Chapter 2

Recent Trends in Solid State Kinetics

2.1 Introduction

Solid state kinetics or heterogeneous kinetics has always been a unique and complex area of research and been subjected to heating debates and controversies. All these controversies can be attributed to the fact that most of the principles in heterogeneous kinetics were adopted from those of homogeneous or solution kinetics. Many methods have been developed during the past few years to study the solid state kinetics. The very first work on the kinetic studies of thermal decomposition was carried out by Kujirai and Akahira in 1925. Afterwards a number of methods have been proposed for the kinetic analyses of thermal decomposition using data obtained from thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) in addition to variety of other methods. Both isothermal and nonisothermal methods were employed to study the kinetics. The nonisothermal methods have the advantage that all the interesting information could be obtained from a single experimental run.

The techniques that can be used to study solid state kinetic data can be classified according to the experimental conditions selected and the mathematical techniques performed. Experimentally isothermal or nonisothermal methods are employed. The mathematical methods employed can be model fitting, single heating rate or the isoconversional methods.
Among these, model fitting methods were the first and most popular method. Single heating rate methods that do not evolve any mechanism functions were also used to study the kinetics.

Even though model-free isoconversional methods have existed in thermal analysis community over many years, only with the International Confederation for Thermal Analysis and Calorimetry (ICTAC-2000) meeting these methods have come to light as a heated discussion among the practitioners of thermal analysis. Since then ample number of literature have appeared in favour of this school of thought. Model-free approaches can be recommended as a trust worthy way of obtaining reliable and consistent kinetic information from both isothermal and nonisothermal data. The important features of model-free methods are that it allows kinetic predictions to be accomplished without evaluating the reaction model and pre-exponential factor. Besides, these methods allow the activation energy to be determined as a function of the extent of conversion.

Isoconversional methods are the representatives of the model-free methods. In the isoconversional methods, the kinetic analysis is carried out over a set of kinetic runs at a fixed value of conversion function. Under these conditions the value of conversion function ($\alpha$) is constant and the reaction rate is a function of temperature only.

This review is an attempt to summarize the methods that have been employed to investigate kinetic analysis of solid state reactions that appear in the recent literature. The review focuses on the isoconversional methods as well as the complementary techniques which are usually employed along with the isoconversional methods. An account on the
conventional single heating rate methods like CR, MKN, HM and MT which are employed in the present investigation and some solid state reaction models are also given in this chapter.

This review is not a comprehensive one rather it provides general information on the recent trends in the literature for the investigation of solid state kinetics using thermo analytical methods.

2.2 Single Heating Rate Methods (non-mechanistic equations)

Conventional methods including the non-mechanistic equations and mechanism based equations to solve the solid state kinetics were reviewed by S. Mathew. In earlier times single heating rate methods were used predominantly to study the solid state kinetics. Several methods have been proposed in this regard. Many of these methods are based on the approximation which can lead to errors. Consequently even with the same experimental data, different evaluation methods may result in different values for the kinetic parameters \( i.e. \) \( E, A \) and \( n. \) All these methods do not evolve mechanism of solid state reactions. It would appear that overwhelming consensus of opinion is that these discrepancies are due to mathematical approximations and not to any flaw in the mathematical method. The basic rate equations in the heterogeneous kinetics can be written as

\[
\frac{d\alpha}{dt} = Ae^{\frac{E}{RT}}(1-\alpha)^n
\]  

(1)

For a linear heating rate, \( T = T_0 + \phi t, \) where \( T_0 \) is the temperature of inception of reaction and \( \phi \) is the heating rate defined by the eqn (2)
\[ \frac{dT}{dt} = \phi \] (2)

Combining eqns (1) and (2), one gets

\[ \frac{d\alpha}{dT} = \frac{A}{\phi} e^{\frac{E}{RT}} (1 - \alpha)^n \] (3)

Eqn (3) may be considered as a general equation relating the parameters \( A \), \( E \) and \( n \). Several authors have given the solution of eqn. (3) in simpler and more practically useful form for calculating the kinetic parameters for the thermal decomposition of solid state reaction of the type

\[ A \text{ (s)} \rightarrow B \text{ (s)} + C \text{ (g)} \]

For monitoring the reaction from mass loss, various forms such as concentration \( C \), weight fraction \( W \), number of atoms \( N \) and volume fraction \( V \) have been used. However, for uniformity a dimensionless quantity, the fractional decomposition \( \alpha \), which at time \( t \) is defined as the fraction of the sample decomposed, is employed.

Therefore,

\[ \alpha = \frac{w_t}{w_\infty} = \left( \frac{m_0 - m_t}{m_0 - m_\infty} \right) \] (4)

where,

\( w_t = \) mass loss at time \( t \)

\( w_\infty = \) maximum mass loss in the TG experiment for the reaction under investigation

\( m_0 = \) initial mass of the sample
$m_t$ = the mass at time $t$ and

$m_\infty$ = the mass at the end of the reaction

Most of the methods for obtaining the kinetic parameters utilise

\begin{align*}
\text{equations (1) or (3) in some form or the other. Three different approaches have been made in this context.}^{15}
\end{align*}

(a) Differential methods
(b) Integral methods
(c) Approximation methods

Among the non-mechanistic equations we have employed four integral methods viz., CR, HM, MKN and MT equations for the present investigation. Hence brief discussions on these methods are attempted.

2.2.1 *Coats-Redfern equation*

Coats and Redfern\textsuperscript{16} evaluated the temperature integral with the aid of Rainville function.\textsuperscript{17} The temperature integral in the right hand side of the following equation

\begin{align*}
\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} &= A \frac{\gamma - E}{\phi R^2 \gamma} d\gamma = A \frac{\gamma - E}{\phi R^2 \gamma} d\gamma \\
&= \frac{\gamma}{\phi R^2 \gamma} d\gamma
\end{align*}

may put in the following form.

\begin{align*}
\frac{AE}{\phi R} \int_0^\infty \frac{e^{-x}}{x^2} dx
\end{align*}

where, $x = \frac{E}{RT}$
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The L.H.S of the equation (5) can be integrated to get the expression,
\[ 1 - (1 - \alpha)^{1 - n} / (1 - n) \] for \( n \neq 1 \) and when \( n = 1 \), the LHS becomes \(-\ln (1 - \alpha)\).

For convenience, this expression will be denoted hereafter by \( g(\alpha) \), where
\[ g(\alpha) = 1 - (1 - \alpha)^{1 - n} / (1 - n) \] (7)

Equation (5) can be written as
\[ g(\alpha) = \frac{A^T}{\phi} \int_0^T e^{-\frac{E}{RT}} dT \] (8)

Using Rainville function, the RHS can be transformed into
\[ \left( \frac{AR}{\phi E} \left( 1 - \frac{2RT}{E} \right) \right) T^2 e^{-\frac{E}{RT}} \] (9)

Combining and rearranging eqns. (5), (7) and (9) we get

\[ g(\alpha) = \left( \frac{AR}{\phi E} \left( 1 - \frac{2RT}{E} \right) \right) T^2 e^{-\frac{E}{RT}} \] (10)

or on linearization

\[ \ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \left( \frac{AR}{\phi E} \left( 1 - \frac{2RT}{E} \right) \right) - \frac{E}{RT} \] (11)

Equation (11) is the Coats-Redfern equation. These authors have shown that for the usual value of \( E \) and temperature range over which reaction generally occurs, the term \( \ln \left( \frac{AR}{\phi E} \left( 1 - \frac{2RT}{E} \right) \right) \) is ‘sensibly constant’ since \( 2RT/E \ll 1 \). A plot of \( \ln \left[ \frac{g(\alpha)}{T^2} \right] \) versus \( 1/T \) would, therefore, be linear. \( E \) and \( A \) can be calculated from the slope and the intercept of the
linear plot. These authors have recommended a trial and error method for
determining the form of g(α), i.e. the value of the ‘n’ is determined by
trial and error. This drawback has been overcome by the use of iteration
methods to get the best fit value of ‘n’ with the aid of a computer.

2.2.2 MacCallum-Tanner equation

To simplify the tedious numerical procedures, MacCallum and Tanner\textsuperscript{13}
used Zsako’s tabulated values and have shown graphically that

1. –log p(x) is a linear function of 1/T , i.e. –log p(x) = X + a/T ,
   where X = intercept and a = slope

2. ‘a’ is a linear function of E, i.e. a = Y + bE, where Y = intercept and
   b = slope

3. log X is a linear function of log E,

   i.e. log X = log Z + c log E, where c and Z are constants.

Therefore –log p(x) = ZE\textsuperscript{C} + (Y +bE)/T

Substituting the evaluated constants, these authors obtained the equation

\[-\log p(x) = 0.483E^{0.435} + \frac{(0.449 + 0.217E \times 10^3)}{T} \]  (13)

Introducing the equation in the logarithmic form of the following eqn.,

\[ g(\alpha) = \left( \frac{AE}{\phi R} \right) = \int x \left( \frac{e^{-x}}{x^2} \right) dx = \left( \frac{AE}{\phi R} \right)[p(x)] \]  (14)

we get the final form of MacCallum-Tanner equation

\[ \log g(\alpha) = \log \left( \frac{AE}{\phi R} \right) - 0.483E^{0.435} \times \frac{(0.449 + 0.217E \times 10^3)}{T} \]  (15)

In this method, the order of the reaction must be determined correctly by
the trial and error method.
2.2.3 Madhusudanan–Krishnan–Ninan equation

Here a two term series approximation\(^{18}\) for solving the Arrhenius temperature integral \(p(x)\) in the following form is used

\[
p(x) = \frac{e^{-x}}{x^2} \left( \frac{x+1}{x+3} \right)
\]

(16)

The values of \(p(x)\) have been computed for a wide range of temperatures (T) and activation energy (E) values covering many of the condensed phase decomposition reactions.

They showed that \(\ln p(x)\) is a linear function of \(x\) and the slope and the intercept of \(\ln p(x)\) versus \(x\) plots are linear functions of \(1/x\) and \(\ln(x)\) respectively. Combining these, eqn. (17) is obtained

\[
\ln p(x) = a + b + c \ln x
\]

(17)

Substituting the numerical values of \(a\), \(b\) and \(c\), we get the MKN equation,

\[
\ln \left( \frac{g(\alpha)}{T^{1.9215}} \right) = \ln \left( \frac{AE}{\phi R} \right) + 3.7721 - 1.9215 \ln E - \frac{0.12039E}{T}
\]

(18)

The kinetic parameters were calculated from the linear plot of the left hand side of the equation against \(1/T\). The values of \(E\) and \(A\) were evaluated from the slope and the intercept respectively.

2.2.4 Horowitz–Metzger equation

Horowitz–Metzger\(^{19}\) made reasonable approximations for the term \(\text{exp}(-E/RT)\) in order to integrate it in the closed form. The equation defines a term \(\theta\), which is related to the inflection temperature, \(T_s\) and temperature under consideration, \(T\) as

\[
T - T_s = \theta
\]

(19)

Where \(\theta\) is a parameter. Assuming \(\theta/T_s \ll 1\), it can be shown that
\[
\frac{1}{T} = \frac{1}{(Ts + \theta)} \approx \frac{1}{Ts \left(1 + \frac{\theta}{Ts}\right)} \approx \frac{1}{Ts} \left(1 - \frac{\theta}{Ts}\right) \quad (20)
\]

Substituting, eqn. (20) in the exponential integral

\[
\int_{0}^{T} e^{-\frac{E}{RT}} dT = \int_{0}^{\theta} e^{-\frac{E}{RT_s}} \left(1 - \frac{\theta}{T_s}\right)^2 d\theta = \frac{RT_s}{E} e^{-\frac{E}{RT_s}} \left(1 - \frac{\theta}{T_s}\right) \quad (21)
\]

Substituting this in eqn. (5),

\[
g(\alpha) = \left(\frac{ART_s^2}{\phi E}\right) e^{\frac{E}{RT_s}} \left(1 - \frac{E \theta}{RT_s^2}\right) \quad (22)
\]

Taking logarithm

\[
\ln g(\alpha) = \ln \left(\frac{ART_s^2}{\phi E}\right) - \frac{E}{RT_s} + \frac{E \theta}{RT_s^2} \quad (23)
\]

A plot of \(\ln g(\alpha)\) versus \(\theta\) will yield a straight line with slope \(= \frac{E}{RT_s^2}\).

Knowing the value of \(E\), \(A\) can be calculated from the above equation.

These authors have also derived the relation \(n = (1 - \alpha_s)^{(1-n)}\) from which \(n\) can be calculated.

The major disadvantage of this method is its dependence on \(T_s\) which is influenced by procedural factors such as sample mass, heating rate etc.

2.3 Model Fitting Methods

Usually the model fitting method can be carried out using Coats Redfern method.
Model fitting method makes use of the equation

\[ \int_0^a \frac{d(\alpha)}{f(\alpha)} = g\alpha = \int_0^r \frac{A}{\phi} \exp\left(-\frac{E}{RT}\right) dT \]  

(24)

where, \( g(\alpha) \) is the reaction model that represents a certain solid-state mechanism. The reaction model may have various forms of \( g(\alpha) \) as given in Table 2.1. The mechanism is obtained by fitting the experimental data into these models and the equation which gives the best fit \( i.e \) with maximum correlation coefficient is selected. The Coats-Redfern method was used for solving the equation. Linear plots of given models of \( \ln g(\alpha)/T^2 \) versus \( 1/T \) were drawn for each model by the method of least squares (where \( g(\alpha) \) is the integral form of \( f(\alpha) \), the reaction model) and the corresponding correlation coefficients were also evaluated. \( E \) and \( A \) were calculated in each case from the slope and the intercept respectively.

### Table 2.1

<table>
<thead>
<tr>
<th>Eqns no</th>
<th>Form of ( g(\alpha) )</th>
<th>Rate controlling process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \alpha^2 )</td>
<td>One dimensional diffusion</td>
</tr>
<tr>
<td>2</td>
<td>( \alpha + (1-\alpha) \ln (1-\alpha) )</td>
<td>Two dimensional diffusion</td>
</tr>
<tr>
<td>3</td>
<td>( [1-(1-\alpha)^{1/3}]^2 )</td>
<td>Three dimensional diffusion, spherical geometry: Jander equation</td>
</tr>
<tr>
<td>4</td>
<td>( (1-2/3 \alpha)(1-\alpha)^{2/3} )</td>
<td>Three dimensional diffusion, spherical symmetry: Ginstling – Brounshtein equation</td>
</tr>
<tr>
<td>5</td>
<td>( -\ln (1-\alpha) )</td>
<td>Random nucleation, one nucleus on each particle: Mampel equation</td>
</tr>
<tr>
<td>6</td>
<td>( [-\ln (1-\alpha)]^{1/2} )</td>
<td>Random nucleation, Avrami equation I</td>
</tr>
<tr>
<td>7</td>
<td>( [-\ln (1-\alpha)]^{1/3} )</td>
<td>Random nucleation, Avrami equation II</td>
</tr>
<tr>
<td>8</td>
<td>( 1-(1-\alpha)^{1/2} )</td>
<td>Phase boundary reaction, cylindrical symmetry</td>
</tr>
<tr>
<td>9</td>
<td>( 1-(1-\alpha)^{1/3} )</td>
<td>Phase boundary reaction, spherical symmetry</td>
</tr>
</tbody>
</table>
In solid state kinetics, mechanistic interpretation usually involves identifying a reasonable reaction model. A model is a theoretical, mathematical representation of what occurs experimentally. In solid state reaction, a model can describe a particular reaction type and translate that mathematically into a rate equation. Many models have been proposed in solid state kinetics and these models have been developed on the basis of certain mechanistic assumptions. Other models are more empirically based and their mathematics facilitates data analysis with little mechanistic meaning. Therefore different rate expressions are produced from these models.

The mechanism of a reaction is a detailed description of the molecular events which corresponds to the progress along the reaction coordinate \( i.e. \) molecular changes, atom reorganisation, which account for the transformation of reactants to products.

Solid state reactions are generally heterogeneous in character. Rate coefficients measured for homogeneous reactions include the variations in the concentrations of reactants, which results from the chemical change. In heterogeneous reactions, rate coefficients include no such consideration of the frequency of occurrence of reaction conditions per unit volume; but it incorporates the geometric changes during reaction. Therefore, the rate of product formation at advancing interface may depend on the effective area and surface concentration of reactants or intermediates. The availability of the active species within the active region may be controlled by the intermediate formation, reactant dissociation and reactant mobility. Hence, the reaction probability depends on both
effective area of heterogeneous interface and the reactivities, number and disposition of participants.

2.3.1 Model classification

Models are either classified in terms of the shape of isothermal curves or mechanistic assumptions. Depending on the shape, there may be acceleratory (in which the reaction rate is increasing), deceleratory (rate decreases as reaction progress), linear (rate remains constant) and sigmoidal. Depending on the mechanisms there may be nucleation, geometric contraction, diffusion and reaction order.\textsuperscript{21}

2.3.2 Model derivation

Sestak and Breggren\textsuperscript{23} have suggested a mathematical form that represents all the models in a single general expression.

\[ g(\alpha) = \alpha^m (1-\alpha)^n (-\ln(1-\alpha))^p, \]  

(25)

where m, n and p are constants. By assigning values for these three variables, any model can be generated. Table 2.1 lists some of the common models employed in the kinetic studies.

2.3.2.1 Nucleation and growth models

The kinetics of many of the solid state reactions can be explained on the basis of nucleation model. Specifically the Avrami models. The imperfections in the solids due to dislocation, cracks, point defect etc. act as the sites for nucleation since the activation energy is minimised in these regions. These sites are called nucleation sites have abnormal environment; they are the sites of crystal imperfections. Decomposition of the solids is favoured here due to the relatively low energy of activation (a
consequence of the strain) required at these sites. The germ nuclei then grow to become the growth nuclei as the decomposition progresses.\textsuperscript{24}

Nucleation has been shown to be a surface phenomenon associated essentially with some surface defects.\textsuperscript{25-26} All thermal decomposition involves nucleation. Experiments have shown that the concentration of the germ nuclei and consequently the rate of nuclei formation depends on the method of preparation, particle size and shape, exposition of the sample to UV or other high energy radiation etc. \textit{i.e.} on the history of the sample.\textsuperscript{27-29}

Avrami\textsuperscript{30} has considered, in solid state reaction, where the rate is governed by the growth of nuclei along the three crystallographic axes and arrived different expressions for the growth of nuclei. They are

For two dimensional growth of nuclei
\[-\ln(1 - \alpha) = kt^2\] \hspace{1cm} (26)

and for three dimensional growth
\[-\ln(1 - \alpha) = kt^3\] \hspace{1cm} (27)

The general form of the Avrami equation is
\[-\ln(1 - \alpha) = kt^n\] \hspace{1cm} (28)

Erofeev\textsuperscript{31} has derived the expression similar to the above equation as
\[-\ln(1 - \alpha) = (kt)^n\] \hspace{1cm} (29)

An alternate approach was made by Mampel\textsuperscript{32} to the problem of ingestion and overlap of nuclei. He considered that each particle in the solid may be nucleated with equal probability. The formation of nuclei (those nuclei
which undergo two dimensional surface growth) can be thought of as a random throwing of discs on to a plane surface. The fraction of the reactant undecomposed at any time corresponds to the uncovered portion of the plane surface. Discs falling within other discs are considered as full-grown nuclei or phantom nuclei and discs which cover one another partially are considered as overlapping nuclei. For particles of small radius, Mampel obtained the relation

\[-\ln(1 - \alpha) = kt\]  

(30)

For highly dispersed systems where random nucleation results in only a single nucleus per particle, the kinetics is described by the above unimolecular law.

2.3.2.2 Geometrical contraction (R) models (Phase Boundary)

These models assume that nucleation occurs rapidly on the surface of the crystal. The rate of degradation is controlled by the progression of the resulting reaction interface towards the centre of the crystal. Depending on the crystal shape, different mathematical models may be derived.

For any crystal particle following relation is applicable

\[r = r_0 - kt\]  

(31)

where \(r\) is the radius at time \(t\), \(r_0\) is the radius at time \(t_0\) and \(k\) is the reaction rate constant. If a solid particle is assumed to have cylindrical or spherical/cubical shape, the contracting cylinder (contracting area) or contracting sphere/cube (contracting volume models) respectively can be derived.
For solid particle with cylindrical symmetry, contracting cylinder model can be applied. The reaction is

\[ 1 - (1 - \alpha)^{\frac{1}{2}} = k_0 t \]  

(32)

For a particle with spherical or cubical shape, contracting volume model can be applied. For this the equation is

\[ 1 - (1 - \alpha)^{\frac{1}{3}} = k_0 t \]  

(33)

2.3.2.3 Diffusion models (D)

For a large number of heterogeneous reactions, the rate controlling process is diffusion. Diffusion may take place either through normal crystal lattice of the product phase or along the crystal surfaces and channels or fissures of imperfect product crystals.\(^ {34} \)

For a one dimensional plane, where the conversion factor (\( \alpha \)) is directly proportional to the product layer thickness,\(^ {35} \) the equation which represents one dimensional diffusion (D1) is

\[ \alpha^2 = kt \]  

(34)

The three dimensional diffusion models can be constructed on the assumption that, the solid particle is spherical in shape. The equation which represents the three dimensional diffusion (D3) is

\[ (1 - (1 - \alpha)^{\frac{1}{3}})^2 = kt \]  

(35)

This equation represents the Jander\(^ {36} \) model.

If a solid particle is cylindrical in shape and the diffusion occurs radially through a cylindrical shell with an increasing reaction zone, a two
dimension diffusion (D2) model can be derived. The equation can be represented as

\[ \alpha + (1 - \alpha) \ln(1 - \alpha) = kt \]  

Ginstling and Bounstein proposed another equation for three dimensional diffusion, discarded the concept parabolic law which holds only at low conversion values. The equation for D4 model is

\[ 1 - \frac{2}{3} \alpha - (1 - \alpha)^{\frac{3}{2}} = kt \]  

Diffusion can also be represented as JMAEK models \[ \left[-\ln(1 - \alpha)^n\right]^{\frac{1}{n}} \], where n becomes 1.5 (one dimension), 2 (two dimensions), 2.5 (three dimensions).

2.3.2.4 Order based (F) models

Order based models are the simplest models as they are similar to those used in homogeneous kinetics. In these models, the reaction rate is proportional to concentration, amount or fraction remaining of reactants raised to a particular power, which is the reaction order. Order based models are derived from the following general equation

\[ \frac{d\alpha}{dt} = k(1 - \alpha)^n \]  

where \( \frac{d\alpha}{dt} \) is the rate of the reaction, k is the rate constant and n is the reaction order. If \( n = 0 \), the zero order model (F0) model is obtained,

\[ \frac{d\alpha}{dt} = k \]
After separating the variables and integrating the equation becomes

$$\alpha = kt$$  \hspace{1cm} (40)

If $n = 1$, the first order model (F1) is obtained

$$\frac{d\alpha}{dt} = k(1-\alpha)$$  \hspace{1cm} (41)

Separating the variables and integrating the equation, we get

$$-\ln(1-\alpha) = kt$$  \hspace{1cm} (42)

The first order model is also called Mampel model, is a special case of the Avrami–Erofeev (A) models where $n = 1$. Similarly, second order ($n = 2$) and third order ($n = 3$) are obtained.

### 2.3.3 Drawbacks of model fitting method

Model fitting methods yield single value of activation energy which cannot account for the variation of activation energy due to the complexity of the solid state reaction. The values obtained by these methods are averages that do not reflect changes in the kinetics and mechanism with the temperature and the extent of conversion. Model fitting methods yield different values of kinetic parameters for the isothermal and non isothermal data.\(^{40}\)

### 2.4 Isoconversional Methods

It is well known that real solid state reactions are too complex to be described by single pair of Arrhenius parameters and the traditional set of reaction models. This has inspired the development of new computational techniques that facilitate the detection of multi step kinetics. Isoconversional method employ multiple temperature program (\(e.g.\)
different heating rates and/or temperatures), because this is the only practical way to obtain data on varying rates at a constant extent of conversion. The isoconversional methods require the knowledge of temperatures $T_\alpha$ at which an equivalent stage (i.e. the stage at which a fixed amount is transformed) of reaction occurs for various heating rates.

Although it had been known since the work of Flynn and Wall that the variation of $E$ was a sign of the process complexity, the $E$ dependencies were not exploited. The full potential of the isoconversional methods has been appreciated as Vyazovkin\textsuperscript{7} brought analysis of the $E$ dependences to the forefront and demonstrated that they can be used for exploring the kinetic scheme of the processes.

The methods take their origin in the single-step kinetic equation

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha)$$  \hspace{1cm} (43)

and make use of the isoconversional principle which states that at a constant extent of conversion, the reaction rate is a function only of the temperature. i.e.

$$\left[ \frac{d\ln(d\alpha / dt)}{dT^{-1}} \right] = \left[ \frac{d\ln k(T)}{dT^{-1}} \right] + \left[ \frac{df(\alpha)}{dT^{-1}} \right] = -\frac{E}{R}$$  \hspace{1cm} (44)

In the above equations $A$ and $E$ are Arrhenius parameters (the pre-exponential factor and the activation energy, respectively), $f(\alpha)$ is the reaction model, $R$ is the gas constant, $T$ is the temperature, $t$ is the time and $\alpha$ is the extent of conversion, which can be determined from TG runs as a fractional mass loss or from DSC runs as a fractional heat release.
The application area of isoconversional analysis has been growing quickly and currently covers a variety of thermally stimulated processes such as decomposition,\textsuperscript{41-50} cure kinetics,\textsuperscript{51-55} crystallisation of glasses\textsuperscript{56-57} as well as of crystallization of polymer melts.\textsuperscript{58-59} It can also be used for obtaining reliable and consistent kinetic data for the pyrolysis of cellulose,\textsuperscript{60} combustion of bio waste,\textsuperscript{61} co-combustion of sewage sludge with straw and coal,\textsuperscript{62} pyrolysis of oil sludge,\textsuperscript{63} wheat straw,\textsuperscript{64} crystallisation kinetics of alloys\textsuperscript{65-66} and combustion of heavy hydrocarbons.\textsuperscript{67}

Recent applications of isoconversional kinetic analysis involve physical aging of glass,\textsuperscript{68} thermal denaturation of collagen,\textsuperscript{69} physical gelation of a gelatin solution and melting of gelatin gel.\textsuperscript{70-72}

In the solid state reactions, a variation in activation energy occurs due to the complex reaction mechanism. Often in a solid sample the reacting entities strongly interact with the neighbouring molecules or particles. Therefore during such a reaction, reactivity may change due to the processes like product formation, crystal defect formation and intra-crystalline strain. Solid state reactivity could also be affected by experimental variables that would change the reaction kinetics. If two or more elementary steps, each having unique activation energy affect the rate of product formation, the reaction is usually considered complex. In such a reaction, a change in activation energy as the reaction progresses would be observed.\textsuperscript{73}

The shapes of the dependence of $E$ on $\alpha$ have been identified for competing,\textsuperscript{74} independent,\textsuperscript{75} consecutive\textsuperscript{76} and reversible\textsuperscript{77} as well as reactions complicated by diffusion.\textsuperscript{78} An increasing dependence of $E$ on $\alpha$ indicates the reaction is competing, independent or consecutive reaction.
These types of reactions are usually observed in the thermal decomposition of polypropylene. The dependence of $E$ on $\alpha$ characteristic of consecutive reaction is also applicable to processes proceeding with a change over from a kinetic to diffusion regime. Such type of reactions usually occurs in reaction like solid $\rightarrow$ solid + gas. The decreasing dependence of $E$ on $\alpha$ corresponds to the kinetic scheme of an endothermic reversible reaction followed by an irreversible reaction. The dehydration reactions in crystal hydrates in Fig. 2.1 as well as other processes involving a reversible step demonstrate these type of reactions.

![Dependence of E on alpha for the dehydration of calcium oxalate monohydrate](image)

**Fig. 2.1.** Dependence of $E$ on $\alpha$ for the dehydration of calcium oxalate monohydrate

If the activation energy remains constant with conversion, the reaction is considered to be a single step reaction and in this case model fitting method can be applied to predict the mechanism of reaction. B. Jankovic and co-workers have employed both model fitting and model-free method to study the dehydration of swollen poly(acrylic acid) hydrogel. In this report conventional model fitting method was employed in the $\alpha$ range 0.5 to 0.9 where the activation energy $E$ was found to be constant. Kinetic
analysis of solid and liquid ammonium nitrate by model-free revealed that E is constant with conversion with a value of 90 kJ mol$^{-1}$ and model fitting method was employed to find the mechanism of the reaction and it was found that the dissociation followed a contracting cylinder model. Various dependencies of E on $\alpha$ and an algorithm to find out the complex solid state processes are given in Fig. 2.2 and 2.3.

Fig. 2.2. Dependence of E on $\alpha$ for various reactions (1) complex process involving competitive reaction (2) reversible reaction (3) reaction complicated by diffusion.
Chapter 2

Fig. 2.3. The algorithm for solving the inverse kinetic problem for some typical cases of complex processes

The commonly employed isoconversional methods are Friedman, $^{84}$ FWO$^{85-86}$ and KAS.$^{87-88}$ Among these FWO is one of the most used methods and has received more than 450 citations. Model-free isoconversional methods can be classified as differential and integral methods based on approximation and equations which do not make use of approximation.

2.4.1 FWO equation

Flynn-Wall$^{85}$ and Ozawa$^{86}$ independently developed an isoconversional method for nonisothermal data, which is commonly referred to as FWO method. This is based on the nonisothermal rate equation

$$\frac{d\alpha}{dT} = \frac{A}{\phi} e^{-\frac{E}{RT}} f(\alpha)$$

(45)

The integral form of the above equation can be written as

$$g(\alpha) = \frac{A}{\phi} \int_{0}^{T} \exp\left(-\frac{E}{RT}\right) dT = \frac{AE}{\phi R} p(x)$$

(46)
Where $g(\alpha) = \frac{\alpha}{\int_0^\alpha f(\alpha)}$, $x = \frac{E}{RT}$ and $p(x)$ is the temperature integral.

Substituting Doyle’s approximation $p(x) \equiv \exp(-1.0518x - 5.331)$ (47) in eqn. (46) and rearranging we get the FWO equation as

$$\ln \phi = \ln \left(\frac{AE}{R}\right) - \ln g(\alpha) - 5.331 - 1.052 \frac{E}{RT}$$ (48)

Thus for a constant value of $\alpha$, the plot of $\ln \phi$ versus $1/T$, gives a straight line with a slope $-1.052E/R$, from which activation energy can be calculated.

2.4.2 Friedman equation

This is a differential method and was one of the first isoconversional methods. The equation is

$$\ln \left(\frac{d\alpha}{dt}\right) = \text{const} - \frac{E}{RT}$$ (49)

The plot of $\ln \left(\frac{d\alpha}{dt}\right)$ against $1/T$ should be a straight line, with slope as $-\frac{E}{R}$, from this we can evaluate the activation energy.

2.4.3 Kissinger-Akahira-Sunose equation (KAS)

This method is based on the Coats Redfern approximation

$$p(x) = \frac{\exp(-x)}{x^2}$$ (50)

$x$ being equal to $\frac{E}{RT}$.

From the eqns (43) and (47) it follows that

$$\ln \frac{\phi}{T^2} = \ln \left(\frac{AE}{Eg(\alpha)}\right) - \frac{E}{RT}$$ (51)
For a constant value of $\alpha$, the plot of $\ln\left(\frac{\phi}{T^2}\right)$ against $1/T$ gives slope as $-\frac{E}{R}$, from this we can estimate the activation energy.

### 2.4.4 Li and Tang equation\(^{90-91}\)

This equation does not make use of any approximation of the temperature integral. The equation can be written as

$$\int_{0}^{\alpha} \ln\left(\frac{d\alpha}{dt}\right) d\alpha = G(\alpha) - \frac{E}{R} \int_{0}^{\alpha} \left(\frac{1}{T}\right) d\alpha$$

(52)

Where $G(\alpha) \equiv \alpha \ln A + \int_{0}^{\alpha} \ln f(\alpha) d\alpha$

(53)

A plot of $\int_{0}^{\alpha} \ln\left(\frac{d\alpha}{dt}\right) d\alpha$ versus $\int_{0}^{\alpha} \left(\frac{1}{T}\right) d\alpha$, at a given $\alpha$, for a set of heating rates, will yield a slope equal to $-\frac{E}{R}$.

### 2.4.5 Advanced isoconversional equation

The isoconversional equation developed by Vyazovkin\(^{92}\) has been extensively used to study the kinetics.\(^{50,62,66,93-97}\) The method avoids the inaccuracies associated with analytical approximations of the temperature integral.

For a set of ‘m’ experiments carried out at different heating rates the activation energy can be determined at any particular value of alpha by finding the values of $E(\alpha)$ for which the function
\[
\sum_{i \neq j} \sum_{m} \left[ \frac{I(E_i, T_{ij}) \beta_j}{I(E_i, T_{ij}) \beta_j} \right] = \Omega
\] (54)

is a minimum. The minimisation procedure can be repeated for each value of \( \alpha \) and hence the dependence of \( E \) on \( \alpha \) can be studied. The values of \( I(E,T) \) may be found by numerical integration as well as with the help of Senum–Yang approximation.\(^9^8\)

Later Vyazovkin\(^9^9\) modified the above equation to account for the random temperature variation. This modified method is not limited to linear heating programs and can be used to analyze kinetics from a non linear heating program. The equation can be represented as

\[
\sum_{i \neq j} \sum_{m} \left[ \frac{J(E_i, T_j(t_{ij}))}{J(E_i, T_j(t_{ij}))} \right] = \Omega
\] (55)

Vyzovkin introduced further modification to the isoconversional method.\(^1^0^0\) This method involves integration over smaller time intervals and the modified equation can be represented as

\[
\sum_{i \neq j} \sum_{m} \left[ \frac{J'(E_i, T_j(t_{ij}))}{J'(E_i, T_j(t_{ij}))} \right] = \Omega
\] (56)

As in the previous methods, the activation energy \( (E) \) at each \( \alpha \) is the value that minimizes \( \Omega \) in the above equation. The advanced isoconversional method (AIC) is claimed to be superior to other isoconversional methods\(^9^2\) because integration over smaller time segments can better account systematic \( E \) variations.
2.4.6 **Advantages of isoconversional methods**

1. It can be used to analyze either isothermal or nonisothermal data.

2. Results from isothermal and nonisothermal experiments are internally consistent.

3. The explicit evaluation of $E-\alpha$ dependency can reveal complexities in the reaction kinetics.

2.4.7 **Drawbacks of isoconversional methods**

Even though isoconversional methods are capable of addressing most of the controversies in solid state kinetics, the method does not yield pre-exponential factor or the model of the solid state reactions. In order to get a complete kinetic picture, the combinations of isoconversional method with some model deriving methods are recommended.\(^7\)

2.5 **Complementary use of Isoconversional Methods with Different Methods**

Based on the results of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) kinetics project,\(^7\) the model-free isoconversional methods and model fitting methods that use multiple heating rate methods are particularly successful in obtaining a better understanding of the solid state kinetics. These methods also produce reasonably consistent kinetic results for isothermal and nonisothermal data and were identified as the most prospective techniques currently available for kinetic analyses.

Khawam and Flanagan have employed isoconversional method in combination with model fitting method to study the desolvation kinetics.\(^5\) In this method the power of isoconversional method has been combined
with the conventional model fitting to get the kinetic triplets \( i.e. \) E, A and \( f(\alpha) \). They employed isoconversional methods to obtain E values which were compared to the values obtained by model fitting methods. The most accurate model was assumed to be the one which is having activation energy closest to those obtained from isoconversional method.\(^5\) But this can be applicable only when the activation energy remains constant with the conversion function.

The combination of isoconversional methods with various methods like invariant kinetic parameters, master plot methods, multivariate nonlinear regression method, single heating rate methods (without model prediction) and model fitting methods are frequently used.

### 2.5.1 Invariant kinetic parameters (IKP)

This method is based on the kinetic compensation effect.\(^{101}\) The experimental values of \( \ln A \) and E are frequently found to demonstrate a linear correlation, also known as a kinetic compensation effect or an isokinetic relationship. The combined use of isoconversional method with invariant kinetic parameters which is based on the compensation is quite successful in predicting the kinetic triplets.\(^{102-105}\)

IKP method requires several \( \alpha-T \) curves recorded at different heating. IKP method gives values of the invariant kinetic parameters \( i.e. \) \( E_{inv} \) and \( A_{inv} \) which correspond to the true kinetic model that describes the investigated process at all heating rates. It is based on the existence of the linear compensation effect between E and \( \ln A \) obtained for the same TG curve by various theoretical kinetic models.

\[
\ln A = a + b \cdot E
\]  
(57)
where $a^*$ and $b^*$ are the compensation effect parameters. These values of $E$ and $\ln A$ are obtained from the slope and intercept of plots $\ln[g(\alpha)/T^2]$ vs. $1/T$ by using model-free Coats-Redfern equation.

If the compensation effect exists, the straight lines $\ln A$ vs. $E$ should be obtained for each heating rate and should intersect at a point that corresponds to the true values of $E$ and $\ln A$ for the true kinetic model, which are called the invariant kinetic parameters. It was shown that the conversion functions calculated by means of the IKP method depend on a set of kinetic models. The IKP method allows us to compute the invariant activation energy, invariant pre-exponential factor and model from the TG data.

### 2.5.2 Master plot method

The combination of master plot with isoconversional methods is successful in predicting the complex nature of the solid state reactions as well as predicting the mechanism of reactions.\textsuperscript{106-110}

The mechanism function $f(\alpha)$ or $g(\alpha)$ of solid state reaction can be found out using master plot method. Master plots are reference theoretical curves depending on the kinetic model but generally independent on the kinetic parameters of the process.\textsuperscript{111} Master plot methods can be of integral or differential approach.

In many cases, the experimental kinetic data can be easily transformed to the experimental master plots and comparison of theoretical master plots drawn by assuming various kinetic models with the experimental master plot allows us to select appropriate kinetic model of the process under investigation.
2.5.2.1 Integral method

In integral method,

\[
g(\alpha) = \frac{AE}{\phi R} p(x)
\]  

(58)

By using a reference point at \( \alpha = 0.5 \) and according to above equation, the following equation is obtained

\[
g(0.5) = \frac{AE}{\phi R} p(x_{0.5})
\]  

(59)

where \( x_{0.5} = \frac{E}{RT_{0.5}} \) and \( T_{0.5} \) is the temperature required to attain 50\% conversion. When eqn (58) is divided by eqn (59),

\[
\frac{g(\alpha)}{g(0.5)} = \frac{p(x)}{p(x_{0.5})}
\]  

(60)

Plotting of \( g(\alpha)/g(0.5) \) versus \( \alpha \) corresponds to theoretical master plots of various \( g(\alpha) \) functions. Both the temperature–conversion (\( \alpha–T \)) profile and the value of \( E \) for the process should be known in advance in order to draw the experimental master plot of \( p(x)/p(x_{0.5}) \) versus \( \alpha \) from the experimental data obtained at a given heating rate. To draw the experimental master plot of \( p(x)/p(x_{0.5}) \) versus \( \alpha \) obtained under different heating rate, an approximate formula of \(^{112}\) of \( p(x) \) was used. Thus eqn. (60) indicates that, for a given \( \alpha \), the experimental value of \( p(x)/p(x_{0.5}) \) and theoretically calculated values of \( g(\alpha)/g(0.5) \) are equivalent when an approximate conversion model is used. Consequently this integral model can be used to determine the reaction model.
2.5.2.2 Differential method

The kinetic rate equation at infinite temperature is obtained by introducing the generalised time $\theta$ defined as

$$\theta = \int_0^1 \exp \left( \frac{-E}{RT} \right) dt$$

(61)

where $\theta$ denotes the reaction time taken to attain a particular $\alpha$ at infinite temperature. Differentiating the above equation leads to

$$\frac{d\theta}{dt} = \exp \left( \frac{-E}{RT} \right)$$

(62)

Combining eqn (43) and (62), the following expression is obtained

$$\frac{d\alpha}{d\theta} = Af(\alpha)$$

(63)

Using a reference point at $\alpha = 0.5$, the following equation is easily derived

$$\left( \frac{d\alpha}{d\theta} \right)_{\alpha=0.5} = \frac{f(\alpha)}{f(0.5)}$$

(64)

where $f(0.5)$ is a constant for a given kinetic model function. The above equation indicates that, at a given $\alpha$, the experimentally determined value of the reduced generalised reaction rate, $\left( \frac{d\alpha}{d\theta} \right) / \left( \frac{d\alpha}{d\theta} \right)_{\alpha=0.5}$, and theoretically calculated value of $f(\alpha)/f(0.5)$ are equivalent when an appropriate $f(\alpha)$ for describing the rate process under investigation is applied. Because both the values depend only on $\alpha$, comparison of the experimental plot of $\left( \frac{d\alpha}{d\theta} \right) / \left( \frac{d\alpha}{d\theta} \right)_{\alpha=0.5}$ against $\alpha$ with the theoretical
plots of $f(\alpha)/f(0.5)$ against $\alpha$, drawn by assuming various $f(\alpha)$ functions, is methodologically identical to the conventional master plot method.

### 2.5.3 Multivariate non linear regression method

Another important method that appears in literature for the model prediction is multivariate non linear regression methods. K. Chrissafis have employed isoconversional methods and multi variate non linear methods for the kinetics of the thermal degradation of poly(ethylene adipate).

This method is based on multiple heating rates and makes the assumption that the parameters of the model are identical for measurements at all heating rates. It allows a direct fit of the model to the experimental data without a transformation, which would distort the error and consequently the result. An additional advantage lies in the fact that there are no limitations with respect to the complexity of the model and consequently it can be applied to multi step reactions.

In multivariate non linear regression method, several dynamic measurements run at different heating rates are brought together during the analysis. The relevant differential equations are numerically solved and the parameters of the differential equations are iteratively optimised. All these can be done using Netzsch Thermokinetic software.

### 2.5.4 Kissinger method

Kissinger’s method which occupies between the model-free and model fitting method, uses several heating rates to investigate the kinetic parameters while a single value of activation energy is obtained. This method is widely used to investigate the kinetics.
method derives the activation energy using the peak temperature at which the maximum reaction rate occurs and the order of reaction using the shape of the mass loss–time curve. The equation can be represented as

\[ \ln \left( \frac{\phi}{T_p^2} \right) = \text{const} - \frac{E}{RT_p} \]  

(65)

\( T_p \) is the peak temperature at different heating rates. The activation energy has been calculated from the linear plots of \( \ln \left( \frac{\phi}{T_p^2} \right) \) against \( 1/T \). Unlike the isoconversional methods, the Kissinger method takes a simplified approach that yields only a single \( E \) value for the whole process.

As a result, the obtained value is sound only if there is no variation of \( E \) throughout the process. Therefore, Kissinger method cannot detect the reaction complexities. The accuracy of this method is higher than that of model fitting but lower than the accuracy of model-free method.

### 2.5.5 Non parametric kinetic method

Non parametric kinetics (NPK) method was introduced by Nomen and Sampere.\textsuperscript{125-126} This method represents a special approach for treating the kinetic data. The method introduces a new point of view in kinetic analysis. It is also based on the single step kinetic approximation, so that the basic relationship for the analysis of kinetic is eqn. (43).

The most significant feature of this method is that its ability to provide information about the reaction kinetics without any assumptions either about the functionality of the reaction rate with the degree of conversion or temperature.

The NPK method uses larger number of points and a wide range of temperatures. This is a model-free method in the sense that it allows for
isolating the temperature dependence of the reaction rate (and therefore activation energy) without making any assumption about the reaction model. Hence it is considered as a model-free method, but due to its complexity, it has been applied very little.

Vlase et. al\textsuperscript{127-128} have analyzed the decomposition kinetics of three structurally similar complexes \( \text{Co}_2\text{Cu}(\text{C}_2\text{O}_4)_3(\text{R-diamino})_2 \) (where R is ethyl, 1,2-propyl, or 1,3-propyl) by applying the method of nonparametric kinetics (NPK) and the method of Ozawa and Flynn and Wall (OFW). They reported that the NPK method yielded an activation energy whose value is similar to the mean value determined by the OFW method.

Mocioiu et. al\textsuperscript{129} have compared the method of invariant kinetic parameters and the isoconversional method as applied to the crystallization kinetics of a silica-soda-lead glass. They find that the method is in agreement with isoconversional methods and that the kinetics follows a Johnson-Mehl-Avrami-Erofeev-Kolmogorov model.

\section*{2.6 Miscellaneous Methods}

Combination of different model invoking equations and isoconversional methods is quite useful for effective kinetic analysis\textsuperscript{130-133}. Isoconversional methods as well as conventional model fitting were used for the thermal degradation process. G. Singh and group have extensively employed isoconversional methods with model fitting for the investigation of energetic materials\textsuperscript{134-138}.

B. Jankovic has employed\textsuperscript{139} Malek method for the model determination of nonisothermal decomposition process of anhydrous nickel nitrate under air atmosphere along with isoconversional method. A combination of
isoconversational method with JMAEK equation is also reported in the literature for kinetic analysis.\textsuperscript{102, 52, 140-141} B. Saha\textsuperscript{142} and co workers have employed a hybrid genetic algorithm (HGA) technique (GA coupled with the local optimization algorithm (LOA)) and a model-free (isoconversional method of analysis to obtain the optimized kinetics triplet values for catalytic (ZSM-5) and noncatalytic decomposition of a waste low-density polyethylene (LDPE) sample.

Gaikwad\textsuperscript{143} and co workers have employed Sharp–Wentworth and Freeman–Carroll methods for the kinetic studies of some coordination polymers of first transition series metal ions \textit{viz.} Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). Coats–Redfern integral and the Achar–Bridly–Sharp differential methods are employed to study ammonium niobium oxalate decomposition.\textsuperscript{144} L. Tian\textsuperscript{145} and co-workers have employed Starink method with isoconversional method to investigate the thermal decomposition of lanthanide complexes. Mahadevan and Augis–Bennet methods has been used for the Crystallisation kinetics of a cesium iron phosphate glass.\textsuperscript{51} M. Kobelnik and co-workers have employed Capela and Ribeiro isoconversional method to study the non decomposition kinetics of iron (III)-diclofenac anhydrous salt.\textsuperscript{146}

\subsection*{2.7 Conclusions}

Even though isoconversional methods are supposed to answer all the controversies evolved in the kinetic analysis so far, yet not free from flaws. Different methods applied to the same nonisothermal data should lead to same value of activation energy. Unfortunately different methods produce different activation energy. Often the Friedman method and FWO method lead to different activation energies. While integral methods like FWO and
KAS methods produce closer values of activation energy. This is one of the controversial aspects of isoconversional methods. Another drawback of isoconversional method is that the methods do not allow calculating the pre-exponential factor ($A$) or the reaction model $f(\alpha)$. In order to have a complete kinetic picture, the knowledge of kinetic triplets ($A$, $E$, $f(\alpha)$) is necessary. The model fitting methods that yield single values of kinetic triplets are unable to reveal the multi step nature of solid state reactions.

The ICTAC-2000 meeting is supposed to be a milestone in the realm of solid state kinetics. In fact the project was a first step in standardizing solid state kinetic analysis methods. The main conclusion of the meeting is that one should use isoconversional methods in combination with different techniques (model fitting method) in order to get realistic kinetic parameters.
References


Recent Trends in Solid State Kinetics


