

Kinetic Analysis of Thermogravimetric Data*

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Thermogravimetric analysis ultimately affords a record of residual weight fraction versus temperature for a sample heated at a fixed rate under a particular set of other experimental conditions.¹ Ideally, a single thermogram is equivalent to a very large family of comparable isothermal volatilization curves and, as such, constitutes a rich source of kinetic data for volatilization. While it is often quite difficult to realize this potential and even more difficult to apply the resulting laboratory test data to practical problems involving different conditions of geometry, function, and environment, the determination is worth undertaking as a first step. In this paper, a procedure for deriving such preliminary kinetic data from the thermogram will be discussed and applied to two simple cases.

PROCEDURE

Kinetics of Volatilization in Thermogravimetry

One of the many kinds of thermogram found for real materials is illustrated in rather idealized form in Figure 1, where w the apparent residual weight fraction calculated on initial weight, is plotted against the temperature in the sample furnace. The apparent weight fraction volatilized is:

$$v = 1 - w \quad (1)$$

The apparent volatilization rate is found by multiplying the thermogram slope, $-dw/dT$, by the constant heating rate B :

$$dv/dt = -Bdw/dT \quad (2)$$

For a particular volatilization step, however, the appropriate residual weight fraction is the true one, h , calculated on the total fraction volatilized during

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that step, rather than on the total initial weight. From Figure 1,

$$h = (w - G)/H \quad (3)$$

where H is the total apparent weight fraction volatilized during the step and G is the apparent weight fraction remaining after the step has been completed. From eqs. (1) and (3):

$$dv/dt = Hdh/dt \quad (4)$$

It should be noted here that H and G are seldom as clearly defined as they are in Figure 1; in many cases, their estimation constitutes one of the major difficulties of kinetic analysis.

Another difficulty arises from the need to take into account the nature of the kinetic process. In general:

$$-dh/dt = rf(h) \quad (5)$$

where r is the empirical rate constant for volatilization, and where the specific form of $f(h)$ depends on the type of kinetic process, as given in Table I for the two simple cases to be discussed in this paper. Inspection of Table I shows that when h has values near unity, the correlative values of $f(h)$ are also near unity.

TABLE I
Two Specific Forms of $f(h)$ and $g(h)$

Order of kinetic process	$f(h)$	$g(h)$
0	1	$1-h$
1	h	$-\ln h$

The constant r must be treated as empirical because its value for a particular substance is not always uniquely determined by the temperature; it may also be trivially dependent on such procedural details as the nature and geometry of the apparatus, the nature of the environmental atmosphere, and the size, shape, and degree of subdivision

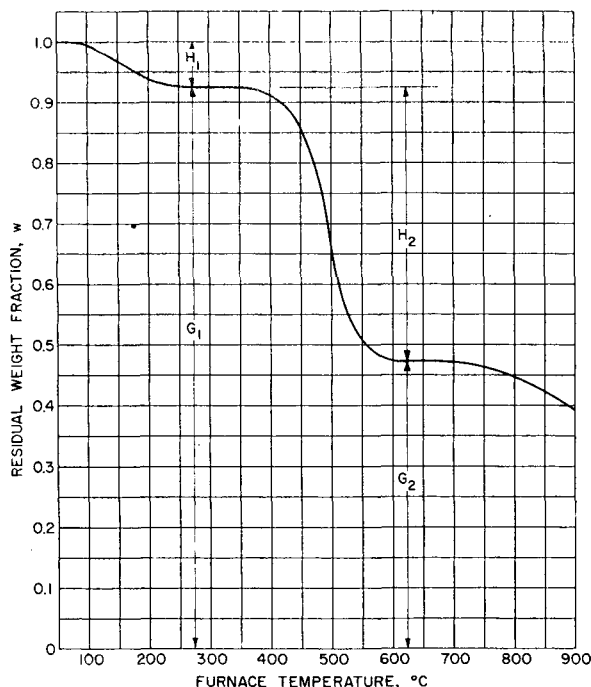


Fig. 1. An illustrative thermogram.

of the sample. Thus, while r is arbitrarily applied as a specific rate constant in this paper, its potential triviality will be constantly emphasized by the use of the symbol r instead of the specific rate constant symbol k .

In this limited sense, then, the relationship between r and the absolute temperature T can be expressed in the form of the simple Arrhenius equation:

$$r = ae^{-b/RT} \quad (6)$$

where a is the apparent frequency factor and b is the apparent activation energy for volatilization, and where R is the molar gas constant. Helpfully, while the value of the constant a is often trivially determined, especially for solid materials, the corresponding value of b is not necessarily trivial. In many instances it can be shown that over at least part of the experimental temperature range, the value of b is the same as that of the activation energy for some fundamental physical or chemical process.²

When the evaluation of the constants in eq. (6) is approached in the usual way by plotting $\log r$ versus $1/T$, it turns out that only a small portion of the thermogram can be utilized, viz., the region where the slope is neither too shallow nor too steep to be measured with sufficient precision.

In fact, in the range of volatilization rates which are small compared to the heating rate, the slopes found from the thermogram are not only imprecise but also inherently inaccurate, being consistently greater than those indicated by comparable isothermal data.³ This effect (which renders thermogravimetric data unsuitable for extrapolation to long times) arises from the fact that in thermogravimetry, the dwell time at each temperature is so brief that no evidence of volatilization can accumulate in the range of small volatilization rates. Consequently, when the initial slopes for a particular volatilization step finally do put in an appearance, they are artificially steep.

The Equation of the Thermogram

One way to avoid the need to deal with a broad range of volatilization rates is to evaluate a and b as constants of the equations of the thermogram rather than of the rate equation. To this end, eqs. (2), (4), and (5) can be used in rewriting (6) as the equation of the true slope of the thermogram:

$$-\frac{dw}{dT} = \frac{af(h)e^{-b/RT}}{B} \quad (7)$$

The equation of the thermogram itself is found by integrating eq. (7), treating a and b as constants:

$$-\int_{h_1}^h \frac{dh}{f(h)} = g(h) = \frac{a}{B} \int_{T_0}^T e^{-b/RT} dT \quad (8)$$

where the specific form of $g(h)$ depends on the nature of the kinetic process, as given in Table I. Here it is seen that when h has values near unity in the neighborhood of T_0 , the correlative values of $g(h)$ are near zero.

From eqs. (4) and (7), a/B can be evaluated on the basis of a single thermogram slope, $(dw/dT)_a$, and the corresponding absolute temperature, T_a , where $f(h)$ has the value $f(h_a)$:

$$\frac{a}{B} = \frac{e^{b/RT_a} \left(\frac{dw}{dT} \right)_a}{Hf(h_a)} \quad (9)$$

The integration of the right-hand member of eq. (8) is accomplished by substitution of u , having values x , for b/RT . Then, x_0 being greater than x ,

$$\int_{T_0}^T e^{-u} dT = -\frac{b}{R} \int_{x_0}^x \frac{e^{-u}}{u^2} du \quad (10)$$

$$-\frac{b}{R} \int_{x_0}^x \frac{e^{-u}}{u^2} du = \frac{be^{-u}}{Ru} \Big|_{x_0}^x + \frac{b}{R} \int_{x_0}^x \frac{e^{-u}}{u} du \quad (11)$$

TABLE II
Table of $-\log p(x)$ and $-\log q(x)$ and Their First Differences

x	$-\log p(x)$	$-\Delta$	$-\log q(x)$	$-\Delta$	x	$-\log p(x)$	$-\Delta$	$-\log q(x)$	$-\Delta$
10	6.417	—	1.074	—					
11	6.928	0.511	1.109	0.035	31	16.472	0.462	1.518	0.014
12	7.433	0.505	1.142	0.033	32	16.933	0.461	1.531	0.013
13	7.933	0.500	1.173	0.031	33	17.394	0.461	1.543	0.012
14	8.427	0.494	1.201	0.028	34	17.853	0.459	1.556	0.013
15	8.918	0.491	1.228	0.027	35	18.312	0.459	1.568	0.012
16	9.406	0.488	1.253	0.025	36	18.770	0.458	1.579	0.011
17	9.890	0.484	1.277	0.024	37	19.228	0.458	1.590	0.011
18	10.372	0.482	1.299	0.022	38	19.684	0.456	1.602	0.012
19	10.851	0.479	1.320	0.021	39	20.141	0.456	1.612	0.010
20	11.328	0.477	1.341	0.021	40	20.597	0.456	1.623	0.011
21	11.803	0.475	1.360	0.019	41	21.052	0.455	1.633	0.010
22	12.276	0.473	1.379	0.019	42	21.507	0.455	1.643	0.010
23	12.747	0.471	1.397	0.018	43	21.961	0.454	1.653	0.010
24	13.217	0.470	1.414	0.017	44	22.415	0.454	1.662	0.009
25	13.686	0.469	1.430	0.016	45	22.868	0.453	1.672	0.010
26	14.153	0.467	1.446	0.016	46	23.321	0.453	1.681	0.009
27	14.619	0.466	1.461	0.015	47	23.774	0.453	1.690	0.009
28	15.084	0.465	1.476	0.015	48	24.226	0.452	1.699	0.009
29	15.547	0.463	1.491	0.015	49	24.678	0.452	1.707	0.008
30	16.010	0.463	1.504	0.013	50	25.129	0.451	1.716	0.009

From eqs. (8) and (11), the equation of the thermogram is:

$$g(h) = \frac{ab}{BR} \left(\frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-u}}{u} du \right) - \frac{ab}{BR} \left(\frac{e^{-x_0}}{x_0} - \int_{x_0}^\infty \frac{e^{-u}}{u} du \right) \quad (12)$$

The second term in eq. (12) is vanishingly small except for imperceptibly small values of $g(h)$, so that eq. 12 reduces to:

$$g(h) = \frac{ab}{BR} \left(\frac{e^{-x}}{x} - \int_x^\infty \frac{e^{-u}}{u} du \right) \quad (13)$$

or, more conveniently:

$$g(h) = \frac{ab}{BR} p(x) \quad (14)$$

The common log of $p(x)$ is given in Table II for the values of x which are ordinarily encountered. The values of $\log p(x)$ were calculated using tabulated values⁴ of e^{-x} and of the exponential integral^{5,6} to six significant figures. Also given in Table II are the first differences in $\log p(x)$ for use in interpolating.

Before b can be evaluated, it is necessary to determine x_a , the value of x at T_a . Once this has been done, b can be found by using

$$b = RT_a x_a \quad (15)$$

From eqs. (9) and (14), b is also given by:

$$b = \frac{RHf(h_a)g(h_a)e^{-x_a}}{p(x_a)} \left(\frac{dT}{dv} \right)_a \quad (16)$$

Then, setting eq. (15) equal to eq. (16):

$$x_a p(x_a) e^{x_a} = q(x_a) = \frac{Hf(h_a)g(h_a)}{T_a} \left(\frac{dT}{dv} \right)_a \quad (17)$$

The common log of $q(x)$ and the corresponding first differences are given in Table II, where the required value of x_a can be found by interpolation.

If, as frequently happens, the nature of the kinetic process is unknown at T_a , b can be roughly approximated by choosing h_a as close to unity as possible in determining $q(x_a)$, taking care to avoid the range of inherently inaccurate gentle thermogram slopes. This approach is analogous to the use of initial volatilization rates as estimates of empirical rate constants in isothermal weight-loss studies. As a rule, a value of h_a near 0.95 is satisfactory, and the corresponding values of $f(h_a)$ and $g(h_a)$ can be taken as 1 and 0.05.

An Approximate Equation of the Thermogram

In many instances, the need to use Table II in determining b can be avoided, since for values of

TABLE III
Values of a'/a for Some Values of x

x	10	15	20	25	30	35	40	45	50
a'/a	0.844	0.888	0.913	0.928	0.939	0.947	0.954	0.958	0.962

x greater than about 15, eq. (13) is usually approximated well enough by a simpler relationship. This is derived⁷ by taking the exponential integral as approximately equal to the sum of the first two terms of the asymptotic expansion:

$$\int_x^\infty \frac{e^{-u}}{u} du \cong e^{-x} \left(\frac{1}{x} - \frac{1!}{x^2} + \dots \right) \quad (18)$$

When eq. (18) is used, eq. (13) becomes:

$$g(h) \cong \frac{ab}{BR} \frac{e^{-x}}{x^2} \quad (19)$$

By use of the definition previously given for x , eq. (19) can also be written:

$$g(h) \cong aRT_a^2 e^{-x} / Bb \quad (20)$$

Then, combining eqs. (9) and (20),

$$b \cong \frac{RT_a^2}{Hf(h_a)g(h_a)} \left(\frac{dv}{dT} \right)_a \quad (21)$$

The value of b found at T_a by eq. (21) is always a little higher than that found by eqs. (17) and (15), but, as will be shown, the approximate equation affords a good first estimate of b even for values of x near 15. As a rule, the error due to approximation is small compared with the experimental errors of thermogravimetric analysis,¹ and with the errors resulting from uncertainty regarding the values of G and H and the nature of the kinetic process. Further, progressively better estimates of b can often be determined by trial and error curve-fitting, and practically the same ultimate value of b is found whether the exact or the approximate thermogram equation is applied.

This is possible because the error in $g(h)$ as computed by eq. (19) instead of eq. (14) can be virtually compensated, for a given value of b , by applying a constant factor to the approximate equation. This is especially true for volatilization steps which are completed within a relatively narrow temperature range. Thus, eq. (19) can be presented as being nearly exact for curve-fitting purposes in the form:

$$g(h) = a'be^{-x}/BRx^2 \quad (22)$$

where a' is the apparent frequency factor for volatilization, multiplied by a correction constant.

The magnitude of the correction can be found from the ratio of eq. (22) to eq. (14), which gives:

$$a'/a = x^2 p(x) e^x = xq(x) \quad (23)$$

That the value of a'/a is nearly constant over a narrow range of x can be seen from Table III.

APPLICATIONS

The use of the exact and approximate equations of the thermogram will next be illustrated in two examples of volatilization via simple kinetics. In both cases, the thermogravimetric data refer to 200-mg. samples heated in a 000 Coors porcelain crucible in a Chevenard thermobalance,¹ at the rate of 180°/hr. in an atmosphere of dry N₂ flowing at 314 cc./min. One sample was a fluid; the other was analyzed in the form of a coarse powder produced by end-milling the solid material under liquid N₂.

Octamethylcyclotetrasiloxane

The evaporation of octamethylcyclotetrasiloxane in dry N₂ affords an example of zero-order volatilization of a liquid, in which case $f(h)$ and $g(h)$ have their simplest possible forms, and the meaning of the constant b is clear. Further, it is known in advance that in the temperature range of the thermogravimetric analysis, observed values of b should be only slightly greater than the reported latent heat of vaporization, 10.85 kcal./mole, at the boiling point, 175°C.⁸

Of great further interest is the fact that this relatively low value of b corresponds to values of x as low as 13 or so, which is about the lowest value encountered in practice, since low activation energies tend to occur with low temperatures. Thus the data for octamethylcyclotetrasiloxane afford an excellent basis for comparing the exact and approximate equations of the thermogram under extremely severe circumstances.

The thermograms for duplicate analyses of the silicone fluid are shown as solid lines in Figure 2, where it is seen that the zero-order volatilization process ends when the residual weight fraction has declined to about 0.09, and the corresponding value of H is 0.910.

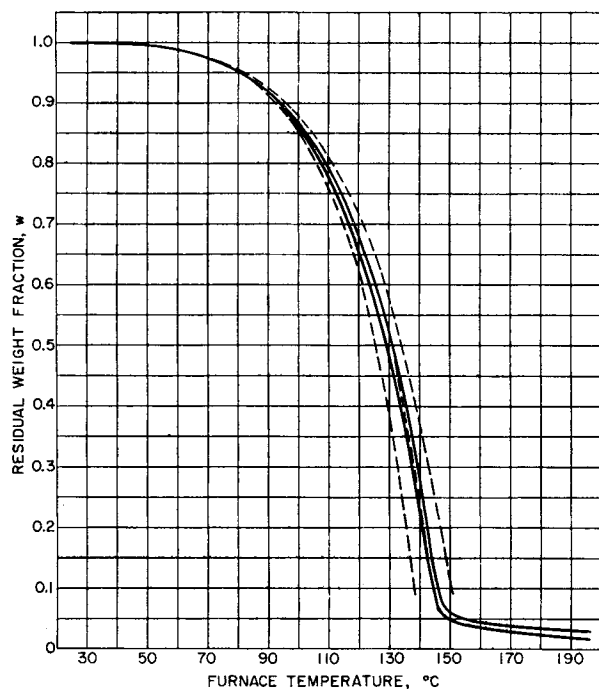


Fig. 2. Thermogravimetric analysis of octamethylcyclotetrasiloxane at 180°/hr. in dry N_2 : solid curves, experimental; lower, middle, and upper dashed curves calculated with $b = 12.75, 11.65,$ and 10.75 kcal./mole, respectively.

In the zero-order case, as given in Table I, $f(h)$ is unity and $g(h)$ is $1 - h$. Further, since the volatilization step of interest begins where w is unity, the sum of G and H is unity. Therefore, using eq. (3),

$$g(h) = 1 - \frac{(w - G)}{H} = \frac{v}{H} \quad (24)$$

Equation (14) then becomes

$$v = (Hab/BR)p(x) = np(x) \quad (25)$$

by using eq. (22), the corresponding approximate equation is found:

$$v = Ha'bc^{-x}/BRx^2 = n'e^{-x}/x^2 \quad (26)$$

For the preliminary evaluation of b , the error of determining the thermogram slope is presumably smallest in the neighborhood of 80°C., where w is 0.95. At this point, where T_a is 353°K. and $g(h_a)$ is $0.05/H$, the slope of the lower curve in Figure 2 was found to be about $1/410$ per degree. By use of these data in eq. (17), $q(x_a)$ was evaluated as 5.807×10^{-2} , whose common log is -1.236 . By interpolation in Table II, the corresponding value of x_a was found to be 15.32. From Eq. (15),

then, b is 10.75 kcal./mole. When b is approximated by using the same data in eq. (21), the slightly higher result is 12.08 kcal./mole.

Thus, even for a rather low value of x_a , the approximate equation has yielded a first estimate of b which agrees within one or two kilocalories with the value calculated by the more nearly exact method. The latter value, however, cannot be taken as a standard of comparison, since it is only as precise as the data used in eq. (17). These primary data, especially the reciprocal thermogram slope dT/dv_a , are subject to appreciable experimental errors, as well as errors in personal judgement. In fact, the value 10.75 kcal. at 80°C. is probably too low, judging from the reported latent heat of vaporization noted earlier.

A more convincing standard of comparison would be a value of b whose use in determining values of $p(x)$ in eq. (25) affords a best fit to all of the zero-order portion of the thermogram. Toward this end, the degree of misfit with b equal to 10.75 kcal./mole was first studied. The value of a/B in eq. (25) was calculated by means of eq. (9) and found to be 1.207×10^4 per degree. The corresponding value of n is 5.942×10^7 , whose common log is 7.774. This value of $\log n$ was checked against the lower curve in Figure 2 at 80°C., by use of the logarithmic form of eq. (25):

$$\log v = \log p(x) + \log n \quad (27)$$

whence

$$\log n = \log v_a - \log p(x)_a \quad (28)$$

The value of $\log n$ found from the data at 80°C., by use of Table II and eq. (28), was 7.778.

With b equal to 10.75 kcal./mole and $\log n$ equal to 7.778, the calculated values of w were found to be too high at temperatures above 80°C., as shown by the upper dashed curve in Figure 2. When the value of b is arbitrarily increased by 2 to 12.75 kcal./mole, the corresponding value of $\log n$ is 9.157, and the calculated values of w are too low at temperatures above 80°C., as shown by the lower dashed curve in Figure 2. Thus the best-fit value of b lies between 10.75 and 12.75 kcal./mole.

This best-fit value of b was sought by matching the data curve at both 80 and 145°C. First a value of b was chosen between 10.75 and 12.75 kcal./mole, and from the corresponding values of x and $\log p(x)$ at 80°C., $\log n$ was evaluated. Then eq. (27) was solved for v at 145°C. for comparison with the data curve. The difference between calculated and observed values was smallest for b

TABLE IV
 Thermogravimetric Data for Octamethylcyclotetrasiloxane

Temperature, °C.	Residual weight fraction and differences ^a					
	<i>w</i>	Δ_1	Δ_2	Δ_3	Δ_4	Δ_5
34	0.998	0	-0.001	-0.002	-0.001	-0.001
50	0.990	0	0.002	0	0.001	0.001
65	0.977	0	0.003	0	0.001	0.001
80	0.950	0	0	0	0	0.001
94	0.894	0.004	-0.001	0.009	0.005	0.006
108	0.796	0.007	-0.017	0.025	0.008	0.010
121	0.634	0.020	-0.042	0.061	0.018	0.022
134	0.388	0.031	-0.118	0.110	0.022	0.022
145	0.090	0.035	-0.259	0.160	0.004	0

^a Δ_1 , upper less lower data curve (solid curves, Fig. 2); Δ_2 - Δ_4 , values from curves calculated from exact equation with $b = 12.75, 10.75,$ and 11.65 kcal./mole, respectively, less w ; Δ_5 , values from curve calculated from approximate equation with $b = 11.65$ kcal./mole, less w .

equal to 11.65 kcal./mole, the corresponding value of $\log n$ being 8.400. As shown by the central dashed curve in Figure 2, the use of these constants affords a good fit to the data curve within experimental error.

Next, the exact and approximate equations of the thermogram were compared by using this best-fit value of b in both of them, specifically, in eq. (27) and in the logarithmic form of eq. (26):

$$\log v = \log n' - 2 \log x - 0.4343x \quad (29)$$

whence

$$\log n' = \log v_a + 2 \log x_a + 0.4343x_a \quad (30)$$

The value of $\log n'$ found from the data at 80°C., using eq. (30), was 8.353.

Happily, as summarized in Table IV, the values of w calculated by the exact and approximate equations were identical within experimental error over the entire experimental temperature range, even though the value of x descended to 14 near 145°C. It is interesting to note also that, in good agreement with Table III, the ratio of n' to n at x equal to 16.61 was found to be 0.897. The corresponding values of a' and a are 2.11×10^3 and 2.35×10^3 per second.

Polytetrafluoroethylene

The volatilization of polytetrafluoroethylene has been studied extensively and related to the thermal decomposition of the polymer essentially to monomer. In isothermal tests *in vacuo* on very minute samples,² the volatilization was clearly first-order at aging temperatures up to 510°C. At the latter temperature, the nature of the process remained dubious until about 20% of

the sample had volatilized. Over the temperature range from 480 to 510°C., however, the apparent activation energy for the volatilization was found to be 80 kcal./mole.

Contrastingly, in isothermal tests in dry N₂ on comparatively bulky 200-mg. powdered samples,³ the kinetic process appeared to be zero-order in the initial stages of volatilization at aging temperatures ranging from 450 to 520°C., tending toward first-order kinetics after 15 to 40% of the sample had volatilized. Further, the apparent activation energy for the initial volatilization was found to be 80 kcal./mole only up to 487°C. At the higher temperatures, the Arrhenius plot of initial volatilization rates curved to a gentler slope, corresponding to a value of b in the neighborhood of 60 to 70 kcal.

Many similar controversies have arisen from supposedly identical studies of the volatilization kinetics of the pyrolysis of complex materials. In part, these appear to have been due to subtle or unmeasured differences in sample composition, or to the sheer imprecision of measurements of rapid volatilization rates. Also, differences in the size, geometry, and degree of subdivision of the sample can affect the findings sufficiently to render the available kinetic data at least partially trivial.

In the preliminary analysis of the thermogram for polytetrafluoroethylene, shown as a solid curve in Figure 3, doubt about the kinetics of volatilization affected the first estimates of b to about the same small extent as did the use of the approximate method of calculation for the exact one. In the computation, T_a was taken as 794°K. (521°C.), where w_a is 0.950 and where $(dv/dT)_a$ was measured as $1/_{351}$ per degree. Assuming first-order kinetics

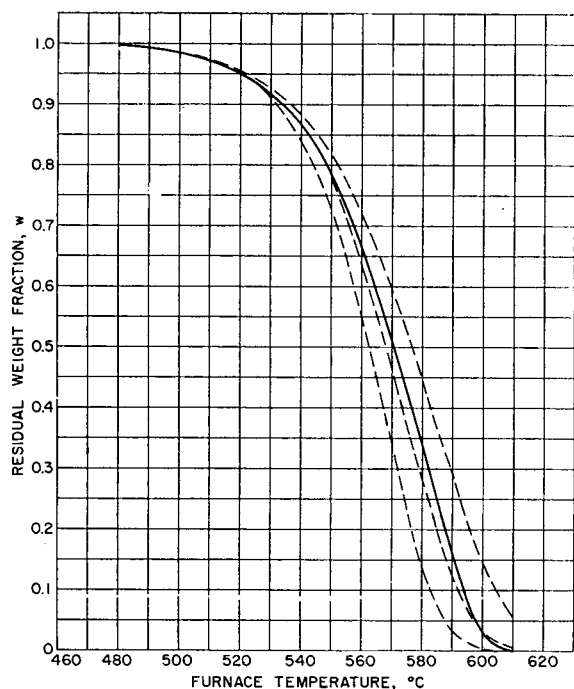


Fig. 3. Thermogravimetric analysis of pulverized polytetrafluoroethylene at 180°/hr. in dry N₂: solid curves, experimental; lower, middle, and upper dashed curves calculated with $b = 80, 70,$ and 60 kcal./mole, respectively.

over the entire thermogram, the data curve in Figure 3 can be construed as representing a case of complete volatilization in a single step, in which case h is equal to w . Then, with $f(h)_a$ taken as w_a , equal to 0.950, and $g(h)_a$ as $-\ln w_a$, equal to 0.051, the value of b given by eqs.(17) and (15) is 70.5 kcal./mole, while that given by eq. (21) is 73.7 kcal./mole. On the assumption of zero-

order kinetics, with H still taken as unity for want of a better notion, the values of b found by the exact and approximate methods are 68.4 and 71.4 kcal./mole.

Since these preliminary calculations suggest that b is at least 60,000, and since the thermogram in Figure 3 ends at about 610°C., the lowest value of x to be expected is about 34. Thus the curve-fitting trials of values of b can safely be accomplished by using the approximate equation

$$-\log w = \frac{(\log e)a'RT^2e^{-x}}{Bb} = n''T^2e^{-x} \quad (31)$$

Taking 70 kcal./mole as a nice round value of b , the corresponding value of n'' found by substituting the data at 794°K. into eq. (31) is 6.572×10^{11} deg.⁻². The calculated thermogram resulting from the use of these values of b and n'' is displayed as the central dashed curve in Figure 3. Being too low, this trial curve indicates that the best-fit value of b is less than 70,000. A measure of the degree of misfit is afforded by the upper and lower dashed curves in Figure 3, drawn on the basis of extreme values of b , 60 and 80 kcal./mole, and the corresponding values of n'' , 1.152×10^9 and 3.734×10^{14} deg.⁻².

As summarized in Table V, a fit to the data curve is more closely approached by taking b equal to 66 or 68 kcal./mole, the corresponding values of n'' being 5.122×10^{10} and 1.822×10^{11} deg.⁻². Probably a slightly better fit over most of the curve could be attained by taking b equal to 67 kcal./mole, but such further refinement cannot be justified, since in the present case, unlike that

TABLE V
Thermogravimetric Data for Polytetrafluoroethylene

Temperature, °C.	Residual weight fraction and differences*						
	w	Δ_1	Δ_2	Δ_3	Δ_4	Δ_5	Δ_6
480	0.995	0.002	0.001	-0.001	0.000	0.001	0.001
500	0.984	0.003	0.002	-0.001	0.001	0.001	0.001
520	0.953	0	0	0	0	0	0
530	0.913	-0.002	0.004	0.011	0.007	0.006	0.006
540	0.862	-0.024	-0.003	0.017	0.006	0.002	0.001
550	0.784	-0.065	-0.015	0.028	0.004	-0.005	-0.006
560	0.667	-0.123	-0.030	0.052	0.007	-0.011	-0.013
570	0.511	-0.180	-0.044	0.083	0.010	-0.016	-0.015
580	0.337	-0.199	-0.057	0.107	0.010	-0.023	-0.023
590	0.174	-0.144	-0.052	0.112	0.008	-0.022	-0.025
600	0.033	-0.031	-0.001	0.115	0.034	0.015	0.014
610	0.008	-0.008	-0.004	0.045	0.006	0	0

* Δ_1 - Δ_5 values from approximate equation with $b = 80, 70, 70, 66,$ and 68 kcal./mole, respectively, less w ; Δ_6 , values from exact equation with $b = 68$ kcal./mole, less w .

of the simple silicone fluid discussed earlier, there is no way of telling whether the misfit near the tail of the curve is due to a change in the value of a' or b , or a change in the nature of the kinetic process, or perhaps some combination of these parameters. If it is a' which changes, however, the same change occurs in a , as shown by the data in Table V calculated for b equal to 68 kcal./mole using

$$-\log w = 2.260 \times 10^{20} p(x) \quad (32)$$

In any case, the value of b , 66–68 kcal./mole, found from the thermogram is within the range, 60–70 kcal./mole, found with considerably greater uncertainty from comparable isothermal aging curves. The values of a and a' corresponding to b equal to 68,000 are 7.60×10^{14} and 7.18×10^{14} per second, as determined at 794°K. Since the correlative value of x is about 43.1, Table III indicates that the ratio of a' to a , 0.945, is slightly low.

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Synopsis

Thermogravimetric data are generally more extensive than are comparable isothermal aging data, and therefore afford

preliminary kinetic information in greater abundance. The kinetic analysis of the thermogram, by use of either its exact equation or a more convenient approximation formula, is straightforward in cases of volatilization via simple kinetics. Application of the analytical procedure to the thermogram for the zero-order volatilization of octamethylcyclotetrasiloxane yielded an estimate of 11.65 kcal./mole as the average heat of vaporization in the temperature range of 80 to 145°C. The apparent activation energy for the first-order pyrolytic volatilization of 200-mg. samples of pulverized polytetrafluoroethylene was estimated to be 66 to 68 kcal./mole in the temperature range of 520 to 610°C.

Résumé

Les données thermogravométriques sont en général plus nombreux que les données de vieillissement isothermes comparables; c'est pourquoi elles donnent une abondante information cinétique préliminaire. L'analyse cinétique du thermogramme, utilisant ou son équation exacte ou une formule approximative plus facile, est applicable dans les cas de volatilisation au moyen de schémas cinétiques simples. L'application du processus analytique au thermogramme pour la volatilisation suivant un ordre zéro de l'octaméthylcyclotetrasiloxane donne une valeur de 11.65 kcal par mole comme chaleur moyenne de vaporisation dans l'intervalle de température de 80 jusqu'à 145°C. L'énergie d'activation apparente pour la volatilisation pyrolytique suivant un ordre un d'une quantité de 200 mgr. de polytétrafluoroéthylène avait une valeur de 66 jusqu'à 68 kcal par mole dans un intervalle de température de 520 jusqu'à 610°C.

Zusammenfassung

Thermogravimetrische Daten sind im allgemeinen in grösserem Umfang vorhanden als vergleichbare Angaben über die isotherme Alterung, und liefern daher eine grössere Menge an vorläufiger, kinetischer Information. Die kinetische Analyse des Thermogramms unter Benützung der exakten Gleichung oder einer bequemeren Näherungsformel ist in Fällen einer einfachen Verflüchtigungskinetik in elementarer Weise durchführbar. Die Anwendung des analytischen Verfahrens auf das Thermogramm der Verflüchtigung nullter Ordnung von Octamethylcyclotetrasiloxan lieferte für die mittlere Verdampfungswärme im Temperaturbereich von 80 bis 145°C einen Wert von 11.65 kcal/Mol. Die scheinbare Aktivierungsenergie der pyrolytischen Verflüchtigung erster Ordnung von 200 mg-Proben von gepulvertem Polytetrafluoräthylen wurde im Temperaturbereich von 520° bis 610°C zu 66 bis 68 kcal pro Mol bestimmt.

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