2.1 INTRODUCTION

Sufficient amount of experimental work has been done in the field of inorganic solids, while the research in organic solids has been limited mainly at the basic level. For long organic molecular solids have been viewed upon as insulators. Much interest in them has been created in an attempt to understand conduction mechanism. The earliest experimental work in the field of organic semiconductors was done on phthalocyanines. Aromatic hydrocarbons are the most extensively studied organic solids to date. Anthracene commands the same place among organic semiconductors as germanium and silicon among inorganic semiconductors.

Within the last decade there has been rapid increase in the work on electrical properties of organic substances. The rising interest in biophysical processes and their relations to the electrical phenomena occurring in vivo also spurred investigation of electrical properties of organic compounds.

The existence of semiconduction property has been demonstrated in a variety of different classes of organic compounds such as condensed aromatic hydrocarbons, charge transfer complexes, pyrolized polymers and stable free
radicals. With few exceptions the electrical conductivities are small and the energies of activation for the conduction process are high. But the fact that even small conductivities are displayed suggests that some kind of intermolecular interaction takes place which, in an electric field, gives rise to electronic conduction. It is suggested that this interaction is due to molecular orbital overlap. The extent of orbital overlap is a function of molecular structure and hence, if semiconduction arises from such overlap, it is not surprising that semiconduction activation energies correlate with properties which are also a function of molecular structure, such as the molecular ionization energy, electron affinity and excitation energy of the ground triplet state transition. 190, 191

Eley et al. 192 - 195 have published the results of an extensive series of investigations on the semiconductivity of organic substances. An excellent series of measurements on the aromatic hydrocarbon crystals have also been reported by Northrop and Simpson. 196 Other published reviews covering much of the same ground includes those of Le Blanc, 197 Inokuchi and Akamatu, 56 Okamoto and Brenner, 57 Kearns, 198 Kommandeur, 199 Lyons and Morris, 200 Hamann, 201 Kallmann and Silver, 202 Brophy and Buttery 55 and Fox, Labes and Weissberger. 203
2.2 FACTORS INFLUENCING ELECTRICAL CONDUCTIVITY:

Electrical conductivity for organic materials is apparently dependent on several variables such as, purity, degree of crystallinity, environment, surface effects, applied field, temperature, pressure, thickness, electrode material, humidity, impurity contents etc. Some of them are discussed briefly below:

(a) Field – The variation of the current through sample with applied voltage is one of the easiest measurements to make since the sample is not disturbed during the process. Such a measurement is important because nature of conduction can often be understood from the value of \( n \) in the expression

\[
I \propto V^n 
\]

The value of \( n \) is 1 when the behaviour is ohmic. A value \( n = 2 \) is given when a space charge limited current flows through a trap free insulator. Rose has shown how to work backward from an experimentally determined \( I - V \) characteristic to obtain the energy distribution of traps and also their number.

Numerous workers have studied the dependence of conductivity on field strength. Hartshorn, Popov, and
Liang\textsuperscript{206} proposed the theories to explain the variation of conductivity with field. Poole\textsuperscript{207} has found an exponential variation of steady state conductivity with field strength which could be represented by

$$\sigma_3 = a \exp(bF)$$ \hspace{1cm} . . . 2.2

where $a$ and $b$ are constants. However, Joffe\textsuperscript{208} states that it is only the steady state conductivity which increases with field and the true conductivity is independent of field strength. According to him this was due to the polarization effects. O' Dwyer\textsuperscript{26} has shown that conductivity will not only be variable on account of field but will also depend on space charge.

Measurements of Riehl\textsuperscript{209} on organic substances have shown that electrical conductivity is proportional to $\exp(-B/T)$ where $T$ is absolute temperature. Electrical conductivity was found to increase with high fields but not the value $B$.

Departure from Ohm's law in high electric fields occurs as a result of activation barrier perturbation even in the absence of thermal and chemical effects. Electrical conductivity thus increases with the field in the high electric field region.\textsuperscript{210} Tomar,\textsuperscript{167} Talwar\textsuperscript{211} and Bhatnagar\textsuperscript{212} have found that electrical conductivity increases with field for Poly-4-methyle
pentene - 1, PVC and Indian sugar cane wax respectively. Recently the effect of field on conductivity of pyrene, xanthene and naphthalene has been reported.

(b) Temperature - Like the current - voltage characteristics, the investigations of current dependence on the temperature give some information on the conduction mechanism. A rise in temperature tends to increase the current and conductivity. Electrical conductivity of organic semiconductors very often follows a relation of the form

\[ \sigma = \sigma_0 \exp(-E/kT) \] or \[ \sigma = \sigma_0 \exp\left(-\frac{E'}{2kT}\right) \] .. 2.3

where \( \sigma \) is the conductivity measured, \( E \) the 'activation energy of conduction', \( \sigma_0 \) pre-exponential factor, \( k \) Boltzmann constant and \( T \) the absolute temperature. The expression of energy term by \( E \) or \( E' \) depends on its interpretation. If the logarithm of the conductivity is plotted against \( 1/T \), two regions, a high temperature region and the other low temperature region depending strongly upon the past history of the crystal result. The high temperature region is independent of past history of the crystal and involves a considerably larger activation energy. The complete conductivity curve is a superposition of two
curves given by \[ \sigma = \sigma_1 \exp \left( -\frac{E_1}{kT} \right) + \sigma_2 \exp \left( -\frac{E_2}{kT} \right) \] \[ \ldots 2.4 \]

where \( \sigma_1 \) and \( \sigma_2 \) are preexponential terms. Out of the two terms in equation 2.4, the first has a small coefficient and small activation energy and predominate at lower temperatures while the other has a larger coefficient and larger activation energy and is predominant at higher temperatures.

The study of conductivity dependence on field and temperature sometimes reveals that current-temperature and current-field curves obtained on increasing and decreasing of temperature or field are quite different and distinct, resulting into a sort of hysteresis loop.

Hysteresis effect has been observed in case of paraffin wax,\(^{219}\) carnauba wax,\(^{220}\) sugar cane wax,\(^{221}\) polyethelene,\(^{166}\) PVC,\(^{211}\) naphthalene,\(^{222}\) \( \beta \)-naphthol,\(^{115}\) xanthene\(^{214}\) and pyrene.\(^{213}\)

(c) Electrode material — Electrical conductivity of the semiconductor or insulator is very much influenced by the material of the electrode used to make electrical contact. An electrode can be (i) blocking, (ii) nonblocking and noninjecting, (iii) injecting, with regard to carriers of either sign. Only type (ii) and (iii) give rise to ohmic behaviour. The I - V characteristic of a semiconductor depends on the electrode-semiconductor work function.
223

O' Dywer has studied the influence of cathode material on the conductivity and breakdown strengths of solids and liquid dielectrics. Reucroft studied the conductivity of anthracene monocystals with different electrodes (sodium, silver, indium) gave the identical results with respect to the magnitude of the conduction current and therefore concluded that the observed electrode barriers are independent of the work function of the individual metallic electrode employed. In view of a report by Boroffka of anthracene conductivity observed some four orders of magnitude higher with the use of copper iodide electrodes as compared with metallic electrode. Electrolytic contacts in anthracene have been extensively studied by Kallmann and Pope, Silver and others and showed that the current-voltage relation of electrolytic contact is linear only above a certain critical voltage level. Eley et al. measured the conductivity of bovine plasma albumen with four electrode metals Cu, Pt, Al and In. Closely similar results were obtained in all cases. Bhatnagar and Srivastav have found the measurable influence of the electrode materials of Zn, Cu and Al on the conductivity of Indian sugar cane wax at 35°C.

(d) Pressure - In general, the electrical conductivity of organic material
increases with increasing pressure. The conductivity of organic material is given by

\[ \sigma = n_0 e \mu \exp \left( -\frac{E}{kT} \right) \]  

when pressure is increased both \( \mu \) and \( E \) may change. The change of \( \mu \) is related with the change of carrier transport in the material and the change of \( E \) is related with the change of the energy gap.

The effect of high pressure on the electrical conductivity of various organic compounds such as polycyclic aromatic hydrocarbons, polymers, charge transfer complexes, free radicals, and organic metallic compounds have been investigated. Eley et al. reported that the effect of pressure was to sharply lower the value of activation energy of loose versus compacted powders of metal-free phthalocyanine by 50% and of isoviolanthrene by 25%. In case of metals, the increase in conductivity has been found to be only 2-fold while for organic substances 100-fold increase in conductivity has been observed by applying suitable pressure. Inokuchi and coworkers have shown that the increase in conductivity observed in quaterylene and violanthrone was close to the mobility increase for anthracene. Consequently, they concluded that the large increase in conductivity was mostly due to the large increase
in concentration of charge carriers. Pohl et al. obtained an expression for pressure dependence of conductivity, which is as follows:

$$\ln \left( \frac{\sigma}{\sigma_0} \right) = \frac{b}{k} P^{1.2} \quad \ldots \quad 2.6$$

where $\sigma_0$ and $b$ are constants for the substance, $P$ is the pressure and $k$ is Boltzmann constant.

(e) **Thickness** - Numerous workers have studied the dependence of electrical conductivity on thickness and found that the $I - V$ characteristics is dependent on the same. According to Wright the current varies as inverse cube of thickness. Sharma has found a linear relationship between conductivity and thickness in sealing wax. Bashara and Dotty have found that SCLC increases with thickness. Recently, Thomas et al. studied SCLC in anthracene and found that the current at fixed voltage, varies inversely with approximately the third power of thickness.

(f) **Humidity** - Numerous workers have found that humidity and also impurities cause the conductivity to increase with field strengths. Barker and Thomas have found a measurable
influence of humidity on conductivity in high field. Moisture affects the conductivity in two ways:

(1) By increasing the dielectric constant and therefore ions concentration by reducing the effective dissociation energy and

(2) Departure from ohm's law in high fields as a result of activation perturbation even in the absence of thermal and chemical effects.

Nanthia et al. have shown that there is an increase in conductivity due to presence of humidity.

(g) Impurity content — The electrical conductivity of organic compound is extremely sensitive to the presence of impurities. The conductivity itself could be used as a measure of purity provided that the absolute value for a given material were known. Effect of purification on the semiconduction of Imidazole were carried out by Brown and Aftergut and found that the presence of two slopes in \( \log \sigma \) versus \( 1/T \) plot is indicative of an impure specimen since further purification gives rise to single slope. Pick and Wissman showed that for naphthalene the activation energy depend on the presence of impurities. Effect of known impurities on electrical properties of hydrocarbons have been investigated by Northrop and Simpson. Okamato and coworkers observed a change in conductivity properties of hydrocarbons,
which has been purified by different methods.

2.3 PRESENT MEASUREMENT TECHNIQUE

In the present investigation steady state dark conductivity has been studied. The degree of accuracy of conductivity depends on the accuracy of measuring current, voltage and dimensions of the sample with the various perturbing parameters.

A sandwich type of cell has been used for the measurement of electrical conductivity. The cell is a three-terminal capacitor employing a guard electrode, a guarded electrode and a unguarded electrode. The use of the guard electrode eliminates the edge capacitance and the capacitance to ground of the high potential electrode in addition to the effect caused by dc surface conductivity and by surface polarization from moisture films etc.

(a) Construction of the conductivity cell - Design of the conductivity cell was based on Bhatnagar and Srivastav's cell. 255

All the metal parts of the cell, except the screws and the locating pins are made out by turning a single solid copper rod of 2.25" in diameter. The cell consists of an outer casing E, provided with a brass terminal T, to which the cylinder B is attached. The guard ring (GR) is screwed to the cylinder B. The central opening of the guard ring is slightly tapered
(Fig. 2.1) Coaxially with the guard ring is situated the guarded electrode (GE), also tapered but in the opposite direction to that of the guard ring, which is held by a circular perspex disc (PD) by means of a fixing nut (N). The disc PD fits accurately the cylinder B.

The perspex disc, the guarded electrode, the guard ring and cylinder B are turned accurately on the lathe, so that they are coaxial. The locating pins (LP) ensure that the capacitor can be dismantled for cleaning etc., and reassembled without sensible loss of accuracy. The perspex disc carrying the guarded electrode can be kept rigidly in position with the help of the clamping cylinder C.

The inner parts carrying the guard ring and guarded electrode are turned accurately on the lathe and common surfaces of B, GR and GE are cut accurately. Finally the surfaces are finished with silicon carbide polishing paper. To avoid field distortions at the edges, care was taken while cutting and polishing to obtain sharp edges of the guarded and the guarding electrodes and accurately plane surfaces.

The high voltage copper electrode (A) is held at a fixed distance from the guard ring by perspex spacers of equal thickness; the ends of the spacers are accurately plane and parallel. The surface of this electrode
Fig. 2.1 Conductivity Cell.
is prepared in the same manner as the common surfaces of the guard ring and the guarded electrode. The electrode is firmly held in position by means of two brass screws which pass through spacers and the insulating washers, both made of perspex.

The inner assembly, after cleaning can be screwed to the container E. The perspex insulating plug (K) is screwed in position by means of a pair of compass. The outer crevices are sealed.

The thermocouple for calibration of the assembly can be inserted through the two sets of port holes (T'). The liquid dielectric under consideration can also be introduced through the hole H. The conductivity cell was calibrated with the help of a thermocouple.

(b) Constants of the conductivity cell - For maximum effectiveness, the width of the guarding electrode should be atleast 2d, where d is the thickness of the sample. The gap between the guarded and guarding electrodes should be as small as possible. Keeping this requirement in view, the edges of the perspex separators have been kept at the distance of 2.391 cm (> 2d) from the inner edge of the guard electrode. The effective radius of the guarded electrode is greater than its actual radius.
The effective radius \( r \) of the guarded electrode is given by Amey and Hamburger formula \(^{256}\)

\[
r = \frac{r_1 + r_2}{2} - \frac{2d}{\pi} \ln \left[ \frac{h \pi (r_2 - r_1)}{4d} \right]
\]

where \( r_1 \) and \( r_2 \) are the radii of the guarded and the guard ring as shown in Fig. 2.2. The effective area \( A \) of the guarded electrode is given by \( A = \pi r^2 \), using the value of \( r \), given by equation 2.7. The value of \( r \) is used in computing the vacuum capacitance \( C_o \) of the cell by the formula

\[
C_o = 0.27816 \frac{r^2}{d} \text{ pf.} \quad \ldots \quad 2.8
\]

The values of various constants are given in Table below.

**Constants of Three - electrode (circular) system**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_1 )</td>
<td>Radius of guarded electrode</td>
<td>0.549 cm</td>
</tr>
<tr>
<td>( r_2 )</td>
<td>Inner radius of guard ring</td>
<td>0.588 cm</td>
</tr>
<tr>
<td>( d )</td>
<td>Thickness of the sample</td>
<td>0.065 cm</td>
</tr>
<tr>
<td>( r )</td>
<td>Effective radius of guarded electrode</td>
<td>0.564 cm</td>
</tr>
<tr>
<td>( A )</td>
<td>Effective area of guarded electrode</td>
<td>1 cm(^2)</td>
</tr>
<tr>
<td>( C_o )</td>
<td>Vacuum capacitance</td>
<td>1.3488 pf</td>
</tr>
</tbody>
</table>
THREE-ELECTRODE SYSTEM

Fig. 2.2
(c) Assembly for preparation of samples — The assembly used for moulding the samples of para-chloroaniline (PCA), manufactured by B.D.H. Poole, England for the present study consists of the following parts:

(i) Lower copper electrode (A) — The lower electrode is plane copper plate of thickness 0.3 cm and of cross-section 9 x 5.8 cm$^2$. The surface is made plane and smooth. Four holes each of 0.476 cm are drilled near edges at the centre of the four sides of this copper plate. The lower electrode in fact is a metallic foil of size 3 x 5.8 cm$^2$, which is pressed on this plate in the centre parallel to its shorter side.

(ii) Sample holder (C) — Plane and smooth mica sheets are selected to make the 'Sample holder' in which the samples are moulded. The pieces of size 4 x 3.5 cm$^2$ are cut out of mica sheets and joined together with a suitable adhesive to form specimen holder of desired thickness. Alternately the desired thickness is obtained by gradually peeling off the layers. A circular cavity (radius 0.6 mm) is cut in centre of mica sheet.

(iii) Mica Frame (D) — This frame is of the same dimension as the lower electrode and can be screwed with the help of four screws
through holes. A circular hole (diam. 2.54 cm) is drilled through it in the centre. This mica frame helps in exerting pressure on the sample holder and also helps in keeping the upper electrode at a fixed position.

(iv) Bridge and fly screw (E) - A brass strip \((18 \times 2 \times 0.3 \text{ cm}^3)\) is bent at right angles at four places and turned into the shape as shown in Fig. 2.38. Two holes near the two ends are drilled, keeping in view that these holes remain in perfect alignment with these in the copper plate and mica frame along their breadth. A threaded hole is drilled at the centre of the bridge. Fly screw is simply a steel screw 6 cm in length. It can pass through the threaded bridge hole and apply a pressure at the centre of upper electrode.

(v) Upper electrode (H) - Upper electrode is a circular copper disc (1 cm radius and 0.3 cm thickness). Both surfaces are made smooth. A hole of nearly 0.15 cm depth is provided at the centre of one surface. Pressure is applied at the hole by screwing the fly screw through the bridge. The upper electrode proper is actually a circular metal foil which is wrapped on to the above circular disc and can be unfolded whenever desired.

(vi) Non-conducting washers (q) - two washers made of perspex fit exactly in
Fig. 2.3 Components of the Assembly used for preparation of samples.
the holes in the copper plate. They help in keeping the upper electrode insulated from the lower electrode. These washers used, are helpful in the formation of electrets.

Different parts of the assembly, assembled together are shown shown in Fig. 2.3.

(d) Method of preparation of samples - Both the electrodes are cleaned with benzene. The copper foil is placed on the polished surface of lower electrode. The sample holder is placed over this foil along with mica frame such that the circular cavity is exactly in the centre of the circular hole in upper mica frame. The mica frame and bridge are fixed on to the copper plate. Small quantity of PCl₅ is taken in a clean glass tube and is melted on an electric heater. Now it is carefully poured in a cavity of the sample holder. The upper electrode is then at once gently placed over it and is pressed with the help of fly screw. The quantity of material in the cavity is so adjusted that a small portion may bulge out on solidification ensuring complete filling of the cavity. The assembly is placed in thermostat and is allowed to cool down to room temperature. After it has acquired the room temperature, the sample is taken out from the assembly and is examined under microscope to check for cracks, good surface finish and uniformity. Samples of 0.65 mm thickness were prepared in this way.
(e) Voltage source — Ten Eveready Min-Max 700-D batteries of 90 volts each supplied by Union Carbide India were used for applying the electric field. This enabled a variation of voltage from 90 volts to 900 volts in the steps of 90 volts. Their use ensure stability of voltage and eliminates the possibility of fluctuation inherent in the mains operated power supplies.

(f) Temperature control — The current through organic semiconductors is highly sensitive to temperature variations and hence temperature control is an important factor. A wide range thermostat manufactured by Baird and Tatlock Ltd., London has been used in the present investigation, in which desired temperature could be controlled from room temperature to 250°C to an accuracy of ± 0.5°C. The samples are uniformly heated and temperature is measured by a thermocouple.

(g) Current measuring instrument — Beckman Uitrohmeter supplied by Beckman Instruments International, Geneva has been used to measure current in the present investigation. High current sensitivity permits measurements to be performed at low applied voltage. The full scale voltage ranges provided 20, 50, 100, 200, 500, 1000, 2000 and 5000 millivolts.
These ranges together with input resistors of $10^6$, $10^8$, $10^{10}$ and $10^{11}$ ohms provided current sensitivities from $5 \times 10^{-6}$ to $2 \times 10^{-13}$ amp. full scale. The current as low as $2 \times 10^{-15}$ amp. may be directly measured.

The absolute accuracy of the reading varies with the input resistor used. With $10^6$ ohms input resistor, the absolute error is less than 2% and with $10^{11}$ ohms the error is between 3 and 5%. The relative error between two readings made using the same input resistor and about the same current is within 1%.

Voltage and current of either polarity may be measured and voltage applied for resistance measurements may be reversed for polarization or dielectric absorption.

(h) Circuit arrangement and current measurement - The circuit arrangement for measuring the current through the specimen is shown in Fig. 2.4. Shielded wires are used in the circuit and all shieldings are properly earthed to avoid instability and other inaccuracies.

Proper input resistor and voltage range along with proper signal polarity is selected. If the order of the current is not known the meter is set to the least sensitive condition and voltage sensitivity and/or input resistor is increased until a substantial meter reading is obtained.
CIRCUIT DIAGRAM FOR CONDUCTIVITY MEASUREMENT

Fig. 2.4
After zeroing the meter with the input resistor and voltage range to be used, the 'Input' switch is turned to 'On' position and the reading of the meter is recorded. The meter reading indicates the voltage developed across the input resistor. The value of current through the sample is given by

\[ I = \frac{\text{Voltage range} \times \text{meter reading}}{R_{\text{input}} \times 100} \text{ Amp.} \quad 2.8 \]

Current density \( J \), electric field \( E \) and conductivity can be calculated with the help of measured current \( I \) by the formulae

\[ \sigma = \frac{J}{E} \quad (\text{ohm}^{-1} \text{ cm}^{-1}) \]

\[ J = \frac{I}{A} \quad (\text{Amp cm}^{-2}) \quad 2.9 \]

\[ E = \frac{V}{d} \quad (\text{volt cm}^{-1}) \]

where \( A \) is the effective area of the electrode and \( d \) is the thickness of the sample.

2.4 DETAILS OF MEASUREMENT :

(a) Variation of current with field - A freshly prepared sample whose conductivity is to be measured is introduced between the electrodes of conductivity cell. The cell containing the sample is then transferred to the thermostat which was
previously set at the desired temperature. This assembly is allowed to remain in the thermostat for 5 hours. This period is sufficient for the sample to attain the thermal equilibrium. After the attainment of thermal equilibrium the field is applied across the specimen and current is measured. It was observed that immediately after the application of the voltage, the current is much greater than in the later periods. It requires about 1 - 2 hours waiting before current reaches its steady value. At higher temperature this period has been found to be comparatively less. The steady values of currents were recorded by varying the fields from 1.38 KV/cm to 13.84 KV/cm. i.e. by varying potentials from 90 volt to 900 volt in steps of 90 volt. The current is also noted while decreasing the value of fields from 13.84 KV/cm to 1.38 KV/cm.

Steady values of the currents were recorded both while increasing and decreasing the field at the following temperatures :

25°, 30°, 35°, 40°, 45°, 50°, 55° and 60°C.

(b) Variation of current with temperature - In this part of measurement, the temperature of the specimen was varied from 25° to 60°C in step of 5°C at a fixed value of field.
The values of the field were the following:
1.38, 2.77, 4.15, 5.54, 6.92, 8.3, 9.7, 11.07, 12.46 and 13.84 KV/cm.

These measurements were carried out on freshly prepared specimen by increasing its temperature from 25° to 60°C and then decreasing it from 60° to 25°C in steps of 5°C at a fixed value of field. The steady value of the current corresponding to each temperature was recorded after allowing a sufficient period required for attaining thermal equilibrium. The measurements were repeated by taking a fresh sample to ensure reproducibility of results.

2.5 CALCULATIONS:

(a) Activation Energy - Variation of conductivity with temperature in each straight portion of graph is governed by the equation

\[ \sigma^* = \sigma^* \exp \left( - \frac{E}{kT} \right) \]  \hspace{1cm} \text{(2.10)}

Relationship between conductivity and inverse of temperature is shown in Figs. 2.19 to 2.22 which have been obtained after plotting log of conductivity versus inverse of temperature (°K) for different fields. A resolution between the conductivities corresponding to high and low temperature regions seems
to have taken place in each case.

Activation energy $E_1$ and $E_2$
corresponding to low and high temperature regions
respectively have been calculated using the formula

$$E = \frac{k \left( \ln \sigma_1 - \ln \sigma_2 \right)}{\left( \frac{1}{T_2} - \frac{1}{T_1} \right)} \quad \text{.. 2.11}$$

where $k$ is the Boltzmann constant.

(b) Calculation of Power 'm' - An approximate linear $I - V$
characteristics (Fig. 2.9) suggests a power law relationship

$$I = KV^m \quad \text{.. 2.12}$$

The power $m$ was estimated by the method of least squares.

Present calculation of power $m$ is somewhat different from the method of least squares. One such method which has been followed here is to introduce new variables, so as to arrive at a more tractable relationship. Thus taking a log of the equation 2.12, one get

$$\log I = m \log V + \log K$$

suppose $\log I = y$, $\log V = x$, $\log K = c$

the equation 2.12 becomes

$$y = mx + c \quad \text{.. 2.13}$$
The problem now has been reduced to the problem of fitting a straight line to a set of points in the $xy$ plane and thus to a simple problem of least squares. Now the power $'n'$ can be computed from the following relation

$$
m = \frac{\sum x \sum y - n \sum xy}{(\sum x)^2 - n \sum x^2} \quad \cdots 2.14
$$

The values obtained in this method sometimes differ from those obtained by solving the original least square equation but these differences are very small.

2.6 RESULTS

(a) $I-V$ characteristics - The $I-V$ characteristics at different temperatures are represented in Figs. 2.5 to 2.8. From these curves, following results are observed:

(i) Order of the variation of current is from $10^{-11}$ to $10^{-6}$ Amp, which is in agreement with reported values for organic semiconductors.

(ii) At all temperatures, the current obtained during increasing and decreasing of field is quite different. The curves obtained for complete cycle of the field show a sort of hysteresis effect. The arrows on each curve show the direction in which
Fig. 2.5 Current-Voltage Characteristics
Fig. 2.6 Current-Voltage Characteristics
Fig. 2.7 Current-Voltage Characteristics
Fig. 2.8 I-V Characteristics
field is varied. The hysteresis effect seems to decrease with increasing temperature.

(iii) At all temperatures the value of current while increasing the field is always greater than that with field decreasing.

(iv) A typical log I - log V characteristics obtained by increasing and decreasing field strength is shown in Fig. 2.9. The I - V characteristics of all samples is marked by two distinct regions. In the low voltage region below about 360 volts (field 5.54 KV/cm), the current varies linearly with voltage, while at higher voltages, the current follows a faster increase. No. sharp knee is observed separating these two regions.

The value of power 'm' is calculated for all samples for both regions of the curves. These values are tabulated in the Table 2.1. From the Table it seems that (a) the values of power 'm' for high field region are always greater than that for low field region. (b) The power being less than one at low field region, while at high field region, the power is greater than one, indicating the departure from Ohm's law in the sense of a faster than linear increase in current. (c) The values of 'm' are smaller for curves obtained by increasing the field than those of curves obtained by decreasing the field.
Fig 2.9 Log I - Log V characteristics.
<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Power ' m ' region corresponding to lower field increasing / decreasing</th>
<th>Power ' m ' region corresponding to higher field increasing / decreasing</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.7905 / 1.4380</td>
<td>1.2392 / 1.5324</td>
</tr>
<tr>
<td>30</td>
<td>0.9218 / 0.9772</td>
<td>1.1799 / 1.4310</td>
</tr>
<tr>
<td>35</td>
<td>0.9330 / 1.0515</td>
<td>1.1256 / 1.3070</td>
</tr>
<tr>
<td>40</td>
<td>1.0678 / 1.1320</td>
<td>1.1820 / 1.3294</td>
</tr>
<tr>
<td>45</td>
<td>0.7209 / 0.7013</td>
<td>0.9659 / 1.0422</td>
</tr>
<tr>
<td>50</td>
<td>0.6119 / 0.6696</td>
<td>1.0332 / 1.1034</td>
</tr>
<tr>
<td>55</td>
<td>0.7392 / 0.7469</td>
<td>1.1895 / 1.2785</td>
</tr>
<tr>
<td>60</td>
<td>0.7959 / 0.7878</td>
<td>1.1517 / 1.2016</td>
</tr>
</tbody>
</table>

(v) Fig. 2.10 shows log J versus $\sqrt{E}$ Schottky plots at different temperatures. These plots are straight lines for field greater than 5.54 KV/cm.

(vi) Log J/$v^2$ versus 1/V plots are shown in Fig. 2.11. These plots are approximately linear for higher field.

(b) Variation of conductivity with field - The variation of conductivity with field has been investigated by plotting log $\sigma$ versus E curves for all temperatures. These plots are shown in Fig. 2.12. The following two points are worth noting:
Fig. 2.10 Log $J$ vs $\sqrt{E}$ plot (Schottky type plot)
Fig 2.11 Log(J/V^2) vs 1/V plot
Fig. 2.12 Variation of conductivity with field (log ρ vs E)
(i) At low field region, the conductivity decreases slowly with increasing the field.

(ii) At high field region, the conductivity increases very slowly with increasing the field and the semi log plots yield straight lines.

(c) Variation of current with temperature — Results of variation of current with temperature are shown in Figs. 2.13 to 2.17. On account of a very large variation of current with temperature (10^{-11} to 10^{-6} Amp) log J versus T curves have been plotted both for increasing and decreasing temperatures. Important features of these curves are:

(i) At all fields, the current—temperature curve does not repeat itself when the temperature is decreased indicating a hysteresis effect. During cooling the current is always higher than that obtained during heating.

(ii) Current of the same order as obtained during the study of variation of current with field at different temperatures was observed when the temperature is varied at each field from 25^\circ C to 60^\circ C.

(iii) As the temperature of the specimen is increased the current rises slowly first from 25^\circ C to 45^\circ C. After 45^\circ C the current shows a rapid rise upto 60^\circ C.

(iv) Richardson Schottky type plots log J/T^2 versus 1/T
Fig. 2.13 Current - Temperature Characteristics (semi log plot)
Fig. 2.14 Current-Temperature Characteristics (semi log plot)
Fig. 2.15 Current-Temperature Characteristics (semi log plot)
Fig. 2.16 Current-Temperature Characteristics (semi log plot)
Fig. 2.17 Current-Temperature Characteristics (semi log plot)
are shown in Fig. 2.18. It is observed that in low
temperature region \( J / T^2 \) rises slowly with
increase of temperature, while in the high temperature
region it rises rapidly, with a sharp knee at about
\( 46^\circ C \) which separates these two regions.

(d) Variation of conductivity with temperature — The
variation
of log of conductivity with inverse of temperature (\( ^0 K \)) are
shown in Figs. 2.19 to 2.23. The important features of
these curves are:

(i) The conductivity rises with temperature at each
field being of the order of \( 10^{-14} \text{ ohm}^{-1} \text{ cm}^{-1} \) at low
temperatures and of \( 10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1} \) at high
temperatures.

(ii) The curves corresponding to all the fields show two
straight lines, one corresponding to low temperature
region and other to high temperature region.

(iii) In the low temperature region, with a rise in the
temperature the conductivity increases linearly to
a certain value, then above temperature of about
\( 46^\circ C \), there follows a quicker increase in the value
of conductivity, also linearly, but the slope of
straight line is different (with different
activation energy). No sharp knee (transition
temperature) is observed separating these two regions.
Fig 2.18 Log $J/T^2$ vs $1/T$ plot (Richardson plot)
Fig. 2.19 Plot of log $\sigma$ vs $1/T$
Fig. 2.20 Plot of log $\sigma$ vs $1/T$
**Fig. 2.21 Plot of \( \log \sigma \) vs \( 1/T \)**

**FIELD 6.92 KV/CM**

**FIELD 8.3 KV/CM**
Fig. 2.22 Plot of log $\sigma$ vs $1/T$
Fig. 2.23 Plot of log $\sigma^-$ vs $1/T$
(iv) From the slopes of the straight portions of the curves, the values of activation energy has been calculated. These values of activation energy are shown in Table 2.2.

<table>
<thead>
<tr>
<th>Field (KV/cm)</th>
<th>Activation energy low temp. region $E_1$ (eV)</th>
<th>Activation energy high temp. region $E_2$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.38</td>
<td>1.84</td>
<td>3.72</td>
</tr>
<tr>
<td>2.77</td>
<td>1.81</td>
<td>3.92</td>
</tr>
<tr>
<td>4.15</td>
<td>1.63</td>
<td>3.98</td>
</tr>
<tr>
<td>5.54</td>
<td>1.52</td>
<td>3.93</td>
</tr>
<tr>
<td>6.92</td>
<td>1.41</td>
<td>4.06</td>
</tr>
<tr>
<td>8.30</td>
<td>1.38</td>
<td>4.08</td>
</tr>
<tr>
<td>9.70</td>
<td>1.37</td>
<td>4.11</td>
</tr>
<tr>
<td>11.07</td>
<td>1.35</td>
<td>4.11</td>
</tr>
<tr>
<td>12.46</td>
<td>1.34</td>
<td>4.11</td>
</tr>
<tr>
<td>13.84</td>
<td>1.32</td>
<td>4.15</td>
</tr>
</tbody>
</table>

(v) It is found that activation energy corresponding to high temperature region is greater than that corresponding to low temperature region. The variation
Fig. 2.24  Variation of activation energy with field.
of activation energy corresponding to low temperature region \(( E_1 )\) and corresponding to high temperature region \(( E_2 )\), with field is shown in Fig. 2.24. The values of activation energy for non-ohmic region centres round 1.3 eV, while for high temperature region it is approximately constant and is of the order of 4 eV.