Chapter - 2

THEORETICAL ASPECTS
2.1 GLASS FORMATION

Glass has been defined in many ways, but two features which are commonly mentioned are

(a) a glass is formed from a highly viscous super-cooled liquid and

(b) the liquid forming glasses, possesses a structural network of short range order, glasses are thus essentially amorphous solids having two characteristic structural features

(a) Short range order

(b) A continuous framework of strong primary bonds

Glass or vitreous solids show continuous change in first order thermodynamic properties such as entropy (S), Volume (V), Heat content (H) and crystallization at any temperature but these become solids through a progressive increase in its viscosity showing discontinuous changes in second order thermodynamic properties, such as specific heat capacity. So vitreous state is continuous with the liquid state and glasses have a structure similar to liquid from which they are formed. The difference between the glass and the corresponding liquid or supercooled liquid may be conventionally demonstrated by a Volume-temperature
relationship of the type shown in figure 2.1. Upon cooling a liquid to below its melting point it will either crystallize or form a glass. If liquid is allowed to crystallize, normally there is a discontinuous change in volume at the freezing point, $T_f$ and the path 'a' is followed. It is not difficult, however, to inhibit crystallization by cooling quickly enough and therefore to supercool liquid below its normal freezing point. On further cooling the supercooled liquid until, in the region of $T_g$, where the viscosity of the liquid has reached about $10^{14}$ poise, the $V$-$T$ slope gradually changes to become approximately parallel to the corresponding line for the crystal and noncrystalline material is said to be in the glassy or vitreous state.

Since the glasses are systems of higher complexity, they require for their characterization a large number of parameters than their crystalline counterparts. The unusual characteristics of glass namely, its chemical stability, inherent transparency, hardness and brittleness and its poor conductivity to heat and electricity are the consequences of its composition, the existence of strong covalent bonds between the atoms and the lack of crystal structure.

Multicomponent alloy glasses which are slowly cooled from their melt, probably approach the ideal state more closely. However, a new difficulty may arise, namely a microheterogeneity caused by the separation of noncrystalline microphases. This is well known phenomenon in
Fig. 2.1 Volume - temperature relationship for glass-forming system.
oxide glasses. The size of micro-phase regions depends upon the thermal history of the glass and constituents additional parameters which may influence the electronic properties of noncrystalline solids. To discuss the kinetics of the phase transitions during the glass formation, it is worth discussing the energetic of transitions of the three states of the matter.

Since molecules in the vapour phase have on the average more potential energy than those of the liquid phase, the process of evaporation must be accompanied by an absorption of energy and conversely, condensation by an evolution of energy. The change in energy (enthalpy change) when a definite quantity of liquid is vaporized, is called the heat of vaporization, $\Delta H_v$. The free energy change $\Delta G_v$ for the process at temperature $T$ is given by

$$\Delta G_v = \Delta H_v - T\Delta S_v \quad \text{(2.1)}$$

Since the vaporization increases the disorder of the system the entropy change, $\Delta S_v$ is positive. The free energy change being zero at equilibrium, the enthalpy change is given by

$$\Delta H_v = T\Delta S_v \quad \text{(2.2)}$$

and the entropy change due to evaporation is

$$\Delta S_v = \frac{\Delta H_v}{T} \quad \text{(2.3)}$$
Similarly, melting or fusion takes place when the free energy change, $\Delta G_f$ of the process is zero.

$$\Delta G_f = \Delta H_f - T_f \Delta S_f = 0 \quad (2.4)$$

Where $T_f$ is the melting temperature which is set by the ratio $\Delta H_f/\Delta S_f$, that is the ratio of the heat of fusion to the change in entropy during fusion. The entropy change is given by

$$\Delta S_f = \frac{H_f}{T_f} \quad (2.5)$$

In case two component A and B are melted together, the free energy of formation of a solution (G) of two component is the function of concentrations only. The molar free energy, $\Delta G_f$, is the free energy change when pure component are melted to the desired compositions, per mole of the final mixture. The change in entropy is predicted as

$$\Delta S_f = - R \left( X_A \ln X_A + X_B \ln X_B \right) \quad (2.6)$$

Where $X_A$ is the molar fraction of component A and $X_B$ is the molar fraction of component B.

The change in enthalpy $\Delta H_f$ is assumed to be equal to the change in energy of mixing $\Delta E_m$. The total
energy of mixture is calculated from bond energies of nearest neighbours. In a mixture with A and B molecules, each with Z nearest neighbours, there are on the average Z $X_A$ molecule of A and $X_B$ molecule of B around any given molecule in the mixture. If energy of A-A bond is $-E_A$, B-B bond is $-E_B$ and A-B bond is $-E_{AB}$, where the E's are positive quantities then the total energy change $\Delta E_m$ per unit volume of the mixture is

$$\Delta E_m = -ZC X_A X_B \left[ E_{AB} - \left( \frac{E_A + E_B}{2} \right) \right] \quad (2.7)$$

Where $C$ is the total concentration of the molecule in the mixture. If the energy of A-B bond is greater (more negative) than the energy of A-A and B-B bonds, than $E_{AB} > (E_A + E_B)/2$, and $E_m$ is negative at all composition. Under these conditions the two components are completely miscible at the temperature where the equations apply. If, however, $E_{AB} < (E_A + E_B)/2$, then there is a tendency for components to segregate and below a certain temperature the mixture separates into two different phases.

The transition from liquid to a glassy solid is accompanied by the abrupt changes in such properties as coefficient of thermal expansion specific heat, specific volume enthalpy and compressibility at an experimental temperature in a glass transition temperature, $T_g$. At such high viscosity, molecular motions are retarded and relaxation times become comparable to (or greater than)
the time generally taken for experimental measurement, thus giving rise to the discontinuity shown in figure 2.1 (55). Thermodynamically, it can be explained as follows. The temperature dependence of volume is related to the entropy $S$ under equilibrium conditions by the standard relations

$$-\left(\frac{\delta V}{\delta T}\right)_P = \left(\frac{\delta S}{\delta P}\right)_T$$

(2.8)

where $P$ is the pressure and $T$ is the temperature. Changing the entropy to the configuration entropy $S_c$ plus entropy from other causes, $S_v$ equation (2.8) may be written as

$$-\left(\frac{\delta V}{\delta T}\right)_P = \left(\frac{\delta S_v}{\delta P}\right)_T + \left(\frac{\delta S_c}{\delta P}\right)_T$$

(2.9)

The equation is obeyed at temperature above the melting point $T_f$ (figure 2.1) where the liquid is thermodynamically stable. In the glass forming materials, the equation (2.9) still continues to be obeyed below $T_f$ since the liquid exists as a metastable (supercooled) phase and exhibits the usual equilibrium properties. However, at temperature near or below $T_g$ where the structure becomes effectively frozen ($\delta S_c/\delta P)_T$ in equation (2.9) becomes negligibly small, consequently with only $S_v$ continuing to change, the slope of volume versus temperature curve decreases. The rotation and translation of the atoms or molecule which are characteristics of liquid state, cease at $T_g$ and only thermal vibrations exist. The contraction cooling below $T_g$ is therefore the result of only
smaller thermal vibrations the glass transition temperature determined by the rate of cooling of the melt also depends upon the thermal history of the materials. Similarly when a glass is reheated, the rate of heating will determine the glass transition temperature. The glass transition temperature is increased by higher cooling rate and reduced by a lower cooling rate (fig 2.2).

2.2 CHEMICAL ORDERING IN CHALCOGENIDE GLASSES

The atom scale structure of glasses is approached by presenting a method for systematically describing the development of the local order in a binary system $A_{1-x}B_x$ ($A = Ge, As; B = S, Se$) where $A$ and $B$ are atomic species from columns a and b of the periodic table (56).

The network structure of an amorphous solid can be specified in three stages:

(i) Atomic co-ordination

(ii) The distribution of bonds between the atoms and

(iii) The molecular structure of the network forming groups.

It is assumed that all bonds within the network are satisfied. In bulk quenched glasses, the co-ordination at each atom satisfied the normal chemical valence given by 8-N rule; 4 for Ge, 3 for As and 2 for S or Se. There are distinctly two ways to specify distribution of bond types in a covalent network. The first is purely statistical and is
known as "Random Covalent Network Model (RCNM). The distribution is completely determined by the two atomic co-

ordination \( Y_a \) and \( Y_b \), and the concentration. When the alloy composition is normalized to one atom, the number of bonds of a particular type, \( N_{ij} \) is given by

\[
N_{AA} = y^2 (1-x)^2 / 4N_t \\
N_{BB} = y^2 x^2 / 4N_t \\
N_{AB} = Y_a Y_b x(1-x) / 2 N_t \tag{2.10}
\]

Where the total number of bonds \( N_t \) is simply one half of the total coordination,

\[
N_t = [ Y_a (1-x) + Y_b x ] / 2 \tag{2.11}
\]

The RCNM includes A-A, A-B, B-B bonds for all compositions other than \( X=0 \) and \( X=1 \). This distribution, therefore, neglects all factors, specially relative bond energies which could promote a non-statistical distribution. The second model for the bond distribution, the chemically ordered network model (CONM) or the chain crossing model (CCM) emphasis just these relative bonds energies and thereby favours heteropolar A-B bond at all concentrations. This model included a compound composition,

\[
X_c = Y_a / (Y_a + Y_b )
\]

in which there are only A-B bonds. The compositions range given by \( 1 > x > x_c \) is called the B-rich alloy regime and contains only A-B and B-B bonds where the range \( x_c > x > 0 \)
Fig. 2.2 The effect of rate of cooling on glass transition temperature (T_g), curve 1, rapid cooling; curve 2, medium rate; curve 3, slow rate.
is called A-rich and has only A-B and A-A bonds. The total number of bonds at any composition is still given by equation (2.11), but now the bond distribution must be specified separately for the alloy regimes defined above, and for the compound composition $X_c$

\begin{align*}
N_{AA} &= 0 \quad N_{AB} = Y_a(1 - x) \quad \text{where} \quad 1 \geq x > x_c \\
N_{BB} &= (Y_a - Y_b)x - Y_a \quad / 2 \\
N_{AA} &= 0 \quad N_{BB} = 0 \quad x = x_c \\
N_{AB} &= (Y_aY_b) / (Y_a + Y_b) \\
N_{AA} &= [Y_a - (Y_a - Y_b)x] / 2 \\
N_{AB} &= Y_bx, \quad N_{BB} = 0 \quad xc > x \geq 0
\end{align*}

Figure 2.3 and 2.4 illustrates the bond distribution for two important classes of alloy systems, $Y_a = 3$, $Y_b = 2$, and $Y_a = 4$, $Y_b = 2$. Here in present study we are concerned with chemically ordered compounds in Se - Te and there alloys with Ga.

(2.3) ELECTRONIC STRUCTURE AND CHARGED DEFECT STATES MODEL

The key to our understanding of the electronic properties of materials is a knowledge of their electronic bond structure. In the case of crystalline semiconductors, sophisticated theoretical models are available for their band structure. This theoretical understanding of crystalline substance is possible because the periodic
Fig. 2.3 Bond counting statistics for the three-two coordinated alloy $A_{1-x}B_x$. The solid lines are derived from the random covalent network model and dashed lines from the chemically ordered network model.
Fig. 2.4 Bond counting statistics for the four-two coordinated alloy $A_{1-x}B_x$. The solid lines are derived from the random covalent network model and dashed lines from the chemically ordered network model.
crystalline symmetry simplifies mathematical problems involved in solving the quantum mechanical wave equations. In amorphous semiconductors, theories of bond structure are crude and qualitative because long-range periodicity is absent. As first pointed out by IOFFE (2) the basic electronic properties of a semiconductor are determined primarily by the character of nearest neighbours rather than long-range order so long as short range order exists, as it does in amorphous semiconductors, the main features of the electronic bond structure are retained. There will be allowed energy bands having non-localized states. The allowed bands will be separated by regions of energy in which localized electronic states exist.

The detailed nature of the electronic structure of any particular solid depends on the compositions, but the general feature of the density of states are determined primarily by the predominant form of bonding. For example, tetrahedrally bonded solids, such as silicon, are characterized by bonding the antibonding bands near the Fermi energy. Sketches or the resulting electronic density of states for both crystalline and amorphous tetrahedral solids are given in figure 2.5. The major difference between the two forms is the possible existence of tails of localized states in the bands of the latter (11,57).

On the other hand, if the material contains a large percentage of chalcogen of (i.e. group VI) atoms, the
a) Sketch of the electronic density of states of a perfect crystalline tetrahedrally bonded solids. \( E_V \) and \( E_C \) are the valance and conduction band edges, respectively, and \( E_F \) is the Fermi energy. \( E_{opt} \) is the approximate value of the optical band gap, while \( E_A \) represents the activation energy for free electron conduction.

b) Sketch of the electronic density of states of an ideal amorphous tetrahedrally bonded solids. \( E_V \) and \( E_C \) are the valance and conduction mobility edges, respectively, the other notations are same as in a).
Antibonding bond
E_e
EA

Bonding band
EV

Density of states/(cm\(^{-3}\)eV\(^{-1}\)) (a)

Energy

Density of states/(cm\(^{-3}\)eV\(^{-1}\)) (b)
presence of high-energy lone pair electrons leads to quantitatively different electronic densities of states, as shown in figure 2.6. The valance band is now non-bonding, and does not contribute significantly to the cohesive energy of the solid (58).

Problem of the origin and distribution of density of the localized states in the forbidden energy gap is not so simple as shown in Fig 2.5 and 2.6. Intuitively one would expect the density and extent of the tails of localized states to depend upon the degree of disorder and hence randomness of the potential. The concept of disorder cannot be quantized easily because the degree of disorder may vary according to the method of preparation of a given material and its intrinsic properties or even from region to region within the same sample. At present, it is not possible to relate the electronic band structure to the degree of disorder in any precise but general way. The problem of understanding the origin and behaviour of the tails of localized states in amorphous materials is the most important and challenging task for physisists. Few models, e.g. DAVIS AND MOTT (59), MARSHAL AND OWEN (60) and STREET AND MOTT (61) can be used to determine the density of localized states in amorphous semiconductors.

A charged defect states model proposed by STREET AND MOTT (61) is described here in detail to account for the origin and distribution of localized states in chalcogenide amorphous semiconductors. This model is based on the idea
Fig 2.6

a) Sketch of the electronic density of states of a perfect crystalline chalcogen solid. The Notations is same as in Fig 2.5(a), except that it is assumed that free hole rather than free-electron conduction Predominates.

b) Sketch of the electronic density of states of an ideal amorphous chalcogen solid. The Notations is same as in Fig 2.5(b), except for the assumptions that free hole rather than free-electron conduction Predominates.
of presence of dangling bonds in amorphous semiconductors. When a co-ordination of any atom is less than optimal, the missing bonds are referred to as dangling. The energy of an atom with a single dangling bond \( E_b \) is greater than the atom in its ground-state configuration where \( E_b \) is the bond strength which is typically 2-6 eV. These dangling bonds are equivalent to surface state but are qualitatively different in several respects. They each involve an unpaired spin, and thus should contribute to both an EPR signal and a Curie term in the magnetic susceptibility. But in addition they produce a very different electronic density of states as is sketched in figure 2.7. The occupied states are non bonding and so are higher in the gap. Since the dangling bond states are quite localized, the unoccupied states are still higher in energy, on the average by the correlation energy \( V \). Street and Mott (61) proposed that a neutral defect which they called a dangling bond would be unstable towards a transformation into a negatively and positively charged pairs. Kastner et al. (63) considered the chemical nature of these defects quantitatively and showed that the lowest energy neutral defect in chalcogenide glasses is a three-fold co-ordination chalcogen atoms which they called \( \Gamma^0 \).

Also following the idea of Anderson (64) lattice distortions of surrounding is assumed to be sufficiently strong that the reaction:

\[
2\Gamma^0 \rightarrow \Gamma^+ + \Gamma^-
\]  

(2.14)
Fig. 2.7 Sketch of the electronic density of states of as deposited evaporated amorphous silicon. The notation is same as in Fig. 2.5 (b). The fermi energy is pinned by the large dangling bond density ($10^{19}$ cm$^{-1}$).
Where $D^+$ represent a positively charged three fold co-ordinated chalcogen atom and $D^-$ represent negatively charged, singly co-ordinated chalcogen atom, is indeed exothermic KASTENER ET AL (63) called such a $(D^+, D^-)$ pair a valance alternation pair (VAP). The reaction (2.14) can take place because spontaneous bond breathing can effectively convert a $D^+$ centre into a $D^-$ centre. Due to this ease or reverse reaction the presence of VAPS ordinarily pins the Fermi-level (65). All defect centre's are therefore, either positively or negatively charged and $D^0$ only occurs by excitation since it takes low energy to produce defect states $(D^+, D^-)$ and as many as $10^{19}$ cm$^{-3}$ such defect states can be present in a typical glass. The resulting band structure as shown in figure 2.8. The distortion is expected because of the strong attraction between $D^+$ and the lone pair electron on a neighbouring atom.

The strong lattice distortion has a profound effect on the energy level of electron at the dangling bonds, yielding properties similar to F-centers or small polarons. Possible transition of an electron between the valance band and $D^+$ are illustrated is a configurational - co-ordinate diagram shown is figure 2.9(a). $E_A$ and $E_C$ are optical excitation and recombination energies and are vertical because of the Frank - condon principle. $E_B$ is the difference between the total energy of the ground and
Fig. 2.8 Sketch of the effective one-electron density of states of a typical chalcogenide glass. The notation is the same as in the Fig. 2.6 (b). The Fermi energy is pinned by the valence-alternation pairs, despite the low density one-electron states at $E_F$. 

\[ \text{Density of states (cm}^{-3} \text{ev}^{-1}) \]
excited states and is the energy of thermal excitation. For simplicity, we assume that the local vibrational frequency is unchanged by the electronic transition and therefore

\[ E_A - E_B = E_B - E_C = W^+ \quad (2.15) \]

where \( W^+ \) is the polaron energy. An equivalent diagram applies to the electron energy levels of the doubly occupied centre. The six important energy levels of the singly and doubly occupied centres are shown in Fig 2.9(b). Levels A, B and C are respectively, \( E_A, E_B \) and \( E_C \) above the valance band and represent the transitions in figure 2.9(a). \( A', B' \) and \( C' \) are the corresponding energies of the doubly occupied centres. \( W^+ \) and \( W^- \) are the respective polarons energies. \( U_C \) is the true corelation energy, the difference between the electron energy of the one electron and the two electron states at identical distortional configurations and \( -V \) is the effective corelation energy when distortion is included. \( E^+ \) and \( E^- \) define the position of the energy levels relative to the band edges.

In chalcogenides, lone pair orbitals form the upper part of the valance band; bonding states are much deeper and antibonding states form the conduction band. A dangling bond interacts primarily with neighbouring lone pairs because bonding electron are located between bonding atoms. \( D^+ \) is strongly attracted to such lone pair, bonding with it by distorting its environment. A large electronic energy is released in this way because the lone pair
a) Configurational - co-ordinate diagram for the singly occupied dangling bond, the lower level represents $D'$ plus the filled valance band. The upper level represents $D'$ with a hole at the top of the valance band.

b) Combined level diagram for singly and doubly occupied dangling bonds, as described in the text. Energy definition of $W_1$, $W_2$ and $U$ are also included.
Fig. 2.9
electrons are transferred into deep bonding states; this in itself argues strongly for local distortions. An extra electron introduced into this \( D^+ \) complex occupies the next highest level, which is the conduction-band-like antibonding orbital. Because of the charge on \( D^+ \), a shallow donor level results. This is represented by level A in Figure 2.9 (b). Thus \( E^+ \) is typical donor binding energy and hence not greater than about 0.1 eV.

In contrast to \( D^+ \), the two electrons on \( D^- \) cannot form a covalent bond with a neighbouring atom but instead occupy a valance-band-like lone pair. An acceptor level is formed because of the charge on \( D^- \) and one finds that \( E^- = E^+ \) using a similar arrangement as for \( D^+ \). The configuration of \( D^* \) lies intermediate between that of \( D^+ \) and \( D^- \) and therefore approximate equality of \( W^+ \) and \( W^- \) is expected. Because of the lattice distortion, it is no longer possible to assign a single energy to a localized states. In particular, the energies of thermal and optical transitions differ by the polaron energy. In this model, the Fermi energy is pinned near the middle of the band gap, at energy \( W_1 + U/2 \) above the valance band. This may be seen by equating the excitation rate of electron from \( D^- \) and \( D^+ \) forming \( 2D^0 \), which is proportional to \( \exp(-U/2 KT) \), with the recombination rate (equation 2.14) which varies as \( n^2 \) where \( n \) is the \( D^0 \) concentration. Thus, from detailed balance.
\[ n = \exp\left(-\frac{U}{2 K T}\right) \]  \hspace{1cm} (2.16)

and \( E_F \) is at energy \( U/2 + W_1 \) above the valence band since \( W_1 \) is the energy required to free a hole from \( D^0 \). The Fermi level is pinned since any additional donor or acceptor states will alter the concentration of \( D^+ \) with respect to \( D^- \), but will not alter \( E_F \) unless their concentration exceeds that of dangling bonds.

2.4 THERMAL ANALYSIS OF NON-ISOTHERMAL CRYSTALLIZATION

Kinetic in Glass Forming Liquids

2.4.1 INTRODUCTION

The last decade has been seen a strong theoretical and experimental interest in the application of non-isothermal experimental analysis techniques to the study of phase transformations. While isothermal experimental analysis techniques are in most cases more definitive, non-isothermal, thermo-analytical techniques have several advantages. The rapidity with which non-isothermal experiments can be performed makes these types of experiments attractive. Non-isothermal experiments can be used to extend the temperature range of measurement beyond that accessible to isothermal experiments. Many phase transformations occur too rapidly to be measured under isothermal conditions because of both transient inherently
associated with the experimental apparatus. Industrial processes often depend on the kinetic behavior of systems undergoing phase transformations under non-isothermal conditions. In this instance a definitive measurement of non-isothermal transformation kinetic is desirable.

The experiments of MEILING and UHLMAN (66) and VERGANO and UHLMANN (67) indicates that the growth rate of crystallites in glass forming liquids is not limited by removal of heat from crystal-liquid interface. The departure in temperature of the interface from that of either bulk phase is negligible. In this light, glass forming liquids may provide unique systems in which to assess the validity of the theoretical models used to describe the process of crystal growth. They provide systems in which temperature of the liquid - crystal interface is well defined by the temperature of the system and therefore, the time evaluation of the crystallization kinetics can meaningfully be measured using thermal analysis techniques.

Thus, it is not surprising that recently differential scanning calorimetry (DSC) and differential thermal analysis (DTA) have been examined as techniques which are applicable to the study of phase transformations involving nucleation and growth, and in particular to the crystallization kinetics of glass forming liquids (68-79). With very few exceptions the analysis of the data obtained has been carried out using the JOHNSON-MEHL AVARAMI transformation rate equation.
2.4.2 JOHNSON - MEHL - AVARMI TRANSFORMATION EQUATIONS

One of the legacies of the classic work done by JOHNSON and MEHL (80) and AVARAMI (81) concerning the kinetics of phase transformation involving nucleation and growth under isothermal conditions in the JOHNSON - MEHL - AVARAMI isothermal equation. This equation is usually written in the following form:

\[ \alpha(t) = 1 - \exp(-k t^n) \]  \hspace{1cm} (2.17)

Here \( \alpha(t) \) is the fraction of transformation completed at time \( t \). \( k \) is a function of temperature and in general depends on both the nucleation and growth rate. \( n \) is a parameter which reflects the nucleation rate and/or the growth morphology. A comprehensive review of the development of this equation can be found in work of CHRISTIAN (84). The isothermal transformation rate, \( d\alpha(t)/dt \) can be easily determined from equation (2.17) by differentiating with respect to time

\[ \frac{d\alpha}{dt} = K n t^{n-1} \exp(-k t^n) \] \hspace{1cm} (2.18)

Because of the explicit relation between \( \alpha \) and \( t \) given by equation 2.17 and 2.18 can be rewritten equivalently as
This equation (2.19) sometimes referred as the JOHNSON-MEHL-AVARAMI transformation rate equation.

2.4.3 APPLICABILITY OF THE JOHNSON-MEHL-AVARAMI TRANSFORMATION RATE EQUATION

The eq. (2.18) and (2.19) as developed by JOHNSON-MEHL-AVARAMI transformation are based on several important assumptions. These assumptions are:

1) Isothermal transformation conditions
2) Spatially random nucleation
3) Growth rate of new phase dependent only on temperature and not time (i.e. linear growth kinetics).

It has been asserted by CHRISTIAN (82) that eq. (2.18) and (2.19) may be used as an approximation for the early stages of diffusion controlled growth transformation process for which assumption (3) may not rigorously hold.

Recently equation (2.19) has been applied without qualification to the analysis of non-isothermal phase transformation (68-75, 77). It has been shown (78) that the JOHNSON-MEHL-AVARAMI transformation rate equation can only be rigorously applied to transformation involving nucleation and growth in a limited number of special cases in a non-isothermal condition. In particular, if it can be
shown that the transformation rate depends only on the state variable of fraction transformed, \( \alpha \) and temperature \( T \), and not on thermal history, non-isothermal as well as isothermal transformation consistent with assumptions (2) and (3) above.

The criteria which are necessary in order to apply eq. (2.19) to the non-isothermal crystallization process in glass forming liquids are thus restrictive. Assumption (3) limits crystallization phenomena whose growth rate is controlled by temperature and is independent of time. An example of such a system is a glass forming liquid which undergoes structurally only a morphological change on crystallization. Assumption (2) further limits the application of (2.19) to systems such as those which demonstrate homogeneous nucleation or heterogeneous nucleation at randomly dispersed second phase particles. Under the restrictions outlined by HENDERSON (78) an example of a system which allows the non-isothermal application of eq (2.19) is one in which the nucleation process takes place early in the transformation and the nucleation rate is zero thereafter. This case has been referred to as site saturation by CAHN (83).

Eq. (2.19) could possibly be used as an approximation for systems in which the above criteria are not obtained. The validity of such approximations would have to be critically examined (78, 82, 83).
2.4.4 APPLICATION OF DSC AND DTA TO THE MEASUREMENT OF CRYSTALLIZATION KINETICS

The application of DSC and DTA to the characterization of phase transformation has been previously examined by several workers (68,74 84to 90). The usual experimentally imposed conditions is that the temperature , \( T \), of the transforming sample is changed at a constant rate , \( r \), with respect to time (i.e. \( dT/dt = r = \text{constant} \)). If sample size is relatively small and good thermal contact is maintained between the sample and the rest of the system , then for sufficiently small values of \( r \), the thermal behaviour of the system can be used to accurately determine the transformation kinetics of the sample.

Figure 2.10 shows a typical DSC or DTA trace associated with a constant scan rate experiment. For DTA the height of the curve at any particular temperature \( T \) is a measure of the difference in temperature , \( T \), between the sample and the reference . For DSC the height of the curve at some particular temperature \( T \) as a measure of the heat evolving from the sample per unit time , \( dH/dt \). For either DTA or DSC under the experimental constraints cited above one can assume that \( dH/dt \propto d\alpha/dt \) (DSC) or \( T \propto d\alpha/dt \) (DTA). This is known as BORCHARD assumptions (86,87). Thus area under the curve from \( t=0 \) to \( t=t_0 \) is proportional to \( \alpha(t_0) \). The constant of proportionality can be determined from the normalization conditions i.e.
Fig. 2.10 Schematic drawing of DSC or DTA trace under constant scan rate conditions for a crystallization process which obeys the Johnson-Mehl-Avrami transformation rate equation.
\[ \int_{0}^{\infty} \left( \frac{d\alpha}{dt} \right) dt = 1 \]  \hspace{1cm} (2.20)

In essence the directly measurable quantities are \( T, \ \frac{d\alpha}{dt}, \ \alpha \) and \( t \).

It must be emphasized that the above justification for the use of thermal analysis technique is predicted on the assumptions that during the crystallization process the temperature of the solid - liquid interface is arbitrarily close to that of either bounding bulk phase and that the sample temperature is homogeneous and can be uniquely determined. This requires that the interface temperature be negligibly affected by the liberation of the latent heat of fusion at the growth interface. UHLMANN et al (66,67) has shown that for the glass forming system of \( \text{Na}_2\text{O} - 2 \text{SiO}_2 \) and \( \text{GeO}_2 \) (67) no increase in the temperature of the growth interfaces could be measured. The quantitative experimental work of BRIGGS (75) on \( \text{CaO-MgO-SiO}_2 \) glasses confirmed that the activation energy for crystal growth as determined by thermal analysis techniques as essentially the same as that determined by direct optical measurement. The recent work of CHEN (77), utilizing DSC techniques successfully compared the activation energy for crystal growth in metallic glasses. Thus there is some credibility to the assertion that DSC and DTA are applicable to the characterization of crystallization kinetics in a variety of glass forming systems.
It should be clearly understood, however, that these techniques are not applicable to glass forming systems in temperature range where the temperature of the melt-crystal interface is affected by the liberation of the latent heat of fusion. LAIRD and BERGEON (91) showed that the glass forming system, PbO - 2 B₂O₃, demonstrated such behaviour in the high growth rate region of temperature PbO - 2B₂O₃ has the latent heat of fusion of 30 K and a maximum growth rate of 2 µm s⁻¹. Under maximum growth rate conditions, the temperature of the interface was determined to be 23°C above that of the bulk phases. MORLEY (92) has also reported heat effects in LiO₂-SiO₂ glass under high growth rate conditions. The maximum growth rate in this instance was approximately 15 µm s⁻¹. Experimentally, such systems present some difficulties. Only the lowest scan rates are appropriate and a high density of initial nuclei is needed, if the material is to fully crystallize before the growth rate becomes too high. Under these conditions, the results should be compared to independent data when possible.

2.4.5 TEMPERATURE DEPENDENCE OF k AND EXPERIMENTAL REQUIREMENTS

There are two cases of interest with respect to the temperature dependence associated with the JOHNSON-MEHL-AVARAMI transformation rate equation. It is expected that in glass forming systems K could demonstrate a simple ARRHENIUS behavior or a VOGEL-FULCHER behavior with
respect to temperature during the crystallization process. Specifically

\[ K = K_0 \exp \left( -\frac{\Delta E}{KT} \right) \]  \hspace{1cm} \text{(Arrhenious) (2.21)}

or

\[ K = K_0 \exp \left[ -\frac{\Delta E}{k(T - T_0)} \right] \]  \hspace{1cm} \text{(Vogel - Fulcher (2.22)}

where \( \Delta E \) is the appropriate activation energy, \( K \) is the BOLTZMAN'S constant, \( T_0 \) is a constant temperature and \( K_0 \) is the appropriate pre-exponential term. It is believed that the temperature dependence of \( K_0 \) can be ignored compared to the exponential term in the context of the analysis though it is not be rigorously true (66, 67 and 93).

Since it is extremely doubtful that both the nucleation rate and the crystalline growth rate will have the same temperature dependence during the observable non-isothermal crystallization process (82, 93). It is clear that the applicability of the simple temperature dependencies cited above for \( K \) will in most instances be limited to cases where \( K \) depends only on the growth rate and not on the nucleation rate. The valid application of the simple temperature dependencies given by equation 2.21 or 2.22 further restricts the temperature range of the possible experiments to temperature regimes where the growth rate is dominated by the molecular mobility in the liquid phase. Specifically, this temperature regime refers to the low
There are three notable and phenomenologically different mechanism which can give rise to this simple temperature relations for crystal growth in certain temperature ranges. First, UHLMANN ET AL (66, 67 and 93) have asserted that for congruently melting glass-forming materials the low temperature crystalline growth rate will be limited by the viscosity of the glass forming liquid. In this instance $\Delta E/n$ can be interpreted as the activation energy for viscous flow. This interpretation has been utilized by CHEN(77) in his treatment of the crystallization kinetics of several metallic glasses utilizing DSC. The success of CHEN'S treatment, however, may in part depend on the linear growth kinetics of the duplex domains often associated with eutectic compositions.

The second mechanism involves the "linear growth kinetics" which can arise in diffusion controlled crystal growth. Recent reports of such forming systems have been given by SCHERER and UHLMANN (94) (K2O-SiO2 glasses) and SHELESTAK ET AL (95) (CaO-MgO-Al2O3-SiO2 glasses). In the latter case JOHNSON-MEHL-AVARAMI equation is found to be applicable when a bulk nucleation catalyst is added. Examples of other such systems have been outlined by UHLMANN (93) have asserted that in many such instances the low temperature side of the peaked growth rate curve associated with this mechanism is dominated by interatomic diffusion in
the liquid. Diffusion controlled growth is characterized by a gradient in the atomic concentrations in the region just ahead of the growth front. The development of this characteristic solute distribution ahead of the interface depends on the interatomic diffusion coefficient and hence, under constant scan rate conditions, on time. If the interatomic diffusion flux in the melt is rapid compared to the crystalline growth rate, then the atomic concentration gradient under constant scan rate conditions will be essentially the same as those observed under isothermal conditions at any given temperature. Under these conditions ∆E/n can be interpreted as the activation energy for interatomic diffusion. The validity of assumptions that concentration profiles ahead of the growth front are the same as those profiles obtained under isothermal conditions could be tested by performing the crystallization process under different scan rates. If the values of the ∆E/n as determined from the two different scan rate experiments differ, then assumptions is in the error. Thirdly it is possible that the devitrification of these compositionally complex glass forming systems may, in other instances, be dominated by other processes at the melt - crystal interface and yet demonstrate "linear growth kinetics". In this case ∆E/n will reflect the activation energy for the rate limiting step for growth occurring at the interface. Thus in order to experimentally obtained the simplified temperature dependance for K given by eq (2.21) and (2.22) in such glass forming liquids, scans from low to high temperature must be
used which allows the melt to fully crystallize at temperature which are dominated by the low temperature growth behaviour.

Moreover, in order for the JOHNSON MEHL - AVARAMI equations to hold under non-isothermal conditions, sufficient randomly distributed nuclei must be present at the initiations of the crystallization process such that possible additional nucleation during the crystallization process has a negligible effect on the overall crystallization kinetics. These actual nuclei might be provided by the addition of nucleation catalysts or by low temperature anneals to provide homogeneously nucleated sites. In the absence of additional nucleation the initial density of the nuclei need not be large. Using the data of MEILING and UHLMANN (66) for Na₂O. 2SiO₂ as an example and assuming isotropic growth, a nucleation density on the order of $1 \times 10^5$ nuclei/cm³ should be sufficient for scan rates of 10°C/min or less. This density corresponds to a crystal size of approximately $2.2 \times 10^{-2}$ cm in the fully crystalized specimen. For high heat of fusion glass forming systems the work of JACKSON ET AL (96) indicates that secondary nucleation can play an important role in the growth kinetics. Depending on the secondary nucleation rate and morphology, this behaviour could have a mitigating effect on the necessary number of initial nuclei and/or the general applicability of the JOHNSON-MEHL-AVARAMI equation.
2.4.6.1 EVALUATION OF THE RELATION BETWEEN $\alpha$ AND $T$ FOR
JOHNSON - MEHL - AVARAMI TRANSFORMATION RATE EQUATION

It has been shown that equation 2.19 can be written as

$$\frac{d\alpha}{dt} = n \frac{K^{1/n}}{f(\alpha)} \left[ \ln(1-\alpha)^{-1} \right]^{((n-1)/n)} \tag{2.23}$$

where

$$f(\alpha) = (1-\alpha) \left[ \ln(1-\alpha)^{-1} \right]^{((n-1)/n)}$$

the generalized temperature dependence of $K$ can be expressed as follows

$$K = K_0 \exp\left[ -\frac{\Delta E}{kT} \right] \tag{2.24}$$

Where $K_0$ is a constant, $E$ is the appropriate activation energy, $k$ is the Boltzmann constant and $T$ is the generalized temperature parameter.

Since $dT/dt = r$, the equation 2.23 is separable in $\alpha$ and $T$ and can therefore be directly integrated.
\[
\int \frac{d\alpha}{(1-\alpha') \left[ \ln(1-\alpha)^{-1} \right] ((n-1)/n)} = \int \frac{T}{n K_0 \exp\left(\frac{-E}{n K T'}\right) \frac{dT'}{r}}
\]

Integration yields

\[
\left[ \ln(1-\alpha)^{-1} \right]^{1/n} = K_0^{1/n} \left( \frac{T}{r} \right) E_2 \left( \frac{\Delta E}{n K T} \right)
\]

(2.26)

Where \( E_2 \) is the exponential integral of order of 2 and is defined as clearly in the work of ABRAMOWITZ and STEGUN (97). It should be emphasized that \( \alpha \) is the fraction transformed at the temperature \( T \), under constant scan rate conditions.

### 2.4.6.2 APPROXIMATION FOR \( E_2 \)

It can be shown (99) that

\[
E_2(y) = \exp[-y/(y+2)] \left( 1 + R \right)
\]

(2.27)

where \( R = 2(y+2)^{-2} + \text{higher order term in } (y+2)^{-2} \). For the expected cases of interest \( R \) can usually be neglected compared to 1. Using approximation given by equation 2.27 and neglecting \( R \) in equation (2.26) yields:

\[
\left[ \ln(1-\alpha)^{-1} \right]^{1/n} = Z \left[ 1 + \frac{2 n K T}{\Delta H} \right]
\]

(2.28)
\[ Z = \left[ \frac{r \Delta E}{n k T^s k^{1/n}} \right] \]  

(2.29)

2.4.6.3 DETERMINATION OF \( \Delta E \) USING A SINGLE SCAN

Rewriting equation 2.26 in a somewhat different form:

\[ \left[ \ln (1 - \alpha)^{-1} \right]^{1/n} = K_0^{1/n} (T/r) \exp \left[ \frac{-\Delta E}{n K T} \right] (E/nKT + 2) \]

(2.30)

The slope of a plot \( \ln \ln(1 - \alpha)^{-1} \) versus \( T^{-1} \) can be determined by taking the derivative of \( \ln \ln(1 - \alpha)^{-1} \) with respect to \( T^{-1} \) thus:

\[ \frac{d[\ln \ln(1 - \alpha)^{-1}]}{d(T^{-1})} = -\frac{\Delta E}{K} - 2nT \left[ 1 - \frac{n K T}{\Delta H + 2n K T} \right] \]

(2.31)

2.4.6.4 DETERMINATION OF \( (\Delta E/n) \) USING A SINGLE SCAN

Taking the natural logarithm of equation 2.23:

\[ \ln \left( \frac{d\alpha}{dt} \right) = -\left( \frac{\Delta E}{n K T} \right) + \ln \left( n K_0^{1/n} \right) + \ln f(\alpha) \]

(2.32)
The slope of a plot \( \ln(\frac{d\alpha}{dt}) \) versus \( T^{-1} \) can be determined by taking the derivative of \( \ln(\frac{d\alpha}{dt}) \) with respect to \( T^{-1} \) and noting that \( f(\alpha) \) is implicitly a function of \( T \).

\[
\frac{d[(\ln(\frac{d\alpha}{dt}))]}{d(T^{-1})} = -\frac{\Delta E}{nK} - K_0^{1/n} \exp\left(-\frac{\Delta E}{nK} T^2\right) \frac{df(\alpha)}{dT} = \frac{T^2}{nr} \exp\left(-\frac{\Delta E}{nK} T_0^2\right) \frac{df(\alpha)}{dT} 
\]

(2.33)

### 2.4.6.5 DETERMINATION OF \( \Delta E/n \) USING MULTIPLE SCAN RATES

**INTEGRAL METHOD**

Integrating equation 2.23 yield;

\[
\int_{0}^{\alpha_0} \frac{d\alpha}{f(\alpha)} = n K_0^{1/n} \left(\frac{T_0}{r}\right) E_2 \left(\frac{\Delta E/n K T_0}{T_0}\right)
\]

where \( \alpha_0 \) is the fraction transformed at temperature \( T_0 \) with scan rate \( r \).

Using the approximation given by equation 2.27 and neglecting \( R \)

\[
\int_{0}^{\alpha_0} \frac{d\alpha}{f(\alpha)} = n K_0^{1/n} \left(\frac{T_0}{r}\right) \frac{\exp\left(-\frac{\Delta E}{n K T_0}\right)}{\frac{\Delta H}{n k T_0} + 2}
\]
for

\[(\Delta E/nkT_o) \gg 2\]

\[
\int_0^{\alpha_o} \frac{d\alpha}{f(\alpha)} = \frac{n^2K_0^{1/n}K}{\Delta E} \left(\frac{T_o^2}{r}\right) \exp \left(-\frac{\Delta E}{nKT_o}\right)
\]

Since

\[
\int_0^{\alpha_o} \frac{d\alpha}{f(\alpha)} = \text{Constant (Independent of } r)\]

\[
(T_o^2/r) \exp \left(-\frac{\Delta E}{nKT_o}\right) = \text{Constant}
\]

or

\[
\ln \left(\frac{r}{T_o^2}\right) = -\frac{\Delta E}{nKT_o} + \text{Constant} \quad (2.34)
\]

Thus by varying the scan rate \( r \) in a series of scans, different values for \( T_o \) will be obtained as determined by measuring \( \alpha_o \) (i.e. by integrating \( d\alpha/dt \)). A plot of \( \ln(T_o^2/r) \) versus \( T_o^{-1} \) will have a slope of \( \left(-\Delta E/nk\right) \). It must be emphasized that \( T_o \) refers to the temperature at which \( \alpha_o \) of the transformation has taken place.
2.4.6.6 DETERMINATION OF CONDITION AT PEAK IN NONISOTHERMAL TRANSFORMATION RATE \( \frac{d\alpha}{dT} \)

(A) CONDITIONS ON \( \frac{df}{d\alpha} \)

At the maximum of the transformation rate

\[
\frac{d^2 \alpha}{dt^2} = 0
\]

Differentiating equation 2.23 with respect to \( t \), yields the following conditions on \( \frac{df(\alpha)}{d\alpha} \) at the peak

\[
\left( \frac{\frac{df}{d\alpha}}{\text{peak}} \right) = \frac{r\Delta E}{(n^2 K T_p^2 K_p^{1/n})} = -\frac{Z_p}{n} \quad (2.35)
\]

(B) CONDITIONS ON \( Z_p \)

calculations of \( \frac{df(\alpha)}{d\alpha} \) yields

\[
\frac{df(\alpha)}{d\alpha} = \frac{n-1}{n} \ln(1-\alpha)^{-1} n + \frac{(n-1)/n}{\ln (1-\alpha)^{-1} n} \quad (2.36)
\]

Substituting equations (2.35) and (2.28) into equation (2.36) yields

\[
Z_p = \left[ \frac{n-1}{n} \left( 1 + \frac{2 n k T_p}{\Delta E} \right) + \frac{1}{n} \left( 1 + \frac{2 n k T_p}{\Delta E} \right)^{-1/n} \right]^{-1/n} \quad (2.37)
\]
In most cases of interest \( Z_p \) will be essentially constant with respect to the scan rate, since \( 2 n k TP/\Delta E \ll 1 \).

In general \( Z_p \) will lie between 1 and 0.9 given reasonable values for \( T_p \) and \( E \).

(C) CONDITIONS ON \( \alpha_p \)

Substituting equations (2.35) and (2.37) into equation (2.36) and taking \( Z_p \approx 1 \), implies

\[
\ln(1-\alpha_p) = 1
\]

on with approximations cited above \( \alpha_p = 0.633 \) (independent of \( r \) or \( n \)). Taking \( Z_p \approx 0.9 \), for \( n = 3 \), then,

\( X_p \approx 0.605 \), For \( Z_p < 1 \), \( X_p \) depends weakly on \( n \) and \( r \).

(D) DETERMINATION OF (\( \Delta E/n \)) USING MULTIPLE SCAN RATES

(PEAK METHOD)

As shown above \( Z_p \) is approximately constant. Using equation (2.29)

\[
Z_p = \frac{r \Delta E}{n K T_p^1 K_p^{1/n}} = \text{Constant}\quad (2.39)
\]

To first order this constant can be taken to be equal to 1. \( T_p \) and \( K_p \) will, however, vary markedly with scan rate.
Therefore, using equation (2.24) in equation (2.39) and taking the natural logarithm.

\[
\ln \left( \frac{r}{T_p^2} \right) = \ln \left( \frac{Zp n k K_0^{1/n}}{\Delta E} \right) - (\frac{\Delta E}{n k T_p})
\]

The slope of a plot of \( \ln(r/T_p^2) \) versus \( T_p^{-1} \) is given by the derivative of \( \ln(r/T_p^2) \) with respect to \( (1/T_p) \)

\[
\frac{d[\ln(r/T_p^2)]}{d(T_p^{-1})} = -\left( \frac{\Delta E}{n k} \right)
\]

(2.40)

The above approximation holds will because \((Zp n k K_0^{1/n} / E)\) is to a good approximation constant.

2.5.1 EVALUATION OF THE JOHNSON – MEHL – AVARAMI TRANSFORMATION PARAMETERS UNDER CONDITIONS OF SINGLE SCAN TECHNIQUE.

Under the assumptions of the simplified temperature dependence for \( K \), the parameters associated with the JOHNSON – MEHL – AVARAMI transformation rate equation which are of fundamental importance are of \( E, n, T_0, K_0 \). The techniques of data analysis given below can be broadly divided into a single scan analysis technique and a multiple – scan analysis technique.
2.5.2 SINGLE - SCAN TECHNIQUE

It has been indicated that a single temperature scan in principle be used to determine all of the parameter cited above. An outline of such a technique is given below.

2.5.3 DETERMINATION OF ($\Delta E/n$)

Using the technique first suggested by PILOYAN (98) and later used by CLINTON(7)) and SESTEK(72) to assess the crystallization kinetics of oxide glasses, it is possible to show that a plot of $\ln(d\alpha/dt)$ versus $1000/T$ will closely approximate to a straight line behaviour with a slope equal to $-\Delta E/nK$. In most instances the effective activation energy for various flow will be at least of the order of 2 to 3 eV during the crystallization process. Since the STOKES - EINSTEIN relation indication that the growth rate for a crystallite should be proportional to the reciprocal of the viscosity one could expect that $\Delta E/n$ would be also be at least of the order of 2 to 3 eV. In this case the second term on the right hand side of the equation (2.33) will be determined by the exponential term, making it negligible.

2.5.4 DETERMINATION OF $\Delta E$ AND $n$

It is also possible to show that a plot of $\ln \ln (1-\alpha)^{-1}$ versus $1000/T$ should be also approximate a linear behaviour. The slope of such a plot will be given by -
E/K. This is exactly the same method outlined by SESTEK (72) and an estimate of the possible error can be made by estimating the second term on the right hand side of the equation (2.31) the determination of $\Delta E/n$ and $\Delta E$ makes it possible to directly determine the parameter n.