# Estimating Isothermal Life from Thermogravimetric Data

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In a previous paper,[1] equations were given for determining from thermogravimetric data the kinetic constants for volatilization under the experimental conditions employed. As a logical extension of this work, a procedure will now be given for estimating isothermal life from the thermogram. This, in turn, will lead to a method of approximating the apparent activation energy for volatilization when the nature of the kinetic process is unknown. Data for polytetrafluoroethylene will be used in illustrating these procedures.

## Equivalent Isothermal and Thermogravimetric Data

The equation of the thermogram has been given[1] as:

$$g(h) = abp(x)/BR \tag{1}$$

where $g(h)$ is a function whose specific form depends on the nature of the kinetic process, $a$ is the apparent frequency factor, $b$ is the apparent activation energy for volatilization, $B$ is the constant heating rate employed in the thermogravimetric analysis, $R$ is the molar gas constant, and $p(x)$ is a function which has been tabulated previously.[1] The value of $h$, the true residual weight fraction corresponding to a particular volatilization step, is given by:

$$h = (w - G)/H \tag{2}$$

where $w$ is the apparent residual weight fraction calculated on the initial weight of the sample, $H$ is the total apparent fraction volatilized during the step, and $G$ is the apparent weight fraction remaining after the step has been completed. The value of $x$ is given by:

$$x = b/RT \tag{3}$$

where $T$ is the absolute temperature. (It should be noted that $p(x)$ is used as a very good approximation to $p(x) - p(x_0)$, where $x_0$ relates to a

volatilization rate which is vanishingly small compared to the smallest rate observable on any reasonable experimental time scale.)

In the isothermal aging case, $g(h)$ is given by:

$$g(h) = rt \tag{4}$$

where $r$ is the apparent rate constant for isothermal volatilization. The temperature dependence of $r$ can be expressed in the form of the simple Arrhenius equation:

$$r = ae^{-b/RT} \tag{5}$$

If samples of the same geometry and degree of subdivision are subjected to isothermal aging and thermogravimetric analysis under otherwise identical experimental conditions, then at identical values of $w$, the corresponding values of $h$ and $g(h)$ from the isothermal and constant heating-rate tests are also identical. Thus, at the isothermal aging time $t_i$, and the absolute thermogravimetric analysis temperature $T_i$ at which the same value of $w$ occurs:

$$rt_i = abp(x_i)/BR \tag{6}$$

Using eq. (5) in eq. (6) yields

$$t_i = be^{b/RT}p(x_i)/BR \tag{7}$$

or, more conveniently:

$$\log t_i = \log (b/BR) + (b \log e/RT) + \log p(x_i) \tag{8}$$

where $T$ is the absolute aging temperature, and where $x_i$ is calculated for the absolute thermogravimetric analysis temperature $T_i$ corresponding to the equivalent aging time $t_i$.

## Heat-up Times

The validity of eq. (7) can be demonstrated by comparing matching sets of isothermal and thermogravimetric data, but before this can be done, allowance must be made for any volatilization occurring

in the isothermal case before it has become iso-thermal. In practice, $t_i$ consists of both the observed time at heat $t_{ia}$ and an equivalent iso-thermal time $t_c$ corresponding to the heat-up time:

$$t_i = t_{ia} + t_c \qquad (9)$$

From eq. (7), it is clear that $t_c$ can be computed readily if the value of $b$ is known and if the iso-thermal aging sample is brought up to temperature at a constant heating rate. Further, since the aging temperature and the corresponding thermo-gravimetric analysis temperature are identical at $t_c$, Equation (7) simplifies to:

$$t_c = (be^x/BR)p(x) \qquad (10)$$

By using eq. (3), eq. 10 can be further simplified:

$$t_c = Txe^xp(x)/B = (T/B)q(x) \qquad (11)$$

The function $q(x)$ has been tabulated previously,[1] but if only a rough approximation of $t_c$ is required, the value of $q(x)$ can be taken as 0.03.

## A Convenient Data Plot

In many cases, it is possible to present the information conveyed by eq. (8) in the more fa-miliar form of a plot of log $t_i$ versus $1/T_i$. If $x_i > 20$:

$$\log p(x_i) \cong -2.315 - 0.4567x_i \qquad (12)$$

Thus eq. (8) becomes:

$$\log t_i \cong \log (b/BR) - 2.315 +$$
$$(b \log e/RT) - (0.4567b/RT_i) \qquad (13)$$

Equation (13) is virtually exact for values of $b/RT_i > 20$.

In addition to convenience in graphing, eq. (13) affords a means of approximating the value of $b$ when, as all too often happens, the nature of the kinetic process is unknown. Given matching sets of isothermal and thermogravimetric data, $t_c$ can be roughly estimated, as suggested under equation (11), whereafter log $t_i$ can be plotted against $10^3/T_i$. If the plot is reasonably linear, its slope $m$ can be measured and used in estimating $b$:

$$b \cong -mR(10)^3/0.4567 = -4351m \text{ cal.} \quad (14)$$

Again, eq. (14) becomes increasingly inexact for values of $b/RT_i < 20$. Further, as will next be shown, $T_i$ must be taken as the actual temperature

in the sample; the use of furnace temperatures introduces large errors.

## Polytetrafluoroethylene Data

Matching sets of isothermal and thermogravi-metric data were available for powdered poly-tetrafluoroethylene produced by end-milling a piece of a Teflon (trademark, E. I. du Pont de Nemours & Company, Inc.) gasket under liquid $N_2$. In both cases, 200 mg. samples of the coarse powder were heated in a 000 Coors porcelain crucible in a Chevenard thermobalance[2] in an atmosphere of dry $N_2$ flowing at 314 cc./min. The same heat-ing rate, 3°C./min. was used in thermogravimetric analysis to complete volatilization and in heating to a furnace temperature of 490°C. for isothermal aging.

Values of $T_i$ based on furnace temperature readings in thermogravimetric analysis are listed in Table I opposite a few selected values of $w$. The corresponding values of log $t_i$ were calculated by use of eq. (8), for $B = 3$°C./min., $R = 1.987$ cal./mole/°C. and $T = 763$°K. The value of $b$ was taken as 68,000 cal./mole on the basis of the value of 66,000 to 68,000 found previously from the thermogram.[1] The resulting working equation is:

$$\log t_i = 23.533 + \log p(x_i) \qquad (15)$$

The corresponding observed values of log $t_i$ were found by using eqs. (9) and (11). The value of $t_c$ found for $x = 44.85$, log $q(x) = -1.671$, is 5.4 min.

TABLE I
Isothermal Life of Teflon from Furnace Temperatures in Thermogravimetric Analysis

| $w$ | $T_i$, °K. | $x_i$ | $\log p(x_i)$ | $\log t_i$ | $\log t_i$ (observed) |
|---|---|---|---|---|---|
| 0.950 | 794 | 43.10 | -22.006 | 1.527 | 1.468 |
| 0.900 | 806 | 42.46 | -21.716 | 1.817 | 1.711 |
| 0.750 | 826 | 41.43 | -21.248 | 2.285 | 2.149 |
| 0.500 | 844 | 40.55 | -20.847 | 2.686 | 2.511 |
| 0.250 | 859 | 39.84 | -20.524 | 3.009 | 2.889 |
| 0.115 | 866 | 39.52 | -20.378 | 3.155 | 3.093 |

Since the values of $x_i$ in Table I are all greater than 20, the data were plotted as suggested by eq. (13) in Figure 1, where it is seen that the agree-ment between calculated and observed data is poor when furnace temperatures are used as estimates of sample temperatures.

In order to determine actual sample temperatures, a dummy run was conducted on an additional sample of polytetrafluoroethylene. In this non-weighing run, one junction of a Pt–PtRh differential thermocouple was immersed in the sample, while the other junction was placed in the thermocouple well of the Chevenard thermobalance. The output of the differential thermocouple was measured on a Leeds and Northrup Model 9835B d.c. microvoltmeter, and recorded along with the furnace temperature.
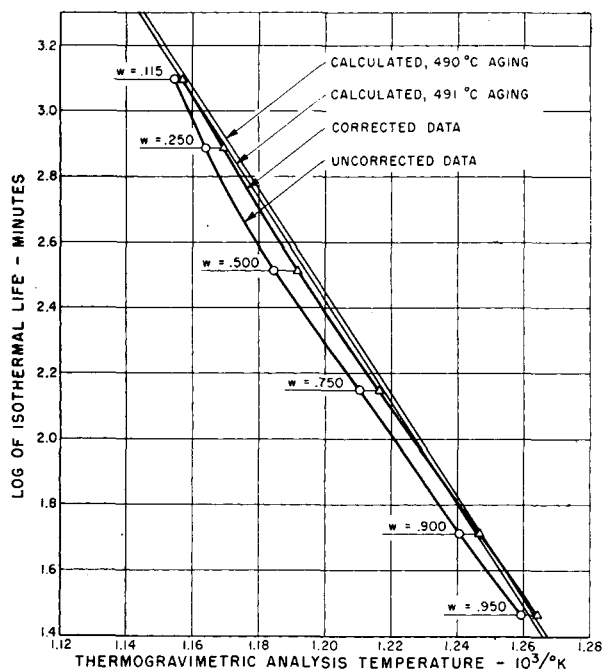


Fig. 1. Equivalent isothermal life of polytetrafluoroethylene from thermogravimetric data.

As expected, the sample temperature was appreciably lower than the furnace temperature during heating periods, and this difference was reinforced during periods of rapid volatilization. On attainment of constant temperature, however, the sample became slightly warmer than the thermocouple well in the absence of any endothermic process. This is because the cool incoming $N_2$ impinged on the thermocouple well.[2] The differences (sample temperature minus furnace temperature) found under the experimental conditions employed in this work are listed in Table II. Also given in Table II are values of $T_i$ corrected to the nearest degree, together with calculated values of log $t_i$ based on a value of $T = 764°K$. Since the value of $t_c$ was virtually unaffected by

## TABLE II
### Isothermal Life of Teflon from Sample Temperatures in Thermogravimetric Analysis

| $w$ | $\Delta T$ | $\Delta T_i$ | $T_i$, °K. | $x_i$ | log $p(x_i)$ | log $t_i$ |
|---|---|---|---|---|---|---|
| 0.950 | −1.2 | −3.3 | 791 | — | — | — |
| 0.900 | +0.8 | −3.6 | 802 | 42.67 | −21.811 | 1.696 |
| 0.750 | +0.8 | −4.2 | 822 | 41.63 | −21.339 | 2.168 |
| 0.500 | +0.8 | −4.8 | 839 | 40.79 | −20.956 | 2.551 |
| 0.250 | +0.8 | −3.6 | 855 | 40.02 | −20.606 | 2.901 |
| 0.115 | +0.8 | −2.1 | 864 | 39.61 | −20.419 | 3.088 |

this change, the observed values of log $t_i$ in Table I stand unchanged.

In Figure 1, it is seen that applying the nearest-degree correction wrought a great improvement in the agreement between calculated and experimental values. Even better agreement should be possible, given precise sample temperatures for an actual weighing run. Unfortunately, this information is not available from the thermobalance presently in use. Even so, however, the corrected data in Figure 1 yield a good estimate of $b$ when used in eq. (14). On treating the data points as belonging to a straight line and omitting the nonisothermal point at $w = 0.950$, the least-squares slope of the corrected data was found to be −15.4. The corresponding value of $b$ is 67,000 cal./mole, in excellent agreement with the value found from the thermogram.[1]

The writer is indebted to Mrs. W. G. Spodnewski, who painstakingly conducted the experimental work.

## References

1. Doyle, C. D., J. Appl. Polymer Sci., 5, 285 (1961).
2. Simons, E. L., A. E. Newkirk, and I. Aliferis, Ana Chem., 29, 48 (1957).

## Synopsis

Equations are given for estimating equivalent isothermal life from thermogravimetric data and for estimating the apparent activation energy for volatilization even though the nature of the kinetic process is unknown. Illustrative data for polytetrafluoroethylene are presented. The importance of using sample temperatures, rather than furnace temperatures, is noted.

## Résumé

On présente des équations pour estimer la durée de vie isothermique équivalente à partir des données thermogravimétriques et pour estimer l'énergie d'activation apparente de la volatilisation même si la nature du processus cinétique est inconnu.  Comme exemple on présente les résultats obtenus dans le cas du polytétrafluoroéthylène.  On note l'importance de l'utilisation de la température réelle des échantillons plutôt que les températures du four.

## Zusammenfassung

Gleichungen zur Bestimmung der äquivalenten, isothermen Lebensdauer aus thermogravimetrischen Daten und der scheinbaren Aktivierungsenergie für die Verflüchtigung werden angegeben, auch für den Fall, dass die Natur des kinetischen Prozesses unbekannt ist.  Zur Illustrierung werden Daten für Polytetrafluoräthylen mitgeteilt.  Auf die Wichtigkeit, die wahre Probentemperatur und nicht die Ofentemperatur zu benützen, wird hingewiesen.