CHAPTER IV

ELECTRICAL CHARACTERIZATION
Electrical characterization forms the backbone of any investigation on solid electrolyte and electrode materials, because the magnitude of ionic and electronic conductivity present in them rates their utilization in electrochemical devices. The charge transference ability of solid electrolytes in terms of optimum ionic conductivity, and mixed (electronic + ionic) conductivity of electrode materials are hallmarks of electrochemical sensors constituents. The first section (A) of this chapter deals with the brief background of complex impedance spectroscopy, general measurement techniques used therein followed by results and discussion. The second section (B) is devoted to temperature and concentration dependent conductivity. The third and last section (C) covers the details of transport number followed by results and discussion.

IV.A COMPLEX IMPEDANCE SPECTROSCOPY

At present, the complex impedance measurements are widely popular as a technique for characterizing both the liquid and the solid electrolytes along with other materials. The complex impedance data analysis can yield near-perfect estimates of bulk conductivity of the materials free from the displacement current and the electrode polarization effects. The latter one is inherent in the steady state dc measurements.

Sluyters et al have extensively used complex impedance method to study the polarization phenomenon of aqueous electrochemical cell [1]. Thereafter, this technique has been considered to be one of the powerful tools to analyze the electrochemical processes in the field of aqueous electrochemistry. Late in 1969 impedance spectroscopy has been first employed by Bauerle to study the basic polarization process in the cell of yttria stabilized zirconia [2]. Since then, this technique has been in vogue for characterizing the wide range of materials, which include polymers, oxides, glasses, halides, etc.

Jonscher has been instrumental in acquiring the huge amount of impedance information pertaining to dielectric loss [3]. In number of instances, the data on
dielectric loss have been used to determine the conductivities of solid electrolyte [4]. Almond and co-workers in 1982 have transformed the Jonscher’s empirical universal dielectric response equation into a form, which is useful for analyzing the small signal ac response of ionic materials [5]. This explains satisfactorily the non-zero dc conductivity and power law behavior in solid electrolyte [5]. The details of these are discussed in the subsequent subsection.

Macdonald and Brachman have developed quantitative methods for analyzing the experimental impedance results of semiconductors [6]. In subsequent years, a particular approach to unify and simplify the results of impedance measurements has been developed. This approach has primarily been based on the most general situation, where three connected arcs appears when the real and imaginary parts of the impedance are plotted parametrically as a function of frequency in the complex impedance plane or Cole-Cole plots [7]. The complex non-linear least squares fit program developed by Macdonald and Brachman proved to be extremely versatile, and allow for the fitting of the data to the different equivalent circuits, which include both the ideal and the distributed elements [6].

The complex impedance spectroscopic (CIS) studies involve measurement of real and imaginary parts of impedance/admittance as a parametric function of frequency over a wide range. In recent years, this technique has become a well-accepted fundamental tool for characterizing ionic conductors in terms of ionic conductivity, electrode polarization, activation enthalpy for ion migration, etc. In more recent past, it has been rightly exploited to probe the solid electrolytes, particularly, to distinguish the inter-grain, intra-grain conduction, micro-heterogeneity and electrode-electrolyte interface. Additionally, impedance spectroscopy and quasi-elastic neutron scattering have been successfully combined to probe the micro-dynamics of polymeric, glassy and crystalline materials. Besides offering these applications, in the characterization of materials, the technique also provides a unique possibility to investigate the motion of charged particles (ions and/or polarons) on very different time scales. Even it resolves the
elementary hopping processes of mobile charges. Hence, it is a very powerful microscope in time.

The CIS technique has been extensively utilized to examine and understand the role of space charge layer forming across (i) conducting/insulator and (ii) conducting/conducting (two- or multi-phase systems) interfaces [7-10]. At appropriate second phase concentration, i.e. at percolation threshold, space charge layer dominates the conduction of composite electrolyte. On the other hand, grain-boundaries have been the limiting factors in effectively employing intrinsic oxygen conductor in devices [11-13].

In the light of above discussion it can be said that, without appropriate technique, the measured results might be assigned to bulk electrolyte, while, in fact, may be envisaged as a combination of all the above mentioned contributions. The analysis of complex impedance data, however, can almost always yield the true bulk conductivity of the material. The major difficulty encountered in the measurement of ionic conductivity of solids has been polarization at the electrode/electrolyte interface, and at the grain-boundaries in the polycrystalline solids. Using ideally reversible or alternatively blocking electrodes, one can principally eliminate the electrode polarization. Hence, apart from investigating genuine impedance dispersion, another main objective in performing frequency dependant measurement is, indeed, to identify and circumvent electrode polarization effects. Additionally, CIS technique can be employed to distinguish the inter-grain (conduction between the grain), intra-grain (conduction within the grain), and their effects on ion migration [14-17]. The chief advantage of impedance spectroscopy over measurements in the time domain is that the measured data can be described analytically, using an equivalent circuit as a model. The elements of an equivalent circuit model represent the various macroscopic processes involved in the transport of mass and charge in solid electrolyte. The details are discussed below.
IV.A.1 THEORY

In impedance measurements, a sine wave is used because when sinusoidal signal applied to a linear system of the type in shown figure IV.1, the input and output have the same form, so the magnitude of the response is directly proportional to the electrical stimulus. At any specific frequency, there is a linear relationship between the input and the output signals. The impedance of such a circuit is the ratio of voltage to current, as Ohm's law holds true in time domain. If the voltage function is given by

\[ V(t) = V_m \exp(j\omega t) \]  

(IV.1)

Then the current function will be given by

\[ I(t) = I_m \exp(j\omega t - \phi), \]  

(IV.2)

where, \( \phi \) represents the phase angle. The negative value of \( \phi \) indicates that the current leads the voltage, and the impedance is composed of a frequency independent resistive term \( R \) and capacitive term \( 1/j\omega C \), where, \( j = (-1)^{1/2} \). Conversely, the positive value of \( \phi \) indicates that the voltage leads the current and \( Z \) is composed of \( R \) and the inductive term \( j\omega L \). The impedance of the circuit, \( Z(\omega) \), can be expressed in both polar as well as Cartesian forms;

\[ Z(\omega) = |Z| \exp(-j\phi) = |Z| \cos(\phi) - |Z| \sin(\phi) = Z_r - jZ_i \]  

(IV.3)

here \( Z_r \) and \( Z_i \) are real and imaginary parts of impedance, respectively. The relations between various quantities are:

\[ |Z| = (Z_r^2 + Z_i^2)^{1/2} \]  

(IV.4)
$$\phi = \text{Arc tan} \left( \frac{Z_i}{Z_r} \right)$$  \hspace{1cm} (IV.5)

Admittance, \( Y = \frac{1}{Z(\omega)} = G + iB \)  \hspace{1cm} (IV.6)

where

\[ G, \text{ conductance} = \frac{Z_r}{Z_r + Z_i^2}, \text{ and } B, \text{ susceptance} = \frac{Z_i}{Z_r + Z_i^2} \]  \hspace{1cm} (IV.7)

The geometric response of a circuit, comprising parallel combination of RC components (Fig. IV.2a), in complex impedance plane is represented in figure IV.2b. Since

\[ G = \frac{1}{R} \text{ and } B = \omega C, \]

\[ Z_r = \frac{G}{G_i + B_i} = \frac{R}{1 + (\omega RC)^2} \]  \hspace{1cm} (IV.8a)

and

\[ Z_i = \frac{B}{G_i + B_i} = \frac{\omega R_i C}{1 + (\omega RC)^2} \]  \hspace{1cm} (IV.8b)

Eliminating \( \omega \) from the above equations (IV.8a) and (IV.8b) followed by rearrangement give,

\[ \left( Z_r - \frac{R}{2} \right)^2 + Z_i^2 = \left( \frac{R}{2} \right)^2 \]  \hspace{1cm} (IV.9)

This is an equation of a circle with radius \( R/2 \) and centre at \((R/2,0)\). The co-ordinates at the top of the arc are \((R/2,R/2)\). Thus, at

Fig.IV.2: (a) An electrical equivalent and (b) Geometric response of circuit in complex impedance plane.
frequency \( \omega = \omega_o \),

\[
Z_i = \frac{R}{2} = \frac{R}{1 + (\omega_o RC)^2}, \quad \text{and} \quad Z_i = \frac{R}{2} = \frac{\omega_o R C}{1 + (\omega_o RC)^2}
\]

Combining and rearranging, it follows that,

\[
\omega_o RC = 1 \quad \text{or} \quad \omega_o = \frac{1}{RC}
\]

Thus, the impedance response of a resistor \( R \) in parallel with capacitor \( C \) will be a perfect semicircle intersecting the real axis at \((R, 0)\) as shown in figure IV.2b. The relaxation time \( \tau_o = RC \) is given by the inverse of frequency at the top of the semicircle. On the other hand, Cole-Coie distribution of relaxation times, the real and imaginary parts of the impedance are given by,

\[
Z_r = \frac{R \left\{ 1 + (\omega \tau_o)^{-\alpha} \sin \left( \frac{\alpha \pi}{2} \right) \right\}}{1 + 2 (\omega \tau_o)^{-\alpha} \sin \left( \frac{\alpha \pi}{2} \right) + (\omega \tau_o)^{2(1-\alpha)}}
\]

\[\text{and}\]

\[
Z_i = \frac{R \left\{ (\omega \tau_o)^{-\alpha} \cos \left( \frac{\alpha \pi}{2} \right) \right\}}{1 + 2 (\omega \tau_o)^{-\alpha} \sin \left( \frac{\pi \alpha}{2} \right) + (\omega \tau_o)^{2(1-\alpha)}}
\]

Similar expressions for real and imaginary parts of the impedance can also be derived for the circuit shown in figure IV.3. For such circuits,

\[
C_v = \beta \omega^{n-1} \quad \text{and} \quad R_v = \frac{1}{\alpha \omega^n}
\]

where, \( n = 1 - \alpha \) and \( \frac{\alpha \pi}{2} = Arc \tan \frac{a}{\beta} \)
\[ G = \frac{1}{R + \alpha \omega^n} \quad \text{and} \quad B = \beta \omega^n \quad \text{(IV.14)} \]

so \[ G = \frac{Z_i}{Z_i^2 + Z_j^2} \quad \text{and} \quad B = \frac{Z_i}{Z_i^2 + Z_j^2} \quad \text{(IV.15)} \]

Reorganisation of equations (IV.12a) to (IV.15), eliminating \( \omega^n \) and replacing \( \alpha / \beta \) with \( \tan(\alpha/2) \) yields

\[
\left( Z_i - \frac{R}{2} \right)^2 + \left( Z_j - \left[ R \tan\left( \frac{\alpha \pi}{2} \right) \right]^2 \right)^3
\]

where, \( r^i = \left( \frac{R}{2} \right)^2 + \left( \frac{R}{2} \right)^2 + \tan\left( \frac{\alpha \pi}{2} \right)^2 \)

This is an equation of a circle with centre \( (R/2, [R \tan\{\alpha \pi/2\}]/2) \) and radius \( r \). Thus, the impedance response of the circuit shown in figure IV.3 or Cole-Cole distribution, yield an arc depressed below the real axis (Figure IV.3b) by an angle \( \alpha \pi/2 \) and intersect at \( (R,0) \) [1]. Co-ordinates at the top of the arc are \( (R/2, \ [R \cos(\alpha \pi/2)]/2 \ (1+\sin(\alpha \pi/2)) \), and the mean relaxation time is inverse of the peak frequency \( f_0 \).
Each of the physical processes taking place in an electrochemical cell, would give a separate semicircle provided their values of relaxation time are widely different. As a first approximation, each of the semicircles in the impedance diagram may be considered as the response of the lump $R-C$ combination. From the correlation between the parameters of semicircle, $R$ and $C$ components, it has been seen that the plotting of such a diagram provides a straightforward determination of the electrolyte resistance irrespective of the degree of electrode polarisation. This is the chief advantage of complex impedance spectroscopy. In addition, this method does not necessarily require the use of reversible electrodes or complicated cell geometry while making a study of the electrode polarisation. Determination of the dielectric properties of the material and an ease of studying the electrode polarisation are the additional advantages of impedance analysis. Complications, however, arise in obtaining an equivalent circuit to be used to simulate the electrode phenomenon. The elements must be present in simulated equivalent circuit accounting for the impedance due to various electrode processes. A few examples with different $R-C$ series/parallel or more complex lumps are illustrated in figure IV. 4a and IV.4b so as to simulate an equivalent electrical $R-C$ circuit for some complicated Cole-Cole plots [18]. A highly convoluted combination of line and semicircle in the impedance plot is sometimes difficult to resolve and then admittance diagrams instead of impedance diagrams are preferred. According to Jonscher [3], there may be a deviation from the ideal behaviour due to some other reasons and this becomes much more pronounced in admittance representation than in the conventional impedance plot [3]. This is possible because the identification of deviation from a straight line is easier than that from a circular arc. The fitting of a straight line is also more accurate than that of a circular arc, which is an added advantage of admittance analysis.
Fig. IV.4a: (a) Series combination of resistor $R_1$ with capacitor $C_1$ and resistor $R_2$ with capacitor $C_2$ connected in parallel, (b) a series combination of resistor $R_1$ with capacitor $C_1$ connected in parallel with $R_2$ and whole circuit is connected in series with capacitor $C_2$, (c) a series combination of resistor $R_1$ with capacitor $C_1$ connected in parallel with $C_2$ and whole circuit is connected in series with capacitor $R_2$, along with corresponding complex impedance plots for different values of components.

Fig. IV.4b: (a) Parallel combination of resistor $R_1$ and capacitor $C_1$ in series with a parallel combination of resistor $R_2$ and capacitor $C_2$, (b), (c) and (d) complex impedance plots for different values of components.

IV.A2 SAMPLE PREPARATION FOR IMPEDANCE MEASUREMENT

For impedance measurements, the specimens were obtained in the form of circular discs of 10mm diameter and 1-2 mm thickness. In order to achieve good ohmic contacts, high quality graphite paint was applied on the both flat surfaces followed by baking them at about 200°C for two hours in an electric furnace. The impedance measurement was taken 500°C. The sample holder assembly for impedance measurement consisting of six well-polished silver electrodes, facilitating spring loading of six samples at a time, allows determining the relative conductivity
performance of sample under identical conditions. The details of the sample holder are discussed below.

IV.A3 EXPERIMENTAL DETAILS

IV.A3.i Design and Development of Sample Holder
A sample holder designed and developed, facilitating spring loading of six samples as well as monitoring gas partial pressure is shown schematically in figure IV.5. The sample holder can withstand temperature up to 1000°C. Part A of the sample holder (Fig. IV.5a) is outer jacket (inserted in furnace) that does not allow any gas to flow in or out. The part B (Fig. IV.5b) is designed to spring load the six samples. The spring (inside water-cooling jacket, which is not shown in figure IV.5b), placed at the top of each alumina pressing rod allows spring loading of sample. The expansion/contraction of solid samples while heating/cooling is compensated by such arrangement. A pre-calibrated thermocouple, placed in a close vicinity of samples, facilitates the measurement of actual sample temperature. The temperature gradient within the area of measurement was seen to be negligible; and O-ring achieves a gas tight fitting between the lower and upper flanges.

Water circulation systems, is provided for cooling the area close to O-ring, to protect it at high temperature so also to retain spring action since, at high temperature spring action reduces. A six core coaxial cable (Teflon coated) of length ≈ 10 cm is used (electrical connection between upper electrodes and switching system) to avoid electrical interference during the impedance measurements. Lower six electrodes, shown in insert of figure IV.5b, are internally linked together with a common point fastened to ‘low’ of the impedance analyzer.

IV.A3.ii Complex Impedance Measurements
Impedance spectra, in general, span more than 17 decades on the frequency scale, ranging about $10^3$Hz - $10^{14}$Hz. Depending upon the frequency range, entire frequency range is divided into following four regions. (i) the low impedance
Figure IV.5: Schematic presentation of sample holder for impedance measurement of six samples

regime, (frequency below a few megahertz). (ii) the radio regime (a few MHz to a few GHz) and (iii) The microwave regime (few GHz to about 150GHz) and (4) far-infrared regime (above 150GHz).

Electrodes are used during measurement only in the first frequency regime. Guided electromagnetic waves are employed in cases of second and third ones, and unguided electromagnetic waves are employed in fourth. Coaxial wave-guides are in practice up to 18GHz. In all above experimental set-ups may differ in technique, but the general procedure towards the materials characterisation is radically same in any regime of the spectrum. The complex impedance is always determined by measuring the amplitude and phases of quantities related to field-induced current in the material. These quantities are voltage and currents, in the first regime. In other cases (electrode-free), the relevant quantities are complex field amplitude of
electromagnetic waves transmitted or reflected by the sample. In this technique $Z(\omega)$ is obtained from the measured data and the boundary conditions at the interfaces that guarantee the continuity of the electric and magnetic field components.

The present work, particularly, focuses the attention on the measurement and analysis in the first frequency regime (up to a few MHz), which is very important from the development of materials from electrochemical device application and microscopic conduction mechanism view points. A standard electrode technique was used as described below.

Prior to the impedance measurement, the spring-loaded samples were heated at a suitable maximum temperature $T_1$ (normally it is below the melting/glass transition temperature or decomposition temperature of the sample) for half an hour as shown in figure IV.6. The soaking time (dwell time) of 30 minutes was seen to be sufficient to homogenize the charge carriers in them, and also simultaneously to remove the moisture content therein, if any. During the cooling cycle, at each set

![Figure IV.6: Temperature profile during the impedance measurement](image-url)
temperatures ($T_2$, $T_3$, and $T_4$...), a dwell time of 30 minutes was given to ensure thermal equilibrium in the samples. The real and the imaginary parts of impedance, 10 minutes prior to an end of dwell time ($t_6$, Figure IV.6), are measured as a function of frequency. The concentration of gases of interest was maintained throughout the experiment.

The impedance data of samples obtained at each temperature were arranged systematically, labeled and stored during the measurements. On line impedance data analysis was used to get various impedance parameters viz. bulk conductivity, ion hopping relaxation time/frequency, distribution in relaxation time and activation enthalpy for ion migration, etc. A brief description of the computer automated measurement system is given below.

**IV.A3.iii Computer-automated Experimental Set-up**

The computer-automated system, for multi-channel complex impedance measurement is depicted schematically in figure IV.7. It consists of: (i) impedance
analyzer (HP 4192A) (ii) R. F. switching system (Keithley 7001 switch main frame) (iii) home made furnace, (iv) gas mixing system, (vi) sample holder (provision to spring load six samples at a time) and (vii) personnel computer (Pentium processor) installed with IEEE-488 GPIB interface and DAC-16 cards.

The HP 4192A LF impedance analyser has a built in capability to measure real and imaginary parts of impedance in the frequency range from 5Hz to 13MHz. A programmable signal level allows applying voltage less than decomposition potential of solid electrolyte. The Keithley 7001 main frame system preinstalled with 6001 r. f. switchboard facilitates selection of 10 samples as per operator’s choice. Both these instruments have built in remote operation capability via IEEE-488 interface bus. The furnace with power pack is used for heating and cooling procedures. Home-made GUI (graphic user interface) computer software was used to acquire the data and subsequent analysis. A desired partial pressure (10 to 10000 ppm) of the gas of interest (SO₂/CO₂) can be maintained around the samples using electronic mass-flow-meter (Teledyne Hastings, USA) with computer interface compatibility.

IV.A4 RESULTS AND DISCUSSION

Figure IV.8 shows the impedance plots of pure Ag₃SO₄. From this figure it is seen that only one perfect semicircle occur in low temperature modification of Ag₃SO₄. It is worth to note the appearance of a small bulge at 415⁰C in the frequency domain 5 to 8 MHz. This show an anomalous feature which continues further at all temperature above 415⁰C. Its reproducibility is checked by repeating the conductivity measurement, and also by using non-blocking silver electrode. The presence of single semicircle along with small bulge indicates that the appearance of this anomalous feature at high frequency is due to passage of current through the Ag₃SO₄ electrolyte (excluding electrode effect). Further, these results rule out the possibility of the appearance of the one of the semicircles for the sample belonging to 1st and 2nd region due to non-blocking nature of the Ag electrode. This results
Fig. (IV.8): Complex impedance plots for pure Ag$_2$SO$_4$ with silver electrodes.

substantiate the occurrence of two semicircles due to the mobility of Ag$^+$ and M$^{2+}$. The typical complex impedance plots for (100-x)Ag$_2$SO$_4$;(x)MSO$_4$ (M = Ba, Ca) systems, at temperature 250°C within the limits of solid solutions (x ≤ 5.27 mole %) are displayed in the figure IV.9. Both compositions exhibit distorted semicircle arc. Since the conductive silver coating on both surfaces of the electrolyte acts as reversible (non-blocking) electrode, no electrode polarisation is reflected in the complex impedance plane. A non-linear least squares (NLLS) fit method was used to ascertain the presence of two overlapping dispersed semicircular arc. In order to accomplish it, the complex impedance data, acquired at a fixed temperature using computer control HP-4192A LF impedance analyser, fitted to the equation

$$Z(\omega) = Z(\infty) + \frac{Z(\infty) - Z(0)}{1 + (J\omega \tau)^\alpha}$$

(IV.17)

where the symbol carries usual meaning. A careful look at the figure IV.9 reveals that the each distorted semicircular arc is a combination of two overlapping dispersed semicircle, which is further suggestive of the presence two different associated relaxation time in the conduction process. On the other hand, a perfect singly semicircular at a fixed temperature is discernable (Fig. IV.9b) for two phase systems, i.e. for (80)Ag$_2$SO$_4$;(20)CaSO$_4$. 

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For clear understanding of the above results, the entire system of $(100-x)\text{Ag}_2\text{SO}_4:(x)\text{MSO}_4$ is divided into two region.

Region I $\text{Ag}_2\text{SO}_4$ solid solution for $x \leq 5.27$ mole % and Region II biphasic mixture for $x > 5.27$ mole %.

**Region-I**

Since the silver coating on both the surfaces of electrolyte acts as an reversible (non-blocking) electrode, no spur or inclined line due to electrode-electrolyte interface is seen. The distorted semicircular arc is the manifestation of ion migration through the sample [39]. A careful look at the figures reveals that the distorted semicircle is a combination of two overlapping depressed semicircles (represented by dished semicircles). This suggests the occurrence of two prominent conduction mechanisms simultaneously under the external perturbation ac signal. Many processes can be envisaged in polycrystalline ion conducting specimens. However, experimental impedance obviously contains major

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**Fig. IV.9:** Complex impedance plots for $(100-x)\text{Ag}_2\text{SO}_4:(x)\text{MSO}_4$ systems, at temperature $250^\circ\text{C}$ (a)$M = \text{Ba}$ and (b) $M = \text{Ca}$

**Fig. IV.9b:** Complex impedance plot for $(80)\text{Ag}_2\text{SO}_4:(20)\text{CaSO}_4$ system at temperature various temperatures
contribution from inter-grain and intra-grain ion migration [39].

There would be a number of macroscopic models to manifest the above two conduction processes subsequently, presence of two semicircular arcs in the complex impedance plane. Instead of a simple arrangement of squares here, a brick wall model is considered as shown in figure IV.10 so as to account for the above conduction processes. Owing to the recent developments in polycrystalline conductors [39], the total intra-grain conduction (conduction within the square) comprises conduction via following two paths. (i) conduction due to mobility of ions parallel to interface in the highly disordered space-charge region \( Y^{\parallel} \) and (ii) conduction due to ionic transport in an interior of the grain (\( Y' \)). Similarly, the conduction across the grains (from one square to other nearby one), which can be denoted by \( Y^{\perp} \). An electrical equivalent of these processes is represented in figure IV.10 (c). The conduction in each sub-region is considered to be due to a series of forward successive jumps of mobile ions in the direction of an applied electric field. Each successive forward hop is represented by a resistor R, the capacitor C connected.
across this resistor accounts for the backward jump followed by the forward one to a nearby vacant site (an unsuccessful jump) which also takes care of the displacement current (Fig. IV.10b) [39]. Here, the geometric capacitance $C_g$ is shunted by a number of parallel current paths and the capacitors in each sub-region takes care of displacement current.

Region-II

As the concentration of added impurity ($\text{MSO}_4$) is further increase beyond 5.27 mole%, the insoluble phase get dispersed into the matrix of $\text{Ag}_2\text{SO}_4$. The evidence of phase separation can be obtained from the corresponding XRD and SEM characterization carried out on these samples, the result of which are discussed in the chapter V. According to the dispersed phase theory for MX/MX' discussed in chapter-1, there is a net transfer of cations ($\text{Ag}^+$ and $\text{M}^{2+}$) from either phase across the interface. The interfacial reaction would be taking place in the wake of free energy association which makes the particular interfacial reaction more favourable to occur than the other. These factors enrich the interstitial ions and vacancy concentration forming a space charge layers close to the contacted region of $\text{Ag}_2\text{SO}_4$ and $\text{MSO}_4$. As a result of this, the mobility of $\text{Ag}^+$ parallel to interface (also term as an ion parculating path) is strongly govern by concentration of the charge carriers present there, as well as any distortion, i.e. likely to place when wrong size $\text{M}^{2+}$ cross over the grain containing predominant concentration of their counter parts. These results are discussed in detail in the next section.

A physical representation of samples belonging to this region is depicted in figure IV.11a. the space charge layer existing between the grain of $\text{Ag}_2\text{SO}_4$ and $\text{MSO}_4$ is indicated. This physical picture can suitably be described by a simple electrical equivalent circuit as shown in figure IV.11b. Each subcircuits in the
dashed rectangle represent the individual grain. Here impedance offered by the
grain shown as a circuit elements, in the dashed rectangle is exceedingly high. On
the other hand, in the two phase mixture of moderately conducting grains, ions are

![Diagram](image)

**Fig IV.11 (a) The interfacial Ag$_2$SO$_4$/MSO$_4$ grain contact involving space charge layer
(b) Equivalent circuit**

more mobile along the space charge layer which as described by Maier(1985). Thus, in the region II, conductivity is solely attributed to the Ag$^+$ migration along the interfacial diffuse space charge layers. Since the surface percolation is most likely to take place rather than the intragrain conduction, almost all current passes through circuit element shown in figure IV.11b corresponding to space charge layers, resulting into single relaxation time. This description is strongly supportive of the resultant single semicircle in the complex impedance plane in the region II, shown as a representative example in the figure IV.9b.
IV.B  TEMPERATURE AND CONCENTRATION DEPENDENT
CONDUCTIVITY

Atomic transport in solid is considered as a field of growing importance in solid-state physics and chemistry. The bulk transport generally refers either to a flux of matter in a chemical potential gradient or flux of charge in an electric potential gradient. The former case results in diffusion and the latter in conductivity.

Exceptionally high ionic conductivity in solid electrolytes is often interpreted in terms of hopping of mobile charge carrier from occupied site to nearby vacant site [19]. The conductivity due to such hopping of ions is, generally, expressed as the product of fractional number of defects $n_d$ and the hopping rate of a defect $\nu_d$ i.e.

$$\sigma \propto n_d \nu_d$$

$$\sigma \propto e^{-\frac{E_f}{kT}}e^{-\frac{E_m}{kT}}$$

(IV.18)

The first term in the equation refers to the thermally activated defect concentration and second term to the temperature dependent hopping rate, which are expressed respectively as

$$n_d = n_0 e^{-\frac{E_f}{kT}}$$

(IV.18a)

$$\nu = \nu_0 e^{-\frac{E_m}{kT}}$$

(IV.18b)

where $E_f$ and $E_m$ are the energy of defect formation and migration respectively. Thus,

$$\sigma \propto e^{-(E_f + E_m)/kT}$$

$$\sigma = \sigma_0 e^{-\frac{E_f}{kT}}$$

(IV.19)

where $(E_f + E_m = E_a)$ is enthalpy of activation for conduction. Therefore, the low activation enthalpy is a better criterion for characterization of fast ion conductor (FIC) then the mere conductivity itself. This important parameter ($E_a = E_f + E_m$) for
a conduction process can only be derived from the temperature dependent conductivity, expressed in terms of a well-known Arrhenius equation.

\[ \sigma = \sigma_0 e^{-\left(\frac{E_a}{kT}\right)} \]  

(IV.20)

where \( \sigma_0 \) is the pre-exponential factor and \( E_a \) is the activation energy. If this relation holds good, then the Arrhenius plot of \( \ln(\sigma) \) versus \( 1/T \) will be a straight line with a slope \( E_a/k \) and the intercept \( \ln(\sigma_0) \). A large number of electrolyte systems showed linear Arrhenius plots and the conductivity in these systems have been explained by using the concepts involved in the Arrhenius model. Essentially, the transitions from given site to the nearby equivalent vacant sites are governed by (i) temperature independent parameters embodied into \( \sigma_0 \), and (ii) a Boltzmann factor describing the temperature dependent probability of hops by surmounting the energy barrier \( \ 'E_a' \). However, it has been observed that, \( E_a \) is the enthalpy or internal energy rather than free energy. Thus, the pre-exponential factor \( \sigma_0 \) contains not only the terms such as attempt frequency \( \omega \) and the jump distance \( \lambda \) but also entropy terms of the form \( e^{-S/R} \) [20].

In 1969, Hildebrand for the first time has pointed out that the original Arrhenius model obscures the role of entropy [21]. Also, it imposes a particular view about the mechanism by which a given transport process proceeds. It is customary to quote activation energy for ionically conducting solids, and thus implicitly to accept the above suggested model as a suitable description of the process. In the ionic conductor in general, it is a normal practice to construct the Arrhenius plots for temperature dependence of conductivity derived from the normal formula for diffusion [22] as given by,

\[ D = D_0 e^{-\left(\frac{E_a}{kT}\right)} \]  

(IV.21)

where \( D_0 = \lambda^2 n \omega / Ne^{-S/R} \), \( n \) is the number of mobile species, \( N \) is the number of sites.
Following the familiar Nernst-Einstein equation derived by Mott and Gurney [23],

$$\sigma / D = n q^2 / kT$$  \hspace{1cm} (IV.22)

where $D$ is the diffusion coefficient, $n$ and $q$ are the number and charge of mobile ions, respectively; $T$ is the temperature (in Kelvin) using IV.21 and IV.22, one arrives at

$$\sigma T = (\sigma T)_0 e^{\frac{E_a}{kT}}$$  \hspace{1cm} (IV.23)

where $(\sigma T)_0 = \frac{\lambda^2 n^2 w^2 q^2}{N \cdot \kappa e^{\delta_{SR}}}$. Hence the activation energy can be obtained from a plot of ln $(\sigma T)$ versus $(1/T)$. It is clear that the slope and intercept of the ln $(\sigma)$ versus $(1/T)$ plots are less defined than for the ln $(\sigma T)$ versus $1/T$ line. The activation energies, however, derived from both the plots are comparable. Therefore, the Arrhenius plots for the conductivity of an ionic solid may be derived either from the expression (IV.20) or (IV.23). It is evident from these equations that if the former is a linear plot then a plot of latter must be curved and vice-versa.

Experimentally, the construction of the Arrhenius plot for a solid electrolyte requires determination of bulk conductivity as a function of temperature, which is directly, obtained from the complex impedance plots obtained at various temperature.

The dc conductivity of all the samples has been calculated at various temperature by using

$$\sigma_b = G \frac{L}{A}$$  \hspace{1cm} (IV.24)

where $G = 1/R_{bulk}$, $L/A$ is the cell constant. $L$ is the distance between two parallel electrodes of equal cross sectional area $A$ and $R_{bulk}$ is the bulk resistance.
IV.B1 THEORY

An attempt has been made to improve the hypothetical model based on the mobility of the ion as function of lattice distortion proposed recently by Singh et al [24]. Ag2SO4 lattice is a Frenkel disorder analogue, where the sublattices of Ag⁺ ions are in the SO₄ tetrahedron, which forms a rigid lattice. With rise in temperature, Ag⁺ sublattice gives Frenkel defects, the interstitial concentration, \( x_i \), of which is given by.

\[
x_i = \exp(-\Delta G_F / kT)
\]

where, \( \Delta G_F \) is the standard free energy of formation of the Frenkel pair, which is constituted by vacancy plus interstitial concentration. Using Kroger-Vink notations, the disorder reaction can be written as

\[
Ag_{Ag} + V_i = Ag^{+}_{Ag} + V_{Ag}^-
\]

Let \( N_i \) and \( N_v \) be the concentration of interstitial ions and vacancies, which are given by \( (Ag_i - V_i) \) and \( (V_i - Ag_{Ag}) \), respectively. The law of mass action for reaction IV.26 is given by

\[
N_i - N_v = k_f \exp[-\Delta G_f / kT]
\]

where \( k_f \) is mass constant.

In order to maintain the thermodynamic stability the local electro neutrality and constancy in chemical potential, then reaction (IV.27) follows:

\[
N_i = N_v = n = (k_f)^{1/2} \exp[-\Delta G_f / kT]
\]

or more explicitly,

\[
N = (k_f)^{1/2} \exp[-\Delta S_m + \Delta S_{cf}] \frac{E_i}{2k} \exp \frac{E_i}{2kT}
\]
where $-\Delta S_{th}$, $\Delta S_{cf}$ and $E_f$ are the thermal entropy, configurational entropy, defect formation enthalpy. A remark may be made here about the temperature dependence of $E_f$. As a matter of fact, temperature increases, the crystalline lattice expands and the binding forces get weakened. Consequently, $E_f$ decreases with temperature. As a first approximation, one may assume a linear relationship between the defect formation enthalpy and temperature given by,

$$ E_f = E_{fo} (1 - \alpha T) \quad \text{(IV.30)} $$

where $\alpha$ is the temperature co-efficient of the defect formation enthalpy and $E_{fo}$ is the equivalent energy of defect formation at absolute zero.

Incorporation of a wrong size aliovalent guest cation, say, divalent, of radius $r_g$ into the host matrix, which is supposed to be substituted partially for the host cation of radius, $r_h$, in the sublattice gives rise to many interesting features. The influence of perturbation of the presence of wrong sized guest cation, $M^{2+}$, is two fold: (i) it distorts $SO_4$ tetrahedron and its surrounding and (ii) being immobile (most divalent cation are immobile, primarily owing to their massive charge to volume ratio) it impedes the pathways of mobile host cation. In particular, if $r_g < r_h$ then the lattice suffers a contraction, and it expands if $r_g > r_h$.

Following one of these incorporations of $M^{2+}$, the lattice generally undergoes a strain locally up to a few atomic distances in the proximity of guest $M^{2+}$ which depends on the value of $(r_g - r_h)$, called distortion factor. Such local lattice expansion / contraction must alter expectedly the values of entropy and the required heat of transition, $\Delta H$ from $\beta$-phase to $\alpha$-phase in $Ag_2SO_4$. Shahi and Wagner have observed results on these lines in case of $AgBr-Agl$ mixed system [25]. The strong dependence of conductivity on lattice volume has also been observed by Secco and Secco [26].

The configurationally entropy, $\Delta S_{cf}$, of the crystal is independent of the distribution of energy in an ensemble. It is determined solely by the number of
different ways in which the ions, cation and anions, may be arranged over the available number of lattice sites. It is, thus given by

$$\Delta S_{cf} = k \log W_{cf} = k \log [(N_a + N_c)! / N_a! N_c!]$$  \hspace{1cm} (IV.31)

here, $W_{cf}$ represents the number of different arrangements of $N_a$ anions and $N_c$ cation over a total of lattice sites, $N_a + N_c$. Since in the case of pure host lattice of Ag$_2$SO$_4$ the distribution of mobile $N_c$ cation with respect to the antagonist anions, $N_a$, does not change, the configurational entropy, $\Delta S_{cf}$, remains invariant. However, in the M$^{2+}$ partially substituted host system, the ions neighboring the guest cation will have a different vibrational frequency $\nu'$, then those at regular undistorted sites, $\nu$, because the ions binding restoring forces are modified. In order to elucidate further, we assume that in the doped crystal each ion neighboring the guest cation, according to Einstein model, is equivalent to three harmonic oscillators of frequency $\nu' \neq \nu$. Thus, considering a two formula unit for the host there will be 12 oscillators of mobile ions per M$^{2+}$ site each possessing a frequency, $\nu'$. That is to say, there will remain $(3N-12)$ oscillators in the host lattice, each of frequency $\nu$, if it is assumed that only one host Ag$^+$ is replaced by guest aliovalent cation, M$^{2+}$. In general, if $m$ mole% of the impurity is doped, then the thermal entropy of equation for M$^{2+}$ doped Ag$_2$SO$_4$ can be given by

$$\Delta S_{th} = [12mk (1 + \log (kT/\hbar \nu')) + (3N-12m) k (1 + \log (kT/\hbar \nu))]$$
$$- [3Nk (1 + \log (kT/4k))]$$  \hspace{1cm} (IV.32)

The first and second terms are due to doped and perfect (undoped) crystals respectively. One then finds an expression for the increase in thermal entropy per M$^{2+}$, given by,

$$\Delta S_{th} = 12 k \log (\nu'/\nu')$$  \hspace{1cm} (IV.33)
Although the employed model is quite simplistic and crude one, nevertheless it demonstrates the fact that $\Delta S_{th}$ is a consequence of the change in frequency of the lattice vibration following the incorporation of a wrong sized dopant cation. Given the validity of this model, substitution of $\Delta S_{th}$ in equation IV.28 leads one to

$$n = \{ (k_r)^{1/2} \left( \frac{\nu}{\nu'} \right)^6 \exp \left( \frac{\Delta S_{th}}{2k} \right) \} \exp \left( \frac{E_r}{2kT} \right)$$

(VI.34)

Moreover, the ionic migration is decided by the types of doping made using iso and aliovalent impurities in the host material; that is it is decided by mainly the ionic size, valency, electronic structure and bonding characteristics of the mobile ion.

The bonding characteristics of the mobile ion to the surrounding environment play an important role in determining the ionic conductivity. Recently, Wuensch has examined the basis for fast cation conductivity in Ag$^+$ and Cu$^+$ halides relative to Na$^+$ and Li$^+$ analogues [27]. The analysis shows that the cation distribution and transport process do not depend solely on the geometry of the anion array, but are also affected by the bonding characteristics and concentration of the mobile ions in a given compound or composition. Similarly, Mehrotra et al, have discussed the crystal chemistry of the thenardite family, all having thenardite type of structure denoted by $A_2TO_4$ [28]. Silver sulphate belongs to this class. In this class, $TX_4$ tetrahedra are almost regular, the co-ordination polyhedra of the six coordinated metal ions are irregular. In addition, these polyhedra vary greatly in shape depending on the different bonding properties of the cation.

In a modified (contracted) lattice of $Ag_2SO_4$ doped with guest cation with $r_g < r_h$, the mobile Ag$^+$ will be bounded more rigidly to the lattice. Evidently, if the dopant ion is such that $r_g < r_n$, the lattice is contracted and hence the $\nu' > \nu$, since the frequency of vibration is directly proportional to the rigidity of the bond. Consequently, such an incorporation is counter productive as the Frenkel defect concentration will be lowered according to equation IV.33; and hence, lesser
number of equivalent sites will be available to the mobile Ag⁺ to hop to. On the other hand, if dopant cation has a greater ionic size than that of the host, i.e. \( r_g > r_b \), then \( \nu' < \nu \) and formation of Frenckel defect will be favoured whereby ionic conduction via Ag⁺ hops is promoted.

In addition to the mutual change in entropy, there will also be change in mutual coulombic interactions between the dopant cation under consideration and its nearest neighbors due to lattice distortion. The expansion, for example, in the localized lattice increases the distance between mobile Ag⁺ and negatively charged O ions of SO₄ and also between the alike nearest ions, thus leading to reduction in the interaction energy. Thus the energy of interaction per dopant cation according to Born [29] and Medelung [30] may be written as

\[
E = -4e^2 \left[ \frac{1}{r} - \frac{1}{\sqrt{2r}} \right] = -4e^2 / r
\]  

(IV.35)

here, the first and second terms are due to coulombic force of attraction and repulsion, respectively. Correspondingly, the activation energy increases when the lattice contraction is effected.

Although, in general, the energies cannot be represented exactly by the above equations, the said treatment provides some useful qualitative and semi quantitative interpretations, which helps in understanding the fundamental conduction mechanism in \( \beta \)-Ag₂SO₄.

**IV.B2 RESULTS AND DISCUSSION**

Arrhenius plots for all the compositions are found to obey Arrhenius law in both \( \alpha \) and \( \beta \) phases. As an example, figure IV.12 depicts such as behaviour for host slow-cooled and quenched Ag₂SO₄. The \( \beta \) phase conductivity in both the cases is seen to be matching closely. An observed, change in slope for slow-cooled Ag₂SO₄ at 416°C with jump in conductivity of the order of a magnitude accounts for
conductivity \( (2.22 \times 10^{-5} \text{ S cm}^{-1} \) at \( 250^\circ \text{C} \) and \( 3.4 \times 10^{-3} \text{ S cm}^{-1} \) at \( 440^\circ \text{C} \) \) and the transition temperature \( 416^\circ \text{C} \) are in close agreement with the earlier reporting [31-33].

![Diagram](image)

**Fig. IV.12**: Plot of \( \log(\sigma T) \) against \( 10^5/T \) for Ag$_2$SO$_4$ prepared using (a) slow-cooling and (b) quenching technique.

On the grounds of room temperature XRD, SEM and FTIR results, as discussed in first section of this chapter (IV.A), all the binary systems are proved to be bi-phase mixture over the entire compositional range except the concentrations of MSO$_4$ (M = Ba, Ca and Mg) less than or equal to 5.27 mole % in Ag$_2$SO$_4$.

Conductivity maximum can be caused by the presence of an intermediate phase, which has conductivity higher than that of pure material. But for the present systems, however, this possibility has to be ruled out since x-ray diffraction results shows the characteristics peaks of Ag$_2$SO$_4$, BaSO$_4$, CaSO$_4$ and MgSO$_4$ only. The present results are similar to those for composite solid electrolyte system of \( MX/MXY \) type [34,35]. In composite system, the conductivity goes through a maximum when second insoluble phase is added. The increase in conductivity has been attributed to the conduction along the interface region between two phases. Concurrently, as the concentrations of either CaSO$_4$ or BaSO$_4$ (in respective system) increases in Ag$_2$SO$_4$ matrix, the total conductivity is also enhances due to formation of highly conductive surface percolation pathways across the interface of
two phases. The maximum conductivity at a particular composition is due to percolation threshold concentration [36,37].

Detailed explanation of conductivity behavior of samples belongs to series I, II and III are given below.

**IV.B2.i SERIES-I: (100-x)Ag$_2$SO$_4$:x)BaSO$_4$**

The bulk conductivity of each sample, at various temperatures, is obtained following non-linear list squares fitting the complex impedance data to equation IV.36 [39].

\[ Y(w) = \frac{Y(\infty) - Y(0)}{1 + (j\omega \tau^*)^{\alpha}} \]  \hspace{1cm} (IV.36)

Variations of $\log (\sigma T)$ with $10^3/T$ (Arrhenius plots) for a few compositions, within the solid-solubility range, are shown in figures IV.13. Insert of this figure shows the variation of conductivity with concentration of BaSO$_4$ at 425°C. The conductivity enhances with increasing BaSO$_4$ concentration in $\alpha$-Ag$_2$SO$_4$ and exhibits a maximum for $x = 5.27$ ($\approx$5% vacancy). Similarly, in the orthorhombic modification of Ag$_2$SO$_4$, the conductivity maximum is observed for the same composition.

The partial replacement of mono-valent Ag$^+$ by the divalent Ba$^{2+}$ not only produces additional vacancies (extrinsic) as per equation IV.37 but also alters the
local environment in the vicinity of guest cation so as to attain thermodynamic, electrical and chemical equilibria.

\[ \text{Ag}_{2-2x}\text{Ba}_{x-x}\text{SO}_4. \]  

(IV.37)

The partial replacement of \( \text{Ba}^{2+} \) not only creates the additional vacancies but also opens the host lattice structure in the vicinity of guest cation [39]. \( \text{Ag}^- \) hopping probability increases in such localized distorted lattice. At low doping levels, the localized distorted structures (open bottleneck with vacancy), which can be termed as bond as per the percolation theory, get interconnected thereby forming the least resistive ion percolating paths. With increasing dopant concentration, extra percolation paths are created which in turn enhances the conductivity. The maximum conductivity at \( x = 5.27 \) is due to the percolation threshold [39].

The Arrhenius plots for two-phase region (\( x = 10-100 \)) are displayed in figures IV.14a and b. The observed break-over in the conductivity at about 412\(^\circ\)C is closely matching with the transition temperature, corresponding to orthorhombic to hexagonal phase transformation in \( \text{Ag}_2\text{SO}_4 \), obtained from DTA and DSC (as discussed in Chapter V). As a matter of fact, the break in Arrhenius plot is always interpreted in term of crystal structural change of the sample. Thus, break-over in
conductivity at about 412°C in all samples evidences the presence of AgSO₄, in them. In other words, all samples (x = 10-90) are bi-phase mixture of β-Ag₂SO₄ and β-BaSO₄ in the temperature range from room temperature to 412°C, which is in agreement with XRD and DTA results.

The variations of conductivity with BaSO₄ concentration at 350°C, depicted in figure IV.15 reveals maximum for 80Ag₂SO₄-20BaSO₄, which happens to be eutectic composition (chapter-V). The smaller the grain size of each phase in eutectic gives large heterogeneous interfacial contact as well as more effective space change layer [40]. According to Jow and Wagner these interfacial space-change layers are highly conducting [40]. Eutectic composition being with

![Conductivity isotherm at 250°C for (100-x)Ag₂SO₄-xBaSO₄ (x=10-90).](image)

minimum grain size contains maximum ion percolating paths whereby maximum in conductivity. These results are in good agreement with reported one [41].

This enhancement in conductivity could be explained in the light of dispersed theory. According to dispersed phase theory for MX/M′X, there is a net transfer of cations from either phase across the interface [34,35]. The disordered reaction using Kroger-Vink notation can be written as

1. \[ \text{Ag}_{\beta \beta}(\text{Ag}_2\text{SO}_4) + x\text{Ba}^{**} = (100 - x)\text{Ag}_{\beta \alpha}(\text{Ag}_2\text{SO}_4) + \{\text{Ba}_{\alpha \alpha}(\text{Ag}_2\text{SO}_4) +\} \text{V}_{\beta \alpha}(\text{Ag}_2\text{SO}_4) \]
Two probable Frenkel analogue interface reactions are

II. \( Ag_{Ag}(Ag_2SO_4) + V_i^{\prime}\) (BaSO\(_4\)) = \( Ag_i^{\prime}(BaSO_4) + V_{Ag}^{\prime}\) (Ag\(_2SO_4\))

II. \( V_i(Ag_2SO_4) + Ba_{Ba}(BaSO_4) = Ba_i^{\prime}(Ag_2SO_4) + V_{Ba}(BaSO_4) \)

The corresponding mass action law takes the form

\[
C_v C_i = C_o \exp \left[-(\Delta G^0)\right]
\]

where \( C_v \) and \( C_i \) are the vacancy concentration in one phase and interstitial concentration in the other in contact, respectively, \( \Delta G^0 \) is free enthalpy for reaction and \( C_o \) is the pre-exponential factor.

If the free energy of reaction I exceeds that of reaction II, it gives rise to additional interstitial \( Ba^{2+} \) in \( Ag_2SO_4 \) leaving behind equivalent vacancies in the \( BaSO_4 \) lattices otherwise the converse is true. Since \( Ba^{2+} \) is more electronegative than \( Ag^+ \), reaction II is thermodynamically favored. In addition, as a result of repulsive interaction, \( Ba^{2+} \) pushes back the surface \( Ag^+ \) into the \( Ag_2SO_4 \). Thus forbidding reaction I, these two factors enrich the interstitial ion and vacancy concentration forming space charge layers close to the \( Ag_2SO_4 \) and \( BaSO_4 \) surface, respectively. The presence of foreign \( Ba^{2+} \) in space charge region at \( Ag_2SO_4 \) surface also leads to the lattice expansion, thus, favoring the \( Ag^+ \) mobility parallel to the interface. The maximum conductivity at 20-mole\% \( BaSO_4 \) is due to optimum percolating paths in the sample.

**IV.B2.ii SERIES-II: (100-x)Ag\(_2\)SO\(_4\) : (x)CaSO\(_4\)**

The plots of log(\(\sigma T\)) versus \(10^3/T\) for \((100 - x)Ag_2SO_4 : (x)CaSO_4\) system for \(x = 0\) to 10, \(x = 10\) to 60 and \(x = 70\) to 100 are displayed in figures IV.16, 17a and 17b, respectively. As seen, in both orthorhombic (stable below 416°C) and hexagonal (stable above 416°C) modifications of \( Ag_2SO_4 \) conductivity obeys the Arrhenius
law (Eq.IV.23). Thus, the thermally activated process governs the conductivity i.e. by thermally activated defects, $n$, given by (Eq. IV.18a).

Note notwithstanding, there is a sudden jump in magnitude of conductivity following transition (similar to the observed in case of pure Ag$_2$SO$_4$) for the samples containing CaSO$_4$ up to 60 mole% (Figure IV.17a). Beyond this composition (Figure IV.17b), however, the slope changes without any jump in conductivity. The changeover in the slope of Arrhenius plots for all samples were found coinciding with the $T_c$ obtained from
DSC and DTA investigations. As said earlier the changeover in the slope of
Arrhenius plot is, in general, ascribed to switch in conduction mechanism either due
to intrinsic / extrinsic effect or structural phase transition in the sample under test.

Figures IV.18a-c display the conductivity behaviour (in both modifications)
of samples with $x = 0$ to 10; $x = 10-60$ and $x = 70-100$ CaSO$_4$ added Ag$_2$SO$_4$,

![Conductivity isotherm](image)

Fig. IV.18: Conductivity isotherm (a) $x = 0$ to 10, for (b) $x = 10$ to 60 and (c) $x = 70$ to
100; in HTR and LTR Regions.

respectively. For clarity, the results are divide into two temperature regions, namely
(1) the high temperature region (hexagonal phase) HTR and (2) the low temperature
region (orthorhombic phase), LTR.

**HTR**

In the high temperature modification (Fig. IV-18a), the conductivity exhibits
maximum at 7.57 mole % (approximate 7% vacancy) CaSO$_4$ within the solid
solubility region. Whereas, in two-phase region (Figs. IV-18b, 18c) it remains fairly
invariant. The conductivity below the transition temperature decreases as shown in
(Figs. IV-18a-c). The maximum conductivity at 7.57 mole %, corresponding to 7%
vacancy is in good agreement with the reporting [39]. The disorder reaction can be written using Krogerr Vink notation as

\[ \text{Ag}_x \text{Ag}_y(\text{Ag}_2\text{SO}_4) + x\text{Ca}^{2+} = (100 - x)\text{Ag}_x\text{Ag}_y(\text{Ag}_2\text{SO}_4) + (\text{Ca}_x\text{Ag})_y(\text{Ag}_2\text{SO}_4) + V_{\text{Ag}}(\text{Ag}_2\text{SO}_4) \]

In HTR, the host Ag₂SO₄ lattice (hexagonal) being more open structure, Ag⁺ squeezes through the lattice with a high elementary hopping probability. The hopping of ions is, however, possible only if an equivalent vacant site is available in its immediate vicinity. On account of the availability of additional vacancies, due to CaSO₄ addition, ion-hopping paths termed as ion-percolating paths for Ag⁺ are created which in turn increases the conductivity. The maximum conductivity at \( \approx 7\% \) vacancy is due to percolation threshold.

At higher CaSO₄ concentration, extrinsic vacancies agglomerate thereby form clusters. These cluster, disrupt the highly conducting percolation paths in lattice leading to a decrease in ion conductivity. Absence of other conductivity maximum at higher CaSO₄ concentration (>10 mole %) is the manifestation of non-existence of new intermediate phase above transition temperature.

**LTR**

In the \( \beta \)-phase, on the other hand, the concentration as well as the type of dopant cation, \( M^{2+} \), added to the host system, largely govern the ionic conductivity of the solid electrolyte. The conductivity in this temperature region is seen decreasing within the solid solubility (up to 5 mole %) and also in multiphase (\( x > 6 \) mole %) regions, in sharp contrast to the observations. The decrease in conductivity in both the solid solubility and the bi-phase regions can be understood as follows.

In the LTR, within the limit of solid solubility region, ionic size and valence of the guest substituting cation chiefly govern the bulk conductivity. Hence, this is treated as an impurity controlled region. The reduction in conductivity, is quite contrast to enhancement in HTR, and this cannot be understood by above discussed classical theory of aliovalent doping. As this theory accounts for the creation of
additional vacancies, to maintain the charge neutrality, whereby an enhancement in \( \sigma \) is generally forgone conclusion. The theory of lattice distortion, due to ionic size mismatch is evoked to explain the decrease in conductivity \([42,43]\). According to latter theory, host lattice expands/contrasts depending on the larger/small size of guest ion vis-à-vis host. Combination of both these theories suggests that the partial replacement of guest \( \text{Ca}^{2+} \) for monovalent host \( \text{Ag}^+ \) not only gives rise to additional vacancies but also introduces local lattice distortion in the vicinity guest ion. Since, \( \text{Ca}^{2+} \) has smaller ionic radius (0.99\( \text{Å} \)) than \( \text{Ag}^+ \) (1.26\( \text{Å} \)), the partial replacement of latter by former leads to an appreciable lattice contraction. This host lattice distortion would be in the vicinity of \( \text{Ca}^{2+} \).

![Diagram](image)

**Fig. IV.19:** The lattice when some of the \( \text{Ag}^+ \) are partially replaced by \( r_s < r_\theta \) along with there modified potential wells.

Hence, an additional vacancy with deeper potential well (Fig. IV.19) offers large activation energy of migration for mobile \( \text{Ag}^+ \). In addition to this, \( \text{Ca}^{2+} \) being divalent has its own self-trapping effect, concurrently is negligibly mobile. As \( \text{CaSO}_4 \) content increases, both these factor contribute to increase in activation energy consequently decrease in conductivity, which is in good agreement with results (Fig. IV.20).
As the concentration of CaSO$_4$ is increased further (Beyond solid solubility limit.) the insoluble phase disperses into Ag$_2$SO$_4$ matrix, which is well substantiated by the experimental findings (XRD), discussed in previous subsection of this chapter. Further supplemented by taking a look at the corresponding microphotographs, where on addition of CaSO$_4$ the grains of the impurity phase are seen dispersed throughout the host matrix, thus confirming the phase separation. In previous investigation the dispersion of second insoluble phase is reported to enhance conductivity [35]. But in this system, CaSO$_4$ dispersed samples, in contrast to these report, conductivity does not exhibit such a trend (Figure IV.18a). These results are explained as under.

Two probable Frenkel analogue interface reaction in this case are given by:

I. \( \text{Ag}_\text{Ag}^+ (\text{Ag}_2\text{SO}_4) + V^+ (\text{CaSO}_4) = \text{Ag}^+ (\text{CaSO}_4) + V^+ (\text{Ag}_2\text{SO}_4) \)

and

II. \( V^- (\text{Ag}_2\text{SO}_4) + \text{Ca}_{\text{Ca}}^- (\text{CaSO}_4) = \text{Ca}^+ (\text{Ag}_2\text{SO}_4) + V^- (\text{CaSO}_4) \)

The corresponding mass action law takes the form

\[ C_iC_j = C_0 \exp (-\Delta G^o) \] (IV.39)

If the free energy for reaction-I exceeds that for reaction-II this gives rise to additional interstitial Ca$^{2+}$ in Ag$_2$SO$_4$, leaving behind equivalent vacancies in the CaSO$_4$ lattice; otherwise the converse is true. Since Ca$^{2+}$ is more electropositive then Ag$^+$ vis-à-vis antagonist SO$_4^{2-}$, reaction-II is thermodynamically more favorable. In addition, as a result of repulsive interaction Ca$^{2+}$ pushes the surface Ag$^+$ back into the Ag$_2$SO$_4$, and thus, forbids reaction-I. These two factors enrich the
interstitial ion and valency concentration forming space charge layers close to the Ag$_2$SO$_4$ and CaSO$_4$ surfaces, respectively (Fig. IV.21). The enhanced defect concentration is given by

$$C_{\nu'c'} = \sqrt{(K_f \varepsilon' / \varepsilon)} = (\varepsilon' / \varepsilon) . c_i / c^o$$  \hspace{1cm} (IV.40)

where $C^o$ is used to normalized the defect concentration and $K_f$ is the electrochemical mass action for reaction-1. The terms $\varepsilon$ and $\varepsilon'$ are the dielectric constants of Ag$_2$SO$_4$ and CaSO$_4$, respectively.

![Diagram](image_url)

**Fig. IV.21:** Schematic representation of defects at Ag$_2$SO$_4$/CaSO$_4$ interface.

The enhanced interstitial divalent cation concentration in the space charge region reduces the hopping rate of mobile Ag$^+$ in want of by near vacancies. Additionally, the foreign Ca$^{2+}$, in the space charge region, at the Ag$_2$SO$_4$ surface blocks the Ag$^+$ mobility parallel to the interface, which otherwise is considered as an ion percolating path [36]. The overall effect is that the interfacial space charge regions are more blocking than percolating the nature, i.e. they form clusters or in other words an agglomeration of interstitial cations. The conductivity in the space charge region is normalized following the relation.
\[ \sigma_n = \frac{\sigma_{\text{interstitial}}}{\sigma_{\text{interior}}} \] (IV.41)

A sudden drop in activation energy (Figure IV.20) for 20 mole% CaSO\textsubscript{4} added to Ag\textsubscript{2}SO\textsubscript{4} sample, in bi-phase region, could be explained as follows.

The precipitation of CaSO\textsubscript{4} in Ag\textsubscript{2}SO\textsubscript{4} matrix modifies the grain morphology of Ag\textsubscript{2}SO\textsubscript{4} and provides improved density of sample as seen earlier in this chapter. Increased packing density reduces the voids in the sample facilitating the inter-grain ion migration leading to decrease in average activation energy for conduction.

**IV.B2.iii SERIES-III: (100-x)Ag\textsubscript{2}SO\textsubscript{4}:(x)MgSO\textsubscript{4}**

Figure IV.22 depicted the variations of log \((\sigma T)\) with \(10^3/T\) for the samples belonging \((100-x)\text{Ag}_2\text{SO}_4:(x)\text{Ag}_2\text{SO}_4 \ (x = 10 \text{ to } 50)\)

![Graph](image)

**Fig. IV.22: Arrhenius plots for Ag\textsubscript{2}SO\textsubscript{4} : MgSO\textsubscript{4} binary system.**

The observed break-over in the conductivity at about 419\(^\circ\)C in this system is also closely matching with the transition temperature, corresponding to orthorhombic to hexagonal phase transformation in Ag\textsubscript{2}SO\textsubscript{4}. Thus break-over in the conductivity at about 419\(^\circ\)C in all samples evidences the presence of Ag\textsubscript{2}SO\textsubscript{4} in them and to
biphasic mixtures. Since the samples deform at temperature greater than or equal to 600°C, conductivity measurement were restricted to below this temperature. A careful look at the figure IV.22a reveals maximum conductivity for 80Ag₂SO₄-20 MgSO₄.

In conclusion, the conductivity of β-Ag₂SO₄ is found to be dependent on ionic size, valence and electronic structure of the guest cation, particularly in the low temperature modification of Ag₂SO₄ (orthorhombic phase). Moreover, bonding characteristic of the mobile ion to the surrounding environment seems to play an important role in determine the ionic conductivity. The ionic migration is decided by mainly the ionic size, valency, electronic structure and bonding characteristics of the mobile ion. Mehrotra et al [28], who have discussed the crystal chemistry of the thenardite family, all have thenardite type of structure denoted by A₂T₂O₄. Further, TX₄ tetrahedral are almost regular the co-ordination polyhedra of the six coordinated metal ions are irregular. In addition, these polyhedra vary greatly in shape depending on the different bonding properties of the cations. The ionic conductivity is found invariant, in general, with respect to these factors in α-Ag₂SO₄. These results could throw light on the Fundamental conduction mechanism in Ag₂SO₄ and also on the criterion of selecting the impurity cation in the binary system. (in solid electrolyte).
IV.C TRANSPORT NUMBER

It is necessary to determine the transport number of a given solid electrolyte first, because this very parameter decides about the suitability of the solid materials to be used in electrochemical devices.

The use of solid electrolyte materials in ideal practical devices demands that they should not exhibit electronic conductivity, even moderately. The conductivity of any sample, in general, is expressed as the sum of the ionic and electronic components, given by

\[ \sigma_{Total} = \sigma_{ion} + \sigma_{ele} \]  \hspace{1cm} (IV.42)

An equivalent circuit as shown in figure IV.23 could present the material that exhibits the mixed i.e. both electronic and ionic conductivities. The transport number, also called transference number of particular species is defined as the fraction of total charge carried by that species. In other words

\[ t_i = \sigma_{ion} / \sigma_{Total} \text{ and } t_e = \sigma_{ele} / \sigma_{Total} \]  \hspace{1cm} (IV.43)

There are various methods which have been used in a number of solid state systems to determine ionic as well as electronic transport number such as (i) Tubandt’s method (ii) EMF comparison method (iii) dc polarization method and (iv) pulse method.

IV.C1 EXPERIMENTAL TECHNIQUES OF TRANSPORT NUMBER DETERMINATION

Various popular methods for determining transport number in solid electrolytes are described in following sections. Although during the course of present study dc
polarization technique was employed for transport number determination, it is certainly worthwhile to discuss various other techniques.

**IV.C1.i Tubandt’s Method**

It is a classical method utilized by Tubandt to determine transport number in electrolytes by validity of Faraday’s Law. It is, particularly, suitable for cation conductors. An electrolytic cell comprises of an identical anode and cathode on either side of the electrolyte disc placed one after the other as shown in figure IV.24. When a suitable amount of current is passed for some time, the mass of cathode and its adjacent disc of the electrolyte increase, while that of the anode and it’s adjacent electrolyte disc decreases. If the mean mass difference after passing known amount of current for pre-decided time is \( m \) and the mass transferred (Theoretical) \( mg \) for an ideal solid electrolyte is calculated by integrating the current through the cell, then ionic transport number \( t_i \) can be obtained by using the equation,

\[
t_i = \frac{m}{mg}\tag{IV.44}
\]

i.e. the ratio of experimentally observed mass difference to the theoretical one equals the ionic transport number.

**IV.C1.ii Emf Method**

This method was described theoretically by Wagner to determine the transport number [38]. Here, electrodes control the activity of the rate determining electro-active species. These measurements are confined to cases where (i) the electrode reactions are highly reversible (in electro chemical sense) (ii) the thermodynamic
parameters for electrodes and reaction products are known and (iii) the activities involved are controllable.

In particular, the condition of reversibility is a crucial one. In such cases the transport number could be determined as follows:

Suppose an ionic conductor is sandwiched between two electrodes with the different chemical potentials \( \mu_1 \) and \( \mu_2 \) is shown in figure IV.25. The electrochemical potential across this cell is given by [44,45],

\[
E = \frac{1}{|Z|F} \mu_2 \frac{1}{|Z|F} \int_{\mu_1}^t_i c_{di} \, dt = \frac{1}{|Z|F} t_i (\mu_2 - \mu_1),
\]

where \(|Z|\) is the absolute value of the valency of the mobile ion in the electrolytes \( F \) is Faraday’s number. For a pure ionic conductor (with \( t_i = 1 \)) the theoretical value of electrochemical potential is

\[
E_{\text{theor}} = \frac{(\mu_1 - \mu_2)}{|Z|F}
\]

Therefore, \( E = t_i E_{\text{theor}} \)

\[
t_i = (1 - t_v) = \frac{E}{E_{\text{theor}}}
\]

Thus from a measurement of \( E \) and prior knowledge of \( E_{\text{theor}} \) the value of \( t_i \) can be obtained.
Two types of electrochemical system are commonly employed to find $t_i$ from this relationship.

i) Solid electrodes having controllable activities of the electroactive species on either side of the electrolytes [46].

ii) System with controlled gas partial pressures $a$ and $a_2$ on either side of the electrolyte [47].

In the latter case, it is important to make use of a protecting gas with the same composition as the one with the lower partial pressure equivalent to that of the active component. To avoid leakage of high active gas to the low active reference gas electrode, the flow direction should be as indicated in figure IV.26.

\[ \begin{array}{c}
\text{Fig. IV.26} : \text{Experimental arrangement for the determination of transport number of controlled gas with different partial pressure.} \\
\end{array} \]

**IV.C1.iii DC Polarization Method**

The partial conductivities of electronic and ionic charge carries can be deduced by using polarization measurements. In this technique, the mixed conductor is subjected to a dc bias, which polarizes the mixed conductor. In Wagner’s method the mixed conductor ($MX$) is placed between the virtually reversible electrode ($M$) and irreversible inert electrode (e.g. graphite or platinum) to form a cell of configuration given below [48].

\[ -(M) \mid MX \mid \text{inert electrode}(+) \]

A dc potential, below the decomposition potential of $MX$ is applied to the cell with a negative pole on the left electrode $M$ of the cell. Since there is no source of $M$ ions at right hand electrode, a steady situation eventually prevails, whereby conduction
is via electrons or holes. In the derivation of this theory there are two implicit assumptions
i) The electronic resistance is a function of the polarization potential
ii) The ionic resistance is not a function of polarization potential.
In an alternative technique, the mixed conductor is placed between two irreversible inert electrodes, and two implicit assumptions are made which are directly opposite to those of Wagner’s theory. They are,
   i) The electronic resistance is unchanged by polarization potential, and
   ii) The ionic resistance changes with time as the polarization builds up.

Danforth and Bocine [49] and also Vest and Tallen [50] derived the following formula for determining the transport number of electrons and ions.

\[
\frac{E_{(0)}}{E_{(\infty)}} = \tau_e = 1 - \tau_i \tag{IV.48}
\]

where \(E_{(0)}\) and \(E_{(\infty)}\) are the voltages at zero and infinite time in response to current step.

**IV.C1.iv Pulse method**

Electronic carriers can respond more readily than ionic carries to the fluctuations in applied potential. A technique based on this fact has been suggested by Yuketo [51]. In this method a dc voltage is applied across an electrolytic cell in-cooperating two similar working electrodes, e. g. \(M/MX/M\). The current time characteristics monitored as a rapid voltage pulse is superimposed. If electronic conductivity is insignificant then the response time of the ions causes smooth rise to the new current plateau corresponding to the higher voltage level and a similar smooth decline when the voltage pulse is removed. If, on the other hand, there is an electronic contribution, the smooth rise and fall are preceded by abrupt jumps. This method has been recently used to study the redistribution of electronic carrier and the motion of ions in Cul [52].
IV.C2 EXPERIMENTAL DETAILS

Under this phase of work, all the compositions of series I-III were scanned at different temperatures. This is done with a special view to assessing the conductivity nature at different temperature in these solids. The experimental set up used for the measurement of transport number (Fig. IV.27) following dc Polarization method, has a computer controlled data acquisition system consisting mainly of digital programmable electrometers (Keithley, Model-617) This instrument has a built-in programmable power supply capable of giving 5mV to 110 V dc output. Moreover, the voltage to current ratio can be accessed directly through it.

A fixed dc bias is applied across the sample, with the application of the bias the polarization starts setting in and conductivity decreases with time till it attains a constant value. At this stage, the observed conductivity is solely due to the contribution of electrons, because of the use of inert electrode. The saturation value
of the conductivity, $\sigma_{sat}$, is equal to the electronic conductivity, $\sigma_e$. AC conductivity which is equal to the total conductivity ($\sigma_{ac} = \sigma_e + \sigma_i$) has been considered to be a zero time conductivity, $\sigma_0$, due to absence of polarization.

The functional dependence of conductivity with time for pure slow cooled Ag$_2$SO$_4$ sample under normal and SO$_2$ partial pressure at 440°C is shown in figure IV.28. It was observed that the conductivity drop off with time at a faster rate if the samples is subjected to the higher temperature, while the rate of fall is slower for lower temperatures.

![Graph showing variation of dc conductivity with time for pure Ag$_2$SO$_4$ at 450°C under normal and SO$_2$ partial pressure.](image)

Fig. IV. 28: The variation of dc conductivity with time for pure Ag$_2$SO$_4$ at 450°C under normal and SO$_2$ partial pressure.

Similarly, the steepness in the time dependent conductivity curve is observed to be greater for those compositions, which showed high, valued of ac conductivity, as studied earlier.

The high values of conductivity, at high temperatures, imply higher mobility of charge carriers, since the defect (Eq. IV.18b) gives mobility. The increase in cation mobility with temperature is obviously due to the fact that at high temperature the lattice is more open, which reduces the enthalpy of defects migration. Thus, within short time saturation in dc conductivity is exhibited due to polarization of mobile ions. In other words, conductivity drops off steeply before saturating with time with a high value of slope $[\delta \rho (w=0)/\delta t]$ which explains the observed conductivity behaviour. Similarly, the increases in zero time conductivity
of the conductivity, $\sigma_{\text{sat}}$, is equal to the electronic conductivity, $\sigma_e$. AC conductivity which is equal to the total conductivity ($\sigma_{\text{tot}} = \sigma_e + \sigma_f$) has been considered to be a zero time conductivity, $\sigma_0$, due to absence of polarization.

The functional dependence of conductivity with time for pure slow cooled Ag$_2$SO$_4$ sample under normal and SO$_2$ partial pressure at $440^\circ$C is shown in figure IV.28. It was observed that the conductivity drop off with time at a faster rate if the samples is subjected to the higher temperature, while the rate of fall is slower for lower temperatures.

![Graph showing the variation of dc conductivity with time for pure Ag$_2$SO$_4$ at 450°C under normal and SO$_2$ partial pressure.]

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at high temperature clearly demonstrate the rise in number of mobile charge carriers contributing to the conduction process. This is quite in accordance with the temperature-activated process of increase in mobile ion concentration given by (Eq. IV.18b)

Thus, in view of the above arguments, it becomes evident that with the rise in temperature, the number of mobile cations, participating in conduction process, increases with enhanced mobility. This explains the rise in conductivity with temperature according to the equation (IV. 23). These results are in good agreement with those discussed earlier on the basis of Arrhenius plots.

The transport number of charge carrier is determine by using the formula,

\[ \tau = \frac{\sigma_0 - \sigma_x}{\sigma_0} \]  

(IV.50)

The values of \( \tau_1 \) and \( \tau_c \) thus, obtained for (94.73)Ag\(_2\)SO\(_4\):(5.27)MSO\(_4\) (M= Ca, Ba and Mg) at various temperature, are given in Table IV.1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>( T = 240^\circ C )</th>
<th>( T = 440^\circ C )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \tau_1 )</td>
<td>( \tau_c )</td>
</tr>
<tr>
<td>Pure Ag(_2)SO(_4)</td>
<td>0.9953</td>
<td>0.0047</td>
</tr>
<tr>
<td>Pure Ag(_2)SO(_4) under partial pressure of SO(_2)</td>
<td>0.9964</td>
<td>0.0036</td>
</tr>
<tr>
<td>M=Ba</td>
<td>0.949</td>
<td>0.051</td>
</tr>
<tr>
<td>M=Ca</td>
<td>0.899</td>
<td>0.101</td>
</tr>
<tr>
<td>M=Mg</td>
<td>0.901</td>
<td>0.099</td>
</tr>
</tbody>
</table>

Table IV.2. presents the transport number at 300, 400 and 500°C for the samples which show maximum conductivity in (100-x)Ag\(_2\)SO\(_4\):(x)BaSO\(_4\) and (100-x) Ag\(_2\)SO\(_4\):(x)CaSO\(_4\) systems.
Table IV.2: Transport number at 300, 400 and 500°C of the samples which show maximum conductivity.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Transport No.</th>
<th>$T = 300°C$</th>
<th>$T = 400°C$</th>
<th>$T = 500°C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 Ag$_2$SO$_4$ : 30 BaSO$_4$</td>
<td>$t_1$</td>
<td>0.9045</td>
<td>0.9761</td>
<td>0.9208</td>
</tr>
<tr>
<td></td>
<td>$t_1$</td>
<td>0.0955</td>
<td>0.0239</td>
<td>0.0792</td>
</tr>
<tr>
<td>80 Ag$_2$SO$_4$ : 20 CaSO$_4$</td>
<td>$t_1$</td>
<td>0.9172</td>
<td>0.9328</td>
<td>0.9784</td>
</tr>
<tr>
<td></td>
<td>$t_1$</td>
<td>0.0828</td>
<td>0.0672</td>
<td>0.0216</td>
</tr>
</tbody>
</table>

From above tables IV.1 and IV.2 it is clear that, the ionic transport number is higher and closer to unity at elevated temperature than that at the lower temperatures. Secondly, the conductivity component due to a clear ionic conduction in all samples, which is obtained as the difference between the total bulk conductivity and post-polarization conductivity due to electronics exclusively is very nearly same as that due to bulk conduction. In other words, the electronic component in the bulk conduction is negligibly small. Hauffe et al [53] have also found the value of ionic transport number of Ag$_2$SO$_4$ to be 0.9975 at 602°C under oxygen partial pressure which is quite consistent with our results ($t_1 = 0.9964$). Amongst all the studied compositions, the highest conductivity giving samples show the transport number nearly equal to unity. The small ionic transport number for M = Ca samples at low temperature is due to very poor electrical conductivity.
REFERENCES:


