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# THERMAL ANALYSIS OF REACTIONS AND TRANSFORMATIONS IN THE SOLID STATE. I. EXPERIMENTAL EVALUATION OF PUBLISHED KINETIC METHODS USING THERMOGRAVIMETRY*

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## ABSTRACT

A review of the non-isothermal mathematical models used to study the kinetics of reactions and transformations in the solid state is presented and their deficiencies discussed. An experimental evaluation of the new tabular method introduced by Gyulai and Greenhow is presented. Thermograms of several compounds of different sample size were obtained at different heating rates and analyzed by the Gyulai–Greenhow technique. The analysis showed a wide variation for the enthalpy calculated by this technique, as a function of the sample size and the heating rate ratios. For example, the calculated enthalpy of desolvation for the tertiary butanol solvate of methyl prednisolone obtained from different runs using the same heating rate but different sample sizes, yielded values between 16 and 95 kcal/mole. Variation in the heating rate ratios also affected the results. The enthalpy of theophylline varied between 17 and 39.6 kcal/mole with different heating rate ratios. Similar differences were found with calcium oxalate samples.

## INTRODUCTION

In the past twenty years, the determination of kinetic parameters from thermogravimetric (TGA) curves has been the subject of extensive experimental and theoretical discussions. In many instances, earlier efforts have not only been disappointing and tedious to carry out, but also subject to many systematic errors, thereby necessitating an arbitrary choice of variable constants. In a great number of these instances, it was therefore possible to change the value of the experimental activation energy dramatically by varying "adjustable" parameters within permissable limits. Such conditions do not inspire great confidence in the apparent activation

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energies so extracted. For this reason, many careful workers preface such results by the word "procedural"[1, 2], meaning that the results could contain variables not extracted by the treatment of the data.

It would be important to eliminate the variability of the extracted parameters as thermogravimetry is a continuous non-isothermal method which has many advantages over currently used isothermal methods. These advantages are that a single experimental curve is sufficient to obtain an estimate of the apparent heat of activation and that the kinetics can be probed over an entire temperature range in a continuous manner without any gaps[3].

The present study was undertaken to investigate the presently utilized, non-isothermal thermogravimetric kinetic methods to study chemical degradation and phase transformation. The study was done in two parts. The first part is concerned with a literature review of methods and their evaluation while the second part is an experimental evaluation of a recently introduced tabular method by Gyulai and Greenhow[4]. For this purpose, experimental data for methyl prednisolone tertiary butanol solvated form (Form $II_b$) desolvation, theophylline phase transformation, and calcium oxalate monohydrate dehydration and chemical degradation was obtained.

## EVALUATION OF PUBLISHED METHODS

A number of non-isothermal methods have been proposed and summarized in several review articles[1, 2, 5–9]. These methods fall into two distinct approaches for the determination of kinetic parameters from thermogravimetric measurements. The two approaches are the differential and the integral methods. These two methods use the general non-isothermal kinetic equation, eqn. (1).

$$\frac{d\alpha}{dT} = \left(\frac{Z}{a}\right) e^{-E^*/RT} f(\alpha) \tag{1}$$

where $a = dT/dt$ or the linear heating rate (°C/min); $Z$ is the Arrhenius pre-exponential factor; $E^*$ the activation energy (kcal/mole); $R$ the gas constant; $T$ the absolute temperature in (K); $d\alpha/dT$ the rate of sample loss per degree; $\alpha$ the fractional weight of the material reacted as a function of the total weight loss; and $f(\alpha)$ a function of the weight loss. Its analytical form depends on the reaction in question.

The most widely used differential method to extract the kinetic parameters from TG curves is the method first introduced by Freeman and Carroll[9]. The method is based on eqn. (1) and on Scheme 1 with the arbitrarily chosen $f(\alpha) = X^n$, where $X$ is the concentration, mole fraction or amount of reactant A, and $n$ is frequently called the reaction order, in analogy with homogenous kinetics.

$$(\text{Solid})_1 \rightarrow (\text{Solid})_2 + \text{gas} \qquad \text{(Scheme 1)}$$

Therefore, the rate expression for the disappearance of reactant A from the mixture can be written as

$$-\frac{dX}{dt} = Z\,e^{-E^*/RT}\,X^n \tag{2}$$

By rearranging eqn. (2), taking the logarithmic form, and then differentiating with respect to $dX/dt$, $X$, and $T$, we arrive at

$$\frac{E^*\,dT}{RT^2} = d\ln\left(-\frac{dX}{dt}\right) - n\,d\ln X \tag{3}$$

Integration of eqn. (3) gives

$$-\frac{E^*}{R}\Delta\left(\frac{1}{T}\right) = \Delta\ln\left(-\frac{dX}{dt}\right) - n\Delta\ln X \tag{4}$$

Dividing eqns. (3) and (4) by $d\ln X$ and $\Delta\ln X$, respectively, gives

$$\frac{E^*\,dT}{RT^2\,d\ln X} = \frac{d\ln(-\,dX/dt)}{d\ln X} - n \tag{5}$$

and

$$\frac{(-\,E^*/R)\Delta(1/T)}{\Delta\ln X} = \frac{\Delta\ln(-\,dX/dt)}{\Delta\ln X} - n \tag{6}$$

From eqns. (5) and (6), a plot of $d\ln(-\,dX/dT)/d\ln X$ versus $dT/T^2 d\ln X$ and $\Delta\ln(-\,dX/dt)/\Delta\ln X$ versus $\Delta(1/T)/\Delta\ln X$ should yield a straight line with slopes of $\pm\,E^*/R$ and intercepts of $n$.

Markowitz and Boryta[10] found that this method could not be used to study reactions in which the sample temperature deviated considerably from that of the furnace. This was the case with highly exothermic reactions such as the reactions of powdered metals with air, oxygen, or nitrogen. Sestak et al.[2] criticized the differential method in that it suffered from an inherent weakness such as the magnification of experimental scatter due to differentiation which thus requires a very precise and tedious recording, since the graphical determination of the rate, $d\alpha/dt$, depends on the sample size, heating rate, and absolute linearity of the heating program. In addition, Sestak et al.[2] criticized the assumption of the existence of a single reaction order, $n$, as an empirical constant. To overcome the disadvantages of the differential method, Sestak et al.[2] suggested the use of a numerical solution for the determination of the rate ($d\alpha/dt$). Flynn and Wall[1] pointed out that the differential method gives a "procedural" $n$ and $E^*$, particularly when an overlapping stage of an independent reaction takes place. This is due to the arbitrary choice of $f(\alpha)$ which does not always account for the right analytical form needed for overlapping reactions and therefore cannot account for multistage reactions.

The integral approach is also based on eqn. (1) which can be rearranged to yield

$$\frac{d\alpha}{f(\alpha)} = \left(\frac{Z}{a}\right)(e^{-E^*/RT})\,(dT) \tag{7}$$

or in the integral form

$$F(\alpha) = \int_{\alpha_0}^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{Z}{a} \int_{T_0}^{T} e^{-E^*/RT}\, dT \tag{8}$$

Where, hence, $\alpha_0$ and $T_0$ are initial conversion and absolute temperature, respectively. Unfortunately, the right-hand side of the equation does not reduce to a finite form under integration, and the analytical form of $f(\alpha)$ is not known. Of the several integral methods proposed in the literature, differences exist in the solution path for eqn. (8). Both exponential[11-14] and tabulated numerical solutions[15-17] to the right-hand side of eqn. (8) have been proposed.

The exponential integration method was introduced by Coats and Redfern[11]. Their approach is based on Scheme 1 and eqn. (8) with the arbitrarily chosen $f(\alpha) = (1 - \alpha)^n$. Integration of the right-hand side of eqn. (8) was done by the substitution $\mu = E^*/RT$, and then use of the approximation relationship presented in eqn. (9) to obtain eqn. (10).

$$\int_{\mu}^{\infty} e^{-\mu}\, \mu^{-b}\, d\mu = \mu^{(1-b)}\, e^{-\mu} \sum_{n=0}^{\infty} \frac{(-1)^n (b)^n}{\mu^{n+1}} \tag{9}$$

$$\frac{1 - (1 - \alpha)^{1-n}}{1 - n} = \frac{ZRT^2}{aE^*} \left[1 - \frac{2RT}{E^*}\right] e^{-E^*/RT} \tag{10}$$

Taking the logarithmic form of eqn. (10) will give eqn. (11).

$$\log \frac{1 - (1 - \alpha)^{1-n}}{T^2(1 - n)} = \log \left[\frac{ZR}{aE^*} \left(1 - \frac{2RT}{E^*}\right)\right] - \frac{E^*}{2.3RT} \tag{11}$$

From eqn. (11), a plot of $\log [1 - (1 - \alpha)^{(1-n)}]/T^2(1 - n)$ versus $1/T$ should yield a straight line with a slope of $(- E^*/2.3R)$.

Zsako and Arz[18] analyzed fifteen thermogravimetric curves of the thermal decomposition of $CaCO_3$ obtained from the literature by means of the Coats and Redfern method and found that the activation energy varied between 26 and 377 kcal/mole and the pre-exponential factors between $10^2$ and $10^{69}$ as functions of the working conditions.

The tabulated integration methods are based on tabulating the value of the integral form of the right-hand side of eqn. (8). Assuming that the amount decomposition at the lower temperature is very small, Doyle[15] substituted zero for $T_0$ in order to be able to use the notation $\mu = E^*/RT$ to obtain

$$F(\alpha) = \frac{Z}{a} \int_{0}^{T} e^{-E^*/RT}\, dT = - \frac{ZE^*}{aR} \int_{\infty}^{y} (e^{y}/\mu^2)\, d\mu \tag{12}$$

where $y$ is the value of $\mu$ at the temperature corresponding to the apparent value of $\alpha$. Introducing the notation

$$P(y) = -\int_{\alpha}^{y} (e^{-\mu}/\mu^2)\, d\mu \tag{13}$$

eqn. (12) becomes

$$F(\alpha) = \left(\frac{ZE^*}{aR}\right) P(y) \tag{14}$$

Using eqn. 14 and a table of $-\log P(y)$, Doyle[15] applied a trial and error curve fitting method for the determination of activation energy. This method is lengthy and $f(\alpha)$ must be known or assumed. Zsako[16] attempted to simplify Doyle's method by using eqn. (14) in the logarithmic form

$$\log\left[\frac{ZE^*}{aR}\right] = \log F(\alpha) - \log P(y) = \text{constant} \tag{15}$$

where the term $\log(ZE^*/aR)$ is constant, and depends only on $E^*$, the nature of the material and the reaction studied, and the heating rate "$a$", but not the temperature of the study. The constant can be calculated for different reaction mechanisms, if $F(\alpha)$ is known or assumed, for each individual value of a series of activation energies using a tabulated value of $\log P(y)$. The apparent activation energy chosen would yield an activation energy which is consistent with the chosen function $F(\alpha)$.

Satava and Skvara[17] have simplified Zsako's tedious procedure by using a graphical comparison of $\log F(\alpha)$ and $\log P(y)$ by means of nomograms. The $\log F(\alpha)$ values for various rate processes are plotted versus the corresponding temperature values on transparent paper on the same scale as the standard plot of $-\log P(y)$ versus $T$. The plot of $\log F(\alpha)$ is placed on top of the $\log P(y)$ diagram so that the temperature scales coincide and it is then shifted along the coordinate until one of the $\log F(\alpha)$ curves fits one of the $\log P(y)$ curves. From this $\log P(y)$ function, the corresponding activation energy, $E^*$, can then be obtained.

Zsako[19] suggested an empirical formula, eqn. (16), for the approximation of $P(y)$ and claimed that errors are less than 0.5% if $y$ is greater than 1.6.

$$P(y) = \frac{e^{-y}}{(y - d)(y + 2)} \tag{16}$$

with $d = 16/(y^2 - 4y + 84)$.

Other methods which involve the use of two TGA curves have been proposed. Reich[20] has published a method which requires two TGA curves with different heating rates for determining the energy of activation. He emphasizes that his method is sensitive to changes in temperature. On the other hand, Chatterjee[21] introduced a method which requires two TGA curves obtained with different sample weights under similar reaction conditions. This method uses the rate expression given by eqn. (17).

$$-\frac{dW}{dt} = Ze^{-E^*/RT}\,W^n \tag{17}$$

or

$$n\log W - \log(-\,dW/dt) = \frac{E^*}{2.30RT} - \log Z \tag{18}$$

Considering two thermograms which are to be obtained by taking two different initial weights of the substance, eqn. (18) can be rewritten as

$$n\log W_1 - \log(-\,dW/dt)_1 = \frac{E^*}{2.303RT} - C \tag{19}$$

and

$$n\log W_2 - \log(-\,dW/dt)_2 = \frac{E^*}{2.303RT} - C \tag{20}$$

The constant will be the same in both cases. The values of $W_1$, $W_2$, and the corresponding $(-\,dW/dt)_1$ and $(-\,dW/dt)_2$ can be determined at selected temperatures from each set of curves and $n$ can be evaluated by

$$n = \frac{\log(-\,dW/dt)_1 - \log(-\,dW/dt)_2}{\log W_1 - \log W_2} \tag{21}$$

A series of values of $n$ can be determined at successive temperatures in order to determine whether or not $n$ changes during a particular reaction. Having determined the value of $n$, the value of $E^*$ can be determined from a single tracing by plotting $[n\log W - \log(-\,dW/dt)]$ versus $1/T$. The slope of the plot of this equation will give the value of $E^*/2.303R$ and the intercept will be equal to the value of the $\log Z$.

Zsako[22] criticized the methods which use more than a single TG curve to obtain the kinetic parameters. He describes these methods as erroneous, illusory, and worthless, since the extracted kinetic parameters obtained depend on procedural variables such as heating rate, sample weight, particle size, compactness, material and geometry of the sample holder, nature and static or dynamic character of the atmosphere, etc. Also, Zsako discussed the influence of the factors on the shape and position (on the temperature axis) of the obtained TG curves. He extended his criticism to Doyle's[15] and his own[16] tabulated methods.

In the case of thermogravimetry, because the shapes of the TG curves and also the kinetic parameters derived from these curves depend on the previously mentioned procedural variables[22-26], investigators tried to explain these variations on the basis of the Arrhenius equation by introducing a new term referred to as the "kinetic compensation effect"[26-31]. This phenomenon is expressed as

$$\log(Z) = aE^* + b \tag{22}$$

Equation (22) predicts that, for the same compound and under different procedural conditions, a plot of $E^*$ versus log($Z$) will give a straight line with a slope equal to "$a$" and an intercept equal to "$b$". Both "$a$" and "$b$" are constant and characterize the family of curves for that compound. Needless to say, this approach requires two empirical parameters for each experimental variable such as heating rate, sample size, etc. It also allows one to predict experimental values of $Z$ given $E^*$ or vice versa, but does not yield a constant value of $E^*$ and $Z$ which are inherent to the reaction or transformation being studied.

In a recent article, Gyulai and Greenhow[4] have combined the tabular integral approach with the somewhat older technique of obtaining two TGA traces of the same compound taken under the same conditions, but at different heating rates. They introduced the notation

$$i = \int_0^T e^{-E^*/RT}\,\mathrm{d}T \tag{23}$$

and rewrote eqn. (8) as

$$\mathrm{F}(\alpha) = (A/a)i \tag{24}$$

To apply this approach using TGA curves taken at two different heating rates, $a_1$ and $a_2$, one must determine the temperature at $a_1$ and $a_2$ at which a percentage conversion $\alpha_1$ is achieved. This is then repeated using a different value for the percentage conversion, $\alpha_2$. In their notation, $a_1$ is the lower heating rate, $a_2$ the higher heating rate, $T_{11}$ the temperature for conversion $\alpha_1$ at heating rate $a_1$, $T_{12}$ the temperature for conversion $\alpha_1$ at heating rate $a_2$, $T_{21}$ the temperature for conversion $\alpha_2$ at heating rate $a_1$, $T_{22}$ the temperature for conversion $\alpha_2$ at heating rate $a_2$. Utilizing the $i$ notation of eqns. (23) and (24), they obtained

$$i_{11} = \int_0^{T_{11}} e^{-E^*/RT}\,\mathrm{d}T; \qquad i_{12} \int_0^{T_{12}} e^{-E^*/RT}\,\mathrm{d}T \tag{25}$$

$$\mathrm{F}(\alpha)_{11} = (A/a_1)i_{11}; \qquad \mathrm{F}(\alpha)_{12} = (A/a_2)i_{12} \tag{26}$$

Since the area under the curve for a constant fraction of conversion is equal for both thermograms, then

$$\mathrm{F}(\alpha)_{11} = \mathrm{F}(\alpha)_{12} \tag{27}$$

and

$$\mathrm{F}(\alpha)_{11}/\mathrm{F}(\alpha)_{12} = (a_2/a_1)/(i_{11}/i_{12}) = 1 \tag{28}$$

or

$$a_1/a_2 = i_{11}/i_{12} \tag{29}$$

They calculated and tabulated values for $i$ as $\log(i)$. These equations imply that one should obtain a series of values for the activation energy, $E^*$, at any percentage conversion, $\alpha_1$, and any two heating rates, $a_1$ and $a_2$. For this method, a plot is made of a series of $E^*$ values as the $x$-axis and the values of $\log(i_{11}/i_{12})$ obtained from the tables as the $y$-axis. The value of $E^*$ for a system can be obtained, where

$$\log(i_{11}/i_{12}) = \log(a_1/a_2) \tag{30}$$

According to the above equations, eqn. (30) should be a unique solution and should present the value of $E^*$ at that particular percentage conversion.

The Gyulai and Greenhow technique will be experimentally evaluated in this study.

## EXPERIMENTAL

### *Materials*

Calcium oxalate monohydrate (Fisher Scientific Co., Fair Lawn, N.J.) was used during this study as supplied. Theophylline monohydrate was prepared by recrystallizing theophylline (U.S.P. grade, Nutritional Biochemical Corp., Cleveland, Ohio) from double distilled water. Anhydrous theophylline was prepared by heating theophylline monohydrate in the oven at 105°C overnight or until its X-ray diffractogram corresponded to anhydrous theophylline. Methyl prednisolone Form $\mathrm{II}_b$, was prepared by recrystallizing methyl prednisolone (The Upjohn Co., Kalamazoo, Mich.) in tertiary butanol (J. T. Baker Chemical Co., Philipsburg, N.J.).

### *Instrument*

The instrument used during this study is a simultaneous thermogravimetric analyzer, TGA, differential thermogravimetric analyzer, DTG, and differential thermal analyzer, DTA (Thermoflex Analyzer, Rigaku/USA, Inc., Wakefield, Mass.).

The thermoflex analyzer is a single furnace instrument in which the DTA cells are mounted on the weighing beam. The differential temperature and sample temperature are measured by the same thermocouple pair. The sample couple is in direct contact with the material undergoing the scan. The DTG signal is generated with an analog system from the TGA signal.

The sample was weighed on a Chan Electrobalance using the thermobalance platinum sample crucible as a tare so that the residual weight could be directly measured after the run. Since the sample mass ranged from 10 to 20 mg, the thermobalance was calibrated for 10 mg full scale. The atmosphere was high purity dry nitrogen (Norwich Cylinder Co.) which was regulated at a constant flow of 160 ml/min. The sensitivity of the DTA was 500$\mu$V. The temperature scale was 30 mV full scale with the temperature calibrated at zero voltage. Temperatures were converted to degrees centrigrade by a table of electromotive force for platinal thermocouples. The heating rate was as stated in the thermogram. DTG sensitivity was 0.5. The chart speed was 10 mm/min for all runs.

## RESULTS AND DISCUSSIONS

To investigate the consistency of the extracted value of $E^*$ under the influence of experimental conditions using the Gyulai and Greenhow method, a program was undertaken to study the kinetics of a wide variety of compounds which undergo different chemical and physical transformations. The chosen compounds and transformations studied were the desolvation of the *t*-butyl alcohol solvate of methyl prednisolone, the phase transformations (sublimation and vaporization) of theophylline, and the dehydration and chemical degradation of calcium oxalate monohydrate. In particular, the investigation was designed to focus on the effect of sample size, heating rate, and heating rate ratios on the calculated heats of activation.

### *Sample size effect on the calculated enthalpy of desolvation of methyl prednisolone*

Three thermograms (A, B, C) of methyl prednisolone Form $II_b$ were obtained using the thermoflex analyser. Two of these thermograms, A and B, were obtained at the same heating rate (10°C/min), but for different sample weights. Thermogram A was generated from 12.74 mg while thermogram B was obtained from 8.05 mg. These two thermograms were compared with thermogram C, which was obtained from 8.66 mg and generated under a heating rate of 2.5°C/min.

For illustrative purposes, Fig. 1 shows thermogram A, a typical tracing for methyl prednisolone Form $II_b$, obtained using the thermoflex analyser. The thermogram is a simultaneous TG–DTG and DTA trace. That is to say, this thermogram provides not only the mass as a function of temperature, but also the change in mass as a function of temperature. It also provides the temperature difference between the sample and an inert reference substance as a function of temperature at a constant heating rate. Gyulai and Greenhow used only the TG trace to calculate their kinetic parameters.

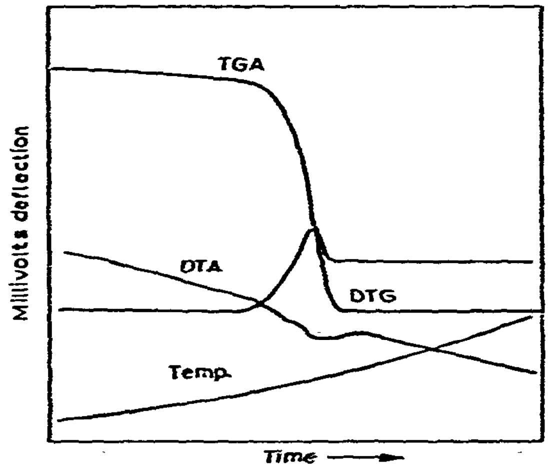

Fig. 1. Simultaneous TG–DTG and DTA thermogram for methyl prednisolone tertiary butanol solvated form (Form $II_b$) desolvation, in nitrogen atmosphere obtained from 12.74 mg as stated under the experimental condition.

TABLE 1

TEMPERATURES OF DECOMPOSITION OBTAINED FROM TWO THERMOGRAMS OF METHYL PREDNISOLONE FORM $II_b$ GENERATED AT TWO DIFFERENT HEATING RATES AT A PARTICULAR PERCENTAGE CONVERSION

| *Thermogram A (10°C/min) versus thermogram C (2.5°C/min)* | | | *Thermogram B (10°C/min) versus thermogram C (2.5°C/min)* | | |
|---|---|---|---|---|---|
| *100α* | $T_{12}$ *(K)* | $T_{11}$ *(K)* | *100α* | $T_{12}$ *(K)* | $T_{11}$ *(K)* |
| 10.1 | 356.1 | 346.6 | 11.1 | 350.1 | 346.9 |
| 21.28 | 365.5 | 351.3 | 19.7 | 354.4 | 350.7 |
| 49.2 | 376.4 | 358.0 | 34.19 | 354.4 | 355.0 |
| 70.48 | 381.4 | 361.6 | 35.85 | 364.7 | 358.3 |
| 92.22 | 389.1 | 366.6 | 81.62 | 370.9 | 363.4 |

TABLE 2

A SAMPLE WORKSHEET TO ILLUSTRATE THE METHOD OF CALCULATION USING 10.1% CONVERSION AS 1 FOR METHYL PREDNISOLONE (USING THE GYULAI AND GREENHOW METHOD)

| $E^*$ | $-\log i_{11}$<br>$T_{11} = 346.6$ K[a] | $-\log i_{12}$<br>$T_{12} = 356.1$ K[b] | $\log (i_{11}/i_{12})$ |
|---|---|---|---|
| 20 | 11.56175 | 11.20265 | −0.3591 |
| 30 | 18.03428 | 17.50674 | −0.52754 |
| 40 | 24.46001 | 23.76415 | −0.69586 |
| 50 | 30.85952 | 29.99531 | −0.86415 |
| 70 | 43.61323 | 42.41256 | −1.20067 |

[a] $a_1 = 2.5$°C/min (run C)

[b] $a_2 = 10$°C/min (run A)

$\log (a_1/a_2) = -0.6021$.

$\log (i_{11}/i_{12}) = \log (a_1/a_2)$ at $E^* = 34$ kcal/mole.

From the thermogram, Fig. 1, the ratio between the initial weight of methyl prednisolone Form $II_b$ and the final weight was found to be equal to 1.215, which is equal to the ratio of the molecular weight of the solvated form (Form $II_b$), to the unsolvated form (Form II). This suggested that Form $II_b$ is a 1:1 solvated form which agrees with the finding of Munshi and Simonelli[32]. Similar results were obtained from thermograms B and C which are not included in this text.

From thermograms A and C, $T_{12}$ at a heating rate of 10°C/min and $T_{11}$ at a heating rate of 2.5°C/min were obtained from a percentage conversion, $\alpha_1$. This procedure was repeated using these two thermograms for a series of percentage conversions, $\alpha_2$, $\alpha_3$, $\alpha_4$, etc. The results were tabulated in Table 1. Using these two temperatures, ($T_{11}$ and $T_{12}$) and a table of log $i$, we calculated $\log(i_{11}/i_{12})$ for a series of values of $E^*$. Since these computations are on the lengthy side, a working sheet was used as an example to illustrate the method of calculations. Table 2 shows this

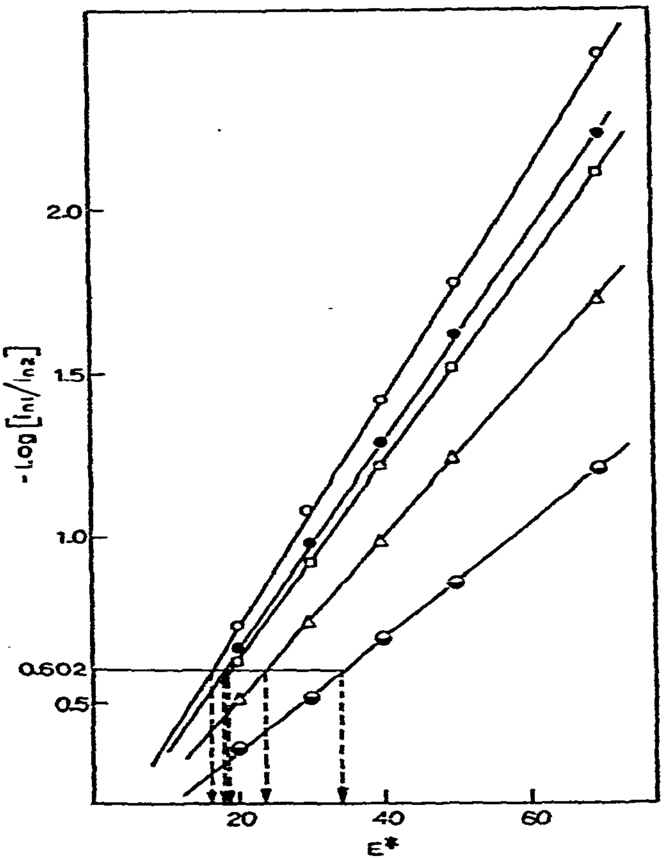

Fig. 2. Log ($i_{n1}/i_{n2}$) versus $E^*$ plot for methyl prednisolone Form II$_b$ desolvation as a function of fraction decomposition ($\alpha$) using two thermograms (A and C) generated under the same conditions as described in the experimental condition, but with different heating rates. Key: A at 10°C/min; C at 2.5°C/min; ○, 92.2% decomposition; ●, 70.5% decomposition; □, 49.2% decomposition; △, 21.3% decomposition; ⊖, 10.1% decomposition.

TABLE 3

EFFECT OF SAMPLE SIZE ON THE CALCULATED ENTHALPY OF METHYL PREDNISOLONE FORM II$_b$ DESOLVATION OBTAINED BY USING GUYLAI AND GREENHOW METHOD

| *Thermogram A (10°C/min, 12.76 mg) vs. thermogram C (2.5°C/min, 8.66 mg)*[a] | | *Thermogram B (10°C/min, 8.05 mg) vs. thermogram C (2.5°C/min, 8.66 mg)*[b] | |
|---|---|---|---|
| *100α* | *E* (kcal/mole)* | *100α* | *E* (kcal/mole)* |
| 10.1% | 34.13 | 11.1% | 94.97 |
| 21.28% | 23.3 | 19.7% | 90.0 |
| 49.2% | 18.89 | 34.19% | 80.9 |
| 70.48% | 17.89 | 53.89% | 55.7 |
| 92.22% | 16.3 | 81.62% | 48.8 |

[a] Calculated from Fig. 2.
[b] Calculated from Fig. 3.

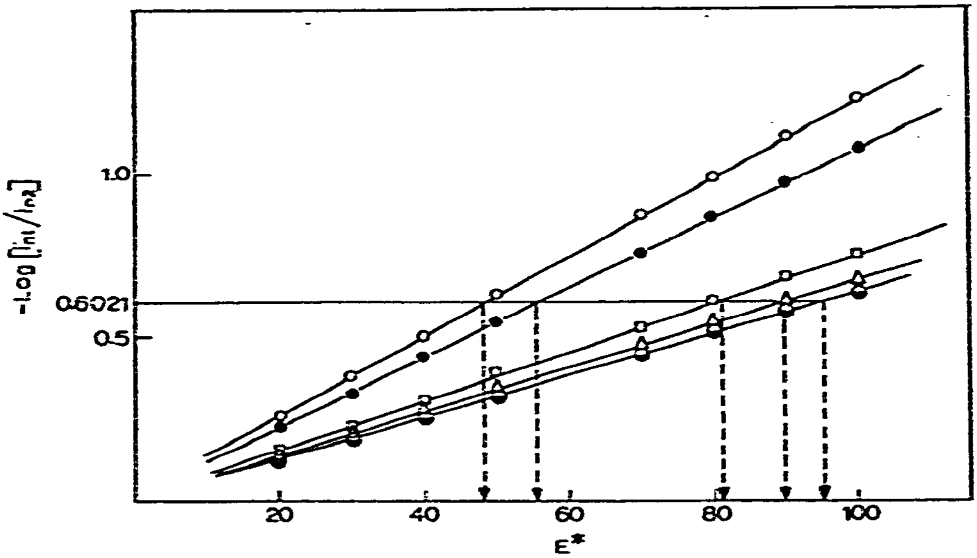

Fig. 3. Log ($i_{a1}/i_{a2}$) versus $E^*$ plot for methyl prednisolone Form II$_b$ desolvation as a function of fraction decomposed ($\alpha$) using two thermograms (B and C) generated as described in the experimental condition but with different heating rates. Key: B at 10°C/min; C at 2.5°C/min; ○, 80.6% decomposition; ●, 53.9% decomposition; □, 34.2% decomposition; △, 19.7% decomposition; ⊖, 11.1% decomposition.

working sheet in which the weight loss corresponding to 10.1% occurs at 346.6 K at $a_1$ = 2.5°C/min. The same percentage conversion at $a_2$ = 10°C/min occurs at 356.1 K. For these two temperatures, $T_{11}$ = 346.6 K and $T_{12}$ = 356.1 K, and log $i$ at 20 kcal/mole were determined using the reciprocal interpolation[4]. The calculated values were 11.56175 and 11.20265, respectively. The difference between these two values will give a value of $\log(i_{11}/i_{12}) = -0.3591$. This operation was repeated for other values of $E^*$. A plot of $-\log(i_{11}/i_{12})$ versus $E^*$ for a series of percentage conversions, shown in Table 2, was made and is shown in Fig. 2. The plot shows a linear relationship from which the enthalpy of desolvation of methyl prednisolone as a function of percentage conversion can be obtained by extrapolation, where $-\log(i_{11}/i_{12}) = -\log(a_1/a_2) = -\log(2.5/10) = 0.602$. The values of enthalpies obtained at different percent conversions are tabulated in Table 3.

The temperatures of decomposition obtained from thermograms B and C at the same heating ratio as thermograms A and C are also listed in Table 1. A plot of $\log(i_{11}/i_{12})$ versus $E^*$ is shown in Fig. 3. The resulting enthalpies of desolvation of methyl prednisolone, Form II$_b$, obtained from Fig. 3 were also listed in Table 3. The data show a wide variation of the calculated enthalpies as a function of the percentage conversion within the same sample and as a function of sample size variation between thermograms A and B. The calculated enthalpies as a function of the percentage conversion using thermograms A and C varied between 16 and 34 kcal/mole while the values obtained from thermograms B and C yielded values much higher than the previous thermograms and ranged between 48.8 and 95 kcal/mole. Close analysis of the sample size effect shown in Tables 1 and 3 shows that the

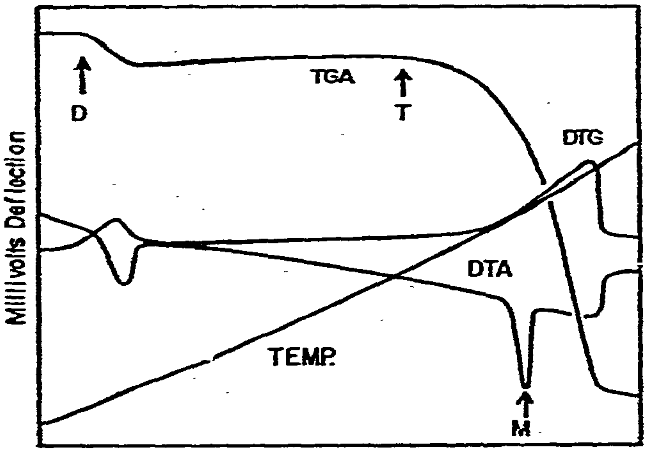

Fig. 4. Simultaneous TG–DTG and DTA thermogram for theophylline monohydrate dehydration and phase transformations in nitrogen atmosphere obtained as stated in the experimental condition.

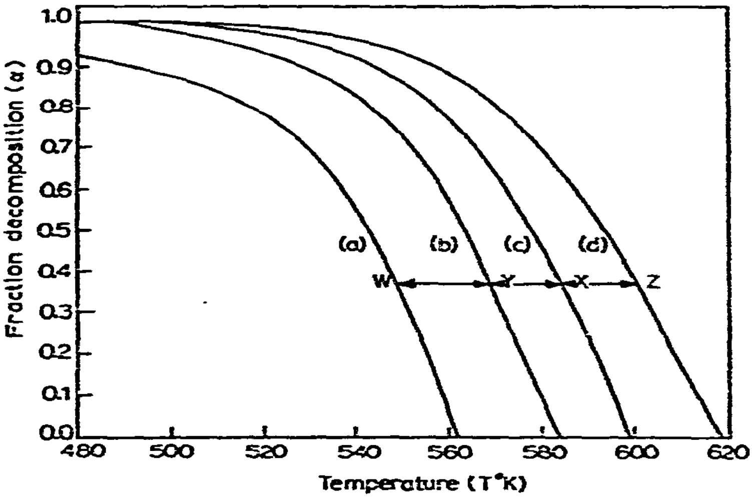

Fig. 5. Thermograms for theophylline (anhydrous) obtained at a constant sample weight (8 mg ± 0.1 mg) and different heating rates. The thermograms were generated as stated in the experimental conditions and scaled for fraction decomposed and linear absolute temperature. Key: (a), 1.25 °C/min; (b) 2.5 °C/min; (c) 5 °C/min; (d) 10 °C/min.

larger the sample size, the greater the temperature difference and the lower the calculated $E^*$.

### *Effect of the heating rate ratio*

Theophylline and calcium oxalate monohydrate were used to study the influence of the heating rate ratio on the calculated kinetic parameters using the Gyulai and

Greenhow method. Several thermograms of these samples at a constant sample weight and different heating rates were generated using the thermoflex analyser to be used in this study.

Figure 4 shows a thermogram for theophylline monohydrate. The thermogram indicates that there are two steps. The first step is dehydration starting at point D on the thermogram and the second step is phase transformation, starting at point T on the thermogram, which is the weight loss due to vaporization of the compound. Since there are weight losses below and above the melting point, M, on the thermogram without any chemical decomposition, sublimation is occurring below the melting point and vaporization is occurring above the melting point. Only the calculations involving the vaporization, the second step, will be used at this point to evaluate the use of Gyulai and Greenhow's technique.

For convenience, the percent conversion as a function of the temperature was determined from the original thermograms and the plots shown in Fig. 5 for four thermograms of theophylline obtained at a constant sample weight (8 mg ± 0.1 mg) and different heating rates. The heating rates chosen were 1.25°C/min, 2.5°C/min, 5°C/min, and 10°C/min. The temperatures of decomposition obtained from sets of

TABLE 4

TEMPERATURES OF DECOMPOSITION OBTAINED FROM TWO THERMOGRAMS OF THEOPHYLLINE (ANHYDROUS) AT TWO DIFFERENT HEATING RATES AT A PARTICULAR PERCENTAGE CONVERSION

| *Run 9 versus run 14*<br>*10°C/min versus 2.5°C/min* | | | *Run 9 versus run 12*<br>*10°C/min versus 1.25°C/min* | | | *Run 13 versus run 12*<br>*5°C/min versus 1.25°C/min* | | |
|---|---|---|---|---|---|---|---|---|
| *100α* | *$T_{12}$ (K)* | *$T_{11}$ (K)* | *100α* | *$T_{12}$ (K)* | *$T_{11}$ (K)* | *100α* | *$T_{12}$ (K)* | *$T_{11}$ (K)* |
| 17.09 | 567.2 | 540.5 | 17.09 | 567.2 | 512.5 | 17.09 | 553.6 | 512.5 |
| 30.76 | 579.3 | 552.2 | 30.76 | 579.3 | 530.1 | 30.76 | 566.5 | 530.1 |
| 51.01 | 593.7 | 563.4 | 51.01 | 593.7 | 543.9 | 51.01 | 578.4 | 543.9 |
| 80.13 | 607.5 | 575.8 | 80.13 | 607.5 | 555.8 | 80.13 | 591.3 | 555.8 |

TABLE 5

THE CALCULATED ENTHALPY OF VAPORIZATION ($\Delta H_v^*$) FOR THEOPHYLLINE USING THE GYULAI AND GREENHOW INTEGRATION METHOD FOR KINETICS

| *Run 9 (10°C/min) versus run 14 (2.5°C/min)* | | *Run 13 (5°C/min) versus run 12 (1.25°C/min)* | | *Run 9 (10°C/min) versus run 12 (1.25°C/min)* | |
|---|---|---|---|---|---|
| *100α* | *$\Delta H_v^*$ (kcal)* | *100α* | *$\Delta H_v^*$ (kcal)* | *100α* | *$\Delta H_v^*$ (kcal)* |
| 17.09 | 39.6 | 17.09 | 17.28 | 17.09 | 22.62 |
| 30.76 | 30.26 | 30.76 | 20.56 | 30.76 | 23.55 |
| 51.01 | 28.22 | 51.01 | 22.94 | 15.01 | 24.62 |
| 80.13 | 28.09 | 80.13 | 23.38 | 80.13 | 24.78 |

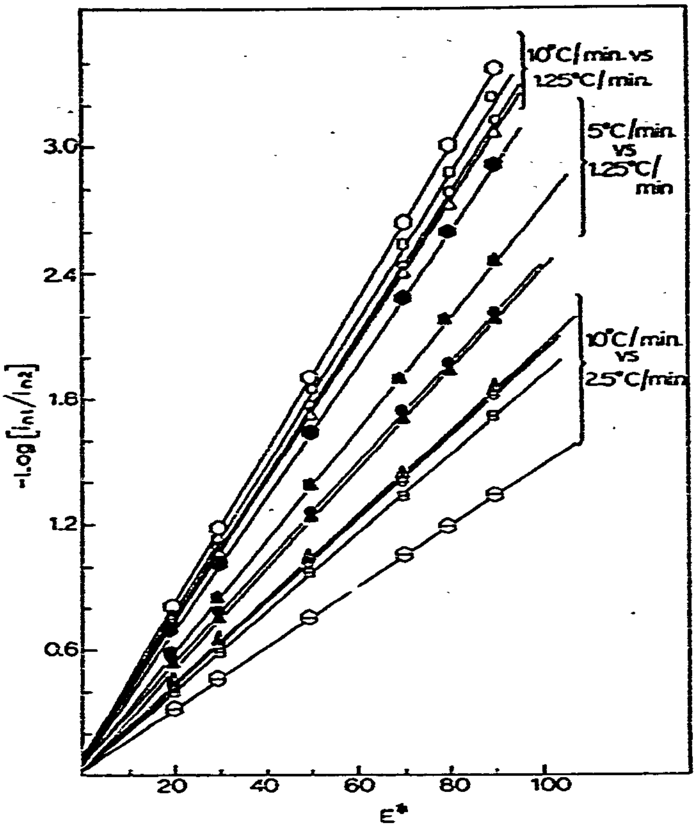

Fig. 6. Log ($i_{s1}/i_{s2}$) versus $E^*$ plot for theophylline phase transformations as a function of fraction decomposition; and heating rate ratios. ○, ⬢, ⊖, 17.1% decomposition; □, ■, ⊟, 30.8% decomposition; ○, ●, ⊖, 51.0% decomposition; △, ▲, ⟁, 80% decomposition, where ○, □, ○, △, were obtained from thermograms (a) and (d) (Fig. 5); ⬢, ■, ●, ▲, were obtained from thermograms (a) and (c) (Fig. 5); ⊖, ⊟, ⊖, ⟁, were obtained from thermograms (b) and (d) (Fig. 5).

two thermograms with different heating rates and having different heating ratios, are listed in Table 4. The resulting log($i_{11}/i_{12}$) versus $E^*$ plots for data in Table 4 are shown in Fig. 6. The enthalpies calculated from Fig. 6 show wide variation, ranging from 17.3 to 39.6 kcal/mole as a function of percentage conversion within the same runs and as a function of the heating rate ratios. The data are summarized in Table 5. Table 5 shows that enthalpies obtained from two thermograms at higher heating rates have higher values with a wide range of variation compared with values obtained from two thermograms generated at lower heating rates, even though they have the same heating rate ratios. The variation gets smaller as we go to higher heating rate ratios. For example, for a heating rate ratio equal to four, ($a_2/a_1$ = 4), obtained from two thermograms generated at 10°C/min, the enthalpies calculated by the Gyulai and Greenhow method range between 28 and 39.6 kcal/mole. On the other hand, the enthalpies calculated from two thermograms generated at 5°C/min and 1.25°C/min vary between 17.3 and 23.5 kcal/mole. This indicates that as we go to lower heating rates having the same ratios, the values of the enthalpies decrease and the range of variation also decreases.

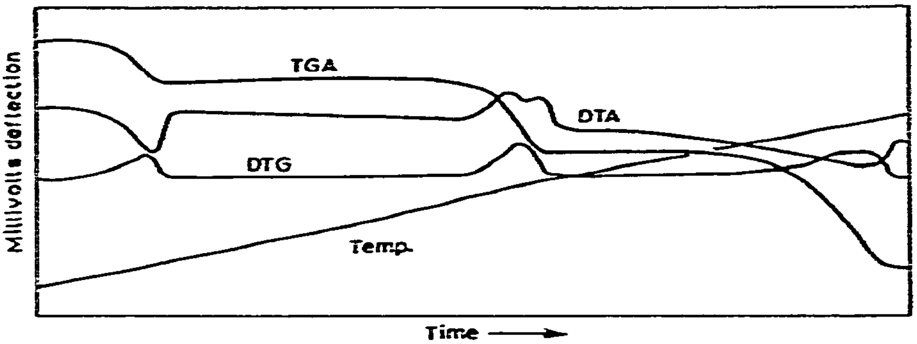

Fig. 7. Simultaneous TG–DTG and DTA thermograms from calcium oxalate monohydrate dehydration and chemical degradation in nitrogen atmosphere, obtained as stated in the experimental conditions.

TABLE 6

TEMPERATURES OF DECOMPOSITION OBTAINED FROM TWO THERMOGRAMS OF CALCIUM OXALATE MONOHYDRATE GENERATED AT TWO DIFFERENT HEATING RATES AT A PARTICULAR PERCENTAGE CONVERSION (DEHYDRATION STEP)

| *Run 2 (20°C/min) versus run 3 (2.5°C/min)* | | | *Run 4 (10°C/min) versus run 3 (2.5°C/min)* | | |
|---|---|---|---|---|---|
| *100α* | *$T_{12}$ (K)* | *$T_{11}$ (K)* | *100α* | *$T_{12}$ (K)* | *$T_{11}$ (K)* |
| 16.67 | 432.1 | 412.4 | 16.67 | 418.8 | 412.4 |
| 40 | 442.3 | 418.8 | 40 | 431.5 | 418.8 |
| 70 | 452.5 | 424.9 | 70 | 437.0 | 424.9 |

For a heating rate ratio equal to eight, the enthalpies calculated from two thermograms at 10 and 1.25°C/min range between 22.6 and 24.8 kcal/mole. The data for theophylline suggests that the higher the heating rate ratio, the less the variation in the calculated enthalpies.

Figure 7 shows a thermogram for calcium oxalate monohydrate generated under a nitrogen atmosphere. The thermogram shows three consecutive phase transformation steps. The first step is the dehydration of calcium oxalate monohydrate to form anhydrous calcium oxalate. The second and third steps show chemical decomposition of calcium oxalate. The chemical decomposition in step two is the release of carbon monoxide to form calcium carbonate which in turn decomposes in the third step to release calcium dioxide to form calcium oxide.

The temperatures of decomposition in step one obtained from sets of two thermograms with different heating rates having different heating ratios, are listed in Table 6. The resulting $\log(i_{11}/i_{12})$ versus $E^*$ plots for data in Table 6 are shown in Fig. 8. The temperatures of decomposition in step two of the calcium oxalate are listed in Table 7 and the corresponding $\log(i_{11}/i_{12})$ versus $E^*$ plots are shown in Fig. 9. By the same token, temperatures of decomposition of calcium carbonate–calcium oxide trans-

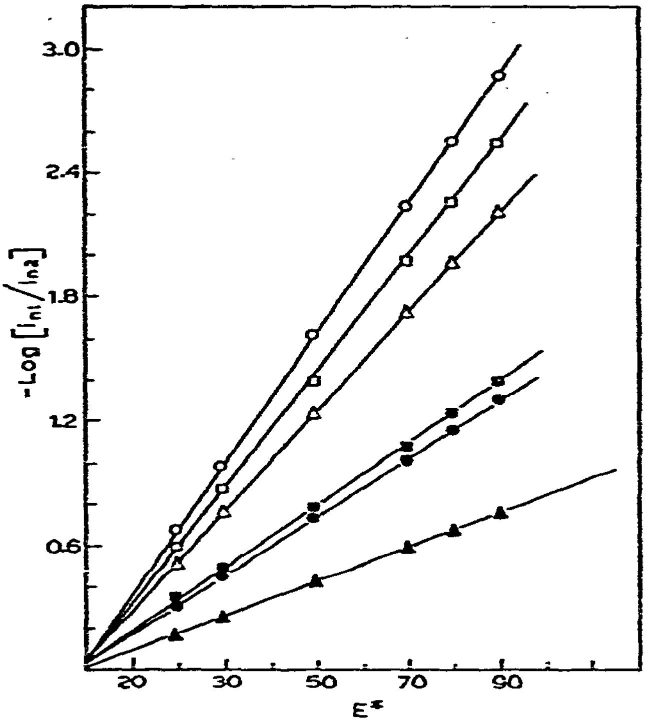

Fig. 8. Log ($i_{n1}/i_{n2}$) versus $E^*$ plot for calcium oxalate monohydrate dehydration (step one) as a function of fraction decomposition and heating rate ratios; △, ▲, 17.7% decomposition; □, ■, 40% decomposition; ○, ●, 70% decomposition, where △, □, ○, were obtained from two thermograms generated at 20°C/min and 2.5°C/min; ▲, ■, ●, were obtained from two thermograms generated at 10°C/min and 2.5°C/min.

TABLE 7

TEMPERATURES OF DECOMPOSITION OBTAINED FROM TWO THERMOGRAMS OF CALCIUM OXALATE MONOHYDRATE GENERATED AT TWO DIFFERENT HEATING RATES AT A PARTICULAR PERCENTAGE CONVERSION (FOR CALCIUM OXALATE–CALCIUM CARBONATE CHEMICAL DEGRADATION)

| *Run 1 (20°C/min) versus run 3 (2.5°C/min)* | | | *Run 4 (10°C/min) versus run 3 (2.5°C/min)* | | |
|---|---|---|---|---|---|
| *100α* | *$T_{12}$ (K)* | *$T_{11}$ (K)* | *100α* | *$T_{12}$ (K)* | *$T_{11}$ (K)* |
| 12.89 | 741.8 | 699.4 | 12.89 | 735.0 | 699.0 |
| 32 | 756.2 | 722.2 | 32 | 755.1 | 722.2 |
| 64.9 | 769.5 | 738.3 | 64.9 | 770.0 | 738.3 |
| 96.89 | 781.8 | 751.2 | 96.89 | 782.5 | 751.2 |

formation are shown in Table 8, and the corresponding log($i_{11}/i_{12}$) versus $E^*$ plots are shown in Fig. 10. The enthalpies calculated from Figs. 8–10 show wide variation. The enthalpies range from 27 to 71.4 kcal/mole for the dehydration step and from 37.2 to 76 kcal/mole for the calcium carbonate–calcium oxide chemical transformation step. Table 9 summarizes these data. The data for step one is in agreement with the

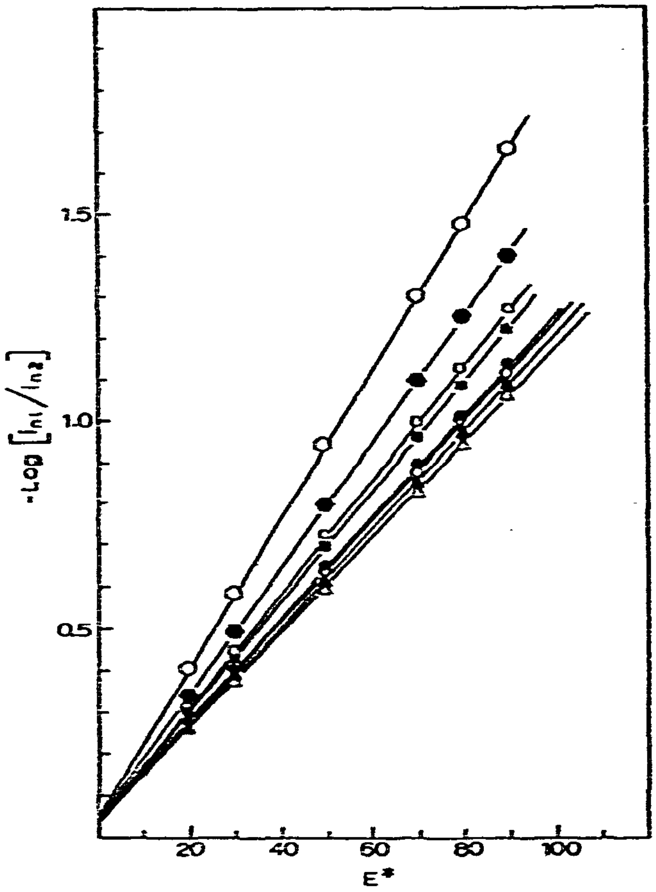

Fig. 9. Log ($i_{n1}/i_{n2}$) versus $E^*$ plot for calcium oxalate–calcium carbonate transformation (step two) as a function of fraction decomposition and heating rate ratios; ⬡, ⬢, 12.9% decomposition; □, ■, 32% decomposition; ○, ●, 64.9% decomposition; △, ▲, 96.9% decomposition, where ⬡, □, ○, △, were obtained from two thermograms generated at 20°C/min and 2.5°C/min; ⬢, ■, ●, ▲, were obtained from two thermograms generated at 10°C/min and 2.5°C/min.

TABLE 8

TEMPERATURES OF DECOMPOSITION OBTAINED FROM TWO THERMOGRAMS OF CALCIUM OXALATE MONOHYDRATE GENERATED AT TWO DIFFERENT HEATING RATES AT A PARTICULAR PERCENTAGE CONVERSION (STEP THREE: CALCIUM CARBONATE–CALCIUM OXIDE CHEMICAL DEGRADATION)

| *Run 1 (20°C/min) versus run 3 (2.5°C/min)* | | | *Run 4 (10°C/min) versus run 3 (2.5°C/min)* | | |
|---|---|---|---|---|---|
| *100α* | *$T_{12}$ (K)* | *$T_{11}$ (K)* | *100α* | *$T_{12}$ (K)* | *$T_{11}$ (K)* |
| 9 | 960.1 | 886.0 | 9 | 940.0 | 886.0 |
| 27 | 990.1 | 920.5 | 27 | 973.0 | 920.5 |
| 50 | 1014.0 | 940.6 | 50 | 995.5 | 940.6 |
| 80 | 1037.4 | 959.5 | 80 | 1014.98 | 959.5 |

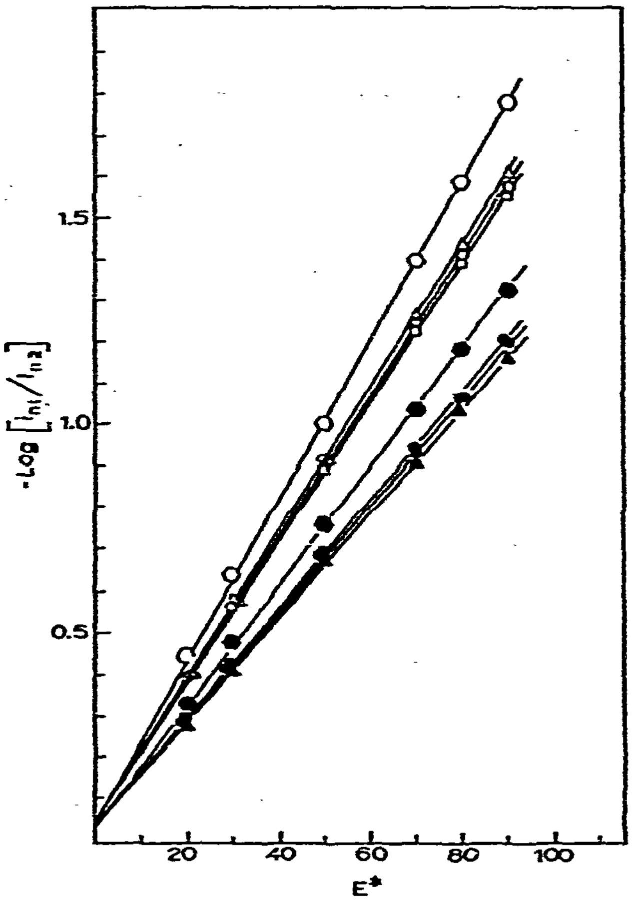

Fig. 10. Log ($i_{n1}/i_{n2}$) versus $E^*$ plot for calcium carbonate–calcium oxide transformation (3rd step in calcium oxalate monohydrate thermogram (Fig. 7) as a function of fraction decomposition and heating rate ratios; ◯, ⬤, 9% decomposition; □, ■, 27% decomposition; ○, ●, 50% decomposition; △, ▲, 80% decomposition, where ◯, □, ○, △, were obtained from two thermograms generated at 20°C/min and 2.5°C/min ⬤, ■, ●, ▲, were obtained from two thermograms generated at 10°C/min and 2.5°C/min.

previous findings on theophylline, in that as the heating rate ratios are increased, the calculated enthalpies get smaller and the variation between these values gets narrower. On the other hand, for steps two and three, which occur in the temperature ranges of 393–495°C and 596–768°C, respectively, the calculated enthalpies for the higher heating rate ratios were higher than those of the smaller heating rate ratios and have a wider range of variation. The last finding is opposite to that in the case of theophylline vaporization and calcium oxalate monohydrate dehydration. This may be due to the fact that calcium oxalate monohydrate dehydration and theophylline phase transformation occur at a lower temperature and in a narrower temperature range.

TABLE 9

THE CALCULATED ENTHALPIES OF DEHYDRATION AND DEGRADATION OF CALCIUM OXALATE MONOHYDRATE USING THE GYULAI AND GREENHOW INTEGRATION METHOD FOR KINETICS

| *Step one* | | *Step two* | | *Step three* | |
|---|---|---|---|---|---|
| *100α (%)* | *ΔH* (kcal)* | *100α (%)* | *ΔH* (kcal)* | *100α (%)* | *ΔH* (kcal)* |
| *Run 2 (20°C/min) versus run 3 (2.5°C/min)* | | *Run 1 (20°C/min) versus run 3 (2.5°C/min)* | | *Run 1 (20°C/min) versus run 3 (2.5°C/min)* | |
| 16.6 | 35.82 | 12.89 | 47.83 | 9 | 43.93 |
| 40 | 30.93 | 32 | 63.57 | 27 | 50.48 |
| 70 | 27.11 | 64.9 | 72.38 | 50 | 49.98 |
| | | 96.89 | 75.95 | 80 | 48.96 |
| *Run 4 (10°C/min) versus run 3 (2.5°C/min)* | | *Run 4 (10°C/min) versus run 3 (2.5°C/min)* | | *Run 4 (10°C/min) versus run 3 (2.5°C/min)* | |
| 16.67 | 71.39 | 12.89 | 37.2 | 9 | 38.97 |
| 40 | 37.85 | 32 | 42.99 | 27 | 43.43 |
| 70 | 40.44 | 64.9 | 46.65 | 50 | 43.32 |
| | | 96.89 | 48.69 | 80 | 44.63 |

## CONCLUSIONS

A literature and experimental evaluation showed that the non-isothermal thermogravimetric techniques published in the literature gave unsatisfactory results, as a wide variation in calculated enthalpies as a function of experimental conditions was observed. All methods, differential, integral or two-curves techniques, make the following assumptions which are often violated.

(a) The equation was derived assuming that all solids decompose to another solid plus gas.

(b) The function of the mass change, f(α), is assumed to be $(1 - \alpha)^n$.

(c) The analysis of data implicitly assumes that the furnace atmosphere does not influence the reaction. This suggests the reaction will be the same under an oxidative or non-oxidative atmosphere, which is not true for many reactions.

(d) The method assumes that the sample temperature is equal to the furnace temperature throughout the specimen, i.e. no thermal gradient.

(e) The method assumes that only one reaction occurs in the system and that the order of the reaction is the same throughout the reaction. This excludes the possibility of multistep reactions.

In addition to the above assumptions, the methods using two thermogram curves either assume a parallel shift of the thermograms on the temperature axis when the two thermograms are generated under two different heating rates, but keeping other conditions constant; or a parallel shift of the thermograms on the temperature axis when the two thermograms are generated from two sample weights keeping other conditions constant.

This assumption does not agree with our observations and findings in Fig. 5. Figure 5 also shows that the lower the heating rate the lower the temperature of decomposition corresponding to a certain percentage conversion. This decrease is not homogeneous since the slopes of these thermograms are different and the distance WY is greater than the distance XZ. Figure 5 shows that this distance is not homogeneous as a function of fraction of decomposition ($\alpha$). This latter observation fully supports our observation that the inconsistencies of the parameters obtained from presently utilized techniques is due to the disregard of the thermal gradients that must exist in the sample.

After a thorough analysis of the techniques, we have rationalized that the major cause of this variation is due to the fact that these methods (including the Gyulai and Greenhow method) do not take into consideration the thermal gradient of the sample or the lag in temperature of the sample from that indicated on the thermogram. As a result, a minor variation in the recorded temperature will yield a range of variations in the calculated $E^*$. The variation of $E^*$ as a function of the sample size can be explained by the fact that the larger the specimen mass, the greater the difference between the sample and furnace temperatures, and the larger the thermal gradient. Also, the specimen mass could alter the heating rate and the degree of gaseous diffusion through the specimen. Similarly, the larger variations seen with higher heating rates can be explained due to the larger thermal gradients and temperature lag of the sample which must exist at the higher heating rates.

It is obvious from the above results that the dissatisfaction often expressed in the literature regarding use of the non-isothermal techniques presently available to researchers is well founded.

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