

## Chapter 3

# Electrical Conductivity of Crystal

### 3.1 Introduction

As in the case of metallic conductors, electrical current can flow through a solution of an electrolyte also. For metallic conductors: current is carried by electrons, chemical properties of metal are not changed and an increase in temperature increases resistance. The characteristics of current flow in electrolytes in these respects are different. The current is carried by ions, chemical changes occur in the solution and an increase in temperature decreases the resistance.

Electrical conductivity (EC) is a measure of the ability of water to conduct an electric current and depends on[1-5]:

- Concentration of the ions (higher concentration, higher EC)
- Temperature of the solution (high temperature, higher EC)
- Specific nature of the ions (higher specific ability and higher valence, higher EC)
- Conductivity changes with storage time and temperature.

The measurement should therefore be made in situ (dipping the electrode in the stream or well water) or in the field directly after sampling. The determination of the electrical conductivity is a rapid and convenient means of estimating the concentration of ions in solution. Since each ion has its own specific ability to conduct current, EC is only an estimate of the total ion concentration[6-8].

Ohm's law defines the relation between potential (V) and current (I). The resistance (R) is the ratio between V and I:

$$R = V / I. \quad 3.1$$

The resistance depends upon the dimensions of the conductor, length,  $L$ , in cm, cross sectional area,  $A$ , in  $\text{cm}^2$  and the specific resistance,  $\sigma$ , in ohm.cm, of the conductor:

$$R = \sigma \times L / A \quad 3.2$$

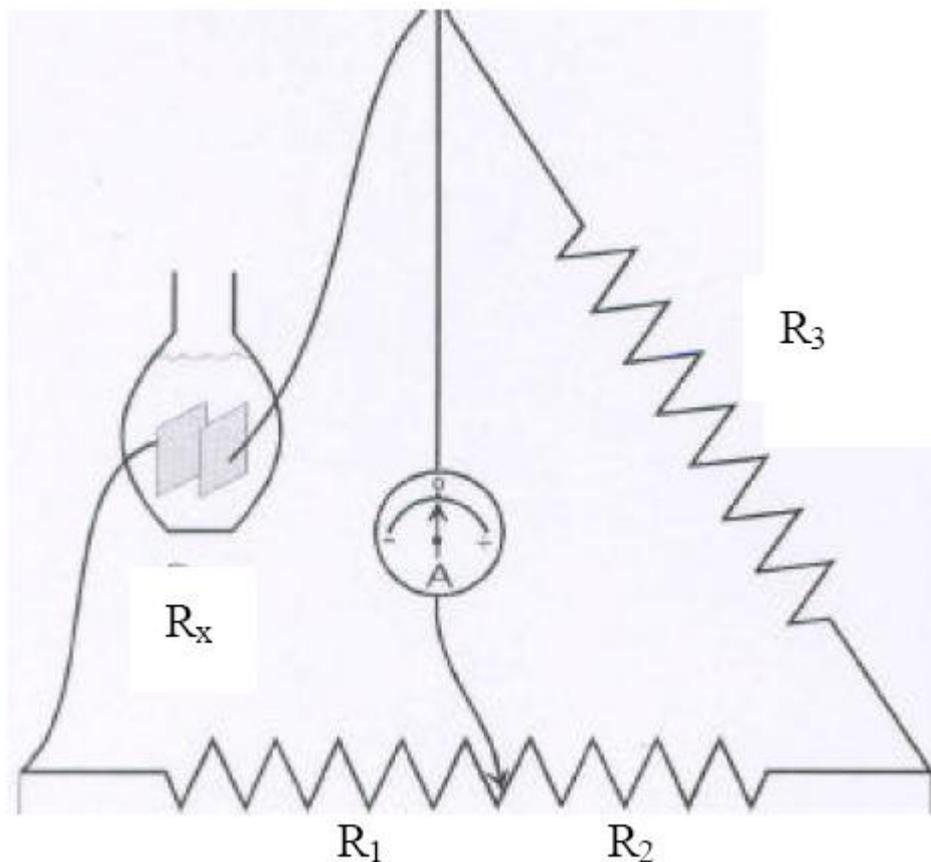
In the present case our interest is in specific conductance or electrical Conductivity (which is the preferred term), the reciprocal of specific resistance,  $k$ , in  $1/\text{ohm.cm}$  or Siemens per centimeter,  $\text{S/cm}$ , which can be thought of as the conductance offered by  $1 \text{ cm}^3$  of electrolyte:

$$K = 1 / \sigma = L / A R \quad 3.3$$

The resistance of the electrolyte is measured across two plates dipped in the liquid and held at a fixed distance apart in a conductivity cell. The ratio  $L/A$  for the cell is called cell constant,  $K_c$ , and has the dimensions  $1/\text{cm}$ . The value of the constant is determined by measuring the resistance of a standard solution of known conductivity:

$$K_c = R \cdot k \quad 3.4$$

In the international system of units (SI) the electrical conductivity is expressed in Siemens which is the reciprocal of resistance in ohm. The older unit for conductance was mho. Report conductivity as milli Siemens per meter at  $25^\circ\text{C}$  ( $\text{mS.m}^{-1}$ ). See table for conversions.



**Figure 3.1 – Schematic Diagram of Conductivity Meter**

An apparatus called a conductivity meter that consists of a conductivity cell and a meter measures conductivity[1-4]. The conductivity cell consists of two electrodes (platinum plates) rigidly held at a constant distance from each other and are connected by cables to the meter. The meter consists of a Wheatstone bridge circuit as shown in the figure. The source of electric current in the meter applies a potential to the plates and the meter measures the electrical resistance of the solution. In order to avoid change of apparent resistance with time due to chemical reactions (polarisation effect at the electrodes) alternating current is used. Some meters read resistance (ohm) while others read in units of conductivity (milli-Siemens per meter). Platinised electrodes must be in good condition (clean, black-coated) and require replating if readings of the standard solution become erratic. Replating should be done in the laboratory. The cell should always

be kept in distilled water when not in use, and thoroughly rinsed in distilled water after measurement.

The design of the plates in the conductivity cell (size, shape, position and condition) determines the conductivity measured and is reflected in the so-called cell constant ( $K_c$ ), Typical values for  $K_c$  are 0.1 to 2.0. The cell constant can be determined by using the conductivity meter to measure the resistance of a standard solution of 0.0100mol/L potassium chloride (KCl). The conductivity of the solution (141.2 mS/m at 25°C) multiplied by the measured resistance gives the value of  $K_c$ , Equation 4. The cell constant is subject to slow changes in time, even under ideal conditions. Thus, determination of the cell constant must be done regularly.

Conductivity is highly temperature dependent. Electrolyte conductivity increases with temperature at a rate of 0.0191 mS/m°C for a standard KCl solution of 0.0100 m.  $R_3 R_x 75$  For natural waters, this temperature coefficient is only approximately the same as that of the standard KCl solution. Thus, the more the sample temperature deviates from 25°C the greater the uncertainty in applying the temperature correction. Always record the temperature of a sample (+0.1°C) and report the measured conductivity at 25°C (using a temperature coefficient of 0.0191 mS/m°C) Most of the modern conductivity meters have a facility to calculate the specific conductivity at 25°C using a built in temperature compensation from 0 to 60°C. The compensation can be manual (measure temperature separately and adjust meter to this) or automatic (there is a temperature electrode connected to the meter).

Current is carried by both cations and anions, but to a different degree. The conductivity due to divalent cations is more than that of mono-valent cations. However, it is not true for anions. The conductivity factors for major ions present in water are listed below[5-7].

**Table 3.1 : Conductivity Factors for ions commonly found in water**

Ion	Conductivity Factor $\mu\text{S/cm per mg/L}$
<b>Cations</b>	
$\text{Ca}^{2+}$	2.60
$\text{Mg}^{2+}$	3.82
$\text{K}^{+}$	1.84
$\text{Na}^{+}$	2.13
<b>Anions</b>	
$\text{HCO}_3$	0.715
$\text{Cl}$	2.14
$\text{SO}_4^{2-}$	1.54
$\text{NO}_3$	1.15

The conductivity of a water sample can be approximated using the following

relationship  $E_c = S (C_i \times f_i)$

in which

$E_c$  = electrical conductivity,  $\mu\text{S/cm}$

$C_i$  = concentration of ionic specie  $i$  in solution,  $\text{mg/L}$

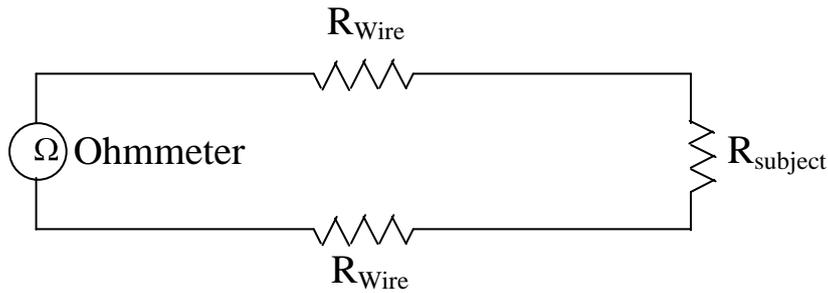
$f_i$  = conductivity factor for ionic specie  $i$

### 3.2 Low temperature resistivity measurements

#### 3.2.1 Experimental Procedure:

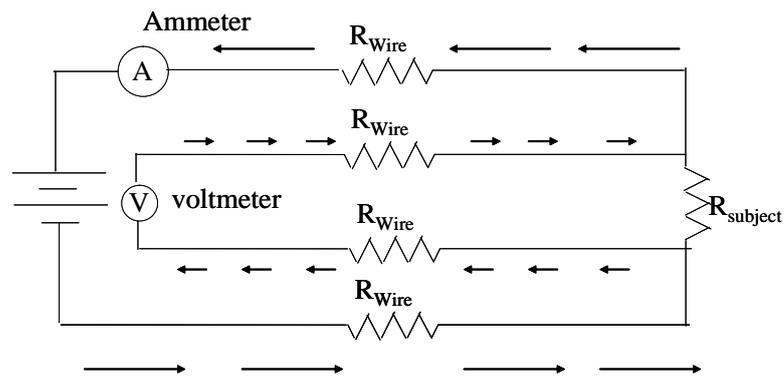
Generally electrical resistivity is measured by two probe method as shown in Fig. 4.1 But in case of two probe method the error due to current

through two contact leads will affect in the measurements in case of small resistance[7-9].



**Figure 3.2 Two probe resistivity measurement.**

To reduce error one can use the “four probe method” as shown in Fig. 4.2 in which two probes are used for passing the current and other two probes are used for measuring voltage. From Fig. 4.2 one can see that voltmeter is connected directly with the sample and the resistance of the voltmeter is very high so no current will pass through the voltage leads[10-14].



**Figure 3.3 Four probe resistivity measurement connection**

The experimental system available at IUC-DAE, Indore consists of advanced current source for passing the current, Schlumberger computing multimeter for measurement of voltage. Measurements down to 10 K are possible by a closed cycle refrigerator system (CCR). The Lakeshore temperature controller is used to control the temperature. In most of the cases a constant current of 10 mA is allowed to pass and the voltage

measured will be of the order of few tens of microvolt. Hence it should be noted here the resolution of the voltmeter should be in nanovolts level for accurate measurements. One can measure the resistivity of four samples at a time by using current scanning card PCL 222A and a scanner for multimeter, PCL 222A is switching board where one can switch between different samples through a computer.

Minate is a 4 Wire Scanner used to measure voltage developed across samples. All the systems are connected with the computer by GPIB (general purpose interface bus) to make the process of measurement automatic. For measurements down to 10K CCR is used. The compressor of this system is separated from the expander but interconnected using flexible helium hoses. Samples are mounted above the expander and contacts of the samples with the expander are made of GE varnish (Thermally conductor and electrically insulator). For the contact of current and voltage leads with the samples silver paste is used. Silicon Diode is used as a temperature sensor. Since the system temperature goes down to 10K one has to keep the samples in vacuum. For this a diffusion pump connected with rotary pump is used which can achieve vacuum upto  $10^{-5}$  mbar. For further protection three shielding are used, one is for thermal shielding to protect thermal effects other is for radiation shielding and the last one is for vacuum shielding. For making connection to the pump with the system vacuum hallow is used, generally thin Cu wires are used as a connecting wire for connection with voltmeter and current source. There may be an error due to induced e.m.f. by the magnetic field developed due to the flow of current through this conductor. To reduce this error one can make the wire by twisting two Cu wires than the magnetic fields due to two conductors will be in opposite direction which will cancel each other's effect. For making connection with each system electromagnetic shielded wires are used where the shielding is made up of conducting wires. This shielding is connected to earth to reduce the noise. There is another source of error due to thermo e.m.f. developed by the temperature gradient in the sample, for this current is repeatedly passed in two opposite directions to reduce the effect of thermo e.m.f.

For resistivity measurement, four contacts were made onto the sample with copper wires and after that current was allowed to pass through outer two contacts and voltage is measured between the inner two contacts as discussed above.

The resistivity calculated using data of resistance of  $\text{Cu}_x\text{WSe}_2$  ( $x = 0, 0.5, 1.0$ ) crystal by normally used resistivity equation[15]

$$\rho = 2\pi s \frac{V}{I} \quad 3.5$$

where,  $s$  = spacing between probes,  $V$  = voltage and  $I$  = current.

and the value of activation energy is calculated using the expression[16]

$$\rho = \rho_0 \exp\left(-\frac{E_a}{KT}\right) \quad 3.6$$

where,

$\rho$  = resistivity at particular temperature

$\rho_0$  = resistivity at room temperature

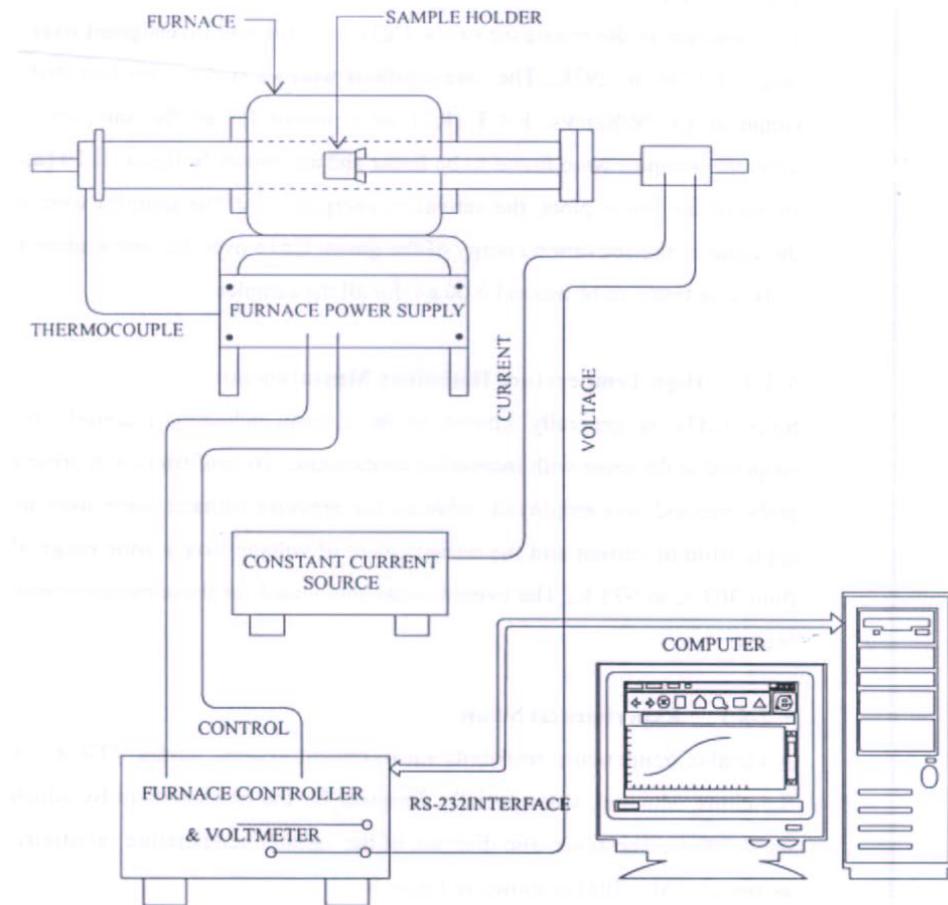
$E_a$  = activation energy

### 3.3 High Temperature Resistivity Measurement

#### 3.3.1 Experimental Procedure :

A variable temperature resistivity measurement system, model VTRM - 408, designed by Scientific Solutions, Mumbai, is specially used for the measurement of resistivity from room temperature to 973K. The schematic diagram of this system is shown in Fig.4.5.

The high temperature resistivity measurement set up consists of the following five units : Sample holder, Furnace, Furnace controller, constant current source and data acquisition source[17-20].



**Figure 3.4 Schematic diagram of high temperature resistivity measurement setup.**

The furnace controller is a programmable digital PID type temperature controller with 10 second PWM output for furnace power supply. The temperature inside the furnace is monitored using thermocouple TC1.

The furnace controller could be operated in two different modes- Step Mode and Sweep Mode. In the Step Mode, the temperature of the furnace was controlled to any desired temperature value within  $\pm 1^{\circ}\text{C}$ , when proper PID values are selected. In the Sweep Mode, the furnace temperature was continuously incremented to any temperature from the lowest ( $25^{\circ}\text{C}$ ) to the maximum temperature ( $700^{\circ}\text{C}$ ) at different sweep rates, say  $1^{\circ}\text{C}$  per minute to  $10^{\circ}\text{C}$  per minute.

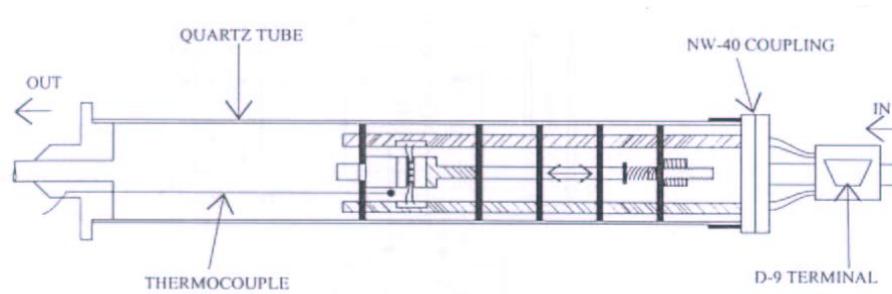
The sample holder assembly consisted of two parts – a quartz tube and the sample holder as shown in the Fig. 4.6. Sample holder was inserted from right end of the quartz tube and could be clamped to it using a NM – 40QC clamp. The thermocouple was inserted from the other end through a nylon neck of the tube. A gas flow or vacuum could be handled through this end.

The sample holder assembly was made up of stainless steel tubes flanges, which could easily withstand 700°C. Thin ( 40 SWG ) stainless steel wires were used as electrical probes. They were brought near the sample through a dual hole ceramic tubes located inside the supporting stainless steel tubes.

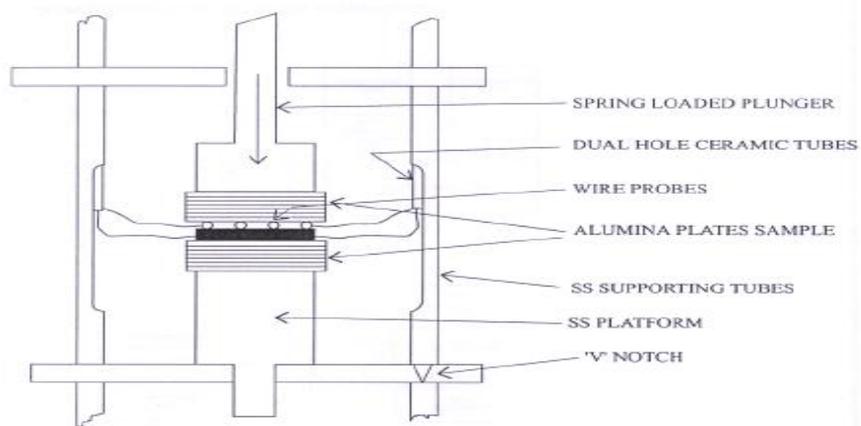
The stainless steel wires were properly positioned and aligned on the lower alumina plate. Over this arrangement, the sample was placed. This sample was then sandwiched between the lower and upper alumina plates using a spring-loaded plunger ( Fig. 4.7). The constant current was passed through the outer leads while the voltage was measured between the inner leads with change in temperature. All the four electrical leads were brought out of the sample holder in a D-type 9- pin connector. Connections to the current source and the voltmeter were made by extending electrical wires from this connector. A 3 ½ digit, 3 range built-in voltmeter in the furnace controller unit measured the voltages from 20 mV to 2000 mV with 10  $\mu$  V resolution for the lowest range. The measurement range can be selected from the front panel switch. Reading on the voltmeter was available on the remote data acquisition personal computer via RS-232 interface lines, which contained information about the sensor temperature, set temperature, percentage power, voltmeter reading and whether the controller action is off or on.

Setting proper PID values in the menu, the furnace was heated and the temperature was increased in accordance with the selected sweep rates. A Q-Basic program directly converted the measured

values of voltage within the inner terminals in terms of resistance values[21-22].



**Figure 3.5 Sample holder assembly.**



**Figure 3.6 Sample holder for high temperature resistivity measurement.**

### 3.4 Experimental

To measure electrical conductivity of all crystal a crystal were combined and form a tablate of 6 mm diameter. Tabulate form of crystal was prepared at S. K. Patel college of Pharmaceutical Education and Research, Ganpat University, Kherva, Gujarat. A rotary Tablet machine was used to prepare tablate of crystals.



**Figure 3.7: Rotary Tablate Machine**

Specification:

**Type:** Minipress – MT – 11

**Pressure:** Hydrostatic

**Company Made:** Karnavati Engineering Pvt. Ltd., Mehsana

**Minimum Quantity:** 100 mg.

**Maximum Quantity:** 1000 mg.

**Used Tool:** B-Tolling (6 mm Diameter)

An electrical conductivity of all crystals was measured at Department of Chemistry, S. P. University, V. V. Nagar, Gujarat. High resistance electrometer was used to measure electrical conductivity shown in figure – 6.3. The temperature was varied for measurement of conductivity of all crystals.



**Figure 3.8: High Resistance Electrometer**

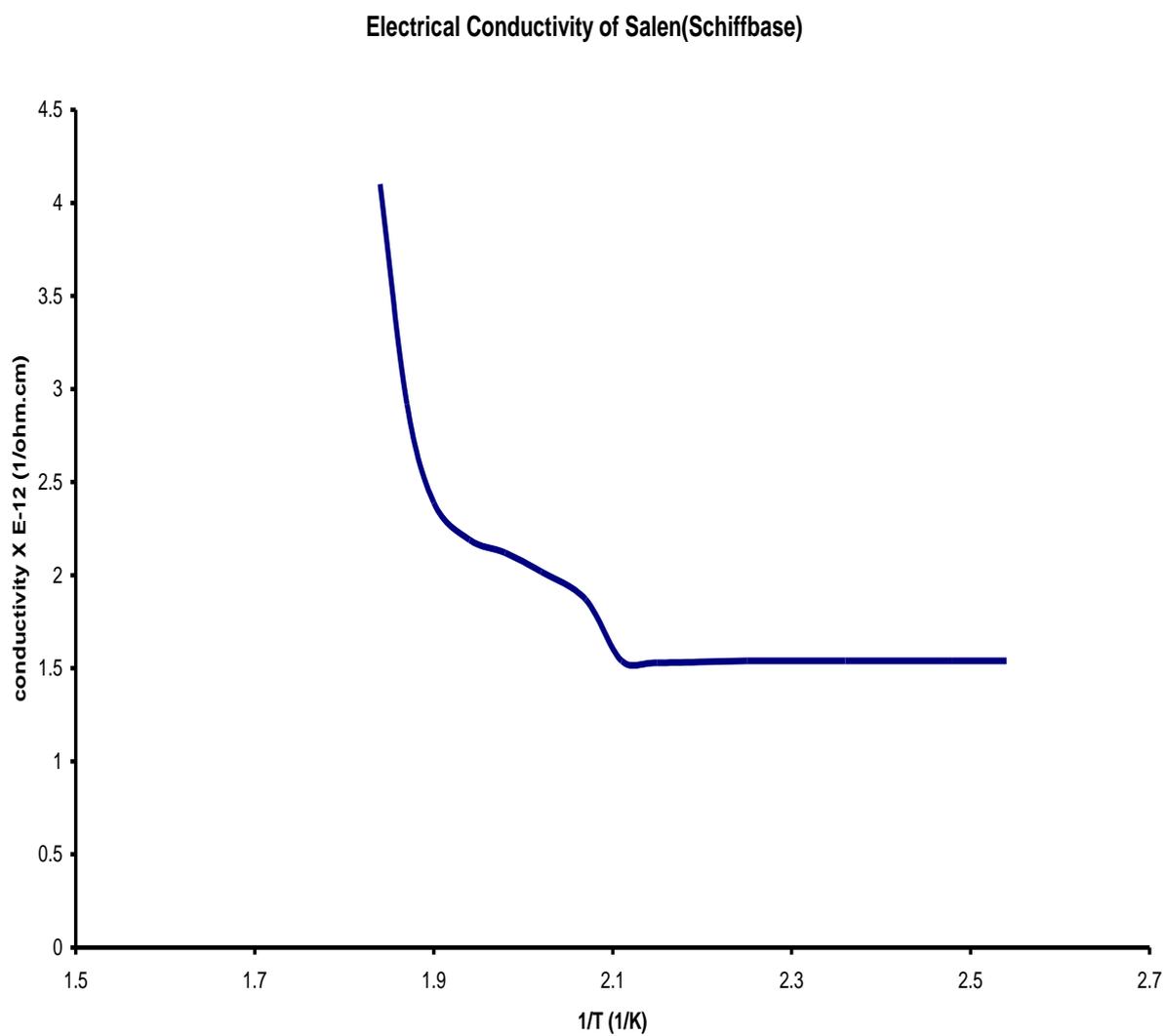
Model Make: Keithley, Germany

Mode: Dynamic

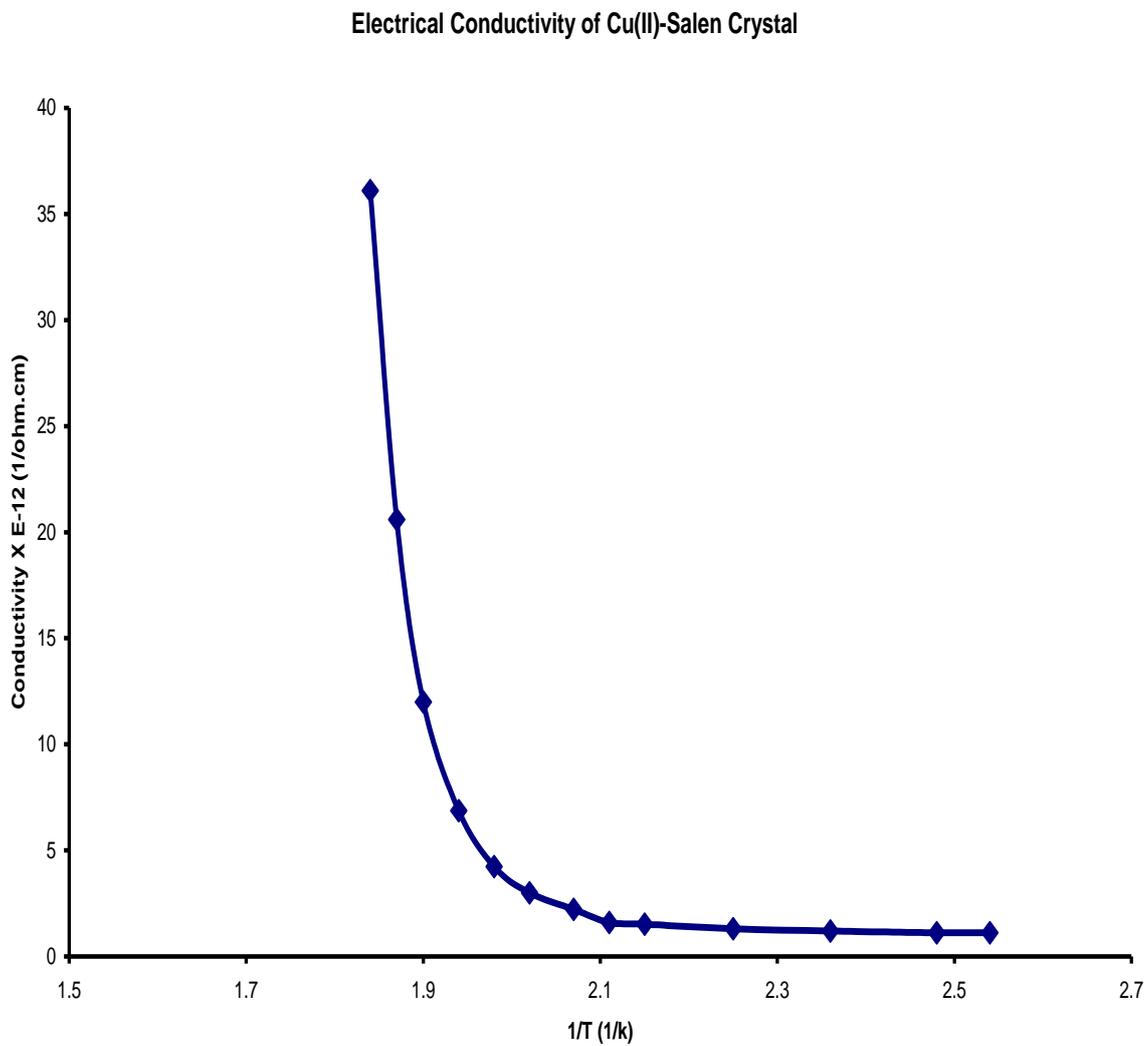
### 3.5 Result and Discussion

**Table 3.2: The Electrical conductivity of azo polymers) at different temperatures.**

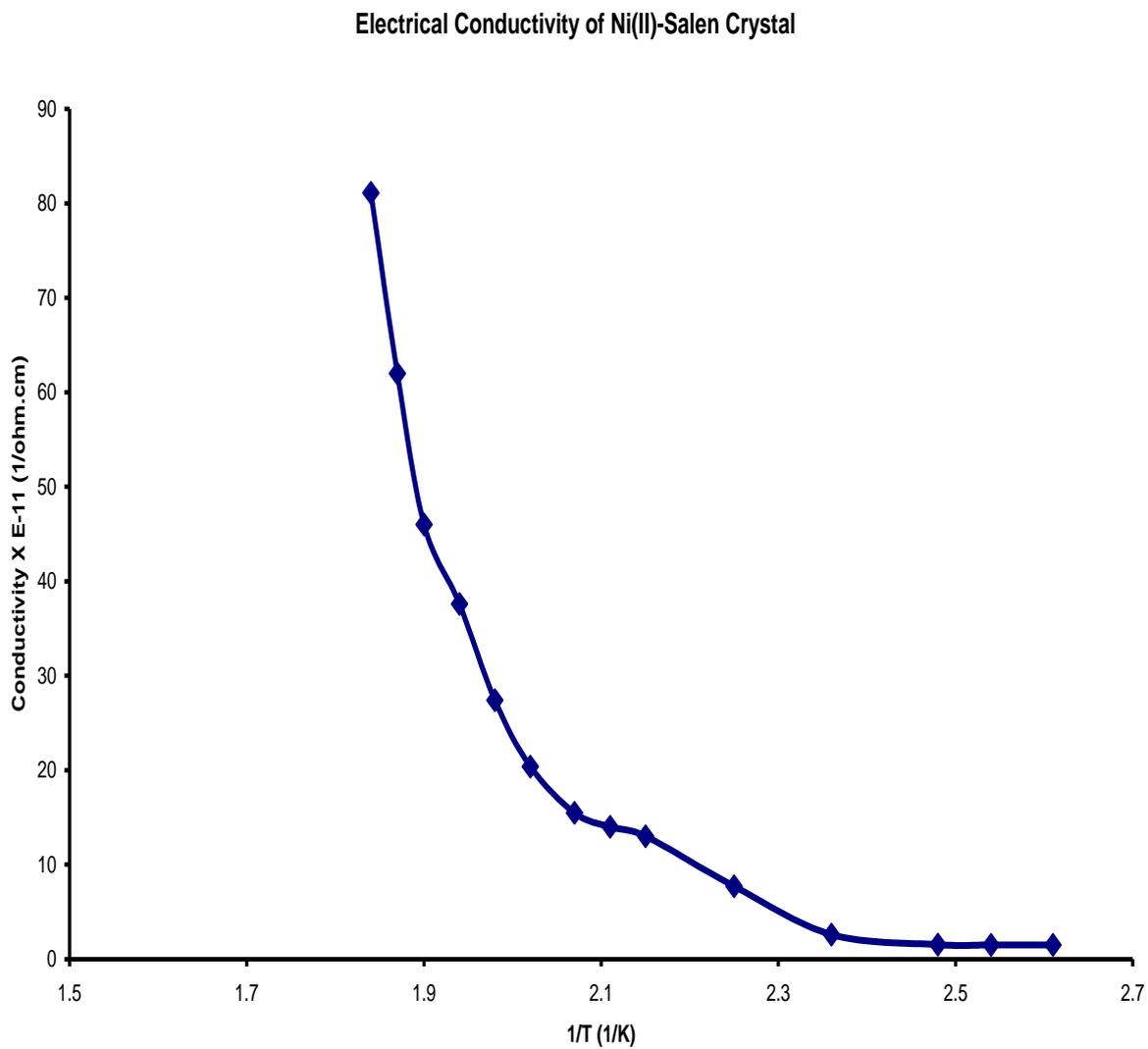
$1/T (^{\circ}\text{K})^{-1}$	Specific conductivity ( $\sigma \text{ ohm}^{-1}\text{cm}^{-1}$ )of samples (at temperature)		
	Salen(Schiffbase)	Cu(II) Crystal	Ni(II) Crystal
3.24	$1.31 \times 10^{-12}$	$1.44 \times 10^{-12}$	$0.57 \times 10^{-12}$
3.09	$1.53 \times 10^{-12}$	$1.70 \times 10^{-12}$	$1.43 \times 10^{-12}$
2.90	$1.30 \times 10^{-12}$	$1.80 \times 10^{-12}$	$0.56 \times 10^{-12}$
2.83	$1.18 \times 10^{-12}$	$1.70 \times 10^{-12}$	$10.2 \times 10^{-12}$
2.75	$1.30 \times 10^{-12}$	$1.60 \times 10^{-12}$	$1.43 \times 10^{-11}$
2.68	$1.37 \times 10^{-12}$	$1.44 \times 10^{-12}$	$1.53 \times 10^{-11}$
2.61	$1.38 \times 10^{-12}$	$1.20 \times 10^{-12}$	$1.52 \times 10^{-11}$
2.54	$1.54 \times 10^{-12}$	$1.11 \times 10^{-12}$	$1.52 \times 10^{-11}$
2.48	$1.54 \times 10^{-12}$	$1.11 \times 10^{-12}$	$1.53 \times 10^{-11}$
2.36	$1.54 \times 10^{-12}$	$1.20 \times 10^{-12}$	$0.26 \times 10^{-10}$
2.25	$1.54 \times 10^{-12}$	$1.31 \times 10^{-12}$	$0.77 \times 10^{-10}$
2.15	$1.53 \times 10^{-12}$	$1.52 \times 10^{-12}$	$0.13 \times 10^{-9}$
2.11	$1.54 \times 10^{-12}$	$1.60 \times 10^{-12}$	$0.14 \times 10^{-9}$
2.07	$1.87 \times 10^{-12}$	$2.22 \times 10^{-12}$	$1.55 \times 10^{-9}$
2.02	$2.02 \times 10^{-12}$	$3.00 \times 10^{-12}$	$2.04 \times 10^{-9}$
1.98	$2.12 \times 10^{-12}$	$4.24 \times 10^{-12}$	$2.74 \times 10^{-9}$
1.94	$2.19 \times 10^{-12}$	$6.87 \times 10^{-12}$	$3.76 \times 10^{-9}$
1.90	$2.39 \times 10^{-12}$	$12.0 \times 10^{-12}$	$4.60 \times 10^{-9}$
1.87	$2.92 \times 10^{-12}$	$20.6 \times 10^{-12}$	$6.2 \times 10^{-9}$
1.84	$4.10 \times 10^{-12}$	$36.1 \times 10^{-12}$	$8.11 \times 10^{-9}$



**Figure 3.9 Electrical Conductivity of Salen(Schiffbase)**



**Figure 3.10 Electrical Conductivity of Cu(II) Crystal**



**Figure 3.11 Electrical Conductivity of Ni(II) Crystal**

Examination of the results presented in Tables - 3.2 reveals that the electrical conductivities of all the crystals are in the range from  $10^{-12}$  to  $10^{-11}$   $\text{ohm}^{-1}.\text{cm}^{-1}$  at  $25^{\circ}\text{C}$ . This show that the conductivity of crystals is rather low at room temperature but the conductivity increase with temperature slowly initially and very rapidly after some point between 410 and  $510^{\circ}\text{K}$  depending upon the nature of the crystals[23-25].

The plots of  $\log \sigma$  vs  $1/T$  (Shown in Figure 3.9 to Figure 3.11) for all samples are found to be linear in the higher temperature range. The temperature at which this occurs is designated as the break temperature. The change in the value of  $\sigma$  beyond this break temperature and in the high temperature range is comparatively faster. Below the break temperature the change in the value of  $\log \sigma$  vs  $1/T$  is slow and regular except in the case of Ni(II) crystal; with these latter three the variation in the value of  $\sigma$  below break temperature is not regular. In these cases the value of  $\sigma$  increases and then decreases and further increases with increase in temperature[26-28].

Usually the break point is associated with thermal degradation of the sample. But the earlier investigation of thermal stability of present crystals show no softening or melting properties at the temperature or entire temperature range in which the present study was carried out. It has been establish that from the conductivity measurements at temperature below the break point that the results of initial measurements on a new sample are not reproducible.

The first measurements give conductivity curves, which lie considerably below and steeper than the stabilized curve as shown in Figure 3.9 to Figure 3.11. This indicates that an orientation effect occurs when an external field is applied and that the curves below the break temperature perhaps are determined by parameters of secondary interest, such as grain size of the sample, molding the pellets- all related to the fact that sample was polycrystalline. Therefore, it may be difficulty to draw

conclusions concerning the properties of the Schiffbase and crystals from these initial parts of the curves.

It is worth noting that the electrical conductivity of crystals highly dependent on the nature of metal atom, nature of used ligand and the size and shape of the macromolecules. In the present cases there would be uncertainty about the structures of crystals because the crystals formed through cross-linking metal bridges between two Ligand chains. Hence information about the electrical properties of crystals will not be appropriate as to permit further conclusion. In fact the results of electrical conductivity of all crystals reveal that they can be ranked as semi conducting material with high resistance[29-32]. It was also observed that Cu(II) and Ni(II) are found to be better conductor and this may due to existence of planer or coplanar structure up to some extents in the crystal.

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