

KINETIC PARAMETERS FROM MAXIMUM REACTION RATE IN DYNAMIC THERMAL ANALYSIS

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In this paper the Peak properties of the dynamic thermograms in DSC, DTA and DTG analysis have been examined. It has been proved that the fraction decomposed at the peak maxima does not depend upon the heating rate and that the peak temperature strongly depends upon the heating rate. An equation for the calculation of activation energy has been derived.

Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) or Differential Thermogravity (DTG) thermograms are rather difficult to analyse, from the view point to get kinetic parameters, as compared to isothermal thermogravimetry (TG) thermograms. The complications arise due to the fact that temperature and the extent of reaction both vary simultaneously with respect to time. Recently, Kishore *et. al.* have shown that DSC dynamic thermograms can be satisfactorily analysed to get kinetic parameters by a method which is free from any kinetic assumptions^{1,2}. The purpose of present paper is to examine in detail the properties of the DTA, DSC or DTG peaks and to find out usefulness of them in deriving simple procedures for obtaining kinetic parameters.

NOMENCLATURE

a	=	fraction of the reactant remaining at any time t
a_m	=	fraction of the reactant remaining at the maximum rate (i.e. at the peak)
$f(a)$	=	arbitrary function of the reactant concentration
$f'(a)$	=	$\frac{df(a)}{da}$
$f''(a)$	=	$\frac{d^2f(a)}{da^2}$
$\frac{da}{dt}$	=	rate of the reaction
T	=	absolute temperature
T_m	=	temperature ($^{\circ}\text{K}$) at the maximum rate (i.e. peak temperature)
T_0	=	temperature ($^{\circ}\text{K}$) at which DSC, DTA, DTG thermograms start appearing
k_k	=	rate constant which depends upon the temperature
k'_T	=	$\frac{dk_T}{dT}$
k''_T	=	$\frac{d^2k_T}{dT^2}$
n	=	order of reaction
E	=	activation energy (kcal mole ⁻¹)
ϕ	=	heating rate $^{\circ}\text{C min}^{-1}$
A	=	frequency factor
$\lambda, \lambda', \lambda''$	=	constants

RESULTS AND DISCUSSION

In order to examine the properties of DSC, DTA and TG (dynamic) thermogram maxima, let us start with the following general kinetic law.

$$-\frac{d\alpha}{dt} = k_T f(\alpha) \tag{1}$$

According to Arrhenius equation

$$k_T = A_{exp} (-E/RT) \tag{2}$$

Since the temperature in a dynamic run varies linearly, we get

$$T = T_0 + \phi t$$

or

$$\frac{dT}{dt} = \phi \tag{3}$$

and also

$$\frac{d\alpha}{dt} = \frac{d\alpha}{dT} \cdot \phi \tag{4}$$

Combining eqns. (1) and (4), we get

$$-\phi \frac{d\alpha}{dT} = k_T f(\alpha) \tag{5}$$

The differential form of eqn. (5) would be

$$\text{or } -\phi \frac{d^2(\alpha)}{dT^2} = \frac{dk_T}{dT} f(\alpha) + \frac{df(\alpha)}{d\alpha} k_T \tag{6}$$

Put

and

$$\frac{dk_T}{dT} = k'_T, \quad \frac{df(\alpha)}{d\alpha} = f'(\alpha) \tag{7}$$

$$\frac{df(\alpha)}{d\alpha} = f'(\alpha), \quad \frac{d^2 f(\alpha)}{d\alpha^2} = f''(\alpha)$$

Equation (6) can now be written as

$$-\phi^2 \frac{d^2 \alpha}{dT^2} = f(\alpha) \left[\phi k'_T - f'(\alpha) k^2_T \right] \tag{8}$$

Equation (8) will hold for the thermogram maxima when the condition for maximum rate is applied i.e.

$$\frac{d}{dT} \left(\frac{d\alpha}{dt} \right) = 0 \text{ or } \frac{d}{dt} \left(\frac{d\alpha}{dT} \right) = 0 \tag{9}$$

Using eqn. (9) and (8), we get

$$\phi k'_T = f'(\alpha) k^2_T$$

or

$$\phi = \frac{f'(\alpha) k^2_T}{k'_T} \tag{10}$$

For getting a similar equation, free from heating rate ϕ , one could proceed with Equation (5) as follows

$$-\phi \int_1^\alpha \frac{d\alpha}{f(\alpha)} = k_T \int_{T_0}^T dT \tag{11}$$

The integral limits are put by considering that initially $\alpha = 1$ at $T = T_0$. Substituting the condition for maxima from equ. (10) in eqn. (11)

$$f'(\alpha) \int_{\alpha}^1 \frac{d\alpha}{f(\alpha)} = \frac{k'T}{k^2T'} T \int_{T_0}^T dT \quad (12)$$

After getting a general equation applicable to the peak of the thermogram, let us now examine the peak properties as follows.

- (I) whether or not T_m depends upon ϕ
- (II) whether or not α_m depends upon ϕ
- (III) whether the knowledge of T_m at various ϕ could be used to calculate E .

In order to test the condition whether T_m depends on ϕ or is independent, the requirement would be that T_0 should not change with ϕ .

Thus

$$f'(\alpha) \int_{\alpha}^1 \frac{d\alpha}{f(\alpha)} = k'T k_T^{-2} \int_{T_0}^T k_T dT = \lambda \quad (13)$$

For the first order reaction ($n = 1$): $f(\alpha) = \alpha$ and therefore eqn. (13) becomes — (14)
 $\log \alpha = k$

and for the n^{th} order reaction, eqn. (13) becomes

$$\frac{n}{n-1} (1 - \alpha^n - 1) = \lambda \quad (15)$$

From eqns. (14) and (15) it is evident that α should be constant during the course of the reaction, if T_m is independent of ϕ , which is practically not possible. It may therefore be concluded that no kinetic law can be obtained from peak properties considering that T_m does not vary with ϕ which suggests that T_m is strongly dependent upon ϕ .

Let us now see if α_m depends upon ϕ or not. The requirement for α_m to depend on ϕ is that

$$\frac{df(\alpha)}{d\alpha} = f'(\alpha) = \lambda' \phi \quad (16)$$

On combining eqns. (10) and (16)

$$\frac{k'T}{k^2T'} \equiv \lambda'$$

or

$$\int \frac{dk_T}{k^2T'} = \lambda' \int dT + \lambda'' \quad (17)$$

or

$$k_T = (C - bT) \quad (18)$$

The condition required for the above equation is just not possible and therefore it suggests that α_m is independent of ϕ , and that it would depend upon the nature of the kinetic law applicable to the process. It is very clearly shown in Table 1 that α_m values remain constant at the peak temperature even when heating rate is varied.

TABLE 1

PEAK TEMPERATURE OF THE LOW TEMPERATURE EXOTHERM OF AMMONIUM PERCHLORATE AT VARIOUS HEATING RATES

Heating Rate (ϕ) ($^{\circ}\text{C min}^{-1}$)	Peak temperature ($^{\circ}\text{K}$)	α_m value at the peak temperature
2	534.0	0.46
4	544.5	0.48
8	556.0	0.45
16	567.5	0.47
32	584.5	0.49
64	601.0	0.45

Let us now obtain the kinetic law from the dependence of T_m on ϕ . Using eqn. (10) and differentiating it with respect to T_m one can obtain the following equation for first order reaction.

$$\frac{d \ln \phi}{dT_m} = \frac{E}{R} T_m^{-2} \left(1 + 2T_m \frac{R}{E} \right) \quad (19)$$

On R.H.S. of eqn. (19) $\frac{2T_m R}{E}$ is much less than unity, therefore eqn. (19) can be written as

$$\frac{1}{T_m^{-2}} \frac{d \ln \phi}{dT_m} \simeq E/R$$

or

$$\frac{d \ln \phi}{dT_m^{-1}} \simeq E/R \quad (20)$$

Equation (20) suggests that the plot of $\ln \phi$ versus $1/T_m$ should yield a straight line which should pass through the origin, and the slope should give the value of E .

Equation (19) on integration yields eqn. (21) which is free from approximation arriving at (20).

$$\phi = B T_m^2 \exp \left(- \frac{E}{RT_m} \right) \quad (21)$$

Equation (21) is celebrated equation by Kissinger³. The E values calculated for various decomposition reaction from eqn. (20) and (21) are given in Table 2 which are quite comparable to each other.

TABLE 2
ACTIVATION-ENERGY (E) VALUES OF VARIOUS COMPOUNDS IN K CAL MOLE⁻¹

Compounds	E (K cal mole ⁻¹) by equation (20)	E (K cal mole ⁻¹) by equation (21)
RDX (ref. 2)	38.0	34.0
Phenylalanine (ref. 4)		
Ist Endotherm	56.6	53.0
IInd Endotherm	51.0	48.0
IIIrd Endotherm	48.0	42.0
Phase-transition endotherm of ammonium per-chlorate (ref. 5)	108.0	102.0
Ammonium perchlorate high-temperature exotherm (ref. 1)	72.0	70.0

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