Chapter 3

Theoretical Aspects of Phase Transformation Kinetics and Evaluation of Thermo-Physical Properties
In this chapter the salient features of modelling of phase transformation kinetics in the purview of dynamic calorimetry measurements and a brief description of quasi harmonic Debye-Gruneisen formalism are presented. The theory of phase transformation kinetics is in fact very broad. But in the current chapter attention is focused on modelling aspects of kinetic issues of diffusion mediated and displacive (martensitic) phase changes in the physical metallurgical context. In precise terms, the non isothermal version of the Kolmogorov-Johnson-Mehl and Avrami (KJMA) model of diffusional phase changes is taken up for detailed discussion. This incorporates different nucleation and growth modes for the overall progress of transformation extent with time under linear heating or cooling rate conditions. For modeling the kinetics of martensitics transformation, the empirical relation given by Koistinen and Marburger is used. Further, the second part of this chapter deals with an analytical description of a particular version of thermophysical equation of state that is known as Debye-Gruneisen formalism. Before proceeding further, the general aspect of kinetics of phase transformation is discussed in the next section.

### 3.1. Basic glimpse of kinetics of phase transformation

A study of phase transformations that occur in solid state is of interest on both basic and applied grounds. Since phase transformations represent the explicit manifestation of thermodynamic instability, a comprehensive mapping of the evolutionary character of different phase fields in terms of appropriate intensive thermodynamic variables such as volume, pressure; temperature is extremely useful in constructing phase diagrams, the use of which in the design of materials is only too obvious [1-5]. If any of the thermodynamic variables suffer a change, correspondingly the Gibb's free energy of the system also changes continuously or discontinuously. Finally if the variation in free energy leads to change in structural details of a phase, then
"Phase transformation" is said to occur. Hence the system undergoes a phase transformation to that new structure [1-5]. The free energy may vary continuously if the thermodynamic variables like temperature or pressure is varied and the rate of variation is actually structure and system dependent. On alteration of the external conditions such as pressure and temperature, the initial state of the system is no more in the equilibrium state.

![Fig.3.1 A schematic of different kinetic pathways offered by three different cooling histories is shown. Paths A and B stand for transformations occurring under isothermal and linear cooling conditions, where as the path C represents a step wise cooling with small incremental isothermal holds. Note that in all the three paths A, B and C the net reduction in Gibbs energy ΔG is the same.](image)

While thermodynamic considerations decide the ultimate stability of condensed systems, it is the time scale that marks the rate of attainment of this true thermodynamic equilibrium, which decides the effective usefulness of a solid as a practically useful engineering material. While thermodynamics classifies phase changes in terms of the nature of discontinuity in appropriate susceptibility functions, the kinetic considerations serve to broaden this classification further [1-5]. The number of kinetic paths available in
general for solid state phase transformations are many and these can be realized by selecting appropriate kinetic path variable [1-5]. Let us consider a system undergoing phase transformation form one state $\alpha$ to other state $\beta$ during cooling from the high temperature. In figure 3.1 the schematic illustration of path variable respect to one kinetic variable, namely cooling rate ($\beta$) is presented. Form figure 3.1, it is clear that system can choose three independent paths which are A, B and C which involve different time durations for the same transformation [1-5]. There are other possible kinetic path variables which includes starting grain size ($d$) or morphology of the material, stress state ($\sigma$) and irradiation level etc. These could act either singly or in combination to decide the overall kinetics of transformation. In the present case, an attempt is made to highlight the role of one important kinetic variable, namely the heating or cooling rate in decisively altering the kinetics of simple structural transformations that occur in metals and alloys. The choice of this variable is based on the fact that it plays a vital role in dictating the final microstructure of many engineering alloys used in strategic applications. The other reason is that relevant experimental kinetic data with sufficient degree of accuracy are easily generated by carrying out the high resolution thermal analysis experiments and the results of which are rather easily processed to obtain information on transformation temperatures, the transformation velocity, especially their dependence on thermal history. In the present study in order to study the phase transformation kinetics heat flux differential scanning calorimeter has been used.

3.2. Isothermal and non-isothermal transformations

As illustrated in figure 3.1, a phase transformation between two phases $\alpha$ and $\beta$ can be realized under varying time ($t$) – temperature ($T$) combinations, known under the generic name of thermal history. In the purely isothermal case, the sample is held at a fixed temperature ($path$ A) the magnitude of which decides effectively the available
chemical driving force ($\Delta^o G$) and diffusional mobility of atoms. Apart from temperature, the time duration of isothermal holds decides the extent of transformation.

The isochronal process involves continuous heating or cooling as a function of time (path B shown in figure 3.1) or with interrupted isothermal holds (path C shown in figure 3.1). The kinetics of such non-isothermal transformations is basically decided by the cooling rate adopted. There is enormous evidence in metallurgical literature, which suggests that on rapid heating or cooling conditions, there is strong possibility that classical nucleation and growth mediated phase changes are inhibited and yield way to martensitic or displacive types of transformation [1-5]. This situation arises because under rapid heating or cooling conditions the diffusion of species become difficult due less available time.

It is generally the case that non-isothermal experiments are easily performed with minimal expenditure of time; but their results are the difficult ones to understand and interpret in concrete terms. From an applied context, most of the industrial heat treatments are done under complex thermal history, thereby necessitating a holistic understanding of both isothermal and non-isothermal phase transformation kinetics. In literature, there are very few rigorous treatments aimed primarily at tackling the problem of phase evolution under varying time-temperature history [6-16] and generally their mathematical complexity comes in the way of their widespread practical appeal. In the next section the theoretical aspect of transformation kinetics of diffusional based transformation under both isothermal and non-isothermal case is discussed in detail.

3.3 Kinetics model for nucleation & growth type transformation

There have been immense efforts from different research groups to develop suitable kinetics models for solid state transformations [8-35]. In past, especially the contributions from Johnson and Mehl [9], Avrami [10-12] and Kolmogorov [13] known jointly as the Johnson-Mehl-Avrami-Kolmogorov model (JMAK) are found to be
significant. The derivation of the KJMA model is based on the combination of three specific independent processes that are nucleation, growth and impingement of growing particles. It has been observed that mode of nucleation and growth can be different depending on the transformation. The nucleation processes considered are either continuous nucleation, when the nucleation rate is changing with temperature or as site saturation if all nuclei are present before the growth starts. Further, the growth processes can be either diffusion controlled, or interface controlled depending on whether overall kinetics is being decided by diffusion or interface mobility [6-16]. In the following sections the derivation of KJMA equation is discussed in detail.

3.4 Rate of transformation

For the analysis of kinetics of solids state transformation experimentally, one needs to measure the variation of a physical property (enthalpy, electrical resistivity, length, hardness, specific volume and magnetization etc.) as a function of time or temperature during the course of a phase change. From such data the degree of transformation $X (0 \leq X \leq 1)$ can be calculated as follow.

$$X = \frac{(P_T - P_0)}{(P_f - P_0)},$$  \hspace{1cm} (3.1)

Where, $P_T$ is the instantaneous physical property measured during the transformation at any temperature $T$, $P_0$ and $P_f$ are the value of $P$ at the start and finish of the transformation, respectively. The transformed fraction does not depend on $t$ or $T(t)$ in a direct way, although the thermal history of the material decides the extent of transformation. In order to correlate the extent of transformation and thermal history, let us now define a path variable $\Omega$ which determines the extent of transformation and depends on thermal history. Therefore one can express the fraction of transformation as follows [14].

$$X = F(\Omega)$$  \hspace{1cm} (3.2)
The above Eq. (3.2) does not impose any constraint on the type of transformation considered. If the transformation mechanism is not changing for a given time-temperature path (t-T), then $\Omega$ can be assumed to be proportional to number of atomic jumps because temperature decides the atomic mobility and time defines the duration of transformation process. Under these circumstances, the thermal history dependence of $\Omega$ can be described in the following way depending on whether process is isothermal or non-isothermal [14].

$$\Omega = k(T(t)). \quad (3.3)$$

$$\Omega = \int k(T(t)) dt. \quad (3.4)$$

In above Eqs $k(T)$ is rate constant and assumed to be of the Arrhenius form.

$$k(T(t)) = k_o \exp \left( - \frac{Q_{eff}}{RT(t)} \right). \quad (3.5)$$

With $k_o$ as the pre-exponential or frequency factor, $Q_{eff}$ is the apparent or effective activation energy for the overall transformation process and $R$ is gas constant. In general terms, $Q_{eff}$ must be treated as dependent on the transformation extent $X(T(t))$ as well, but for reasons of convenience and simplicity, is often taken to be a constant. In the reported literature, the kinetic theories for non-isothermal phase transformations have been derived from the theory of isothermal transformations in conjunction with additivity rule [14] given below.

$$\int_0^\tau \left( \frac{dt}{\tau^{iso}} \right) = 1. \quad (3.6)$$

Where, $\tau^{iso}$ is the time required during one isothermal step. In words, it can be stated that if a non isothermal transformation is composed of a series of isothermal processes then the total time required follows by adding relative durations of time spent at each temperature and equating this sum to one. But it must be remembered that this will only hold when process is isokinetic [6]. If a non-isothermal experiment is described as a
series of isothermal anneals, each of infinitesimal length of time, and Eq. (3.3) is applied to each time step [14-15] for overall isochronal (i.e. constant heating rate) experiments. Then only the outcome will be in accordance with the Eq. (3.4). In the classical methodology adopted for analysing the kinetics of a nucleation and growth type of transformation as studied by thermal analysis methods, the following separable functional representation is often invoked to represent the instantaneous reaction rate from Eq. (3.2) [14-17].

$$\frac{dX}{dt} = \left(\frac{dF(\Omega)}{d\Omega}\right) \left(\frac{d\Omega}{dt}\right).$$  \hspace{1cm} (3.7)

If we assume that the time gap between two isothermal processes under isothermal transformation is infinitesimal then $d\Omega = k(T(t))dt$, this leads to Eq. (3.4), therefore with the help of Eq. (3.3) and Eq. (3.4), we can write [25].

$$\frac{dX}{dt} = k(T(t)) \frac{dF(\Omega)}{d\Omega}. \hspace{1cm} (3.8)$$

From the above equation it is clear that the rate of transformation can be described if both the terms are clearly defined in Eq. (3.8). The first term is standard Arrhenius term and therefore one need to have a clear idea about the second term alone.

3.5. **Transformation mechanism: nucleation and growth**

The overall kinetics of phase transformation can be described in terms of fraction transformed as function of time/temperature. The overall fraction transformed is function of nucleation and growth. In the next section the detailed descriptions of nucleation and growth modes are discussed.

3.5.1. **Nucleation modes**

There are four different categories of nucleation modes; (1) continuous nucleation (2) site saturation nucleation, (3) mixture of continuous and site saturation nucleation, (4) Avrami nucleation.
The continuous nucleation means the rate of nucleation is monotonically increasing with time. The rate of nucleation is decided by the number of critical nuclei present and the rate of jump of atoms across the interface from parent to the critical nuclei of the product phase. The jump frequency through the interface can be described in the form of Arrhenius form \( \exp(-Q_N/RT) \) [6] where \( Q_N \) stands for activation energy for nucleation. The number of critical nuclei depends on an activation energy \( \Delta G^* \) and it can be approximated in the following form [7].

\[
\Delta G^* \approx \frac{C}{\Delta T^2}.
\]  \hspace{1cm} (3.9)

Where \( C \) is constant relatively intensive to temperature and \( \Delta T \) is under cooling or overheating. Hence the nucleation rate per unit volume can be written as [7].

\[
\dot{N}(T) = N_0 \exp \left(-\frac{Q_N}{RT}\right) \exp\left(-\frac{\Delta G^*}{RT}\right).
\]  \hspace{1cm} (3.10)

If \( \Delta T \) is very high then \( \Delta G^* \) will be very small and in this case nucleation rate will only depends on the mobility of the atoms across the interface and the Eq. (3.10) can be written as follow [6-7].

\[
\dot{N}(T) = N_0 \exp \left(-\frac{Q_N}{RT}\right).
\]  \hspace{1cm} (3.11)

The main features of continuous nucleation is that at \( t=0 \) the number of nuclei of supercritical size will be zero.

In the case of site saturation nucleation the nucleation rate does not change during transformation and it remains constant throughout the transformation, in this case the rate of nucleation can be defined as follows [6-7].

\[
\dot{N}(T) = N \delta(t - 0).
\]  \hspace{1cm} (3.12)

Where \( \delta \) denotes Dirac function and \( N \) is number of nuclei presents at \( t=0 \).

It has often been observed that mixed mode of nucleation are present during phase transformation in real system. Under this category there are some nuclei already
present at $t=0$ and other formed during the course of transformation. The rate of nucleation for mixed mode is just the weighted average of the rate of continuous and site saturation nucleation. The rate of nucleation for mixed mode can be written in the following way [6-7].

$$\dot{N}(T) = \dot{N}^0 \delta(t - 0) + N_0 \exp \left( -\frac{Q_N}{RT} \right). \quad (3.13)$$

In Eq. (3.12), $N$ and $N_0$ represents the relative contribution from two different modes.

In the case of Avrami nucleation mode the nuclei of supercritical size formed from the nuclei of subcritical size, such that the total number of nuclei of supercritical and subcritical remains constant. Therefore the rate change of supercritical nuclei number can be expressed as follow [10-12].

$$\dot{N} = i\dot{N}_{sub}. \quad (3.14)$$

Where $i\dot{N}$ is the rate at which subcritical nuclei change to supercritical nuclei and it can be expressed in the following form

$$i\dot{N} = \eta_0 \exp \left( -\frac{Q_N}{RT} \right). \quad (3.15)$$

with $\eta_0$ pre-exponential factor. Upon integration of Eq. (3.14), after separation of variables, using Eq. (3.15) and the boundary condition that the number of subcritical nuclei equals $N$ at $t=0$, it is obtained for the rate of formation of supercritical nuclei at $t=t^\ast$.

$$\dot{N}(T) = \eta_0 \dot{N} \exp \left( -\int_0^{t^\ast} i\dot{N} \, dt \right). \quad (3.16)$$

By variation of $\eta_0$, the mode of nucleation can be varied from site saturation ($\eta_0$ infinitely large) to continuous nucleation ($\eta_0$ infinitely small).

3.5.2. Growth modes

In a more general way two types of growth modes are identified, one of which is
diffusion controlled growth where long range diffusion is involved. Under diffusion controlled growth mode the product phase has different composition than parent phase. The second category of growth mode is interface controlled. The interface controlled growth mode involves short range diffusion and overall composition of the product phase is same as the parent phase.

In the case of diffusion controlled growth, long range diffusion in the matrix governs the growth of the new phase particles. The diffusion length, $R$ is proportional to square root of time and it can be expressed in the following form [6-7].

$$R = (Dt)^{1/2}. \quad (3.17)$$

Where $D$ is diffusion coefficients, Eq. (3.17) is valid under isothermal condition only and it is also known as parabolic growth. Under non-isothermal condition the diffusion length can be approximated as follow [6-7].

$$R = \left[ \int DT(t)dt \right]^{1/2}. \quad (3.18)$$

Further the temperature dependence of diffusion coefficient can be described according to following equation

$$D(T(t)) = D_0 \exp \left( -\frac{Q_D}{RT} \right). \quad (3.19)$$

with $D_0$ as the pre-exponential factor and $Q_D$ as the activation energy for diffusion. The growth laws given in Eq. (3.17 & 3.18) are only valid in very large matrix of parent phase and holds only in the initial stages of transformation until there is no impingement. [18]. If Eq. (3.17 & 3.18) holds together then the volume of growing particle will be

$$V = gR^d. \quad (3.20)$$

Where $g$ is particle geometry factor and $d$ is the dimensionality of the growth.

In the case of interface controlled growth model the particle growth is governed by the mobility (driving force normalized velocity) of interface between product and parent. The velocity of the interface is decided by the net jump of atoms from the parent
phase to the new growing phase per unit of time. The jump of atoms is determined by the
difference in the Gibb’s free energy for an atom between parent and product phase.
However, the transfer of the atom is inhibited due to formation of new interface which in
turn create an energy barrier for the jump of atoms across the interface. If $\Delta G^a$ is the net
free energy difference between parent and product phase, then the net flux of atoms
jumping from the parent to the product phase across the interface can be approximated as
follow [6-7].

$$J = J_0 \exp \left( -\frac{\Delta G^a}{RT} \right).$$  \hspace{1cm} (3.21)

In Eq. (3.21) $J_0$ is the pre exponential factor. Further in the case of interface controlled
growth the volume of growing particle can be written as follows [15-17].

$$V = g(\int J dt)^d.$$  \hspace{1cm} (3.22)

The Eqs. (3.20 & 3.21) for both diffusion and interface controlled growth model can be
combined and given in compact form. At any time $t$ the volume $V$ of growing particle
that nucleated at time $t_0$ is given by [15-17]

$$V = g(\int \vartheta dt)^d/m, \hspace{1cm} (3.23)$$

$$\vartheta = \vartheta_0 \exp \left( -\frac{Q_g}{RT} \right). \hspace{1cm} (3.24)$$

with $\vartheta_0$ as the pre-exponential factor for growth, $Q_g$ the activation energy for growth, and
$m$ as the growth mode parameter. For the case of diffusion controlled growth, $m=2$, $Q_g$
equals $Q_D$ (activation energy for diffusion) and $\vartheta_0$ equals $D_0$. For the case of interface
controlled growth $m=1$, $Q_g$ equals $\Delta G^a$ (interface energy barrier) and $\vartheta_0$ equals $J_0$.

3.5.3. Effect of impingement on growth

The volume of the growing particle given by Eq. (3.23) is referred to as the
extended volume, which counts for the entire transformed volume without considering
impingement of transformed domains, is a virtual concept [14-17]. Thus the overlapped
domains should be counted twice or even multiple-times in order to obtain the virtually
defined extended volume. In reality, the particles are not growing into an infinitely large
parent phase and the extended volume does not account for the overlap of particles (hard
impingement) and their possibly surrounding diffusion fields (soft impingement).
Therefore, the relationship between the extended volume $V_{ext}$ and the actual volume $V'$
transformed phase is needed. If it is assumed that the nuclei are randomly dispersed
throughout the space and suppose that at a given time $t$ the actually transformed volume
is $V'$ and during the course of transformation after an infinitesimal time laps of $dt$, if the
extended and the actual transformed volumes are increase by $dV_{ext}$ and $dV'$. Then from
the change of the extended volume $dV_{ext}$, only a part will contribute to the change of the
actually transformed volume $dV'$, namely a part as large as the untransformed volume
fraction $(V-V')/V$. where $V$ is the total volume of the system. Therefore the change in the
real volume can be expressed as follow [14-17].

$$dV' = \left( V - \frac{V'}{V} \right) dV_{ext}.$$  \hspace{1cm} (3.25)

Further the degree of transformation can be defined as.

$$X = \frac{V'}{V}.$$  \hspace{1cm} (3.26)

After integrating Eq. (3.25), one can get the following expression for extent of
transformation [14-17].

$$X = \frac{V'}{V} = 1 - \exp \left( \frac{V_{ext}}{V} \right).$$  \hspace{1cm} (3.27)

3.5.4. **Overall transformation kinetics**

The overall transformation kinetics describes the relationship between fraction
transformed and time for different reaction temperature. Actually it is function of both
nucleation and growth rate. The empirical expression describing the overall
transformation kinetics can be obtained by substituting the expression for extended
volume in Eq. (3.26)

\[ X = \frac{V^t}{V} = 1 - \exp \left[-\{k(T)t\}^n\right]. \quad (3.28) \]

Where \( k(T) \) is rate constant and is function of \( T \) and \( n \) is time exponent. Note that this
equation cannot be derived for a mixture of the nucleation models. Eq. (3.28) has first
been derived by Johnson and Mehl (for the case of isothermal transformations with
continuous nucleation [9] and by Kolmogrov and Avrami (for isothermal transformations
with continuous nucleation and site saturation) and therefore it is referred as the KJMA
equation with Avrami exponent \( n \) [10-12].

3.5.5. Formulation of Kolmogrov-Johnson-Mehl and Avrami model for isothermal
and non-isothermal transformations

By combining Eq. (3.3) & Eq. (3.28), the expression for fraction transformed
under isothermal case can be rewritten as follow.

\[ X = F(\Omega) = 1 - \exp[-\Omega^3]. \quad (3.29) \]

However, for the case of non-isothermal annealing, on the basis of nucleation and growth
models, an equation for \( V_{ext} \) can be derived and after substitution into Eq. (3.28) leads to
a KJMA-like equation and also fulfill the prescription of Eq. (3.2) with \( \Omega \) defined
according to Eq. (3.3). Additionally, if a KJMA-like equation can be obtained then the
associated kinetic parameters \( n, Q \) and \( k_0 \) can be given in terms of appropriate nucleation
and growth models even in the case of non-isothermal transformation. In the following, it
will be shown that this is possible for at least in the case of isochronal annealing as long
as the nucleation process involved is either site saturation or continuous nucleation.

Considering the case of isochronal annealing, the phase transformation
temperature under dynamic heating condition can be expressed as follows.

\[ T(t) = T_o + \beta t. \quad (3.30) \]
Where $T_o$ is the start temperature (at $t=0$) of the experiment and $\beta$ is the constant heating rate. The above formulation can be analogous to that for isothermal transformations with certain mathematical intricacy. The integral in Eq. (3.22) cannot be evaluated analytically in general. An Arrhenius term can be obtained by substitution of Eqs. (3.5) and (3.30) into Eq. (3.20) and integrated over time as follows [17].

$$\Omega = k_o \int_0^t \exp \left( -\frac{Q_{eff}}{R(T_o + \beta t)} \right) dt. \quad (3.31)$$

The above equation can be also be integrated over temperature by replacing time with temperature by using of Eq. (3.30). The integration in Eq. (3.31) is performed over a new time parameter $t'=t + T_o / \beta$ by invoking $dt=dt'$ and $T_o+\beta t'=\beta t=T(t')$. The boundaries for the integration then become $T_o/\beta$ and $t'$. If on heating $T_o$ is chosen small, such that $\beta (T-T_o) \approx 0$, the start of the new time scale (i.e. $t'=T_o/\beta$) can be shifted to $t'=0$ without changing the value of the integral [19]

$$\Omega = k_o \int_{T_o/\beta}^{t'\prime} \exp \left( -\frac{Q_{eff}}{R\beta'} \right) dt' = k_o \int_0^{t'\prime} \exp \left( -\frac{Q_{eff}}{R\beta'} \right) dt'. \quad (3.32)$$

With this it become possible to obtain an analytical integration by using a series expansion of type [15-17]

$$\int_0^\infty e^{-xt} t^n dt = \frac{e^{-x}}{x} \left[ 1 - \frac{n}{x} + \frac{n(n+1)}{x^2} \right]. \quad (3.33)$$

With the help Eq. (3.33), $\Omega$ can be approximated as follow

$$\Omega = \left( k_o R \beta t^2 \big/ Q_{eff} \right) \exp \left( -\frac{Q_{eff}}{R\beta} \right) \left[ 1 - 2 \frac{R\beta'}{Q_{eff}} + 6 \left( \frac{R\beta'}{Q_{eff}} \right)^2 \right]. \quad (3.34)$$

Further the back substitution $t'=T(t')/\beta$ can be made so that there is no time parameters ($t$ or $t'$) is involved anymore. On basis of Eq. (3.34), explicit analytical equations can be
derived for the degree of transformation in the case of isochronal annealing, and for specific nucleation and growth models following the recipe indicated at the beginning.

For pure site saturation and for pure continuous nucleation or both in combinations with growth according to Eq. (3.24), KJMA like equations can be obtained that will be compatible with Eq. (3.1) with \( \Omega \) as given by Eq. (3.2) and \( k \) given by Eq. (3.5). In this way explicit expression for \( n \), \( Q \) and \( k_o \) can be obtained in terms of the operating nucleation and growth mechanisms and corresponding expressions are listed in table 3.1

From table 3.1 it can be seen that for the nucleation and growth cases the KJMA parameters pertaining to isothermal annealing and to isochronal annealing are equal (except for the correction factor \( s \) given below as in Eq. (3.35) [17].

\[
s = \frac{(n - 1)!}{n^{n-1}} \left( \frac{(Q_N + (n - 1)Q_g)^n}{\prod_{j=0}^{j=n-1}(Q_N + jQ_g)} \right)^n \tag{3.35}
\]

In above table \( m \) decides the mechanism of transformation and for interface controlled \( m = 1 \) and for diffusion controlled process \( m = 2 \). The second term \( d \) is the dimensionality of growth. Further, the expressions for the overall, effective activation energy, \( Q \), given in table 3.1 can be represented by a single equation, incorporating the exponent \( n \), the ratio of the number of growth dimensions and the growth mode, \( d/m \), and the separate activation energies for nucleation, \( Q_N \), and for growth, \( Q_g \), as follows [17].

<table>
<thead>
<tr>
<th>Continuous Nucleation</th>
<th>Isothermal</th>
<th>Isochronal</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>( d/m+1 )</td>
<td>( d/m+1 )</td>
</tr>
<tr>
<td>( Q )</td>
<td>( (n-1)Q_N+Q_g/n )</td>
<td>( (n-1)Q_N+Q_g/n )</td>
</tr>
<tr>
<td>( k_o )</td>
<td>( n^{\frac{gN_o\theta_0^{n-1}}{n}} )</td>
<td>( n^{\frac{gN_o\theta_0^{n-1}}{n}} s )</td>
</tr>
</tbody>
</table>

Table 3.1
Listing of different kinetics parameters under isothermal and isochronal condition

<table>
<thead>
<tr>
<th>Continuous Nucleation</th>
<th>Isothermal</th>
<th>Isochronal</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )</td>
<td>( d/m )</td>
<td>( d/m )</td>
</tr>
<tr>
<td>( Q )</td>
<td>( Q_N )</td>
<td>( Q_g )</td>
</tr>
<tr>
<td>( k_o )</td>
<td>( n^{\frac{gN^*\theta_0^n}{n}} )</td>
<td>( n^{\frac{gN^*\theta_0^n}{n}} )</td>
</tr>
</tbody>
</table>
\[
Q_{\text{eff}} = \left\{ \left( \frac{d}{m} \right) Q_g + \left( n - \frac{d}{m} \right) Q_N \right\} / n. \quad (3.36)
\]

The above equation holds for both isothermal and isochronal annealing.

### 3.6. Determination of kinetics parameter from DSC results

From the experimental DSC peak profile as shown in figure 3.2 as a model, the fractional extent of transformation as a function of temperature \( X(T) \), is estimated using the following expression.

\[
X(T) = \frac{\int_{T_s}^{T} \varphi(T) dT}{\int_{T_s}^{T_f} \varphi(T) dT}. \quad (3.37)
\]

Here, the integral in the numerator, namely, \( T_s \int_{T_s}^{T} \varphi(T) dT \), stands for the partial area under the peak in the temperature domain \( T_s - T \) as shown in figure 3.2 by crossed lines. The denominator \( T_s \int_{T_s}^{T_f} \varphi(T) dT \) stands for the total peak area covering the entire transformation temperature range \( (T_s - T_f) \). Eq. (3.37) assumes that transformation is complete upon reaching \( T_f \), although this is certainly not true for higher heating rates. The transformation plots obtained using Eq. (3.37) is displayed in figure 3.3. In the

![Fig. 3.2. Schematic of DSC peak profile used for calculating phase fraction](image-url)
present study the transformation plots are fitted with the following non-isothermal version of the Kolmogorov-Johnson-Mehl-Avrami (KJMA) formalism for the fraction transformed $X(T)$ as a function of temperature at constant heating rate ($\beta$) [17]

$$X(T) = 1 - \exp\left[-k^n\left(\frac{R(T - T_S)^2}{\beta Q_{\text{eff}}}\right)^n\right]. \quad (3.38)$$

The above expression assumes site saturation type of nucleation. It may be noted that in the above model, we have chosen $T - T_S$, the temperature increment with respect to the experimentally observed threshold or onset temperature ($T_S$) as the independent variable, since this corrects in an apparent manner for the error incurred in not accounting precisely for the true start of the transformation corresponding to near zero transformed fraction ($X = 0$). In above equation $k$ is Arrhenius rate constant and $n$ is the so-called Avrami or transformation exponent.

3.7. Martensitic Transformation: Koistinen-Marburger Relation

The kinetics of martensitic transformation is modelled after the popular relation

![Isochronal Transformation Diagram](image_url)

**Fig. 3.3.** Phase fraction curve obtained using Eq. (3.38)
proposed by Koistinen and Marburger on empirical grounds [32]. In what follows, we use this relation in a slightly modified form, in order to incorporate explicitly the cooling rate in it.

\[ X(T) = \exp \left\{ - \left[ \left( \frac{b'}{\beta} \right) \left( M_s - T \right) \right]^n \right\} \quad (3.39) \]

Here \( X(T) \) is fraction of martensite formed at temperature \( T \). In the above expression, \( \beta \) is the cooling rate in K sec\(^{-1} \), \( M_s \) is the onset temperature in Kelvin and \( n \) is a constant. By setting \( (b'/\beta)^n = b \), a simple two parameter description of martensitic transformation after the well-known empirical framework of Koistinen and Marburger (K-M) can be readily obtained [32]. It must be added that in the original K-M prescription, \( n \) is taken to be unity [32]; but we allowed it to vary here in order to get better numerical agreement. The results of fitting of the experimental data obtained on uranium using Eq. (3.39) will be discussed later. However, it is useful to note that, since Eq. (3.39) is empirical in origin, it is not possible to provide a physicochemical basis for the cooling rate variation of parameter \( b \). The negative value of \( n \) arises from the fact that with positive values for the argument (\( T_s - T \)), the transformation extent \( X(T) \) increases with decreasing temperature.

The K-M equation was justified by Magee on phenomenological grounds in the following manner [33]. Magee assumed that in a finite temperature drop \( dT \), the number of new martensitic plates per unit volume of austenite \( dN \), is proportional to the increase in chemical driving force, \( \Delta G_v \). That is,

\[ dN = k_m d(\Delta G_v) \quad (3.40) \]

\( k_m \) is the proportionality constant for martensite transformation. If \( dy \) is the corresponding change in volume fraction of martensite in this temperature interval \( dT \), then,

\[ dy = VdN_v \quad (3.41) \]

\( V \), is the average volume of the newly formed plates, and \( dN_v \) is the change in the number of plates per unit volume. Setting \( dN_v/dN = 1-y \), we get,
\[ V(1 - y)k_m \Delta S_v (\Delta T). \]  
\[ (3.42) \]

In Eq. (3.42), we have used, \( d(\Delta G_v)/dT = \Delta S_v \) the entropy of transformation. Thus, in final analysis

\[ \int \frac{dy}{1 - y} = \int V k \Delta S_v \Delta T \]  
\[ (3.43) \]

Integration by variable separable, yields with the assumption that \( V k_m \Delta S_v \) is a constant and that \( dT = \Delta T = M_s - M_f \), the temperature interval between martensite start and finish temperatures. Thus,

\[ \ln(1 - y) = V k_m \Delta S_v [M_s - M_f]. \]  
\[ (3.44) \]

Thus, we get the K-M relation, with the tacit identification that \( V k_m \Delta S_v = b \), the K-M constant in the empirical equation. The effect of altering \( \beta \), the cooling rate has to do with the constant \( k_m \), since \( \Delta S_v \) and \( V \) are independent of thermal history. But this aspect is not probed in this study any further.

3.8. Quasi harmonic theory

In recent years many first principles and semi-empirical modelling methodologies have been developed alongside with advances in experimental techniques and these have been successfully applied for many metallic alloys to derive basic thermodynamic properties in a self-consistent manner [36-46]. Harmonic approximation given by Debye model has been widely used to calculate the vibrational free energy. But under harmonic approximation it has been assumed that the frequency of vibration is independent of volume as well the temperature and there is no inter-phonon interaction. The vibrational free energy can be expressed analytically by the phonon frequency alone. However, the harmonic approximation failed to explain thermal expansion. In order to explain anharmonicity, quasi-harmonic Debye-Grünesien formalism has been developed. This considers the volume dependence of frequencies but ignored the temperature effect on frequencies. Based on the knowing of the vibrational spectrum obtained by experiment or
calculated precisely with numerical methods such as density functional perturbation theory or frozen phonon method, quasi harmonic formalism has been found to reproduce thermodynamic properties quite consistently with experimental results. However, many investigations also discover that the quasi harmonic formalism is inadequate in the region of high pressure and high temperatures [36-50]. At high temperatures, the intrinsic phonon interaction (anharmonicity) neglected by quasi harmonic formalism becomes prominent in many materials. But as of today invoking the intrinsic anharmonicity in a rigorous way is quite difficult; however there is significant improvement in this field [36-50].

Accordingly, in the present study, we have adopted this method for obtaining reliable first-order estimates of thermal quantities, including heat capacity and thermal expansion in an integrated and self-consistent manner. In the following section, a brief familiarizing account of this formalism is provided.

The Debye-Grüneisen quasiharmonic formalism is quite a robust method for modelling the vibrational contribution to thermal properties and requires only standard input data [36-50]. The details of this model are adequately described by the monograph of Anderson, for example [45]; only a brief familiarizing account is given here. In essence, the quasi-harmonic approximation involves the treatment of the volume dependence of the vibrational frequencies through the Mie Grüneisen parameter $\gamma_G$ which has been brought into play for explaining the thermal expansion effects arising out of lattice anharmonicity. The Grüneisen parameter ($\gamma_G$) may be defined as [45].

$$\gamma_G = -\frac{d \ln \omega}{d \ln V} \approx -\frac{d \ln \theta_D}{d \ln V}. \quad (3.45)$$

In the above expression $\omega$ is frequency of lattice vibration, $\theta_D$ is Debye temperature and $V$ is (molar) volume of solid. Eq. (3.45) is an approximation to $\gamma_G$ under the validity of Debye model [45]. Basically $\gamma_G$ has been introduced to relate thermal properties with
elastic properties of materials [45]. In more basic way $\gamma_G$ can be defined as change in pressure of a material resulting from increase in energy density at constant volume.

$$\gamma_G = V \left( \frac{\partial P}{\partial E} \right)_V .$$  \hspace{1cm} (3.46)

Where $E$ stands for energy density, $V$ is molar volume and $P$ is pressure. If the change in pressure is exactly proportional to the change in energy density then $\gamma_G$ will be independent of both $P$ and $T$, and experiments show this to be nearly correct if one considers the case for the variation of $\gamma_G$ with $T$ at constant $V$. In fact, the proportionality constant usually lies between 1 and 2. Further, $\gamma_G$ can be expressed in terms of measured physical properties as follows.

$$\gamma_G = \left( \frac{\partial P}{\partial E} \right)_V = \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial E}{\partial T} \right)_V .$$  \hspace{1cm} (3.47)

Further, the numerator and denominator in Eq. (3.47) can be defined in the following forms.

$$\left( \frac{\partial P}{\partial T} \right)_V = \alpha_V B_T .$$  \hspace{1cm} (3.48)

$$\left( \frac{\partial E}{\partial T} \right)_V = C_V .$$  \hspace{1cm} (3.49)

With the help of Eqs.(3.46, 3.47, 3.48 & 3.49) we can get $\gamma_G$ in the following form.

$$\gamma_G = \frac{\alpha_V B_T V}{C_V} .$$  \hspace{1cm} (3.50)

In the above expression, $\alpha_V$ is the volume thermal expansivity, $B_T$ is the isothermal bulk modulus and $C_V$ is the isochoric or constant volume specific heat. Thus $\gamma_G$ given by Eq (3.50) is composed of individual measurable physical properties, each of which varies significantly with temperature, but the ratio of these properties as given by Eq. (3.50) does not vary greatly with temperature, and sometimes not at all.
The starting point of Debye-Grüneisen quasiharmonic formalism is that for a condensed system at equilibrium, the total pressure acting on the system $P$ is assumed to be composed of two components. Of these, the cold or potential pressure, corresponding to zero Kelvin temperature is a function of only volume. The other thermal pressure component (at fixed volume) is a function of only temperature. Thus,

$$P_{\text{total}} = P_o(V) + P_{\text{th}}(T,V). \quad (3.51)$$

Where $P_o$ is the zero Kelvin cold pressure arising due to cohesive forces of the solid, which can be expressed in terms of the Helmholtz free energy $F$ as follow.

$$P_o = -\left(\frac{\partial F}{\partial V}\right)_T. \quad (3.52)$$

It is clear from above equation that a complete description of $P_o$ could be obtained by calculating Helmholtz free energy as a function of volume at 0 K using a suitable ab-initio method or through semi-empirical inter atomic potential schemes or from suitable empirical P-V equations of state [44-46]. Irrespective of the methodology employed, it is clear that at equilibrium conditions,

$$dP = 0 \text{ and hence } P_o = P_{\text{th}}. \quad (3.53)$$

The thermal pressure can be estimated from the following fundamental thermodynamic identity given in Eq. (3.48) [42].

$$\left(\frac{\partial P_{\text{th}}}{\partial T}\right)_V = \alpha_v B_T = \gamma_v C_V / V. \quad (3.54)$$

It is true that in the real case $\gamma_v$ is temperature dependent [45-47], which can be treated accurately if details of experimental phonon spectrum data are available [45]. On the contrary, with little or no details of phonon dispersion, it is customary to neglect this temperature dependence of $\gamma_v$ in many first order calculations of thermal effects at moderate pressures [45]. Sometimes, $\gamma_v(V)$ dependence is also empirically approximated in terms of a simple power law, namely
\[(\gamma_o / \gamma_o) = \left( \frac{V_T}{V_o} \right)^q \quad (3.55)\]

In the above expression, \(\gamma\) is the reference volume Grüneisen parameter and \(q\) is the power law exponent [45]. In many simulations that \(q = 1\), is often assumed. However, in the present study, the thermal pressure component is treated in the following manner. Integrating Eq. (3.54) along the isotherm, one can write

\[\int dP = - \int \left( \frac{\alpha \gamma B_T}{V} \right) dT = - \int \left( \gamma_o \frac{C_V}{V} \right) dT. \quad (3.56)\]

By taking \((\gamma / V) = (\gamma_o / V_o)\), the value at the reference temperature of 298.15 K, it is easy to simplify the above approximation as follows.

\[P_o - P_{th} = \left( \frac{\gamma_o}{V} \right) \int C_V dT = \left( \frac{V_o}{V_o} \right) E_{vib} \quad (3.57)\]

In above expression \(E_{vib}\) is the internal energy, which is a function of volume and hence temperature. \(P_o\) can be expressed by adopting for example, the popular Murnaghan equation of state [45, 46], which considers the linear variation of the bulk modulus \(B_T\) with pressure with proportionality constant being the isothermal pressure derivative of bulk modulus \(B'_T\) [45]. It may be added that Murnaghan equation of state holds good only for small excursions from equilibrium volume. Finally at thermodynamic equilibrium the condition that \(P_o = P_{th}\), must hold good. Accordingly, the basic Mie-Grüneisen thermal equation of state can be re-expressed in the following manner [45].

\[V_T = V_o \left\{ \frac{E_{vib}}{Q_o - rE_{vib}} \right\} + 1 \quad (3.58)\]

More details on Mie-Grüneisen quasi-harmonic formalism can be obtained from the recent monograph of Anderson [45]. Where \(Q_o = B_o V_o / \gamma_o\) and \(r = (B'_T - 1)/2\); \(V_o\) is the volume, \(B_o\) is isothermal bulk modulus and \(B'_T\) is the pressure derivative of bulk modulus at 298.15 K. In order to evaluate the consistent temperature dependence of volume using
Eq. (3.58), one need to have accurate estimation of $E_{\text{vib}}$, $B_T$, $B'_T$ and $\gamma_G$, and these discussed in ensuing sections

3.8.1. Evaluation of vibrational energy

The internal energy and specific heat at constant volume can be described in terms of either Debye or Einstein model with a constant $\Theta_D$ or $\Theta_E$. Alternately one can incorporate the temperature dependence of $\Theta_D$ via Grüneisen parameter defined in Eq. (3.45) [45]. In the current study, we however adopted a constant value of $\Theta_D$ as this gives satisfactory results. The temperature dependence of $E_{\text{vib}}$ as well as $C_v$ have been estimated using the Debye formula [45]. The choice of this formula is that it satisfactorily approximates the integral especially at the low temperature. In terms of Debye model, the vibrational free energy can be written as [44-46]

$$E_{\text{vib}} = 9NK_B T \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D} D \left( \frac{x^3 dx}{e^x - 1} \right)$$

(3.59)

In above expression $x_D = \theta_D/T$ and $\theta_D$ is Debye temperature. The Debye temperature in the present study has been taken from the literature and preference is given for calorimetric based data. On the other hand, the estimation of other parameters namely, isothermal bulk modulus $B_T$, its pressure derivative $B'_T$ and Grüneisen parameter $\gamma_G$ are discussed in the following sections.

3.8.2. Estimation of isothermal bulk modulus and its pressure derivative

In order to obtain a reliable estimate of isothermal bulk modulus and its partial derivative first we have scrutinized the literature and given the priority to $P-V$ based data. The available $P-V$ data has been re-analyzed in the present study using linearized form of Murnaghan equation of state given by Smith [49]. Therefore, the advantage of this linear transformation of raw $P-V$ data is that appropriate choice of the empirical equation of state can be made for proper treatment of the experimental data. The equation which relates the scaled $P-V$ quantities is given below [48].
\[ P/\mu = (B_T)^{1/2} + s[P\mu]^{1/2}. \] (3.60)

In the above equation, \( \mu = 1 - V/N_o \) and \( s = (B_T' + 1)/4; \) \( V_o \) is the volume at atmospheric pressure, \( V \) is volume at any pressure \( P \).

In the second scheme we have collected the data on isothermal bulk modulus and corresponding lattice parameter for different homologous compounds. Based on previous systematic studies carried out on minerals [45], it is well known that bulk modulus and corresponding molar volume for homologous compounds or elements obey the following relation.

\[ B_T V^n \equiv \text{constant} \] (3.61)

The above equation holds good for many isostructural elementals and compounds.

3.8.3. Estimation of Grüneisen parameter

The other important quantity required for calculating the temperature dependence of volume under Debye-Grüneisen formalism is the Grüneisen parameter (\( \gamma_G \)). There are various methods which have been adopted to calculate \( \gamma_G \) in terms of experimentally measured thermo physical properties or based on lattice dynamics [45]. There are two types of Grüneisen parameters one of which is known as macroscopic or thermal Grüneisen parameter and other is referred as microscopic Grüneisen parameter. Thermal Grüneisen parameter can be evaluated either in terms of macroscopic first order properties that includes heat capacity, thermal expansivity, bulk modulus and molar volume or in terms of equation of state properties such as pressure derivative of bulk modulus [45]. Thus, Grüneisen parameter in terms of macroscopic physical properties can be written as follows [43].

\[ \gamma_G = \alpha_B B_T V / C_V = \alpha_B B_S V / C_p. \] (3.62)

On the other hand if one considers the theory of lattice dynamics then the Grüneisen parameter can be evaluated in terms of intrinsic elastic constants. In the
present case for evaluating \( \gamma \), the famous equation of state known as Slater formula which has been employed and the respective formula can be written as follow.

\[
\gamma^G = \frac{1}{2} \left( \frac{dB^T}{dP} \right) - \frac{1}{6}
\]  

(3.63)

If for a given material \( B^T \) is known then \( \gamma \) can be calculated using above equation.

3.8.4. Calculation of thermal expansivity and heat capacity

Having thus estimated all the required quantities, the temperature dependence of volume can be calculated using Eq. (3.58). Further from the derivative of Eq. (3.58) gives thermal expansivity data and it is expressed in Eq. (3.64).

\[
\alpha_V = \left[ \frac{(Q_o C_V)}{\{r(r - 1)E_{vib}^2 - Q_o E_{vib}(2r - 1) + Q_o^2\}} \right].
\]

(3.64)

Subsequent to the estimation of thermal expansion, the harmonic contribution to isochoric heat capacity \( C_{hv} \) has been estimated from the temperature derivative of Eq. (3.59). The dilatational and the electronic contributions to heat capacity have been estimated from the following relation [45].

\[
C_p = C_{hv} (1 + \alpha_V \gamma^G T) + \Gamma_e T.
\]

(3.65)

The last term, \( \Gamma_e T \) accounts for the small, linear electronic contribution to the heat capacity. The details regarding the actual implementation of Debye-Gruneisen model for obtaining self consistent estimates of thermal expansion and heat capacity for UFe\(_2\) and URh\(_3\) intermetallic compounds are presented in Chapter 7.
3.9. References