SEMI-ANNUAL STATUS REPORT

for the period
May 1, 1965, to November 1, 1965

to

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MULTIDISCIPLINARY RESEARCH IN SPACE-RELATED SCIENCE AND TECHNOLOGY

NASA Grant NGR 44-007-006

By

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INTRODUCTION

Research in the space-related sciences and technology has been carried out for some years at Southern Methodist University at a low level of activity. In November of 1963, a university-wide Committee for Space Research was established for the purposes of (1) determining the level of undeveloped research interests among faculty members capable of conducting investigations related to space science and technology, and (2) assisting faculty members in gaining financial support for research projects in space-related areas of study.

Effective May 1, 1965, the University received a grant from the NASA for "Multidisciplinary Research in Space-Related Science and Technology" for a period of three (3) years in the amount of $200,000 with a first year level of effort at $100,000. With these funds five (5) projects were initiated. They are

1. Electrostatic and Electrokinetic Phenomena of the Interface Between Two Immiscible Liquids Containing Soluble Electrolytic Species.
2. Thermal Conductivity of Low Vapor Pressure Materials: Sodium Vapor.
3. RC Distributed Circuit Study.
4. Impedance Characteristics of Irradiated Thin Films.
5. Studies in Ultrasonic Paramagnetic Resonance.

This report documents the personnel conducting the investigations, the major items of equipment purchased (over $1000), and the status of the five projects for the period May 1, 1965, to November 1, 1965. It should be noted that, in order to phase the research with the University calendar, all projects were officially initiated on June 1, 1965.

PERSONNEL

During the subject period the following personnel were engaged in research on the projects indicated.

1. Project: Electrostatic and Electrokinetic Phenomena of the Interface Between Two Immiscible Liquids Containing Soluble Electrolytic Species

   Personnel: Dr. J.J. Banewicz, Principal Investigator
   Dr. J.A. Maguire, Associate Investigator
   Mr. Andrew Bramley, Research Fellow (1/2-time)

2. Project: Thermal Conductivity of Low Vapor Pressure Materials: Sodium Vapor

   Personnel: Dr. H.A. Blum, Principal Investigator (1/4-time)

3. Project: RC Distributed Circuit Study

   Personnel: Dr. K.W. Heizer, Principal Investigator (1/4-time)
   Dr. Y. Fu, Associate Investigator (1/4-time)
   Mrs. J. Fu, Research Fellow (1/2-time)

4. Project: Impedance Characteristics of Irradiated Thin Films

   Personnel: Dr. L.L. Howard, Principal Investigator (1/2-time)
   Mr. R.F. Eberline, Research Fellow (1/2-time)
   Mr. D.S. Glass, Research Assistant (1/8-time)

5. Project: Studies in Ultrasonic Paramagnetic Resonance

   Personnel: Dr. G.C. Wetsel, Jr., Principal Investigator (1/4-time)
   Mr. A.D. Dunkin, Research Fellow (1/2-time)

EQUIPMENT

During the subject period two pieces of equipment costing in excess of $1000 have been purchased. These are itemized below:

Project: Thermal Conductivity of Low Vapor Pressure Materials:
Sodium Vapor
Equipment: 1 Lindberg Hevi-Duty 3-Zone Tube Furnace Model 54677,
(to 2200F, 5" ID x 36"L) E.H. Sargent Company.
Purchase Price: $1042.00

Project: Studies in Ultrasonic Paramagnetic Resonance
Equipment: 1 Varian 12-inch Electromagnet System, consisting
of 1 V-3600 Electromagnet and 1 Special V-FR2501
Fieldial Magnetic Field Regulated Power Supply,
Varian Associates.
Purchase Price: $15,530.00

PROJECT STATUS REPORTS

1. Project Title: Investigation of the Electrostatic and Electrokinetic Phenomena of the Interface Between Two Immiscible Liquids Containing Soluble Electrolytic Species

Investigator (s): Dr. J.J. Banewicz
Dr. J.A. Maguire
Department: Chemistry

The initial phase of this investigation has involved the construction of a high sensitivity, conductance bridge and the selection and purification of the solvent and solute species. Therefore, this progress report will be composed of three sections: apparatus, solvent and solute.

Apparatus

A high sensitivity, A.C. conductance bridge has been assembled. A schematic diagram of this bridge is shown in figure 1. This is a modification of a Jones-Shedlovsky Bridge with a Wagner earthing device. The ratio arms E-A and A-F consist of two 100Ω, type 500-D General Radio, precision resistors. Using these resistors, a 1:1 correspondence between the value of the unknown resistance R_x and the resistor R_1 is obtained. By replacing these resistors with either a 10Ω (G.R. type 500-B) or 1KΩ (G.R. type 500-H) resistor ratios from 1:100 to 100:1 can be obtained. The measuring resistor, R_1, is a precision, 0→11,000Ω decade resistor, variable

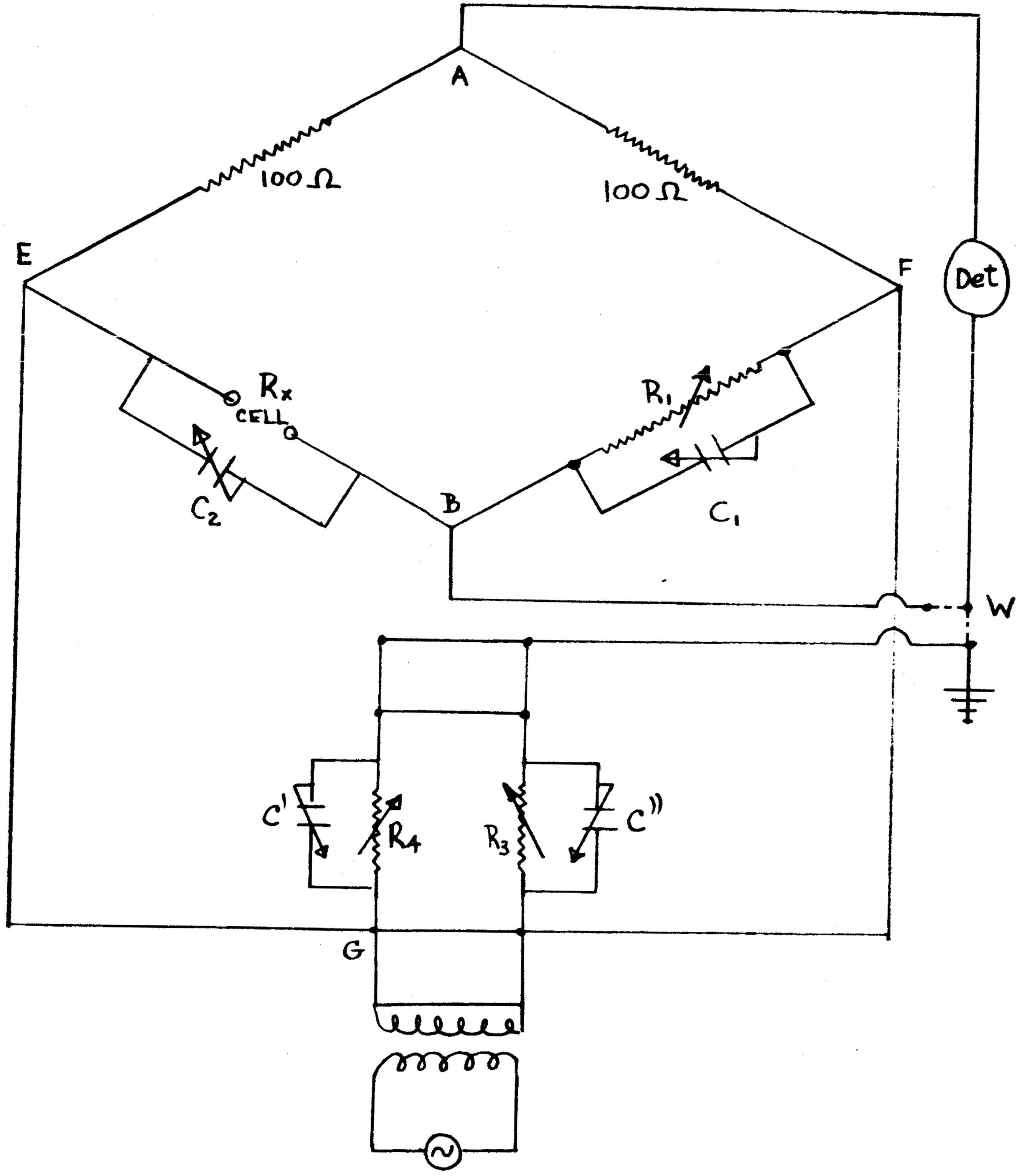

FIGURE 1

Figure 1. Schematic Diagram of Conductivity Bridge

in 0.1Ω steps (Leeds and Northrup- 4755 Decade). Using these combinations, resistances from .001Ω to 1.1MΩ can be measured directly. Since the absolute values of the capacitances will be of no great importance in determining resistance, no detailed description of the capacitors need be given here.

The bridge balance is determined using a General Radio, Null Detector (Type 1212-A). The bridge design also permits the use of an oscilloscope as a balancing detector. The voltage source is a Hewlett-Packard Oscillator, Model 650-A. This generator is capable of supplying voltages up to 3 volts at frequences from 0 to 10 MC. The Wagner earthing device is already described in the literature and will not be discussed here. A block diagram, showing the wiring set-up is shown in Figure 2.

The conductivity cell used is a standard, Washburn cell. The temperature of the cell is controlled to within ± .005°C with a Sargent s-67428 Bath. To insure anhydrous conditions, the bath liquid is inhibited mineral oil. The temperature of the bath is measured using a 18° to 31°C thermometer, readable to 0.001°C.

Solvent

The solvent systems in this investigation will consist of water in conjunction with some organic solvents that have high dielectric constants and are immiscible with water. The first such system will be water-valeronitrile (C_4H_9CN). Purification procedures for water are well known, but not much information is available in the literature concerning the purification of valeronitrile.

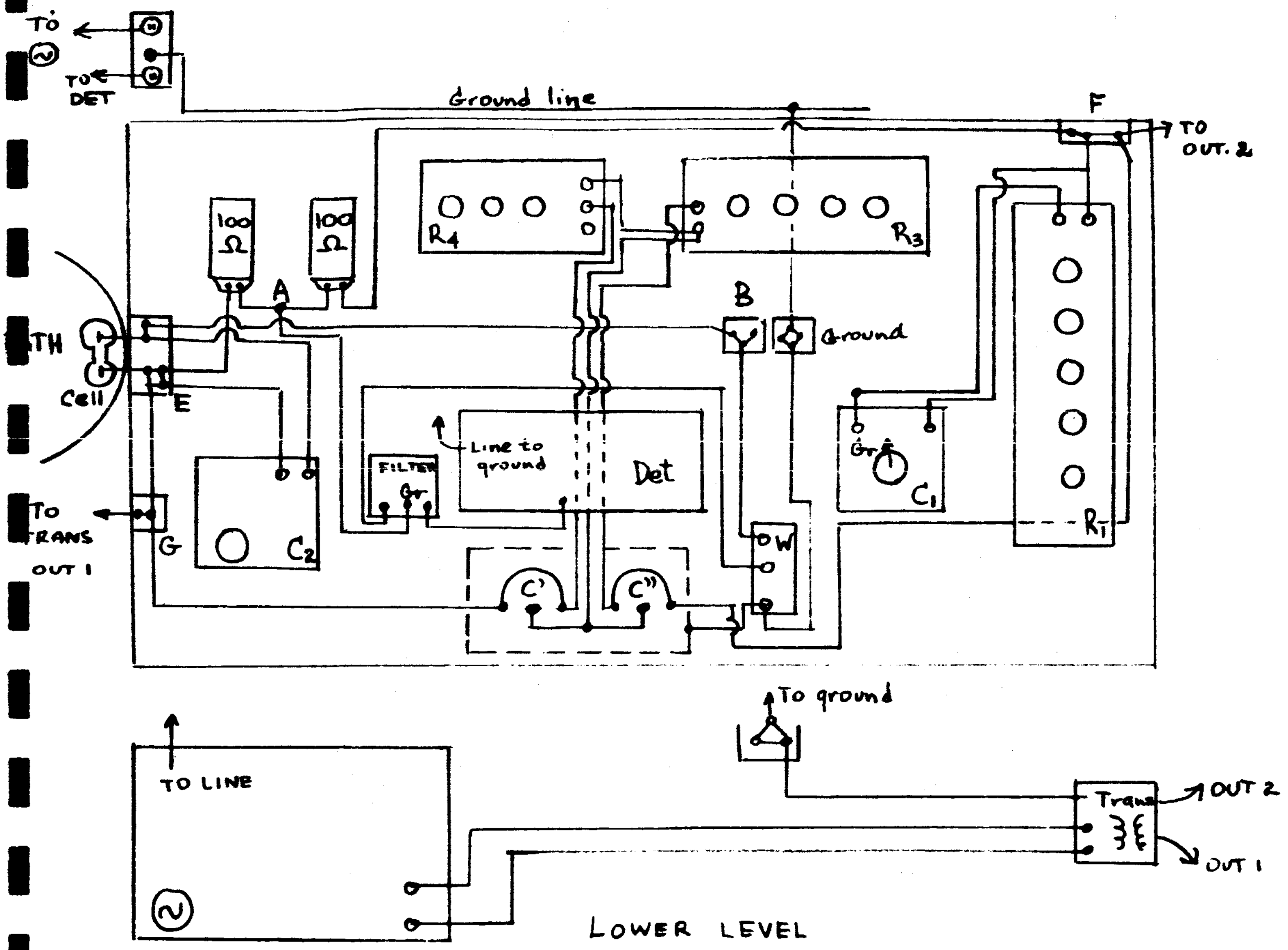

FIGURE 2

Figure 2. Block Diagram of Conductivity Bridge

The impurity content of the valeronitrile was determined using gas phase chromatography. This method of analysis proved to be much more precise than the measurement of physical properties, such as boiling point and electrical conductivity. It was found that successive extractions of the valeronitrile with various selected reagents, followed by drying and fractional distillation in a Todd Distilling Column with about 60 theoretical plates produced valeronitrile containing virtually no impurities as measured by gas chromatography. The purification procedure was checked by measuring the ultraviolet absorption spectrum of the valeronitrile.

Due to the high cost of the commercially available valeronitrile, it proved more convenient to synthesize the nitrile in this laboratory.

Solute

The solutes to be used in this study are transition metal salts. The first salt chosen for extensive study was PtI_4. This substance was prepared by the reaction of chloroplatinic acid and potassium iodide according to the method of Lassagne and Pigeon*. Analysis was performed by heating a known weight of the compound at 1000°C for four hours and weighing the residual platinum. Analysis showed the formula to be $PtI_{3.9}$. The nonstoichiometry of this compound has been discussed in the literature, and formulas ranging from $PtI_{3.7}$ to $PtI_{3.9}$ have been reported. This compound is soluble in valeronitrile. Spectroscopic evidence indicates that in valeronitrile

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* J.L. Lassagne Ann. Chim. Phys. 51, 113 (1832)
L. Pigeon ibid. 2, 496, (1894)

the PtI_4 undergoes solvation reactions forming several different species. There is strong indication that PtI_2 and nitrile complexes derived from the dissociation of I_2 are among the substances formed. Fortunately, the decomposition products, PtI_2 and I_2, are available and exhibit unique absorption spectra. An extensive photometric study of this system is now being conducted.

Since the behavior of PtI_4 in valeronitrile is apparently complex, other transition metal compounds less susceptible to reduction are being studied. Among these are the nickel halides and the copper (II) halides. The valeronitrile complexes of these salts are being prepared and characterized.

The results from the study of these complexes will be used to determine the nature of the diffusing species in the nitrile solvent. This information will be necessary in interpreting conductivity results. In case the behavior of the transition metal salts proves to be too complicated in the two solvent systems, use will be made of less interesting but simpler salts such as LiI or KI as solutes.

2. Project Title: Determination of Thermal Conductivity of Low Vapor Pressure Materials: Sodium Vapor

Investigator: Dr. H. A. Blum

Department: Mechanical Engineering

INTRODUCTION:

Potential use of liquid metals as working substances in compact turboelectric systems for space vehicles has resulted in an extensive program for studying the heat transfer and fluid dynamics behavior of liquid metals. The thermal conductivity of sodium vapor has not been measured even though it is important to know this property for many heat transfer problems. If sodium vapor were monatomic there would be ways to estimate this property for at least the low density conditions. As pointed out by Stone, Ewing, et al. (Ref. 1) and by others, sodium in the vapor phase is a mixture of monatomic, diatomic, and tetraatomic molecules. This complicating factor makes it unlikely that reliable predictions of the thermal conductivity can be made. Furthermore, it indicates that in the experiments which we are planning to make we should expect an effect of pressure as well as temperature on the thermal conductivity which would be a function of the composition of this vapor mixture.

OBJECTIVES:

We would like to be able to measure the thermal conductivity of sodium vapor between 800 and 2000F by a steady state approach.

CURRENT STATUS:

In the original proposal we indicated that a modification of the method proposed by Vines (heat transfer across an annulus) (2) would enable us to accomplish our objective. In the report period we have also studied the application of methods by Rothman and Bromley (3) and Nuttall and Ginnings (4) who have measured thermal conductivity of gases across the gap between parallel plates. The possibility of measuring the thermal conductivity by heat transfer from a hot wire across a gap to a surrounding cylinder as exemplified by Zollweg and Gottlieb (5) was also studied in some detail. While all three steady state methods have certain advantages and disadvantages, the overwhelming factors in our selection were first that we could avoid experimenting with insulating seals for the lead wires associated with thermocouples and heaters and that measurements would be more easily obtained. By the end of the next period (June 1, 1966) we hope to have an apparatus built and calibrated.

THE APPROACH:

For heat transfer across an annulus between two parallel cylinders equation one is appropriate.

$$k = \frac{q \ln d_2/d_1}{2\pi L \Delta T} \tag{1}$$

where k = thermal conductivity BTU/hr. ft. °F

q = heat transfer BTU/hr.

A = cross section perpendicular to heat flow ft^2

ΔT = temperature drop across gap °F

d_2, d_1 = outer and inner diameters across gap ft

L = length of cylinder ft

The experimental plan will involve the following:

1. The cell as pictured in Figure 1 will be placed in a three-zone tubular furnace. Instead of a stub coming out of the cell as pictured in Figure 1, there will be a stainless steel tube that will run to a manifold. A vacuum will be maintained in the cell to approximately 10-5 mm and then the furnace will be heated to approximately 1000F. The central heaters will be adjusted until the temperature of the inner cylinder is approximately 10°F above the furnace temperature. The guard heaters will be adjusted in order to prevent heat transfer along the length of the metal cylinders. The power consumed to maintain this temperature difference will be due to the combination of radiation plus some lateral losses. This procedure will be followed throughout the temperature range of interest for various temperature differences across the gap.

2. Pure argon will fill the thermal conductivity cell. This argon will have been purified by flowing it through a molecular sieve followed by a hot titanium getter. For the same temperature drop across the gap in a series of experiments conducted within the temperature range of interest we can determine, after measuring the power consumption, (corrected for radiation) a thermal conductivity of argon and check it against values in the literature.

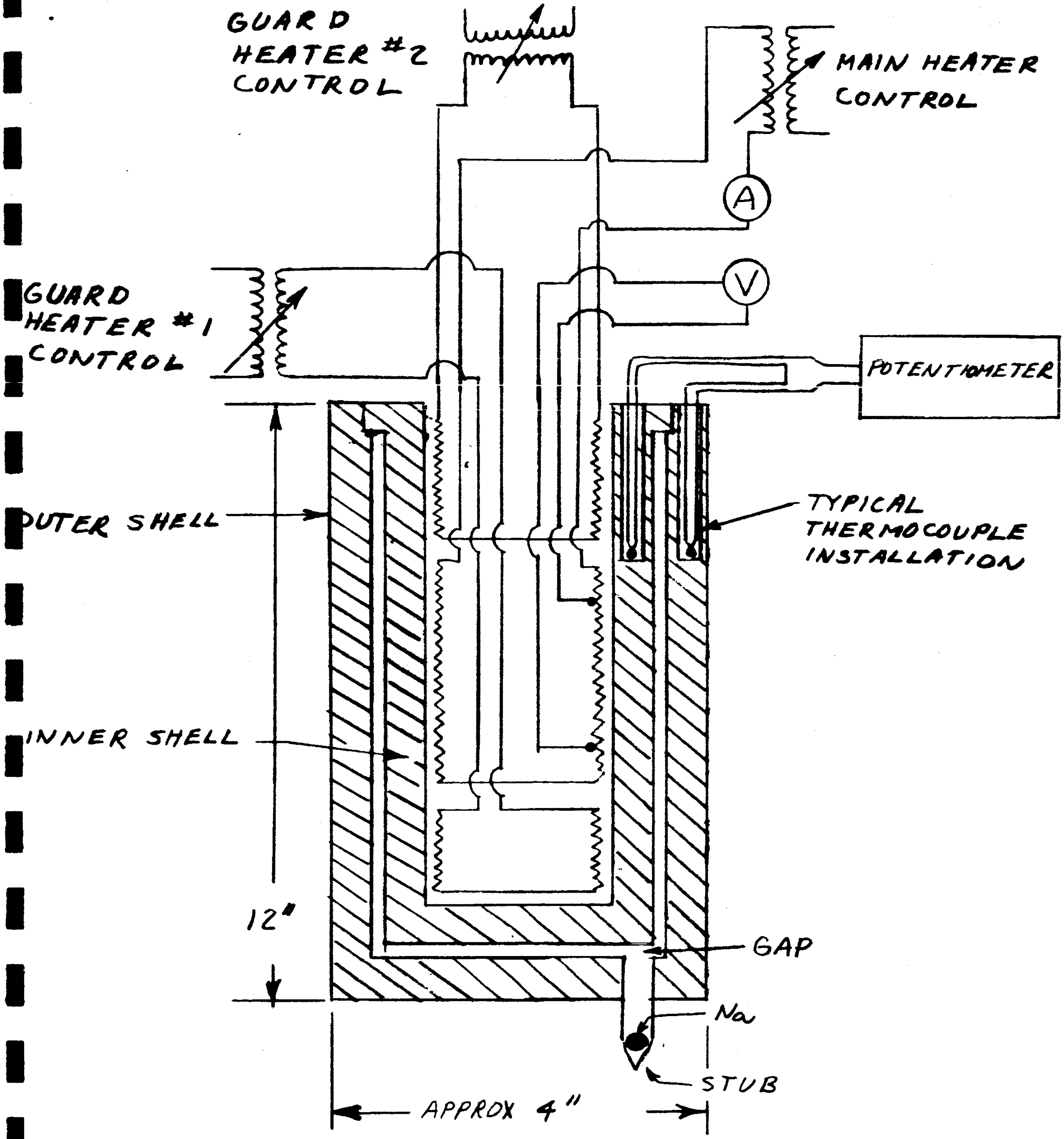

Figure 1. Sodium Vapor Thermal Conductivity Cell and Controls

3. The thermal conductivity cell will be placed in a dry box. The dry box air will be replaced by argon. Within the dry box there will be an ampoule of pure sodium (0.5 grams), some tools, and fittings. The stainless steel tubing which had been used in the previous steps will have been broken except for about an inch or an inch and a half coming out of the cell. With the dry box filled with argon the vial of sodium will be broken and the sodium will be placed in the now open stub coming out of the thermal conductivity cell. A fitting will be made to connect the tubing to a vacuum system where we will try to obtain vacuum of about 10-6 mm. When this is obtained the tubing will be crimped shut to insure the maintenance of a vacuum and to isolate the sodium from other parts of the system. Now the thermal conductivity cell with its associated thermocouple and heater leads will be placed in the furnace and the gas thermal conductivity will be determined. From the thermodynamic property data provided by Ewing, Stone et al (1) we can be assured of having both liquid and vapor in equilibrium throughout the temperature range providing there is a sufficient mass of sodium in the system. From their vapor pressure data we will know the pressure of the system if we can measure the temperature. Knowing then the volume, the pressure, and the temperature we can estimate the composition (e.g. Na, Na_2) as obtained from the previously referenced work.

Chromel-Alumel thermocouples at the same position across the gap (Figure 1) will be coupled together to measure the temperature difference. These will be checked against each other in the previously mentioned multi-zone furnace (Figure 2). The temperatures will be measured by means of a laboratory potentiometer. It is expected that temperature difference can be determined to about 0.1°F. The power will be determined by measuring the heater voltage across a fixed length of the cell and by measuring the current in the heater line. From this total power measurement will be subtracted the power required to maintain the same temperature difference when the vacuum experiments were conducted. The diameters will have been measured prior to the sealing of the bottom plate. It has been estimated, in view of the fact that the cell will be made entirely of stainless steel, that the gap measurement at room temperature will be identical to that at the high temperature levels. Considering the expected errors in the measurements of the temperature difference, the gap, and the heat transfer, we anticipate keeping the error in the thermal conductivity determination to approximately 5%.

EXPERIMENTAL ERRORS AND MISCELLANEOUS CALCULATIONS:

The factors which could introduce errors in our proposed measurements are heat losses, heat transfer by radiation, convective heat transfer, temperature jumps at low gas pressures, and eccentricity between the "concentric" cylinders. A detailed discussion of these errors is presented by Tsederberg (9).

End losses can be handled in several ways. For example, by use of guard heaters within the inner cylinder, it is possible to create a sufficient length of isothermal section for measurements. Another approach is to build two cells, one of which is longer than the other. Assuming

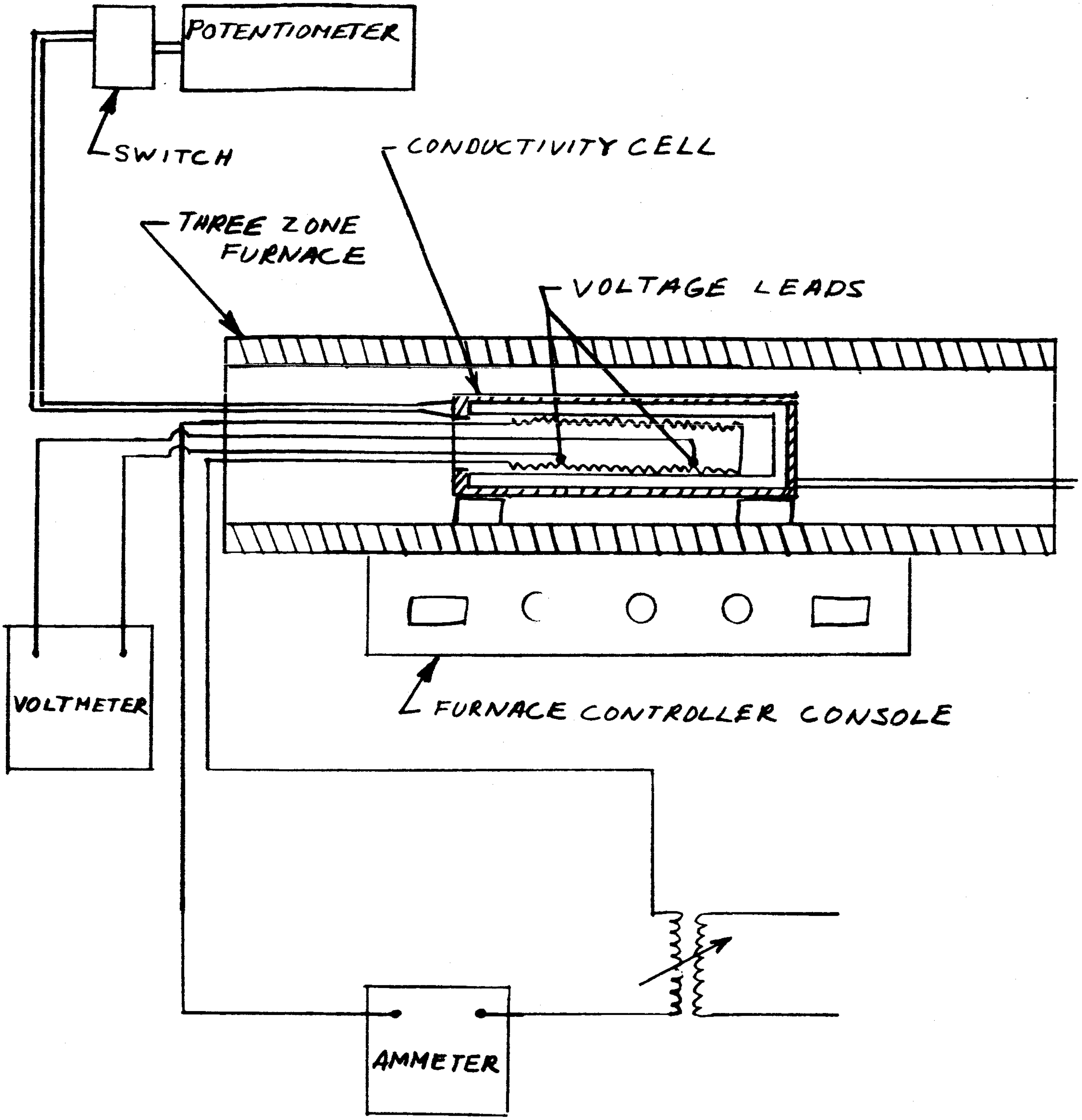

FIGURE 2
SODIUM VAPOR THERMAL CONDUCTIVITY SYSTEM

end effects are identical in both systems, for same ΔT and diameter ratios:

$$q_{T_A} - q_{EL} = \frac{2\pi L_A\, k(\Delta T)}{\ln \frac{d_2}{d_1}}$$

$$q_{T_B} - q_{EL} = \frac{2\pi L_B\, k\, (\Delta T)}{\ln \frac{d_2}{d_1}}$$

$$q_{T_A} - q_{T_B} = \frac{2\pi (L_A - L_B)\, k\, \Delta T}{\ln \frac{d_2}{d_1}}$$

where

q_{T_A} = Total power measured in an experiment with length, L_1

q_{T_B} = Same as above for length, L_2

q_{EL} = End losses

Concerning radiation, we have estimated with a wall emissivity of 0.06 that the percentage of heat transferred across the gap by radiation will be about 20% of the total heat transfer at 1800F providing absorption of the sodium vapors is negligible and that the temperature difference across the gap is approximately 10°F. We propose to obtain this emissivity by brushing on a gold preparation and baking it on in the furnace.

For enclosed air spaces convection can be neglected when the Grashof number is less than 2000 for horizontal layers heated from below (8) (opposite to the way we would do it) and less than 8000 for vertical spaces. It was not possible for us to calculate these numbers for sodium since we do not know the properties so we calculated values for common gases whose properties are available. For example, using carbon dioxide, a maximum temperature difference across the vapor of 100°F, and a 5/64" gap (much larger than we will probably use), the Grashof number varied from 13.2 at 500°F to 0.526 at 1500°F. The Fr number for gases such as air, steam, oxygen and other common gases are much lower. We assume that Grashof numbers for sodium vapor would also be low.

At this point we have not made any calculations concerning the temperature jump error at low gas pressures. We do not expect this to be a serious problem in view of the fact that our lowest pressure of interest is approximately 1 mm and the highest pressure will be approximately 1 atmosphere.

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(2) Vines, R. G., "Measurement of the Thermal Conductivities of Gases at High Temperatures," Journal of Heat Transfer, February 1960.

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(4) Nuttall, R. L. and Ginnings, D. C., "Thermal Conductivity of Nitrogen from 50° to 500°C and 1 to 100 Atmospheres," Journal of Research of the National Bureau of Standards, Vol. 58, No. 5, May 1957.

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(6) Coffman, W. A., "A Study of Thermal Conductivity Measuring Methods for Low Vapor Pressure Materials," Engineering Report, November 15, 1963.

(7) Blum, H. A., "Measurement of Vapor Thermal Conductivities: Low Vapor Pressure Materials," Fourth Thermal Conductivity Conference, San Francisco, October 1964.

(8) Kreith, Frank, "Principles of Heat Transfer," p. 318, International Textbook Co., Scranton, 1958.

(9) Tsederberg, N. V., "Thermal Conductivity of Gases and Liquids," (In English), M.I.T. Press, Cambridge, Massachusetts, 1965, p. 12-14.

3. Project Title: RC Distributed Circuit Study

Investigator(s): Dr. K. W. Heizer

Dr. Y. Fu

Department: Electrical Engineering

Introduction:

In order to make RC Distributed Circuits usable, it is necessary that the problems of analysis, approximation and synthesis be solved. The problem of analysis consists of determining the driving point and transfer immittances of given structures as well as determining the mathematical properties of the immittances. The problem of approximation is to develop a means whereby a desired response can be approximated sufficiently closely by a function which has the allowed physical properties. The synthesis problem is to devise a means whereby given a set of physically realizable properties, the structure configuration may be determined.

These problems are somewhat interrelated so that none can be completely solved without some knowledge of the others. However, the initial study requires attack in the order given, with a continued parallel effort.

Work Completed:

The rectangular two-dimensional RC Distributed Network problem with arbitrarily-shaped electrodes has been solved. The description of such an n-port network has been given in terms of its short-circuit admittance parameters. By controlling the boundary conditions and the shape of the electrodes, a set of poles is obtained that was not present in the one-dimensional problem. The residue of each of these poles may also be controlled.

An analytic solution has been obtained for the case of the uniform resistive sheet with a number of parallel conducting strips. This makes possible the determination of the number of strips necessary in a given case to approximate the one-dimensional solution.

Additional properties for the one-dimensional problem have been determined and generalized for the n-port structure.

A number of low-pass filter functions have been determined in the form which is possible to obtain with distributed networks.

Some work has been completed synthesizing a given transfer function by means of a Distributed RC Network with a Negative Impedance Converter, a lumped resistance and a lumped capacitor.

Work in Progress:

A method has almost been completed to synthesize the shape of the electrodes to approximate a given transfer function. This is a method using a high speed digital computer with the aid of the analytic solution of the properties when the shape is known.

A paper is in preparation by Julia Fu and Yumin Fu on the generalized one-dimensional n-port structure with examples using an active element.

Another paper is in preparation by K. W. Heizer giving the solution to the two-dimensional structure with an example using the computer synthesis technique.

4. Project Title: Impedance Characteristics of Irradiated Thin Films

Investigator(s): Dr. L. L. Howard

Department: Electrical Engineering

Introduction:

This is the first report of progress toward determination of the effect of electron beam irradiation upon the complex impedance characteristics of thin films.

The principal purpose of initial research efforts has been to attempt to verify and extend previously-observed thin film impedance characteristics. Toward this end eleven sets of four bismuth films each have been prepared by evaporation. The initial resistance values of these films range from 11 ohms to 395 ohms. Infra-red transmission measurements on these films are almost complete, and analytical work which should yield impedance values and equivalent circuits will begin soon.

The effort to establish that these films are similar to those on which previous impedance characteristics were observed has included also a continuing measurement of resistance drift with time. In addition, a preliminary electron microscope study, both of the structure and of the effect of electron beam irradiation, has been carried out. All of these observations tend to indicate that the films and their behavior are similar to the films of previous work.[1,2,3]

Superscripts refer to numbered items in the List of References

This report will document most of the important details of the research to date in the study of bismuth film characteristics.

Electron Micrographs:

A major part of the study of complex impedance characteristics has involved the relation of film structure to equivalent (and probably also to actual) circuits. This structure may be examined using electron micrographs.

Good sharp electron micrographs of bismuth films (particularly of films unchanged by irradiation or evaporation) are not easy to obtain because of bismuth's low melting point and because of its activity in the electron beam; nevertheless, specimens of the films prepared in the laboratory have been examined for structure similarity and for similarity of previously-observed activity in the electron beam, and have been found to have characteristics which appear to be similar to those formerly observed. A constant source of dismay, however, was the inability 1) to get enough film illumination to be able to study the structure in the microscope; and 2) to stabilize the activity so that it, too, could be studied in the microscope under variation of various parameters. The plans of Southern Methodist University to procure an electron microscope has made it possible, however, to plan research considering that these problems will be largely resolved. Proof of this came during an appraisal of the Hitachi HU11B2 microscope (the instrument ordered later by the University). At that time the principal investigator was for the first time able to examine a typical bismuth film for long periods under high illumination and high magnification. The electron micrograph shown in Figure 9 of Ref. 4 (attached) was made at that time. It is unique; and yet it is considerably below the ultimate capability of the microscope. There is "information" in the grain boundaries which has not been previously displayed or discussed. Analysis of this information and its revelance to bismuth characteristics will be given after more study of it has been carried out on the University's own microscope.

Resistance Drift

An outstanding characteristic of bismuth films previously examined has been their drift of resistance with time. This was true of a "first generation" of these films, which were formed at pressures of approximately 3×10^{-5} Torr, and also of a "second generation," formed at approximately 3×10^{-6} Torr. The "third generation," having been formed at approximately 3×10^{-7} Torr, is already displaying the same general characteristics. A plot of these characteristics is shown in Fig. 10 of Ref. 4. With no longer time experience than that shown, it appears that the break in long-term "change" characteristics will occur at approximately the same values of initial resistance: between 300 and 400 ohms.

Infra-Red Transmission

Infra-red transmission measurements (at $2\mu < \lambda > 15\mu$) are carried out with the films positioned in special adapters as shown in Fig. 11 of Ref. 4. These adapters are mounted on the source housing of a Beckman IR-5 spectrophotometer made available to this laboratory through the courtesy of Dr. Harold Jeskey of the Southern Methodist University Department of Chemistry.

Figure 12 of Ref. 4 gives a complete set of infra-red transmission characteristics for films in the resistance range of interest. These data are new and are being used to determine complex impedance information. It is expected that perhaps the complex impedance postulation (based upon structure) may be able to explain the shape of these curves.

Crystallite Change During Irradiation

It has been pointed out above that the films described herein are different from those previously deposited in that these films were deposited at a lower pressure, i.e., at approximately 3×10^{-7} Torr. They appear to behave in a manner similar to that of previously deposited films, however, in that electron beam irradiation excites considerable activity in them.

This activity was observed when a specimen was examined in the RCA EMU-3 electron microscope, but was difficult to control adequately. When a specimen was placed on the cold stage in the Hitachi microscope, however, it was possible to exercise considerable control over the activity. Control was so good, in fact, that the change of crystallite orientation could be stopped essentially at any stage. Figure 13 of Ref. 4 is an example of this control. The left-hand view was made first; then irradiation was allowed to take effect; then finally, the right-hand picture was made.

There are many changes in the crystallite structures. Some of the most obvious are: the band in the crystallite in the upper left corner has disappeared in the "after" view; the grey crystallite in the center has turned white in the "after" picture; next to it the bands in the crystallite have changed markedly between pictures. The most unusual thing is the fact that only very isolated radical changes (all white to all black, and vice versa) have occurred. Usually there is a predominance of radical change. Temperature control of a cold stage should make it possible to obtain the amount of change desired.

NOTE: A complete copy of a progress report on this project is attached as a supplement. Also attached is another complete report on Dr. Howard's thin films research entitled, "The Development of a High Vacuum System."

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4. L. L. Howard, R. F. Eberline, D. S. Glass, Thin Films Research Laboratory Progress Report No. 1, Southern Methodist University, December 1, 1965.
5. L. L. Howard, D. S. Glass, Thin Films Research Laboratory Technical Report No. 1, Southern Methodist University, Oct. 1965.

5. Project Title: Studies in Ultrasonic Paramagnetic Resonance

Investigator: Dr. G. C. Wetsel, Jr.

Department: Physics

Abstract:

The method of ultrasonic paramagnetic resonance (UPR) is applicable to the study of the direct or "one-phonon" process of spin-lattice interaction in paramagnetic crystals. The purpose of this investigation is to obtain information concerning the direct process in crystals of calcium fluoride containing paramagnetic ions from the lanthanide and actinide groups, utilizing the method of UPR. This report contains brief discussions of the theory, experimental method, and progress to date.

Theory:

One assumes in the theoretical approach to the problem that the spin Hamiltonian for the paramagnetic ion in its host crystal is known. The direct spin-lattice interaction is described by an effective Hamiltonian, linear in the lattice strain, of the form[1]

$$H_{SL} = \sum_{ij} V_{ij} u_{ij} , \qquad (1)$$

where V_{ij} depends on the electron coordinates and u_{ij} is a component of the macroscopic elastic strain tensor. The particular form of H_{SL}, of course, depends on the particular ion and its host lattice. Two dissimilar cases will be considered below.

The attenuation of an elastic wave is found by treating the spin-lattice Hamiltonian as a time-dependent perturbation on the eigenstates of the spin Hamiltonian. The result is[2]

$$\alpha = (nh\nu/2h^2\rho v^3)\left|\langle i|H_{SL}|j\rangle\right|^2 g(\nu), \tag{2}$$

where α is the exponential attenuation factor per unit length, n is the population-density difference for the two energy levels of interest, ρ is the density of the sample, v is the velocity of the ultrasonic wave, $g(\nu)$ is the normalized resonance line-shape function, and $\langle i|H_{SL}|j\rangle$ is the matrix element of the spin-lattice Hamiltonian for the two energy levels. Experimental determination of the attenuation thus allows evaluation of H_{SL}.

A. U^{4+}:CaF2

Tetravalent uranium, an actinide, has two 5f electrons, which are responsible for its paramagnetic properties. The free-ion ground state, $^3H_4$, splits into three singlets and three non-Kramers doublets in the crystalline field of calcium fluoride. A doublet and a singlet lie lowest in energy, with the ground state a doublet. The doublet and singlet are considered to form a split triplet described by a spin Hamiltonian of the form [3]

$$H_S = g_{\parallel}\beta B_z S_z + g_{\perp}\beta B_{\perp} S_{\perp} + D[S_z^2 - 1/3S(S+1)] , \tag{3}$$

with effective spin, S = 1. The zero-magnetic-field splitting of the doublet and singlet is given by D, and the other symbols have their usual meaning.

The spin-lattice Hamiltonian corresponding to this description is[3]

$$H_{SL} = \sum_{ij} D_{ij} S_i S_j \quad , \tag{4}$$

where

$$D_{ij} = \sum_{ijk\ell} G_{ijk\ell} u_{k\ell} \; . \tag{5}$$

The tensor of which $G_{ijk\ell}$ is a component is called the spin-lattice coupling tensor.

B. Ce^{3+}:CaF_2

Trivalent cerium, a lanthanide, has one 4f electron, which is responsible for its paramagnetic properties. The free-ion ground state, $^2F_{5/2}$, splits into three Kramers doublets in the crystalline field of calcium fluoride. The spin Hamiltonian for the ground state is

$$H_S = g_{\parallel} \beta B_z S_z + g_{\perp} \beta B_{\perp} S_{\perp} \quad , \tag{6}$$

with effective spin, S = 1/2. The corresponding spin-lattice Hamiltonian is

$$H_{SL} = \sum_{ij} D_{ij} B_i S_j \quad , \tag{7}$$

where D_{ij} is defined as in equation (5).

The attenuation of elastic waves by trivalentcerium should be magnetic field dependent and the attenuation of elastic waves by tetravalent uranium should not, in the first approximation. Also, because of the Kramers doublet nature of Ce^{3+}, the interaction should be much weaker than that of the Kramers doublet U^{4+}. Similar arguments can be given for other rare earth ions in calcium fluoride.

Experimental Method:

Ultrasonic paramagnetic resonance involves the measurement of the attenuation of a high-frequency elastic wave in a paramagnetic crystal when the crystal is located in an external magnetic field of magnitude corresponding to electron paramagnetic resonance at the frequency of the elastic wave. A block diagram of the UPR spectrometer is given in Figure 1.

A piezoelectric quartz transducer is bonded to the specially fabricated paramagnetic sample and placed in a tunable, reentrant, resonant cavity. The cavity is immersed in a bath of liquid helium in the inner dewar of a double dewar cryostat placed between the pole pieces of a twelve-inch Varian electromagnet with special field-control and field-sweep power supply. Pulses of electromagnetic energy at a frequency of approximately 9.3 gigahertz and a duration of the order of one microsecond are transmitted from an RK6229 tunable magnetron at a repetition rate of 100 to 1000 pulses per second to the sample cavity. By means of the piezoelectric effect, the pulses of electromagnetic energy are converted into pulses of elastic energy by the transducer. The elastic wave propagates through the bonding material into the sample and reflects from the other end of the sample. The resulting pulse-echo pattern excites echo pulses of electromagnetic energy in the cavity by means of the inverse piezoelectric effect. These pulses travel through a precision calibrated attenuator and are detected by a superheterodyne receiver. The detected output of the receiver is sent through the Hewlett-Packard Display Scanner to a recorder. This recorder signal is a DC level which depends on the amplitude of some chosen echo. If the magnetic field is then swept linearly, the recorder presents a graph of amplitude of the n'th echo as a function of magnetic field. The precision attenuator allows one to measure the attenuation in decibels by comparison.

Discussion:

During the course of this investigation, it is planned that the direct spin-lattice interaction of ions from the lanthanide group such as Ce^{3+}, Pr^{3+}, Yb^{3+}, Tm^{3+} be compared with the interaction of ions from the actinide group such as U^{4+}, U^{3+}, all in calcium fluoride. The expected experimental results will allow the determination of the proper spin-lattice Hamiltonian for the ions, and therefore provide important information about the direct process.

During the first six months of this project, the major effort has been given to the design, construction, and/or purchase of the components of the UPR spectrometer and its support equipment. Because of the complex experimental problem of generating and detecting high-frequency elastic waves, it is necessary to have some means of testing the bonds at room temperature. This cannot be done at 9.3 gigahertz because of the very strong intrinsic attenuation of the sample. However, it is possible at room temperature for frequencies of the order of one gigahertz. Because of this need, and the applicability of the lower frequency equipment to many other ultra sonics studies in solids, funds have been provided by Southern Methodist University for the microwave ultrasonics apparatus illustrated in Figure 2.

At present, final design and construction of the apparatus is in progress, and should be completed within the next two months. It is expected that all necessary components will be operational by then and the proposed experimental investigation can begin.

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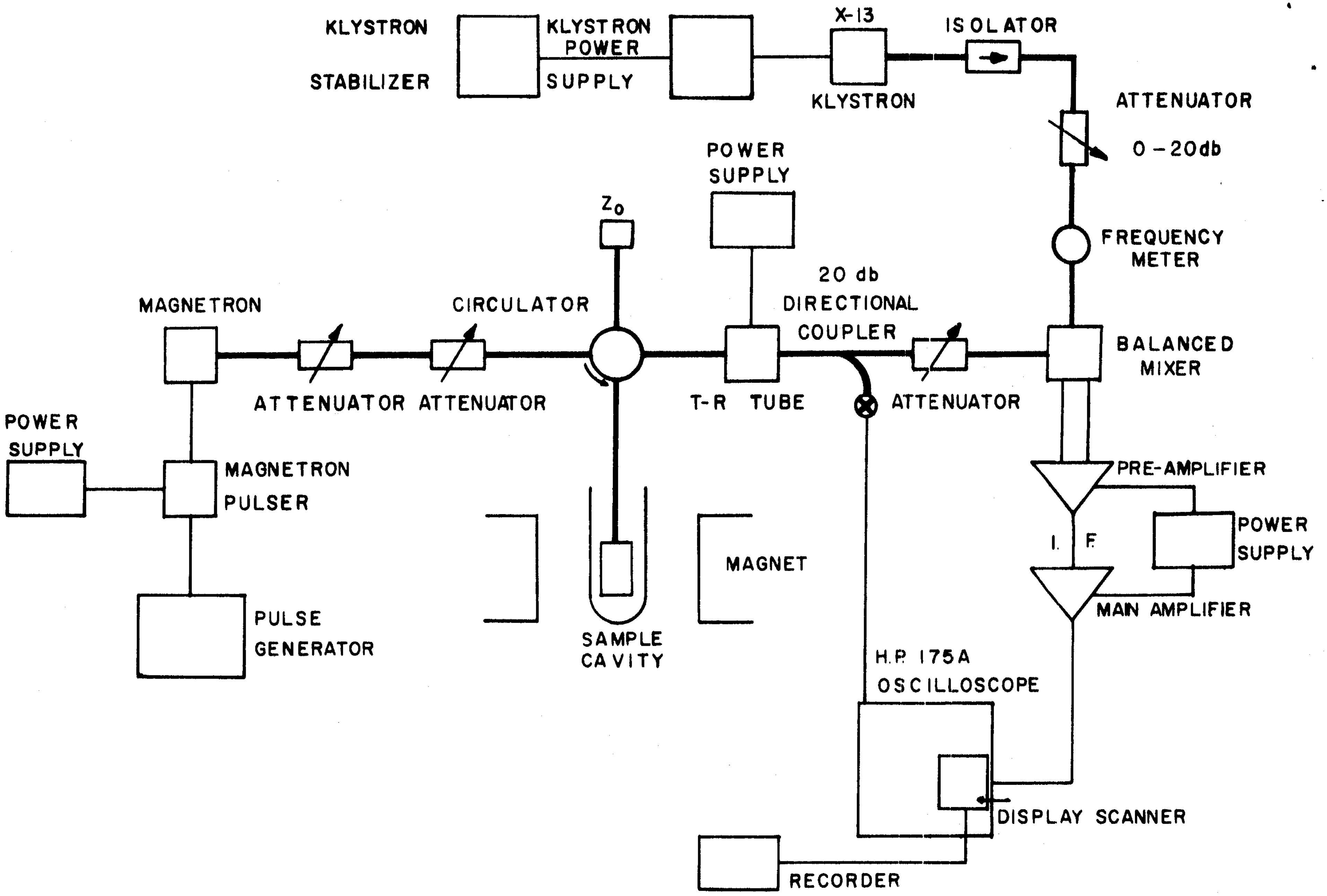

Figure 1

ULTRASONIC-PARAMAGNETIC-RESONANCE SPECTROMETER

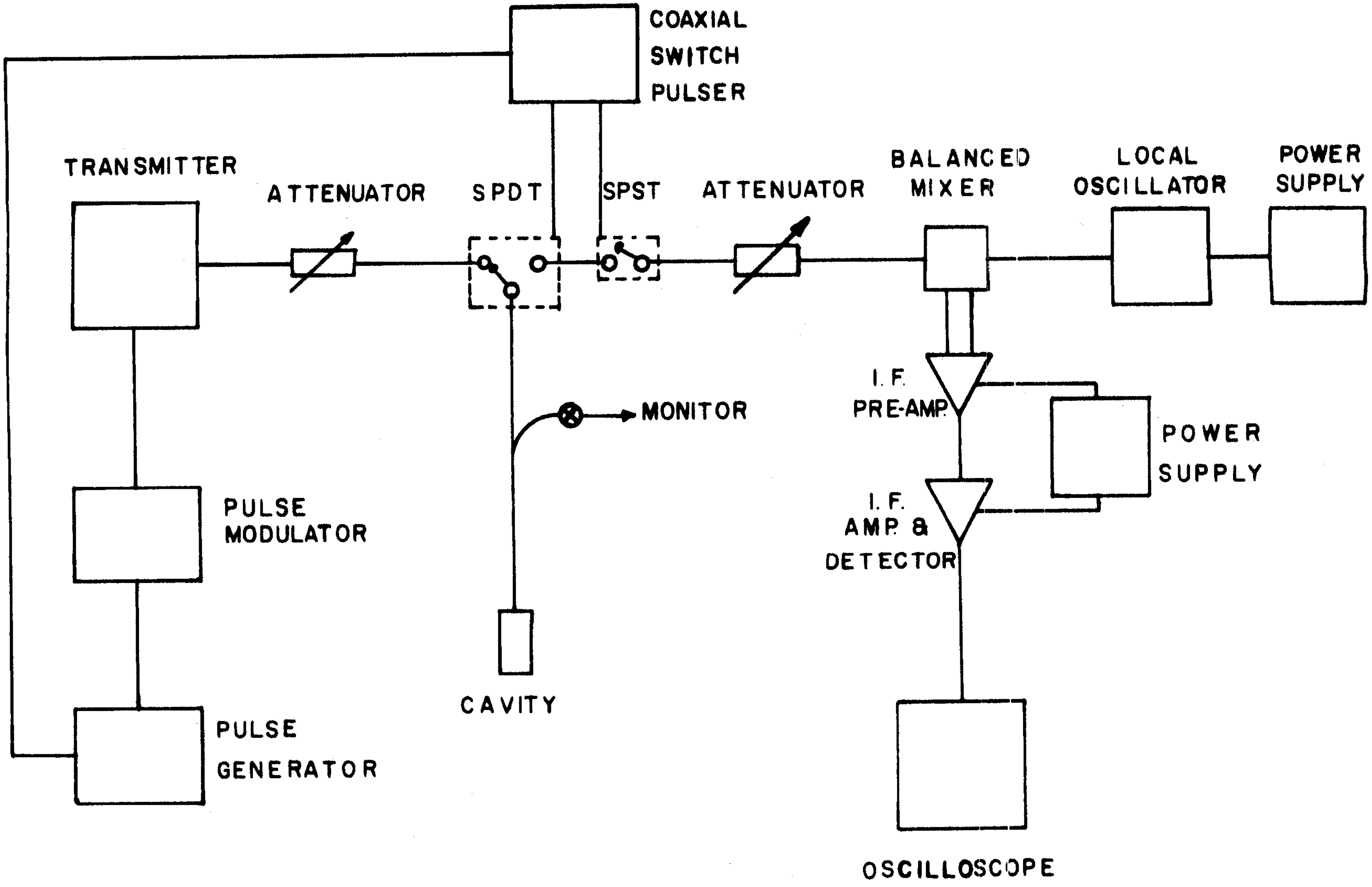

Figure 2

MICROWAVE ULTRASONICS APPARATUS