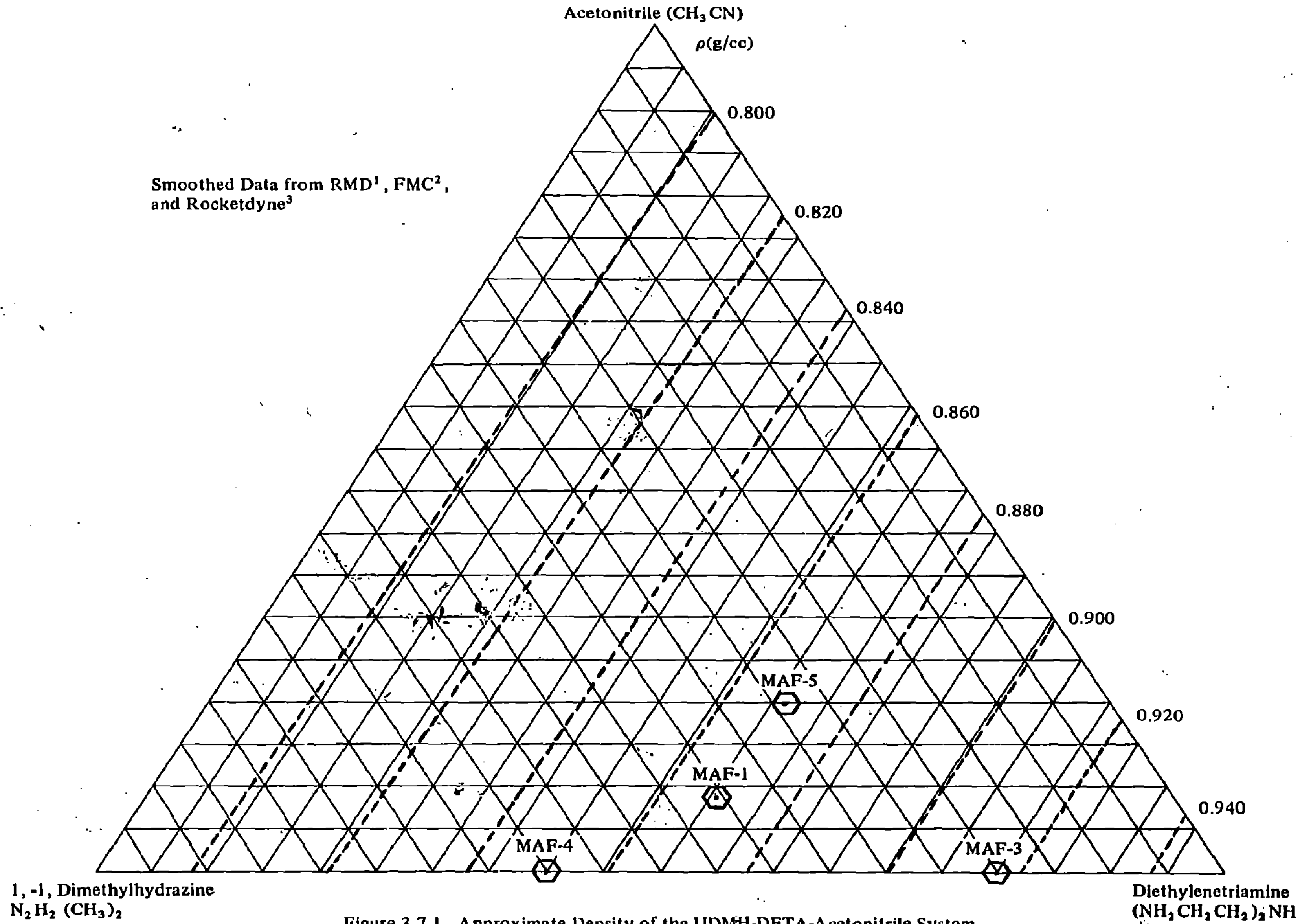


Figure 3.7-1. Approximate Density of the UDMH-DETA-Acetonitrile System (g/cc at 25°C (77°F))

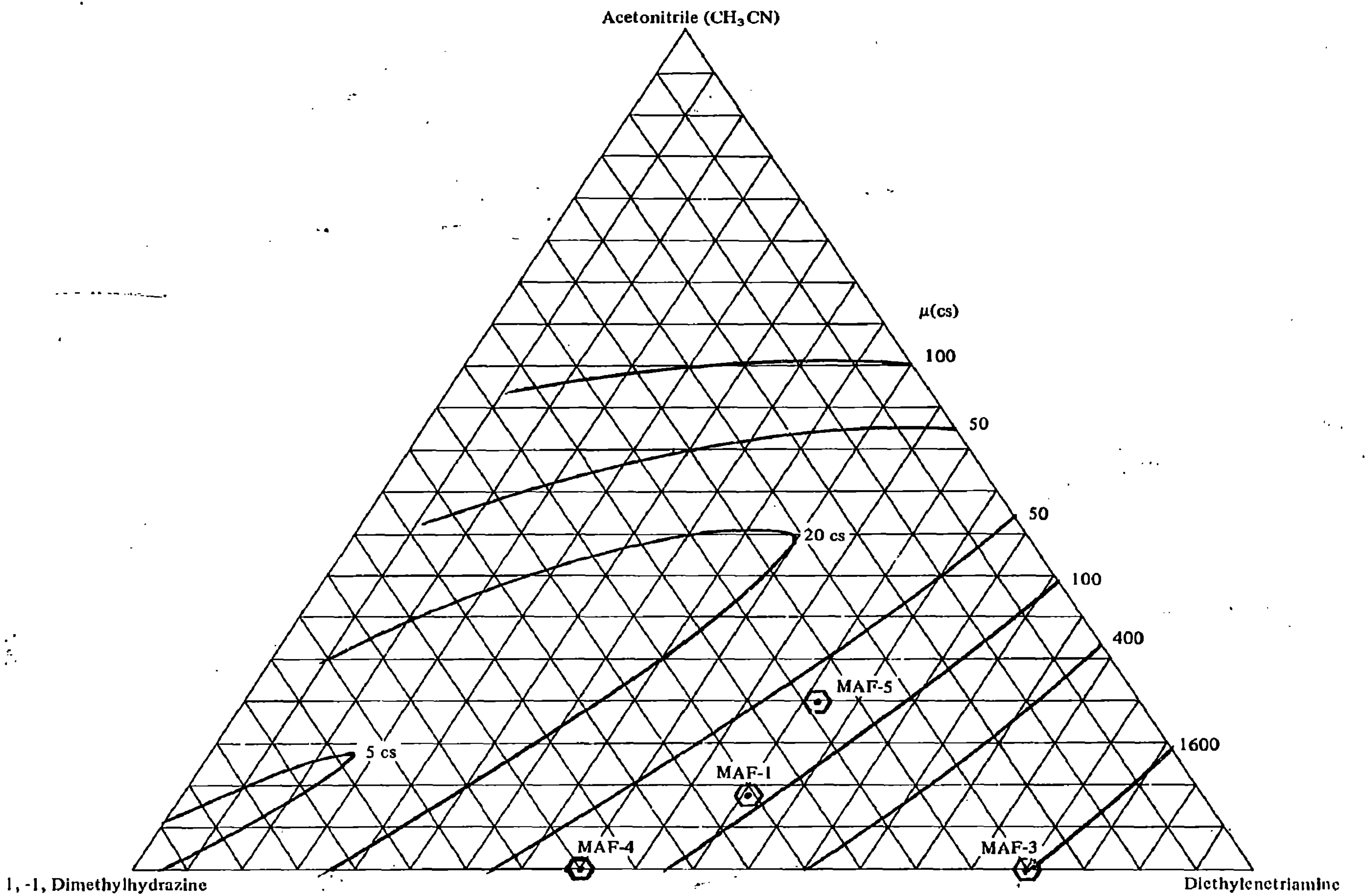


Figure 3.7-2. Approximate Viscosity of the UDMH-DETA-Acetonitrile System (Centistokes, at -65°F) Smoothed Data from RMD[1], FMC[2], and Rocketdyne[3]

3.8.1 DENSITY

3.8.2 MELTING POINTS

3.8 THE N_2H_4-UDMH-$N_2H_5NO_3$ SYSTEM

3.8.1 Density

The only data for the density of a three component blend reported was for MHF-2. The plot in Figure 3.8-1 is based mainly on this point and generally follows the departure from theoretically predicted density which is suggested by the well-established edges.

This data should be used only for the most approximate engineering estimates in light of the lack of measured values.

3.8.2 Melting Points

The melting points of five ternary blends were reported by RMD(6). These data were smoothed along the line joining these blends and hydrazine and used as a basis for forming the plot in Figure 3.8-2, along with the established data for the N_2H_4-$N_2H_5NO_3$ and the N_2H_4-UDMH binary systems.

These data are at best highly provisional, and should be used only for engineering approximations.

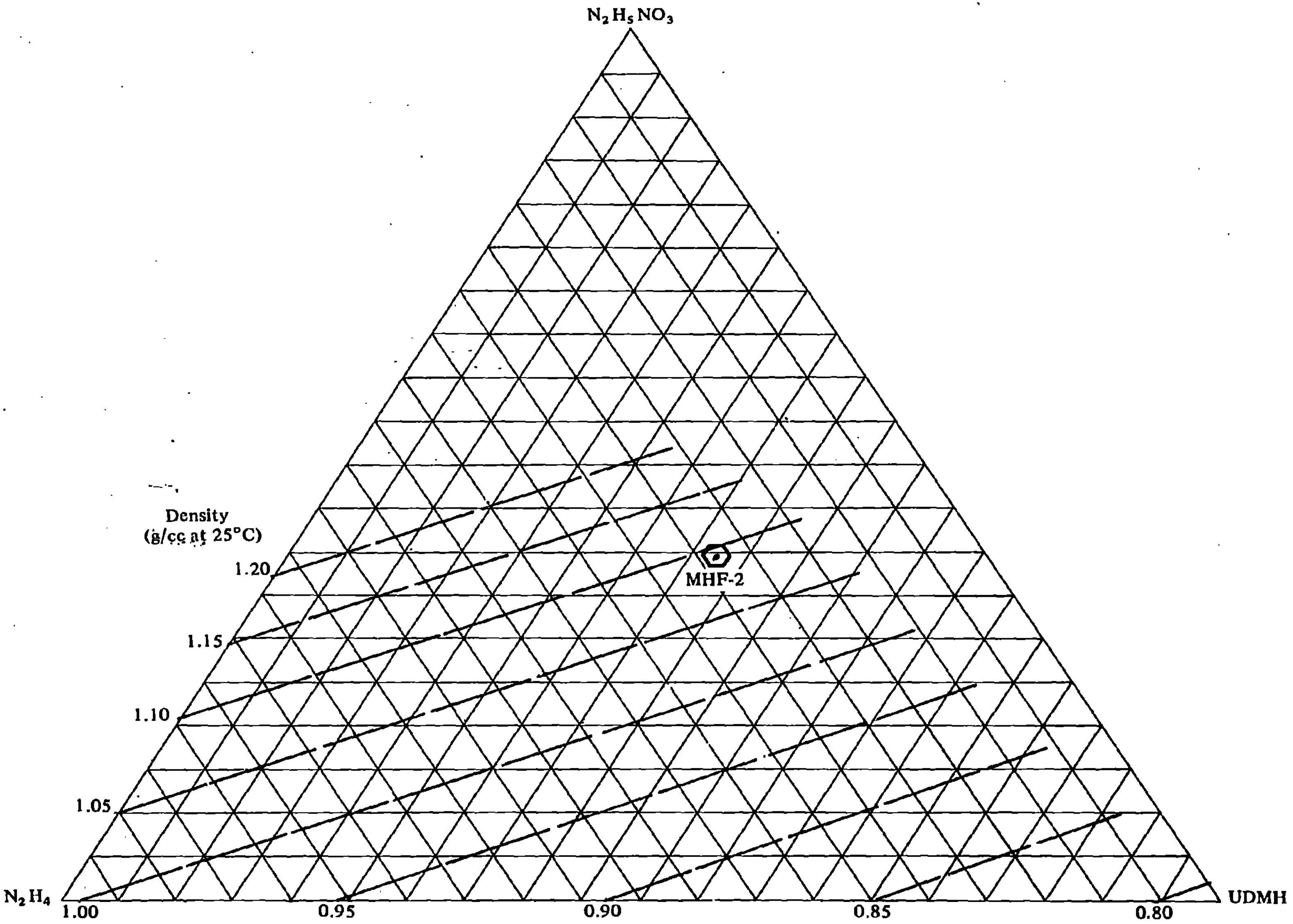


Figure 3.8-1. Density in the Hydrazine-1, 1-Dimethylhydrazine-Hydrazinium Nitrate System, (g/cc at 25°C (77°F) MHF-2 Data: RMD[6]

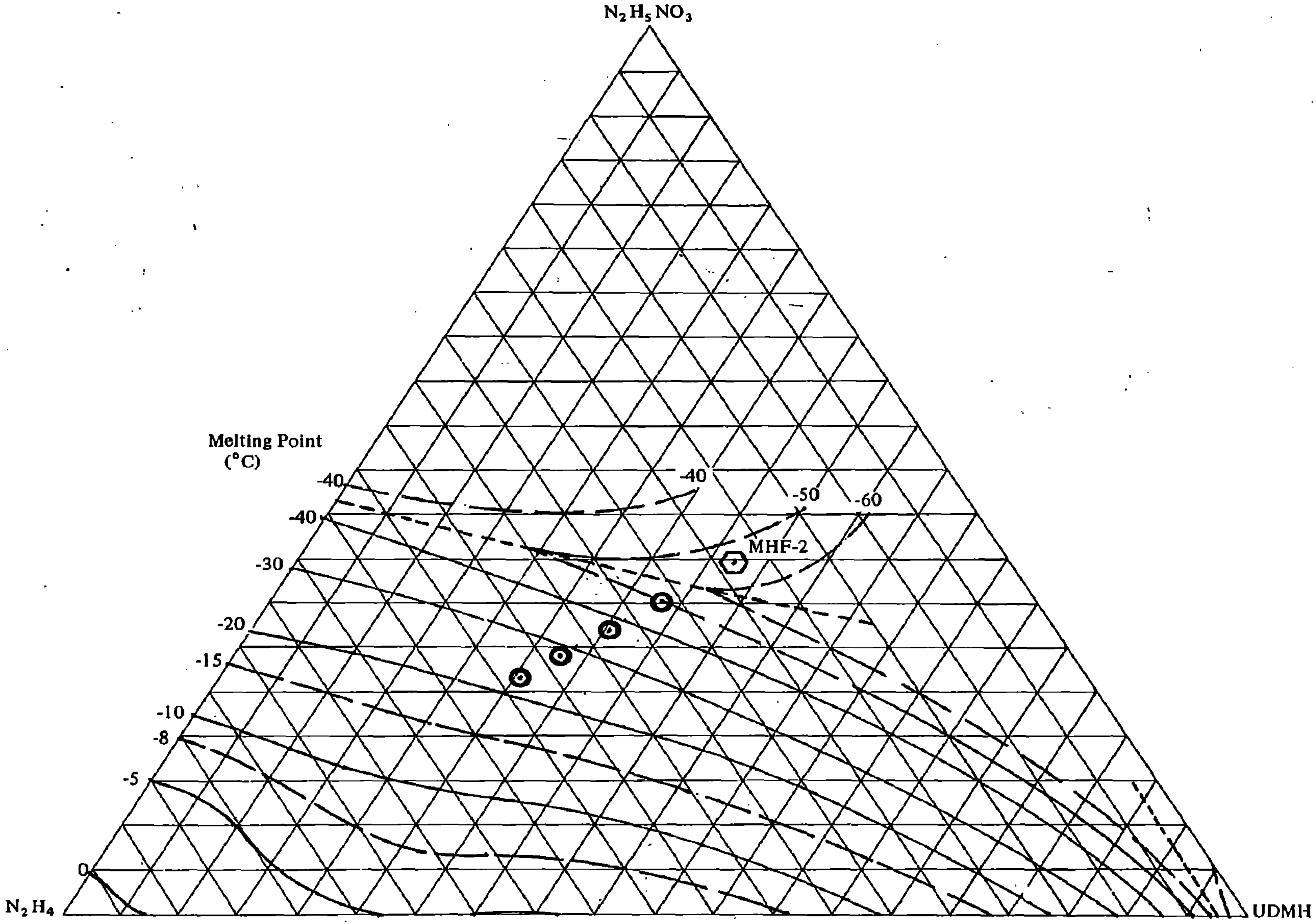


Figure 3.8-2. Melting Point in the Hydrazine-1, 1-Dimethylhydrazine-Hydrazinium Nitrate System, (Degree C) (Indicated Points, Data from RMD[6])

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3.9 REFERENCES

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4.0 HANDLING - STORAGE AND COMPATIBILITY

4.1 INTRODUCTION

4.1.1 GENERAL

4.1.2 ORGANIZATION

4.1.3 SCOPE

4.1.4 USAGE LIMITATIONS

4.1 INTRODUCTION

4.1.1 General

This section presents a summary of data on the long term storage capability and materials compatibility of the various fuels and blends based on the hydrazines and amines, and the recommended procedures for handling and storing such fuels.

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 (4.3 and 4.4) will provide guidelines for the selection of materials to be used in specific applications.

Additional information concerning the decomposition of the propellants will be found in Section 6.0, however, the gross effect of propellant decomposition - pressure buildup - is described in this section (subsection 4.3).

The generally recommended equipment, procedures and precautions for transferring and storing the propellant (handling) are presented in Section 4.2.

4.1.2 Organization

This section is divided into three major subsections as described above. These appear in the table of contents on the divider 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.

4.1.3 Scope

Subsection 4.2 deals with accepted methods of transferring propellants between storage, shipping, and usage functions as practiced by major manufacturers and users, and when in concurrence with other standard handling manuals concerned with these propellants. Propellants requiring identical procedures and equipment are discussed together as a group.

Some of the propellants which have found little or no use have had very little or no handling information documented. These are related, wherever possible, to similar compositions, with an appropriate warning about the possible consequences of the composition differences.

Subsection 4.3 deals with the gross effects of propellant decomposition in sealed containers, i.e., that of pressure build-up. Information on the causes of and nature of the decomposition itself is presented in more detail in Section 6.0.

Subsection 4.3 is concerned only with the effect of various materials and storage temperatures on the pressure build-up at various ullages. This subsection is divided into a brief discussion for each group of propellants, followed by a graphical and tabular summary of the quantitative data which have been reported. Propellants which show similar behavior are discussed together as groups.

Where no clear-cut trends in behavior were found to occur with composition, no attempt is made to generalize results or recommendations to propellants for which no data are available.

Subsection 4.4, compatibility, deals mainly with the effect of the propellants and their vapors on materials in contact with them. The compatibility ratings, however, do include some provision for decomposition of the propellant, to the extent that materials causing excessive decomposition are placed in the lowest, or worst, rating category.

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 hydrazine and amine-type fuels.

The differences between various other rating schemes is also briefly discussed. All of the fuels considered, except those containing hydrazinium nitrate, 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 frequency of usage, availability of data, and commonality of ingredients. This results in N_2H_4, UDMH, and the 50-50 blend being considered as the first group with the largest quantity of available data.

4.1.4 Usage Limitations

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

4.2 HANDLING AND TRANSFER

4.2.1 GENERAL

4.2.1.1 Special Exceptions

4.2 HANDLING AND TRANSFER

4.2.1 General

(U) All of the hydrazine-based and mixed amine fuels, with the exception of DETA, ammonia and MAF-2, contain hydrazine or hydrazine derivatives. Therefore, handling, transfer and storage procedures which apply to one fuel, are found generally to apply equally well to all of the propellants. Therefore, all of the MHF blends, MAF-1, 3, 4 and 5, the BAF blends, 50/50, MGGP-1, hydrazine, MMH, and UDMH are generally covered by the same transfer and handling procedures.

(U) Ammonia is covered by separate procedures which reflect its lower fire and toxicity hazards and its higher vapor pressure. (See Section 5.0 on Safety). Although little information is available on DETA, it is handled more like the hydrazines, than like ammonia, and, therefore, procedures applicable to the hydrazine derivatives should be equally applicable to DETA.

(U) No handling procedures were ever established for MAF-2 or its ingredients, and the effects of environmental factors on MAF-2 are unknown. If MAF-2 or its ingredients are ever handled, procedures used for the hydrazines should be used provisionally, with additional caution, and the quantity of propellant involved should be limited until more is known about it.

(U) Since most of the fuels are good solvents, certain materials may be dissolved, blistered, decomposed or otherwise damaged if contacted by the fuels. Precautions should be maintained against spillage, and the compatibility with various materials must be considered.

(U) The decomposition of the fuels caused by contamination, improper materials, or heat can contribute to pressure buildups resulting in container rupture, spillage, fire and/or explosion. The use of proper materials and the maintenance of cleanliness is mandatory. (See Sections 4.3, 4.4, 5.0 and 6.0).

4.2.1.1 Special Exceptions

The following Special Exceptions are to be noted:

(C) MHF-1, 2, 4, 5, 5B and MGGP-1 contain hydrazinium nitrate and represent somewhat more of a hazard (see Section 5) especially if the fuel is burning. Extra attention should be paid to variables such as contamination, improper materials, and hot environments, to avoid potential fires, explosions or pressure buildups. These fuels should not be disposed of by burning, unless it is done in protected and isolated explosion-proof high-temperature-resistant equipment. Dilution with water during burning will reduce the temperature and reduce the explosive tendencies.

(U) Some of these fuels will freeze upon exposure to normally-encountered cold climates. The most notable case is hydrazine with a melting point of 34 F. Experience with freezing hydrazine has shown that the fuel contracts upon freezing, resulting in no harm to the container. This, and similar fuels, however, can be difficult to melt since the shrunken solid does not contact the container walls, except at the bottom. Other candidates for freezing include the 50 N_2H_4/50 UDMH blend (melting point 20 F), and nearly any other blend which is composed of more than three-fourths hydrazine.

4.2.2 Handling And Transfer Of Ammonia

4.2.2.1 General

Anhydrous ammonia differs from the hydrazine based fuels in several major respects; it is mildly cryogenic, having a high vapor pressure, and making it desirable to store it in refrigerated and/or insulated equipment. It is also usually stored as a liquified gas under pressure to raise its boiling point. Other noteworthy features of ammonia are that it is less toxic, its vapor has a narrower flammable range, and it is not subject to explosive decomposition.
to explosive decomposition.

Nevertheless, ammonia should be handled only by properly trained personnel, and stored in materials which are known to be compatible with it. The fact that ammonia is stored under pressure as a liquified gas must be kept in mind at all times. Since ammonia is a refrigerant, it can undergo rapid cooling when expanding through orifices, resulting in freezing of moisture.

The most complete and up to date sources of detailed handling, storage, and safety procedures include the American Standards Association, CGA, Pamphlet G-21 (1); the D.O.D. Handbook entitled "The Handling and Storage of Liquid Propellants", (2) and the product bulletins of ammonia manufacturers.

4.2.2.2 Materials for Ammonia Transfer Equipment

Pipes, fittings and valves should be clean and composed of materials compatible with ammonia. Nickel and stainless steel alloys are widely recommended by all sources for all practical temperatures. Mild steel is recommended for ambient temperatures only, and in piping, black iron (extra heavy, schedule 80) is recommended. Aluminum alloys can be used for low temperature transfer operations.

Copper, brass, bronze, zinc and their alloys must be absolutely prohibited from use with ammonia as these will react rapidly and spontaneously, especially if the ammonia contains small amounts of water. Galvanized pipe should never be used.

All valves as well as pipe should be rated for at least 300 psig service. All regions of the piping system where ammonia may be trapped should contain relief valves set to no more than 300 psig. (Note: the A.S.A. recommends 250 psig).

Pipe joints may be of welded construction (preferred), or freshly made glycerine-litharge joint cement may be used on threaded joints. Plastic-lead thread compounds may be used on temporary set-ups. Pipe flanges should be generally of a type which contain at least four bolts.

Marking of piping systems shall be in accordance with MIL-STD-101A. The primary warning color is brown, and the secondary color is yellow. Ammonia systems shall also contain adequate pressure gauges and liquid level gauges.

Further details concerning equipment for transfer and handling of ammonia can be found in the ASA pamphlet G:2.1 on anhydrous ammonia, the DOD Manual on the handling and storage of liquid propellants, or in the manufacturers' literature.

Detailed information on the toxic and fire hazards of ammonia, as well as safety precautions, are presented in Section 5.0 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 ammonia.

4.2.2.3 Ammonia Transfer Procedures

Since ammonia is usually cold, care should be taken that the temperature is suitable for the materials and design of transfer systems and containers. Mild steel, for example, should not be used at temperatures significantly below normal ambient, due to the occurrence of cold embrittlement.

In filling cylinders or other containers, care must be taken to prevent overfilling. Since liquid ammonia expands considerably upon warming, a sufficient vapor space must always exist above the liquid to allow for warming to the maximum temperatures anticipated.

A table of maximum allowable liquid volume loadings is presented below (Table 4.2.1) as a function of temperature for three values of filling density. The filling density is a rating for the container expressed as the weight of gas (and liquid) in the tank divided by the weight of water which the tank will hold. The volume loading is the percent of the tank volume occupied by the liquid phase.

Adequate liquid level indicators must be installed in all containers to enable proper control of the liquid volume loading.

TABLE 4.2.1 MAXIMUM SAFE LIQUID AMMONIA VOLUME LOADINGS AT VARIOUS TEMPERATURES AND FILLING DENSITIES. REFERENCE (2)

TEMPERATURE OF LIQUID IN TANK °F	LOADING DENSITY (%) OF TANK VOLUME		
	56% FILLING DENSITY	57% FILLING DENSITY	58% FILLING DENSITY
30	87.3	88.9	90.4
40	88.3	89.9	91.5
50	89.5	89.9	92.7
60	90.6	92.2	93.9
70	91.8	93.4	95.1
80	93.1	94.7	96.4
90	94.4	96.1	97.8
100	95.8	97.6	99.3

interior dip tube inlet, which curves to the cylinder wall opposite the valve outlet, to be exposed to vapor. After some ammonia has been released from a cylinder, it could be placed upright, however, the horizontal position facilitates heat transfer to the liquid, which is spread over a large area of the cylinder wall. Heat transfer is necessary to vaporize the ammonia as vapor is drawn off.

Never place an ammonia cylinder in a heating bath, or otherwise attempt to heat it artificially in order to release more vapor. This is a very hazardous operation and could rupture the cylinder. Also, care should be exercised in manifolding two cylinders together, since liquid could flow from the warmer to a colder cylinder, overfilling the latter. Manifolded cylinders should always be weighed before closing them off, to guard against overfilling.

A cylinder is considered empty when the pressure gauge reads 25 psig or less, and there is no condensation on the cylinder wall.

To withdraw liquid ammonia from a cylinder, the cylinder should be placed horizontally with the butt end 2 inches above the valve end, and with the valve outlet pointing upward. This places the eductor tube in the liquid. The ammonia is pushed out by its own vapor pressure. It can then be allowed to flow into a container of lower pressure and temperature, or it can be pumped into another container. Pumps or compressors must be designed for ammonia service and have a working pressure of at least 300 psig. (The ASA (2) requires 250 psig.)

Ammonia is usually transferred from tank cars or trucks by the compressor method. A compressor is connected with its suction side to the storage tank vapor space and pressure differential thus created between the tank car and the storage tank pushes the liquid ammonia into the storage tank through a line connecting the liquid valves of both truck and car. When all liquid has been transferred, some of the vapor may also be removed from the tank car or truck by closing off the liquid line, reversing the compressor (by way of appropriate valving), and drawing vapor through the compressor to the storage tank.

Extreme caution must be taken not to reduce the pressure in the tank car below 15 psia (ambient) to avoid air entering the system. During unloading, a pressure differential of about 30 psig should be maintained. This differential will drop by 5 or 10 psi when the tank car is empty of liquid and approximately 500 lbs of ammonia vapor remains.

After the desired amount of vapor has been drawn off, all block valves are closed and the pressure in the transfer lines is relieved by a bleed valve. The flexible hoses are then removed, the tank car valves closed, and the cover dome secured.

If unloading into low pressure systems, it may not be necessary to use a compressor. In this case, vapor pressure will force the liquid out of the tank car. The pressure on the tank car should not exceed 175 psig.

The procedures for transferring ammonia from main storage to ready storage or process is essentially the same as described above. Tanks with bottom outlets can also be equipped with liquid pumps to expedite transfer, or gravity feed may be used.

In all cases, extreme caution should be used not to overfill the container being filled. All equipment should

4.2.2.4 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 ammonia gas mask, and proper protective clothing and other measures is discussed in Section 5.2.3.1 of this Handbook.

In case of an accident, large amounts of water is the most effective means of counteracting ammonia exposure. First Aid is covered in more detail in Section 5.2.4.1.

4.2.3 Handling and Transfer to Hydrazine Substituted Hydrazines and Blends

- 4.2.3.1 General
- 4.2.3.2 Materials in Transfer Equipment
- 4.2.3.3 Transfer Procedures
- 4.2.3.4 Personnel Protection

4.2.3 Handling And Transfer Of Hydrazine, Substituted Hydrazines And Blends

4.2.3.1 General

(U) Hydrazine, substituted hydrazines, DETA, and blends of these materials are highly toxic and flammable liquids. In the vapor phase, some of these fuels may be subject to explosive decomposition. Unlike ammonia, these fuels have a relatively low vapor pressure, and consequently they are usually shipped and otherwise handled in nonpressurized bottles, drums, or tank cars. (See the appropriate subsection on shipping for the individual propellants in Section 2.0.)

(U) The handling and transfer of these propellants should be conducted by properly trained personnel. The propellants should be stored in materials which are known to be compatible. Since the most compatible materials differ for different propellants, the storability and compatibility of various materials should be determined. Sections 4.3 and 4.4 provide guidelines for the storability and compatibility with materials.

(C) The product bulletins of manufacturers of hydrazine, MMH, and UDMH such as Olin Mathieson and the FMC Corp. provide extensive information in handling, storage and safety procedures. In addition, the DOD Handbook entitled "The Handling and Storage of Liquid Propellants". (2) dated January 1963, in a valuable source of information for hydrazine, MMH, and UDMH. In general, the blended fuels require handling and transfer procedures identical to those for the neat propellants of which they are composed. MHF-5 and MHF-5B, which are representative of the hydrazinium nitrate containing blends, require additional caution due to the presence of nitrate ions which promote chemical reactions with materials of construction, and rapid, hot, flare-like burning, if set on fire. The residues left by MHF-5 and similar blends after evaporating contain hydrazinium nitrate which is shock sensitive in concentration higher than about 25 - 35%. (See Section 3.4.4.) Reference 3 presents a comprehensive treatment of handling and transfer procedures for MHF-5 and 5B which are also applicable to MHF-1, 2 and 4.

4.2.3.2 Materials in Transfer Equipment

(U) Equipment used in transfer and storage of the propellants should be constructed of materials which are compatible with the propellant under all conditions of direct contact. In general, the materials deemed by most sources to be suitable for use with hydrazine, MMH, UDMH, and related blends are the aluminum alloys, stainless steels, Inconel, and titanium-6Al-4V. Metallic materials not recommended for use with these propellants include K-monel, brass, cadmium, copper, hastelloy, silver, and zinc. Non-metals which are provisionally suitable for use with these fuels include teflon, mylar, polyethylene, graphite and asbestos. No sealant or lubricant has been found which is completely suitable for all of these propellants, however "Apiezon L" and "Reddy Lube 200" have been found provisionally suitable. The use of polyvinyl chloride, polyvinyl alcohol, neoprene, and kel-F 800 should be avoided.

(U) For any permanent facilities or long term exposure, proposed materials of construction should be tested under the expected actual conditions of use, or detailed data should be consulted, if available for those conditions. The detailed behavior of materials will differ for the various propellants and under varying conditions. (See Sections 4.3 and 4.4 for additional information.) The hydrazinium-nitrate containing propellants are generally more reactive and corrosive in the presence of materials. Detailed information on equipment design, welding, cleaning, passivation, and inspection will be found in References 3 (MMH, MHF-3), 4 (MHF-5, 5B) 5, (UDMH, 50/50) and 6 (Hydrazine), as well as in the propellant manufacturer's brochures.

4.2.3.3 Transfer Procedures

(U) Procedures for the handling and transfer of hydrazine, MMH, UDMH, and blends, including MHF-5, have been established and documented by the CPIA(2), Rocketdyne (3), (4), (6), Bell Aerosystems (5), and the propellant manufacturers. The procedures differ very little from one propellant to another, and since their toxicity, vapor pressure, and fire hazards are similar, this commonality of procedures is justifiable for all propellants of this family with only minor exceptions for MHF-1, 2, 4, 5, 5B, and MGGP-1.

(U) The exceptions apply to the higher corrosivity, greater reactivity, and the explosion hazards associated with propellants containing hydrazinium nitrate in solution. Generally, transfer should be conducted in materials which have been proven safe for use with these propellants, and by personnel who have been completely familiarized with the handling of hydrazinium nitrate containing blends. Greater care should be taken with these blends to avoid exposure to heat, especially in the form of local hot spots in the handling equipment. Liquid MHF-1 has been known to detonate violently when heated to approximately 500 F in confined spaces such as in regenerative cooling passages.

(U) In transferring propellants from 55-gallon drums or other shipping containers, the most common method of unloading is the pressure-unloading method in which dry ditrogen gas pressure is applied to the container to be emptied. Unloading by way of a transfer pump in the discharge line has also been used with success.

In transferring propellants, all personnel not concerned with the operation shall evacuate the area, and sufficient warnings shall be displayed to prevent personnel from inadvertently entering the area.

In unloading drums, (ICC 5C and 5G) and eductor pipe is fitted to the drum as shown in figures 4.1 and 4.2. A dry nitrogen supply is used to pressurize the drum to no more than 5 psig. Even if a transfer pump is used, the volume left by the receding propellant in the drum must be filled with dry nitrogen. Under no circumstances should air be allowed to enter a container containing hydrazine type propellants as an explosive vapor mixture could result.

Personnel conducting the transfer operation should be properly clothed to facilitate spill- and fire-control, should a spill occur. Under no circumstances should open flames or other sources of heat be permitted in the area.

In unloading propellant from tank cars or tank trucks, the transfer lines and associated equipment are arranged as shown in figure 4.3. Both the tank car and the storage (receiving) tank should be equipped with sufficient vent lines, safety valves and control devices to prevent overpressurization, overfilling, or air from entering the system. Details of a typical tank car dome and eductor assembly are shown in figure 4.4. If a transfer pump is used, an additional vent line and associated valving must be added just downstream (on the output side) of the pump. The pressure limits for tank cars and trucks vary with container design and are usually specified by ICC or state and local regulations. If the rated pressure is unknown, transfer should be conducted by a pump, and in any case, nitrogen pressure should never exceed 5 psig.

The procedures for transfer of propellants from main storage to ready storage or vehicle (missile) tankage is essentially the same as described above, except that in many cases, special procedures have been established for loading vehicle (missile) tankage. In all cases, caution must be exercized not to overfill or overpressurize containers and not to allow air or other contaminants from coming into contact with the propellants. All equipment should be cleaned and electrically grounded.

4.2.3.4 Personnel Protection

The personnel involved in the handling and transfer of hydrazine, substituted hydrazines, and their blends should wear adequate protective clothing. The facilities should include safety showers and eye wash fountains, located conveniently near the transfer operation. Additional sources of water should be available for fighting fires or diluting spills.

Section 5.2.3 of this handbook describes the head, face, body, hand, and foot protection to be worn by personnel.

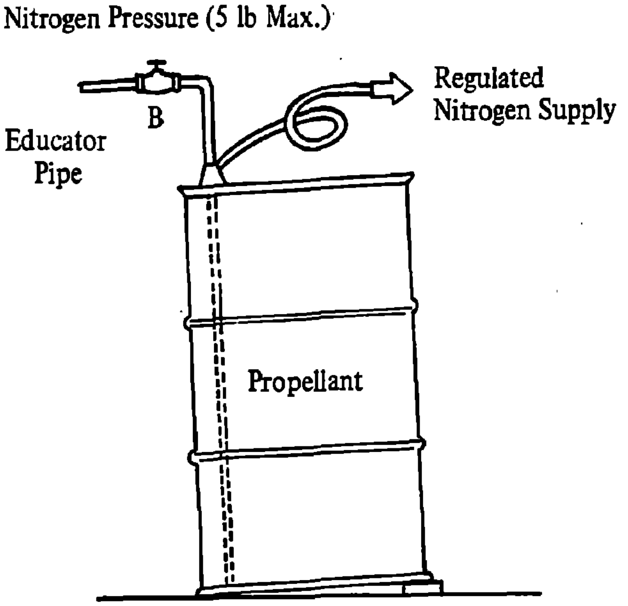

Figure 4.1. Method for Unloading Propellant from Drums

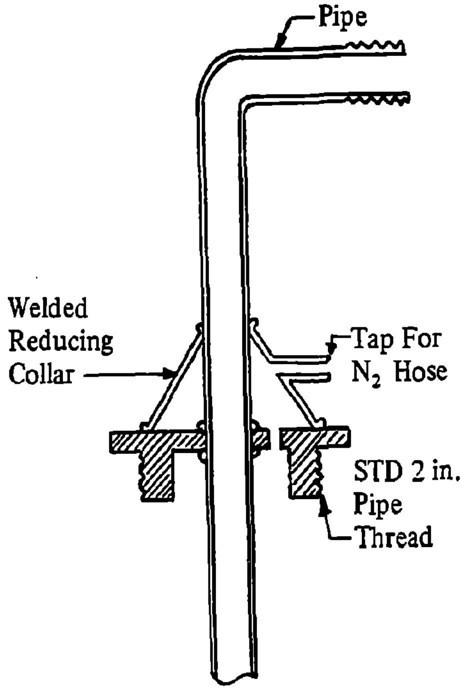

Figure 4.2. Details of Stainless Steel Eductor Pipe

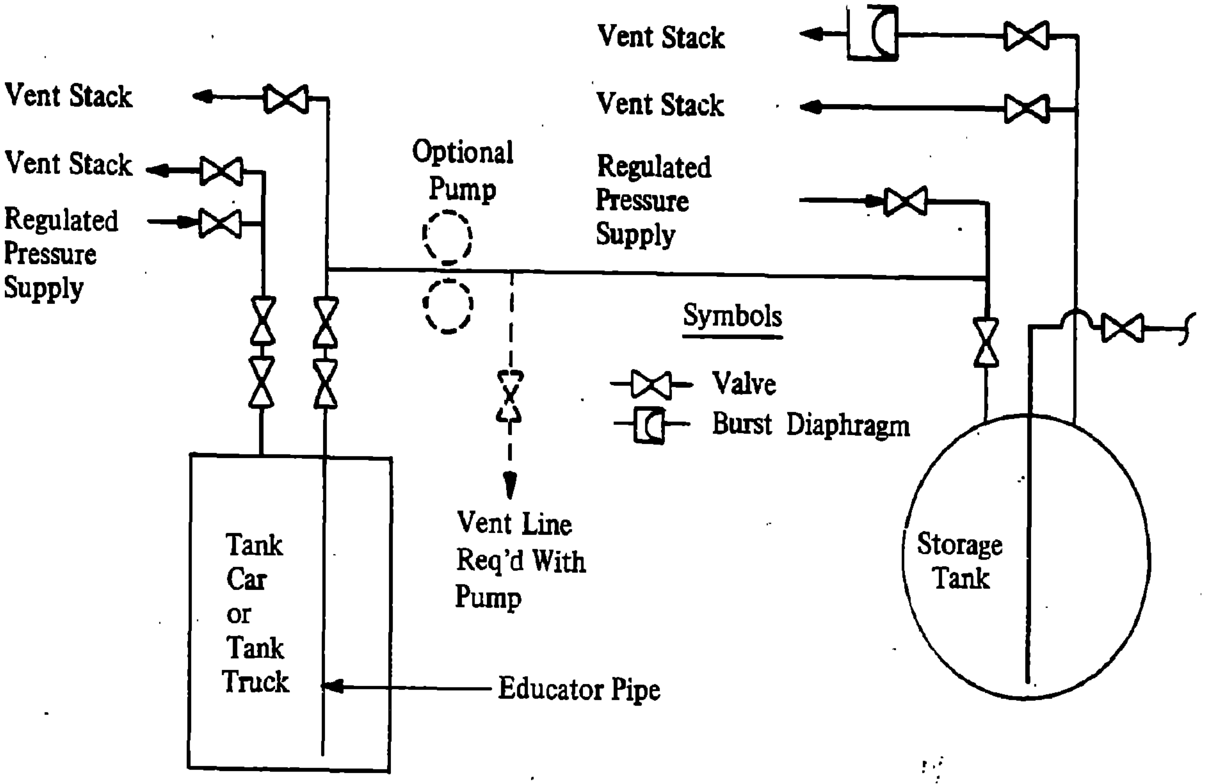

Figure 4.3. Transfer from a Tank Car or Tank Truck by the Pressure Unloading Method

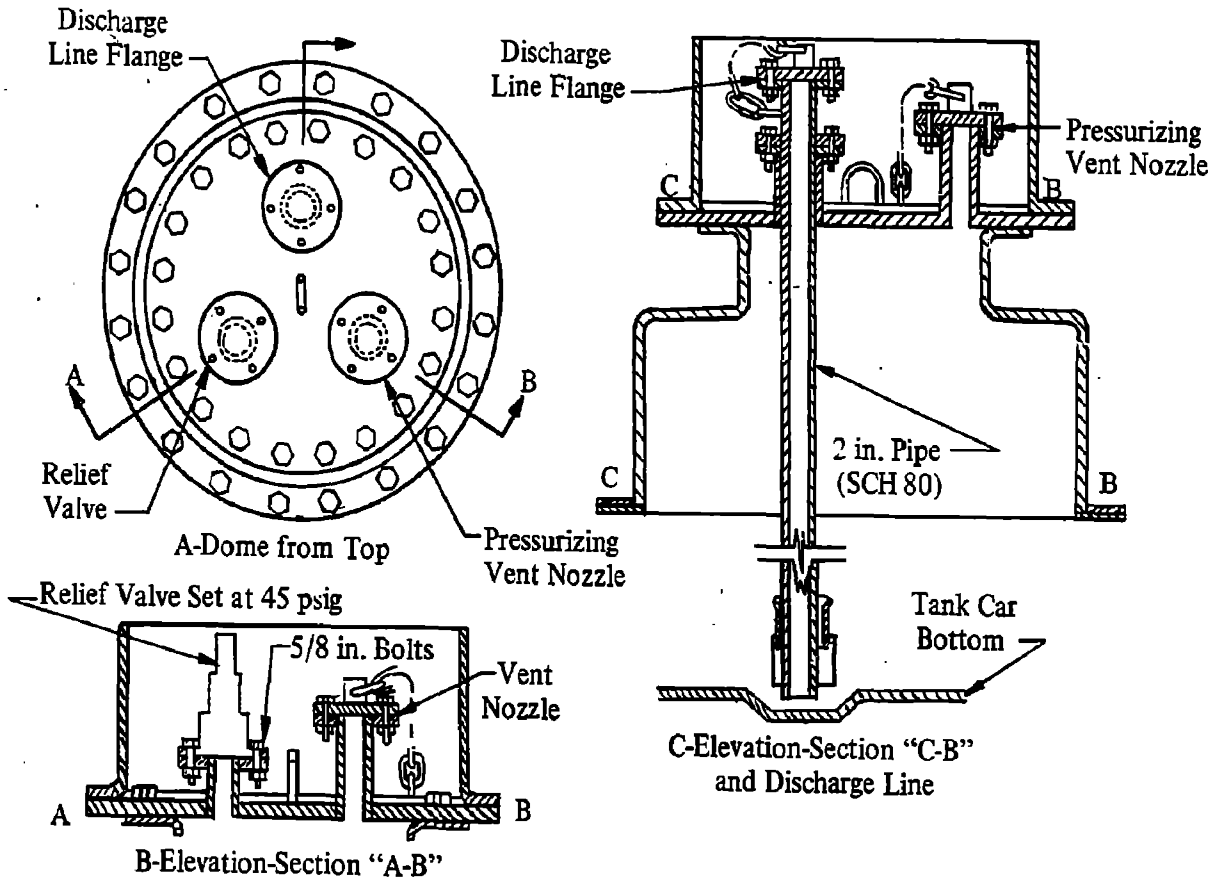

Figure 4.4. Tank Car Dome and Eductor Pipe Details

4.2.4 Handling and Transfer of Mixed Amine (MAF) Fuels and Diethylenetriamine (DETA)

4.2.4.1 General

The Mixed Amine Fuels, except MAF-2, contain mainly UDMH and DETA, and some acetonitrile (CH_3CN). The technical literature from the manufacturers of DETA (Carbide and Carbon Chemicals Co., and Pennsalt Mfg. Co.) indicate that there are no special handling problems associated with DETA as compared with UDMH. Otherwise, there is very little information on the handling and transfer of the MAF blends. RMD(7), FMC Corp.(11), and Riehl(8),(9) studied the handling characteristics of MAF-1 and MAF-4 (U-DETA), respectively. The storage and handling of DETA and other amines is briefly discussed in Kirk-Othmer (10). The information presented below is taken from these sources. It will be seen that, in general, the handling and transfer procedures for UDMH and the other hydrazine fuels are applicable to the MAF blends. Although there is no information in the literature for MAF-2, the procedure outlined for MAF-1 should apply.

4.2.4.2 Materials in DETA and MAF Transfer Equipment

Materials used in transfer equipment for DETA or mixed amine fuels should be compatible with the propellant under all conditions of direct contact with both the liquid and vapor. As with the hydrazines; stainless steel, aluminum alloys, and inconel seem to be the most widely accepted and recommended materials(7,10). There is some indication that mild steel produces discoloration of the amine propellants,(10) however, steel or black iron, free of rust, presents no corrosion problem. There is no indication of whether titanium alloys are compatible with amines. Copper, brass, bronze and zinc and similar alloys are not recommended for use with mixed amine fuels.

Nonmetals reportedly compatible with MAF's include teflon, Kel-F(7). Rubber, neoprene, and silicone products, on the other hand, are attacked by amines, and should be avoided. The use of Kel-F in fuels containing UDMH should also be avoided. Additional materials, not covered in the literature on amines may be compatible. Tests of the specific materials being considered, should be conducted under the conditions of usage, before being installed.

4.2.4.3 Transfer Procedures

The transfer procedures for amines are essentially the same as those for the hydrazines and the MAF and BAF blends. Since most of the amines are somewhat less corrosive, flammable, volatile, and toxic than UDMH, UDMH becomes the dominating factor in blends containing it.

Transfer procedures are outlined in greater detail in subsection 4.2.3.3 of this handbook.

4.2.4.4 Personnel Protection

The equipment and facilities for personnel protection against the amines are essentially identical to those recommended for the hydrazines. Reference should be made to Sections 4.2.3.4 and 5.2 of this handbook.

4.2.4.5 Storage of MAF-Fuels Exposed to Air

Figures 4.5 and 4.6 illustrate the effect of accelerated storage of MAF-4 (40% DETA, 60%) in the air. The accelerated storage effect was created by bubbling air and nitrogen through the liquid thereby exposing a large surface of the liquid to the air or nitrogen. Nitrogen was used as a control for comparison purposes. The effects of the accelerated storage on physical properties as a function of composition was noted. The data indicated that this drastically accelerated storage in air had only a small effect on the properties at a given composition. The change in composition is a result of the evaporation of the more volatile UDMH. This data can be applied provisionally to other compositions of UDMH and DETA in addition to MAF-4. MAF-3 contains 80% DETA and 20% UDMH.

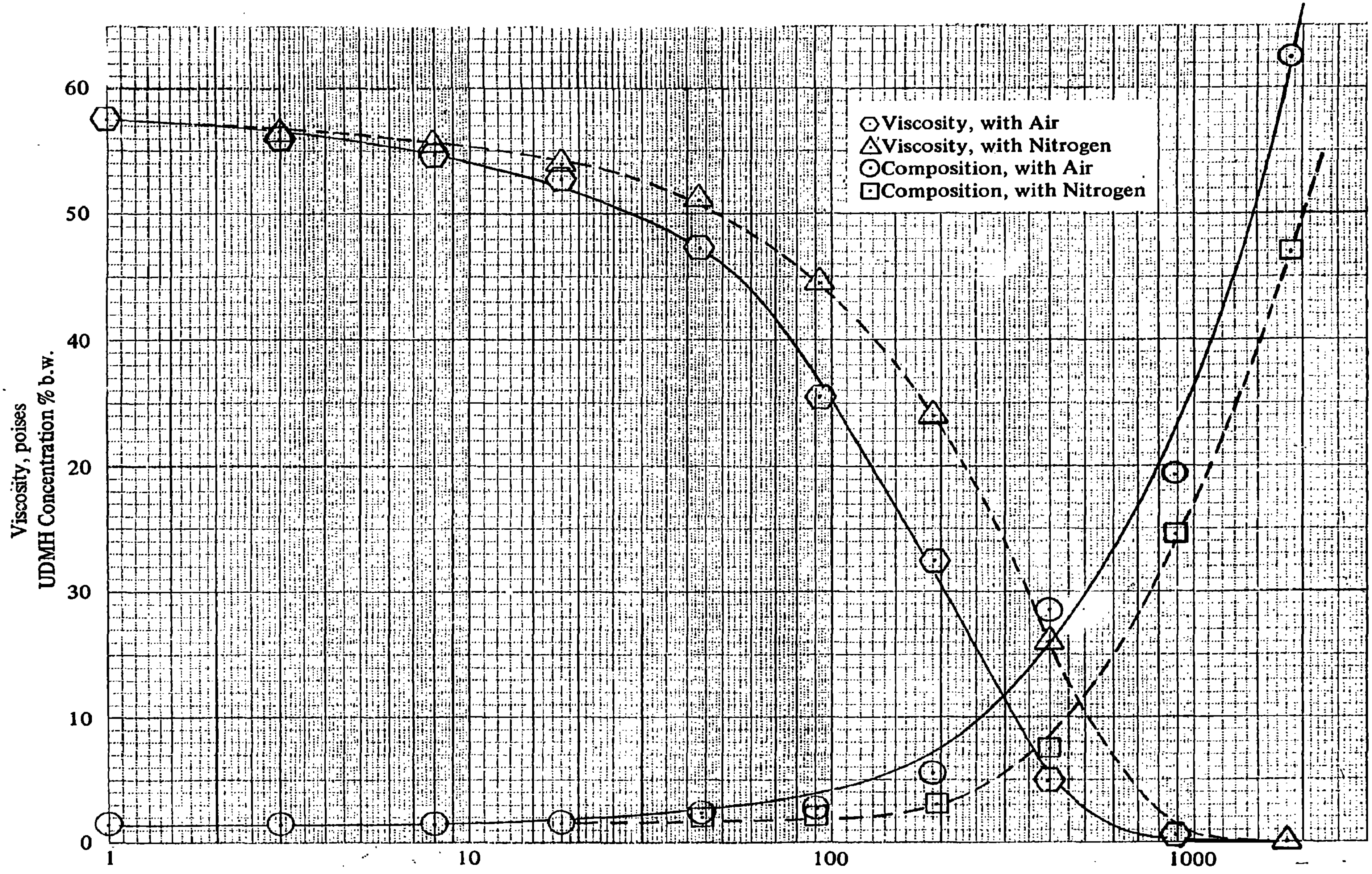

Figure 4.5. Effect of Bubbling Air and Nitrogen Through MAF-4: Composition and Viscosity versus Volume of Gas. Data from FMC (11)

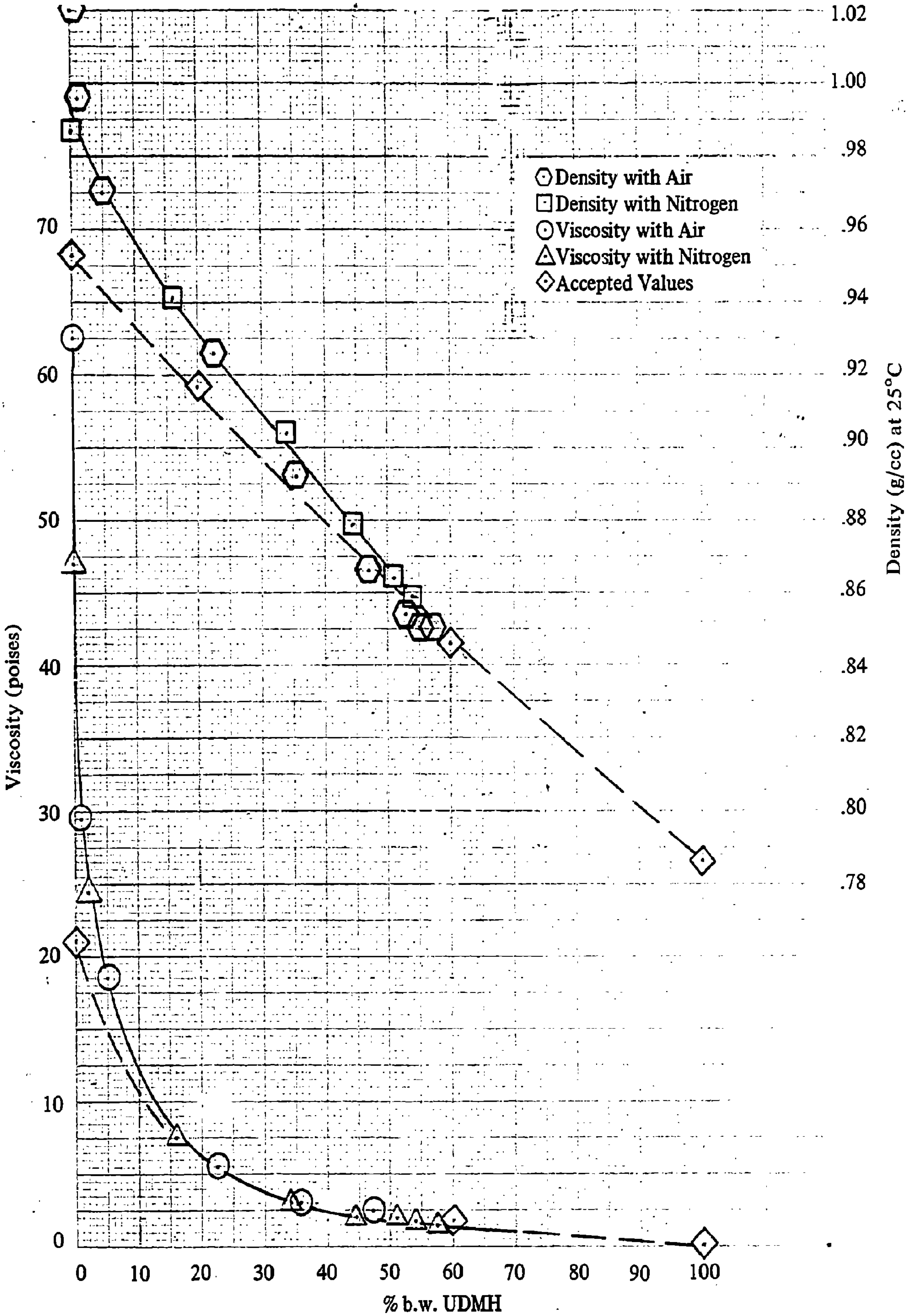

Figure 4.6. Effect of Bubbling Gas through MAF-4 on Density and Viscosity versus Composition. Showing Comparison with Accepted Values. Ref. (11)

4.2.5 Disposal and Pollution Control of All Hydrazine Based Fuels, DETA and Ammonia

4.2.5 Disposal and Pollution Control of All Hydrazine Based Fuels, DETA and Ammonia

(U) Disposal of these propellants shall be conducted in a manner such that the following requirements can be met.

1. Discarded fuels or byproducts should not be able to collect in areas where they can do harm later.
2. Fuels should be disposed of in a way which will prevent toxic vapors from reaching work - or inhabited areas.
3. Fuels 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.

(U) All of the fuels in question can be disposed of by burning completely, or by chemical neutralization.

(U) Small amounts of the fuels can be flushed away with a large excess of water. Exceptions are MAF-1 and MAF-5 which should be burned and/or neutralized due to their cyanide content. Large amounts should always be burned or neutralized.

(U) Burning of MAF-1 or MAF-5 can also release cyanides, due to the methyl cyanide content of the fuels. The combustion products should be passed through a scrubber, and the residuals further neutralized chemically.

(C) The products of combustion should be passed through a scrubber system in populated areas, or otherwise through a vent stack at least 50 feet higher than the highest nearby working area. Additional precautions should be taken when burning MHF-1, 2, 4, 5, 5B or MGGP-1 or any other mixtures containing nitrate or oxidizing salts, due to the explosion hazard. Such operations should be conducted in remote areas in explosion proof equipment. In addition, copious quantities of water should be available for cooling and/or dilution of such fires.

(U) Chemical neutralization of the fuels or the scrubber products is best accomplished by chlorination of the water solutions of the fuel. The chlorine serves to break down the toxic ingredients through oxidation. The alkalinity of the resulting water solution can be neutralized via hydrochloric acid (muriatic acid). Further cleaning of the water can be achieved by passing through activated charcoal or sand and gravel beds or by adding alum floc to precipitate out impurities. A second effective method of chemical neutralization is the use of hydrogen peroxide solutions (H_2O_2 + H_2O). The peroxide serves the same oxidation purpose as the chlorine. Again dilute HCl can be used to neutralize excess alkalinity. Further cleaning of the resulting water solutions is accomplished as above until the water meets local or state cleanliness standards.

> CAUTION - Do not mix concentrated hydrogen peroxide or HCl with concentrated fuel solution. Such a practice is highly dangerous since an explosive reaction may result.

4.3 STORABILITY AND PRESSURE RISE DATA

4.3 STORABILITY AND PRESSURE RISE DATA

4.3.1 General

(U) Propellant storability depends on several factors relating to propellant stability, propellant effects on materials, material effects on the propellant, contamination, and environment.

(U) In general, the hydrazine derivatives, blends of hydrazine derivatives, ammonia, and amines are easily stored for long periods of time at ambient outside conditions, providing suitable containers are provided, and proper procedures are followed.

(U) The proper selection of a container material, adequate container strength, cleanliness, and protection from wide extremes of heat and cold will minimise the possibility of loss or contamination of the propellant.

(U) The following paragraphs describe more specifically the proceedures, limitations, cautions, and pressure rise experience for the specific propellants, ingredients and blends covered in this handbook.

(U) Many of the materials requirements and procedures described previously in transfer (Section 4.2) apply as well to storage.

4.3.2 Storage Procedures

4.3.2.1 Hydrazine, Substituted Hydrazines, and Blends Containing Hydrazines and Amines.

(C) This subsection applies to hydrazine, UDMH, MMH, 50/50 blend, the MHF-blends, MAF-blends, and BAF-blends. Ammonia is treated separately mainly due to its vapor pressure (sect 4.3.2.2). MHF-1, 2, 4, 5, 5B and MGGP-1 require additional care in the materials selection and storage environmental factors, due to the hydrazinium nitrate content which renders these blends more reactive, in general than the blends not containing hydrazinium nitrate. These blends are discussed further in sections 4.3.2.3 and 4.3.3.

(U) Hydrazine and hydrazine type fuels should be stored in containers composed of materials known to be compatible with the fuels for long storage periods and under all environmental conditions anticipated for the storage area. Materials generally recommended for use include 300-series found acceptable include polyethylene, teflon, glass, nylon, butyl rubber, pyrex, and graphite. When in doubt concerning the compatibility of a given material and propellant combination, sections 4.3.3 and 4.4 should be consulted. No lubricants have been found which are totally acceptable for long term use, although in storage containers, these are not required. "Apiezon L" and "Reddy Lube 200" have found some success in transfer equipment. (See Section 4.2.) Materials which are not acceptable for use with these fuels include the following:

UNSUITABLE MATERIALS FOR STORAGE OF HYDRAZINES AND BLENDS

Brass, all types
Bronze, all types
40 E and 7075 Alluminum Alloys
Copper
Gold
Lead
Zinc
Magnesium
Molybdenum over 1/2% in alloys
Silver
Tin
Stellite alloys (other than No. 21)
Mild steel
4130 and 4340 steels

(U) Nickel, Inconel, and Chromel A seem to be margmally acceptable in these fuels for moderate time periods. In many cases the behavior of these metals differ from one fuel to another and it is recommended that Section 4.4 be consulted for additional information.

(U) Hydrazine-based propellants can usually be stored in their shipping containers until use. It is recommended that shipping containers and other storage vessels be protected from weather and other hazards.

(U) All storage containers must be fitted with a rupture disk and pressure relief valve above the vapor space. The storage area must be well ventilated and far removed from sources of heat, sparks or open flames.

(U) Large storage containers should be surrounded by sufficient diking to completely contain the liquid in the event of the rupture of a full container.

if the other chemicals (such as oxidizers) are reactive with the hydrazines.

The storage area should have adequate facilities for fire fighting and decontamination in the event of a spill. Other protective equipment should be available as described in Sections 4.2, and 5.2.5 through 5.2.8.

The recommended material for piping, fittings, and tankage for use with ordinary pressures (less than 250 psig) is schedule 40 stainless steel, with welded connections, or standard AN stainless tubing with flare fittings.

4.3.2.2 Ammonia Storage Requirements

Anhydrous ammonia is usually stored at pressures above 40 psig. Since its boiling point at this pressure is only 25.8 F, and even insulated vessels take up heat from the atmosphere, ammonia evaporated to maintain this temperature must be vented. Vented gas is usually compressed and condensed or absorbed in water to make by-product aqua ammonia.

For storing large quantities of anhydrous ammonia, refrigerated storage at ambient pressure requires smaller investment than conventional storage at ambient temperature. Cost of refrigerated facilities is determined by the time allowed for filling. An insulated 600,000 ft^3 tank of 106 ft overall diameter will accommodate nearly 10,000 tons of anhydrous ammonia at -27 F and 0.5 psig. Hortonspheres(10) which are designed for operation at 40-50 psig, may be used if refrigeration for this level of pressure is available.

Not more than 50,000 gal of ammonia should be stored in an unrefrigerated tank. Storage tanks must not be filled to more than 56% of the water weight capacity of the container at 60 F. These tanks should be fabricated of compatible material and designed for a minimum working pressure of 300 psig.

To prevent possibility of rupturing a storage vessel and releasing its total contents to the atmosphere, each storage tank should be equipped with two spring-loaded relief valves set at a pressure not to exceed the design working pressure of the tank. The discharges from relief valves should be piped to a stack which discharges at least 6 ft above any surrounding platform or working area. Tanks should be located outdoors or in specially constructed buildings. Ventilation to avoid pocketing of ammonia under roofs should be provided for indoor tanks. Outdoor tanks should be painted white, or some other heat-reflecting color. Each tank should be electrically grounded. When insulation is provided, it should be water-resistant to prevent possible damage.

It is recommended that refrigerated tanks be provided with thermal insulation at least equivalent to the following thicknesses of mineral wool felt.

Storage Temperature, °F	Thickness, Inches
35-60	3-4
25-35	4-5
15-25	5-6
0-15	6-7

Each storage tank should be equipped with liquid level gages. The refrigerated storage tanks should be designed for a working pressure of not less than 60 psig, protected by relief valves for design pressure, and at least two compressors should be provided for the refrigeration system. When underground storage tanks are used, the top of the container should be below the frost line, and at least 2 ft below the surface of the ground. Such tanks should be given an external corrosion-resistant coating, and should be anchored or weighted securely to prevent floating if ground water conditions make this a possibility.

Ammonia piping should be designed for 300 psig working pressure, and be of compatible materials. Standard (schedule 40) steel piping may be used if joints are welded. Extra heavy (schedule 80) should be used if piping contains screwed joints. Steels and stainless steels are the most widely recommended materials of construction.

Galvanized iron, copper, brass, zinc, bronze, and other metals prohibited for hydrazine service (Section 4.3.2.1) should never be used for ammonia.

Further discussion of equipment associated with transfer and storage of ammonia is presented in Section 4.2.2.

4.3.2.3 Additional Storage Requirements for Fuels Containing Hydrazinium Nitrate.

In general, fuels containing hydrazinium nitrate are more corrosive, more reactive, and are more subject to interactions with materials of construction and impurities. These factors are highly aggravated by elevated temperatures.

Materials and equipment used for storage of these fuels should be composed of stainless steel (series 300) or aluminum alloys (except 40 E and 7075).

Extremely careful attention should be given to cleaning and passivation of the system, and to anticipated thermal environments. These fuels should be stored in a cool

(U) place, and all containers should be equipped with pressure relief devices above the vapor space, set to pressures below the working pressure of the container.

(C) Detailed information concerning passivation and cleaning of equipment is given for MHF-5 and 5B in Reference 3. These formulations are representative of the hydrazinium nitrate containing blends.

(U) General information and safety precautions regarding transfer of these blends is given in Sections 4.2.3 and 5.0. Since the buildup of pressure from decomposition of the fuel in various containers is a problem at elevated temperatures, Section 4.3 should be consulted for a survey of pressure rise experience.

(U) It is recommended that MHF-1, 2, 4, 5 and 5-B and MGGP-1 be stored in an isolated location and that such storage areas be separated from other chemicals and equipment by explosion-resistant barricades. To avoid the possibility of fire or explosion, the fuels should be stored in a cool place and copious quantities of water should be available for fire fighting or neutralization of spills.

4.3.3 Pressure-Rise Data

4.3.3.1 General
4.3.3.2 Factors Effecting Pressure Rise
4.3.3.3 Material Effects on Pressure Buildup
4.3.3.4 Propellant Effects
4.3.3.5 MHF-3 Storage Data

4.3.3 Pressure - Rise Data

4.3.3.1 General

(C) Pressure rise data is presented herein for various propellants in heremetic storage within vessels of various materials and at various ullages and temperatures. Figures 4.7 through 4.11 show pressure versus time plots for methylhydrazine; 1,1-dimethylhydrazine; MHF-1, MHF-5 and 5B, and BAF-1185. MHF-1, 5, and 5B are shown together since they all contain the same three ingredients, MMH, Hydrazinium nitrate, and hydrazine. Figure 4.11 illustrates the results of tests conducted by various investigators on the effect of ullage on pressure-rise rate for those propellants having significant pressure rise.

4.3.3.2 Factors Effecting Pressure Rise

(U) Major factors which effect the rate of decomposition (gassing) of the propellants were found to be temperature, material type, and cleanliness, and the presence of impurities, multiple materials, etc. Excessively high rates of pressure buildup were found by RMD(12) in the case of dissimilar materials being exposed to blends containing the salt hydrazinium nitrate in solution. This is due to electrochemical reactions brought about by the presence of dissimilar metals in contact with the ionic (conducting) salt solution. In almost all cases of high pressure buildups, a synergistic effect between temperature and the catalytic action of the metal was a determining factor. At a given gas production rate, the pressure rise rate should be inversely proportional to the ullage volume if decomposition is occurring mainly in the liquid phase. In cases (Figure 4.11) where the pressure rise rate departs drastically from this inverse dependence on ullage, a principal source of gas production must be in the vapor phase.

4.3.3.3 Material Effects on Pressure Buildup

(U) The figures show, that among the candidate materials, aluminum alloys are superior to the stainless steels, and that the poorest material for long term storage pressure rise is rusted mild steel. The rust, of course, is a well-known promoter of decomposition in hydrazines. Titanium alloy and 17-7 PH stainless steel seem to be intermediate in performance between the aluminum alloys and the other stainless steels. It would appear, that in hermetic sealed storage the aluminum alloys are best for long term storage of hydrazine type fuels.

(U) Experimental verification of storability is recommended, however, in all instances where hermetic sealed storage is contemplated for operational systems.

1. Most Promising	Aluminum Alloys
2. Moderately Promising	Titanium Alloys and 17-7 Ph Stainless
3. Least Promising	Other Steels
4. Not to be considered for any application	Alloys containing Copper, Zinc, etc.

4.3.3.4 Propellant Effects

(U) The propellants which have proven to give the best results are those neat fuels and blends which do not contain water, nitrates, or other oxidizing substances. Thus, high purity N_2H_4, MMH, UDMH and DETA and/or blends of these will give the least pressure buildup in properly passivated approved materials.

(U) The next most difficult group of blends from a pressure buildup standpoint, are those containing water. Typical among these are MHF-6, BAF-1014, BAF-1185 and impure blends from the first category. These water containing blends combine the corrosive effects of the water and of the propellant. The pressure buildup, however, is only slightly greater, on the average, than for the purified neat fuels.

(U) The propellants MHF-1, 2, 4, 5, 5B and MGGP-1 present by far the greatest problem from a pressure-rise standpoint. The presence of the strongly oxidizing nitrate ions in the solution create an environment which encourages extensive metal-nitrate-fuel reactions. These reactions then produce a synergistic effect with the propellant's tendency to undergo decomposition and oxidation reactions within itself, since the metal compounds formed by the reaction with the nitrates become catalysts for further heterogeneous decomposition of the fuel.

(U) In general, the propellants can be grouped by storage pressure rise tendencies as follows:

1. Low Rates of Pressure Rise:

   N_2H_4
   MMH
   UDMH
   DETA
   NH_3
   50/50
   MHF-3
   MAF-1, 3, 4, 5

2. Moderate Rates of Pressure Rise:

   Impure (water containing) members of the above list.

3. High Rates of Pressure Rise:

MHF-1, 2, 4, 5, 5B
MGGP-1

It can be seen from the above table and the table shown under material effects (Subsection 4.3.2.3) which combination of materials and propellants present the most and/or the least problems.

It is recommended that the above tables serve only as preliminary guidelines in the selection of materials, along with the pressure rise and compatibility data.

It is to be noted that some of the propellants are included in groups only by inference in that no data are available on such propellants as BAF-1014, MAF-5, or MHF-4. No data exists on MAF-2, and it was not included, since none of its ingredients are common to the other propellants.

4.3.3.5 MHF-3 Storage Date

Tables 4.1 and 4.2 give a summary of the results of storage of MHF-3 under varying conditions and in various materials for different lengths of time. Table 4.1 concerns the behavior of MHF-3 in containers of various materials without specimens. Table 4.2 contains storability data for MHF-3 in glass containers containing metal specimens. Parameters such as surface to volume ratio of the material, storage temperature and time, and ullage have been studied for their effects on the pressure buildup resulting from decomposition. Table 4.3 gives the results of chemical analyses of MHF-3 after various storage tests. These samples taken from tests shown in Table 4.1 are indicated using the index number from Table 4.1. Most of the data shown has been abstracted from reference 4 although the original sources of data are also indicated.

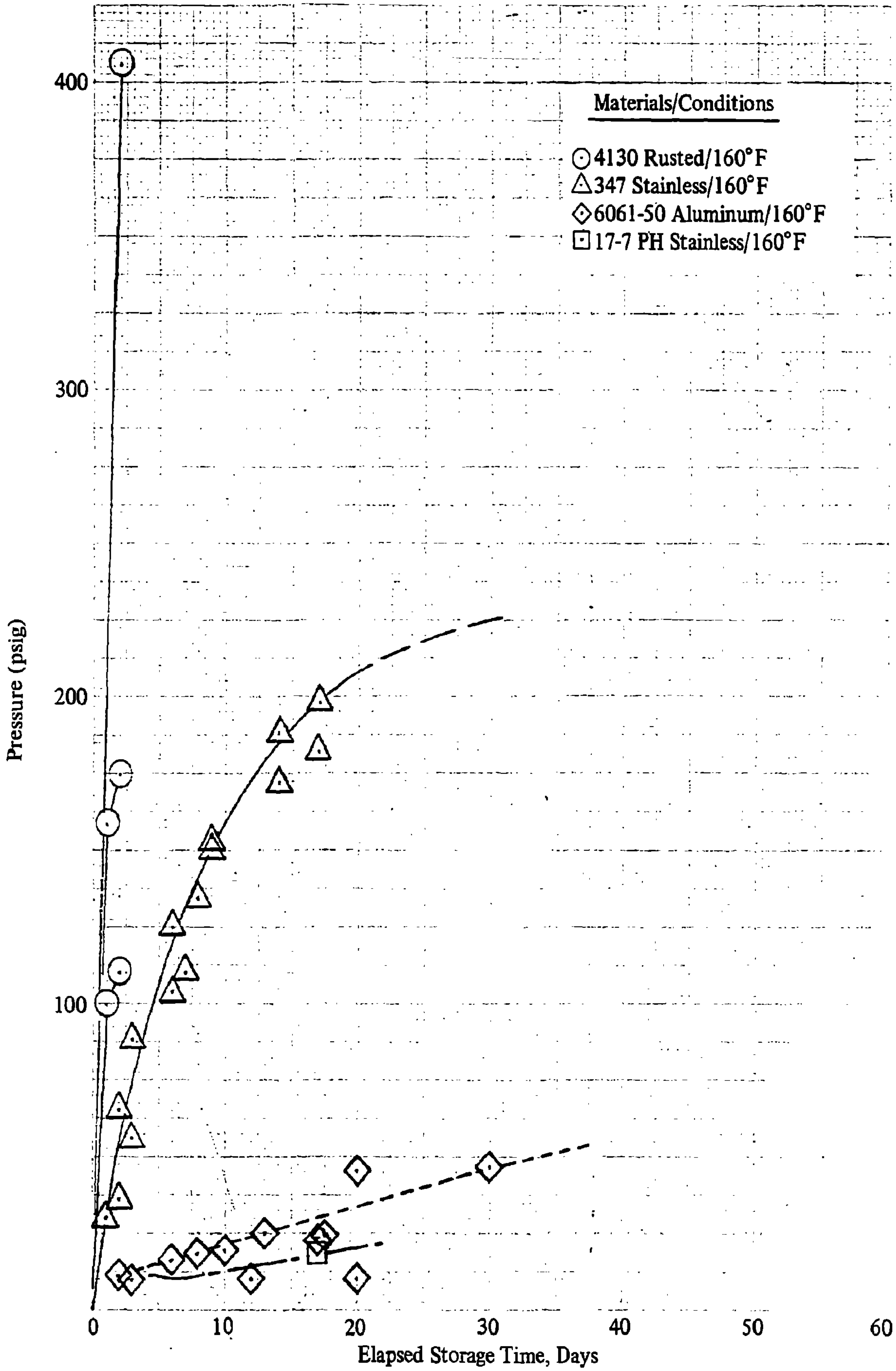

Figure 4.7. Pressure versus Time Curves for MMH From Ref. 22

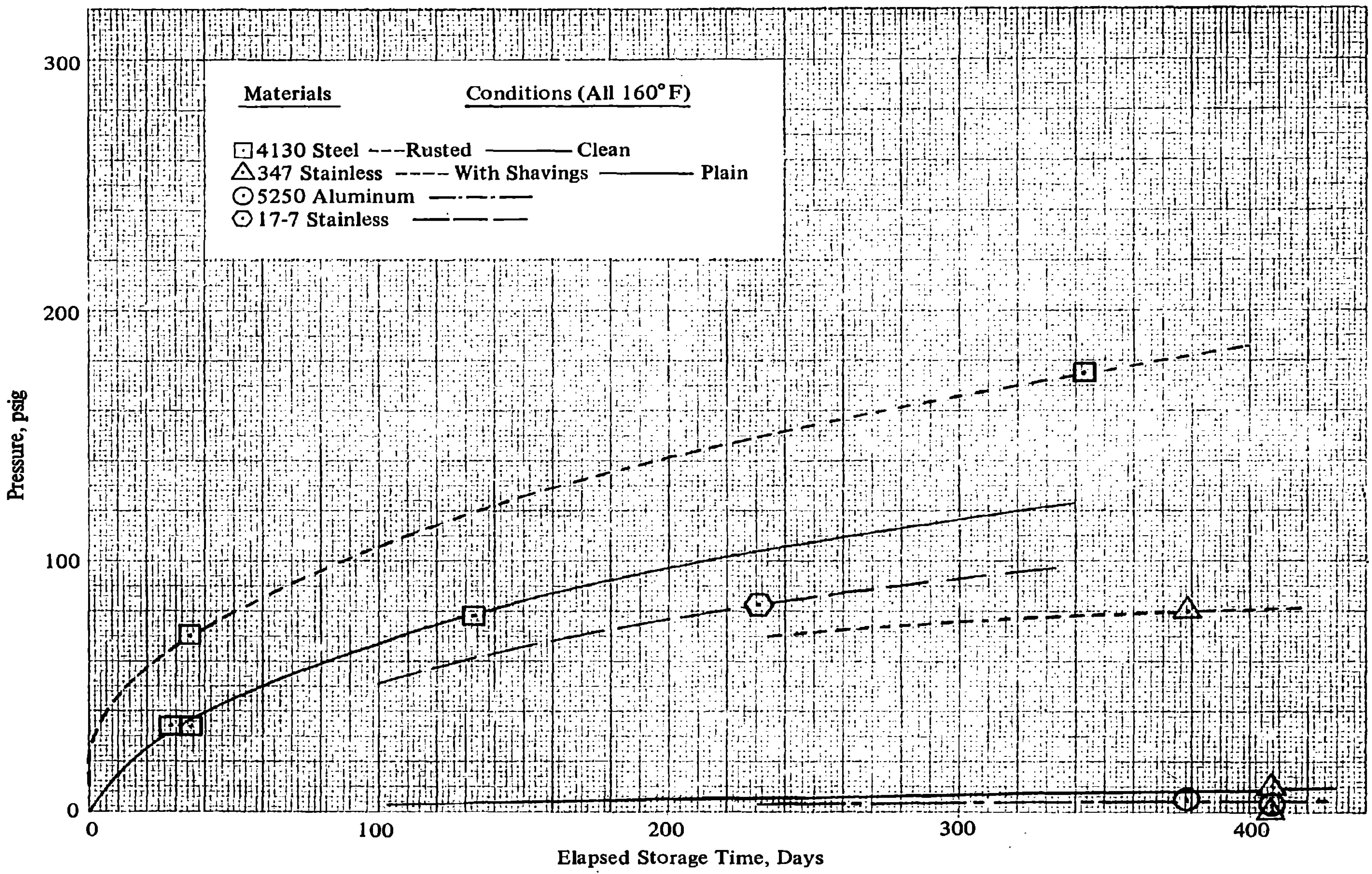

Figure 4.8. Pressure versus Time Curves for UDMH From Ref. 22

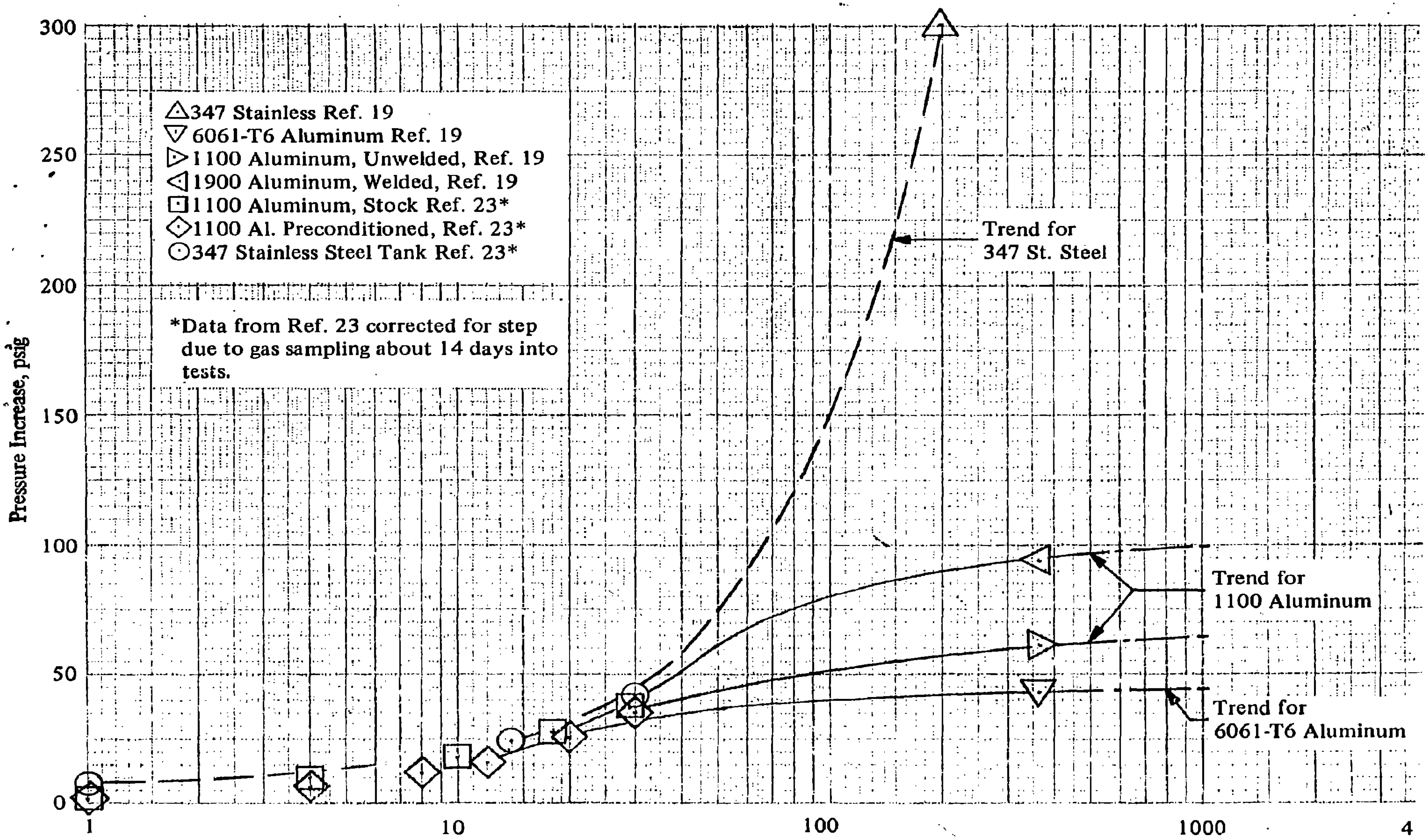

Figure 4.9. Pressure Rise Data for Long Term Storage of BAF-1185 in Various Tankage Materials. 100°F for First 30 Days (19 and 23) Followed by 165°F for Remainder of Test (19)

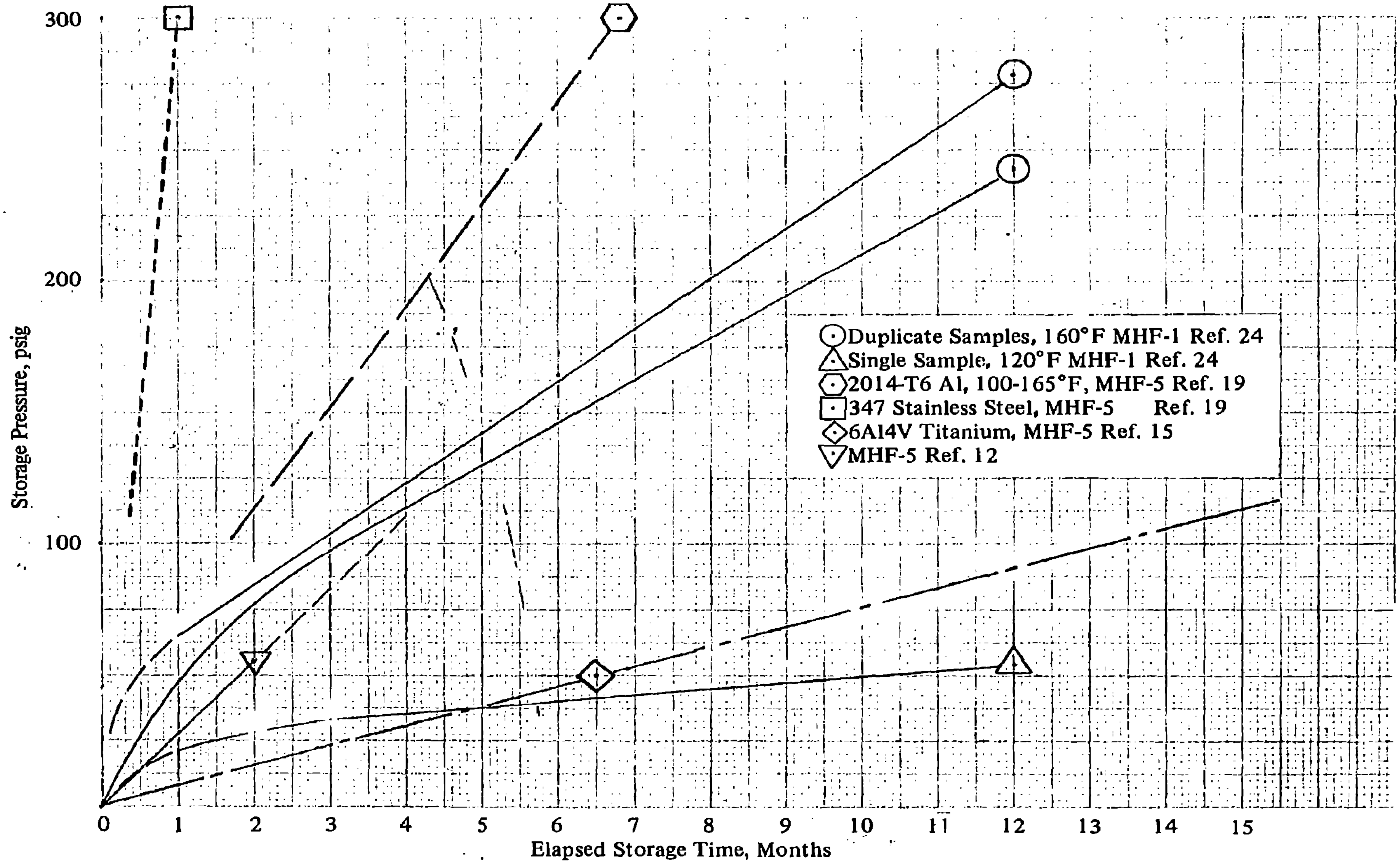

Figure 4.10. Pressure Rise Data for MHF-1 and MHF-5 Storage in Aluminum and Stainless Steel Containers at 5% Ullage Data and Smoothed Curves from References 12, 15, 19, 24

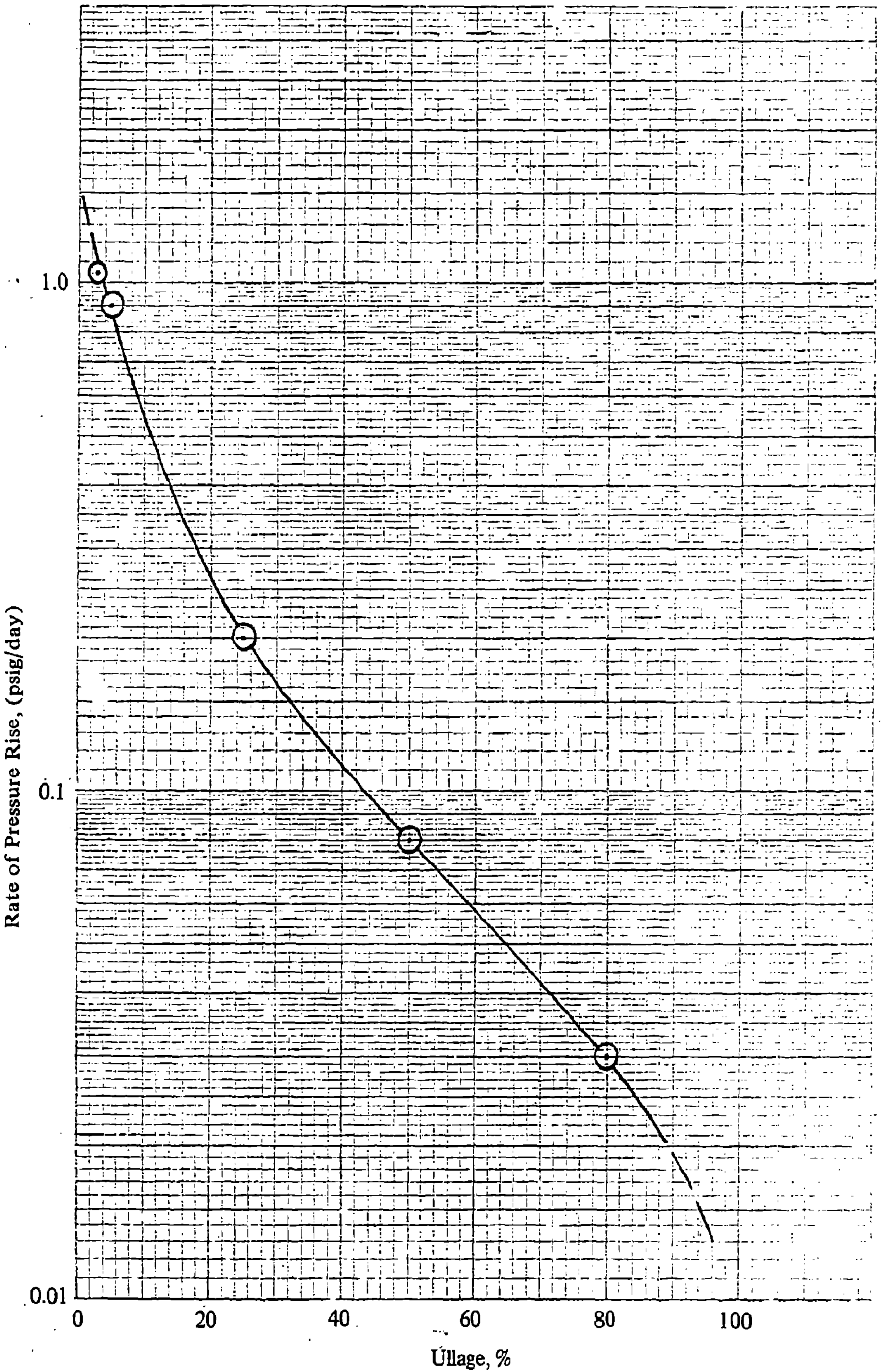

Figure 4-11. Pressure Rise Rate versus Ullage for MHF-5 in Aluminum

TABLE 4.1 MHF-3 STORABILITY DATA IN INDICATED CONTAINERS WITHOUT SPECIMENS

NO.	CONTAINER MATERIAL	ULLAGE, PERCENT	SURFACE TO VOLUME, INCH^{-1}	STORAGE TEMP. F	STORAGE TIME, DAYS	FINAL PRESSURE, PSI	AVERAGE PRESSURE RISE/RATE PSI/DAY	REF.
1	Glass	3.4	-	100	60	-	0.005	13
2	Glass + Alum Vent Valve	8	-	130	60	-	0.01 ±0.01	14
3	Glass	18	-	130	60	-	0.015 ±0.01	14
4	Glass	28	-	130	60	-	0.008 ± 0.01	14
5	Glass	11	-	145	60	-	0.002 ±0.006	14
6	Glass	38	-	145	60	-	0.004 ±0.006	14
7	Glass	11	-	160	60	-	0.03 ±0.06	14
8	Glass	27	-	160	60	-	0.0055 ±0.006	14
9	Glass	60	-	160	60	-	0.06 ±0.006	14
10	Glass + Alum Vent Valve	79	-	160	60	-	0.012 ±0.01	14
11	Glass	38	-	180	60	-	0.012 ±0.006	14
12	Glass	50	-	160	1	0.60	0.60	15
	Glass	50	-	160	10	1.24	0.069	15
	Glass	50	-	160	20	1.69	0.045	15
	Glass	50	-	160	60	3.38	0.042	15
13	Al-1100-0* + Weld Sample	48.9	3.3	100	28	0	0	16, 17, 18, 19
14	Al-1100-0* + Weld Sample	46.4	3.3	165	35	9	1 to 3	16, 17, 18, 19
	Al-1100-0* + Weld Sample	46.4	3.3	165	140	27	0.12 after 60 days	16, 17, 18, 19
	Al-1100-0* + Weld Sample	46.4	3.3	165	365	49		16, 17, 18, 19
15	Al-1100-0* + Weld Sample	50.5	3.3	100	28	0	0	16, 17, 18, 19
16	Al-1100-0* + Weld Sample	48.1	3.3	165	35	7	1.0	16, 17, 18, 19
	Al-1100-0* + Weld Sample	48.1	3.3	165	35 to 77	16	0.21	16, 17, 18, 19
	Al-1100-0* + Weld Sample	48.1	3.3	165	77 to 365	45	0.10	16, 17, 18, 19
17	Al-2014-T6 + Weld Sample	48.9	3.3	100	7 to 28	0	0	16, 17
18	Al-2014-T6 + Weld Sample	46.4	3.3	165	28 to 77	58	1.2	16, 17
	Al-2014-T6 + Weld Sample	46.4	3.3	165	77 to 210	163	0.79	16, 17
	Al2014-T6 + Weld Sample	46.4	3.3	165	210 to 315	240	0.73	16, 17
19	Al-2014-T6 Plain	50.5	3.3	100	1 to 28	0	0	16, 18, 19
20	Al 2014-T6 Plain	48.1	3.3	165	28 to 56	0	0	16, 18, 19
	Al-2014-T6 Plain	48.1	3.3	165	56 to 63	7	1.0	16, 18, 19
	Al-2014-T6 Plain	48.1	3.3	165	63 to 365	30	0.076	16, 18, 19
27	AISI 347 + Weld Sample	48.9	3.3	100	7 to 28	0	0	16, 17, 18, 19
	AISI 347 + Weld Sample	46.4	3.3	165	28 to 35	20	2.9	16, 17, 18, 19
	AISI 347 + Weld Sample	46.4	3.3	165	35 to 365	221	0.61	16, 17, 18, 19

* Gauges were 247 stainless steel; pipe connecting gauges was 304 stainless.

TABLE 4.1 (CON'T)

NO.	CONTAINER MATERIAL	ULLAGE, PERCENT	SURFACE TO VOLUME, INCH^{-1}	STORAGE TEMP. F	STORAGE TIME, DAYS	FINAL PRESSURE, PSI	AVERAGE PRESSURE RISE/RATE PSI/DAY	REF.
28	Inconnel 718 Plain	48.1	3.3	165	7 to 14	0	0	16
	Inconnel 718 Plain	48.1	3.3	165	14 to 98	45	0.54	16
	Inconnel 718 Plain	48.1	3.3	165	98 to 231	103	0.44	16
30	AM 355	5	3.3	100	1 to 5	-	1.6	13
	AM 355	5	3.3	100	5 to 50	-	0.31	13
	AM 355	5	3.3	100	50 to 116	-	0.07	13
22	Al-2024	48.1	3.3	160	390	13	0.035	14
23	Al-6061-T6 + Weld Sample	50	3.3	165	134	-	0.209, 0.216	20
24	Al-6061-T6 + Weld Sample	50	3.3	165	21	-	0.86	19
	Al-6061-T6 + Weld Sample	50	3.3	165	70	23		19
	Al-6061-T6 + Weld Sample	50	3.3	165	140	29	0.10 after 25 days	19
	Al-6061-T6 + Weld Sample	50	3.3	165	210	35.6		19
	Al-6061-T6 + Weld Sample	50	3.3	165	365	52		19
	Al-6061-T6 + Weld Sample	50	3.3	165	204	35		15
25	Al-6061-T6 Plain	50	3.3	165	21	17.5	0.83	19
	Al-6061-T6 Plain	50	3.3	165	70	22		19
	Al-6061-T6 Plain	50	3.3	165	140	27	0.10 after 25 days	19
	Al-6061-T6 Plain	50	3.3	165	210	33.5		19
	Al-6061-T6 Plain	50	3.3	165	365	52		19
	Al-6061-T6 Plain	50	3.3	165	204	32		21

TABLE 4.2 MHF-3 STORABILITY DATA IN GLASS CONTAINERS WITH INDICATED METAL SPECIMENS

NO.	SPECIMEN MATERIAL IN GLASS REACTOR	ULLAGE, PERCENT	SURFACE TO VOLUME INCH^{-1}	STORAGE TEMP. F	STORAGE TIME, DAYS	FINAL PRESSURE, PSI	FINAL SMOOTHED PRESSURE RISE/RATE, PSI/DAY	REF.
34	AM 350	80	0.61	160	60	-	0.085 ±0.01	14
35	Ti-13V-11Cr-3Al	80	0.66	160	60	-	0.015 ±0.01	14
36	AFC-77	80	0.67	160	60	-	0.015 ±0.01	14
37	AM 357	80	0.71	160	60	-	0.033 ±0.01	14
38	AM301, M34045	20	0.20	130	60	-	0.01 ±0.01	14
39	AM 301 (Sheet)	20	0.32	130	60	-	0.027 ±0.01	14
40	AM 350	20	0.16	130	60	-	0.045 ±0.01	14
41	Ti-13V-11Cr-3Al	20	0.24	130	60	-	0.023 ±0.01	14
42	AFC-77	20	0.18	130	60	-	0.020 ±0.01	14
43	AM 357	20	0.21	130	60	-	0.031 ±0.01	14
44	18% Ni Maraging Steel Fusion Welded	20	0.19	130	60	-	0.33	14
45	18% Ni Maraging Steel Fusion Welded	20	0.20	130	60	-	0.20	14
46	18% Ni Maraging Steel Fusion Welded	18 or 38	0.19	130	60	-	0.25	14
47	18% Ni Maraging Steel Fusion Welded	18 or 38	0.31	130	60	-	0.65	14
48	18% Ni Maraging Steel Fusion Welded	18 or 38	0.44	130	60	-	1.24	14
49	18% Ni Maraging Steel Fusion Welded	80	0.74	160	60	-	0.51	14
50	18% Ni Maraging Steel Fusion Welded	80	0.80	160	60	-	0.27	14
21	Al-2014	80	2.05	160	60	-	0.999 ±0.006	14
31	Al-2014	80	1.68	160	60	-	0.18 ±0.01	14
32	AM 355 Fusion Welded	80	1.07	160	60	-	0.10 ±0.01	14
33	AM 301, M34045	80	0.88	160	60	-	0.026 ±0.01	14
26	Al-7178	80	2.21	160	60	-	0.95 ±0.006	14
29	Inconnel 718	50	1.95	160	30	-	0.63	15

TABLE 4.3. CHEMICAL ANALYSIS OF VARIOUS SAMPLES BEFORE AND AFTER STORAGE IN SELECTED MATERIAL CONTAINERS (REFS. 18, 19)

CONDITION AND CONTAINER MATERIAL	COMPOSITION, WEIGHT PERCENT						FUEL COLOR	TABLE 4.1 INDEX NO.	REF.
	N_2H_4	NH_3	H_2O	MMH	IMPURITIES	ANILINE			
Fuel Prior to Test	12.30	0.10	2.60	84.80	0.01	0.04	Colorless	-	18, 19
Al-1100-0 (a)(b)	13.33	3.74	1.42	81.51	0.00	0.00	Pale Amber	13, 14	
Al-1100-0 (b)	13.81	0.00	1.40	83.80	0.00	0.00	Pale Amber	15, 16	
Al-2014-T6 (a)(c)	47.35	0.00	1.37	57.79	0.00	0.00	Colorless	17, 18	
Al-2014-T6 (b)	14.20	0.00	1.43	84.57	0.00	0.00	Pale Yellow	19, 20	
347 Stainless Steel (a)(b)	12.50	0.00	1.50	83.37	0.00	0.00	Dark Amber	27	
347 Stainless Steel (d)	10.20	2.40	3.10	83.40	0.82	0.00	Redish Brown	-	
Inconel 718 (e)	12.86	0.00	1.86	85.04	0.00	0.00	Pale Amber	28	
Fuel Prior to Test	14.39		0.53	84.97	0.11	-	Colorless	-	19
Al-6061-T6 (a)(f)	13.52		0.48	83.23	2.77	-	Colorless	23, 24	
Al-6061-T6 (f)	13.52		0.48	82.78	3.22	-	Colorless	25	

(a) Weld sample in the container

(b) One year storage (30 days at +100 F and 335 days at +165 F)

(c) Removed from the study after 350 days of storage (30 days at +100 F and 320 days at +165 F) due to an indicated pressure leak. Pressure dropped from 272 to 63 psig. The reason for the constituent difference in this container is unknown; the fuel was not MHF-3.

(d) Removed from the study due to a pressure leak after 193 days of storage (30 days at +100 F and 163 days at +165 F).

(e) Removed from the study due to a pressure leak after 245 dyas of storage (30 days at +100 F and 215 days at +165 F).

(f) One year storage at 165 F.

4.4 COMPATIBILITY OF MATERIALS

4.4 COMPATIBILITY OF MATERIALS

4.4.1 General

4.4.1.1 Introduction

The selection of materials for use in contact with the hydrazine and amine fuels is determined both by the effect of the propellant on the material, 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. Although the compatibility of materials with a propellant is usually based primarily on the material's corrosion rate, emphasis with hydrazine-type propellants must also be placed on the effect of the material on the propellant's stability.

The effect of materials on the propellant has been classed as the heterogeneous or catalytic decomposition behavior of the propellant. Both intentional and unintentional catalytic decomposition are discussed in Section 6.0 of this Handbook. The gross effects of both thermal and heterogeneous propellant decomposition pressure buildup in sealed containers, are summarized in Section 4.3.

The effect of a propellant on materials has been generally classified as the materials compatibility of the propellant. The effects of the materials on propellant decomposition, however, have also been included in the compatibility ratings recommended by the Defense Metals Information Center(1) and other agencies. 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.

4.4.1.2 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 lower 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 conditons of its intended use before it is placed in service.

4.4.1.3 Content

This subsection contains tables of compatibility ratings based on the rating schemes shown in Section 4.4.1.4, below. Also are included tables of compatibility data which were presented in terms other than the standard ratings.

The first set of tables deals with N_2H_4 $50N_2H_4/50UDMH$, and UDMH. They are placed together for ease of comparison and due to their wide usage.

The next set of tables contain data for MMH, and MHF-3, shown together due to their related compositions. The third set of tables contain data on the MAF fuels.

Ammonia compatibility data are presented separately. in the final table. No data were found for MAF-2 and 5, MHF-2 and 4, or BA-1014. MHF-1, and 5, and MGGP-1 are covered in Section 4.3.3. Comparisons and limitations of use are discussed in Section 4.4.1.5.

This subsection presents reported compatibility ratings, and data on corrosion rates and volume and weight changes for metals and non-metals. 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 the corrosion rate in mils/year. The compatibility ratings presented are based primarily on these data, and to some extent on propellant decomposition.

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.

4.4.1.4 Compatibility Rating Schemes and Criteria

The compatibility classification scheme adopted in this Handbook for materials is based on the rating schemes recommended by the Defense Metals Information

(U) Center(25), and those used by Battelle Memorial Institute in their liquid propellant handbooks(26), Bell Aerosystems in the Titan II Propellant Handbook(5), Rocketdyne, in their MHF-3 and MHF-5B Handbooks(3),(4), and various manufacturers in their product bulletins.

(U) The several services which used the rating schemes were in essential agreement on the metals. There is a greater degree of uncertainty with the non-metals, where some services classified materials purely on a subjective or qualitative basis, and others, on a semi-quanitatives basis. The schemes of References(4) and (5) are adopted in combined form for this Handbook.

(U) The following tables present the rating schemes for metals (Table 4.4.1) and non-metals (Table 4.4.2). These schemes provide a standard by which to judge the compatibility of material and propellant combinations, but are by no means a precise indicator of what to expect in terms of pressure rise, material corrosion, volume changes, etc. Some detailed information of this type will be found in the references cited.

4.4.1.5 Usage Limitations and Special Provisions

(U) The propellants vary widely in the quantity of data available for them. Thus, the specific propellants for which little or no compatibility data exist are:

No Data	Little Data
MHF-2	MHF-1
MHF-4	MAF-1
MAF-2	DETA
MAF-5	MHF-5B
BA-1014	MHF-6
MAF-3	

It is possible to make generalizations to some of these propellants, although extreme caution should be exercised

(C) MHF-1 and MHF-2 are related to MHF-5 for which considerable pressure rise data exist. Both, however, contain considerably more nitrate ions than MHF-5, and can be expected to be proportionately more corrosive, giving lower ratings or more pressure rise than MHF-5.

(C) MHF-4 is very near the composition of MHF-5 with 2% less nitrate content. It can be assumed, provisionally, that materials will give the same behavior with MHF-4 as with MHF-5. Materials in contact with MHF-5B, also very close to MHF-5 (same nitrate content) can also be assumed, provisionally, to have the same behavior as with MHF-5.

(U) Materials in contact with BA-1014, midway in composition between hydrazine and BAF-1185, can be assumed, provisionally, to have the same rating as with

(U) TABLE 4.4.1 COMPATIBILITY CLASSIFICATIONS - METALS

CLASS	CORROSION RATE MILS/YEAR	DECOMPOSITION	USAGE LIMITATIONS
A	Less than 1.0	None	No Limitations. Typical use involves constant contact with the fuel. Metals can be considered for long term storage.
B	1.0 to 5.0	Slight Degradation over a period of time.	Restricted to transient or limited contact. Not recommended for long term storage.
C	5.0 to 50	Limited Decomposition may occur on contact.	May only be used in areas where brief contact can occur. Not recommended for use where contact occurs regularly.
D	More than 50	Considerable decomposition may occur. May cause ignition or explosion.	Metals are totally unsuitable for use under any conditions. Contact may create a hazardous condition.

CLASS	VOLUME CHANGE %	DUROMETER READING CHANGE	PROPELLANT DECOMPOSITION	USAGE LIMITATIONS
A	0 to less than 25% swelling.	± 3	None	Satisfactory under conditions indicated. No significant changes noted in material or propellant.
B	Less than 10% shrinkage-Less than 25% swelling	± 10	Slight	Material will undergo slight but significant changes in physical properties. Not recommended for long term contact.
C	Less than 10% shrinkage-Less than 25% swelling	± 10	Moderate	May be used where moderate physical and chemical degradations are tolerated over short time periods. Repeated or prolonged use could result in substantial breakdown.
D.	More than 10% shrinkage - More than 25% swelling	Over ± 10	Severe	Unsatisfactory for use in any application under indicated conditions. May create a hazardous condition, ignition or explosion.

hydrazine or BAF-1185, whichever is lower. Similarly, materials in contact with MHF-6 can be assumed to have the lowest rating of MHF-3 or BAF-1185.

Little is known about the ingredients of MAF-2 in any concentrations. Therefore, the compatibility of materials with it is only a matter of conjecture.

MAF-3 can be treated in accordance with the fact that its composition is between that of MAF-4 and neat DETA. MAF-5 has a higher methylcyanide content than MAF-1. MAF-1 should, however, serve as a provisional guideline for MAF-5.

The determination of swelling, hardness changes, corrosion rates and decomposition is subject to considerable variations from sample to sample and between investigators depending on many intangible factors. This is why semi-qualitative ratings are used, and it is the reason why results should not be considered exact, repeatable or absolutely final.

4.4.2 COMPATIBILITY OF HYDRAZINE, UDMH, AND 50-50

4.4.3 COMPATIBILITY OF MHF-3, MMH, AND OTHER MMH-CONTAINING BLENDS

4.4.4 MATERIALS COMPATIBILITY OF THE MAF FUELS AND DETA

4.4.5 MATERIALS COMPATIBILITY OF NH_3

4.4.2 Compatibility of Hydrazine, UDMH, and 50-50.

Hydrazine, UDMH, and the 50-50 blend have been studied more extensively than any of the other hydrazine-type fuel blends. The extensive data on compatibility ratings for various materials as a function of temperature and exposure duration are compiled below in table 4.4. This data should supplement the brief materials recommendations made in section 4.2.3.2, before final material selection is made.

In general, UDMH is slightly more compatible with metals than hydrazine, but slightly less compatible with nonmetals. The compatibility of 50-50 blend is roughly comparable to hydrazine and UDMH. The table should be consulted for individual differences and trends between the different fuels, temperature, and exposure duration.

Specific corrosion rate data are presented in table 4.5 for coupons immersed in 50-50 blend, and in table 4.6 for a comparison of welded and unwelded coupons in 50-50 blend.

When data was found in more than one reference, the earliest, or most original source is cited in the reference list (Section 4.5). In some cases an original source could not be located. In these cases, the earliest obtainable source was cited.

4.4.3 Compatibility of MHF-3, MMH and Other MMH-Containing Blends

MHF-3, MMH and the MHF and BAF blends have overall compatibility characteristics similar to the other hydrazines and 50-50 blends discussed in Section 4.4.2.

MHF-3 and some of the other MHF blends have been studied extensively as candidates for use in prepackaged propulsion units. Most of the data have been expressed in the literature in terms of pressure buildup instead of A, B, C, or D ratings. Tables 4.7 and 4.8 present detailed pressure rise data for MHF-3 in various materials of construction(13, 14). Further data for MHF-3 and other blends are discussed and presented in Section 4.3.3.

Research is currently underway on the compatibility of MMH in stainless steel and titanium alloy. These tests, being conducted by Bell Aerospace Company for the Air Force Minuteman III program, indicate good compatibility between the propellant and material.

In general, blends containing more than 2% water or hydrazinium nitrate are more corrosive than neat fuels. Also, hydrazinium nitrate promotes more rapid decomposition of the propellant in the presence of materials. (See Section 6.2.) Data on pressure rise of MHF-3 and other blends is presented in Section 4.3.3. Results indicate considerable difficulty in hermetically sealed storage of such blends at elevated temperatures.

4.4.4 Materials Compatibility of the MAF Fuels and DETA

Fuels in the UDMH-DETA-Acetonitrile system including MAF-1, 3, 4, and 5 and neat Diethylenetriamine have similar compatibility characteristics. MAF-1 and 4 are the only fuels for which a usable quantity of data have been obtained. DETA and MAF-3 and 5 would have similar compatibility characteristics, and this similarity can be used as a basis for preliminary estimates.

MAF-2, belonging to another family of acetylenic amines may not be similar to the other MAF fuels. No compatibility data is available on MAF-2 since most work on this family was conducted in laboratory glassware. A small number of brief engine tests were conducted in stainless steel hardware. The results were inconclusive.

Table 4.9 summarizes the compatibility ratings for various materials in MAF-4.

4.4.5 Materials Compatibility of NH_3

Anhydrous ammonia is compatible with most metals and alloys excluding those of copper at ambient temperatures. Silicon-iron, the noble metals, noble metal alloys and tantalum are all good, up to at least the boiling point of water.

For moist ammonia, only tantalum and the noble metals are in Class A, that is, have less than 1 mil per year corrosion rate. Nickel, cast irons with copper content, mild steel, cast iron, inconel and lead are in Class B, that is, have less than 5 mils per year corrosion rate. Copper and copper alloys are Class B in dry ammonia and Class D in moist ammonia (greater than 50 mils). The recommended materials for ammonia containers are steel, stainless steel, or aluminum alloys.

When the highest temperatures involved are likely to be very far outside the normal ambient range, as in a rocket motor, stainless steel of 300 or 400 series can be used.

Graphite materials are considered best for handling ammonia gas at very high temperatures. Monel and nickel may also be used at elevated temperatures.

Most of the normal organic materials are not approved for use with ammonia. Teflon, Kel-F, pure asbestos sheets (J-M60) are among the materials that may be used for some ammonia services.

greases and oils with ammonia or equipment used to handle ammonia, but silicones and fluorolubes can be used. Before any lubricant is used with ammonia, compatibility studies should first be conducted. The recommended gasket material is hard-finished, rubber-frictioned asbestos sheet (J-760) groove.

Data on ammonia compatibility is presented in Table 4.10.

TABLE 4.4. COMPATIBILITY OF MATERIALS IN UDMH, 50-50 BLEND AND N_2H_4

MATERIALS	UDMH			50-50				HYDRAZINE		
	RATING	MAX T, °F	REF.	RATING	MAX T, °F	EXPOSURE TIME, DAYS	REF.	RATING	MAX T, °F	REF.
Stainless Steels										
303	A		37	A	160	90	27	D		28
304L				A	160	90	29	A		28
				A	60	270	46			
316	A	140	38,39,40 41,42,43	A	160	90	27	D		28
				D	→160		34,35			
321	A	160	38,39,40	A	160	90	27	B		28
				A	60	270	46			
347	A		37	A	160	90	29	A		28
				A	60	270	46			
15-7 PH MO Cond. A	B		37	A	160	90	27			
17-4 PH	A		37	A	160	90	27	A	140	39
				C	160		33	D	160	39
17-7 PH Cond. A				A	160	90	27			
AM 355 Cond. H				A	160	180	27			
AM 350 SCT	A		37	A	160	90	29			
AM 350				D	160		31,34			
410 H & T				A	160	90	27			
440 C				A	160	90	27	D		28
440 C (Annealed)				A	150	7	30			
301				B			34			
302	A		37	B	140		31	B		28
302				A	80		36			
317				D	160		31	D		28
321	A	160	38,39,40, 43	A	140		34,31	B		28
321				B	68		36			
410	A	160	41	B	77		31,33,36	B		28
430				B			33,36	B		28
W				B	77		31,33	B		28
17-7 PH	A	160	38,39,40	A	140		36	A	75	39
A286	A	85	38,40	D	160		31,34			
315								D		28
416	A		37					D		28
420 F								D		28
430 F								D		28
440 A								D		28
329								D		28
422	A		37							

TABLE 4.4 (CONT)

MATERIALS	UDMH			50-50				HYDRAZINE		
	RATING	MAX T, °F	REF.	RATING	MAX T, °F	EXPOSURE TIME, DAYS	REF.	RATING	MAX T, °F	REF.
Stainless Steel (Cont)										
17-7 PH	A		37							
Haynes Alloy 25	A		37	A	160	90	27			
Hastelloy F (65% Mo)	A		37							
Hastelloy X (9% Mo)	A		37							
Hastelloy C (17% Mo)	A		37							
Hastelloy B (28% Mo)	A		37							
Mild Steel	A		37	D	80		33			
1020 Alloy Steel	A		37	A	60	270	46			
4130 Alloy Steel	A		37	A	60	270	46			
A 286	A		37	A	60	270	46			
Platings										
Cadmium				D	60	360	5			
Chromium				A	60	360	5			
Copper				D	60	360	5			
Gold or Berylco 25				A	160	90	27			
Nickel, Electrolytic				A	60		5			
Nickel, Electrodeless				A	160	133	29			
Silver				A	60	360	5			
Tin				A	60	360	5			
Zinc				D	60	360	5			
Aluminum Alloys										
1100	A	160	39,43	A	60	270	46			
2014-T4				A	60	270	46	A	80	39
2014-T6 Sheet,				A	160	270	27			
Unwelded				A	60	90	46			
Welded				B	60	270	46			
				A	160	14	27			
Spot Welded				D	60	270	46			
Extrusions, All.				A	160		27,29,46			
2024-T6				A	160	90	27			
2219-T81 Unwelded				A	60	270	46			
Welded				A	60	270	46			
3003-H14				A	150	7	30			
5086-H36 Unwelded				A	160	90	27			
Welded				A	160	14	27			

TABLE 4.4 (CONT)

MATERIALS	UDMH			50-50				HYDRAZINE		
	RATING	MAX T, °F	REF.	RATING	MAX T, °F	EXPOSURE TIME, DAYS	REF.	RATING	MAX T, °F	REF.
Magnesium Alloys										
HM2/A-T8				D	60	30	5			
AZ31				D	150	7	5			
Cobalt Alloys										
Haynes Stellite 6K				A	160	90	29			
Haynes Stellite 21				A	160	90	29			
Misc. Metals										
Brass	A	75	39,42,43					B		28
	D	75	2							
Cobalt								D		28
Copper	A	145	38,39,44					D		28
	D	75	40,42							
Inconel	A		37					B		28
Inconel X								B		28
Iron								D		28
Lead								D		28
Magnesium	A	140	39					D		28
Berylco 25				A	160	90	27			
Maganese								D		28
Molybdenum	B	86	39					D		28
Monel	A	140	39,42,43					A	80	42
								D	80	45
								B		28
Nickel	A	140	39,42,43	A	160	90	27	A		42,44,47
								D		39,45
Chromel-A								A	80	47
								D	80	39
								B		28
Nichrome								A	80	39,47
								B	80	28
Silver								A	80	39
								D	75	42,44
								B		28
Stellite								C	77	47
								B		28
Tantalum	A	140	39					A	80	42,44
Tin								D		28

TABLE 4.4 (CONT)

MATERIALS	UDMH			50-50				HYDRAZINE		
	RATING	MAX T, °F	REF.	RATING	MAX T, °F	EXPOSURE TIME, DAYS	REF.	RATING	MAX T, °F	REF.
Aluminum Alloys (Cont)										
5254-F				A	160	90	27			
5456-H24, All				A	60	270	46	A	140	39
5456-H321 Unwelded				A	160	90	27			
Welded				A	60	180	46			
6061-T6 Unwelded	A		37	A	160	90	27			
All				A	60	270	46			
6066				A	160	90	27			
7075-T6	A		37	A	160	90	27			
				A	60	180	46			
356	B	140	39,43	A	160	90	27	A	160	39
				A	60	180	46			
5086-H34	A	145	44							
5154-H34	A	145	38,40							
6063-T6	A	145	38,40							
2017	A	75	39,43					A	160	39
4043								A	160	39
6061	B	160	39,43					A	160	39,44
716								A	140	39
Tens - 50				A	160		27			
25								A		28
250								A		28
25H								A		28
35								A		28
25H								A		28
24ST								A		28
40E								B		28
43	A		37					B		28
52ST								A		28
61ST								A		28
75ST								A		28
XA-545								B		28
716								B		28
1100-H14	A	145	38,40,44							
1200-H14	A	145	38,40							
2024-T3	A	145	38,40,44							
3004-H34	A	145	38,40							

TABLE 4.4 (CONT)

MATERIALS	UDMH			50-50				HYDRAZINE		
	RATING	MAX T, °F	REF.	RATING	MAX T, °F	EXPOSURE TIME, DAYS	REF.	RATING	MAX T, °F	REF.
Misc. Metals (Cont)										
Nilvar				A	60	270	46			
Ni-Span C				A	60	90	46			
Titanium Alloys										
Titanium B120VCA				A	60	270	46			
				A	160	90	27			
Titanium A110-AT	A	130	39	A	160	90	27			
Titanium C120AV	A	160	38,39,40, 44	A	160	90	27			
				A	60	270	46			
Misc.										
Tungsten Carbide				A	160	90	5			
Zinc	D	75	39	D	60		5	D	Room	39,44
Plastics and Elastomers										
Cellulose Acetate								D	75	44
Diallyl Phthalate	D	75	43					D		28
Epon (All, epoxy)				D	60 and up	1	5	B	80	47
Polyvinyl Alcohol	D	75	43,44					D	75	44
Ethyl Cellulose								C	75	44
Furan Resin	A	75	43					B		28
Hycar (2202)				B	60	1	5	B		28
				C	60	270	46			
				D	60	30	46			
Kel-F				D ("5500")	60		46	B		28
Kel-F "300" (Unplasticized)				B	60	360	46			
				D	80	8	5			
Lacto Preme								D		28
Lucite								B		28
Melamine Formaldehyde								B		28
Nylon	A	130	41					B		28
Phenolic				D	60	–	46	B		28
Polyester (Mylar)				D	60	10	5	D		28
				D	80	1	5			
Polyethylene	B		37	See below				A		28
Polystyrene								D		28
Koroseal								B		28
Vinylite	D	32	41					B		28

TABLE 4.4 (CONT)

MATERIALS	UDMH			50-50				HYDRAZINE		
	RATING	MAX T, °F	REF.	RATING	MAX T, °F	EXPOSURE TIME, DAYS	REF.	RATING	MAX T, °F	REF.
Plastics and Elastomers (Cont)										
Natural Rubber								D		28
Synthetic Rubber								B		28
Polyethylene (lo-density)				A	60	360	46			
Polyethylene (Hi-density)				D	160	30	27			
"Marlex 50" (Hi-density)				A	60	270	46			
"Marlex 50" (Hi-density)				B	60	360	46			
Polyelefin, Insulation										
(White)				A	160	30	27			
(Black)				C	160	30	27			
Polypropylene (Hercules)				A	60	180	46			
Polypropylene (Chicago Molded Products)				A	160	30	27			
Polyamide-Nylon				A	80	50	5			
Zytel 31				D	80	60	5			
				D	160	7	27			
Zytel 63				D	80	—	5			
Zytel 101				A	60	360	46			
				B	80	50	5			
				D	80	55	5			
				D	160	7	27			
Teflon filled with graphite, asbestos, or molydisulfide				A	60	360	46			
"Armalon" 7700+ Teflon				C	60	270	46			
"Armalon" 7700L+ Teflon				C	60	270	46			
Teflon "FEP"				A	60	180	46			
				B	60	270	46			
				A	80	60	5			
				D	160	30	27			
Annealed "Kel-F"				D	160	6	5			
				B	60	30	46			
				C	60	270	46			
Fluorobestos and Asbestos				A	60	90	5			
TFE-Felt 7550				B	60	270	46			
Fluorogreen				A	60	180	46			
Saran				D	60	10	5	D		28
				C	80	—	5			
Silastic								B		28

TABLE 4.4 (CONT)

MATERIALS	UDMH			50-50				HYDRAZINE		
	RATING	MAX T, °F	REF.	RATING	MAX T, °F	EXPOSURE TIME, DAYS	REF.	RATING	MAX T, °F	REF:
Plastics and Elastomers (Cont)										
Teflon "TFE"	A	160	39,43,44	A	60	270	46	A		28
				A	80	125	5			
				B	160	30	27			
Tygon	D	75	41	D	80	—	5	B		28
Veloform								D		28
Asbestos								B		28
Glass	A	160	41					A		28
Graphite								B		28
Nat. Carbon CCP-72 and Purepon P3N				A	160	30	29			
Graphitar No. 14 and 39				D	160	30	29	B		28
Pipe Joint Compounds										
AN-C-53								B		28
Oxyseal				B	80	14	27	B		28
Thread-Tite								B		28
Silicone Lubricants										
DC-200 Series								B		28
D6-550								B		28
DC-710								B		28
Lead - Tin Solder	(Metals)							B		28
Silver Solder	(Metals)			A	60	270	46	B		28
Varnish	D			D				B		28
Wood								D		28
Wool								D		28
Gold	(Metals)							A	75	42
Buna N Rubber	B	80	41	D	60	30	5			
Butyl Rubber	A	140	41	See below						
	D	140	39							
Polyvinyl Chloride, All				D	60 and up		5			
Neoprene Rubber	A	68	39	D	60	30	46			
	D	75	45	B	80	2	5			
				D	80	9	5			
Delanium	A	75	43					A	140	39
All Coatings				D	All	30	27,29			

TABLE 4.4 (CONT)

MATERIALS	UDMH			50-50				HYDRAZINE		
	RATING	MAX T, °F	REF.	RATING	MAX T, °F	EXPOSURE TIME, DAYS	REF.	RATING	MAX T, °F	REF.
Laminated Glass										
Silicone				A	60	30	46			
				C	60	90	46			
Phenolic				C	60	30	46			
				D	60	90	46			
Epoxy				C	60	90	46			
				D	60	180	46			
Polyester				D	60	30	5			
Polyformaldehyde				B	60	30	46			
(Delrin)				D	60	90	46			
Polycarbonate				D	60	10	46			
(Lexan)				D	80	—	5			
Polyvinyl Fluoride (Tedlar)				B	60	180	46			
Polyvinylidene Fluoride				B	80	30	29			
(Kyrer)				A	80	30	5			
				D	160	30	29			
Plexiglas CR39				D	60	9	5			
Plexiglas II				D	80	1	5			
Hypalon 20										
Butyl Rubber				D	80	7				
Parco 823-70				B	80	1	5			
				C	80	27	5			
805-70				B	80	1	5			
				C	80	16	5			
				D	80	31	5			
				C	160	2	27			
F-120-55				D	60	—	5			
Silicone A-7001				D	60	—	5			
Narmco X3168				D	60	—	5			
P-4010				A	60	—	5			
30000				A	60	—	5			
H-Film				D	160	—	5			

TABLE 4.5. CORROSION DATA FOR METAL COUPONS IN 50-50 BLEND

Propellant Quantity:	One fluid ounce per test tube
Specimens:	Rectangular coupons approximately five square inches in area
Number of Specimens:	Three per material in individual test tubes
Condition:	Partial immersion - Static
Time:	Three days
Temperature:	160°F ±5°F
Apparatus:	Nitrogen blanket in pressure tight, screw top, aluminum-foil gasketed culture test tube
Data:	Average of three specimens

MATERIAL	% WEIGHT CHANGE	CORROSION RATE - MPY	REMARKS
ALUMINUM ALLOYS			
2014-T6 WROUGHT	-0.0039	0.134	No change in appearance in all the aluminum alloys.
2024-T6	-0.0027	0.096	
5086-H36	-0.0022	0.079	
5254F	-0.0034	0.119	F is as fabricated.
5456-H321	-0.0017	0.060	
6061-T6	-0.0012	0.040	
7075	-0.0022	0.077	
A110 AT TITANIUM	-0.0014	0.047	
C120 AV TITANIUM	-0.0020	0.068	
BERYLCO 25	-0.0042	0.147	No change in appearance.
STAINLESS STEEL			All the stainless steels exhibited a minor discoloration in the vapor phase and/or at the liquid vapor interface.
304L	-0.0030	0.108	
316 ANNEALED	-0.0020	0.067	
321 ANNEALED	-0.0052	0.171	
347 ANNEALED	-0.0048	0.163	
15-7PH CONDITION A	-0.0037	0.119	PH is precipitation hardened.
17-7PH CONDITION A	-0.0043	0.141	
AMS 355 CONDITION H	-0.0036	0.080	
410 HARDENED AND TEMPERED (H&T)	-0.0122	0.329	Rusted in vapor phase.
COATINGS			
GOLD PLATING ON BERYLCO 25	None	None	No visible change in appearance.
CATALAC PAINT ON MILD STEEL	--	-	The coating peeled off in 3 to 4 days. There was evidence of lifting on the edges in 10 to 15 minutes.

TABLE 4.6. CORROSION DATA FOR TENSILE COUPONS IN 50-50 BLEND

Propellant Quantity:	7.5 fluid ounces per flask
Specimen:	Tensile specimen - approximately 5.5 square inches in area
Number of Specimens:	Three per material in one test vessel
Condition:	Full immersion - Static
Time:	14 days
Temperature:	160°F
Apparatus:	Erlenmeyer flask (about 8 ounces) with reflux condenser
Data:	Average of three specimens

MATERIAL	WELDED		UNWELDED		BRAZED		SOLDERED	
	% WEIGHT CHANGE	RATE MPY	% WEIGHT CHANGE	RATE MPY	% WEIGHT CHANGE	RATE MPY	% WEIGHT CHANGE	RATE MPY
ALUMINUM ALLOYS								
2014-T6 MANUAL WELD	-0.0002	0.003						
2014-T6 MACH. WELD	-0.0035	0.037						
2014-6061 MANUAL WELD	-0.0033	0.034						
5086 H-36	+0.0004	–	-0.0004	0.003				
5456-H321	-0.0008	0.007	-0.0025	0.021				
6061-T6	-0.0080	0.059	-0.0057	0.042	-0.0457	0.343		
STAINLESS STEELS								
303							Tin Soldered -0.0006	0.009
304L ANNEALED	-0.0012	0.009	+0.0024	–	Nicrome Brazed +0.0014	–		
321 ANNEALED	+0.0013	–	+0.0028	–				
347 ANNEALED	+0.0020	–	+0.0029	–	Silver-Brazed +0.0025	–		
410 H&T	-0.0546	0.317	-0.0108	0.064				

TABLE 4.7 MHF-3 COMPATIBILITY
(Initial Pressure = 36 psig)

Test Container Material		Ullage (% Volume)	Temp. (°F)	Surface Area to Liquid Volume Ratio	Pressure Rise (mm Hg/day)		Decomp. Ratio $\frac{R_{metal}}{R_{neat}}$	Extrapolated Decomp. Rate (mm Hg/day)		
					Decomp. Rate	After (days)		Ullage	S/V Ratio	Press. Rise
AFC-177	(Ref. 14)	79	160	0.67	0.7	55	1.2			
AM357		79	160	0.71	1.7	55	2.8			
18% Ni M.S.		79	160	0.74	26.4	55	44.0			
Neat Control		79	160	—	0.6	55	—			
AFC-77		18	130	0.18	1.0	60	1.4			
AM 357		18	130	0.21	1.6	60	2.3			
18% Ni M.S.		18	130	0.20	10.5	60	15.0			
18% Ni M.S. (fusion welded)		18	130	0.19	16.3	60	23.3			
18% Ni M.S., Ni coated (aged)		18	130	0.19	5.3	60	7.6			
Nickel Sheet		18	130	0.19	15.2	60	21.7			
Neat Control		18	130	—	0.7	60	—			
Al 7178		80	160	2.21	4.9	60	1.4	5	0.21	62.4
Al 2014		80	160	2.05	5.1	60	1.4	5	0.21	65.2
AM 355		80	160	1.68	9.3	60	2.4	5	0.21	109.6
AM 355 (fusion welded)		80	160	1.07	5.2	70	2.5	5	0.21	112.0
AM 355, M34045		80	160	0.88	1.4	60	1.3	5	0.21	60.4
AM 350		80	160	0.61	4.4	60	2.1	5	0.21	93.6
Ti Alloy		80	160	0.66	0.8	55	1.1	5	0.21	48.0
AM 350		20	130	0.16	2.3	60	2.3	5	0.21	7.7
AM 301, M34045		20	130	0.20	0.5	50	1.0	5	0.21	3.4
AM 301 (sheet sample)		20	130	0.32	1.4	50	1.6	5	0.21	5.4
Ti Alloy		20	130	0.24	1.2	60	1.5	5	0.21	5.0
Neat Control		80	160	—	0.6	60	—	5	0.21	45.6

TABLE 4.8. MHF-3 COMPATIBILITY

(Steady State Values - after 60 days of test) (Ref: RMD (14))

			MEASURED			EXTRAPOLATED				
TEST COUPON SAMPLE	METAL ALLOY TYPE	TEMP. (°F)	ULLAGE (%)	S/V RATIO (cm^{-1})	PRESS. RISE (mmHg/day)	ULLAGE (%)	S/V RATIO (cm^{-1})	GAS EVOLUTION RATE [PRESSURE RISE]		PRESS. AFTER 2 YR.
								(mmHg/day)	(psi/day)	Storage (psi)
Neat Control		130	20	—	0.7	5	—	0.7	0.014	10
		160	80	—	0.6	5	—	—	—	—
Al 2014		130	20	—	—	5	0.21	—	—	—
		160	80	2.05	5.1	5	0.21	4.0	0.079	58
Al 7178		130	20	—	—	5	0.21	—	—	—
		160	80	2.21	4.9	5	0.21	3.4	0.066	48
AM 301, M34045		130	20	0.20	0.5	5	0.21	0.7	0.014	10
		160	80	0.88	1.4	5	0.21	3.8	0.074	54
AM 301, Sheet Sample		130	20	0.32	1.4	5	0.21	2.0	0.039	28
		160	80	—	—	5	0.21	—	—	—
AM 350		130	20	0.16	2.3	5	0.21	11.9	0.230	168
		160	80	0.61	4.4	5	0.21	—	—	—
RMD 6073-Q1		100	5	?	3.626					
AM 355		*130*	*20*	—	—	5	0.21	—	—	—
		160	80	1.68	9.3	5	0.21	9.7	0.188	137
AM 355, Fusion Welded		*130*	*20*	—	—	*5*	*0.21*	—	—	—
		160	80	1.07	5.2	5	0.21	13.5	0.261	191
AM 357		130	20	0.21	1.6	5	0.21	4.5	0.087	64
		160	80	0.71	1.7	5	0.21	7.2	0.139	101
AFC-77		130	20	0.18	1.0	5	0.21	2.4	0.046	34
		160	80	0.67	0.7	5	0.21	1.3	0.025	18
Titanium Alloy	*(13% V, 11% Cr, 3% A1)*	*130*	20	0.24	*1.2*	5	0.21	2.3	0.044	32
		160	80	0.66	0.8	5	0.21	2.0	0.039	28
18% Ni Maraging Steel		130	20	0.20	10.5	5	0.21	46.4	0.897	655
		160	80	0.74	26.4	5	0.21	145.1	2.807	2049
			80	0.80	13.7	5	0.21	65.4	1.265	923
18% Ni M.S., Fusion Welded		130	20	0.19	16.3	5	0.21	77.8	1.505	1099
		160	80	—	—	5	0.21	—	—	—
18% Ni M.S., Nickel Clad		130	20	0.19	5.3	5	0.21	23.5	0.455	332
		160	80	—	—	5	0.21	—	—	—
A Nickel, Sheet Sample		130	20	—	—	5	0.21	72.4	1.40	1022

TABLE 4.9. MAF-4 COMPATIBILITY

(DATA FROM REF. 8)	"A" or "B"	"B" or "C"	D
Metals			
Aluminum			
QQ-A-318 (Plain)	x		
325 (6061 Anod)	x		
327 (6061 Anod)	x		
351 (2017 Anod)	x		
345 (3003 Anod)	x		
245 (2024 Anod)	x		
362 (2024 Alclad)	x		
561 (1100 Anod)	x		
601 (356 Anod)	x		
601 (356 Plain)	x		
5052			
Steels 304	x		
307	x		
MIL-5-7081 Plain	x		
18-8 St. S. 5059	x		
18-8 St. S. 6721	x		
18-8 St. S. 7720	x		
18-8 St. T. 8506	x		
Chrome Plated - S. 6758	x		
Lead - Nionel Alloy	x		
Copper - Plain			x
Braze			x
Wire			x
Zinc			x
Alum. Bronze			x
QQ-B-671			x
Cadmium - Plain			x
Plating			x
Brass			x
QQ-B-611			x
Silver Braze			x
MIL-B-7883			x
Plastics and Elastomers			
Silicone Rubber Ams 3305	x		
Hydrapol O.T.	x		
Mylar A	x		
Silicone DC-160			x
Silicone SE 450-24/4B			x
Silastic 152 & 250			x
Kel-F			x
Hewett Rubber			x
Goodyear			
Redwing			x
N Plioweld 1551			x
Buna N			x

TABLE 4.9. (CONT)

(DATA FROM REF. 8)	"A" or "B"	"B" or "C"	D
Oils			
Dow Corning			
Silicone 500	x		
Silicone 200; μ = 300 cs	x		
Silicone 200; μ = 10 cs			x
Silicone 129 b			x
Silicone 310			x
Silicone 550			x
Glo Graphite - Suspension			x
Varnaton			x
Octoil			x
Kel-F Oil 10			x
With Wax 150			x
Kel-F Oil 1			x
Motor Oil			x
Insta. Oil			x
MIL 5606			x
Cellulube 90, 150			x
Pyraul.(Mansanto)			x
Areclor 1254			x
G.E. Silicone 81743			x
Grease			
Apiezon -L & -T		x	
Lubriseal		x	
Alcolube		x	
Ward's Bearing Grease		x	
Parker Water Oilube 50		x	
Parker G-363 Grease			x
Parker Fuel Lubc 44			x
MIL-G-4343			x
Lubeiko-M1 (Hi Temp)			x
Dow Corning 4, 33, 55, 44, 11, 20, 41, High Vacuum			x
Texaco TG-1888; Unitemp			x
Kel-F B-12			x
Kel-F 40			x
Podbelniak High Temp.			x
Podbelniak 2713			x
Cosmolube 1			x
Cosmolube 101			x
J. Crane Lubricant 1, 1A, 11			x
Jan-A-669 Grease			x
Led Plate 250			x
Metco Valve Lube			x
Mogul Taper Valve Lubricant			x

TABLE 4-10. AMMONIA COMPATIBILITY

MATERIALS	RATING CLASS	MAX. TEMP. °F	REF.
Metals			
Stainless Steels			
304L	A	AMB* (dry)	31
316	A	AMB (dry)	31
302	A	AMB (dry)	31
430	A	AMB (dry)	31
Hastelloy F (65% Mo.)	B	AMB (dry)	31
Hastelloy X (9% Mo.)			
Hastelloy C (17% Mo.)	B	AMB (dry)	31
Hastelloy B (28% Mo.)	B	AMB (dry)	31
Mild Steel	A	AMB (dry)	31
Hastelloy D	B	AMB (dry)	31
Brass	D		5
Cobalt	D		5
Copper	D		5
Inconel	B	75 (l)	42, 48
Iron	B	75 (l)	40, 42
Lead	B	75 (l)	42
Tantalum	A	212 (l)	48
Plastics and Elastomers			
Kel-F	B	Hot (l)	41
Phenolic	B	Hot (l)	41
Polyethylene	B	Hot (l)	41
Teflon	A	77 (dry)	31
Misc.			
Glass	A,B	77 (dry)	31
Graphite	A	>2,000 (dry)	42
Solder			
Gold	A	Liquid	42, 48
Platinum	A	Liquid	42, 48
Zr - Platinum	A	Liquid	48
Rh - Platinum	A	Liquid	42

*Ambient ≈ 70°F

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4.5 REFERENCES

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5.0 SAFETY

5.1 INTRODUCTION

5.1.1 General

5.1 INTRODUCTION

5.1.1 General

(U) The purpose of the Safety Section of this Handbook is to present and evaluate information concerning hazard characteristics of the hydrazine based propellants, together with procedures and equipment employed for their safe handling.

(U) 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.

(U) The reader is further cautioned that, while every reasonable effort has been made to assure the information given in this section, the authors and Bell Aerospace Company make no warranty nor do they assume legal responsibility for its correctness.

(C) The safety-related characteristics of the fuel blends are determined by the corresponding characteristics of their major constituents. It is postualted herein that the most hazardous constituent defines the hazard of the blend. Thus, the toxic and fire hazards of MHF-3 blend are assumed to be those of its most toxic and flammable constituent, MMH. However, in the case of MHF-5 blend, the toxic and fire hazards are those of MMH, but there is an additional explosion hazard due to the presence of hydrazinium nitrate.

(U) 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 major constituent chemicals are described (hydrazine, UDMH, etc.). At the end of each section, the blends are listed and referenced to the appropriate hazard paragraphs.

5.2 TOXICITY

5.2.1 General Introduction

5.2 TOXICITY

5.2.1 General Introduction

The propellants considered in this Handbook are all classified as toxic substances, and prolonged exposure to high concentrations of vapor or ingestion of sizeable doses is potentially lethal. Tests to determine lethal doses and concentration-time combinations have been conducted on several types of animals, the largest being the dog. Experience with human exposure is very limited; however, exposure limits have been established for most of the neat ingredients.

Ammonia, for which the most data is available, is one of the least toxic of the fuels considered here. It is therefore treated separately from the others. (Sections 5.2.2.1, 5.2.3.1 and 5.2.4.1) The hydrazines, and fuels containing N_2H_4, MMH and UDMH are treated as a group in Sections 5.2.2.2, 5.2.3.2 and 5.2.4.2. Finally, the amines and MAF fuels are considered in Sections 5.2.2.3, 5.2.3.3, and 5.2.4.3.

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.

Exposures are expressed as concentration and exposure duration for exposure to vapors in the air; and as dosages referred to as a fraction of body weight for ingestion. In tests on animals, the lethal dosage is defined as the dosage which kills 50% of test subjects. The dosage is expressed as LD_{50} in milligrams of substance per kilogram of body weight (Mg/kg). The concentration of vapors in air is expressed in terms of parts of vapor per million parts of air (ppm). In both instances, the basic unit is one millionth part of the whole.

Tests with animals are obviously not directly applicable to humans due to the size difference; however, it has been found to provide an approximate indication of the relative toxicity of various substances. Also, on a mg/kg basis, the dosage tolerance of humans has usually been found to be within the range obtained for various animals.

Table 5.2-1, below, lists the recommended MAC for all of the hydrazine and Amine fuels for eight-hour exposure.

Table 5.2-2 summarizes all blends indicating the component from which the principal hazard arises.

TABLE 5.2-1 MAXIMUM ACCEPTABLE CONCENTRATIONS

FUEL	MAC	FUEL	MAC
Ammonia	100	MAF-5	0.5**
DETA	20	MGGP-1	1.0**
Hydrazine	1.0	MHF-1	0.5**
MMH	0.5	MHF-2	0.5**
UDMH	0.5	MHF-4	0.5**
50-50	0.5	MHF-5	0.5**
MHF-3	0.5	MHF-5B	0.5**
MAF-3	1.0*	MHF-6	0.5**
MAF-4	0.5**	BA-1014	1.0*
MAF-1	0.5**	BAF-1185	0.5**
MAF-2	20*		

* Estimated for this work.

** Based upon most toxic and highest vapor-pressure ingredient.

TABLE 5.2-2 HAZARD CLASSIFICATION OF HYDRAZINE-TYPE FUEL BLENDS

BLEND	PRINCIPAL HAZARDS TOXIC HAZARD	 FIRE HAZARD	 EXPLOSION HAZARD
50-50 Hydrazine/UDMH	UDMH	UDMH	Hydrazine
MHF-1	MMH	MMH	HN
MHF-2	UDMH	UDMH	HN
MHF-3	MMH	MMH	MMH
MHF-4	MMH	MMH	HN
MHF-5 and MHF-5B	MMH	MMH	HN
MHF-6	MMH	MMH	MMH
MAF-1	UDMH	UDMH	UDMH
MAF-2			
MAF-3	UDMH	UDMH	UDMH
MAF-4	UDMH	UDMH	UDMH
MAF-5	UDMH	UDMH	UDMH
BA-1014	MMH	MMH	Hydrazine
BAF-1185	MMH	MMH	MMH
MGGP-1	Hydrazine	Hydrazine	HN

5.2.2 Hazards and Exposure Limits

5.2.2.1 Ammonia

The hazards of ammonia, which is much less toxic than the hydrazines, are covered adequately by References 3, 9, and 13. Reference 12 presents a very useful table of physiological responses and allowable exposures to various concentrations of ammonia which is reproduced here along with additional data from other sources (Table 5.2-3). The original source of the data is unknown, but it is in close agreement with other sources(3, 12, 14).

Although ammonia is not classified a systemic poison, its liquid and vapor are caustic and can be toxic in relatively high concentrations. Fortunately the odor detection level of about 50 ppm is below the MAC (maximum allowable concentration for a daily 8 hour exposure) of 100 ppm. Contact with the liquid can cause damage to the skin or eyes in the form of burns or blindness. Thermal burns, because of the low temperature of the liquid, are another consideration.

5.2.2.2 Hydrazine, Substituted Hydrazines, MHF-Fuels, BAF Fuels, and MGGP-1

Hydrazine, UDMH, MMH and mixtures of these are toxic liquids and they give off toxic fumes.

Inhalation of N_2H_4, MMH or UDMH vapors will cause dizziness, nausea, chest pains, coughing, wheezing, and/or hoarseness appearing gradually over long exposure periods(1). The actual symptons will depend on the degree of exposure and the individual. Exposure of the eyes to the vapor can cause itching, swelling of the mucous membranes, painful blistering, and burns similar to those caused by a welding arc, respectively, depending on the degree of exposure(2).

The MAC (Maximum Allowable Concentration for an eight-hour daily exposure) for N_2H_4 vapors is 1.0 ppm and that for MMH and UDMH is 0.5 ppm. Since UDMH is the more volatile compound, the 50-50 blend of N_2H_4 and UDMH give off principally UDMH vapors, and an MAC of 0.5 ppm is recommended for 50-50(3, 9, 10). A similar condition exists for fuels containing MMH. The MAC values for the fuels established by the American Conference of Governmental Industrial Hygienists (ACGIH) as of 1963, are shown in Table 5.2-4. In the case of mixtures, attention to the most toxic component is recommended.

TABLE 5.2-3 PHYSIOLOGICAL RESPONSE TO VARIOUS CONCENTRATIONS OF AMMONIA(13, 3)

NH_3 CONCENTRATION (ppm IN AIR)	PHYSIOLOGICAL RESPONSE (WHEN INHALED)
50-53 (Ref. 13)	Odor detectable by most persons.
100 (Ref. 13)	Maximum allowable concentration for repeated 8-hour daily exposure.
300 (Ref. 13)	Maximum allowable concentration for one-time, up to 1-hour exposure.
408 (Ref. 13)	Least amount causing immediate irritation to throat.
698 (Ref. 13)	Least amount causing immediate irritation to the eyes.
1,720 (Ref. 13)	Least amount causing coughing - no permissible exposure.
2,000 (Ref. 3)	Dangerous for short exposures (1/2 hour). Produces severe toxic effects; may be fatal after short exposure.
2,500 (Ref. 13)	
5,000 (Ref. 3)	Rapidly fatal.
(CONCENTRATION IN AIR OR LIQUID (WATER))	**PHYSIOLOGICAL RESPONSE (ON EXPOSED SKIN)**
10,000 (1%) (Ref. 3)	Midly irritating to moist skin.
30,000 (3%) (Ref. 3)	Stinging, chemical burns, blistering, respectively, depending on exposure duration.

Ingestion or skin contact with adsorption will cause caustic burns, headache, dizziness, nausea, or may even prove fatal, depending on the severity and duration of contact. In this respect, hydrazine tends to cause surface burns, whereas UDMH tends to be absorbed, causing internal effects. Hydrazine is considered by some to be up to 15 times more toxic than UDMH in contact with the body, or up to 3 times more toxic when ingested(11). UDMH, and MMH on the other hand, tend to be most dangerous from the inhalation of vapors.

The effects of these fuels have been determined on various test animals by various investigators. Table 5.2-4 also indicates the LD_{50} (Dosage Lethal to 50% of test specimens) determined from References 4, 5, 6, 7 and 8. Most of the data in References 2, 3, and 7 are based on the data reported in 4, 5, 6, and 8. Where available, a range of values is presented to indicate the scatter evident between different individual specimens and investigators.

Hine Laboratories, Inc.(8) conducted tests with mice weighing between 20 and 30 grams, in which they were injected with various amounts of hydrazine, UDMH, and MMH. Some of the animals were given antidotes to test their effectiveness. The results of these tests were an LD_{50} for hydrazine of 70 mg/kg of body weight and an LD_{50} for MMH of 78 mg/kg which indicated hydrazine to be more toxic than MMH. This information contradicts most other sources. Tests by Cornell Labs(5), for example, give an LD_{50} for hydrazine of 64 mg/kg and an LD_{50} for MMH of 28 mg/kg when injected into rats weighing between 18 and 24 grams. These data are in closer agreement with the other sources. All data are summarized in Table 5.2.4. Reference 5 also states that hydrazine has a depressant action on rats; lowering their body temperature and pulse rate, whereas, MMH and UDMH were found to be stimulants.

With the exception of ammonia which is less toxic than the hydrazines, the detection of these fuels by their odor should not be relied upon for sufficient warning of their presence in dangerous concentrations, over long time periods, since their MAC is below the detectable level. Considerable disagreement exists between References 2 and 8 regarding the detectable odor of hydrazine. It is, therefore, recommended that the higher limit be assumed until the discrepancy is resolved. Hydrazine vapors also cause olfactory fatigue, reducing the possibility of detecting odors.

For shorter duration, one-time exposures to the hydrazines and their mixtures, higher concentrations have been found to be tolerable. Since most propellant handling operations involve contact with fuels for brief and irregular periods, these moderately higher concentrations may not create an undue hazard, provided that the contact is brief and adequate ventilation is provided. No specific limits for short duration exposures have been established.

Tests have been conducted on the effects of short term UDMH exposure on dogs and rats by Weeks, et al(12). Dogs were found the most susceptable in this, and other work. In 5 to 60 minute exposure, no adverse effects were observed on dogs exposed to 50 ppm for 1 hour; 200 ppm for 15 minutes or 600 ppm for 5 minutes. Since UDMH is more toxic than hydrazine from an inhalation standpoint, it is believed that similar results for hydrazine would be a conservative prediction.

5.2.2.3 Amines, and MAF Fuels

The mixed amine fuels (with the exception of MAF-2) contain UDMH, DETA and Acetonitrile. Therefore, in the absence of extensive information in the specific blends, the toxicity of the MAF fuels must be determined from their most toxic ingredients. Since UDMH is the highest vapor pressure component, the toxicity of UDMH vapors (Section 5.2.2.2) should be the overriding consideration. Although the odor of UDMH offers sufficient warning of hazardous concentrations for short term exposure, the detectable odor is above the 8-hour MAC, and personnel should evacuate the area, or obtain respiratory protection, immediately.

DETA is an amine and it is toxic. The toxic effects are caused by both the amine vapor and the liquid itself. Irritating effects on the eyes have been observed. A maximum allowable concentration of 20 ppm (parts per million) in air has been recommended from studies made at the Jefferson Medical College. If liquid amine remains in contact with the skin, burns similar to caustic burns will result. Care should be taken to avoid contact of the liquid amines with any part of the body. Clothing contaminated with amines should be removed. The lower volatility of DETA accentuates the hazard of contact poisoning by these blends, MAF-3 being more hazardous than MAF-4 which is then more hazardous than UDMH.

The combinations of UDMH and DETA present the maximum hazard of both fuels in the blends. For this reason, the MAF-fuels are to be considered more hazardous in general than either of the constituents alone.

Acetonitrile (methyl cyanide) is a saturated aliphatic cyanide and reliable toxicological data are not available except that saturated aliphatic and aromatic cyanides when very pure are no more toxic than many chemicals commonly regarded as relatively harmless. Technical grades of methyl cyanide may contain small quantities of methyl isocyanide which is highly toxic. The quantity of this compound in MAF-1, however, is expected to be less than 1% by weight.

Studies have shown that at normal temperatures, saturated vapor concentrations of DETA produced little or no

TABLE 5.2-4
SUMMARY OF TOXIC HAZARDS OF PROPELLANTS

FUEL	UDMH(REF)	50–50(REF)	N_2H_4(REF)	MMH(REF)
• MAC (ppm) *	0.5	0.5	1.0	0.5
Odor (ppm) Detectable	6-14(4)		3.83*	1-3
• Mice LD$_{50}$ Injected mg/kg	115(8)		70(8) 57 - 62(6)	78(8)
• Mice LD$_{50}$ Orally mg/kg			59(6)	
• Mice LC$_{50}$ ppm in Air 4 hr. exposure	172(4)			
• Rats LD$_{50}$ Injected mg/kg	98 - 106(5)		55 - 59(6) 61-67(5)	26 - 30(5)
• Rats LD$_{50}$ Orally mg/kg			60(6)	
• Rats LC$_{50}$ ppm in Air 4 hr. Exposure	252(4)		200 - 630(4)	
1 hr. Exposure	1410			
• Dogs LD$_{50}$				
Injected mg/kg	60(4)			
Evap. on skin	1040(4)			
ppm in Air (4 hrs.)	111(4)			
(1 hr.)	980			
• Rabbits LD$_{50}$ Injected mg/kg				14
• Humans, LD$_{50}$ Estimated ppm in Air (4 hrs.)			570.	74.

* The recommended MAC for MHF-1, MHF-2, MHF-3, MHF-4, MHF-5, -5B, MHF-6, BAF-1185 and BA-1014 is 0.5 ppm.

toxic effects in rats exposed for eight hours. However, tests of the skin penetration of liquid with quinea pigs revealed a LD_{50} of 0.17 ml/kg (approximately 160 mg/kg).

In order of DETA concentration, the following table summarizes the hazards from MAF-fuels and DETA:

a. DETA is extremely hazardous from liquid contact, but only slightly hazardous from vapor inhalation.

b. MAF-3 is just as hazardous as DETA from the standpoint of skin contact. It is also a hazard from the standpoint of UDMH vapor inhalation, although not quite as much as for pure UDMH. The partial pressure of UDMH gas over MAF-3 is roughly one-half the partial pressure of UDMH gas over neat UDMH liquid.

c. MAF-1 and MAF-5 should be considered just as hazardous as DETA from skin contact, and in addition more hazardous than MAF-4, from UDMH vapor toxicity. The partial pressure of UDMH over MAF-1 is roughly two-thirds the vapor pressure of neat UDMH.

d. MAF-4 still must be considered as hazardous as DETA from a skin contact standpoint. The partial pressure of UDMH over MAF-4 is about three-quarters that of UDMH over pure UDMH. It, therefore, should be treated as if it were UDMH from a vapor toxicity standpoint.

No toxicity information for MAF-2 is available. MAF-2 is a blend of glycidyl/propargyl amines, and the information given for DETA should apply. In addition, MAF-2 has a lower vapor pressure than the aliphatic amines, reducing the hazard from vapor toxicity. The hazards from skin contact with the liquid, however, should be considered as great as for DETA.

5.2.3 Preventive Measures

5.2.3.1 Ammonia Safety Precautions

The following safety precautions have been simultaneously recommended by the American Standards Association, the CPIA, (Defense Dept. Handling Manual), and the manufacturers:

a. Personnel should be educated in the nature and characteristics of ammonia; in the use of all safety equipment; proper materials for contact with ammonia; and self aid and first aid.
b. Personnel shall work in groups of two or more when handling or transferring ammonia.
c. Personnel involved in transfer or handling of ammonia shall wear protective clothing of cotton or rubber, and impermeable gloves and boots. Sleeves and trouser legs should cover glove gauntlets and boots, respectively.
d. Respiratory protection such as an approved ammonia gas mask or self-contained breathing apparatus (approved by the U.S. Bureau of Mines) shall be worn if the ammonia concentration exceeds 3 percent, or in any emergency condition where the concentration is unknown, or in any confined space or oxygen-deficient atmosphere.
e. Safety showers and eye-wash facilities shall be provided close by, and these shall be inspected regularly and prior to any operation involving anhydrous ammonia.
f. Safety clothing, breathing apparatus and other equipment shall be periodically inspected and maintained in good condition.
g. Prior to operations, all transfer lines, valves, and connections shall be checked to ensure proper operation and shall be free of leaks and contamination.
h. All possible sources of ignition shall be eliminated.
i. Contaminated areas and equipment shall be immediately flushed throughly with water.
j. If a defective container or other hazardous situation arises in an inhabited area, the local police and fire authorities shall be advised of the situation immediately and steps shall be taken to remove personnel from endangered areas. The use of large quantities of water is the most effective way of reducing the vapor pressure and fire hazard from ammonia.

5.2.3.2 Hydrazine and Hydrazine Derivatives

In general, the safety precautions outlined for ammonia, above, apply equally to the use of the hydrazines and amines. It is pointed out that the MAC of hydrazine and hydrazine derivatives (Section 5.2.2.2) is much lower than for ammonia, being 1.0 ppm for hydrazine, 0.5 ppm for MMH and UDMH, and 20 ppm for neat DETA. The use of respiratory protection in the form of self-contained breathing apparatus is mandatory when necessary to work in areas where the concentration is above the MAC for prolonged periods of time.

Specific requirements for hand, foot, head, body and face protection have been derived by government and industry and are summarized below:

a. Hand and Foot Protection - Fuel and oxidizer protective gloves covered by Military Sepcification MIL-G-43196(3) shall be worn. Natural rubber, reclaimed rubber, or GR-S rubber safety shoes, or an overboot designed to be worn over regular safety footwear and high enough to fit comfortably under the legs of protective trousers, shall be worn. Contaminating agents shall be removed promptly, and the footwear shall be inspected frequently.
b. Head, Face and Body Protection - Under normal conditions, a plastic face shield, rubber or plastic wrist and arm protectors, and a rubber-type apron shall be worn. Whenever there is a possibility of gross splashing, protective clothing covered by Military Specification MIL-C-12527A shall be worn. Rubber or rubberized items of clothing impregnated with a corrosion-resisting plastic, such as Teflon or Kel-F, and vinyl-coated cotton also are approved.

5.2.4 First Aid

5.2.4.1 Ammonia

A survey of the available literature on accepted first aid procedures for ammonia and hydrazine has revealed substantial agreement between the different authoritative sources. The major differences between ammonia and hydrazine are that the vapor toxicity of ammonia is less than for hydrazine, and that extensive contact with liquid ammonia could cause freezing. The following first aid procedures are recommended for ammonia.

<u>If Ammonia Contacts the Skin or Clothing</u>: Promptly flush with copious quantities of water. Exposed areas could be effected by frostbite and/or alkali burns and should be treated accordingly. Remove contaminated clothing immediately and call a physician in cases of serious exposure. Water should be tepid if there are signs of frostbite. In facility design, safety showers should be provided at convenient locations.

<u>If Ammonia Contacts the Eyes</u>: Flush eyes with copious quantities of tepid water for approximately 15 minutes. Call a physician as soon as possible. If necessary to choose between flushing with water and seeking help, flush for 10 minutes, then seek help and then resume flushing. Do not put anything but water in the eyes.

<u>If Ammonia Vapors are Inhaled</u>: The exposed individual should try to avoid breathing until he reaches fresh air or is able to put on protective respiratory equipment. If breathing stops involuntarily, apply artifician respiration, preferably with the aid of oxygen. Call a Physician immediately in case of serious exposure.

<u>Other First Aid</u>: Due to the painfully irritating nature of high concentrations of ammonia, and the possibility of temporary blindness, a person exposed to sudden high concentrations may sustain other injuries while attempting to get clear of the area. Any such injuries should be treated accordingly and a physician should be called immediately.

5.2.4.2 Hydrazine, Substituted Hydrazines, MHF Fuels, and MAF Fuels

A survey of the most widely accepted first-aid procedures for all of the hydrazines, and the blended fuels containing hydrazine and/or hydrazine derivitives has revealed little or no difference in recommended procedures from one propellant to another. Therefore, the following procedures, common to all of the hydrazine-based fuels should be followed. The principal sources of information which were surveyed include "The Handling and Storage of Liquid Propellants," (D.D.R. & E.) 1963 (20); Olin Mathieson and FMC Corp. Product Bulletins; and the Rocketdyne "Condor Propellant Handbook" (15).

<u>If Propellant Contacts the Skin or Clothing</u>: Exposed areas should be flushed immediately with large quantities of water, and affected areas should be treated for alkali burns. It is very important that large quantities of water be used as the heat of dilution is high. Small amounts of water may cause blistering. Contaminated clothing should be removed immediately. A physician should be summoned as soon as possible. In facility design, safety showers should be provided at convenient locations.

<u>If Propellant Contacts the Eyes</u>: The eyes should be repeatedly and completely flushed with large quantities of water for approximately 15 minutes. The patient should be placed in the care of an authorized physician, preferably an Ophthalmologist, as soon as possible. If necessary to choose between flushing the eyes with water and seeking help, flush for 10 minutes, then seek help, and then resume flushing. Do not put anything but water in the eyes. (Eye-wash basins should be available at convenient locations).

<u>If Propellant Vapors are Inhaled</u>: The exposed individual should hold his breath if possible or breath in a shallow manner until fresh air is reached or until protective equipment can be put on. If breathing has stopped involuntarily, apply artificial respiration. The exposed individual should be removed immediately from further exposure, kept quiet, and be placed in the care of an authorized physician as soon as possible. In the meantime, if necessary, first aid treatment can be administered as established by the responsible medical authority. In case of convulsions, short-and-quick-acting barbiturates may be administered by a physician with due regard to depression of respiration.

5.2.4.3 DETA and Mixed Amine Fuels

Very little information is available on the first aid procedures for the MAF fuels, and DETA. It has been found, however, that first aid procedures are very similar for many propellants. Since amines are strongly poisonous by contact and by ingestion, the first aid procedures established for skin and eye contact, and ingestion of the hydrazines should be supplemented by additional flushing and washing with soap and water. In cases of vapor inhalation, the procedures for the hydrazines will apply. This is especially true of MAF-1, 3, 4 and 5 which contain UDMH and whose vaport will be predominantly UDMH.

For All Types of Exposure to DETA and MAF fuels, follow the procedures outlined in Section 5.2.4.2 for the hydrazines, and call a physician.

In Cases of Contact with liquid, it is recommended that the amount of flushing and/or washing required be increased. Washing with soap and water is recommended.

5.2.5 Detection of Fumes

Although a number of devices have been proposed from time to time for the detection of fumes of hydrazine and its derivatives, 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 for MMH and UDMH is an order of magnitude higher than the recommended MAC for an 8-hour day exposure. Further, hydrazine-type 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. (Ref. 15). Area fume-monitoring devices are described in section 5.2.7, below.

5.2.6 Leak Detection

A number of methods are available for the detection of small leaks in equipment containing ammonia, hydrazine, or hydrazine derivatives. Chemical methods depend on the rapid reaction of acid fumes with these fuels to form solid salts. The simplest method consists of a cotton swab soaked in 6 N hydrochloric acid. When brought in proximity to a leak, the HCl and amine fumes react to form a dense white smoke. A number of proprietary preparations are on the market which are more pleasant to use than hydrochloric acid, and are equally sensitive. These are supplied in plastic squeeze bottles or in aerosol cans. When sprayed on a leak they generate a copious white foam. An example is "Leak-Tec Formula No. 17 AM" made by American Gas and Chemicals, Inc., New York, N.Y. 10021. This preparation will detect ammonia leaks of as small as 0.1 ounce per year.

5.2.7 Area Monitoring

Two types of area monitor have been applied to hydrazine fume detection; the colorimetric type and the conductivity type. The colorimetric method depends on the development of a color in a reagent by exposure to hydrazine-type fumes. By comparison with standard calibrated color specimens, the vapor concentration of the unknown sample can be determined. The most frequently used reagent for hydrazine and its derivatives is p-dimethylamino benzaldehyde which develops a yellow color when exposed to hydrazine-type fumes. This reagent is specified in ASTM Standards, Part 10, 14258-8 (1961) and in Navy Specification MS 17869 (Weps), and is used in testers made by Hach Chemical Co., Ames, Iowa, and by The Mine Safety Appliance Co., Pittsburgh, Pa. The MSA Universal Tester, as an example, uses a hand pump to draw a known volume of air through a piece of filter paper treated with the reagent. The paper is then removed from the tester and compared with a color standard. It is sensitive to concentrations of 0.5 to 10 ppm of hydrazine-type fuels. It does not distinguish between hydrazine and MMH or UDMH, but this is unimportant for area monitoring purposes.

The conductivity method depends on the change in electrical conductance of a solution due to the presence of an ionizable solute. In the Toxic Gas Detector (made by Davis Instruments Div, Automatic Sprinkler Corp., Newark, N.J.) a known volume of air containing the suspected vapor is bubbled through a known volume of de-ionized water. The change in conductivity of the water unbalances a Wheatstone bridge and produces a current indication on the meter. The instrument is calibrated for various kinds of gases but will not distinguish one from another. (This, again, is not an important deficiency for an area monitoring device.)

The MSA "Billion-Aire", a continuous recording instrument based on suppression by contaminants of an alpha particle induced ion current, has been calibrated for ppm concentrations of UDMH and MMH in air.

5.2.8 Dosimeters

A colorimetric dosimeter badge was developed by the Mine Safety Appliance Co., for the USAF Aero Medical Research Laboratory, Bindone*, dispersed on Eastman Chromogram Sheet, was used as the sensing element in the badge. It produces a purple color of intensity proportional to the integrated dose. Synthetic color comparison standards were developed. The range of the badge is approximately 100 to 1800 ppm-minutes.

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*Bindone = ($\Delta^{1,2'}$ - Bindan) - 1'. 3,3' Trione

5.3 FIRE AND EXPLOSION HAZARDS

5.3 FIRE AND EXPLOSION HAZARDS

5.3.1 General

All of the fuels covered in this Handbook are flammable in air, and may ignite spontaneously in the presence of oxidizing materials. The DOD Contractors Safety Manual (Reference 19) classifies ammonia in Hazard Group I (Fire Hazard) and hydrazine, MMH, UDMH, MAF fuels, and blends of these as Hazard Group III (Fire and Explosion Hazard). Mixtures containing hydrazinium nitrate are not specifically covered in the DOD Contractors Safety Manual. However, those mixtures containing 25 percent or more of hydrazinium nitrate should be classified in Hazard Group IV (Mass Detonating Explosives).

A list of the tests conducted to evaluate the hazard potential of liquid rocket propellants is given in Table 5.3-1.

TABLE 5.3-1 LIST OF SAFETY TESTS USED TO DETERMINE FIRE AND EXPLOSION HAZARDS

TEST	USED TO DETERMINE
Drop Weight Test	Whether prop. detonates. How much energy required.
Card Gap Test	Whether prop. 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 Diam. 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 fuels follows.

5.3.2 Ammonia

5.3.2.1 General

Ammonia (anhydrous) is shipped in compressed gas cylinders, tank trucks and tank cars under the I.C.C. green label as a "nonflammable compressed gas". The flammability limits at atmospheric pressure are 16 to 25 percent by volume of ammonia in air. An ammonia-air mixture in a standard quartz bomb did not ignite spontaneously at temperatures below 850 C (1562 F). When an iron bomb, having some catalytic effect, was used, the ignition temperature was 650 C (1204 F) (Reference 14). Ammonia vapor is lighter than air; thus, a small leak in an unconfined space can be expected to disperse rapidly without building up flammable concentrations. However, large spills represent a serious fire hazard. The flammable concentration range is also broadened and the hazard increased by the presence of strong oxidizers such as liquid oxygen or nitric acid. The flammability limits of ammonia in air and in oxygen are shown in figure 5.3-1, (Reference 16).

Ammonia fires are difficult to extinguish. If possible, the first step in combating an ammonia fire is to cut off the supply of ammonia. Water in large quantities (at least 100 pounds per pound of ammonia) is the only recommended fire fighting agent. Fog nozzles or sprays are preferred to solid streams. The water acts to reduce the temperature, and also to absorb and dilute the ammonia and lower its vapor pressure. Any ammonia containers in the vicinity of the fire should be sprayed with water to keep their temperature down and avoid pressure bursting. When the fire is extinguished, continue to spray the area with water until the ammonia concentration is reduced to a safe level. (A concentration of 50 ppm is detectable by odor, but is not irritating.)

Explosion hazards with ammonia are of two distinct types: (1) pressure rupture of containers and pipelines, (2) admixtures with oxidizing chemicals.

5.3.2.2 Pressure Ruptures

The liquid density of anhydrous ammonia decreases rather rapidly with increasing temperature. Thus, if a container of ammonia is overfilled and its temperature is subsequently increased, the ullage volume can be reduced to zero and the container subjected to excessively high hydrostatic pressures due to liquid expansion. In order to prevent pressure ruptures, a number of requirements and recommended practices are called out in the regulations for design and operation of ammonia systems. Details are given

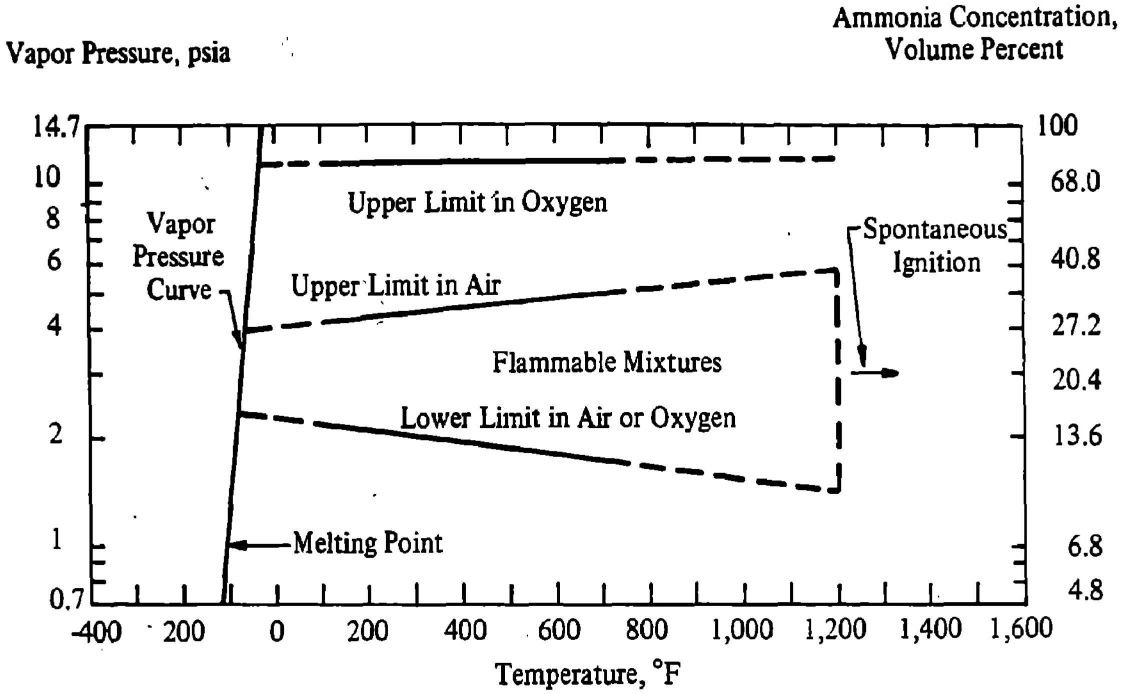

Figure 5.3-1. Flammability Characteristics Diagram of Ammonia in Air And In Oxygen at Atmospheric Pressure

in Reference 14. Briefly, the filling density of an unrefrigerated ammonia container is limited to 56 percent of the weight of water at 60 F that the container will hold, or the liquid filling volume is limited to 82 percent of the container volume. Additionally, containers are required to have one or more spring-loaded tamper-proof safety valves. Relief valves are also required in piping systems in locations where liquid may be trapped between two valves. An important warning is given in Reference 20. Great care should be exercised in manifolding two or more liquid containers together. Valves on such an installation should never be reclosed after being opened, unless it is possible to determine immediately the liquid level in each container. A slight temperature difference between two containers will cause liquid to flow from the warmer to the cooler container, possibly overfilling the latter.

5.3.2.3 Admixtures of Ammonia with Oxidizing Chemicals

Ammonia-air and ammonia-oxygen mixtures can exist without reacting, and accumulations of these mixtures in confined volumes are very hazardous. The TNT equivalent of LO_2-ammonia mixtures is 10-20 percent (Reference 19). Similarly, ammonia can react without ignition with chemicals such as mercury, halogens, nitric acids, hypochlorites, etc. forming compounds which are dangerous explosives. Ignition of these explosive mixtures may occur after a considerable amount has accumulated. These hazards can best be prevented by storing and handling ammonia in well ventilated areas free from oxidizers, oil, heat, and sparks. Any spillage of ammonia should be flushed immediately with large amounts of water fog or spray. Ammonia should never be allowed to come in direct contact with mercury (as in a manometer or a vacuum pump). An accumulation of salts around a fitting or a valve in an ammonia system is evidence of a leak and possible reaction of ammonia vapor with acid -fumes. Such salt accumulations may be hazardous and should be flushed off with water before any attempt is made to repair the leak.

5.3.3 Diethylenetriamine (DETA) and Mixed Amines

Diethylene Triamine (DETA) is not classified by I.C.C. as a dangerous article. Its flash point is variously reported as from 135 to 215 F. (This wide discrepancy is due to the fact that commercial grades of DETA may contain up to 9 percent of other amines. The purer grades will have the higher flash points.)

Since DETA is used as a blending ingredient in the MAF-series fuels, it will not be encountered in the "neat" form as a rocket propellant. The fire and explosion hazards associated with the MAF-series fuels are essentially those of the other major ingredient, UDMH.

In a fire involving one of the MAF fuels, (except MAF-2) the UDMH component will quickly burn away, leaving a much slower burning residue of DETA. Fire fighting methods are the same as those for UDMH fires, (i.e., water spray, alcohol-type foam). It has been observed that the fumes from a DETA/air fire contain significant amounts of hydrogen cyanide up to 1.5 percent. (Reference 21). When approaching a fire, either a full face gas mask with ammonia canister, or a closed breathing apparatus should be worn.

Residues from a DETA supported fire should be flushed with large quantities of water. The residues are essentially nontoxic but are strongly alkaline.

5.3.4 The Hydrazines

The flammability characteristics of hydrazine, and of the substituted hydrazines, differ significantly from those of hydrocarbons, in consequence of their endothermic composition.

The flammability regimes of anhydrous hydrazine in air are shown in Figure 5.3-2 (Reference 16), which is plotted on a grid of log vapor pressure versus temperature. The scale on the right of the figure gives the volume concentration of saturated vapor in air at one atmosphere pressure. The region in the lower left of Figure 5.3-2 is the oxidation region. Hydrazine vapor in air can be ignited (in an ASTM open cup apparatus) at a minimum temperature of 105 F, corresponding to a vapor concentration of 4.7 percent by volume. At lower temperatures, the concentration of saturated vapor in air is too low to be ignitable. For this reason, the Interstate Commerce Commission regulations classify hydrazine as a Corrosive Liquid (white label) rather than as a flammable liquid. However, liquid hydrazine will inflame when spilled on rusty iron at 75 F, and it is known to ignite spontaneously with a large number of solid and liquid oxidizers at much lower temperatures (Reference 17).

As the temperature is increased, hydrazine vapor concentrations pass through the stoichiometric mixture ratio and become fuel rich. Unlike hydrocarbon fuels, however, there is no rich mixture flammability limit. At a temperature of approximately 150 F, it is possible to sustain a decomposition flame in hydrazine vapor, even in the absence of air. The decomposition flame regime boundaries are not clearly defined, but may be considered as extending from 35 percent to 100 percent vapor concentration. In the presence of catalytic surfaces (iridium, cobalt, etc.) decomposition flames may be sustained at much lower temperatures. The spontaneous ignition temperature of hydrazine vapor in air is again very sensitive to the presence of catalytic surfaces. The Bureau of Mines (Reference 16) reports the spontaneous ignition temperature of hydrazine/air mixture as 520 F in glass, and 315 F in stainless steel (a nominally compatible material). Even at 520 F, hydrazine decomposition is principally catalytic in nature. Spontaneous ignition of hydrazine can also occur when exposed to large surface areas such as rags, cotton waste, sawdust, etc. These materials should not be kept around hydrazine storage and handling areas.

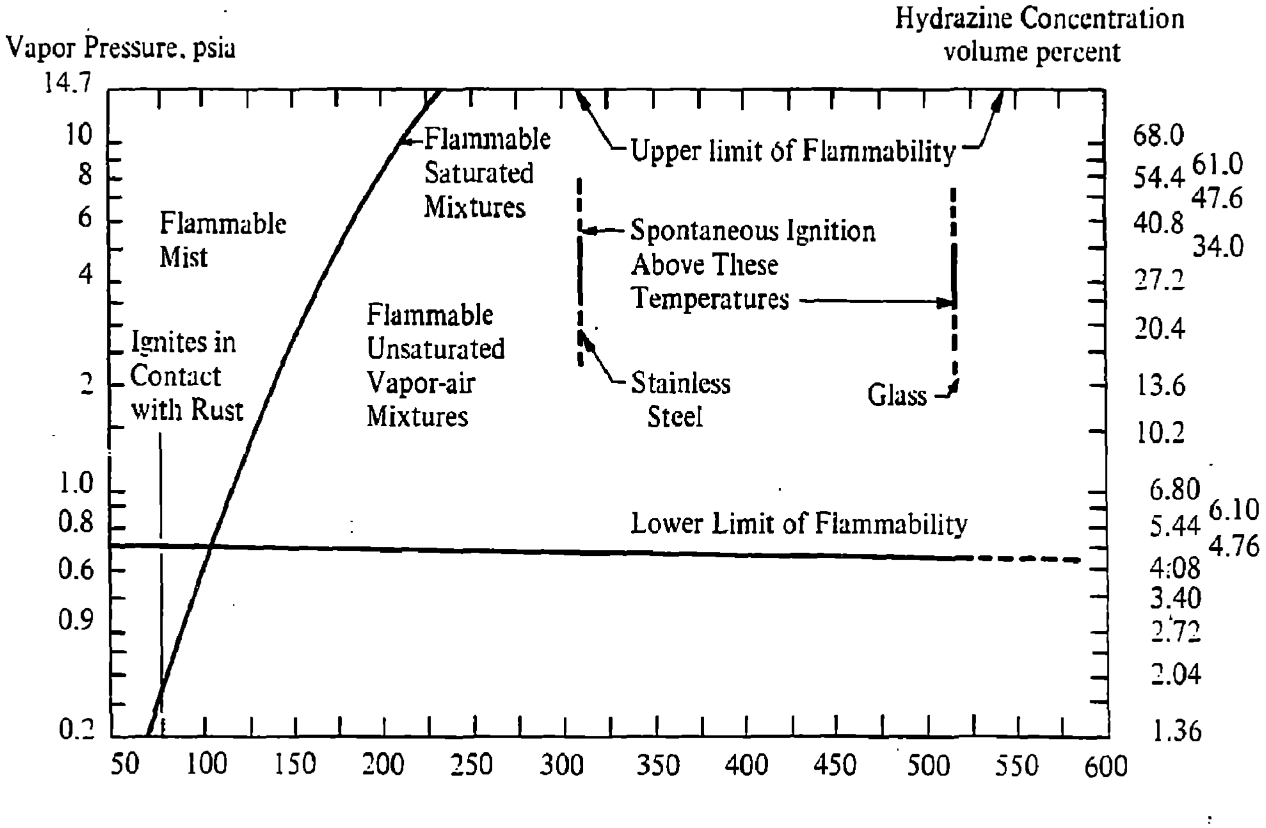

Figure 5.3-2. Flammability Characteristics Diagram of Anhydrous Hydrazine in Air at One Atm. Pressure (14.7 psia)

Dilution of hydrazine vapor will decrease its flammability, but all diluents are not equally effective. Olin Mathieson (Reference 2) recommends nitrogen as a "padding" for hydrazine in storage containers. Dilution of liquid hydrazine with water will reduce its flammability. Atlantic Research Corp. (Reference 18) reports that water solutions of hydrazine at any concentration below 40 percent cannot be ignited. A 50 percent solution will burn only near its boiling point. The flash and fire points of hydrazine-water solutions are shown in Figure 5.3-3. Carbon dioxide reacts with hydrazine vapor and does not reduce flammability. Chlorobromomethane and bromo-trifluoromethane have been found to be reactive with hydrazine.

Monomethyl hydrazine (MMH) and unsymmetrical dimethyl hydrazine (UDMH) have flammability characteristics similar to those of anhydrous hydrazine. Due to their higher volatility, both MMH and UDMH have flash points at much lower temperatures than hydrazine, and both are consequently classified by I.C.C. as flammable liquids (red label). Flammability limits of MMH and UDMH are given in Figures 5.3-4 and 5.3-5. (Reference 16.)

The presence of N_2O_4 vapors in air drastically reduces the spontaneous ignition temperatures of the hydrazine fuels. It can be seen from Figure 5.3-6 (Reference 22), that UDMH ignites spontaneously at room temperature in those N_2O_4 air mixtures containing more than 8 percent N_2O_4. Similarly MMH and hydrazine ignite spontaneously in mixtures containing more than 11 and 14 volume percent, respectively. At higher liquid temperatures, spontaneous ignition occurs at lower N_2O_4 concentrations. The effect of liquid temperature on the S.I.T. of hydrazine is shown in Figure 5.3-7.

Chemical analysis of the combustion products from air-supported fires of UDMH and MAF have revealed that these fumes contain significant amounts of hydrogen cyanide (Reference 21). This is not predicted by thermodynamic calculations, and is thus a product of incomplete reaction. Up to 1.5 percent has been observed in free air flames. When fighting a fire involving UDMH or MAF, either a full face gas mask with ammonia canister, or a closed breathing apparatus should be worn.

Investigations of fire fighting methods for hydrazine fuels have been conducted by Atlantic Research Corp. (Reference 18) and by the Bureau of Mines (Reference 23). The first step in combatting a hydrazine fire is, if possible, to isolate it from other fuel or oxidizer supplies. If plenty of water is available, a drenching water spray is an effective extinguishing agent. The water acts to cool the hydrazine and to lower its vapor concentration through formation of the hydrate. Water fogs have been found to be less effective

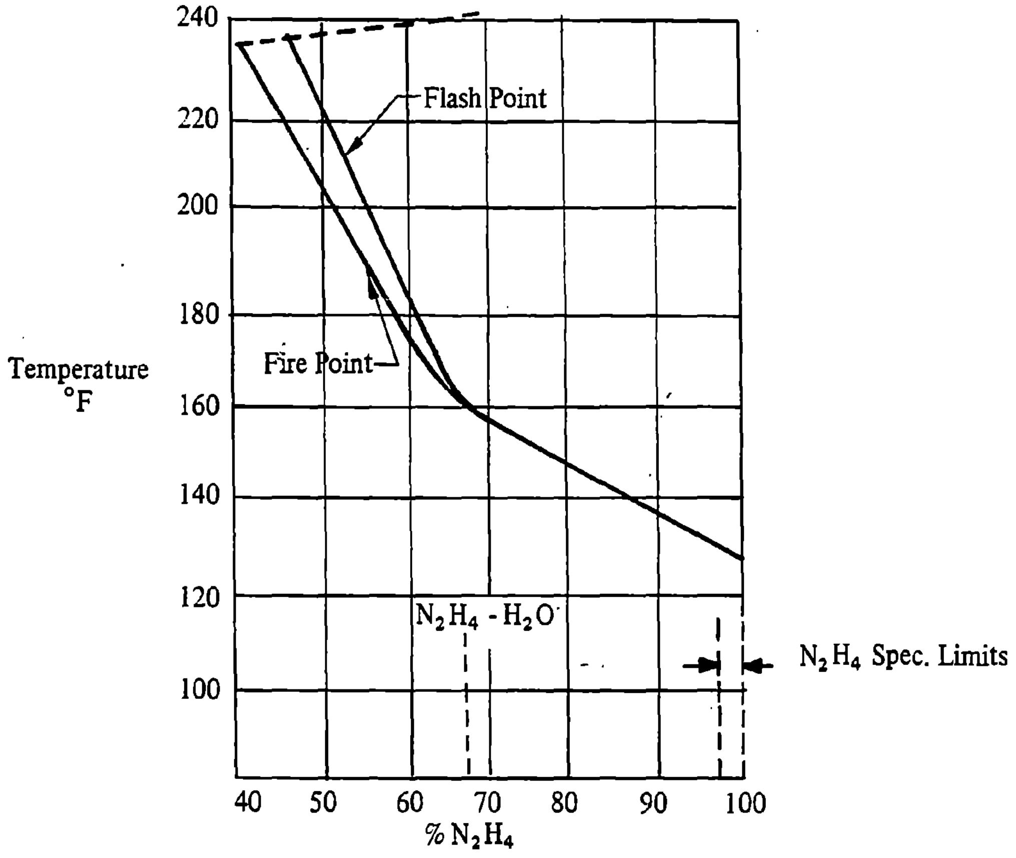

Figure 5.3-3. Flash and Fire Points of Hydrazine-Water Mixtures.

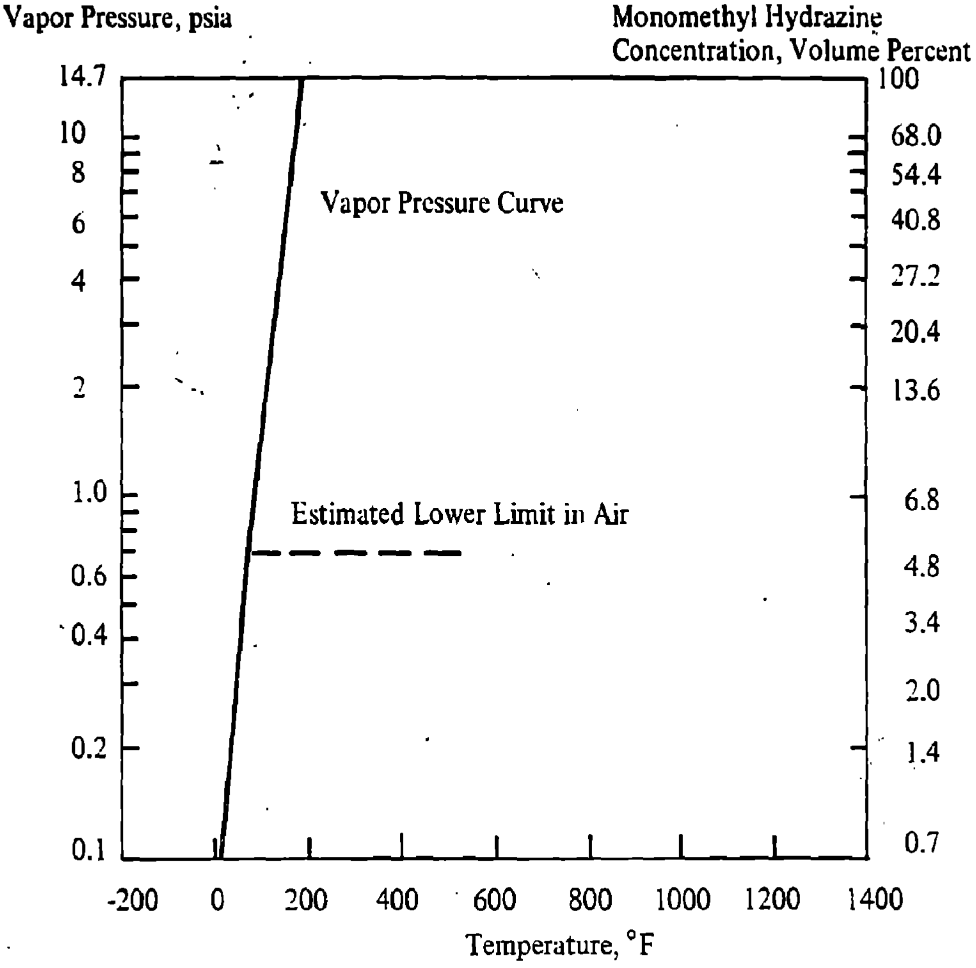

Figure 5.3-4. Flammability Characteristics Diagram of Monomethyl Hydrazine in Air at Atmospheric Pressure

than coarse sprays, because of vaporization of the water droplets in the flame. If water supplies are limited, other agents can be used. An "alcohol-type"* foam is more effective than water spray in extinguishing deep pools of burning fuel. Only about 1/3 as much water is required with the foaming agent as in a water spray for equal effect. Dry sodium bicarbonate, applied rapidly at a rate of 0.017 lb per square foot minimum is effective in extinguishing a flame. However, since it does not cool the fuel, reignition is a possibility. Carbon dioxide fire extinguishers are not effective. Halogenated hydrocarbon fire extinguishing agents react with a hydrazine flame, resulting in increased intensity and production of dense fumes. These agents are considered hazardous and are not recommended for hydrazine fires.

Fires involving hydrazine and a strong oxidizer such as nitrogen tetroxide are extremely intense and may be punctuated with vapor explosions. Such fires should be approached with extreme caution and only with adequate safety equipment. Water spray, in large quantities, is the only recommended agent for fighting such fires (References 15 and 16).

After a hydrazine fire has been extinguished, the liquid residues will still contain enough hydrazine to be a toxic hazard to animal and vegetable life. These residues must not be allowed to flow into a stream or sewer until they have been neutralized. If the residue consists of an area of earth saturated with a hydrazine/water solution, natural air oxidation can be expected to decontaminate the area within a few days. More rapid decontamination can be effected by spraying the area with a 5 percent hydrogen peroxide solution. Larger quantities of liquid residue should be contained in a holding pond. where it can be neutralized with calcium hypochlorite, chlorine, or hydrogen peroxide, before releasing into a sewer or storm drain, (See References 1 and 15).

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* A foam designed for combatting alcohol fires, as for example, Aerofoam 99, manufactured by National Foam Systems, Inc.

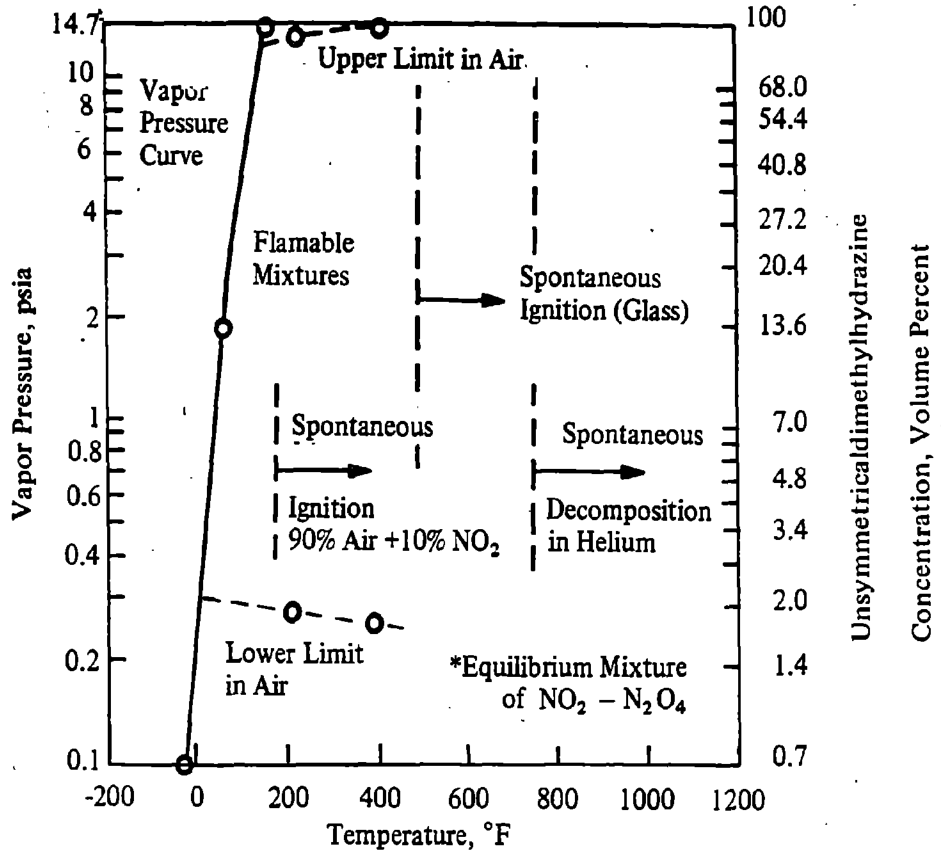

Figure 5.3-5. Flammability Characteristics Diagram of Unsymmetrical-dimethylhydrazine in Air and in Nitrogen Dioxide at Atmospheric Pressure

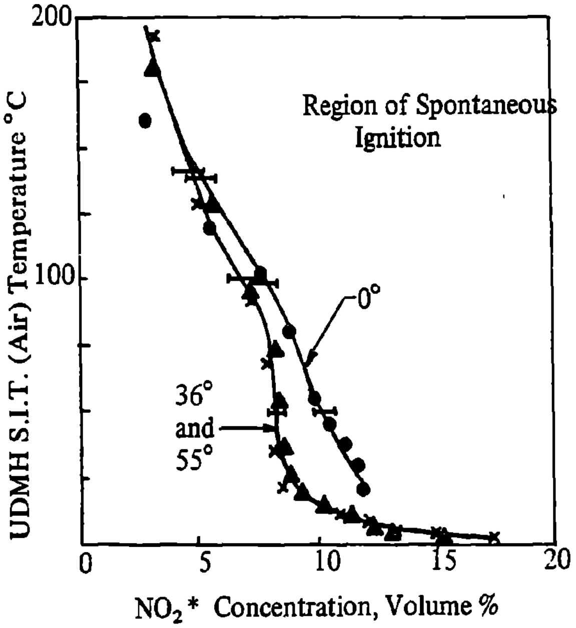

Figure 5.3-6. Minimun Spontaneous Ignition Temperatures of Liquid UDMH at Various Initial Temperatures In NO_2*-Air Mixtures at 740 ±10 mm. Hg Pressure As a Function of NO_2* Concentration

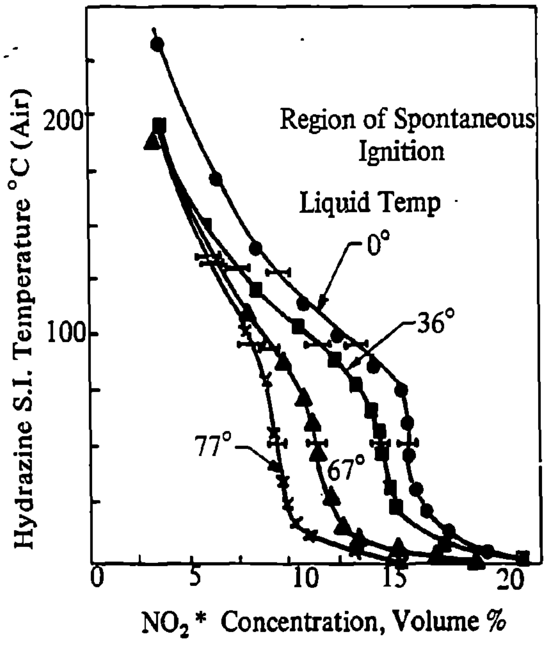

Figure 5.3-7. Minimum Spontaneous Ignition Temperatures of Liquid Hydrazine at Various Temperatures in NO_2*-Air Mixtures at 740 ±10 mm. Hg Pressure As a Function of NO_2* Concentration

5.3.5 Hydrazinium Nitrate (HN)

Hydrazinium Nitrage (HN) is an ingredient of MHF-1, MHF-2, MHF-4, MHF-5 and other fuel blends. Neat HN is a white crystalline solid; however, it is seldom encountered in this form. It is more often produced in situin solution with hydrazine or methylhydrazine.

Fires involving hydrazinium nitrate solutions are very intense, and "flare burning" is often encountered. In common with other oxidizer-supported fires, water spray in large quantities is the best fire-fighting agent.

Pan-burning tests of MHF-5 blend have been conducted by Thiokol/RMD (Reference 27). It was observed that fires of this blend could be allowed to burn to dryness without detonations. However, when fires were smothered before completion, it was observed that the residues contained higher concentration of HN than the original blend. Residues containing 70 percent or more of HN were shock sensitive and exploded in the drop-weight tester.

The detonability of the hydrazine - MMH - HN system of blends is reported in Section 3.4.4 of this Handbook. It will be noted from Figures 3.4-4 through 3.4-6 that all of the MHF-series of blends fall below the detonable range of HN content. Similarly, the detonability of the hydrazine - HN - water blends is reported in Section 3.5.4 and shown in Figure 3.5-4. From the above information, it may be concluded that the MHF-series blends (except MHF-2) and the MGGP-1 blend belong in DOD hazard classification Group III rather than Group IV.

Liquid MHF-2 blend, containing 40.2 percent HN, is believed to be detonable; however, no card-gap test data on this blend has been reported. MHF-2 should be classified in Hazard Group IV. MHF-3 contains no hydrazinium nitrate and should be classified in Hazard Group III.

Storage of solid hydrazinium nitrate or solutions containing more than 25 percent HN in hydrazine is not encouraged, since these materials are subject to the regulations for Group IV or Class 7 explosives (Reference 19).

5.3.6 Explosion Hazards

5.3.6.1 Sensitivity

Most sources agree that liquid hydrazine, MMH, and UDMH cannot be exploded by shock, friction, or electric discharge. The Bureau of Mines (Reference 24) reported that liquid hydrazine could not be detonated with a No. 10 Army detonator plus a booster charge of 20 grams of tetryl, even at 221 F. Card gap tests and trauzl block tests of the three fuels have always been negative. The authors know of no recorded cases of liquid MMH or UDMH explosions. However, the record for anhydrous hydrazine is not completely clean. Attempts to use hydrazine as a regenerative coolant have been generally unsuccessful (Reference 25, 26) due to uncontrolled thermal explosions in the cooling passages. Bell Aerosystems (Reference 26) reported two identical cases in which pressurized liquid hydrazine at 250 F was detonated by burnout of an electrically heated wire during pool boiling heat transfer tests. On the other hand, containers filled with hydrazine have been immersed in fire until they burst, without exploding. The authors conclude that, while explosion of liquid hydrazine is possible under some circumstances, it is unlikely that these circumstances would be encountered in a fire.

The vapors of hydrazine and its derivatives can be decomposed explosively by a variety of initiating mechanisms, such as flame, electric sparks, shock compression. The Bureau of Mines (Reference 23) notes that there is little question but that mixtures of UDMH with air can be detonated. If ignited, a deflagration-to-detonation transition can occur, given a sufficient volume of vapor. Overpressure ratios can be as high as 100:1 in detonations; thus, they can be very destructive. The most dangerous period occurs at the moment of ignition of vapors following a large spill. In the case of blends, the vapor phase consists almost entirely of the most volatile component. Thus, the hazards of MAF-1 should be expected to be equivalent to UDMH, and the hazards of MHF-3 should be equivalent to MMH.

The detonability and explosion hazard classification of blends containing hydrazinium nitrate is discussed above in Section 5.3.5.

5.4 REFERENCES

5.4 REFERENCES

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6.0 CATALYSTS AND CATALYTIC DECOMPOSITION

6.1 INTRODUCTION

6.1.1 GENERAL

6.1.2 TERMINOLOGY

6.1.3 MATERIAL COVERED

6.1 INTRODUCTION

6.1.1 General

The purpose of this section is to provide the handbook user with information on the stability and decomposition characteristics of the hydrazine family of propellants. Only the basic knowledge on each subject is provided in this section. References are supplied to allow more detailed information to be obtained.

6.1.2 Terminology

Propellant decomposition in this section refers to the breakdown of the basic chemical components into smaller molecular species or intrachemical reaction for multicomponent fuels as opposed to chemical reaction with other chemicals to form reaction products.

This chemical breakdown can be initiated by various means, each of which entails introduction of energy into the propellant in sufficient quantity to break the weakest chemical bonds. The energy can be supplied directly by heat, i.e., thermal, through the use of a catalyst or from a radiation source. These methods of initiating breakdown will be classified as the types of decomposition.

If the propellant decomposition occurs in the absence of foreign matter, the reaction is said to be homogeneous. If, however, it is necessary to have a second substance present to aid the reaction, such as a solid body, the reaction is considered heterogeneous.

A third factor to consider in regard to decomposition processes is whether it occurs in the liquid or vapor phase. In this section reactions occurring in both phases will be discussed.

For each type of propellant decomposition, the characteristics of the type of decomposition, past experience in this field, and existing systems in which the decomposition techniques are employed, are described. In addition the effects of impurities on each of the above factors is included in the discussion.

6.1.3 Material Covered

The thermal stability of the hydrazine fuels is a critical property. The rate of decomposition of the fuels under given conditions is a measure of their stability. The less readily they decomposed the more stable the fuel. The fuels must be sufficiently stable to enable their use in regenerative cooling, yet be able to undergo controlled decomposition in thermal bed reactors. The effect of pressure in conjunction with temperature provide a guide to the use limits of the propellants.

Since the hydrazine blend fuels are currently the most widely used for monopropellant gas generators and engines, their catalytic decomposition characteristics are critical. In this section the nature of the catalytic reactions, the types of catalysts evaluated, specific industry experience with catalysts and the effects of impurities on the decomposition reaction are reviewed.

A second type of decomposition, termed radiolytic describes the general class in which some form of radiant energy is used to induce fuel decomposition. The use of heterogeneous, or homogeneous radiolytic catalysis is discussed for use with propellants in liquid and gas phases. The different sources of radioactivity are discussed as part of the number of radiolytic systems which have been evaluated. Each of the propellants evaluated will be discussed separately.

The last type of fuel decomposition to be discussed is thermal. In the recent prepackaged propellant systems increased interest has been shown in thermal decomposition as a means of obtaining a low cost method of decomposing hydrazine and hydrazine blend fuels. The types of thermal sources, industry experience with various thermal decomposition systems and the effects of impurities on the decomposition reaction are discussed.

The discussion of thermal stability and decomposition in this section describes the work done with chemically pure propellants to evaluate their rate of decomposition as a function of temperature. The effect of other factors are mentioned, but not discussed in detail, since they are discussed in the Thermal Decomposition or Catalytic Decomposition sections.

6.2 THERMAL STABILITY AND DECOMPOSITION

6.2.1 CRITERIA OF EVALUATION

6.2.2 EFFECT OF IMPURITIES

6.2.3 INDUSTRY EXPERIENCE WITH HOMOGENOUS THERMAL DECOMPOSITION
  6.2.3.1 Hydrazine
  6.2.3.2 UDMH
  6.2.3.3 MMH
  6.2.3.4 MHF-1
  6.2.3.5 MHF-2
  6.2.3.6 MHF-3
  6.2.3.7 MHF-5

6.2 THERMAL STABILITY AND DECOMPOSITION

6.2.1 Criteria of Evaluation

There are no standarized methods for testing the thermal stability of propellants. Usually the stability of a propellant is evaluated in a bomb. equipped with a pressure measuring device which is heated in a bath at constant temperature. Observations are made of the time required for a predetermined pressure to develop. A variation of the method involves raising the temperature of the bomb at a constant predetermined rate and observing the temperature at which spontaneous decomposition occurs. Generally. the measurements are fairly crude due to uncertainty of heat transfer. and decomposition may be proceeding at a different rate. well below the temperature recorded at the decomposition temperature. Actually the temperature at which the rate of decomposition is rapid enough to give definite evidence of decomposition. in a short time interval. is measured. Further. since stability test results vary greatly depending on the material of construction of the test apparatus. these tests always include a factor of compatibility. as well as. thermal stability. This type of test may be adequate for studying the thermal stability of propellants for normal use, but may be totally inadequate as a criterion for the usefullness of propellants to be stored in packaged liquid rocket units. Even small amounts of gases irreversibly generated could be serious in a sealed propellant tank (4).

In order to provide a baseline, only the thermal stability tests performed in glass ampoules or other glass devices are considered for this discussion.

6.2.2 Effect of Impurities

There are three factors (related directly to the test specimen) which provide uncertainty into the thermal stability measurement. Two of these pertain to impurities in the propellant under study, the third pertains to the surroundings in which the propellant is in contact. In the first case the impurity is actually consumed in the reaction. This condition can be detected readily if the impurity is present in relatively small amounts. because the reaction rate will decrease before the composition of the major components has been significantly altered. Impurity catalysis is somewhat more troublesome. especially where the catalyst is unknown. It is sometimes possible to detect a catalyst impurity by comparing reaction rates of identical reaction mixtures after successive purification of each of the components. However. since the catalyst may be present only in microquantities. ordinary purification procedures may not reduce the catalyst concentration. For the purpose of avoiding the effects of impurities, effort was concentrated on purified components and on the establishment of reliable reaction rate data for extended periods of time. for all of the tests reviewed.

An evaluation of the effect of surroundings includes: varying the gaseous atmosphere in which the propellant is tested. varying the materials in which the tests are conducted. including pretreating the surfaces with the propellant as a form of passivation and varying of the surface area to volume ratio to obtain surface area effects.

6.2.3 Industry Experience with Homogeneous Thermal Decomposition

6.2.3.1 Hydrazine

Thermal stability tests have been done on hydrazine by Rocketdyne, References (4) and (39), Princeton. (3). Reaction Motors. (21) and (22). NASA Lewis. (30). Watertown Arsenal. (26). Aerojet. (15). Olin Mathieson. (48) and NOTS. (17).

The tests at Rocketdyne with purified hydrazine. ~ 100% showed that decomposition measurements at constant temperature in glass ampoules varied if the surface of the glass wasn't properly passivated. The decomposition tests with Olin Mathieson chemically purified hydrazine showed an activation energy of 19 kcal/mole. compared to RPL purified hydrazine with an activation energy of 7 kcal/mole (4d). At 275 C (527 F) tests on the purified hydrazine demonstrated average decomposition rates of 0.043% after 13 hours. Based on this it was concluded by Rocketdyne that hydrazine was inherently more stable than normally considered. however. the need for high purity was specified (4d).

Tests to evaluate the effect of gas-to-liquid ratio on propellant decomposition was performed at 128 C (262 F) by Rocketdyne (4a). using passivated glass ampoules for the propellant. The results showed that the percent of hydrazine decomposed was independent over gas-to-liquid ratios up to 30:1 (the test limits). Table 6.2-1 (Reference 4d. p. 6) shows the average decomposition rate of hydrazine in percent decomposed per hour.

Work done by Princeton (3) to evaluate the thermal decomposition of hydrazine in the presence of silica. platinum and tungsten. showed that the material used affected the hydrazine decomposition reaction. This supports previous indications that any determination of the thermal stability of hydrazine must specify the container material used.

TABLE 6.2-1 EVALUATION OF HYDRAZINE DECOMPOSITION RATE

SAMPLE	AMPOULE	TEMP	AVERAGE RATE, PERCENT DECOMPOSED PER HOUR		
			1.5 mm	2.0 mm	3.0 mm
Olin Mathieson Purified	Pyrex	171°C			0.0075
RPL Purified	Pyrex	171°C			0.0075
Olin Mathieson Purified	Pyrex	210°C	0.087	(0.065)*	(0.043)
Olin Mathieson Purified	Quartz	210°C	(0.080)	0.060	(0.040)
RPL Purified	Quartz	275°C	(0.070)	(0.052)	0.035

* Values in parenthesis are corrected for internal diameter of ampoule, assuming the rate is inversely proportional to the diameter.

Reaction Motors performed thermal stability measurements on hydrazine supplied by Olin Mathieson Chemical Corporation, which assayed at 99.6 - 99.7% pure. Experiments were performed in glassware which was scrupulously clean and had been passivated with the hydrazine. Plots of pressure rise for mercury in the manometer vs. time, were used to evaluate the rate of decomposition. The rate of pressure rise for the hydrazine at 70 C (158 F) is shown in Figure 6.2-1 (Reference 21 p. 63) for a 5% ullage system. These test results conflict with work done on a follow-on effort wherein similar stability tests were performed. The follow-on tests performed with 10% ullage showed a much greater decomposition rate, Figure 6.2-2 (Reference 22, p. 35). This is inconsistent with the effects of ullage on decomposition rate, discussed in Reference 21, but may be due to other changes in test conditions not presented.

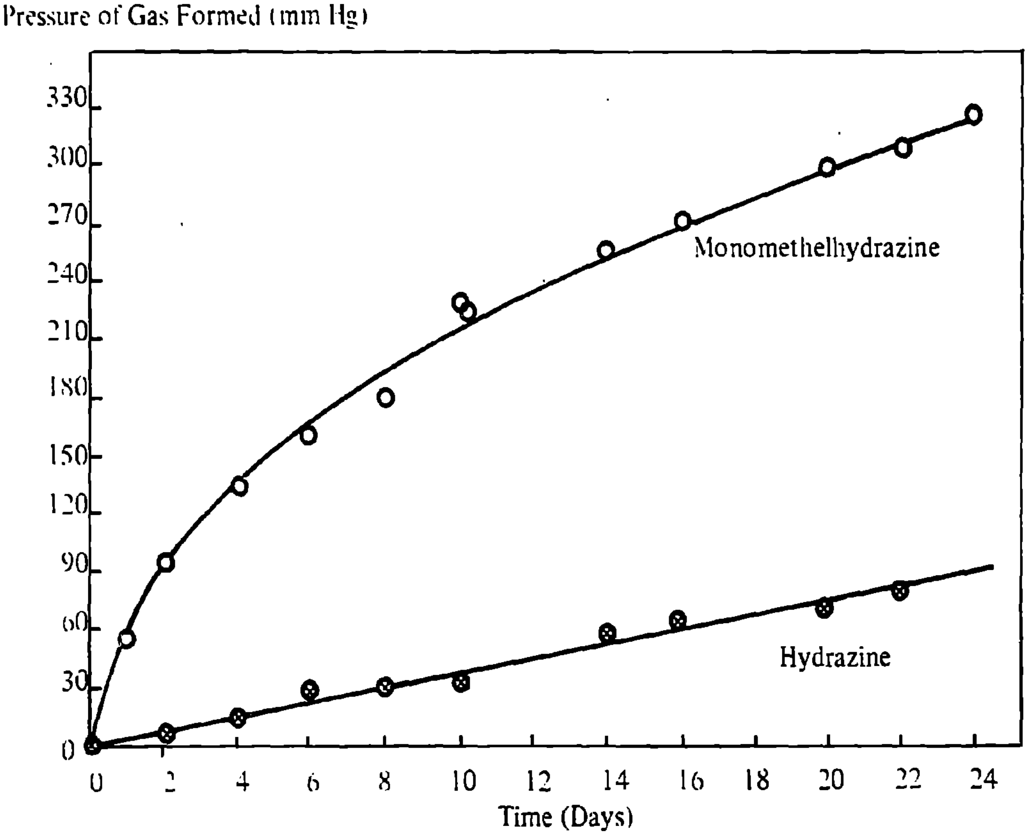


Figure 6.2-1. Rate of Gas Evolution for Monomethylhydrazine at 70°C with 5% Ullage

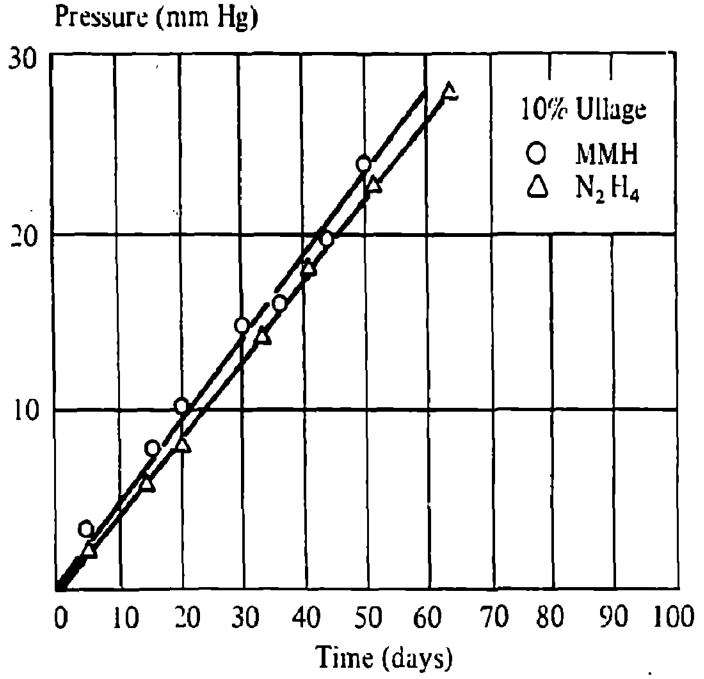


Figure 6.2-2. Rate of Decomposition of N_2H_4 and MMH at 160°F with 10% Ullage

NASA Lewis (30) used highly purified hydrazine, prepared in a nitrogen atmosphere, in outgassed Pyrex tubes, to evaluate propellant decomposition rates. The hydrazine was produced by ammonalysis of hydrazine sulfate, followed by fractional distillation. This process yielded hydrazine which was 99.90 to 100.00% pure material. Based on rate of decomposition vs. temperature evaluated over a temperature range of 175 C to 250 C, an activation energy of 72.7 kcal/mole was obtained for hydrazine. This differed significantly from the Rocketdyne work reported earlier.

Olin Mathieson (48), under subcontract to Aerojet, reviewed the literature on stability tests of hydrazine. They concluded that difficulties had been encountered in obtaining reproducible hydrazine decomposition rates, because of the uncontrolled variables of wall effects, catalysts, impurities, concentrations and methods of determining the extent of decomposition. Based on the literature survey, Olin concluded that hydrazine does not decompose at an explosive rate below 500 F. Industry experience subsequent to this report has indicated this value to be 150 F higher than the safe operating limit.

Olin stated that although there is no experimental data to establish the fact all tests indicate that homogeneous reactions occur in the liquid phase at sufficiently elevated temperatures.

The work conducted at Rocketdyne (4), discussed previously, substantiates this hypothesis in their evaluation of the effect of gas to liquid ratio on the decomposition rates Olin also stated that heterogeneous reactions are involved in the thermal decomposition of hydrazine vapor or liquid. In the absence of oxidants, explosions due to N_2H_4 instability have occurred, only when there has been a net generation of vapor in contact with a sufficiently hot surface.

6.2.3.2 UDMH

Tests to determine the ignition temperature of UDMH were conducted at NASA Lewis (45). They employed a glass flask, which was part of a National Bureau of Standards standard test apparatus. This apparatus is described in The Journal of Research for the National Bureau of Standards, Volume 53, July 1954, pages 49-66. The tests used a small charge of fuel which was sprayed into the preheated flask. Thus the test was not designed to measure decomposition of a bulk fluid. The self-ignition temperature of UDMH was determined to be 454 F, in the presence of air. The spontaneous decomposition temperature, in which air was not present was 740 F.

An evaluation was done at the Naval Ordnance Test Station (17), to evaluate the thermal decomposition of UDMH. Tests in a pyrex reactor, using a helium atmosphere, showed that the activation energy of UDMH was 28.7 kcal/mole. It was determined that the reaction was mainly controlled by the thermal energy and not surface catalysis at the wall.

No data was available in the literature pertaining to decomposition rates for this propellant.

6.2.3.3 MMH

Thiokol-RMD (21) evaluated the thermal stability of 99.55% MMH, obtained from the Dynex Chemical Corporation. Well passivated, scrupulously clean glassware was used for these tests. Figure 6.2-1 (Reference 21. p. 63) shows the rate of rise of the manometer as a function of time for MMH, with 5% ullage, at 70 C (150 F). Similar tests in a follow-on program (Reference 22) showed that at 160 F, with a 10% ullage system, the decomposition rate of MMH is 0.45 mmHg/day.

TABLE 6.2-2 COMPARISON OF THE DECOMPOSITION RATES OF MHF-1 AND MHF-1 COMPONENTS

FUEL MIXTURE	RATE* (mm Hg/DAY)
MHF-1	10.0
MMH-20% $N_2H_5NO_3$	5.0
N_2H_4-20% $N_2H_5NO_3$	1.0
N_2H_4	0.1**
MMH	0.1**
MMH-14% N_2H_4	0.3

* In an 85% ullage system at 160°F.

** Extrapolated from 10% ullage systems.

6.2.3.4 MHF-1

The only organization which conducted thermal stability evaluation of MHF-1, was Thiokol-RMD, (21, 22 and 23). Their experience indicated that samples of MHF-1 prepared from different batches of starting material had different thermal stability properties. Using the glass thermal stability apparatus filled to 20% of full volume with liquid (80% ullage), decomposition rate measurements were made at 160 F. Table 6.2-2 (Reference 23, p. 45) presents the results of these measurements. These results compare well with results obtained on earlier tests discussed in References 21 and 22.

The dependence of decomposition rate on the ullage volume of the experimental vessel was shown to be important (Reference 22). At a temperature of 160 F the decomposition rate of a fresh mixture of MHF-1 changed from 4.0 mmHg/day to 30 mmHg/day as the ullage changed from 85 to 50%. The effect of temperature on decomposition rate is shown in Table 6.2-3.

TABLE 6.2-3 MHF-1 EFFECT OF TEMPERATURE ON DECOMPOSITION RATE

	Moles gas x 10^5 Instantaneous Rate in gm. fuel-day		
Days Temp (°F)	10	20	30
200	0.73	0.61	0.40
176	0.20		
163	0.08		
140	0.05	0.04	0.03

As expected, the rate of decomposition increases with temperature at faster rates at the higher temperatures (Reference 22). Figure 6.2-3 shows the effect clearly.

The rate data shown in these tests confirmed that the rate of decomposition of fuel is relatively slow at 160 F, approximately 3 x 10^{-6} moles per day per gram of fuel.

6.2.3.5 MHF-2

The only evaluation of this propellant reported in the literature, was conducted by Thiokol-RMD (22). Although the physical properties were discussed, no details were presented on the thermal stability evaluation. Their tests at 160 F, in 85% gas volume, showed that decomposition rates of 5.4, 4.5 and 4.0 mm of Hg/day were observed after 10, 20 and 30 days of exposure respectively.

6.2.3.6 MHF-3

Thiokol-RMD (22) evaluated the thermal stability of MHF-3 in the same apparatus and test methods used for hydrazine, MMH and MHF-1. Table 6.2-4 (Reference 22, p. 37) presents a tabulation of the decomposition rates of the various hydrazine fuel blends. Based on this the MHF-3 was considered more stable than MHF-1 (10 mmHg/day versus 35 mmHg/day).

6.2.3.7 MHF-5

Thiokol-RMD performed the thermal stability evaluation on MHF-5 using the extra clean, passivated apparatus shown in Figure 6.2-4 (Reference 5, p. 43). The rate of gas evolution measured at temperatures of 100, 120 and 160 F at 6% ullage was determined. Based on the gas evolution rate as an inverse function of time, the calculated activation energy for the reaction is 19,200 cal.

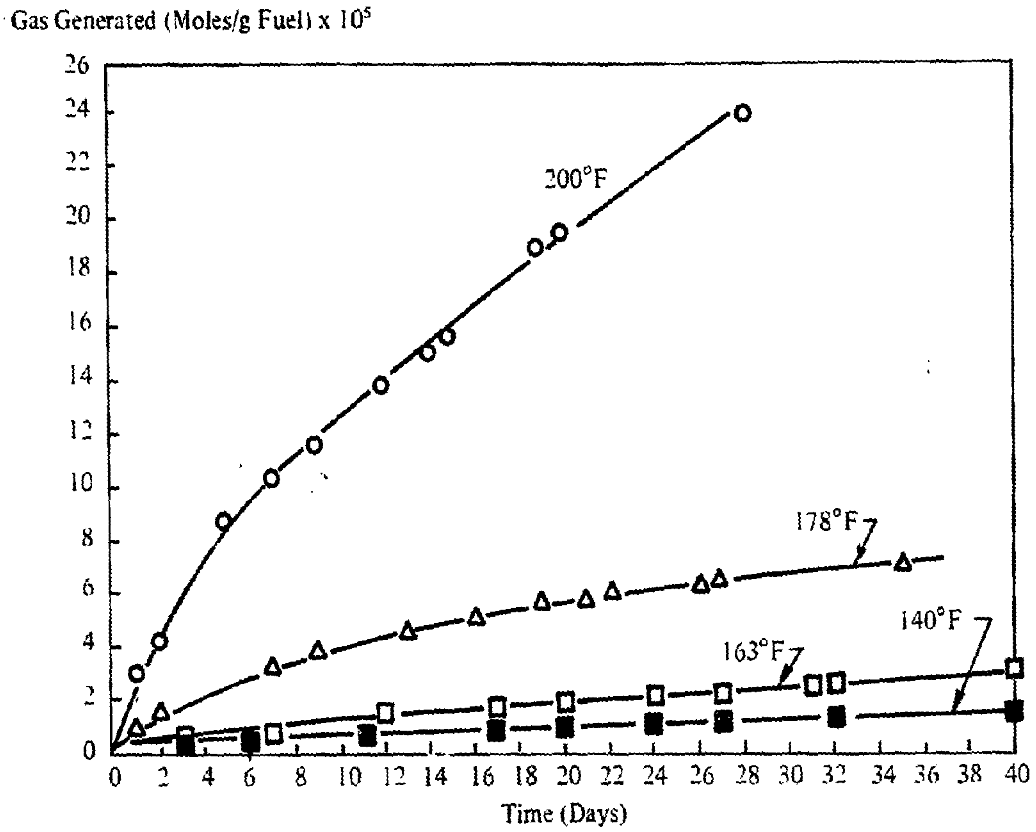
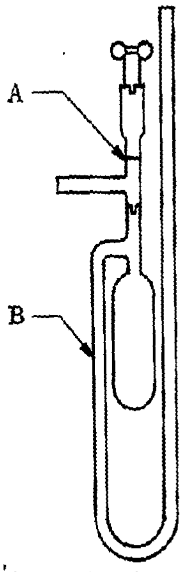


Figure 6.2-3. Rate of Gas Evolution from MHF-1 as a Function of Temperature

TABLE 6.2-4 THERMAL STABILITY OF MHF-1 AT 160°F

RUN NO.	INSTANTANEOUS RATES (mm Hg/DAY)				
	DAYS	20	40	60	80
1		1.9	1.6	1.3	1.2
2		0.9	0.9	0.8	0.8



A. Fisher & Porter Lab-Crest 4mm Needle Valve, 90° Side-Arm Sealed on Reactor Reservoir

B. Capillary Tubing 8mm OD; 2mm ID

Figure 6.2-4. Laboratory Thermal Stability Apparatus

6.3 CATALYTIC DECOMPOSITION

6.3.1 Shell 405 Systems

6.3.1.1 Introduction

The use of a catalyst to obtain decomposition of hydrazine and the hydrazine fuel blends necessitated the development of materials with very specific properties. The catalyst is divided into two parts, a support material which provides the structure for the catalyst and a transition metal which causes the decomposition process to occur in the propellant. The support material should have high crush strength, high porosity (large internal surface area), physical stability at maximum reactor temperatures, thermal shock resistance, and should be chemically inert to NH_3 and H_2 to 1200 C (2192 F). In addition the support material should have a high heat of wetting to assist starting (high surface area). Reference 1 presents a list of these desirable properties and a review of the efforts made by Shell to obtain suitable catalysts meeting these requirements. The metals which catalyze the propellant decomposition should be highly active, dispersible in a porous support, chemically stable in hot NH_3, N_2 and H_2 gases, not capable of being sintered at 2192 F and available commercially.

The large scale use of hydrazine for auxiliary propulsion systems is largely attributed to its ability to undergo catalytic initiation of decomposition. The materials which can be used to initiate this decomposition range from common iron oxide to the rare metal iridium. It is not difficult to get the hydrazine to decompose, but it is difficult to obtain a catalyst which retains its activity after reasonable periods of operation. Extensive evaluation was performed to develop catalysts which met the following criteria:

(a) able to initiate decomposition at temperatures as low as 0 F
(b) capable of repeated cold starts
(c) nonhygroscopic, to avoid absorbing atmospheric water during storage
(d) melting temperature above 2500 F
(e) ignition delay below 0.5 second
(f) adequate physical strength
(g) capable of supporting decomposition at 0.065 lb/sec-in.^{2} propellant bed loading
(h) able to obtain desired decomposition with reasonable catalyst bed length

A catalyst was developed to meet these criteria, by Shell Development Corporation, under NASA Contract NAS7-97. This catalyst was designated Shell 405. This contract ran from January 1962 to March 1964 (Reference 1). In this section a review will be presented of this program and the major developments with hydrazine.

6.3.1.2 Catalyst Development

The first user of hydrazine monopropellant reactors was the Jet Propulsion Laboratory for their Mariner engines. These reactors used a catalyst which had to be warm in order to operate. The catalyst consisted of an alumina substrate pellet with iron, cobalt and nickel deposited on it (Reference 20).

The initial heat up requirement for the JPL catalyst prevented its use in missions which required multiple restart capability. Since most ACS and space propulsion missions do require restart capability a program to develop the spontaneous catalyst was undertaken.

Shell Development Company (1) evaluated various transition metal catalysts and alumina and carbon substrates, for the ambient temperature decomposition of hydrazine. The program resulted in the availability of a catalyst which demonstrated all of the original criteria listed above. Materials which showed possible use for catalysts were: Ru-Ir, Ir, Ru, Ru-Pt and Fe-Co-Ni-Rh. In this work, other metals were evaluated and found to be incapable of providing fast spontaneous decomposition of hydrazine.

The most promising substrate material evaluated was alumina due to its high temperature capability and inertness to the high temperature decomposition products. The alumina supports were evaluated for the effects of different surface area on activity and stability.

The catalyst beds were found to vary in operation according to the size of the particles used. The smaller size of catalyst 20 - 30 mesh sieve size, provided the greatest rate of decomposition, with the highest bed pressure drop. The largest size of catalyst 1/8 in. cylindrical pellets, were the strongest substrates, providing the lowest pressure drop, with the smallest decomposition rate.

The Shell 405 catalyst currently has the best combination of desirable properties. The remainder of the section will be devoted to its use by other organizations for thrust chambers and gas generators using hydrazine.

6.3.1.3 Catalyst Properties and Handling

An extensive discussion of the properties and handling of the Shell 405 catalyst was presented by Shell (1) under laboratory and test cell conditions at sea level. TRW (6) performed evaluations on the effect of vacuum operation on the catalyst in a reactor. In addition they evaluated the effect of various operational duty cycles on the catalyst durability. All work on these evaluations was done with hydrazine fuel only.

Under contract NAS 7-97 Shell evaluated the effects of humidity, hot air and ammonia vapor on the catalyst. Table 6.3-1 (Reference 1, page 25) presents a tabulation of these tests. Apparently the presence of air at 550 C (1022 F) had a significant degrading effect after 1 hour of exposure.

Under contract NAS 7-520 TRW (46) evaluated the behavior of Shell 405 catalyst during and after exposure to extended vacuum storage, standard solvents, high and low temperatures, and oxidation/reduction cycling. Eighteen weeks vacuum storage at 10^{-6} Torr caused no apparent physical degradation of the catalyst. Methylene chloride, trichloroethylene, Freon and distilled water did not show any harmful effects on the catalyst. The bed temperature affected the start response when varied from 100 F down to 0 F. A marked decrease in start response was observed between these two temperatures. Laboratory tests by United Aircraft (7) quantified the degradation of the activity of Shell 405 catalysts resulting from heating in an inert gas or N_2, NH_3 or H_2. This quantification was in the form of measuring total surface area and available metal surface area. Hydrogen chemisorption was used to identify the available metal surface area, while N_2 absorption was used to identify the total available surface area. Detailed test results are presented in the report.

6.3.1.4 Applications of Catalyst Systems

Shortly after Shell developed the 405 catalyst, development programs and in-house studies were performed to evaluate its capabilities in reactors. An extensive program was performed by Rocket Research Corp. (41) and (42) under NASA Contract NAS 7-372 to develop design and scaling criteria for monopropellant hydrazine reactors, employing Shell 405 spontaneous catalyst. A brief review of the important considerations covered in this work is presented here.

The number of injection holes, the distribution of the injection holes the distance of the injector face from the catalyst bed and the optimum injector pressure drop were determined. Various arrangements of the different size catalyst material, i.e., 20 - 30 mesh and 1/8 in. pellets, were evaluated. The optimum bed length for obtaining hydrazine decomposition was evaluated, with the consideration of pressure drop as a function of bed length included. The relation of injection velocity to start response was investigated. This was associated with the injection flow rates and overall bed loadings on the catalyst bed (flow rate divided by cross-sectional area of bed). The important outcomes of this program, plus input from the experience of other investigators will be discussed in the reactor design section.

An analytical study was performed by United Aircraft on catalytic reactors for hydrazine decomposition (28). The study included the development of computer

TABLE 6.3-1 SUMMARY OF EXPOSURE TESTS OF SHELL 405 CATALYST

CATALYST TREATMENT	RESULTS
Moist air (100% relative humidity) for 24 hours. (8.1% w gain).	An increased delay was observed on first shot (42→155 msec). Second shot was normal.
Dry CO_2 gas, 1 hour (1% w gain).	Fired OK. First shot obscured by leaky feed valve. Second shot normal.
Radiation (10^8 rads gamma rays from Co source).	No effect.
Sodium from 1 N NaOH (1% Na on Catalyst).	No effect for first 8 shots. At 9th shot, delay was somewhat longer, and at 10th shot much longer than normal.
SO_2 absorbed on catalyst from stream of N_2 containing 1% SO_2. (1% SO_2 on Catalyst).	The first shot was normal except for slightly high bed temperature. The second shot had a long ignition delay of 552 msec indicating poisoning.
Air at 200°C, 1 hour.	No effect.
Air at 550°C, 1 hour.	Did not fire cold. Fired when warm but slow (183 msec). Much catalyst broken.
Air at 550°C, then reduced with H_2 at 550°C.	Fired cold, but with delays 2-3 times normal.
Absorbed ammonia 1.5% w gain from NH_3 stream.	Slightly longer delay for first shot, second shot normal.
Ammonia flush between shots (100% NH_3 stream).	Somewhat increased delays when fired at ambient temperature. Much longer delay when fired cold. The effect was temporary. Firing restored catalyst.

programs to calculate the temperature and reactant concentration distributions as functions of time and axial position in typical reaction chamber configurations. The computer model considers both thermal and catalytic decomposition of reactants, along with simultaneous heat and mass transfer between the free-gas phase and the gas within the pores of the catalyst pellets. Correlation was made between the test data and the program.

The two major monopropellant hydrazine engine development programs undertaken with Shell 405 catalyst were performed by Rocket Research Corporation and Hamilton Standard (43) and (29). Both of these programs were performed to develop 23 lbf monopropellant thrustors for advanced post boost propulsion applications.

Flightweight engines fabricated and tested by RRC (43) were used to evaluate steady state operation, pulse mode reproducibility, thermal environment effects and start response capability. Pulse widths of 10, 30, 90 and 240 milliseconds were demonstrated at duty cycles ranging from 88% down to 0.6%. The engine performance was evaluated for the various duty cycles. The testing included maintenance of 400 F maximum outer wall temperature and injector operation at 1200 F stabilized temperature. Vibration tests of the system were included in the evaluation series.

Hamilton Standard (29) subjected their flightweight engines to the following tests: sea level and vacuum performance, fuel temperature limit testing, "buried" configuration tests, vacuum thermal tests, vibration tests and valve response tests. The pulse and thermal duty cycles were similar to those performed by Rocket Research which were described above.

The reports on both of these programs contain oscillograph traces and detailed data on the test results.

6.3.2 Other Catalyst Systems

6.3.2.1 Introduction

Although the Shell 405 catalyst system has higher desirable properties, it uses iridium, which is a strategic metal, as the catalyst. This factor led to exploratory programs to develop other catalysts which were adequate to meet limited mission requirements. In addition work was conducted with propellants other than hydrazine to develop systems which operate at -65 F for military applications.

6.3.2.2 Catalyst Development

Catalyst systems evaluated for hydrazine and its blends employed the following substrate materials: Al_2O_3, Al_2O_3 + 6% SiO_2, MgO and other refractory oxides. Metals used for catalysts included: a cobalt-nickel combination, ruthenium and a ruthenium - platinum combination. A brief review of hydrazine decomposition programs with these catalysts is presented, followed by a review of decomposition programs with propellants other than N_2H_4.

6.3.2.3 Hydrazine/Catalyst Systems

The earliest catalyst development program, in which hydrazine was decomposed in a monopropellant reactor, was performed by JPL. Under this program an iron-nickel-cobalt combination was deposited on aluminum oxide pellets to form a catalyst system that needed heat for restarts. A hypergolic start using an N_2O_4 slug to initially decompose the hydrazine and heat up the bed, was used for the early Ranger and Mariner Thrustors.

In order to alleviate the need for the hypergolic starts, yet retain the ability to get warm bed restarts, Shell Development Company used ruthenium as a catalyst. The ruthenium is less expensive than the iridium, but it does not provide the indefinite cold start capability. This catalyst, designated Shell-X in the commercial version, therefore, is adequate for limited types of duty cycles.

The Air Force has undertaken an effort with the Esso Research and Engineering Company (47) to develop a low cost catalyst. Development efforts led to the conclusion that the rhuthenium metal on a PTN (Esso proprietary designation), MgO or Al_2O_3 substrate presented the most promising approach. Although none of these systems demonstrated the unlimited restart capability of Shell 405, the ruthenium - aluminum oxide system did demonstrate ten cold starts. Rocket Research (27) attempted to fabricate a stronger version of the Shell 405 catalyst, by sintering the granular beds into a single unit. Although there was some increase in strength the final product had a high pressure drop and could not reproducibily be fabricated.

6.3.2.4 Hydrazine - Hydrazine Nitrate/Catalyst Systems

An effort to develop a higher performing monopropellant/catalyst system was performed by Shell Development Company (2) under an AFRPL Contract. This program was conducted with hydrazine-hydrazine nitrate propellant and an Al_2O_3 catalyst. Tests showed that the high temperatures developed during the propellant decomposition caused partial sintering of the catalyst with a loss of macro surface area. The incorporation of SiO_2 into the substrate, between 6 and 10 percent, provided a system with improved stability.

6.3.2.5 MGGP-1/Catalyst System

The Naval Ordnance Test Station (12) performed a program to define the parameters controlling the catalytic decomposition of hydrazine blends at -65 F. Tests demonstrated that starts could be obtained with Shell 405 and the propellant at -65 F, however, the start response traces were erratic. Increased bed length caused an increase in the ignition delay and a decrease in exhaust gas temperature, which is similar to the results obtained from pure hydrazine. Mass flux values as high as 0.156 $lb/sec\text{-}in^2$ were demonstrated for the reactors. Catalysts evaluated were iridium on Harshaw 1404 alumina support, iridium-ruthenium metal on extruded carbon support and a combination of both. Detailed discussion of the performance with each of these catalysts is presented in the report.

6.4 RADIOLYTIC DECOMPOSITION

6.4 RADIOLYTIC DECOMPOSITION

6.4.1 Introduction

The process of decomposing the hydrazine fuels requires an initiating energy source. In the case of radiolytic decomposition the energy may come from one of several types of sources. These include energy from the sun, the Van Allen radiation belt, isotope radioactive decay, and leakage from nuclear reactors used in space propulsion. In order to understand the interaction between the radiation source and the propellant, a brief review is presented below of the terminology encountered in the literature (19). The energy source will deliver its dose of radiation in units called roentgens (r). This unit is defined as the quantity of X or gamma rays which will produce, as a consequence of ionization, one electrostatic unit of electricity which is 3.3 x 10^{10} coulombs of electricity. The coulomb is defined as the charge accruing from the flow of one ampere of electricity for one second. These values are based on 1 cc of dry air as measured at 0 C (32 F) and 1 atmosphere pressure. Since a singly charged ion carries 4.80 x 10^{10} electrostatic units, 1 roentgen, forms 2.08 x 10^9 ion pairs in 1 cc of dry air. In terms of standard electrical units, each ion pair requires about 32.5 electron volts (ev) for formation. The absorption of this energy is defined by another unit, the rad. The rad is defined as 100 ergs/gm of material.

6.4.2 Industry Experience

6.4.2.1 Hydrazine

NASA Lewis (31) performed evaluations on the effects of ionizing radiation on the space stability of chemical rocket propellants. The program consisted of a survey of the effects of X-rays (0.1 to 1.0 angstroms) on liquid and vapor samples of N_2H_4 in borosilicate glassware at room temperature. Intensities of 1 x 10^2 to 1 x 10^3 roentgens per minute were imposed on the samples. The liquid samples had 0.9 percent N_2H_4 decomposition from a total dose absorption of 9.5 x 10^5 rads. The vapor samples had 3 percent decomposition from a total dose absorption of 13 x 10^5 rads. These results confirmed earlier tests by NASA Lewis (30) on hydrazine vapor radiated with a dose of 590 kilo roentgens.

6.4.2.2 Monomethylhydrazine (MMH)

Aerojet - General Corporation (50) conducted a program to evaluate the effects of reaction radiation from a nuclear space propulsion system on monomethylhydrazine propellant. As part of this program samples of MMH in Type 304 stainless steel capsules were radiated with 1 x 10^8 roentgens at ambient temperature and pressure. There was a significant pressure buildup in the container, with approximately 21 ml of gas being produced per ml of liquid, based on 1 atmosphere pressure and 77 F temperature. Decomposition gas analysis revealed 28 mole % H_2, 41 mole % N_2, and 31 mole % CH_4; with minor amounts of oxygen, ammonia, and MMH vapor. This decomposition corresponded to 4.5% decrease in pure MMH.

6.4.2.3 UDMH

The Naval Radiological Defense Laboratory (44) performed tests to develop decomposition suppression methods for irradiated UDMH. When a 100 ml sample of propellant absorbed 8.5 x 10^6 rads an average of 199.0 ml of total off-gas was generated at 25 C, 1 atmosphere. The decomposition products were 48.6% H_2, 45% N_2, and 6.4% CH_4. The use of methyl methacrylate scavenger reduced the off-gas volumes by 18.2%.

A literature search referenced in the report revealed that UDMH has been shown to decompose by 8% when gamma-irradiated to 1.2 x 18^8 roentgens.

As discussed previously in reference to hydrazine, NASA Lewis performed evaluations on the effects of ionizing radiation on the space storability of UDMH propellant. The program consisted of a survey of the effects of X-rays on liquid and vapor samples of UDMH in borosilicate glassware at room temperature and intensities of 1.0 x 10^2 to 1 x 10^3 roentgens per minute. With a 7.5 x 10^5 rads absorbed dose, on a 1.20 gm sample, the decomposition of UDMH was 4.7%. The major products from the UDMH were N_2, H_2, NH_3, N_2H_4, CH_3-NH_2, and $(CH_3)_2NH$.

6.4.2.4 N_2H_4/UDMH (50-50)

This Aerojet Program was oriented towards evaluation of the radiation effects on N_2H_4/UDMH fuel, when kept exposed to the radiation from a space propulsion nuclear reactor (Reference 50). A literature search, performed at the beginning of the program, revealed that earlier work had been done with Cobalt 60 gamma radiation of 50-50 and its individual constituents. Samples of the 50-50 in 2 ml glass ampoules were subjected to 10^7 rads over a period of time, with no significant decomposition experienced.

On the Aerojet program, samples were sealed in stainless steel containers, in 100 ml lots, then subjected to radiation rates ranging from 1.2 x 10^6 roentgens/hr to 1.7 x 10^6 roentgens/hr. The samples had experienced only a 0.4 percent decomposition after this exposure, indicating little problem existed from this type of radiation and level. Physical properties of the propellant were measured and presented in the report.

6.4.3 Summary

Although there is a potential benefit to be gained from the use of radiation as a means of decomposing monopropellants, all work reported to date shows that work has been oriented in the other direction. As nuclear propulsion is given greater consideration for actual missions and becomes a more active field, more effort may be placed on the use of nuclear energy as an energy source for the controlled decomposition of monopropellants.

6.5 THERMAL DECOMPOSITION OF HYDRAZINE FUELS

6.5 THERMAL DECOMPOSITION OF HYDRAZINE FUELS

6.5.1 Introduction

The potential use of the hydrazine fuels for gas generators and attitude control thrusters has been increased through the development of thermal beds. These beds use an outside source of heat to cause decomposition of the initial slug of fuel, which is sustained by the exothermic decomposition of the subsequent fuel flows entering the heated chamber. The propellants which have been evaluated in thermal bed tests were: hydrazine, MMH, UDMH, MHF-3 and MHF-5.

The heat sources evaluated by industry include: electric heating coils, solid propellant grain exhaust gases, solid oxidizers, liquid hypergolic slugs and a catalytic top layer of decomposition bed. The thermal beds used include: firebrick, hot chamber walls, porous ceramic structures, metallic spheres and metallic wire screens. The injectors used for delivering the propellant were: showerhead, vortex, spray and staged tube types. In this section the industry experience with each of the propellants will be discussed, regarding the initiators used, the types of beds, the types of injectors and the test results.

6.5.2 Industry Experience

Although the freezing point requirements for military application negate the use of neat hydrazine as a monopropellant, it was used for thermal bed testing as a convenient baseline. The experience gained with this propellant will be discussed first, followed by a discussion of the other propellants.

6.5.2.1 Hydrazine

Thermal bed testing was conducted with hydrazine by TRW (34), the Naval Weapons Center, China Lake, California, (14) and the Army Missile Command, Huntsville, Alabama (9).

TRW performed preliminary tests with a Nichrome wire and a wound steel coil in a reaction chamber, to determine the temperature required to initiate the hydrazine decomposition. Using a 50 in.^{3} stainless steel chamber, the minimum temperature of 1000 F was required before the hydrazine decomposition could be sustained.

Oxidizer ignition tests were performed with an N_2O_4 slug initiation. The ratio of N_2O_4 to injected hydrazine was between 0.4 to 0.6, with an initial burst of oxidizer lasting for 0.3 to 0.6 seconds. Bed loading for this test was approximately 0.006 lb/sec in.^{2}. The longest duration demonstrated was 25 minutes.

The Naval Weapons Center did an extensive amount of test and development effort on the thermal bed gas generators, for a bootstrap, positive expulsion system. I_2O_5, a solid powder, was used as the initiator. Since this material is hygroscopic, it must be sealed in plastic or coated, prior to use, to prevent deterioration from atmospheric moisture. The I_2O_5 was placed in an initiator cup, between the injector face and the thermal bed. The bed material for these tests was alumina 1/8-in. pellets. Bed loadings of 0.4 lbs/sec-in.^{2} were demonstrated during 20 seconds of pulsing operation. Since most of the thermal bed work done by the Navy used mixed hydrazine fuel propellants further test work is described in the sections on MHF-3 and MHF-5 fuels.

The Army Missile Command at Huntsville (9) did extensive thermal bed testing to evaluate the best system of initiation, bed material and injector configuration for a bootstrap variable demand gas generator system. Oxidizers tested included $KMnO_4$, I_2O_5, HIO_3, and mixtures of I_2O_5 and $KMnO_4$. Data are presented on the amount of initiator used for different bed loadings with hydrazine propellant and a firebrick bed. A more detailed discussion of this organization's work is presented in Reference 8. In this report, a more comprehensive list of oxidizers evaluated in laboratory drop tests is presented. This includes metal additives in the $KMnO_4$ and chromic oxides. In addition, different methods of depositing the oxidizing initiator on the thermal bed were evaluated. The two types of thermal bed materials evaluated by the AMC were K-26 firebrick supplied by Babcock and Wilcox and porous honeycomb ceramic, designated Torvex, by DuPont.

The subscale thermal bed tests performed by the Army used showerhead and spray-type injectors. Test results for the firebrick with I_2O_5 initiator showed the need for axially drilled holes, which provided improved flow distribution to the oxidizer. Equations are presented for the design of the thermal beds which are closely related to catalyst bed designs. This subject is discussed in the reactor design section.

6.5.2.2 MHF-3

In order to overcome the high freezing point problem of hydrazine and meet the -65 F starting requirements of the Air Force and Navy, the MHF-3 propellant was developed. With this goal in mind, Thiokol-RMD performed an extensive program to develop a thermal bed gas generator system to be used with this propellant. (References 10 and 18).

The MHF-3 thermal bed tests, described in Reference 18, incorporated starts with solid propellant cartridge grains or solid oxidizer initiators. The solid propellant was Minuteman-type propellant (70% AP, 10% Al/20% PBAA), which decomposed to provide hot exhaust gases to ignite the initial flow of fuel. The solid oxidizer employed was I_2O_5 powder, which was sealed in a thin polyethylene bag and located at the injector face, upstream of the thermal bed. The polyethylene bag was used to prevent moisture absorbtion by the I_2O_5 during storage. The evaluation of alternate initiator sources is discussed in the report.

The thermal bed materials evaluated were copper, stainless steel and porcelain. The test results indicated no discernable difference in bed temperature profiles with any of the materials. The test reactor used was 1.08-inch diameter, 4 inches long. Bed flowrates up to 0.02 lb/sec were demonstrated, yielding 0.0218 lb/sec in^2 bed loading.

Using a copper bed with I_2O_5 initiator, in an uninsulated bed, a maximum unit shutdown period of 17 minutes was demonstrated. Details of over one hundred tests with varying hardware parameters, are presented in the report.

Under the "Monopropellant Gas Generator" Program sponsored by the Navy, RMD (10) performed system development effort. In these tests only I_2O_5 was used as the initiator, with spheres as the thermal bed. The use of 5 grams of I_2O_5 powder, sealed in polyethylene bags, is discussed, relative to the short ignition delays, (less than 0.150 seconds) and the pressurization cycles. Spray cone nozzles were used for the MHF-3 injection.

Since most of Ref. 10 is oriented toward the expulsion cycle, more emphasis is placed on the gas generator operation in the system, than as a single component. A solid squib initiator was used for prepressurizing the ullage into which the gas generator fires. Results of approximately 50 tests are presented in the reports.

A NOTS Program (35) involving an N_2H_4 thermal bed also included test work with MHF-3 propellant. Of these two tests, one was an on/off duty cycle with a maximum off time of 181 seconds, while the second test performed was a 57 second steady state test. The maximum bed loading demonstrated was 0.025 lb/sec-in^2 at 970 psia chamber pressure.

6.5.2.3 MHF-5

A program to develop a bootstrap monopropellant thermal bed gas generator system was performed by the Naval Weapons Center, China Lake (14).

The MHF-5 tests were performed with a 3.2-inch diameter x 4.0-inch long bed, which used an I_2O_5 initiator inserted upstream of Monel spheres. Up to 50 grams of I_2O_5 starter was tested with bed loadings up to 0.40 lb/sec-in^2 in steady state. The maximum pulse bed loading demonstrated was 0.45 lb/in^2-sec. A series of 52 tests are discussed with the gas generator part of the bootstrap system. All of the high bed loadings were obtained with a distributed flow-type (staged) injector.

During this program, a 60 second steady state run, restart capability with bed temperatures as low as 700 F and a five-to-one throttling capability were demonstrated.

Thermal beds using MHF-5 propellant were evaluated by Thiokol-RMD (18 and 10b). This program demonstrated the effect of bed length on bed temperature profile. Bed materials evaluated were: Harshaw HA-3 nickel catalyst pellets, copper, stainless steel, and porcelain. During this test program, the ability of MHF-5 to operate with a shorter bed length than MHF-3 was demonstrated.

6.5.2.4 UDMH

A program was conducted by JPL (37) to evaluate thermal decomposition of UDMH to enable this low freezing point propellant to be used in a system. Smooth reliable thermal decomposition was obtained with a chamber having a characteristic length (L*) of 5000 in. C* values around 3200 ft/sec were demonstrated at 300 psia chamber pressure. Using fuel that was not preheated, the minimum L* in which decomposition was sustained was 2100 in. Although carbon deposits were present from the exhaust products, the percent produced was below the predicted values, based on thermodynamic calculations.

6.6 REACTOR DESIGN TECHNOLOGY

6.6.1 CATALYST ROCKET ENGINES AND GAS GENERATORS DESIGN TECHNOLOGY

6.6.2 THERMAL BED GAS GENERATOR TECHNOLOGY

6.6 REACTOR DESIGN TECHNOLOGY

6.6.1 Catalyst Rocket Engines and Gas Generators Design Technology

Although the design of monopropellant reactors is still an art, enough experience has been gained to document the critical factors in reactor design. An intensive design study was performed by Rocket Research Corporation (41, 42) to obtain design and scaling criteria for monopropellant hydrazine rocket engines and gas generators. The Army Missile Command (8) performed a development program with various propellants, initiators, and thermal beds to establish thermal bed design criteria. A summary of the primary conclusions reached from each of the programs is presented in this section.

Rocket Research Corporation (41, 42) performed an experimental and analytical study of engine operation at thrust levels of 0.5, 5, and 50 lbf. Based on this program, a number of empirical equations relating basic engine parameters were derived.

Since only the showerhead injector scheme was evaluated, the injector discussion will be limited to this type. However, other organizations have successfully demonstrated thrustor operation with spray nozzles and staged injectors. Injector pressure drops of 10 - 20 percent of chamber pressure were adequate in obtaining stable operation. Although performance and start response are not greatly affected by the number of injection orifices, consideration must be given to localized flow per area of bed and the time lag in propellant distribution. If the flow per area of bed is too great, the catalyst bed will degrade. However, if there are too many flow distribution channels to a large number of orifices, the fill time will adversely affect the start response.

The size of 405 catalyst used was found to influence the performance, start response, pressure drop, durability, and stability of the thrustor. The smaller particles provide faster decomposition rates, with higher performance per unit bed length. Since they provide a larger surface area, there is also a greater pressure drop as the particles get smaller, accompanied by increased pressure stability. Tests showed a direct degradation in chamber stability when the top layer of the bed was changed from granular, 20 - 30 mesh size catalyst, to 1/8-inch pellets. Therefore, smaller size catalyst should be kept at the top of the bed. The optimum bed length found by Rocket Research depended on the overall thrustor size. The catalyst particle diameter should be less than 1/8 the diameter of the reactor inside wall to get good bed packing. For beds using two layers of catalyst, the granular size catalyst should be approximately 2-inches long. The exact size depends on the thrust level, but the maximum length of fine mesh should be 0.3-inch. The pellets should be used in adequate amounts to provide the desired degree of decomposition as indicated by the temperature and composition of the N_2H_4 decomposition gases.

Based on general experience in the industry, current state-of-the-art engines, using showerhead injectors, should use long duration bed loading of about 0.045 lb/sec of propellant per square inch of catalyst bed. Injectors using tubes feeding into the catalyst bed allow "staged" operation, in which propellant is simultaneously fed into the catalyst bed at different locations along its length. These staged injectors can operate at higher bed loadings, approaching 0.2 lb/sec-in^2.

The Rocket Research Corp. reports (41, 42) provide data for calculating catalyst bed length and pressure drops with known bed configurations.

6.6.2 Thermal Bed Gas Generator Technology

The majority of the literature available on the design of thermal bed gas generators is from the Naval Ordnance Test Station (14, 35) the Army Missile Command (8, 9), and Reaction Motors Division of Thiokol Chemical Corporation (10, 18). Each of these organizations has evaluated various types of initiators, injector configurations and bed materials. An attempt by the Army Missile Command (8) to define design equations for the thermal bed showed they were basically the same as developed by Rocket Research for the Shell 405 catalytic bed.

An overall review of the work conducted in the field shows that the best available designs (highest bed loading and start response configurations) use a staged injector, with I_2O_5 initiator and ceramic or steel balls. The reports referenced above provide an excellent review of the state-of-the-art efforts in thermal bed design.

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6.7 REFERENCES

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7.0 APPENDICES

7.1 INDEX OF PROPELLANTS, ACRONYMS AND COMPOSITIONS

FUEL	COMPOSITION OR FORMULA	OTHER NAMES	SECTIONS
			(PROPERTIES)
Ammonia	NH_3		2.1
DETA	$C_4N_3H_{13}$	Diethylenetriamine	2.2
Hydrazine	N_2H_4		2.3
MMH	$N_3H_3CH_3$	Methylhydrazine	2.4
UDMH	$N_2H_2\ (CH_3)_2$	1, 1-Dimethylhydrazine	2.5
50/50	51.Min.N_2H_4-47.min.UDMH-2.Max. impur	Aerozine-50	2.6, 3.2, 3.8
MHF-1*	45.3 MMH-23.3N_2H_4-31.4 HN	Hydrazoid N	2.14, 3.4
MHF-2	36.5 UDMH-40.2HN-23.3 N_2H_4		2.15, 3.8
MHF-3	86.MMH-14.N_2H_4		2.7, 3.3, 3.4
MHF-4	50.5 MMH-32.5N_2H_4-17.0HN		2.16, 3.4
MHF-5	56.0 MMH-26.N_2H_4-19.HN		2.17, 3.4
MHF-5B	58.0 MMH-23.N_2H_4-19.HN		2.18, 3.4
MHF-6	73.0 MMH-16.5N_2H_4-10.5H_2O		2.19, 3.3
MAF-1**	40.5 UDMH-50.5 DETA-9.0 CH_3CN	Mixed Amine Fuel	2.10, 3.7
MAF-2	48.3 DiPGA-42.6 PRODGA-9.1 TRIPRAM	MIGA	2.11
MAF-3	20.0 UDMH-80.0 DETA		2.8, 3.7
MAF-4	60.0 UDMH-40.0 DETA	U-DETA, HYDYNE	2.9, 3.7
MAF-5	29.5 UDMH-50.5 DETA-20.0 CH_3CN		2.12, 3.7
BA-1014	23.96 MMH-66.67N_2H_4-9.37H_2O		2.20, 3.3
BAF-1185	50.45 MMH-29.83N_2H_4-19.73H_2O		2.21, 3.3
MGGP-1	62.09 N_2H_4-10.49HN-27.42H_2O		2.13, 3.5

*MHF = Mixed Hydrazine Fuel

**MAF = Mixed Amine Fuel

7.2 UNITS AND CONVERSION FACTORS

7.2.1 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 of 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)

7.2.2 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:***

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 water saturated with air at one atmosphere) is .01°K less than the triple point temperature or 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}.

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* Nat'l. Bur. St. (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)

7.2.3 Basic Constants

CONSTANTS	SYMBOL	1963 VALUE
Velocity of light (vacuum)	c	2.997925 x 10^{10} cm/sec
Avogadro number	N	6.02252 x 10^{23} molecules/mole
Faraday constant	$\mathcal{F}$	96,487 coulombs/mole
Plank's constant	h	6.6256 x 10^{-27} erg - sec
Pressure-volume product for one mole of gas at 0°C and zero pressure	$(PV)^{P=0}_{0°C}$	2271.06 joules/mole 22413.6 cm^3 atm/mole

7.2.4 Derived Constants

CONSTANT	SYMBOL	1963 VALUE
Elementary charge (charge on the electron)	$e = \mathcal{F}/N$	4.80298 x 10^{-10} e.s.u
Gas constant	R	8.31433 joules/deg-mole 1.98717 cal/deg-mol
Boltzman constant	$K = R/N$	1.38054 x 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 x 10^{13} joules/g
Constant relating wave number and energy	$Z = nhc$	11.96255 joules-cm/mole 2.85912 cal-cm/mole

7.2.5 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/in.^{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	$\frac{1.798796}{\text{M.W.}}$	BTU/lb
cal/g-mole-°K	0.9993312	BTU/lb-mole-°R
cal/g-mole-°K	$\frac{0.9993312}{\text{M.W.}}$	BTU/lb-°R
joules/g	0.429922	BTU/lb
joules/g-mole	$\frac{0.429922}{\text{M.W.}}$	BTU/lb-mole
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
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.

TABLE OF CONVERSION FACTORS (CONT)

MULTIPLY	BY	TO OBTAIN
Standard Acceleration of Gravity (g)		
980.665 cm/sec^2		
32.174049 ft/sec^2		
Gas Constant (R)		
$8.31433 \frac{\text{joule}}{\text{g-mole-}^\circ\text{K}}$		
1.98717 cal/g-mole-°K		
$0.0820561 \frac{\text{liter-atm}}{\text{g-mole-}^\circ\text{K}}$		
$1545.32 \frac{\text{lb-ft}}{\text{lb-mole-}^\circ\text{R}}$		
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		

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13. ABSTRACT

The Hydrazine Fuels Handbook is a compilation of engineering information on the physical and chemical properties, storage and handling, production, transportation, safety, and the thermal and catalytic decomposition of the hydrazine family of fuels and their blends. It contains information on the following propellants:

Ammonia
Diethylenetriamine
Hydrazine
Monomethylhydrazine
1, 1-Dimethylhydrazine
50/50, N_2H_4/UDMH
MAF-1
MAF-2
MAF-3
MAF-4
MAF-5
MHF-1
MHF-2
MHF-3
MHF-4
MHF-5
MHF-5B
MHF-6
BA-1014
BAF-1185
MGGP-1

This 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.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Propellants						
Fuels						
Hydrazine						
Monopropellants						
Properties						
Handling						
Safety						
Storage						
Chemistry						
Handbooks						
Amines						
Ammonia						
MAF-Fuels						
BAF-Fuels						
MHF-Fuels						
Mixtures						