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	spentcatalyst
Determination of the concentration of the active elements	Phase compositiion of the catalyst prepared	in situ evaluationof 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			
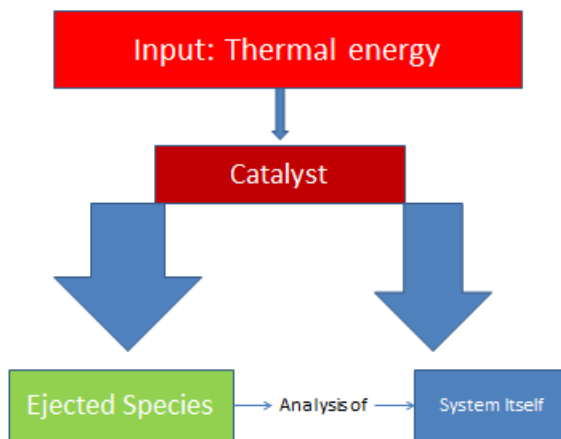
Figure 1.1: Flow diagram of catalyst studied by thermal input

Table 1.2: Conventional Thermo-analytical Techniques

Technique	Abbrviation	Physical property measured
Thermogravimetry	TG and DTG	weight/change in weight of the sample
Differeential 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-Mechnical 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 exloited 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
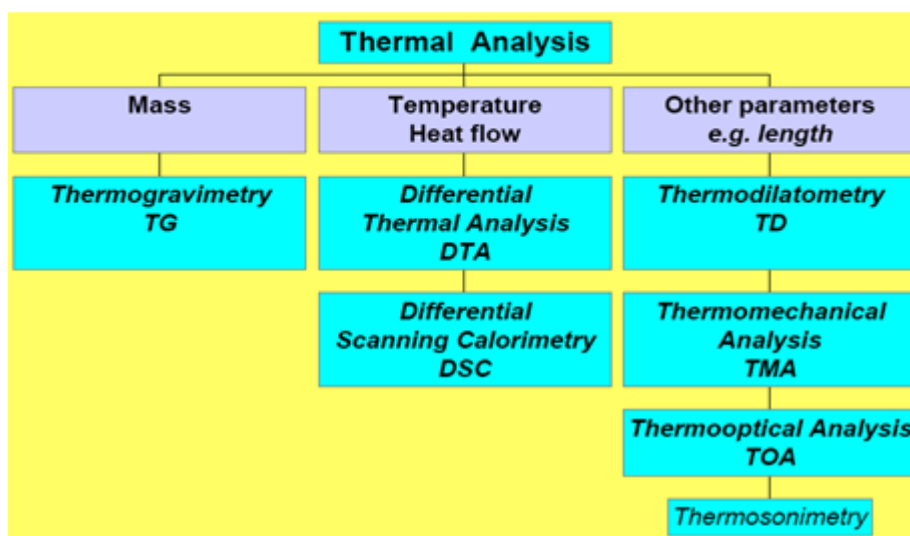
Figure 1.2: Thermal analysis techniques the measured parameter can be mass, temperature, heat flow, dimension, optical or magnetic property

or spectral analysis in terms of power, accuracy and time but still many laboratories are employing thermo-analytica 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 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 evaulation of the kinetic triplet namely activation energy, pre-exponential factor and g(α) or f(α) 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 short comings 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 It is community for long time on the use of thermmo-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 occuluded material in porous media like zeolite, decomposition of salts in the formation of catalysts.

6.Characterization of materials like glass transition temperature, analysis of

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 stes 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/cm^3 while the density of air at 1273 K is 0.3mg/cm^3. Consider a smaple of 20 mg with a density of 1g/cm, 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,

MABC = $(\rho_a - \rho_n)$ (V$_x$ - V$_S$) equation 1

MABC = $m_0(\rho_a - \rho_n)[1/\rho_x - 1/\rho_s]$ 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

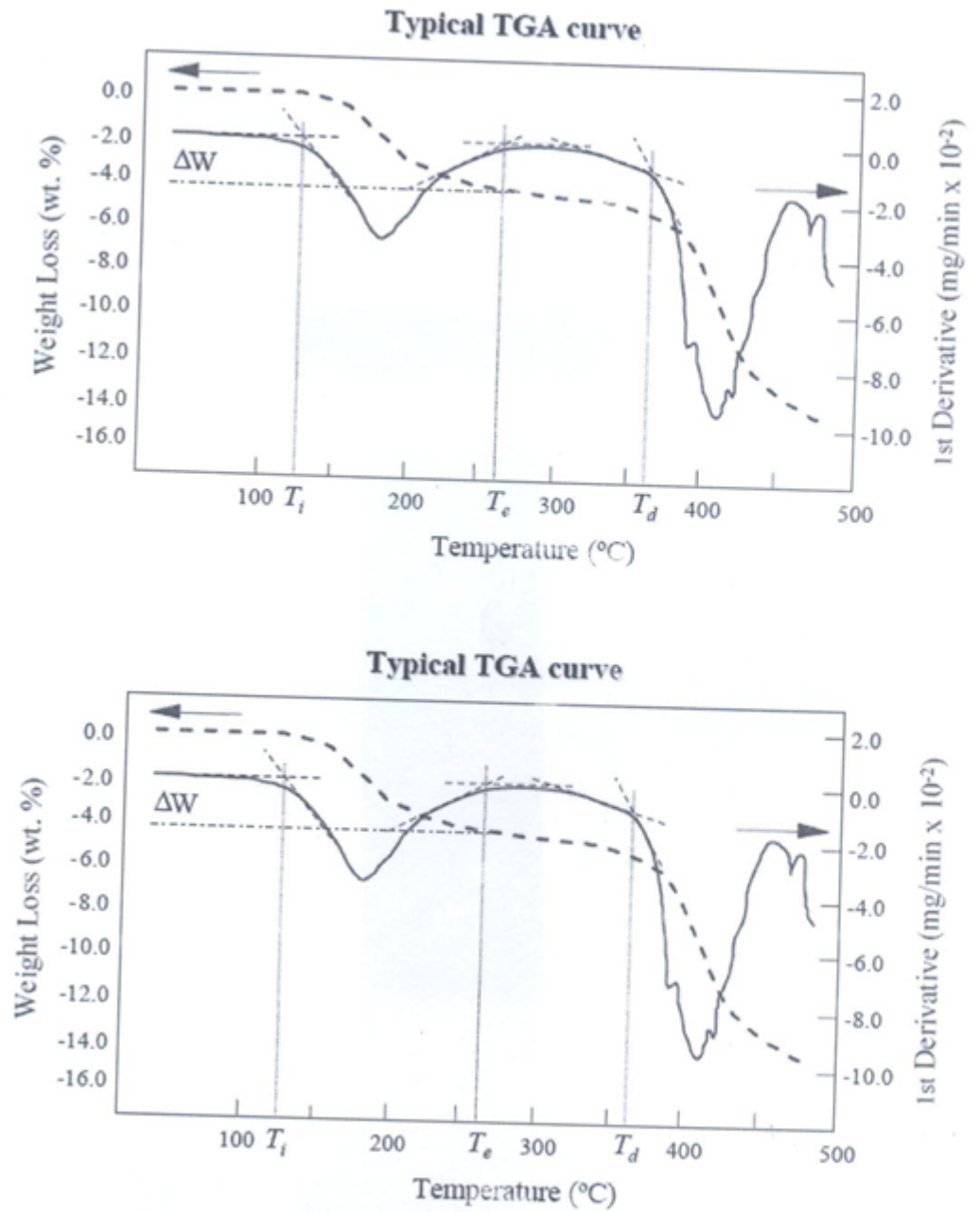## Typical TGA curve

Typical TGA curve

Figure 1.3: Typical TG curve shown in dashed line and DTG given by the continuous line
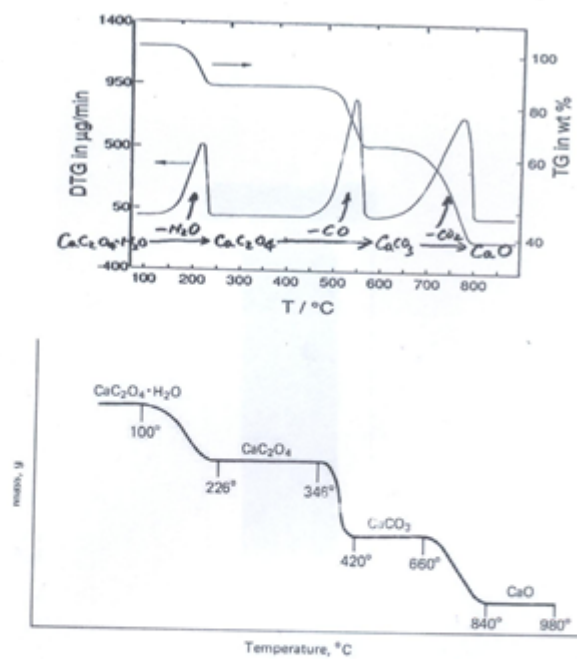
Figure 1.4: Thermo-gravimetric trace for the decomposition of calcium oxalate(one can notice that the trace provides information on the steps and also the species involved in the decomposition process)

Table 1.3: Variables for MABC equations

Variable	description of the variable
ρ_a	air density at the time of measurment in mg/cm^3
ρ_n	density of normal air that is 1.2mg/cm^3
m_0	nominal mass in grams
V4-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 wight of the sample as a function of temperature (capacity upto 1 gram typical sample in milligraams). 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 recant 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-converison levels. Accordingly based on Arrhenius type expression of relevance is Arrhenius type expression of relevance is $\ln(d]alpha/dt) = (-E/RT_i)$ - ln f(α)

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(α) 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 beating rate is easier the expression can be rewritten $\ln((d\alpha/dT)\beta) = -(E/RT_i)$ - ln f(α)

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 transforation 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(α) 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

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

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
			Gupta et al	A2
]hline p(y) iso conversion method	plot of (T_i/β) versus $1/T_i$	B	generlised Kissinger	A3
Maxmimum 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 $\ln(\beta/T^2{}_i)$ 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 isoconverson method has very much reduced. Any new procedure must be capable of demonstrating onmore 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 conventinally 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 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-Blotzmann 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 canapproximate 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

Table 1.5: Table 3.1. Typical physico-geometric kinetic models for treating the conversion (α = fraction reacted) versus time data for solid stated reactions.

Designation of the model	f(α)	g(α)
Random Nucleation	$1-\alpha$	$-\ln(1-\alpha$
Generalized nth order	$(1-\alpha)^n$	$(1/n)(1-(1-\alpha)^{n-1}$
Power law	$(2\alpha)^{1/2}$	$(\alpha)^{1/2}$
Power Law	$(3\alpha)^{2/3}$	$(\alpha)^{2/3}$
Power law	$(4\alpha)^{3/4}$	$(\alpha)^{3/4}$
1D or 2D Avrami-Erofeyev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-[n(1-\alpha)]^{1/2}$
2D or 3D Avarami-Erofeyev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
3D Avaramin-Erofeyev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Prout-Tomkins	$\alpha(1-\alpha)$	$\ln[\alpha/(1-\alpha)]$
Contracting area	$2(1-\alpha)^{1/2}$	$2[1-(1-\alpha)^{1/2}]$
Contracting Volume	$3(1-\alpha)^{1/3}$	$[1-(1-\alpha)^{1/3}$
Generalized method of Sestak	$(1-\alpha)^n \ (\alpha)6n$	
One Dimensional diffusion	$(1/2)\alpha$	$(\alpha)^2$
Two dimensional diffusion	$[-\ln(1-\alpha)^{-1}$	$[(1-\alpha)\ln(1-\alpha)]+ \alpha$
Three dimensional diffusion Jander	$3(1-\alpha)^{2/3} +[1-(1-\alpha)^{1/3}]$	$[1-(1-\alpha)^{1/3}]^2$
Three dimensional diffusion Ginstling-Brounshtein	$[3/2(1-\alpha)^{-1/3} -1]$	$[1-(2\alpha/3)-(1-\alpha)^{2/3}$
Zero order	1	α
First order	$1-\alpha$	$-\ln(1-\alpha)$
Second order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
Third order	$(1-\alpha)^3$	$0.5(1-\alpha)^{-2}-1$

implying the other statistics can approximate to MB statistics.

The kinetic data of solid state reactions are treated conventionally with a different model as compared to the reactions taking place in homogeneous solutions[3]. The reaction is considered to initiate and propagate at the interface of the solids and various types of kinetic expressions have been employed to represent the dimensionality and the progress of the reaction at the interface. These models are based on the consecutive steps of nucleus formation and the growth of the nucleus in one or two or three dimensions. It is therefore clear how the dimensionality is introduced in the kinetic expressions of solid state reactions. It is known that the concentration term in solid state reactions does not change with time though the amount converted can change. Hence using concentration terms in the kinetic expressions of solid state reactions is inappropriate.A brief summary of the various kinetic expressions normally employed to treat the isothermal kinetic data of solid state reactions is given in Table 3.1. These model kinetic expressions can be analyzed in terms fo classifications like models based on nucleation, geometrical contraction or expansion, deceleratory or acceleratory or sigmoid type of kinetic curves, models based on diffusion and models based on reaction orders. Many of these models are unique to treatment of solid state reactions. Similarly,non-isothermal data have been analyzed based on various models. Typical expressions employed for treating kinetic data on non-isothermal measurements are assembled in Table 3.2. Most of these expres-

Table 1.6: Typical expressions for treating non-siothermal data in thermal methods

Model	Relationship	Ref
Ozawa method	$(\log\beta) = \text{Log}(AE/R)\text{-}2.314\text{-}0.456(E/RT)\text{-}(\log g(\alpha)$	6,7
Coats and Redfern	$[\log(1\text{-}(1\text{-}\alpha)^{1-n}/T^2(1\text{-}\alpha) = \log(AR/\beta E)(1\text{-}(2RT/E))\text{-}$ $(E/2.303RT)$ for n is not equal to 1	8,9
Coats and Redfern	$\log(\text{-}\log(1\text{-}\alpha)/T^2) = \log(AR/\beta E)(1\text{-}(2RT/E)\text{-}$ $(E/2.303RT)$ for n is equal to 1	8,9
Freeman and Carrol	$(\Delta \ln(d\alpha/dT)/\Delta\ln(1\text{-}\alpha)) = \text{-}E((\Delta)(1/T)/R\Delta\ln(1\text{-}\alpha))\text{+}n$	10
Friedman	$(\ln(\beta dx/dT)) = [\ln A\text{+}n\ln(1\text{-}\alpha)\text{-}E/RT$	11
Flynn-wall	$[(\log\beta)] = [(\log(AE/R)\text{-}2.314\text{-}0.4567(E/RT)]$	12

sions given in Table 3.2 have been derived on some specific models conceived by the respective authors. It is not clear which one of these expressions is more suitable to treat the non-isothermal data for an unknown system and in the absence of such a guideline, it has been customary to apply more than one of these expressions for the same set of experimental data on non-isothermal kinetics and then compare the values of the derived parameters like activation energy, $E-a$, and the pre-exponential factor (A) of the Arrhenius equation. These values are given in Table 3.3. Typical models for the treatment of non-isothermal data (only typical ones are given and for others the readers are referred to the original literature [6-17]. Though, the non-isothermal data have been analyzed for consistency or to interpret the mechanism of the solid state reactions using any one of the equations given in the table, the results have led to many unclear situations since the derived parameters of E_a and A from various models are mostly not consistent and hence the interpretation has to resort to some selection which could not be unbiased. Secondly, since not all the models employed for treating a set of non-isothermal kinetic data , the selection and supposed applicability of the model chosen appear to be arbitrary. Whenever, inconsistency is found in the values of the parameters of E_a and A, the analysis are most often silent or only looks at them as though the models are different, even then the suitability of one model over the other is not explicit. In order to substantiate the contention that the parameters of E_a and A have not been consistent, a chosen set of data collected from literature are given in Table 3.3.. The data given in Table 3.3. should not be taken as representative ones available in literature. No attempt has been made to collect the data extensively. Galway[27] has observed that the value of pre-exponential factor for nearly 50%(this estimate appears to be arbitrary) of solid state decompositions like in the range of 1068 - 10^{14} s^{-1}. In reality for most of the solid state reactions, the values of pre-exponential factor vary widely and the spred is certainly too large and mostly differ fro the standard value of 10^{13} s^{-1} a value derived from Polyani-Wigner model.One can raise several questions based on the magnitude of the values of E_a and A reported in literature for the kinetics of solid state reactions. It is not the intention to list all the questions but only to indicate a few of them.
1. What is the significance of the values of A higher than 10^{13} s^{-1}?
2. What interpretation can be offered when the observed values of A is far less than 10^{13} s^{-1}?
  (iii) The values of activation energy do not usually lie in the range of 100-

Table 1.7: Values of E$_a$ and A deduced for some typical solid state reactions includes examplesof decomposition, dehydration, solid state inorganic and organic reactions and Phase changes

Reaction	E$_a$ (kJ/mol)	A$(min^{-1})/(sec^{-1})$	Ref
Decomposition of ply carbonates			
Coats and Redfern	15.6	-	18
Freeman and carrol	360.4	-	
Decomposition of Borax pentahydrate	'	'	'
Dehydration	92.0	2.35x10^{10}	19
Decomposition	15.9	2.04	
Formation of Nb$_3$Sn			
Kissinger	312		20
Flynn-Wall	312		
Melting of ice	28.5	10^9(sec^{-1}	21
Decomposition of Gd$_2$Mo$_7$O$_{24}$14.5H$_2$O			
Horowitz-Metzer	30.6	2.3x10^2	22
Coats and Redfern	28.1	1.9x10^2	
β to γ phase transition			
Avarami-Erofeyev	89±8	4.6x10^9	23
Cardow model	142±14	2.0X10^{17}	
Nuceation growth	70±4	1.1x10^8	
SiC from CNT and Si	96±30		25
Zinc oxalate-Isothermal			26
Simple power law	250.5	3.0x10^{18}	
Unimolecular law	258.3	2.8x10^{21}	
Dynamic method			
Coats and Redfern	257.5	4.8x10^{20}	
Zsako	214	2.6x10^{17}	
Nickel oxalate -isothermal method			26
1.Prout-Tompkins	54.6	3.7x10^4	
Contracting cube law	82.0	6.9x1067	
Avarami-Erofeyev	66.2	8.0x10^4	
Unimolecular law	137.5	1.8x10^{11}	
Nonisothermal method			
Coats and Redfern	160.6	1.1x10^{13}	
Asako	140.8	2x10^{12}	
Thorium oxalate Isothermal method			26
Exponential law	147.4	6.8x10^{11}	
Contracting cube law	226.1	1.2x10^{17}	
Non-isothermal data			
Coats and Redfern	209.9	9.4x10^{16}	
Contracting cube law	173.9	3x10^{13}	
Unimolecular law	173.9	1x10^{1}4	

200kJ/mol, which is normal for bond breaking and bond forming steps being rate determining. If the values obtained were to be too low or too high, how are they to be rationalized? Galwey and Brown [28,29] have made a detailed analysis of the aspect of the applicability and justification of the use of Arrhenius type equation for the evaluation of tow important kinetic parameters for solid state reactions. The reasons and arguments proposed by them can be summarized as follows: (i) The mechanism of reaction in solid state may be different from that occurring in homogeneous systems, where movement and collision are envisaged as initiating steps of the reaction. In solids, the species are immobilized and hence this type of collisions may not be the initiator of the reaction.

(ii) The reactions (at least some of the reactions in the solid state) may be due to bond activation through electronic energy or through phonon activation.

(iii) If softening and melting were to precede the solid state reaction, then one can visualise the reaction sequence as in homogeneous medium.

(IV)The variation of E with α the extent of reaction (smooth or abrupt) denotes the nature of consequctive steps involved in solid state reactions

(v) If the solid state reaction proceeds by the development and growth of a reaction interface, then the local strain, imperfections, the crystalline phases of the reactants and products all will contribute to the acceleration or deceleration of reaction rates as well as for the change in E_a with α. It is not yet clear how the various forms of the intervening phase, like a molten product, a defect crystalline phase or reorganizations in reactant (like removal of water) could provide a chemical environment where the conventional Polanyi-Wigner treatment will be much applicable as in homogeneous phase.

(vi)In terms of energy transfer, the species in the interfacial zone is more ordered in homogeneous liquid medium,but less ordered as compared to the fully crystalline phase. The in-between crystalline phases (interface region) may provide additional allowed energy levels in the forbidden regions of energy bands in the solid. The electronic energy levels though normally follow Fermi-Dirac statistics, can approximate to Maxwell-Boltzmann distribution under the temperature conditions employed in the solid state reaction. If this situation prevails then one can justify the use of Arrhenius equation for evaluating E_a and pre-exponential factor.

(vii) if on the other hand phonons are the mode of activation, then one can expect the Bose-Einstein statistics will approximate to Maxwell-Boltzmann distribution for the conditions prevailing under reaction conditions and hence the use of Arrhenius equation can still be justified.

Though the summary of the arguments given justify the use of Arrhenius type of relationship to evaluate the kinetic parameters (E_a and A) it ha snot provided any explanation for the variation of E_a and ln A. These variations are considered in terms of compensation between E_a and ln A or by the variation of one (E_a or ln A) while the other remains constant.

The linear relationship between E_a and ln A is termed as compensation effect in the literature. The observance of this effect is usually identified by the inherent 'heterogeneity' of the surface and hence the changes in reactivity of these sites. However a simple linear variation between E_a aned ln A for sites varying reactivity is not expected unless one has to invoke additional internal reorganizations which can give rise to smooth variation in both E_a an ln A. It must be remarked that these solid state reactions were to involve an intermediate vapourization and condensation steps, then it is probable that one can still invoke Arrhenius

type of equation for evaluating E_a and ln A. However, not all solid state reactions do proceed by evaporation of reactant and condensation of the product.

It is appropriate to quote Prof Flynn at this stage. 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 a kinetic analysis of them [30].

Even if one were to admit inexperience in treating kinetic data from thermal analysis, the physical significance of the kinetic parameters derived from the analysis is not clear yet. Secondly, it is yet to be resolved, why the same experimental data can be fitted to various models simultaneously? Do they reflect on the closeness of the models, or the inadequacy of the treatment of data based on the models chosen. The widely practiced method of extracting Arrhenius parameters from thermal analysis experiments involves 'force fitting' of experimental data to simple reaction order kinetic models [31]. The 'force fit' may not be suitable for the anaylsis of data of thermal analysis, outside the applicable range of variables and hence can be of limited utility for drawing mechanistic details of the reaction,. It should be remarked that the concept of kinetic order of the reaction has to assume a new significance in the case of solid state reactions.

Even for simple decomposition reactions, the available models cannot appropriately take into account like sintering before decomposition, simultaneous existence of polymorphoic transition. It should be recognised that the models proposed are oversimplified and envisages one nucleation site per particle. There can be multiple and different types of nucleation simultaneously and their growth may be a complex function which cannot be treated in terms of simple geometrical considerations. The direct observation of the texture and morphology of the substances have to be coupled with the kinetic fit of the data for developing a model and draw meaningful deductions regarding nucleation and growth.

The values of the activation energy for solid state reactions can be rationalized only in some simple restricted conditions. For example for the two systems if g($|alpha$) and A were to be equal then, the magnitude of E_a can be used to postulate on the reaction kinetics. However, even in these cases, if E_a were to vary with α, the fraction of the reaction, then it denotes changes in reactivity as a result of extent of reaction and the complex nature of the reaction. There is overwhelming tendency to compare E_a values obtained for isothermal and non-isothermal experimental conditions. Even though time and temperature are mathematically related by the heating rate (β =dT/dt), it is not clear how the species of the system will respond to the bimodal variation. Whether the changes observed will be an arithmetic sum or product of the variations observed with each of these variables. It appears that it is neither of these two mathematical functions. In conclusion, one can state that if carefully used and complemented with other techniques, the analysis of solid state kinetics can provide indications on the reaction mechanism and may yield information on reactivity which can be exploited for synthetic strategies.

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Table 1.8: calibration standards useful in DTA measurements

Calibrant	transion temperature (K)	heat of reaction(J/g)
KNO_3	400.7	54.06
In	430	28.41
Sn	504.9	59.66
SiO_2	846	10.25
K_2SO_4	856	46.61
K_2CRO_4	938	52.63
$BaCO_3$	1083	
$SrCO_3$	1198	