

NETZSCH-ITAS AWARD (1987) PAPER

KINETICS OF SOLID STATE THERMAL DECOMPOSITION REACTIONS

K. N. Ninan

ANALYTICAL AND SPECTROSCOPY DIVISION, SPPC,
VIKRAM SARABHAI SPACE CENTRE
TRIVANDRUM-695022, INDIA

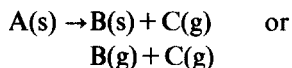
The study of solid state reactions is a challenging task since solids are extremely complex and exhibit an almost infinite variety in their compositional and structural features. The study has three aspects: phenomenological, thermodynamic and kinetic. The kinetic aspect is concerned with the rate of transformation of the reactants into the products and the mechanism of transformation. The reaction occurring in liquid or gas phase is expressed as a function of concentration of the reactants. But the concentration term usually has little significance in a solid state reaction, as the reacting species are very restricted in their motion and, therefore, cannot be described by simple statistical laws.

Solid state reactions can be classified into four categories; (i) reaction of a single solid (like solid state decomposition), (ii) solid-gas reaction, (iii) solid-liquid reaction and (iv) solid-solid reaction. The present paper deals with the first category of reactions, providing a personal view of the kinetic aspects of solid state reactions.

The most widely used thermal technique to study the kinetics of solid state thermal decomposition reactions is TG. The data obtained from TG are more quantitative than those obtained from DTA or DSC, as mass measurement has an order of magnitude higher accuracy and precision, as compared to the measurement of ΔT (DTA) or dH/dt (DSC). A statistical analysis to demonstrate the variance of the kinetic parameters obtained from TG, DTA and DSC has shown that the results obtained from TG have better precision than those from the other two methods [1]. However, TG is a limited technique in the sense that the study is limited to reactions which involve a mass change. (The equations and methodologies described here are applicable to any other thermal technique also.)

Kinetic analysis of experimental data

The general approach in kinetic analysis is to obtain an equation for the rate of the reaction. In the case of a decomposition reaction:



this is the rate of mass-loss which can be expressed in terms of a dimensionless quantity, called the degree of transformation or fractional decomposition, α , defined at time t as:

$$\begin{aligned} \alpha_t &= M_t/M_\infty && \text{(TG)} \\ &= A_t/A_\infty && \text{(DTA/DSC)} \end{aligned}$$

where M and A refer to mass loss and area respectively at time t and at the completion of reaction (∞).

The rate of a solid state decomposition reaction $d\alpha/dt$ depends on the reactant as well as the temperature of the reaction, so that it can be described as two separate functions of temperature and conversion as:

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

where the first function $k(T)$ is temperature dependent and $f(\alpha)$ is a function of the actual composition of the sample. For most reactions, the temperature dependence is found to be Arrhenius type, so that the term $k(T)$ can be identified as the rate constant k , related to temperature as:

$$k = A \exp[-E/RT] \quad (2)$$

where A = pre-exponential factor, E = energy of activation, R = gas constant and T = temperature. If a reaction is proven as iso-kinetic over the range of temperature studied, the Arrhenius equation can be inserted into equation (1) to give:

$$d\alpha/dt = A \exp[-E/RT] \cdot f(\alpha) \quad (3)$$

There are two basic approaches in solving this equation.

Mechanism-non-invoking methods

The mechanism-non-invoking method is a simple extension of homogeneous kinetics, wherein it is assumed that

$$f(\alpha) = (1 - \alpha)^n \quad (4)$$

where n is the order of reaction in homogeneous kinetics. For solid state reactions, it is unjustifiable to use the term order of reaction in the same sense as used in homogeneous kinetics. So, in our work n has been described as "order parameter", implying to have only empirical significance. Its physical significance is questionable and undefined. Substituting for $f(\alpha)$ in equation (3) we get

$$d\alpha/dt = A \exp[-E/RT] \cdot (1-\alpha)^n \quad (5)$$

The kineticist is concerned with finding out the three basic parameters, viz. A , E and n for a given reaction. There are two approaches for this: the isothermal and the non-isothermal methods.

Isothermal kinetics

Isothermal kinetics is the conventional method for evaluation of kinetic parameters and it is based on the rate equation:

$$d\alpha/dt = k(1-\alpha)^n \quad (6)$$

For the correct value of n , a plot of $(d\alpha/dt)$ vs. $(1-\alpha)^n$ will give a straight line with slope = k . However, the accuracy of evaluation of the tangent $(d\alpha/dt)$ is basically poor, and hence an integral approach is preferred. Rearranging equation (6) and integrating, we get:

$$[1 - (1-\alpha)^{1-n}]/1-n = kt \quad (7)$$

which applies for all values of n , except $n=1$, for which the equation is:

$$-\ln(1-\alpha) = kt \quad (8)$$

The LHS of equations (7) and (8) is called $g(\alpha)$ for convenience. Thus, a plot of $g(\alpha)$ vs. t will give a straight line with slope = k . The plots can be made for various values of n and the order parameter is chosen as the one which gives the best straight line. The rate constant k is evaluated at different temperatures and from $\ln k$ vs. $1/T$ plots E and A are calculated.

An a priori knowledge of the correct form of $g(\alpha)$ or the correct value of n is required for the evaluation of kinetic parameters by this method, unless one resorts to the iteration method of trying various values of n or $g(\alpha)$. It has been attempted to circumvent this problem, by a "g(α) free" approach. From equations (2) and (7):

$$g(\alpha) = kt = A \exp[-E/RT] \cdot t \quad (9)$$

or

$$\ln t = \ln g(\alpha) - \ln A + E/RT \quad (10)$$

Since $\ln g(\alpha)$ is very small in comparison to $\ln A$, E and A can be obtained from plots of $\ln t$ vs. $1/T$, and usually $t_{1/2}$ i.e., the time taken for $\alpha=0.5$ is taken for this

purpose. We have evaluated the dependence of the kinetic parameters on the specific α value chosen for the plot [2]. For the dehydration of zinc oxalate dihydrate, the kinetic parameters were computed from $\ln t$ vs. $1/T$ plots for α from 0.1 to 0.9 in the increment of 0.1 and the results are given in Table 1, which show a pronounced dependence of E and A on the α value chosen. It is, therefore, necessary

Table 1 Dependence of kinetic parameters on α

α	E , kcal mol ⁻¹	A , s ⁻¹	r
0.1	35.525	7.187×10^{16}	0.9988
0.2	31.316	3.480×10^{14}	0.9999
0.3	28.913	1.740×10^{13}	0.9997
0.4	27.744	4.350×10^{12}	0.9995
0.5	26.954	1.794×10^{12}	0.9992
0.6	26.065	6.266×10^{11}	0.9986
0.7	25.644	4.158×10^{11}	0.9989
0.8	24.884	1.755×10^{11}	0.9982
0.9	24.431	1.198×10^{11}	0.9980

to exercise caution in calculating E and A from $\log t$ vs. $1/T$ plots. One has to see the dependence of the kinetic parameters on the α value chosen in such cases.

Non-isothermal kinetics

The great advantage of TA techniques of obtaining the results from a single measurement is in the use of non-isothermal methods. For a linear heating rate ($\phi = dT/dt$), the rate equation becomes:

$$d\alpha/dT = (A/\phi) \exp[-E/RT] \cdot f(\alpha) \quad (11)$$

All the methods for obtaining the kinetic parameters from the above equation fall into two distinct categories, viz., the differential method and the integral method. The most widely used differential method is probably the Freeman-Carroll equation [3]. The difficulty in the correct estimation of a continuously varying slope as in a TG curve makes the integral methods more acceptable for the evaluation of the kinetic parameters.

On rearranging and integrating the rate equation between the limits of $\alpha = 0$ at T_i and equal to α at T , we get

$$\int_0^\alpha d\alpha/(1-\alpha)^n = (A/\phi) \int_{T_i}^T \exp[-E/RT] \cdot dT \quad (12)$$

The integral form of the left hand side of the equation is $g(\alpha)$, as discussed earlier. The right hand side of the equation cannot be integrated in a closed form. Different

authors have used many techniques to evaluate the exponential integral. The techniques fall into three distinct groups: (i) approximation method, (ii) series expansion method and (iii) numerical solution method, using tabulated values.

Approximation method

These methods employ an approximation related to a particular experimental value, usually the inflection point T_s of the TG curve. The van Krevelen equation [4] is probably the first equation in this series. The Horowitz–Metzger equation [5] is more popular and simpler to use:

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{(1-n)} \right] \approx \ln \frac{ART_s^2}{\phi E} - \frac{E}{RT_s} + \frac{E\theta}{RT_s^2} \quad (13)$$

Series expansion method

The solution of the exponential integral is done as an infinite series of which the first two terms are considered generally. In this category, the most popular method is probably the Coats–Redfern equation [6] and a number of investigators have used this method:

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{(1-n)T^2} \right] = \ln \left[\frac{AR}{\phi E} \left(1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (14)$$

Numerical solution method

In this method the rate equation is integrated as:

$$g(\alpha) = \frac{AE}{\phi R} \left[\frac{-e^x}{x} + \int_{-\infty}^x \frac{e^x}{x} dx \right] = \frac{AE}{\phi R} p(x) \quad (15)$$

where $x = -E/RT$. The function $p(x)$ has been expanded using different methods and the values of $p(x)$ have been calculated and tabulated for limited ranges by many workers (e.g., Ref. [7]). From the tabulated values of $g(\alpha)$ and $p(x)$, a trial and error curve fitting method is employed for the determination of the kinetic parameters.

This is a tedious process, and MacCallum and Tanner [8] suggested a simplification to overcome the problem. From different curve fittings with the tabulated values of $p(x)$, they derived an equation for calculating the kinetic parameters:

$$\log \left[\frac{1 - (1 - \alpha)^{1-n}}{(1-n)} \right] = \log \frac{AE}{\phi R} - 0.483E^{0.435} - \frac{(0.449 + 0.217E) \times 10^3}{T} \quad (16)$$

Madhusudanan-Krishnan-Ninan (MKN) equation [9]

We have introduced a new simple approximation for solving the $p(x)$ function in the form

$$p(x) = \frac{e^{-x}}{x^2} \left[\frac{(x+1)}{(x+3)} \right] \quad (17)$$

The $p(x)$ values obtained with this have been compared with conventional series solutions like semi-convergent series, Scholmilch approximation, Van Tets series, etc. (Table 2). It is found that the differences are in the 5th or 6th significant figure only.

Table 2 Comparison of $p(x)$ values

x	Semi-convergent	Scholmilch	Van Tets	Two-term
10	14.77857	14.77537	14.77507	14.77222
15	20.53528	20.53499	20.53494	20.53388
20	26.08300	26.08295	26.08294	26.08244
25	31.51215	31.51214	31.51214	31.51186
30	36.86509	36.86509	36.86508	36.86492

Using this approximation, the values of $p(x)$ have been computed for the values of E in the range of 60–400 kJ mol⁻¹ in the increment of 10 and T in the range of 300–800 K in the increment of 10. These ranges cover many of the condensed phase reactions. We have then shown that $\ln p(x)$ is a linear function of x , and the slope and intercept of $\ln p(x)$ vs. x curves are linear function of $1/x$ and $\ln(x)$ respectively. Combining these we get:

$$\ln p(x) = a + bx + c \ln x \quad (18)$$

Substituting the numerical values of a , b and c , introducing for $p(x)$ in equation (15) and rearranging we get the MKN equation:

$$\ln \left[\frac{1 - (1 - \alpha)^{1-n}}{(1-n)T^{1.9215}} \right] = \ln \frac{AE}{\phi R} + 3.7721 - 1.9215 \ln E - \frac{0.12039E}{T} \quad (19)$$

The validity of our equation has been tested using a theoretical TG curve, generated by us as well as the Gyulai-Greenhow theoretical TG data [10]. The results are given in Table 3, which show the suitability of our equation for the evaluation of kinetic parameters.

Table 3 Computation of energy of activation from theoretical TG curves

<i>E</i> , theoretical, kJ mol ⁻¹	<i>E</i> , calculated,	Kinetic equations
	99.44	Coats-Redfern
100 (MKN curve)	98.60	MacCallum-Tanner
	99.63	MKN
251.16 (GG data)	251.33	Gyulai-Greenhov
	251.09	MKN

Mechanism-based kinetic equations

So far, the discussion has been concerned with the right hand side of the general kinetic equations:

$$d\alpha/f(\alpha) = k dt \quad (\text{isothermal}) \quad (20)$$

$$d\alpha/f(\alpha) = (A/\phi) \exp[-E/RT] \cdot dT \quad (\text{non-isothermal}) \quad (21)$$

In the mechanism-non-invoking equations we have assumed that $f(\alpha) = (1-\alpha)^n$ which is a mere extension of the assumptions used in homogeneous kinetics. But the mechanism-based kinetic equations are based on the assumption that the form of $f(\alpha)$, or $g(\alpha)$ in the integrated form, depends upon the reaction mechanism.

The heterogeneous processes can be divided into three basic steps: (i) transport of matter or diffusion; (ii) nucleation and growth of nuclei, and (iii) phase-boundary reactions. Various equations have been derived for all these three processes, assuming different physico-geometric models and nine of them have been briefly listed by Satava [11] (Table 4). The reaction mechanism is obtained from the one which gives the best linear curve with the experimental data and the kinetic parameters are calculated from the slope and intercept, as usual.

Dependence of kinetic parameters on procedural factors

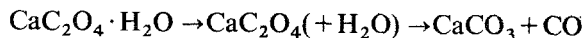
The results obtained from thermoanalytical measurements are known to be affected by a number of procedural factors [12], the most important among which are the heating rate and sample mass (m). The kinetic parameters calculated from the TA curves should, therefore, depend on ϕ and m . A search through literature reveals, for certain reactions, an alarmingly wide range of kinetic parameters obtained for varying experimental conditions. For e.g.: sets of values of $E = 157 \text{ kJ mol}^{-1}$ and $A = 10^4 \text{ s}^{-1}$, and $E = 3828 \text{ kJ mol}^{-1}$ and $A = 10^{157} \text{ s}^{-1}$ have

Table 4 Mechanism based equations

Eq. No.	Form of $g(\alpha)$	Rate-controlling process
1	α^2	One-dimensional diffusion
2	$\alpha + (1 - \alpha) \ln(1 - \alpha)$	Two-dimensional diffusion
3	$[1 - (1 - \alpha)^{1/3}]^2$	Three-dimensional diffusion, spherical symmetry—Jander equation
4	$\left(1 - \frac{2}{3}\alpha\right) - (1 - \alpha)^{2/3}$	Three-dimensional diffusion, spherical symmetry—Ginstling–Brounshtein equation
5	$-\ln(1 - \alpha)$	Random nucleation—one nucleus on each particle
6	$[-\ln(1 - \alpha)]^{1/2}$	Random nucleation—Avrami equation I
7	$[-\ln(1 - \alpha)]^{1/3}$	Random nucleation—Avrami equation II
8	$1 - (1 - \alpha)^{1/2}$	Phase boundary reaction—cylindrical symmetry
9	$1 - (1 - \alpha)^{1/3}$	Phase boundary reaction—spherical symmetry

been reported for the thermal decomposition of CaCO_3 under two sets of experimental conditions [13, 14]. Obviously, such values reported as kinetic parameters do not convey any meaning. To describe a reaction, one has to ideally get a set of kinetic parameters which are invariant with procedural factors. In the absence of any sound theoretical approach, the best suited will be an empirical one to get mathematical correlations between kinetic parameters and procedural factors, so that at least within certain ranges such reactions are represented by some constant numbers. One limited attempt has been to use the kinetic compensation effect, $E = a + b \log A$; but it does not give a correlation with procedural factors.

In our laboratory, we have attempted to obtain quantitative correlations between kinetic parameters and procedural factors, using standard model compounds such as calcium oxalate monohydrate which gives non-overlapping and clear-cut stoichiometric reactions of both types i.e., a reversible dehydration (Stage I) and a non-reversible decomposition reaction (Stage II).



The kinetic parameters were computed from TG curves recorded for seven heating rates (1–100 deg/min) and seven sample masses (1–20 mg) [15]. It was observed that for Stage II the values of E and A are randomly fluctuating and are not dependent on the procedural factors, whereas for the dehydration reaction (Stage I), E and A decrease systematically with increase in either heating rate or sample mass. The systematic dependence could be mathematically correlated as:

$$E \text{ (or } \log A) = C_1 + C_2/\phi \quad (\text{for constant } m) \quad (22)$$

$$E \text{ (or } \log A) = C_3 - C_4m + C_5m^2 \quad (\text{for constant } \phi) \quad (23)$$

It was further attempted [16] to see whether this trend or fluctuation for Stage I and II respectively, are due to the fact that non-mechanistic equations were used for the computation of the kinetic parameters. In other words, what will the kinetic parameters be, if the mechanism-based equations are used. The TG data were evaluated using the nine mechanism-based equations [11] and as many as four to five equations gave linear curves in most of the cases. An arbitrary comparative method [17] was, therefore, resorted to establish the reaction mechanisms as phase boundary reaction with spherical symmetry i.e., $g(\alpha) = 1 - (1 - \alpha)^{1/3}$ for Stage I, and phase boundary reaction with cylindrical symmetry i.e., $g(\alpha) = 1 - (1 - \alpha)^{1/2}$ for Stage II. The kinetic parameters were evaluated using these mechanistic equations. Here again, for Stage II, E and A randomly fluctuated, whereas for Stage I, they showed a similar systematic trend which could be represented by identical mathematical correlations.

Thus, it can be seen that for the dehydration reaction, with increase in either heating rate or sample mass, the values of E and A decrease. It was, therefore, attempted to superimpose the effects of ϕ and m to get the effect of their simultaneous variation [18]. Five heating rates were employed and at each heating rate five sample masses were used. The three integral equations and the mechanism-based equation were used to calculate the kinetic parameters. As expected, it was found that

$$E \text{ (or } \log A) = C_1 + C_2/\phi \quad (\text{for constant } m) \quad (22)$$

The correlation constants, C_1 and C_2 decreased systematically with sample mass, which can be represented as:

$$C_1 \text{ (or } C_2) = a + b/m \quad (24)$$

Combining these two we get

$$E \text{ (or } \log A) = a_1 + b_1/m + a_2/\phi + b_2/\phi m \quad (25)$$

A multiple regression analysis was carried out to get the simultaneous effects of m and ϕ as:

$$E \text{ (or } \log A) = k_1 + k_2/\phi + k_3/m \quad (26)$$

With this type of correlation, we can get E and A for any value of m and ϕ .

Since some people claim that these types of variations are the property of non-isothermal methods, while isothermal methods are free of such problems, it was attempted to see whether such fluctuations and trends are prevalent in isothermal

experiments also [19]. The two stages of reaction were monitored with 7 sample masses and at an average of 5 isothermal temperatures for each m . It was found that for stage II, there was no correlation of E or A with sample mass. They randomly fluctuated as in the case of non-isothermal experiments. However, for stage I, they showed a systematic decrease which could be mathematically expressed as E (or $\log A$) = $C_1 - C_2m + C_3m^2$, similar to what was obtained for the non-isothermal method.

The study was extended with mechanism-based approach also [20]. Here the isothermal method offers a great advantage of having no ambiguity in inferring the reaction mechanism, which was found to be difficult for the non-isothermal method. The mechanism was found to be phase boundary reaction with cylindrical symmetry following the equation, $1 - (1 - \alpha)^{1/2} = kt$ for both the stages. However, as far as the kinetic results are concerned, they showed the same range and fluctuation for stage II and trend for stage I, as in the case of the non-mechanistic method. In another study [21] with a modified isothermal method similar correlations between kinetic parameters and sample mass were derived for the dehydration of $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. The reliability of all these correlations was evaluated by statistical analysis using the F test, and it was found that they have a confidence level of better than 99% in almost all the cases.

Multiple correlations such as:

$$T_i = \left(\frac{C_3}{\phi} \right) m^{C_2/E} \quad (27)$$

$$T_\alpha = \left(\frac{C_4}{\phi} \right) m^{C_5/E} \quad (28)$$

were derived to describe the interdependence of kinetic parameters and experimental variables in the case of TG, DTA and DSC [22, 23].

The kinetic data thus computed and correlated, have practical application to predict the reaction rate at other temperatures. Thus, in the prediction of the pyrolysis rate of the thermal protection systems used in rockets. Arrhenius type equations are used. However, the heating rates experienced for rockets during their ascent are different from those available in usual thermoanalytical equipments. Such correlations between kinetic parameters and heating rates would, therefore, make thermal studies more useful in evaluating the thermal protection systems. The effect of heating rate on the thermal decomposition kinetics of fibre glass phenolic used as ablative thermal protection systems of rockets has recently been reported [24]. However, the kinetic parameters are not significantly affected by heating rate or sample mass for the thermal decomposition of functionally terminated polybutadiene prepolymers used as composite solid propellant binders [25].

Conclusion

There is an everlasting controversy between isothermal and non-isothermal and between mechanistic and non-mechanistic approaches. At least in our study, we do not find any reason for condemning one in preference to the other; each has its own merits and drawbacks. The mechanism of a thermal decomposition reaction cannot be assigned unequivocally from the mathematical curve fitting of the TG data alone, whereas the isothermal mass-loss data give a better insight into the reaction mechanism. As far as the values of the kinetic parameters are concerned, there is no significant difference between isothermal and non-isothermal methods or between mechanistic and non-mechanistic approaches, in the sense that they show the same degree of fluctuation or trend, as the case may be. Thus, for the purpose of calculating the kinetic constants, the non-isothermal method has the advantage of greater simplicity. However, one has to ascertain the influence of procedural factors on the kinetic parameters before making any conclusion regarding the kinetics and mechanism of a solid state thermal decomposition reaction. Finally, it may be possible to superimpose the effects of the individual procedural factors, in order to predict the kinetic parameters for any set of experimental parameters.

The significance of the kinetic parameters for a solid state reaction is also a subject of controversy. Some suggest that heterogeneous reactions are not activated processes and that the only rate controlling process is the heat exchange between the reacting mass and its surroundings [26]. However, the majority feel that since the temperature dependence of the reaction rate is Arrhenius type, the reaction must involve an activated process. There is yet another school which thinks that the kinetic constants are just mathematical parameters, having empirical rather than any theoretical significance.

Because of these raging controversies, condensed phase kinetics has sometimes been outrightly condemned, in comparison to solution or gas phase kinetics. However, it may be remembered that the homogeneous kinetics was in no better shape in its formative years about a century back. The solid state kinetics, in particular the non-isothermal method has made its headway only during the last three decades with the advent of modern thermoanalytical methods and is poised to adorn the same high pedestal in the near future.

* * *

The author wishes to thank Prof. C. G. R. Nair, Dr. V. R. Gowarikar, Mr. M. R. Kurup and Dr. K. V. C. Rao for their encouragements. Thanks are due to Prof. P. M. Madhusudanan and Dr. K. Krishnan for helpful discussions and to Director, VSSC for the kind permission to publish this work.

References

- 1 P. M. Madhusudanan, K. Krishnan and K. N. Ninan, Proc. 3rd National Sym. Thermal Anal., Trivandrum, 1981, p. I. 46.
- 2 K. Krishnan, K. N. Ninan and P. M. Madhusudanan, Thermochim. Acta, 79 (1984) 279.
- 3 E. S. Freeman and B. Carroll, J. Phys. Chem., 82 (1958) 394.
- 4 D. W. van Krevelen, C. van Heerden and F. J. Huntgen, Fuel, 30 (1951) 251.
- 5 H. H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.
- 6 A. W. Coats and J. P. Redfern, Nature, 201 (1964) 68.
- 7 J. Zsakó, J. Phys. Chem., 72 (1968) 2406.
- 8 J. R. MacCallum and J. Tanner, Eur. Polym. J., 6 (1970) 1033.
- 9 P. M. Madhusudanan, K. Krishnan and K. N. Ninan, Thermochim. Acta, 97 (1986) 189.
- 10 G. Gyulai and E. J. Greenhow, J. Thermal Anal., 6 (1974) 279.
- 11 V. Satava, Thermochim. Acta, 2 (1971) 423.
- 12 W. W. Wendlandt, Thermal Methods of Analysis, 3rd edn., J. Wiley, N. York, (1986).
- 13 P. K. Gallagher and D. W. Johnson, Thermochim. Acta, 6 (1973) 67.
- 14 P. K. Gallagher and D. W. Johnson, Thermochim. Acta, 14 (1976) 255.
- 15 C. G. R. Nair and K. N. Ninan, Thermochim. Acta, 23 (1978) 161.
- 16 K. N. Ninan and C. G. R. Nair, Thermochim. Acta, 30 (1979) 25.
- 17 P. H. Fong and D. T. Chen, Thermochim. Acta, 18 (1977) 273.
- 18 K. N. Ninan and C. G. R. Nair, Thermochim. Acta, 37 (1980) 161.
- 19 K. N. Ninan, Thermochim. Acta, 74 (1984) 143.
- 20 K. N. Ninan, Thermochim. Acta, 98 (1986) 221.
- 21 K. Krishnan, K. N. Ninan and P. M. Madhusudanan, Thermochim. Acta, 90 (1985) 229.
- 22 P. M. Madhusudanan, K. Krishnan and K. N. Ninan, Thermal Analysis, Vol. I (Proc. 7th ICTA, CANADA), J. Wiley, N. York, 1982, p. 226.
- 23 K. Krishnan, K. N. Ninan and P. M. Madhusudanan, Thermochim. Acta, 71 (1983) 305.
- 24 K. N. Ninan, J. Spacecraft and Rockets, 23 (3) (1986) 347.
- 25 K. N. Ninan and K. Krishnan, J. Spacecraft and Rockets, 19 (1) (1982) 92.
- 26 A. L. Draper, Proc. 3rd Toronto Sym. Thermal Anal., 1970, p. 63.