

ELECTRICAL CONDUCTIVITY
OF
LOW DIELECTRIC CONSTANT LIQUIDS

by
Evelyn Maureen White

Submitted in Partial Fulfillment
of the Requirements for the
Degree of Master of Science

at the
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Signature of Author:
Department of Chemical Engineering

Certified by:
K. A. Smith, Thesis Supervisor

Accepted by:
G. C. Williams, Chairman,
Dept. Committee on Graduate Theses



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Submitted to the Department of Chemical Engineering in August, 1975, in partial fulfillment of the requirements for the degree of Master of Science at the Massachusetts Institute of Technology.

ABSTRACT

This experimental investigation was carried out in order to determine the electrical characteristics of several hydrocarbons of low dielectric constant. All measurements of the conductivity were below 1 picomho/m ($=10^{-12}$ A/V-m = 10^{-14} ohm $^{-1}$ cm $^{-1}$). This category includes most petroleum products, petroleum distillates made conductive by adding anti-static additives, and liquified gases.

Of particular interest was the determination of the electrical conductivity of liquified natural gas (LNG), which is given special consideration due both to its increasing usage and to the electrostatic hazards associated with its transfer and storage. Electrostatic potentials can be generated during the flow of these insulating liquids and, if the voltage is sufficient, it will produce a spark. Liquified natural gas and many other petroleum products are highly combustible and the electrical conductivities of these liquids are among the properties related to the hazards of their combustion, since the conductivity controls the rate at which charges accumulate and are dissipated. At the very low conductivities found for several of these liquids ($< 10^{-15}$ ohm $^{-1}$ cm $^{-1}$), high velocities and long residence times are necessary for static charge buildup to occur. However, any charge accumulation which does take place would require a long relaxation time to dissipate.

Two methods were used to measure the electrical conductivities: (1) direct current measurements, and (2) liquid capacitance measurements. In preliminary tests the conductivities of several petroleum solvents were measured. A comparison of this data with published values for these liquids indicated that the apparatus was working properly. Any variation between these two sets of values could be accounted for by the presence of small quantities of dissolved ionic impurities such as dissociated aqueous salts, chlorides, sulfur compounds, and water. Support for this explanation partially stems from the different readings obtained for reagent grade toluene and purified toluene.

Another type of ion has been postulated to exist in these insulating liquids. Work done by other investigators indicates that "chemically pure liquids," although showing no electrical conductivity of their own, are slightly ionized by natural background radiation. These ions are continually being formed as others are lost by recombination. Because of the very small extent of ionization in these pure liquids, their electrical conductivities are much lower than for the less pure liquids.

From the present study, it has been found that the maximum electrical conductivity for ING is below 10^{-17} ohm⁻¹cm⁻¹. This extremely low value indicates that any electrostatic charges which do accumulate during LNG transfer operations would persist over a long time interval. The author is in agreement with conclusions reached from other studies that cryogenic fluids are nearly perfect insulators and that the observed conduction is due to the presence of charge carriers produced from atmospheric radiation.

Thesis Supervisor:

Kenneth A. Smith
Professor of Chemical Engineering

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
August 11, 1975

Professor Frederick J. McGarry
Secretary of the Faculty
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Dear Professor McGarry:

In accordance with the regulations of the Faculty,
I herewith submit a thesis, entitled "Electrical Conductivity
of Low Dielectric Constant Liquids" in partial fulfillment
of the requirements for the degree of Master of Science
in Chemical Engineering at the Massachusetts Institute of
Technology.

Respectfully submitted,

(

Evelyn Maureen White

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I. SUMMARY

A. Basic Concepts

1. Conductivity

The conductivity of a substance can be determined in several ways; for example, by applying a certain voltage to a substance and recording the resulting current. The current reading can be substituted into Ohm's Law, which in its most general form is expressed as:

$$\mathcal{K} = j / E$$

where the electrical conductivity, \mathcal{K} , is in A/V-cm (= ohm⁻¹cm⁻¹), the current density, $j = I/a$, is in A-cm⁻², and the electric field strength, $E = V/L$, is in V-cm⁻¹. In terms of the specific resistance of a cylindrical conductor, the relationship becomes:

$$\mathcal{K} = (L/a)(1/R) .$$

The quantity, L/a , is called the cell constant and must be computed for each conductivity cell.

2. Relaxation Time or Half-Value Time

The conductivity of a substance is conveniently discussed in terms of a related concept, the time constant or half-value time. This quantity can be defined, for a homogeneous liquid completely filling a container, by considering the charges carried in the substance. These charges will decay according to an exponential law and the time constant for this decay depends only on the properties of the liquid, and not for example on the geometrical shape of the measuring cell (16).

3. Dielectric Constant

The dielectric constant represents the property of an insulating material which, when used in a conductivity cell, increases the capacitance relative to that of a vacuum. If the capacitance does not increase, then the dielectric constant equals one (11). Substances with dielectric constants falling in the range 6 to 1 are the insulating dielectrics which are the liquids under consideration in this study. Because of the low dielectric constants of these hydrocarbons ($\epsilon \approx 2$) in comparison to water ($\epsilon \approx 80$), ions are attracted together to a far greater extent in hydrocarbons, and therefore, the degree of dissociation is smaller than in water (8). With a very small degree of dissociation, there will be fewer charged species present and therefore the conductivity will be much lower.

4. Effect of Molecular Structure and Substitution

The electrical conductivity and dielectric constant of a substance are fundamental characteristics reflecting the composition and molecular structure. Structurally, hydrocarbons can be sub-divided into open-chain and aromatic compounds. Heptane is an example of a compound belonging to the aliphatic group. Due to the stability imposed by the strong bonding, these hydrocarbons lack a mechanism for electrical conduction of their own in the absence of ionic contaminants. In contrast to this is the aromatic compound benzene which is reported to show a

slight conductivity of its own. This conduction phenomena has been further linked to both excited π electrons and the migration of holes and electrons (2). Correlations between molecular structure and conductivity were made and the electrical conductivity of LNG was postulated to fall in the range $10^{-18} \Omega^{-1}$ and $10^{-20} \Omega^{-1} \text{cm}^{-1}$.

B. Introduction

1. Generation of Static Electricity

It has long been known in the petroleum industry that substantial charges can be generated in well-grounded equipment during flow of low conductivity liquids (13). A crude picture has been constructed of the phenomena which occur during static charge generation. It is known that at the inter-face between a liquid and another substance, there is a tendency for repulsion between positive and negative ions and this displaces them from their normal equilibrium state. The ions of one polarity aggregate at the interface, while ions of the opposite polarity stay in the liquid. Thus, if a liquid is held in a pipe, the wall of the pipe will accumulate positive ions, for example, and the liquid will build up a charge with an equivalent quantity of negative ions. The fluid travelling through the pipe will carry, in this case, more negative electricity into the storage tank. The charged liquid will now transfer its net charge to the grounded walls of the tank. In studying the mechanism for static electrification, it is necessary that the electrical conductivity be determined, since it is an important

factor controlling both charging and relaxation phenomena.

2. Discharge of Electricity

A brief description is provided of the prerequisites for ignition of a combustible material. Electrical discharges occur during the flow of ions and electrons in an electric field separated by two or more electrodes. Recent work has shown that in very low conductivity liquids the mechanism providing for spark formation involves inhomogeneities within the substances which provide a conduction path. Such regions can result from the presence of particulate matter or from two-phase flow which often occurs during cooldown of the system (12).

3. Theoretical Models of Electrical Conduction

Two theoretical models have emerged to explain the phenomena occurring during conductivity measurements of insulating liquids. In summary, these two theories differ in that:

(1) Gavis's theory for fairly high conductivity liquids holds that electric double layers form at the electrodes (3, 21). He provides an equation for the transient current when applying a potential difference. Gavis bases his theory on the assumption that rapid re-dissociation occurs and therefore that polarization is not caused by depletion of ions.

(2) In Silver's theory, an attempt is made to analyze the relation between current, voltage, and

electrode distance (35). Silver shows how the theory can be used to obtain values for the rate constant of the dissociation reaction.

4. Objectives of the Thesis

- (1) To construct an apparatus for measuring very low electrical conductivities of hydrocarbons.
- (2) To determine the electrical conductivities by two different dc methods, in order to obtain a criterion for the accuracy of the readings.
- (3) To compare the experimental readings with values published in the literature.
- (4) To modify the apparatus so that conductivities of cryogenics, such as liquid nitrogen and LNG, could be determined.

C. Experimental Apparatus and Procedure

1. Comparison Between Alternating Current and Direct Current Methods

Alternating current methods are commonly used for determining relatively high electrical conductivities of liquids. Utilization of this method has the advantage of eliminating polarization effects, which otherwise complicate the measurements. However, it is frequently necessary to measure very low electrical conductivities ($<10^{-5} \Omega^{-1} \text{cm}^{-1}$) by means of dc measurements.

2. Apparatus

The measurements of electrical conductivities were made by placing the fluid inside a conductivity cell consisting of two, electrically insulated concentric

cylinders. Data was obtained using a Keithley 610C electrometer and was recorded on a Hewlett-Packard 7004B X-Y recorder.

3. Procedure

Before each measurement was taken the two cylinders were washed withalconox solution and rinsed with distilled water. A small amount of the same liquid to be measured was used for a final rinse before a current reading was made. For each measurement the conductivity cell was filled with 900 ml of fluid and adequate time was allowed for charge relaxation to occur. The electrical conductivities of several hydrocarbons and petroleum solvents were measured. These include: n-heptane, reagent grade toluene, low quality "purified" toluene, carbon tetrachloride, xylene, liquified commercial grade methane, and liquified technical grade methane.

Some modifications had to be made in the experimental apparatus for determination of the conductivities of cryogens. The conductivity cell was surrounded by a coolant in order to slow down the boil-off rate of the liquid. All batteries and electrical equipment were isolated from the measuring cell so that possible spark formation at an electrical connection could not ignite the LNG.

Two different methods were used to determine electrical conductivities. These include direct current measurements and liquid capacitance measurements.

4. Measurement of Very Low Conductivities

a. Direct Current Measurements

Direct current measurements were taken by continuously applying 240 volts from a dry storage battery to the conductivity cell and recording the current flowing between the cylinders. The conductivities corresponding to these currents were computed using the equation:

$$\begin{aligned} \kappa &= (L/a)(1/R) \\ &= (L/a)(I/V) \quad . \end{aligned}$$

Before conductivities could be determined from this relationship, the cell constant (L/a) had to be calculated. This was done by calibrating the cell with a solution of known conductivity. The solution used was 0.01 N KCl. The cell constant was calculated to be 30.70 cm or 0.0326 cm⁻¹.

b. Liquid Capacitance Measurements

In this measurement the liquid hydrocarbon or solvent was used as the dielectric in a capacitor. The conductivity was computed from the time required for the potential to decay. This method required calibration of the apparatus to find its total capacitance. Once this value was obtained conductivities were calculated by measuring the voltage drop during a given time interval, using the equation:

$$\kappa = \left[(C_t + C_c(\epsilon - 1)) / C_c \right] \times (\epsilon_0 / t) \times \ln(V_1 / V_2)$$

where C_t is the total capacitance of the system, C_c is the calculated capacity of the empty cell, t is the time required for the potential drop, and V_1 and V_2 were the initial and final voltages, respectively.

D. Results and Discussion

1. Experimental Difficulties - Variation of Conductivity with Time

For measurements less than 1 picomho/m in liquids, several experimental complications arise which become harder to deal with as the conductivity decreases.

Among the problems encountered are:

- (1) Difficulties associated with the dc method, especially polarization effects.
- (2) Difficulties associated with the decrease of conductivity with time. Because of the decay of conductance, it remains unclear as to which current reading gives the true conductivity.

2. Analysis of Current-Time Curves

Formidable problems arise in trying to interpret charging current versus time curves, as there are probable several inter-related mechanisms taking place. Due to certain differences in the time constants for these phenomena, an attempt was made to differentiate between various regions of the current-time curve according to the appropriate mechanisms (8). It was concluded that

the combined effects of cell capacitance, polarization, electrolysis, and ion depletion are responsible for the short-time phenomena causing the initial drop in the current.

Once the steady state current was reached, the conductivity remained constant for a brief period. Then a slow phenomena followed which produced very small decreases in the current over a long period. This decrease is attributed to the presence of non-depleting ions in a state of partial dissociation.

3. Interpretation of the Phenomena

The problem thus arises as to how to define conductivity since the current is continually varying with time. Various extrapolations along the current-time curve have been suggested to represent the true conductivity. These include: zero time current, infinite time current, and steady state current. The convenient and reproducible portion of the charging current versus time plot was found to occur at the steady state current value. All readings, therefore, represent these currents.

4. Results of Conductivity Measurements

Direct current and liquid capacitance measurements were taken of several hydrocarbons and petroleum solvents. Good agreement was found to exist between these different methods and published values. Small variations between these readings could be attributed to ionic contaminants in the solution. The tests of two grades of liquified natural gas showed that the maximum conductivity reading

for LNG was below $10^{-17} \Omega^{-1} \text{cm}^{-1}$.

E. Conclusions

The extremely low value for the electrical conductivity of liquified natural gas indicates that a relatively long residence time is necessary for charge accumulation or dissipation to occur. Therefore, under ordinary operating conditions, problems with electrostatic charge generation do not appear to be hazardous. Nevertheless, the potential danger of building up electrostatic charges within the flowing liquid in the presence of particulate matter inside the pipe or during two-phase flow which occurs as the system is cooled down, is greatly increased.

F. Recommendations

A recommendation for continued investigation with LNG involves a study of the charging tendency to evaluate the ease of generating electrostatic charges under a variety conditions. If the charge generation appears to be significant then investigations should be continued with scale-model equipment.

II. BASIC CONCEPTS

A. Conductivity

A great deal of experimental work has been carried out in the petroleum industry to demonstrate that pure aliphatic hydrocarbons possess no electrical conductivity of their own (3, 18, 19). The extremely low electrical conductivities which these volatile products are nonetheless found to measure originates from the presence of small quantities of ions. Shell Oil Company reports that its refinery and petrochemical raw materials, intermediates, and finished products contain ion concentrations of approximately 10^{-11} to 10^{-12} gram ion/liter (34). The source of these ions comes from trace amounts of foreign contaminants and it is the motion of such discrete charged particles that provides the mechanism for electrical conduction.

The conductivity of a substance can be determined in several ways; for example, by applying a certain voltage to a substance and recording the resulting current. The current reading can be substituted into Ohm's Law, which in its most general form is expressed as:

$$\mathcal{K} = j / E$$

where the electrical conductivity, \mathcal{K} , is in A/V-cm ($= \text{ohm}^{-1} \text{cm}^{-1}$), the current density, $j = I/a$, is in A-cm^{-2} , and the electric field strength, $E = V/L$, is in V-cm^{-1} . In terms of the specific resistance of a cylindrical conductor, the relationship becomes:

$$\mathcal{K} = (L/a)(1/R)$$

since the resistance, R , is defined as the ratio of the voltage gradient to the current density. Thus, the conductivity is proportional to the length of the measuring cell, L , and is inversely proportional to its cross-sectional area, a . The quantity, L/a , is called the cell constant and must be computed for each conductivity cell due to the lack of uniformity in dimensions.

According to this equation the electrical conductivity is expressed in mho per meter ($\Omega^{-1} \text{m}^{-1}$). The tabulated conductivities of different substances were found to vary in order of magnitude (extreme ranges are practically from infinity down to zero) probably more than any other material property (42). Because of the small values dealt with in petroleum products, a new unit has been defined and is frequently used to substitute for the low powers of ten. This "conductivity unit" has been arbitrarily denoted as a submultiple of $10^{-12} \Omega^{-1} \text{m}^{-1}$, so that (19):

$$1 \text{ conductivity unit} = 1 \text{ picomho/m} = 10^{-14} \Omega^{-1} \text{cm}^{-1}$$

B. Relaxation Time or Half-Value Time

The conductivity of a substance is conveniently discussed in terms of a related concept, the time constant or half-value time. This quantity can be defined, for a homogeneous liquid completely filling a container, by considering the charges carried in the substance. These charges will decay according to an exponential law and the time constant for this decay depends only on the properties of the liquid, and not for example

on the geometrical shape of the measuring cell (16).

This can be shown as follows. The amount of charge, Q , (in coulomb) in a liquid can be equated to the integral of the dielectric displacement D (in Q/m^2) over a surface, a , (in m^2) such that:

$$Q = \int D \, da$$

The current I (in ampere) is equal to $-dQ/dt$ (where t is the time in seconds) which, in turn, is related to the integral of the current density j (in A/m^2) over this surface:

$$-dQ/dt = \int j \, da \quad .$$

Both D and j can be associated through the field strength E (in V/m) by the equations:

$$D = \epsilon \epsilon_0 E \quad \text{and} \quad j = \kappa E$$

where ϵ is the dielectric constant relative to empty space (dimensionless) and ϵ_0 is the dielectric constant of empty space ($\epsilon_0 = 8.854 \times 10^{-12}$ A-sec/V-m). As a result, if (κ/ϵ) remains constant, then these equations can be combined to give the expression:

$$dQ/Q = -(\kappa/\epsilon\epsilon_0) \, dt$$

or,

$$Q = Q_0 e^{-t/\tau}$$

where $\tau = \epsilon\epsilon_0/\kappa$ is the time constant. This value is thus independent of the shape or size of the measuring cell.

Another quantity, the half-value time, $t_{1/2}$ is defined as $e^{-t_{1/2}/\tau} = 1/2$, so that (16):

$$t_{1/2} = (\epsilon\epsilon_0/\kappa) \ln 2 = 0.6931 \epsilon\epsilon_0/\kappa \quad .$$

For most hydrocarbons ($\epsilon \approx 2$) it was found that

the conductivity and time constant varied as shown in Table I,

Table I

Variation of Conductivity and Relaxation Time
for Most Hydrocarbons

Conductivity (ohm ⁻¹ cm ⁻¹)	τ (sec)	$t_{\frac{1}{2}}$ (sec ^{1/2})
10 ⁻¹¹	0.02	0.013
10 ⁻¹²	0.2	0.13
10 ⁻¹³	2	1.3
10 ⁻¹⁴	20	13
10 ⁻¹⁵	200	130

from reference (16). Since the difference between the relative dielectric constant, ϵ , of hydrocarbons changes very little, then any differences in the relaxation time and half-value time are, therefore, almost entirely caused by a variation in the conductivity. A consequence of this fact is that the relaxation time and half-value time may range from an extremely short fraction of a second for the non-hazardous crude oils to minutes or hours for the dangerous purified products.

C. Dielectric Constant

The dielectric constant represents the property of an insulating material which, when used in a conductivity cell, increases the capacitance relative to that of a vacuum. If the capacitance does not increase, then the dielectric constant equals one (11). As early as 1893, Nerst and Thomson stated

that the dielectric constant is the primary factor to be considered in classifying various solutions according to their electrical conductivity (19). The relationship between the conductivity and the dielectric constant is diagrammatically illustrated in Table II, although this correlation is not actually a functional one (8).

Table II
Relationship Between Conductivity
and Dielectric Constant

κ	10^5	1	10^{-5}	10^{-10}	10^{-15}	10^{-20}
ϵ	80		20	6	3	2
Conductors			Dielectrics			
			Semi-Conductors	Insulators		

The first row provides values for the conductivity in $\Omega^{-1} \text{cm}^{-1}$ and the second row lists the dielectric constants ϵ . The divisions on this scale are logarithmic. Substances with dielectric constants falling in the range 6 to 1 are the insulating dielectrics which are the liquids under consideration in this study. Because of the low dielectric constants of these hydrocarbons ($\epsilon \approx 2$) in comparison to water ($\epsilon = 80$), ions are attracted together to a far greater extent in hydrocarbons and, therefore, the degree of dissociation is smaller than in water (8). Walden states that the dissociation constant is roughly proportional to the dielectric constant taken to the third power (19). This has been

found for several electrolytes, mainly organic salts, in different solvents varying from isobutyl alcohol ($\epsilon = 6$), other alcohols ($\epsilon = 25$ to 35), and nitriles ($\epsilon = 27$ to 36), to water ($\epsilon = 80$). This relationship accounts for the low conductivities of hydrocarbon solutions (20). In another study done by Mecke and Feininger, the degree of dissociation of various alcohols and phenols was found in solvents of very low dielectric constant (chlorobenzene, benzene, and cyclohexane). The results indicated that the dissociation constant and dielectric constant were related exponentially (19). Due to the low dielectric constants, then according to either of these relationships, the dissociation constants will also be small. With a very small degree of dissociation, there will be fewer charged species present and therefore the conductivity will be much lower.

D. Effect of Molecular Structure and Substitution

The electrical conductivity and dielectric constant of a substance are fundamental characteristics reflecting the composition and molecular structure. For example, the effect of substitution of a chlorine atom on benzene ($\epsilon = 2.28$) to yield chlorobenzene ($\epsilon = 5.61$) accounts for a factor of over 1000 in the electrical conductivity (8). In this study we are interested in substances which consist only of carbon and hydrogen. Chemically, they are very inert, since they contain no oxygen or nitrogen atoms and therefore do not readily attack other substances.

Structurally, hydrocarbons can be subdivided into open-chain and aromatic compounds. Heptane is an example of a compound belonging to the open-chain or aliphatic group. Since it is one

of the saturated hydrocarbons containing no double bonds, it is very stable and relatively difficult to modify either chemically or physically. This stability is due, in part, to the ability of carbon to form strong σ bonds with hydrogen and other carbon atoms. Due to the stability imposed by the strong bonding, these hydrocarbons lack a mechanism for electrical conduction of their own in the absence of ionic contaminants.

In contrast to this is the aromatic compound benzene which is reported to show a slight conductivity of its own. Benzene has a greater stability than one would expect for a compound with six carbon-carbon σ bonds and three carbon-carbon π bonds (10). The added stability is caused by the delocalization of the three π -bonding electrons over six carbon atoms (33). Such a resonating structure, which provides greater stability for the molecule, is believed by Forster and others to be responsible for electrical conduction through an electron transfer mechanism. This conduction phenomena has been further linked to both excited π electrons and the migration of holes and electrons (2).

The effect of substitution on hydrocarbons, although not the subject of this investigation, has been examined by several other researchers (19). The data showing greater electrical conduction in many halogenated species was a useful correlation used in the liquified methane studies. The maximum value for electrical conduction of LNG was determined to be lower than $10^{-17} \Omega^{-1} \text{cm}^{-1}$. In another study done by Willis, electrical conductivities of cryogens were measured to as low as $10^{-20} \Omega^{-1} \text{cm}^{-1}$ (for carbon monoxide) using a very refined apparatus (43). Among the other cryogens tested was chlorotrifluoromethane (Freon-13) which is

structurally similar to methane in having a single carbon atom at its center, but is different in its substituents. The conductivity for freon-13 was found to be $2.6 \times 10^{-18} \Omega^{-1} \text{cm}^{-1}$ from electrometer amplifier measurements which the author felt were reasonably accurate (43). From a consideration of the molecular symmetry, bond properties (especially bond energies), electronegativity, and ionization potentials of the substituents, it was concluded that the electrical conductivity of freon-13 would be greater than that of methane. This is due to the stronger tendency for charge carrier generation to occur in this molecule by ionizing radiation (10, 32).

A further correlation was made in estimating where the conductivity for liquified methane would fall in relation to the other cryogens. This correlation comes from a consideration of the stability of π -bonds and the effect of bond energies on the tendency of charge carrier formation. The configuration of carbon monoxide, with ten valence electrons, predicts one σ bond and two π bonds (10). The stabilizing effect of two π bonds and the correspondingly large bond energy for CO (255.8 kcal/mole, which is larger than the 225 kcal/mole bond energy for N_2) suggests that the less stable methane molecule may have a conductivity greater than $10^{-20} \Omega^{-1} \text{cm}^{-1}$. Therefore, a likely range for the electrical conductivity of methane is believed to fall between $10^{-18} \Omega^{-1} \text{cm}^{-1}$ and $10^{-20} \Omega^{-1} \text{cm}^{-1}$.

III. INTRODUCTION

A. Generation of Static Electricity

It has long been known in the petroleum industry that substantial charges can be generated in well-grounded equipment during flow of low conductivity liquids (13). Generation of static electricity is primarily a fire hazard and there have been several reports of serious fires and explosions in which the cause was attributed to static electricity (45). This problem has become more acute due to the large volumes and flow rates employed in the transfer of petroleum distillates and LNG (26). Consequently, much research has been conducted to evaluate what factors contribute to the buildup of static charges.

A crude picture has been constructed of the phenomena which occur during static charge generation. It is known that at the inter-face between a liquid and another substance; either a solid (e.g. a liquid contained in a vessel); a liquid (e.g. two immiscible fluids in contact); or a gas (e.g. air just above a liquid) there is a tendency for repulsion between positive and negative ions and this displaces them from their normal equilibrium state. The ions of one polarity aggregate at the interface, while ions of the opposite polarity stay in the liquid. Thus, if a liquid is held in a pipe, the wall of the pipe will accumulate positive ions, for example, and the liquid will build up a charge with an equivalent quantity of negative ions. The fluid travelling through the pipe will carry, in this case, more negative electricity into the storage tank. The

charged liquid will now transfer its net charge to the grounded walls of the tank.

In studying the mechanism for static electrification, it is necessary that the electrical conductivity be determined, since it is an important factor controlling both charging and relaxation phenomena. In high conductivity liquids, charge buildup is rapidly dissipated to the surrounding walls (34). In general, the buildup of an electrical charge within a flowing liquid presents the greatest danger when its conductivity lies within the range of 10^{-10} to $10^{-15} \Omega^{-1} \text{cm}^{-1}$. This hazard is increased by a combination of the following effects: the ionization at these conductivities is adequate to cause significant charge buildup at intermediate flow rates, and, a relatively long time is necessary for charge dissipation. This problem has been controlled for many hydrocarbons by the addition of anti-static additives (ASA), which raise the conductivity of the liquids so that charges can no longer accumulate to a hazardous degree. At lower conductivities, net charge accumulation does not readily occur. However, if there is any charge buildup, it will not dissipate easily and the liquid will stay charged over a much longer time interval (34). In this study, LNG was found to fall into the latter conductivity grouping. Therefore, any charge accumulation which might occur in this liquid would require a long residence time for appreciable dissipation to occur (26).

B. Discharge of Electricity

A brief description is provided of the prerequisites for ignition of a combustible material. Electrical discharges occur during the flow of ions and electrons in an electric field separated by two or more electrodes. As the molecules collide, there is a transfer of energy from the electrons and ions being accelerated in this field, to the substance separating the electrodes (38). As a consequence of this dissipation of energy, other active molecular species are formed and a rise in temperature occurs (29). The specific energy necessary for ignition of an explosive mixture is a function of the mixture's composition (38). However, any flammable mixture of methane and air has a small enough ignition energy to be ignited by an ordinary electrostatic spark-discharge (12).

Several investigators still express confusion about how these sparks are created in highly insulating fluids (12, 26). Although significant potential differences can form, there is still a problem in collecting enough electricity to make an intense spark. More recent work has shown that in very low conductivity liquids the mechanism providing for spark formation involves inhomogeneities within the substances which provide a conduction path. Such regions can result from the presence of particulate matter or from two-phase flow which often occurs during cooldown of the system (12). Previous investigators have indicated that impure gas or liquid streams could produce significant charges, although no conclusions were reached concerning specific impurity levels or flow rates.

C. Theoretical Models of Electrical Conduction

Two theoretical models have emerged to explain the phenomena occurring during conductivity measurements of insulating liquids. In summary these two theories differ in that:

- (1) Gavis's theory for fairly high conductivity liquids holds that electric double layers form at the electrodes (3, 21). He provides an equation for the transient current when applying a potential difference. An important factor determining the size of the transient includes the ratio of the double layer thickness, δ_1 , to the plate distance, d . Its rate of decay is affected by a sum of exponentials, the smallest of which is $\exp(-t/\tau)$. To give an example of the size of the double layer: for hydrocarbons ($\epsilon \approx 2$) at 10-1000 picomho/m, $\tau = 1.8 - 0.018$ seconds, and $\delta_1 = 0.04 - 0.004$ mm (for a diffusivity $D = 10^{-9} \text{ m}^2/\text{s}$) (18).
For conductivity values falling in this range, since δ_1 is small with respect to the electrode distances and τ is small with respect to usual measuring times, then it can be concluded that the transient is small and should decay rapidly. Gavis bases this theory on the assumption that rapid redissociation occurs and therefore that polarization is not caused by depletion of ions.
- (2) In Silver's theory, which has been accepted by several researchers studying insulating liquids, an attempt is made to analyze the relation between current, voltage,

and electrode distance (35). Data collected by Forster in his studies of the conductivity of benzene were used in support of his hypothesis. In this model, ions are formed in spaces of finite thickness in volumes surrounding the electrodes. The result of this mathematical formulation is that the observed conductivity depends on V/d^2 , and on two constants. Silver shows how the theory can be used to obtain values for the rate constant of the dissociation reaction.

D. Objectives of the Thesis

- (1) To construct an apparatus for measuring very low electrical conductivities of hydrocarbons.
- (2) To determine the electrical conductivities by two different dc methods, in order to obtain a criterion for the accuracy of the readings.
- (3) To compare the experimental readings with values published in the literature.
- (4) To modify the apparatus so that conductivities of cryogens, such as liquid nitrogen and LNG, could be determined.

Liquid methane is the form of natural gas often used in storage and transfer operations primarily because of the small volume of the liquid in comparison to the gas. At its normal boiling point of 111.8°K , liquid methane has $1/625$ the volume of gaseous methane at standard temperature and pressure (12). Therefore, it is of special interest to obtain a better knowledge of the electrical properties of LNG.

IV. EXPERIMENTAL APPARATUS AND PROCEDURE

A. Comparison Between Alternating Current and Direct Current Methods

Alternating current methods are commonly used for determining relatively high electrical conductivities of liquids. Determination of the conductivities of aqueous solutions can easily be made to an accuracy within 0.1% of the actual value. Utilization of this method has the advantage of eliminating polarization effects, which otherwise complicate the measurements. However, it cannot be successfully used for the determination of low conductivities. Then the capacitative current in the measuring cell becomes so much greater than the resistive current that it prevents an accurate measurement from being taken (19). This is because the two currents become out of phase and can only be separated with expensive equipment (18).

Therefore, it is frequently necessary to measure very low electrical conductivities by means of dc measurements. Kraus and Fuoss, in their classical investigation on the properties of electrolyte solutions, established a quantitative criterion for determining when dc methods should be employed: dc measurements were taken whenever the conductivities of the solutions were below $10^{-5} \Omega^{-1} \text{cm}^{-1}$ (20). As a consequence, all conductivities reported in this study represent dc measurements.

B. Apparatus

During dc measurements of electrical conductivities, the fluid was contained within a conductivity cell consisting of two

concentric cylinders. Both the outer cylinder and the inner solid bar were made of 304 stainless steel. The actual dimensions of the apparatus are provided on the vertical cross-section appearing in Figure I. This conductivity cell was electrically insulated with a teflon lid which held the inner cylinder in place. A small opening in the teflon lid allowed for a piece of shielded cable to connect the inner cylinder to a power supply. Another cable was soldered to the outer cylinder to provide a connection to the electrometer input. All leads were made of teflon-insulated, coaxial shielded cable. The outer cylinder was electrically insulated by resting it on a tiered teflon stand, which provided a wide cross-sectional conduction path of short length for external charges to dissipate. The cell was placed inside a carefully grounded Faraday cage during measurements.

Data was obtained using a Keithley 610C electrometer and was recorded on a Hewlett-Packard 7004B X-Y recorder. Two hours were always allowed for the electrometer to warm up so that no drift of the needle would occur. With good electrical insulation, this electrometer can read currents as low as 10^{-15} amps. However, because of extraneous charges picked up at the electrical junctions, the noise level of the electrometer and cables was found to be 1.3×10^{-13} amps. For current measurements, the response time of this instrument was reported in the instruction manual to be two seconds when used on the fast feedback mode. Much scatter was obtained under these conditions so that currents were measured using the normal response, which is somewhat slower.

C. Procedure

Before each measurement was taken the two cylinders were washed withalconox solution and rinsed with distilled water. A small amount of the same liquid to be measured was used for a final rinse before a current reading was made. For each measurement the conductivity cell was filled with 900 ml of fluid and adequate time was allowed for charge relaxation to occur. Initial tests were taken of heptane, which had a very low conductivity of about $3.40 \times 10^{-15} \Omega^{-1} \text{cm}^{-1}$. In later measurements, the conductivity of heptane was varied by adding small quantities of Shell's anti-static additive ASA #3, which is a mixture of chromium dialkylsalicylate, calcium didecyl sulfosuccinate, copolymer of lauryl methacrylate and methyl-vinylpyridine, in a hydrocarbon solvent (14).

The electrical conductivities of other hydrocarbons and petroleum solvents were measured. These include: reagent grade toluene, low quality "purified" toluene, carbon tetrachloride, xylene, liquified commercial grade methane, and liquified technical grade methane. Typical analyses of these two grades of methane were reported by the distributor as follows (30):

Table III

Typical Analysis of
Technical Grade Methane

Component	Mole %
methane	98.5
ethane	0.5
nitrogen	0.6
oxygen	0.1
carbon dioxide	0.1
propane	0.1
higher alkanes	0.1

Table IV

Typical Analysis of
Commercial Grade Methane
(Tennessee natural gas)

Component	Mole %
methane	93.63
carbon dioxide	0.70
nitrogen	0.47
ethane	3.58
propane	1.02
isobutane	0.21
<u>n</u> -butane	0.19
isopentane	0.06
<u>n</u> -pentane	0.06
hexane	0.02
heptanes plus	0.06

Some modifications had to be made in the experimental apparatus for determination of the conductivities of cryogenics. The conductivity cell had to be placed in a large dewar flask which contained cryogenic fluid. This served as a coolant for the conductivity cell to slow down the boil-off rate of the liquid. All parts of the cell were precooled in liquid nitrogen and the level of cryogen in the conductivity cell was maintained when boil-off did occur. A further precaution was taken to isolate all batteries and electrical equipment from the measuring cell so that possible spark formation at an electrical connection could not ignite the LNG.

Two different methods were used to determine electrical conductivities of these cryogenic fluids. These were the same procedures as followed for measurements of petroleum solvents and include:

- (1) direct current measurements, using the fluid as a conductor and measuring the current flow; this

value was then substituted into Ohm's Law in order to determine the conductivity (3, 18).

- (2) liquid capacitance measurements, which involve a determination of the relaxation time for the liquid of known dielectric constant; this was accomplished by measuring the rate of voltage decay in the capacitor (26, 34).

D. Measurement of Very Low Conductivities

1. Direct Current Measurements

Direct current measurements were taken by continuously applying 240 volts from a dry storage battery to the conductivity cell and recording the current flowing between the cylinders. The conductivities corresponding to these currents were computed using the equation:

$$\begin{aligned} \kappa &= (L/a)(1/R) \\ &= (L/a)(I/V) \end{aligned}$$

Before conductivities could be determined from this relationship, the cell constant (L/a) had to be calculated. This was done by calibrating the cell with a solution of known conductivity. The most commonly used solution is potassium chloride because of numerous studies done measuring its conductivity at various concentrations and temperatures in cells of uniform length and area. In computing a value for the cell constant, 900 ml of 0.01 N KCl solution were placed in the conductivity cell (42). The circuit

consisted of a voltage divider which would measure the potential difference across a 1% precision resistor and the conductivity cell, as shown in Figure II. The following equations were used in the computation of the cell constant. A value for the current was obtained using the relationship:

$$I = V_1/R_1$$

where V_1 was the voltage measured on the electrometer and R_1 was the 226 Ω 1% precision resistor. The circuit was rewired so that V_2 could be measured on the electrometer. The two voltages, V_1 and V_2 , were found to be 39.60 volts and 4.67 volts, respectively. After the current was substituted into the following equation, the voltages were used to obtain the resistance of the solution, R_2 :

$$\begin{aligned} R_2 &= V_2/I \\ &= (V_2/V_1) R_1 \end{aligned}$$

From this equation the resistance of the solution, R_2 , was calculated to be 26.65 Ω . Since the conductivity of 0.01 N KCl equals 0.00122238 $\Omega^{-1}\text{cm}^{-1}$ under these experimental conditions, then the cell constant becomes:

$$\begin{aligned} L/a &= RK \\ &= 26.65 \times 0.00122238 \\ &= 0.0326 \text{ cm}^{-1} \end{aligned}$$

or its reciprocal: $a/L = 30.70 \text{ cm}$

Once the cell constant was obtained, the current readings were converted into the corresponding conductivities by means of Ohm's Law. The results of the direct

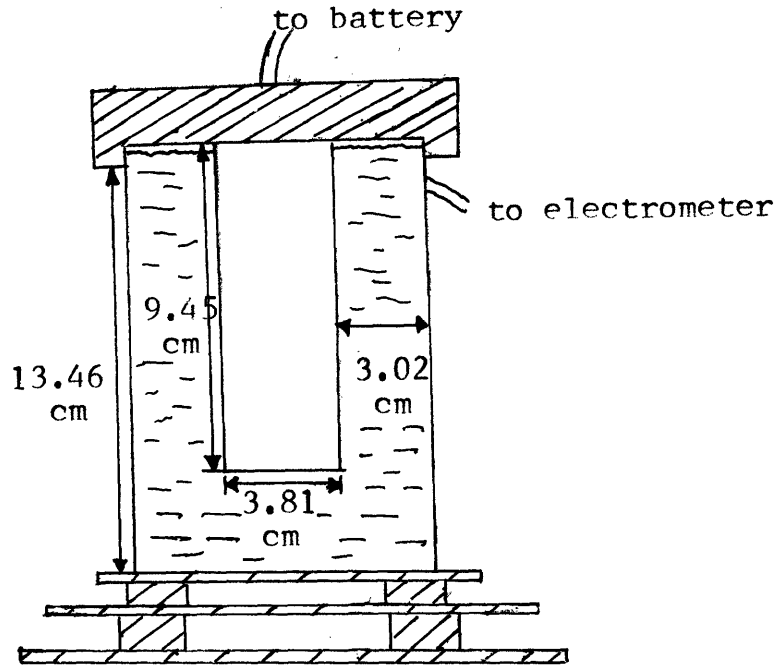


Figure I.

Vertical Cross-Section
of Conductivity Cell

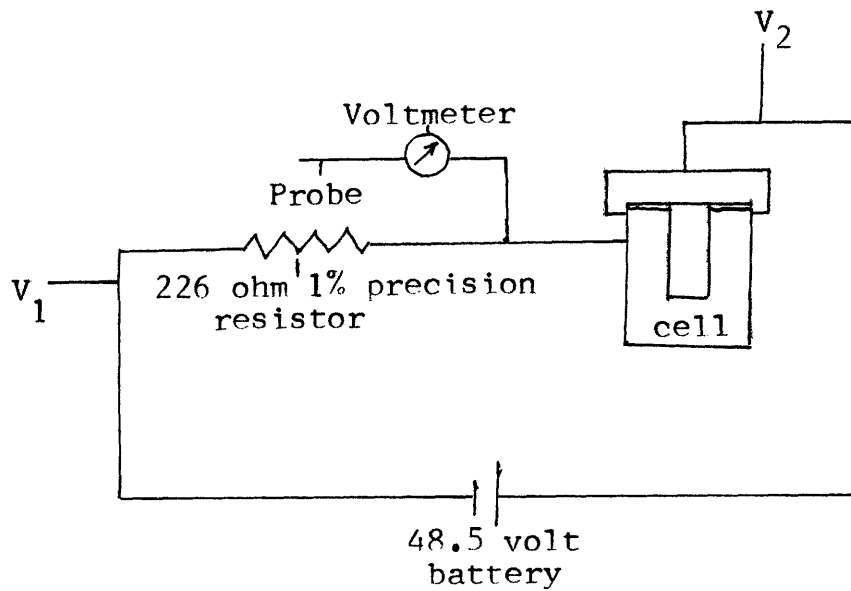


Figure II.

Apparatus for Measuring
Cell Constant

current conductivity measurements are listed in Table V, of the "Results" section.

2. Liquid Capacitance Measurements

The other method employed in the determination of the conductivities of low dielectric constant liquids was liquid capacitance measurements. The liquid hydrocarbon or solvent was used as the dielectric in a capacitor. The conductivity was computed from the time required for the potential to decay.

This method required calibration of the apparatus to find its total capacitance. Therefore, values had to be either known or computed for the following quantities:

C_c = the capacity of the empty cylinders in vacuo, as calculated from their geometrical shape (37)

C_k = the known value of the calibration capacitance (500 pF and 800 pF)

ϵ = the dielectric constant of the liquid .

The total capacitance, C_t , of the system was obtained by placing a capacitor in parallel with the electrometer, applying a known voltage, and recording the length of time required for a specific potential drop. This was repeated without the capacitor in parallel. The system capacitance was found by comparing the two decay times for the same voltage drop, with a known capacitor in parallel (t_2) and without one (t_1). These values were substituted into the following equation to obtain C_t :

$$C_t = (t_1/t_2 - t_1) C_k - C_c (\epsilon - 1) .$$

Several runs were taken to obtain consistent results and the average of these values was used.

The conductivity of air was also measured with and without the capacitor in parallel and negligible differences were found, with the conductivity approximately equal to $10^{-17} \Omega^{-1} \text{cm}^{-1}$ (also reported in reference 26). It is believed that this is the value where external leakage to the system becomes important, since moisture and dirt at the open end of a connector can effect the readings. Therefore, $10^{-17} \Omega^{-1} \text{cm}^{-1}$ was believed to be the lowest value which could accurately be measured with this apparatus.

The voltage drops occurring during a given time interval were calculated, in order to determine the conductivities. These values could then be substituted into one of the equations below.

(a) For high conductivity liquids the following equation applies:

$$\chi = [(C_t + C_c(\epsilon - 1) + C_k)/C_c] \times (\epsilon_0/t) \times \ln(V_1/V_2)$$

(b) For low conductivity fluids, the appropriate equation is:

$$\chi = [(C_t + C_c(\epsilon - 1))/C_c] \times (\epsilon_0/t) \times \ln(V_1/V_2)$$

where the symbols denote:

C_c = the calculated capacity of the empty cell, pF

ϵ = the dielectric constant of the liquid (for most hydrocarbons $\epsilon = 2$)

ϵ_0 = the absolute dielectric constant of vacuum

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ A-sec/V-m}$$

C_t = total capacitance of the system, pF

C_k = applied capacitance, pF

t = time required for the potential drop

V_1 = initial voltage

V_2 = final voltage

The computed conductivities are given in the "Results" chapter. Here again, $10^{-17} \Omega^{-1} \text{cm}^{-1}$ was the minimum conductivity value measured, since the recordings are affected by external leakage below this.

V. RESULTS AND DISCUSSION

A. Experimental Difficulties - Variation of Conductivity with Time

For measurements less than 1 picomho/m in liquids, several experimental complications arise which become harder to deal with as the conductivity decreases. Among the problems encountered in low conductivity measurements are:

- (1) Difficulties associated with the type of measurement used (i.e. the necessity of employing dc methods which causes polarization of the electrodes; a limitation in the applied field strength), and,
- (2) Another difficulty is that the conductivity of the hydrocarbons varies with time, usually decreasing. This may be attributed to particulate suspensions which are slow at establishing an internal equilibrium of their own. Because of the decay of conductance, it remains unclear as to which current reading would give the true conductivity. This is a very controversial subject among investigators and most of the evidence is circumstantial. Therefore, the current-time curves must be analyzed in terms of the phenomena occurring before any conclusions can be drawn.

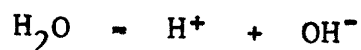
B. Analysis of Current-Time Curves

Formidable problems arise in trying to interpret charging current versus time curves, as there are probably several inter-related mechanisms taking place, for example: cell capacitance, polarization, electrolysis, and ion depletion (8, 15, 18).

Strictly speaking, such processes cannot be separated because they overlap. Due to certain differences in the time constants for these phenomena, an attempt was made to differentiate between various regions of the current-time curve according to the appropriate mechanisms (8).

A more detailed analysis of the mechanisms occurring is facilitated by considering another plot: log current against time. During the initial two second period, three distinct linearizations are obtained. The comparatively short, steep initial region is generally attributed to the effect of charging the conductivity cell, which acts like a capacitor. The cell capacitance effect is due to the movement of ions in the solution and because of this it is related to and overlaps with the mechanism occurring in the second region. This broader line is attributed primarily to the polarization of molecules by the field. It was experimentally proven long ago by Whitehead (1933) that the observed shape of these curves is in large part caused by polarization within the liquid dielectric (8). The separation of positive and negative ions requires a corresponding increase in charges on the electrodes and this explains much of the initial current drop (15). The closer this polarized state approaches its final form of charge separation, the lower the charging current becomes until finally the relatively constant current is left.

The term polarization is often used loosely to denote electrolysis (28). It has been suggested that water is dissociated by electrolysis according to the simple equation:



Experimental support for the occurrence of ion depletion is obtained by repeatedly measuring the charging current for the same solution. Results for the first recording appear in Figure IV). Subsequent readings were taken at different time intervals and these later curves (all similar to one another; see Figure V) differed from the initial measurement in having a markedly sharper drop off during the first two seconds. Ion depletion was found, as expected, to be an irreversible process, in contrast to polarization which is completely reversible. This depletion phenomena was also found to be more pronounced at lower conductivities, which agrees with the findings of others. Therefore, in conclusion, the combined effects of cell capacitance, polarization, electrolysis, and ion depletion are believed to be responsible for the short-time phenomena in the current drop and provide an approximate value for the quantity $(\kappa_o - \kappa_m)$, where κ_o is the initial recorded conductivity which drops to a fairly constant value, κ_m .

Once the steady state current was reached the conductivity remained constant for a brief period. Then a slow phenomena followed which produced very small decreases in the current over a long period. One would expect that as the current continued to flow, the source of ions would become extremely limited. In trying to account for the continuous decrease in current, Gemant discusses another type of ion (18). This second type of ion is described as molecular size electrolytes in a state of partial dissociation. Because these ions are in equilibrium with other molecules and are continually being regenerated, their effect upon the conductivity is negligibly small. On this basis they

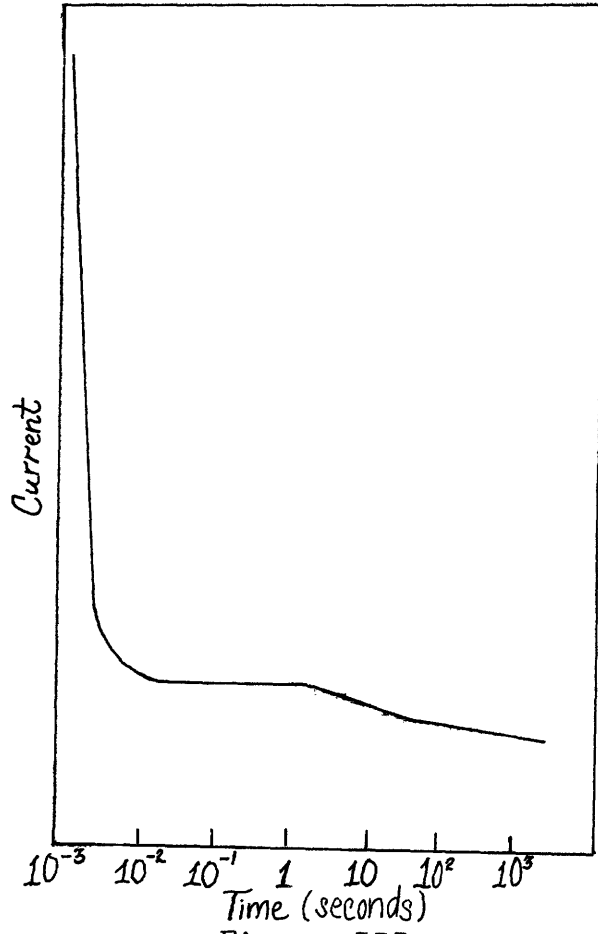


Figure III.

Typical Current versus Time Curve
for an Insulating Liquid
(Ref. 8)

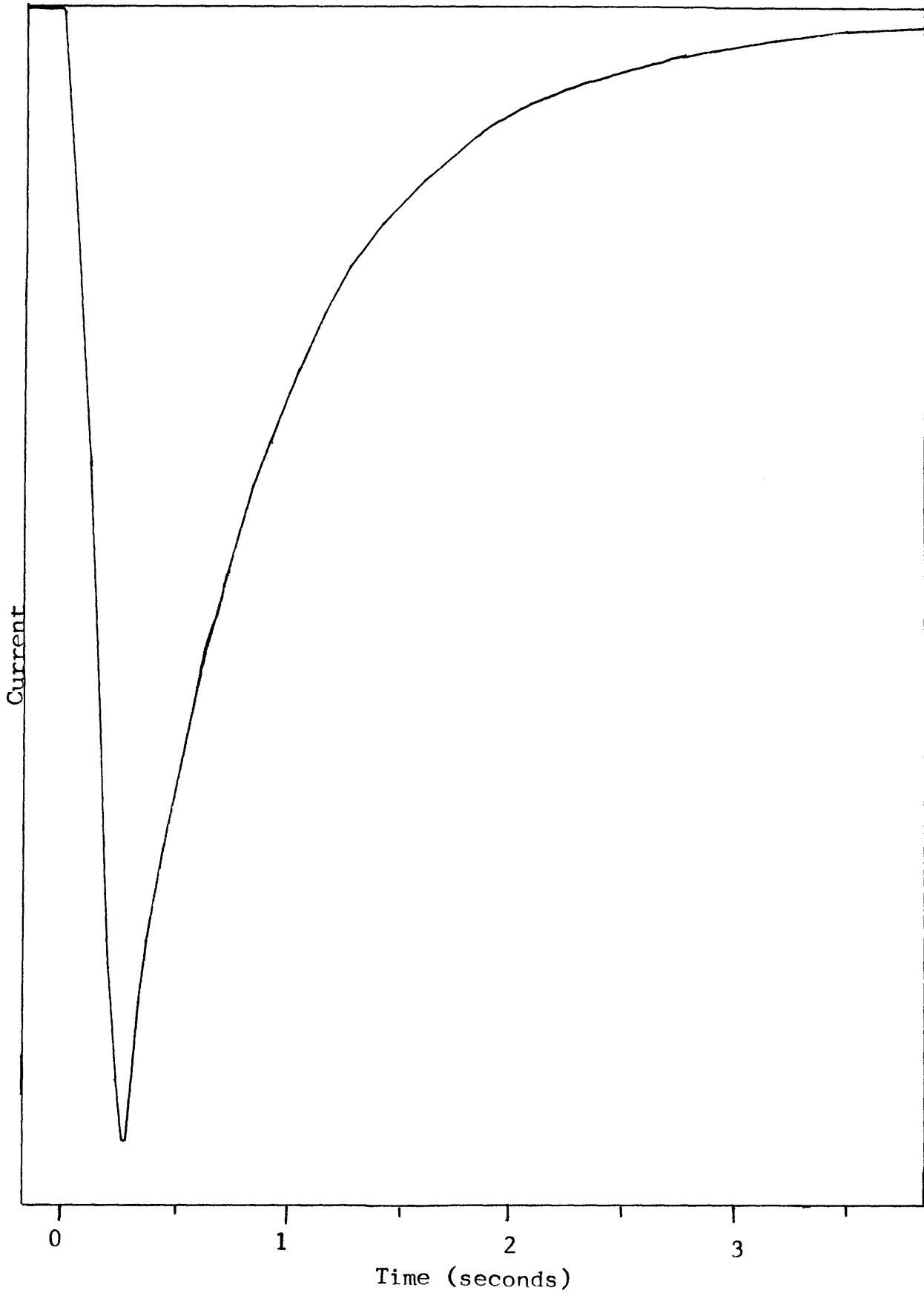


Figure IV.

Initial Current versus Time
Plot for n-heptane

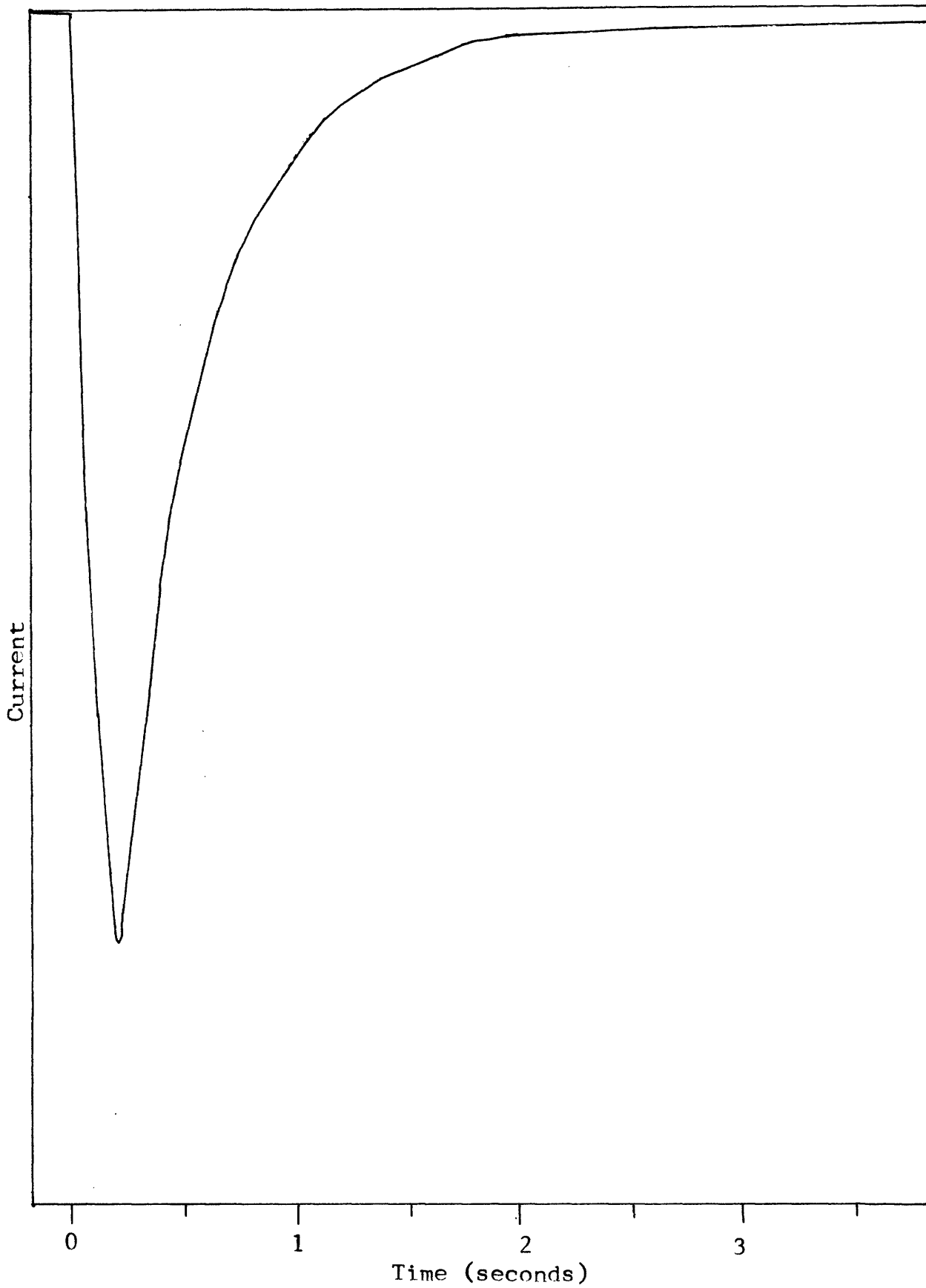
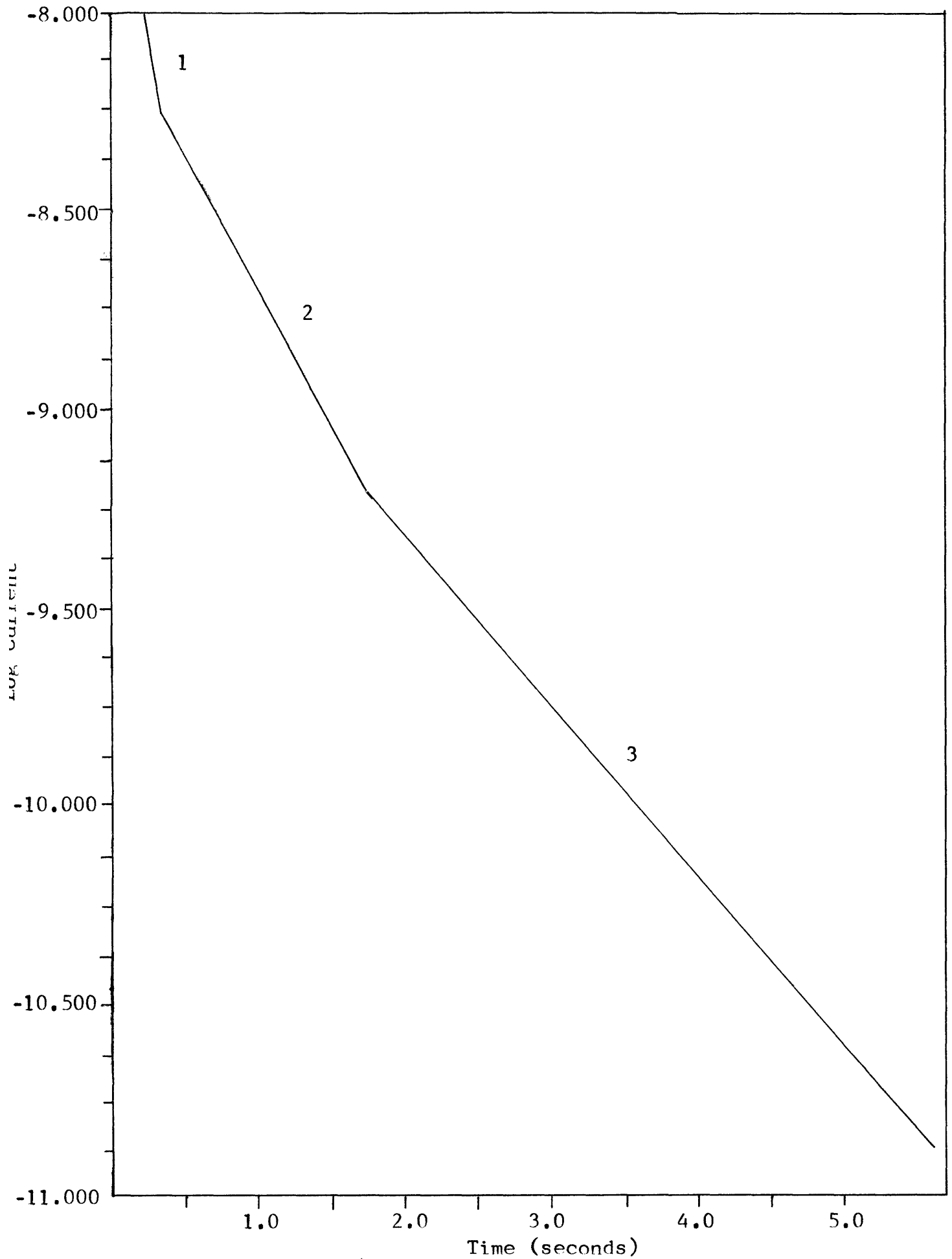


Figure V.

Subsequent Current versus Time
Plot for n-heptane



and follows the law of mass action. If the symbol c is used to represent the equal concentrations of positive and negative ions and c_w represents the water concentration, then $c^2/c_w = K_w$ or $c = \sqrt{c_w K_w}$ where c_w is usually a small quantity in insulating liquids. For example, if a liquid contains 0.1% water, $c_w = 0.001$ (8). For the low dielectric constant liquids under study, K_w should be of the order of magnitude, 10^{-25} , while c is of the order of 10^{-14} (in mols per liter) (8).

Although there is strong evidence to suggest that the capacitance and polarization phenomena occurring during the first few milliseconds result in this part of the curve, the actual peak value is quantitatively useless. This is because the inertia of the electrometer needle is so great during this instantaneous rise, that when the curve stops short of the true peak value (due to the instruments slow response time in comparison to the phenomena described) errors in the readings are often obtained.

Just as regions one and two of the log current versus time plot overlap and are mechanistically interrelated, likewise there is an association between the phenomena occurring in regions two and three. The predominant effect in region three is believed to be ion depletion. This is more generally referred to as the "dc cleanup effect" (18). Gemant explains this phenomenon in terms of the type of electrolyte dissolved in the homogeneous media (9). This type of ion is described as existing "in a state of total dissociation" (8). Because the ions are not in equilibrium with molecules, they are thus "depleting" (18). This type of ion is removed from the liquid fairly rapidly and is believed to cause a sharp drop in the charging current.

are called "non-depleting ions" and are responsible for a very slow decrease in current (18).

In a discussion of the ions causing electrical conduction, the existence of ionized species in the extremely low conductivity cryogenic fluids, like LNG, deserves mention. Most cryogenics are in a fairly pure state because at such low temperatures impurities will freeze out of the liquid. Therefore, it is believed that no intrinsic mechanism exists within a cryogen for the formation of charge-carriers (43). All charge-carriers present are generated through ionizing radiation from the atmosphere. The voltage dependence which exists is attributed to the interactions between recombination rates and applied gradients. Because the charge-carriers are created in pairs having opposite charge in close proximity to one another, the recombination rate is high (43). This rate is slightly dependent on the ionization potential and is largely dependent on the molecular type (43). Further support for the hypothesis that ions are created to a limited extent by natural background radiation comes from studies done of a liquid shielded by a lead container which absorbs the incoming radiation (8). The measured conductivities were much lower in this case than for conductivity measurements taken without shielding the liquid from radiation effects. Therefore, such a mechanism which involves the loosening of electrons from the molecules is highly probable (9).

C. Interpretation of the Phenomena

The problem thus arises as to how to define conductivity since the current is continually varying with time. An adequate solution

to this question is not simple and this is why it is hard to gather reliable data on the subject. Different theories have been proposed concerning specific current values which are stated by their authors to represent the "true conductivity" of a liquid. Various extrapolations along the current-time curve have been suggested which include:

- (1) Zero Time Current. In describing conductivity measurements for a solution of n-heptane containing anti-static additive, Koszman presents his conclusion that ion depletion may have a significant effect on the readings, necessitating "extrapolating current measurements as a function of time back to zero time" (6).
- (2) Infinite Time Current. Current readings, I_f , were recorded over a very long interval by Guizonnier et al. for a transformer oil (18). After four days the current was found to be almost constant. The authors discovered that the resistance of their dc cell, V/I_f , was increasing as the applied potential was allowed to increase, so that final conductivities decreased with increasing potential:

$$V/I_f = a + bV$$

The field strength employed by Guizonnier was fairly small (< 2 kV/cm) and no counter emf was present. These phenomena were attributed to the creation of space charges and to the depletion of charged particles from the bulk of the liquid.

In another set of experiments, findings inconsistent with Ohm's Law, such as the above results, were avoided

if the liquid between the electrodes was continually replenished.

Gavis draws the conclusion: "According to the view presented here, polarization is not caused by ion depletion or by deposits on the electrode surface. Therefore, current-time plots should not be extrapolated back to zero time in order to obtain true conductivities, but rather to infinite time" (3).

- (3) Steady State Current. Gemant, in numerous writings, has described a series of pitfalls involved in dc conductivity measurements (8). He has concluded that the steady state region of the curve represents a relatively true value of conductivity, particularly due to the non-reproducibility of the other measurements and difficulties involved in these methods.

In attempting to reach some conclusion about which current reading to use in computing the conductivity, several complications had to be resolved. It was found from this experimental work that the current continued to decrease very slightly over a period of several hours. Therefore, Guizonnier's findings that four days were required to obtain a nearly constant current were not surprising. However, due to the time period necessary to measure this conductivity, κ_{∞} , the infinite time method was found to be highly impractical. Furthermore, the differences in conductivity obtained after about five minutes were reasonably insignificant.

Many more difficulties and inconsistencies arose in attempting to justify an extrapolation of current back to zero time. First, a consideration must be given to the effect of ion depletion on

these measurements. One of the reasons which researchers cited in favor of extrapolation back to zero time was to eliminate the effect of ion depletion. However, there is strong evidence which implies that ion depletion occurs early in the recording as a sharp drop from peak value to the steady current, as discussed when analyzing these curves. In the process of selecting points from the early part of the curve and replotting them as log current versus time, these investigators are also including the effect of ion depletion. This error could become considerable at lower conductivities where ion depletion becomes important.

An even greater error in the extrapolation back to zero time is due to the fact that this value is really much smaller than the actual peak current. An incorrect reading is obtained because the rather long response time of the electrometer (minimum of two seconds on the fast mode), which cannot accurately record a peak which occurs during the first few milliseconds. The true peak current is much higher. This was found by recording the current with respect to time on an oscilloscope with a much faster response time. A value for the peak was not obtained, however, because it extended over the measurable range on the oscilloscope.

A third finding which illustrates that the peak recordings are quantitatively useless concerns the recording needle on the electrometer. Due to the extremely high instantaneous peak value, it was concluded that the needle attains enough inertia to make peak values measured somewhat inconsistent. This effect was found to cause errors of about 45% in peak value readings. A similar result was found by Gavis and Koszman: "The reproducibility of the data was such that conductivities below $10^{-14} \Omega^{-1} \text{cm}^{-1}$ were

reliable only to within 50%" (6).

Thus the convenient and reproducible portion of the charging current versus time plot was found to occur at the steady state current value. Although ion depletion and electrolysis serve to shift the time at which this current is reached during repeated measurements of a solution, the reading itself is entirely reproducible. All readings, therefore, represent these currents.

D. Results of Conductivity Measurements

Direct current and liquid capacitance measurements were taken of several hydrocarbons and petroleum solvents. The results are summarized in Table V. Good agreement was found to exist between these different methods and published values. Therefore, it was concluded that the apparatus was working properly. Small variations between these readings could be attributed to ionic contaminants in the solution. This explanation comes from the measurements of reagent grade toluene and "purified" toluene, the latter which has more impurities and a correspondingly higher conductivity.

The tests of two grades of liquified natural gas showed that the maximum conductivity reading for LNG was below $10^{-17} \Omega^{-1} \text{cm}^{-1}$. A limitation was reached at this conductivity value because below this number external leakage becomes an important factor. Commercial grade methane (Tennessee natural gas) with a high impurity level was the sample more likely to provide a measurable conductivity. However, as expected, many of these impurities, such as carbon dioxide and water, froze out and appeared during liquification of the methane gas as a small white layer on the bottom of the

dewar flask. Therefore, there was not a sufficient quantity of impurities present to produce a measurable electrical conduction equal to or greater than $10^{-17} \Omega^{-1} \text{cm}^{-1}$.

Table V

Results of Conductivity Measurements by
Direct Current and Liquid Capacitance
Methods.

Liquid	Direct Current Conductivity (ohm ⁻¹ cm ⁻¹)	Liquid Capacitance Conductivity (ohm ⁻¹ cm ⁻¹)	Conductivity of Pure Liquid*
n-heptane	3.40 x 10 ⁻¹⁵	3.86 x 10 ⁻¹⁵	< 1 x 10 ⁻¹⁴
toluene (reagent grade)	4.78 x 10 ⁻¹⁵	4.46 x 10 ⁻¹⁵	< 1 x 10 ⁻¹⁴
toluene ("purified")	9.35 x 10 ⁻¹³	6.81 x 10 ⁻¹³	< 1 x 10 ⁻¹⁴
carbon tetrachloride	1.72 x 10 ⁻¹⁵	3.84 x 10 ⁻¹⁵	4 x 10 ⁻¹⁸
xylene	2.90 x 10 ⁻¹⁵	2.83 x 10 ⁻¹⁵	< 1 x 10 ⁻¹⁵
liquid methane (com. grade)	< 10 ⁻¹⁷	< 10 ⁻¹⁷	-
liquid methane (tech. grade)	< 10 ⁻¹⁷	< 10 ⁻¹⁷	-

*References 26, 42, 43

VI. CONCLUSIONS

It was concluded that the source of the observed electrical conduction in long chain hydrocarbons (greater than five carbons) such as heptane is different than in the shorter liquified hydrocarbons such as methane. Since the longer hydrocarbons are liquid at room temperature they will dissolve small quantities of impurities fairly readily and these contaminants provide a mechanism for the electrical conduction. In cryogenics, however, these impurities freeze out of the liquid phase so that the solutions are relatively pure. There is little tendency for these stable molecules to produce a conductivity of their own by shifting electrons. In Willis's studies of low temperature fluids, the same conclusion was reached that there is no intrinsic mechanism for charge carrier generation within the cryogen itself (43). The charge carriers which do form are produced by ionizing radiation from the atmosphere.

The extremely low value for the electrical conductivity of liquified natural gas ($< 10^{-17} \Omega^{-1} \text{cm}^{-1}$) indicates that a relatively long residence time is necessary for charge accumulation or dissipation to occur. Therefore, under ordinary operating conditions, problems with electrostatic charge generation do not appear to be hazardous. Nevertheless, the potential danger of building up electrostatic charges within the flowing liquid in the presence of particulate matter inside the pipe or during two-phase flow which occurs as the system is cooled down, is greatly increased.

VII. RECOMMENDATIONS

It was found in another investigation done of the electrical conductivity and charging tendency in liquid hydrogen, that electrostatic charge formation in well-grounded equipment can be significant under certain operating conditions (26). Therefore, a recommendation for continued investigation with LNG involves a study of the charging tendency to evaluate the ease of generating electrostatic charges. Tests should be done under a variety of flow conditions, including two-phase flow and flow over large surfaces such as filters. In addition, various contaminants should be added to evaluate the effect of different impurity levels. If the charge generation appears to be significant then investigations should be continued with scale-model equipment.

APPENDIX A

List of Symbols

a	area of electrode, cm
c	concentration, mols per liter
C	capacitance, pF
D	dielectric displacement, Q-m ⁻²
δ	electrical double layer thickness, mm
E	electric field strength, V-cm ⁻¹
ϵ	dielectric constant relative to empty space
ϵ_0	dielectric constant of empty space ($\epsilon_0 = 8.854 \times 10^{-12}$ A-sec/V-m)
I	current, ampere
j	current density, A-cm ⁻²
κ	conductivity, ohm ⁻¹ cm ⁻¹
L	length of electrode, cm
Q	charge, coulomb
R	resistance, ohm
t	time, seconds
$t_{1/2}$	half-value time, seconds
τ	relaxation time, seconds
V	voltage

APPENDIX B

Physical Constants of Methane (30)

Molecular Weight	16.043
Specific Volume (70°F, 1 atm)	23.7 cu.ft./lb. (1479.5 ml./g/)
Boiling Point (1 atm)	-258.7 °F (-161.5 °C)
Freezing Point (1 atm)	-296.7 °F (-182.6 °C)
Triple Point	-296.5 °F (-182.5 °C)
Triple Point Pressure	0.115 atm
Specific Gravity (60°F, 1 atm)	0.5549
Density, Gas (0°C, 1 atm)	0.79 g./l.
Density, Liquid (b.p.)	0.4256 g./ml/
Critical Temperature	-115.8 °F (-82.1 °C)
Critical Pressure	673.3 p.s.i.a.
Critical Density	0.162 g./ml.
Latent Heat of Vaporization (b.p.)	121.54 cal./g.
Latent Heat of Fusion (t.p.)	13.875 cal./g.
Specific Heat, Gas (60°F, 1 atm)	
C	0.5271 cal./g.-°C
C _P	0.4032 cal./g.-°C
V	
Flammable limits in Air	5.3-14% (by volume)
Gross Heat of Combustion (60°F, 1 atm)	1011.6 BTU/cu.ft.

APPENDIX C

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