

Estimation of Kinetic Parameters from Thermogravimetric Traces

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Synopsis

A novel and comparatively simple procedure is described for the estimation of values of kinetic parameters from thermogravimetric traces. The expressions derived are assessed for their facility and reliability by utilizing data from theoretical and experimental thermograms. Calculated values of parameters agree well with assumed or reported values.

INTRODUCTION

It is desirable in polymer degradation studies to be able to estimate values of kinetic parameters, such as overall activation energy E and reaction order n , from thermogravimetric traces. Several recent reports have appeared which describe relatively simple methods for determining one of the above parameters; subsequently, the other parameter may be obtained by means of another procedure.^{1,2} Methods proposed for the simultaneous estimation of E and n often involve tedious expressions and simplifying assumptions and may suffer from one or more disadvantages.³⁻⁶ The purpose of this paper is to present a previously unreported procedure which allows a comparatively simple determination of E and n by essentially the same method.

THEORY

If, as is generally assumed, the Arrhenius equation is valid in pyrolyses, one may write,

$$R_T = [A/(RH)] \exp \{-E/RT\} W^n \quad (1)$$

where R_T is the slope of the primary thermogram, A is the frequency factor, (RH) is the rate of heating (= constant), W is the weight fraction of material remaining, and R and T are the gas constant and absolute temperature, respectively. When a weight fraction of inactive material, W_R , remains after a pyrolysis, W in eq. (1) is replaced by W_c , where, $W_c = W - W_R$.

Upon expanding eq. (1) in an asymptotic series^{7,8} and assuming that $(2RT/E) \ll 1$ (usually true in polymer pyrolyses), eq. (1) becomes

$$-\int_{W_0}^W dW/W^n = [A/(RH)] (RT^2/E) \exp \{-E/RT\} \quad (2)$$

Combining eqs. (1) and (2), eliminating the term $[A/(RH)]$, and generalizing by allowing for an inactive residue, one obtains,

$$E/R = S/[W_c \ln (W_{0,c}/W_c)] \quad \text{For } n = 1 \quad (3)$$

and

$$E/R = S(1 - n)/W_c^n (W_{0,c}^{(1-n)} - W_c^{(1-n)}) \quad \text{For } n \neq 1 \quad (4)$$

where

$$S = dW_c/d(1/T)$$

$$W_{0,c} = W_0 - W_R$$

From eqs. (3) and (4), it may be readily shown that,

$$S_1/S_2 = (W_{1,c}/W_{2,c}) \log (W_{0,c}/W_{1,c}) / \log (W_{0,c}/W_{2,c}) \quad \text{For } n = 1 \quad (5)$$

and

$$S_1/S_2 = (W_{1,c}/W_{2,c})^n [1 - (W_{1,c}/W_{0,c})^{(1-n)}] / [1 - (W_{2,c}/W_{0,c})^{(1-n)}] \quad \text{For } n \neq 1 \quad (6)$$

TESTING OF THE THEORETICAL EQUATIONS

Utilization of Theoretical Thermograms

Theoretical plots of W or W_c versus $1/T$ were constructed, utilizing eq. (2), in order initially to assess the facility and reliability of eqs. (3-6). Some of the plots are shown in Figure 1. In all of the plots, the value of (RH) was held constant and arbitrarily assumed to be unity, whereas, the assumed values of A , n , and E were varied (see Table I). Various kinetic parameters obtained from the curves, by utilizing eqs. (3-6), were compared with the assumed values.

Estimation of n . Prior to determining the overall activation energy of a pyrolysis by the procedure employed in this paper, it is necessary to estimate the reaction order n . From eqs. (5) and (6), it can be seen that for a particular, arbitrarily selected ratio $W_{1,c}/W_{2,c}$ and value of W_R , the corresponding ratio, S_1/S_2 , may be calculated for various values of n . Such calculated values were used to construct the theoretical curves depicted in Figure 2. In this figure, the various values of W_1/W_2 or $W_{1,c}/W_{2,c}$ and of W_R are given, from which the ratio S_1/S_2 was calculated. The curves in Figure 2 were then utilized to estimate values of n for the various theoretical (and experimental) thermograms. These values are listed in Table I and agree well with the assumed values of n .

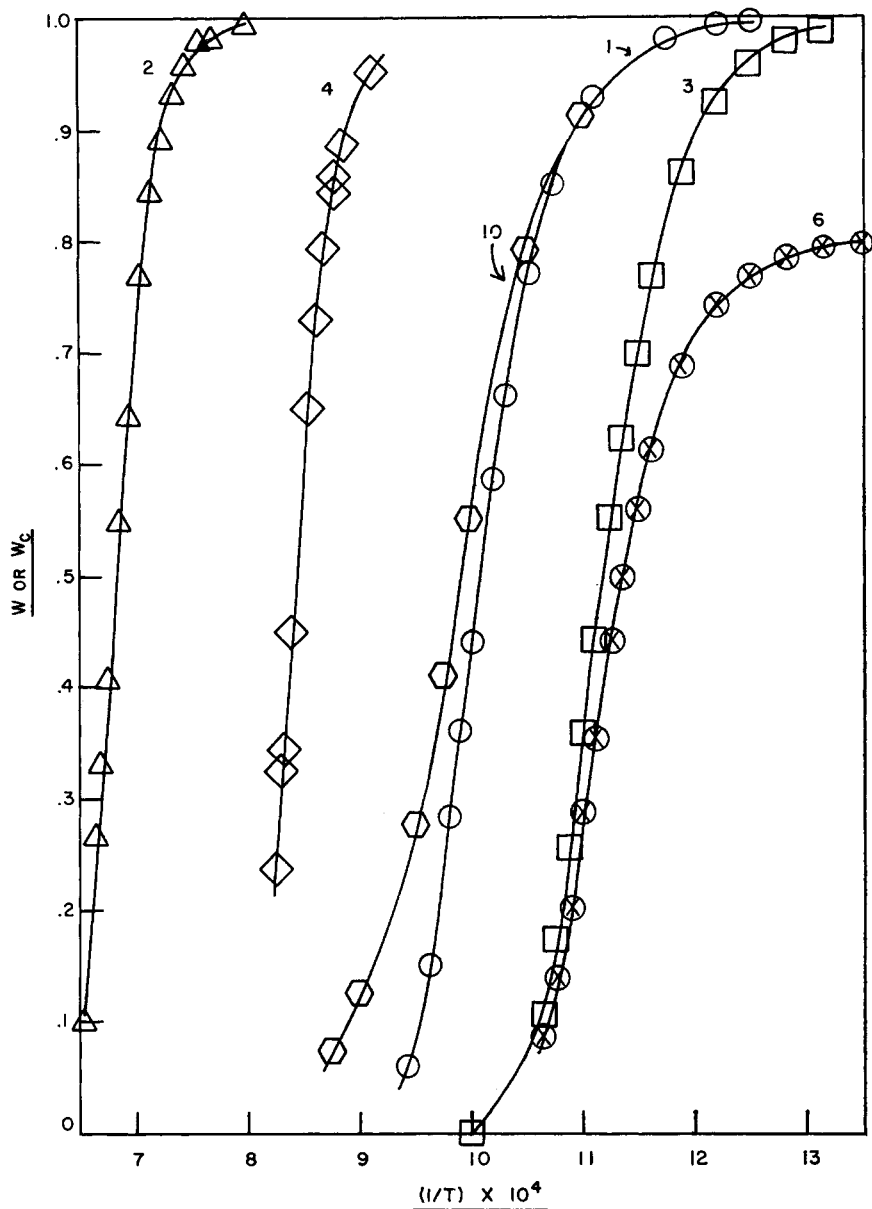


Fig. 1. Weight fraction remaining W vs. reciprocal temperature $1/T$ for various values of E , n , and A .

It may be of interest to note here, that eqs. (5) and (6) may be employed to obtain a simple expression involving n . Thus, at values of W of 0.8 and 0.1, values of S_1/S_2 (designated as $S_{0.8}/S_{0.1}$) were calculated for various values of n , letting $W_R = 0$. The following values of n and $S_{0.8}/S_{0.1}$ respectively, were obtained: 0, 0.22; $1/4$, 0.31; $1/2$, 0.43; 1, 0.78; $1\frac{1}{2}$,

TABLE I
Evaluation of Kinetic Parameters from Theoretical and Experimental Thermograms

Theoretical curve no. or polymer	Weight fraction of residue W_R	Frequency factor A		Reaction order n		Activation energy E , kcal./mole	
		Assumed or reptsd.	Calcd.	Assumed or reptsd.	Calcd.	Assumed or reptsd.	Calcd.
1	0	9.1×10^6	13×10^6	1	0.90	40	41 ± 1
2	0	1×10^{10}	1.3×10^{10}	1	0.95	80	81 ± 1
3	0	1×10^8	1.7×10^8	1	1.15	40	41 ± 1
4	0	1×10^{13}		1		80	82 ± 1
5	0.10	1×10^8	0.5×10	1	0.94	40	43 ± 1
6	0.20	1×10^8		1	1.08	40	45 ± 1
7	0	9.1×10^6	0.305	0	-0.1	40	42 ± 3
8	0	9.1×10^6	0.395	$1/2$	0.44	40	42 ± 1
9	0	9.1×10^6	0.563	$1 1/2$	1.42	40	43
10	0	9.1×10^6	0.642	2	1.88	40	43 ± 1
Teflon ^a	0		0.50	1.02 ± 0.07	0.97 ± 0.13	70 ± 5	75 ± 1
Polyethylene ^b ≈ 0			0.48	ca. 1	0.95 ± 0.05	61-67	62 ± 1

^a Data of Fuoss et al.⁹ and Anderson.¹⁰

^b Data of Anderson and Freeman.³

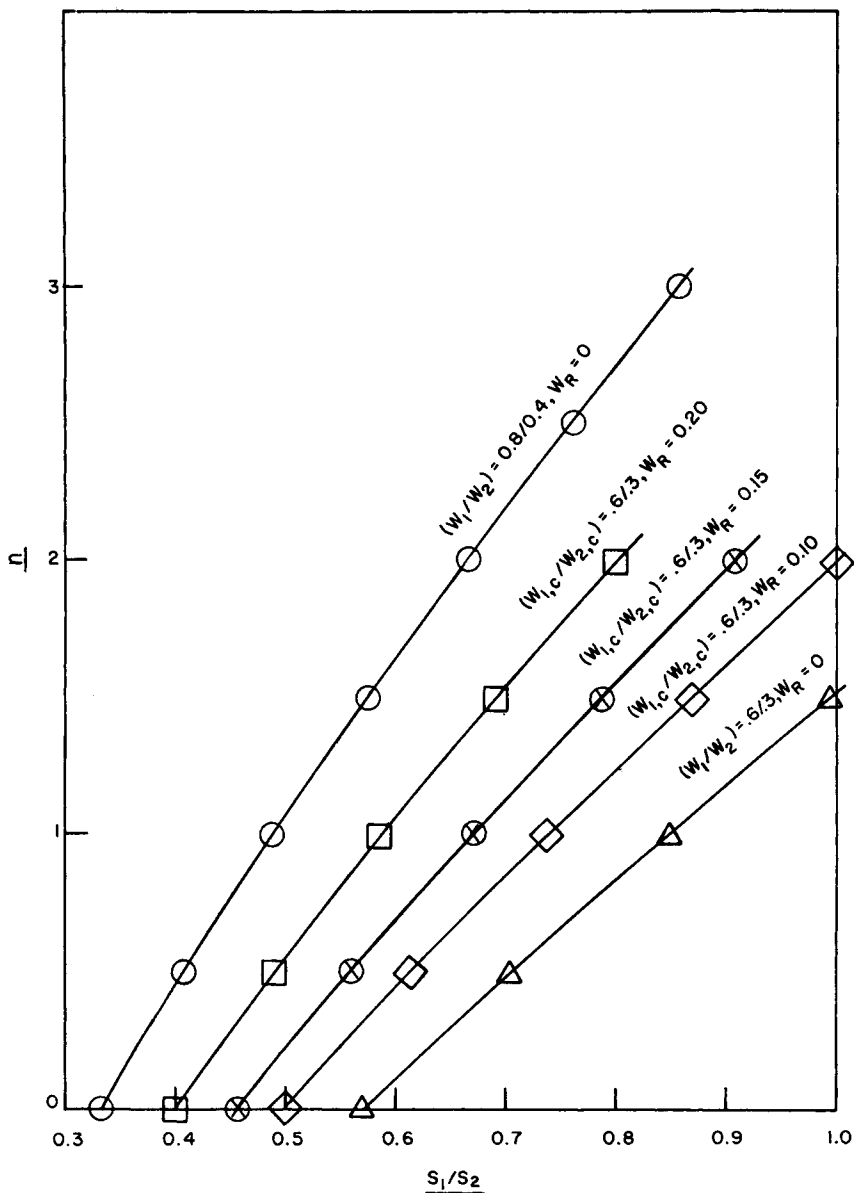


Fig. 2. Theoretical plots of reaction order n vs. S_1/S_2 for various values of W_1/W_2 or $W_{1,c}/W_{2,c}$ and W_R .

1.23; 2, 1.77. From these values, the following approximate expression may be written for values of n from about $1/4$ to 2:

$$S_{0.8}/S_{0.1} \approx D(T_{0.8}/T_{0.1})^2 \approx 0.8n \quad (7)$$

where

$$D \equiv (dW/dT)_{0.8}/(dW/dT)_{0.1}$$

Since the value of $T_{0.1}/T_{0.8}$ is generally a little larger than unity, eq. (7) may be written as,

$$D \approx n \quad (8)$$

Equation (8) may be used when it is desired to obtain a rapid and approximate estimation of n from a primary thermogram which possesses a value of W_R of zero.

Estimation of E . After the value of n has been determined, as described above, the value of n may be substituted into eqs. (3) and (4) to obtain the value of the overall activation energy. Values of E were obtained from data obtained from the theoretical curves (see Fig. 1), and were found to agree well with assumed values (cf. Table I). From values of $S_{0.8}$, $S_{0.6}$, $S_{0.4}$, and $S_{0.3}$, which were used in the evaluation of n , an average value of E was estimated. After values of E and n have been estimated, the value of the frequency factor A may be ascertained subsequently by means of eq. (1).

Estimation of A . From eq. (1), it may be shown that

$$\log A = \log \{ [S(RH)/W^n] (1/T)^2 \} + E/2.3RT \quad (9)$$

Equation (9) may be utilized to calculate values of A . Thus, several calculated values of A are given in Table I along with assumed values.

Utilization of Experimental Thermograms

Values of kinetic parameters were determined from experimental thermograms as described above. Experimental thermograms of Teflon⁹ and polyethylene³ were examined. Calculated and reported parameter values are listed in Table I, and were found to agree to about the same extent as in the case of calculated and assumed parameter values. It is interesting to note that for Teflon, the value of D [cf. eq. (7)] was found to be approximately 0.95.

Appreciation is expressed to D. W. Levi for his review and helpful criticisms of the manuscript.

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Résumé

Un méthode nouvelle et comparativement simple est décrite pour estimer les valeurs des paramètres cinétiques à partir des résultats thermogravimétriques. Les expressions dérivées à partir des résultats des thermogrammes théoriques et expérimentaux s'imposent par leur facilité et leur cohérence. Les valeurs calculées pour les paramètres s'accordent avec les valeurs prévues et rapportées.

Zusammenfassung

Ein neuartiges und verhältnismässig einfaches Verfahren zur Bestimmung der Werte kinetischer Parameter aus thermogravimetrischen Diagrammen wird beschrieben. Die abgeleiteten Ausdrücke werden in Bezug auf ihre Handlichkeit und ihre Verlässlichkeit durch Verwendung von Daten aus theoretischen und experimentellen Thermogrammen überprüft. Die berechneten Werte der Parameter stimmen gut mit den theoretischen und experimentellen Werten überein.

Received March 5, 1965