

A QUICK, DIRECT METHOD FOR THE DETERMINATION OF ACTIVATION ENERGY FROM THERMOGRAVIMETRIC DATA

The determination of kinetic parameters such as energy of activation from thermogravimetric data is receiving considerable attention. Coats and Redfern (1) have reviewed several of these methods briefly. An extensive critical review of methods will be published soon (2).

The determination of an activation energy parameter from a single integral TGA curve (weight loss vs. T) has been found to involve cumbersome curve-fitting techniques or the determination of a value for an often spurious order parameter, n . In cases where a simple order is not followed, such a procedure may lead to disastrous results (2,3).

Although several "differential" methods, based on rate of weight loss vs. temperature data at several heating rates, are able to circumvent these difficulties (2,4), they suffer from a chronic weakness—the magnification of experimental scatter, which renders their application to actual experimental data difficult if not impossible.

In this letter, we present a quick, simple method for determining activation energies directly from weight loss vs. temperature data at several heating rates.

Without any loss of general applicability, we define the degree of conversion, C , such that $1 - C$, the residual fraction, equals the weight of material loss divided by the total weight loss as T or $t \rightarrow \infty$. The thermogravimetric rate is given by eq. (1)

$$dC/dT = (A/\beta) f(C) e^{-E/RT} \quad (1)$$

where T = absolute temperature, β = constant heating rate, A = pre-exponential factor of the Arrhenius equation, E = energy of activation, R = the gas constant, and $f(C)$ = a function of degree of conversion (weight loss).

Assume that A , $f(C)$, and E are independent of T and that A and E are independent of C (it will be shown that the method, itself, permits a test of these assumptions). Then, one may separate the variables and integrate to obtain (6),

$$\begin{aligned} F(C) &= \int_0^C dC/f(C) = (A/\beta) \int_{T_0}^T e^{-E/RT} dT \\ &= (AE/\beta R) \{e^{-E/RT}/(E/RT) + \int_{-\infty}^{-E/RT} (e^x/x) dx\} \\ &= (AE/\beta R) p(E/RT) \quad x = E/RT \end{aligned} \quad (2)$$

TABLE I

Logarithm of Exponential Temperature Integral Function
and Its Differences for Various E/RT

E/RT	$\log p(E/RT)$	$\Delta \log p(E/RT)$
7	4.8301	—
8	5.3699	0.5398
9	5.8980	0.5281
10 ^a	6.4167	0.5187
20 ^a	11.3277	0.4770
30 ^a	16.0104	0.4629
40 ^a	20.5967	0.4558
50 ^a	25.1295	0.4515
51	25.5806	0.4511
52	26.0314	0.4508
53	26.4820	0.4506
54	26.9323	0.4503
55	27.3823	0.4500
56	27.8319	0.4496
57	28.2814	0.4495
58	28.7305	0.4491
59	29.1794	0.4489
60	29.6281	0.4487

^a For detailed values in the range $10 \leq E/RT \leq 50$, see reference (6).

since at the lower limit, T_0 , the integral is negligible for usual polymer degradation cases. Equation (2) expressed in logarithmic form is

$$\log F(C) = \log(AE/R) - \log \beta + \log p(E/RT) \quad (3)$$

Doyle (5) has found that for $E/RT \geq 20$, $\log p(E/RT)$ may be closely approximated by eq. (4),

$$\log p(E/RT_i) \cong -2.315 - 0.457 E/RT_i \quad (4)$$

Therefore, eq. (3) becomes

$$\log F(C) \cong \log AE/R - \log \beta - 2.315 - 0.457 E/RT \quad (5)$$

"Differentiating" eq. (5) at constant degree of conversion results in

$$d \log \beta / d 1/T \cong (0.457/R) E$$

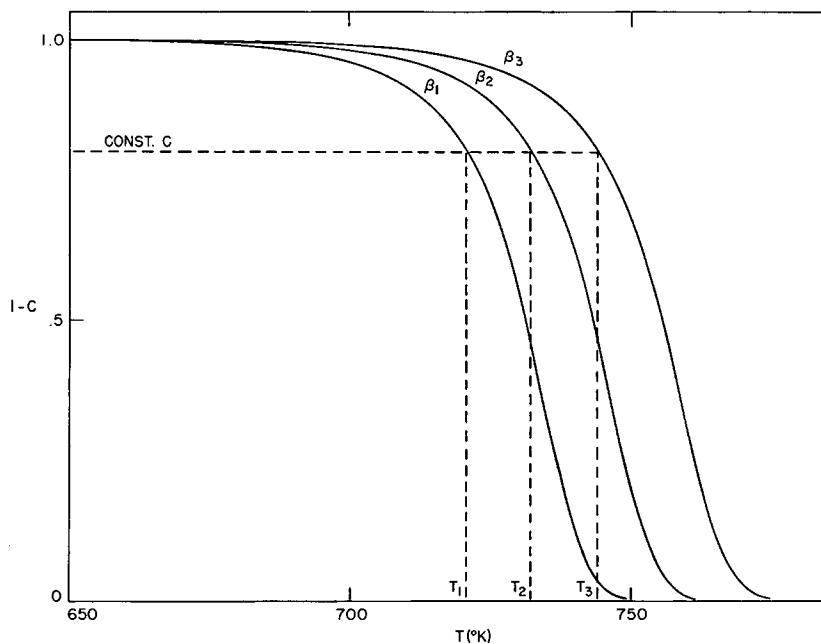


Fig. 1. Residual fraction vs. temperature for three rates of heating: $\beta_1 = 0.05$ °C./sec.; $\beta_2 = 0.10$ °C./sec.; $\beta_3 = 0.20$ °C./sec. Case B [ref. (3)]: $E = 60,000$ cal./mole; $A/\beta_2 = 10^{16}/^\circ\text{C}$.

or, for $R = 1.987$ cal./mole-°K.,

$$E \cong -4.35 \, d \log \beta / d \, 1/T \quad (6)$$

In actuality, β has discrete values, $\beta_1, \beta_2 \dots$ rather than continuous ones; therefore, Δ 's rather than derivatives would be more precise mathematically, but the results would be identical.

Table I is a condensed table of $\log p(E/RT)$ values for various E/RT . It extends the range of Doyle's data (6) from $10 \leq E/RT \leq 50$ to $7 \leq E/RT \leq 60$. For $20 \leq E/RT \leq 60$, the slope whose average value of 0.457 is used in eq. (4) varies about $\pm 3\%$.

Therefore, from weight loss vs. temperature thermograms at several heating rates, one may determine the corresponding temperatures at a constant weight loss. This is illustrated in Figure 1 for theoretical curves for a case often found in polymer decomposition where the isothermal rate goes through a maximum value (3). Then, from the slope of a plot of $\log \beta$ vs. $1/T$, the activation energy may be calculated by eq. (6). This procedure may be repeated at other values of $1 - C$, thus testing the constancy of E with respect to C and T . This is illustrated in

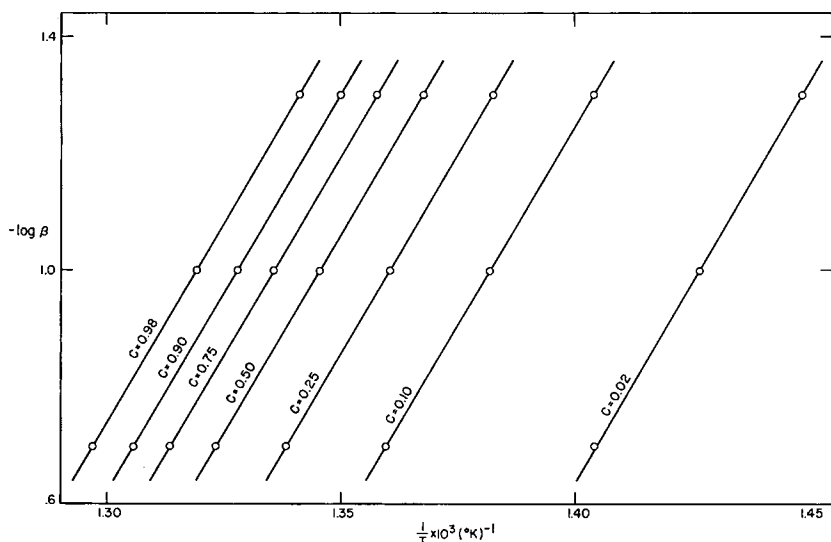


Fig. 2. Logarithm of heating rate vs. reciprocal absolute temperature (same parameters as in Fig. 1).

Figure 2 for the above case for $\beta = 0.05, 0.1$, and 0.2°C./sec. and $C = 0.02, 0.10, 0.25, 0.50, 0.75, 0.90$, and 0.98 . The values of E calculated from the slopes of the curves in Figure 2 from eq. (6) are given in Table II ($E_{\text{approx.}}$). These should be compared with the theoretical value, $E_{\text{theor}} = 60,000$ cal./mole.

Once the approximate E has been determined, the constant in eq. (6) may be easily recalculated for the appropriate E/RT from Table I. These new values (column 4, Table II) may be utilized to redetermine the corrected activation energies listed in the last column of Table II.

Utilizing the above successive approximation method, activation energies for cases where $E/RT < 20$ should be susceptible to accurate determination.

In summary, this method for determining the activation energy from TGA plots involves only the reading of the temperature at a constant weight loss from several integral thermograms at different heating rates. From the slope of $\log \beta$ vs. $1/T$, the activation energy may be closely approximated by means of eq. (6). From the approximate E/RT value, the constant, -4.35 , may be improved upon to obtain more accurate activation energies. The independence of E from C and T may be tested by determining E at various values of constant weight loss.

TABLE II
Calculated Activation Energies for Case B with
Maximum Isothermal Rate at $C = 0.5$ (3)

C	$E_{\text{approx}}(\text{const.} = 4.35),$ cal./mole	$E/RT_{(\text{approx})}$	Reevaluated constant	$E_{\text{corrected}},^a$ cal./mole
0.02	59,100	42.8	4.401	59,800
0.10	59,100	41.5	4.396	59,700
0.25	59,400	40.8	4.392	60,000
0.50	59,100	40.4	4.390	59,400
0.75	59,500	40.1	4.388	60,000
0.90	59,500	39.8	4.387	60,000
0.98	59,500	39.6	4.386	60,000

^a $E_{\text{theor}} = 60,000$ cal./mole.

References

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