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MOLECULAR STRUCTURES STUDIES AND OTHER RELATED RESEARCH

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Research Institute

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13. ABSTRACT

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Overhaul of a Bendix TOF mass spectrometer was completed. Thermal conductivity as a function of crystal lattice defects was determined for NaCℓ and BeO. An apparatus used to determine heats of vaporization was refined and calibrated.

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FOREWORD

This report was prepared by the University of Dayton Research Institute under Air Force Contract F33615-69-C-1330. The work was initiated under Project No. 1360, "Chemical, Physical and Thermodynamic Properties of Aircraft, Missile and Spacecraft Materials", Task No. 736001, "Thermal and Chemical Behavior of Advanced Weapon System Materials". The project engineer was Mr. Hyman Marcus (AFML/LPT), Thermo and Chemical Physics Branch, Materials Physics Division, AF Materials Laboratory, Wright-Patterson AFB, Ohio 45433.

The report covers exploratory research conducted during the period January 1969 through October 1971. The manuscript was released by the authors in December 1971.

This technical report has been reviewed and is approved.

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SECTION 1

MICROBEAM PROBE X-RAY ANALYSIS

1.1 Description. Analyses of a wide variety of solids submitted by the Air Force Materials Laboratory (AFML) were performed by the University of Dayton Research Institute (UDRI), utilizing X-ray emission spectroscopy with an electron microbeam probe X-ray analyzer.

Research was conducted on analysis techniques and characterization of solid surfaces with primary emphasis on the chemical combination effects on fine features of soft X-ray emission spectra recorded by the electron microbeam probe. Specific areas of research included instrumentation for automatic data acquisition, reduction, and plotting of soft X-ray spectral data as well as analytical applications. The data acquisition system consisted of the usual signal amplification electronics plus a digital drive spectrometer stepping motor and digitized data output via a printing scale /timer and a model ASR-33 Teletype with papertape output of data.

Initially the data were processed and plotted utilizing Air Force computer facilities. The data were later processed and plotted using a commercial time-sharing computer system through a Typagraph terminal conveniently located to the microprobe room. This provided a much faster turn-around time for data reduction and plotting and thus made possible the routine application of the fine features of soft X-ray emission spectra to the characterization of solid surfaces.

In addition to data reduction and plotting, other software was developed for curve integration, spectral stripping and the capability of making replica self-absorption spectra utilizing emission spectral data generated by the electron microbeam probe. Replica self-absorption spectra are similar to the photon absorption spectra and in many cases, especially with the electron microbeam probe, offer the only means to determine absorption edge positions. Replica X-ray absorption spectra are constructed by plotting the natural logarithm of intensity ratios from two emission spectra of the same emission band obtained at different accelerating voltages. A computer program was written to calculate these Ln values for corresponding energy positions. It then outputs the X-Y values in plotting format for plotting by the Typagraph terminal.

Specific research of the applications of chemical combination effects on soft X-ray spectra included the following.

(a) Determination of the oxidation state of iron in iron oxides found in high strength steels, such as D6ac.

(b) Characterization of Aℓ-Cu alloys in Aℓ-Cu thin films, diffusion couples, and hypervelocity impact specimens.

(c) Characterization of boron suboxide phases with the fine features of both oxygen K and boron K emission spectra.

(d) Characterization of SiO thin films with SiK_B emission spectra.

Additional instrumental analytical techniques were developed in the area of content mapping of solid surfaces with the electron microbeam probe and the X-ray data generated. Three advantages of content mapping over conventional scanning X-ray images are: (a) quantitative information as to elemental density and distribution; (b) enhancement of contrast for specimens having an enriched element density with slight variation and (c) enhanced contrast of elemental density and distribution for specimens under high magnification with poor contrast.

1. 2 Air Force Publications.

AFML-TR-70-80, "Bonding and Chemical Combination Studies Using the Electron Microbeam Probe."

AFML-TR-70-146, "Content Mapping Techniques for Qualitative and Semiqualitative Analysis with the Electron Microbeam Probe."

AFML-TR-70-253, "Electron Microbeam Probe Characterization of Aℓ-Cu Alloys with Aℓ and Cu Soft X-ray Spectra."

AFML-TR-70-290, "Computer Plotted Soft X-ray Spectra to Facilitate Chemical Combination Studies with the Electron Microbeam Probe."

1. 3 Journal Publications.

"Content Mapping with an Electron Microbeam Probe." American Laboratory, 10 (December 1970).

"Computer Plotted Soft X-ray Spectra to Facilitate Chemical Combination Studies with the Electron Microbeam Probe," Applied Spectroscopy, 25: 518 (1971).

"Characterization of SiO Using Fine Features of X-ray Emission Spectra," Vacuum, 21: 165 (1971).

"Soft X-ray Contact Radiography Using a Cold Cathode Discharge," Materials Evaluation 29: (October 1971).

1.4 Papers Presented.

"Bonding and Chemical Combination Studies Using the Electron Microbeam Probe, 21st Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio (March 1970).

"Content Mapping Techniques for Qualitative and Semiquantitative Analysis with the Electron Microbeam Probe," 21st Mid-American Symposium on Spectroscopy, Chicago, Illinois (June 1970).

"Changes in the Fine Features of X-ray Emission Spectra from Aℓ-Cu Alloys Using the Electron Microbeam Probe," Fifth National Conference on Electron Probe Analysis, New York, New York (July 1970).

"Computer Plotted Soft X-ray Spectra to Facilitate Chemical Combination Studies with the Electron Microbeam Probe," Ninth National Meeting of the Society of Applied Spectroscopy, New Orleans, Louisiana (October 1970).

"Boron Bonding Studies Using the Electron Probe," 22nd Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio (March 1971).

"Chemical Bonding Studies on Boron Institial Compounds," Sixth National Conference on Electron Probe Analysis, Pittsburgh, Pennsylvania (July 1971).

"Electron Microprobe Instrumentation for Soft X-ray Spectroscopy," Sixth National Conference on Electron Probe Analysis, Pittsburgh, Pennsylvania (July 1971).

"Characterization of SiO Using Fine Features of X-ray Emission Spectra," Sixth National Conference on Electron Probe Analysis, Pittsburgh, Pennsylvania (July 1971).

"Some Special Techniques for Electron Probe Soft X-ray Analysis," Midwest Probe Users' Group Meeting, Wright-Patterson Air Force Base, Ohio (July 1971).

The above publications and papers were coauthored by W. L. Baun, AFML/LPA, and J. S. Solomon, University of Dayton Research Institute.

SECTION 2

X-RAY DIFFRACTION RESEARCH AND DEVELOPMENT

Throughout the contractual period, various projects were initiated and progress reported in the form of Technical Reports. The projects which were initiated are as follows: (2. 1) Powder Camera Modification; (2. 2) Computer Controlled Data Acquisition Proposal; (2. 3) Iron-Oxygen System Investigation; (2. 4) Characterization of Surfaces; (2. 5) Laser Window Program; (2. 6) Structural and Orientational Aspects of Graphitized Fibers; (2. 7) Low-Temperature Analysis of Some Sugars. Projects (2. 1) and (2. 6) have been summarized into Technical Reports AFML-TR-71-26 and AFML-TR-69-53, respectively. Project (2. 7) is entitled "X-ray Diffraction Studies of the Role of Hydrogen Bonding in the Low-Temperature Behavior of Materials," and is in press. Project (2. 1) entitled "Back-Reflection Camera on a Budget," has also been accepted for printing in the summer issue of Siemens Review, August 1971. Brief summaries of the above mentioned projects are outlined in the following paragraphs.

2. 1 Powder Camera Modification. A Siemens 2-radian powder diffraction camera was modified to meet the requirements of a Seeman-Bohlin back-reflection focusing type. Essentially, the specimen was transferred from the geometrical center of the camera to the circumference. Provisions for oscillating the specimen were met by constructing a spring-loaded shaft attached to a slab-like specimen holder and housed in a brass cylinder. A driver arm connected to the shaft and driven by a motor provided the oscillatory motion. The apparatus was tested and found to be quite satisfactory for most requirements.

2. 2 Computer Controlled Data Acquisition Proposal. Due to the increasing interest in cell parameters as a function of temperature and in the linear thermal coefficient of expansion (paragraph 2. 5), new equipment was proposed to provide a much needed means of data collection and reduction. The equipment was computer oriented and increased the reproducibility of data to an accepted level.

2. 3 Iron-Oxygen System. This project was in direct support of the F-111 program. The main interest was to correlate X-ray data with physical and chemical properties of damaged aircraft parts due to failure or other cause. A literature search was conducted and tables were prepared correlating data of various investigators pertaining to oxidation mechanisms.

2.4 Characterization of Surfaces. This project was recently initiated to determine, by X-ray diffraction and/or X-ray fluorescent techniques, the coating thicknesses of oxide and other layers on various substrates such as copper, iron, etc. Preliminary studies in this area included a literature search and the oxidation of 5 mil Ta and Nb sheets. Sixty references were gathered. The references have been placed on cards and all pertinent information written on the back of each card. A file is being maintained under the title of "Characterization of Surfaces" and all new references can be added with the intent of composing an extensive coverage of reading materials in this area. The X-ray data obtained so far do not look too promising as the oxide layer thickness seems to be a function of both time and temperature. However, only the two metals, Ta and Nb, have been investigated so far and these have the property of forming protective suboxide layers.

2.5 Laser Window Program. This program was recently initiated by the Materials Physics Division of AFML. Due to the nature of this program, new equipment and updating of existing equipment were proposed. The new equipment consists mostly of the data collection type, i.e., step scanning controller with a printing time-scaler and teletype scanner. This equipment is needed for precise determinations of lattice parameters. In addition, a low-temperature camera capable of maintaining any temperature between -180°C and 200°C was designed. The plans have been submitted to the machine shop for fabrication. The camera was used in conjunction with an existing diffractometer and NIM electronics package for precise determination of thermal expansion coefficients. All calculations were accomplished through the CDC 6600 computer system by means of paper tape input.

The camera design was a modification of Jetter's[1] and consisted essentially of an evacuable chamber in which was housed a coolant flask. The specimen holder was constructed of a copper block with insulated Nichrome wire wound about its interior. The holder was connected to a copper finger extending to the bottom of the flask. A beryllium window in the chamber allowed the X-ray beam to pass through the camera striking the specimen and diffracting to the detector (scintillation counter).

Coolants consisting of liquid nitrogen, dry ice and acetone, ice and water, etc., were added to the flask and with proper heating control, temperatures between -190°C and 200°C were maintained.

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[1] Review of Scientific Instruments 28, 12, 1087 (1957).

2.6 Structural and Orientational Aspects of Graphitized Fibers. This project was initiated to better understand the structural properties of graphitized fibers. An in-depth search was made to cover all previous investigations of the same nature. The challenge was quite demanding and led to enlightening results. Through the course of this work, curve fitting and unfolding techniques were satisfactorily applied, while new techniques added further information not yet published in the literature. For example, it was found that all fibers investigated in this work were composed of several similar structures. One published paper[2] states that no fiber has produced diffraction data showing more than one component. This conflicting data will, without a doubt, prompt more research in this area.

2.7 Low-Temperature Analysis of Some Sugars. The ultimate goal of this project was to correlate temperature dependent changes in vibrational spectra with structural changes found by X-ray diffraction and thus to gain an understanding of the role of hydrogen bonding in determining the temperature dependence of materials properties.

The recorder output was used as input to a least squares unit cell refinement program for the 7094 computer system. Only four of the eight compounds investigated yielded satisfactory data, but this was enough to make some concluding remarks. In particular, the new results did not contradict the model of Sklar, et al.[3] assigning the entire unit cell shrinkage to hydrogen bond contraction. This model, then, should have been retained for comparison to infrared data, at least until more extensive X-ray data was available.

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[2] Rosalind E. Franklin, "The Structure of Graphitic Carbons", ACTA Cryst., Vol IV, Pg. 257 (1951).

[3] N. Sklar, M. E. Senko and B. Post, "Thermal Effects in Urea: The Crystal Structure at -140°C and at Room Temperature," Acta Cryst. 14, 716 (1961).

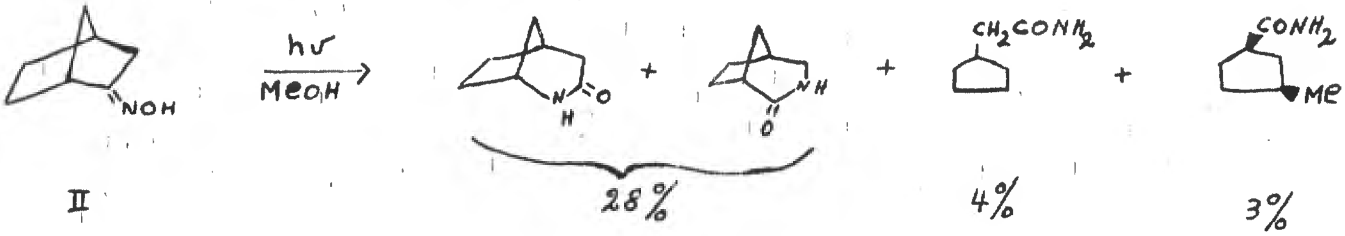
SECTION 3

PHOTOCHEMISTRY

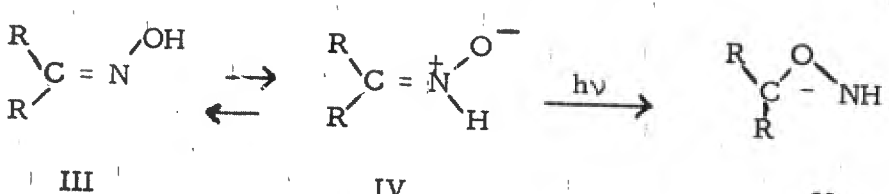
3.1 <u>Ketoxime Photochemistry.</u> The photolysis of camphor oxime (I) yields,

I

in addition to parent ketone, various nitriles as the only reported products.[1] This result is at variance with the normally observed photochemical rearrangement of oximes to amides.[2-5] One possible cause for the anomalous behavior of I might be the ring strain associated with the bicyclo (2.2.1) heptyl system. We have been able to exclude this explanation by studying the closely related compound, norcamphor oxime (II)[6] and demonstrating its rearrangement to amides.



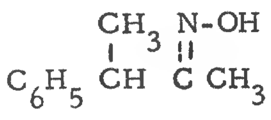
The photochemical rearrangement of oximes (III) to amides proceeds via an intermediate oxaziridine (V).[4,5] It has been suggested[7] that the immediate precursor of V is the prototropic tautomer (IV)



III IV V

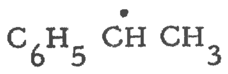
This proposal is in agreement with our reported finding[6] that irradiation of II in methanolic solutions of sodium methoxide results in a dramatic decrease in reaction rate, and a reduced concentration of oxaziridine intermediate.

Since the divergent photochemistry of I did not seem to be a result of strain associated with the bicyclic system, we turned our attention to the effect of α-substituents on the course of ketoxime photochemistry. Previous workers[1] had suggested that nitrile formation arose from homolytic carbon-carbon bond cleavage on either side of the oximino function. Such cleavage in II would produce a 2° radical, whereas a more stable 3° radical would be obtained from similar cleavage of I. Accordingly, we decided to study the photochemistry of 3-phenyl-2-butanone oxime (VI).[8] Homolytic bond cleavage in VI would result in the formation



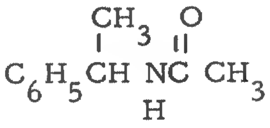
$C_6H_5\overset{\overset{CH_3}{|}}{CH}\overset{\overset{N-OH}{\|}}{C}CH_3$

VI



$C_6H_5\dot{C}HCH_3$

VII



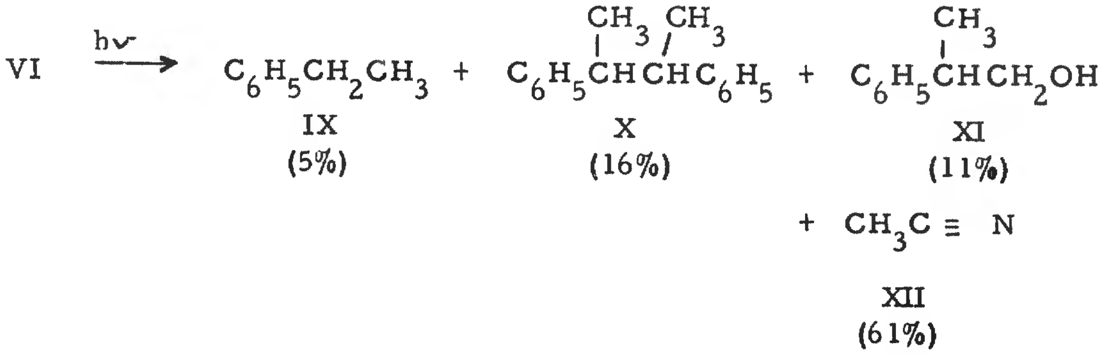
$C_6H_5\overset{\overset{CH_3}{|}}{CH}\underset{H}{N}\overset{\overset{O}{\|}}{C}CH_3$

VIII

of a resonance stabilized α-phenethyl radical (VII). Observation of products derived from VII would lend support to the hypothesis that radical stability is responsbile for the occurrence of cleavage versus rearrangement. This study had the additional feature of being fail-safe. If our hypothesis were incorrect and rearrangement to N-α-phenethyl-acetamide (VIII) occurred, we would be able to demonstrate the stereochemistry of the rearrangement. This could be done quite simply by hydrolyis of VIII to α- phenethylamine, and comparison of the absolute configuration of this amine with that of the starting oxime prepared from starting materials of known configuration.[9]

Irradiation of a 1% methanolic solution of VI for 18 hours using an ultraviolet source having maximum intensity at 2537Å resulted in exclusive cleavage of the starting material as summarized below (Scheme 1).[10] Under these conditions, 30% of VI remained unreacted.

Scheme 1



$$VI \xrightarrow{h\nu} \underset{\substack{IX\\(5\%)}}{C_6H_5CH_2CH_3} + \underset{\substack{X\\(16\%)}}{C_6H_5\overset{CH_3}{CH}\overset{CH_3}{CH}C_6H_5} + \underset{\substack{XI\\(11\%)}}{C_6H_5\overset{CH_3}{CH}CH_2OH} + \underset{\substack{XII\\(61\%)}}{CH_3C\equiv N}$$

Compounds IX, X, and XI may be considered to arise from α-phenethyl radicals (Scheme 2).

Scheme 2

$$\text{VII} + CH_3OH \longrightarrow \dot{C}H_2OH + \text{IX} \quad \text{(hydrogen abstraction)}$$

$$2\ \text{VII} \longrightarrow \text{X} \quad \text{(dimerization)}$$

$$\text{VII} + \dot{C}H_2OH \longrightarrow \text{XI} \quad \text{(radical combination)}$$

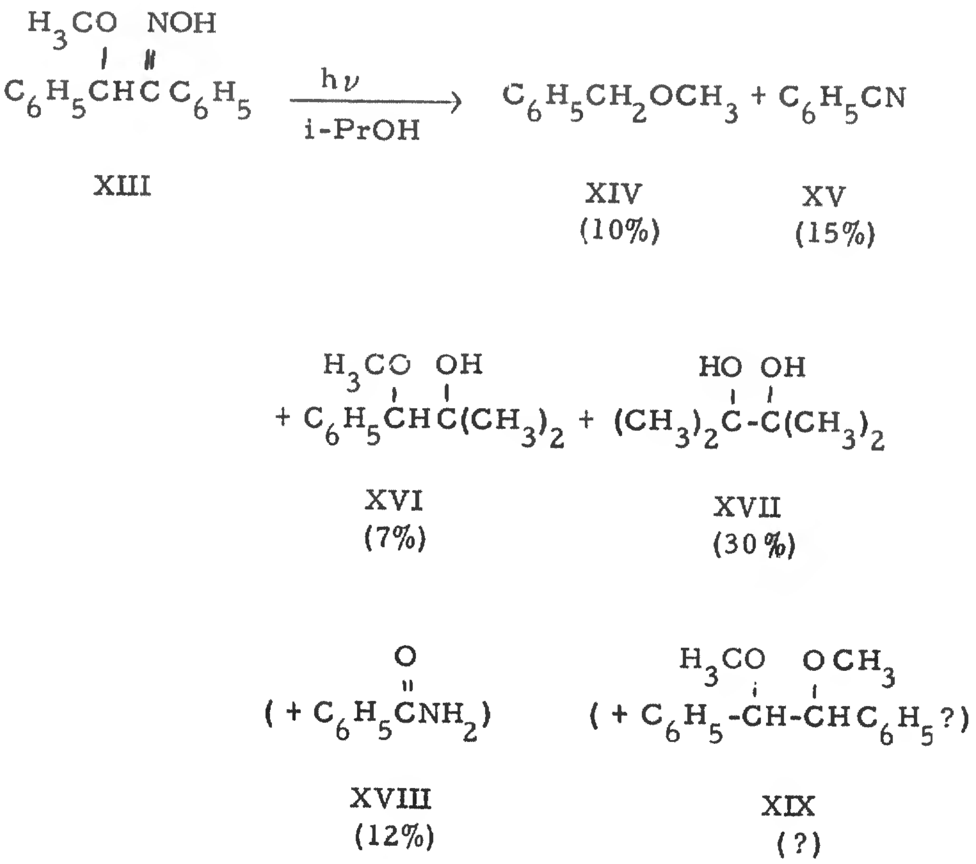
Further evidence for the intermediacy of VII and corroboration of Scheme 2 was obtained from two additional experiments. Substitution of isopropyl alcohol for methanol as solvent resulted in an increase in the yield of ethylbenzene (IX) and a decrease in 2, 3-diphenylbutane (X). This is in accord with the greater ease of hydrogen atom abstraction from isopropyl alcohol relative to methanol. Use of ethanol as the solvent resulted in elimination of XI as a product, with concomitant formation of 3-phenyl-2-butanol in its place. This, of course, supports radical combination as the mode of formation of XI.

Under photolytic conditions then, VI fragments into α-phenethyl radicals and a nitrogenous moiety. The latter is the source of acetonitrile, while the former gives rise to the other photoproducts. Since 30% of VI was unreacted after irradiation, exact material balance requires a 70% yield of acetonitrile. The sum of the yields for all other products should also be 70%. The observed yield of 61% for acetonitrile is acceptable, but the material balance for the other photoproducts is too low (32% total). Chromatography of the photolysate on silica gel afforded a fluorescent material as well as a resinous product in the later fractions (methanol-chloroform), both of which were nonvolatile. We have made no attempt to identify these components, but they are undoubtedly responsible for the poor material balance obtained for the nonnitrogenous products by gas chromatography.

Attempts to elucidate the multiplicity of the excited state were inconclusive. Attempted sensitization with p-dichlorobenzene and toluene resulted in decreased consumption of oxime (i. e. quenching). Irradiation in the presence of 1, 3-pentadiene (quencher) did result in a decrease in the reaction rate. However, oxime was consumed, and none of the normal photoproducts were observed.

As a further test of our hypothesis regarding the importance of radical stability in determining the course of oxime photochemistry, irradiation of methylbenzoin oxime (XIII) was undertaken. In addition, it was hoped that this study would provide information regarding the structure of the photolytically generated nitrogenous cleavage produce (vide infra).

Scheme 3



$$\underset{\text{XIII}}{C_6H_5\overset{H_3CO}{\overset{|}{C}}H\overset{NOH}{\overset{\|}{C}}C_6H_5} \xrightarrow[\text{i-PrOH}]{h\nu} \underset{\substack{\text{XIV}\\(10\%)}}{C_6H_5CH_2OCH_3} + \underset{\substack{\text{XV}\\(15\%)}}{C_6H_5CN}$$

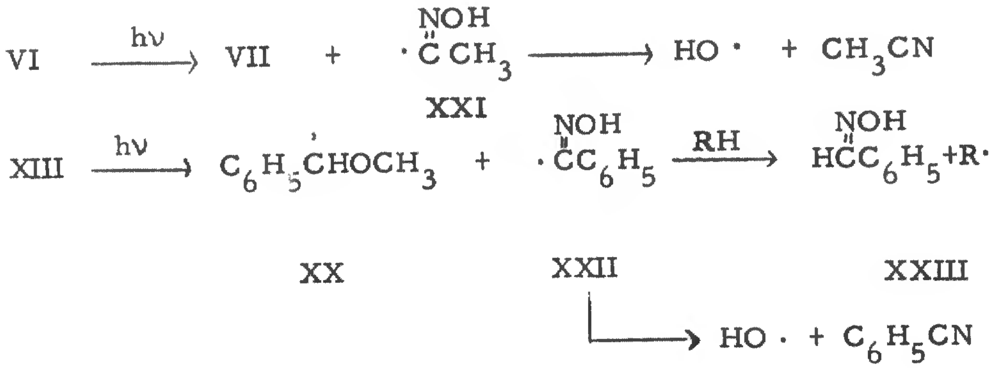
$$+ \underset{\substack{\text{XVI}\\(7\%)}}{C_6H_5\overset{H_3CO}{\overset{|}{C}}H\overset{OH}{\overset{|}{C}}(CH_3)_2} + \underset{\substack{\text{XVII}\\(30\%)}}{(CH_3)_2\overset{HO}{\overset{|}{C}}\text{-}\overset{OH}{\overset{|}{C}}(CH_3)_2}$$

$$\underset{\substack{\text{XVIII}\\(12\%)}}{(+ C_6H_5\overset{O}{\overset{\|}{C}}NH_2)} \quad \underset{\substack{\text{XIX}\\(?)}}{(+ C_6H_5\text{-}\overset{H_3CO}{\overset{|}{C}}H\text{-}\overset{OCH_3}{\overset{|}{C}}HC_6H_5?)}$$

The results indicate (Scheme 3) that a free radical cleavage process is occurring. Thus, the formation of XIV, XV, and XVI compares favorably with the formation of IX, XII, and XI in the previous photolysis of 3-phenyl-2-butanone oxime (VI). Complete analogy between the two reactions would require the presence of the dimerization product XIX (analogous to X). Synthesis of an authentic sample of XIX is underway, and when completed will allow us to examine the photolysate for this product.

The presence of benzamide (XVIII) in the photolysate is strongly suspected. Tentative identification has been achieved on the basis of gas chromatography retention times, but more conclusive proof (isolation) is mandatory because of the important mechanistic implications suggested by its presence. Our studies give indisputable proof for the intermediacy of α-phenethyl (VII) and α-methoxybenzyl (XX) radicals in the photolytic cleavage of VI and XIII. These radicals may arise from the primary photochemical process[11] (Scheme 4), or they may result from decomposition of initially generated imino radicals[12] (XXIV and XXV, Scheme 5). Both schemes can account for the formation of nitriles, but obtention of benzamide (XVIII) from the

Scheme 4



$$\mathrm{VI} \xrightarrow{h\nu} \mathrm{VII} + \cdot\overset{\mathrm{NOH}}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3} \longrightarrow \mathrm{HO}\cdot + \mathrm{CH_3CN}$$

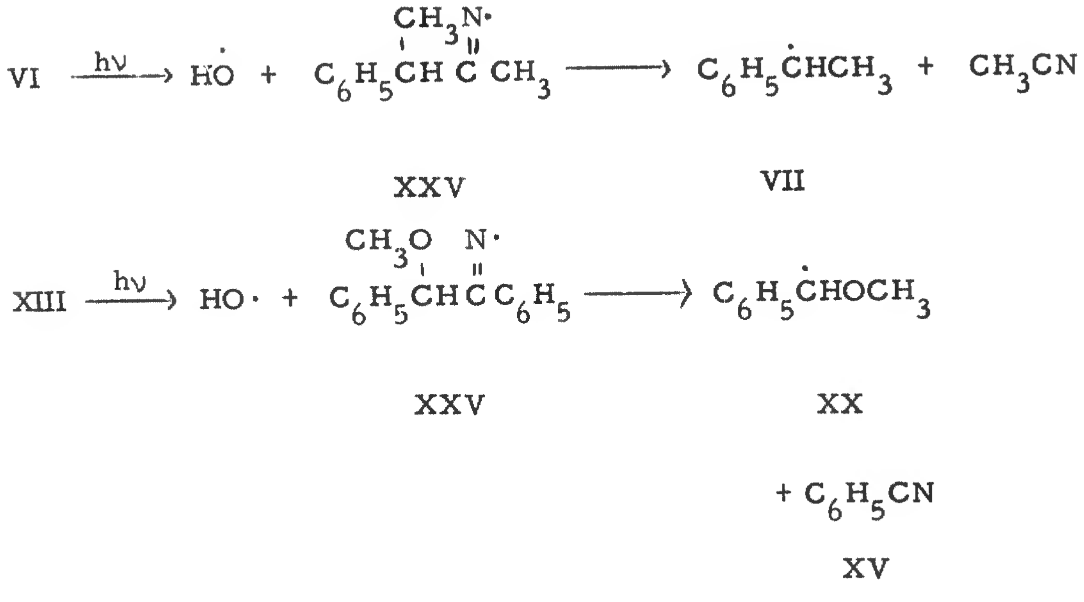
XXI

$$\mathrm{XIII} \xrightarrow{h\nu} \mathrm{C_6H_5\dot{C}HOCH_3} + \cdot\overset{\mathrm{NOH}}{\overset{\|}{\mathrm{C}}}\mathrm{C_6H_5} \xrightarrow{\mathrm{RH}} \mathrm{H}\overset{\mathrm{NOH}}{\overset{\|}{\mathrm{C}}}\mathrm{C_6H_5} + \mathrm{R}\cdot$$

XX XXII XXIII

$$\mathrm{XXII} \longrightarrow \mathrm{HO}\cdot + \mathrm{C_6H_5CN}$$

Scheme 5



$$\mathrm{VI} \xrightarrow{h\nu} \mathrm{H\dot{O}} + \mathrm{C_6H_5}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{H}\overset{\mathrm{N}\cdot}{\overset{\|}{\mathrm{C}}}\mathrm{CH_3} \longrightarrow \mathrm{C_6H_5\dot{C}HCH_3} + \mathrm{CH_3CN}$$

XXV VII

$$\mathrm{XIII} \xrightarrow{h\nu} \mathrm{HO}\cdot + \mathrm{C_6H_5}\overset{\mathrm{CH_3O}}{\overset{|}{\mathrm{C}}}\mathrm{H}\overset{\mathrm{N}\cdot}{\overset{\|}{\mathrm{C}}}\mathrm{C_6H_5} \longrightarrow \mathrm{C_6H_5\dot{C}HOCH_3} + \mathrm{C_6H_5CN}$$

XXV XX

XV

photolysis of XIII may be rationalized only on the basis of Scheme 4. Thus, hydrogen abstraction from solvent by the imidoyl radical XXII to yield benzaldoxime (XXIII) and subsequent photolytic rearrangement of XXIII[4] would be expected to produce benzamide.

In summary, the photochemical cleavage of ketoximes appears to proceed via a homolytic bond cleavage similar to the Norrish Type I cleavage of ketones. The stability of the intermediate radicals is an important factor in determining whether a given ketoxime undergoes cleavage to nitrile, or rearrangement to amide.

During the course of our studies the need arose to determine the configuration of several ketoximes. The classical method of assigning ketoxime stereochemistry on the basis of the Beckmann rearrangement is time consuming and not completely reliable. We discovered configurationally dependent shifts in the NMR signals for hydrogens alpha to the oximino function to be induced by the addition of hydrochloric acid vapor to benzene solutions of ketoximes. In this solvent the syn-and anti-alpha hydrogens are magnetically nonequivalent and give rise to separate NMR signals. Upon addition of hydrochloric acid vapor (Figure 1), the α-hydrogens syn to the hydroxyl group shift upfield, while the anti-alpha hydrogens move downfield. Hence, configuration is assigned rapidly and confidently on the basis of the direction of shift. A detailed account of this work has been published[13], and a patent application is in the process of being filed.

We are pleased to acknowledge the cordiality and intellectual stimulation provided by members of the Exploratory Studies Branch of the Materials Laboratory at Wright-Patterson Air Force Base.

3.1.1 References

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6. B. L. Fox and H. M. Roseberg, Chemical Communications, 1115 (1969).

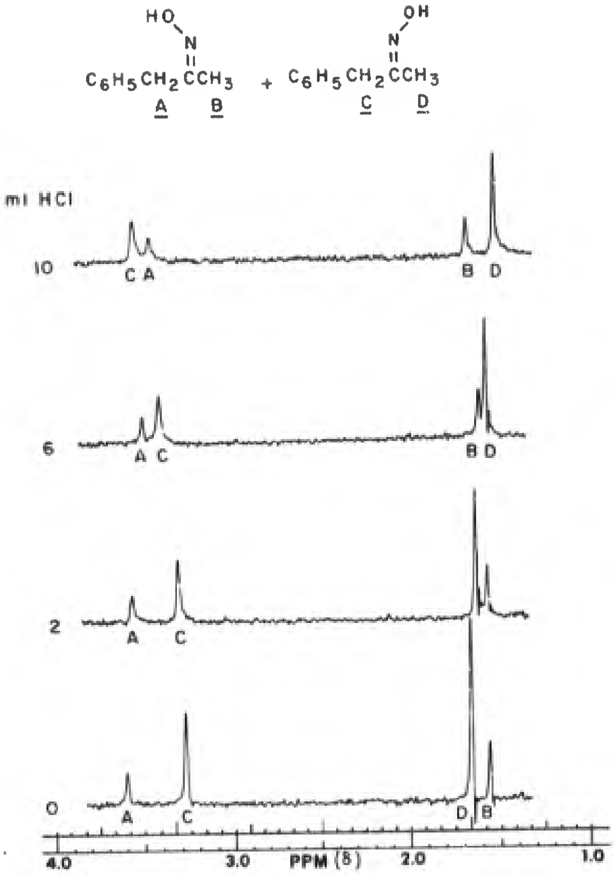

Figure 1.

Figure 1. Effect of Hydrogen Chloride on the NMR Spectrum of a Mixture of Phenylacetone Oximes.

7. G. G. Spence, E. C. Taylor, and O. Buchart, Chemical Review, 70: 231 (1970).

8. J. E. Reboulet, Master's Thesis, University of Dayton, 1970.

9. D. J. Cram, Journal of the American Chemical Society, 71: 3863 (1949).

10. Product distributions were determined by quantitative glpc, and are the average of at least two different reactions conducted simultaneously.

11. Similar radicals have been proposed to account for the formation of nitriles from oxime benzoates; cf. H. Ohta and K. Tokumaru, Chemical Communications, 1601 (1970).

12. Such radicals have been proposed to account for nitrile formation in the photolysis of azines; cf. R. W. Binkley, Journal of Organic Chemistry, 34: 3218 (1969).

13. B. L. Fox, J. E. Reboulet, R. E. Rondeau, and H. M. Rosenberg, Journal of Organic Chemistry, 35: 4234 (1970).

3.2 Liquid Crystals. During the time covered by this contract, interest developed in nonanil liquid crystals at the Materials Laboratory at Wright-Patterson Air Force Base. Low-temperature liquid crystalline materials having broad nematic ranges have potential applicability to numerous Air Force devices.

We have synthesized a series of difluorostilbenes, and have tested them for liquid crystal behavior. By careful control of reaction conditions, 1:1 adducts [(trifluorostyrenes (1)] of tetrafluoroethylene (TFE) and aryl lithiums were prepared, isolated, and subsequently converted to difluorostilbenes (II) by reaction with an aryl lithium. The results of our

$$\mathrm{ArLi} + \mathrm{CF_2{=}CF_2} \longrightarrow \underset{\mathrm{I}}{\mathrm{ArCF = CF_2}}$$

$$\mathrm{I} + \mathrm{Ar'Li} \longrightarrow \underset{\mathrm{II}}{\mathrm{ArCF = CF\,Ar'}}$$

studies are summarized in Table I.

Table I

Comp. No.	Ar	Ar'	m. p.	Liquid Crystal
1	C_6H_5	C_6H_5	71-73°	No
2	p-$CH_3C_6H_4$	p-$CH_3C_6H_4$	110-112°	No
3	C_6H_5	p-$CH_3C_6H_4$	≈ 25°	No

Although the two-step synthetic route to difluorostilbenes allows the preparation of unsymmetrical materials, yields, are quite low. Frequently encountered by-products are biphenyls from the oxidation of the aryl lithiums. These are not insurmountable problems and future studies are planned.

Earlier workers[1, 2] have failed to report the stereochemistry of the difluorostilbenes prepared by this method. Due to the asymmetry of compound 3, the coupling constant for the magnetically nonequivalent fluorines should allow a stereochemical assignment to be made. We observed a coupling constant of 120 Hz, which indicates the trans - configuration. This result is encouraging, since trans-dichlorostilbenes have recently been shown to exhibit nematic phases at room temperature[3]. Hence, there is good reason to expect suitably substituted trans-difluorostilbenes, synthesized by the method given above, to be liquid crystals.

3.2.1 References.

1. S. Dixon, Journal of Organic Chemistry, 21: 400 (1956).

2. T. McGrath and R. Levine, Journal of the American Chemical Society, 77: 4168 (1955).

3. W.R. Young, A. Aviram and R.J. Cox, Angew. Chemical International, Edit., 10: 410 (1971).

SECTION 4

THERMODYNAMICS

During the contractual period, investigations were performed in three areas utilizing three major pieces of equipment. Additional work was accomplished not directly pertinent to the above mentioned areas of investigation and is listed separately in Paragraph 4.4.

4.1 Thermodynamic Work Using the Bendix Time-Of-Flight Mass Spectrometer. The Bendix Time-of-Flight Mass Spectrometer (cut away view of heating and ionizing areas in figures 2 and 3) is used to detect ion species of any ionizable material by high voltage pulsing of the ionized material down a lengthy "flight" tube. The material to be studied is placed in a Knudsen Cell, (several other vaporization and material introducing methods are available) the system (heating zone and flight tube areas) is evacuated and heat is applied to the cell via radiation (twin filaments placed close to the cell) and electron bombardment (the cell is electrically insulated from ground and an appropriate positive high voltage is applied).

As the material is vaporized it passes upward through a series of collimators and finally enters the ionizing area (8 in Figure 2) as a uniform stream. The material is continually ionized by an electron flow at a 90 degree angle to the flight tube, and simultaneously a progressive high voltage pulse is applied (normally at a rate of 10,000 times per second) via a series of collimating plates directly in line to the detector.

The ionized material then gathers momentum proportional to its mass/charge ratio and is picked up by the detector -- the lighter ions with fewer units of charge arriving first and the heavier and/or greater charged ions arriving later.

The signal is then amplified and the entire mass spectrum can be displayed on a suitable oscilloscope. Several analogs are supplied with a gate circuit which enables the operator to manually or electrically scan the mass spectrum and display the relative ion peak intensities on a suitable recorder. The analogs also provide for monitoring of one mass peak with precision so that an extended record can be kept of the mass peak's intensity over a period of time with respect to temperature of the vaporizing sample. Many factors are involved as to the overall height or intensity of a particular mass peak.

(a) The temperature of the vaporizing material must remain constant. A slight change in temperature affects the total number of atoms and/or molecules in the ionizing stream per unit time.

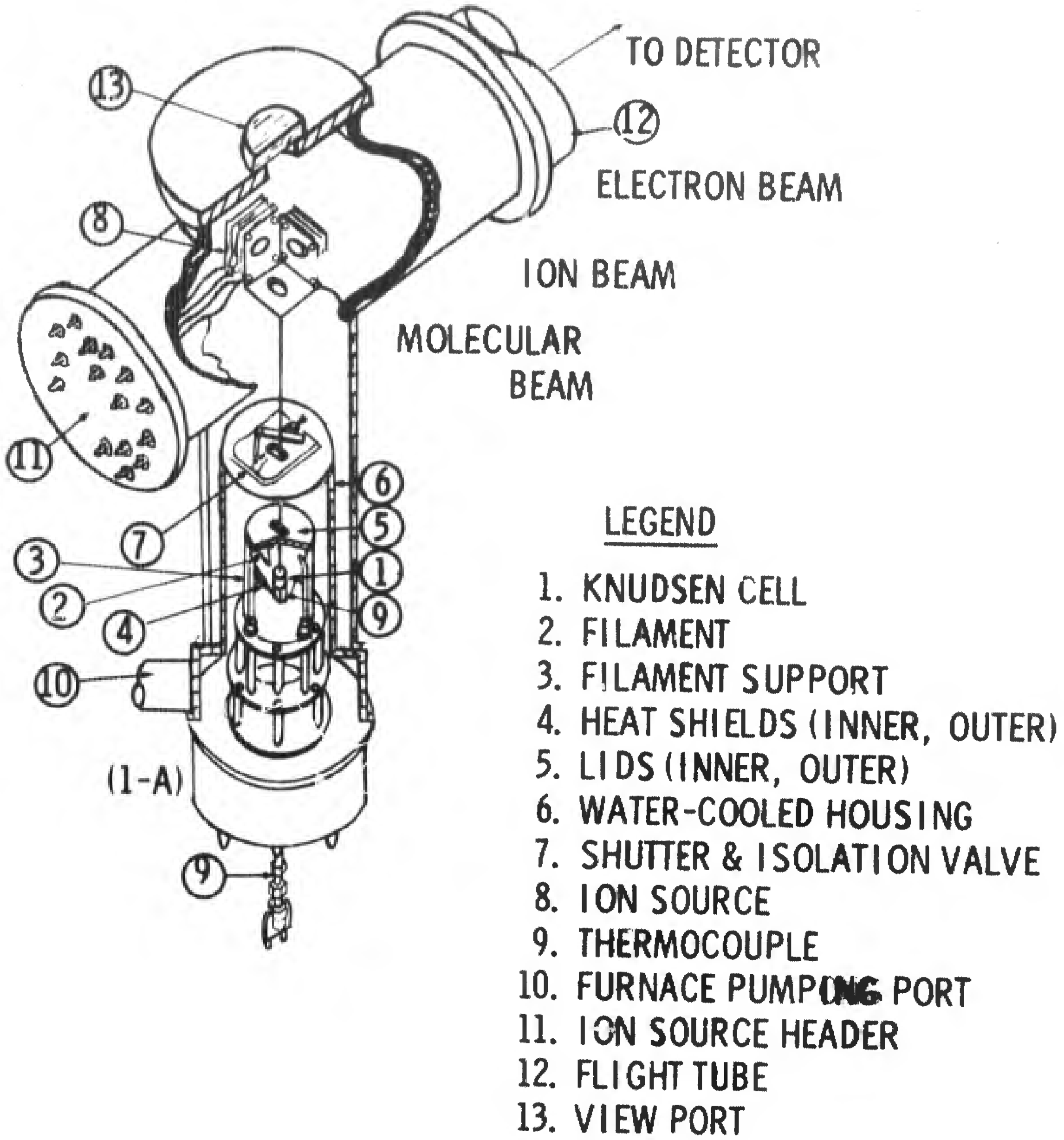

Figure 2. Knudsen Cell and Ionizing Area.

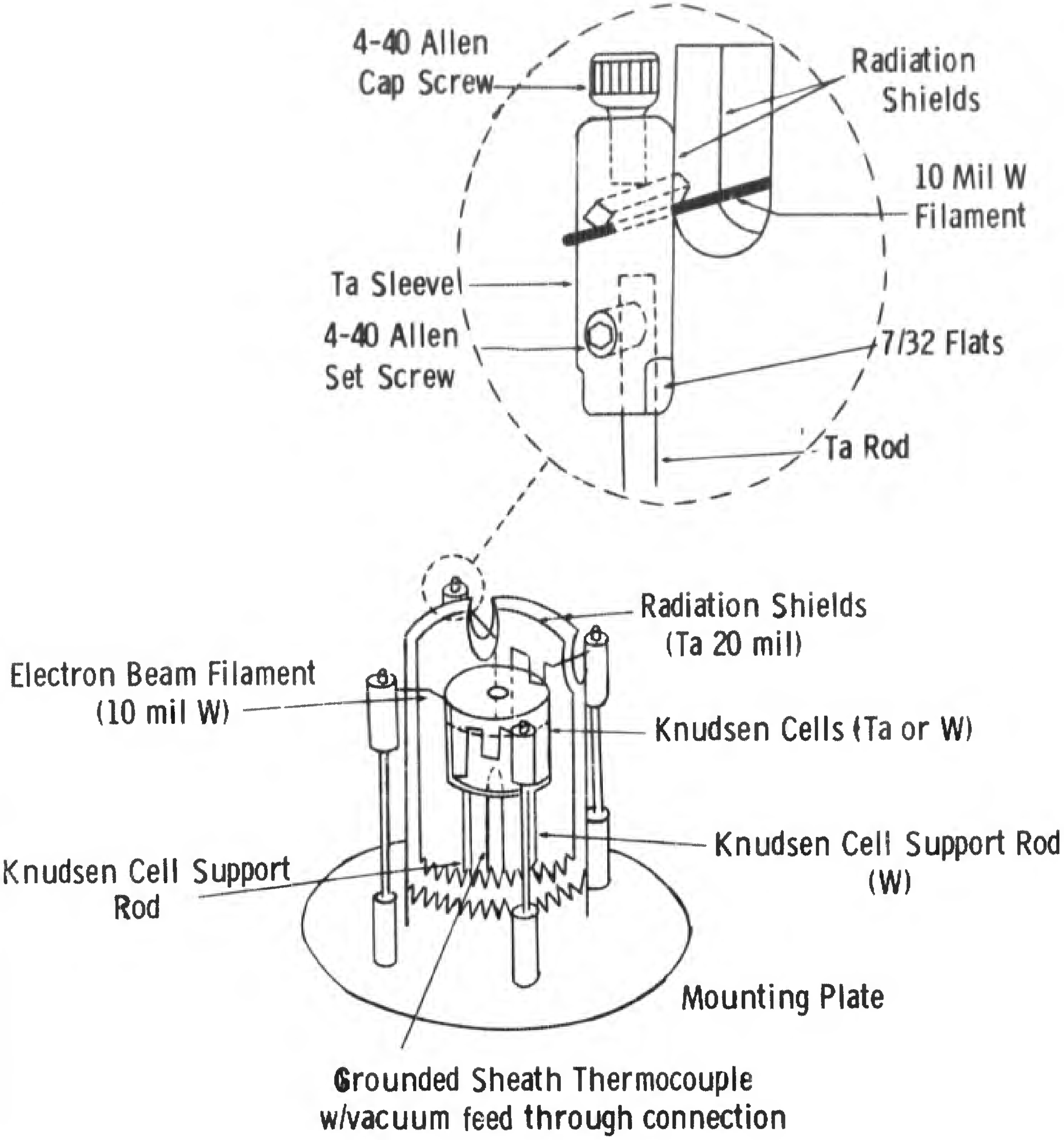

Figure 3. Physical Arrangement of Experimental Equipment With Exploded View of Filament Holder.

(b) The position of the Knudsen cell with respect to the collimators.

(c) The intensity of the ionizing beam (subject to power supply of line voltage changes.)

(d) The nature and age of the electron beam filament.

(e) The ionizing nature of the investigative material.

(f) The uniformity of the progressive high voltage pulsing collimators (deposited material on these plates will alter nature of pulse).

(g) Overall vacuum of evacuated area.

(h) The amount of mercury contamination present on all electrical parts of the evacuated system (a mercury diffusion pump is used for high vacuum).

(i) The horizontal and vertical focusing of the ion beam as it travels down the flight tube.

(j) The ion focusing device.

(k) The state or age of the ion multiplier and the stability of the voltage requirements surrounding its use.

(l) The stability of the analogs. The analog is the only instrument to qualitatively watch the peak height intensity -- the intensity being a combination of overall amplification and gate width.

It was felt that a general overhaul of the unit was necessary before any serious work could be done. The following tasks were performed to better the overall operation of the unit.

(a) The mechanical sections of the Bendix were completely disassembled including the structural supports and vacuum system and all items were given a thorough cleaning and inspection.

(b) The vacuum system was changed slightly to allow for more efficient pumping of the Knudsen cell chamber and for compactness.

(c) The unit was moved to an adjacent wall to provide access to the rear and more room for incoming equipment.

(d) The filament electrode connections for the Knudsen cell heating chamber supplied with the instrument were found to be inadequate so a better clamping arrangement was sought. Drawings for a screw type connection were obtained and the electrode terminals altered accordingly.

(e) The analog units supplied with the Bendix were checked for linearity and calibrated using a known input voltage.

(f) Several recorders were located and put into repair for their use on the Bendix as well as other incoming equipment.

(g) A voltage divider was constructed to limit the output voltage of the analogs and to provide exact rating to various recorders that may be used.

Several runs were made on the Bendix using silver as the investigative material. The results of one of these runs is illustrated in Figure 4.

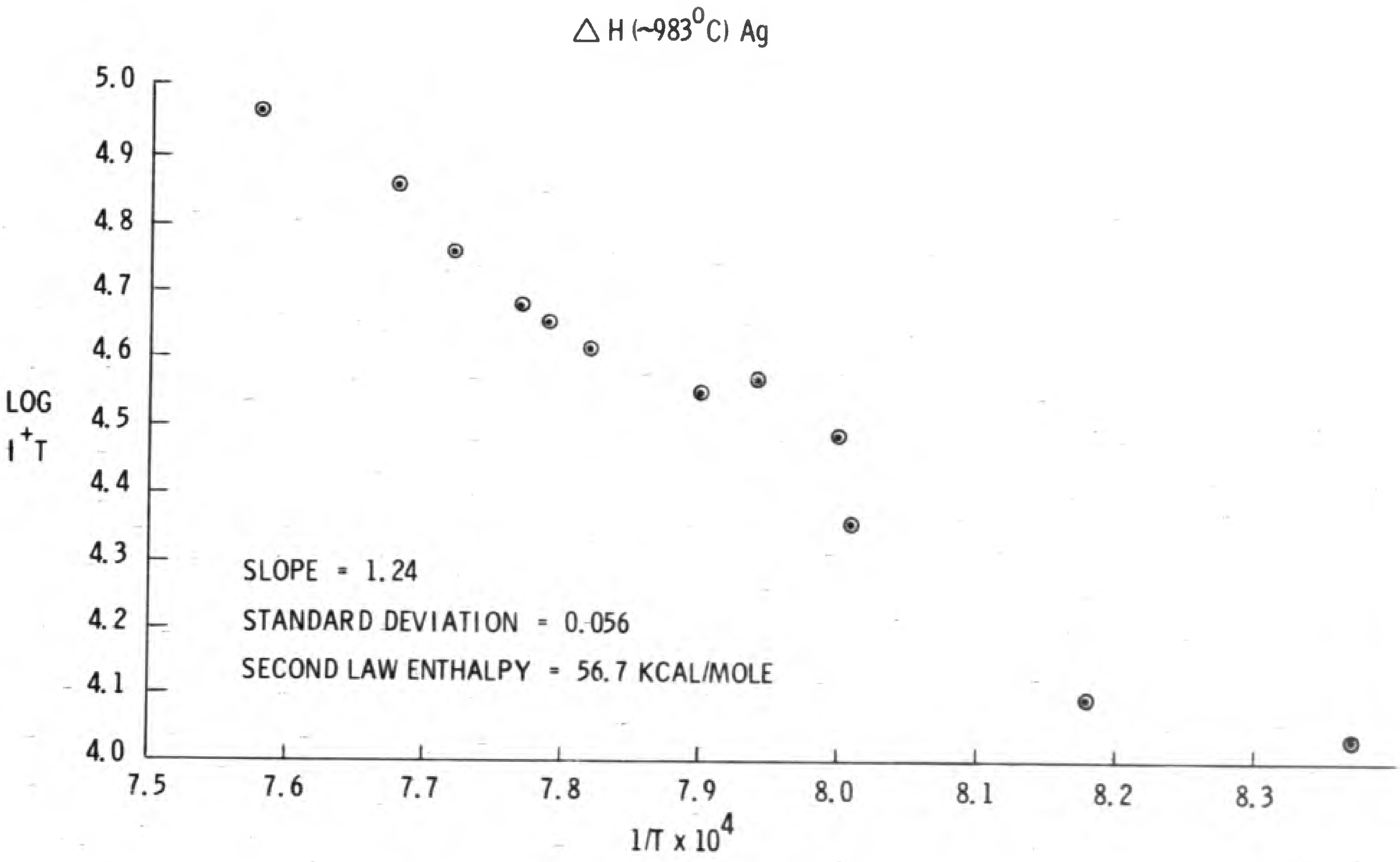

Figure 4. Heat of Vaporization of Silver

The data analyzed from these several runs were lacking in both accuracy and precision. Thermodynamic evaluations using the instrument were not reproducible due to the inherent instability of the ion collection system. Since it was not economically feasible to alter the system to provide the stability required the unit was left idle thereafter.

Two computer programs were written for mass spectrometric use. The first was written by the operator, the second by computer services at the request of the operator. The first was designed to accept the necessary thermodynamic inputs of temperature and associated peak height and determine from a best fit of a linear relation to the peak height, temperature data points by the method of a least square analysis the following quantities, the slope and the intercept of the linear relation, the enthalpy of the vaporization of the material and the standard deviation of these quantities and the average temperature over which the data was collected. The second program is designed to display statistical information regarding isotopic peak height probabilities based on natural abundances of the elements. Since the mass spectrometer evaluates ions by their mass/charge ratio, the mass spectrum of molecules and multi-elemental single ion species is arrayed according to the statistical combination of their isotopes. An example of this is given in Table I.

When the element silicon is ionized, some Si_2^+ is present. The program will calculate all of the isotopic combinations Si_2^+ and print out the ratio of these combinations with respect to the highest calculated (observed) peak. The program was set up to accept three element molecules. with up to five atoms for each element and up to seven possible isotopes for each atom.

4.2 Thermal Conductivity

4.2.1 Thermal Conductivity of NaCℓ as a Function of Crystal Lattice Defects:

The measurement of the lattice component of the low temperature thermal conductivity (phonon energy transport) of materials is of interest because of the strong relationship between lattice parameters, crystal properties, and the thermal conductivity between 0 and 40°K. It is, therefore, desirable to refine low temperature conductivity measurement techniques. Such refinements include those of temperature measurement and thermometer and specimen attachment techniques. The first part of the work was concerned with the calibration of the "thermometers", followed by calibrating the entire apparatus by measuring the thermal conductivity of a well characterized sodium chloride single crystal. The second phase of the work correlated the dislocation densities with thermal conductivity (see Figure 5); the dislocation densities were reduced by annealing the crystals for varying lengths of time.

A thermal conductivity apparatus was used to verify the thermal conductivity theory in a single-crystal halide (NaCℓ). Many modifications

TABLE I

Calculation of the Si_2^+ Mass Spectrum

Mass Number	Fractional Abundance	Mass Number			Mass Spectrum Array Ratio
		28	29	30	
		.9221	.047	.0309	56 Highest peak observed
28	.9221	.8503	.0433	.0285	57 0.1 of peak 56
29	.047	.0433	.0022	.0014	58 0.07 of peak 56
30	.0309	.0285	.0014	.0009	59 0.003 of peak 56
					60 0.001 of peak 56

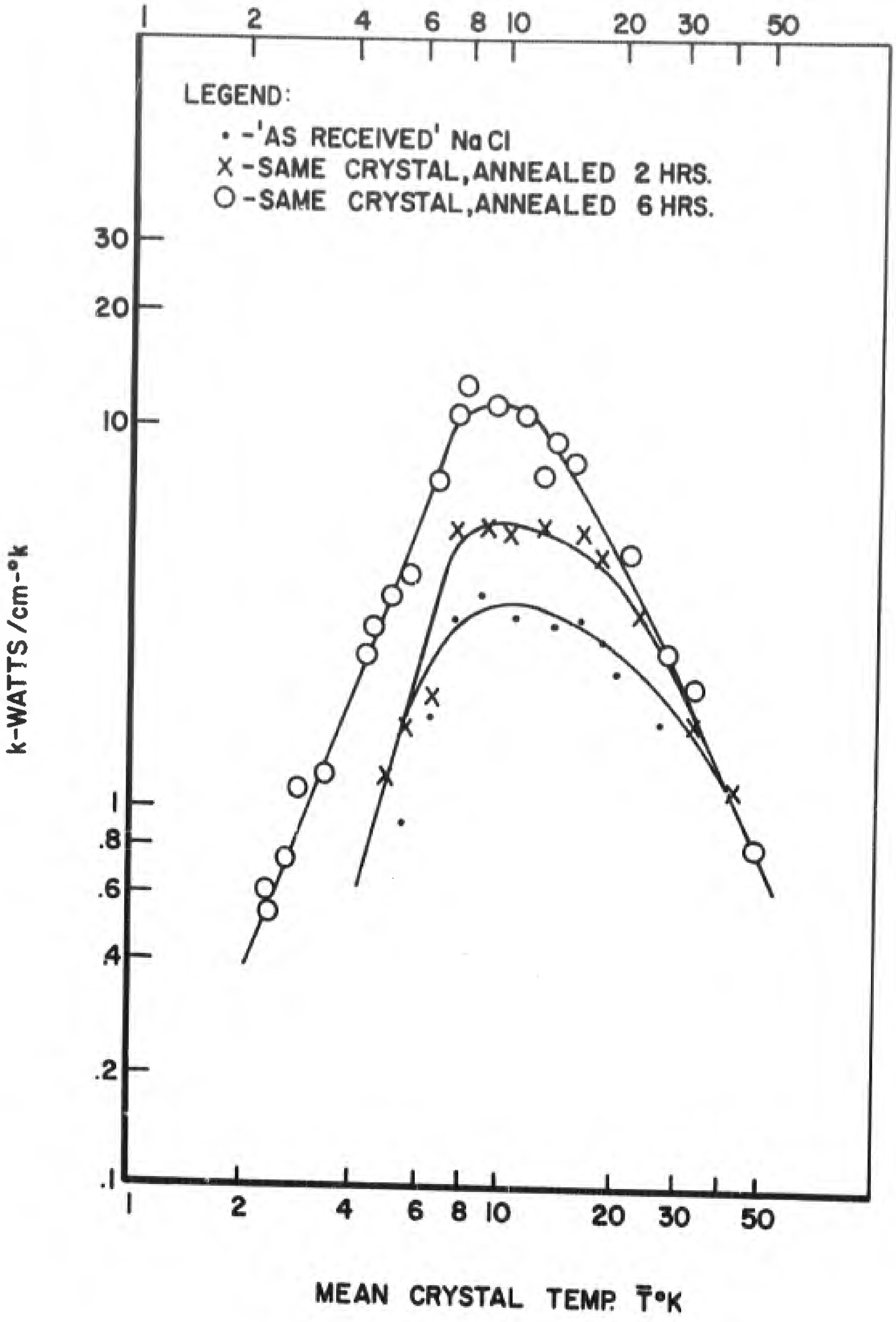

Figure 5. The Effect of Anneal On Thermal Conductivity

of the apparatus (Figures 6 and 7) were found to be necessary and subsequently accomplished.

Three runs were made. Run number one was the crystal "as-received"; run number two was the same crystal annealed two hours; and run number three was the same crystal annealed six hours. The crystal "as-received" was cleaved perpendicular to the axis of the cylinder and the new surface etched. Relative dislocation densities were obtained by a visual count of both positive and negative etch pits as seen on a 500 x -4 x 5 inch photo. Twenty photos were taken of each crystal surface and the counts averaged so as to obtain a good statistical average. An empirical correlation was then made relating the dislocation density and the thermal conductivity.

Two computer programs were written for use with this thermal conductivity apparatus. The purpose of the first program was to generate a table for the determination of the temperature of a germanium diode used in the thermal conductivity apparatus. The second program was written as an attempt to evaluate the data obtained from thermal conductivity measurements on a selected single crystal. The least square method of data analysis was applied in linear and polynominal form to the data received, in an attempt to observe whether the experimental curves computed fit existing formulas found in the literature.

4.2.2 BeO Thermal Conductivity.

An apparatus was constructed for the evaluation of the thermal conductivity of beryllium oxide.. The apparatus is basically the same as that used previously to determine the thermal conductivity of NaCℓ (see Figure 6) Numerous components were charged to accommodate a much smaller crystal (0.9 x 0.9 x 10 mm). The support mechanism, heater, heat sink, differential and reference thermocouples were necessarily modified. Techniques were developed to reduce or eliminate heat leaks through the eight instrument leads. A number of successful runs have been made. The instrumentation as shown in Figure 7 was also used in this evaluation. Some preliminary data is shown in Figure 8.

4.3 Calibration of an Apparatus to Determine Heats of Vaporization.

An apparatus to be used for weight-loss and high-temperature kinetic studies was refined and calibrated by running a Langmuir evaporation of nickel.

The three major components of the apparatus are; a vacuum system, an induction furnace, and a Cahn type RH electrobalance (see Figure 9). Within the vacuum system, the sample is suspended from the electrobalance into the induction coil. This method provides clean heating and reduces gas absorption prior to weighing.

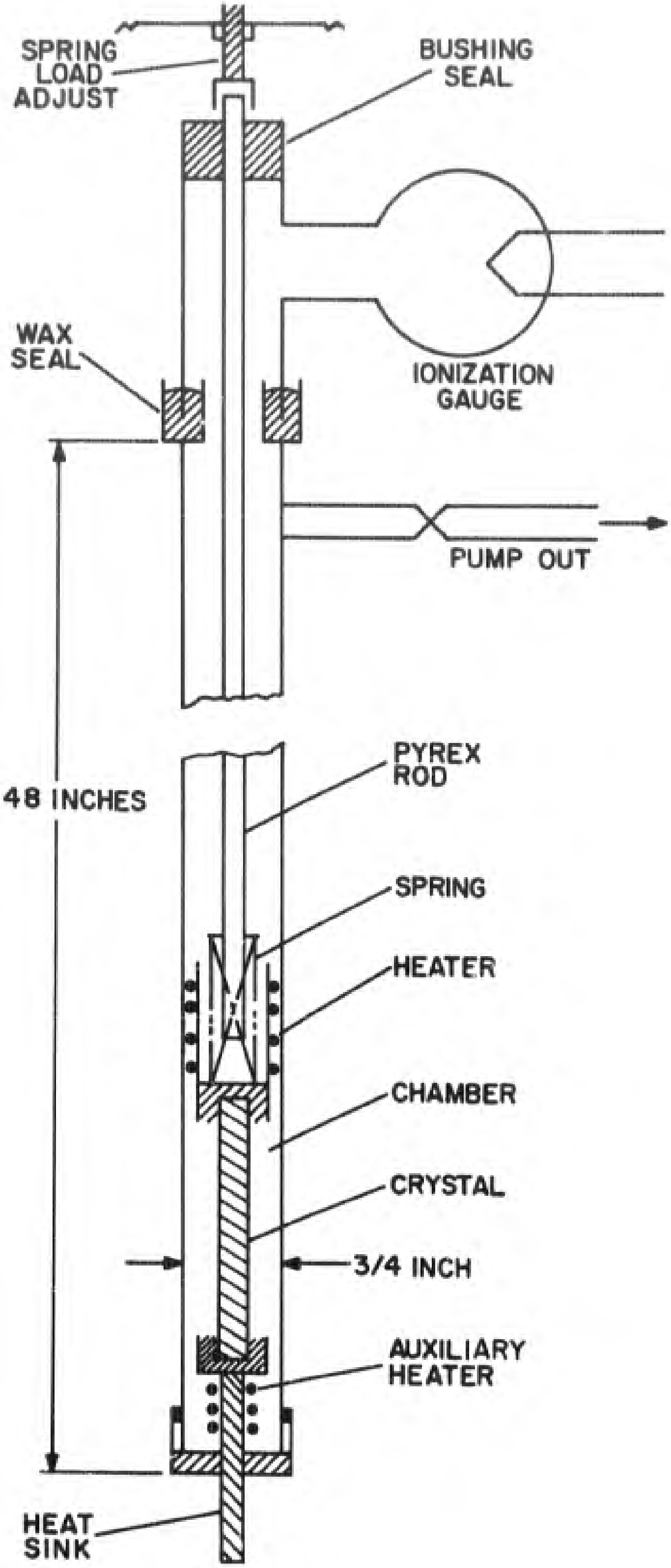

Figure 6. Thermal Conductivity Apparatus.

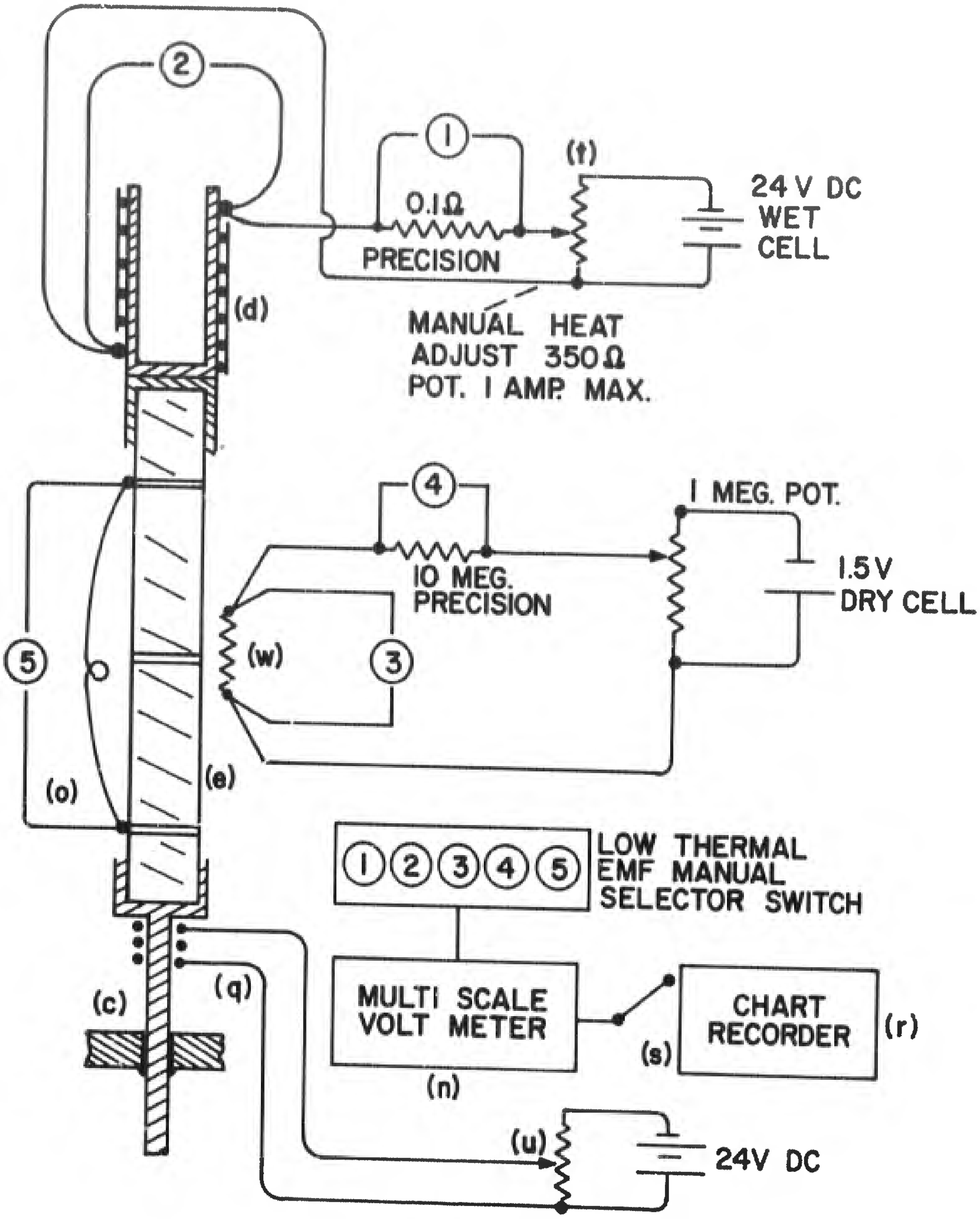

Figure 7. Instrumentation and Crystal Attachment

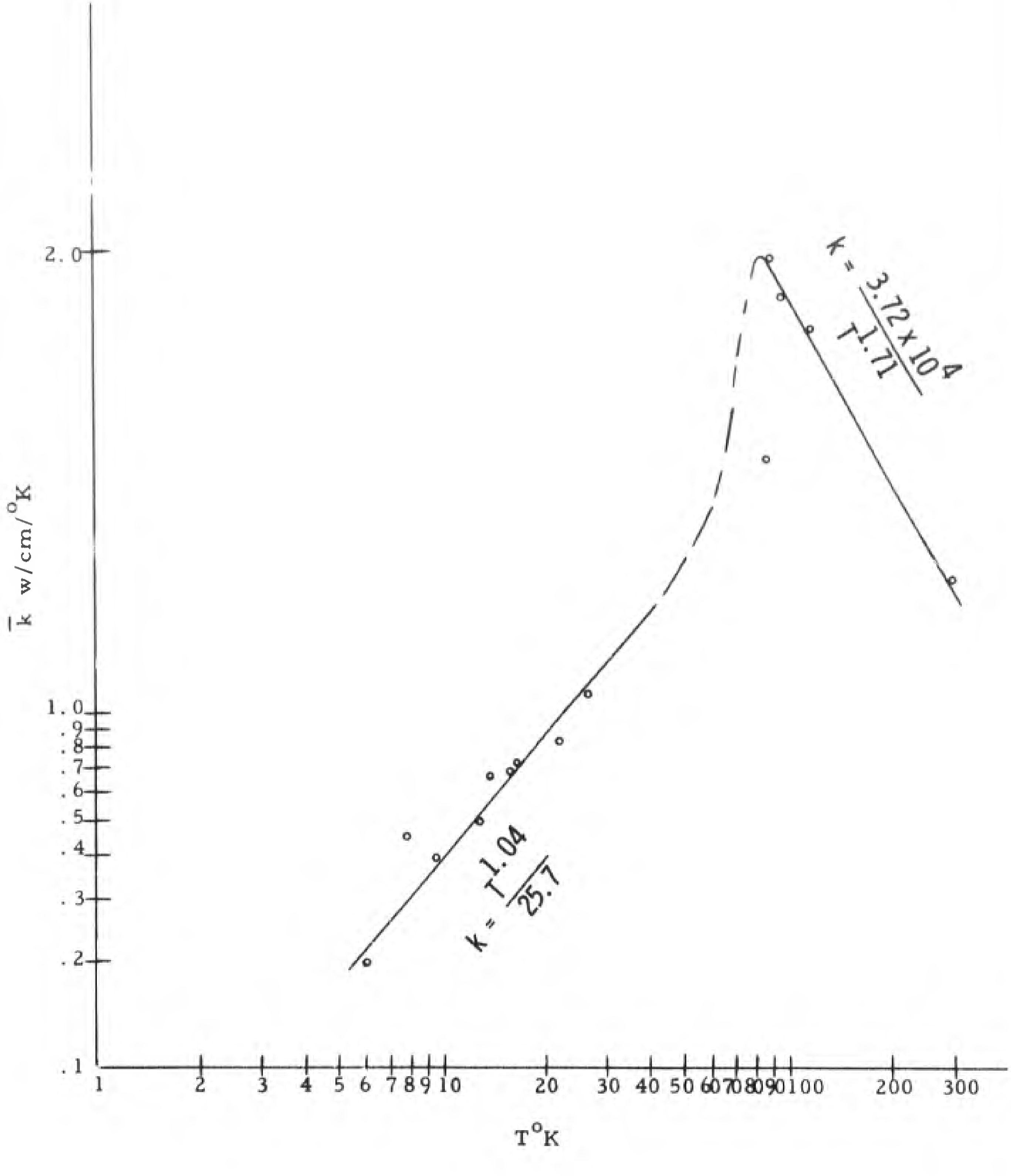

Figure 8. Thermal Conductivity of Single Crystal BeO Run 2 (20 September, 1971) Along Long Axis (C Axis).

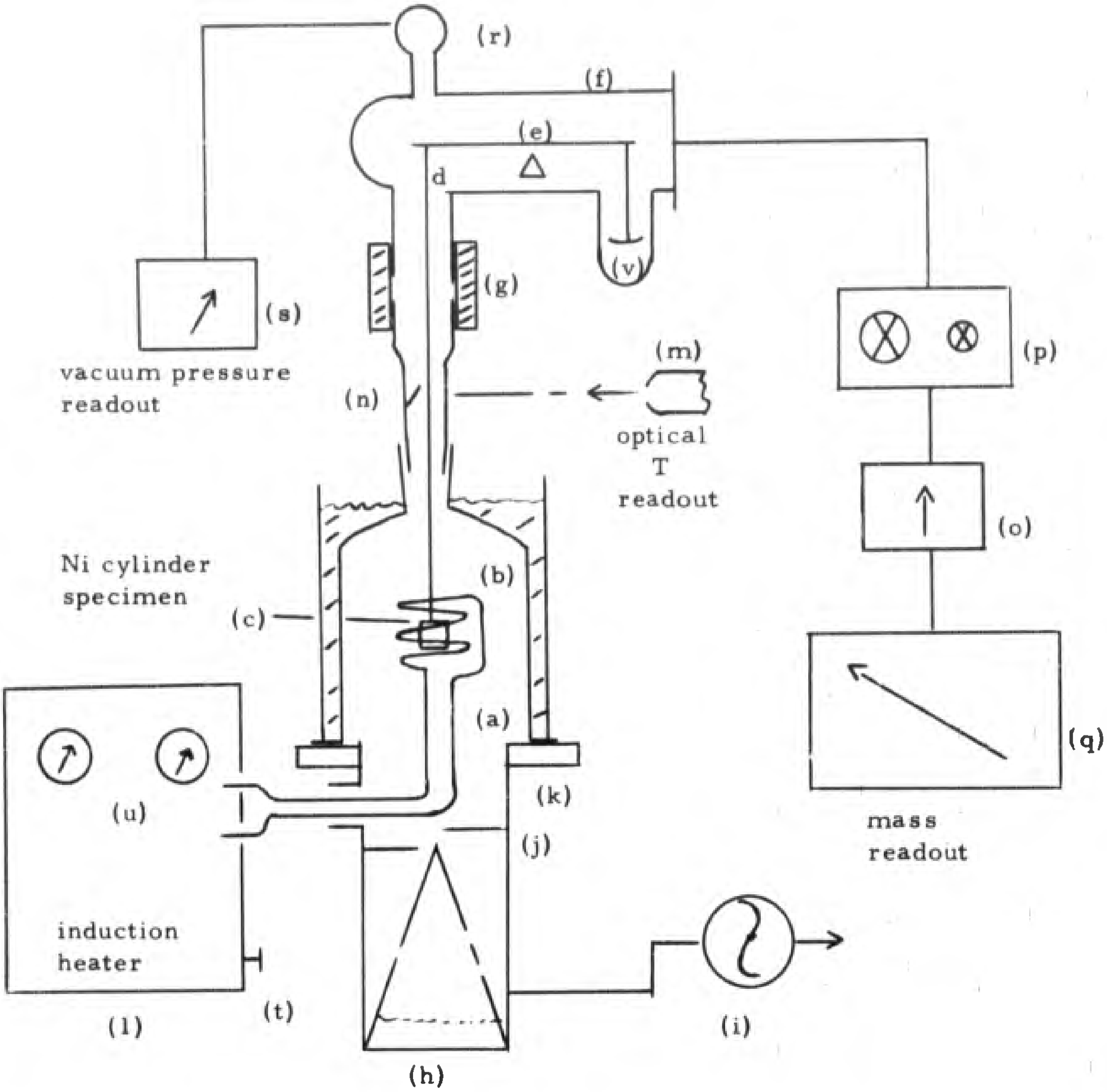

Figure 9. Vacuum - Induction Furnace Coupled to Microbalance.

Numerous procedures were tried to better insulate and couple the induction furnace to the system, thus enabling higher temperatures for extended periods of time.

Further, a computer program was developed to determine the deviations of heats of vaporization.

4.4 Additional Work

(a) Several panels were cut and a thermocouple readout system to be used with a Nuclide Mass Spectrometer was installed.

(b) A connection was made for an automatic liquid nitrogen filler to be used with a Nuclide Mass Spectrometer.

(c) A filtered and pressure regulated air outlet system was installed to more conveniently clean the delicate components associated with the thermal conductivity and Cahn-micro balance apparatus.

(d) Assistance was given in revamping a spectrophotometer located in Building 17 at Wright-Patterson Air Force Base.

(e) Two holders were designed and made for use with a spectrophotometer located in Building 56 at Wright-Patterson Air Force Base, because existing holders were too small to use with the single crystals being evaluated.

(f) Several drawings were made and a liquid nitrogen heat exchanger coil and manifold system designed, and fabricated for use with the spectrophotometer located in Building 17 at Wright-Patterson Air Force Base. The heat exchanger heats liquid nitrogen from a pressurized dewar to approximately +150°F. The temperature of the purging gas is monitored by a thermocouple readout system built into the heat exchanger apparatus, and controlled by two valves located just in front of the manifold outlet. The purpose of the manifold purge system is to eliminate unwanted peaks in the spectrum caused by water, carbon dioxide, etc.