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THE ELECTRICAL CONDUCTIVITY OF SOME CRYOGENIC FLUIDS

By

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ABSTRACT

Cryogens (liquefied gases with low boiling points) are, in general, excellent insulators. Prior to this investigation, no measurements of conductivity in cryogens had been successful. An upper limit of conductivity in the range 10^{-15} to 10^{-17} mho/cm had been established for some cryogens. Data from the organic chemicals and petroleum industries indicated that fluids with conductivities in the 10^{-11} to 10^{-15} mho/cm range could present electrostatic potential hazards, particularly in situations of large volume storage and high flow rates. The advent of large capacity dewars and associated high flow rates of cryogens in the aerospace industry led to concern about this hazard. Liquid hydrogen, because of the associated explosion hazard, was of particular interest. Measurements of the electrical conductivity of several cryogens were proposed to determine under what conditions, if any, cryogens could present an electrostatic potential hazard.

Apparatus was designed and fabricated which could condense and hold a sample of the cryogen under investigation for a period of several hours. This sample volume incorporated paths for electrical conduction through the cryogen. An equation was derived for the resistivity (reciprocal of conductivity) of the material contained in the sample volume in terms of the geometry and the resistance

measured through the sample material. Correction for fringing fields was made by comparison of the calculated and the measured capacitance of the system.

The resistance was measured by two methods. The primary method was the measurement of the current produced by a known potential difference. An electrometer amplifier with a maximum sensitivity of 10^{-15} ampere full scale was employed for this measurement. The second method used was to observe the decay of an applied charge with an electrostatic voltmeter. The RC time constant of the system was on the order of 6×10^5 seconds so only small voltage increments were obtainable in the time available.

Measurements were made on six cryogens. These were liquefied hydrogen, deuterium, argon, nitrogen, carbon monoxide, and chlorotrifluoromethane.

The resistivity or conductivity of the cryogens appears to be a function of the applied voltage gradient. In other words, the cryogens tend to act as constant current sources. Electrometer amplifier data indicated a resistivity range of 5.75×10^{15} ohm-cm at 245 volts/inch for deuterium to about 10^{20} ohm-cm at the same gradient for carbon monoxide. Electrostatic voltmeter data agreed to within a factor of four for the four most conductive cryogens with poorer agreement in the cases of the two least conductive fluids.

It is postulated, on the basis of measurements made by others on gases and data taken in this investigation, that cryogens are intrinsically perfect insulators. Observed conduction is believed to be due to the presence of charge carriers produced by ionizing radiation present as natural background. In the case of deuterium, the presence of tritium as an impurity in a concentration of about one part per billion produced enough radiation to make quantitative calculations possible and good support for this hypothesis was obtained. A calculation for the remaining cryogens, based on a reasonable assumption of local cosmic ray activity, indicates sufficient energy availability to account for the observed currents.

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INTRODUCTION

The usual design practice for electronic instrumentation to be installed in cryogens (liquefied gases with low boiling points) is to consider thermal stresses, seals for the necessary wires, spark hazard, heat dissipation, and similar physical problems. No consideration is given to leakage currents through the cryogen from exposed elements of differing potential since, for practical purposes, the electrical conductivity of cryogens is not significant.

In recent years however, cryogenic systems of large volume and flow rates have come into existence. Dewars with capacities of hundreds of thousands of gallons and associated flow rates of thousands of gallons per minute have created the possibility of an electrical problem of another nature, that of electrostatic potentials. The petroleum and organic chemicals industries have been aware of this problem for some time and have established that the dangerous range of conductivity appears to be from 10^{-11} mho/cm to 10^{-15} mho/cm for quite pure liquids.¹ A determination of the electrical conductivity of cryogens to determine whether electrostatic potentials can be generated was thus desirable. Liquid hydrogen, because of the possible explosion hazard, was of particular interest.

¹ D. I. Saletan, "Electrostatic Considerations in the Organic Chemicals Industry," Paper presented to the AIChE, New York section, Oct..23, 1958.

A literature search for this property in cryogens produced little information. Wolfke and Keesom² attempted to determine this property for liquid helium and they concluded that the conductivity was less than 10^{-15} mho/cm since that was the maximum sensitivity of their apparatus and no conductivity was observed.

The first measurements in connection with the present work were made in 1961 on liquid hydrogen. The apparatus consisted of two concentric brass cylinders suspended from a polytetrafluoroethylene (Teflon) ring and immersed in a dewar of liquid hydrogen. The ratio of the voltage drop across the input impedance of a voltmeter to the drop across the series connected annulus gave an impedance ratio. Knowledge of the meter input impedance, applied voltage, and geometry then permitted calculation of the desired information.

Three serious limitations were found in this arrangement. The boiling of the liquid hydrogen introduced a large noise signal, the system was very susceptible to electrostatic perturbations, and the leakage resistance limited conductivity determinations to 10^{-16} mho/cm.

In the same year Cassutt et al.,³ also investigated the electrostatic hazard problem. The apparatus used had a limit of measurement

² W. H. Keesom, Helium, (Amsterdam: Elsevier, 1942) p. 324.

³ L. Cassutt, D. Biron, B. Vonnegut, Advances in Cryogenic Engineering, VII ed. K. D. Timmerhaus, (New York: Plenum Press, Inc., 1962), pp. 327-35.

which led to the conclusion that liquid hydrogen had a conductivity of less than 10^{-17} mho/cm. The conductivity of liquid hydrogen was the only data reported.

Liquid hydrogen did not appear to represent an electrostatic potential hazard. The failure to measure any detectable current left an area of uncertainty. No information was obtained which might indicate under what circumstances, if any, liquid hydrogen could become sufficiently conductive to generate electrostatic potentials. Further, other cryogens had not received even as much attention as liquid hydrogen. More sensitive measurements applied to a range of cryogenic fluids were proposed in order to determine what conductivity, if any, cryogens possess and what mechanisms appear to be significant in producing any observed electrical conductivity.

CHAPTER I

MEASUREMENT TECHNIQUES

Three aspects of the problem were considered in the design of better apparatus for making conductivity measurements of cryogens.

1. The apparatus should provide conduction paths of large cross section and short length through the cryogen while maintaining excellent electrical isolation of structural members. It was felt that only in this fashion could measurable currents be obtained.
2. The sample volume should be able to hold the cryogen under investigation for several hours with no boiling taking place in the sample. This suggested a closed container immersed in a condensing bath.
3. A method of measuring small currents or large resistances with suitable transition between ambient and cryogenic environments was needed.

Figures 1 through 5 show the resulting design. Figure 1 shows a vertical section through the apparatus. A dewar was placed on a base and a flange placed on the open end. This flange was held in place and rendered leak tight by a flat gasket and a system of tie rods to the base. A cover plate which was bolted to this flange and sealed by an O ring in a groove had all of the necessary pass throughs, seals, and the sample volume mounted on it.

Figure 2 is a section through the sample volume. A family of six concentric annuli are formed by nesting 2, 4, and 6 inch OD tubing into 1, 3, 5, and 7 inch OD tubing with the 7 inch tubing forming the wall of the closed container. Hard drawn brass tubing with one-eighth inch wall was chosen. Such tubing can be obtained within only a few thousandths of round, which is necessary to obtain good concentricity of the annuli. The resulting annuli are therefore three-eighths of an inch wide. Radial centering was accomplished by nonconductive screws at the bottom and a pin of the same material at the top. The 2, 4, and 6 inch cylinders were made into a rigid structure by a cross structure at the top with a hole for the centering pin. The electrical connection was made by bringing a wire through a glass to metal seal. This also provided for vertical positioning of the cylinders by making the test lead and seal carry the weight of the inner electrode. The centering devices were thus essentially load free.

Figure 3 is a photograph of the apparatus assembled. Purge and sample gas bottles are on the left, the dewar with pressure gauges and the electrometer amplifier measuring head in place are adjacent to the gas bottles, and the bench has on it such items as meters, capacitance bridge, electrometer amplifier, and a recorder. Figure 4 shows the sample volume out of the dewar. Wiring for the level sensors and the heater tape used to drive off the sample at the end of a run

can be seen. Figure 5 is a close-up of the flange from which the sample volume was suspended. Attention is directed to the clear plastic transition piece between the electrometer measuring head and the metal shield over the seal. This piece served the dual purposes of electrical isolation of the measuring head while maintaining a continuous dry gas purge on the seal and also permitted visual check that electrode contact was achieved between the electrometer measuring head and the test lead.

The initial assembly of this design provided a sample volume 28 inches long immersed in a dewar 34 inches deep. After assembly the leakage resistance was measured and proved to be about 2×10^{11} ohms. The conduction path provided by this geometry would have permitted resistivity measurements of about 10^4 times the leakage resistance or about 10^{15} ohm-cm. The limit of measurement under these conditions would, therefore, have been about 10^{-15} mho/cm. To reduce the leakage current a search was made for materials of lower surface and volume conductivity than glass and nylon. The materials also had to be amenable to fabrication into screws, seals, etc. Calculations indicated that measurements on samples one-fourth inch in diameter with electrodes one-half inch apart would closely simulate the leakage path of the apparatus. The results of this investigation are presented in Table 1.

FIG. 1. VERTICAL SECTION OF TEST APPARATUS

FIG. 2. VERTICAL SECTION THROUGH SAMPLE VOLUME

Figure 3
Experimental Apparatus

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Figure 4

Sample Volume Removed from Dewar

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Figure 5
Top View of Apparatus

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TABLE 1
EFFECT OF VARIOUS CLEANING PROCEDURES
ON SEVERAL INSULATING MATERIALS

Treatment	Resistance in ohms of materials							
	Quartz	Acrylic	Teflon	Glass	Nylon	Epoxy	Cork	Wood
Alcohol wash	--	3.6×10^{11}	5×10^{13}	5×10^{11}	3×10^{12}	1.3×10^{11}	3×10^{11}	--
Alcohol wash and bake	10^{15}	1.2×10^{15}	5×10^{14}	3×10^{14}	6×10^{12}	3×10^{12}	--	10^{11}
Wash, ultra- sonic clean, bake, and ceresin wax coat	10^{16}	10^{16}	----	----	----	----	--	--

The important item to note in Table 1 is the effect of the ceresin coating. Ceresin exhibits a volume conductivity of less than 2×10^{-18} mho/cm as does fused quartz which has been cleaned with chromic acid. However, at 90% humidity, ceresin has a surface conductivity of less than 10^{-17} mho/cm compared to a value of 5×10^{-9} mho/cm for quartz.⁴ Ceresin is a wax and thus does not have the mechanical properties for support structures. It possesses a great utility as a coating for cleaned surfaces to prevent re-adsorption of moisture and was so employed.

The approximately 10^{-14} mho/cm volume conductivity of glass led to a redesign of the glass to metal seal. A graded seal with a quartz section going through Pyrex to glass to metal was fabricated as a substitute.

The nylon centering pin was replaced by a thin wall acrylic tube and the nylon screws were replaced by acrylic screws. All parts were cleaned in alcohol and trichloroethylene, cleaned in an ultrasonic cleaner, and baked at 100°C for twelve hours. Higher temperatures were detrimental to acrylic parts. A container of molten ceresin was placed in the oven and all parts dipped prior to removal from the oven. The apparatus was assembled as quickly as possible and then evacuated to a pressure of less than five microns of mercury absolute pressure to prevent recontamination of insulator surfaces. The only exception was the outer surface of the graded seal, which was exposed to the atmosphere.

⁴ Handbook of Chemistry and Physics, ed. C. D. Hodgman, (32d ed.; Cleveland: Chemical Rubber Pub. Co., 1950) pp. 2114-15.

A metal shield was fabricated for this seal which permitted access to the test lead. A process of drying and purging this surface will be described below. This arrangement yielded a leakage resistance of between 10^{15} and 10^{16} ohms. The sample volume was reduced from 28 inches in length to 10 inches at this time. This greatly simplified the practical problem of condensing and holding a sample.

Relationships of Geometry and Resistivity

The conductivity of the cryogenic sample was the parameter to be determined and the relationship between conductivity and resistance or current measurements must be established from geometrical considerations.

Consider two perfectly conductive cylinders of radii r_i and r_o as shown in Figure 6. If a material of conductivity σ fills the annulus between the cylinders and a potential difference V exists between the cylinders, a current will flow in the dielectric material.

Figure 6.-Annulus and radii

The following assumptions are made:

1. The cylinders are of length L .
2. End effects are negligible, i.e., $L \gg r_o - r_i$.
3. The total current between the cylinders is I .

Consider an annular segment at r of thickness dr . By symmetry, this is an equipotential surface. Because of the current I , a voltage drop dV exists across the segment. The definition that $R = \rho L/A$ where ρ is the reciprocal of σ leads, for constant ρ and A to $dR = \rho/A dL$. For this geometry dL is equivalent to dr and $A = 2\pi rL$. Substitution gives $dR = (\rho/2\pi L)(dr/r)$. From this

$$V = \int_{r_i}^{r_o} dV = \frac{\rho I}{2\pi L} \int_{r_i}^{r_o} \frac{dr}{r} = \frac{\rho I}{2\pi L} \ln \frac{r_o}{r_i} \quad (1-1)$$

$$\rho = \frac{2\pi L}{\ln r_o/r_i} \frac{V}{I} \quad (1-2)$$

The ratio V/I has the units of resistance and will be noted as R , a measured resistance. Thus,

$$\rho = \frac{2\pi L}{\ln r_o/r_i} R \quad (1-3)$$

For the case under consideration, I is the sum current from a number of parallel paths. Solving Equation 1-2 for current and expressing each of the component currents in this form yields

$$I = \frac{2\pi LV}{\rho} \left(\frac{1}{\ln r_1/r_2} + \frac{1}{\ln r_2/r_3} + \dots \right) \quad (1-4)$$

Equation 1-4 can be solved for ρ .

$$\rho = 2\pi LR \left(\frac{1}{\ln r_1/r_2} + \frac{1}{\ln r_2/r_3} + \dots \right) \quad (1-5)$$

Substitution of the dimensions of the apparatus, expressed in centimeters, gives ρ in units of ohm-cm.

$$\rho = 2\pi R \left[\frac{17.62}{\ln \frac{6.75}{6}} + 15.24 \left(\frac{1}{\ln \frac{5.75}{5}} + \frac{1}{\ln \frac{4.75}{4}} + \frac{1}{\ln \frac{3.75}{3}} + \frac{1}{\ln \frac{2.75}{2}} + \frac{1}{\ln \frac{1.75}{1}} \right) \right] \quad (1-6)$$

or

$$\rho = 3083R \text{ ohm-cm} \quad (1-7)$$

It is useful to calculate the capacitance of the system since it provides a method of correcting for fringing fields. Because of the overlapping of cylinders and the proximity of end plates, this was not an optimum cylindrical geometry and appreciable fringing was present.

The capacitance of a cylindrical capacitor is given by

$$C = \frac{2\pi \epsilon S}{\ln r_o/r_i} \text{ farad where } \epsilon \text{ is approximately } \frac{1}{36\pi \times 10^9} \text{ for a vacuum.}$$

S is equivalent to L in Equations 1-1 through 1-5, but is expressed in meters. The radii are again r_o and r_i . The total capacitance is the sum of the parallel capacitances or

$$C_t = \frac{S}{36\pi 10^9} \left[\frac{1}{\ln r_1/r_2} + \frac{1}{\ln r_2/r_3} + \dots \right] \quad (1-8)$$

Comparison with Equation 1-5 reveals that C_t and ρ differ only by a constant and R , an experimentally determined value. Since the dielectric constant of many cryogenics is known, the capacitance can be both calculated and measured. Comparison of the two values will yield a correction term. In Equation 1-8 this may be considered a correction on S . The effect of the fringing field is to increase the measured capacitance above the calculated value and S must be multiplied by the ratio $C_t^{\text{measured}}/C_t^{\text{calculated}}$ which will be designated C_c . By analogy, the effect on Equation 1-7 is to correct it to

$$\rho = C_c 3083R \text{ ohm-cm} \quad (1-9)$$

Equation 1-8 and the dimensions of the apparatus give a calculated value for C_t of 270.7 picofarad. A correction for the capacitance of the test lead may seem necessary. This capacitance can be shown by calculation to be only 0.204 picofarad. The resolution of the capacitance bridge used was one picofarad so the term will be neglected.

Measurement of Large Resistance

The classical method of measuring a large resistance is with an electrostatic voltmeter. Such a meter has a very high internal impedance and an associated shunt capacitance. Meter deflection is caused by torsional forces induced by placing a charge on this

capacitance. The resistor under test is connected across the input terminals and the meter charged to full voltage. The time rate of decay is noted to determine the unknown resistance. In this experiment an electrostatic voltmeter was used, but not as the primary method of measurement due to limitations which severely limited the accuracy obtainable. The meter used was a 120 volt model with an internal impedance of more than 10^{16} ohms and an internal capacitance of 200 picofarads at 120 volts. The system capacitance, with a sample in place, measured approximately 600 picofarads. The parallel resistance of the meter, the sample, and the support structure was about 10^{15} ohms. The RC time constant was on the order of 6×10^5 seconds or more than six days. Since two to three hours was all the time available for this measurement, only small voltage increments could be obtained.

The primary method of measurement was based on the measurement of the steady state current produced by a fixed potential across the sample. For this measurement a vibrating reed type of electrometer amplifier with a full scale sensitivity of 10^{-15} ampere and a recorder output was available.

Certain parameters of both measuring instruments had, of course, to be determined. Consider first the case where resistance of the sample was measured with an electrostatic voltmeter. Such a meter acts like a capacitance in parallel with an internal leakage resistance.

Since the sample volume is also effectively a parallel resistance and capacitance, the total system consists of two capacitances in parallel with two resistances. In principle, knowledge of the values of three of these components and observation of the voltage decay characteristic suffices to determine the value of the fourth component.

The capacitances involved were quite easy to measure directly. The internal resistance R_i of the voltmeter must be determined in an indirect manner. The technique involves charging the meter to full scale voltage and observing the voltage decay. The input capacitance is a function of the voltage indication however, and a simple RC time constant solution is not adequate. A solution to this type of problem has been obtained using Lagrange's equation.⁵ The solution is

$$R_i = \frac{t_1}{\frac{3}{4} \frac{\alpha^2}{K} (E_o^2 - E_f^2) + C_o \ln E_o / E_f} \quad (1-10)$$

for which t_1 is the time in seconds after the meter is disconnected from the voltage source, E_o is the initial voltage, E_f is the final voltage and K is the spring constant of the movement. The equation for meter capacitance defines C_o and α .

$$C = C_o + \alpha \theta \quad (1-11)$$

⁵ M. B. Broughton, "On Finding the Leakage Resistance of Electrostatic Voltmeters," IEEE Transactions on Education, E-VII (March, 1964), pp. 41-42.

In Equation 1-11, θ is the angle of meter movement in radians, α has units of farad per radian, and C_0 is a constant in farads.

The meter employed was a Sensitive Research Instrument Model ESD. This is a 120 volt, full-scale unit with 1% of full scale accuracy. Solution of Equation 1-10 required experimental evaluation of K , C_0 , and α . Measurements of meter geometry provided a relationship between voltage indication and angle in radians. Capacitance measurements then permitted solving for C_0 and α with the result that

$$C = (15.1 + 154.7 \theta) 10^{-12} \text{ farad} \quad (1-12)$$

The referenced publication⁶ includes the equation $\theta = \frac{\alpha}{2K} V^2$. From this, K could be derived and had a value of $9.6 \times 10^5 \frac{\text{farad volts}^2}{\text{radians}^2}$ over the range of 110 to 120 volts. Substitution into Equation 1-10 gives

$$R_1 = \frac{t}{1.87 \times 10^{-16} (E_O^2 - E_F^2) + 15.1 \ln E_O/E_F} \quad (1-13)$$

Several determinations were made for R_1 as given in Table 2. The resulting value for R_1 is 4.37×10^{16} ohms with a standard deviation of 0.38×10^{16} ohms.

⁶ Ibid.

TABLE 2
DETERMINATION OF ELECTROSTATIC VOLTMETER
INTERNAL RESISTANCE, R_i

Time, seconds	E_o , volts	E_f , volts	R_i , ohms
16,500	119.8	117.7	4.67×10^{16}
18,300	119.6	117.2	4.03×10^{16}
20,100	120	117.0	3.90×10^{16}
34,200	120	115.9	4.87×10^{16}
19,200	120	117.45	4.39×10^{16}

The only parameter to be established for the electrometer amplifier was the value of a feedback resistor. The particular instrument used was an Applied Physics Corporation Model 30. Figure 7 shows schematically how this instrument operates.

Figure 7.-Functional diagram of electrometer amplifier

The sample volume is shown on the left as contained between two electrodes with the structural leakage represented by the parallel resistance R_l . One side of this system is at ground potential G_1 , which happens to be local earth ground. The system is connected by a lead to the electrometer which has a reference ground potential G_2 . If a potential difference V is applied between G_1 and G_2 a current will tend to flow through R_l and the sample to the upper plate of C_v . C_v is a variable capacitor of the vibrating reed type and in accordance with the relationship $V = Q/C$, the charge accumulation on C_v appears as a varying voltage which is capacitively coupled into the electrometer amplifier. The amplifier output is demodulated to produce a DC voltage. The DC voltage is indicated on the 0-1 millivolt meter and is of such a polarity as to cause a current through feedback resistor R_{fb} which tends to neutralize the charge on C_v . The voltage across C_v is thus kept as near zero as the gain of the amplifier will permit and the steady state current in R_{fb} is equal to the current through R_l and the sample. It should be noted that current from G_1 to G_2 by other shunt paths does not enter the measuring loop and that therefore exceptionally good isolation is not a requirement. Three values of R_{fb} were used in the course of the experiment. These were 0.964×10^{12} ohms, 0.999×10^{10} ohms, and 0.996×10^9 ohms.⁷ The current fed back for a one millivolt indication

⁷ Office Memorandum from A. N. Shopp, Standards Laboratory, "Determine Value of Three Electrometer Input Resistors," July, 1964.

on the meter and a nominal 10^{12} ohm feedback resistor would be 10^{-15} ampere. This establishes the maximum sensitivity of the instrument.

CHAPTER II

EXPERIMENTAL PROCEDURES AND DETERMINATIONS

Six gases were chosen for evaluation. These were hydrogen, deuterium, argon, nitrogen, carbon monoxide, and chlorotrifluoromethane (Freon 13). The six included a simple molecule and its isotope, an inert gas, a common gas, and two of differing degrees of chemical complexity and molecular weight. The normal boiling points of these gases varied from 35 to 348 degrees Rankine.

Limitations were placed on the choices available since only liquid hydrogen, liquid nitrogen, liquid argon, and dry ice (solid CO₂) were available as refrigerants. In principle, a wide range of sample temperatures are available by varying the pressure on the condensing bath. From a practical viewpoint, the pressure variation with temperature is so great that equipment design and safety precautions become difficult.

Experimental Procedure

A typical experimental run is best described with reference to Figure 8. At the start of a run all valves were closed except VV1 and VV2. The sample volume was pumped down to a pressure of a few microns absolute. A pump and backfill purging cycle was employed to assure that all volumes which might contaminate the sample were filled only with pure sample gas. The quartz seal was dried by remelting

the ceresin coating with a stream of hot air. The metal shield was then replaced and a dry helium gas purge was maintained inside the shield for the duration of the run. The bath volume was then filled through the bath fill valve, BFV, to chill the apparatus to operating temperature. Bath liquid level was held between limits determined by the liquid level sensors. These sensors were one-tenth watt, thirty-ohm carbon resistors operating at about one-fourth watt dissipation. No damage occurs at this dissipation due to the low environmental temperature. A distinct difference in current occurs as the power dissipation changes during transition of the sensor from gas to liquid or liquid to gas.

When the apparatus was cool the sample gas was introduced. Condensation to the liquid phase occurred when the sample gas supply pressure was sufficient. Monitoring of both the quantity of gas still in the supply cylinder and the liquid level in the sample volume permitted termination of the condensation process when the sample was within three-eighths of an inch from the top of the sample volume. The time required to reach this stage was about four hours. The electrostatic voltmeter was then connected and charged to 120 volts. Periodic readings were taken for about two hours. The voltmeter was then replaced by the measuring head of the electrometer amplifier. Batteries were used to supply excitation of 6, 22.5, 45, 70, and 92 volts.

The resulting current indications of the electrometer were recorded on a strip chart recorder for several minutes at each potential. The polarity of the excitation was then reversed and a second set of data was taken. Finally, a capacitance measurement was made. During this time the sample volume was closed to all vents. The sample pressure was noted so that the relationship between vapor pressure and temperature could be employed to determine the temperature and density in the sample.

The sample was then vented through a gas meter with boiling induced by means of an electric heater. As soon as the liquid was evaporated the heater was turned off and a third set of electrometer data was taken with the sample volume filled with gas at about one local atmosphere pressure (about 585 mm Hg) and near the liquefaction temperature. Finally, the sample volume was pumped to a few microns of mercury absolute pressure and a fourth set of electrometer data was taken to get a measure of the leakage current with the equipment near the operating temperature.

Since such parameters as dielectric constant, density, and temperature depend upon the test conditions, these conditions, which will be useful in the discussion to follow, are tabulated in Table 3.

The conversions from vapor pressure to the other parameters are listed in references 3, 6, 8, 10, 14, 15, and 18. Deuterium gas and Freon 13 gas data could not be found directly and were calculated from the gas laws and compressibility factors.⁸

⁸ B. F. Dodge, Chemical Engineering Thermodynamics, (New York: McGraw-Hill Co., Inc., 1944) p. 161.

TABLE 3

SAMPLE PRESSURES AND IMPORTANT DEPENDENT PARAMETERS

Cryogen	Vapor Pressure mm Hg Absolute	Temperature deg Rankine	Liquid Density lb/ft ³	Gas Density lb/ft ³	Dielectric Constant
Deuterium	167	35	10.675	0.104	1.279
Argon	602	153.4	88.39	0.275	1.527
Freon 13	825	348	94	0.324	2.32*
Nitrogen	592	135	50.87	0.218	1.44
Hydrogen	585	34.8	4.54	0.059	1.23
Carbon Monoxide	1127	152.8	48.7	0.086	1.55*

* Not found in the literature search. Calculated as indicated in text.

Capacitance Measurements

The correction term to be derived from capacitance measurements is first considered. Dividing the measured capacitance by the dielectric constant for the particular cryogen gives a value for the capacitance of that portion of the system which contains the sample. Table 4 below gives the results for four of the cryogens. Two determinations are given for nitrogen and hydrogen. These represent two different runs made several days apart.

TABLE 4
CAPACITANCE MEASUREMENTS OF FILLED SAMPLE VOLUME

Cryogen	Measured Capacitance in Picofarads	Measured Capacitance, Divided by Sample Dielectric Constant
Deuterium	413	322.9
Argon	483	316.3
Nitrogen	460	319.4
Nitrogen	461	320.1
Hydrogen	398	323.7
Hydrogen	398	323.7

The data in Table 4 yield an effective capacitance for the sample volume of 321 picofarads with a standard deviation of 2.7 picofarads. No value could be found for the dielectric constants of liquid carbon monoxide and liquid Freon 13. The capacitance measurements taken for these fluids were divided by the 321 picofarad value obtained by use of the other four cryogens to give the dielectric constants shown in Table 3 for these two substances.

The ratio of measured capacitance to calculated capacitance is thus 1.185 and Equation 1-9 can be modified to correct for fringing fields.

$$\rho = 3.65 \times 10^3 \text{ R ohm-cm} \quad (2-1)$$

Resistance Measurements

The resistivity and its reciprocal, conductivity, can now be calculated on the basis of a measurement of R, the resistance of the current path through the cryogens. The primary method was measurement of the current which resulted from a known applied potential. Current measurements were made with gas and liquid in the sample volume and with the volume evacuated. Both positive and negative potentials were established between G_1 and G_2 . No significant variation in current magnitude was observed with change in polarity. A small current was often observed when G_1 and G_2 were shorted together. This anomaly

appears to be due to two different mechanisms. The primary reason was drift in the amplifier and its associated zero circuit, which was battery supplied. Frequent re-zero adjustments were necessary and contributed to the scatter in the data. Even when the zero was carefully adjusted a very small current, usually less than 10^{-15} ampere, would appear. This is probably due to random charge accumulations on the electrodes since the current varied in polarity and the average value over a period of several minutes appeared to be zero. The recorded output of the electrometer amplifier was examined for intervals which were apparently free of any change in average value, and which did not contain large perturbations such as those caused by line transients. Intervals of at least one minute duration were then integrated by means of a planimeter to obtain the average value of the current over the interval. These average values are plotted in Figures 9 through 26. Further smoothing was accomplished for most of these figures by calculating least square fit analytic functions. These functions, with the mean square error or standard deviation, are given in Table 5. No equation is given for gaseous deuterium and argon. In these instances a saturation effect was observed and an analytic function for the entire interval was not attempted.

The current observed when the sample volume was cold but evacuated is considered to represent the leakage. This current is subtracted from the currents observed with gas and liquid in the sample volume to obtain a net current due to the presence of the cryogen alone. Dividing this net current by the corresponding potential yields a value of resistance for the current path through the cryogen.

Fig.9 Current in Liquid Deuterium

K&E 5 X 5 TO THE 1/2 INCH 358-6
KEUFFEL & ESSER CO. MADE IN U.S.A.

Fig. 10 Current in Gaseous Deuterium

Fig. 12 Current in Liquid Argon

Fig. 13 Current in Gaseous Argon

Fig. 14 Leakage Current for Argon Run

K&E 5X5 TO THE 1/2 INCH 358.6
KEUFFEL & ESSER CO. MADE IN U.S.A.

Fig. 15 Current in Liquid Freon 13

K&E 5X5 TO THE 1/2 INCH 359-6
KEUFFEL & ESSER CO. MADE IN U.S.A.

Fig. 16 Current in Gaseous Freon 13

Fig. 17 Leakage Current for Freon 13 Run

Fig. 18 Current in Liquid Nitrogen

K&E 5X5 TO THE 1/2 INCH 358-6
KEUFFEL & ESSER CO. MADE IN U.S.A.

Fig. 19 Current in Gaseous Nitrogen

Fig. 20 Leakage Current for Nitrogen Run

K&E 5 X 5 TO THE 1/2 INCH 358-6
KEUFFEL & ESSER CO. MADE IN U.S.A.

Fig. 21 Current in Liquid Hydrogen

Fig. 22 Current in Gaseous Hydrogen

Fig. 23 Leakage Current for Hydrogen Run

Fig. 24 Current in Liquid Carbon Monoxide

K&E 5 X 5 TO THE 1/2 INCH 358-5
KEUFFEL & ESSER CO. MADE IN U.S.A.

Fig. 25 Current in Gaseous Carbon Monoxide

K&E 5 X 5 TO THE 1/2 INCH 358-6
KEUFFEL & ESSER CO. MADE IN U.S.A.

Fig. 26 Leakage Current for Carbon Monoxide Run

TABLE 5

EQUATIONS OF OBSERVED CURRENTS AND STANDARD DEVIATION OF THE DATA

Condition	Equation, $6 \leq V \leq 92$	Standard Deviation
Liquid deuterium	$I = (2.58 + 8.25 \times 10^{-2} V - 5.13 \times 10^{-4} V^2) 10^{-11}$	2.5×10^{-12}
Gaseous deuterium	No equation, saturated at 4.8×10^{-11} ampere	-- --
Leakage, deuterium	$I = (3.4 + 2.33 \times 10^{-1} V) 10^{-16}$	2.36×10^{-16}
Liquid argon	$I = (7.0 + 2.11V - 8.9 \times 10^{-3} V^2) 10^{-14}$	5.9×10^{-16}
Gaseous argon	No equation, saturated at 1.5×10^{-13} ampere	-- --
Leakage, argon	$I = (1.89 + 2.23 \times 10^{-2} V) 10^{-14}$	3.1×10^{-16}
Liquid Freon 13	$I = (9.4 + 9.79 \times 10^{-2} V) 10^{-14}$	2×10^{-16}
Gaseous Freon 13	$I = (-2.23 + 4.15 \times 10^{-1} V) 10^{-14}$	1.6×10^{-16}
Leakage, Freon 13	$I = (3.96 + 3.31 \times 10^{-1} V) 10^{-16}$	1.4×10^{-16}
Liquid nitrogen	$I = (3.1 + 4.55 \times 10^{-2} V - 2.73 \times 10^{-4} V^2) 10^{-14}$	4.1×10^{-16}
Gaseous nitrogen	$I = (4.0 + 1.51 \times 10^{-1} V - 6.39 \times 10^{-4} V^2) 10^{-14}$	1.1×10^{-14}
Leakage, nitrogen	$I = (3.31 + 3.57 \times 10^{-1} V) 10^{-16}$	2.5×10^{-16}
Liquid hydrogen	$I = (1.34 + 7.37 \times 10^{-3} V) 10^{-14}$	9×10^{-16}
Gaseous hydrogen	$I = (2.39 + 9.79 \times 10^{-3} V) 10^{-14}$	3.8×10^{-16}

TABLE 5-Continued

Condition	Equation, $6 \leq V \leq 92$	Standard Deviation
Leakage, hydrogen	$I = (4.03 + 7.1 \times 10^{-2}V)10^{-15}$	1.9×10^{-16}
Liquid carbon monoxide	$I = (2.92 + 4.02 \times 10^{-2}V)10^{-14}$	7.5×10^{-16}
Gaseous carbon monoxide	$I = (4.93 + 1.87 \times 10^{-1}V - 2.66 \times 10^{-3}V^2 + 1.29 \times 10^{-5}V^3)10^{-13}$	3×10^{-16}
Leakage, carbon monoxide	$I = (2.35 + 4.36 \times 10^{-2}V)10^{-14}$	3.6×10^{-14}

This is then used in Equation 2-1 to calculate the resistivity. Table 6 shows the relationships used in the calculation and Figures 27 through 32 show the results graphically. The leakage current is comparable in magnitude to the net current in the cases of nitrogen and hydrogen and larger in the case of carbon monoxide. This produces an uncertainty in the measurement which becomes worse at higher potentials. This increased uncertainty is due to the fact that cryogenes, as can be seen from the Net Liquid column of Table 6, tend to act as constant current sources while the leakage current is proportional to applied potential. Nitrogen and carbon monoxide resistivities are plotted as two curves in Figures 30 and 32. One curve is plotted directly from the tabulations in Table 6. The other, linear, plot is based on the average value of the current over the voltage interval. Significant disagreement between the methods begins to be apparent above 60 to 70 volts.

The electrostatic voltmeter measured the resistance of the sample volume directly. Data were taken in the same manner as for the determination of R_1 , the internal resistance. The connection of the sample volume changed only the value of the C_0 term in Equation 1-10. The value of R obtained may be defined as R_m which represents the parallel impedance of R_1 and the apparent resistance R_a of the sample volume.

TABLE 6

ELECTROMETER AMPLIFIER DATA AND RESISTIVITY DETERMINATIONS

Volts	Currents					Ohms Resistance Through Liquid	Resistivity, ohm-cm, liquid
	Liquid	Gas	Leakage	Net Liquid	Net Gas		
Deuterium							
6	3.05×10^{-11}	4.5×10^{-11}	0.55×10^{-14}	3.05×10^{-11}	4.5×10^{-11}	1.97×10^{11}	0.75×10^{15}
22.5	4.17	4.7	0.93	4.17	4.7	5.4	1.97
45	5.25	4.8	1.44	5.25	4.8	8.57	3.13
70	5.84	4.8	2.0	5.84	4.8	12.0	4.38
92	5.82	4.8	2.48	5.82	4.8	15.8	5.77
Argon							
6	1.93×10^{-13}	6.4×10^{-14}	2.02×10^{-14}	1.73×10^{-13}	4.38×10^{-14}	3.46×10^{13}	1.26×10^{17}
22.5	5.0	11.4	2.39	4.76	9.0	4.73	1.73
45	8.39	14.5	2.89	8.10	11.6	5.55	2.03
70	11.1	15.0	3.45	10.8	11.6	6.51	2.38
92	12.6	15.0	3.94	12.2	11.1	7.55	2.76
Freon 13							
6	9.99×10^{-14}	0.262×10^{-14}	0.59×10^{-14}	9.4×10^{-14}	-- --	0.64×10^{14}	0.233×10^{18}
22.5	11.61	7.11	1.14	10.47	5.97×10^{-14}	2.15	0.785
45	13.81	16.45	1.88	11.93	14.57	3.77	1.38
70	16.25	26.83	2.71	13.54	24.12	5.17	1.89
92	18.41	35.97	3.44	14.97	32.53	6.15	2.24

TABLE 6-Continued

Volts	Currents					Ohms Resistance Through Liquid	Resistivity ohm-cm, liquid
	Liquid	Gas	Leakage	Net Liquid	Net Gas		
Nitrogen							
6	3.36×10^{-14}	4.89×10^{-14}	0.545×10^{-14}	2.82×10^{-14}	4.34×10^{-14}	0.213×10^{15}	0.078×10^{19}
22.5	3.99	7.08	1.13	2.85	5.95	0.789	0.288
45	4.60	9.52	1.94	2.66	7.58	1.69	0.617
70	4.95	11.1	2.83	2.12	8.27	3.30	1.20
92	4.98	12.5	3.61	1.37	8.90	6.73	2.46
Hydrogen							
6	1.39×10^{-14}	2.45×10^{-14}	0.45×10^{-14}	9.41×10^{-15}	2.0×10^{-14}	0.638×10^{15}	0.233×10^{19}
22.5	1.51	2.61	0.56	9.45	2.05	2.38	0.869
45	1.67	2.83	0.72	9.51	2.11	4.73	1.73
70	1.86	3.08	0.90	9.58	2.18	7.31	2.67
92	- - -	3.29	1.06	- - -	2.23	- - -	- - -
Carbon Monoxide							
6	3.16×10^{-14}	6.0×10^{-13}	2.6×10^{-14}	5.59×10^{-15}	5.74×10^{-13}	0.107×10^{15}	0.39×10^{19}
22.5	3.82	7.99	3.33	4.91	7.66	0.458	1.67
45	4.73	9.21	4.31	4.16	8.78	1.08	3.94
70	5.73	9.56	5.40	3.30	9.02	2.12	7.74
92	6.61	9.95	6.36	2.54	9.31	3.62	13.2

Fig. 27 Resistivity of Liquid Deuterium

Fig. 28 Resistivity of Liquid Argon

K&E 5 X 5 TO THE 1/2 INCH 358-6
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Fig. 29 Resistivity of Liquid Freon 13

142 5X5 TO THE 1/2 INCH 358-6
KEUFFEL & ESSER CO. MADE IN U.S.A.

Fig. 30 Resistivity of Liquid Nitrogen

Fig. 31 Resistivity of Liquid Hydrogen

K&E 5X5 TO THE 1/2 INCH 358-6
KEUFFEL & ESSER CO. MADE IN U.S.A.

Fig. 32 Resistivity of Liquid Carbon Monoxide

The equation for two parallel resistances R_1 and R_a is

$$R_m = \frac{R_1 R_a}{R_1 + R_a} \quad (2-2)$$

This can be solved for R_a , resulting in

$$R_a = \frac{R_1 R_m}{R_1 - R_m} \quad (2-3)$$

R_a is itself a parallel impedance composed of the leakage path R_l and the sample path R_s . The process above can be repeated to get an equation for R_s .

$$R_s = \frac{R_l R_a}{R_l - R_a} \quad (2-4)$$

The values of R_l from Figures 10, 13, 16, 19, 22, and 25 and the values of R_a calculated from Equation 2-3 permit calculation of R_s in Equation 2-4. The resistivity can then be calculated from Equation 2-1. Table 7 presents the data and resistivity determinations for the electrostatic voltmeter measurements.

A comparison of the resistivity values given by the two methods is given in Table 8 with the ratios shown. The resistivity given for the electrometer amplifier measurements has been extrapolated to 120 volts for convenience.

TABLE 7

ELECTROSTATIC VOLTMETER DATA AND RESISTIVITY DETERMINATIONS

Cryogen	Time, seconds	E_o , volts	E_f , volts	C_o , picofarads	R_m , ohms	R_a , ohms	R_s , ohms	ρ , ohm-cm
Nitrogen	7,200	118.7	113.3	475	3.2×10^{14}	3.2×10^{14}	3.61×10^{14}	1.32×10^{18}
Nitrogen	5,700	119.8	118.2	476	8.8×10^{14}	8.98×10^{14}	1.32×10^{15}	4.82×10^{18}
Hydrogen	6,300	120	119.2	413	2.25×10^{15}	2.37×10^{18}	2.85×10^{15}	1.04×10^{19}
Hydrogen	9,000	120	117	413	8.49×10^{14}	8.66×10^{14}	9.23×10^{14}	3.37×10^{18}
Deuterium	210	120	110.4	428	5.82×10^{12}	5.82×10^{12}	5.82×10^{12}	2.12×10^{18}
Argon	6,000	119.9	111.7	498	1.68×10^{14}	1.68×10^{14}	1.75×10^{14}	6.39×10^{17}
Carbon Monoxide	3.960	120	118	511	4.56×10^{14}	4.61×10^{14}	5.77×10^{14}	2.11×10^{18}
Freon 13	3.600	120	117.6	761	2.33×10^{14}	2.33×10^{14}	2.52×10^{14}	9.2×10^{17}

TABLE 8
COMPARISON OF RESISTIVITIES AS DETERMINED BY TWO METHODS

Cryogen	Electrostatic Voltmeter Measurement, ohm-cm	Electrometer Amplifier Measurement, ohm-cm	Ratio, EA/EVM
Deuterium	2.12×10^{16}	7.4×10^{15}	0.35
Argon	6.39×10^{17}	3.23×10^{17}	0.50
Freon 13	9.2×10^{17}	2.6×10^{18}	2.83
Nitrogen	1.32, 4.82×10^{18}	1.85×10^{19}	3.84*
Hydrogen	3.73, 10.4×10^{18}	4.6×10^{19}	13.6*
Carbon Monoxide	2.11×10^{18}	1.06×10^{20}	50.2

*Ratio uses the determination with the longest time base when two values are given.

It will be noted that the agreement is best for the three best conductors, fair for the next best, and worst for the two least conductive fluids. The carbon monoxide run was complicated by larger than usual leakage current. This was probably due to the difficulty of maintaining the outer surface of the glass seal dry for the run interval of over 17 hours.

CHAPTER III

MECHANISMS INFLUENCING CONDUCTIVITY

The electrical conductivity of cryogens was a relatively unknown property at the beginning of this investigation. Inability to measure any current at all would not have been surprising since previous investigations had been unsuccessful. Since a small but finite current was observed, the question of mechanism and determining parameters must be considered.

The measurements made on gases at standard temperature and pressure (hereafter simply STP) make a good starting point. During the decade between 1900 and 1910 the electrical conductivity, if any, of air was a matter of some discussion and dissent. Careful measurements established that some conduction did take place. Any assumption of an internal mechanism of ion generation, such as thermal agitation, was rejected. Ionizing radiation was postulated and a number of experiments to verify this led to the discovery of cosmic rays.⁹ The conclusion that cosmic rays exist and induce ion pairs was generally accepted by 1926. On this basis and considering also the low temperatures of cryogens, which further reduces the possibility of thermal ion production, it is postulated that cryogens are intrinsically

⁹L. Janossy, Cosmic Rays, (Oxford: Clarendon Press, 1950) pp. 1-3.

perfect insulators with all observed conduction due to ionizing radiation produced charge carriers.

A quantitative analysis of the process is quite difficult for a number of reasons. First, the energy available for the process is very small. The integrated energy flux for all cosmic radiation is about 3×10^{-3} erg/cm²/second, or about the same as starlight.¹⁰ Second, the energy arrives in a complex distribution of particles of differing interactions with matter. This distribution is affected by altitude, latitude, local surroundings such as building walls, apparatus arrangement, solar activity, etc. Finally, the process is random and the level of activity in the sample exhibits an erratic time dependence.

Behavior of Deuterium

The anomalous behavior of deuterium provided an unforeseen measure of assistance with this problem. All gases were procured in as pure a state as commercially feasible and analyzed on a mass spectrometer for impurity levels as low as 50 parts per million. At this level the deuterium seemed quite pure. The conductivity was, however, almost four orders of magnitude greater than hydrogen. This did not seem reasonable on the basis of only the mass difference

¹⁰S. A. Korff, The Natural Radiation Environment, (Rice University Semicentennial Publications, 1964) pp. 427-40.

of the isotope. The process for producing deuterium led to suspicion of the presence of a small amount of tritium, the radioactive isotope of hydrogen. Apparatus was located capable of detecting tritium in concentrations as low as about one part in 10^{10} . Tritium proved to be present in the deuterium in slightly under one part per billion.¹¹ The beta particle emission of even this small concentration is so large compared to natural background that quantitative analysis becomes possible.

First consider the gaseous phase. From Table 3 the deuterium gas density was 0.104 lb/ft^3 when the current of Figure 10 was measured. The sample volume was 0.168 ft^3 or 4.755 liter. Deuterium gas has a density of 0.0104 lb/ft^3 at STP so the sample volume represented 47.55 liter of STP deuterium. There was thus approximately 4.755×10^{-8} liter of tritium present. The specific activity of tritium is 2.7 curies per milliliter at STP where a curie is defined as 3.7×10^{10} decays or particle emissions per second. The total rate of particle generation was therefore about 4.74×10^6 betas per second.

Two factors must now be determined. One is the loss of beta particles to the brass of the structure. This can be estimated by determination of the path length of a beta particle in deuterium. The second factor is the number of ion pairs generated by a beta particle.

¹¹Office Memorandum from M. F. Milligan, Health Division, "Tritium Content of Deuterium Gas," July 22, 1964.

The maximum energy of a beta particle is determined by binding energy considerations. The interaction of neutrinos causes the beta particles to appear with a spectrum of energies with only a small percentage near the theoretical maximum. This leads to definitions of the average and the root mean square energies which enter into path length calculations.

A comparison has been made between the behavior of mono-energetic beta particles and spectral beta particles which leads to the following equation for maximum path length R_0 for particles in the energy range $E = 0.01$ to 3 Mev.¹²

$$R_0 = 412 E^n \quad (3-1)$$

where R_0 has the dimensions of milligrams per square centimeter.

The exponent n is in turn given by

$$n = 1.265 - 0.0954 \ln E \quad (3-2)$$

the maximum energy for a tritium beta particle is 0.0179 Mev.¹³

In Equation 3-1 this gives a value for R_0 of 0.543 mg/cm^2 . The density of the deuterium gas gives, in the units of specific volume,

¹²R. D. Evans, The Atomic Nucleus, (New York: McGraw-Hill Book Co., Inc., 1955) pp. 625-27.

¹³R. S. Shankland, Atomic and Nuclear Physics, (2d ed., New York: McMillan Co., 1960) p. 378.

$V_g = 0.6 \text{ cm}^3/\text{mg}$ and the maximum range of a tritium beta is 0.326 cm. The electrode spacing in the apparatus is 0.953 cm. It thus appears that some beta particles will be lost. The above considers the most energetic particles. The rms energy of the particles is given by reference 18 above to be about 0.45 E maximum or 8.05 kev. If path length is calculated for the rms energy particle, it is about 0.062 cm. The beta particle loss to the brass structure will thus be neglected to a first approximation.

Now consider the formation of ion pairs. The ionization potential for beta particles in deuterium does not seem to be available. Typical values from Table 9 are 37 electron volts/ion pair for hydrogen, 36 ev/ion pair for nitrogen, and 34.7 ev/ion pair for carbon monoxide. The small variation among gases suggests that use of the hydrogen value for deuterium will not be greatly in error. Using the rms energy of 8.05 kev and 37 ev/ion pair for calculation, a single beta particle will yield about 220 ion pairs. The decay rate of 4.74×10^6 per second will thus yield about 10^9 ion pairs/second in the sample volume. The saturation current observed was 4.8×10^{-11} ampere. A current of 4.8×10^{-11} ampere times 6.24×10^{18} electrons per ampere results in 3×10^8 electrons per second. There is thus quite good agreement between calculated and observed charge carrier generation rate when it is considered that particle loss and recombination effects have been neglected.

A "collection efficiency" may be defined as the ratio of charge

carriers collected to charge carriers generated. It is 0.15 for this case since an ion pair represents two charge carriers.

When the liquid phase is considered, significant differences in behavior appear. The maximum path length for a beta particle becomes 0.0032 centimeter and particle loss is now certainly negligible. The ion pairs generated increase directly with the density to a value of 10^{11} ion pairs/ second. The observed current is 5.85×10^{-11} amperes or 3.66×10^8 electrons/second. The collection efficiency is now only 0.0017 indicating that the recombination rate has increased greatly. The density ratio of liquid to gas is 106.75 and the collection efficiency ratio of gas to liquid is 88.2 suggesting that the recombination rate of ions is nearly proportional to density.

An experimental investigation of recombination rate and carrier mobility in liquid hydrogen was performed by Zessoules, et al.¹⁴ A much larger radiation level was employed to induce charge carriers. The conclusion reached was that only about 2×10^{-4} of the induced carriers were available for "volumetric recombination," the rest disappearing relatively instantaneously. This factor would predict about 2.14×10^7 ion pairs/sec available for current under the conditions in the liquid deuterium or a current of 4.18×10^7 electrons per second compared to the observed 3.66×10^8 . The agreement is

¹⁴ N. Zessoules, J. Brinkerhoff, and A. Thomas, Recombination and Mobility of Nuclear Radiation Induced Ionization in Liquid Hydrogen, (Waltham, Mass.: Tracerlab, Inc., February, 1962)

only fair but the much lower charge carrier density in the deuterium may have lowered the recombination rate, making more than the 2×10^{-4} fraction available for conduction.

Natural Background and Remaining Cryogens

The remaining gases can be treated only on the assumption of a constant radiation flux of unknown magnitude. Comparisons can be drawn which may be instructive. The radiation for these cases differs in that it consists mostly of high energy particles which will penetrate completely through the apparatus giving up energy by ionization. Losses of particles in the structure are not a consideration. The lack of good quantitative data does raise the question of whether enough energy is available from cosmic radiation to produce the observed currents. A high energy particle flux of about two particles per square centimeter per minute per steradian is believed to be correct to within about 30 percent.¹⁵ These particles give up energy at the rate of 2.6 million electron volts per centimeter in argon gas at STP. Most particles come from above so a solid angle of π steradians can be assumed. Also, these particles give up about 32 electron volts to produce an ion pair. These values and the density of liquid argon given in Table 3 give a

¹⁵ Interview with A. D. McGuire, Group P-11, Los Alamos Scientific Laboratory, July, 1964.

charge carrier generation rate of about 3×10^{10} ion pairs per second. The current, from Table 6, was about 1.2×10^{-12} ampere maximum or about 8×10^6 electrons per second. The background radiation is thus at least adequate to generate the observed currents.

For comparative purposes, Table 9 is presented below. Since ion pair generation is a function of density, the ratio of liquid density to gas density should give the ratios of ion pair formation. Due to recombination rate variations, the currents are not in proportion to ion generation rate. The ratios of observed currents are therefore equivalent to the ratios of the collection efficiencies. Division of the ion generation ratio by the current ratio then gives a measure of the relationship between density and recombination rate.

Three types of behavior appear as a result of this comparison. Argon has a relatively low dependence of recombination rate on density. Four gases, three of which are diatomic, have a recombination ratio which increases with density with factors of from 0.82 to 3.5 times the density ratio. Carbon monoxide shows an enormous density dependence by comparison. The set of data for this cryogen is the poorest taken and of dubious reliability. This is due in large part to the very poor conductivity of the liquid phase; however, the gaseous phase is in quantitative agreement with other gases. The qualitative relationship to the other cryogens is thus probably valid.

TABLE 9

IONIZATION POTENTIALS, DENSITY, CURRENT AND RECOMBINATION RATIOS OF LIQUID TO GAS PHASES

Cryogen	Ionization Potential, ev/ion Pair ^{16,17,19}	Liquid/Gas Density Ratio	Liquid/Gas Current Ratio	Liquid/Gas Recombination Ratio
Deuterium	----	102.6	1.22	84
Argon	24.9, 26.9, 24, 27, 25.9, 25.5	321.4	11.0	29.2
Freon 13	----	290.1	0.56	518
Nitrogen	36, 36, 35.8, 33.6	233.3	0.286	816
Hydrogen	36, 31, 38, 37	76.9	0.439	175
Carbon Monoxide	34.7	566.3	0.0045	126,000

¹⁶B. Rossi, High Energy Particles, (New York: Prentice Hall, Inc., 1952), p. 47 and p. 124.

¹⁷W. P. Jesse and J. Sadauski, Phys. Rev. 97, 1955, p. 1668.

¹⁸W. E. Burcham, Nuclear Physics, an Introduction, (New York: McGraw-Hill Book Co., Inc., 1963) p. 174.

CHAPTER IV

CONCLUSIONS

It does not appear to be strictly correct to speak of the electrical conductivity of cryogenic fluids in the sense of Ohms law. Although a current can be passed through a cryogen, only a weak dependence on the applied gradient exists. In other words, the conductivity is not a constant as in an ohmic material, but a function of the applied potential. The cryogen acts nearly as a constant current source. This is believed to be because no intrinsic mechanism of charge carrier formation exists within the cryogen itself. All charge carriers present are generated by ionizing radiation present as natural background. Such voltage dependence as exists is due to interactions between recombination rates and applied gradients. Because the charge carriers are generated in pairs of opposite charge in near proximity to one another, the recombination process is dominant and increases with increasing density. The recombination rate is weakly dependent on ionization potential and strongly dependent on molecular type. An inert gas such as argon does not exhibit much tendency to form negative ions.¹⁹

¹⁹E. W. McDaniel, Collision Phenomena in Ionized Gases, (New York: John Wiley and Sons, Inc., 1964) pp. 370-85.

Since such ions, formed by attachment of electrons to uncharged atoms, would result in a greatly reduced mobility for the negative charge carrier, this process may be significant. The process of negative ion formation can occur in carbon monoxide only by a dissociative process.²⁰ It is tempting to postulate this as the mechanism which causes the high apparent recombination rate, but not enough is known about the parameters involved to present such a hypothesis.

The results of this investigation have led the author to more questions than answers. The effects of electrode spacing, radiation level and type, both higher and lower gradients, and impurities in the gaseous and liquid phases on recombination rates and carrier mobilities are unanswered. Indeed mobilities are not even known. Further, the significance of electrical conductivity data for all pure liquids, where no internal charge carrier generation mechanism is apparent, are questioned. It seems entirely possible that the data are affected by technique, location, and other parameters.

The electrostatic hazard problem does not seem to be significant under ordinary conditions. The effect of a very small amount of tritium in deuterium does suggest that in certain situations, such as cryogenic flows in the presence of a nuclear reactor or other source of intense radiation, enough conductivity may be achieved

²⁰ Ibid., p. 385.

to present a problem. This could take the form of electrostatic potentials and possibly instrumentation interferences. Fluids which already fall into the range of conductivities which are troublesome might well be rendered less troublesome by the addition of small quantities of such radioactives as tritium.

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