

AD-A194 679

THE ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANTS
(3RD) HELD IN ABERD. (U) ARMY BALLISTIC RESEARCH LAB
ABERDEEN PROVING GROUND MD E FREEDMAN ET AL. MAR 88

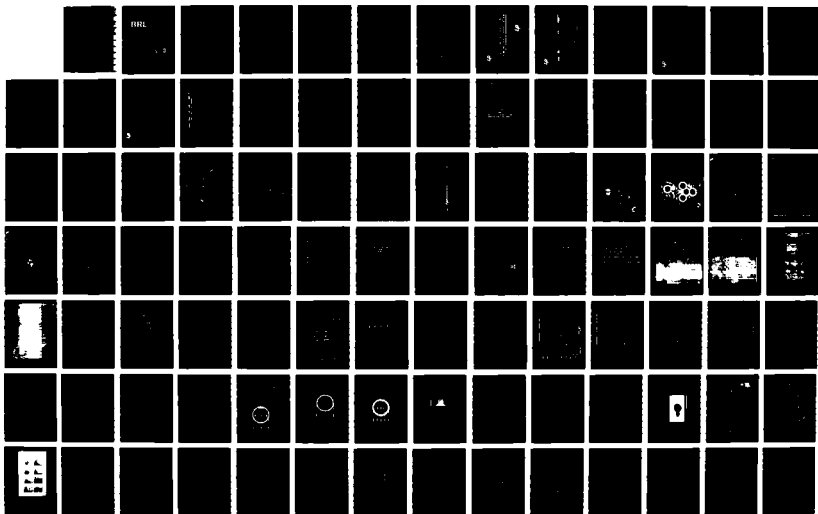
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AD-A194 679

SPECIAL PUBLICATION BRL-SP-73

BRL

1938 - Serving the Army for Fifty Years - 1988

THE THIRD ANNUAL CONFERENCE ON
HAN-BASED LIQUID PROPELLANTSELI FREEDMAN
J. Q. WOJCIECHOWSKI

MARCH 1988

DTIC
ELECTE
JUN 15 1988
S E D

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U.S. ARMY LABORATORY COMMAND

BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

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AD A194679

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			Physical properties Combustion		
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→ This report contains the abstracts and viewgraphs of the 17 papers presented at the BRL's Third Annual Conference on HAN-Based Liquid Propellants. Topics discussed → Ballistic Research Lab → hydroxylammonium nitrate → 790111					
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Revised: Liquid gun propellants

INTRODUCTION

The US Army is currently investigating the use of liquid propellants (LPs) in large and medium caliber guns. These LPs are characterized by the use of hydroxylammonium nitrate (HAN) as their oxidizer. On 25-27 August 1987, the Third Annual LP Conference on HAN-Based Liquid Propellant Flames, Properties and Structure, was held at the BRL with Dr. Walter F. Morrison as General Chairman. The papers presented at this highly successful conference were given by people from academia, industry, and other government agencies.

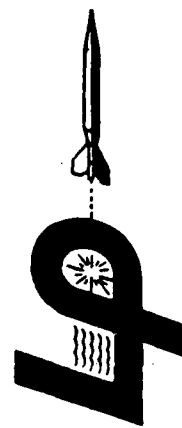
This report is a compilation of the abstracts and viewgraphs of these papers where available. The final program is included in appendix A and a list of attendees in appendix B.

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LIQUID PROPELLANT GUN DEMONSTRATION PROGRAM

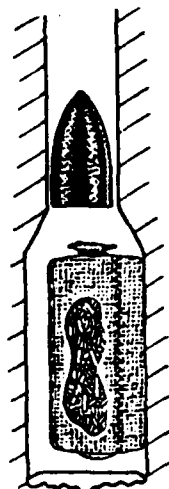




LIQUID PROPELLANT GUN DEMONSTRATION PROGRAM

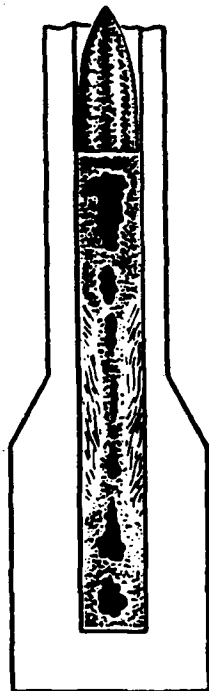
COMBUSTION CONTROL

SOLID PROPELLANT



- UNDERSTOOD
- BUT
- MATURE

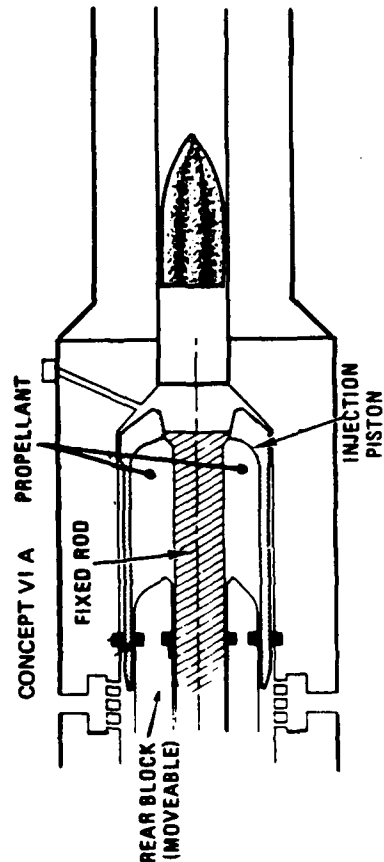
LP BULK LOADED



- SIMPLE
- BUT
- DIFFICULT TO CONTROL

REGENERATIVE IGNITION

- BALLISTIC CONTROL
- BUT
- MECHANICALLY MORE COMPLEX



LIQUID PROPELLANT GUN TECHNOLOGY PROGRAM

PROGRAM OBJECTIVES

- **DEMONSTRATE A 'BRASSBOARD' 155mm RLPG ARTY
SYSTEM IN AN M109 SPH WITH A SPECIFIC LIQUID
PROPELLANT**
 - **BALLISTICALLY VIABLE**
 - **MILITARILY PRACTICAL**

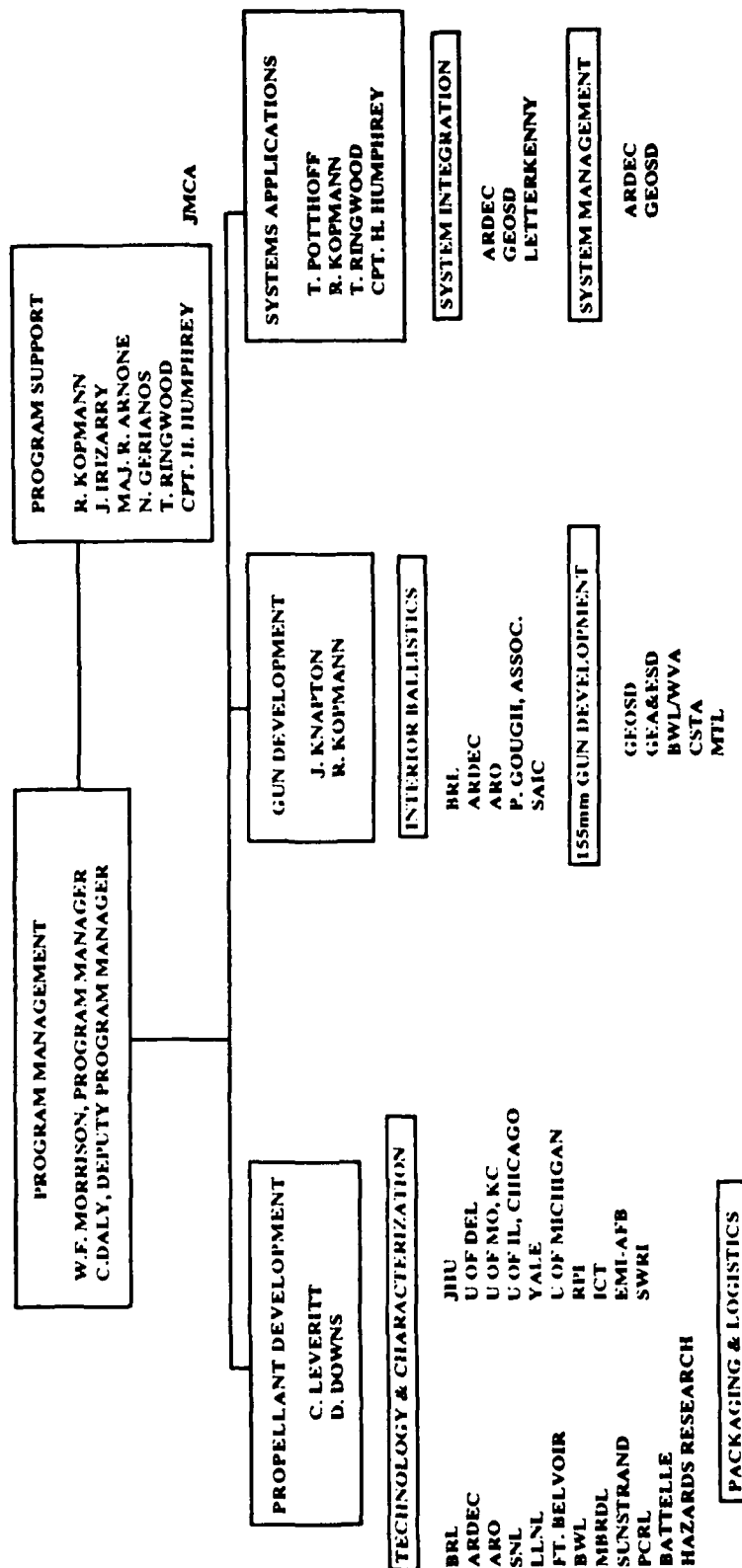
- **DEVELOP TECHNOLOGY BASE REQUIRED TO TAKE
SYSTEM INTO FSD**
 - **HAN-BASED LIQUID PROPELLANT**
 - FORMULATION**
 - CHARACTERIZATION**
 - PRODUCIBILITY**
 - PACKAGING AND HANDLING**

 - **REGENERATIVE LPG**
 - BASIC DESIGN PRINCIPLES
& METHODOLOGY**
 - COMPONENT TECHNOLOGY**
 - DEMONSTRATED BALLISTIC
PERFORMANCE**
 - RAM & PRODUCIBILITY DATA (LIMITED)**
 - SPECIFIC 'PROTOTYPE' DESIGN**

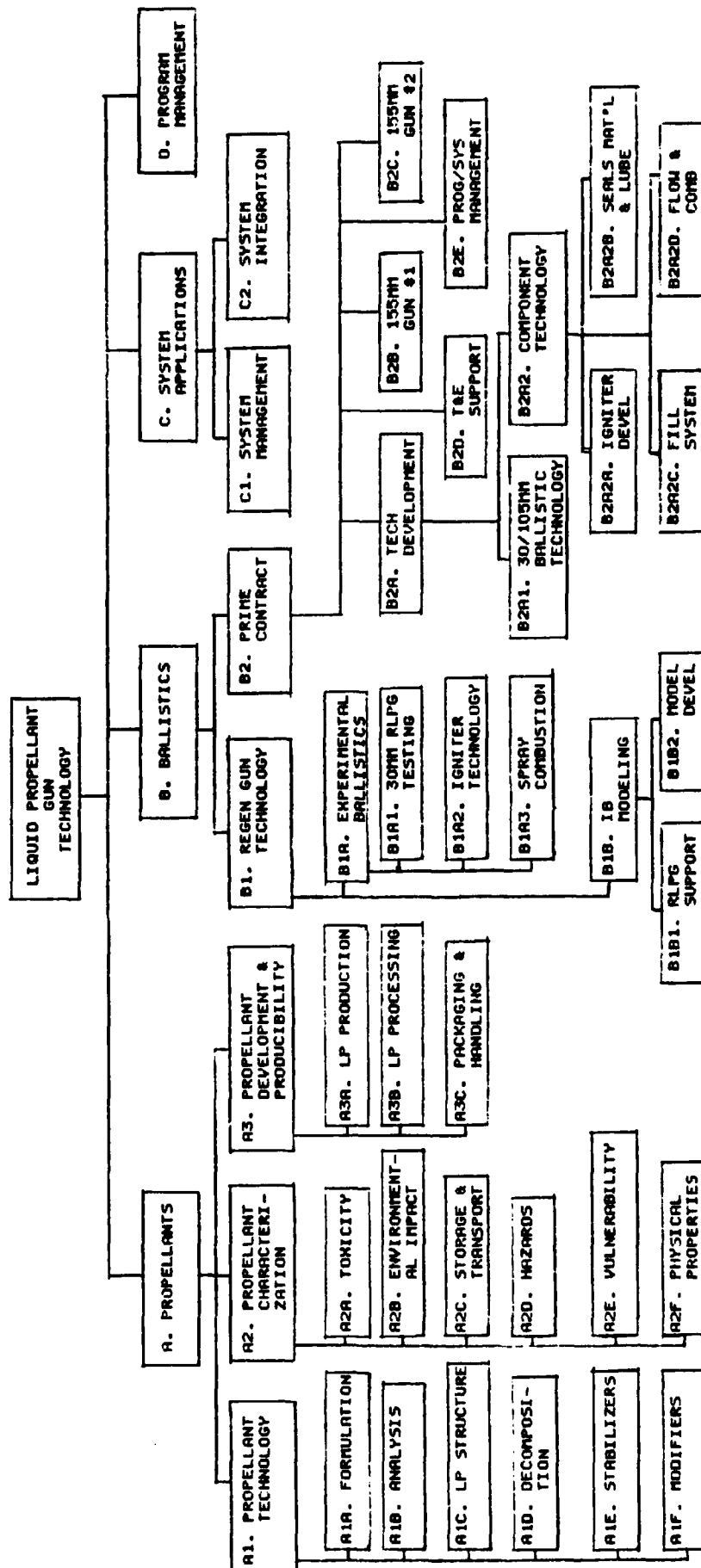
 - **SYSTEM INTEGRATION**
 - M108/9 EXPERIENCE**
 - INITIATE ILS ACTIVITIES**
 - INVOLVE DEVELOPMENT COMMUNITY**
 - PAPER CONCEPT STUDIES**

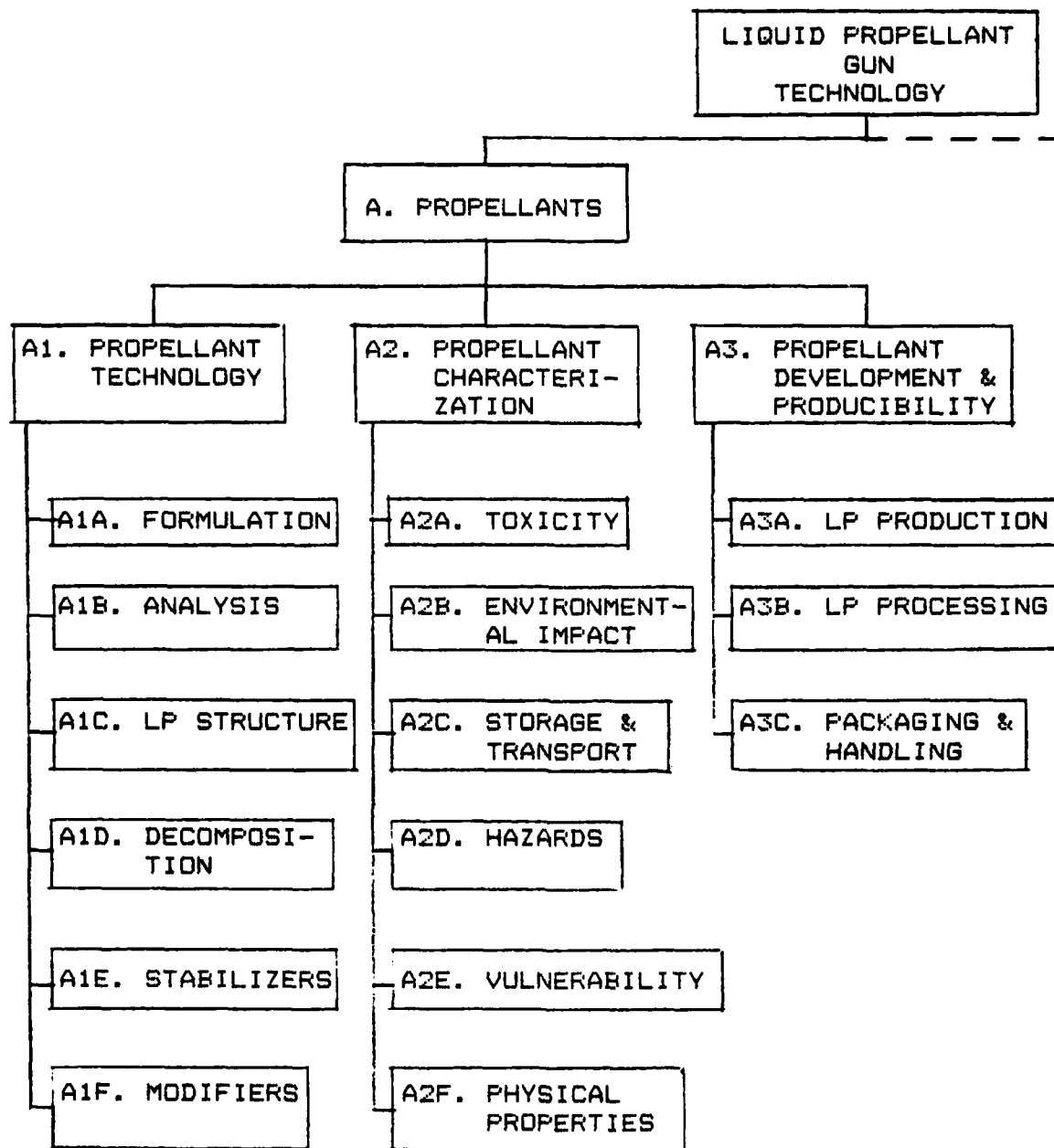


LIQUID PROPELLANT GUN DEMONSTRATION PROGRAM



• JOINT LABCOM - ARDEC PROGRAM
• EXTENSIVE INDUSTRY & ACADEMIC PARTICIPATION





LIQUID PROPELLANT
GUN
TECHNOLOGY

B. BALLISTICS

B1. REGEN GUN
TECHNOLOGY

B1A. EXPERIMENTAL
BALLISTICS

B1A1. 30MM RLPG
TESTING

B1A2. IGNITER
TECHNOLOGY

B1A3. SPRAY
COMBUSTION

B1B. IB
MODELING

B1B1. RLPG
SUPPORT

B1B2. MODEL
DEVEL

B2. PRIME
CONTRACT

B2A. TECHNOLOGY
DEVELOPMENT

B2A1. 30/105MM
BALLISTIC
TECHNOLOGY

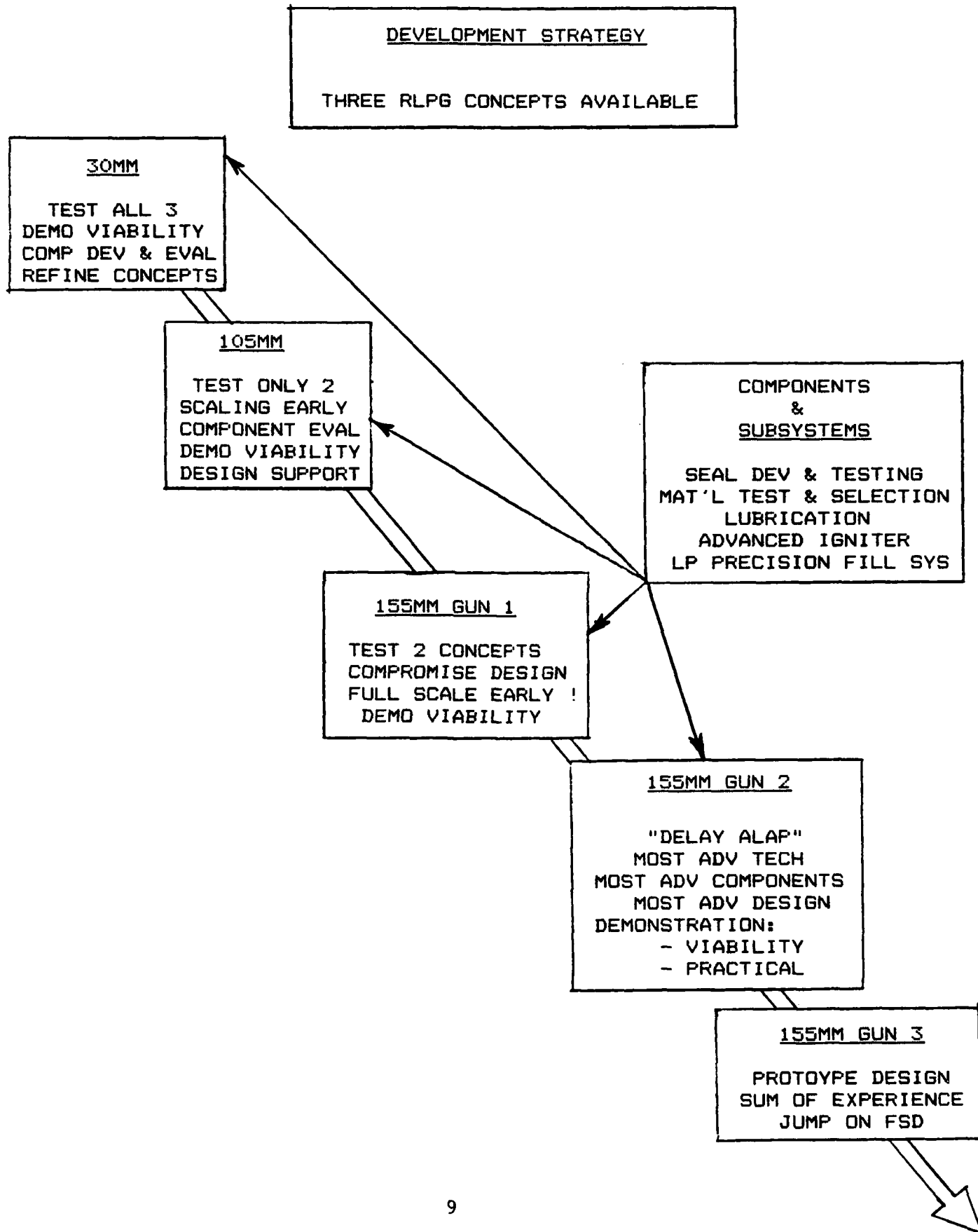
B2A2. COMPONENT
TECHNOLOGY

B2B. 155MM GUN #1

B2C. 155MM GUN #2

B2D. TEST & EVAL
SUPPORT

B2E. PROGRAM/SYS
MANAGEMENT





LIQUID PROPELLANT GUN DEMONSTRATION PROGRAM

CURRENT ARMY PROGRAM

ACCELERATED D-155

1ST GENERATION: 155 mm TEST FY 88

2ND GENERATION: 155 mm TEST FY 89

CONTINUOUS ZONING
BURST FIRE

COMPONENT DEVELOPMENT

800 TO 1000 ROUNDS IN 155 mm

3RD GENERATION DESIGN FOR FSD

— TECHNICAL MATURITY TO SUPPORT FSD —

GE CONTRIBUTION

PROJECTILE AUTOLOADER

FIRE CONTROL

TURRET ELEVATION DRIVES

VEHICLE INTEGRATION

— SYSTEM LEVEL GROUNDWORK —
FOR FUTURE DEVELOPMENT

LP WEAPONIZATION DEMO

155 mm RLPG CANNON MOUNTED ON SPH

MUZZLE VELOCITY: 210 TO 825 m/s

RATE OF FIRE: 3 TO 10 rds/min

BURST FIRE DEMONSTRATION

3 ROUNDS TIME-ON-TARGET

— LP IN ADVANCED INDIRECT FIRE ROLE —

LIQUID PROPELLANT GUN TECHNOLOGY

TECHNICAL RISKS AND UNKNOWNNS

PROPELLANT

- HIGH TEMPERATURE
- CONTAMINATION

RLPG

- RELIABILITY AND MAINTAINABILITY
(RLPG MORE COMPLEX)
 - SEAL LIFE
 - COMPONENT DEVELOPMENT
- SCALING FROM 105MM to 155MM

MAY 86

ABSTRACT
SOLID + LIQUID PHASE EQUILIBRIUM FOR THE WATER + HYDROXYLAMMONIUM
NITRATE SYSTEM

by
J. Bevan Ott and Johanne Artman
Department of Chemistry
Brigham Young University
Provo, Utah

The binary solid + liquid phase diagram has been measured for the water + hydroxylammonium nitrate (HAN) system. The phase diagram is a simple eutectic system with the eutectic at 231.5 K (-41.7°C) and a mole fraction of HAN of 0.281 (wt fraction of HAN = 0.676). The phase diagrams expressed in terms of mole fraction x and weight fraction f are shown in figures 1 and 2.

The enthalpy of fusion of the HAN was determined from the solid + liquid results to be 11 ± 2 J/mol. The HAN was obtained from Southwestern Analytical Chemicals, Inc. as an approximately 2.8 molar solution. The water was removed by vacuum drying over a three month time period, but the sample was still not pure. We estimate the impurity level from the change in melting temperature with fraction melted to be 0.040 mole fraction. We are at present trying to determine the nature of the impurity.

We obtained a melting temperature for the impure sample of HAN of 315.95 K (42.7°C). The melting point corrected to zero impurity would be 317.7 K (44.5°C).

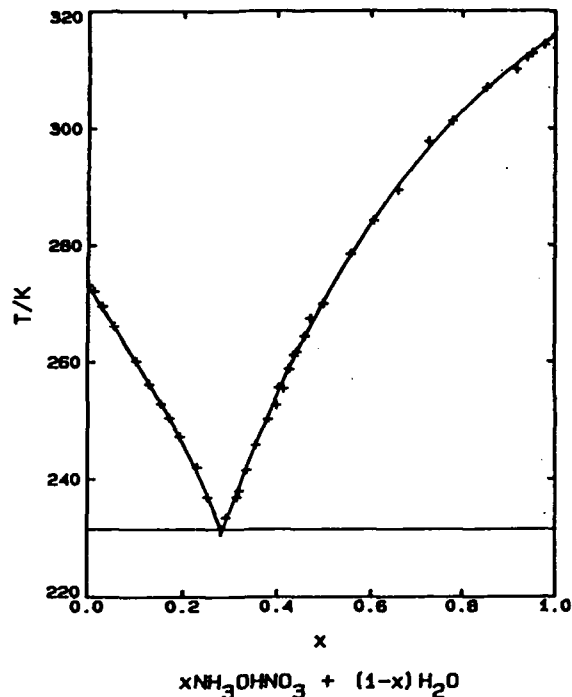


Figure 1. Solid + liquid-phase diagram for HAN + water expressed in terms of Kelvin temperature vs. mole fraction HAN

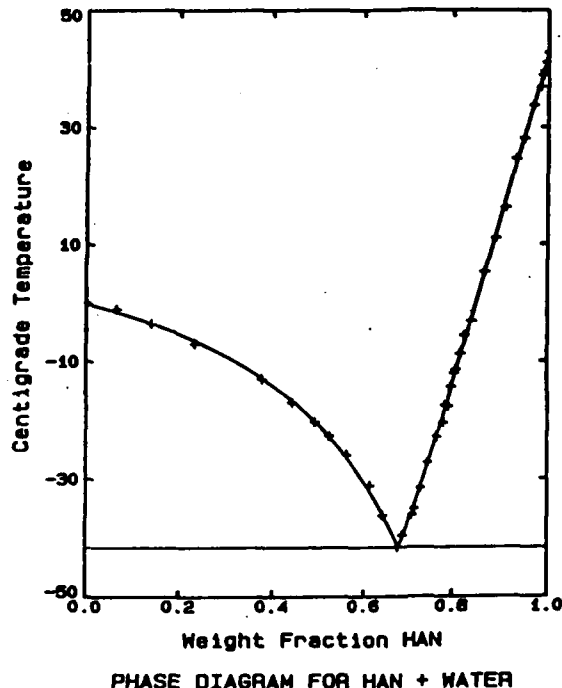


Figure 2. Solid + liquid-phase diagram for HAN + water expressed in terms of centigrade temperature vs. weight fraction HAN

DIFFRACTION STUDIES OF HAN

F. K. Ross and Q. Xie
Research Reactor
University of Missouri
Columbia, MO 65211
(314-882-5237)

The objective of this research program has been to provide information about the structures of crystalline and liquid HAN. To this end, we developed techniques for crystallizing HAN, determined the structure of the crystalline material by X-ray diffraction(1), improved the structural model by providing a single crystal neutron diffraction study(2) and during the past year have concentrated on measuring the diffraction from liquid samples. The crystal data is used to develop a description for the potential of HAN, but obviously is not necessarily an ideal example of the liquid state. The liquid scattering information is intended to test the ability of the model to reproduce the measurable properties of the liquid and, in conjunction with theoretical studies, to provide a better understanding of the liquid.

Diffraction data have been acquired for HAN, for fully deuterated HAN and for a "null" isotopic mixture (64% hydrogen of scattering power $-.374f$ and 36% deuterium of scattering power $+.667f$). In addition, we have continued earlier X-ray diffraction studies with the inclusion of a pyrolytic graphite crystal to produce monochromatic radiation and with the development of a liquid cell for use in the flat-plate geometry. The monochromator is necessary to produce a diffraction pattern which can be deconvoluted from the source spectrum and the latter geometry makes up for some of the intensity loss incurred. Flat-plate geometry also reduces the severity of the absorption corrections incurred for the cylindrical samples (HAN liquid in a quartz capillary tube) reported last year (2). Background scattering from the container is still a problem though, and we find rather bothersome partial crystallinity in both the thin-wall quartz tubing used for the neutron studies and in the stretched Mylar window of our new X-ray cell. Efforts to improve the removal of container scattering from the diffraction pattern are underway.

The weakness of the diffracted intensity in the X-ray experiment suggests that this work might be more appropriately performed at a synchrotron laboratory. Such an experiment is being considered, but it also requires the use of a sample cell. Our X-ray experiments are still providing much useful information to aid in planning the synchrotron experiment.

-
- (1) A. L. Rheingold, J. T. Cronin, T. B. Brill and F. K. Ross, *Acta Cryst.*, (1987).C43,402-404.
 - (2) F. K. Ross, Conference on HAN-Based Liquid Propellant Flames, Properties and Structure, BRL, Aberdeen Proving Grounds, July 29-31, 1986.

* Research Supported by Army Research Office grant DAAG29-85-K-0064.

DIFFRACTION STUDIES OF HAN

F. K. Ross and Q. Xie
Research Reactor
University of Missouri
Columbia, MO 65211

Research supported by the Army Research Office,
"Structure, Potential Energy and Thermodynamic
Properties of Hydroxylammonium Nitrate", R. D.
Murphy and F. K. Ross.

OBJECTIVES

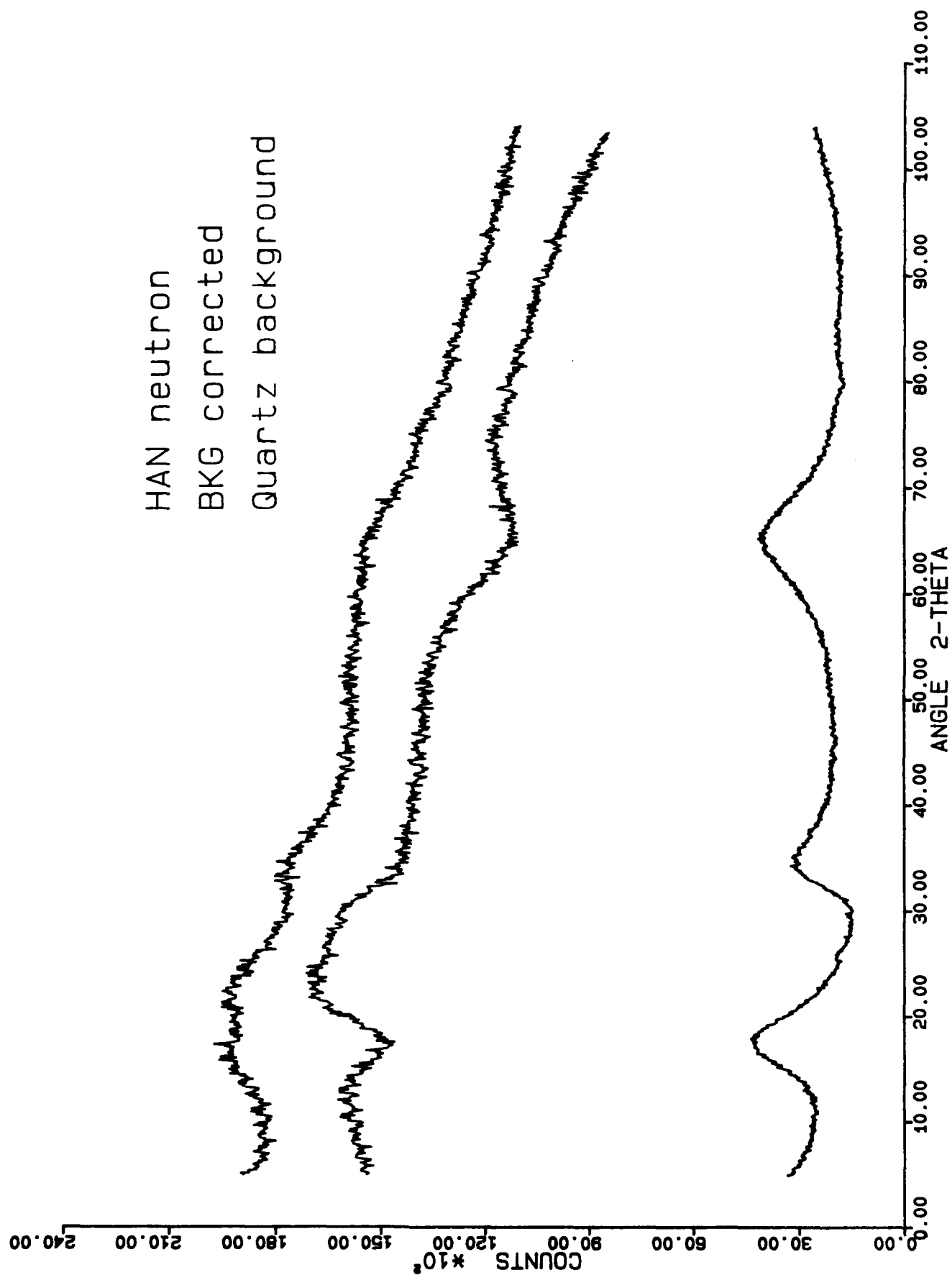
1. Crystallize HAN and determine (crystal) structure.
 - a) X-ray diffraction (HAN, d4-HAN)
 - b) Neutron diffraction
 - c) Search for other structures or phases

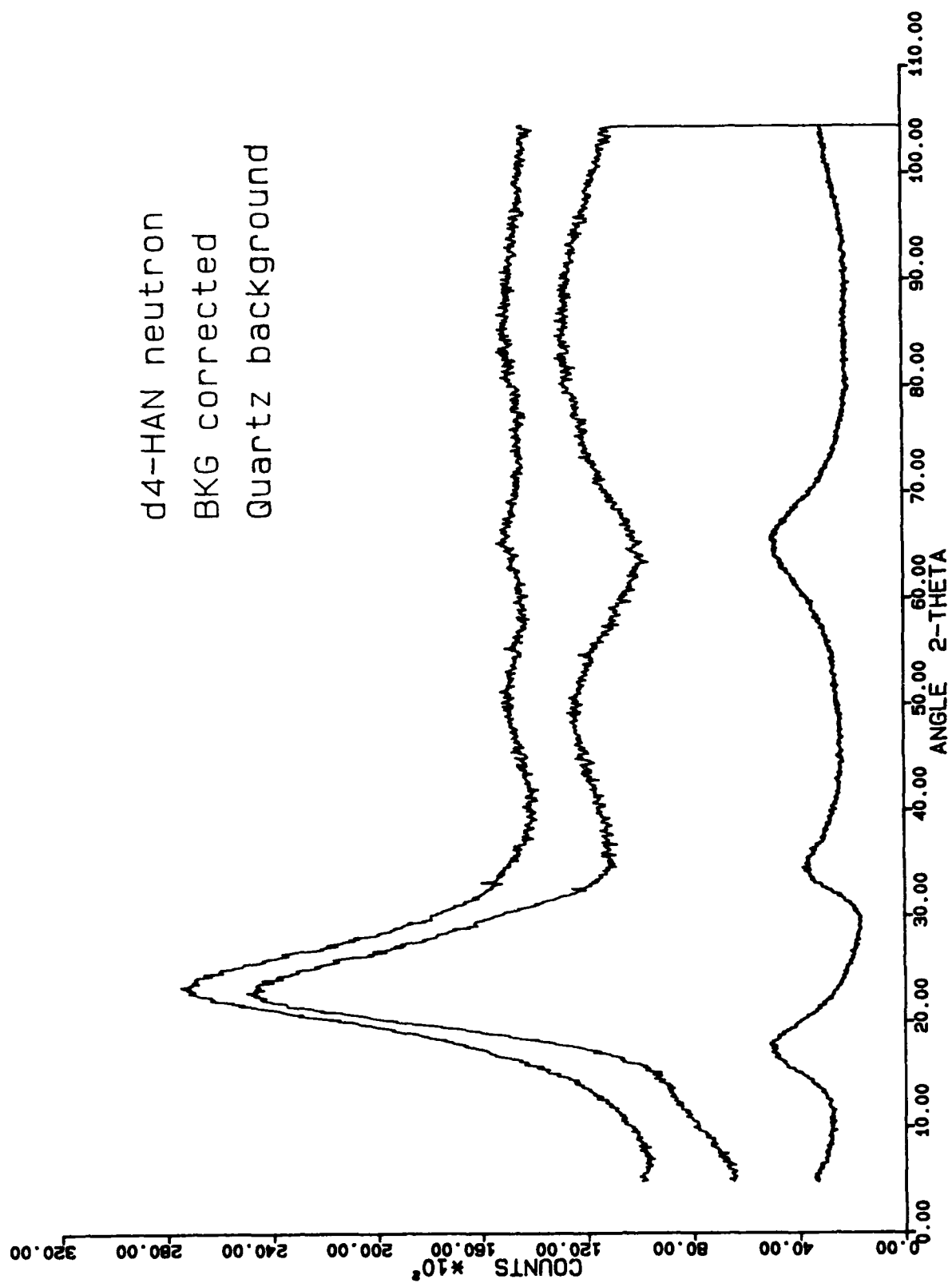
2. Monte Carlo calculations (R. D. Murphy, UMKC) .
 - a) Generate potential from structure parameters
 - b) Calculate thermodynamic properties from the potential
 - c) Use potential to calculate liquid scattering (diffraction)

3. Measure liquid scattering (diffraction) .
 - a) Neutron - HAN, d4-HAN, 36/64% null isotope mixture
 - b) X-ray

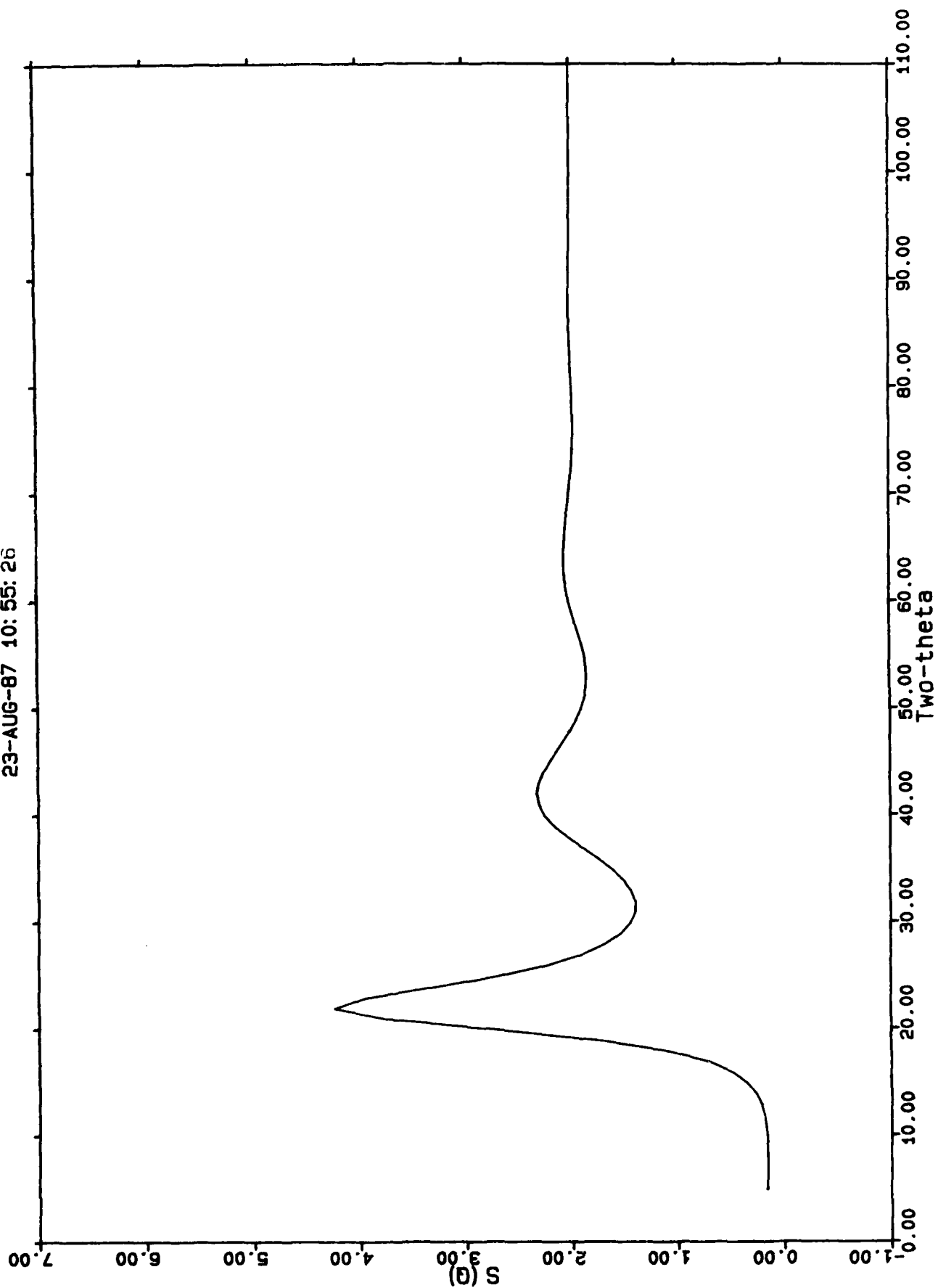
FUTURE DIRECTIONS

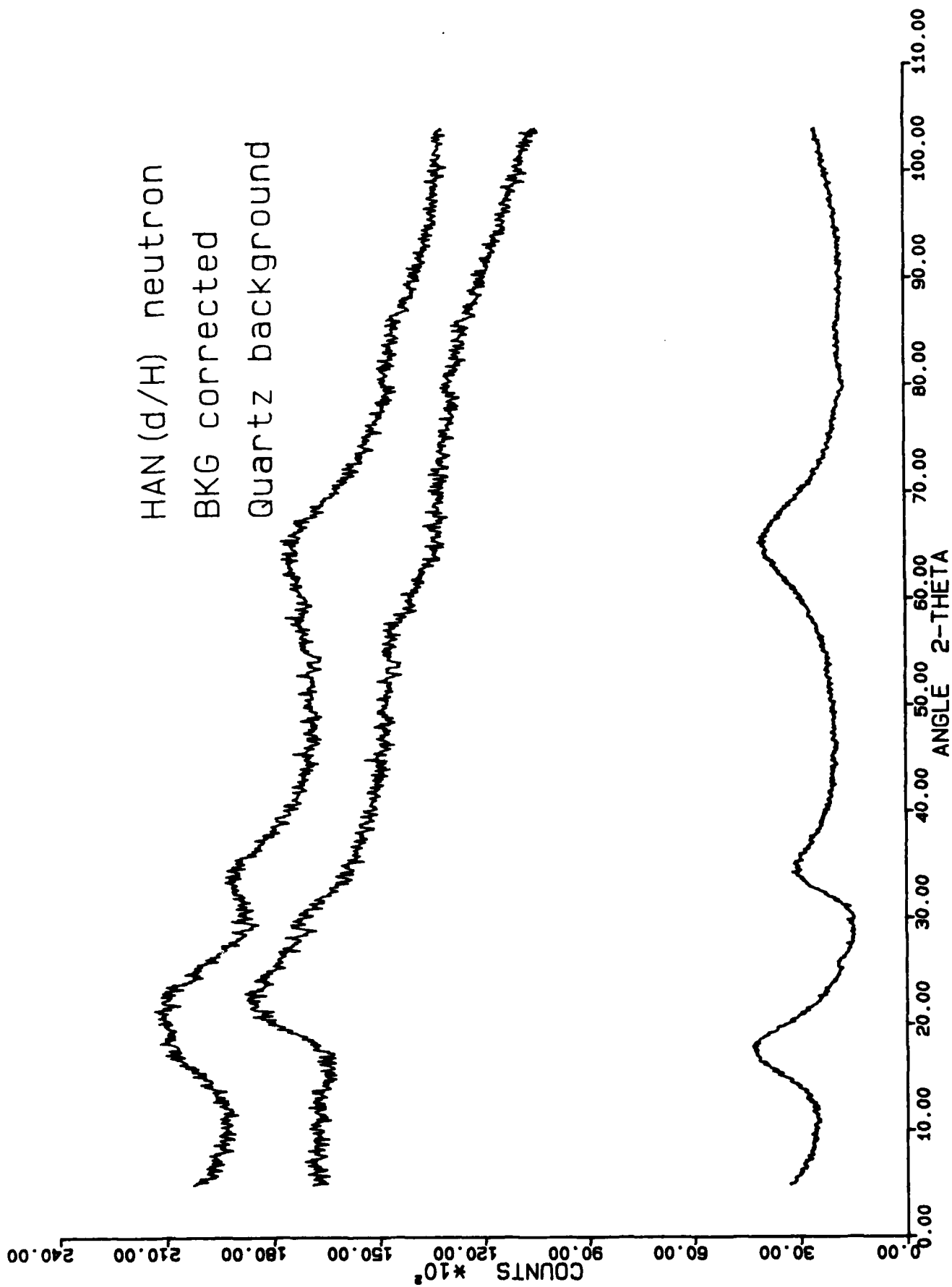
1. LIQUID X-RAY SCATTERING AT SHORTER WAVELENGTHS
($Mo = 0.71 \text{ \AA}$, $Ag = 0.56 \text{ \AA}$)
2. FOCUSING MONOCHROMATORS
3. ...
4. ELECTRON DENSITY ANALYSIS
 - e^- density maps
 - electrostatic potential maps
 - multipole model refinement



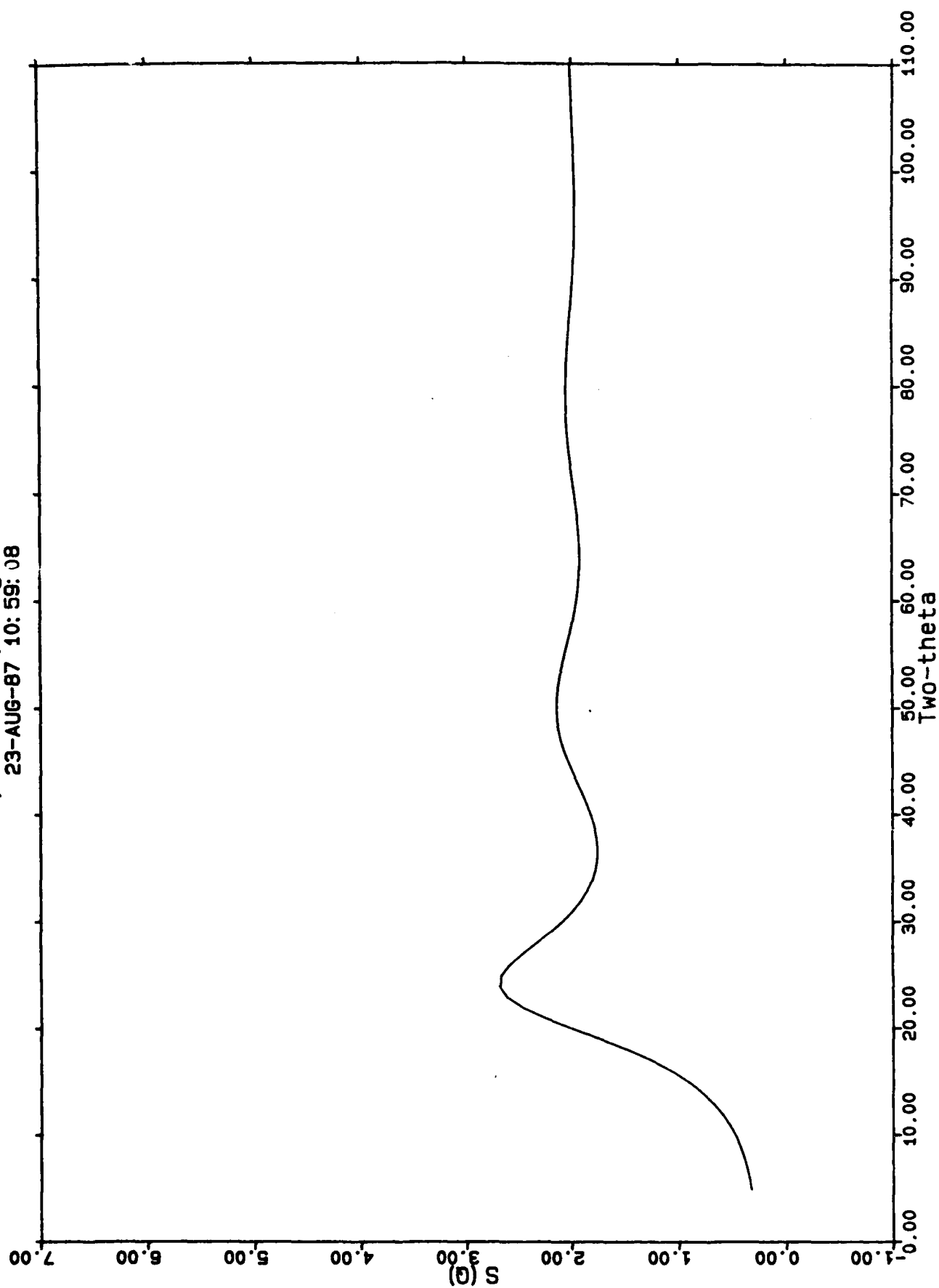


HAN - eta=.45, chi=.50, sigma=.80, dia.=4.0
23-AUG-87 10:55:26

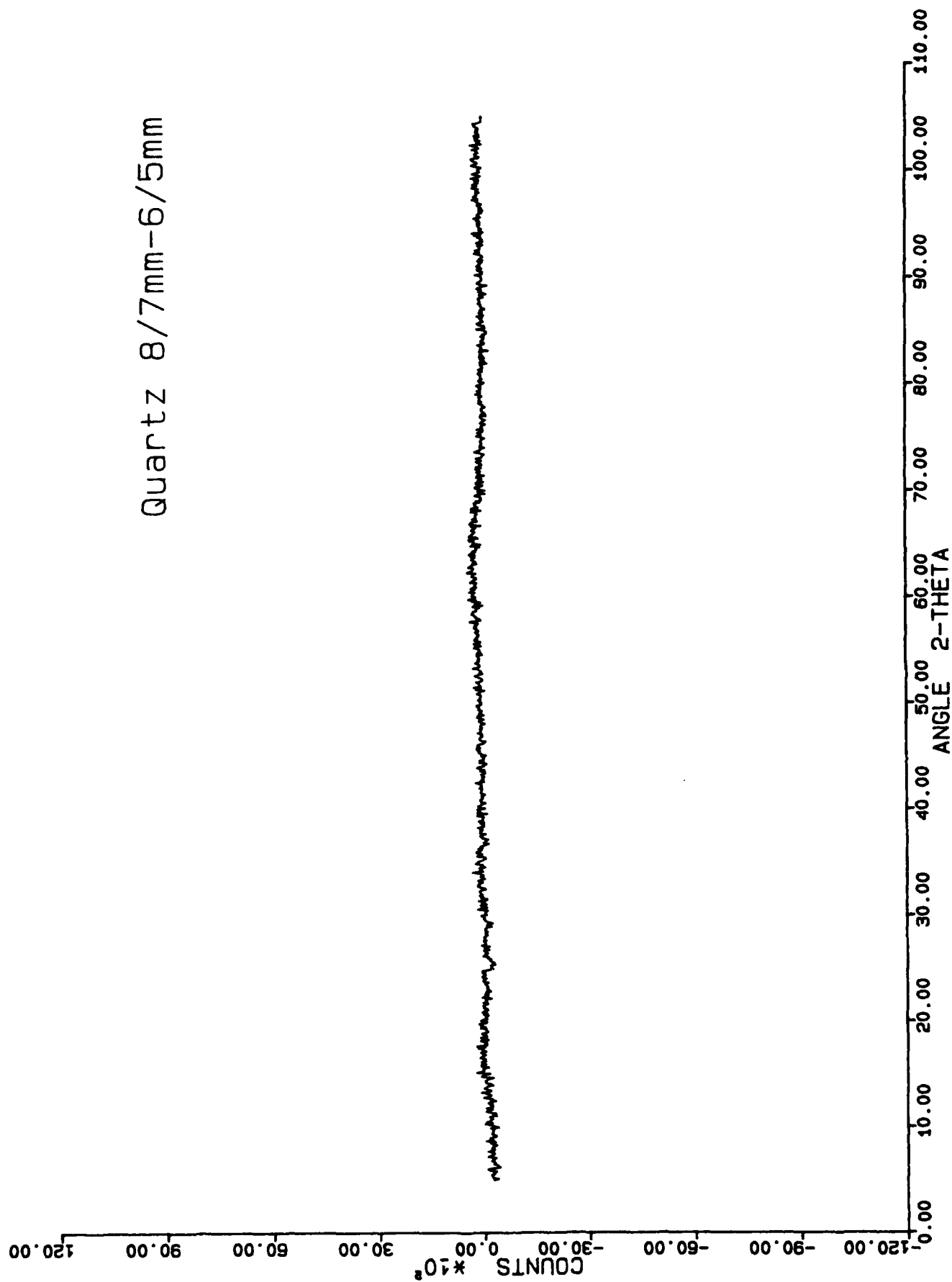




HAN - eta=.25, chi=.50, sigma=.90, dia.=3.2
23-AUG-87 10:59:08

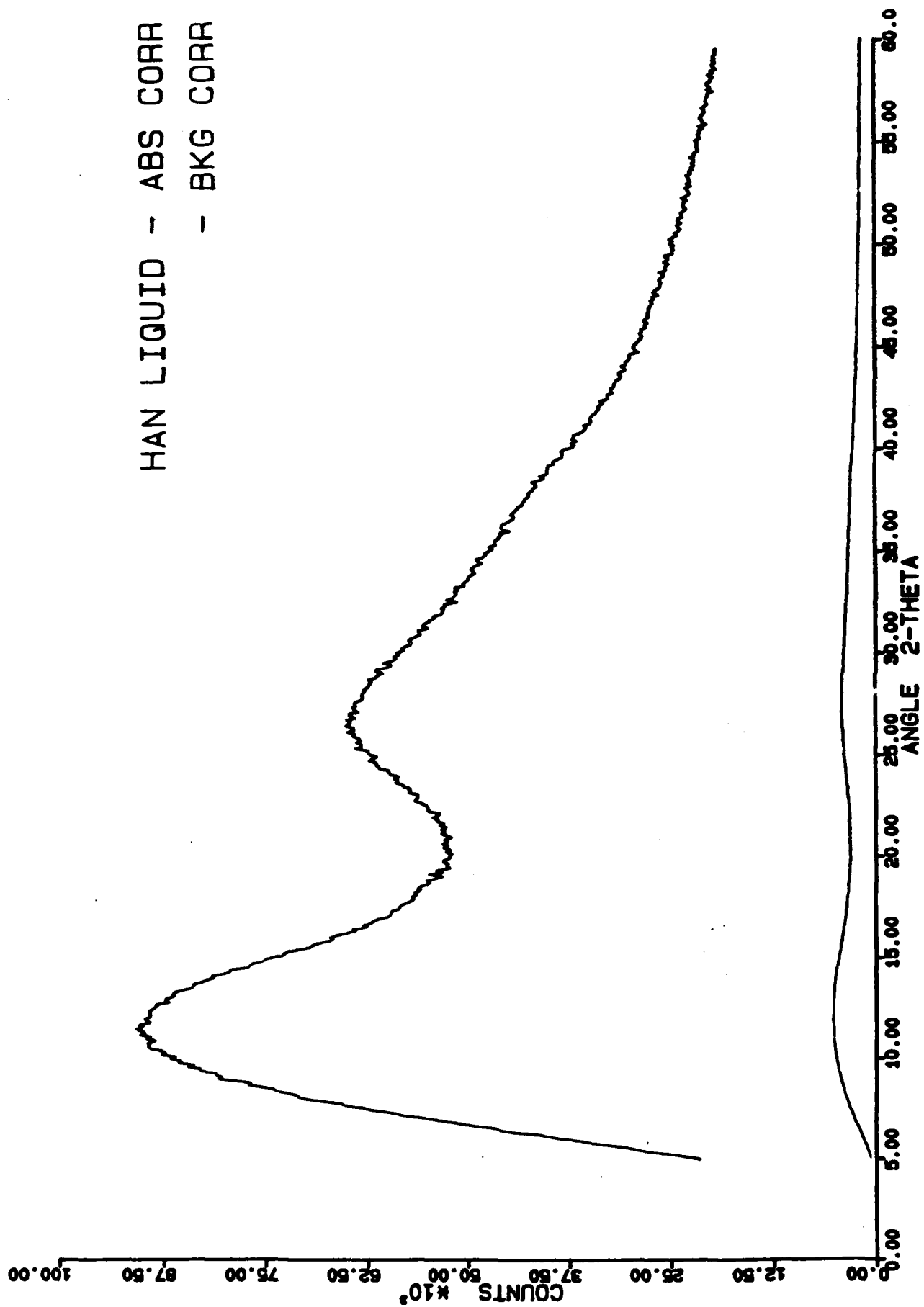


Quartz 8/7mm-6/5mm

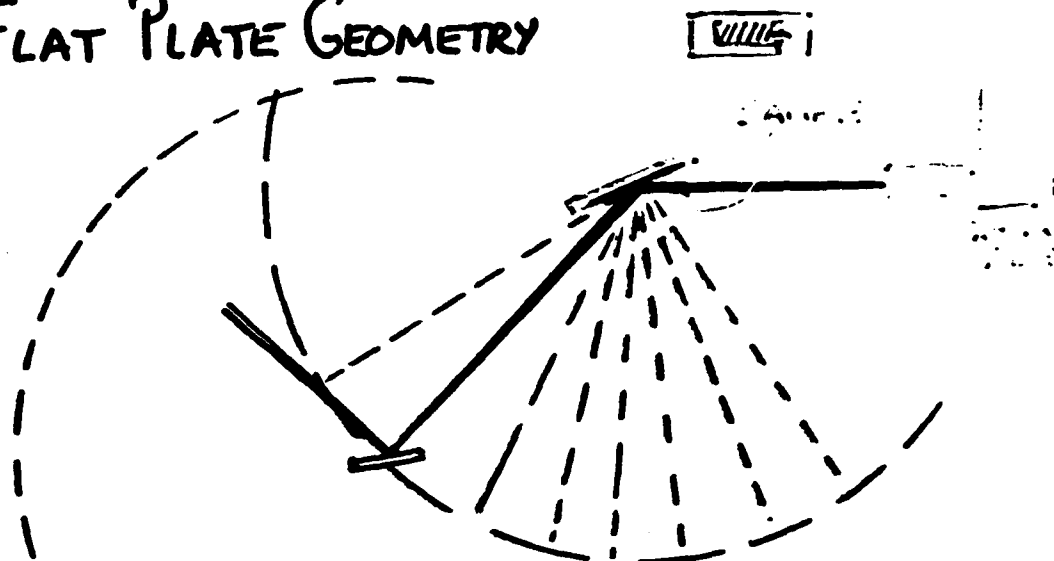


SAMPLE PREPARATION

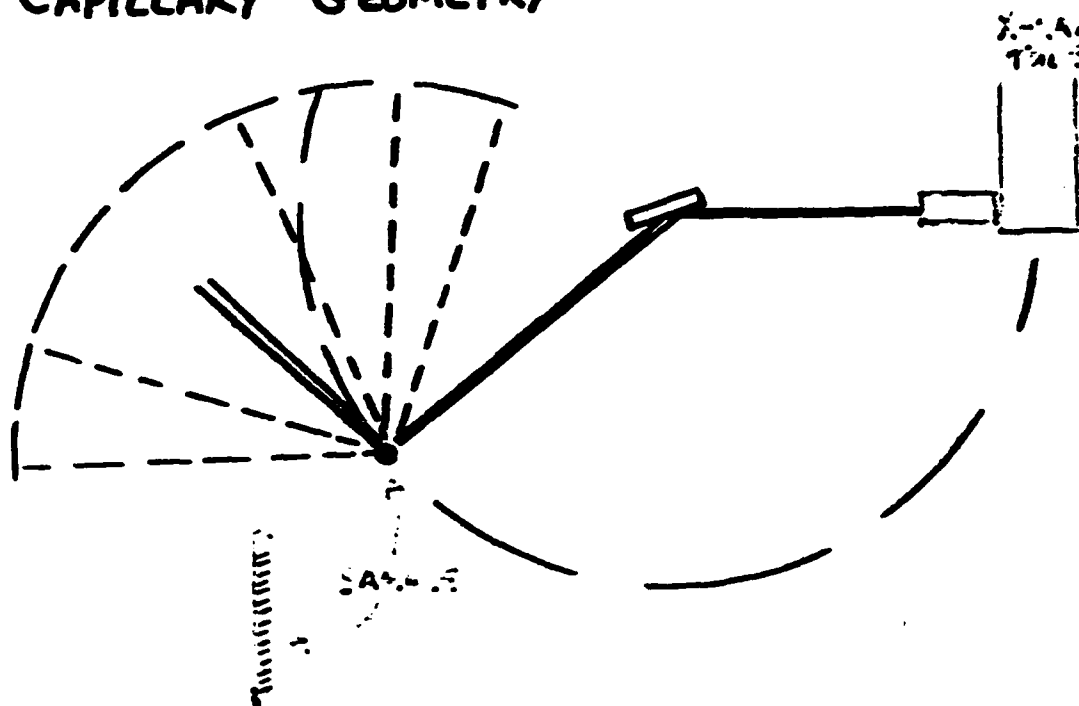
- a) Rotary evaporate 18% solution (S. W. Analytical Chemicals) to about 90 weight percent HAN.
- b) Vacuum dehydrate at 60-70 degrees C for several hours.
- c) Transfer hot liquid (pipet, hypodermic syringe, etc.); use dry atmosphere glove-box if necessary.
- d) Isotopic exchange - dilute dehydrated sample in 99.9% deuterated water (usually for 99.5% exchange in three dilutions).
- e) Seal samples in thin-wall quartz tubes or load into polyethylene cell for liquid X-ray scattering.



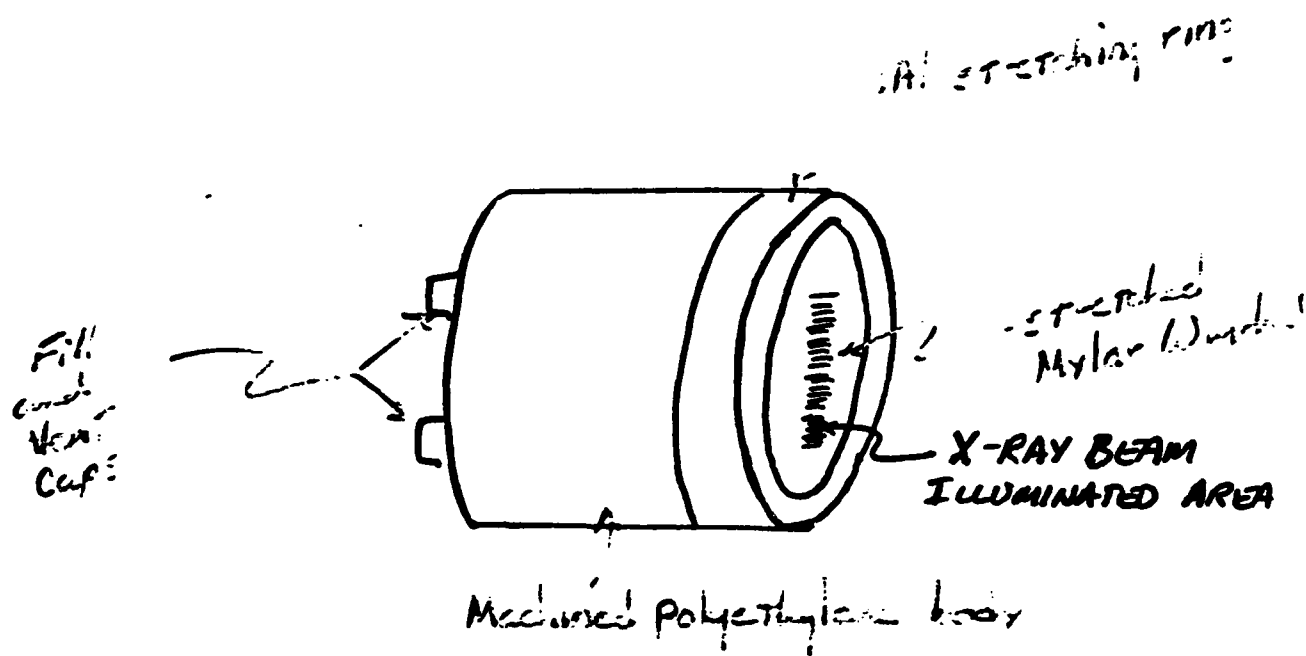
A. FLAT PLATE GEOMETRY

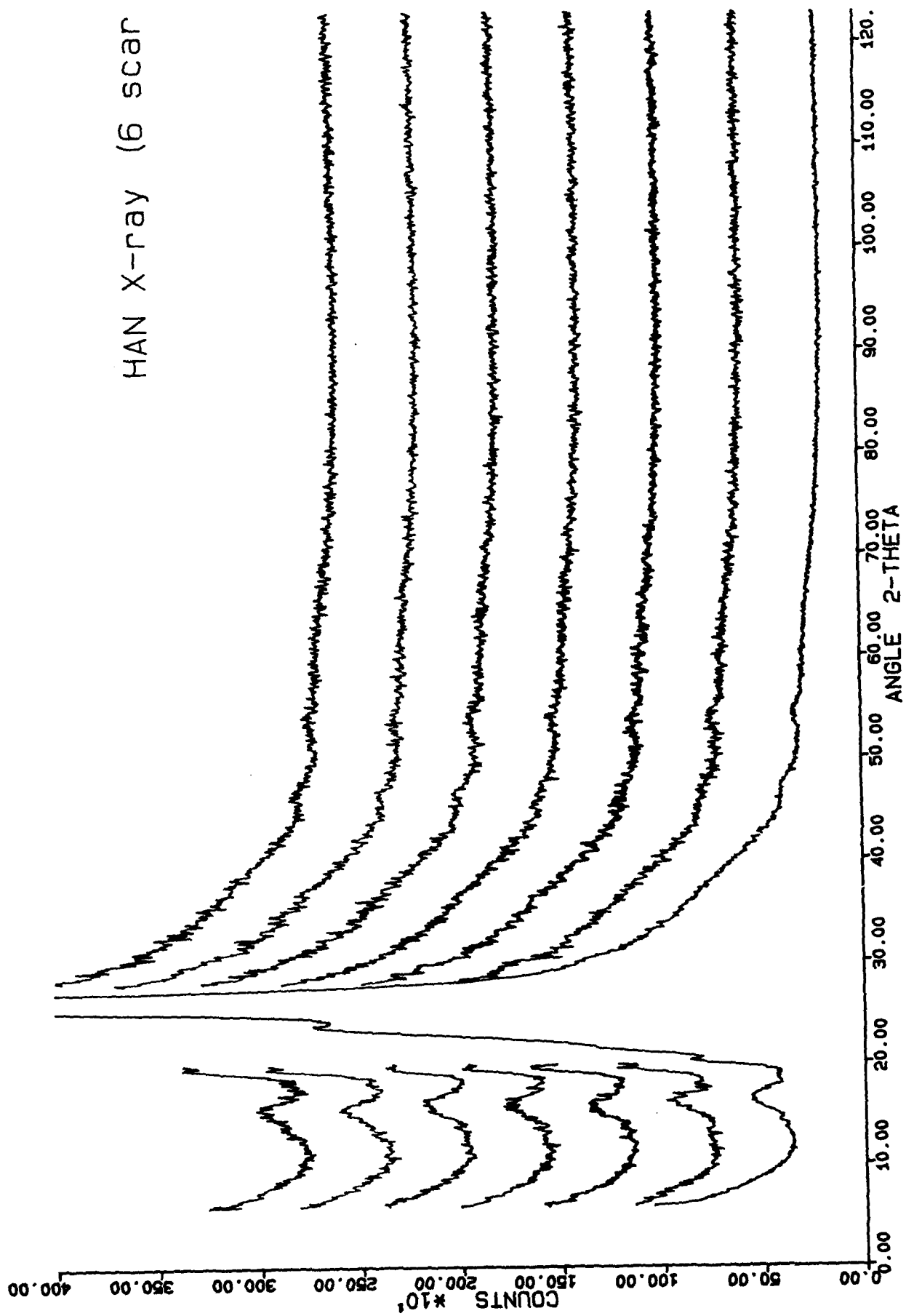


B. CAPILLARY GEOMETRY

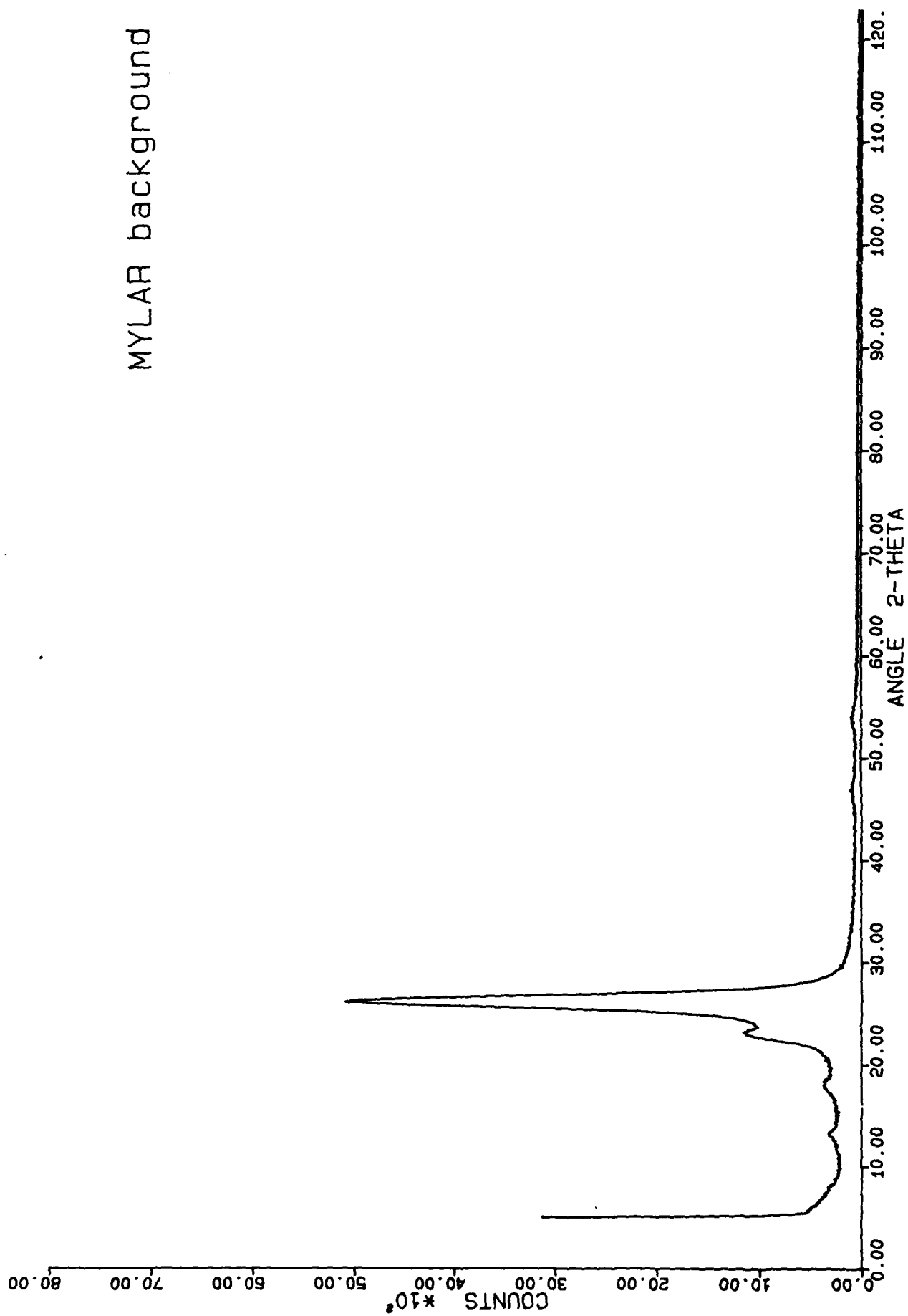


High Pressure Cell For X-ray
 Spectroscopy

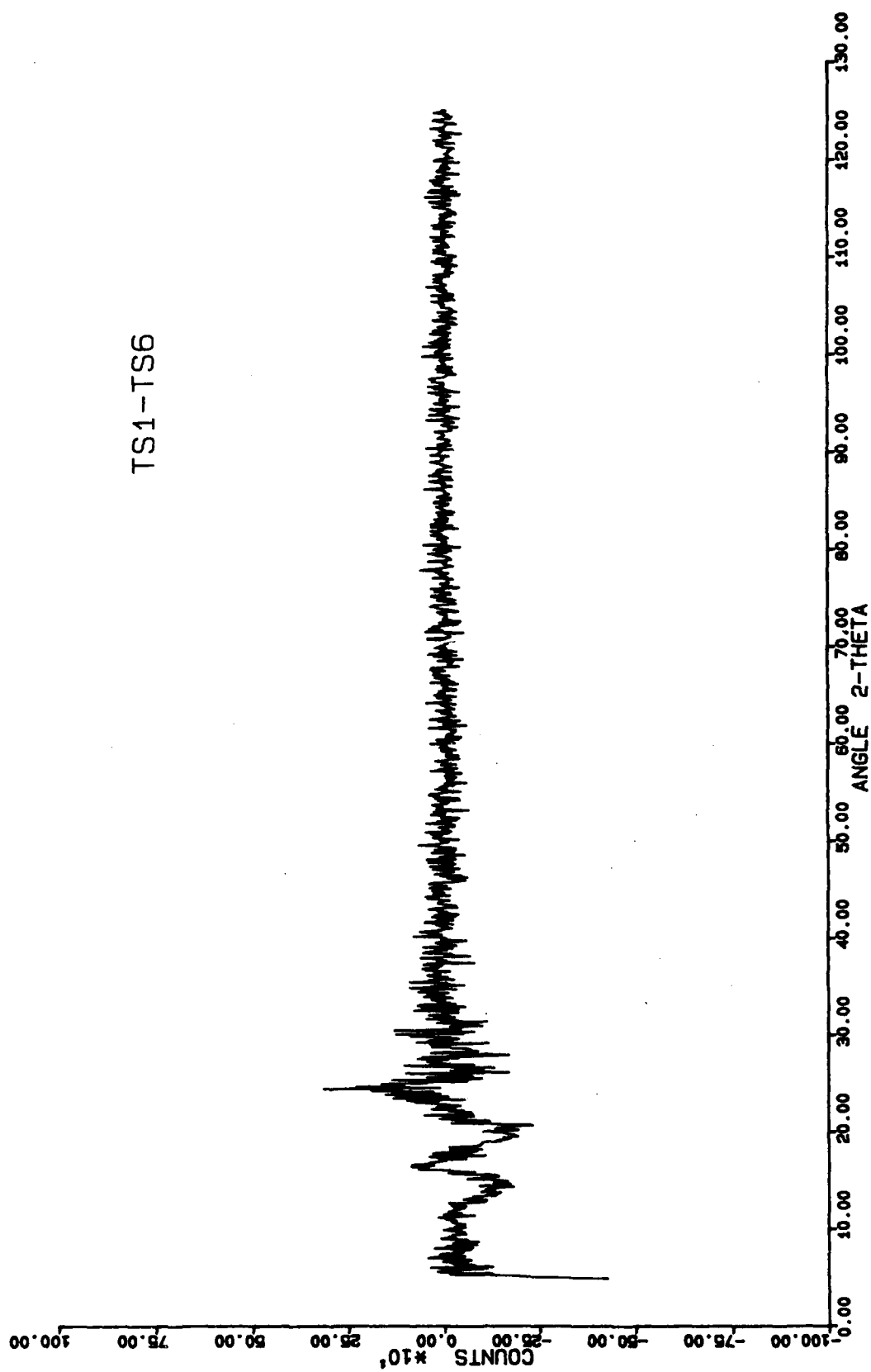




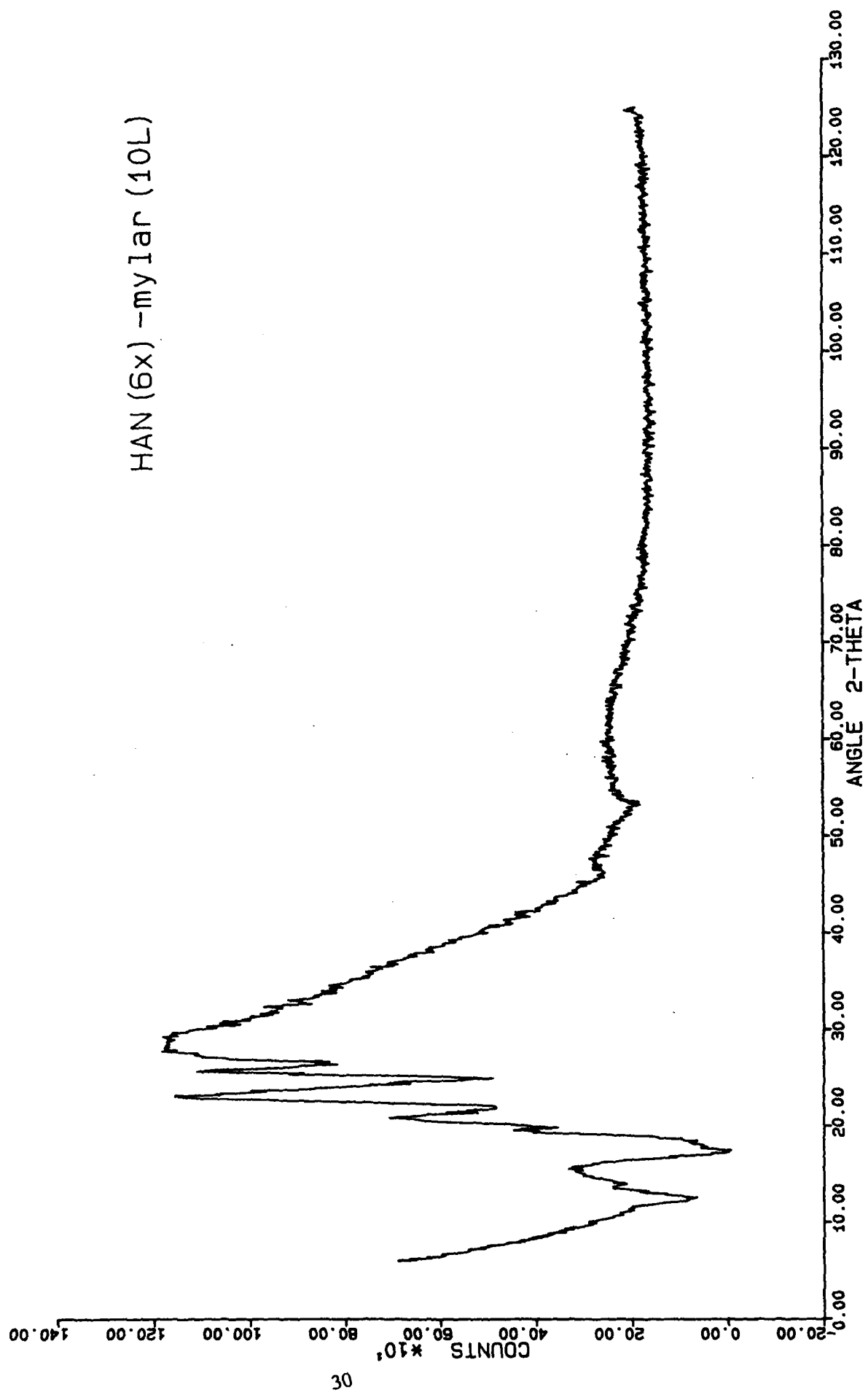
MYLAR background



TS1-TS6



HAN (6x) -mylar (10L)



LIQUID SCATTERING SUMMARY

NEUTRON

- 1) d4-HAN - better statistics (x2)
- 2) HAN, Null isotope - x5 to x10 statistics improvement
incoherent background subtractions
multiple scattering corrections

X-RAY

- 1) better liquid cell windows
- 2) energy sensitive detector (HgI2)
- 3) focussing monochromator
- 4) shorter wavelengths (smaller window effect)
- 5) synchrotron experiment

MODELS

- 1) pursue Percus-Yevick model with non-spherical shape, with form factor, etc.
- 2) Monte Carlo calculations underway with neutron data
need better potential for hydroxylammonium ion
need more crystal structure data (other salts)

NO_3^- X-N
 $\text{O}_1, \text{O}_2, \text{O}_3$ plane
 H atoms omitted

Distances from plane

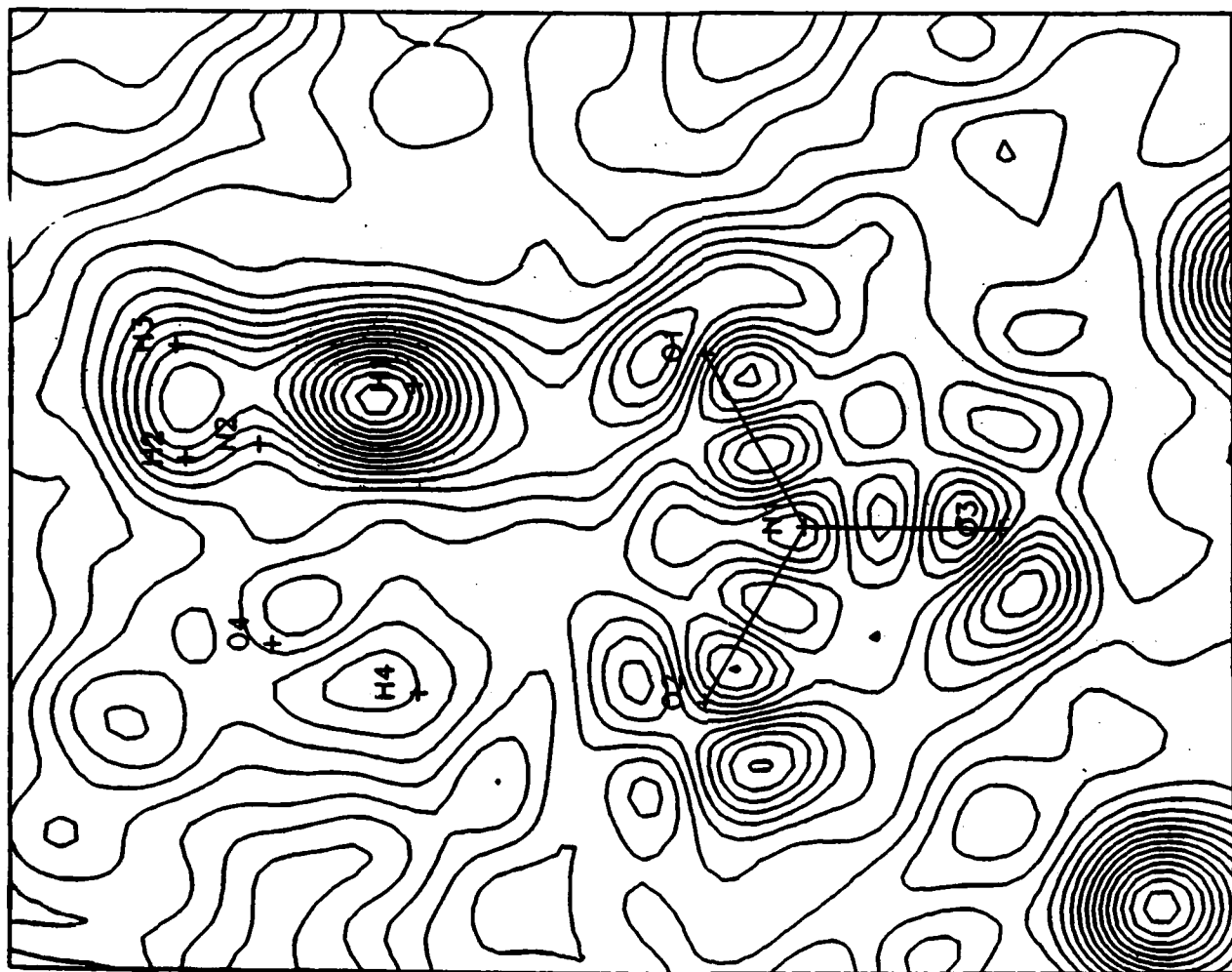
N_1 $-.006 \text{ \AA}$

N_2 $-.051$

H_1 $+0.077$

H_4 $-.50$

O_4 $-.68$



3.80

Y

-3.80

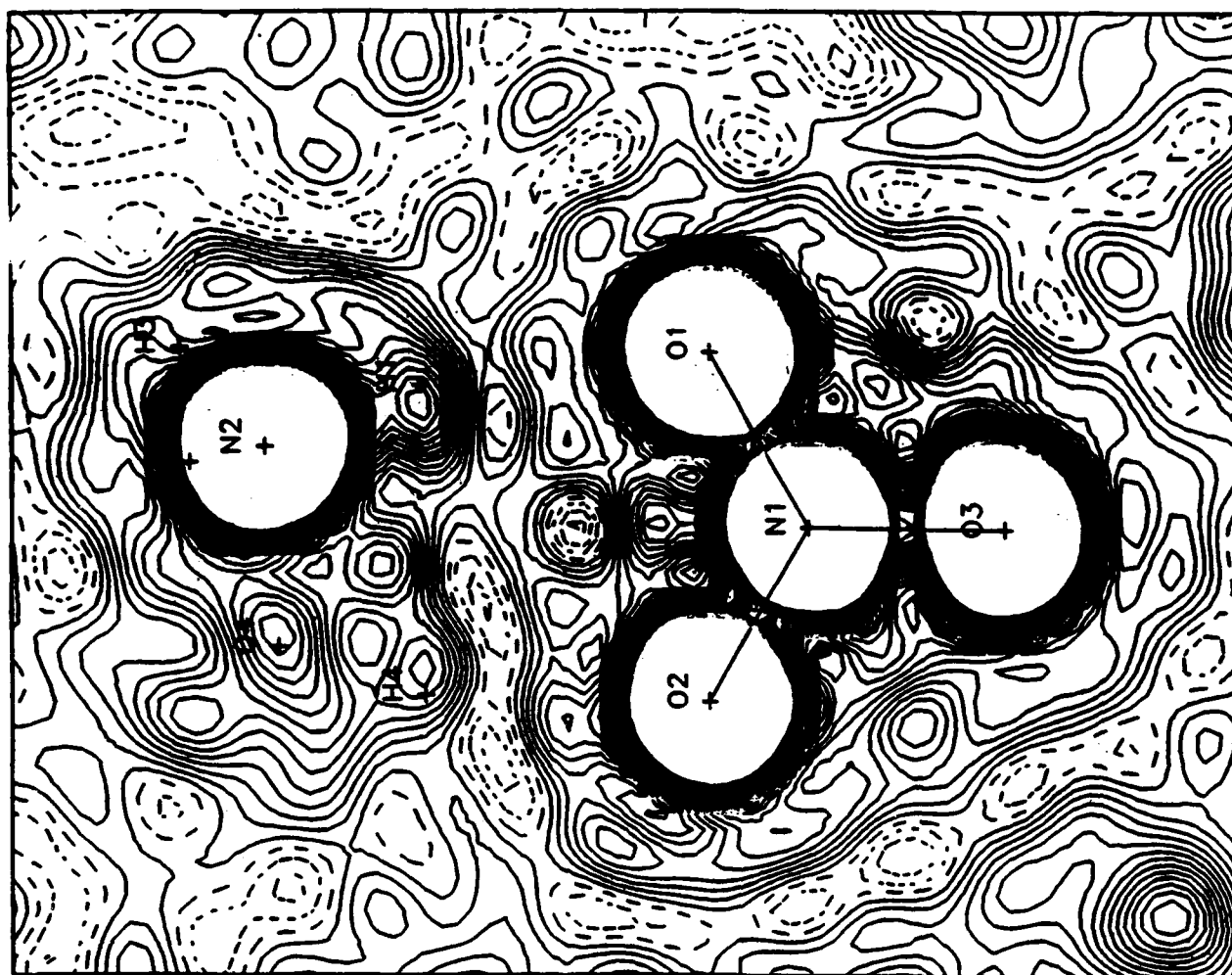
HAN HAN

3.00

X

-3.00

HAN X-N
 Hydrogens included
 $0.1 \text{ e}^-/\text{\AA}^3$ contours
 F_{obs}



3.80

Y

-3.80

HAN HAN

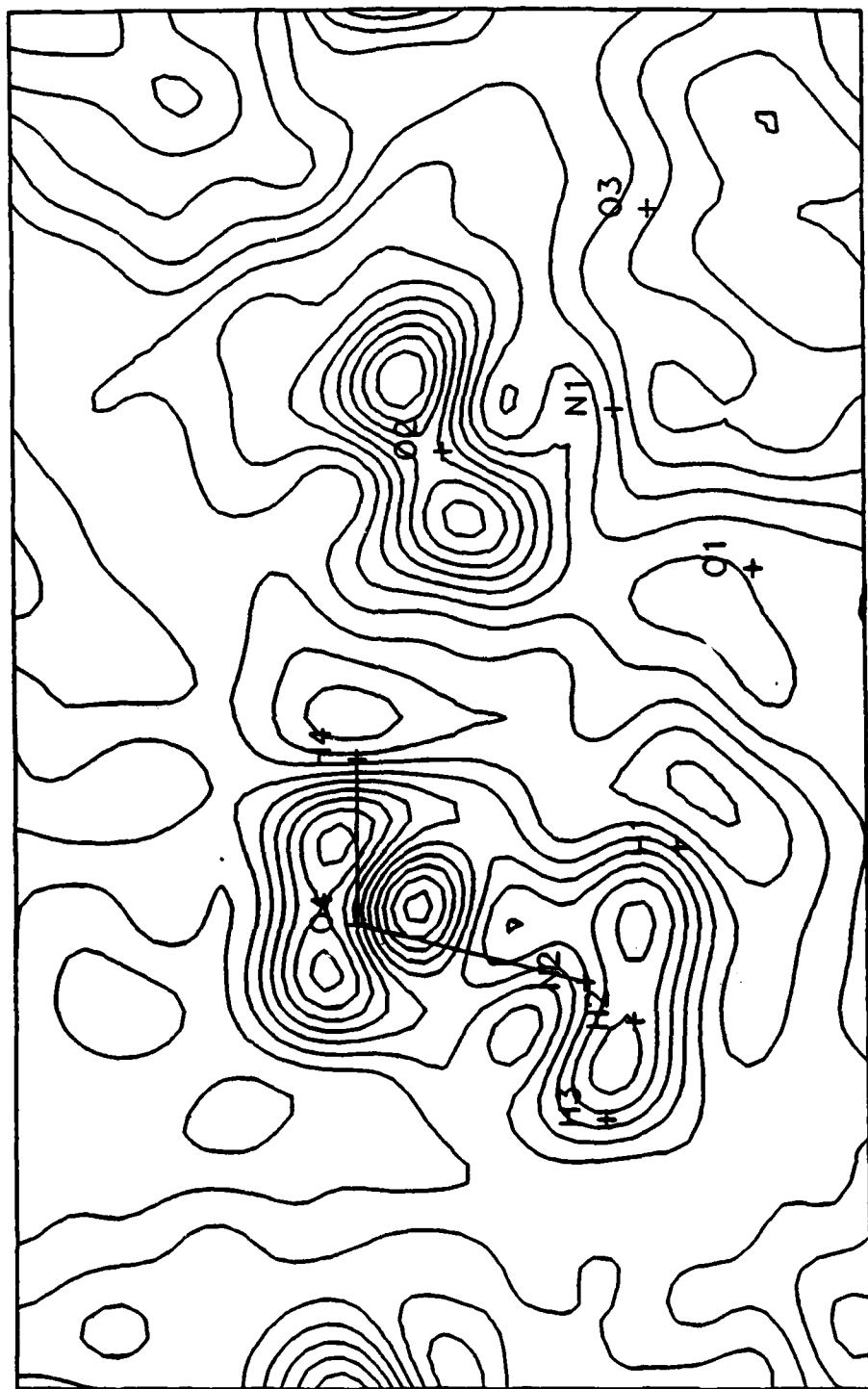
3.00

X

-3.00

$\text{NH}_3\text{-OH}^+$ X-N
 N-O_1 plane
 H
 H atom included

CONTOUR INTERVAL = .05 E/A3



4.00

X

4.00

2.50

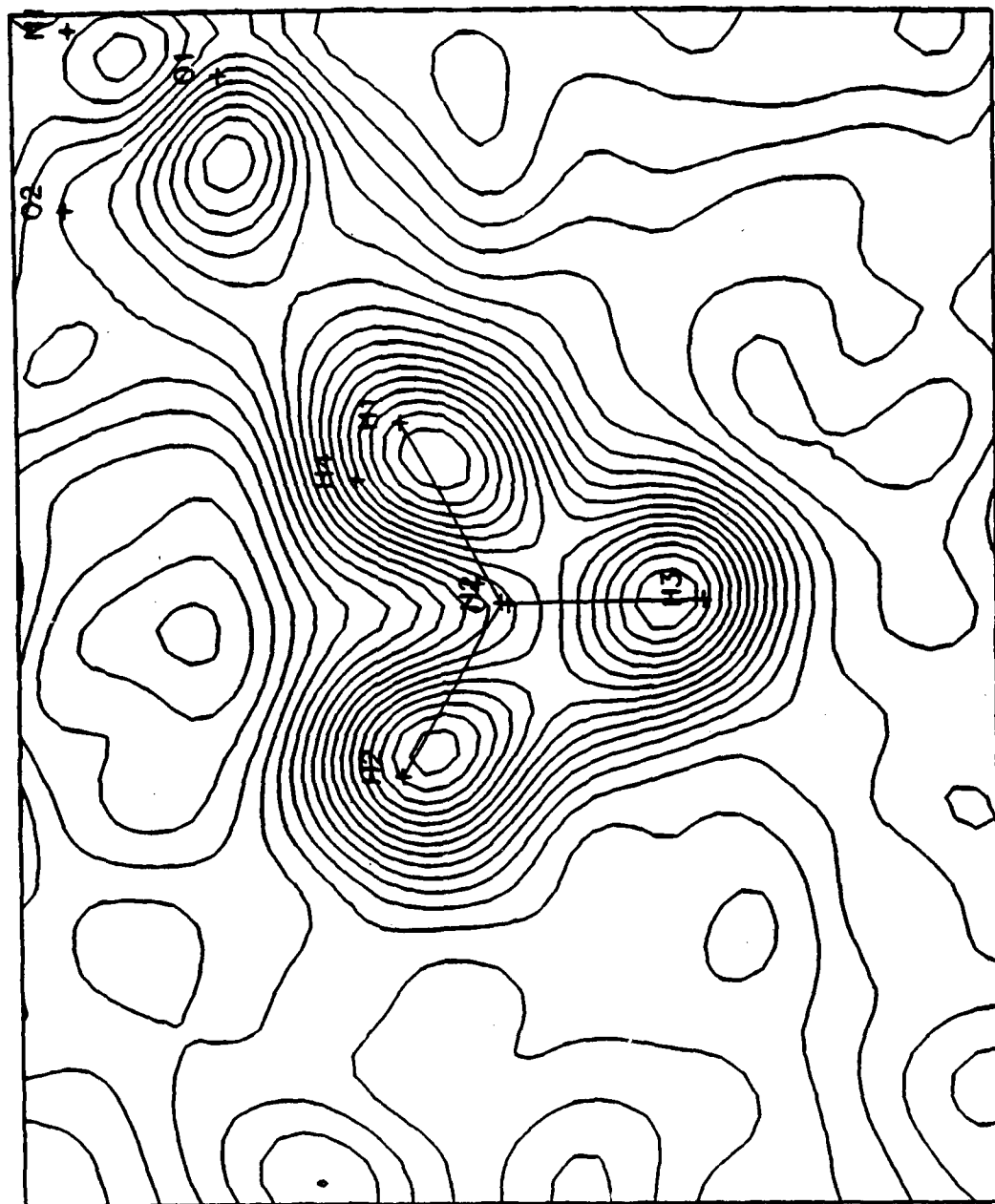
Y

-2.50

HAN HAN

$+H_2O - NH_3$ X-N
 plane of H_1, H_2, H_3
 Helium omitted.

CONTOUR INTERVAL = .05 E/A3

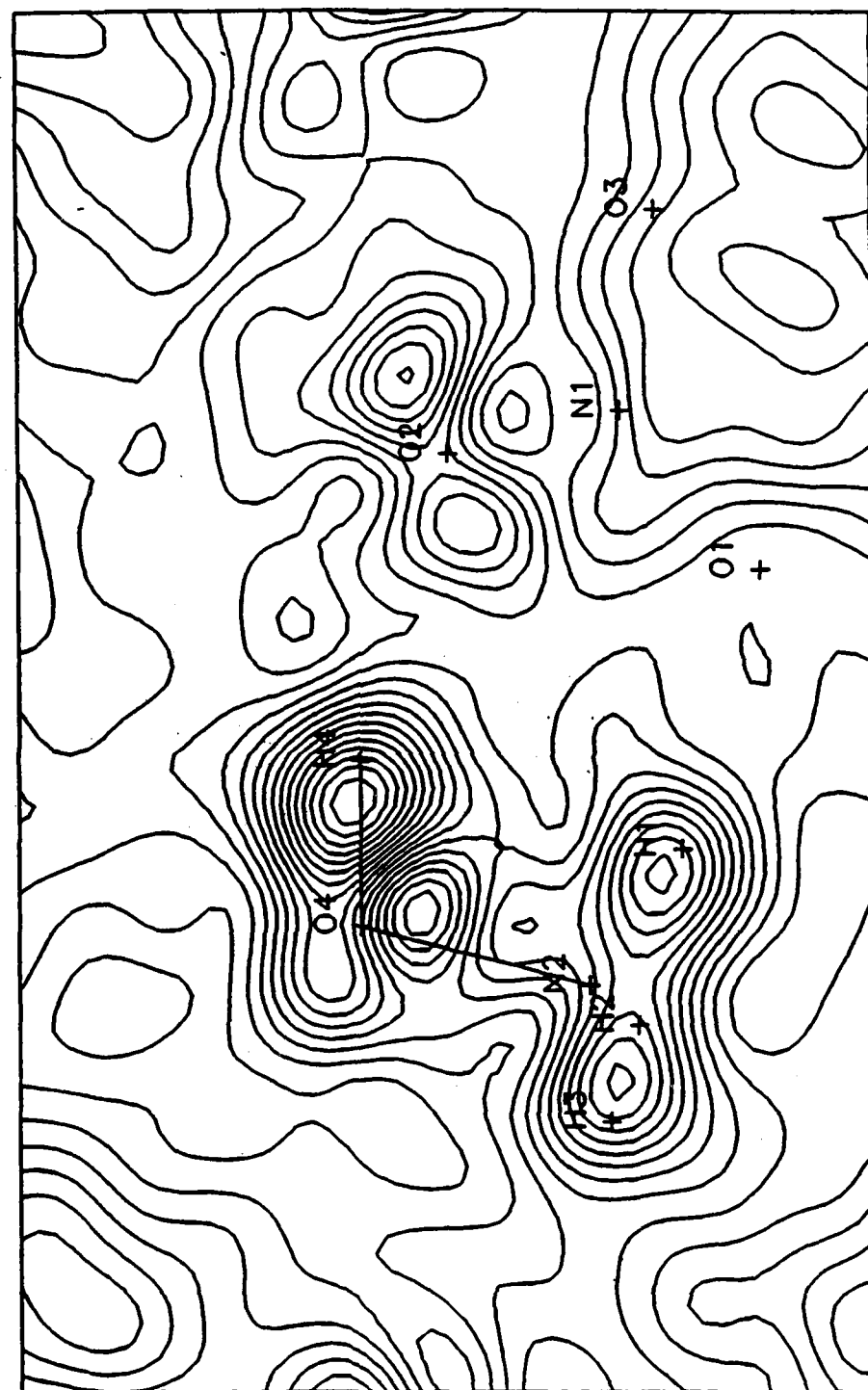


HAN HAN

NH_3OH^+ X-NI
N-O₄ plane

Hydrogen Omitted

CONTOUR INTERVAL = .05 E/A3



4.00

X

4.00

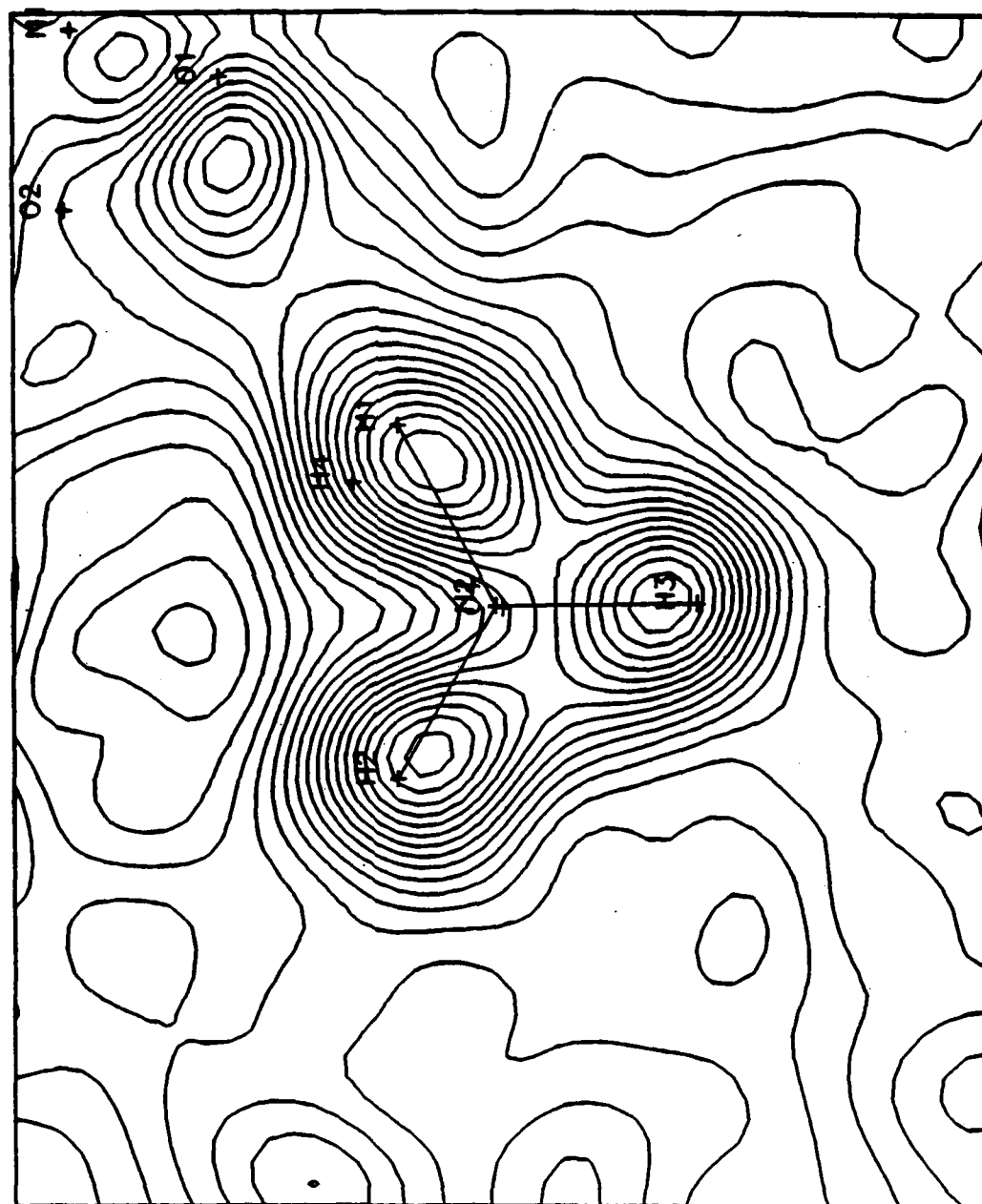
2.50

Y

-2.50

HAN HAN

CONTOUR INTERVAL = .05 E/A3



2.80

X

-2.80

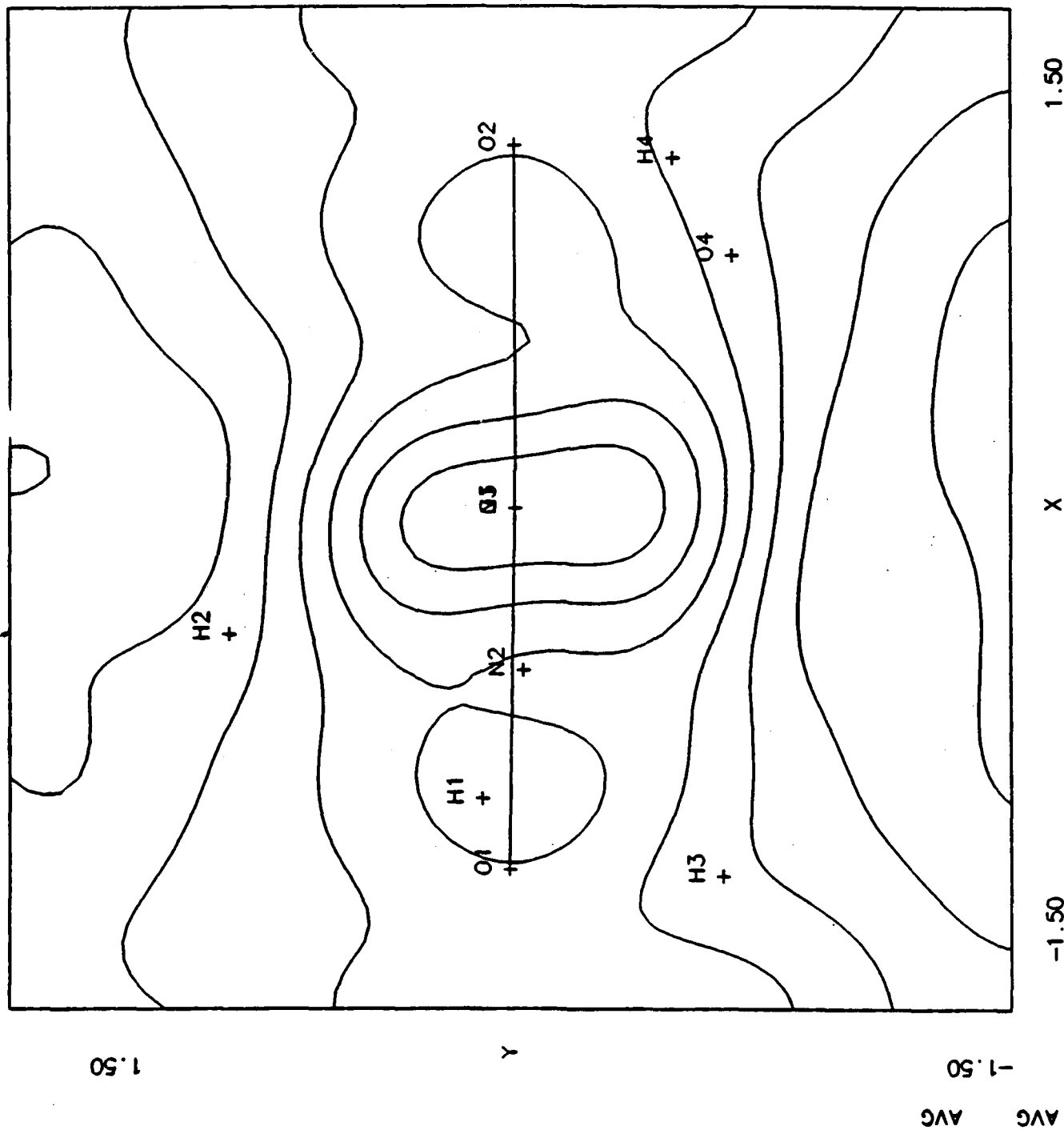
HAN HAN

-2.30

2.30

Y

NO_3^- X-N
 average $\bar{c}$ density
 at mid-point of
 O_3-N_2 bond.



High Pressure Spectroscopy and the Structure of HAN
Mark A. Davies* and Robert A. Fifer, BRL

Infrared spectra of aqueous solutions of deuterated hydroxylammonium nitrate (dHAN, 11 M in D_2O) have been recorded at pressures ranging from 1 bar to 17.5 kbar. Such data are needed as input and validation for theoretical models used to predict the physical properties of propellants, particularly in the environment of gun barrels at the time of ignition.

Because all protons of HAN are labile, the remaining hydrogen (3%) is distributed between water and the hydroxylammonium ion ($DO-H$, ND_3OH , HND_2OD). The isolated O-H and N-H vibrations are isotopically uncoupled from O-D and N-D vibrations, eliminating shifting and splitting of vibrational bands due to intramolecular coupling. Correlations between measured O-H bond distances with uncoupled vibrational frequencies allows the distribution of various O-H...O distances, where the O atoms are connected by a hydrogen bond, to be determined.

Pressures were generated using a diamond anvil high pressure cell. The sample was confined between the diamonds using a tantalum gasket. Pressures were measured using the known frequency shift of crystalline quartz as a function of pressure.

The N-O stretch shifts from 991.7 cm^{-1} to 1012.2 cm^{-1} and the nitrate ion bending mode shifts from 825.7 cm^{-1} to 816 cm^{-1} . The intensity of the N-O stretch, greater than that of the 1045 cm^{-1} nitrate ion symmetric stretch at atmospheric pressure, decreases with pressure and is less than that of the 1045 cm^{-1} band at 17.5 kbar. Spectra of the O-H stretching region (above

3000 cm^{-1}) are also shown. Spectral bandwidths of O-H vibrations are much narrower at high pressures. At this time, it has not been determined if a phase change has occurred.

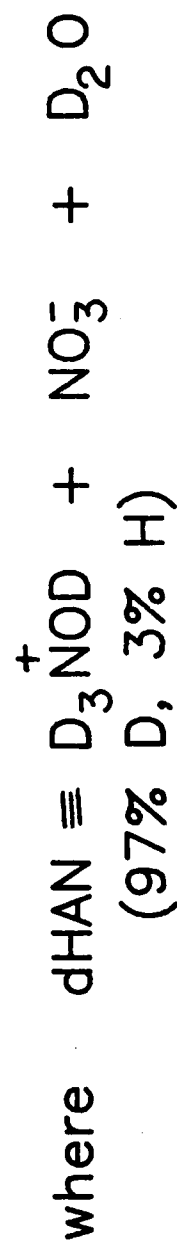
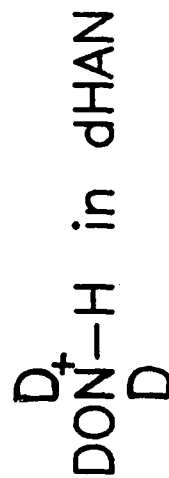
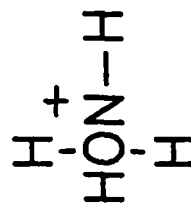
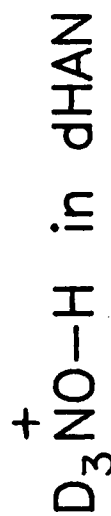
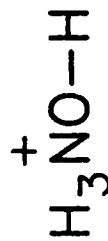
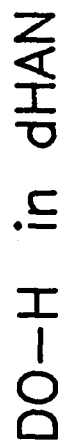
Future studies will include spectroscopic measurements over smaller pressure increments than those used in these preliminary experiments, as well as concentration and temperature dependence studies at high pressures. In addition, it is hoped that the HAN band positions at various pressures can be calibrated against the crystalline quartz standard, eventually eliminating the need for the addition of the pressure standard to the sample.

* National Research Council Postdoctoral Associate

Isotopic Uncoupling Spectroscopy

uncoupled vibration

species measured



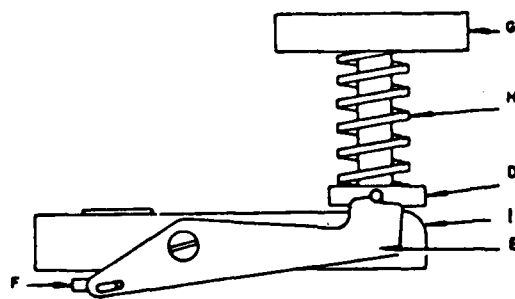
ADVANTAGES OF FTIR

speed of data aquisition
lack of sample fluorescence
lack of diamond fluorescence

DIAMOND ANVIL CELL ADVANTAGES

**simplicity of operation
small sample volumes**

Figure 2. Diamond anvil optical cell. Cross-section of cell: A, Diamonds; B, piston (composed of two parts held together by screws which provide for relative movement of the two parts for alignment purposes); C, hardened steel cylinder; D and F, two presser plates connected by the lever arms, E; G, screw; H, calibrated spring; I, steel body.



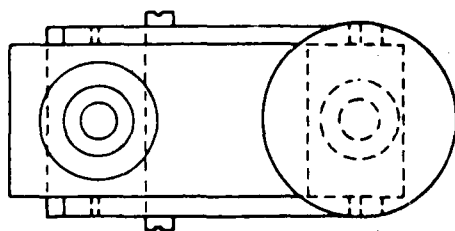
SIDE VIEW

Length: 12.0 cm.

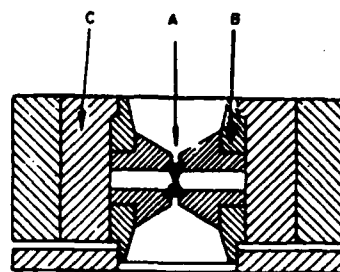
Base Height: 2.5 cm.

Width: 7.5 cm.

Spring Height: 3.5 cm.



TOP VIEW



DETAIL OF DIAMOND CELL

PROBLEMS

- 1. absorption strength necessitates very short path lengths**
 - a) difficulty in making gaskets**
 - b) pressure standard (ruby or quartz) must be ground to very small size**
- 2. light throughput is small due to small gasket aperture size**

EXPERIMENTAL

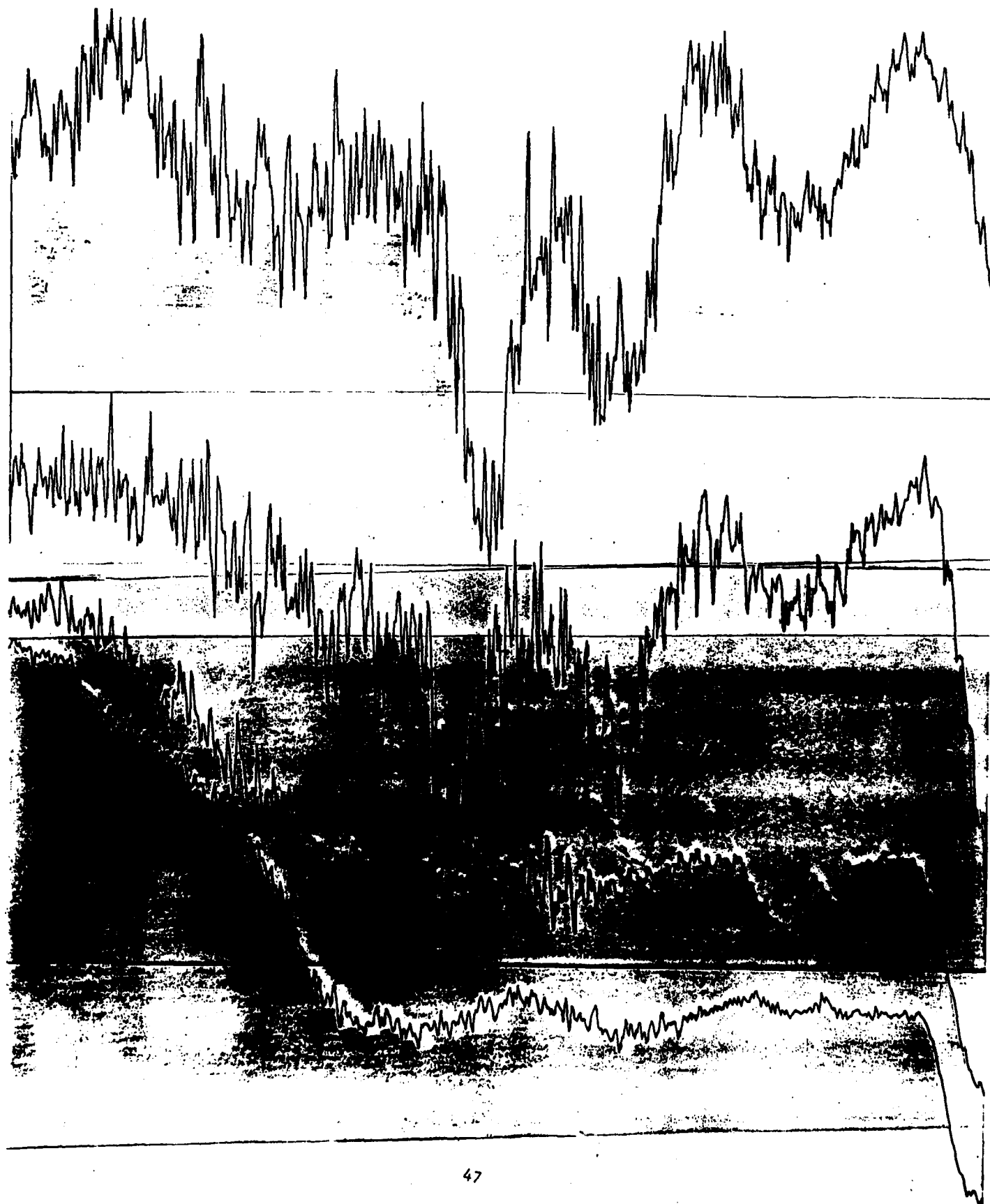
**Mattson Sirius 100 FTIR w/ beam condensing optics
DAC by High Pressure Diamond Optics Inc., Tucson, AZ
4 cm⁻¹ resolution**

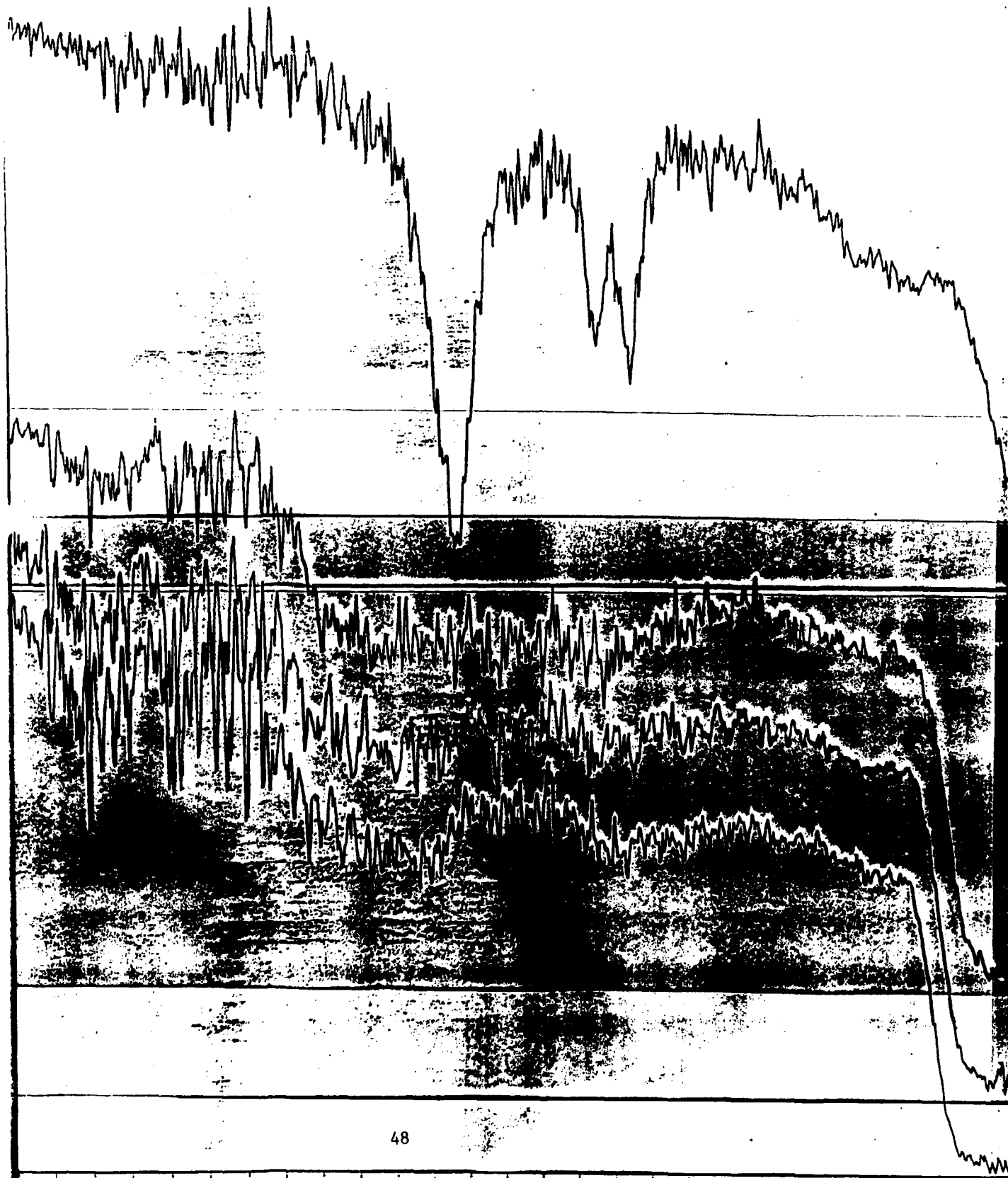
400 scans per spectrum

**Tantalum gaskets, 0.4mm - 0.5 mm diameter
20 micron pathlength (before pressurization)**

**Pressures were calibrated against a crystalline quartz standard
(Wong, Moffatt, Baudais, Appl. Spectrosc. 39, 4, 733, 1985)**

**Calibration was carried out externally using a gasket of the same
thickness as that used in the experiment. KBr transmitted the
pressure.**





48

3800

3600

3400

3200

3000

2800

2600

Wavenumber

600

800

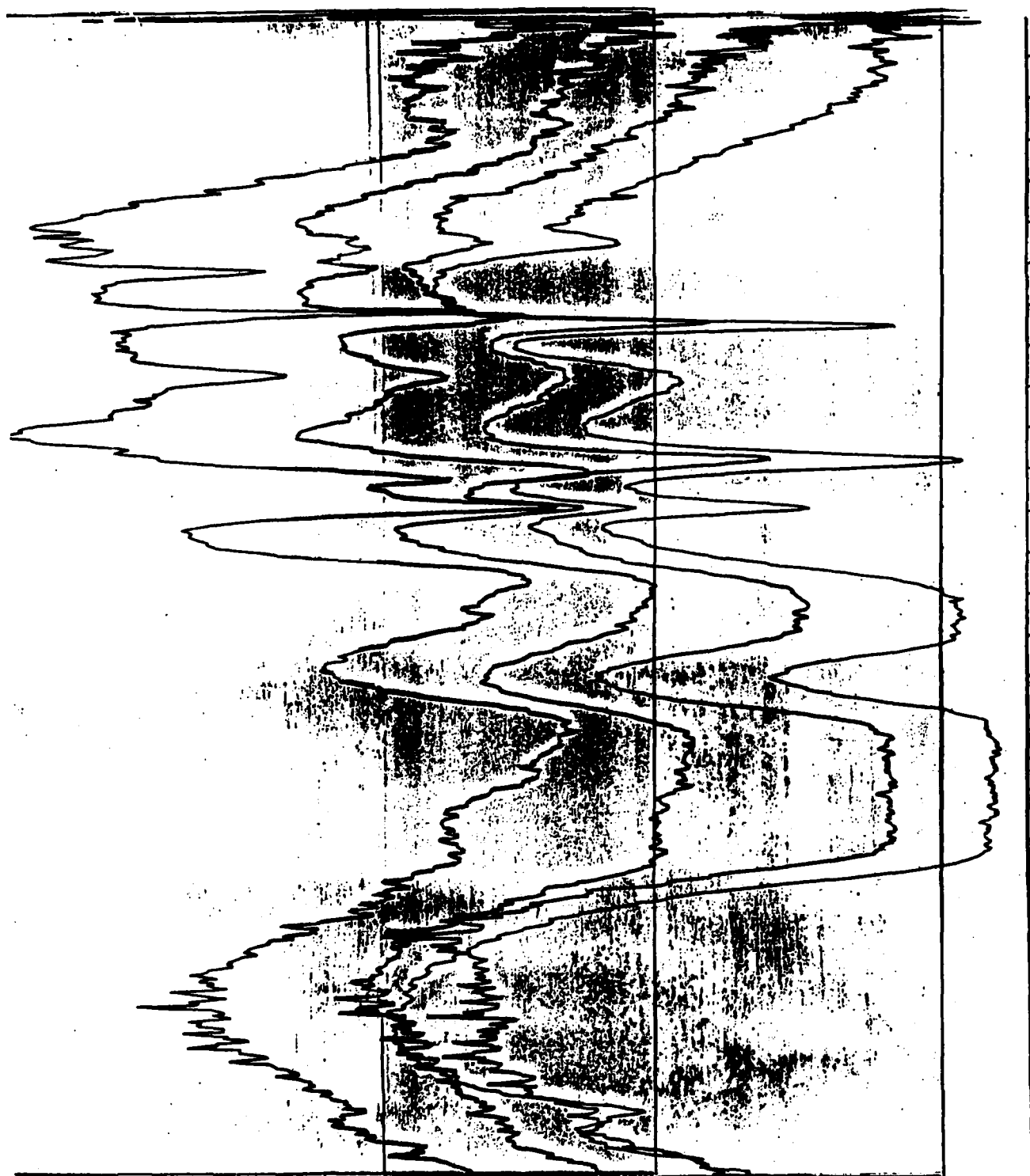
1000

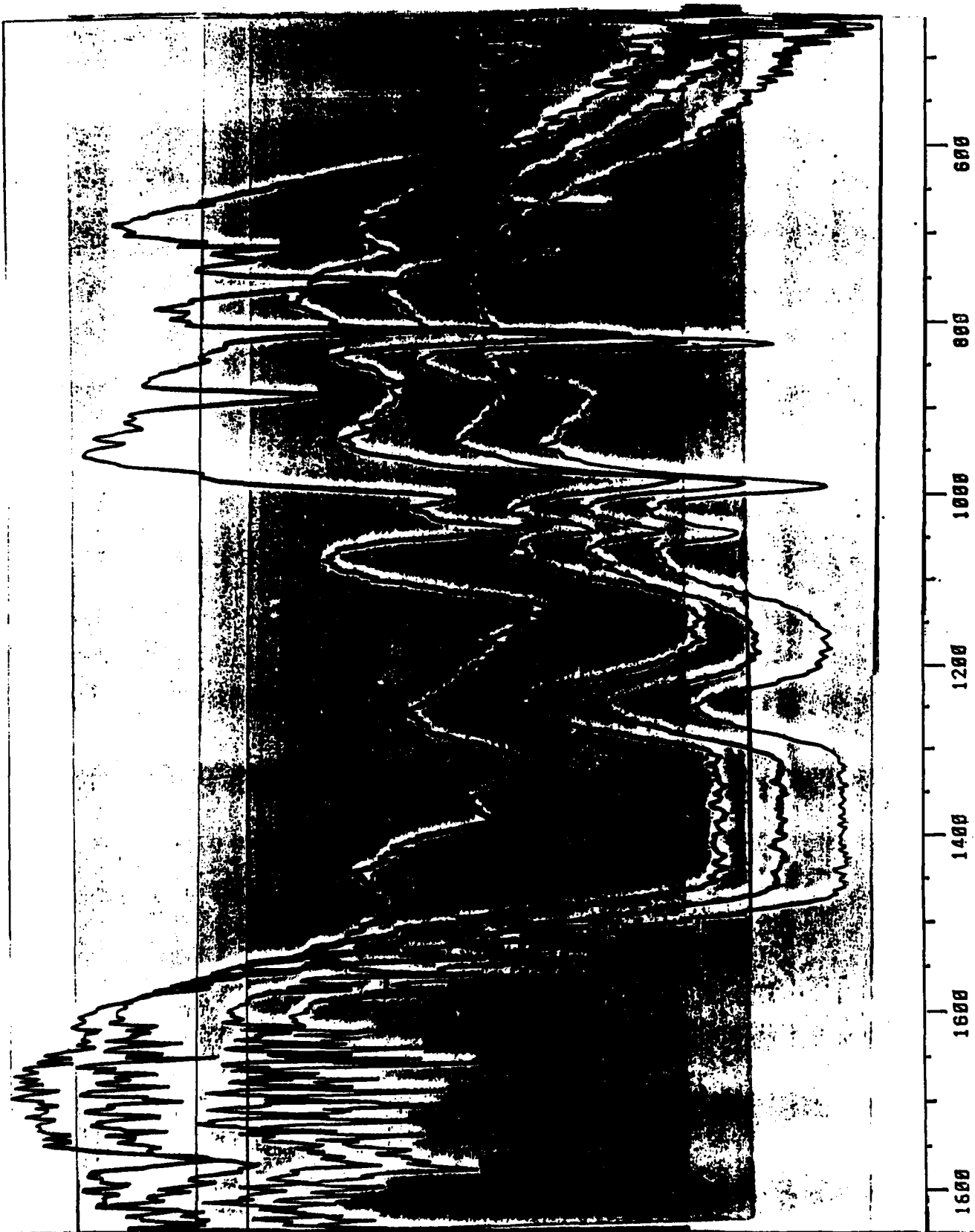
1200

1400

1600

1800





FUTURE WORK

**calibrate pressure sensitive HAN lines against quartz or ruby
(make HAN into its own pressure gauge)
use smaller pressure increments & determine onset of decomposition
concentration & temperature effects**

ACKNOWLEDGMENTS

**R. Fifer
N. Klein
L. Decker
M. Decker
R. Sassé
Prof. P. Garn**

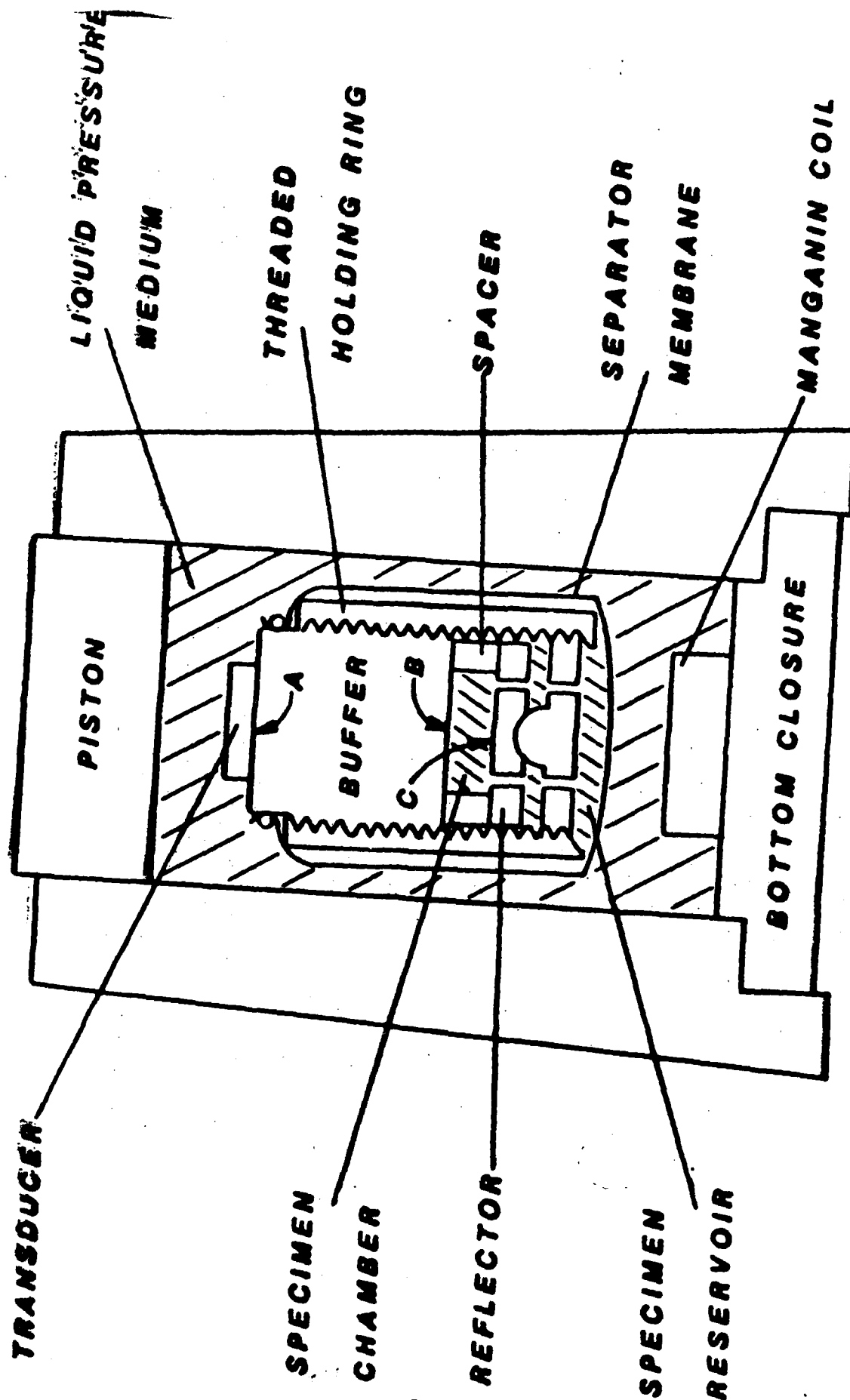
National Research Council

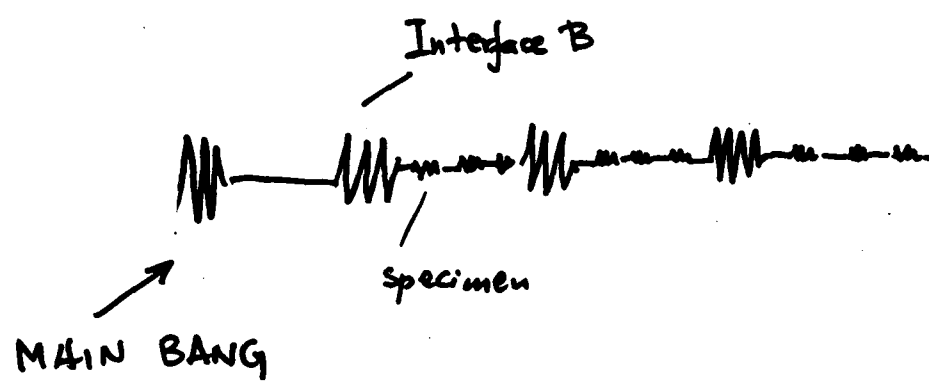
RAMAN SPECTROSCOPY OF AQUEOUS SOLUTIONS AT HIGH TEMPERATURES AND PRESSURES. P. D. Spohn and T. B. Brill, University of Delaware, Newark, De 19716.

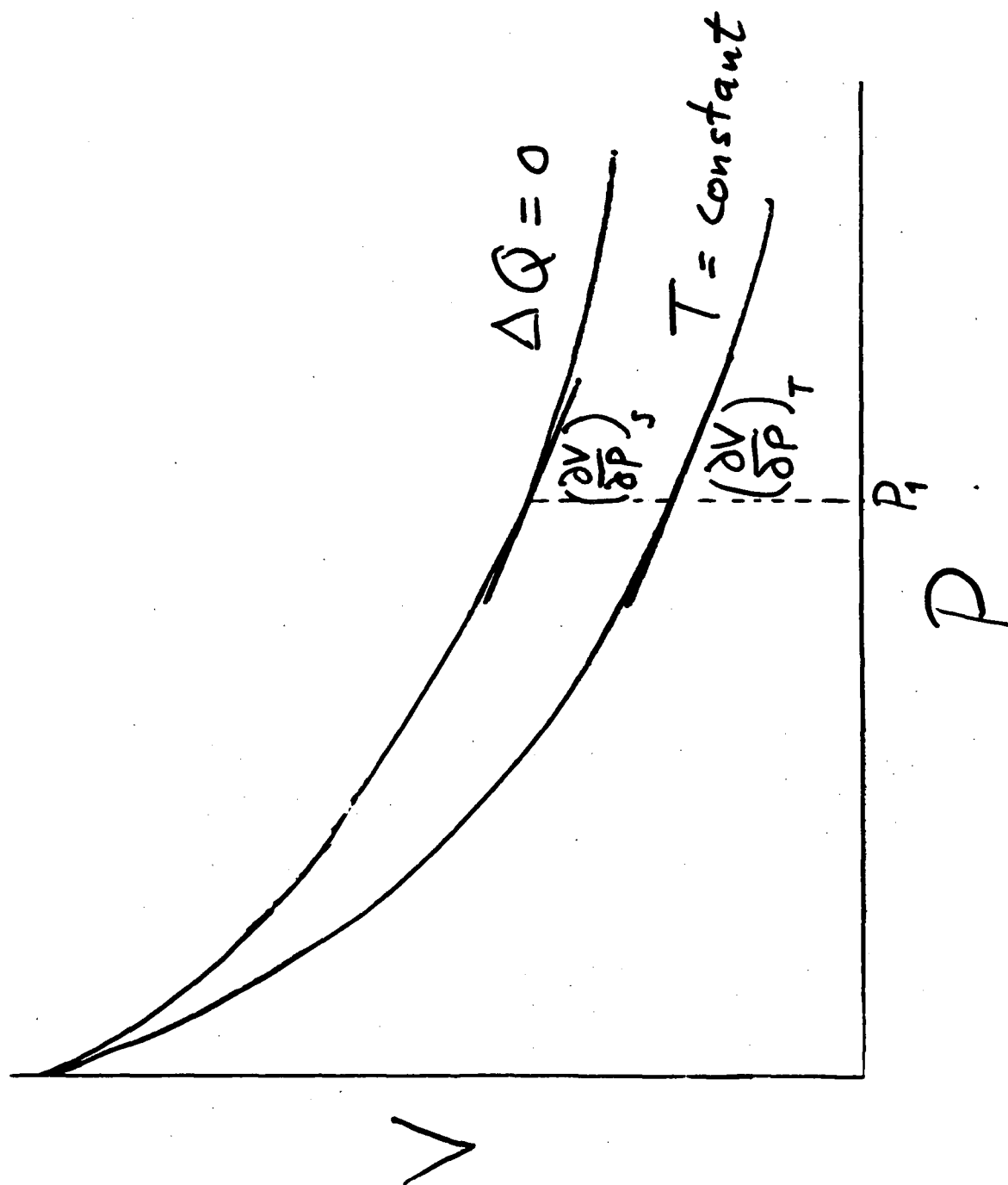
Raman spectroscopy has been shown to provide information on the microscopic organization of the aqueous nitrate ion. Previous studies have been limited to lower temperatures due to the corrosivity that is inherent in these systems. The development of a cell capable of containing corrosive salts under extreme conditions (450° C, 5000 psi) will be described. The study of aqueous inorganic nitrate salts under these conditions will be presented. The possibility of elucidating microscopic structures for metal-nitrate salts and metal-nitrate-HAN mixtures from these studies will be examined.

THE HIGH PRESSURE SOUND VELOCITY,
EQUATION OF STATE AND THERMODYNAMIC PROPERTIES
OF AQUEOUS MIXTURES OF HAN AND TEAN

J. FRANKEL & H. DOXBECK







THE SOUND VELOCITY MEASURES AN

ADIABATIC PROPERTY:

$$\frac{1}{K_s} = \rho v^2$$

where $K_s = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_s$ and $K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$

on an isothermal curve

BUT WE CAN RELATE THEM

$$K_T = K_s + \frac{TV\beta^2}{C_p}$$

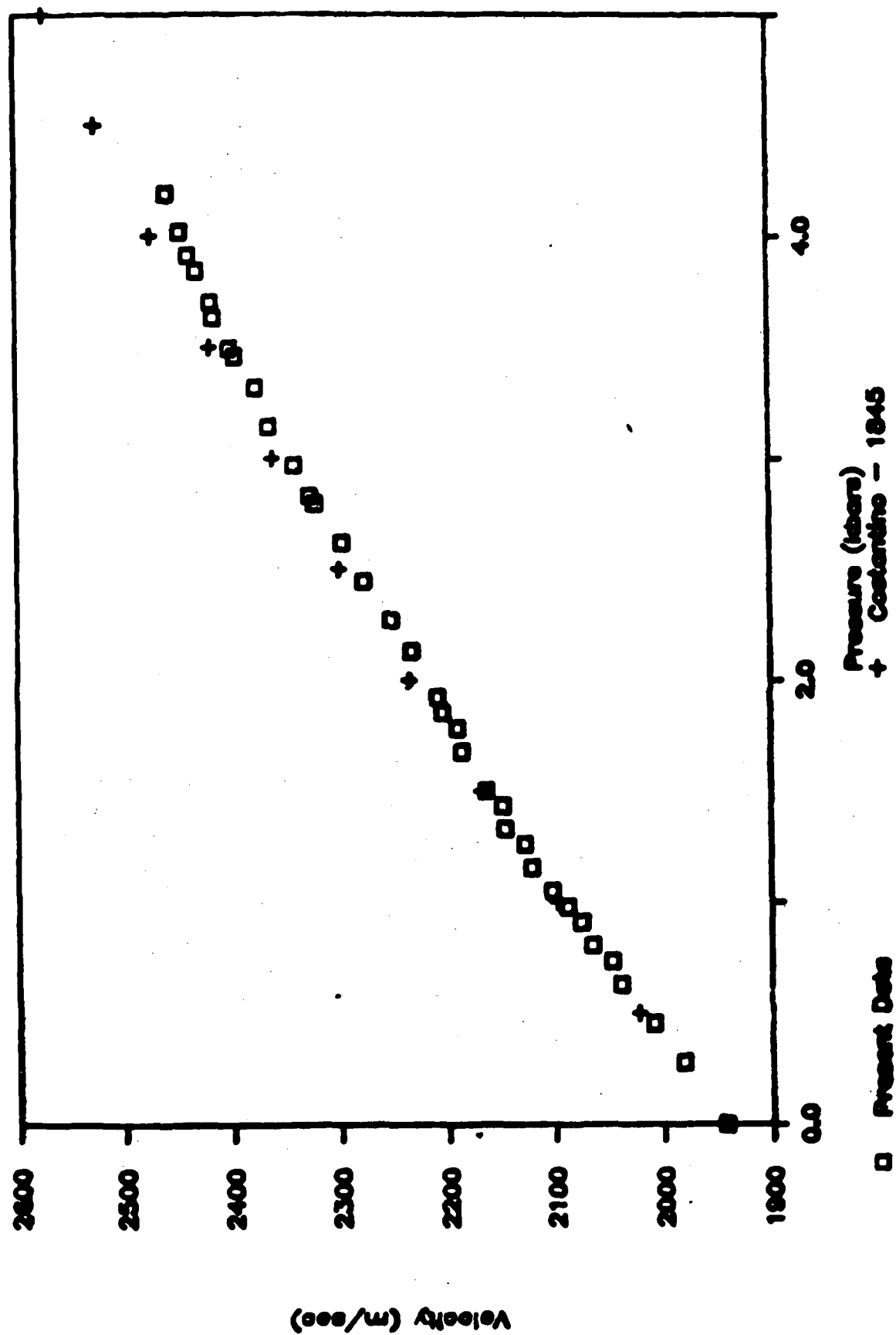
HENCE $\left(\frac{\partial V}{\partial P} \right)_T = -\frac{TV\beta^2}{C_p} - \frac{V^2}{v^2}$

AND FINALLY:

$$\rho(P) - \rho(P_0) = \int_{P_0}^P \frac{dP}{v^2} + \int_{P_0}^P \frac{T\beta^2}{C_p} dP$$

from Maxwell relations the Pressure dependence is found $\left(\frac{\partial \beta}{\partial P} \right)_T = -\left(\frac{\partial K_T}{\partial T} \right)$; $\left(\frac{\partial C_p}{\partial P} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P$

Comparison of Velocity Data



Comparison of Change in Density Data

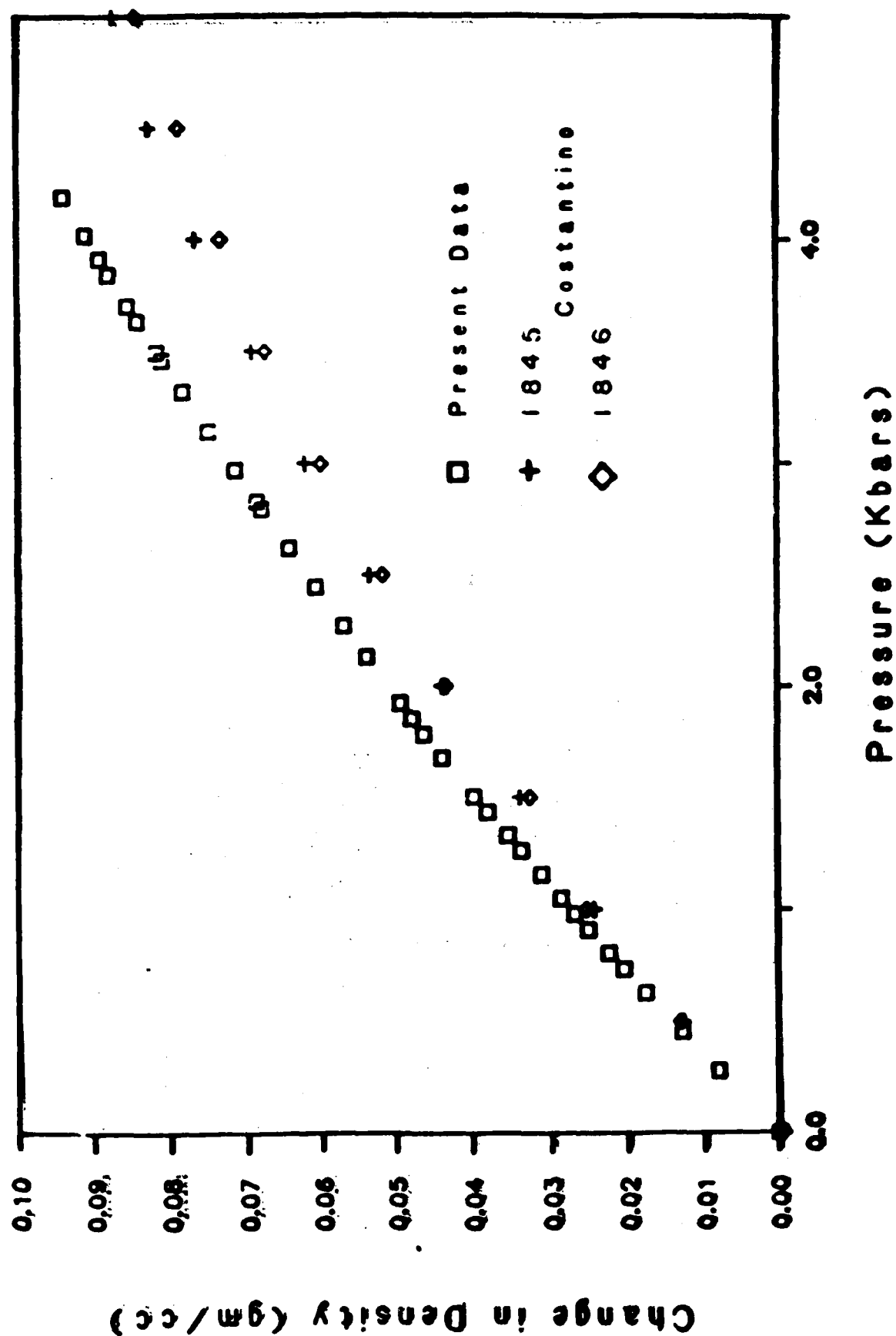
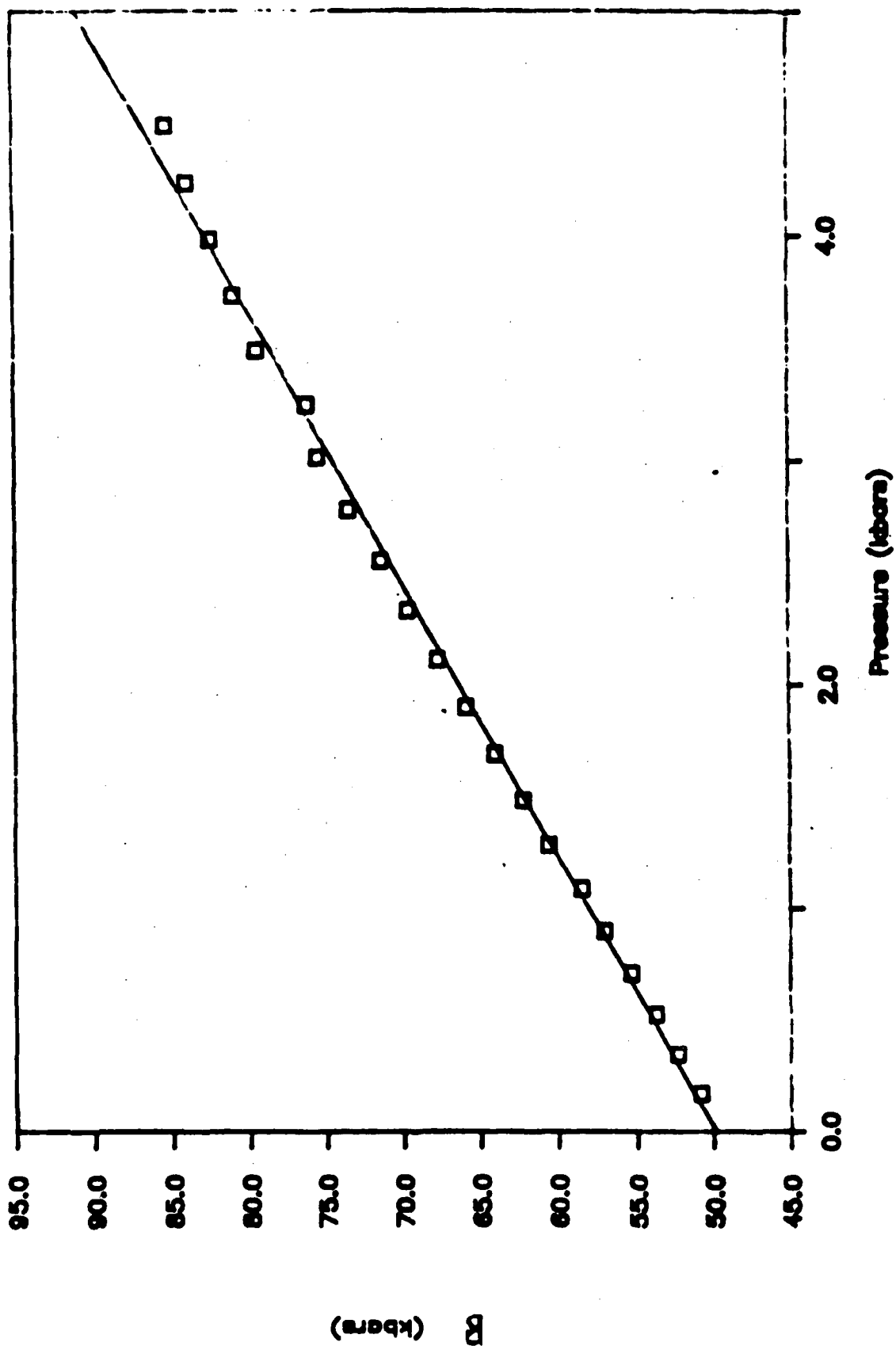


TABLE 2. Pressure and Temperature Dependence of Thermodynamic Quantities* (Obtained Here)

Equation	Units
$v(T) = 1966 - 1.703T$	m/sec, °C
$K_T(T) = 1.954 \times 10^{-5} + 5.200 \times 10^{-6}T$	bar ⁻¹ , °C
$v(P) = 1942.79 + 0.154P - 6.482 \times 10^{-6}P^2 - 1.638 \times 10^{-10}P^3$	m/sec, bar
$\rho(P) = 1.4532 + 2.9387 \times 10^{-5}P - 2.1711 \times 10^{-9}P^2 + 1.2192 \times 10^{-13}P^3$	gm/cm ³ , bar
$B(P) = 48679 + 10.848P$ (Tait Equation)	bar, bar
$C_p(P) = 2.29 + 9.78 \times 10^{-6}P$	joules/ gm K, bar
$\beta(P) = 4.898 \times 10^{-4} - 5.20 \times 10^{-8}P$	K ⁻¹ , bar
$K_T(P) = 2.02 \times 10^{-5} - 3.38 \times 10^{-9}P + 3.36 \times 10^{-13}P^2$	bar ⁻¹ , bar

*Pressure dependence found at room temperature (23°C).
Temperature dependence found at one atmosphere.

Tait Equation



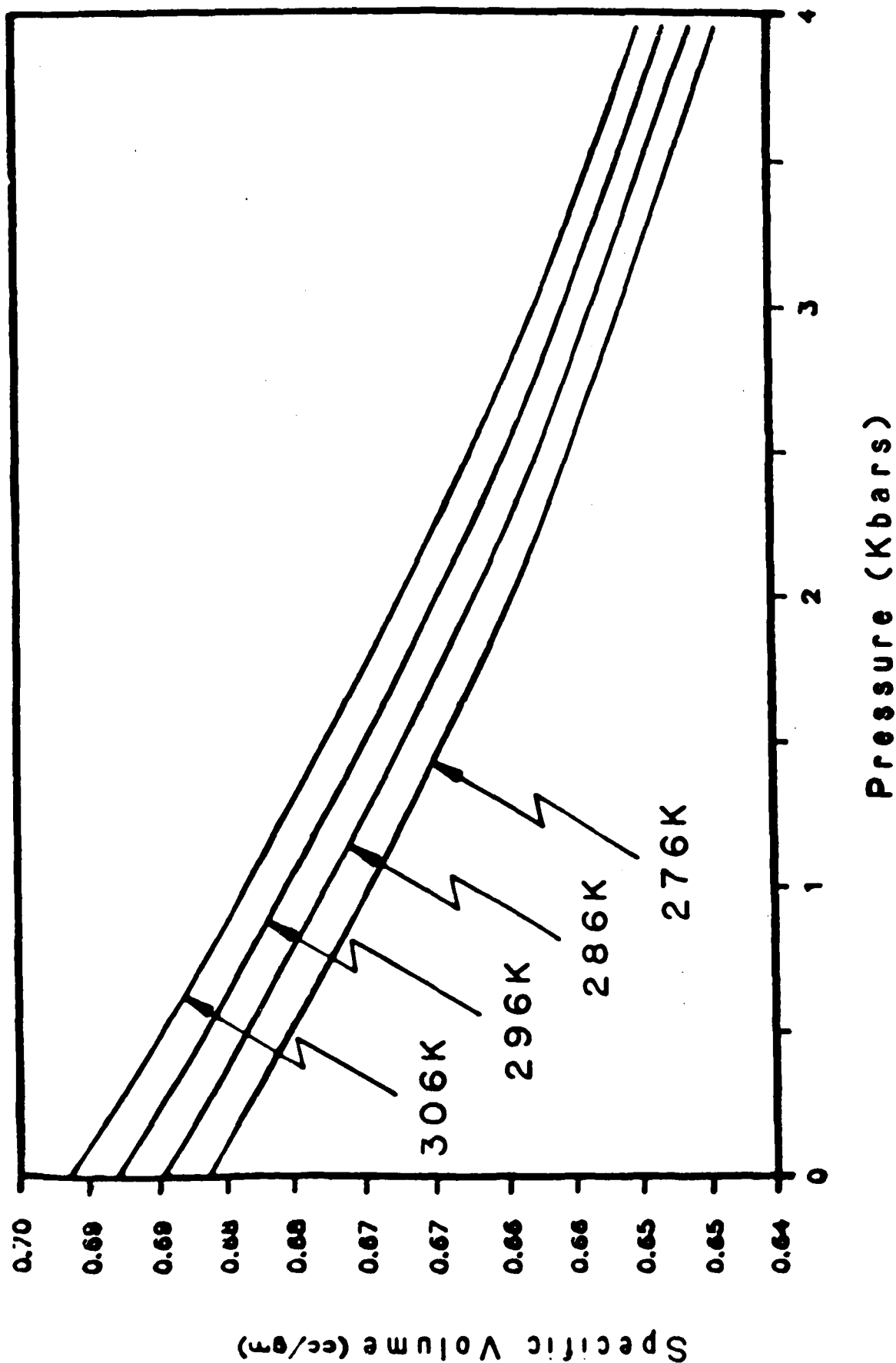
To OBTAIN THE TEMPERATURE DEPENDENCE

FOR PHASE REGIONS WHERE NO PHASE CHANGE

TAKES PLACE

$$\frac{dv}{v} = - \int_{P_i}^P K_T(P) dP + \int_{T_i}^T \beta dT$$

Complete Equation of State



Stimulated Raman Scattering and Explosive Vaporization Induced by Laser
Radiation on a Water Droplet Containing Nitrate

David H. Leach and Richard K. Chang

Yale University
New Haven, Connecticut 06520

Abstract

When micrometer-size droplets are irradiated by a visible laser beam, they can be envisioned as a lens to concentrate the incident radiation inside the droplet and as an optical cavity to provide feedback for the internally generated nonlinear radiation. Because of the concentrated internal intensity and optical feedback, the threshold for stimulated Raman scattering (SRS) from water droplets containing NH_4NO_3 can be readily achieved at low input intensity (e.g., less than 1 GW/cm^2). The SRS spectra contain the following peaks: (1) first-order SRS peaks of the stretching modes of NO_3^- and O-H; (2) nth order SRS peaks of these stretching modes with the (n-1)th order SRS as the pump source; and (3) morphology-dependent resonance peaks superimposed on the SRS of the stretching mode of O-H. Chemical species identification can be made from the energy shift of the SRS peaks. The absolute size of the droplet can be deduced from the wavelength spacing of the morphology-dependent peaks. The ratio of NO_3^- and H_2O concentration within the droplet can be qualitatively estimated from the SRS intensity

ratio of the NO_3^- mode and the O-H mode, even when the NO_3^- concentration is below 0.2 M.

At input intensities higher than that necessary to achieve SRS from a single droplet, laser-induced breakdown (LIB) can occur within the droplet shadow face. The LIB is caused by the following two processes: (1) multiphoton ionization to produce the few priming electrons and (2) cascade multiplication which rapidly increases the plasma density in subnanoseconds. Once LIB has been achieved during the rising portion of the input pulse, the transparent droplet is transformed into an optically opaque droplet which can absorb the remaining portion of the laser pulse.

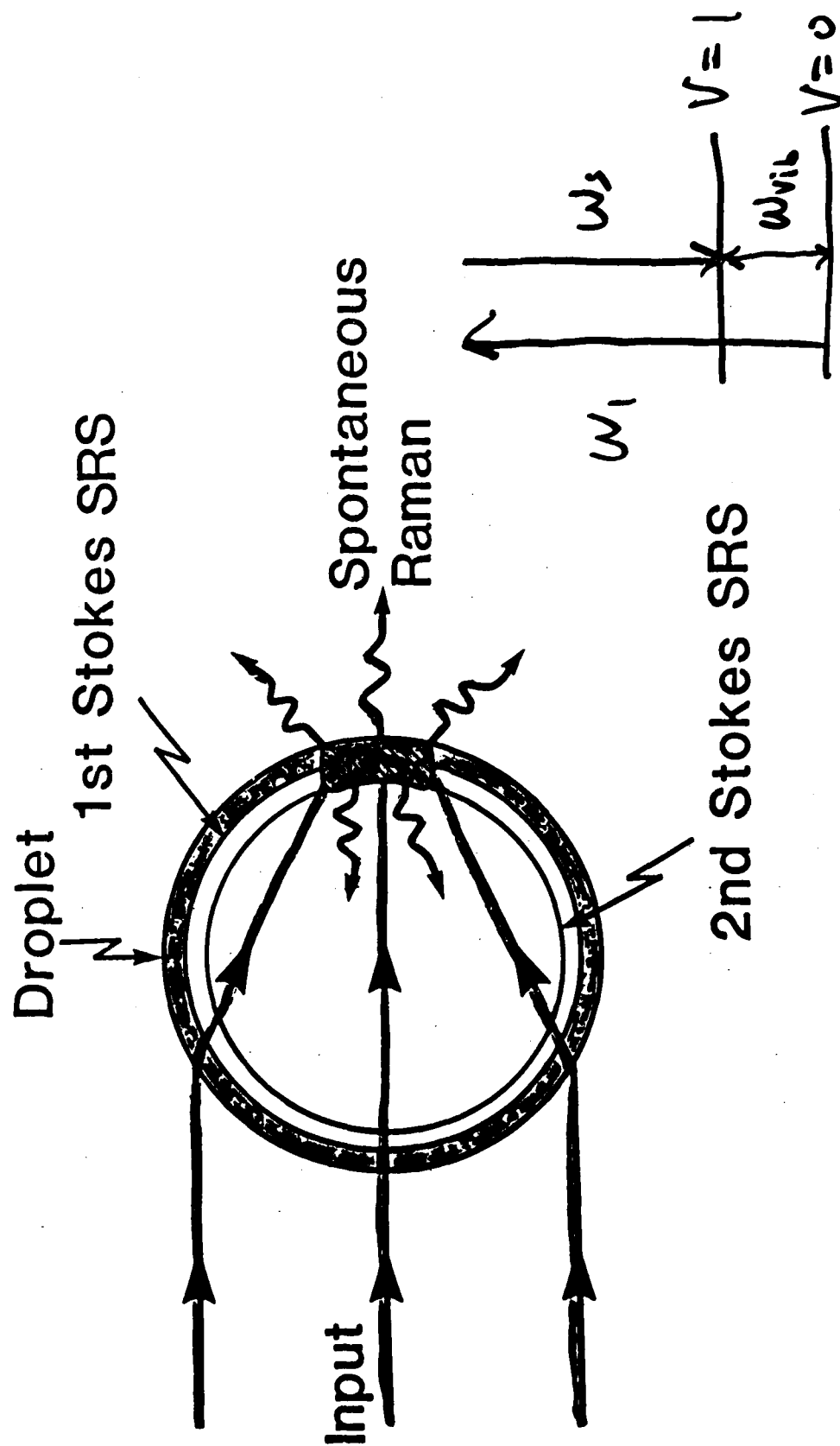
LIB has been investigated in droplets containing 5 M NH_4NO_3 with a spatially resolved spectroscopic technique, which can detect the discrete emission peaks from atomic H (Balmer lines) and once ionized N and O at various locations within the plasma plumes ejected from the shadow face and the illuminated face of the droplet. Since the linear Stark parameters of H are well known, the electron density within these plumes can be estimated from the spatially varying lineshape of the H Balmer emission peak. Although the connection between LIB and electrode ignition of liquid propellents is not clear at this moment, the spectroscopic techniques we have developed to investigate the LIB associated plasma plumes from droplets should be applicable to the study of plasma ignition of liquid propellents with electrodes.

Partial support of U.S. Army Research Office (Contract No. DAAL03-87-K-0076) is acknowledged.

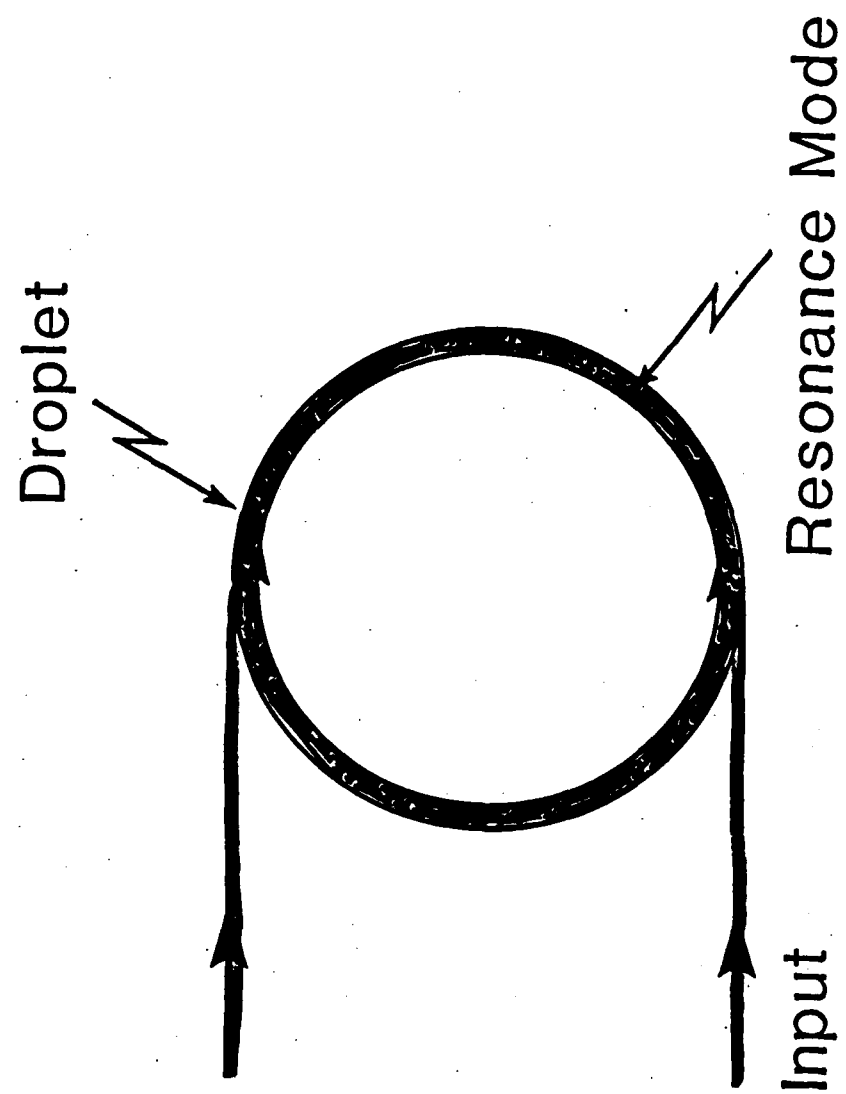
Stimulated Raman Scattering
and
Explosive Vaporization
Induced by Laser Radiation
on
a Water Droplet Containing Nitrate

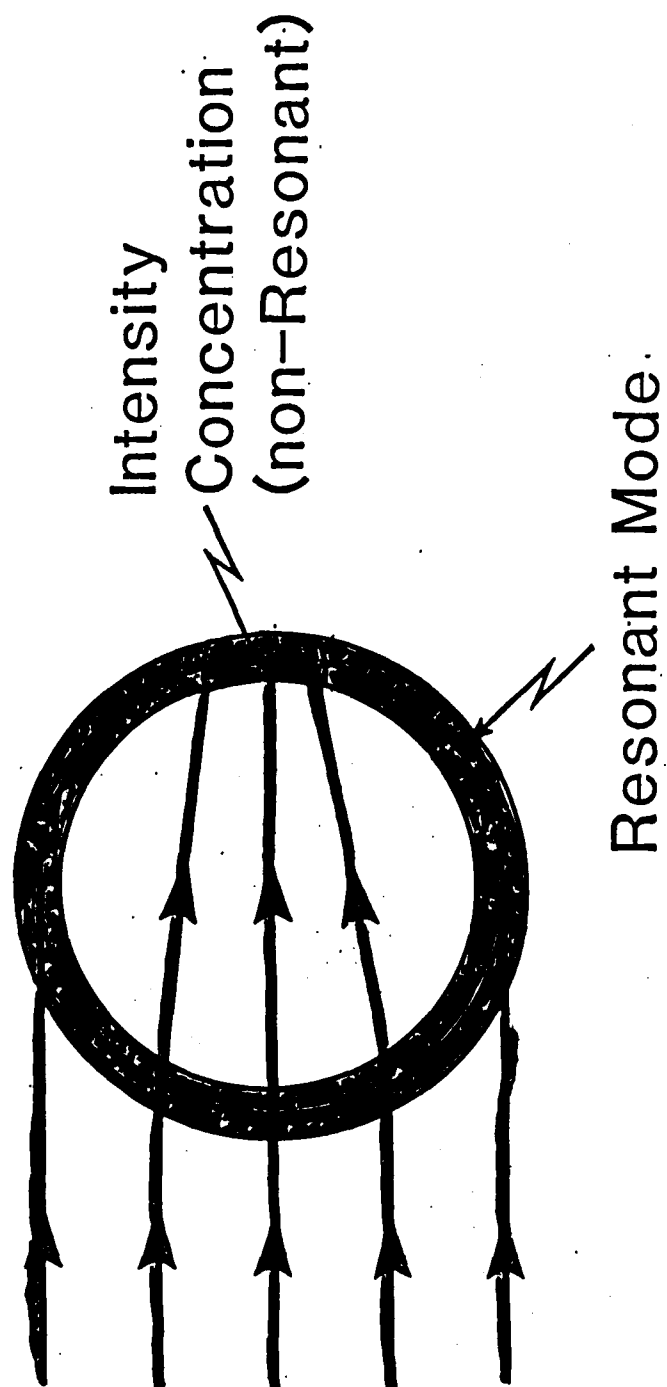
BRL
August 25, 1987

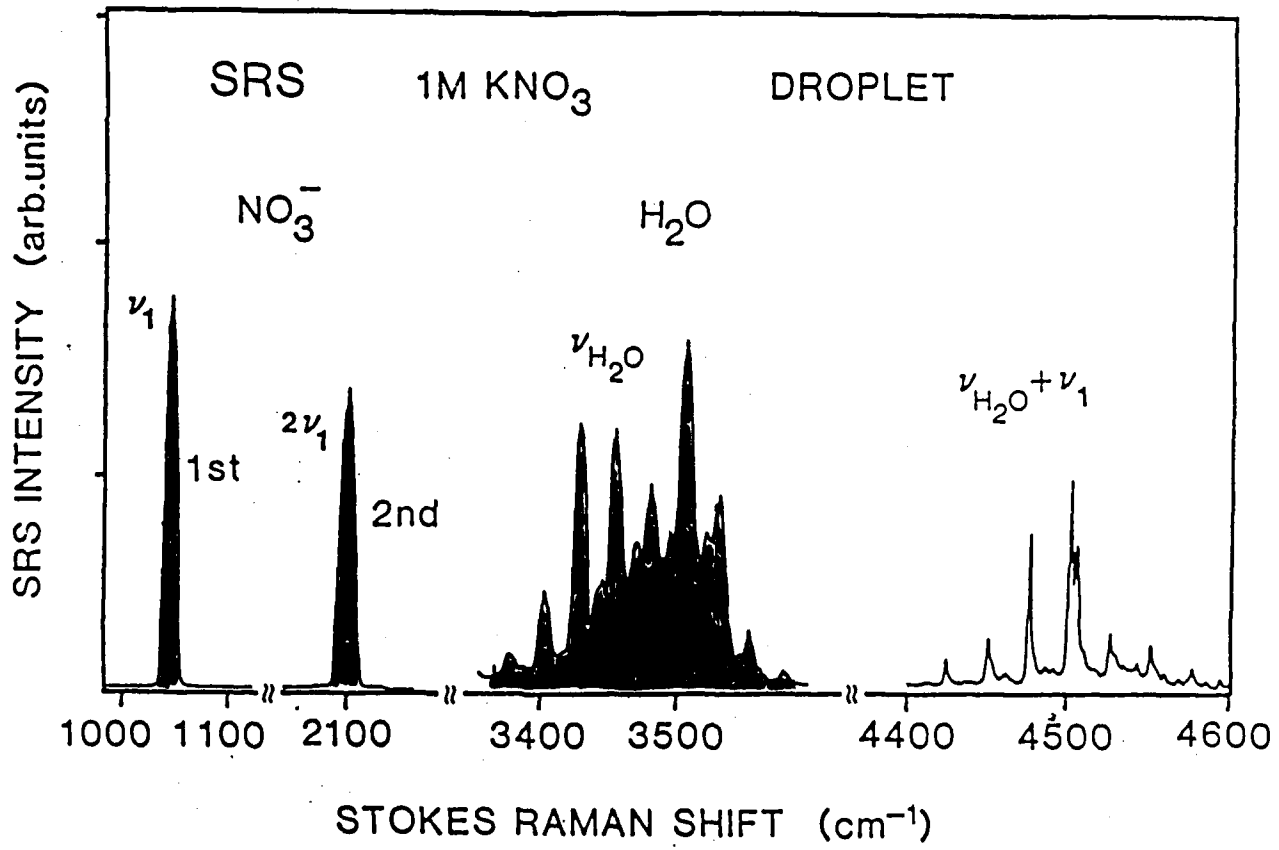
David H. Leach
Richard K. Chang
Yale University

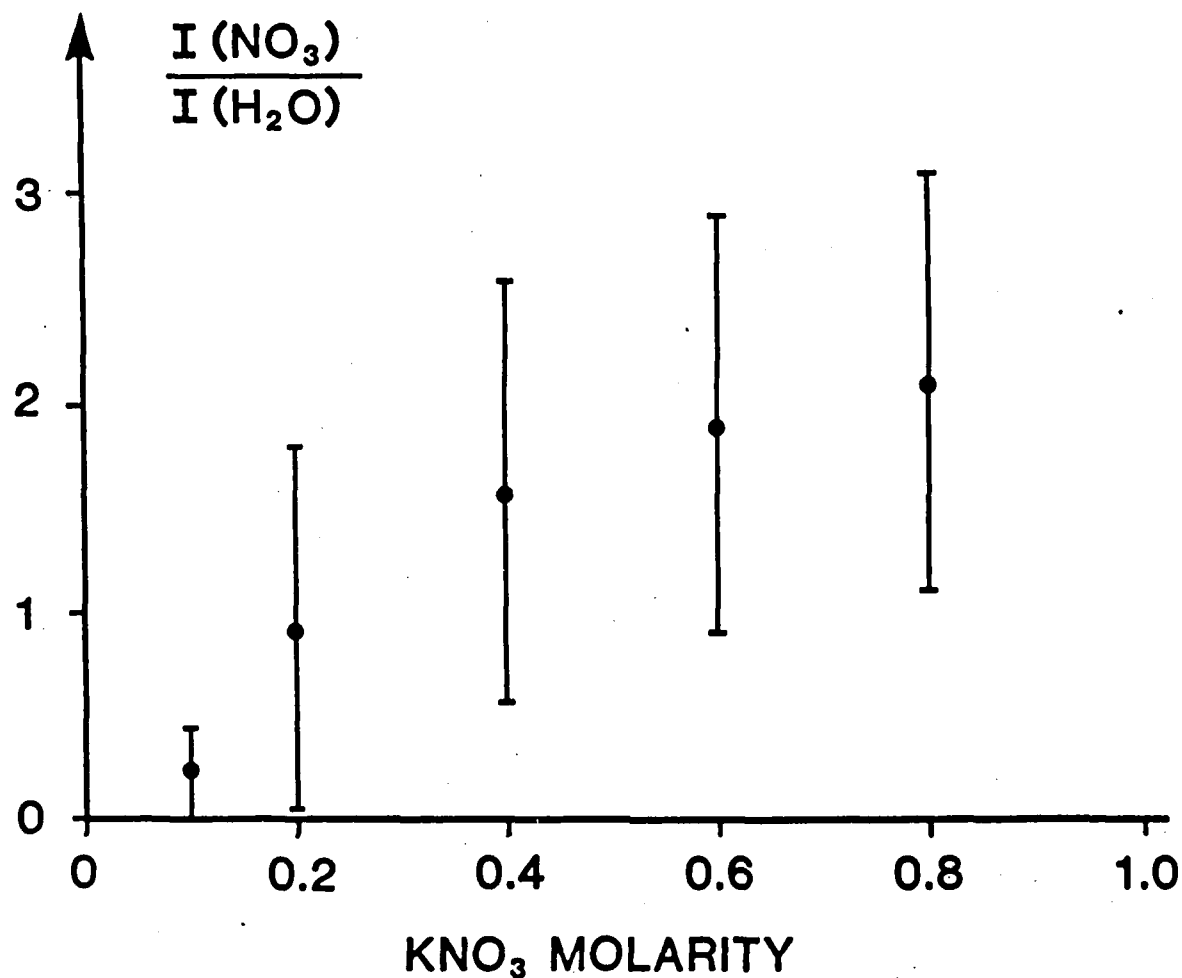


$$\omega_s = \omega_1 - \omega_{vib}$$





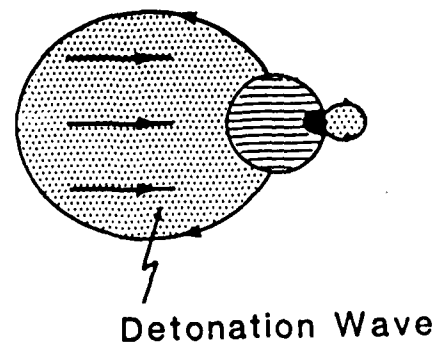
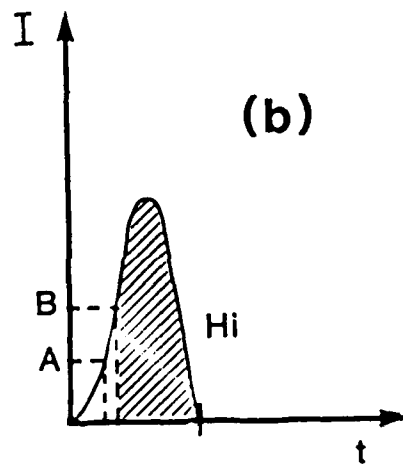
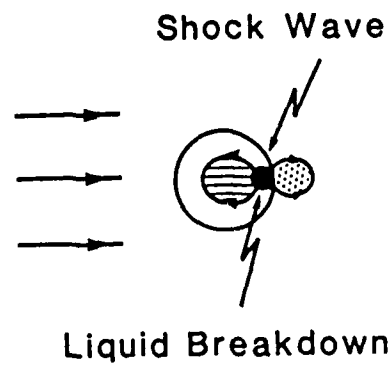
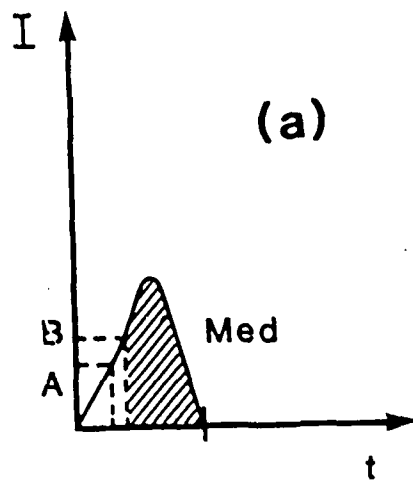




Intensity ratio of the NO_3^- mode at 1050 cm^{-1} and the O-H stretching mode at 3460 cm^{-1} as a function of the KNO_3 molarity. Each point represents the mean value of at least 10 measurements with 90% of all measurements falling within the error margin.

Stimulated Raman Scattering Conclusions

- 1) Species identification via molecular vibrational frequency**
- 2) Resonance mode spacing provides size information**



Shadow side Illuminated side

Forward Backward

4 0 -4 -8 r/a



Spectrograph

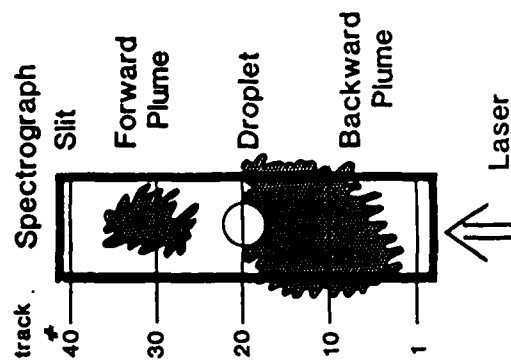
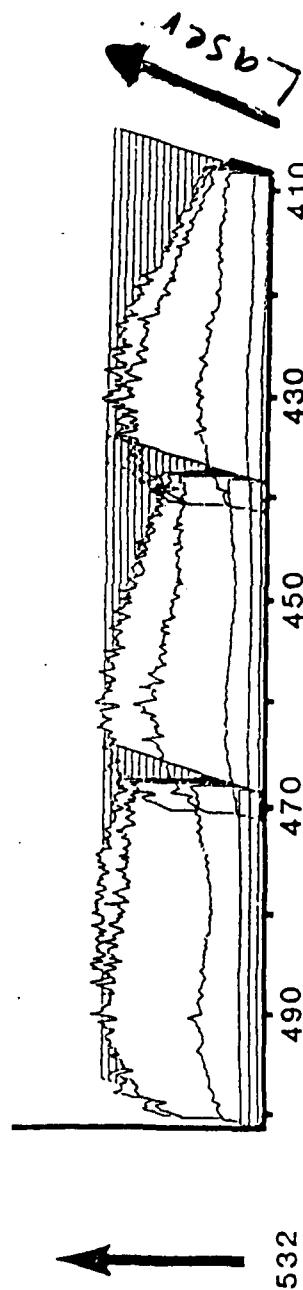
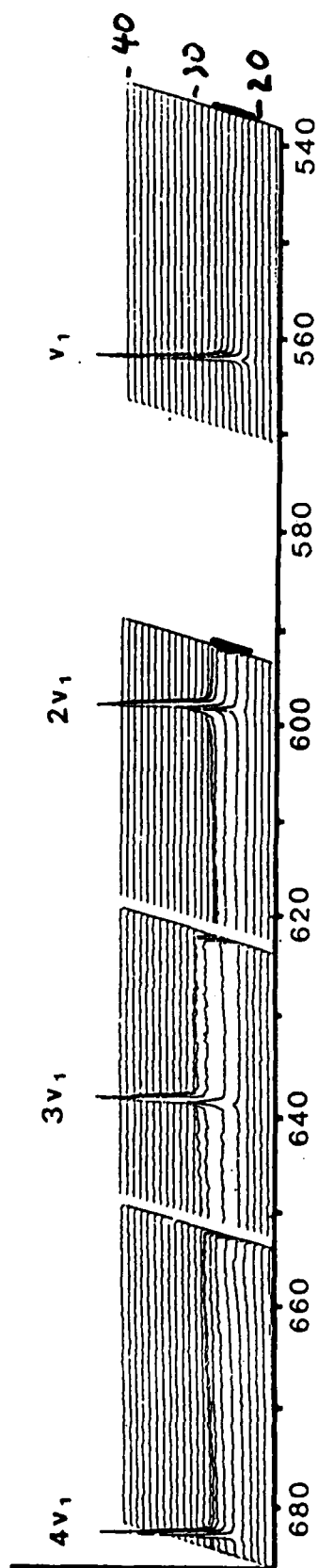
Slit

Laser Direction



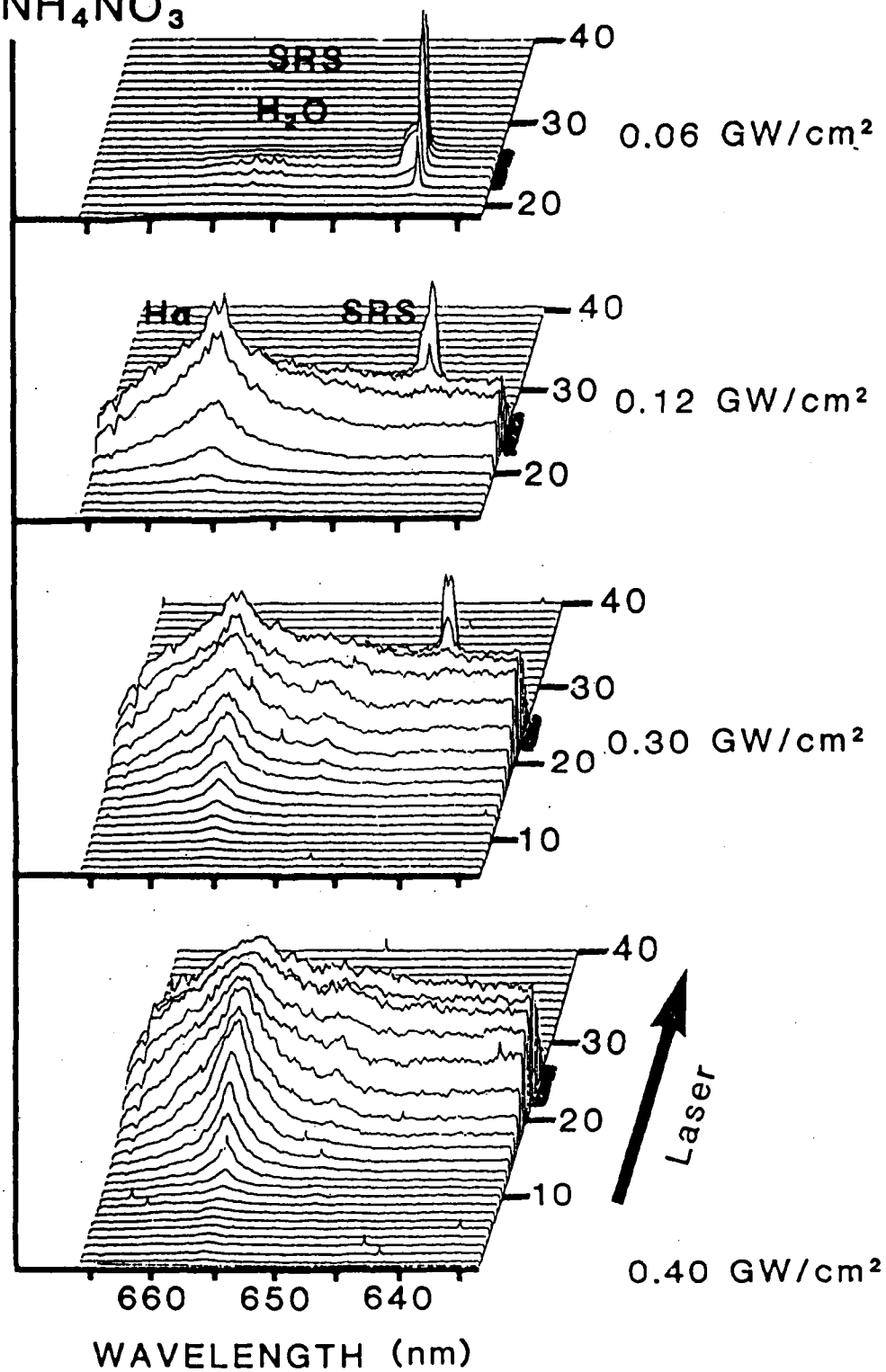
5M NH_4NO_3 LOW INTENSITY MULTI-SHOT

INTENSITY (arb. units)



5M NH_4NO_3

INTENSITY (arb. units)



$t_{\text{delay}} (\mu\text{sec})$

0.25

a



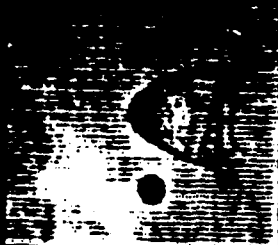
e



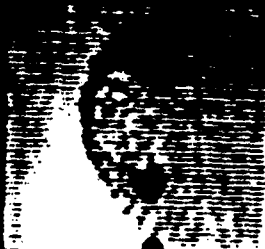
2.0

0.5

b



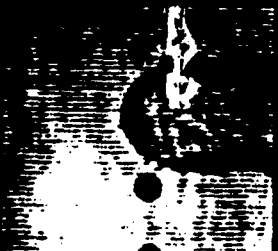
f



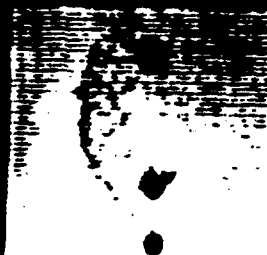
3.0

1.0

c



g



4.0

1.5

d



h



5.0

$I_0 = 1 \text{ GW/cm}^2$

DROPLET COMBUSTION OF HAN-BASED

LIQUID PROPELLANTS

C. K. LAW

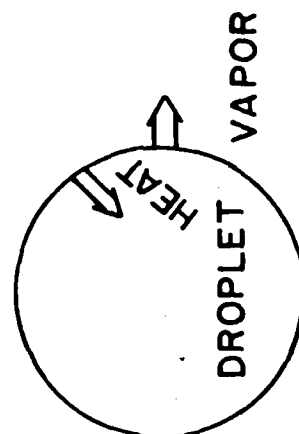
UNIVERSITY OF CALIFORNIA AT DAVIS

**WORK SUPPORTED BY
ARMY RESEARCH OFFICE**

AMBIENCE

HEAT

DIFFUSIVE - CONVECTIVE
REGION

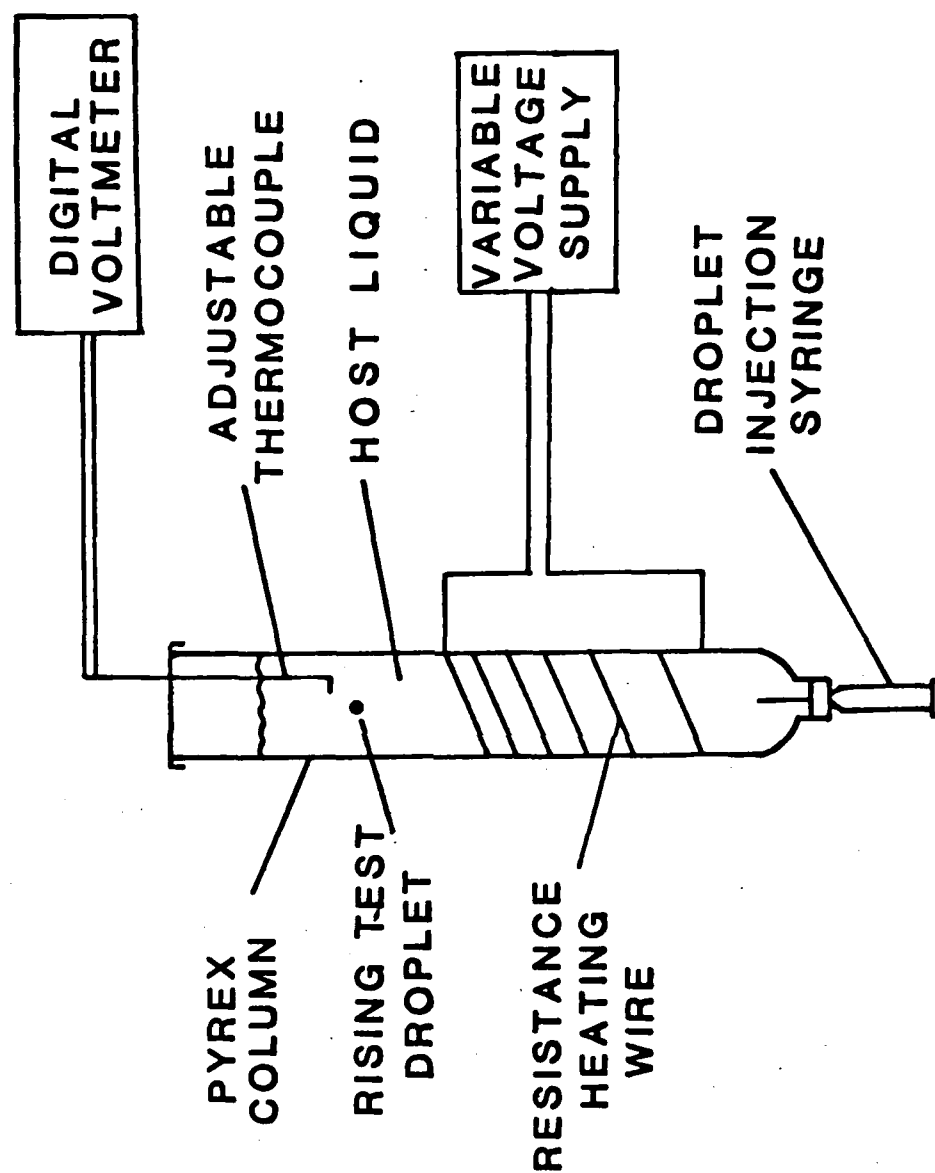


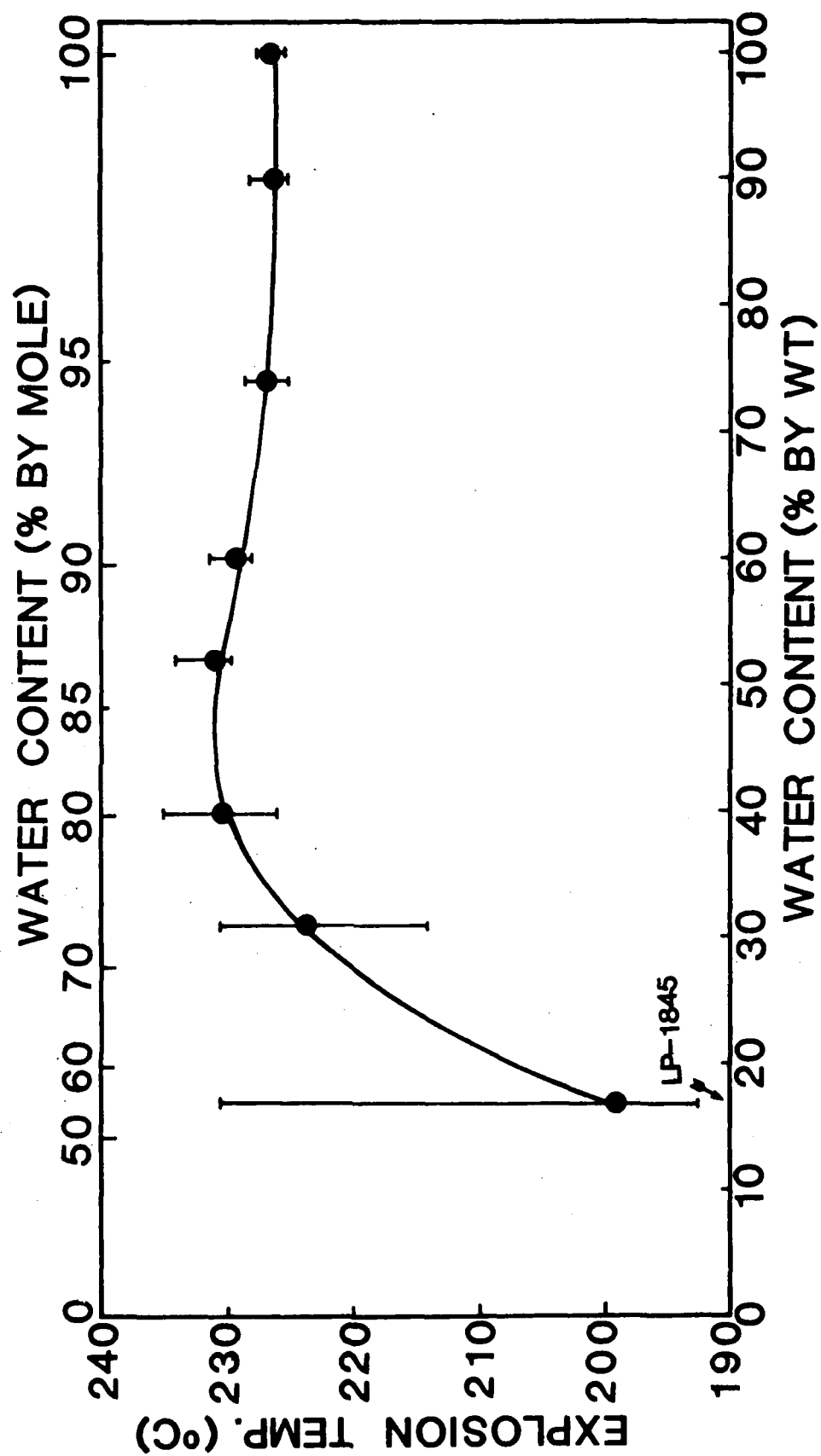
OBJECTIVES

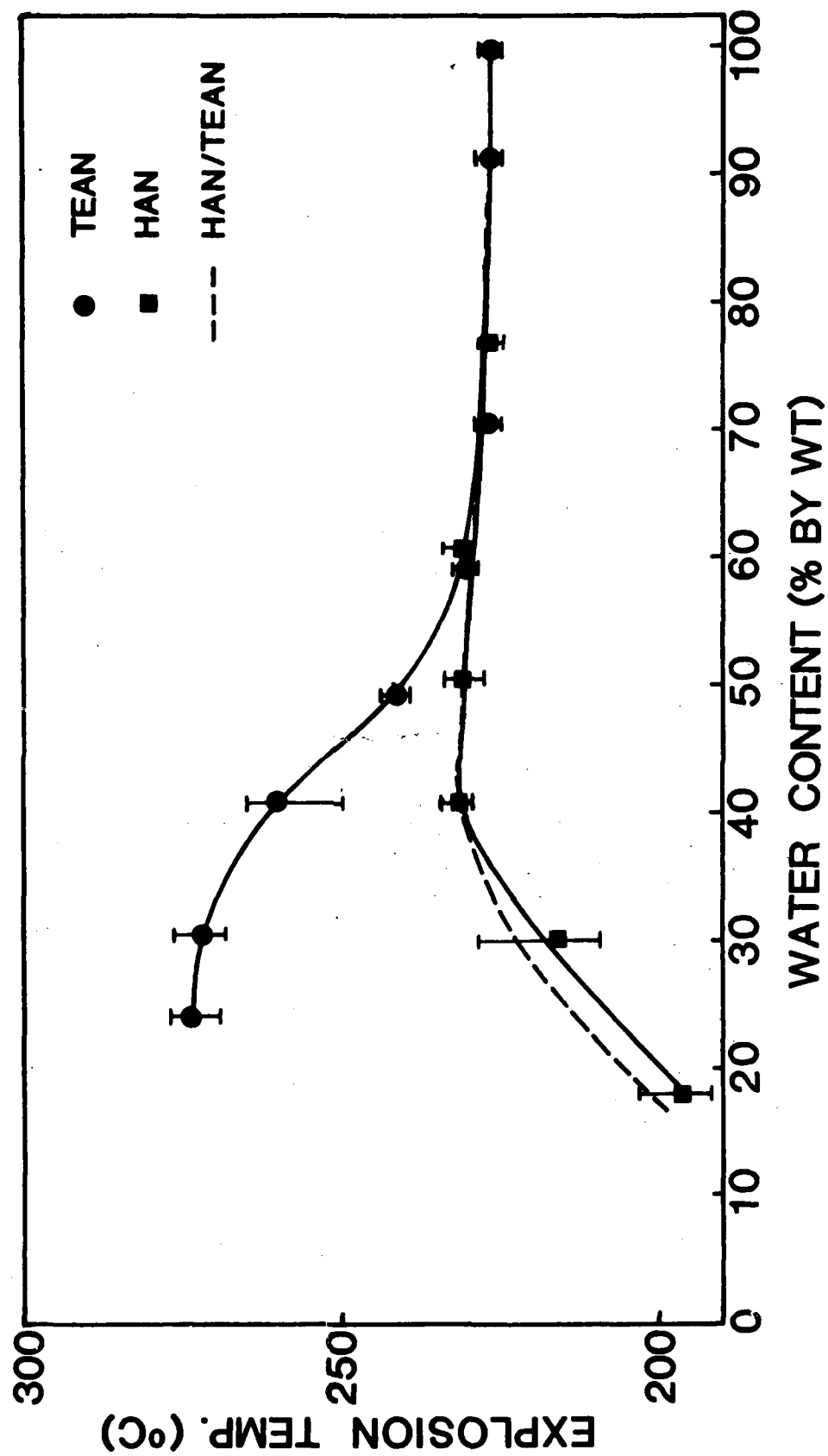
- 1. TO DETERMINE DROPLET EXPLOSION TEMP.**
- 2. TO STUDY DROPLET COMBUSTION CHARACTERISTICS**

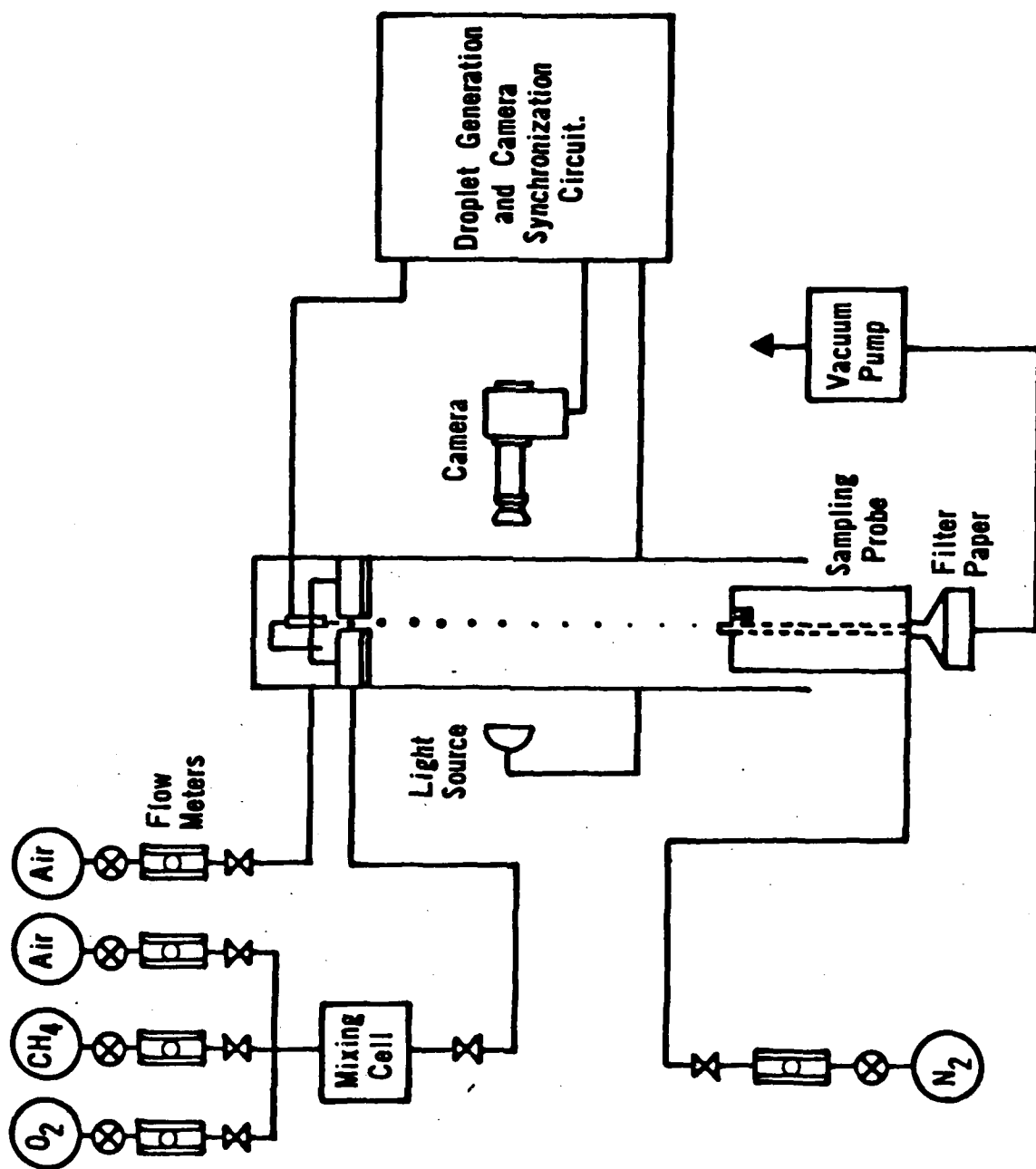
INCLUDING:

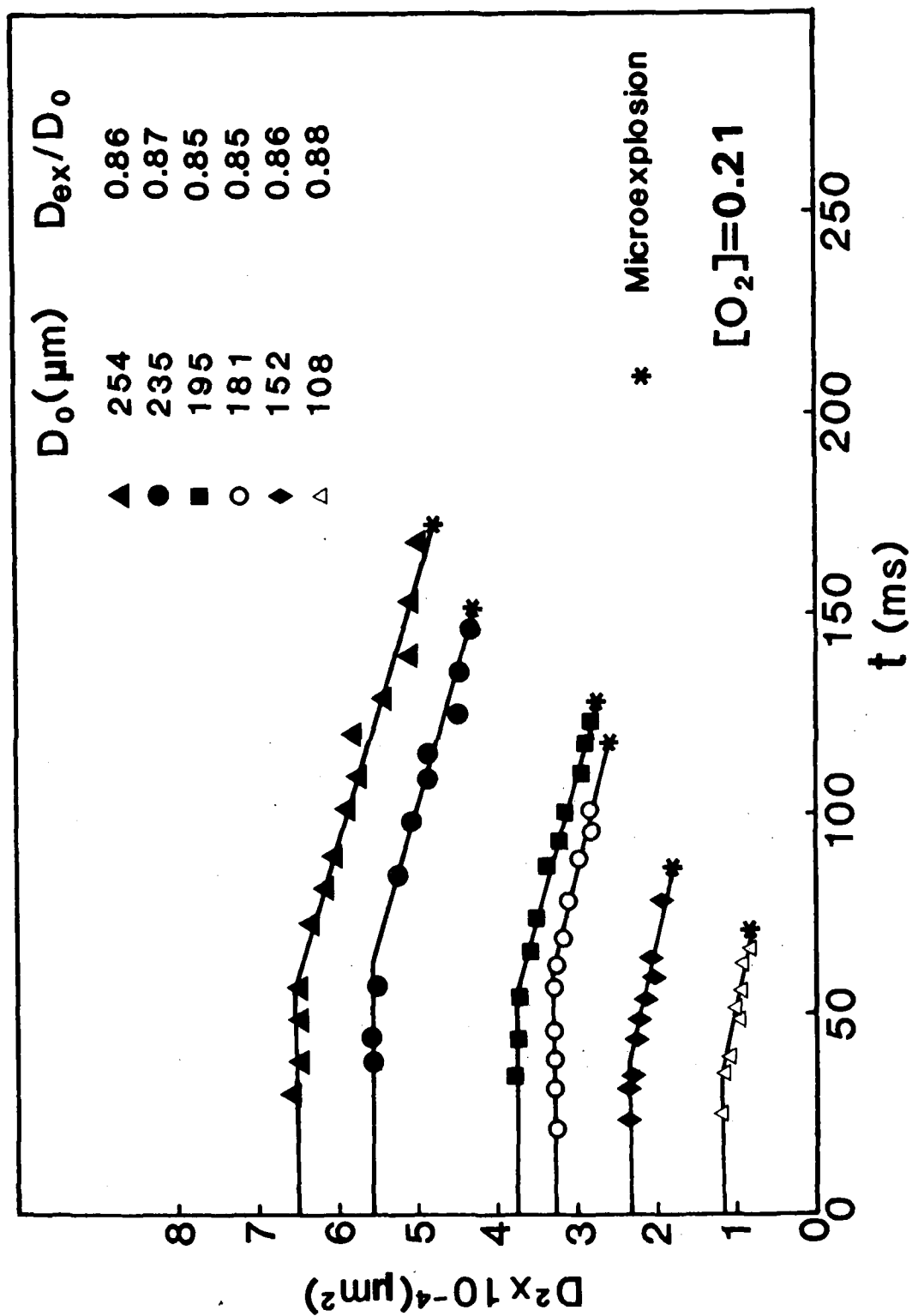
- * HEAT-UP TIME**
 - * GASIFICATION RATE**
 - * EXPLOSION TIME/SIZE**
- AS FUNCTIONS OF**
- * OXYGEN CONTENT IN ENVIRONMENT**
 - * WATER CONTENT IN PROPELLANT**
 - * DROPLET SIZE**

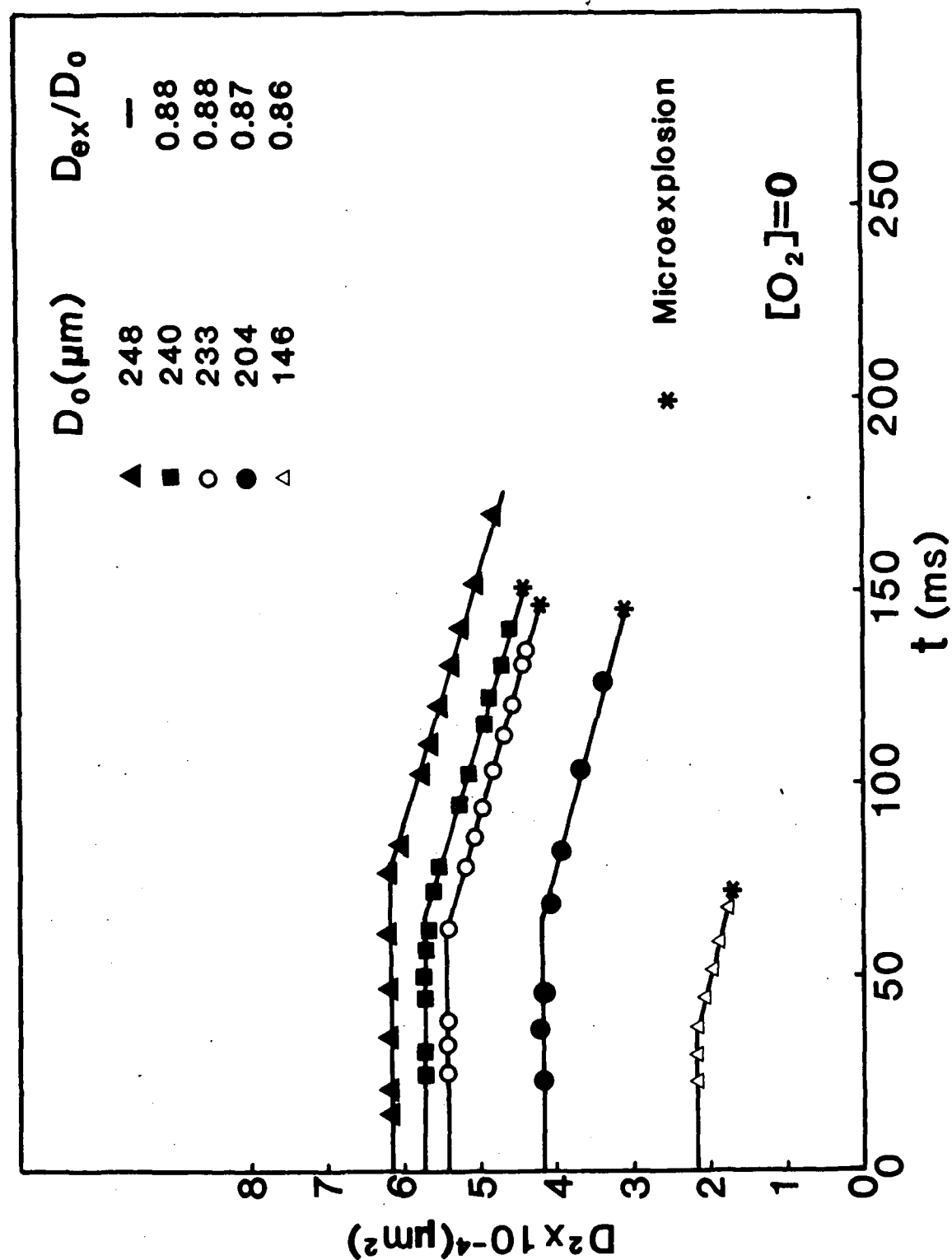


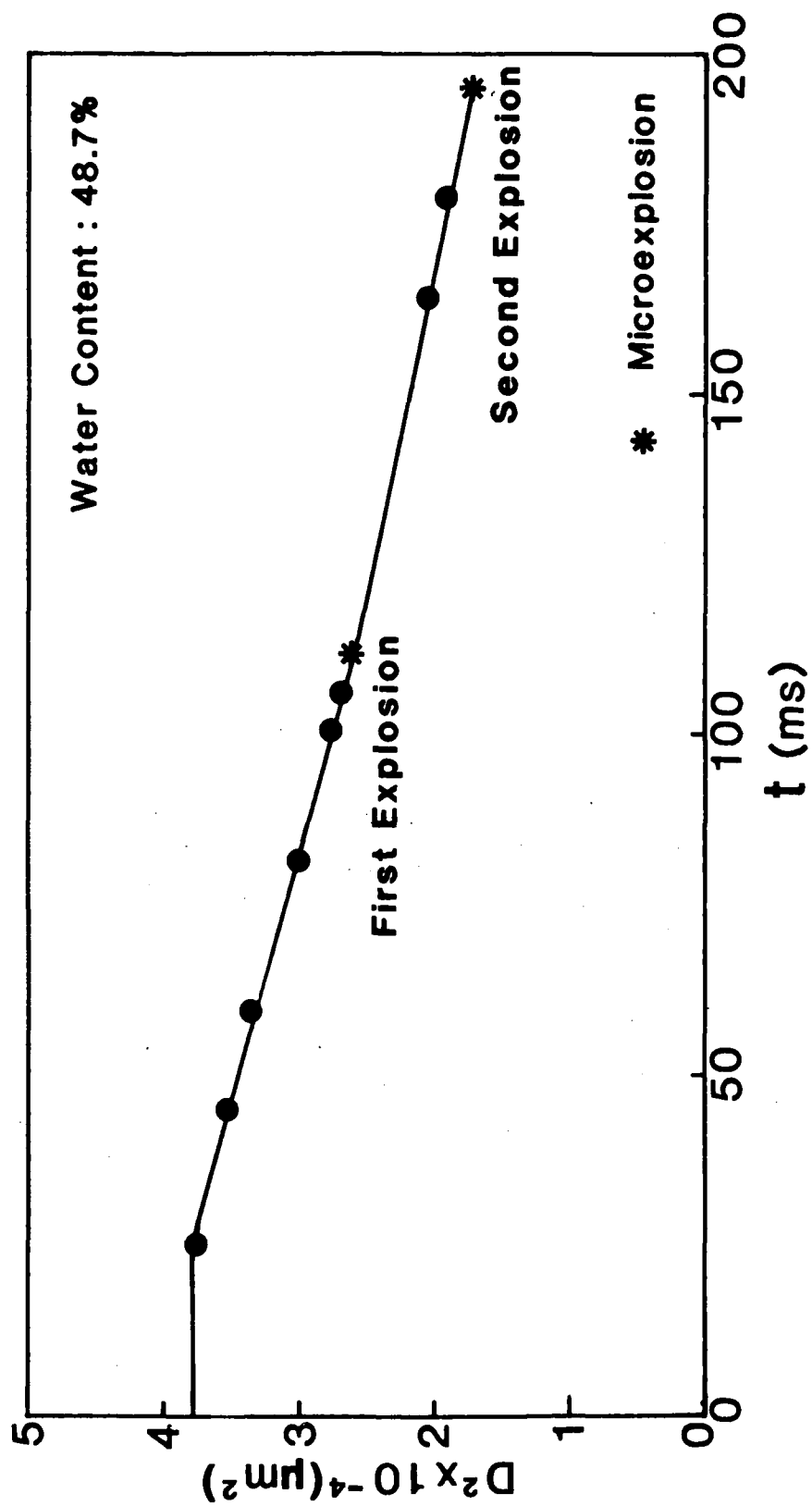


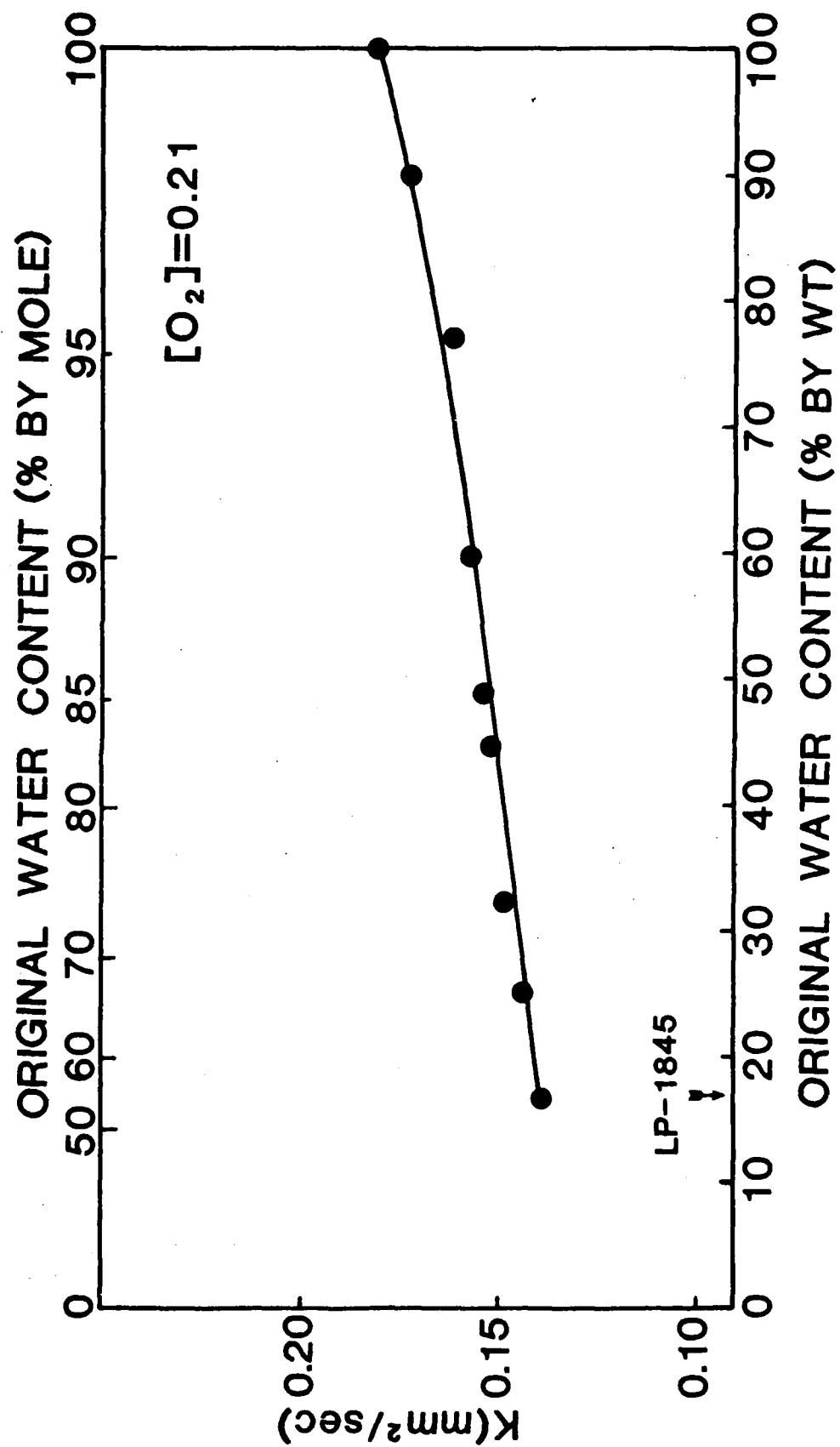


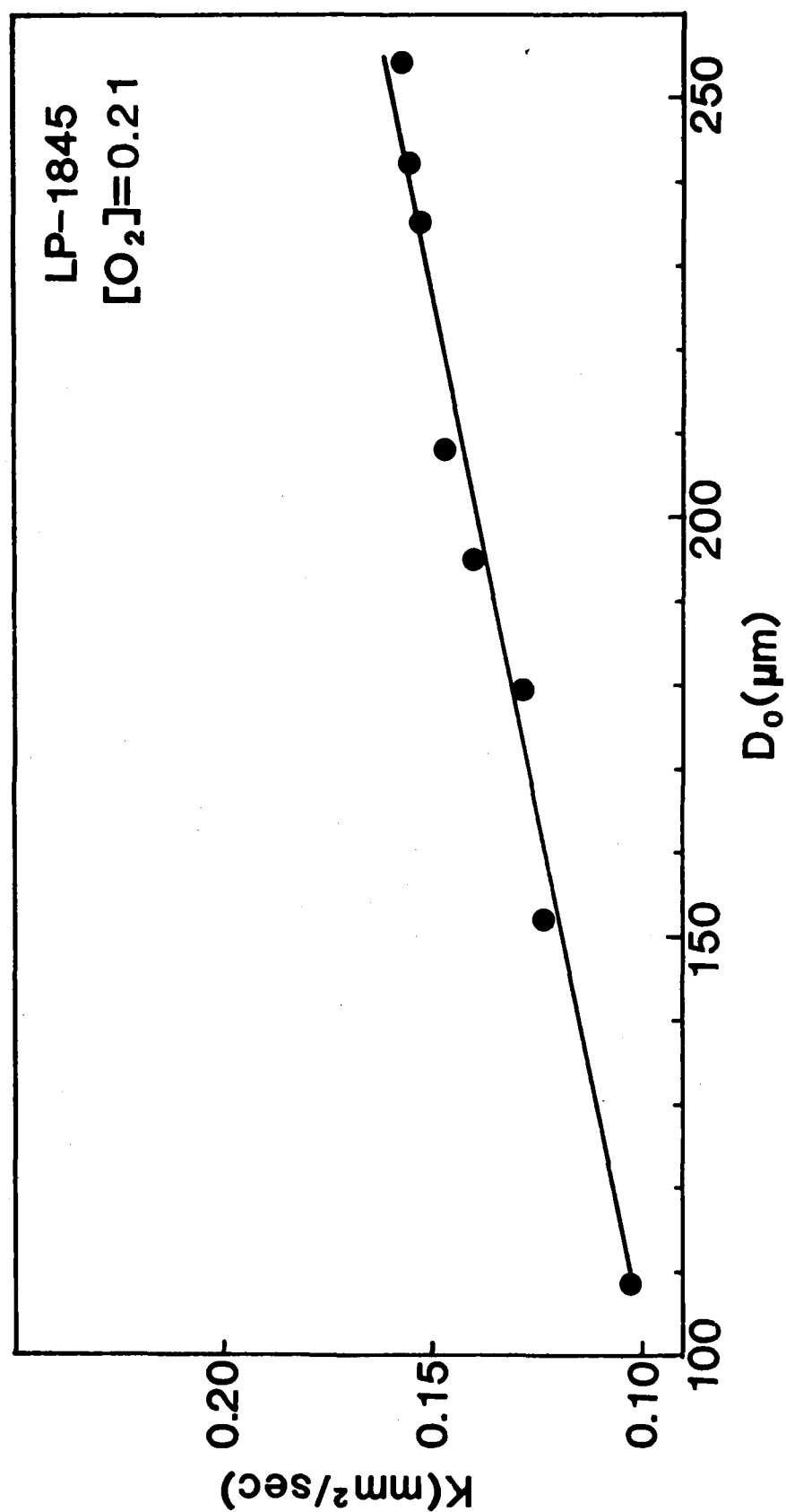


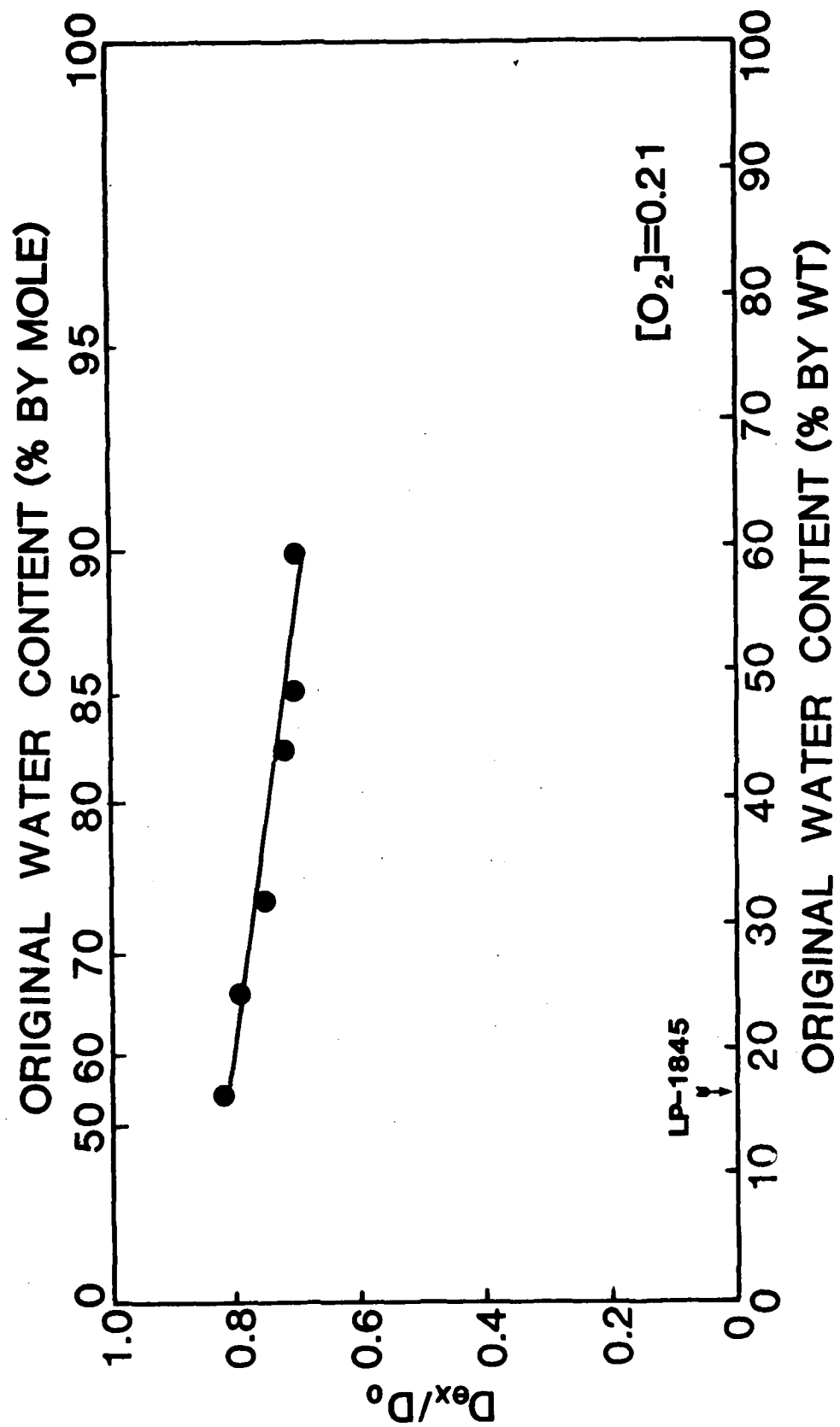




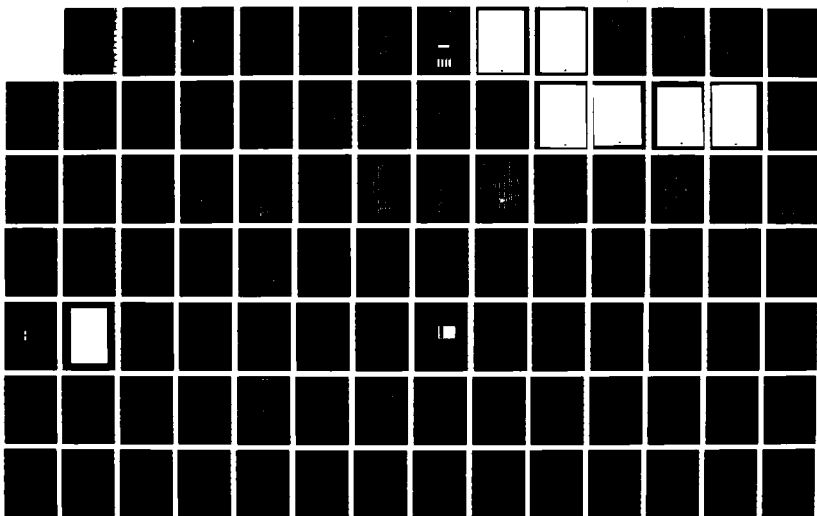


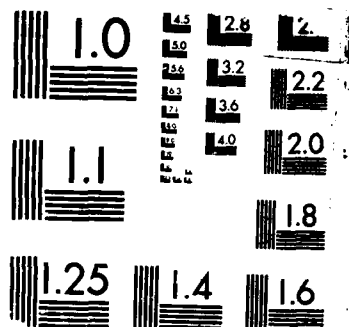




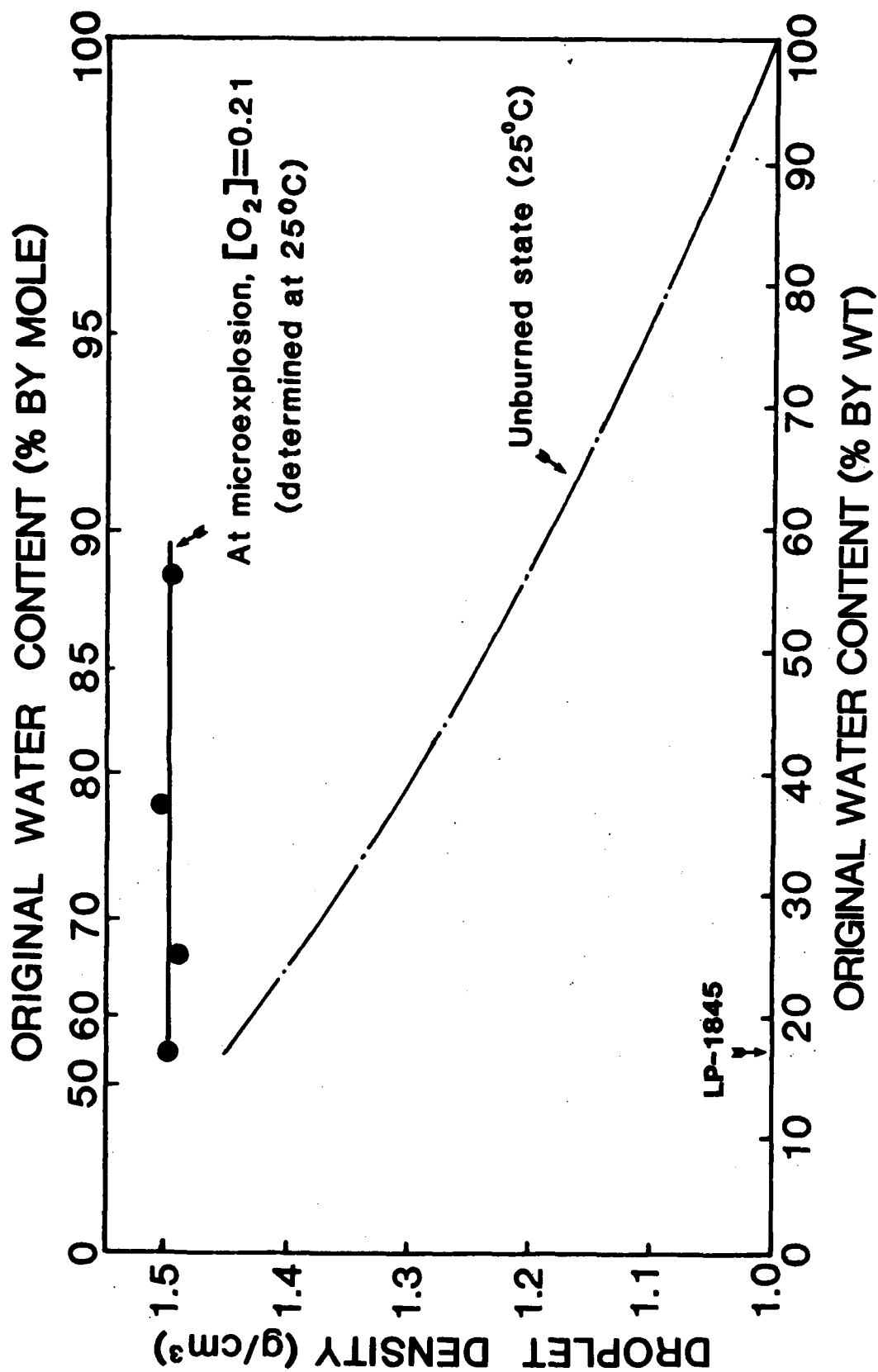


AD-A194 679 THE ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANTS 2/3
(3RD) HELD IN ABERD. (U) ARMY BALLISTIC RESEARCH LAB
ABERDEEN PROVING GROUND MD E FREEDMAN ET AL MAR 88
UNCLASSIFIED BRL-SP-73 F/G 19/1 NL





MICROCOPY RESOLUTION TEST CHART
 NBS 1963-A



SUMMARY (1)

A. DROPLET EXPLOSION TEMP. EXPERIMENT

1. EXPLOSION TEMP. AROUND 200°C

2. EXPLOSION INDUCED BY

* LIQUID-PHASE REACTION FOR WATER CONTENTS
LESS THAN 30-40 PERCENT

* HOMOGENEOUS NUCLEATION OF WATER FOR
HIGHER WATER CONTENTS

3. HAN INITIATES LIQUID-PHASE REACTION

SUMMARY (2)

B. DROPLET COMBUSTION EXPERIMENT

1. INITIAL DROPLET HEATING PERIOD INCREASES
WITH INCREASING SALT CONCENTRATION
2. WATER IS THE DOMINANT VAPORIZING SPECIES
3. MILD LIQUID-PHASE REACTION EXISTS
4. A CRITICAL SALT CONCENTRATION (1.5 g/cm^3)
SEEMS TO EXIST AT WHICH DROPLET
MICROEXPLOSION OCCURS

DSC OF LIQUID PROPELLANTS AND CRYSTALLINE HAN

Leon Decker and R.A. Fifer
U.S. Army Ballistic Research Laboratory
Aberdeen Proving Ground, MD 21005-5066

ABSTRACT

A DSC stability test has been developed for monitoring the stability of HAN-based liquid propellants, and the destabilizing effects of metal impurities. The test involves simultaneous ignition temperature (Tig) measurements for eight samples (2.3 mg each) heated in glass capillaries in a DSC pressurized to 6.9 MPa (1000 psi). Data are given for neat propellant "1845", as well as for samples of the propellant "doped" with 3-150 ppm of iron or copper. The results show that 5 or 10 ppm of either metal leads to a measurable decrease in Tig, and that the decrease in Tig per unit metal concentration is greatest at the lowest metal concentrations. From the signs and shapes of the DSC peaks under different conditions, it thus been found that when water vaporization is suppressed, there are no detectable endo- or exotherms prior to ignition, and that the first gas-producing reaction is apparently endothermic. When water vaporization is suppressed, the Tig for HAN-based propellants are much higher ($>200^{\circ}\text{C}$) than previously suspected.

A preliminary examination of two crystalline forms of HAN indicate that the heats of fusion of both forms (alpha-HAN = 27.0 ± 1.8 cal/gm; beta-HAN = 26.7 ± 1.8 cal/gm) are, within experimental limits, identical. Much more work needs to be performed to properly characterize the experimental material.

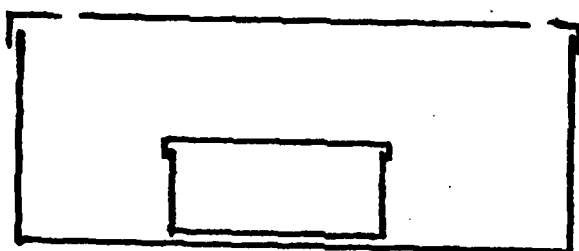
**DSC STABILITY TEST FOR LIQUID PROPELLANTS
AN UPDATE**

**WHY: ONSET TEMPERATURE IS A QUICK GAUGE OF "QUALITY"
PROVIDES A MEANS OF DETERMINING DETERIORATION DUE TO
AGING AND/OR TRANSITIONAL METAL IMPURITIES**

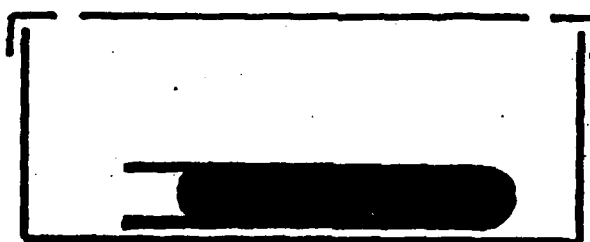
**REF: R.A. FIFER, L.J. DECKER, P.J. DUFF, "DSC STABILITY TEST
FOR LIQUID PROPELLANTS", 22nd JANNAF COMBUSTION MEETING,
CPA PUB. 432, VOL. II, P. 203, OCTOBER, 1985**

SAMPLE CONFIGURATIONS:

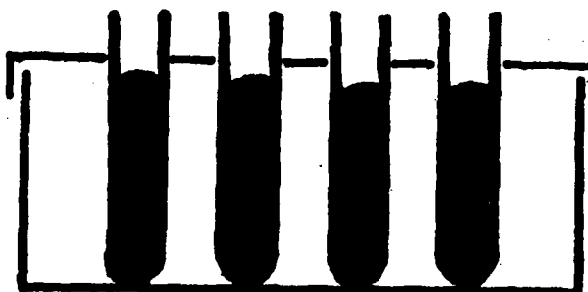
METAL PAN (GOLD, ALUMINUM, PLATINUM)



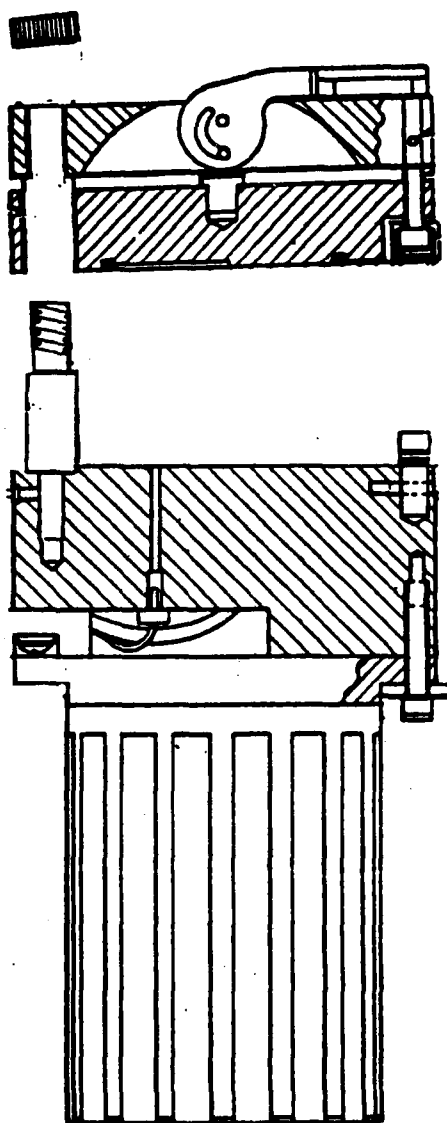
HORIZONTAL CAPILLARY: 4MM X 1.2MM I.D.



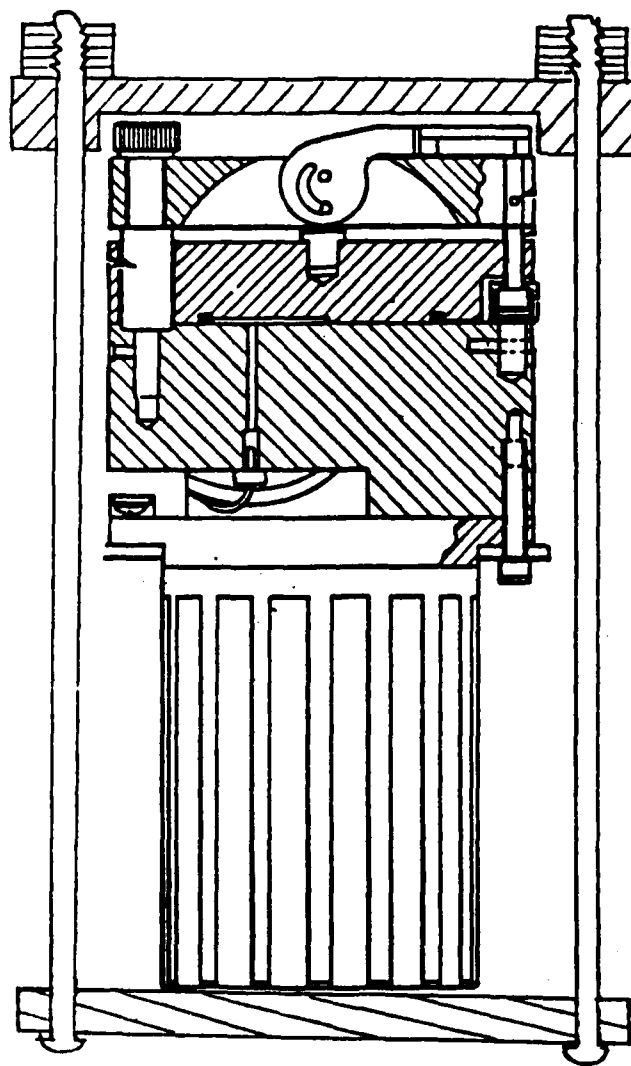
VERTICAL CAPILLARIES (MULTIPLE SAMPLES)



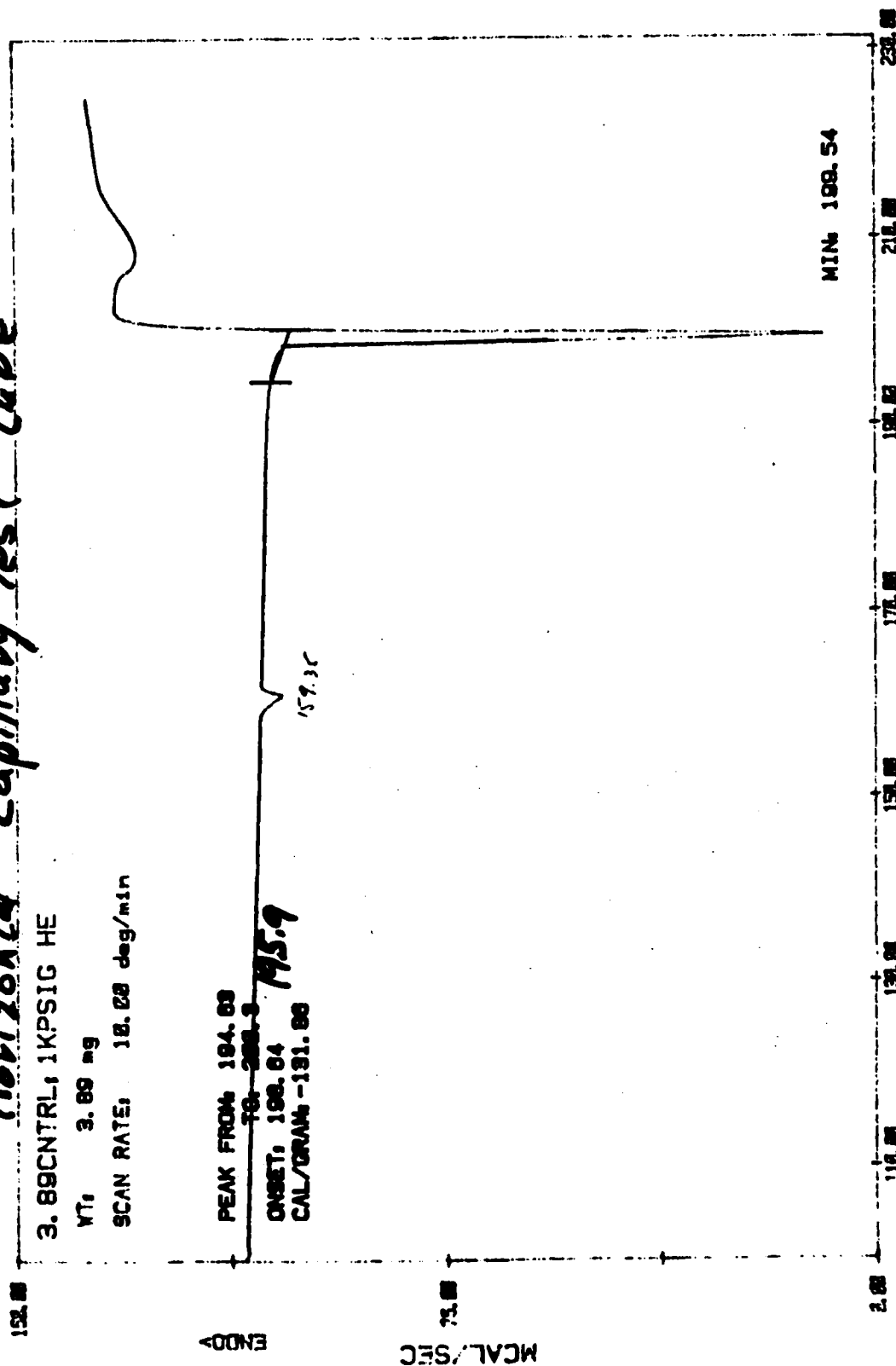
PERKIN-ELMER DSC HEAD



**PERKIN-ELMER DSC HEAD AS MODIFIED FOR
HIGH PRESSURE (1000 PSIG)**



Horizontal capillary test tube



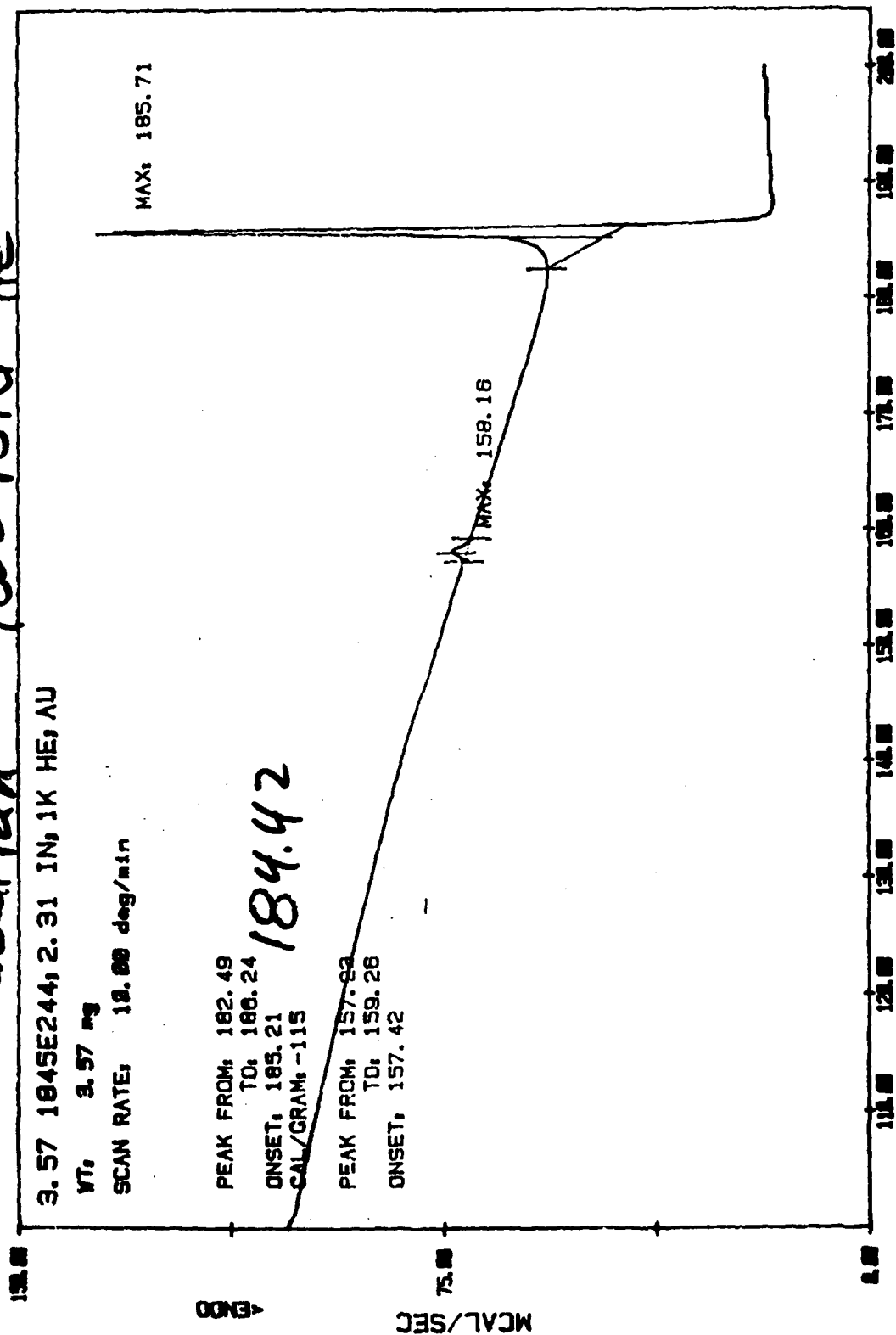
DSC

TEMPERATURE (C)

LEON FILE: 50251.04

DATE: 85/01/25 TIME: 08:17

Gold Pan 1000 PSIG He

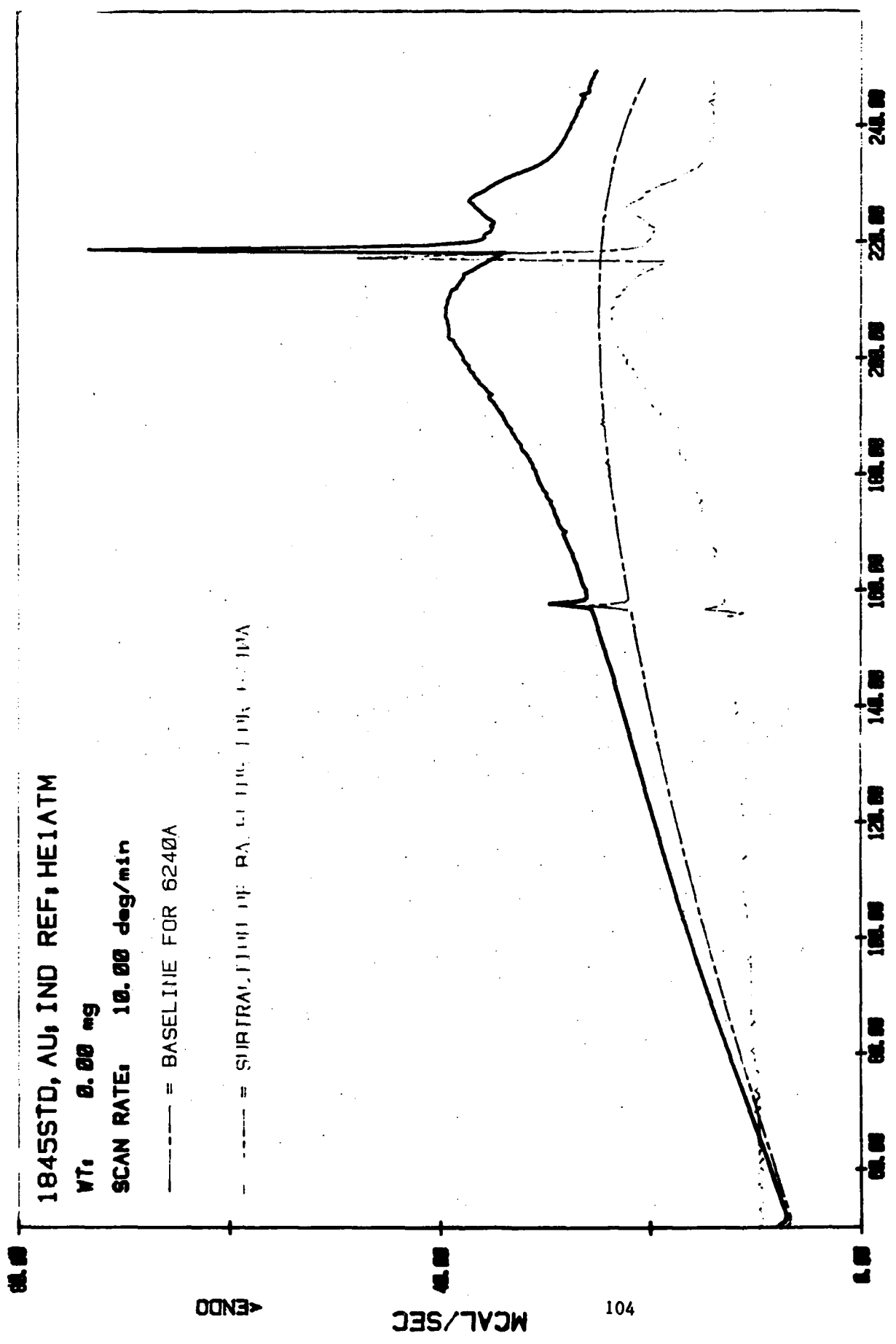


DSC

TEMPERATURE (C)

LEON FILE: 51022.D4

DATE: 05/07/11 TIME: 15:47

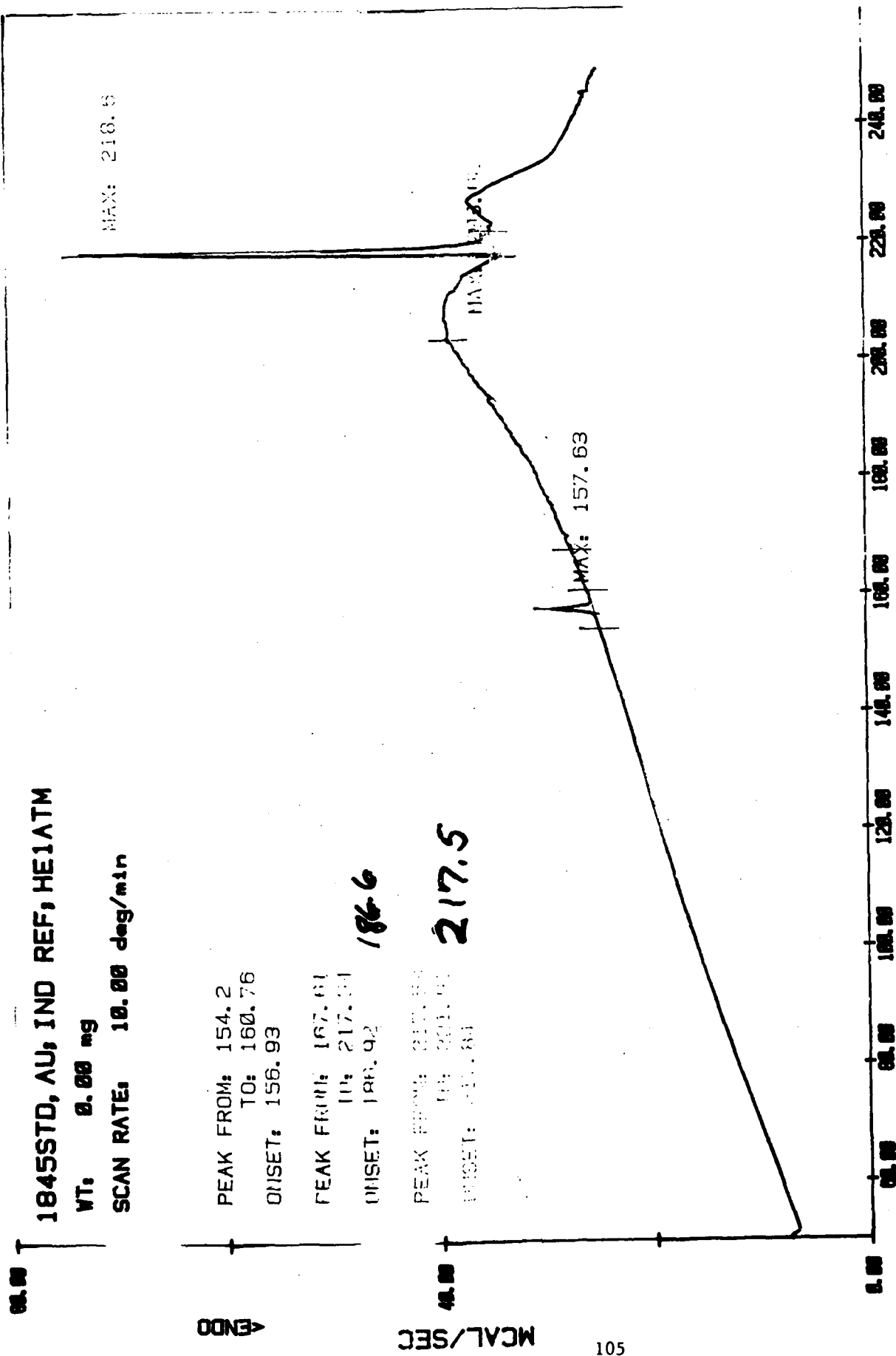


DSC

TEMPERATURE (C)

LEON FILE: 6240A.D4

DATE: 00/00/20 TIME: 13:40



DSC

TEMPERATURE (C)

FILE: 62401.D4

DATE: 00/00/20 TIME: 13.40

ANALOG: IPAN 1K PSIG HE Glass Cap. Test tube

4.68 "IPAN" 59HE1K; 4.45IN/REF

WT: 4.68 mg

SCAN RATE: 10.00 deg/min

ENDO

PEAK FROM: 201.13
TO: 207.48
ONSET: 204.74
CAL/GRAM: -193.98

155.6

205.74

MIN: 205.58

MCAL/SEC

111.00 131.00 151.00 171.00 191.00 211.00 231.00 251.00

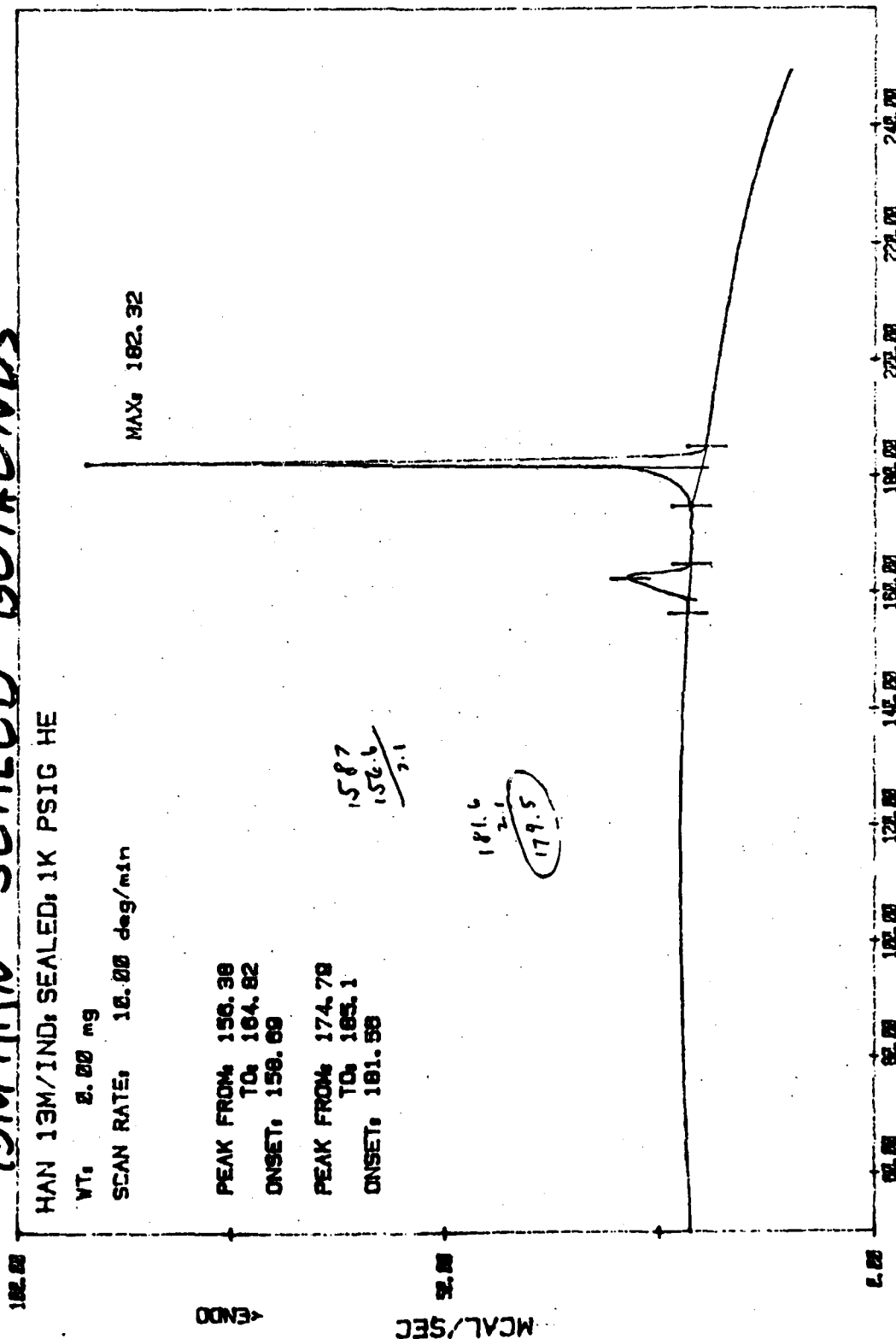
DSC

TEMPERATURE (C)

LEON FILE: 42718.D4

DATE: 84/09/27 TIME: 12:36

13M HAN SEALED BOTRENDIS CAPILLARY



HAN 13M/IND: SEALED: 1K PSIG HE

WT: 2.00 mg

SCAN RATE: 10.00 deg/min

LEON FILE: 6181C.D4

DATE: 06/08/90 TIME: 11:30

TEMPERATURE (C)

DSC

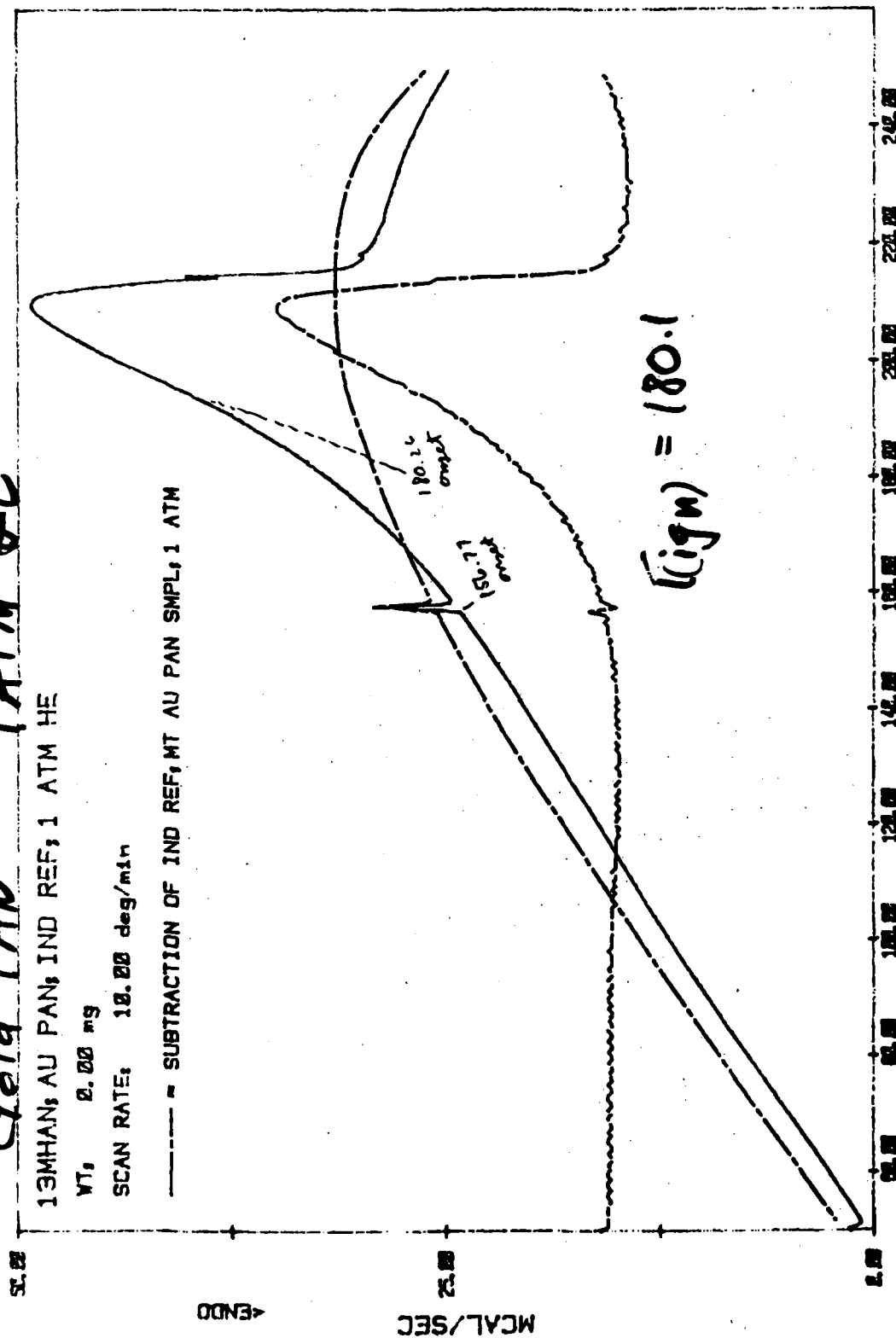
Gold PAN 1 ATM HE

13MHAN, AU PAN, IND REF, 1 ATM HE

WT, 2.00 mg

SCAN RATE: 10.00 deg/min

--- = SUBTRACTION OF IND REF, MT AU PAN SMPL, 1 ATM



LEON FILE: 82302.D4

DATE: 88/08/27 TIME: 15:45

TEMPERATURE (C)

DSC

HAN 15.11M SEALED CAPILLARY

HAN15.11M BL1846899: SEALED

WT: 0.00 mg

SCAN RATE: 10.00 deg/min

PEAK FROM: 150.77
TO: 155.78
ONSET: 150.91

*assume 2.5 C correction as
in preceding.*

159.7
2.5

157.4

MIN: 180.71

ENDO

MCAL/SEC

LEON FILE: 61828.D4
DATE: 08/07/01 TIME: 10:19
TEMPERATURE (C)
DSC

Platinum Pan

1845E244, PT, 1K PSIG HE

WT: 5.78 mg

SCAN RATE: 10.00 deg/min

END

END

MCAL/SEC

Subtraction

Blank

Run

15.19

143.1

143.1

10.00 11.00 12.00 13.00 14.00 15.00 16.00 17.00 18.00 19.00 20.00 21.00 22.00 23.00 24.00

DSC

TEMPERATURE (C)

FILE: 53324.24

DATE: 88/10/29 TIME: 14:47

QUENCHED PRIOR TO INITIATION

**13.24 M HAN IN GOLD PANS 1 ATM HE QUENCHED AT 150C
WEIGHT LOSS CORRESPONDS TO 100% OF WATER**

**1845 STANDARD IN HORIZONTAL GLASS CAPILLARIES
QUENCHED AT 190C
WEIGHT LOSS CORRESPONDS TO 47% OF WATER**

**1845 STANDARD IN VERTICAL GLASS CAPILLARIES
QUENCHED AT 165C
WEIGHT LOSS CORRESPONDS TO 70% OF WATER**

ADVANTAGES OF GLASS CAPILLARY TEST TUBES

INERT

LOW SURFACE TO VOLUME RATIO

MULTIPLE SAMPLE CONFIGURATIONS POSSIBLE

Penetration Temperature (Fig) vs. Metal Concentration

164° 1845 with Fe, Cu

Multiple Vertical Glass Capillaries

1000 psi, 1 deg min

Id for 1844

SUMMARY

SUPPRESSION OF WATER VAPORIZATION (PRESSURIZED DSC,
LOW SURFACE TO VOLUME RATIO) RAISES $T(\text{ONSET})$

LOW CONCENTRATIONS OF Cu^{+2} AND Fe^{+3} PRODUCE THE
GREATEST DECREASE IN $T(\text{ONSET})$ PER UNIT METAL
CONCENTRATION $d(T)/dM$

THE DESTABILIZING EFFECTS OF Cu^{+2} AND Fe^{+3} ARE OF
EQUAL MAGNITUDE
(OBSERVABLE AT CONCENTRATIONS AS LOW AS 5 PPM)

DSC OF CRYSTALLINE HAN

TWO POLYMORPHS REPORTED

**R.A. FIFER, "INFRARED SPECTRA AND POLYMORPHISM IN CRYSTALLINE
HAN", 23RD JANNAF COMBUSTION MEETING, CIA PUB. 457, VOL III,**

P.159, OCTOBER, 1986

WHY?

CONTRIBUTES TO GENERAL BODY OF KNOWLEDGE

PROVIDES REFERENCE MATERIAL

PREPARATION OF HAN CRYSTALS

SUPERNATANT FLUID (MOTHER LIQUOR)
35, 50, 65C/VACUUM

DRY BOX ATTACHMENT TO DSC

STORAGE OF MATERIAL BETWEEN RUNS

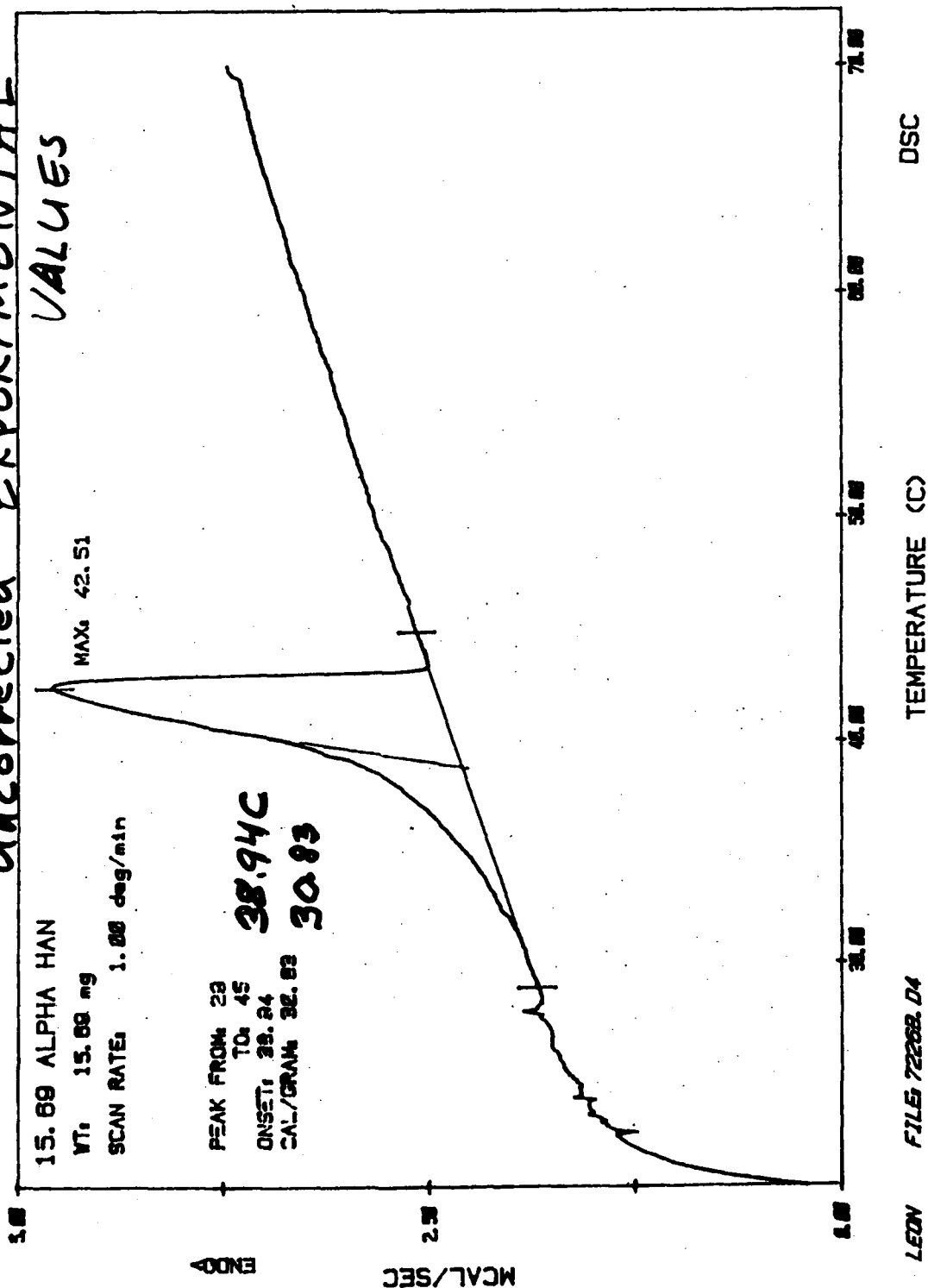
EXPERIMENTAL PROCEDURES

RESULTS

ONSET VARIED FROM 40C (35/YAC/DAYS) TO 36C (65/YAC/18HRS)
LATENT HEAT OF FUSION VARIED FROM 40 (35/YAC/DAYS) TO 27 CAL/GM
(65/YAC/18HRS)

Uncorrected EXPERIMENTAL

VALUES



LEON FILE: 72268.D4

DATE: 87/08/14 TIME: 10:29

ALPHA HAN: LATENT HEAT OF FUSION

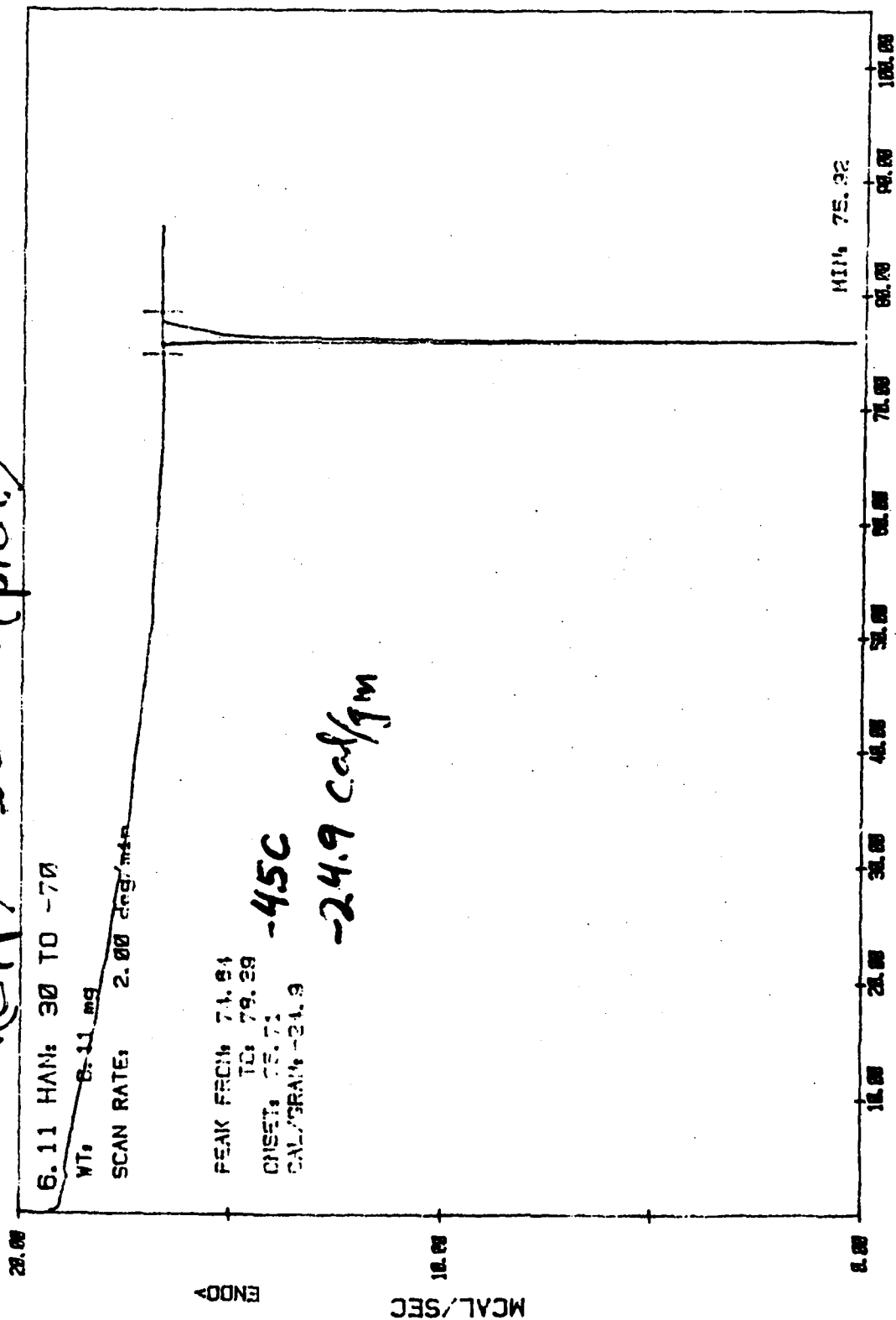
RUN ID	ONSET	CAL/GM	C/MIN	THERMAL RANGE
7230F	35.89C	25.60	+2	-30 TO +70C
7230D	36.21C	29.33	+1	+20 TO +70C
7229B	34.76C	24.95	+2	+20 TO +70C
7231D	36.00C	36.00	+2	+20 TO +70C

← CORRECTED
VALUES

$$ONSET = 35.72 \pm 0.65$$

$$CAL/GM = 26.97 \pm 2.05$$

$T_{exp} = 30 - T_{plot}$



DSC

TEMPERATURE (C)

LEON FILE: 7230E.D4
 DATE: 07/08/10 TIME: 14.04

BETA HAN: HEAT RELEASED DURING CRYSTALLIZATION

RUN ID	ONSET	CAL/GM	C/MIN	THERMAL RANGE
7230G	-47.37C	-27.38	-2	0 TO -70C
7230E	-46.81C	-24.97	-2	+30 TO -70C ←
7229F	-46.38C	-26.06	-2	+30 TO -70C
7229E	-47.46	-29.55	-2	+30 TO -70C
7229D	-50.65	-25.65	-2	+30 TO -70C

ONSET = -47.73 ± 1.69 CAL/GM = -26.72 ± 1.81

INDICATIONS ARE THAT THE ALPHA AND BETA FORMS HAVE
EQUAL OR NEARLY EQUAL (WITHIN EXPERIMENTAL LIMITS)
LATENT HEATS OF FUSION

FURTHER CHARACTERIZATION OF THE CRYSTALS BEING
STUDIED ARE NECESSARY

CONCLUSIONS

WOULD BE NICE, BUT WOULD YOU SETTLE FOR SOME QUESTIONS?

FUTURE WORK

CHARACTERIZE CRYSTALLINE FORMS
SPECTROSCOPICALLY

RUN BOTH FORMS THROUGH PROGRAMMED TEMP INCREASE TO OBTAIN
APPROPRIATE T(ONSET) AND LATENT HEAT OF FUSION
PROGRAM LIQUID THROUGH TEMP DECREASE TO CRYSTALLIZATION, THEN
CHARACTERIZE THE CRYSTAL SPECTROSCOPICALLY

OBSERVE STORED CRYSTALS TO DETERMINE IF THE TWO FORMS ARE
INTERCONVERTIBLE, EITHER PARTIALLY OR TOTALLY

OBSERVE STORED CRYSTALS FOR POSSIBLE DETERIORATION
EVOLVED GASES, WATER FORMATION, CHANGES IN HEAT OF FUSION,
MELTING TEMPERATURE, IGNITION TEMPERATURE

Fast Thermal Decomposition of Liquid Propellant 1845

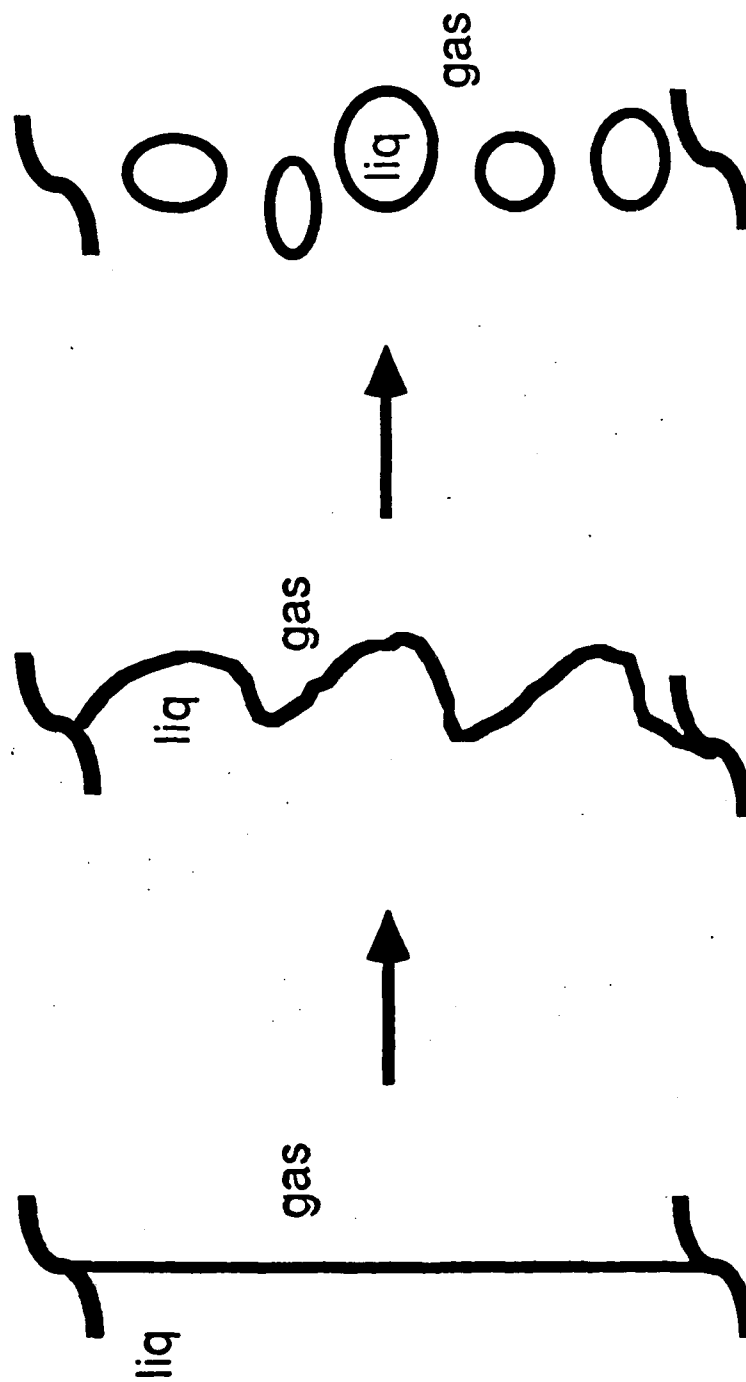
J.T. Cronin, T.B. Brill. Department of Chemistry
University of Delaware, Newark, DE 19716

The high rate ($>100^{\circ}\text{C}/\text{sec}$) decomposition characteristics of liquid propellant LP1845 will be described with the rapid-scan FTIR/thermal profiling technique. The decomposition characteristics of HAN and TEAN were examined and then compared to the pyrolysis behavior of LP1845. A five step process that describes the major events occurring during the fast thermal decomposition/ignition of LP1845 will be presented. A progress report on the acoustic levitation project will be presented.

Stability Characteristics of Deflagrating Liquid Propellants

Rob Armstrong
and
Steve Vosen
Combustion Research Facility
Sandia Labs, Livermore 94550

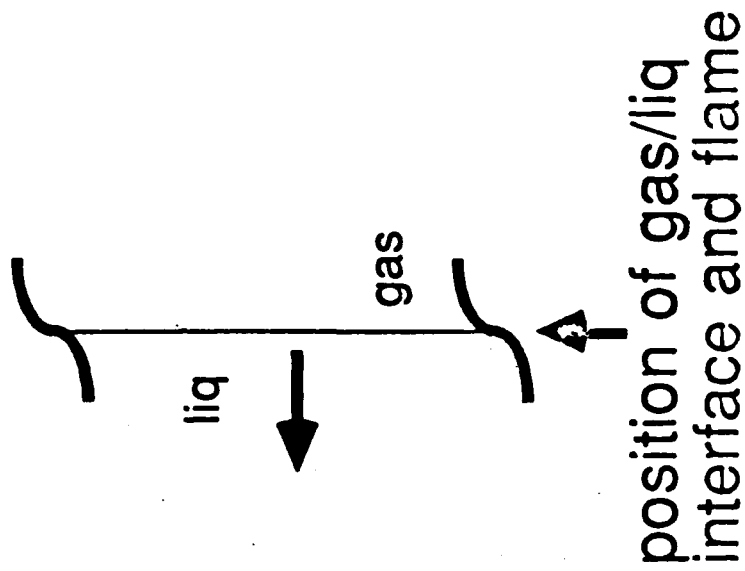
Why stability?



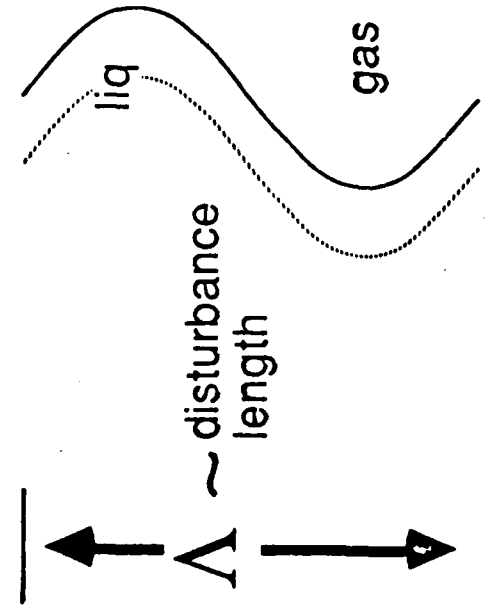
shows the length scale of fluid-mechanical breakup (droplet size)

Initial state from which stability is determined

- steady, planar burning



Previous investigations



$$\lambda \sim \text{thermal-diffusive distance} \\ \approx 10\mu - 1\mu$$

• Landau (1944), Zeldovich (1980)

• Frankel & Shivashinsky (1982),
Pelce & Clavin (1982)
Matalon & Matkowsky (1982)

$$\omega = \omega_1 (\lambda/\Lambda) + \omega_2 (\lambda/\Lambda)^2 + \dots \quad (\text{disp. rel'n})$$

- to this approximation there is no contribution from viscous forces, diffusive forces have stabilizing influence
- smallest wave numbers (largest length disturbance)

Experimental evidence

- it is clear that the small wave number disturbances are observed
- S. Vosen has evidence for a "fog" of small ($10\mu - 1\mu$) droplets also

physical origin?

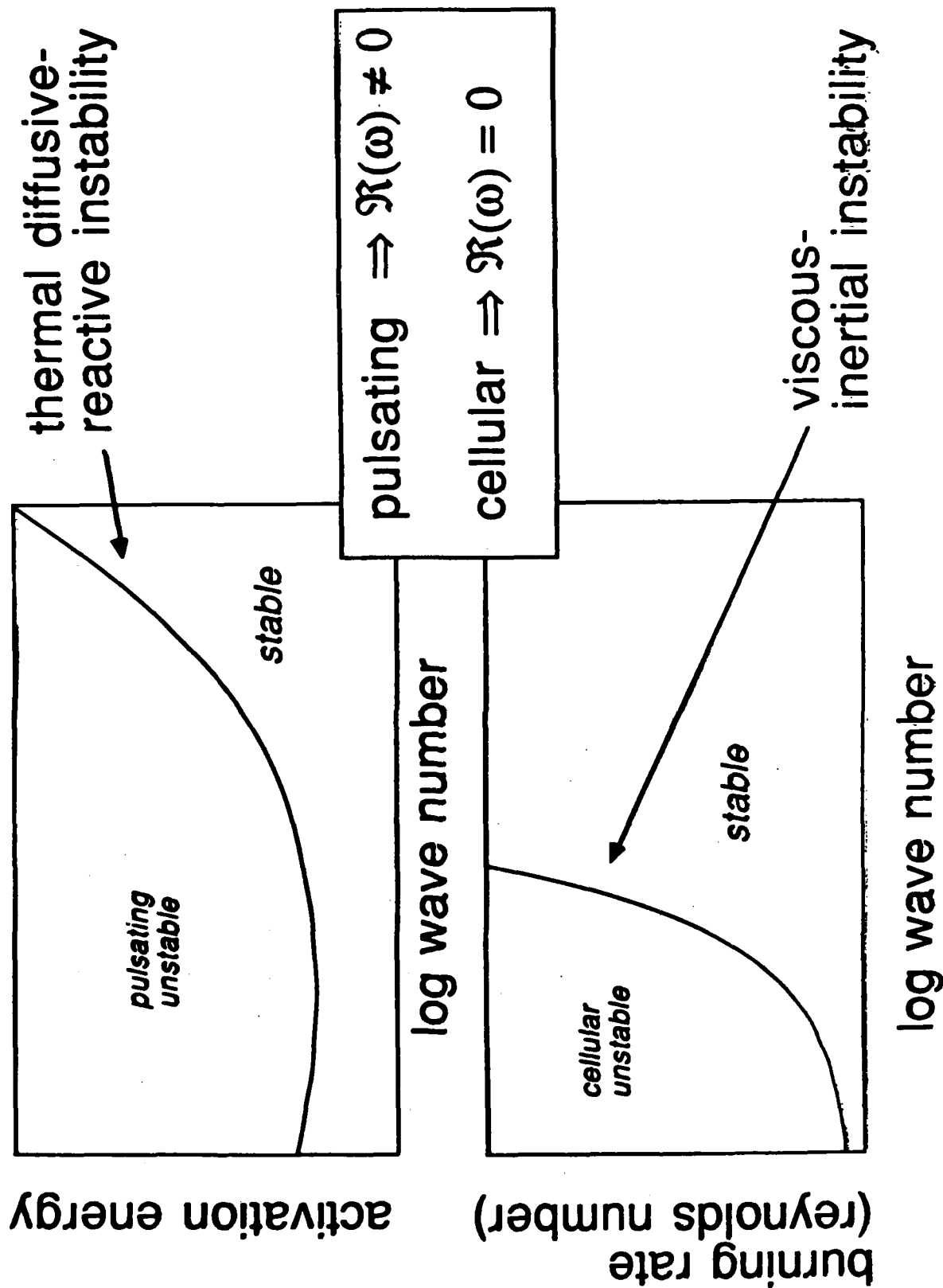
- impossible for fluid mechanical turbulence to be responsible
- is on the correct length scale over which thermal - diffusive processes are active

Experimental evidence (cont'd)

possible mechanisms:

- thermal-diffusive, reactive interaction (known to exist for solid propellants)
- thermal-diffusive, surface tension gradient interaction
- thermal-diffusive, homogeneous shear

Two length scale problem

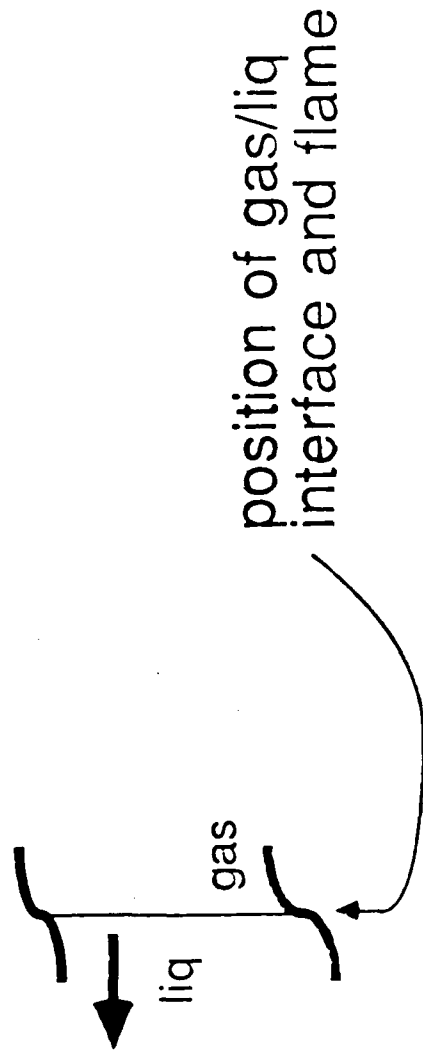


Combine the two in a way relevant to liquid prop. combustion

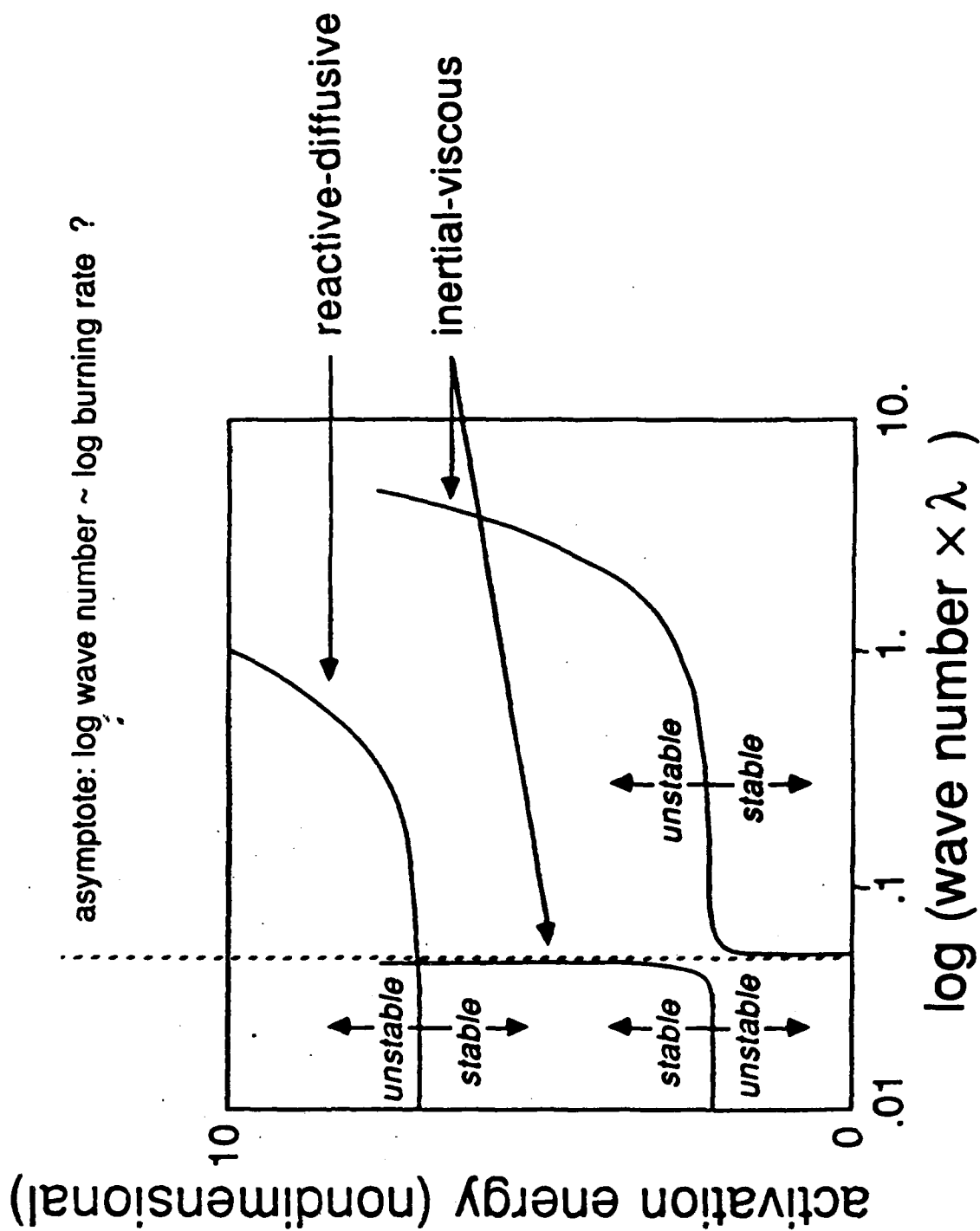
- do not wish to use a perturbative approach that is asymptotic to either the thermal or inertial length scales
- would like to treat all of these forces as equals
- as a result a very large system must be dealt with (which is the reason for the asymptotic approach in the first place)
- we have used advanced techniques to accomplish the solution in the same analytic way as a human would do "by hand"
- disadvantage is that the system must be couched in general fashion
- takes the form of a linear operator in fourier - laplace whose determinant forms the dispersion relation

Model system

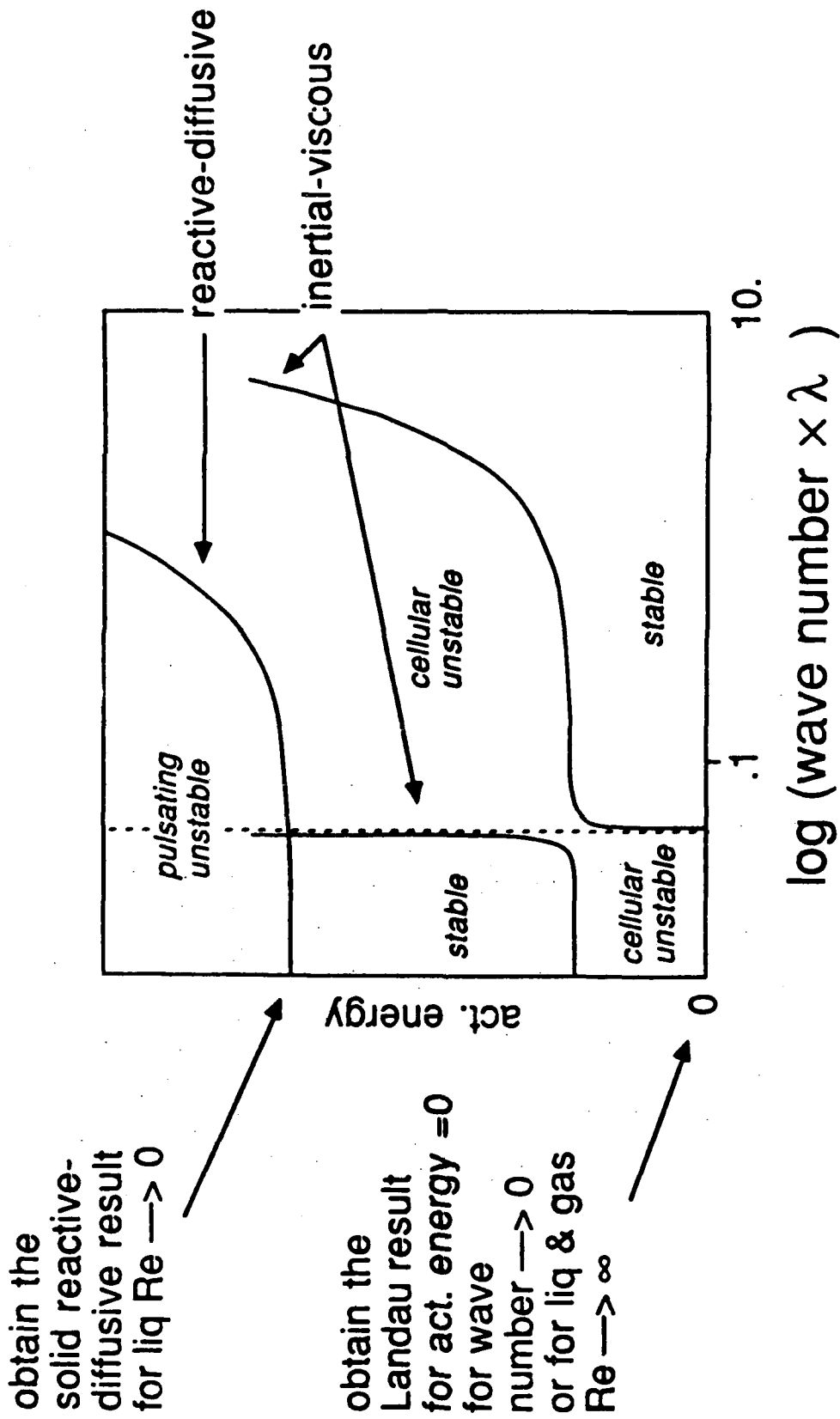
- flame is at the gas/liq interface
- rate of reaction has Arrhenius kinetics
- include full transport (fluid-thermal) and surface tension
- does not require a " λ/Λ " series expansion, only assumes that the reaction zone is thin
- recognizes a large Lewis number in the liquid phase and a general "jump" in transport properties across the gas/liquid boundary



Results



More results



cellular $\Rightarrow \Re(\omega) = 0$ pulsating $\Rightarrow \Re(\omega) \neq 0$

Conclusion

things done

- formalism developed to enable the solution of this large system (including surface tension & gravity)
- found the stability map for liquid propellant model without gravity & surface tension
- have found the exact analytic asymptotic limit for same for wave number $\rightarrow 0$

things to do

- discover the nature of the singularity in the inertial-viscous stability boundary
- include surface tension and gravity
- better chemistry

Summary

- if wave number implies droplet size then this theory predicts that "fog-like" droplets can occur due to diffusive-reactive instability.
- the presence of small droplets is likely to modify burning rate of a secondary flame

THE COMBUSTION OF HYDROXYLAMMONIUM NITRATE BASED LIQUID PROPELLANTS *

Steven R. Vosen
Combustion Research Facility
Sandia National Laboratories
Livermore, CA 94550

ABSTRACT

To better understand the physical processes which occur during the combustion of liquid propellants (LP), a strand burner was used to study hydroxylammonium nitrate based LP flames. By observing the combustion of LP in such an arrangement, much has been deduced of the physical processes that occur during LP ignition and combustion, at pressures which are relevant to LP gun ignition.

Combustion experiments were performed in which mixtures of the salts hydroxylammonium nitrate (HAN) and triethanolammonium nitrate (TEAN) in water were ignited by an electric discharge, in a pressure vessel at pressures of up to 34 MPa (5000 psi). Specifically, the mixtures discussed in this paper are the propellant designated as LP 1846 (60.8 % HAN, 19.2 % TEAN, and 20.0 % water by weight) and HAN/water mixtures. The mixtures were loaded into a container (strand burner) that had a 5 mm (0.20 inch) square cross section, was 40 mm (1.57 inch) deep, and was open on top. Electrodes in two sides of the burner allowed for a discharge through the mixtures, and quartz windows on the other sides allowed for observation of LP combustion. The burner was located in a pressure vessel with a volume (.013 m³, 0.46 ft³) large enough to ensure that only small changes in pressure occurred during combustion.

Images of the combustion were obtained through windows in the pressure vessel by backlit photography, and were recorded on a video system at a rate of 60 frames per second, with an exposure of 100 microseconds. These images clearly show the movement of a liquid-gas interface and a bright flame during LP combustion.

The following conclusions have been made based on photographs of LP and HAN/water combustion, samples of combustion residue in the combustion chamber, and the pressure in the chamber:

- 1) As reported by other experimenters, it has been confirmed that there is a decrease in the average volumetric burning rate of LP in the pressure range of 6.7 to 34 MPa (1000 to 5000 psi).
- 2) There are two regions in the LP flame where reactions occur: at the liquid-gas interface and above the liquid-gas interface.

* This work was supported by a memorandum of understanding between the Department of Energy and the Department of the Army.

- 3) For the pressure range studied, HAN decomposition governs the overall combustion rate of HAN-based propellants.

**THE COMBUSTION OF HAN BASED
LIQUID PROPELLANTS**

STEVEN R. VOSEN

**COMBUSTION RESEARCH FACILITY
SANDIA NATIONAL LABORATORIES
LIVERMORE, CALIFORNIA**

**Work supported by a Memorandum of Understanding
between Department of the Army and DOE**

Approach

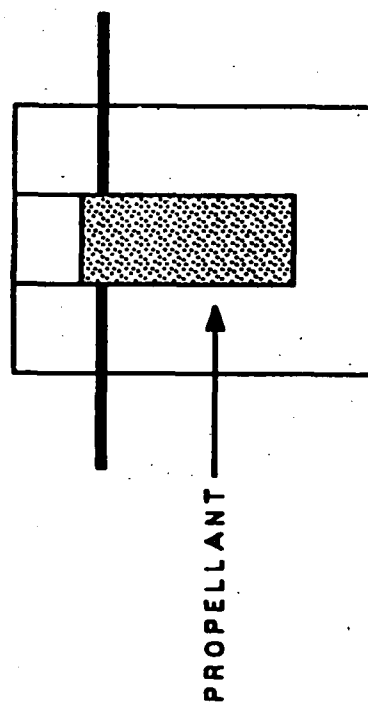
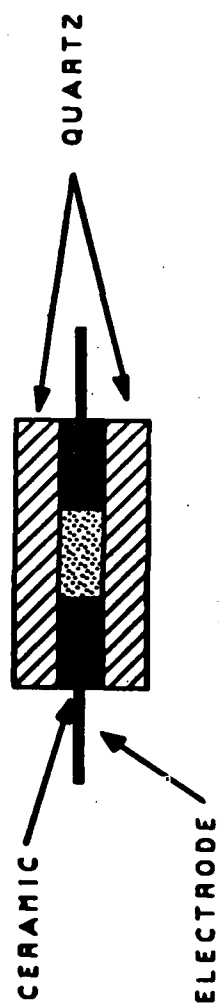
BURN LIQUID PROPELLANTS IN A CONTROLLED ENVIRONMENT TO DETERMINE

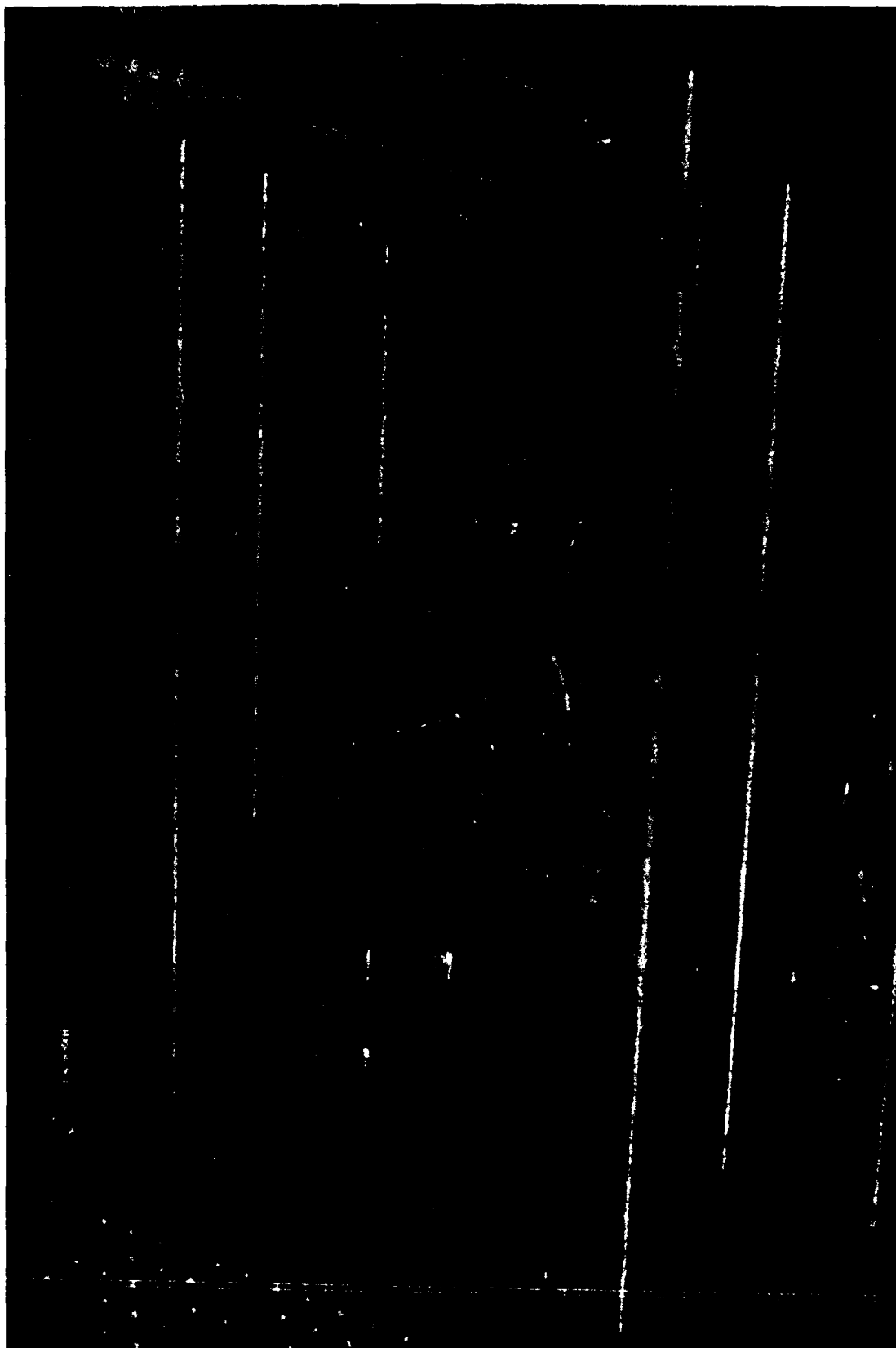
- Burning Rates
- Where Reactions Occur
- Importance of Two-Phase Region
- Flame Stability

Experimental Conditions

- Constant Pressure (1500 - 5000 psi)
- Burn a Column of Fluid (5 mm X 5 mm X 25 mm)
- Electric Discharge Ignition (20 J in 30 μ sec)

Burner





The rate of combustion is given by:

$$\dot{m} = \rho_u S_u A_f$$

↑
Flame area.
"Laminar Burning Speed"

S_u is a function of Chemistry

A_f is a function of:

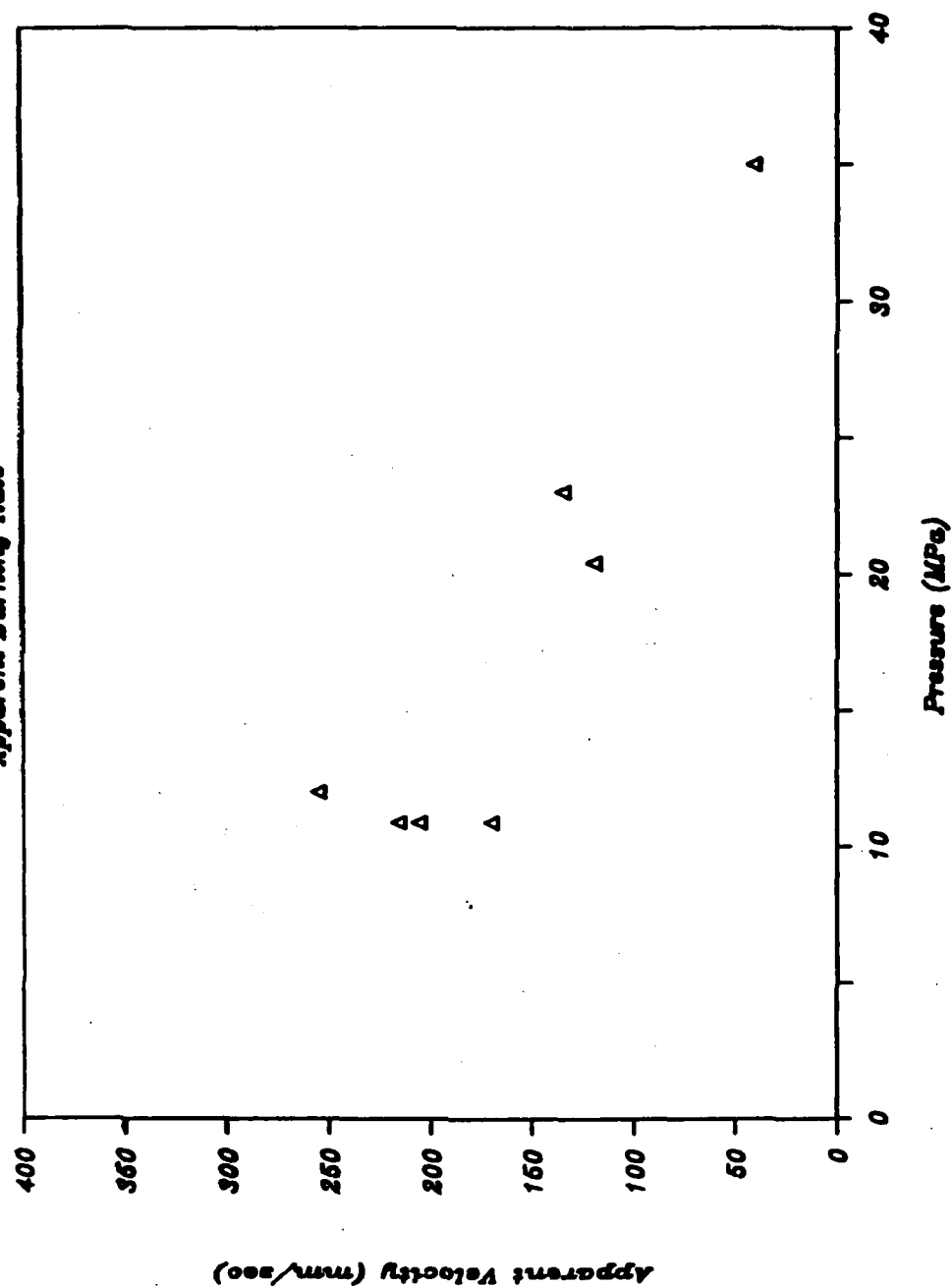
- 1) Turbulence
- 2) Instabilities

Observations

- Regression Rate Decreases with Pressure
- Two Zone Flame Structure
- Burning is Oscillatory

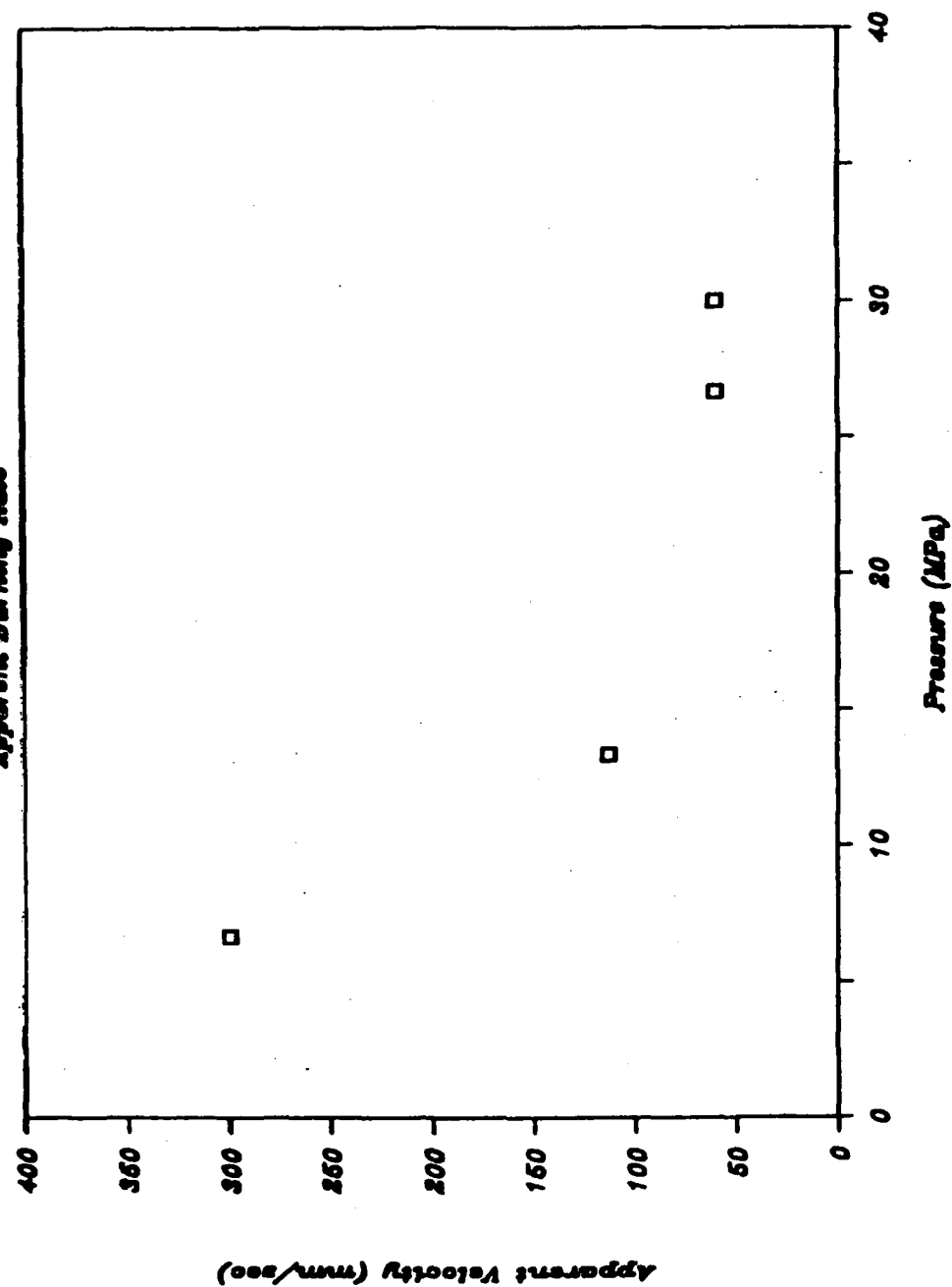
LP 1845

Apparent Burning Rate



LP 1846

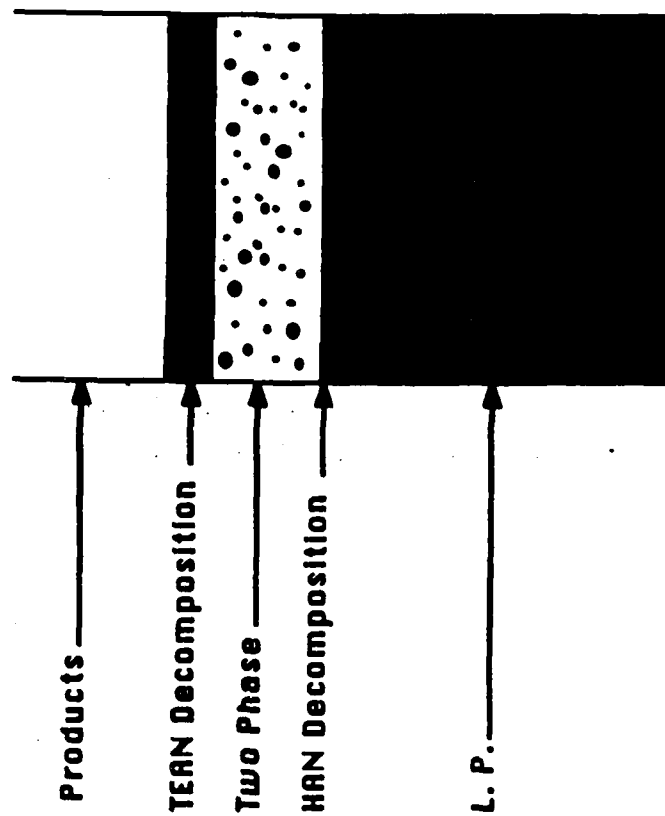
Apparent Burning Rate



Effect of Spark Location

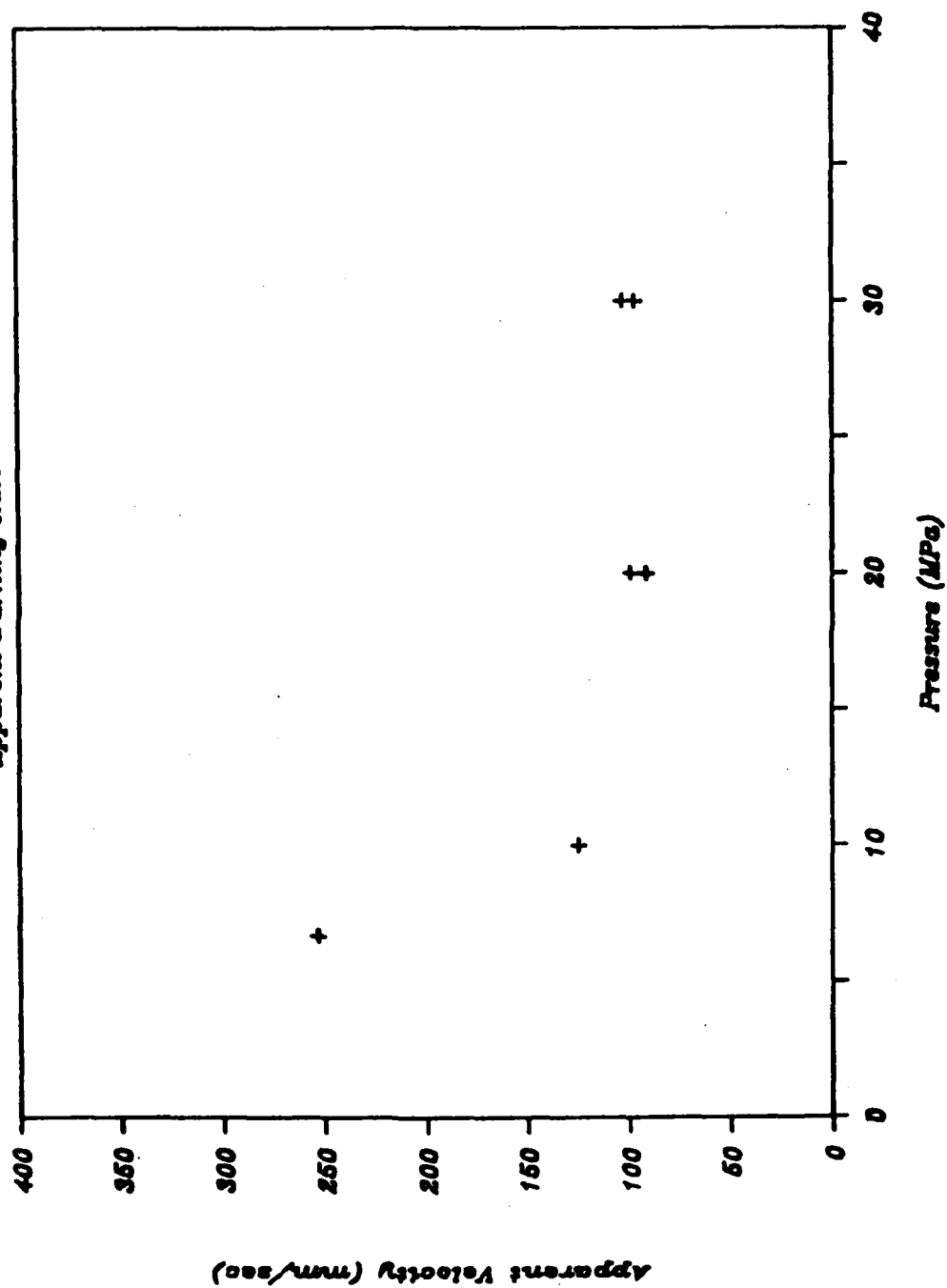
- Ignition below surface:
Visible flame stands off from liquid surface
No liquid is ejected from flame
Large pressure rise
- Ignition at surface:
No visible flame is present
TEAN is ejected from the burner
Small pressure rise

Model of HAN-TEAN-H₂O Combustion



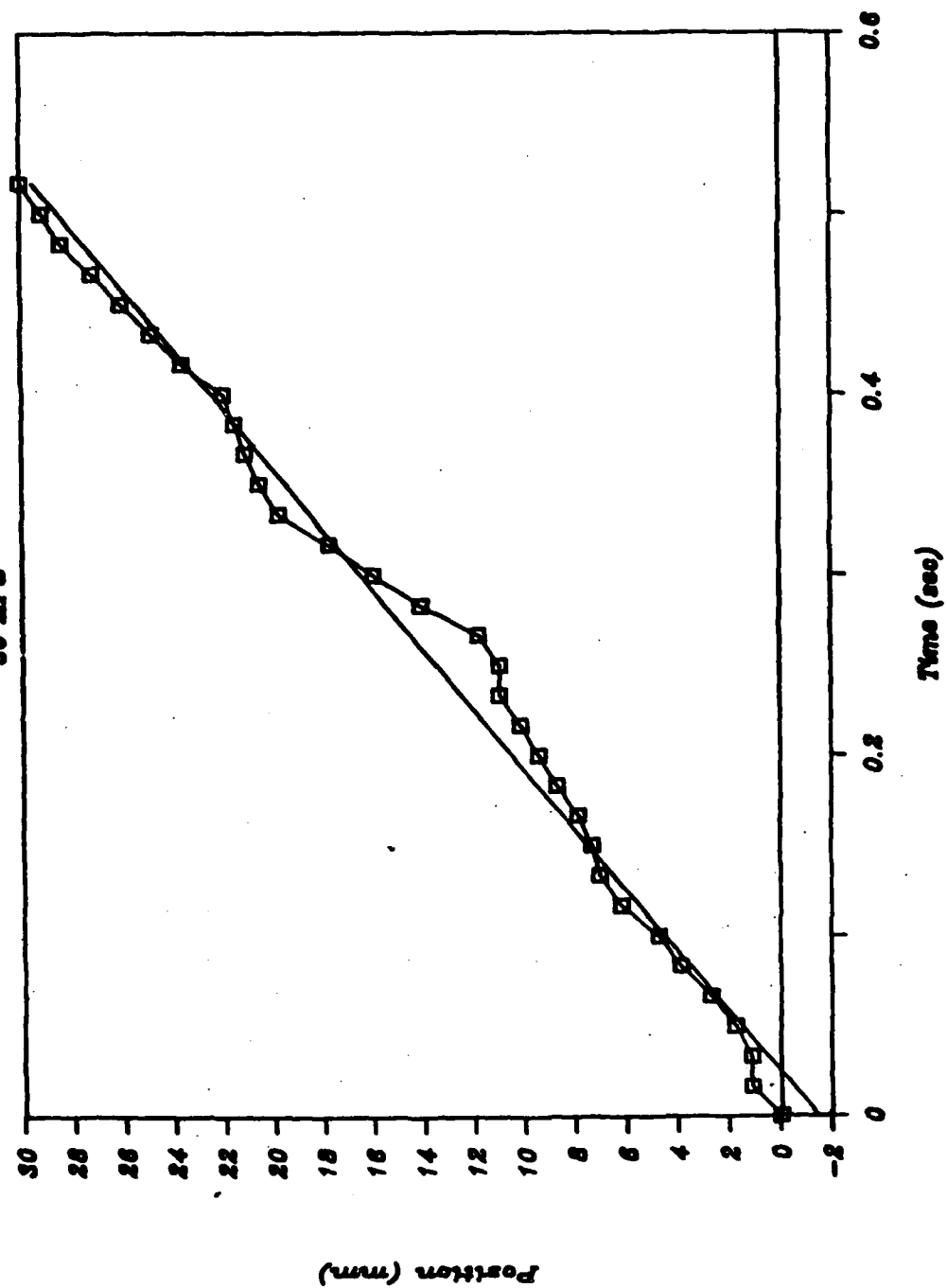
9.16 M HAN

Apparent Burning Rate

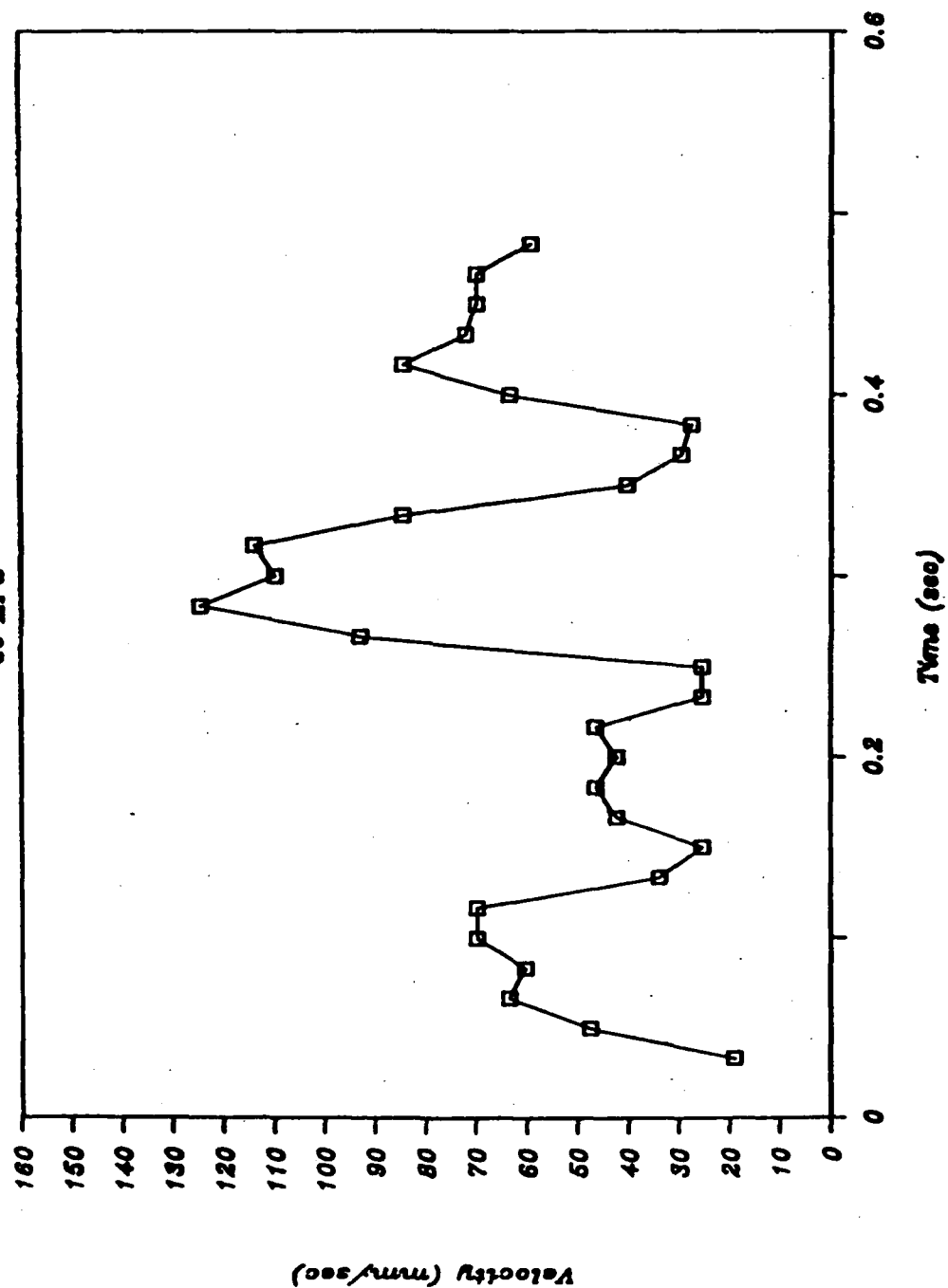


LP 1846

30 MPa

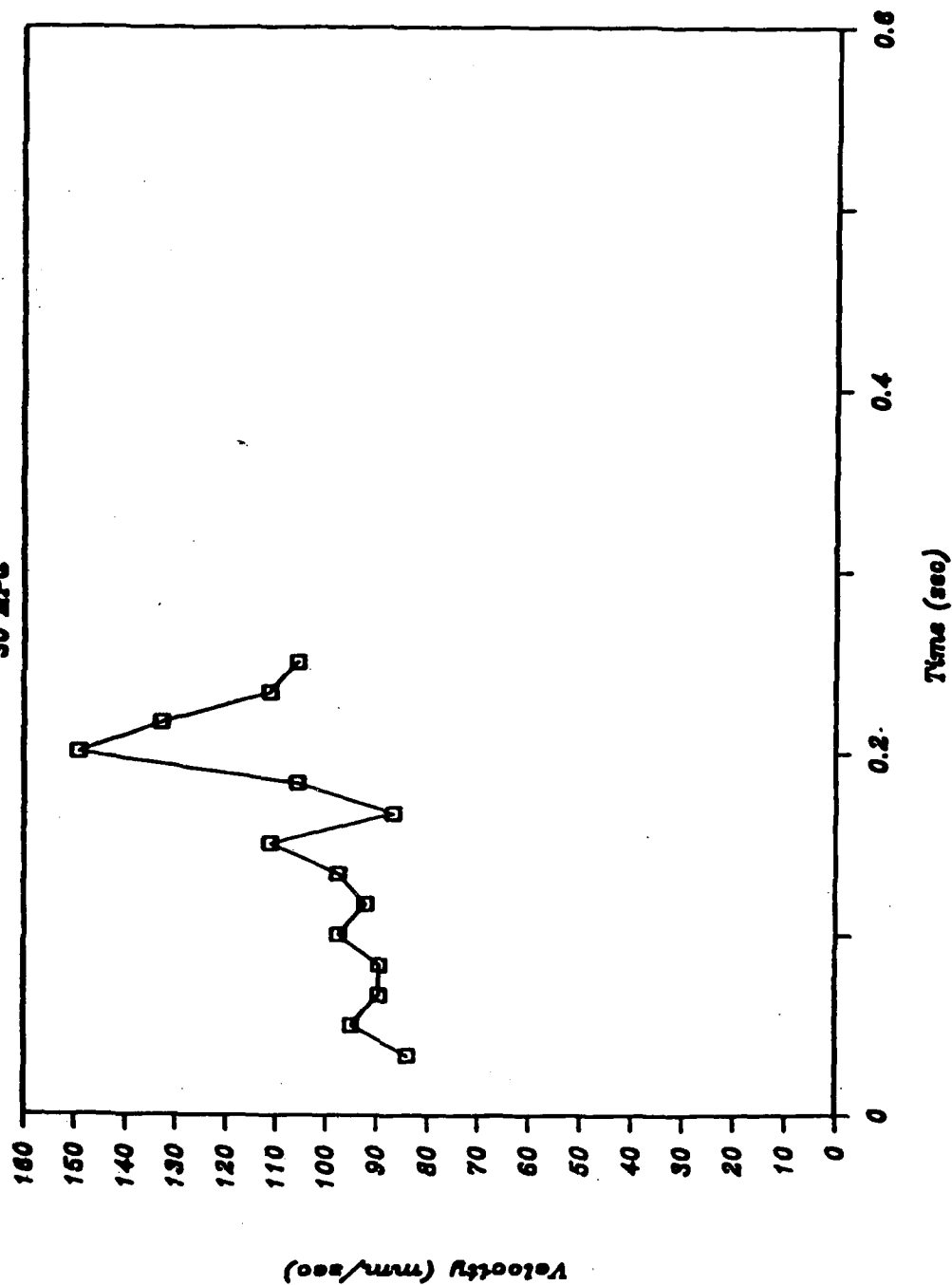


LP 1846
30 MPa



9.16 M HAN

30 MPa



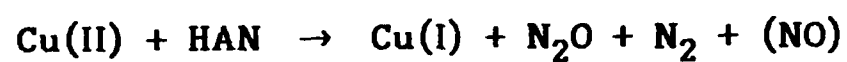
CONCLUSIONS

- HAVE VERIFIED THAT THE OVERALL REGRESSION RATE OF L.P. decreases with pressure
- HAN decomposition also proceeds at a rate which decreases with pressure
- OSCILLATIONS occur which make it difficult to determine a laminar burning Speed

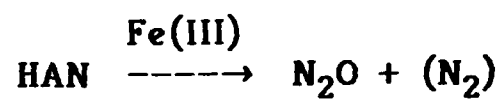
Requirements for Sequestering Agent

- 1) In low concentration, <1% by weight, must be able to strongly complex metal ions in presence of ten molar HAN**
- 2) Must overcome nominal pH 4 in HAN**
- 3) Complexed metal ions must be unreactive towards HAN**
- 4) Must be chemically inert in harsh HAN environment (for years?)**

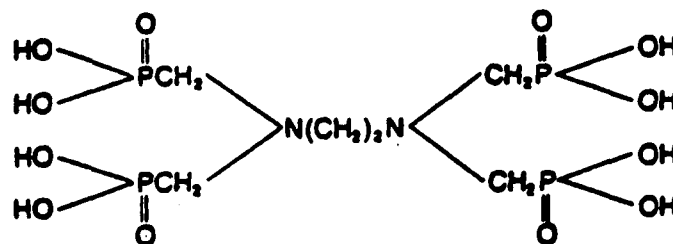
Stoichiometric Metal Ion Impurities



Catalytic Metal Ion Impurities

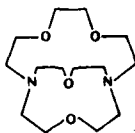


Dequest 2041 (Monsanto)

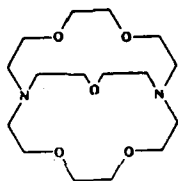


- 1) White solid, 94% purity (Monsanto)
- 2) White solid, 97% purity (Monsanto)
- 3) White solid, >99% purity (Dow)
- 4) Fully deprotonated form L^{8-} (ten protonation sites)

Kryptofix 211



Kryptofix 221



Donor atoms (O and N) enclosed in macrocyclic ring system.

Cryptate stability usually determined largely by match of ionic radius of metal ion and cavity radius of cryptand.

General Observations of Dequest Agents and Iron(III)

- 1) Fe(III) is promptly and extensively precipitated by 2041 and 2060 in both 2.8 M HAN and water (pH < 6), even at 0.5 mM Fe(III) and Dequest agent.
- 2) Solids obtained from either medium are very similar with a given Dequest agent. Fe(III)/Dequest ratio ca. 1:1 for 2041 and 3:2 for 2060.
- 3) Supernatants slowly deposit additional solid. Supernatants appear to be largely colloidal, but clearly contain complexed Fe(III).
- 4) Other metal ions [Cu(II), Co(II), Ni(II), Zn(II), Mn(II)] do not form precipitates, but are strongly complexed.
- 5) Iron(II) does not immediately form a precipitate, but later forms a white solid similar to that with iron(III).
- 6) The iron(III)-Dequest solids dissolve above pH 5-7 to form a yellow solution.

FIGURE ONE

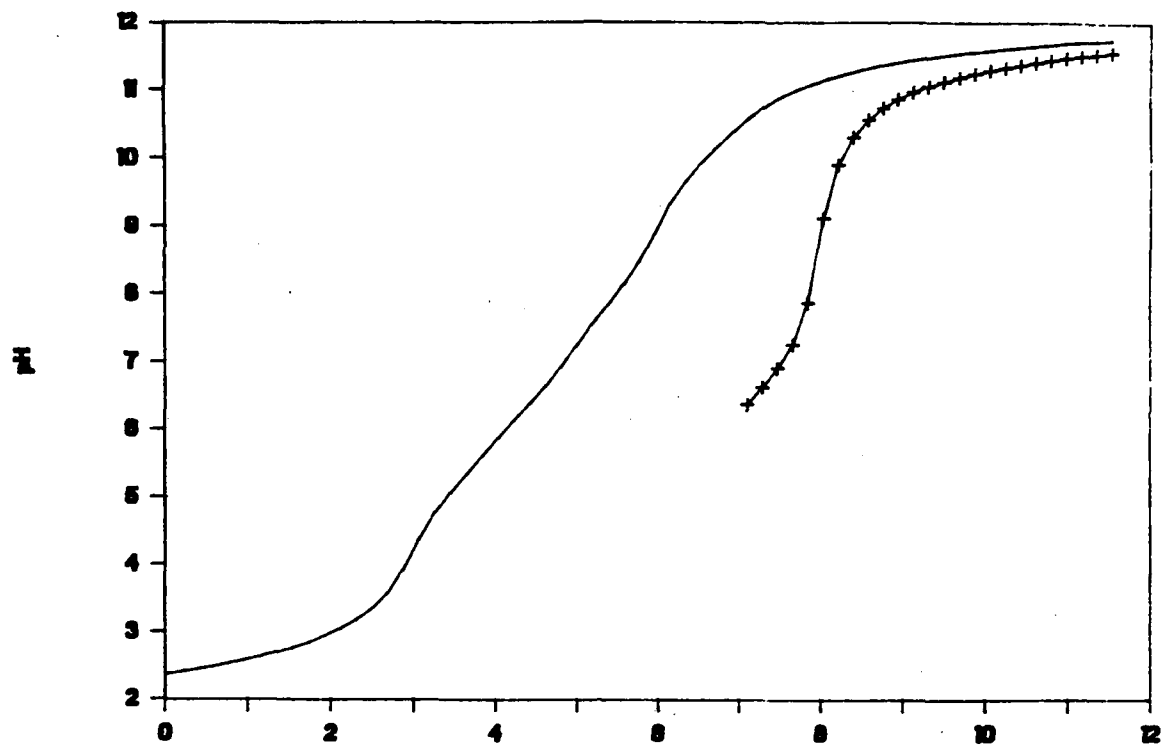
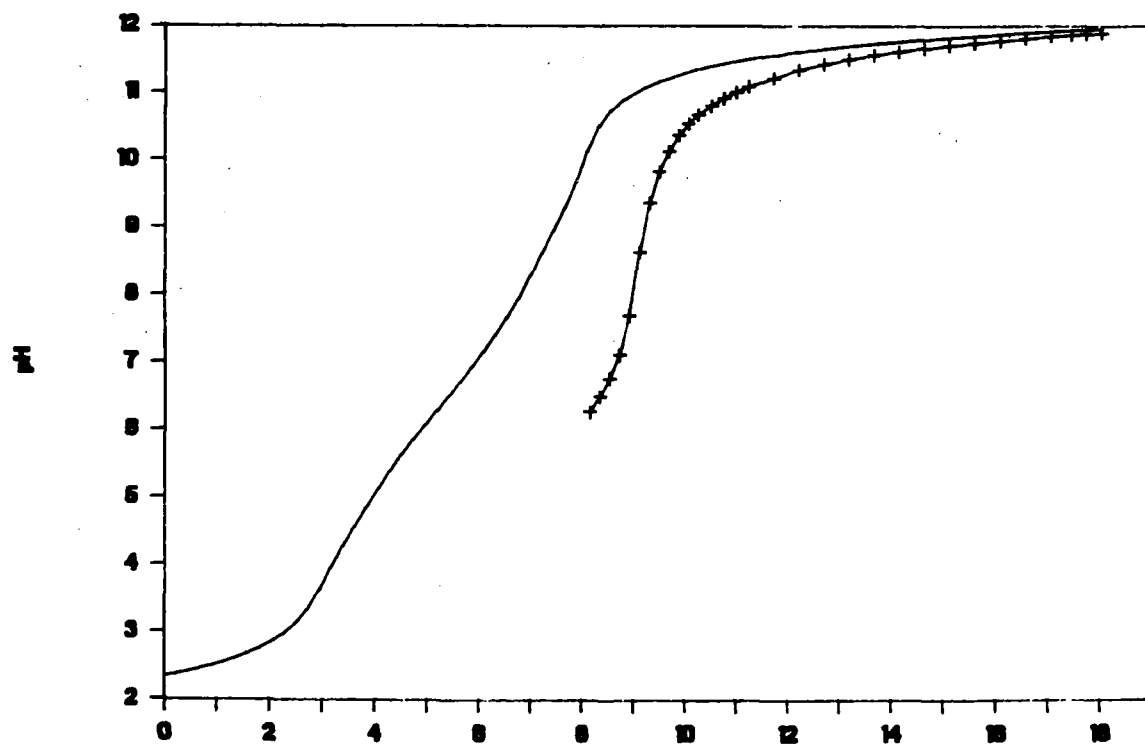
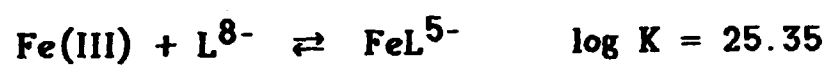


FIGURE TWO



2041



2060



Making the
HAN-ELECTROCHEMICAL

CONNECTION

Ronald L. Dotson

and

James A. Leistra

Olin Corporation

ABSTRACT

~~~~~

Hydroxylammonium nitrate, HAN, in high purity is a valuable chemical which can be produced by several different methods. It is active both as oxidizing and reducing agent, thereby making the electrochemical connection with its preparation and applications. The electrochemical synthesis of HAN has been the subject of considerable interest within recent years within Olin, and a process for its production being developed.

This talk provides a descriptive introduction to the fundamental properties of HAN and then moves quickly to the Olin approach to electrochemical synthesis from the viewpoint of electrochemical engineering. From this perspective the discussion emphasizes some of the unique design tools which the electrochemical engineer uses from both materials science and process design standpoints, that are not common to classical chemical engineering, such as current distribution, fluid flow patterns, mass and charge transfer under electrical load. Electrochemical engineering unifies the concepts of electrode reactions that are approached as heterogeneous catalysts, where the rates of the electrode reactions are controlled not only by the catalytic properties of the electrode substrate but also by the interplay of mass transfer mechanisms that determine the diffusion rate of electroactive species at the conductive and electroactive interfaces.

The discussion emphasizes the importance of correct choice of electrodes as well as materials and apparatus, and is given in four segments following the Introduction, Thermodynamics, Electro-kinetics, Transport and Separation, and finally last but not least Reactor Design.

---

## HAN-ELECTROCHEM-CONNECTION

\*DESCRIPTIVE INTRODUCTION

\*THERMODYNAMIC PROPERTIES

\*ELECTROKINETICS

\*MASS TRANSPORT/SEPARATION

\*PARALLEL PLATE REACTOR

\*CONCLUSIONS

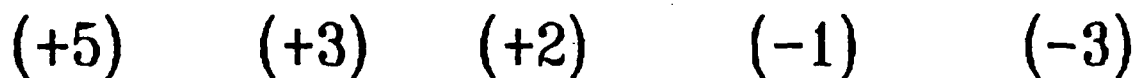
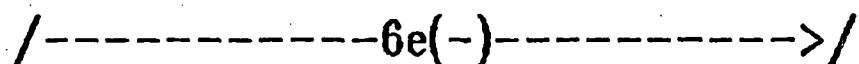
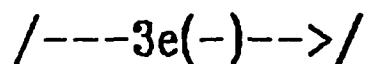
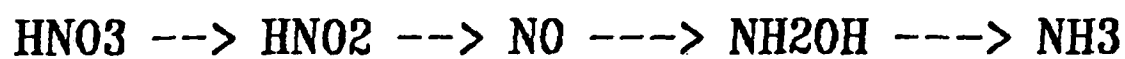
THE REDOX PROPERTIES OF  
HYDROXYLAMMONIUM NITRATE



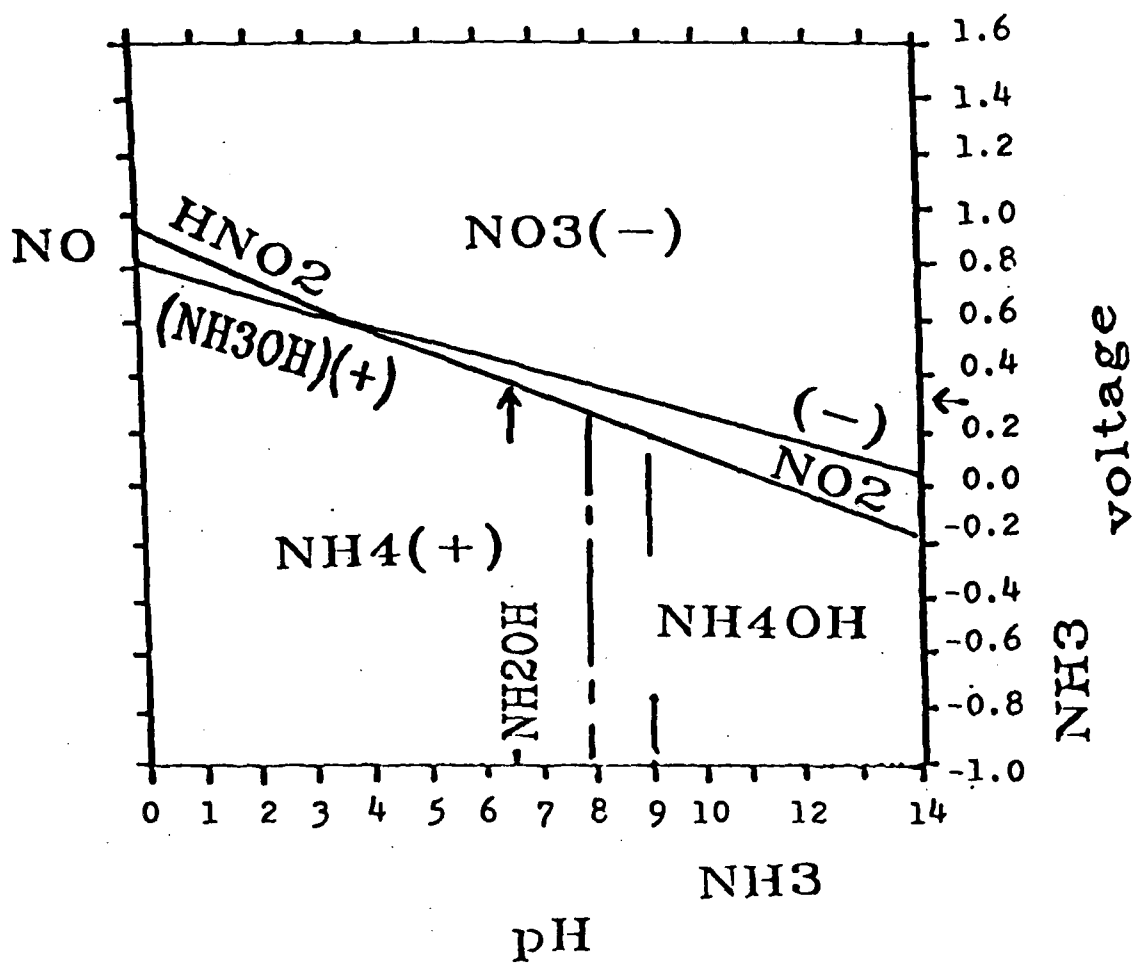
PROVIDE THE  
HAN-ELECTROCHEMICAL  
CONNECTION

HYDROXYLAMMONIUM NITRATE IS DIFFERENT  
FROM THE OTHER HYDROXYLAMMONIUM SALTS

HAN can be formed by action of  
nascent hydrogen on Nitrogen Oxides:



# POURBAIX DIAGRAM



## THERMODYNAMICS

### GIBBS RELATION

Relates the Gibbs free energy to cell voltage.

$$dG = -nFE$$

$$E(\text{volts}) = -4.184 \text{ dG(cals)}/96,490n$$

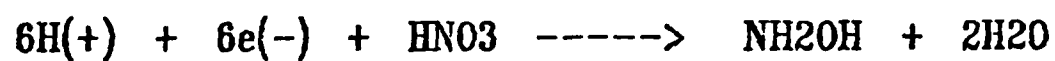
### GIBBS-HELMHOLTZ EQUATION

$$dG = dH - T[dS] = dH + T\{d(dG/dT)\}_p$$

$$E = T(dE/dT)_p - dH/nF$$

## THERMODYNAMICS FOR NITRATE REDUCTION TO HAN

### \*CATHODE HALF CELL REACTION



### \*NERNST EQUATION

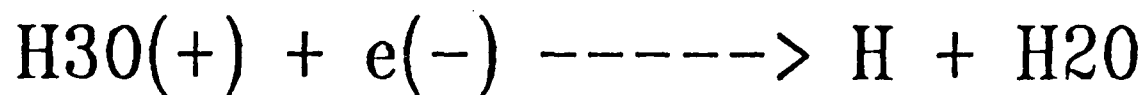
$$E = -0.720 + 0.069 \text{ LOG } [\text{H}(+)]$$

---

# REACTION MECHANISM

## \*ELECTRODE KINETICS

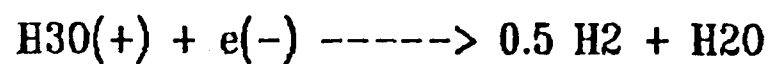
### CHARGE TRANSFER STEP:



## PARAMETERS FOR ELECTRODE KINETICS

Tafel Equation:

$$\eta = (2.303RT/\alpha zF) \log [i_0/i]$$



$$E = -2.303RT/F \log \{[H_2]/[H^+]\}$$

$$E = -1.984E-4 (T) [pH]$$

## MASS TRANSFER LIMITATIONS

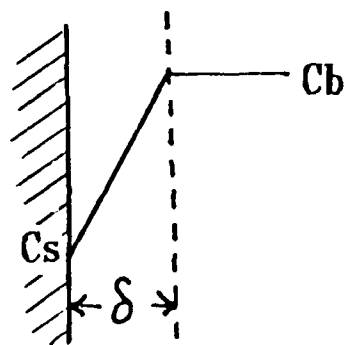
### Concentration Polarization

#### Fick's Law

$$N_o = D/\delta (C_b - C_s)$$

#### Faraday's Law

$$i/zF = D/\delta (C_b - C_s)$$



Nernst Diffusion Layer

## MASS TRANSFER LIMITATIONS

### Concentration Overpotential

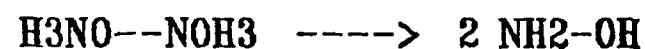
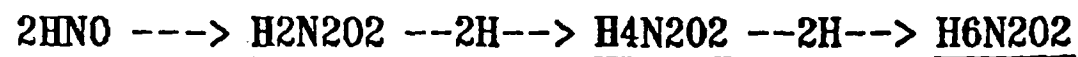
$$i(L)/zF = k C_b$$

$$C_b/C_s = i(L)/[i(L) - i]$$

$$\eta = a + b \log i + c \ln i(L)/[i(L) - i]$$

## PROPOSED REDUCTION MECHANISM

Hyrodimerization of Nitro Groups  
by Indirect Coupling on Cathodic Mercury



## MASS TRANSFER IN ELECTROCHEMICAL SYSTEMS

$$1. \vec{N}_i = -z_i u_i F c_i \vec{\nabla} \Phi - D_i \vec{\nabla} c_i + c_i \vec{v}$$

$$2. \partial c_i / \partial t = - \vec{\nabla} \cdot \vec{N}_i + R_i$$

$$3. \sum_i z_i c_i = 0$$

$$4. \vec{i} = F \sum_i z_i \vec{N}_i$$

# APPLICATION TO ELECTROLYTIC PRODUCTION

OF HAN

For Binary Electrolyte

$$\partial c / \partial t + \vec{v} \cdot \vec{\nabla} c = z_+ u_+ F \vec{\nabla} \cdot (c \vec{\nabla} \Phi) + D_+ \nabla^2 c$$

$$\partial c / \partial t + \vec{v} \cdot \vec{\nabla} c = z_- u_- F \vec{\nabla} \cdot (c \vec{\nabla} \Phi) + D_- \nabla^2 c$$

Subtracting Yields

$$(z_+ u_+ - z_- u_-) F \vec{\nabla} \cdot (c \vec{\nabla} \Phi) + (D_+ - D_-) \nabla^2 c = 0$$

Substituting for the Potential Yields

$$\partial c / \partial t + \vec{v} \cdot \vec{\nabla} c = D \nabla^2 c$$

$$\text{Where } D = (z_+ u_+ D_- - z_- u_- D_+) / (z_+ u_+ - z_- u_-)$$

## CURRENT DISTRIBUTION AT ELECTRODE SURFACE

Velocity (y-direction) = 0

Only the cation reacts at the cathode

Cation Flux

$$N_+ = i/z_+ F = -z_+ u_+ F v_+ c (\partial \Phi / \partial y) - D_+ v_+ (\partial c / \partial y)$$

Anion Flux

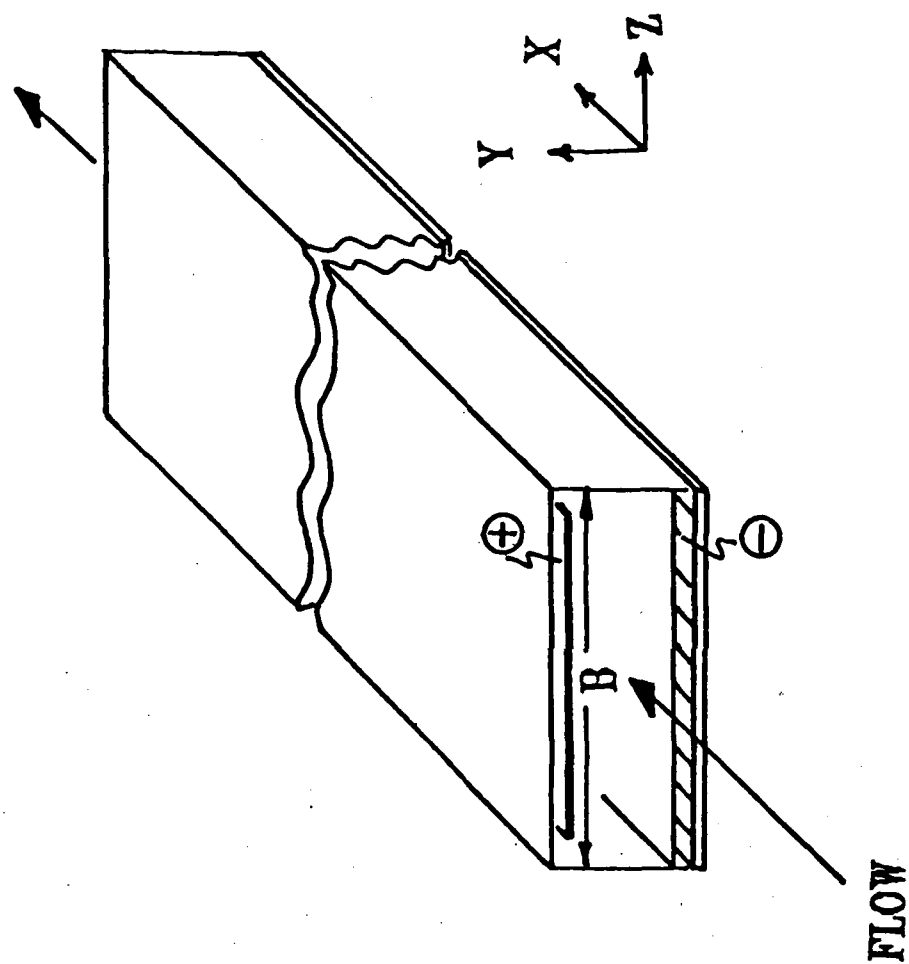
$$N_- = 0 = -z_- u_- F v_- c (\partial \Phi / \partial y) - D_- v_- (\partial c / \partial y)$$

$$\text{Where } c = c_+ / v_+ = c_- / v_-$$

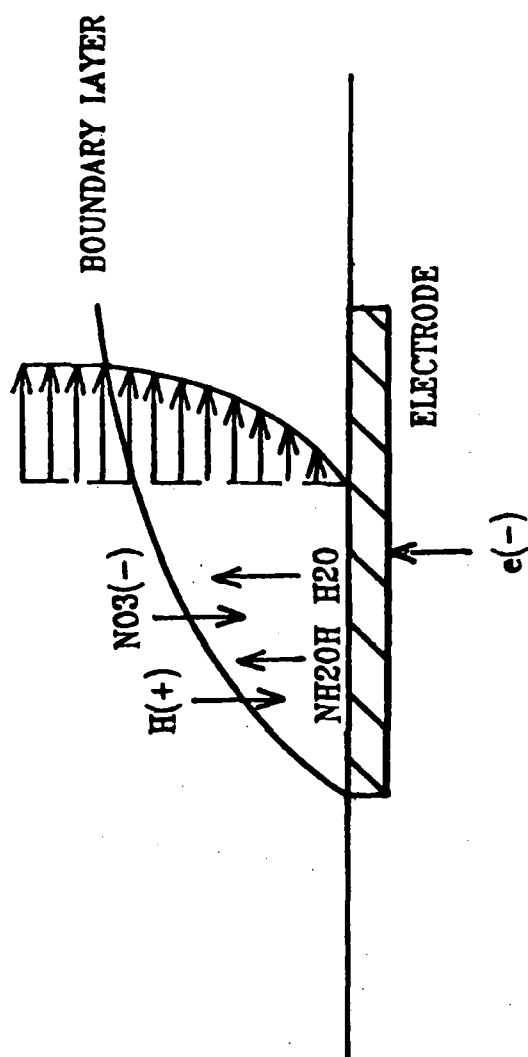
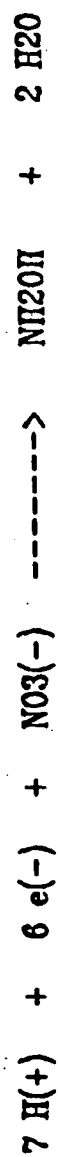
Eliminating the Potential Gradient

$$i/z_+ v_+ F = -[(z_- u_- D_+ - z_+ u_+ D_-) / z_- u_-] \partial c / \partial y$$

PARALLEL PLATE REACTOR WITH ELECTRODES  
OF FINITE WIDTH

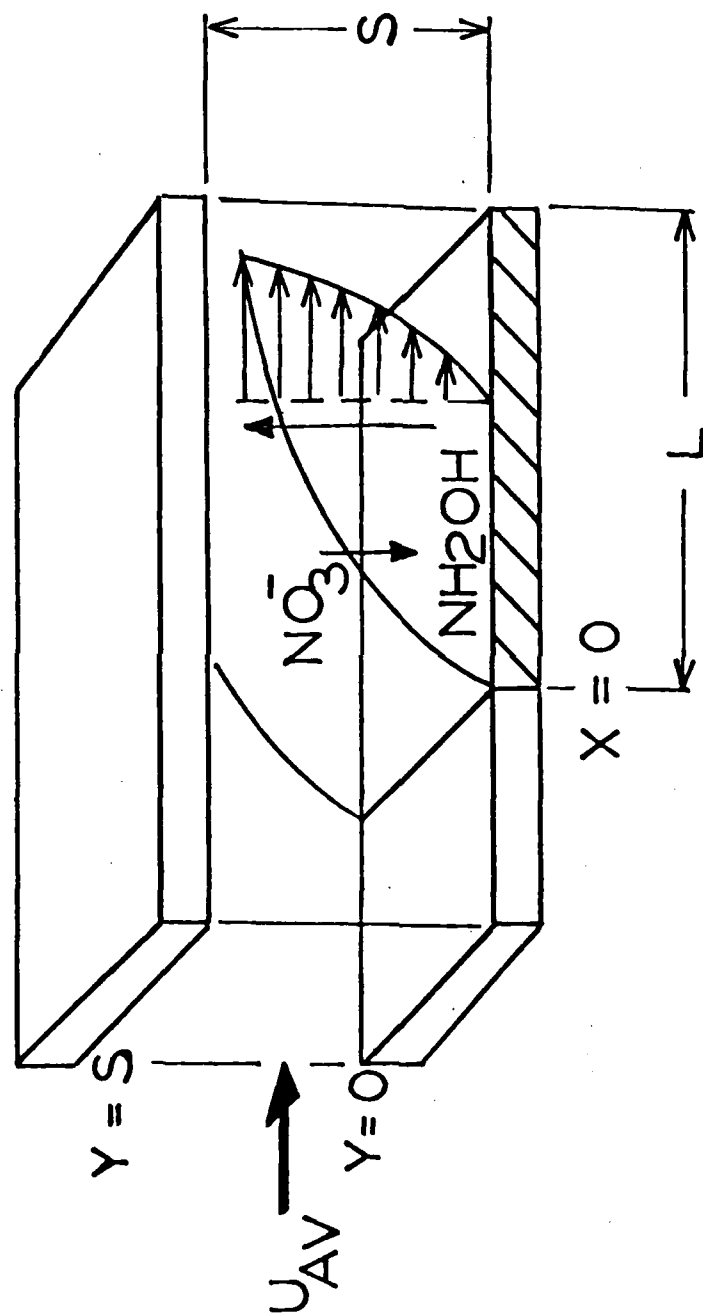


FLOW AND MASS TRANSFER IN THE HYDRODYNAMIC ENTRANCE  
REGION OF A PARALLEL PLATE ELECTROCHEMICAL REACTOR



# PARALLEL PLATE REACTOR

Hydrodynamic entrance length  
under laminar, forced-flow conditions



## PARALLEL PLATE REACTOR

Goal:  $i_x = \text{fcn}(x)$

$$i_x = z F K_x (C_b - C_s)$$

where  $K_x = [-D/(C_b - C_s)] (\partial C/\partial y)_y = 0$

or  $i_x = z F (C_b - C_s) Sh_l D/d_e$

where  $Sh_l = K_x d_e/D$

## PARALLEL PLATE REACTOR

### General Differential Equation

$$\frac{\partial C_j}{\partial t} + \vec{u} \cdot \vec{\nabla} C_j = z_j u_j F \vec{\nabla} \cdot (c_j \vec{\nabla} \Phi) + D_j \nabla^2 C_j$$

For steady state operation  
small potential gradient  
2 - dimensional flow

$$u_x \left( \frac{\partial C}{\partial x} \right) + u_y \left( \frac{\partial C}{\partial y} \right) = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right)$$

For fully developed laminar flow  
negligible diffusion in x - direction

$$u_x \left( \frac{\partial C}{\partial x} \right) = D \left( \frac{\partial^2 C}{\partial y^2} \right)$$

## PARALLEL PLATE REACTOR

Need an expression for  $u_x = \text{fcn}(y)$

from Navier-Stokes equation

$$u_x = 6 U_{av} [y/S - y^2/S^2]$$

from Leveque approximation

$$u_x = 6 U_{av} y/S$$

Therefore:

$$[6 U_{av} y/S] \partial C / \partial x = D (\partial^2 C / \partial y^2)$$

with  $C = C_s$  at  $y = 0$  for  $x > 0$

$C = C_b$  at  $x = 0$  for  $0 < y < S$

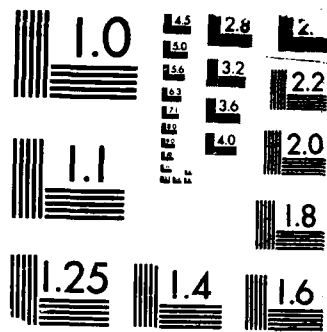
THE ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANTS  
(3RD) HELD IN ABERD. (U) ARMY BALLISTIC RESEARCH LAB  
ABERDEEN PROVING GROUND MD E FREEDMAN ET AL. MAR 88  
BRL-5P-73 F/G 19/1

3/3

**UNCLASSIFIED**

F/G 19/1

NL



MICROCOPY RESOLUTION TEST CHART  
 NBS 1963-A

## PARALLEL PLATE REACTOR

Solution to the basic differential equation

$$K_x = (D/0.893) [2 U_{av} / (3 D \times S)]^{1/3}$$

$$Sh_l = 1.23 [Re Sc d_e / x]^{1/3}$$

or for the whole reactor

$$Sh_{av} = 1.85 [Re Sc d_e / L]^{1/3}$$

with

$$i = z F (C_b - C_s) Sh D / d_e$$

# **EMULSIFIED HAN-BASED PROPELLANTS**

**BY**

**NEALE A. MESSINA**

**PRINCETON COMBUSTION RESEARCH LABORATORIES, INC.**

**A PRESENTATION AT**

**U.S. ARMY BALLISTIC RESEARCH LABORATORY  
CONFERENCE ON HAN-BASED LIQUID PROPELLANT  
STRUCTURE AND PROPERTIES**

**26 AUGUST 1987**

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## **ACKNOWLEDGEMENT**

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(SBIR) PROGRAM
- U.S. ARMY ARDEC CONTRACT DAAA21-86-C-0232
- COTR: DR. ARTHUR BRACUTI

## **PROGRAM PLAN**

---

- **FORMULATION: IDENTIFICATION OF CANDIDATE FUELS**
- **THERMOCHEMICAL EQUILIBRIUM PERFORMANCE**  
(LPG 1845 BASELINE; IMPETUS = 980 j/g,  $T_f = 2723$  K)
- **PROCESSING OF 13M HAN/FUEL/EMULSIFYING AGENT**
  - **FORMULATION WITH THEORETICAL IMPETUS  $\geq 980$  j/g**
  - **PERMANENCE OF EMULSION**
  - **OXIDIZER DROPLET SIZE**

## **PROGRAM PLAN (CONT'D)**

---

- **RHEOLOGICAL PROPERTIES**
  - **SHEAR STRESS VERSUS SHEAR RATE; THIXOTROPY**
  - **YIELD POINT BEHAVIOR**
  - **DYNAMIC LOADING THROUGH GUN VALVE**
- **IMPACT SENSITIVITY**
- **THERMAL INITIATION CHARACTERISTICS**

## **WHY COMPOSITE (HETEROGENEOUS) EMULSIFIED LPS?**

---

- **OPERATIONAL SHORTCOMINGS OF BULK-LOADED LIQUID  
MONOPROPELLANT GUNS**
  - **INCONSISTENT BALLISTIC PERFORMANCE, UNPREDICTABLE  
IGNITION, OCCASIONAL HIGH PRESSURE PEAKS**
  - **BALLISTICS ARISE OUT OF INTERACTION BETWEEN  
HYDRODYNAMIC INSTABILITIES AND COMBUSTION OF  
HIGHLY VARIABLE SURFACE AREA OF MONOPROPELLANT  
CHARGE; TAILORING IS A PROBLEM**
  - **SENSITIZATION OF BULK MONOPROPELLANT CHARGE;  
COMPRESSION IGNITION SENSITIVITY ASSOCIATED  
WITH ENTRAPPED BUBBLES AND ULLAGE**

## **WHY COMPOSITE (HETEROGENEOUS) EMULSIFIED LPS ?(CONT'D)**

---

- **OPERATIONAL SHORTCOMINGS OF REGENERATIVE LIQUID  
MONOPROPELLANT GUNS**
  - **SENSITIVITY/HAZARDS OF LIQUID MONOPROPELLANT;  
COMPRESSION IGNITION, FRICTIONAL SENSITIVITY OF  
HIGH SPEED FLOW IN NARROW GAPS**
  - **LOW PRESSURE COMBUSTION INADEQUACIES**

## **WHAT DO COMPOSITE (HETEROGENEOUS) EMULSIFIED LPs OFFER?**

---

- WELL-DEFINED SURFACE AREA OF OXIDIZER DROPLETS  
EXISTS AS SITES FOR COMBUSTION REACTIONS
- GAS GENERATION RATE LESS SENSITIVE TO SURFACE AREA  
GENERATION DUE TO HYDRODYNAMIC BREAK-UP  
AND INSTABILITIES
- RATE OF REACTION "DESIGNED" INTO PROPELLANT BY  
SUITABLE CHOICE OF OXIDIZER DROPLET SIZE,  
IMMISCIBLE FUEL COMPONENT, STOICHIOMETRY

## WHAT DO COMPOSITE (HETEROGENEOUS) EMULSIFIED LPs OFFER? (CONT'D)

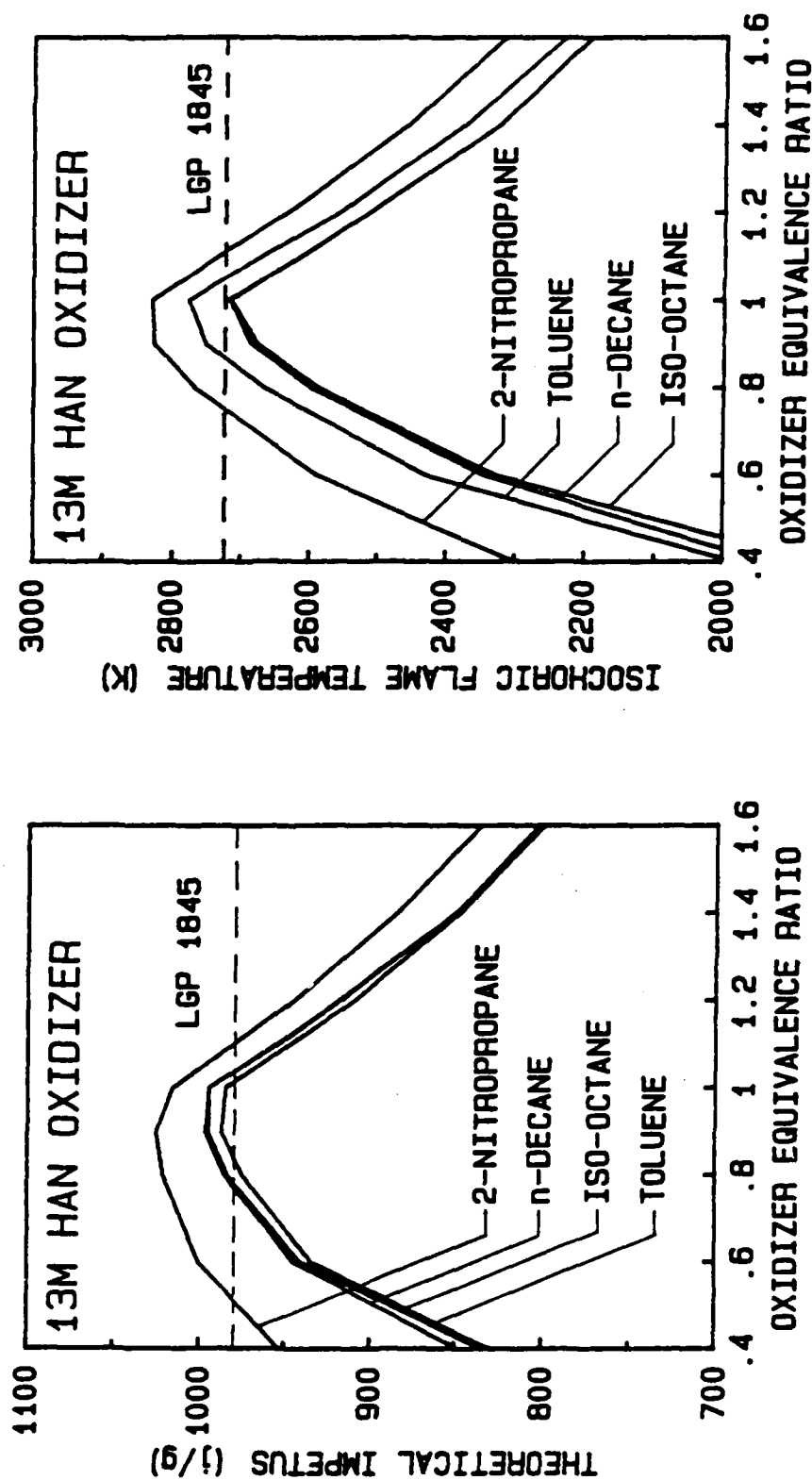
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- OBVIATE NEED FOR MISCIBILITY AS REQUIRED FOR SOLUTION  
MONOPROPELLANTS
- POTENTIAL REDUCED SENSITIVITY DUE TO HETEROGENEITY  
(INTERDIFFUSION PROCESS AT INTERFACES)
- GROWTH POTENTIAL TO HIGH ENERGY FORMULATIONS  
FOR 120mm TANK GUN

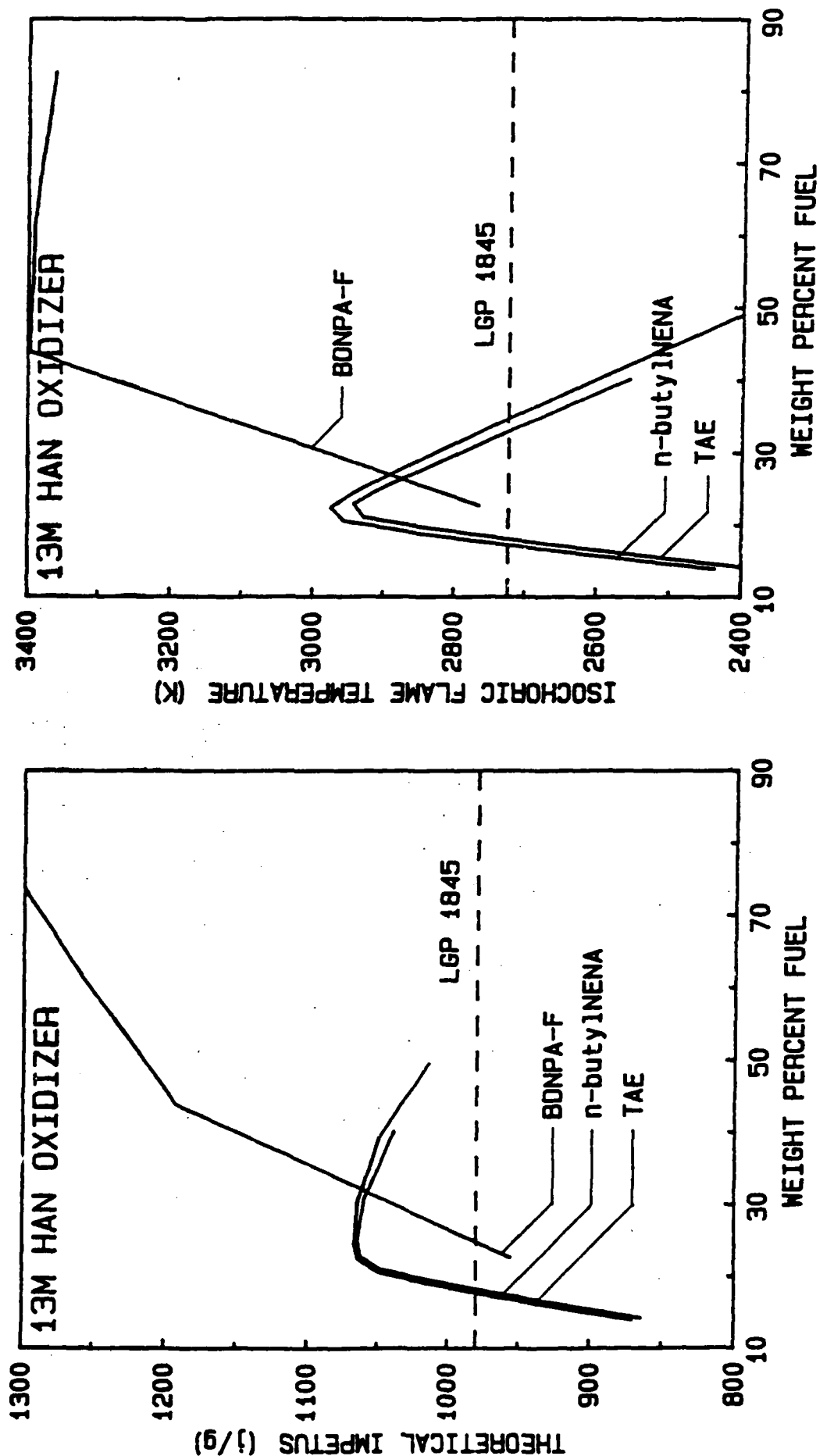
## **COMPOSITE EMULSIFIED PROPELLANT CONSTITUENTS, "WATER-IN-OIL" EMULSIONS**

- **CONCENTRATED AQUEOUS SOLUTION OF 13M HAN,  
DISPERSED PHASE OXIDIZER**
- **HYDROCARBON FUEL IMMISCIBLE IN WATER**
  - ALIPHATIC HYDROCARBONS (n-DECANE, ISO-OCTANE)
  - AROMATIC HYDROCARBONS (TOLUENE)
  - HIGH ENERGY NITROPLASTICIZERS (BDNPA-F, n-butyINENA)
- **EMULSIFYING AGENT (HYDROPHILE/LIOPHILE BALANCE)**
  - FATTY ACIDS
  - FATTY ACID ESTERS
- **WIDE RANGE OF PERFORMANCE VALUES ATTAINABLE**
- **DROPLET SIZE ADJUSTABLE**
  - < 1 MICRON (MICROEMULSION)
  - 10-100 MICRON (MACROEMULSION)

# EQUILIBRIUM THERMOCHEMISTRY



# EQUILIBRIUM THERMOCHEMISTRY



## **EMULSIFICATION TECHNIQUES**

---

- **SONIFICATION (HIGH FREQUENCY VIBRATION)**
- **MICROFLUIDIZATION (IMPINGING STREAMS)**
- **MECHANICAL MIXERS, TUMBLERS**
- **ROTOR-IN-STATOR HOMOGENIZERS**

PROPELLANT PROCESSING

| CONSTITUENT<br>WEIGHT PERCENT |                  | MEAN<br>DROPLET SIZE<br>(MICRON) | MAX<br>DROPLET SIZE<br>(MICRON) | PERMANENCE<br>SIZE<br>(DAYS) | CONSISTENCY <sup>†</sup> |
|-------------------------------|------------------|----------------------------------|---------------------------------|------------------------------|--------------------------|
| HAN                           | H <sub>2</sub> O | FUEL                             |                                 |                              |                          |
| 74.8                          | 17.3             | 7.9 n-DECANE                     | 0.5-1                           | 3                            | >30                      |
| 74.8                          | 17.3             | 7.9 n-DECANE                     | 1-10                            | 50                           | >30                      |
| 74.8                          | 17.3             | 7.9 ISO-OCTANE                   | 1-5                             | 100                          | 21                       |
| 74.1                          | 17.1             | 8.8 TOLUENE                      | 1-15                            | 250                          | >7                       |
| 24.3                          | 5.6              | 70.1 BDNPA-F                     | 1-5                             | 5                            | 21                       |
| 49.3                          | 11.4             | 39.3 n-butyINENA                 | --                              | --                           | NOTE 1                   |
|                               |                  |                                  |                                 |                              | 10                       |

<sup>†</sup>10 ≡ PASTE-LIKE

1 ≡ WATER-LIKE

NOTE 1. FUME-OFF OBSERVED WITHIN 8 HR TO THREE DAYS OF STORAGE

**PRINCETON**  
**COMBUSTION**  
**RESEARCH**  
**LABORATORIES, INC.**

---

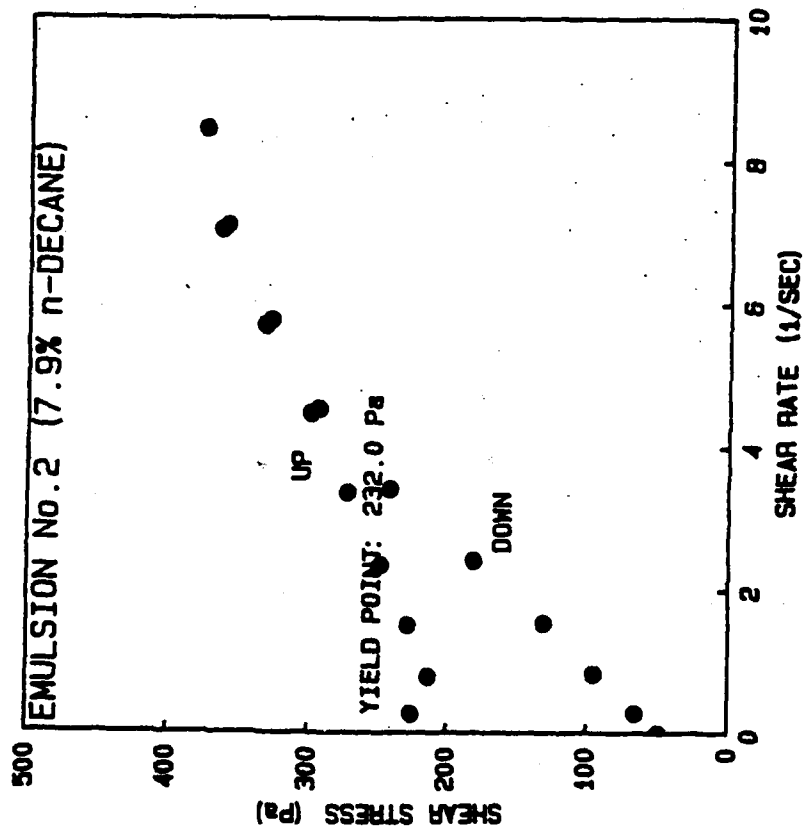
**PHOTOMICROGRAPHS**  
**OF EMULSIFIED HAN-BASED LIQUID PROPELLANTS**

## **RHEOLOGICAL PROPERTIES**

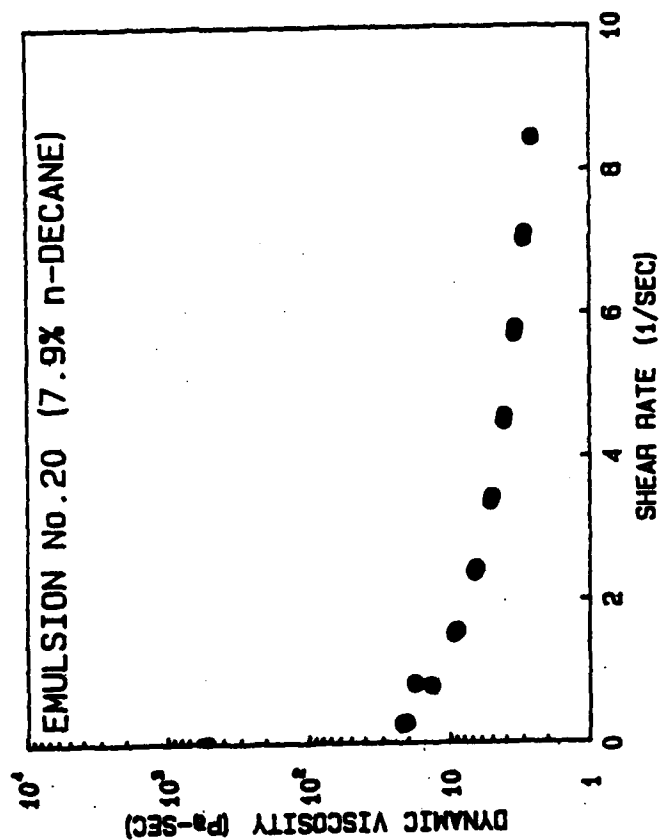
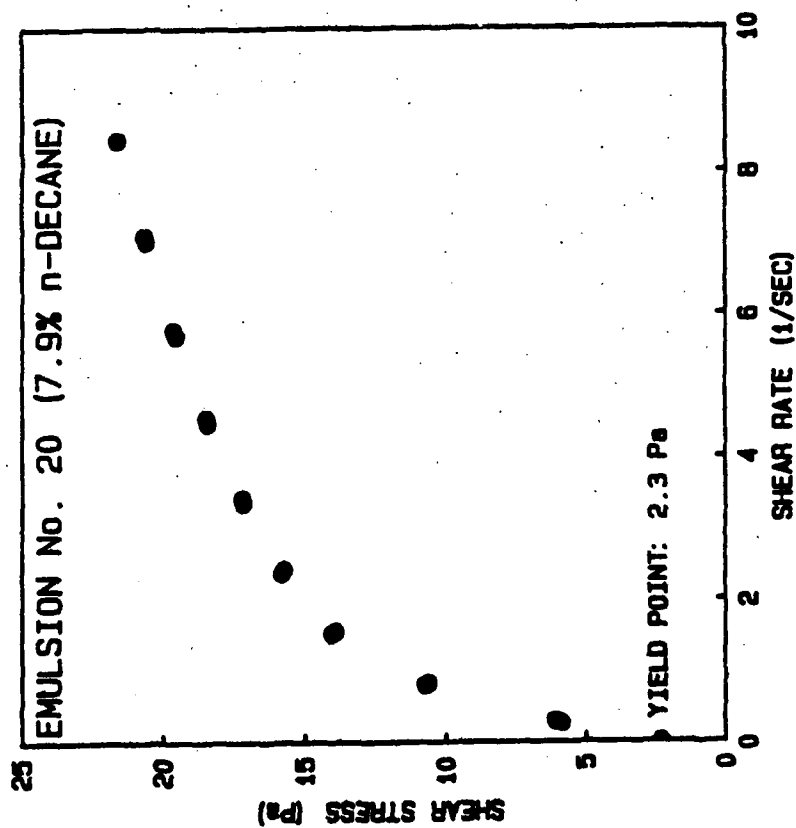
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- **NON-NEWTONIAN LIQUIDS**
- **THIXOTROPIC, TO VARYING DEGREES**
- **YIELD POINT EXHIBITED, 2.3 Pa - 232 Pa**

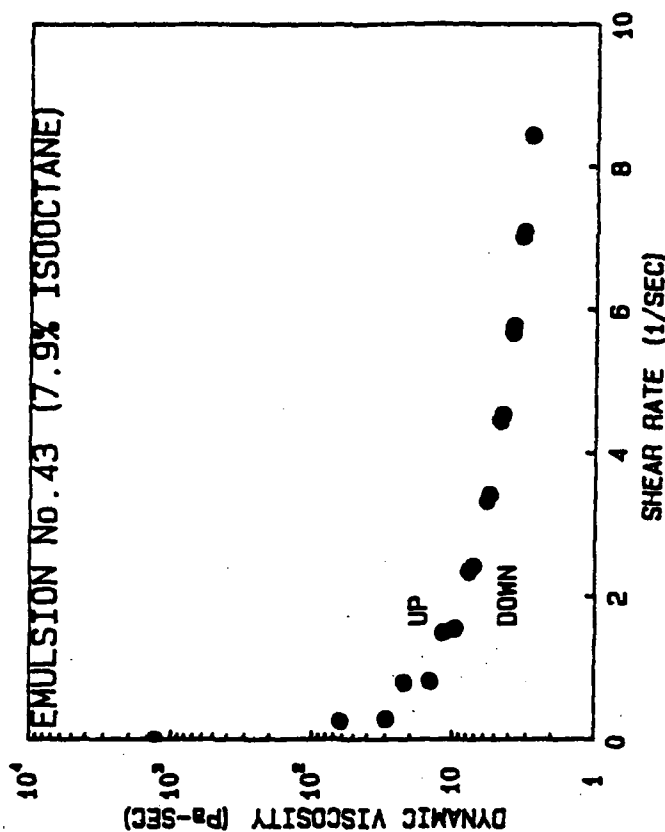
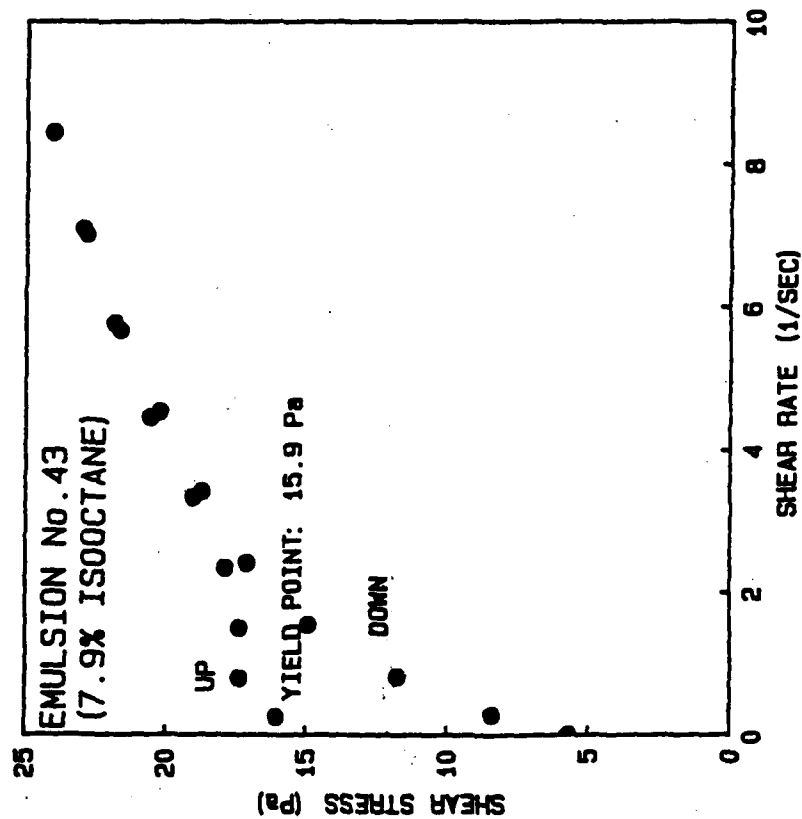
# RHEOLOGICAL PROPERTIES



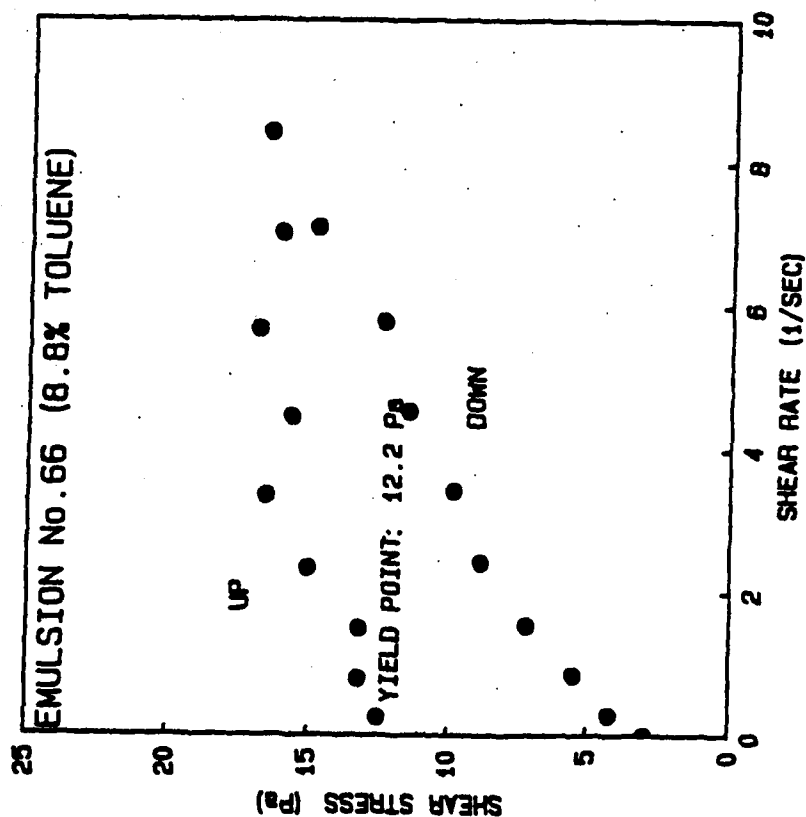
## RHEOLOGICAL PROPERTIES



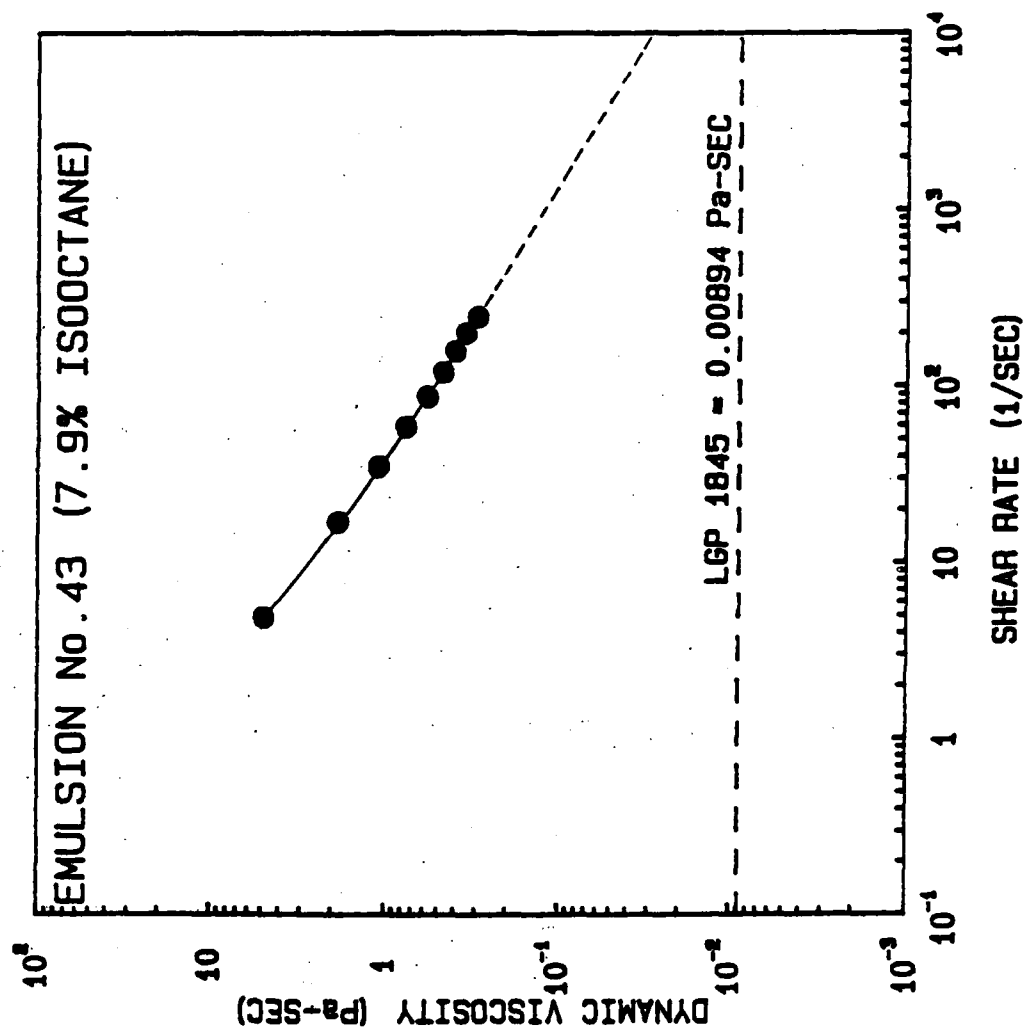
# RHEOLOGICAL PROPERTIES



# RHEOLOGICAL PROPERTIES

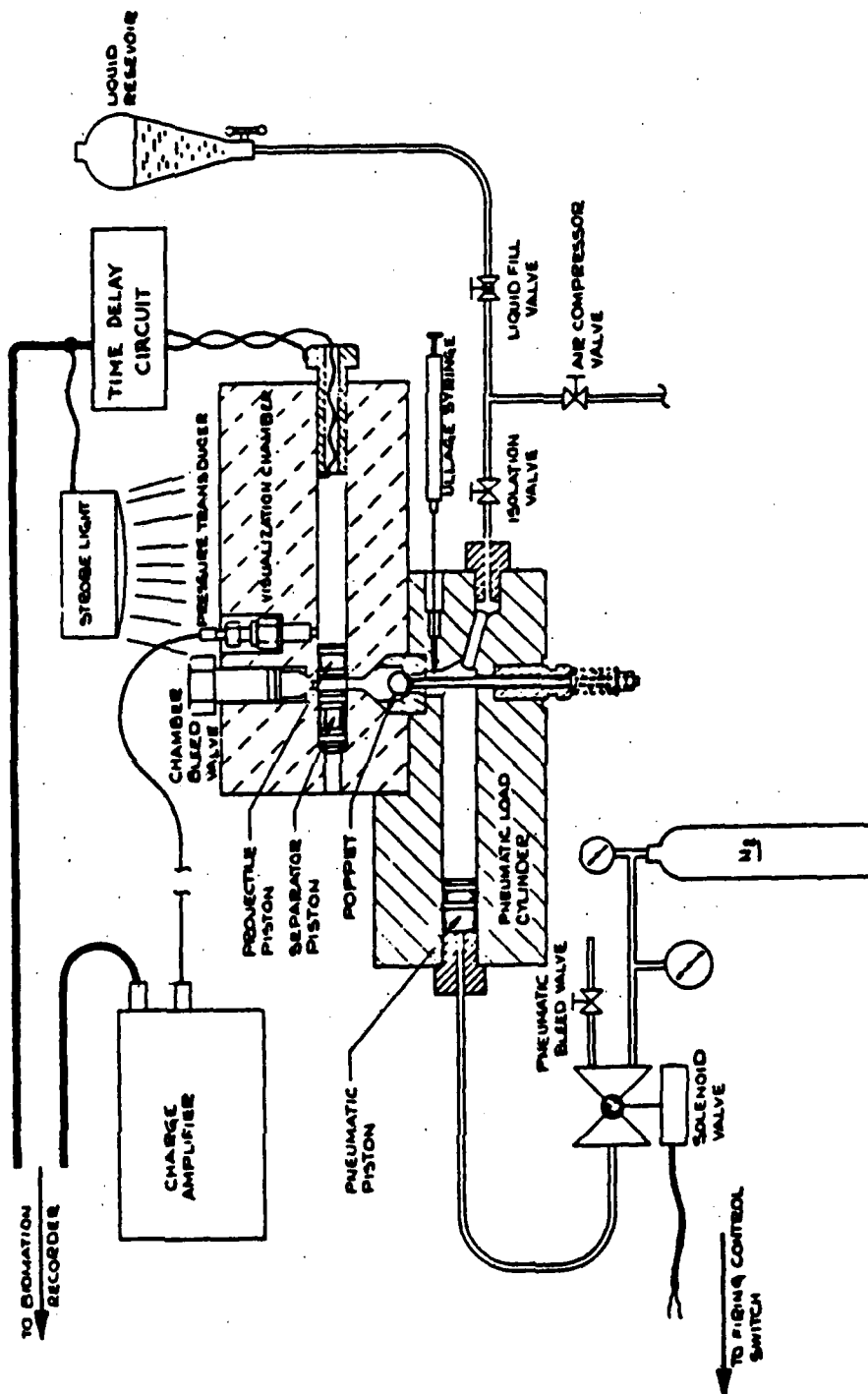


## HIGH SHEAR RATE BEHAVIOR

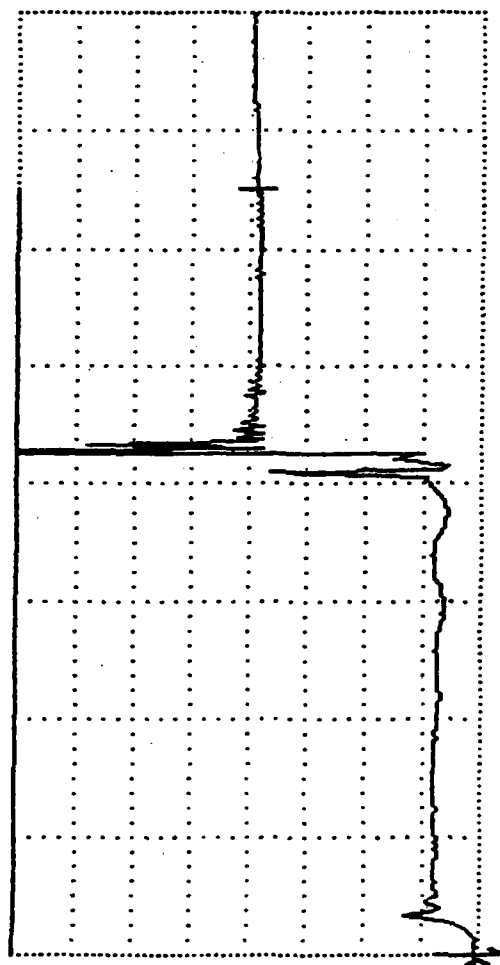


# DYNAMIC LOADING BEHAVIOR THROUGH GUN VALVE

PRINCETON  
COMBUSTION  
RESEARCH  
LABORATORIES, INC.



**DYNAMIC LOADING**  
**EMULSION NO. 20(n-DECANE)**



**SCALING**

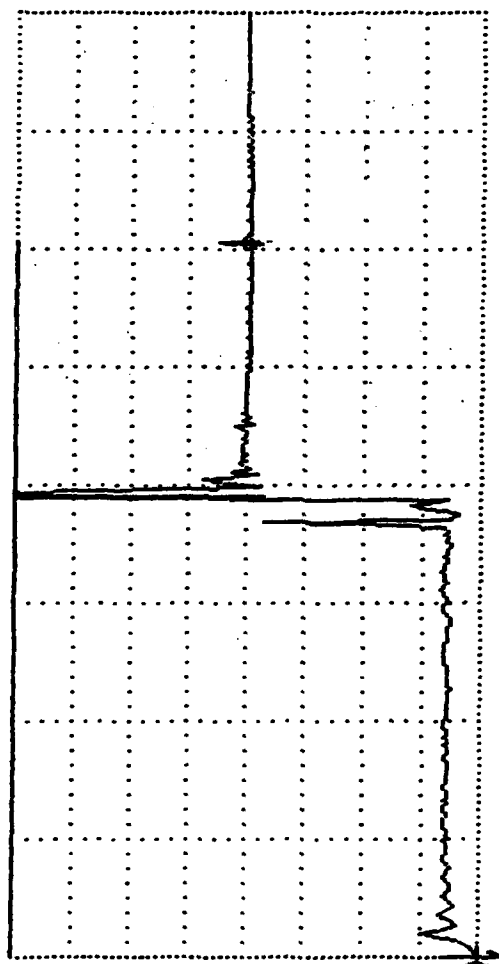
**PRESSURE: 100PSI/DIV**

**TIME: 5 msec/DIV**

**t INJECT = 21.2 msec**

**P EQUIL = 382 PSIG**

**DYNAMIC LOADING**  
**LGP 1845**



**SCALING**

**PRESSURE: 100PSI/DIV**

**TIME: 5msec/DIV**

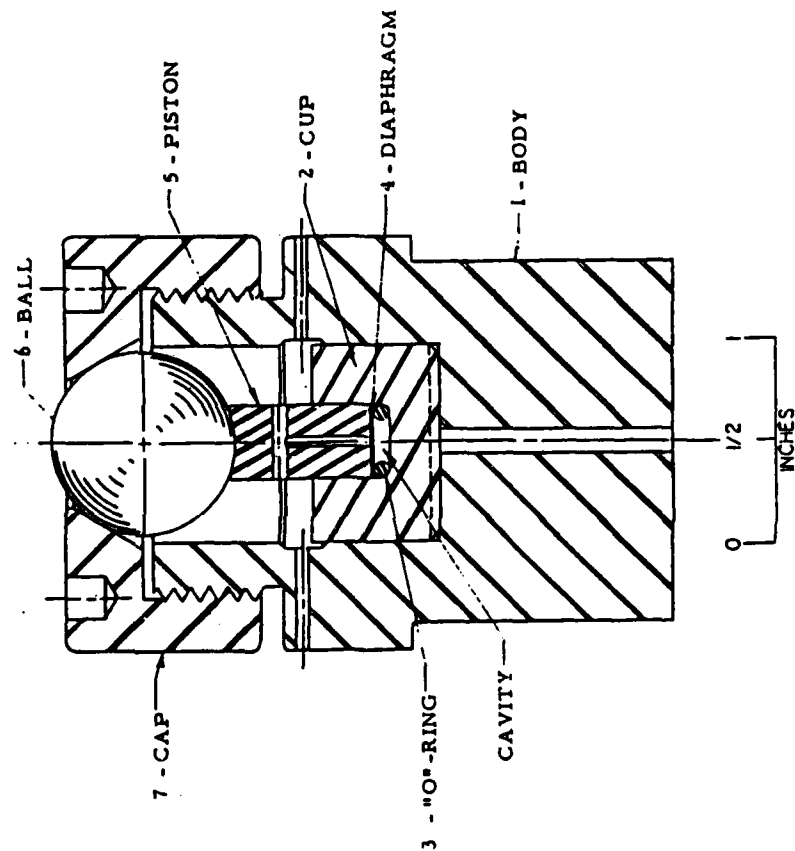
**$t_{INJECT}$  = 19.3 msec**

**$P_{EQUIL}$  = 400PSIG**

**TECHNOPRODUCTS DROP WEIGHT TESTER; 4 kg WEIGHT**

**HYDRAULIC LIMIT (85%) = 157.9 kg-cm**

**SAMPLE HOLDER**



# IMPACT SENSITIVITY FOR SOLUTION MONOPROPELLANTS

50% IGNITION POINT (kg-cm)

| PROPELLANT   | PREVIOUS TESTS                                           | CURRENT STUDY |
|--------------|----------------------------------------------------------|---------------|
| Otto Fuel II | 8.5 - 70 <sup>4</sup><br>98 <sup>1</sup>                 | 102.0         |
| NOS-365      | >100 <sup>3</sup><br>98 <sup>1</sup><br>152 <sup>2</sup> | 140.8         |
| LGP 1845     | >100 <sup>1</sup><br>152 <sup>2</sup>                    | 154.6         |

- REF. 1 STOBIE, U.S. ARMY BRL  
2 CRUICE, HAZARDS RESEARCH  
3 SMITH, NSWC  
4 MASON, BUREAU OF MINES

**IMPACT SENSITIVITY FOR  
HETEROGENEOUS EMULSIONS**

| PROPELLANT      |              | 50 % IGNITION POINT<br>(kg-cm) |
|-----------------|--------------|--------------------------------|
| EMULSION NO. 20 | (n-DECANE)   | 156.0                          |
| EMULSION NO. 43 | (ISO-OCTANE) | 155.0                          |
| EMULSION NO. 66 | (TOLUENE)    | >158.0                         |
| EMULSION NO. 38 | (BDNPA-F)    | 20.0                           |

## **CONCLUSIONS**

- STABLE "WATER-IN-OIL" HETEROGENEOUS EMULSIFIED LPS  
HAVE BEEN PROCESSED WITH 13M HAN AS THE DISPERSED  
OXIDIZING PHASE
- DISPERSED PHASE OXIDIZER PARTICLE SIZE RANGE IS TAILORABLE  
WITHIN WIDE LIMITS
- A ROTOR-IN-STATOR HOMOGENIZER WITH SPEED CONTROL  
IS SUITABLE FOR PREPARING LABORATORY LOTS UP TO 0.5 LITER
- THEORETICAL IMPETUS LEVELS EQUAL TO OR GREATER THAN  
SOLUTION MONOPROPELLANT LGP 1845 ARE EASILY ACHIEVABLE  
FOR 13M HAN/COMMERCIALLY AVAILABLE HYDROCARBONS,  
FOR SLIGHTLY FUEL RICH FORMULATIONS

## **CONCLUSIONS (CONT'D)**

- **SELECTED HETEROGENEOUS EMULSIONS DEMONSTRATE  
INSENSITIVITY TO IMPACT, EXCEPT FOR THE FORMULATION  
BASED ON BDNPA-F ENERGETIC NITROPLASTICIZER**
- **EMULSIFIED LPS ARE PSEUDOPLASTIC IN FLOW BEHAVIOR,  
SEVERAL DEMONSTRATING THIXOTROPY. THEY ARE READILY  
PUMPED THROUGH A GUN VALVE AT PRESSURES TYPICAL  
OF LPG SYSTEMS, I.E., 500 PSIG**

## **RECOMMENDATIONS FOR ADDITIONAL CHARACTERIZATION**

- **ADDITIONAL PHYSICAL PROPERTIES CHARACTERIZATION**
  - DENSITY
  - TIME DEPENDENT THIXOTROPY OF SHEARED PROPELLANT SAMPLES
  - DROPLET SIZE DISTRIBUTION OF SHEARED PROPELLANT SAMPLES
  - FREEZING POINT
- **COMBUSTION PERFORMANCE IN A CLOSED BOMB TYPE APPARATUS**
- **IGNITABILITY CHARACTERIZATION USING PYROGENIC  
IGNITION SOURCE**
- **FLOW AND COMBUSTION DIAGNOSTICS IN A HIGH PRESSURE  
ENVIRONMENT, SIMULATING 30mm RLPG FLOW RATES**
- **20mm MANN BARREL TESTS UTILIZING STANDARD,  
20mm CASED CARTRIDGE AND PROOF SLUG  
WITH TAILORED IGNITION SYSTEM**
- **FORMULATION TAILORING FOR HIGH PERFORMANCE SYSTEMS**

# THE DIFFUSION AND MIXING CHARACTERISTICS OF LGP 1845 AND WATER

Cris A. Watson and John D. Knapton  
U.S. Army Ballistic Research Laboratory  
Aberdeen Proving Ground, MD 21005-5066

## ABSTRACT

An approximate value for the diffusion coefficient of liquid gun propellant (LGP) 1845 into water was obtained using a two color mixing method. The two components, water and propellant, were dyed separate colors and the mixing region was measured as a function of time. Using the experimental mixing length, the diffusion coefficient was calculated. As a check on the procedure, methanol and glycerine were also tested. The diffusion values obtained in the experiments for methanol and glycerine were  $1.28\text{E}^{-5} \text{ cm}^2/\text{s}$  and  $1.73\text{E}^{-5} \text{ cm}^2/\text{s}$ , respectively. The diffusion coefficient for LGP 1845 into water is  $1.59\text{E}^{-5} \text{ cm}^2/\text{s}$ . A prediction for the diffusion coefficient of hydroxylammonium nitrate into water was also calculated and found to be  $1.4\text{E}^{-5} \text{ cm}^2/\text{s}$ . The short term mixing characteristics of LGP and water was also investigated. The results indicated that the propellant and water will not mix properly unless agitated.

**THE DIFFUSION AND MIXING  
CHARACTERISTICS OF LGP 1845  
INTO WATER**

**CRIS WATSON & JOHN D. KNAPTON**

**U.S. ARMY ALLISTIC RESEARCH LABORATORY**

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## OUTLINE

OBJECTIVE

EXPERIMENTAL APPROACH

EQUATIONS

DIFFUSION RESULTS

MIXING CHARACTERISTICS

SUMMARY

## **OBJECTIVE**

DETERMINE THE DIFFUSION COEFFICIENT AND  
EXPLORE THE MIXING CHARACTERISTICS OF A  
HAN-BASED LIQUID MONOPROPELLANT  
INTO WATER

# EXPERIMENTAL APPROACH

TWO COLOR

MIXING TECHNIQUE

LGP 1845

STANDARDS

METHANOL

GLYCERIN



B

MIXING REGION

A

## EQUATIONS

FICK'S RATE EQUATION:

$$J(a,b) = - D(a,b) \rho \frac{dW(a)}{dz}$$

.

.

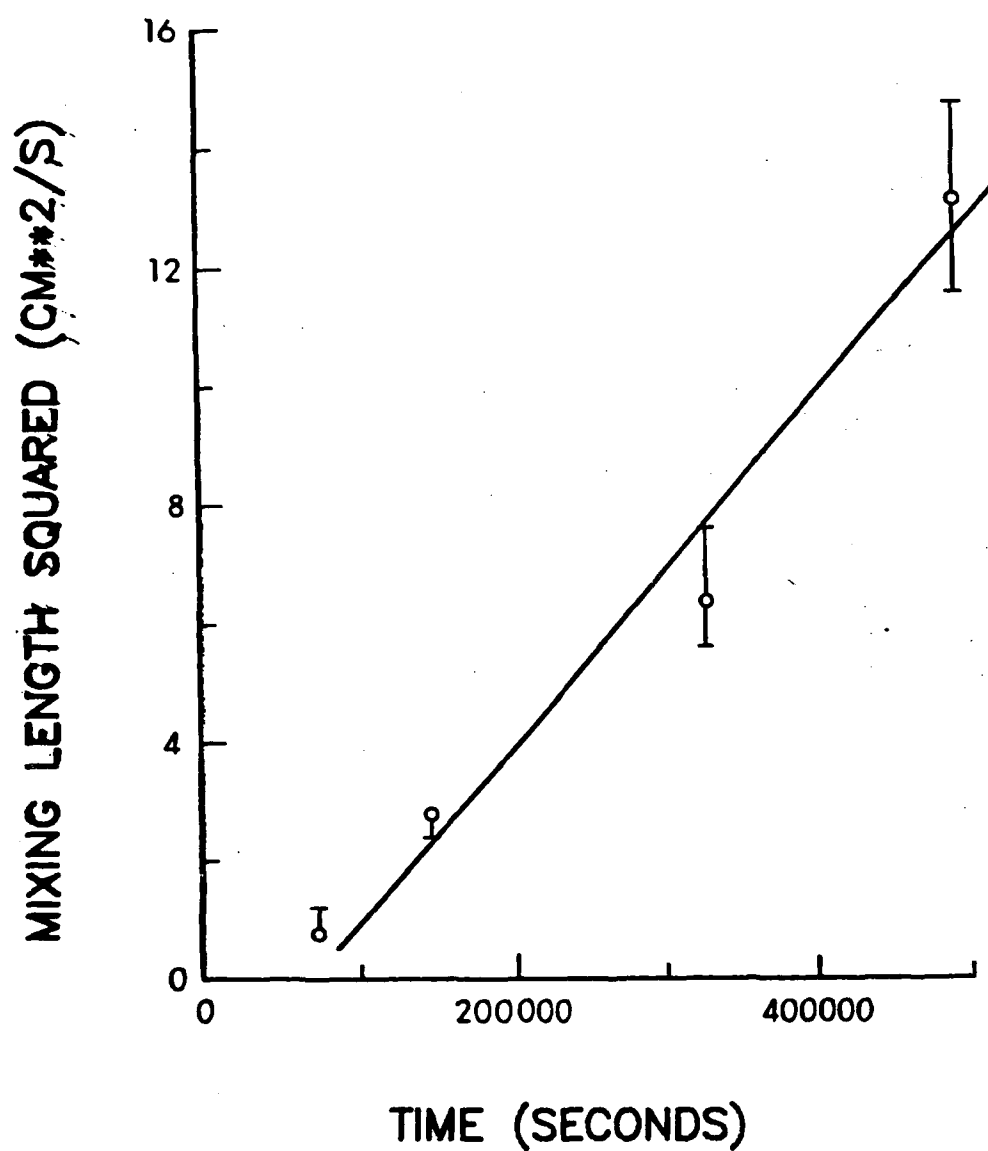
.

$$D(a,b) = + \frac{\rho_a \Delta z^2}{(\rho_a + \rho_b) \Delta \tau}$$

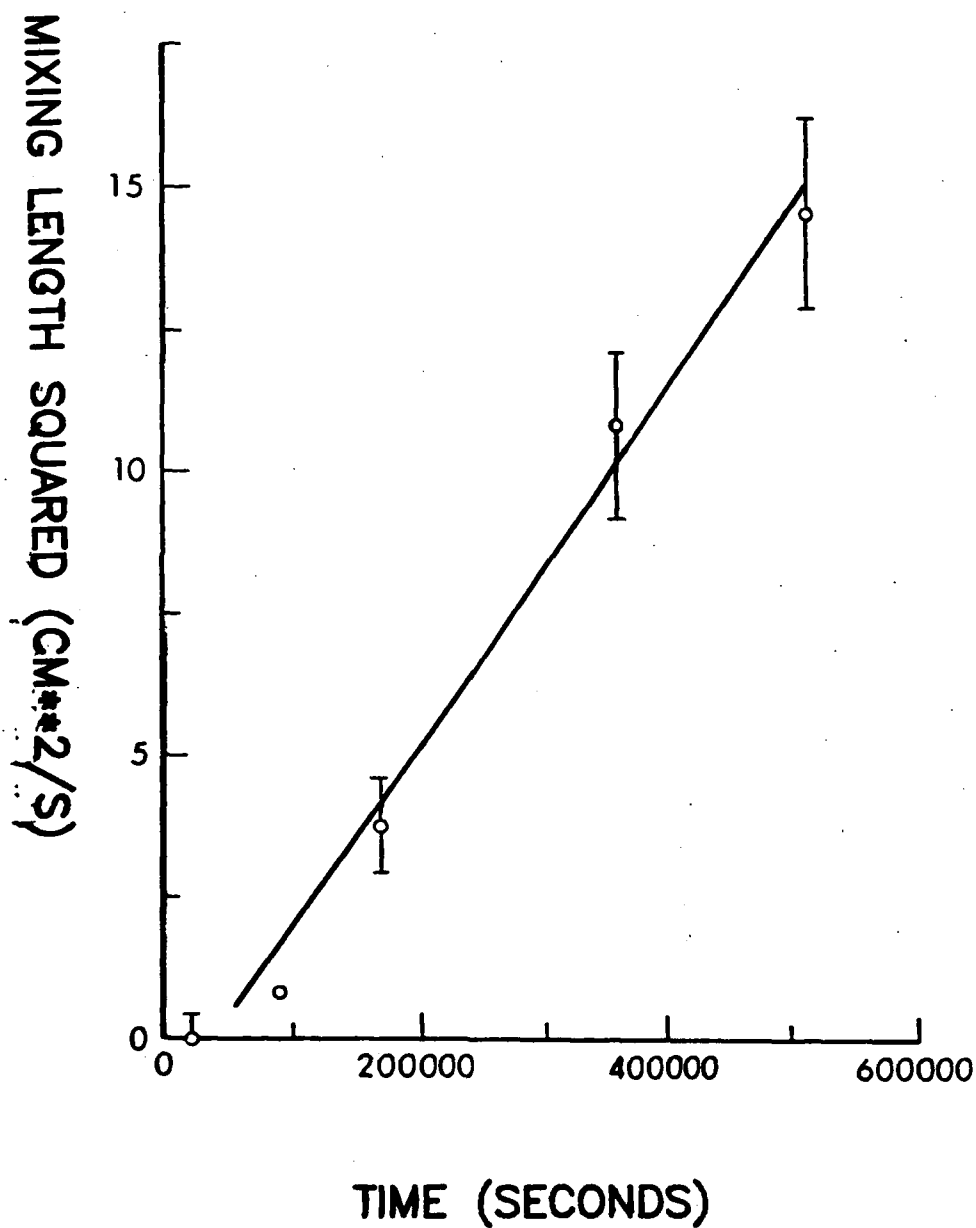
PREDICTION:

$$D = (8.93E-10) * T_o \left( \frac{l_o^* l_r^o}{\Lambda_o} \right) \left( \frac{(z^+ + z^-)}{(z^+ * z^-)} \right)$$

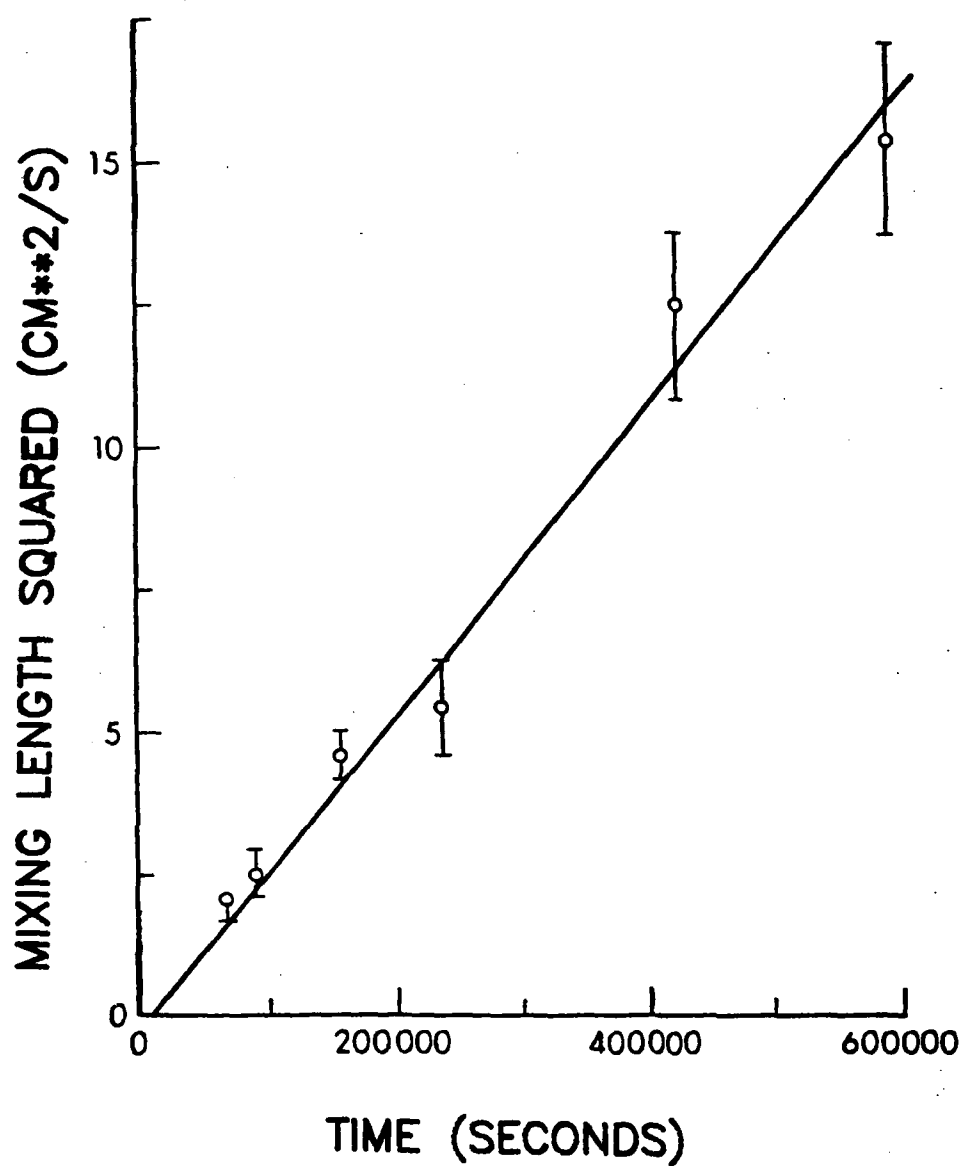
# EXPERIMENTAL RESULTS FOR METHANOL



# EXPERIMENTAL RESULTS FOR GLYCERIN



## EXPERIMENTAL RESULTS FOR LGP 1845



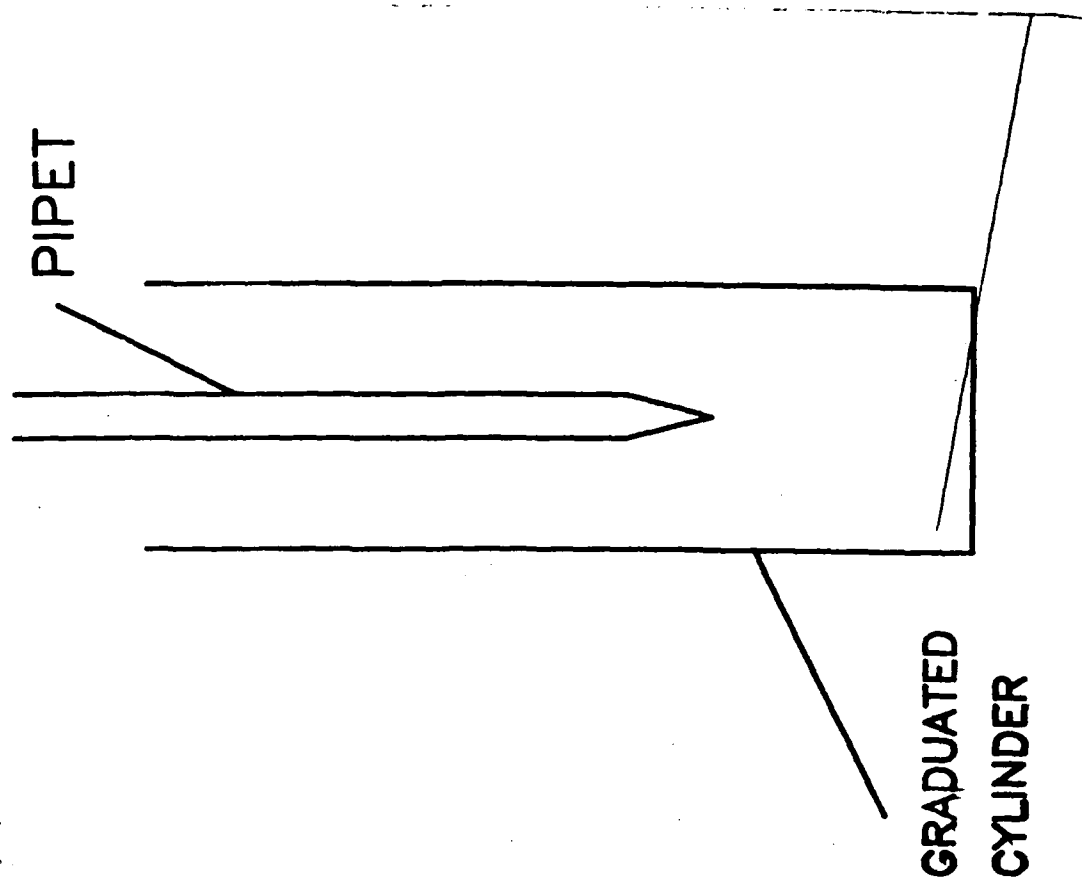
# **DIFFUSION EXPERIMENT RESULTS**

| TEST LIQUID | DIFFUSION COEFFICIENT (CM <sup>2</sup> /S) |                                          |
|-------------|--------------------------------------------|------------------------------------------|
|             | BOOK VALUE                                 | EMPIRICAL                                |
| LGP 1845    | N/A                                        | 1.59 E-5                                 |
| METHANOL    | 1.28 E-5                                   | 1.23 E-5                                 |
| GLYCERIN    | 0.94 E-5                                   | 1.73 E-5                                 |
| *<br>HAN    | N/A                                        | <div>PREDICTED</div> <div>1.43 E-5</div> |

\* AT INFINITE DILUTION

## EXPERIMENTAL SETUP

1. WATER INTO LP  
AT THE BOTTOM
2. WATER INTO LP  
AT THE MIDDLE
3. LP INTO WATER  
AT THE MIDDLE



## Physical Properties of Liquid Propellants With Dissolved Gases

S. Murad  
Chemical Engineering Department  
University of Illinois at Chicago  
Box 4348, Chicago, IL 60680  
Tel: (312) 996-5593

### ABSTRACT

The solubility of three important gases (argon, nitrogen, and methane) has been estimated in liquid propellants using an extended corresponding states theory, and some recently obtained experimental data of Koski (see following abstract), over a range of temperatures, for pressures up to 1000 bars. The effect of these dissolved gases on physical properties such as surface tension are then estimated.

The solubility of the gases have been estimated by using the fundamental equation.

$$f^{(G)} = x \gamma^* H^0 \exp \left[ \int \bar{V} / RT dP \right]$$

where  $f^{(G)}$  is the fugacity of the gas phase,  $x$ , the mole fraction of the dissolved gas in the propellant, and  $\gamma^*$ ,  $H^0$ ,  $\bar{V}$ , are the activity coefficient, Henry's constant, and partial molar volumes respectively of the dissolved gas in the liquid propellant. The values of  $f^{(G)}$ ,  $\gamma^*$ ,  $H^0$ , and  $\bar{V}$  are then estimated using the corresponding states theory, and limited experimental data. This technique can also be easily extended to examine mixtures of gases in liquid propellants.

After the solubilities of the gases in liquid propellants have been estimated, they can be used to estimate their effect on various physical properties, such as density, surface tension, etc. We will show some of our results for surface tension of liquid propellants under pressure, and compare the results with those obtained when gas solubilities are ignored.

## SOLUBILITY OF GASES IN LP 1846

Walter S. Koski  
Department of Chemistry  
The Johns Hopkins University  
Baltimore, MD 21218

The solubility of various gases has been measured in LP 1846 using chromatographic techniques. The temperature range for most of the gases was from  $-15^{\circ}$  to  $30^{\circ}\text{C}$  in 5 degree intervals. The order of increasing gas solubilities was nitrogen, oxygen, argon, methane, krypton, and xenon. These measurements permitted the determination of the free energy, enthalpy, and entropy changes for the solution process. The behavior of oxygen was anomalous since it apparently slowly reacts with the hydroxylammonium ion to produce  $\text{N}_2\text{O}$ .

APPENDIX A



CONFERENCE ON HAN-BASED LIQUID PROPELLANT FLAMES,  
PROPERTIES, AND STRUCTURE

Final Program

All sessions will be held in Bldg 330.

Tuesday, 25 August

8:30 am WELCOME. Walter F. Morrison, Program Manager, LP Program

8:40 am ARRANGEMENTS & SIMILAR FOLDEROL. Eli Freedman, ABCB, BRL

SESSION I: Nathan Klein, BRL, presiding

8:45 am THE PHASE DIAGRAM OF HAN-WATER. J. Bevan Ott,  
Brigham Young University

9:30 am DIFFRACTION STUDIES OF HAN. Fred Ross, University of  
Missouri at Columbia

10:15 am break

10:45 am HIGH PRESSURE SPECTROSCOPY AND THE STRUCTURE OF HAN.  
Mark Davies and Robert A. Fifer, BRL

11:15 am RAMAN SPECTROSCOPY OF AQUEOUS SOLUTIONS AT HIGH TEMPERATURES  
AND PRESSURES. Peter Spohn and T.B. Brill, Univ of Delaware

11:45 Lunch

SESSION II: Josephine Wojciechowski, BRL, presiding

1:30 pm EQUATION OF STATE OF HAN SOLUTIONS. Julius Frankel, BWL

2:00 pm EXPLOSIVE VAPORIZATION OF INDUCED BY LASER RADIATION ON A  
WATER DROPLET CONTAINING NITRATE. David Leach and  
R.K. Chang, Yale University

2:30 pm break

3:00 pm DROPLET COMBUSTION OF HAN-BASED LIQUID PROPELLANTS.  
C.K. Law, University of California, Davis.

3:45 pm adjourn

Wednesday, 26 August

SESSION III: Madelyn M. Decker, BRL, presiding

- 8:30 am DSC OF LIQUID PROPELLANTS AND CRYSTALLINE HAN. Leon Decker and R.A. Fifer, BRL
- 9:00 am DECOMPOSITION STUDIES OF LP 1845. James T. Cronin and T.B. Brill, University of Delaware
- 9:30 am STABILITY CHARACTERISTICS OF DEFLAGRATING LIQUID PROPELLANTS. R.C. Armstrong and S.R. Vosen, Sandia Labs
- 10:00 am break
- 10:30 am THE COMBUSTION OF HAN-BASED LIQUID PROPELLANTS. S.R. Vosen, Sandia Labs
- 11:00 am A LIQUID PROPELLANT DECOMPOSITION/REACTION MODEL. H.A. Dwyer and B.R. Sanders, Sandia Labs
- 11:30 am STABILIZATION OF HAN SOLUTIONS AGAINST TRANSITION METAL ION IMPURITIES. Richard C. Thompson, Univ of Missouri--Columbia
- 12:00 lunch

SESSION IV: Charles S. Leveritt, BRL, presiding

- 1:30 pm ELECTROCHEMICAL STUDIES RELATED TO HAN. R.L. Dotson, Olin Corp.
- 2:00 pm PRELIMINARY STRAND-BURNING RATES FOR HAN-BASED GELLED PROPELLANTS. D.S. Chiu, ARDEC
- 2:30 pm break
- 3:00 pm EMULSIFIED HAN-BASED PROPELLANTS. Neale Messina, PCRL
- 3:30 pm DIFFUSION STUDIES IN LP 1846. Cris Watson, BRL
- 4:00 pm adjourn
- 6:30 pm DINNER

Thursday, 27 August

SESSION V: Eli Freedman, BRL, presiding

- 8:30 am PHYSICAL PROPERTIES OF LIQUID PROPELLANTS WITH DISSOLVED GASES. Sohail Murad, University of Illinois at Chicago
- 9:00 am SOLUBILITY OF GASES IN LP 1846. Walter Koski, JHU
- 9:30 am A NEW DETERMINATION OF THE ENTHALPY OF COMBUSTION OF TRIETHANOLAMMONIUM NITRATE. Jennifer C. Colbert and Eugene S. Domalski, US National Bureau of Standards
- 10:00 am break
- 10:15 am GENERAL DISCUSSION
- 12:00 Final Adjournment



APPENDIX B



# ATTENDEE LIST

Nollie Swynnerton  
Southwest Rsch Institute  
6220 Culebra Road  
San Antonio, TX 78284  
(512) 522-2167

Robert W. Shaw  
US Army Research Office  
PO Box 12211  
Research Triangle Park, NC  
27709-2211  
(919) 549-0641

Paul Bunyan  
British Government  
RARDE  
Powder Mill Lane  
Essex, England

Ronald Dotson  
Olin Corporation  
24 Science Park  
S. Winchester Ave  
PO Box 30-9644  
New Haven, CT 06511  
(203) 271-3330

James A. Leistra  
Olin Corporation  
24 Science Park  
S. Winchester Ave  
PO Box 30-9644  
New Haven, CT 06511  
(203) 785-5242

Marshall Humphrey  
Jet Propulsion Lab  
4800 Oak Grove Drive  
Pasadena, CA  
(818) 354-3523

Clifford M. Moray  
Jet Propulsion Lab  
4800 Oak Grove Drive  
Pasadena, CA  
(818) 354-8078

David S. Dandy  
Sandia National Laboratory  
PO Box 969  
Livermore, CA 94550  
(415) 422-1810

Billy R. Sanders  
Sandia National Laboratory  
Division 8363  
PO Box 969  
Livermore, CA 94550  
(415) 422-3113

A. MacPherson  
Leigh University  
Bethlehem, PA 18017  
(215) 758-4105

Bob J. Agow  
Aerojet  
PO Box 15699C  
Sacramento, CA 95813  
(916) 355-5401

J. Bevan Ott  
Brigham Young Univ  
Dept of Chemistry  
Provo, Utah 84602  
(801) 378-3669

William O. Seals  
US Army ARDEC  
Picatinny Arsenal, NJ  
07806-5000  
(201) 724-5378/4776

Jim Cronin  
University of Delaware  
Chemistry Dept  
Newark, DE 19711  
(302) 451-2459

Peter Spohn  
University of Delaware  
Chemistry Dept  
Newark, DE 19711  
(302) 451-2459

Paul Marinkas  
US Army ARDEC  
ATTN: SMCAR-AEB  
Picatinny Arsenal, NJ  
07806-5000  
(201) 724-2259

Fred Ross  
University of Missouri  
Research Reactor  
Columbia, MO 65211  
(314) 882-4211

Richard Thompson  
University of Missouri  
Dept of Chemistry  
Columbia, MO 65211  
(314) 882-7356

Robert Pate  
General Electric  
OP 43-220  
100 Plastics Ave  
Pittsfield, MA 01201  
(413) 494-4283

R. W. Carling  
Sandia National Laboratory  
Division 8357  
Livermore, Ca 94550  
(415) 422-2206

R. C. Armstrong  
Sandia National Laboratory  
Livermore, CA 94550  
(415) 422-2470

S. Vosen  
Sandia National Laboratory  
Livermore, CA 94550  
(415) 422-3434

Richard Chang  
Yale University  
New Haven, CT 06520  
(203) 432-4272

David Leach  
Yale University  
New Haven, CT 06520  
(203) 432-4234

Gerry Doyle  
GEO Centers  
315 Richard Mine Rd  
Wharton, NJ 07805  
(201) 366-9802

Stanley Griff  
GEO Centers  
Wharton, NJ 07805  
(201) 366-6908

Jean-Paul Picard  
US Army ARDEC  
ATTN: SMCAR-AE  
Picatinny Arsenal, NJ  
07806-5000

Walter Koski  
John Hopkins University  
Department of Chemistry  
Charles and 34th Sts  
Baltimore, MD 21218

Julius Frankel  
CCAC  
Watervliet Arsenal  
Watervliet, NY

Sohail Murad  
U. of Illinois at Chicago  
Dept of Chemical Engr  
Box 4348  
Chicago, IL 60680

Abhanasia Geranios  
US Army ARDEC  
ATTN: SMCAR-FSS-DA  
Picatinny Arsenal, NJ  
07806-5000

Harry A. Dwyer  
Sandia Corporation  
Combustion Research Lab  
Livermore, CA

Chung K. Law  
U. of California at Davis  
Dept of Mech Engr  
Davis, CA 95616 (916) 752-8928

Ballistic Research Laboratory  
Aberdeen Proving Ground, MD  
21005-5066

Neale A. Messina  
Princeton Combustion Rsch Lab  
475 US Highway One  
Monmouth Junction, NJ  
(609) 452-9200

Eli Freedman  
Nathan Klein  
Madelyn Decker  
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Michelle A. Robeson  
Olin Corporation  
24 Science Park  
New Haven, CT 06511  
(203) 789-6048

A.J. Bracuti  
US Army ARDEC  
Picatinny Arsenal, NJ  
(201) 724-3788

Donald S. Chiu  
US Army ARDEC  
Picatinny Arsenal, NJ  
(201) 724-3788

Derek C. Stetter  
US Army ARDEC  
Picatinny Arsenal, NJ  
(201) 724-5626

John Scudiere  
General Electric Ord Div  
100 Plastics Ave  
Pittsfield, MA  
(413) 494-4227

Jennifer C. Colbert  
National Bureau of Stds  
Bldg 222, Room B-348  
Gaithersburg, MD 20899  
(301) 975-2579

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