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KINETICS OF PHASE TRANSFORMATIONS IN AMORPHOUS MATERIALS BY DSC. PART I

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ABSTRACT

New analytical methods are introduced for the determination of kinetic parameters of crystallization of an amorphous alloy from DSC transformation exotherms Isothermal and heating rate methods, as well as a method for separation of two superimposed crystallization reactions are discussed The basic operating principles and accuracy of the two currently most popular DSC instruments (the DuPont 1090 (E I Dupont de Nemours Inc , Wilmington, DE, U S A) and the Perkin Elmer DSC7 (Perkin Elmer Corporation, Norwalk, CT, U S A)) in the context of glass crystallization kinetics are critically evaluated and compared

1 INTRODUCTION

Thermoanalytical techniques, especially differential scanning calorimetry (DSC), have become popular and convenient tools for the characterization of phase transformations in glasses, amorphous alloys and polymeric materials, without resorting to tedious experiments commonly utilized in classical nucleation and crystal growth studies (e g a combination of X-ray diffraction, microscopy, electrical conductivity, etc , on a series of aged samples)

Much work has been published [1–14] on methods by which various kinetic information may be obtained via DSC, as well as the correctness of different mathematical approaches to generate two-dimensional plots used to calculate transformation parameters from DSC experimental data. Yinnon and Uhlmann [15] point out that most of these are in fact identical procedures and many are of questionable validity In this work, we describe procedures which, although requiring computer computation, are conceptually straightforward, and have the advantage of not needing to make

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questionable assumptions to force manipulated data into two-dimensional plots

An unfortunate situation in this area of growing experimental interest is the descriptive term given to two devices of entirely different design, namely DSC In this work, we shall show that the basic operating principles of the DuPont 1090 and 9900 DSC, and the Perkin Elmer DSC7 are dissimilar, in Part II of this series we shall show that the data generated by these devices under identical programming conditions are also different

2 DEVICE CONSIDERATIONS

2 1 *DuPont 1090 and Perkin Elmer DSC7, differences in basic design*

The basic cell designs for the Perkin Elmer and the DuPont instruments used in this study are shown in Fig 1 [16,17] The Perkin Elmer cell (Fig 1(B)) is a massive block of metallic alloy which is constantly maintained at some refrigerated temperature (i e that of flowing water or liquid nitrogen). There are two isolated positions in the cell for the sample and the reference, each of which have an individual resistance heater and a platinum resistance thermometer.

If the temperature of the sample and reference is uniformly raised, and a transformation begins to take place within the sample, the DSC automatically adds or subtracts heat from the capsules so that the temperature difference between the two is always zero, and their individual temperatures are equal to the programmed value For example, if the sample is converting exothermically from the glassy to crystalline states, the DSC will automatically "back off" on the heat input to the sample and also accelerate the heating of the reference, thus maintaining the "null" balance This occurs during part of an electronic switching cycle. During the other part of the

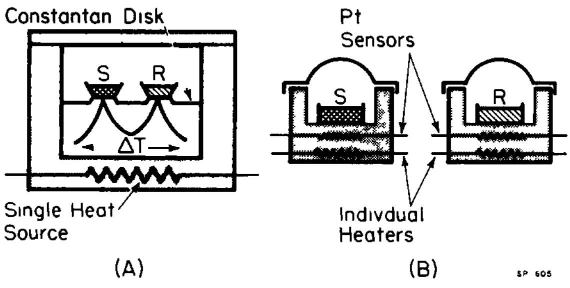

Fig 1 Schematic diagrams of (A) DuPont 1090 and 9900 and (B) Perkin Elmer DSC7 thermal analysis devices

cycle the device adds or subtracts heat equally from both sample and reference to keep their temperatures at the programmed value These cycles switch back and forth many times per second [16]

The amount of electrical energy per unit time which the DSC must alter from the programmed value (in order to maintain the heating schedule) is assumed to be proportional to the energy per unit time expended or absorbed by the sample during the transformation The electrical energy imparted to the heating elements in order to maintain the null balance is the measured quantity Units of power can be recorded versus time and/or programmed temperature in computer memory for subsequent retrieval and data manipulation

The DuPont instrument operates on the principle of a traditional DTA (differential thermal analyzer) [18] Both sample and reference are contained in the same cell and are heated by a single resistance heater (Fig 1(A)) The sample temperature, as well as the difference between sample and reference temperature, is measured by a sensitive thermocouple system placed in mechanical contact below the sample and reference capsules A separate control thermocouple is not in thermal contact with sample or reference

As the temperature of the cell is raised at a programmed rate, any difference between the temperature of the sample and reference is measured as a millivoltage output from the differential thermocouple This millivoltage as a function of time and temperature is automatically (and perhaps misleadingly) converted to units of energy per unit time via a calibrated conversion factor in the computer software

2 2 *Theoretical basis of operation of DTA and DSC*

The development of the relationship between changes in sample enthalpy and device output and its derivations are well treated in the literature [19–21] For the DuPont system, dynamic heat balance requirements yield [21]

$$\frac{\mathrm{d}H}{\mathrm{d}t} = \frac{1}{R}(T_s - T_r) + (C_s - C_r)\frac{\mathrm{d}T_r}{\mathrm{d}t} + RC_s\frac{T_s - T_r}{\mathrm{d}t} \tag{1}$$

where $\mathrm{d}H/\mathrm{d}t$ is the time rate of change in sample enthalpy due to a transformation within it, T_s and T_r are sample and reference temperatures respectively, C_s and C_r are heat capacities, and R is the thermal resistance between the location of the transformation and the temperature measuring device (assumed to be the same for both sample and reference) For small values of thermal resistance, the first term dominates and $\mathrm{d}H/\mathrm{d}t$ is proportional to the differential temperature The smaller the thermal resistance, the smaller the lag time between when a transformation commences and when the differential thermocouple detects it

For the Perkin Elmer system the heat balance is derived as [21]

$$\frac{\mathrm{d}H}{\mathrm{d}t} = -\frac{\mathrm{d}Q}{\mathrm{d}t} + (C_s - C_r)\frac{\mathrm{d}T_f}{\mathrm{d}t} - RC_s\frac{\mathrm{d}^2Q}{\mathrm{d}t^2} \tag{2}$$

where $\mathrm{d}Q/\mathrm{d}t$ is the heat flow generated by the device to compensate for heat released via a sample transformation Low values of R would make the third term negligible For a heating rate study the second term will be a constant offset from zero, before and after the transformation, and can be brought close to zero by a careful match of sample and reference heat capacities This term becomes significant for isothermal studies, and its contribution is discussed in detail in Part II of this series

2 3 Problems with the DuPont design for crystallization kinetics

The relationship between $\mathrm{d}H/\mathrm{d}t$, temperature difference and thermal resistance in eq (1) takes the form of a thermal Ohm's law, current, potential difference, and resistance respectively Since $\mathrm{d}H/\mathrm{d}t$ is a material property, decreasing R must act to decrease $T_s - T_r$ proportionally Thus, the response time of the instrument is limited by its ability to resolve temperature differences beyond the noise level

This consideration introduces a problem when analyzing data from this device As a crystallization reaction proceeds, the temperature of the sample deviates from that of the programmed level (for either a heating rate or isothermal run) and this deviation is the quantity measured as the dependent variable Unlike the Perkin Elmer device, the system makes no effort to maintain the sample at the programmed temperature The DuPont DSC simply records the millivoltage corresponding to the difference in temperature between sample and reference as a function of sample temperature The heating ramp or isothermal hold is controlled by a thermocouple external to both sample and refence

Figure 2 illustrates how substantially T_s can deviate from the programmed value

Using the programmed isothermal or heating rate temperature in any theoretical analysis (as discussed later) is clearly erroneous, the magnitude of the error increases with the increasing exothermic nature of the sample Since crystallization transformations are taken to have an Arrhenius temperature dependence, the transformation rate will increase exponentially with temperature deviation When undertaking crystallization studies using the DuPont system, it is tacitly assumed that the magnitude of the temperature error is negligible The validity of this assumption, however, will always be open to question

The Perkin Elmer system's design acts to maintain the sample at the programmed temperature, but this device does not escape sample temperature deviation under conditions of large sample mass, rapid heating rate or

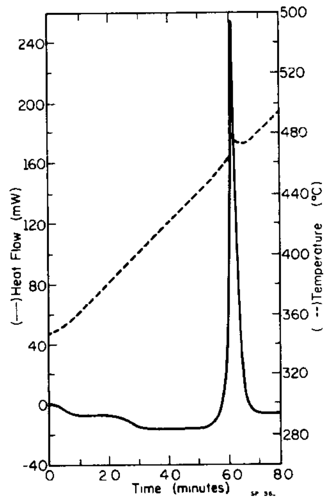

Fig 2 Heating rate study of a large mass of granular $CdGeAs_2$ The exothermic nature of the transformation raised the temperature of the sample by ca 20 ° C

highly exothermic transformations This will be illustrated in the following section

In fairness, error of this sort appears only to be introduced in the DuPont system for transformations from the non-equilibrium state toward the equilibrium state, devitrification being an example Data collected from melting or solidification reactions, in which the sample converts from one equilibrium phase to another, are not affected in the same way During this sort of transformation, the sample will resist any temperature change until the phase change is completed (Le Chatelier's principle) The sample acts to maintain a known temperature, namely the melting temperature, meanwhile the reference temperature increases at a known rate, causing the device to indicate an endothermic transformation Hence, through calibration with a standard material, this device should generate accurate thermodynamic and kinetic data for these types of transformations

2 4 Transformation avalanche

Two amorphous samples of different mass, yet transformed under the same temperature programme, should ideally transform identically with time However, crystallization reactions appear highly mass sensitive on the DuPont 1090 and moderately mass sensitive on the Perkin Elmer DSC7, as shown in Fig 3

Figure 3 shows the exotherms for moderate and exceedingly massive sample loadings (made up of equally sized granules) in both devices All samples were heat treated through their transformations at 20 ° C min^{-1}

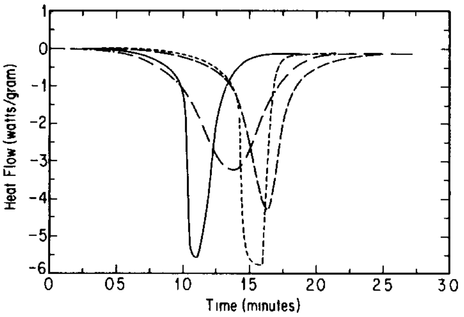

Fig 3 Effect of sample mass on the crystallization exotherm (———) DuPont 9900, 61 4 mg, (– –) DuPont 9900, 10 5 mg, (- - - - - -) Perkin Elmer DSC7, 56,6 mg, (— — —) Perkin Elmer DSC7, 12 4 mg

As can be seen for both devices, the more massive exotherm reaches a peak and terminates at earlier times, the difference in the Perkin Elmer system being not as great as in the DuPont system

The non-compensation design of the DuPont cell is clearly the cause of this system's higher mass sensitivity As the transformation begins, heat is released from the reaction zones within the sample granules, increasing the temperature within the capsule As the temperature of the granules increases, so does the rate of the transformation (following the exponential Arrhenius temperature dependence), which in turn increases the temperature of the sample even more, and so on, causing the glass to "avalanche" toward the ordered state

The compensation design of the Perkin Elmer device has been shown to be inadequate to arrest the effect of the larger mass at the relatively rapid heating rate of 20 °C $\min^{-1}$ This discrepancy will be reduced with decreasing heating rate, giving the system more time to compensate for the exothermic sample transformation This is confirmed in Part II of this series where the calculated activation energy of crystallization of $CdGeAs_2$ is shown as a function of heating rate

It is evident that a sample with as little mass as possible (without going below the sensitivity level of the device to measure temperature difference) is optimal To obtain reproducible data from the devices, we have found ca 5–10 mg to be an acceptable level for $CdGeAs_2$, but this mass will, of course, vary with the exothermic nature of the substance under investigation

It should be noted that the mass sensitivity of the Perkin Elmer instrument would not be known by looking solely at the instrument output The system provides heat flow data as a function of time or temperature, yet the temperature is the programmed temperature (set point), not the actual sample temperature Time and temperature are converted via the heating rate This misleading data presentation was overcome in the present study

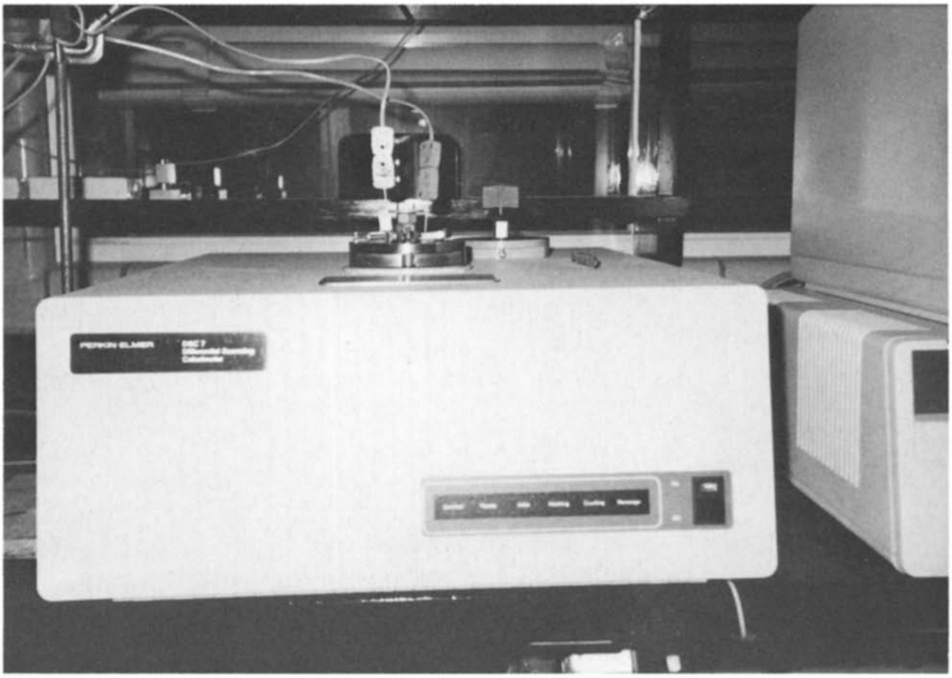

Fig 4 Alternative cell top used to measure sample deviation from programmed value The chromel–alumel differential thermocouple leads to a digital recorder

by machining a new top to the cell which permitted thin chromel–alumel thermocouple wire to run through, and into small holes in platinum caps to the sample and reference cells, forming beads in contact with the sample and the reference capsules, as shown in Fig 4

The capsule tops were crimped down to be in mechanical contact with the sample and reference granules (while still maintaining a hermetic seal)

The millivoltage output from this differential thermocouple was recorded as a function of time digitally * (10 points per second). The millivoltage difference was converted to a temperature difference via an expansion polynomial, and this in turn was converted to sample temperature by adding in the programmed temperature of the reference These sample temperature versus time data were correlated with the system heat flow versus time data to obtain the heat flow versus sample temperature data for the Perkin Elmer system shown in Fig 5

The substantial mass sensitivity of both instruments is well illustrated in Fig 5 which shows that for excessive sample masses in both instruments, the sample temperature by no means follows the heating rate.

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* Bascom-Turner Digital Recorder Model 4000, Bascom-Turner Instruments

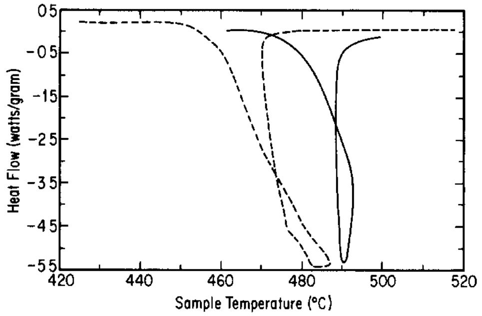

Fig 5 Illustration of effect of excessive sample mass on the devitrification behavior of CdGeAs$_2$ (------) DuPont 9900, 61 4 mg, (———) Perlin Elmer DSC7 41 4 mg

2 5 *Heating rate error*

Amorphous samples which have been fabricated identically, should ideally have exactly the same heat of transformation (which is the integrated area under the peak), regardless of the heating rate This appears to hold true in the Perkin Elmer instrument but is not as stable in the DuPont Heats of crystallization as a function of heating rate for recrystallized CdGeAs$_2$ are plotted in Fig 6

The deviation in area in Fig 6 does not seem appreciable until the higher heating rates (70 and 90°C min^{-1}), and thus the use of only slow to moderate heating rates should minimize error in peak area or shape

2 6 *Isothermal temperature runup limitations*

For an ideal isothermal study, one would like to raise the temperature of the sample to a given level infinitely quickly, (i e in zero time), and instantly hold that temperature with the device taking real data at exactly $t = 0$ This,

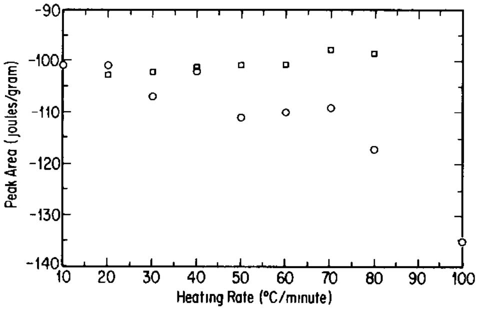

Fig 6 Effect of heating rate on peak area o, DuPont 1090, □ Perkin Elmer DSC7

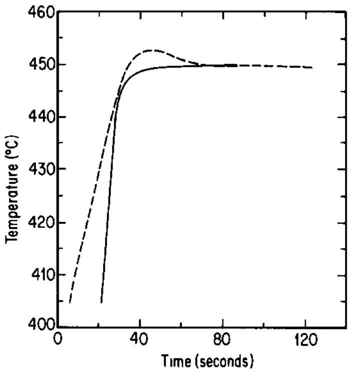

Fig 7 Comparison of junction between rapid heating rate and isothermal portions of DSC temperature programmes using powdered alumina as sample and reference (———) Perkin Elmer DSC7, (- - - - - -) DuPont 9900 Sample temperatures in the Perkin Elmer DSC7 were measured externally (see Fig 4)

of course, is not possible since heat transfer delay limits the heating rate, and the limitations of cell design restrict the sharpness of the "junction" between the heating rate and the isothermal portions of the heating schedule Instrument specifications indicate that the Perkin Elmer DSC7 has a maximum heating rate of 500 °C/min^{-1} while the Dupont 1090 and 9900 maximum is 100 °C/min^{-1} As before, an external thermocouple system was used to determine sample and reference temperatures in the Perkin Elmer system

A comparison of the junctions for both devices, using powdered alumina as both sample and reference, is provided in Fig 7

Figure 7 shows that the Perkin Elmer device, using a heating rate of 300 °C min^{-1}, negotiates the junction quite well, with comparatively minor undershoot, while the DuPont instrument tended to overshoot and relax slowly back to the programmed isothermal value

The small cell size along with the constant thermal competition with cold surroundings make rapid changes in the temperature/time programme feasible in the Perkin Elmer system The DuPont system is simply air-cooled, resulting in much poorer sensitivity to sharp changes in heating schedule A correction for the DuPont apparatus will be discussed in section 3 3 of Part II

Another disadvantage of the DuPont instrument is that its comparatively slow maximum heating rate shortens the range of isothermal temperatures through which data may legitimately be taken Certainly, the crystallization reaction must not be well under way until the isothermal temperature is reached As an illustration, at a heating rate of 100 °C min^{-1}, a crystallization reaction of $CdGeAs_2$ is one fifth completed at ca 493 °C, whereas at 200 °C min^{-1} the reaction is one fifth completed at ca 518 °C degrees

3 METHODS FOR DETERMINING CRYSTALLIZATION KINETICS FROM DSC DATA

3 1 *DSC isothermal transformation theory*

The fraction crystallized as a function of time may be determined [22–24] from the heat flow versus time DSC output simply by dividing successive partial areas under the corrected transformation peak by the entire peak area This will result in the standard "S"-shaped fraction crystallized versus time curve

For an ideal isothermal study, the manipulation of equations is quite straightforward The relationship between fraction crystallized and time for a nucleation and growth process is expected to follow the Johnson–Mehl–Avrami transformation equation [25]

$$F = 1 - \exp(-kt^n) \tag{3}$$

where, F is the time dependent fraction crystallized, t is time, k is a time independent (but temperature dependent) constant, and the exponent, n, is a constant dependent on the mechanism of crystallization Taking logarithms and rearranging we obtain

$$\ln(\ln(1 - F)) = \ln k + n \ln t \tag{4}$$

A plot of $\ln(\ln(1 - F))$ as a function of $\ln t$ will yield the value of n and k For a number of isothermal runs at different temperatures, k versus T data may be established The exponent n should be invariant with isothermal temperature so long as the mechanism of the transformation is not altered

The temperature dependence of k is generally considered to demonstrate a simple Arrhenius behavior

$$k = k_0 \exp\left(\frac{-E_c}{RT}\right) \tag{5a}$$

or

$$\ln k = \ln k_0 - \frac{E_c}{RT} \tag{5b}$$

where k_0 is the pre-exponential constant (which varies negligibly with temperature as compared to the exponential term over moderate temperature intervals), E_c is the activation energy of crystallization, R is the gas constant, and T is temperature A plot of $\ln k$ versus $1/T$ will yield the activation energy of crystallization

3 2 *Isothermal transformation theory of superimposed reactions*

We have found that in isothermal studies with the Perkin Elmer device, two overlapping peaks appear on the generated DSC traces for $CdGeAs_2$

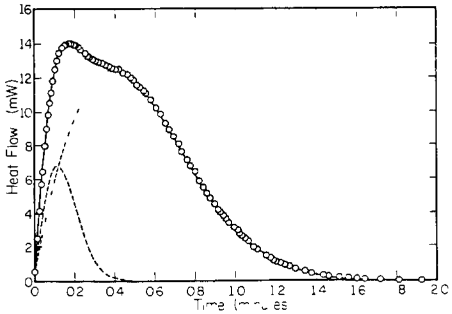

Fig 8 (o) Exothermic DSC output for crystallization of amorphous $CdGeAs_2$ at an isothermal temperature of 495° C on the Perkin Elmer DSC7 (———) SAS fit of eqn (9) to that data, (- - - - - -) calculated isolated peaks via a plot of each term of the sum in eqn (9)

(section 3 4 of Part II) We have developed a method of determining separate activation energies and crystallization mechanism constants for the two superimposed DSC transformation peaks

We define the fraction crystallized as

$$F = \frac{\int_{-\infty}^{t} \dot{H}\,\mathrm{d}t}{\int_{-\infty}^{\infty} \dot{H}\,\mathrm{d}t} \tag{6}$$

where $\dot{H}$ is $\mathrm{d}H/\mathrm{d}t$ determined by the DSC The integral in the denominator is simply the total area, A, under the DSC peak, thus eq (6) can be expressed in differential form

$$\dot{H} = A\frac{\mathrm{d}F}{\mathrm{d}t} \tag{7}$$

We can assume that the DSC generated peak in Fig 8 is the sum of two superimposed peaks (shown as dotted lines in the figure)

$$\dot{H}_{\mathrm{T}} = H_1 + H_2 \tag{8}$$

If we further assume that the individual peaks fit the Avrami expression, then eqn (8) can be rewritten as

$$\dot{H} = A_1\left[k_1 n_1 t^{n_1 - 1} \exp(-k_1 t^{n_1})\right] + A_2\left[k_2 n_2 t^{n_2 - 1} \exp(-k_2 t^{n_2})\right] \tag{9}$$

where A_1 is the area under the isolated first peak and A_2 is the area under the second The areas of the individual peaks must add up to the total area of the experimentally determined peak, A_{T}

$$A_2 = A_{\mathrm{T}} - A_1 \tag{10}$$

Thus, only five coefficients must be determined namely A_1, k_1, k_2, n_1 and n_2

The values of the above five coefficients can be determined by using the non-linear regression package of the Statistical Analysis System (SAS) * The program uses Marquart's method of minimization of least-squares error after reasonable guesses of initial values are provided

3 3 DSC heating rate transformation theory

Although theoretically straightforward, isothermal methods introduce a number of complications due to the discontinuity of the temperature program at the (rapid heatup to isothermal) junction, which necessitate the corrections discussed in Part II of this series, and limit the temperature ranges in which the study may be made Heating rate methods are attractive due to the uniformity of the temperature schedule, yet a theoretical complication is introduced by the inclusion of a temperature dependence in the Avrami expression

Differing mathematical methods for obtaining activation energies from heating rate studies have been a topic debated in recent literature [15,24] Many of the methods generate an "effective" activation energy, E_c/n, in which the activation energy of the transformation is tied to the mechanism constant [14,26]

We propose a very straightforward method, which appears to be a considerably more reasonable approach than those presently available If we simply insert the Arrhenius temperature dependence into the Avrami expression we obtain

$$F = 1 - \exp\left[-k_0 t^n \exp\left(\frac{-E_c}{RT}\right)\right] \tag{11}$$

The heating rate ϕ is simply the DSC change in temperature per change in time

$$\phi = \frac{T_2 - T_1}{t_2 - t_1} \tag{12}$$

From eq (11) it is clear that when $F = 0$, time must also equal zero since k is non-zero and n is positive and finite Thus, we can assign t_1 to be zero time at the initial deflection of DSC trace from its baseline, at its onset temperature $T_1 = T_{onset}$ Since the heating rate is known, we can convert T_2 and t_2 to floating variables so that eqn. (12) can be rewritten as

$$T = \phi t + T_{onset} \tag{13}$$

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* SAS Institute Inc , Cary, NC 27511, U S A

Combining eqns (11) and (13) we obtain

$$F = 1 - \exp\left[-k_0 t^n \exp\left(\frac{-E_c}{R(\phi t + T_{\text{onset}})}\right)\right] \tag{14}$$

or in logarithmic form

$$\ln[-\ln(1-F)] = \ln k_0 + n \ln t - \frac{E_c}{R}\left[\frac{1}{\phi t + T_{\text{onset}}}\right] \tag{15}$$

Equation (15) is of the form of a plane $z = ax + by + c$, where $z = \ln[-\ln(1-F)]$, $a = n$, $x = \ln t$, $b = E_c/R$, $y = 1/(\phi t + T_{\text{onset}})$, $c = \ln k_0$ The coefficients of this equation may be obtained by a least squares fit of the data to this plane, where the only statistical error will be in the z dimension since the x and y dimensions are in terms of the independent variable time This 3-dimensional least squares analysis is explained in detail in other work [27] The "best fit" coefficients result from the solution of three simultaneous equations (16–18) where eqn (18) is a correction to that in ref [27]

$$\sum_{i=1}^{N} z_i x_i = a \sum_{i=1}^{N} x_i^2 + b \sum_{i=1}^{N} x_i y_i + c \sum_{i=1}^{N} x_i \tag{16}$$

$$\sum_{i=1}^{N} z_i y_i = a \sum_{i=1}^{N} x_i y_i + b \sum_{i=1}^{N} y_i^2 + c \sum_{i=1}^{N} y_i \tag{17}$$

$$\sum_{i=1}^{N} z_i = a \sum_{i=1}^{N} x_i + b \sum_{i=1}^{N} y_i + cN \tag{18}$$

The coefficients a and b thus establish independent values for the activation energy of the transformation, E_c, and the exponent, n, characterizing the transformation mechanism

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