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REACTION KINETICS BY THERMAL ANALYSIS

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The application of thermal analysis in the study of reaction kinetics and reaction mechanisms in combination with presently available powerful analytical tools, in the sphere of materials with particular reference to high energy materials is presented and discussed. Also an attempt has been made to correlate the kinetic data obtained by TA with the performance characteristics, for some important materials.

Reaction kinetics by thermal analysis (TA) constitutes one of the most important facets in the application of TA to the study and evaluation of materials [1, 2]. The breaking of one or more constituents of the reactant into simpler atomic groupings brought about by temperature increase, particularly in a solid, is an important distinct class of solid state reactions and has both scientific and practical significance. The reactivity of the solid phase is primarily determined by the bond structure and imperfections of solids along with thermodynamics. The structure, lattice vibrations and defects in a crystal in thermodynamic equilibrium are governed through minimisation of Gibb's free energy, determined by the interaction energy and entropy giving rise to a transformation under favourable conditions.

Nucleation involves conversion of a small volume of reactant into a stable particle of the product. Growth, the continued reaction, occurs preferentially at the interfacial zone of contact between these two phases. Nucleation and growth obey different kinetic expressions. The rate equations generally valid for solid state reactions are acceleratory, deceleratory or sigmoidal in nature. There can be appreciable deviations in the behaviour pattern in real systems from the idealised model.

The kinetics of a solid state reaction can be studied by both isothermal and nonisothermal methods. The results of such studies are kinetic curves that illustrate the relationship between the transformation degree α and time t. Then comes the choice of a kinetic equation adequately representing the experimental data.

In general the Avrami–Erofeev equation (AE) [3–6]

$$[-\ln(1-\alpha)]^{1/n} = k(t-t_0)$$

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where the exponent $n = \beta+\lambda$
β: number of steps involved in nucleation,
λ: number of dimensions in which nuclei grow,
k: rate constant,
t_0: initial time,
t: time
has been found to hold for many solid phase decompositions, phase transformations etc.

When nucleation is restricted to specific crystallographic surfaces, the advancing interface reaction may be expressed as [7]

$$1-(1-\alpha)^{1/n} = k\cdot t$$

where,
n: number of dimensions in which the interface advances.
For chain type reactions, the Prout–Tompkins equation [8]

$$\ln[\alpha/(1-\alpha)] = k\cdot t+C$$

has found application to many systems.
For diffusion controlled reactions, the expression

$$-\log(1-\alpha) = (k\cdot t)^m$$

where $m = \beta+\lambda/2$,
β & λ: as referred above
has been generally found valid.

The structure, at lower temperatures, is basically determined by the energy of interaction but at higher temperatures the entropy predominantly influences the configuration. A variety of structural imperfections of chemical importance may also occur in solids. Four major classes of structural abnormality are to be considered. These may be point defects [9–11] consisting of vacancies in the crystal lattice or interstitial or substitutional disorders. Dislocations [12–15] are unidimensional defects and are important in solid state reactions for they can act as preferential nucleation sites for the formation of new phases, serve as fast diffusion paths and as sites of repeatable growth within a crystal. Stacking faults are two dimensional defects corresponding to irregularities in the stacking of certain lattice planes. Pores and microscopic inclusions are three dimensional crystal defects which significantly affect the reactivity of solids. In polycrystalline materials the grain structure, shape, size and orientation are important as they influence the physical properties and the reactivity. In multiphase solids heterogeneous microstructures depending on the number and composition of phases is significant.

The course of solid state thermal decomposition depends on a number of external and internal factors and the study of thermal dissociation involves the identification of the stages of decomposition and products of the reaction, determination of the kinetics of each stage, construction of the mathematical model and development of the general theory for thermal decomposition.

The determination of the extent of reaction, mass loss, enthalpy change and product gas evolution has found wide application. Therefore, thermal methods of investigation coupled with mass spectrophotometry, gas chromatography, X-ray diffractometry, microscopy and infrared spectroscopy have found profitable application in the investigation of the reactions of solids [16–18].

Under isothermal conditions, a finite time is required to heat the sample to the reaction temperature of interest, so the initial α *vs.* t curve cannot strictly refer to isothermal conditions and thus calls for the design of the experiment, so as to minimise this effect.

Reaction rates related to α and temperature T by different independent functions. At constant temperature,

$$\mathrm{d}\alpha/\mathrm{d}t = A \cdot f(\alpha); \qquad f(\alpha) = k \cdot t$$

If the rate constant "k" varies with "T" in accordance with the Arrhenius equation, then

$$\mathrm{d}\alpha/\mathrm{d}t = A \cdot f(\alpha) \cdot \exp(-E/RT)$$

The validity of this expression depends on the obedience of the rate process to a single rate equation over the whole range of α and also obedience to the Arrhenius equation for the range of temperature studied. At a constant rate of heating, $\mathrm{d}T/\mathrm{d}t = b$,

$$\begin{aligned}\mathrm{d}\alpha/\mathrm{d}T &= \frac{\mathrm{d}\alpha}{\mathrm{d}t} \cdot \frac{\mathrm{d}t}{\mathrm{d}T} \\ &= k \cdot f(\alpha)/b\end{aligned}$$

It is therefore, logical to deduce that it might be possible, by varying the temperature linearly, to determine the complete kinetic behaviour in a single experiment. Both integral and differential methods [19–23] have been proposed to arrive at a suitable and amenable kinetic expression under dynamic temperature conditions for use in thermal analysis. Despite many studies so far carried out by nonisothermal technique on reaction kinetics, it is yet to find complete acceptance amongst the various workers.

It is, however, surprising that for a number of systems [24] the first order equation provides a satisfactory approximation and the value of frequency factor and activation energy obtained have been found to be reasonably accurate though it may not have much of a mechanistic significance and may not represent the exact kinetic relationship.

To arrive at the probable mechanism of transformation, thermal analysis data are to be supplemented with data from other experimental techniques as the mechanism has to be worked out at the molecular, micro and macro level for solid state reactions.

Essential factors in employing TA for kinetic studies is a proper selection of the main parameters of the analysis, sample size, kind of atmosphere and rate of temperature rise during the experiment.

For kinetic studies slower rates of heating are to be preferred as this way a broader peak/change with better resolution is obtained. The reaction, under these conditions, will be more truly temperature dependent and the thermal lag is minimised. For some materials where there is a possibility of explosion, a slower rate of heating is preferred for safety reasons and for suppressing the accelerating effect of the high exothermicity on the transformation rate.

Characteristic transformation temperatures recorded at lower rates of heating approach the temperatures of thermodynamic equilibria of the reactions and these data may often be used directly in a statistical treatment of the thermal decomposition data of solids. Quasi-isothermal, quasi-isobaric TG was introduced by Paulik and Paulik [25] to reduce the deviations from thermodynamic equilibrium due to the dynamic nature of classical thermal analysis.

The heating rate also influences the local atmosphere inside the sample and on its surface. An increase in the heating rate gives rise to an associated increase of the rate of thermal decomposition. This has a bearing on the diffusion of the gases in the bulk of the sample, and their escape into the surrounding atmosphere.

Transformations occurring at a definite temperature therefore may not take place simultaneously in the whole volume of the sample, but proceed gradually from the surface to the centre of the sample along the moving front of the temperature wave. In other case, there can be a rate gradient from the surface to the centre of the sample corresponding to the temperature gradient [26–27]. Large samples, in addition, give rise to diffusional barriers for the gaseous products of the reaction.

The present tendency is to use a small sample size as this reduces the temperature gradient between the wall of the crucible and the bulk of the sample, due to the limited thermal conductivity of the samples in general. The particle size, particle size distribution [28–29], mode of packing, heat of reaction, history of the sample, atmosphere [30] can also effect significant modification of the kinetics. Considering the thermal homogeneity and resolution, smaller sample holders are preferred. Thermocups have been found to have several advantages in this respect.

Application of spectral techniques to thermal analysis has contributed substantially to the capability of TA in the study of reaction kinetics. In FTIR–EGA [31, 32] the released components can be scanned continuously by a

Fourier transform infrared (FTIR) spectrophotometer, the resultant FTIR evolution profiles—plots of absorbance *vs.* sample temperature—characterise the pyrolysis. It is also possible to get structural information on the changes in the reactants as the temperature is raised using a heated sample cell. IR scans of changing structures give detailed spectral information on thermally induced structural changes. An absorbance plot indicating changes in functional groups with temperature, a sort of chemigram, using compressed spectral plots can help follow individual components when several different components are evolved simultaneously in a transformation. The mole ratios of the components released and remaining can be worked out to arrive at finer details.

A comparison of characteristic band intensities of some aminoguanidine nitrates [33] and polynitro [34] compounds at selected thermal decomposition temperatures at regular time intervals have revealed a preferential loss in the intensity of certain functional groups. Photomicrography at suitable magnification as the sample is heated gives information on the morphological and other changes which greatly contributes to the kinetic understanding.

Kinetic data obtained on some high energy materials [35] using thermal analysis are given in Table 1.

Kinetic data obtained by TA have been correlated with performance characteristics in many systems [36–45]. Kinetic data by TA have been found to be useful in

Table 1 Kinetic parameters of the thermolysis of some explosives

Substance		Temp., K	Equation, $f(\alpha)$		E, kJ/mol	log A
1 Nitroamino guanidine	I	423–433	AE	$n=3$	143	10.4
	II	433–451	AE	$n=3$	137	11.0
2 Diaminoguanidine nitrate		501–516	AE	$n=2$	125	9.4
		501–516	Mampel	$n=3$	131	10.6
3 Triaminoguanidine nitrate	I	446–463	AE	$n=2$	167	16.1
	II	463–483	AE	$n=3$	127	10.0
4 Triaminoguanidine picrate		443–448	AE	$n=3$	267	31.0
5 1,3,5 Triamino trinitro benzene		546–560	AE	$n=2$	234	
6 Trinitrosotriaza cyclohexane (TRDX)		406–418	AE	$n=1$	153	22.4
		406–418	AE	$n=1$	233	31.0
7 Trinitrotriaza cyclohexane (RDX)		458–478		$n=0.6$	173	22.2
8 Tetranitrotetraza cyclooctane (HMX)		508–528	AE	$n=1$	251	27.4
		508–528	AE	$n=2$	266	32.7

optimising pyrotechnic compositions [46–48] for delay, illumination, smoke etc. as a direct correlation has been observed. Initial thermal decomposition for explosives have been correlated with their detonation parameters. Extensive application of the kinetic data obtained by TA concerning their performance characteristics has been found for a variety of materials like polymers [49–52], coals [53] elastomers etc. and in metallurgy [54, 55].

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Zusammenfassung — Es wird die Anwendung der Thermoanalyse bei der Untersuchung der Reaktionskinetik und des Reaktionsmechanismus in Zusammenwirkung mit den gegenwärtig zur Verfügung stehenden leistungsfähigen analytischen Werkzeugen auf dem Gebiet von Materialien mit speziellem Bezug auf energiereiche Stoffe dargestellt und besprochen. Es wurde auch versucht, die durch TA erhaltenen kinetischen Daten einiger wichtiger Stoffe mit deren Leistungskenndaten in Beziehung zu stellen.

Резюме — Представлено и обсуждено применение термического анализа в комбинации с другими доступными аналитическими методами для изучения реакционной кинетики и механизма реакций высокоэнергетических материалов. Предпринята также попытка скоррелировать кинетические данные, полученные методом ТА, с эксплуатационными характеристиками некоторых особо важных материалов.