CHAPTER-I

GENERAL INTRODUCTION
The present work is directed to to construct binary phase diagram of $\text{Ag}_2\text{SO}_4$ -
$\text{MgSO}_4$ (M = Ca, Ba and Mg) systems with a view to find suitable electrolyte for SO$_2$,
gas sensor applications. In such work, one of the important tasks was to find out
to what extent $\text{MgSO}_4$ (M = Ca, Ba and Mg) are soluble in room temperature
(orthorhombic) as well as high temperature (highly conducting hexagonal) phase of
$\text{Ag}_2\text{SO}_4$. Another tasks was, whether thermodynamical stability range of hexagonal
phase can be extended to lower temperatures by the addition of $\text{CaSO}_4$ /$\text{BaSO}_4$
/$\text{MgSO}_4$ in $\text{Ag}_2\text{SO}_4$, and also to find out existence of other unknown high
conducting phase in $\text{Ag}_2\text{SO}_4$–$\text{MgSO}_4$ binary, if any. Last but not least, look was to
determine the mechanical strength suitable for sensor application. The first section
of this chapter is devoted to general introduction to solid electrolytes and second
one to general phase diagram of binary system.

1.A SOLID ELECTROLYTES

Ionic compounds are usually insulators in solid state and good conductors in liquid
state, where the liquid state can be a melt or an aqueous solution. In some cases,
however, there is exceptionally a high electrical conductivity in a solid phase [1].
Such solids are now termed as solid electrolytes or super ionics solids. During
recent years much attention has been paid to this class of solid materials. The
current interest is to a great extent due to their technological applications in high
energy density battery systems, fuel cells, sensors, etc. [2, 3]. More precisely, a
substance can be called as solid electrolyte provided its ionic conductivity is
extremely larger than the electronic one.

Unlike liquid electrolytes, these materials often show significant electronic
conductivity due to the passage of electrons and/or holes. For the application, such
as an electrode it is advantageous for a material to be mixed conductor with high
electrolytic as well as electronic conductivity. On the other hand, use of mixed
conductor as an electrolyte would cause internal short-circuiting and subsequent
self-discharge. Hence, it is inevitable to use a solid exhibiting high ionic conductivity but negligible electronic conductivity.

In the light of above stringent requirements, solid electrolytes are to be engineered with the normal ion conductors wherein the electronic conductivity although measurable, is too low for practical applications [4-8]. The recent discovery of new materials with exceptionally high ionic conductivity proves their superiority over liquid electrolytes. The solid electrolyte based devices exhibit (i) long shelf-life (8-10 years), (ii) wide temperature range of operation, and (iii) less complex. Additionally, these systems are, particularly, exciting because they are inherently robust, compact, container free and spill proof.

I.A.1 CHARACTERISTICS OF SOLID ELECTROLYTES
Solid electrolyte materials posses the following characteristics [9]
i) High electrolytic conductivity.
ii) Low electronic conductivity.
iii) Good mechanical integrity.
iv) Good mechanical adhesion to suitable electrode materials with which they are chemically and electrochemically compatible.
v) Stability in presence of electric field.
vi) Chemical compatibility with reaction products.
vii) Low activation energy of migration and
viii) Easy conduction between inter-granular and intra-granular boundaries.

A number of structural features have been found to characterize the solids, which exhibit high ionic transport properties. One of the most common features of majority of the crystalline super ionic solids has been their typical crystal structure wherein, the number of symmetrically and energetically equivalent sites for the mobile ions are larger than the number of mobile ions. Mere fulfillment of this condition does not guarantee the high ionic conductivity, unless the additional condition of low activation energy for the ionic motion is fulfilled. After a close
scrutiny of the characteristic properties of a number of super ionic conductors, within the framework of their structural aspects, Reau et al [10] have formulated the following criteria for high ionic conductivity in solids

i) Small ionic radius and the charge of the mobile ion.
ii) High ionic polarizability of the constituent ions.
iii) Weak binding energy between the mobile and antagonist ions.
iv) Low co-ordination number of mobile ion.
v) Low melting point.

I.A2 CLASSIFICATION OF SOLID ELECTROLYTES

Solid electrolytes can be classified in a number of ways on the basis of their specific characteristics. This is because of the availability of solid electrolytes in a wide range and in a variety of forms. For simplicity and considering the scope of present work, they are divided into five groups as displayed in the following flow chart.

<table>
<thead>
<tr>
<th>Doping</th>
<th>Nature of transition</th>
<th>Nature of substances</th>
<th>Number of conducting ions</th>
<th>Ion contributing to conduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Defect Type</td>
<td>a) Class-I (normal melting)</td>
<td>a) Crystalline</td>
<td>a) Unipolar</td>
<td>a) Silver ion conductor</td>
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<tr>
<td>YCl₃[11]</td>
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<tr>
<td>b) Molten sub-lattice type</td>
<td>b) Class-II (First order transition)</td>
<td>c) non-crystalline (amorphous)</td>
<td>d) Bipolar (both anion and cation contribute to the process)</td>
<td>b) Copper ion conductor</td>
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<tr>
<td>CuBr, AgI, CuI[12,13],</td>
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<tr>
<td>i) cationic conductors</td>
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<td>CuBr, AgI, CuI[12,13],</td>
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<tr>
<td>ii) anion conductors</td>
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<tr>
<td>B₂O₃[11]</td>
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<tr>
<td>c) Layered or tunnel structure type</td>
<td>f) Class-III (Faraday transition)</td>
<td>c) Composites</td>
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<tr>
<td>Na₂S[14], Li₂SO₄[15]</td>
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<tr>
<td>i) cation conductors</td>
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<td>Na₂S[14], Li₂SO₄[15]</td>
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<tr>
<td>ii) anionic conductors</td>
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<tr>
<td>SrCl₂[16], PbF₃[17], CaF₂[18]</td>
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<tr>
<td>g) Polymer electrolytes</td>
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<tr>
<td>h) Proton conductors</td>
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<tr>
<td>d) Halide ion conductor</td>
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<tr>
<td>e) Alkali ion conductor</td>
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</tbody>
</table>

FLOW CHART - 1
I.A2.i Crystalline Solid Electrolytes

One of the most distinct features of super-ionic crystals has been the abrupt change of ionic conductivity by several orders of magnitude that takes place at temperature just below the melting point of these crystals [19]. Clearly the structure plays an important role in the microscopic ion diffusion through solids, and hence, the materials are classified on the basis of their crystal structures.

O’ Keeffe, on the other hand, empirically classified some ionic solids into three categories with respect to fast ionic conduction [11,12]. According to him class-I solids have been those which do not undergo any transformation from non-conducting to the conducting state, but become highly conducting only upon melting. In contrast, class-II solids have been characterized by first order transition to a high conducting state with an entropy change comparable to the entropy of fusion. In class-III solid, the non-conducting to the conducting transformation has been not a first order transition, but spreads over a substantial temperature range through which the conductivity passes smoothly from values typical to the normal salts to those of ionic melts. In some electrolytes heat content exhibit likewise a continuous function of temperature over the entire range of transformation. This transformation has been named after Faraday who was the first to point out its existence in some ionic solids.

I.A2.ii Non-Crystalline Solid Electrolytes

Amorphous or glass like material has attracted a great deal of attention in the application of electrochemical devices for a number of reasons. Additionally, they are easy to prepare and cheaper than crystalline ceramics. It has also been found that the influence of grain – boundaries is nil. The added advantages are (i) they can be easily formed in thin film configuration and (ii) can also be shaped into the desired shape and form. On the basis of ion contribution to the conducting process, glasses can be further categorized into two major subclasses: (i) Anionic conducting
glasses e.g. fluoride glasses and (ii) cationic conducting glasses e.g. sulphide and oxide glasses.

I.A2.iii Composite Solid Electrolytes
The ionic conductors belonging to this class have been heterogeneous multiphase, typically two-phase solid systems. Also known as (i) dispersed solid electrolyte systems (DSES), (ii) ion conductors containing dispersed second phase particles and (iii) heterogeneously doped materials [26].

The significant enhancement in ionic conductivity of LiI and other materials has been observed by adding small particles (sub-micron) of insulating second phase like Al₂O₃ or SiO₂ [20-27]. A detailed theoretical treatment of the conductivity enhancement studies on the mixture of two ionic conductors has been proposed by Maier [28]. There are two main aspects in understanding the abnormal conductance of composite materials: (i) the microscopic mechanism which determines the magnitude of the conductivity along and across the interface [29] and, (ii) on greater macroscopic level by considering percolation theory [30].

I.A2.iv Polymer Solid Electrolytes
Polymer solid electrolytes have attracted a great deal of attention, in more recent past owing to their use as electrolyte in high energy density batteries at temperatures up to 150°C, and as conducting coating to remove static surface charges. As compared to liquid electrolytes, polymer solid electrolytes offer the advantage of a large electro-activity domain and cleaner working conditions. Advantages compared to the other solid electrolytes include easier implementation and low working temperature.

These materials are solid solution of alkali metal salts like LiClO₄, NaI, etc. in propylene oxide [31]. Physical properties of these compounds are similar to those of the thermoplastics to rubbery elastomers. They have shown, the conductivity
between $10^{-2} - 10^{-3} \text{ S cm}^{-1}$ at 120°C, which decreased rapidly to $10^{-7} \text{ S cm}^{-1}$ at room temperature.

**I.A2.v Solid Proton Conductors**

The most recent investigations of solid electrolytes have been directed towards the great proton conductivity in some acid salts as well as crystalllohydrates [32-34]. The best proton conductors are acidic and basic hydrates like HUP, PSA, PMA, etc. [35].

**I.A3 CRITERIA FOR HIGH IONIC CONDUCTIVITY IN SOLID ELECTROLYTES**

The high ionic conductivity of solid electrolyte is brought about by combination of (i) a high concentration of mobile charge carries (ions) and (ii) a low enthalpy of activation for ion migration from occupied site to nearby vacant one. Holzapfel and Rickert pointed out that the common property of all the best solid electrolytes has been that they can be optimized both with respect to the ion mobility and the density of mobile ion [36]. In general, it could be stated that the solid electrolyte should have the following basic features (i) the origin of formation of the sublattice disordering required for electrolytic conductivity, and (ii) ion transport through such disordered structures.

The mobility of one ion species can be determined by the presence of vacancies or ionic defects in the crystal lattice. If an ion near vacancy jumps to the vacancy due to thermal vibration or electric field, new vacancy at ion site will be created in this process and ions shall, thus, carry current from one end to the other. Following two processes are responsible for producing vacancies in crystal lattice:

i) By thermal vibrations of the ions at lattice sites, which can result in an ion vacancy at the lattice site, and ion itself goes interstitially (Frenkel defect).

The concentration of such thermal vacancies is low, but increases rapidly
with temperature and exhibit the conductivity of the order of $10^7 - 10^4$ S cm$^{-1}$ [37].

ii) In some complex lattices, the ion has no definite site but can occupy one of the several symmetrically equivalent sites with almost equal probability. It is then said that the sublattice of this ion is disordered, in contrast to the rigidly ordered sublattice of other ion. Since an ion at a given moment can occupy only one site, other equivalent sites play the part of vacancies.

Most of the solid electrolytes have been seen to attain a high electrical conductivity above a certain temperature, which may or may not be well defined. Increase in temperature leads to an enhancement in conductivity gradually or abruptly. An abrupt jump in conductivity is associated with distinct structural change (e.g. $\square - \square$ transition in AgI), but some times this is not so clear. Structures, which allow fast ion transport, are generally disordered channelled or layered [38]. Ion-ion interactions or correlation have also been seen stimulated sharp changes in conductivity [39-46].

I.A4 THEORETICAL ASPECTS

Some of the important theoretical aspects pertinent to the present work are discussed briefly in the following sub-sections.

I.A4.i Dispersed Phase Theory

In many soft framework electrolytes, e.g. LiI [47] and in some glasses [48] it has been demonstrated that the presence of a dispersed insulating second phase enhances the conductivity by several orders. A large number of mechanisms have been discussed for this behavior, including transport along the dislocation loops of grain-boundaries, and high strain fields at the interface.

Roman et al have used a three-component percolation type model to discuss the increased conductivity [49]. In their theory, they included three regions, namely a conductive phase describing the interface, the ionic conductor and the insulating phase. A three-component electrical network model has been used which stresses
the roll of interface percolation [49, 50]. Two threshold concentrations have been obtained, which define a range of concentrations for which the static conductivity passes through a broad maximum. Dudeny has suggested noticeable space – charge effect in the multiphase systems, which also governs the conductivity behavior microscopically [51]. The space-charge theory relevant to the present work is given below [52].

I.A4.ii  Mechanism of Formation of Space Charge Region Across Interface of Two Phases.

For the Frenkel disorder crystal (\(M^\circ X\)), the disordered reaction in terms of Kroger – Vink notation is given by,

\[
M_M + V_i = M_i^* + V_M^*
\]  \hspace{1cm} (A)

where, \(M\) denotes the cation or it’s regular lattice site, \(v\) and \(i\) are the vacancy and interstitial site, respectively, and ‘\(\cdot\) respective to, denotes the charge of the defect (positive respective to negative) relative to the perfect lattice. The above relation (A) can be split into two so as to understand the mechanism of formation of space charge region microscopically as,

\[
M_M + V_S = M_S^* + V_M^*
\]  \hspace{1cm} (A1)

\[
M_S^* + V_i = M_i^* + V_S
\]  \hspace{1cm} (A2)

The former relation (A1) represents the bulk vacancies and later (A2) expresses the formation reaction for bulk interstitials, which accompanies with annihilation of \(M\) ions at the surface (denoted by \(S\)). Further, the standard free enthalpies \(\Delta_f G^0\) and \(\Delta_f G^\circ\) characterize both the reactions. If the free energy of reaction (A1) exceeds the free energy of reaction (A2), then the cations will be enriched at the surface and vacancy concentration \(N_v\) will be larger in comparison with the bulk concentration \(N_v\), and vice versa for the alternative case. This locally realized space charge (Fig. 1.1a) will be fixed in the equilibrium \((N_i^* = N_i)\) and resultant electric field in its
energetic influence is compensated by the variation of the chemical potentials. The fall of $N_r$ respective to $N_i$ with distance inside the grain, shown in figure I.2b, is characterized by Debye length, which is much steeper than an exponential decrease.

$$\lambda = \left[ \varepsilon \varepsilon_0 kT / 2e^2 C_x \right]^{1/2}$$

(1.1)

where $\varepsilon$ and $\varepsilon_0$ are the relative and absolute dielectric constants, respectively, $e$ the electron charge, and $C_x$ the particle density of the defects in the interior.

In multiphase systems, a second insoluble phase $MX'$ instead of vacuum is in contact with $MX$. In such case, a partial transfer of $M'$ from one solid to the other (Fig. I.1a) occurs near the interface until the difference of the chemical potentials is balanced by the electric field energy. As a result, vacancy concentration is enhanced in the space charge region of the one phase and the interstitial concentration in the other phase. Because of such transfer of ions, the condition of electro-neutrality at the boundary region has been relaxed, and replaced by the general Poisson’s equation,

$$\rho(x) = -\varepsilon \varepsilon_0 (\delta^2/\delta x^2) \Phi(x)$$

(1.2)

where, $\rho$ is the charge density, and $\Phi$ and $x$ as the electric potential and the distance from the surface (Fig. I.1b). The transfer of a mobile ion splits up the concentration profile as shown in figure (I.1)

In case of multiphase system consisting of Frenkel disordered ion conductors $MX$ and $MX'$ (with same mobile cations), the enhancement in conductivity due to space charge region is given by,
\[
\Delta G = \left[ \frac{4 k_f \alpha^a a}{2 R^2 e^2 \varepsilon_0} \right]^{1/4} (\mu + \mu')
\]

where \( k_f \alpha^a a \) is the mass action constant and \( \mu \) is the mobility of cation in space charge region. The primed quantities refer to \( MX' \). Therefore, the effective conductivity of two-phase mixture of \( MX \) and \( MX' \) increases with increasing contact area. The superposition of the individual conductive region (bulk + space charge layer at the interface of \( MX \) and \( MX' \)) is a very difficult problem. However, it depends on the volume fraction, grain size and shape, Debye length as well as conductivity and distribution of the individual phases. An appropriate approach to above problems is Landauer's average medium method.

In conclusion it can be said that each of the above theories has been presented with a special view to explain qualitative as well as quantitative behavior of different materials. However, no attempt has yet been made to develop a generalized theoretical background, which will provide the guidelines for tailoring new materials with required properties for the technological applications. Nevertheless, the above models cater to the needs of the present study.

I.A5 GENERAL APPLICATIONS OF SOLID ELECTROLYTES

Solid electrolytes have been used in a good number of device applications. Some of the important features from this viewpoint are listed below before discussing the actual applications.

i) The material provides an imperious barrier to gases and liquids. They, however, allows one or more ions to migrate through its lattice when a tendency of such a migration exists.

ii) A solids electrolyte allows the measurement of the difference of chemical potentials of the migrating species of on either side in terms of electrolyte force in a properly constituted cell and

iii) Solid electrolytes are stable compounds, which do not get easily corroded by high temperature environment.
The chief applications of solid electrolytes can be categorized according to their characteristics as discussed below.

I.A5.i **Closed Circuit Applications**

The two main principles governing the closed circuit applications are as follow:

i) The emf of a solid electrolyte galvanic cell gives thermodynamic information concerning chemical potentials or activities at the electrodes provided conduction is completely ionic.

ii) The current through the cell, the solid electrolyte sandwiched between anode and cathode, is a measure of rate at which the particular ion is passes through the electrolyte. The free energy change is related to emf, $E$, of the cell by,

$$\Delta G = -nFE$$  \hspace{1cm} (I.4)

where $n$ is the valency of the ions, and $F$ is Faraday constant (96500 coulomb)

Thus, the measured emf directly yields free energy change. An exact determination of $\Delta G$, however, needs precise value of the transference number of ions, $t_i$. In several cases $t_i \approx 1$, and hence, a direct relationship should not be assumed. Practical examples are given below.

I.A5.ia **Fuel Cells**

Fuel cells are devices in which a type of electrochemical species is being continuously consumed; and the output is a continuous electrical voltage and current. Solid electrolyte based fuel cells comprise oxide electrolytes such as calcia stabilized zirconia (CSZ) with cell configuration.

$$\text{pt} / \text{Air (O}_2) / \text{CSZ} / (\text{H}_2, \text{H}_2\text{O}) \text{ or CO or CH}_4/\text{pt}$$

The gaseous fuel H$_2$, CO or CH$_4$, produced by reforming or natural gas or gasification of coal, can be used. On the cathode side, oxygen is continuously fed and is reduced according to reaction.
\[ O_2 + 4e^- + 2V_\text{O}_2^- \leftrightarrow 2O_\text{O} \]

Here, \( O_\text{O} \) means oxygen ions in the lattice, and \( V_\text{O}_2^- \) implies oxygen ion vacancy with effectively two positive charges, which exist at high temperature in the electrolyte lattice. At the anode, oxygen is continuously consumed or burned with the fuel, and the electrons released at the anode by electrochemical oxidation flow through the external circuit back to the cathode. Thus, electrical energy is supplied to the consumer. The open circuit voltage (OCV) \( E_o \) by this effective voltage available is,

\[ E = E_o - IR_i - V_p \]

(1.5)

where \( IR_i \) is ohmic losses (\( R_i \) is internal resistance of the cell) and \( V_p \) is polarization losses at the electrodes. Thus, the voltage efficiency \( \eta = E/E_o \).

**I.A5.ib Electrochemical Capacitors**

The double layer capacitance between an inert electrode like carbon and solid electrolyte like \( \text{Rb}_2\text{Ag}_3\text{I}_5 \) can be as high as 20 \( \mu \text{F/cm}^2 \). High capacitance could be obtained by optimizing the total interface area, e.g., 10\( \text{F/cm}^2 \). However, the voltage limits to 0.6 volts because, the electrolyte decomposes at higher voltages. The cell \( \text{Ag/RbAg}_4\text{I}_5/C \) developed by Raleigh is being considered for energy storage because of the very high capacity [3].

**I.A5.ic Coulometers and Timer Switches**

The cell \( \text{Ag/RbAg}_4\text{I}_5/Au \) can serve as a coulometer. Anode is made up of the same material as the mobile ion species in the electrolyte and the other electrode must be insoluble to moving ion. During charging, when a current passes, silver is deposited over the gold electrode. The deposited mass can be known from Faraday's law. During stripping a reverse current is passed and silver is transported back to the silver electrode. During this process, the cell voltage is determined by Ohmic losses in the electrolyte. The same voltage is of the order of a few milli-volt. When
all the silver is stripped from the gold electrode, a sudden rise in voltage occurs, which is used as a signal of trigger. The interval between the two successive voltages can be used for timing purpose. Such electrochemical switches can be constructed to operate over time range between seconds to months.

IA5.id Solid State Batteries
The discovery of highly conducting solid electrolytes or fast ion conductors brought about the possibility of developing altogether new batteries characterized by ruggedness, high energy density, long shelf life and miniaturized size.

IA5.ii Open Circuit Applications
In these applications the solid electrolyte is normally employed in a suitable cell, which can measure concentration of gaseous species. An example for the open circuit application is the solid electrolyte cell as $O_2$ and $SO_2/SO_3$ sensors. This is useful for the measurement and monitoring of industrial pollutants containing $SO_2$ and $SO_3$, $Ag_2SO_4$, $Na_2So_4-I$, $Li_2SO_4$ and other two phases binary sulphates are being actively explored for $SO_x$ sensor application. The reaction in the cell at the gas electrode- electrolyte interface is given as:

$$SO_3 + \frac{1}{2} O_2 + 2e \rightarrow SO_4^{2-}$$

The resulting Nernst equation for the following cell

$$SO_3 + O_2 / Pt / Na_2SO_4-I / Pt / SO_3 + O_2$$

$$E = \frac{RT}{2F} \log \left[ \frac{(P_{O_2'})^{1/2}P_{SO_3}}{(P_{O_2})^{1/2}P_{SO_3}'} \right]$$

(1.6)

The primed quantities are due to reference gas In air, the expression 1.6 simplifies to
\[ E = \frac{RT}{2F} \log \left[ \frac{P_{SO_3}}{P_{SO_2}} \right] \]

Therefore, by knowing the reference gas partial pressure, one can monitor the pressure of the pollutant in terms of the emf generated. Results obtained during the present work on electrochemical solid-state gas sensor are discussed in chapter V.

As it is said that the present thesis is focussed on the construction of binary phase diagram, it was thought imperative to discuss relevant parameters prior to the general description of phase diagram.

LBI PHASE

A phase is physically distinct, chemically homogeneous and mechanically separable region of heterogeneous system, e.g. Ice/water/vapor are the phases of the same chemical substance, water.

The gaseous state is always a single phase because, the atoms (or molecules) in the gas are mixed at atomic (or molecular) level, whereas, the liquid solution is also single phase but liquid mixture form two separate phases.

In solid state, the different chemical compositions and different crystal structure are possible, therefore, solid may consist of several phases. Whereas, solid solution has the atoms mixed at the atomic level within unit cell and is, therefore, a single phase. The number of phases, which can be formed by any gives substance or group of substances increases, in general, with the number of participating substances, but it may vary considerably. According to phase rule, the number of solid phases in equilibrium can never be greater then number of component plus two, while in the case of liquid, number of liquid phases never be greater than the number of components [53].

The phase diagrams are maps that give the relationship between phases in equilibrium in a system as a function of temperature, pressure and composition.

In order to construct a phase diagram one need to know the transition
temperatures at number of different compositions of the components. While constructing a phase diagram on the basis of a number of transition points at different composition, one must be sure that Gibbs phase rule is obeyed. According to Gibb’s phase rule \( p + f = c + 2 \) [54]. Phase diagram can never be understood in absence of the number of equilibrium that occurs and these are described below.

A system may be considered homogeneous when it is uniform throughout it’s volume, so that it’s properties are the same in all parts. Any equilibrium occurring in a homogenous system is termed as a homogenous equilibrium. On other hand, heterogeneous system consists of two or more distinct homogeneous regions. Surface or interface at where occurs a sudden change in physical and chemical properties separates the homogeneous regions or phases from one another. For system to be in equilibrium, it must be in thermal, mechanical and chemical equilibrium.

Thermal equilibrium exists whenever there is no flow of heat from one part of system to another i.e., two parts are at same temperature. In mechanical equilibrium, pressure is constant throughout the system. The chemical equilibrium of the system exists when the rate of each forward reaction equals to the rate of the corresponding backward reaction. The chemical potential of a particular species must be uniform in all parts of the system. In terms of the Gibbs free energy \( G \), the condition for equilibrium is given by \( (dG)_{T,P} = 0 \).

I.B2 DEGREE OF FREEDOM
The number of degree of freedom of a system is same as the number of variable factor, temperature, pressure and concentration of the components, which must be arbitrarily fixed in order that the condition of the system may be perfectly defined. Within the system, there are variables that specify the compositions of the phases present. Composition are expressed as weight present (or atom percent) so that the number of variable required to specify completely the composition of a phase is \( (c - 1) \).
If there are $p$ phases in a system, the total number of composition variable is $p (c - 1)$. Including the two external variables (pressure and temperature), the total number of variables is $p (c - 1) + 2$. The number of independent variables among these gives the degree of freedom $f$. The degree of freedom cannot be greater than the total number of variables. We may also speak of the variance of the system and describe a system, as being invariant, univariant, and bivariant or multivariant according to whether the number of degree of freedom is none, one, two or more than two [55]

**I.B2.i PHASE RULE**

For a system, in which one phase contain two components, then to specify completely the composition of a phase we require one variable. This variable is the ratio of two components in that particular phase. If one phase of a system contain three components then to specify completely the composition of a phase one require two variables. Generally, if there are $c$ components in one phase than to specify completely the composition of a phase one require $(c - 1)$ variable. For a system of $p$ phases there must be $p (c - 1)$ such variables. Including the two external variables (or pressure and temperature), the total number of variable is

$$p (c - 1) + 2$$  (I.8)

For one component in two phases $\alpha$ and $\beta$, their equation chemical potential are same i.e., $\mu_\alpha = \mu_\beta$. For one component in three phases $\alpha$, $\beta$ and $\gamma$, there will be two equations $\mu_\alpha = \mu_\beta$ and $\mu_\alpha = \mu_\gamma$. In general for $p$ phases it would be possible to write $(p - 1)$ equation for each component. For $c$ component the number of equations must be $c (p - 1)$.

$$(\text{No of variables}) - (\text{No of equation}) = \text{No of independent variable}$$  (I.9)

use (I.8) and in (I.9) leads to
\[ p + f = c + 2 \]  \hspace{1cm} (I.10)

**LB3  HUME ROTHERY RULE**

A number of metal dissolve in each other forms a solid solution. Solid solution is analogous to liquid solution. The mixing of the element in the solid is on the atomic scale. When the solute atom is much smaller than solvent atom, it may dissolve interstitially occupying void space in the parent structure, e.g. carbon in fcc iron and occupies the octahedral voids in the fcc structure. When the solute and solvent atoms are of comparable sizes, the solute substitutes for the solvent atom or regular atomic site. Hume Rothery has framed empirical rules that govern the formation of substitution solid solution. Extensive solid solubility by substitution occurs, when

i) The solute and solvent atoms do not differ by more than 15% in diameter.

ii) The electro negativity difference between the element is small and

iii) The valiancy and the crystal structure of the elements are the same.

Ag – Au, Cu – Ni, Ge – Si system satisfy the Hume Rothery condition very well, therefore, system form complete solid solution, i.e. the two elements mix in each other in entire compositional range.

Substitutional solid solutions have usually a random arrangement of constituent atom on the atomic sites, especially at elevated temperature. This is so, as configurational entropy makes a greater contribution in lowering the free energy with increasing temperature \((G=H-TS)\). This random arrangement of constituent atoms in a solid solution may change over to an order arrangement on cooling to lower temperature provided ordering lowers the enthalpy of the crystal sufficiently.

**LB4  CLASSIFICATION OF PHASE DIAGRAM**

Phase diagrams are classified on the basis of the number of components in the system. Single component systems have unary diagrams, two components systems have binary diagrams, three component systems give rise ternary diagrams and so on.
1.B4.i Single Component Systems or Unary Phase Diagram

In single component systems, there is no composition variable, and only other variables are temperature and pressure. For single-phase region, \( C = 1 \) and \( P = 1 \) then by using phase rule \( F = 2 \). Therefore, for single-phase region, both temperature and pressure can be varied independently within the limits prescribed by the boundaries of the regions. When two phases are in equilibrium \( F = 1 \) i.e., either temperature or pressure can be varied independently but not both. Two-phase equilibrium exists along the phase boundaries.

Three-phase equilibrium exists at points on the phase diagram, where three phase boundaries meet, such points are called triple point. Here \( F = 0 \), neither temperature nor pressure can be varied arbitrarily. Three phases will co-exist at only one particular combination of pressure and temperature. If we alter pressure and temperature from fixed triple point value, one or two of the phases will disappear.

1.B4.ii TWO COMPONENT SYSTEMS OR BINARY PHASE DIAGRAMS

Two-component systems have binary phase diagrams. In two-component systems, one has three variables and these are temperature, pressure and composition. Here there is a need of three-dimensional diagram to plot the variation in pressure, temperature and composition. In order to simplify the representation of the phase relationship on paper, binary phase diagrams are usually drawn at atmospheric pressure, showing variation in temperature and composition only. To denote this, the phase rule for binary phase diagrams is frequently written in a modified form as \( p-f = c +1 \) [56].

The simplest binary phase diagram is obtained for a system exhibiting complete liquid solubility as well as solid solubility. The two components dissolve in each other in all proportions both in the liquid and solid state e.g., phase diagram (Fig. 1.2) of \( \text{Al}_2\text{O}_3 \) and \( \text{Cr}_2\text{O}_3 \). There are only two phases on the phase diagram, the liquid and the solid phases. The single-phase regions are separated by two-phase region (L+S), where both liquid and solid co-exist together. In all binary phase
diagrams, a two-phase region separates single-phase region as given by the “1 - 2 - 1” rule. As one moves from a single-phase region (1), into two-phase region (2) and this again into single-phase region (1). The phase boundary between the liquid and the two-phase region is called the liquidus. The boundary between the solid and the two-phase region is called solidus. When only one phase is present, the composition axis gives the composition of that phase directly.

When two phases are present, their compositions would be different. Here at the temperature of interest $T$, a horizontal line called the tie-line is drawn. The point of intersection of the tie-line with the liquidus and solidus give, respectively, the liquid and solid composition. $C_l$ and $C_s$ are in equilibrium with each other. The solid solubility is, therefore, limited in a number of binary system. But it is never zeroed. A very small quantity of any component will always dissolve in another component as this increases the configurational entropy and lowers the free energy of the crystal.

In present work, author examines two-component system. If the components are completely miscible either in the form of solid solution or in the form of liquid then such types of system can be separated in four groups, which will be described now.
Group-I: The only solid phases are the pure components. Since only pure components can occur as solid phases, the only possible systems are $S_1 - L$, $S_2 - L$ and $S_1 - S_2 - L$, where $S_1$ and $S_2$ represent the crystalline components and $L$ the liquid solution. According to the phase rule a system that consists of only two phases, $S_1 - L$ or $S_2 - L$, will be bivariant, and two of the variables, pressure, temperature, and composition, must be given definite values before the system is entirely defined.

Under a given pressure, the system $S_1 - S_2 - L$ can exist only at single definite temperature and the composition of the liquid phase will also be definite. If the equilibrium is represented in a temperature-composition diagram, the system $S_1 - L$ and $S_2 - L$ will be represented by curves, whereas, the system $S_1 - S_2 - L$ by a point. Since the freezing-point of a liquid is normally lowered by dissolving another substance in it, it follows that if a quantity of the components $B$ is dissolved in molten $A$ (Fig. 1.4) The temperature at which solid $A$ will be in equilibrium with the solution will be below the freezing-point of pure $A$.

The curves $AC$ and $BC$ are called freezing point curves. The curve $AC$ represents the composition of solutions, which are in equilibrium, at different temperatures, with the solid component $A$ and the curves $BC$. Similarly, the composition of solution in equilibrium with solid $B$. At the point $C$ where the two curves cut, both solid components can exist in equilibrium with a liquid solution of definite composition, corresponding with the point $C$. This point is called an eutectic.

At all temperatures, below the eutectic horizontal $DE$ only the solid components or mixtures of the solid components can exist as stable systems. When the temperature and composition are represented by a point in the area $ACD$, solid component $A$ can exist along with liquid solutions.

What happens if a liquid solution $E$. [Fig. 1.3: The only solid phases are the pure components.]
having a composition lying to the left of the eutectic point C, is cooled down? The solid component A will begin to crystallize out when the temperature reaches the point G on the curve AC. If the temperature is allowed to fall still further, more and more of component A will crystallize out, and the composition of the liquid will alter in the direction of C following the curve AC. When the composition of point C is reached, solid B can also begin to crystallize out. If one continues to withdraw heat from the system, solid A and solid B will separate out together, while the temperature remain constant. Since the composition of the solution must also remain constant, it follows that the components A and B must crystallize out from the eutectic solution in constant proportions. The solid, which separates out, is not a compound but a mixture of two solid phases.

**Group-II:** This group includes binary of where compound are formed with an incongruent melting point. When two components can form a stable compound possessing a congruent melting–point, i.e. capable of existing as a solid compound, in equilibrium with a liquid of the same composition, a third equilibrium curve must be added to the curves discussed in preceding section. Since the compound has a definite congruent melting–point and the melting–point will be lowered by dissolving in the liquid either of the pure components, it follows that the melting point of the compound must be a maximum point on the equilibrium curve (point D, Fig I.4). Such a maximum is known as a eutectic. The points A, B, C and D are the congruent melting–point of components A, B, Ax and By, respectively. Curve AC gives the composition of liquid mixtures

![Fig I.4 A compound, A,B, with a congruent melting point, is formed.](image)
of A and B in equilibrium at different temperatures with the component A as solid phase. Curve BE gives the composition of solutions in equilibrium with component B as solid phase and. Curve CDE gives the composition of solutions in equilibrium with the compound as solid phase. The points C and E are eutectic points. If more than one compound with congruent melting point can be formed, a series of curves similar to CDE will be obtained, one for each compound. Point D suggests two-component system consisting of two phases, a solid and a liquid, and according to phase rule the variance should be two. However, the congruent melting point varies only with the pressure, and the system is, therefore, univariant. The variance of the system has been diminished. Such a point is called as indifferent point.

**Group III:** This group encompasses the binary systems in which the compounds are formed with an incongruent melting point. When a compound is formed which undergoes decomposition with formation of another solid phase at a temperature below the congruent melting point of the compound, the equilibrium diagram assumes the general form shown in figure I.5. This corresponds to the case where a compound can exist only in contact with solutions containing an excess of one of the components.

The metastable continuation of the equilibrium curve for the compound is indicated by the dotted line, the summit of which would be the congruent melting point of the compound. Before this temperature is reached, however, the solid compound ceases to be stable, and undergoes decomposition into another solid phase and liquid at the point D. Since
the composition of the liquid formed is not the same as that of the compound, this point is known as incongruent melting–point or peritectic point.

The solid solutions or “mix-crystals” are formed. The introduction by van’t Hoff of the term solid solution resulted from the discovery of a number of deviations from the Raoult-Van’t Hoff law for the depression of the freezing point by dissolved substances. In all cases, the depression was too small; in some cases, the freezing-point was raised. To explain these irregularities, Van’t Hoff assumed that the dissolved substance crystallized out along with the solid solvent. He has showed how this would account for the deviations from the law of depression of the freezing point, which had been developed on the assumption that only the pure solvent crystallizes out from the solution.

Since there are two solutions, the liquid and the solid, and since the concentration of the components in these two phases is generally dissimilar, the curves will be required, one relating to the liquid phase, the other relating to the solid. The temperature – concentration curve for the liquid phase (AC, BC in figure 1.6) is called the freezing-point curve or the solidus curve.

Several different cases where solid solutions are formed are known. To understand the phase diagrams constructed during the present work it is sufficient to study the two components, which do not form a continuous series of solid solutions.

As is evident from figure (1.6), addition of B raises the melting point of A, and the concentration of B in the solid solution will be greater than in liquid solution. This is represented in the figure by the curve AD. On the other hand, addition of A lowers

![Diagram](image_url)
the melting – point of B, and two curves BC and BE are obtained for the liquid and solid phases respectively. At the temperature of the line CDE, the liquid solution of the composition represented by C is in equilibrium with the two different solid solutions represented by D and E. At this temperature, therefore, the “t-c” curve for the solid phase exhibits a discontinuity. And since the solid phase undergoes change at this point, the freezing point curve must show a break. Such a break is a peritectic point of the same type as is observed with an incongruently melting compound.

In the case of figure I.7, the freezing – point of each of the components is lowered by the addition of the other, until at least a point is reached at which the liquid solution solidifies to a mixture or conglomerate of two solid solutions. At the eutectic point the liquid solution is in equilibrium with two different solid solutions, the composition of which is represented by D and E, respectively. If, therefore, a fused mixture containing the two components A and B in the proportions represented by C is cooled, it will when the temperature reaches the point C, solidifies completely to a conglomerate of two solid solutions D and E.

Fig I. 7 The freezing-point curve exhibits a eutectic point.
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