Chapter 1

General Introduction
INTRODUCTION

The solid-state sciences include what is now the largest sub-area of physics and the material engineering sciences. The last thirty years have been marked by the rapid expansion of this field and chemists have contributed to and have been benefited from the development in this important area of science and engineering.

New dimensions to the importance of solid-state reactions have been added by their fast growing applications [1-4] in metallurgy, ceramic technology, electrochemistry, lasers, semi-conductors, polymers, manufacture of artificial gems, catalysts, spinels and refractory materials. Spinels obtained from various oxides and their solutions are used in television, radar and jet planes. Solid-state may act as a useful matrix [5] to put in practice control over the rate, isomer distribution and stereo-chemistry of organic reactions. New technologies based on nuclear energy, space exploration and solid-state electronic devices have stressed the need for high temperature solid-state materials and for a systematic understanding of their chemical behaviour.

The advances made in the superconducting materials during the past few years have led to an increased awareness of the importance of solid-state chemistry that can be judged by the fact that a full issue of Chemical Review
In solid-state reactions, the restricted movement of the reactant molecules provides the restricted opportunity to reach each other in sharp contrast to the fluid phase reactions where random and frequent contact between reactant molecules is a natural consequence of the kinetic nature of reactants. Reactions in the solid state are characterized by (a) chemical process leading to the formation of solid state product or products, and (b) the diffusion process of elementary particles within their interior. Reactions in solid state are free from the complications arising out of solvent and their rates in general are very slow. Hence, usually solid-state reactions are diffusion controlled and are more apposite to kinetic and mechanistic studies and very apt for the discovery of new species [6-9]. In solid-state reactions, at least one component diffuses into the other for the reaction to be initiated and propagated. Therefore, lattice parameters play a very important role in determining the kinetics and mechanism of such reactions [10,11]. In order to understand solid-state reactions, first of all it is necessary to explain the transport of matter in the reaction product. Since this transport in solids is due primarily to the mobility of point defects, it is therefore necessary to understand the behaviour of defects. Furthermore, as the solid-state processes involve movement
of the interphase boundary, the mathematical formulation of the rate processes must be expressed in terms of space and time coordinates.

After some acquaintance with solid phase diffusion in metals had been gained, the systematic study of reactions between solids was taken by Faraday [12]. In 1885, Spring [13,14] asserted to have observed reactions between inorganic solids, but his explanation was not very clear. Robert-Austen [15] noted the diffusion of gold in lead at various temperatures. Cobb [16] observed reactions in solid-state between quartz and alumina with calcium carbonate or calcium sulphate. It is evident from the monograph of Hedvall [17] and Jost [18] that intensive investigations in this field were carried out during second to fourth decade of the twentieth century. Hedvall [19,20], in 1914 and in the subsequent years, demonstrated that reactions in solid state occur frequently and represent indeed an important branch of chemistry. In the middle of the year 1920, Hedvall observed that reactions could be carried out by the motion of lattice ions. This was concluded from the fact that reaction commenced to take place at about the same temperature at which ionic conductivity became noticeable. The discovery that some solid-state transformations occur very rapidly at low temperatures led to scientific inquisitiveness on solid-state reactions.
Pukaill prepared a number of compounds by solid-state interaction which could never be prepared classically and, thus, established the importance of solid-solid reactions. His work was followed by Hedvall. An extensive list of such compounds, along with the raw materials and reaction temperatures, has been prepared by Singer and Singer [21].

In 1927, Jander [22] for the first time presented a mathematical analysis of solid-solid reactions. Jander's model was modified and further developed by a number of workers. Hedvall [17], Tammann [23] and their colleagues made classical studies of the solid-state reactions of inorganic substances. Hedvall [17] proposed that solids are more reactive when they are formed at the lowest possible temperatures as he studied the effect of the thermal history on the reactivity of solids. It was noticed by Hedvall that polymorphic changes in reacting solids cause a considerable increase in the rate of reaction. This effect is known after his name as 'Hedvall effect'. Tammann established a definite relation between the melting point of a solid and its reactivity. The surface mobility is believed to become appreciable when the ratio, \( \alpha \), of the absolute temperature of an ionic solid to its melting point on the absolute scale becomes 0.3. The temperature corresponding to \( \alpha = 0.5 \) is known as the Tammann temperature, at which the solid is
expected to undergo a solid-state reaction at an appreciable rate. The reaction temperatures have been shown by Hedvall [17] and his collaborators to be approximately the same for different reactions of the same solid. The study of mechanism of reactions frequently involves the identification of the diffusing species. This has been achieved beautifully by Wagner [24] for the formation of Ag₂S. Tarnishing, decomposition, polymer degradation, polymerization and oxidation reactions have been extensively studied and reviewed [25-36]. Consequently, the basic features of inorganic solid-state reactions were made clear and they have been summarized in the treatise edited by Garner [28].

The general problem of the study of solid-state reactions is two-fold. One is the experimental determination of reaction rate and morphology as a function of all independent variables, and, the other is the calculation of the reaction rates and the prediction of the morphology under a given set of independent variables in terms of known thermodynamic and transport properties of the system under consideration. These require a knowledge of the atomistic mechanism of the fundamental steps such as nucleation, phase boundary reaction, sintering and diffusion. However, as Stringer et al. [37] have pointed out, theoretical models are in general not adequate for interpretation of real cases and
to account for the kinetic analysis, more data and observations are needed. Real systems are usually in a state of considerable imperfections. Indeed, enhanced and desirable activity and lattice reactivity are often obtained by producing a solid in the form of an imperfect crystal. Lattice imperfections influence all types of elementary steps in a solid-state reaction. They often provide preferred sites for reaction and nucleation, either in bulk of the solid or at the surface.

Obviously, for a quantitative treatment of the reaction kinetics, one has to make several assumptions. Among them, the most important are the assumptions of local thermodynamic equilibrium in the solid phases taking part in the reaction and a thermodynamically well-defined system in which the proper number of independent thermodynamic variables are predetermined. This is why the solid-solid reactions in binary or quasibinary systems have been quantitatively studied. In principle, the knowledge of point defect thermodynamics, thermodynamic properties of the system and that of Fick's law are sufficient to treat the kinetic problems quantitatively. The treatment can be satisfactorily applied to precipitation and decomposition reactions in solids, taking into account the elastic part of the chemical potential [38,39]. Similarly, the relevant problem associated with solid-state electrical battery working with solid electrolytes can be solved by taking into
consideration the diffusion theory in ionic crystal together with point defect thermodynamics [40].

The gradient of chemical potential is a local driving force for the fluxes of the components. There are other solid-state reactions in heterogeneous systems which proceed under the action of other kinds of driving forces such as relative temperature gradients or phase boundary free energies. This kind of reaction under the action of a temperature gradient has been analysed in detail [41], and the solid-state reactions driven by phase boundary free energies are the so called 'Ostwald ripening process' [42].

The reaction between heterogeneous phases, where phase boundary controls the overall rate, are very important and have been studied in a number of solid-gas reactions where a linear rate law indicates that diffusion control does not play the preponderant role [43]. Although it has been found in a number of solid-state reactions in ionic systems that the linear rate law is the initial rate determining step, the atomistic reaction mechanisms are not yet understood. This is due to the fact that in contrast to gas-solid reactions, it is extremely difficult to study the linear reaction rate as a function of the component activities at solid-solid interfaces. But a knowledge of the reaction rate as a function of the independent variables is a pre-requisite for a correct analysis of the atomistic
reaction steps of a phase boundary reaction.

Thermodynamics of solids has many unique features and plays an important role in understanding the reactivity of solids. The equilibrium is usually not possible in reactions in the solid state except for cases of miscibility of reactants and product(s) phases. The reactions in solid state proceed exothermally until at least one of the reactants is completely consumed. In practice, though, complete reaction is difficult to achieve, it is imperative that mixtures of fine powders be pulverized repeatedly to remove the barrier of product stratum between the reactants. The conditions for equilibrium have been discussed fully by Tammann [23]. For achieving equilibrium either gaseous or liquid phase must be present in reaction or the heat of reaction must be small and the entropy difference of reactants and product should not be zero. In the last case, equilibrium occurs at a single temperature, where the stability of the system is reversed. Below the equilibrium temperature, the products are formed and above the equilibrium temperature they are decomposed into the reactants, the reaction being always exothermic.

Most of the solid-state reactions essentially involve lattice rearrangements. The entropy contribution to the free energy change of reaction is very small because order-disorder changes contribute little to the entropy
change of the reaction. Therefore, the expression \( \Delta G = H - T \Delta S \) turns to \( \Delta G \approx \Delta H \), i.e., \( \Delta H \) more or less governs the sign of \( \Delta G \). In 1967, Duncan and Stewart [44] gave a conceptual explanation based on statistical mechanics to correlate the disorder (entropy) with the occurrence of the most probable lattice rearrangements. Navrotsky and Kleppa [45] made experimental investigations for various systems and found a constant value of \( \Delta H \) for all the spinel formation reactions. The deviation of \( \Delta H \) value from the constant value has been attributed to the structural differences and the site preference characteristics of cations. Stone and Tillev [46] suggested that these differences also affect the reactivity of compounds. Kroger [47], and Toropov and Barazakovskii [48], calculated thermodynamic parameters from the emf measurements of a solid cell consisting of the reactants and a solid electrolyte in the form of pellets. Free energy values of reactions are now widely obtained by this method.

The fact that solid substances can act as ionic conductors is known since the end of last century. The solid electrolytes, i.e., solid compounds with practically pure ionic conductivity was first established by transference measurements [49-51]. Following early reports of ionic conductivity, Nernst developed a high temperature cell [52] using mixed oxide solid ionic conductor. A material is said
to be solid electrolyte only when it is in a phase that possesses a structure conducive to ionic mobility. A renewed interest [53-55] in solid electrolytes parallel to fuel cell research has developed during last twenty years. New solid electrolytes having conductivities comparable to aqueous electrolyte solution have been discovered recently. Apart from the application in fuel cells and in solid batteries, solid electrolytes are important in the field of photography and for the determination of thermodynamic data at high temperatures.

To understand solid-state processes it is necessary to understand the properties of solids which may be classified as (i) structure sensitive properties and (ii) structure-insensitive properties [56]. Structure-insensitive properties are well defined under given external conditions and are independent of dimensions of the specimen, whereas structure-sensitive properties are influenced by factors like the mode of preparation of the specimen, the pretreatment, the particle size and the shape. To the structure-sensitive group of properties belong, among others, the chemical formula, the lattice dimensions, the true density, the specific heat, the thermal expansion and for ideal lattices the electrical conductivity and the absorption spectra. Like other properties, usually the chemical reactivity is structure-sensitive and is structure-insensitive in only a few instances. Structure-insensitive
reactions, although of little practical significance, provide the fundamental ingredient for a general comprehension of structure-sensitive reactions.

It is very important to note that all these conclusions are based only on the study of inorganic reactions. Nothing has been mentioned about the organic solid-state reactions in the monographs of Hannay [32] and Budnikov [57]. The solid-state chemistry by Garner [28] includes only one chapter devoted to organic thermal decomposition. Rastogi et al. [8] calculated the values of different thermodynamic parameters in their studies on a number of organic solid-solid reactions.

Many natural processes take place within, or on the surfaces of crystals. To understand these processes, the most fruitful approach is to study reactions in or on crystalline solids. Such reactions also hold considerable promise for the synthetic chemists since many of them are highly selective, giving very pure products which may not be available from solution processes. With the rise of structural crystallography and solid-state physics, the science of solid-state organic chemistry, and particularly the area of lattice-control over reaction pathways, seems to have entered a burgeoning period [58-60]. With deeper understanding of packing effects and of topochemistry, solid-state organic chemistry could be planned and
exploited. The combination of organic solid-state chemistry and X-ray crystallography has proved to be invaluable for structure-reactivity correlation studies. Interest in conducting polymers as a new class of electronic materials has generated entirely new scientific concepts as well as the potential for new technology [61-66]. Schmidt and co-workers [67] reviewed a variety of experimental observations in terms of the topochemical postulate, which states that the reactions in crystals proceed with a minimum of atomic and molecular movements, and are thus determined by the structures of the starting materials.

The crystallization process, from solution or melt, may be associated with a change in molecular conformation and may be considered as a rudimentary form of chemical reaction. This is more convincing where different isomers are involved [68-70]. Many organic compounds are polymorphic. Thus, if these molecules are of different geometries, the solid-solid phase transformation, or recrystallization, is also a chemical reaction [71-72].

Conformational effects have also been studied [73-75] with a clear participation of packing influence. Bernstein and Schmidt [76] concluded that, in an appropriately dichloro-substituted anil, intramolecular interaction would be greatest when the molecule is planar. Indeed, it was found that in one of the two crystalline
modifications of 4,4-dichloroanil the molecules are planar [76] and that the UV-absorption spectrum of this crystalline material is very similar to those of stilbene and azobenzene [77]. However, dichloro-substitution is not sufficient to ensure planarity, even when the molecules do arrange themselves in closed-packed stacks with marked overlapping [75]. The distinction in conformation within the family of anils has not yet been utilized chemically.

An example in which a particular configuration is essential for reaction, but in which other effects are clearly operative, has been described by Heggie and Sutherland [78]. Compound (a) in the solid yields the products (b) and (c), but the reaction does not occur in solution. This is interesting to note that the reaction is slowed down when the solid is covered with ether. It was suggested that the reaction in the solid involves some species which is soluble in ether.
Several interesting thermal reactions involving extensive molecular rearrangements have been studied by the school of Curtin and Paul where they have obtained information on the loci of the reactions by microphotography of reacting single crystal [79, 80]. As an example, we take the air oxidation of several steroidal 11-β-ols to 11-ones in the solid [81, 82]. The reaction, which has synthetic potential, is highly sensitive to the nature of R, implying control by the crystal lattice since the oxidation in solution shows no such sensitivity. In some cases, the molecular packing rather than molecular conformation dominates the chemistry. This is most striking when a substance crystallizes in several different modifications all containing molecules of essentially the same conformation yet undergoing different reactions [67].

The impetus on investigation of solid-state polymerization was provided by the initial expectation that this reaction would be lattice-controlled and would therefore result in highly stereoregular polymer. However,
this expectation proved to be unfounded with vinyl monomers [83]. A number of literature references [84-86] on photopolymerization in the crystalline state, during last decade, show a tremendous progress that has been made in this area. The reactions [87-90] of organic solids with gases have been a subject of renewed interest. The reactions of gases such as \( \text{O}_2 \), \( \text{NO} \) and \( \text{SO}_2 \) with \( \gamma \)-irradiated solid aliphatic carboxylic acids and amides have been under investigation and may have important implications for such biological problems as diffusion in membranes [91]. Reactions of organic solids with liquids have also been studied [92-95] but are relatively few.

Organic solid-solid reaction has unique features. Self-diffusion in organic crystals is generally very slow [96] since organic molecules tend to be bulky and irregularly shaped. In such cases, the reaction occurs by diffusion either at the surface or through the vapour. The rate of reaction, therefore, might then be influenced by the crystal structures of one or both. The reaction of solid picric acid with a number of solid hydrocarbons and naphthols, which apparently proceeds in part via the vapour phase and in part by surface diffusion, leading to the formation of charge transfer complexes, has been studied by Rastogi and co-workers [97]. Ghera and Shoua [98] used the reaction between solid zinc acetate and solid N-acetyl-\( \beta- \)
hydroxy-amines to produce $\Delta^2$-oxazolines. The reaction appears to proceed via a complex in which the zinc is coordinated to the amide carbonyl, and configuration is retained.

Solid-state decomposition includes the subject of explosives and has been reviewed by Dunstan [99]. Interest in explosives has led to intensive studies of the kinetics of decomposition of solid azides and of a wide variety of other salts and oxides, some of them containing organic functions [100]. McBride has studied decomposition reactions of various azo-compounds [101,102] and peroxide [103] and has obtained considerable information on the atomic movement during the process.

The phenomenon of topoaxy is of growing interest to the organic solid-state chemists. Gougoutas [104] has reviewed some fascinating studies that have been done in this field. The quest for organic reactions of high specificity and stereoselectivity has led chemists to explore a variety of reaction conditions, some of which have the clear aim of imitating the reactions of the nature [105].
As the chemical combination in solids is possible only at the phase boundary between adjacent phases, the solid-state reactions are independent of the number of reactants and are considered as reactions between two components only. The formation of the ternary compounds $2\text{CaO}.\text{Al}_2\text{O}_3.\text{SiO}_2$ and $\text{CaO}.\text{Al}_2\text{O}_3.2\text{SiO}_2$ from quartz, alumina and calcium oxide is a clearcut illustration of such consideration. It was found [106] that two of the three components combine in the first step and then the third component reacts with this combination in the second step. That is why the classification of solid-state reactions is done on the basis of the reaction between two components.

The simplest and most common is the additive type reaction, where the reactants may be elements or compounds. If the product is not miscible with the reactants, it appears as a separate new phase between the reactants. If it is partially or totally miscible with either of the reactants, it is generated as one or two new phases with the original phases. If the reactants form products of different compositions then several phases may be present between the reactants.

Tarnishing of metals, in which a salt (oxide, halide, sulphide etc.) is formed by reaction with a non-metal, is an example of reaction between elements. A
coherent diffusion layer may be formed in all instances in which the equivalent volume of salt is greater than that of the metal [107]. Tarnishing reactions that are structure-insensitive are outstanding illustrations of the fundamental mechanism of reactions of solids.

Reactions between elements and compounds [108] constitute a comparatively small group of combinations like the following.

\[
\begin{align*}
\text{Mn} + \text{Mn}_3\text{O}_4 & \rightarrow 4\text{MnO} \\
\text{Fe} + 2\text{FePO}_4 & \rightarrow \text{Fe}_3(\text{PO}_4)_2
\end{align*}
\]

Addition reactions between compounds mostly consist of binary compounds, with some exceptions, for example, the formation of magnesium ortho-silicate from the meta-silicate and magnesium oxide [109,110]. The technically important spinel forming reactions belong to this class and may be considered to be made up of the following two steps:

\[
\begin{align*}
\text{A}_2\text{O}_3 + \text{B}_2\text{O}_3 & \rightarrow \text{A}[\text{B}_2]\text{O}_4 \quad \text{normal spinel} \\
\text{A}_2\text{O}_3 + \text{B}_2\text{O}_3 & \rightarrow \text{B}[\text{A}\text{B}]\text{O}_4 \quad \text{inverse spinel}
\end{align*}
\]

where \( A = \text{Mg, Ca, Ni, Cu, Co, Zn, Pb, Cd, Ba, Sr} \)

\( B = \text{Fe, Al, Si, Sn, Mn, Ti, Cr, Mo, W, B, V, Ge, Ga, PbSi, Pb}_2\text{SiO, Tl}_2\text{CrO}. \)

No general rules have been found for additive reactions except that the reaction temperatures often approximately coincide with the temperature at which self-diffusion becomes appreciable within one of the reactants [23]. Tammann and Mansuri [111] for the first time proposed
the relation of the temperature of measurable self-diffusion to the absolute melting temperature. The ratio between two temperatures is nearly 0.3 for metals, 0.5 for inorganic substances and 0.9 for organic compounds.

The second mode of reaction between two solids is by exchange of constituents. Following are the typical examples of such reactions studied [7,23,112,113].

\[
\begin{align*}
\text{Mg} + \text{ZnS} & \quad \longrightarrow \quad \text{MgS} + \text{Zn} \\
\text{CaO} + \text{PbCl}_2 & \quad \longrightarrow \quad \text{CaCl}_2 + \text{PbO} \\
\text{Hg}_2\text{Cl}_2 + \text{I}_2 & \quad \longrightarrow \quad \text{HgCl}_2 + \text{Hgl}_2 \\
\text{PbS} + \text{CdSO}_4 & \quad \longrightarrow \quad \text{PbSO}_4 + \text{CdS}
\end{align*}
\]

An extensive investigation of the exchange reactions between alkali halides [114] exhibited that in instances in which the lack of miscibility precluded establishment of equilibrium; large cations combined with large anions and small cations with small anions — for instance, sodium bromide and potassium chloride react to form sodium chloride and potassium bromide — whereas no reverse reaction takes place. This indicates that reactions in systems without miscibility have to proceed exothermally.

Exchange reactions of the type \( \text{ABX} + \text{CB} \quad \longrightarrow \quad \text{CBX} + \text{AB} \) comprise a large group of reactions which have been explored by Hedvall [115-118]. Some reactions, which at first glance appear to proceed as additive reactions, are
actually the exchange reactions, for example, the formation of cobaltite from Co$_3$O$_4$ and ZnO [119] or of ferrites from Fe$_3$O$_4$ and MgO, CoO, NiO, MnO [120] takes place as below.

\[
\text{ZnO} + \text{CoO} \rightarrow \text{ZnO} + \text{Co} \text{O}_3 + \text{CoO}, \text{ etc.}
\]

Solid-state decomposition reactions giving gaseous products have been widely studied [121-123]. Solid-state transformations leading to all solid products are rare. High pressure decomposition of titanate spinels, $M_2TiO_4$ to $MTiO_3$ with ilmenite structure has been reported at various temperatures [124].

\[
M_2TiO_4 \rightarrow MTiO_3 + MO
\]

where $M = Mg^{+2}$, $Fe^{+2}$ and $Co^{+2}$

It has been suggested that decomposition of silicate spinels may occur in a similar manner in the lower mantle of the earth. Such reactions are, therefore, of considerable geo-chemical interest.

**ROLE OF DEFECTS IN SOLID-STATE REACTIONS:**

The reactivity of solids is due to the presence of defect in structure. Thus the qualitative description of defects in crystalline solids is necessary for understanding the reactivity of solids. The simplest case of defects, i.e., the mistakes at isolated or fairly isolated atomic sites, are termed point defects as they generally involve
the absence of single atoms at discrete points within the normal lattice of solids. A suitable classification for qualitative description of crystalline defects can be achieved by first considering the so-called point defects and then proceeding to higher dimensional defects. The point defects are essentially responsible in controlling the rate at which solids react. An understanding of point defect behaviour is, therefore, fundamental to the understanding of a wide variety of solid-state reactions. These defects also play their role in controlling the physical properties of many materials, particularly the electronic properties of semiconductors and the colours of insulators. Point defects are of atomic nature whose effect is limited only to their immediate surroundings. Examples are vacancies in the regular lattice or interstitial atoms. Dislocations are classified as linear or one-dimensional defects. Grain boundaries, phase boundaries, stacking faults and surfaces are two-dimensional defects. Finally, pore and macroscopic inclusions are three-dimensional crystal defects. The role of lattice defects in solid-state reactions is important because diffusion processes in solids are controlled by the concentration and mobility of such defects. The simple lattice defects, vacancies and interstitial atoms, take part in a variety of processes leading to phase changes, precipitation, order-disorder transformation and chemical reaction in solids.
It is also possible for one or more lattice defects to associate with one another, that is, to cluster together. This type of defect is termed as an associated defect. An associated defect would represent a Schottky defect if the two vacancies of both a cation and an anion were associated as vacancy pair. In addition to these imperfections, there may be the charged defect also in which some fractions of electrons will be free to move through the crystal. Although the electrons are the only charged particles that exist in the structure, it often simplifies the matters to think about the sites where electrons are missing. This type of 'electron vacancies' is called an electron hole or simply a hole. However, very few efforts have been made to correlate such effects to specific problems of phase transition and chemical reactions in solid-state [125]. Besides the electrons and holes, the atomic defects can also carry a charge. In ionic crystal, this may be considered to be the normal state of affairs. In real crystals the atoms are vibrating, and that they will move towards or away from a vacancy if one is created, depending upon the bonding in the crystal under consideration. This process is called relaxation. If the reactions between point defects in order to maintain the internal equilibria are homogeneous, it can be shown that their relaxation times are small compared to the time of the solid-state reaction [126]. The relaxation time, in all the
other cases where the relaxation of internal equilibria
depends on the density of the sources and sinks of point
defects, may be calculated with the help of suitable models
\[127,128\] or measured independently \[126,129\].

Diffusion occurs through lattice defects because
the direct interchange of atoms is not favoured for energy
reasons, particularly, in case of close-packed structures.
Successive interchange of lattice atoms with an interstitial
atom may also cause diffusion. But, the interstitial can not
be produced in a significant quantity by thermal means as
the energy of formation of the same is quite high.
Generally, the diffusion occurs by vacancy mechanism because
the energy of formation and of migration of a lattice
vacancy is not high. The vacancy mechanism is far more
prevalent than others. An excess concentration of vacancy in
metal can be produced in several ways, such as quenching,
plastic deformation and irradiation \[130\]. At a temperature
where vacancies are mobile, the excess vacancies must tend
to anneal out of the sample. During their migration the
excess vacancies cause atomic interchange and therefore may
influence many diffusion controlled solid-state processes
\[131,132\].

Dislocations are linear or one-dimensional defects
and are mainly responsible for the plastic behaviour of
solids. The idea of dislocation was developed by Taylor
Two characteristics of dislocations are specifically important in solid-state reactions, namely, (a) they can serve as a site of repeatable growth within a crystal and, (b) they can act as fast diffusion paths. Dislocations also act as preferential nucleation sites for the formation of new phases.

Interfaces are two-dimensional defects and play an important role in solid-state reactions. During heterogeneous reaction, mass transport occurs across interfaces. As sites of repeatable growth, interfaces can permit equilibrium between point defects to be attained. In sintering process they serve as vacancy sinks and as paths of rapid transport. The interfaces which occur most frequently in crystals are outer surfaces, phase boundaries and grain boundaries.

The concept of non-stoichiometric compound is important and is defined as one which can take any composition between the approximate limits. A typical example is given by vanadium monoxide, which can take any composition between the approximate limits of VO$_{0.8}$ to VO$_{1.27}$, and does not exist at the precise composition VO$_{1.0}$. This example reveals two characteristics of such compounds; firstly, they invariably have irrational formulae, and secondly, they are found to possess appreciable composition range. Defects in solids are able to alter its composition,
and a phase with homogeneity range can be defined in the broadest sense as a solid solution where one or more kind of atoms are gained or lost [135]. The extent to which a binary compound can exist as a unique phase can be measured by a variety of physical and chemical techniques and many classes of inorganic compounds are reported to have wide composition limits reflecting high concentration of random defects. To quote an example, the high temperature form of Nb$_2$O$_5$ has a complex X-ray powder diagram and preparation in the region NbO$_{2.5}$-NbO$_2$ [136] could, therefore, be described as a non-stoichiometric compound with a wide homogeneity range. This could have been caused either by the presence of additional niobium atoms interstitially, which could increase the density or by vacancies, following the removal of oxygen atoms, which would decrease it.

Recent studies on the conductivities of rare gas solids and many halides (lithium halides, strontium fluoride) have shown that bulk properties of these compounds are associated with point defects [137]. Studies [138] on transition metal oxides suggest that point defects are responsible for diffusion. Danilenko et al. [139] have described the method for calculating the interaction characteristics of impurity atoms with metal grain boundaries.
In high temperature chemical processes, the role of point imperfections tend to predominate over one played by the line imperfections and the process of diffusion is favoured by the migration via point defects. This forms the basis of Wagner’s theory [140] of high temperature oxidation. The theory proved to be very successful in describing the high temperature oxidation of a number of metals [105].

DIFFUSION IN SOLIDS:

Diffusion in solids is largely due to the mobility of point defects. One of the most significant aspects of point defects in solids is the way in which they facilitate the movement of atoms or ions through the structure. The process or thermal activation causes vacancies to migrate by exchanging places with neighbouring atoms or ions. Similarly, interstitial atoms also migrate from one interstitial site to another by thermal activation. The defect mobilities put atoms of a solid in a state of continual migration from site to site throughout the crystal.

Diffusion in solids due to atomic movement through the crystalline lattice has been termed as volume, lattice or bulk diffusion and has been a subject of thorough study. Atoms or ions can diffuse not only through point defects but
along surfaces, grain boundaries, dislocations or other macroscopic defects in the crystals as well. As the regular crystal geometry is disrupted in these regions, atom movement in these cases is often much faster than in volume diffusion.

According to Frenkel and many others, the diffusion mechanism can be classified depending on the type of elementary jumps as follows [141,142]:

1. Rotation mechanism [143] such as exchange mechanism or ring mechanism. This occurs in an idealized crystal structure,

2. Defect mechanism [144-146] such as interstitial mechanism, interstitialcy mechanism, crowdion mechanism, vacancy mechanism etc.,

3. Grain boundary and dislocation mechanism [147-149], and


The mode of the mechanism of diffusion that will be operational in a particular case can be decided on the basis of the following considerations.

1. The mechanism of diffusion which requires the lowest activation energy is preferred. On the
basis of the comparison of the activation energy with the heat of sublimation, it can be predicted as to which one is likely to occur. For activation energy higher than the heat of sublimation, diffusion occurs by defect mechanism. On the other hand, when the activation energy is equal to the heat of sublimation, diffusion via vapour phase is likely. This can be explained as follows. Take the reaction

\[
A (S) + B (S) \longrightarrow AB (S)
\]

If the surface area of grains of reactant B is \( Ao \), the number of molecules of A striking these grains from the vapour \( \frac{dn}{dt} \) would be given by

\[
\frac{dn}{dt} = Ao \frac{P}{\sqrt{2MR}}
\]

where \( P \) refers to pressure; \( R \), the gas constant; \( T \), the temperature; and \( M \), the molecular weight. Now if vapour behaves ideally, it follows that -

\[
\frac{dn}{dt} = Ao \frac{Po e^{-\Delta sH/RT}}{\sqrt{2MR}}
\]

where \( Po \) is a constant and \( \Delta sH \) is the heat of sublimation. For a small temperature range, \( \sqrt{T} \) would not
vary much, and the vapour phase diffusion would approximate the heat of sublimation.

A very low value of activation energy for diffusion would indicate either surface migration or grain boundary diffusion.

2. If the initial rate of reaction is directly proportional to the dissociation pressure of the species, the reaction would occur via the vapour phase. This follows from the equation -

\[
\frac{dn}{dt} = \frac{A_0 \cdot P}{\sqrt{2MRT}}
\]

3. To know whether the reaction is occurring via vapour phase diffusion or by surface migration, the reactants are once placed adjacent to each other and then separated from each other by an air-gap. If the reaction rate is same in two cases, it means that the reaction is occurring via vapour-phase. If there is no reaction in the second case, it signifies that there is no vapour phase diffusion. If the rate decreases with increasing length of the air-gap, then this suggests that diffusion is taking place by surface migration.
4. Inert markers can also be employed [150] in ascertaining whether diffusion occurs by defect mechanism or not in reactions where penetration inside the grain is not possible and are just interface reactions. If the displacement of inert marker is proportional to the square root of diffusion time, then the diffusion occurs by the defect mechanism.

In a solid-state reaction, two solids react to form a product layer which separates them. Thus, a solid-state reaction progresses through three steps in series, namely, self-diffusion of reactant species, its diffusion through the product layer and its diffusion and reaction in the other reactant. This is important to note that counter-diffusion may also be involved in the process [151,152].

The speed at which atoms or ions move through a solid is conveniently expressed in terms of diffusion coefficient. The diffusion coefficient of an atom varies comparatively with the change in external circumstances. The geometry of the crystal structure and temperature affect the movement of the atom through it. Nonetheless, diffusion coefficients also depend upon whether a chemical reaction accompanies the atom movement, the number of defects present, and so on.
Certain metals [153] like $\beta$-zirconium, $\beta$-hafnium, and $\beta$-uranium and $\beta$-plutonium show a deviation from a normal self-diffusion. There has been no satisfactory explanation for this anomalous behaviour. It seems that owing to difficulty in getting these metals pure, the diffusion is enhanced due to the excess intrinsic vacancy concentration associated with impurities such as oxygen, or it may be due to a different mechanism in operation either alone or together with a vacancy mechanism. The involvement of dislocation mechanism is another possibility, because of an unusually high dislocation content that may arise on account of the phase change, necessary in all cases to reach the diffusion temperature, and which may be retained during the diffusion because of the high impurity content. Another important factor is the diffusion of very dilute solutes or impurities in metals [153,154]. The main features of this impurity diffusion are the total obedience to the Arrhenius equation with values of activation energy, $E$, and frequency factor, $A$, that do not differ significantly from the values for solvent diffusion rates justify the assumption of a vacancy mechanism for both. But measurements on impurity diffusion in Aluminium show some deviation from normal behaviour, but this does not warrant to propose another mechanism [155]. Nevertheless, more profound deviations from normal behaviour are noted [154-156] for the diffusion of noble metals and some other transition metals such as Cd,
Co, etc., in solvent as alkali metals and of Ag in PbS [157]. Such behaviour warrants another mechanism and it is believed that this fast impurity diffusivity is due to the solute being dissolved interstitially and its diffusion is by interstitial or interstitialcy mechanism [158,159].

The effect of the activity of one of the components on self-diffusion has been studied in several binary compounds especially oxides [160]. For example, the observation of a cation diffusion coefficient proportional to $\delta$ in an oxide $M_{1-\delta}O$ provides some evidence of a cationic vacancy mechanism. The effect of cation non-stoichiometry and acceptor (Na$^+$, K$^+$) and donor impurities on self-diffusion [161] of Ca and W in CaWO$_4$ was studied and results were found to be related to the vacancy mechanism of diffusion. Similarly cation self-diffusion and impurity diffusion in ferric oxide were studied [162] and diffusion coefficient of Fe was measured as a function of temperature. Various diffusion studies indicate that cation self-diffusion occurs by interstitial mechanism and impurities also diffuse by an interstitial mechanism. In some work this fact has been utilised and evidence for interstitial uranium diffusion in UO$_2$ [163], cation vacancy diffusion in MnO [164] and NiO [165] and anion interstitial diffusion in CaF$_2$ and BaF$_2$ [166] and in UO$_2$ [167] have been explained on the basis of defect theory. Comprehensive evidence of mechanism has not been found for diffusion of both species in a binary
compound. Even in important oxides with rock-salt structure, the diffusion mechanism of oxygen is not clearly understood. It has been proposed that interstitial diffusion of the anion occurs in these materials [168], but studies on pure and doped CoO provide good support for anion-vacancy diffusion [169]. It is also a possibility that diffusion mechanisms change with temperature and direct concentrations.

The separation of impurities from solids can be done by thermal diffusion. The kinetics of impurity separation was done by thermal diffusion [170] taking the life time of the atom on the surface with respect to desorption and the effect of electron wind on the diffusion of the impurity atoms. Fundamental studies of more concentrated solutions have mostly been associated with the phenomenon of chemical diffusion — Kirkendal effects, Darken equations, vacancy wind effects etc..

If a reaction is considered in which the composition of a solid phase changes with time due to the inter-diffusion of two components A and B, then the inter-diffusion coefficient may best be defined in terms of the difference of velocity, $\Delta V$, of the two components or equivalently in terms of the difference in fluxes of A and B; thus [171] —
where \( C_A \) and \( C_B \) are mole fractions, and \( J_A \) and \( J_B \), the fluxes of \( A \) and \( B \); and \( V \), the molar volume. The flux is related to the velocity by \( \dot{V}C = JV \) and depends on the coordinate system so that the diffusion coefficients, \( D_A \) and \( D_B \), may be defined as:

\[
D_A = V \cdot J_A / \Delta C_A \quad \text{and} \quad D_B = V \cdot J_B / \Delta C_B
\]

so that \( D = C_B D_A + C_A D_B \).

If both chemical and tracer diffusions occur by the same mechanism, then it may be shown [172] that:

\[
D_A = D_A^* \left( \frac{\sin a}{\sin c} \right)
\]

where \( D_A^* \) is the tracer diffusion coefficient and 'a' the thermodynamic activity.

The activity in these equations refer to the activity in the crystal undergoing diffusion and may include the effects of stress and electrostatic potential [172].

The general problem of inter-diffusion in multicomponent systems is much more complicated. One can sometimes usefully define an effective binary diffusion coefficient relating to the flux of a species to its concentration gradient [173]. A general discussion of this problem has been done by Kirkaldy [174].
REACTION MECHANISM AND KINETIC MODELS:

Although the solid-state reactions got recognition as early as in the 1800's and in the beginning of 1900's, as evidenced by Faraday [12], Spring [13] and Cobb [175], no significant contribution was made towards understanding the mechanism until after 1910. Some of the earliest quantitative works on the kinetics of solid-phase reactions were done by Hedvall [176], Tammann [177], Wagner [178], Huttig [43] and Jander [179], and others supplemented and developed the Tammann-Hedvall theory.

The kinetic equation representing the reaction $A(S) + B(S) \rightarrow C(S)$, in a mixture of fine powders, is based on the following assumptions:

1. The reaction starts only at the contact points of components A and B;
2. The rate of reaction is proportional to the number of contact points;
3. The number of contact points may depend on the reaction time;
4. The component A is able to diffuse through the layer of the reaction product; and
5. The reaction mixture consists of particles of similar size.
The main features of different models on the basis of rate controlling mechanism in solid-state reactions can be outlined as follows:

(a) Product-layer diffusion control.
(b) Nuclei growth control.
(c) Phase boundary reaction control.

**Product-layer Diffusion Control Model:**

In reactions involving solids, the reactants are not mixed on an atomic or molecular level and must, therefore, diffuse and penetrate into each other if the reaction is to start and propagate within the solid phase, and thus, space coordinates become a controlling factor.

Wagner and Schottky [180] proposed a thermodynamic theory of solids which takes into account imperfections and impurities. They suggested two fundamental processes that are involved in a solid-state reaction.

--- Phase boundary process such as chemical reaction itself, i.e., breaking and reforming of bonds, formation of nuclei and growth of the reaction product.

--- Transport of matter to the reaction zone, i.e., the diffusion through the layer of the reaction product.
Solid-state reactions, therefore, may be treated as a chemical and geometrical reshuffling of the solid phases. In general both the transport and phase boundary processes involve a series of individual steps. In such a sequence, each individual step will have a specific rate constant associated with it. "A virtual maximum rate" may then be defined as the rate that would be found if equilibrium were established for all previous steps. Under these conditions, the reaction with the lowest "virtual maximum rate" controls the overall rate of the reaction. Thus for a solid-state reaction, the rate is controlled either by the combination at the interface or by the transport of the reactants to the reaction zone.

Wagner and Schottky [180] developed a well known parabolic rate law assuming a unidirectional diffusion across the product layer. As the reaction proceeds, the reactants have to diffuse across the product layer for the reaction to sustain itself. The rate or growth of the product layer is given as:

\[
\frac{dy}{dt} = \frac{K}{D}y
\]

where \( y \) is the thickness of the product layer, \( t \) is the reaction time, \( D \) is the diffusion coefficient of the migrating species and \( K \) is the proportionality constant. Assuming the diffusion coefficient to be independent of
time, and the area of contact as constant, we get,

\[ y^2 = 2KDt + C \]

with the boundary condition, \( y = 0 \) at \( t = 0 \), the equation becomes

\[ y^2 = 2KDt = K_Pt \]

This equation is the well known parabolic rate law where \( K_P \) is the parabolic rate constant.

Ceramic processes are mostly accomplished by an intimate mixing of fine powders. Using oversimplifying assumptions, Jander [22] arrived at an expression for the reaction rate of powders, which has been widely used, although its physical basis is unreal. He based his model on the following assumptions:

1. The reaction under consideration can be classified as an additive reaction.

2. Nucleation followed by surface diffusion, occurs at a temperature below that needed for bulk diffusion so that a coherent product layer is present when bulk diffusion does occur.

3. The chemical reaction at the phase boundary is considerably faster than the transport process and thus, the solid-state reaction is bulk diffusion controlled.

4. Bulk diffusion is unidirectional.
5. The product phase is not miscible with any of the reactant phase.

6. The reacting particles are all spheres of uniform radii.

7. The ratio of the volume of the product layer to the volume of material reacted is unity.

8. The increase in thickness of product layer follows the parabolic rate law.

9. The diffusion coefficient of the species being transported is not a function of time.

10. The activity of the reactants remain constant on both sides of the reaction interface.

Jander also made the rather drastic assumption of a constant cross-sectional area and an unchanging volume or density during the progress of a reaction, and developed a well known expression that goes after his name.

\[ k_j t = \left[ 1 - (1 - x)^{1/3} \right]^2 \]

The equation relates the fraction of reaction, \( x \), completed in time \( t \), with the rate constant \( k_j \). The Jander's equation has been applied to many systems \([181-185]\).

Kroger and Ziegler \([186,187]\) indicated that Jander's assumption of a constant diffusion coefficient was not applicable to all solid systems, particularly during the early stage of a reaction. They used most of the Jander's assumption, except that of constant diffusion coefficient,
and instead assumed that the diffusion coefficient and instead assumed that the diffusion coefficient of the transported species was inversely proportional to time. This is equivalent to assuming that the rate of change of product layer thickness is inversely proportional to time which is the basis of Tammann's [23] theory. From this they derived the following equation known as Kroger-Ziegler equation:

\[ k_{K-Z} \ln t = (1 - (1 - x)^{1/3})^2 \]

Zhuravlev, Lesokhin and Tempel'man [186] modified the Jander's equation assuming the activity of the reaction substance to be proportional to the fraction of unreacted material \((1-x)\). Their relationship between fraction of reaction completed and time is:

\[ k_{Z-L-T} t = \left( \frac{1}{(1-x)^{1/3} - 1} \right)^2 \]

Ginstling and Brounshtein [189] arrived at a model using Jander's assumptions with the exception of parabolic rate law. They indicated that parabolic rate asserted that the reaction surface remained constant; however, when they considered spherical particles, this surface area actually decreased as the reaction proceeded. They discarded the parabolic rate law in favour of an equation relating the growth of the product layer to Barrer's growth of the product layer equation [190] for steady state heat transfer.
through a spherical shell. They arrived at the following final form,

\[ k_{G-B} t = \left[ 1 - \frac{2}{3} x - (1-x)^{2/3} \right] \]

Carter [191,192] further improved the Ginstling-Brounshtein model by accounting for the differences in the volume of the product layer with respect to that of the volume of the reactants. He also introduced a new term, \( Z \), to account for the change in volume, and obtained the equation,

\[ k_{C-V} t = \frac{Z - (Z-1)(1-x)^{2/3} - [1 + (Z-1)x]^{2/3}}{(Z-1)} \]

Valensi [193] developed the same solid-state reaction model mathematically from a different starting point. Hence, this equation is referred to as Carter-Valensi equation. Geiss [194] has shown that Carter-Valensi equation becomes significant only when the ratio of volume of product formed to volume of reactants consumed exceeds a value of two.

Dunwald and Wagner [195] derived an equation for solid-state reaction analysis using a solution to Fick's second law of diffusion into or out of sphere. Serin and Ellickson [196] expressed the Dunwald-Wagner equation in
terms of fractional completion of the process.

\[ k_{D-W} t = \frac{\pi^2 D t}{r^2} = \ln \left( \frac{6}{\pi(1-x)} \right) \]

All models, discussed above, have their limitations in a way that they are all based on the reaction of spherical particles of uniform radius; still, they have been shown to represent many solid-state reactions in a satisfactory way [197]. There have been attempts to introduce particle size gradation into a workable model. But, these have resulted in models that involve complicated mathematics and contain parameters that are difficult to measure.

Several empirical and semiempirical rate laws such as the following have been proposed to describe the course of different diffusion controlled solid-state reactions.

i) \[ Y^2 = kt \]

ii) \[ Y^3 = kt \]

iii) \[ Y^2 + Yb = kt \]

iv) \[ Y = kt \]

v) \[ Y = k \log t \]

vi) \[ Y^2 = 2kt \exp[-Py] \]

Generalized equations \( y = kt^n \) and \( y^n = kt \) have also been used by Rastogi [198] and Beg [199] respectively. In these equations, \( y \) is the thickness of the product layer,
t is the time and k, b, n and P are constants.

Nuclei Growth Control Model:

The models of the solid-state reactions for powdered compacts that have been discussed so far are based on the assumption that initially surface diffusion rapidly coats the surface of the reacting particles with a continuous product layer. The subsequent rate of reaction is taken to be the rate of diffusional growth of the product layer. However, there is another way of looking at the initial product formation and subsequent growth. This approach considers the nucleation of products at active sites and the rate at which the nucleated particles grow. Welch (2001) suggests that such a mechanism is possible when the product phase is partially miscible in one or the reactants.

Many mathematical models (201-208) have been advanced relating nucleation and nuclei growth rates to the kinetics of phase transformation and decomposition. The general form of the expression for conversion time relationship is represented as:

\[ \ln (1 - X) = -(kt)^m \]

where \( m \) accounts for the reaction mechanism — number of nuclei present, composition of parent and product phases,
and geometry of the nuclei. If a reaction is represented by this model, a plot of In [ln 1/(1-x)] versus In t gives a straight line with slope \( m \) and intercept \( m \ln k \).

Applications of nuclei growth model to solid-state reactions are few. Huibert and Klawitter [209] applied it to the reaction between ZnO and BaCO₃.

Phase Boundary Reaction Control Model:

When the diffusion of the reactant species through the product layer is fast compared to the reaction, the solid-state reaction is said to be phase boundary controlled. According to Laidler [210], when a discontinuous product phase occurs, the rate determining step may be the chemical process occurring at the phase boundary.

Different models have been developed for different geometries and corresponding boundary conditions. For a sphere reacting from the surface inwards, the fractional reaction completed, \( x \), and time, \( t \), are related by —

\[
kt = \left[ 1 - (1 - x)^{1/3} \right]
\]

which is identical to the expression derived for gas-solid reaction by Levenspiel [211]. For a circular disk reacting from the edge inwards, or for a cylinder, the reaction is —

\[
kt = \left[ 1 - (1 - x)^{1/2} \right].
\]
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