CHAPTER 1

INTRODUCTION

Thermal Analysis methods & Catalysis

Thermal analysis refers to the variety of techniques developed and used in which any physical property of a substance is continuously measured as a function of temperature (thought temperature and time may be related by the term called heating rate dT/dt), the temperature profile can be a prefixed schedule like temperature programming or temperature jump or flash methods.

Thermal analysis techniques are used 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.

Catalysts by nature are inorganic / organic solids. In the process of application, they undergo physical as well as chemical transformations at every stage, like, preparation, evolution of the active phases, reaction, ageing, deactivation and regeneration. The wealth of information that could be generated throughout the life cycle of the catalyst (from the Cradle to the Coffin) by application of appropriate analytical techniques is listed in Table I.1

Table.1 Type of information that can be generated with respect to a catalyst

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 solution phase while preparing 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 product concentrations	The changes in the surface composition of the ageing catalyst	Analysis of the coke species formed
Types of preparation techniques	Dispersion and distribution of the active phase	Kinetics and mechanism of the reaction that		

employed		takes place		
	Surface composition of the catalyst			

Amongst various analytical techniques, Thermal analysis methods occupy an unique place, capable of rendering useful information on catalysts at every stage.

The study of solids employed as catalysts has been centred 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 known, thermal activation has always been the most adopted method due to reasons like easy adoptability, facile amenability for analysis and examination under controlled conditions (both atmosphere and temperature)

Thermal energy as input

↓

Catalyst

Ejected species ← **Analysis of** → **System itself**
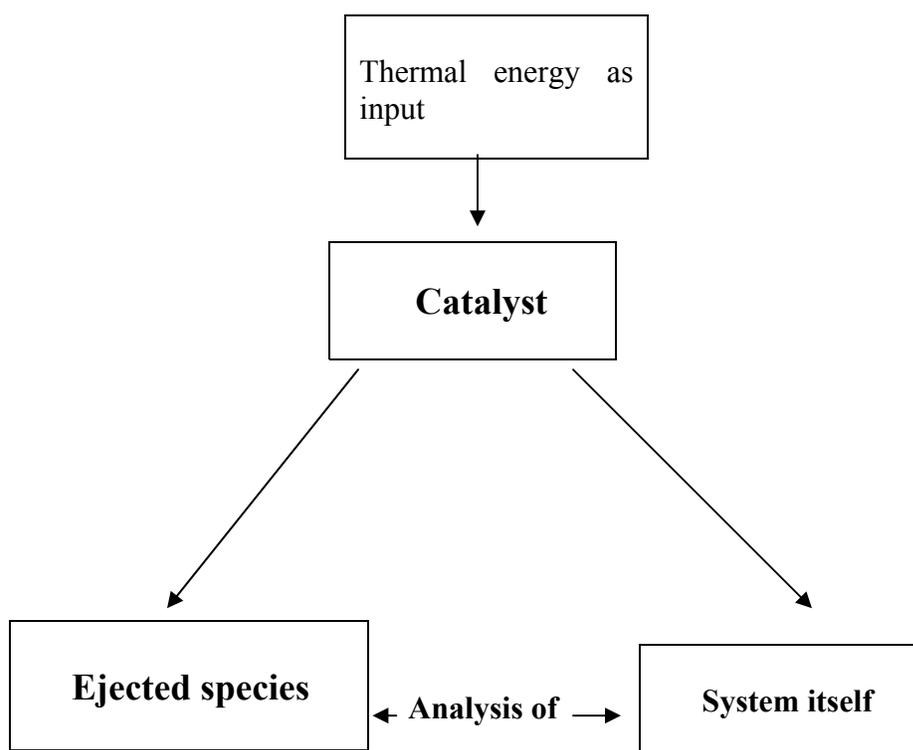
The analysis of ejected/ evolved neutral species has been the predominant method in thermal analysis though ejected electrons (thermionic emission) and other species can also be analyzed.

Thermal analysis generally denotes the group of methods by which the physical or chemical properties of a substance, a mixture and/or a reactant are measured as a function of temperature or time ($T = T_0 + \beta t$) whilst the sample is subjected to a controlled

temperature program. The program may involve heating or cooling (dynamic), or holding the temperature constant (isothermal), or any sequence of these.

New 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 a number of new 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, TG-IR and TEOM (Tapered Element Oscillating Microbalane) have further sharpened the application potential of thermal analysis methods

This does not mean that the 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 also be considered in this monograph.

The list of such conventional techniques has been given in Table I.2.

Table I.2. Conventional thermo-analytical Techniques

Technique	Abbreviation	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	Rate of change of enthalpy
Evolved Gs 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		Change in optical property
Thermomagnetometry		Change in magnetic property
Thermoelectrometry		Change in electrical property
Thermoacoustimetry		Change in acoustic signal

Differtial microcalorimetry	DMC	Enthalpy difference between sample and reference

The classification of the conventional thermal method, shown in TableI.2.. can also be visualized in terms of a flow diagram and one such flow diagram is shown in Fig.1.1.
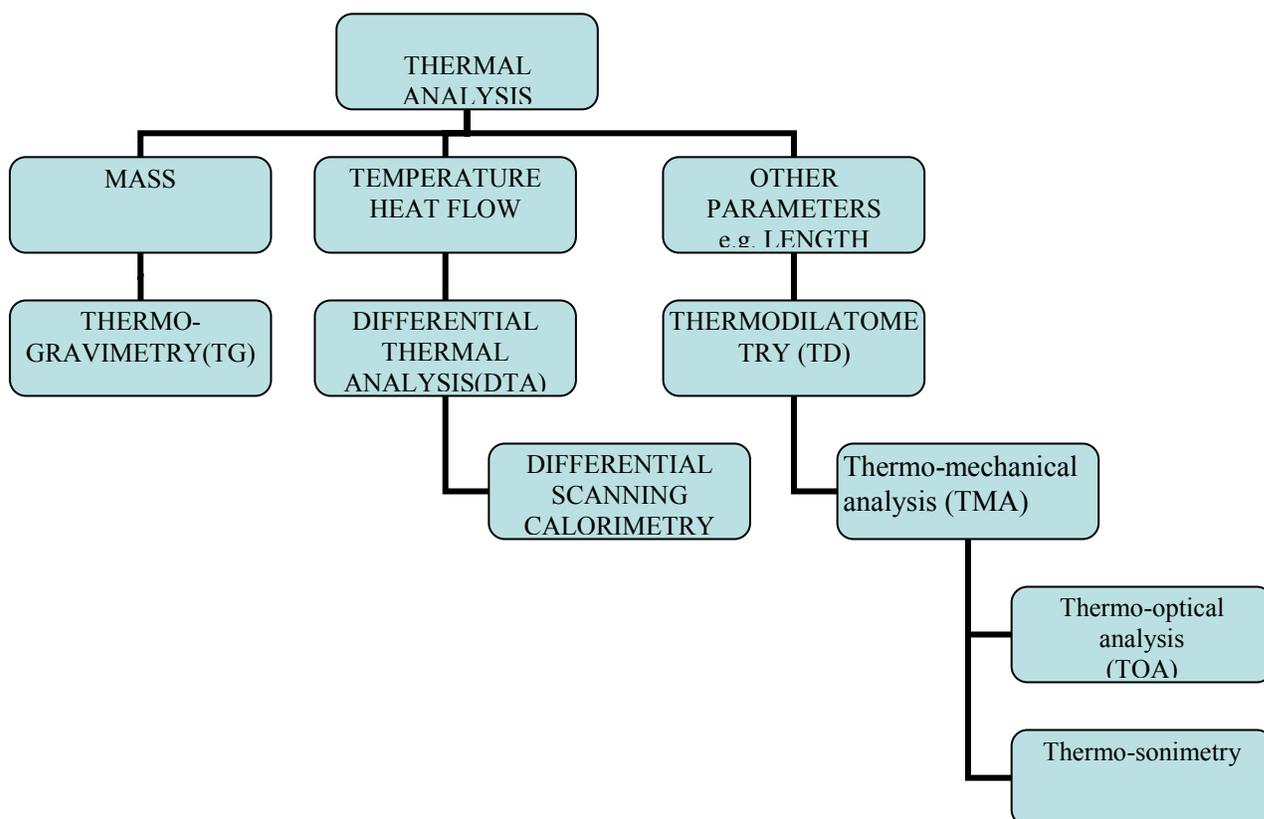

Fig.1.1. Thermal Analysis refers to a number of methods that measure change in any property of a system with respect to temperature, when it is subjected to a controlled temperature variation. The measured parameters can be mass, temperature or heat flow or other properties, dimensions, or optical or magnetic property.

Impact of Thermal analysis on Catalysis research

The justification for a separate monograph on thermal methods in catalysis is necessitated by the fact that the number of publications in this area is always on the increase and more and more applications are brought to focus.

A simple search for thermal methods in catalysis turned out 69186 entries (as on 23rd June 2009) with 61222 journal references, 7365 book and 599 reference entries. A more simple approach would be to see how year wise this topic has been covered by publications. In Table 1.3. the necessary data are assembled.

Table 1.3. The number of entries on the topic thermal methods in catalysis year wise

S.No	Year	No of entries
1	2005	3972
2	2006	4195
3	2007	5033
4	2008	5221
5	2009 (part)	4265

A variety of sources cover the original research in this area and a sample of the journals which has published more than 500 research articles are shown in Table 1.4. This compilation is only to give an idea of the coverage of resources available for this field.

Table 1.4. Journals that cover most of the articles under the title thermal methods in catalysis

Journal	Number of articles
Applied Catalysis A: General	3577
Studies in Surface Science and Catalysis	3503
Journal of Catalysis	3435
Surface Science	2417
Journal of Molecular Catalysis A: Chemical	1937
Applied Catalysis B: Environmental	1586
Journal of Organometallic Chemistry	1495
Microporous and Mesoporous Materials	1228
Chemical Engineering Science	1038
Tetrahedron	976
Journal of Molecular Biology	878
Applied Catalysis	853
Inorganica Chimica Acta	808
Catalysis Communications	712
Carbon	693
Polyhedron	645
Themochimica Acta	641

| Journal of Molecular Catalysis | 624 |
| Applied Surface Science | 587 |

It may be argued that thermo-analytical methods cannot compete with other analytical techniques like electro-analytical 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. It is argued that nearly 35% of the analytical research laboratories still use thermo-analytical techniques.

Secondly the possibility of temperature programming has led to some remarkable developments in the kinetic study of the processes. However, though these studies have been exploited extensively to derive essentially the two important kinetic parameters namely the activation energy and Arrhenius factor. The evaluated values obtained for these two parameters have to be carefully analyzed since in most cases the abnormal values have been reported.

It is appropriate to quote 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 (like the present author) feel obliged to perform a kinetic analysis of 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, 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 can be used to help in 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. These 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 thermal 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 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 them 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 catalytic systems.   These can be summarized as follows:
 1. Determination of thermal constants like Heat of fusion, specific heat , freezing point and melting point.
The MP of pure metals (Au, Pb, Sn etc) is often used for calibration of DTA/DSC. The area under a melting endotherm is proportional to the latent heat of fusion of the sample.

2. Phase changes and phase equilibria
Solid to liquid phase change or liquid to gaseous state, or phase changes in solids

3. Structural changes
Solid-solid transitions where a change in crystal structure occurs.
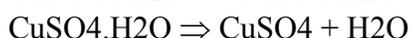
4. Thermal stability
One can monitor the thermal stability of an oxide, particularly stability of a porous material.

5. Thermal decompositions
   ❖   Decomposition of a polymer.
   ❖   Decomposition of template or an occluded material from a zeolite. Thermal decomposition of copper sulphate ($CuSO_45H_2O$) and other salts used for the formation of active catalysts.
   For example the decomposition of copper sulphate can be represented by the following equations
   $CuSO4.5H2O \Rightarrow CuSO4.3H2O + 2H2O$
   $CuSO4.3H2O \Rightarrow CuSO4.H2O + 2H2O$
   $CuSO4.H2O \Rightarrow CuSO4 + H2O$

6. Characterization of materials. (for example)
   ➢   Determination of glass transition temperature.
   ➢   Analysis of Portland cement versus high alumina cement.

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

The listing given is not exhaustive and the application often depends on the innovation of the investigator.   On the whole thermal methods have assumed an importance place in the characterization of catalysts.   The presentation in this monograph is restricted to demonstrate the use of various thermal analysis methods in the elucidation of catalytic systems only.

CHAPTER II

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 percentage weight loss (note not the absolute weight) as 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 the data is possible.

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 factors. 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 a 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 air decreases with increasing temperature as follows: 298 K - 1.29 mg/ml; 498 K - 0.62 mg/ml; 698 K - 0.41 mg/ml. The effect of buoyancy on measurment of weight is illustrated.

The effect of buoyance can be illustrated by a simple example. The density of air at 298 K is 1.3 mg/cm^3, while the density of air at 1273 K is 0.3

mg/cm^3. Consider for a sample of 20 mg with density 1g/cm^3, 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 = $(\rho_a - \rho_n)$ (Vx – Vs) or   (Eq. 1)

MABC = m_0 $(\rho_a - \rho_n)$ [$(1/\rho_x) - (1/\rho_s)$]   (Eq.2)
where the symbols are defined in Table 2.1.

Table 2. 1. Variables for *MABC* equations

Variable	Description of Variable
ρ_a	air density at the time of the measurement in mg/cm^3
ρ_n	density of "normal" air; i.e., 1.2 mg/cm^3
m_o	nominal mass (in grams)
V_x	volume of the unknown weight, X in cm^3
V_s	volume of the reference standard, S in cm^3
ρ_s	density of reference standard, S in g/cm^3
ρ_x	density of unknown weight, X in g/cm^3

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

Typical thermo gravimetric traces (plots of mass versus temperature) are given inFig.II.1. and the trace obtained for Calcium oxalate is shown in Fig.II.2.

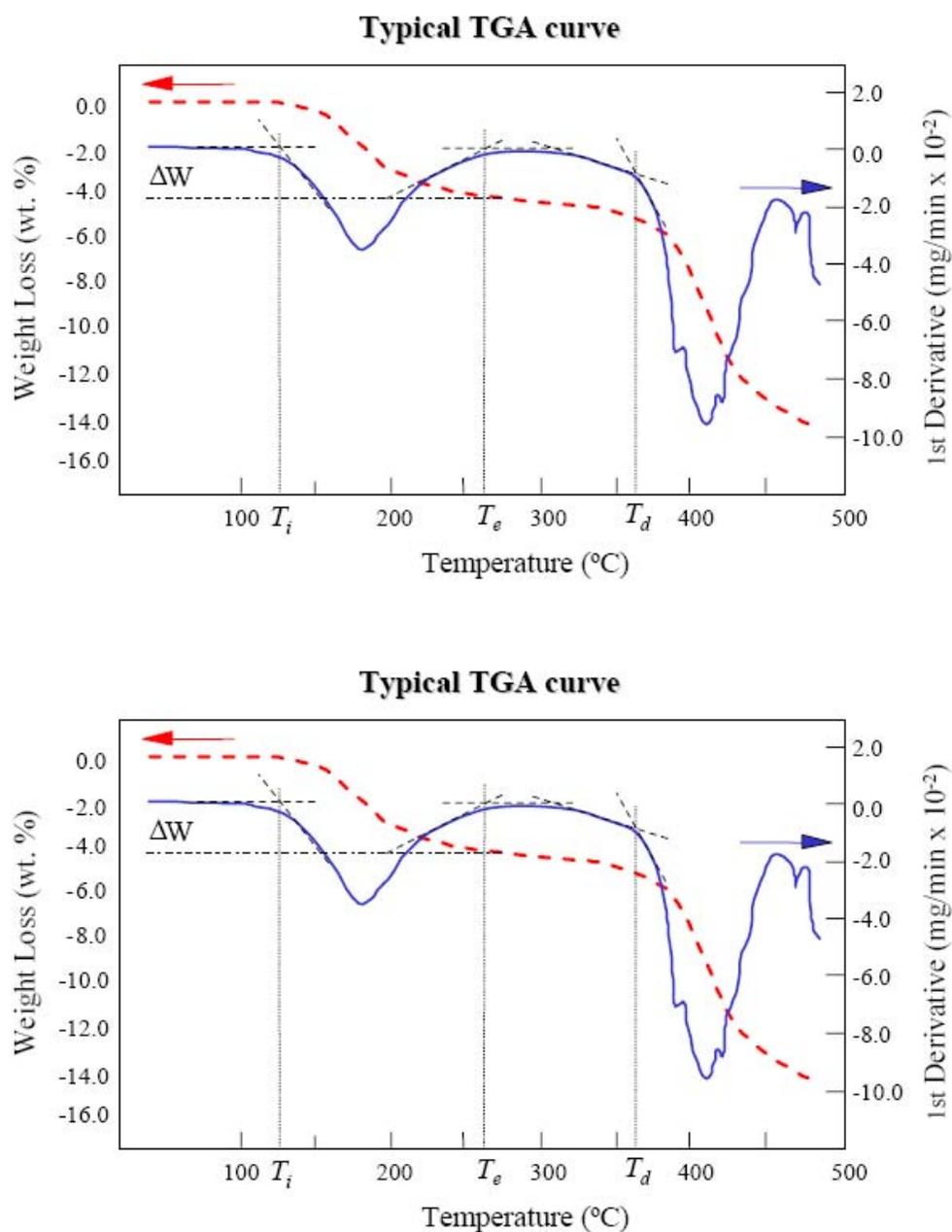**Typical TGA curve**

Typical TGA curve

Fig. II.1   Typical TG curve shown in red (dotted line) and DTG representation given by the continuous line in the figure.
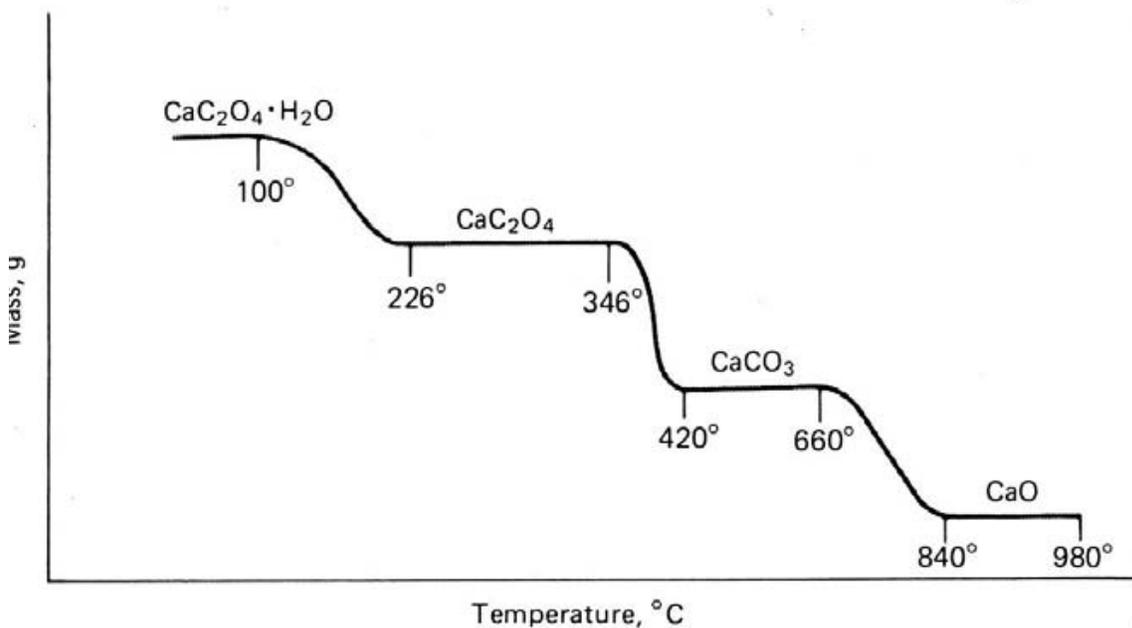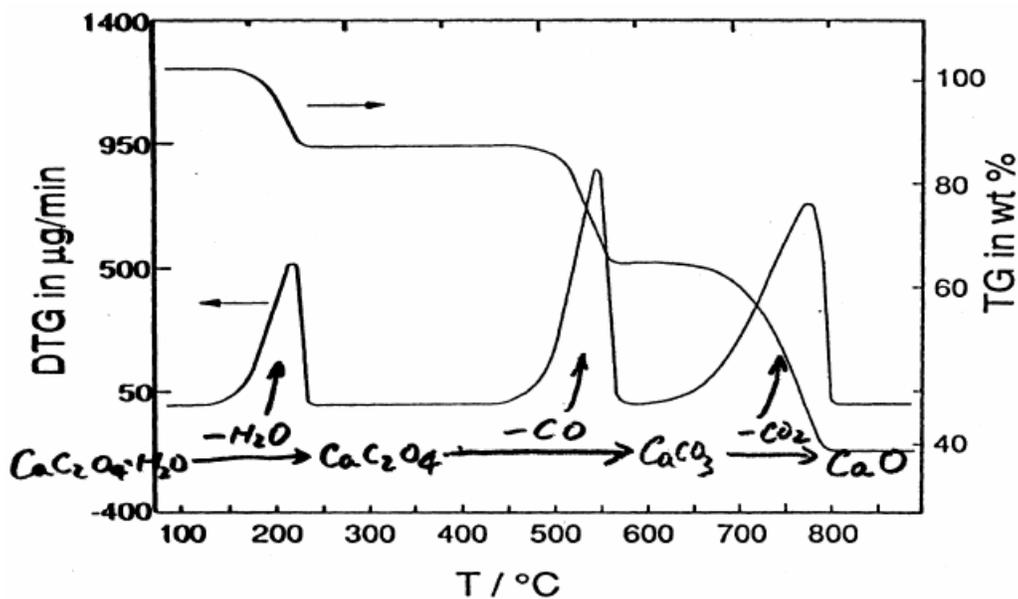
Fig.II.2.   Thermo gravimetric trace for the decomposition of calcium oxalate (one can notice that the trace provides information on the steps and also the species involved in the decomposition process).

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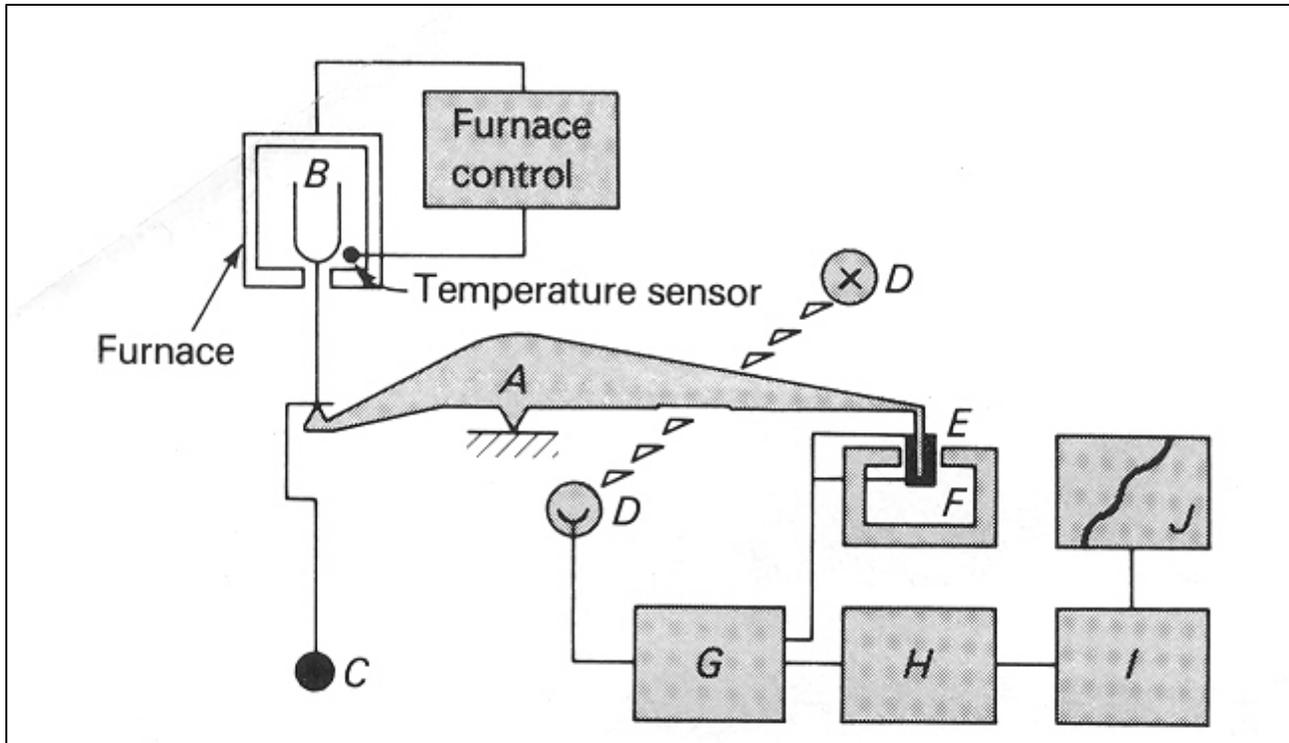

Fig.2.1. A schematic diagram of a typical thermo gravimetric apparatus [A – beam; B – Sample cup; C –Counter weight; D – Lamp and photodiode ; E – Coil; F – Magnet; G – control amplifier; H – Tare calculator; I – Amplifier
J – Data station]

It can be seen that a typical thermo balance consists of a high precision balance, a furnace for achieving high temperatures, e.g, 1800K, a temperature programmer, data acquisition system and auxiliary equipment to provide inert atmosphere.

Requirements of a normal TG balance are :
1. A thermo balance should provide accurate weight of the sample as a function of temperature. (capacity up to 1g, typical sample in mg). Its reproducibility should be very high and also should be highly sensitive.
2. It should operate over a wide temperature range, say from 298 K to 1000/1500 K
3. The design of thermo balance should be such that 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 GC or IR or to QMS 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 isoconversion have been advocated in recent times by Starink [1].   He has classified the available methods and also the methods developed by him as Type A and Type B methods.

Type A method or Friedman type method

This method essentially concerns the determination of the rate at the stages of isoconversion.   Since it depends on the determination of a parameter, it does not require any mathematical approximation.   In this method one must determine the rate of the reaction at $T_f(\beta)$ (where T refers to the temperature subscript 'i ' denotes isoconversion levels and β refers to the heating rate).   Hence one has to determine the rate at isoconversion levels at different heating rates. In addition, one should also note the temperature where the rate is measured for the isocoversion levels. Accordingly based on Arrhenius type expression the equation of relevance is

$$\ln (d\alpha/dt) = (-E/RT_f) - \ln f(\alpha)$$

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_f, and the transformation rate $d\alpha/dt$ at that fixed conversion can be plotted according to the above equation..   The slope of a plot of $\ln (d\alpha/dt)$ versus $1/T_f$ 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

$$\ln [(d\alpha/dT)\beta] = (-E/RT_f) - \ln f(\alpha)$$

This method thus becomes model free method.   Though this A 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.

  M.J.Starink, Thermochim Acta, 404, 163 (2003); http://eprints.soton.ac.uk/18822/; Journal of Material Science, 42, 483 (2007).
1.H.L.Friedman, J.Poly Sci., C 6, 183 (1964)
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[25] S. Vyazovkin, V.V. Goriyachko, Thermochim. Acta 194 (1992) 221.
[26] S. Vyazovkin, A.I. Lesnikovich, Russ. J. Phys. Chem. 62 (1988) 2949.

Type B Isoconversion method

This method is called the generalized Kissinger method and is one of the best known 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;

$(d\alpha/dt) = f(\alpha)\, k(T)$ 1

The temperature dependent function can be replaced by Arrhenius type of expression

$(k) = (k_0) \exp - (E/RT)$ ...2

If the combined expression is integrated by separation of variables one gets

$\int_0^\alpha (d\alpha/f(\alpha)) = (k_0/\beta) \int \text{Exp}\,(-E/RT)dT = (k_0 E/\beta R) \int_{yf}^{Tf} \exp(-y)/y^2\, dy$

Where $y = E/RT$, $y_f\ E/RT_f$, T_f is the temperature at an equivalent (fixed) state of transformation, β is the heating rate. The integral in equation (3) is termed as temperature integral or Arrhenius integral $p(y)$.

Integrating in parts and assuming $y_f \gg 1$ one gets
$(p(y)) \approx \exp (-y/y^2)$

Taking logarithm for expression3 and inserting p(y) one obtains

$(\ln \int_0^\alpha d\alpha/f(\alpha) = \ln (k_0 E/\beta R) + \ln 1/\beta y_f^2 - y_f$

At constant fraction transformed, this leads to

$(\ln (\beta/T^2_f) = - (E/RT_f) + C$

Plot of $(\ln(\beta/T_f)$ versus $1/T_f$ should yield the value of E/R. This method is usually called the Kissinger-Akahira-Sunrose (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 another chapter.

At this stage, it is necessary that one comments on the methods that have been evolved and this has been attempted in Table 2.1.

Designation of the method	Procedure adopted	Type code	Best known methods	Ref
Rate –iso-conversion method	Plot of $\ln(d\alpha/dt)$ versus $1/T_f$	A	Friedman	1
			Gupta et al	2
(p(y)) – Iso-conversion method	Plot of (T_f/β) versus $1/RT_f$	B	Generalised Kissinger	3
Type B Maximum rate method	Plot of (T_p/β) versus $1/RT_p$	B	Kissinger	4
			Flynn correction of	5
Type B iterative method	Type B followed by iterative method	B	Ozawa method	
			Starink method	6
			Lyon method	7

1.H.L.Friedman, J.Polym.Sci., 6,183 (1964).
2.A.K.Gupta, A.K.Jena and M.C.Chaturvedi, Scr.Metall., 22,369(1988).
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7.R.E.Lyon, Thermochimica Acta, 297,117 (1997).

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.

References

[1]M.J.Starink, Thermochim Acta, 404, 163 (2003); http://eprints.soton.ac.uk/18822/; Journal of Material Science, 42, 483 (2007).
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[3]A.K.Gupta, A.K.Jena and M.C.Chaturvedi, Scr.Metall., 22,369 (1988)
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CHAPTER III

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APPROPRIATENESS OF ARRHENIUS EQUATION FOR KINETIC ANALYSIS OF SOLID STATE REACTIONS

It is necessary that at this stage, one considers the appropriateness of employing Arrhenius type of expressions for the evaluation of the activation energy of reactions studied by thermal methods. Hence this aspect has been considered in this chapter. This question it must be stated, has been persistently posed before also a number of times in the literature.

The kinetic parameters for solid state reactions (decomposition, phase change or compound formation) have been conventionally evaluated by treatment of isothermal or non-isothermal data of fraction reacted (α) as function of time in the case of isothermal studies and (α) as a function of temperature employing the conventional Arrhenius equation in the form, $k = A \exp(-E_a/RT)$. The applicability of Arrhenius equation for homogeneous molecular level reactions is well known and has been established beyond doubt since these systems obeys 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 'theoretically sterile' since the constants of these proposed equations do not lead to any deeper understanding of the steps of 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 by interface sites and their energy levels. These energy states though normally obey for Fermi-Dirac 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 Arrhenius equation for treatment of solid state reaction kinetics implying the other two statistics can approximate to MB statistics.

The kinetics of solid state reactions is conventionally treated 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 its growth in one, two or three dimensions. A brief summary of the various kinetic expressions normally employed to treat the isothermal kinetics of solid state reactions is given in Table.III.1. These model kinetic expressions can be analyzed in terms of 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 also been analyzed based on various models. Typical expressions employed for treating kinetic data of non-isothermal measurements

Table 1 Some of the typical physico-geometric kinetic model functions for treating the conversion (α, fraction reacted) versus time data for solid state reactions.[3-5]

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	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
2D or 3D Avrami-Erofeyev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
3D Avrami-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	$2(1-\alpha)^{1/2}$	$2\,[1-(1-\alpha)^{1/2}]$
Contraction volume	$3(1-\alpha)^{1/3}$	$[1-(1-\alpha)^{1/3}]$
Generalized model of Sestak	$(1-\alpha)^n\,\alpha^m$	-
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	$(1-\alpha)^3$	$0.5(1-\alpha)^{-2}-1$

assembled in Table III.2. Most of these expressions given in Table III.2 have been derived on some specific models as conceived by the respect authors. It is not clear, which 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 derived parameters like activation energy E_a and the pre-exponential factor (A) of the Arrhenius equation. These values are Table III.2. Typical models for the treatment of non-isothermal data (only typical ones are given and for other models the readers are referred to the original literature [6-17])

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

analyzed for consistency or to interpret the mechanism of the solid state reaction. However, this situation has led to many unclear situations, since the derived parameters of E_a and A from various models are not mostly consistent and hence the interpretation has to resort to some selection which could not be unbiased. Secondly, since not all the models are employed for treating a set of non-isothermal kinetic data, the selection and supposed applicability of a chosen model appears 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 considered.

In order to substantiate our 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 III.3. The data given in Table.III. 3 should be taken as representative ones available in literature. No attempt has been made to collect the data extensively.

Galwey [27] has observed that the value of pre-exponential factor for nearly 50% (this estimate appears to be arbitrary) of solid state decompositions lie in the range of 10^8 – 10^{14} S^{-1}. In reality for most of the solid state reactions, the values of the preexponential factor vary widely and the spread is certainly too large and mostly differ from the standard value of 10^{13} S^{-1} based on Polyani-Wigner model. One can rise 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 our intention to list all these questions but only to indicate a few of them.

(i) What is the significance of values of A higher than 10^{13} S^{-1}?

(ii) What interpretation can be offered when the observed values of A is far less than $10^{13} S^{-1}$?

Table III.3.Values of E_a and A deduced for some typical solid state reactions (includes examples of decomposition, dehydration, solid state inorganic and organic reactions and

phase-changes)

Reaction	E_a (kJ/mol)	(A) (min^{-1}/sec^{-1})	Ref
Decomposition of poly carbonates Coats and Redfern Freeman and Carrol	 15.6 360.4	 - -	18
Decomposition of Borax pentahydrate Dehydration Decomposition	 92. 15.9	 2.35×10^{10} 2.04	19
Formation of Nb_3Sn Kissinger Flynn-wall	 312 312		20
Melting of ice	28.5 ± 3	10^9 (sec^{-1})	21
Decomposition of $Gd_2Mo_7O_{24}14.5$ H_2O Horowitz- Metzer Coats and Redfern Piloyau-Novikova	 49.2 30.6 28.1	 2.3×10^2 1.9×10^2	22
($\beta - \gamma$) phase transition in sulanilamide Avramin-Erofeyev Cardow model Nucleatin Growth	 89 ± 8 142 ± 14 70 ± 4	 4.6×10^9 2.0×10^{17} 1.1×10^8	23
Paddy husk	125.9	3.7×10^9	24
SiC from CNT and Si	96 ± 30	-	25
Zinc Oxalate – isothermal method Simple power law Unimolecular law	 250.5 258.3	 3.0×10^{18} 2.8×10^{21}	26

Dynamic method			
Coats and Redfern	257.5	4.8×10^{20}	
Zsako	215	2.6×10^{17}	
Nickel oxalate isothermal method			26
1. Prout –Tompkins	54.6	3.7×10^4	
2. Contracting Cube law	82.0	6.9×10^7	
3. Avrami-Erofeyev	66.2	8.0×10^4	
4. Unimolecular law	137.5	1.8×10^{11}	
Non-isothermal method			
Coats and Redfern	160.6	1.1×10^{13}	
Asako	140.8	2×10^{12}	
Thorium oxalate- Isothermal method			26
Exponential law	147.4	6.8×10^{11}	
Contracting cube law	226.1	1.2×10^{17}	
Non-isothermal data			
Coats and Redfern	209.9	9.4×10^{16}	
Zsako			
Contracting cube law	173.9	3×10^{13}	
Unimolecular law	173.9	1×10^{14}	

(iii) The values of activation energy do not usually lie in the range of 100-200 kJ/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 two important kinetic parameters (activation energy and pre exponential factor) 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 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 visualize 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 consecutive 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 of 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 as much applicable as in homogeneous phase.

(vi) In terms of energy transfer, the species in the interracial 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 for 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 ln A) it has not 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 and ln A for sites of varying reactivity is not expected unless one has to invoke additional internal reorganizations which can give rise to smooth variation in both E_a and 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 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 (like the present author) 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 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 analysis 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 polymorphic transition. It should be recognized that the models so far 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 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 ($\beta = dT/dt$), 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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Calibration standards useful in DTA measurements

CALIBRANT	Transition 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	

Typical DSC curve
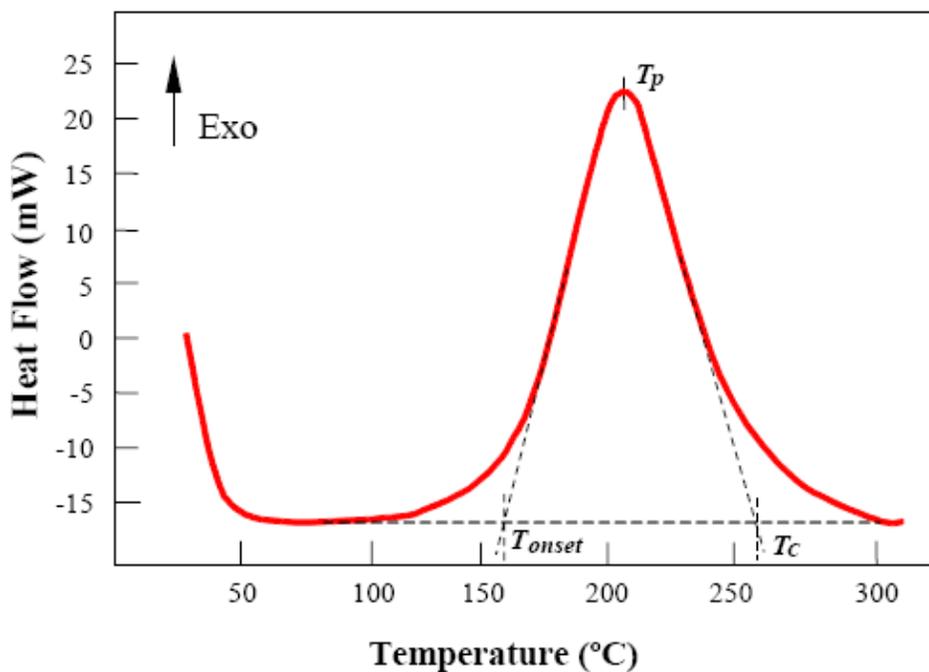
As stated in an earlier chapter, thermal desorption method is amenable for estimation of kinetic parameters. The kinetic triplet normally considered in thermal methods includes the activation energy, frequency factor and the functional dependence of the conversion. In these three parameters, the importance of activation energy and frequency factor need not be re-emphasized. Since heating rate β is related by the relation dT/dt between temperature and time, kinetic analysis seems to be feasible. In addition normally in thermal desorption measurements, the system is far from equilibrium and hence once can use only kinetic expressions for treating such measurements. Normally in every temperature programmed measurement, β, the heating rate is constant and it is possible to obtain the temperature of desorption rate maximum T_{max} (= maximum rate of desorption).

Polanyi-Wigner equation can be expressed as

$$(r_{des}) = -\frac{d\theta}{dt} = \vartheta_n(\theta) \exp(-[\Delta E_{des}^{PW}(\theta)]/RT)(\theta)^{n(\theta)} \qquad (1)$$

Since $\beta = \frac{dT}{dt}$ or $dt = (\frac{1}{\beta})dT$, equation (1) can be rewritten as

$$\frac{d\theta}{dT} = -\frac{1}{\beta}\vartheta_n \exp[-[\Delta E_{des}^{PW}(\theta)]/RT](\theta)^{n(\theta)}$$

At the maximum of the desorption rate at T_{max}

$$\frac{dr_{des}}{dt}\Big|T_{max} = 0$$

This condition must be satisfied since $r_{max} = -\frac{d\theta}{dt} = -\beta\frac{d\theta}{dT}$

$$0 = \frac{d^2\theta}{dT^2}\Big|T_{max} = n.\theta^{n-1}.\frac{d\theta}{dT} + \theta^n\{-\Delta E_{des}/RT_{max}^2\}$$

However

$$\frac{d\theta}{dT} = -\frac{1}{\beta}\vartheta_n.\exp\{-\Delta E_{des}^{PW}/RT\}.\theta^n$$

And hence substituting this value of $\frac{d\theta}{dT}$ *and solve for* { $\Delta E_{des}/RT_{max}^2$ } one gets,

$$\frac{\Delta E_{des}}{RT_{max}^2} = \frac{1}{\beta}\vartheta_n.n.\theta^{n-1}\exp\{-\Delta E_{des}^{PW}/RT_{max}\}.$$

When the reaction order is taken as 1 (n=1) then T_{max} *is independent of the coverage but depends only on the heating rate*

Therefore one can write that

$$\frac{\Delta E_{des}}{RT_{max}^2} = \frac{1}{\beta}.\vartheta_1.\exp(-\frac{\Delta E_{des}}{RT_{max}})$$

Taking logarithm and rearrangement gives

$$(\ln\frac{T_{max}^2}{\beta}) = \frac{\Delta E_{des}}{RT_{max}} + (\ln\frac{\Delta E_{des}}{\vartheta R})$$

In this expression to make it dimensionless each parameter is divided by its own unit, for example $\hat{T} = T/K$)

Now if one were to plot $(\ln\frac{T_{max}^2}{\beta})$ *versus* $\frac{1}{T_{max}}$ for a series of heating rate β, then from the slope of the straight line plot one can calculate ΔE_{des} and ϑ_1 can be obtained from the intercept.

The corresponding expression for a second order desorption process is

$$\frac{\Delta E_{des}}{RT_{max}^2} = \frac{2}{\beta}.\vartheta_2.\theta(T_{max}).exp\left(-\frac{\Delta E_{des}}{RT_{max}}\right)$$

Since in a second order desorption process, the trace is symmetric with respect to T_{max} and hence the θ at T_{max} is half the value of desorption. Inserting that the total θ desorbed $= 2.\theta$, the expression obtained is

$$(\ln \frac{T_{max}^2}{\beta}) = \frac{\Delta E_{des}}{RT_{max}} + (\ln \frac{\Delta E_{des}}{\vartheta_2 R\theta_0})$$

Plotting Left hand side versus $1/T_{max}$ as function of heating rate will provide means for calculating ΔE_{des} from the value of the slope and if θ_0 is known, then the frequency factor ϑ_2 can be calculated from the value of the intercept.

However Redhead derived a simplified relation between ΔE_{des} versus $\frac{1}{T_{max}}$. He made the assumption that activation parameters are independent of surface coverage and the desorption followed first order kinetics.

He used the following equation

$$\frac{\Delta E_{des}}{RT_{max}^2} = \frac{1}{\beta}.\vartheta_1.exp\left\{-\frac{\Delta E_{des}}{RT_{max}}\right\}$$ and solved for ΔE and obtained a relation

$$\Delta E_{des} = RT_{max}\{(\ln[\vartheta_1 T_{max}/\beta]) - \ln\frac{\Delta E_{des}}{RT_{max}}\}$$

The $\{\ln \frac{\Delta E_{des}}{RT_{max}}\}$ is small compared to the first term $\ln \frac{\vartheta_1 T_{max}}{\beta}$ especially when $10^8 < \frac{\vartheta_1}{\beta} < 10^{13}$ K^{-1}. Therefore one can extract the value of the activation energy ΔE_{des} from a single desorption trace at a particular heating rate β and observing T_{max} and using the same to calculate ΔE_{des}.

Another simplified method has also been introduced by Habenshaden and Kuppers. If one were to evaluate the leading edge of the desorption trace at the same value of θ, then one can plot $\ln r_{des}$ versus 1/T according to the logarithmic form of Polanyi-Wigner equation

$$\{\ln r_{des} = -\frac{\Delta E_{des}}{RT} = \ln \vartheta + n \ln \theta\}$$

The slope of this Arrhenius type of plot the value of ΔE_{des} can be calculated. From the intercept of this plot the value of the frequency factor can be calculated if one knows the order of desorption kinetics and also the coverage where the leading edge has been measured.

Even though there is advantages since the assumptions made are limited, a general drawback of this procedure is that the leading edge has the signal/noise data plugged and hence the error involved may be greater when low coverages are considered for leading edge analysis.

There is yet another way of analyzing thermal desorption trace by using a plot of

$\{\ln - \frac{r_{des}}{\theta^n}\}$ versus 1/T for various values of n = 1, 2, or 3. Assuming the activation parameters are independent of temperature and coverage, then a straight line will be obtained if the correct value of n is used. Since

$$\{\ln -(d\theta/dt)/\theta_n^2\} = -\frac{\Delta E_{des}}{RT} + \{\ln \vartheta_n\}$$

The value of activation energy ΔE_{des} and ϑ_n can be determined.
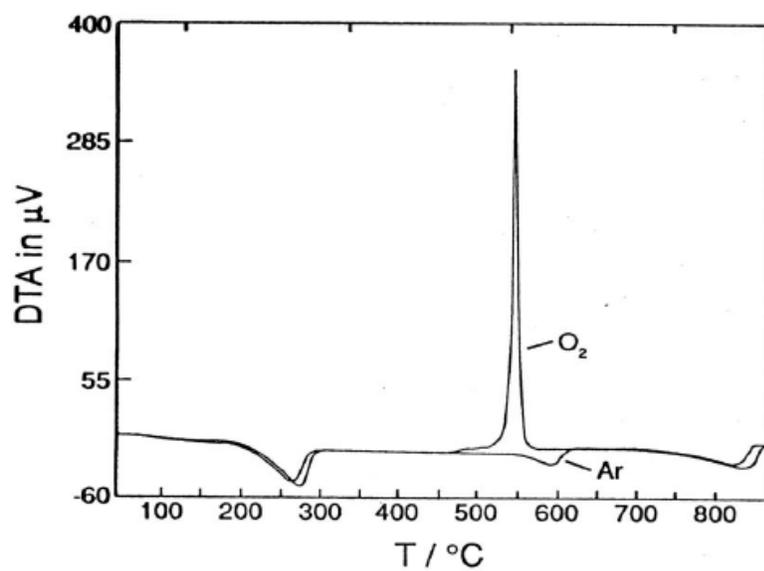
DTA curves for the thermal decomposition of $CaC_2O_4 \cdot H_2O$ at 20 °C min^{-1} in O_2 and Ar

Appendix 1

NOMENCLATURE IN THERMAL ANALYSIS

The evolution of nomenclature in Thermal analysis has a long history.   It started with for *better thermal analysis* in 1977 and has undergone various changes and the evolution is continuing due to changes that are taking place in instrumentation and also other theoretical development.   In this appendix, an adopted version of nomenclature from the site http://www.ictac.org/ictacnews/articles/dec04/ICTAC%20Nomenclature.pdf is given. For any authentic version readers are referred to the ICTAC site http://www.ictac.org.

Thermal Analysis (TA) is a group of techniques either alone or in combination (multiple techniques) which can be used to study the properties of a system as a function of temperature.   The variation in temperature can be related to time in the form of the heating rate β. The heating rate normally employed is linear by the relation $T = T_0 + \beta t$, thought other forms of heating schedule can also be follow
ed like holding the temperature at a particular value (isothermal) or other functional dependence of heating rate. Conventionally the temperature is programmed and this can indicate an increase, or decrease in temperature, a periodic change, or a constant temperature or any combination of these.

Key words normally employed in the definition of Thermal Analysis:

· **Techniques** – a technique is characterized by the property that is being investigated. One such classification is given in Table   ….. in chapter 1.
· **Relationship** – this denotes that either sample property is monitored as a function of temperature (*controlled-temperature program*), or the temperature is measured as a function of the samples property like phase transformation or dehydration and so on (*sample controlled heating*).
 . **Sample** – denotes the system that is being investigated during the entire experiment (starting material, intermediates and final products) and the atmosphere in which the system is being investigated. The whole can be considered as equivalent to the thermodynamic **system.**
 . **Property** – denotes any physical or chemical property of the sample.

In the following only the essential terminology and glossary are given.   For a complete listing the reader is referred to the original documents referred. The system followed is the word or words the qualification and then what the word denotes are given in this sequence.

adiabatic, (adjective)- implies that the thermal analysis is carried out with no heat enters or leaves the system.
atmosphere,(oun)n, - the gaseous environment of the sample during thermal analysis either effected or generated as result of thermal treatment.
calorimetry, (noun) – method where in heat involved is measured.

combined, or hyphenated (adjective) – the combination of two or more techniques (this can include thermal and non thermal techniques as well like TGA-FTIR).

controlled temperature program,(noun) – the temperature ramp imposed on the sample during the course of the thermal analysis.

cooling curve or heating curves, (noun) - the experimental traces during colling or heating.

derivative, (adjective) – pertaining to the first derivative (mathematical) of any trace with respect to temperature or time.

differential, (adjective) – difference in measured quantities usually between a sample and a reference or standard material.

dynamic, Static(adjective)- a prefix to indicate the changes in the parameter.

gas flow, (noun) - the passage of gas from one part of the system to another.

high pressure, (HP, adjective) – a prefix applied to the technique name to indicate that the pressure of the experiment is above ambient.

isobaric, (adjective)- a prefix indicating experiment is carried out at constant pressure.

isothermal, (adjective), - a prefix indicating that the temperature is maintained constant throughout the experiment

micro-, (adjective),- a prefix used to denote that the technique measures small quantities, either with respect to the amount of sample studied, or with respect to the change in the properties measured.

modulated, (adjective)- a prefix indicating that a parameter changes in a periodic manner.

modulated temperature, (MT, adjective), - a prefix indicate that a temperature modulation has been applied.

photo-, (adjective), - prefix to indicate that the experiment involves the illumination of the sample or measures the amount of light emitted from a sample. Where possible the wavelength range of the light should be specified.

sample-controlled, (adjective) – prefix o indicate that a property of the sample is used either continuously to control the sample heating. With no prefix, it is assumed that the experiment is following a controlled temperature program.

scanning, (adjective), – a prefix indicating a specified experimental parameter, usually temperature, is changed in a controlled manner.

stepwise, (adjective) – prefix indicating discrete, discontinuous changes in an experimental parameter like force, temperature etc.

tan δ, n – is the dimensionless ratio of energy lost to energy returned during one cycle of a periodic process. For example $\tan \delta = E'' / E'$, in DMA.

thermal curve or more correctly thermo-analytical curve (noun) – any graph of any combination of property, time, temperature derived from a thermal analysis technique.

thermo-, (adjective)- a prefix indicating the use of changing temperature during the experiment.

Reporting Experimental Conditions

The details of how a   technique is used, additional experimental parameters and constraints employed must be reported alongside the data in all published work. It is important to separate the technique (instrumentation) from the way in which it is used (experiment). Of course, the make and model number should be included in all reports,

papers and studies as well as an experimental section that describes in full all experimental parameters.

The reader is referred to the ICTA publication "Reporting Experimental Results" (Lombardi 1977) for specific guidelines.

It should be normal practice to use the standard IUPAC quantities, units and symbols when reporting any work in thermal analysis. These are listed in I.Mills, T. Cvitaš et.al., *Quantities, Units and Symbols in Physical Chemistry.*

Symbols describing specific events or materials in thermal analysis
In general, symbols should be in *italic* type, or, if vectors, in ***bold italic type.***
Units do not take plural.
Subscripts should be restricted to single letters.
If the subscript relates to an object or property, it should be a CAPITAL letter.

"m_S" = mass of the sample

T_R = temperature of reference .

T_C = Curie Temperature

If the subscript refers to a phenomenon, it should be lower case:

T_m = melting temperature

T_g = glass transition temperature.

If the subscript refers to a specific event, time or point, it should be lower case or figures:

T_i = initial temperature

'm_f = final mass

T_p = peak temperature

'$t_{0.5}$' = time of half reaction

Changes in extensive thermodynamic quantities X due to an event y should be represented by $\Delta_y X$:

$\Delta_{vap}H$ = enthalpy of vaporization

$\Delta_r G$ = Gibbs free energy of reaction.

Symbols for the physical state of the material should be put in brackets after the formula symbol:

$\Delta_{vap}H = H(g) - H(l)$