

Chapter 1

INTRODUCTION

1.1 Thermal methods and Catalysis

Thermal analysis refers to the variety of techniques developed and used in which any physical property of a given system is continuously measured as a function of temperature, though temperature and time may be related by the term called the heating rate namely dT/dt , this aspect will be taken up in a subsequent chapter in detail) and the temperature profile can be a prefixed schedule like temperature programming or temperature jump or flash heating. Thermal analysis techniques are employed in virtually every area of modern science and technology. The basic information that the variety of techniques can provide includes crystallinity, specific heat, expansion and information on a variety of physical and chemical transformations that can take place on the sample under inspection. As stated above this technique can be applied to any sample but this compilation will mainly consider the use of these techniques in the field of catalysis.

Catalysts are by nature inorganic/organic solids. In the process of application, they undergo physical as well as chemical transformations at every stage or unit operations like preparation, evolution of the active phase, reaction, ageing, deactivation and regeneration. The amount of information that could be generated throughout the life cycle of the catalyst (from the Cradle to coffin) by application of appropriate analytic techniques is summarized in Table. 1. Among all the available surface analytical techniques, thermal analysis methods occupy a special place since it is capable of rendering useful information on catalysts at every stage.

The study of solids employed as catalysts has been centered on examining the surface and bulk transformations that take place as a result of input of various forms of activation. Even though a variety of activation procedures are known, thermal activation has always been the most adopted method due to the reasons like easy adaptability, facile amenability for analysis and examination under controlled conditions (both atmosphere and temperature) The analysis of ejected/evolved neutral species has been the predominant method in thermal analysis though ejected electrons (thermionic emission and other species can also be analyzed. Thermal analysis generally denotes the group of methods by which the physical or chemical properties of a substance, a mixture and/or a re-

Table 1.1: Type of information that can be generated with respect to catalyst by thermal methods

Preparation stage	characterization of the catalyst	Evaluation stage	ageing of the catalyst	spent catalyst
Determination of the concentration of the active elements	Phase composition of the catalyst prepared	in situ evaluation of the catalyst	Solid state transformations that occur in the catalyst	inactive phases
Species that can be present in the the solution phase while preparing the the catalysts	Electronic properties of the catalyst	Transient surface species that would be generated	structural transformations that occur during ageing	poisons present on the catalyst surface
Solid state transformations that will occur in the preparation step	structural details of the catalyst	Identification and estimation of the reactant and the product concentrations	the changes in the surface composition of the ageing catalyst	analysis of the coke species formed
Types of preparation techniques Employed	Dispersion and distribution of the active phase	Kinetics mechanism of the reaction that takes place		
	surface composition of the catalyst			

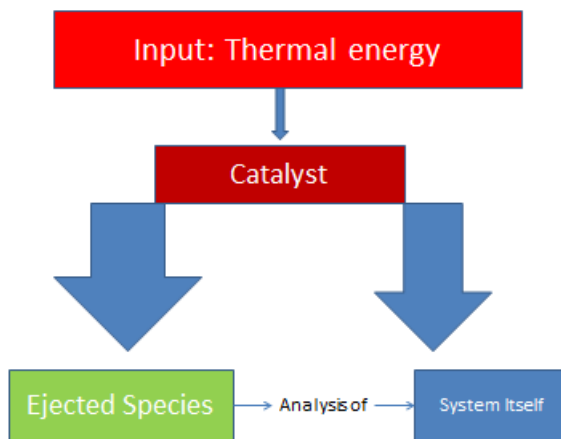


Figure 1.1: Flow diagram of catalyst studied by thermal input

Table 1.2: Conventional Thermo-analytical Techniques

Technique	Abbrviation	Physical property measured
Thermogravimetry	TG and DTG	weight/change in weight of the sample
Differential thermal Analysis	DTA	Difference in temperature between the sample and a thermally inert reference material both heated identically
Differential Scanning calorimetry	DSC	Rateof change in enthapy
Evolved Gas Analysis	EGA	Nature of gases evolved
Thermodilatormetry		Change in the dimension of the sample under zero load
Thermo-Mechanical Analysis	TMA	change in Visco-elastic properties under non-oscillatory load
Dynamic Mechanical Analysis	DMA	Change in visco-elastic properties under oscillatory load
Thermooptometry	TOA	change in optical property
Thermomagnetometry		change in magnetic property
Thermoelectrometry		change in electrical property
Thermoacousticmetry		change in acoustic signal
Differential micrcalorimetry	DMC	Enthaply difference between sample and reference

actant are measured as a function of temperature and/or time while the sample is subjected to a controlled temperature programming. The programme may involve heating or cooling(dynamic or holding the temperature constant or any sequence of these.

1.2 Techniques based on temperature Programming

The possibility of temperature ramp has been exploited in the field of catalysis for a number of years. Originally this method was adopted in the name of flash desorption [1] to study the adsorption of gases on metallic wires and filaments. The introduction of temperature programming has led to the development of number of techniques which are usually denoted as Temperature Programmed Techniques (TPX) where X can take alphabets like D for desorption, R for reduction, O for oxidation, S for sulphidation, RS for Reaction Study and so on). Emergence of hyphenated techniques like TPD-MS and TG-IR, TEOM(tapered element oscillating microbalance) have further sharpened the application potential of thermal analysis methods. This does not mean that conventional thermal methods like Thermo-gravimetry(TG) and its differential mode (DTG),Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC), Thermo-Mechanical Analysis (TMA) have not been exploited in the study of catalysts and the phenomenon of catalysis. They have been extensively employed and these aspects will be considered in this monograph. The list of conventional techniques is given in Table 1.2. It may be argued that thermo-analytical methods cannot compete with other analytical techniques like electro-analytical

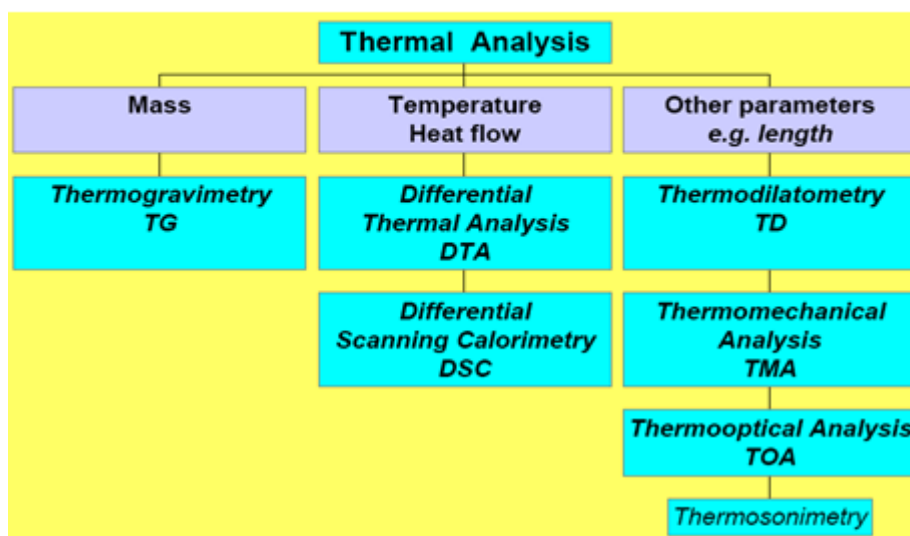


Figure 1.2: Thermal analysis techniques the measured parameter can be mass, temperature, heat flow, dimension, optical or magnetic property

or spectral analysis in terms of power, accuracy and time but still many laboratories are employing thermo-analytical methods for a variety of analytical situations. Second the possibility of temperature programming has led to some remarkable developments in the study of the kinetics of the processes. These studies have been extensively employed to derive the two important kinetic parameters namely the activation energy and the Arrhenius factor. The evaluated values for these two parameters have to be analyzed since in most cases abnormal values have been reported. It is appropriate to quote Prof Finn. He said "the unfortunate fact is that since in thermal analysis, properties of the system are measured as a function of both time and temperature, all thermo-analytical results are potentially kinetic data and many people ill grounded on kinetics feel obliged to perform kinetic analysis on them"

As stated above, the evaluation of the kinetic triplet namely activation energy, pre-exponential factor and $g(\alpha)$ or $f(\alpha)$ are obtainable by temperature programming methods. However, the kinetic data derived from thermal methods are always considered with some skepticism -why is this so? The values obtained for the kinetic triplets do not have much physical meaning but can help in predicting the rate of the processes for conditions when the collection of experimental data is impossible. The kinetic parameters do not have a physical meaning and hence can be used to elucidating the solid state reaction mechanisms. But in reality the truth is in between these two extremes.

It should be remarked that ambiguity inescapably accompanies interpretation of kinetic data obtained in thermal methods. This situation may arise because of the shortcomings from computation methods or experimental shortcomings. Experiments are often done either isothermal or under iso-conversions or under suitable heating rates, all these are unable to provide the details of all that take place under methods. The reactions do not follow normally simple stoichiometry like dehydration decomposition- a single set of kinetic triplet can at best describe a simple reaction at the most or if the mechanism is independent of temperature and the progress of the reaction. Finally non-isothermal kinetics is not obliged to give the same results as isothermal kinetics. There is enough support for both for and against. In this monograph an attempt has been made to address these questions which have been haunting the scientific community for long time on the use of thermo-analytical methods. It is realized that one may not be able to offer solutions for all of them at least one can make an attempt to understand and also to delineate them for evolving possible solutions in future. On the whole, various thermal methods can be employed for studying various properties of catalyst systems. These can be listed briefly as follows:

1. Determination of thermal constants like heat of fusion, specific heat, freezing point, melting point and thermal expansion
2. Phase changes and phase equilibria - solid to liquid phase change or liquid to gaseous phase change or phase changes in solids.
3. Structural changes solid solid transitions where a change in crystal structure occurs.
4. Thermal stability - one can monitor the thermal stability of an oxide, particularly stability of a porous material.
5. Thermal decomposition - decomposition of polymer, decomposition of template or an occluded material in porous media like zeolite, decomposition of salts in the formation of catalysts.
6. Characterization of materials like glass transition temperature, analysis of

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Portland cement etc

7. Extent of adsorption, desorption, reaction, reduction, oxidation, coking/decoking, sulphidation and many other processes involved in the preparation of catalysts and their use in catalytic reactions.

The listing is not comprehensive. The application depends on the innovation of the investigator. On the whole thermal methods have assumed an important place in the characterization of catalysts.

2. Thermogravimetric analysis in catalysis

This is the simplest of the thermal analysis wherein one measures the weight changes that occur as a result of programmed heating of the substance. The result is usually represented as percent weight loss (note not the absolute weight) as a function of temperature. It is also possible to depict the results in differential form also called DTG since it is known that in the differential form the signals are more prominent and also useful quantitative extraction of data is possible.

1.2.1 Buoyancy effect of sample container

It denotes the apparent gain in weight when an empty, thermally inert crucible is heated. It has three components namely (i) decreased buoyancy of atmosphere around the sample at higher temperatures; (ii) the increased convection effect and (iii) the possible effect of heat from the furnace on the balance itself. Modern instruments take care of these effects. A blank run with an empty crucible is always preferable. The buoyancy effect stems from the famous Archimedes principle namely, any object when wholly or partially immersed in a fluid, is buoyed up by the force equal to the weight of the fluid displaced by the object. In the case of temperature, it is connected to the density of the gaseous atmosphere varying with temperature. For example the density of air decreases with increasing temperature as follows at 298 K 1.29 mg/ml; at 498 K it is 0.62 mg/ml; and at 698 K it is 0.41 mg/ml. The effect of buoyancy on measurement of weight is illustrated. The effect of buoyancy can be illustrated with a simple example. The density of air at 298 K is 1.3mg/cm³ while the density of air at 1273 K is 0.3mg/cm³. Consider a sample of 20 mg with a density of 1g/cm³, the magnitude of the air buoyancy correction (MABC) will work out to be of the order of 0.1% if one makes use of any of the following equations,

$$\text{MABC} = (\rho_a - \rho_n) (V_x - V_s) \text{ equation 1}$$

$$\text{MABC} = m_0(\rho_a - \rho_n)[1/\rho_x - 1/\rho_s] \text{ equation 2}$$

the definitions of the symbols are given in Table.

Typical thermo-gravimetric traces (plot of mass versus temperature) are given in Fig.2.1.

In general a range of materials can be studied by thermo-gravimetry that include biological materials, building materials and catalytic materials, glasses and ceramic materials. The information that can be obtained from simple thermo-gravimetric traces are composition, moisture content, solvent content, additives

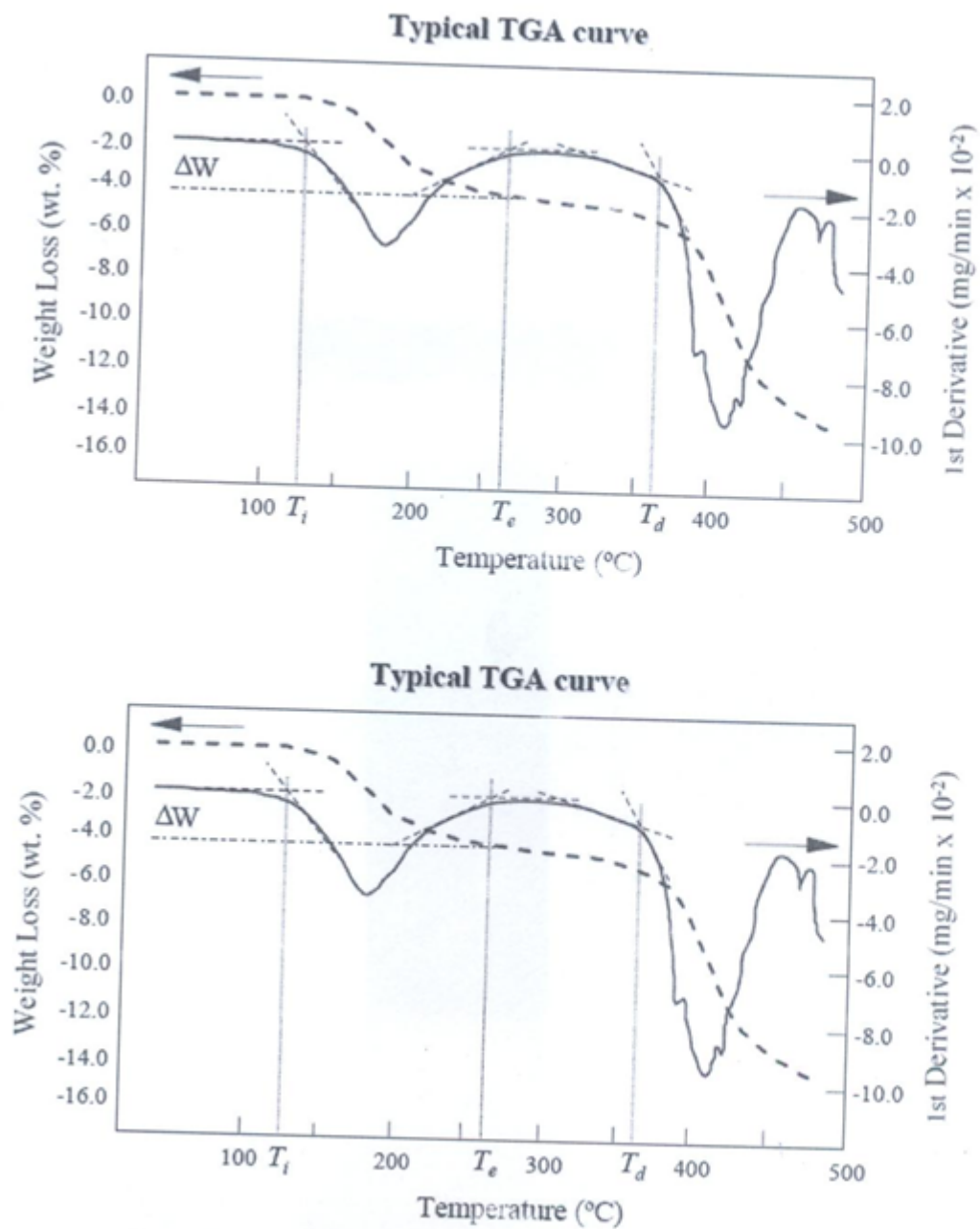


Figure 1.3: Typical TG curve shown in dashed line and DTG given by the continuous line

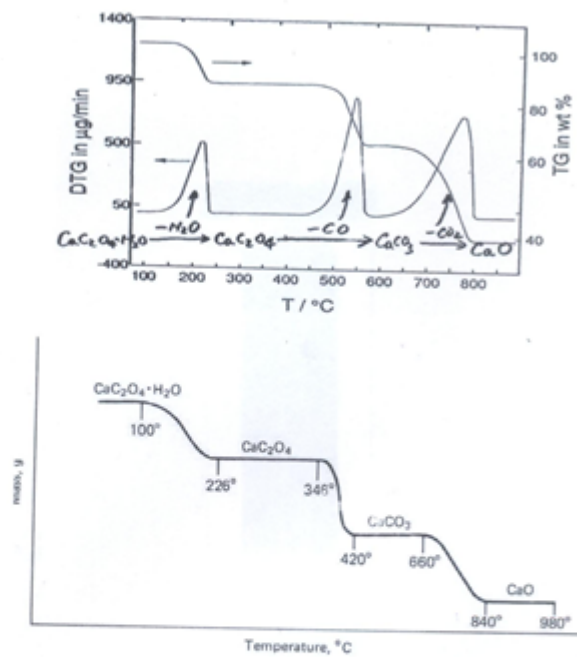


Figure 1.4: Thermo-gravimetric trace for the decomposition of calcium oxalate (one can notice that the trace provides information on the steps and also the species involved in the decomposition process)

Table 1.3: Variables for MABC equations

Variable	description of the variable
ρ_a	air density at the time of measurement in mg/cm^3
ρ_n	density of normal air that is $1.2\text{mg}/\text{cm}^3$
m_0	nominal mass in grams
V_{4-x4}	volume of the unknown weight in cm^3
V_s	volume of the reference standard in cm^3
ρ_s	density of the reference standard in g/cm^3
ρ_x	density of unknown weight in g/cm^3

[For more details on this correction factor refer to http://ts.nist.gov/WeightsAndMeasures/upload/Sop_2_Mar_2003.doc]

if present, polymer content, filler content, dehydration, decarboxylation, oxidation, reduction, decomposition, and in short where ever there is a weight change in the material. Conventionally therefore, phase change which will also occur as a function of temperature cannot be studied by thermogravimetry.

It can be seen that a typical thermobalance consists of a high precision balance, a furnace for achieving high temperature say 1800 K, a temperature programmer, data acquisition system, and auxiliary equipment to provide inert atmosphere. Requirement of a normal Thermogravimetric balance are:

1. A thermo-balance should provide accurate weight of the sample as a function of temperature (capacity upto 1 gram typical sample in milligrams). Its reproducibility should be high and also to be highly sensitive.
2. It should operate over a wide temperature range say from 298K to 1000/1500 K.
3. The design of the thermobalance should be such that the sample container is always located within a uniform hot zone inside the furnace.
4. The sample container should be such that it does not react with the sample at any given temperature.
5. The balance should not be subject to radiation or convection effects arising from the proximity of the furnace.
6. It will be advantageous if thermo balance can be coupled to a Gas Chromatograph or to a Quadrupole Mass spectrometer for catalytic studies.

The determination of kinetic parameters from thermal analysis has some limitations as mentioned before. In order to overcome these limitations various methods of analysis of data have been resorted to. Among the various methods that have been adopted, the methods based on iso conversion have been advocated in recent times especially by Starink. He has classified the available methods and also the methods developed by him as Type A and Type B methods.

1.2.2 Type A method or Friedman type method

This method essentially concerns the determination of the rate at the stages of iso-conversion. Since it depends on the determination of the a parameter it does not require any mathematical approximation. In this method one must deter-

mine the rate of the reaction at $T_i(\beta)$ (where T refers to the temperature, subscript "i" denotes iso-conversion levels and β refers to the heating rate). Hence one has to determine the rate at iso-conversion levels at different heating rates. In addition, one should also note the temperature where the rate is measured for the iso-conversion levels. Accordingly based on Arrhenius type expression of relevance is $\ln(d\alpha/dt) = (-E/RT_i) - \ln f(\alpha)$

Thus if a range of linear heating rate experiments at different heating rates β are done then times at which a fixed stage of the reaction is achieved can be noted for each linear heating rate experiment and hence $f(\alpha)$ will be a constant. Thus by measuring the temperature T_i and the transformation rate $d\alpha/dt$ at that fixed conversion can be plotted according to the above equation. The slope of the plot of $\ln(d\alpha/dt)$ versus $1/T_i$ can be used to calculate the value of the activation energy. Since time and temperature are related functions and measuring heating rate is easier the expression can be rewritten $\ln((d\alpha/dT)\beta) = -(E/RT_i) - \ln f(\alpha)$

Thus this method become model free method. Though this method does not involve any mathematical approximations, it introduces some measurement uncertainties as the measurement of rate of conversion, the estimation of $d\alpha/dT$ is sensitive to determination of the baseline and thus depends how best the thermal analysis equipment is calibrated.

Type B Isoconversion method

This method is called the generalized Kissinger method and is one of the commonly used isoconversion methods. The transformation rate can generally be expressed as a product of two functions namely, one depending on temperature and the other depending on the fraction transformed as follows

$(d\alpha/dt) = f(\alpha) f(T)$ The temperature dependent function can be replaced by Arrhenius type of expression $k = k_0 \exp(-E/RT)$ If the combined expression is integrated by separation of variables one gets

$$\int_0^\alpha d\alpha/f(\alpha) = (A/\beta) \int_0^{T_f} \exp(-E/RT) dT = (A/\beta)(E/R) \int_{y_i}^\infty \exp(-y)/(y^2) dy$$

where $y = (E/RT)$, $y_i = E/RT_i$, T_i is the temperature at an equivalent fixed state of transformation and β is the used heating rate. The integral on the right side of the equation is called the temperature integral or Arrhenius integral $p(y)$

$$\int_{y_i}^\infty \exp[(-y)/(y^2)] dy = p(y_i)$$

Taking logarithm and inserting $p(y)$ one obtains

$$\ln \int_0^\alpha d\alpha/f(\alpha) = \ln(AE/\beta R) + \ln(1/\beta Y_i^2) - Y_i$$

At constant fraction transformed, this leads to

$$\ln(\beta/T_i^2) = (-E/RT_i) + C$$

Table 1.4: comparison of the methods

designation of the method	procedure adopted	type code	Best known methods	ref ¹
Rate, iso-Conversion method	Plot of $\ln(d\alpha/dt)$ versus $1/T_i$	A	Friedman	A1
Rate, iso-Conversion method	plot of (T_i/β) versus $1/T_i$	B	Gupta et al generalised Kissinger	A2 A3
Maximum rate method	Plot of (T_i/β) versus $1/T_i$	B	Kissinger	A4
		B	Flynn	A5
Iterative method	Iterative	B	Starink method	A6 and A7

Plot of $\ln(\beta/T_i^2)$ versus $1/T_i$ should yield the value of E/R . This method is usually called the Kissinger-Akahira-Sunose (KAS) method though a similar method was developed by Vyazovkin and his coworkers. A similar expression is also available for treating the thermal desorption traces to evaluate the activation energy and frequency factor and this will be taken up in a subsequent chapter. At this stage, it is necessary that one comments on the methods so far considered and this is attempted in Table 1.4. ¹ It is appropriate to close this section on the kinetic analysis of isoconversion method by quoting the statements of Starink. He states that the need for further work on activation energy analysis of the isoconversion method has very much reduced. Any new procedure must be capable of demonstrating on more accuracy on the derived parameters. In the next chapter, the implications of this statement will be examined in detail.

1.3 References

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2 Appropriateness of Arrhenius Equation for Kinetic Analysis of Thermal Methods

It is necessary at this stage, one considers the appropriateness of employing Arrhenius type of expressions for the evaluation of activation energy of reactions studies by thermal methods. It is known and established beyond doubt that Arrhenius equation gives fairly good measure on the activation barrier for chemical reactions if the reaction rates or rate constants are determined at specific temperatures. It is necessary that we point out that this type of question on the application of Arrhenius type expression for the evaluation of kinetic parameters for the data on thermal analysis has been raised a number of times persistently in the literature.

The kinetic parameters for typical solid state reactions (like decomposition, phase change, or compound formation) have been conventionally evaluated by the treatment of isothermal or non-isothermal data of fraction reacted (α) as a function of time in the case of isothermal studies or as a function of temperature employing the conventional Arrhenius equation in the form $k = A \text{Exp}(-E/RT)$. The applicability of Arrhenius equation for homogeneous molecular level reactions is well known and has been established beyond doubt since these systems obey the Maxwell-Boltzmann distribution. However, alternate functions like relating $\ln k$ with T or $\ln K$ with $\ln T$ in addition to $\ln k$ versus $1/T$ have also been proposed, but these relations have been considered as 'theroreitclaly sterile' since the constants of these proposed equations do not lead to any deeper understanding of the steps in the chemical reaction [1]. Galwey and brown [2] have raised this aspect in one of their innumerous publications in this area and provided a number of arguments justifying the use of Arrhenius equation to treat the kinetics of solid state reactions. The main argument provided by them concerns that solid state reactions are mostly promoted at and by the interface sites and their energy levels. These energy states though normally obey Fermi Diract statistics for electrons and Bose-Einstein statistics for phonons both these statistical functions can approximate to the conventional exponential function (Maxwell-Boltzmann Distribution (MB). Since obedience to Maxwell Boltzmann statistics is the key for the application of Arrhenius equation, they justified the use of this equation for treatment of solid state reaction kinetics

implying the other statistics can approximate to MB statistics.