

## THE PRACTICE OF OBTAINING KINETIC DATA BY DIFFERENTIAL SCANNING CALORIMETRY\*\*

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### ABSTRACT

Over a period of time we have studied a variety of chemical reactions by different thermal-kinetic methods. The data obtained have been highly practical in defining processing, storage, and safety conditions for active materials. Not all kinetic approaches, however, were found to be equally reliable and no single method was satisfactory for all reactions. Our experiences with isothermal and dynamic methods are discussed in terms of their applications, accuracy, and experimental requirements. A simple isothermal test is recommended to check the validity of experimentally obtained activation energies and Arrhenius frequency factors. A combination of programmed and isothermal techniques is described for characterizing unresolved, multi-stepped reactions.

Industrial samples are quite often less than ideal materials for kinetic analyses. Multiple reactions and problems due to impurities and volatility occur frequently. A number of thermal-kinetic approaches were tried on a variety of reactive samples and their performance evaluated. Our experience and conclusions with these techniques are discussed below.

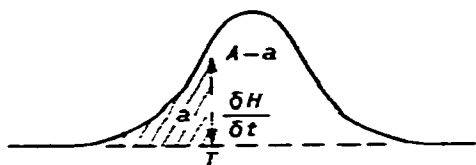
### I. HEAT EVOLUTION METHOD

The method which measured the heat evolution of a temperature programmed sample was first described by Borchardt and Daniels<sup>1</sup> for solutions and later by Uricheck<sup>2</sup> for solids by differential scanning calorimetry (DSC). The reaction heat is obtained from curve displacement as a function of temperature as in Fig. 1. Rate constants and the activation energy are calculated as shown.

For simple, first order reactions of relatively non-volatile materials, the method works well, is fairly rapid, and allows a precision for  $E$  of about 0.5-1 kcal mol<sup>-1</sup>. For example, it has worked well for some organic peroxides, azides, azidoformates, and a polysulfone<sup>3</sup>. However, the method has frequently given incorrect  $E$  values as shown by a few examples in Table 1.

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$$(1) \quad k = \frac{\delta c / \delta t}{(1-c)^n} = \frac{\delta H / \delta t}{(A-a)} \quad \text{1st order}$$

$$(2) \quad \frac{\delta \log k}{\delta(1/T)} = \frac{E}{2.3R}$$

Fig. 1. Borchardt and Daniels method.

TABLE I

COMPARISON OF ACTIVATION ENERGIES OBTAINED FROM HEAT EVOLUTION AND OTHER METHODS

	$E$ (kcal mole <sup>-1</sup> )	
	Heat evolution	Other methods <sup>b</sup>
Nitrocellulose	50-70	41
Dicumyl peroxide	25	35
Torak <sup>a</sup>	45	27
Compound A	33-38	25

<sup>a</sup> Hercules registered trademark for *O,O*-diethyl *S*-[2-chloro-1-(*N*-phthalimido)ethyl] phosphorodithioate. <sup>b</sup> Other methods include Heating rate vs. Peak temperature method, isothermal test procedures, and known sample properties.

As the results in Table I show, errors in the Heat evolution method can be on the high or low side. The Arrhenius plots obtained for these compounds showed good linearity. In some cases the source of error could be detected as small, broad endo- or exothermic events on the main reaction curve. In others, however, incorrect activation energies were obtained without visible evidence of interfering events. This technique should be used with considerable caution.

A similar technique was described by Rogers and Morris<sup>4</sup> for a rapid estimate of  $E$ . The technique measures early peak displacements ( $S$ ) versus temperature and plots  $2.3R\Delta(\log S)$  versus  $\Delta(1/T)$  to obtain  $E$ .

A rapid estimate of  $E$  can also be made from the differential form of the Arrhenius equation  $d \ln k/dT = E/RT^2$ . For the temperature interval  $\Delta T$ , where the reaction rate doubles, the expression becomes  $\ln 2/\Delta T = E/RT^2$ . Rearranging gives  $E = 1.37T^2/\Delta T$ . By measuring the temperature interval  $\Delta T$  during which the curve displacement from the baseline doubles, an estimate of  $E$  can be obtained. Measurement is made early on the reaction curve to avoid depletion error. As in the other methods measuring heat evolution (or curve displacement), the presence of extra endo- or exothermic activity will cause error.

## II. VARIABLE HEATING RATE METHOD

The expression  $F(c) = (AE/\beta R) \rho(x)$  has been derived and used by a number of authors as the basis for kinetic calculations<sup>5-9</sup>. Flynn and Wall<sup>10</sup> and Ozawa<sup>11</sup> have used Doyle's approximation<sup>6</sup> for  $\rho(x)$  to obtain the usable relationship  $\Delta \log \beta/\Delta(1/T) \simeq 0.457 E/R$  where  $\beta$  is the program heating rate and  $T$  is the temperature for a constant degree of conversion. As Ozawa pointed out<sup>12</sup>, Horowitz and Metzger's observation<sup>13</sup> that conversion at the reaction peak is constant, enables the relation to be readily applied to DSC analysis. By measuring reaction peak maximum temperatures as a function of the heating rate and plotting  $\log \beta$  vs.  $1/T_{\max}$ , the activation energy can be obtained by the above equation to within  $\pm 3\%$ . For more accurate computer calculation of  $E$ , McCarty's<sup>14</sup> approximation for  $\rho(x)$  can be used to give the expression

$$E = R \left( \frac{\Delta \ln \beta}{\Delta(1/T)} \left[ \frac{1}{(X+3)} - \frac{1}{X} - \frac{1}{(X+1)} - \frac{1}{(X+4)} - 1 \right] \right)$$

where  $X = E/RT$ . Since  $X$  contains both  $E$  and  $T$  as variables, the expression is reiterated with respect to  $X$  until  $E$  changes by less than  $0.05 \text{ kcal mol}^{-1}$  on successive calculations.

The heating rate versus peak temperatures ( $\beta$  v.  $T_{\max}$ ) method has been applied successfully to many types of reactions. Examples are given in Table 2.

TABLE 2  
KINETIC DATA FROM  $\beta$  VS.  $T_{\max}$  METHOD

Material	$E$ (kcal mol <sup>-1</sup> )	Log $Z$ (min <sup>-1</sup> )
Ferric ammonium ferrocyanide	25.0	9.9
Alkyl-azido formate	30.3	15.0
Nitrocellulose	41.6	18.5
Dicumyl peroxide	35.2	17.0
Torak® (pesticide)	26.8	11.3
Epoxy resin (commercial)	11.3	4.6
Thermosetting resin	reaction 1	21.5, 21.2
	reaction 2	24.8, 24.9
	reaction 3	39.4
Calcium oxalate <sup>11</sup>	78.1	28.6
Nylon 6 <sup>11</sup>	36.2	10.9
Polysulfone <sup>3</sup>	73	

The accuracies of the kinetic values have been checked by an isothermal test procedure (discussed later) and for the thermosetting resin, by processing experience. The thermosetting resin undergoes a complex multi-step polymerization. The reaction, discussed later, would have been difficult to characterize by other means. The advantages of the Heating rate vs.  $T_{\max}$  method are simplicity of measurement, applicability

to many types of reactions, relative insensitivity to secondary reactions, solvent effects, and baseline problems. However, we know of two instances in which this method will not work. One is the analysis of a material such as methyl parathion, which undergoes an isomerization change at reaction temperatures<sup>15</sup>. The second involves materials which decompose with melting, e.g., diazodinitrophenol<sup>16</sup>, cupferron tosylate and the explosive, HMX<sup>17</sup>. The methyl parathion behavior is probably rare. Decomposition with melting can often be identified at fast program rates ( $\sim 10$  to  $20^\circ\text{C min}^{-1}$ ), by a small initial melt endotherm and a characteristic shape shown in Fig. 2. Both types of samples can be characterized by isothermal methods discussed later.

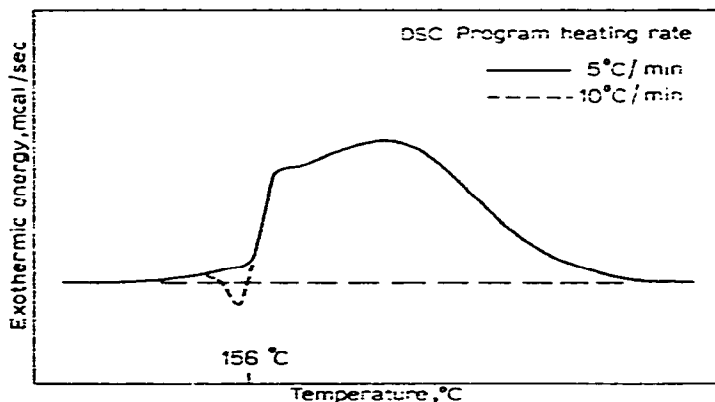


Fig. 2. Reaction exotherm of diazodinitrophenol.

The Arrhenius frequency factor  $Z$ , is most conveniently obtained from an equation derived by Murray and White<sup>18</sup> and others<sup>12,19</sup>. The first-order form used by Rogers and Smith<sup>20</sup> for obtaining  $Z$  is  $Z = (\beta E/RT_{\text{max}}^2) \exp(E/RT)$ . Since the same parameters ( $\beta$ ,  $T_{\text{max}}$ ) are used for  $E$  and  $Z$  calculations, no additional measurements need be made. A  $Z$  value is automatically computed for each heating rate, and agreement is generally within about  $\pm 2\%$  of the average. Reaction rates extrapolated from  $E$  and  $Z$  values by this method have been very satisfactory with respect to known materials properties. Although Ozawa's order-independent methods for frequency factor determinations are available<sup>11,12</sup>, we generally have not found it necessary to apply them.

### III. ISOTHERMAL METHODS

#### *Isothermal aging method*

Programmed kinetic methods are for the most part carried out under accelerated conditions at high temperatures. Rate data are then extrapolated down to more useful temperatures. However, there are a number of situations in which it is necessary to carry out the reaction at low temperatures. Such instances would be when vapor phase reactions, volatility or pressure problems, and high temperature degradations interfere with the analysis. Undesirable crystal-crystal and solid-liquid changes

which might change the reaction rate would also be avoided. A low temperature isothermal method which is useful in these cases has been described<sup>16</sup>. In practice, the technique consists of aging samples at an appropriate reaction temperature and then programming the residual fraction in a DSC or quantitative DTA. The decrease in reaction peak area per unit weight as a function of aging time yields a rate constant at that temperature. Repeating the procedure at more than one aging temperature enables calculation of the kinetic constants. Table 3 shows the data for the isothermal aging of camphor furoxan which undergoes decomposition with melting. The slope of the Arrhenius plot,  $\Delta \ln K/\Delta (1/T)$ , is equal to  $E/R$  and  $E = 20.1$  kcal/mol. Fig. 3 shows the decrease in area of the samples after aging at 105°C for 30, 60, and 90 min.

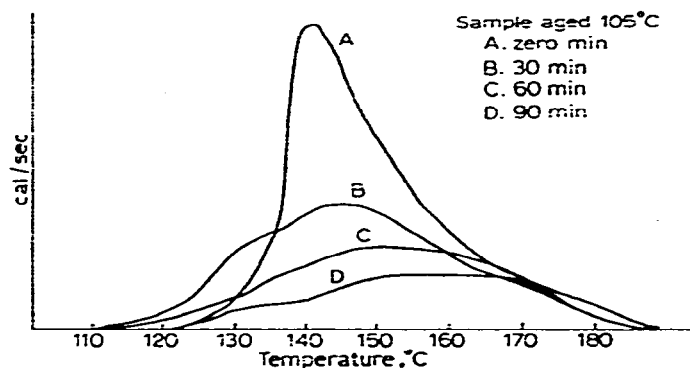


Fig. 3. Reaction exotherms of camphor furoxan after isothermal aging.

TABLE 3

ISOTHERMAL REACTION DATA FOR CAMPHOR FUROXAN PEAK AREA  
(in<sup>2</sup>/mg sample)

Temperature (°C)	Aging time (min)				-ln K
	0	30	60	90	
105	3.67	3.36	2.45	2.14	4.896
110	3.67	2.70	1.80	1.40	4.516
115	3.67	2.02	1.41	0.83	4.208

#### *Isothermal test for kinetic values*

In the evaluation of programmed methods for kinetic data a test was needed to check the activation energies and frequency factors obtained. A single run isothermal test was used as the simplest and most direct means of confirmation. Basically the test consists of predicting a convenient half-life for the reaction at some temperature, using the kinetic values in question. The sample is then aged for the predicted time at the proper temperature and then programmed in the DSC or DTA. If the reaction peak area per g of sample is indeed half the original within a few percent, the prediction was correct and the reaction kinetics verified. For example,

a commercial epoxy resin was examined by the " $\beta$  vs.  $T_{max}$ " method and found to have values for  $E$  of  $11.3 \text{ kcal mol}^{-1}$  and  $\log Z$  of  $4.605 \text{ min}^{-1}$ . The curve area under the running conditions was  $9.01 \text{ in}^2$ . Substituting the values for  $E$  and  $Z$  in the Arrhenius equation enabled calculation of rate constants  $K$ , for various temperatures. The first-order equation  $t_{1/2} = \ln(2)/K$  was then used to calculate a reaction half-life at  $100^\circ\text{C}$ . The sample was aged at  $100^\circ\text{C}$  for the predicted half-life time, cooled and programmed in the DSC. The reaction peak area then measured  $4.4 \text{ in}^2$  vs.  $9.0$  for the original material under the same conditions, which essentially confirmed the kinetic values. This method is used to support kinetic data on all unknown systems.

#### IV. COMBINATION OF TECHNIQUES TO ANALYZE A COMPLEX SYSTEM

Materials have been studied which undergo complex reactions and produce unresolved thermal peaks. An example is the polymerization thermogram of a thermosetting resin shown in Fig. 4. The kinetic values and heats of the individual reactions may be calculated by a combination of programmed and isothermal techniques. The approach is demonstrated for a hypothetical product having three reaction phases with properties as given in Table 4.

Both  $E$  and  $Z$  values for the first two reactions can be calculated from heating rate vs. peak temperature measurements previously described. Reaction rate constants can then be calculated for a range of temperatures by the Arrhenius equation. Because of the difference in activation energy, at some low temperature the rate for reaction 2

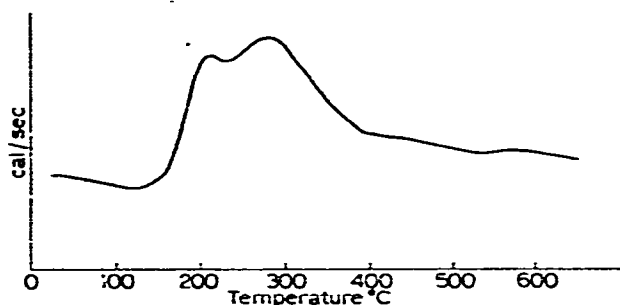


Fig. 4. Thermal curve for the complex polymerization reaction of a thermosetting resin.

TABLE 4  
REACTION PROPERTIES OF A HYPOTHETICAL MATERIAL

Reaction step	Activation energy $E$ ( $\text{kcal mol}^{-1}$ )	Frequency factor $\log Z$ ( $\text{min}^{-1}$ )	Reaction heat ( $\text{cal g}^{-1}$ )
Reaction 1	20.0	10.0	50
Reaction 2	25.0	11.0	65
Reaction 3	40.0	15.0	85

The above reactions would show a reaction curve as in Fig. 5.

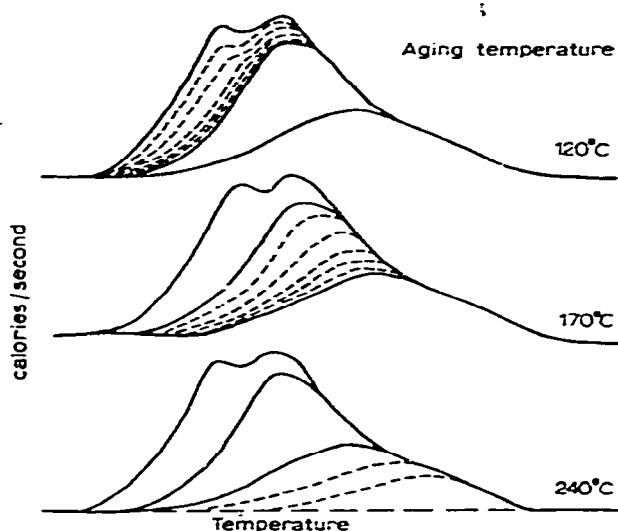


Fig. 5. Reaction exotherms for hypothetical compound after isothermal aging at indicated temperatures.

will be considerably lower than that for reaction 1. For example at 120°C, reaction 1 is 60× faster than reaction 2. The peak area due to reaction 1 can be estimated by isothermally aging equal weight samples at 120°C for various times, programming them in the DSC and superimposing the curves as in Fig. 5a. In this case the area decrease with time  $a_m$ , slows considerably after about 35 min due to the depletion of the first reactant. A rough estimate of the area due to reaction 1,  $A_1$ , can be made by inspection of the superimposed curves. At some appropriate higher temperature (e.g., 170°C) the procedure can be repeated for reaction 2 as in Fig. 5b. An estimate of the peak area for this reaction  $A_2$  can be made. However, this will be very approximate due to the undefined contributions of the first and third reactions.

More exact areas can be obtained by adjusting their estimated value until calculated residual fractions agree with those obtained from the reaction kinetics. Areas measured for reaction 1 are corrected for reaction 2 contribution by  $a_1 = a_m - A_2(1 - e^{-k_2 t})$  where  $a_1$  is the area decrease due to reaction 1,  $A_2$  is the total area estimate for reaction 2 and  $k_2$  is the calculated rate constant for reaction 2. Residual fractions  $(1 - C)$ , are obtained from an  $(A_1 - a_1)/A_1$  calculation for each aging time  $t$  ( $A_1$  is estimated). A plot of  $(1 - C)$  vs.  $t$  is made. A second plot of  $(1 - C)$  vs.  $t$  is made from reaction 1 kinetic values since  $k_1 = Z_1 e^{-E_1/RT}$  and  $(1 - C) = e^{-k_1 t}$ . The two plots are shown in Fig. 6. As shown, if  $A_1$  is estimated too high or too low, the resulting  $(1 - C)$  vs.  $t$  plot will curve away from the true line.  $A_1$  is adjusted until the best match is made. The dashed lines show the small effect of a  $\pm 20\%$  error in estimating  $A_2$  in the correction of the  $a_1$  data.

A value for  $A_2$  can be obtained in the same manner after subtracting out the  $A_1$  area from the data.  $A_3$  is obtained by difference. The kinetic values for the third peak may be determined by isothermal aging as in Fig. 5c, at two or more temperatures. A rate constant is obtained from  $(A_3 - a_3)/A_3 = e^{-k_3 t}$  where  $a_3$  is the area decrease for

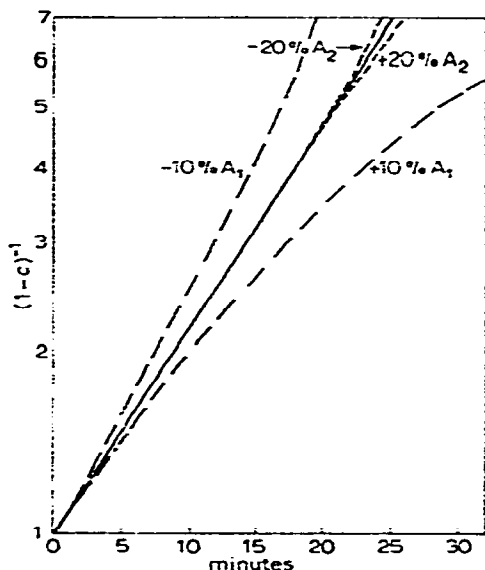


Fig. 6. Residual fraction  $(1 - C)$  vs. aging time for reaction 1.

aging time  $t$ . For two aging temperatures,  $E$  and  $Z$  can be calculated from  $E = R \ln(k_2/k_1)/(1/T_1 - 1/T_2)$  and  $Z = k/e^{-E/RT}$ . Aging temperatures of 240 and 270°C would have been convenient for the third reaction. Reaction heats are calculated from the determined area values.

#### V. CRITICAL HEATING CONDITIONS

A basic assumption in thermal kinetic analysis is that the sample temperature is essentially uniform. For very small samples the non-uniformity is fairly small and does not seriously distort the kinetic values. In larger samples, however, the self-insulating properties of the sample become significant and, for large heats of reaction, the center temperature can reach runaway conditions. Critical thicknesses of samples as a function of their kinetic values and heats of reaction can be shown by use of the Frank-Kamenetskii relation<sup>21</sup>. In terms of the critical sample thickness, the equation is:

$$D = 2 \left( \frac{\delta \lambda R T^2}{E C_0 Q Z e^{-X}} \right)^{1/2}$$

where  $D$  = critical thickness (cm);  $\delta$  = critical constant depending on geometric configuration of sample (0.88 for slab);  $R$  = gas constant ( $1.987 \text{ cal mol}^{-1} \text{ deg}^{-1}$ );  $T$  = temperature (K);  $E$  = activation energy ( $\text{cal mol}^{-1}$ );  $Q$  = heat of reaction ( $\text{cal g}^{-1}$ );  $C_0$  = density (concentration) of reactant ( $\text{g ml}^{-1}$ );  $Z$  = Arrhenius frequency factor ( $\text{sec}^{-1}$ );  $X = E/RT$ ;  $\lambda$  = thermal conductivity ( $\text{cal deg}^{-1} \text{ sec}^{-1} \text{ cm}^{-1}$ ).

#### *Isothermal methods*

When samples are reacted isothermally, the above equation applies as written. Calculations for Fig. 7 are made for liquid samples where  $\lambda = 3 \times 10^{-4} \text{ cal}$



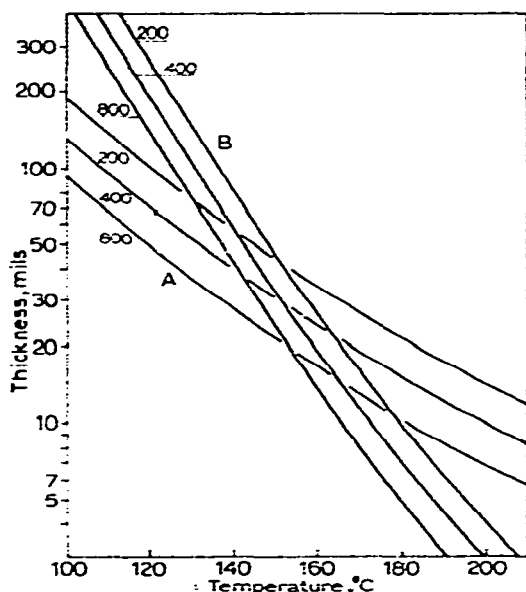


Fig. 7. Critical thickness vs. isothermal temperature conditions for a liquid sample with thermal conductivity of  $3 \times 10^{-4}$  cal deg $^{-1}$  sec $^{-1}$  cm $^{-1}$ . Heats of reaction are 200, 400 and 800 cal g $^{-1}$ . Kinetics of: (A)  $E = 20$  kcal mol $^{-1}$ ,  $Z = 1 \times 10^{10}$  min $^{-1}$ ; and (B)  $E = 40$  kcal mol $^{-1}$ ,  $Z = 1 \times 10^{20}$  min $^{-1}$ .

deg $^{-1}$  sec $^{-1}$  cm $^{-1}$ ,  $C_0 = 1$  g ml $^{-1}$  and slab or disk shaped as in an aluminum pan container. The figure shows critical temperature/thickness parameters for such samples, with  $E = 20$  and 40 kcal mol $^{-1}$  and  $\log Z = 10.0$  and 20.0 min $^{-1}$ , respectively. These samples programmed at 10°C min $^{-1}$  would have a peak maximum at about 165°C. The curves show that these samples even with high heats of reaction are fairly "safe" below 10°C of the peak temperature if their liquid depth is less than about 20 mils. Should the liquid collect in the round corners of the sample sample pan, the effective thickness increases and the critical temperature becomes lower for a given amount of sample. The Frank-Kamenetskii model assumes perfect heat transfer at the sample/container boundary. If the container lid is not in effective contact with the liquid sample—as the case with a "ring" shaped sample or in the commercial DuPont or Perkin-Elmer sealed capsule pans, the effective thermal resistance is increased and the critical temperature is again lower. For powdered samples, the medium is discontinuous and heat transfer proceeds at point contacts and through the gaseous medium. Assuming a decrease in sample thermal conductivity of about 1/9 for a powdered sample, the critical thickness reduces to a third of that shown in Fig. 7 for the same temperature. Thus, for the more energetic materials, the sample layer should be under 10 mils for temperatures within 20°C of the programmed peak.

#### *Programmed case*

To calculate critical program rates as a function of thickness requires modifi-

cation of the Frank-Kamenetskii equation to a first-order form. For programming, the  $C_0$  term is a function of the residual fraction. At any time during the reaction, the critical thickness  $D$  is:

$$D = 2 \left( \frac{\delta \lambda R T^2}{EQZ e^{-x}} \right)^{1/2} / (C_0 [1 - C])^{1/2}$$

The change in the residual fraction with program rate is given by the first-order expression  $(1 - C) = e^{(-AE/R\beta)\rho(x)} = e^{-\theta}$ . Substituting gives

$$D = 2 \left( \frac{\delta \lambda R T^2}{EQC_0 Z e^{-x} e^{-\theta}} \right)^{1/2}$$

Solution of the equation for various heating rates ( $\beta$ ) and temperatures yields the data for the plot in Fig. 8. The boundary line drawn tangent to the temperature curves represents the peak maxima for the various heating rates. The tangent also

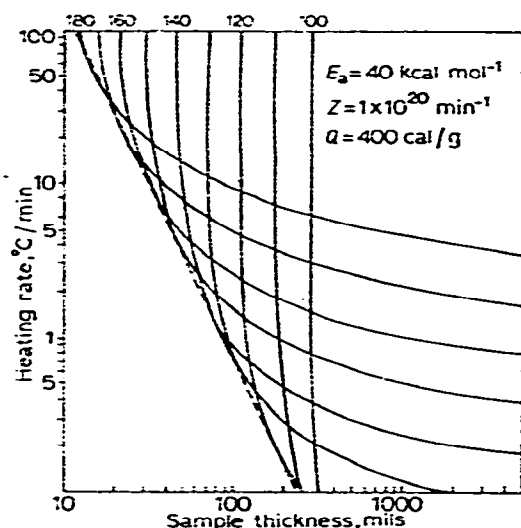


Fig. 8. Boundary conditions for critical program rate and sample thickness.

defines the critical heating rate/sample thickness parameters for programming through the reaction peak without causing a runaway reaction. Fig. 9 shows the critical boundaries for a liquid sample with the kinetics and reaction heats described earlier. Fig. 10 shows the relationships for a powdered sample with an effective thermal conductivity of about  $3 \times 10^{-5} \text{ cal deg}^{-1} \text{ sec}^{-1} \text{ cm}^{-1}$ . Here, the limiting sample size for a material of  $E = 40$ ,  $Z = 1 \times 10^{20}$ , and  $Q$  a modest  $200 \text{ cal g}^{-1}$ , would need to be under 11 mils for a heating rate of  $10^\circ \text{C min}^{-1}$ . For powdered samples of hard refractory-like materials, the thermal conductivity approaches that of the surrounding gas and the critical thickness decreases correspondingly.

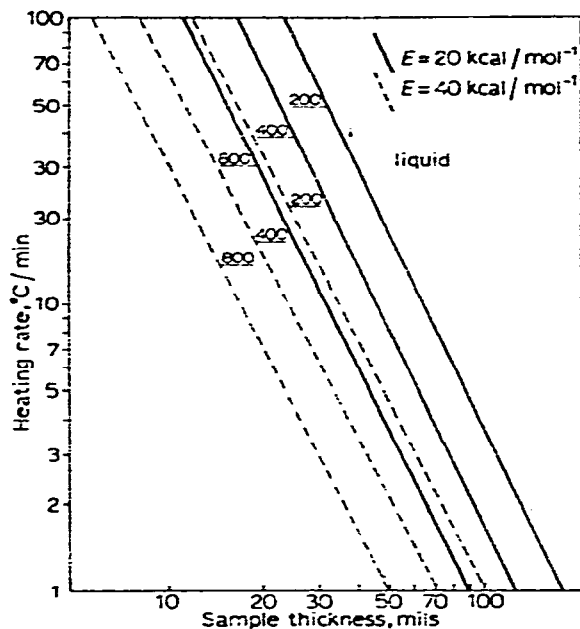


Fig. 9. Critical sample thickness vs. program rate for liquid sample with thermal conductivity of  $3 \times 10^{-4}$  cal deg $^{-1}$  sec $^{-1}$  cm $^{-1}$  and heats of reaction of 200, 400 and 800 cal g $^{-1}$ . —, for  $E = 20$  kcal mol $^{-1}$ ,  $Z = 1 \times 10^{10}$  min $^{-1}$ ; --, for  $E = 40$  kcal mol $^{-1}$ ,  $Z = 1 \times 10^{20}$  min $^{-1}$ .

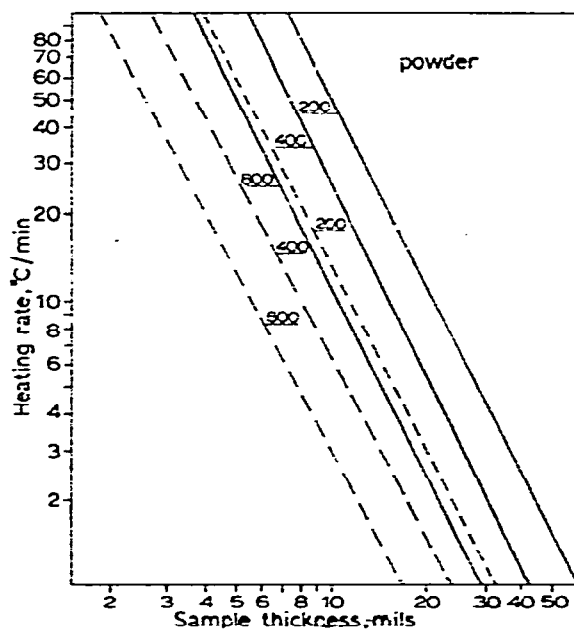


Fig. 10. Critical sample thickness vs. program rate for powdered sample with thermal conductivity of  $3.3 \times 10^{-5}$  cal deg $^{-1}$  sec $^{-1}$  cm $^{-1}$  and heats of reaction of 200, 400 and 800 cal g $^{-1}$ . —, for  $E = 20$  kcal mol $^{-1}$ ,  $Z = 1 \times 10^{10}$  min $^{-1}$ ; --, for  $E = 40$  kcal mol $^{-1}$ ,  $Z = 1 \times 10^{20}$  min $^{-1}$ .

*Other methods*

Two isothermal methods described by R. N. Rogers appear to be worthwhile additions to the thermal-kinetic arsenal. By observing the behavior of the after peak part of the reaction curve, Rogers was able to rapidly obtain kinetic data on samples that decompose with melting<sup>17</sup> and vapor phase reactions occurring in relatively volatile samples<sup>22</sup>. Since these techniques are carried out at relatively high reaction rates, samples should be small, especially for highly energetic materials, to avoid runaway conditions.

## SUMMARY

While heat generation measurements allow convenient and rapid estimates of kinetic values in some cases, incorrect results often occur and the technique should be used with caution. Good results have been obtained on a broad variety of reactions with heating rate-vs.-peak temperature methods. Isothermal measurements are effective when interfering events preclude high temperature, programmed test methods. A simple, isothermal half-life test is recommended as a check on the validity of kinetic values derived from programmed techniques. A combination of isothermal and programmed methods may unravel complex reactions and unresolved peaks. Calculations show that runaway reactions are possible with DSC and DTA size samples.

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