

A GENERAL INTEGRAL TECHNIQUE FOR KINETIC ANALYSIS OF TEMPERATURE-PROGRAMMED THERMOGRAVIMETRY

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A general integral technique for analyzing the first-order kinetics of temperature-programmed thermogravimetry has been developed. The method has been successfully applied to calculate the kinetic parameters of the thermal decomposition reaction of poly(tetrafluoroethylene).

Thermogravimetry (TG) is a thermal analysis method that has been broadly employed in polymer characterizations. Many attempts have been made to use the analytical method for kinetic studies of polymer degradation reactions [1]. However, the success of such an application depends significantly on the data interpretation techniques associated with the specific chemical system being investigated. It is apparent that an efficient data reduction technique can drastically reduce the task that one may encounter in experimental work.

In the past decade or so, many efforts have been made in data analysis techniques for TG kinetics. The topic has been extensively reviewed elsewhere [1–3]. In this paper, a general integral technique for the first-order reaction kinetics of temperature-programmed TG measurements is investigated. The data analysis technique is applied to calculate the kinetic parameters of the thermal decomposition reaction of poly(tetrafluoroethylene), Teflon PTFE, in vacuum [4].

Kinetic analysis

A simple decomposition process in the solid phase can be expressed by the rate equation [4–7]:

$$V = - \frac{d\alpha}{dt} = k_n f, \quad (1)$$

where the symbols and notations are defined under “Nomenclature”; f is a function of α^* and n .

* The definition of α adopted in this paper make the data processing clearer, but it should be realized that the definition used is the opposite of that normally used.

With the simplest case of a first-order reaction where $n = 1$, f can be shown equal to α ; Eq. 1 becomes

$$V = - \frac{d\alpha}{dt} = k_1 \alpha. \quad (2)$$

Using numerical methods and computer programming techniques, the differential form in Eq. 2 was applied successfully to interpret the TG kinetics of the thermal decomposition process of Teflon PTFE [6].

However, Eq. 2 cannot be integrated in a closed form when k_1 is a function of temperature as the situation encountered in a programmed-heating experiment. In general, the integral method is handled by series expansions [1, 5] or a graphical technique [7] involving some degrees of approximations. In this work, the integration of Eq. 2 is performed by a numerical method. The results obtained should be explicit because the increment of integration can be made as small as desired.

For a temperature-programmed experiment with a linear heating rate r , Eq. 2 can be expressed in an integral form as described in Eq. 3 after incorporating in it the Arrhenius relation,

$$- \ln \alpha = \frac{Z}{r} \int_{T_1}^{T_2} \exp \left(- \frac{E_a}{RT} \right) dT. \quad (3)$$

Again, the symbols and notations of Eq. 3 are referred to under "Nomenclature". For simplicity, the following definitions for Q and A are adopted:

$$Q = - \ln \alpha, \quad (4)$$

and

$$A = \int_{T_1}^{T_2} \exp \left(- \frac{E_a}{RT} \right) dT. \quad (5)$$

It is clear that the variable Q can be derived from the measured quantity and that the variable A is the term that cannot be integrated into a closed form.

In the present studies, Eq. 5 was integrated by a numerical method using a trapezoidal formula [8] with a 1K increment in temperature. The integration was carried out from absolute zero up to the desired temperatures. Similar calculations using an integration interval of 0.01 K showed no significant effect on the integrated results of Eq. 5. The results of the numerical integration performed on Eq. 5 with various E_a values are presented in Fig. 1 in a semi-logarithmic form so that a wide range of information can be covered. It is interesting to note that for large values of E_a or at high temperature, the plots in Fig. 1 are practically linear. This fact reduces the tedious work involved in the numerical integration operation because only two points are needed to complete the plot under these conditions. The plots given in Fig. 1 also are necessary for the subsequent data reduction processes.

If an arbitrary and convenient reference point "S" on a TG curve is taken, the derivation given in Eq. 6 can readily be arrived at from Eqs 3, 4 and 5.

$$\frac{Q}{Q_s} = \frac{A}{A_s} \quad (6)$$

Although it is simple and straightforward, Eq. 6 is the key to the present data reduction technique; it gives a direct correlation between the measurable quantity Q/Q_s and the quantity A/A_s that can be obtained only by numerical integrations.

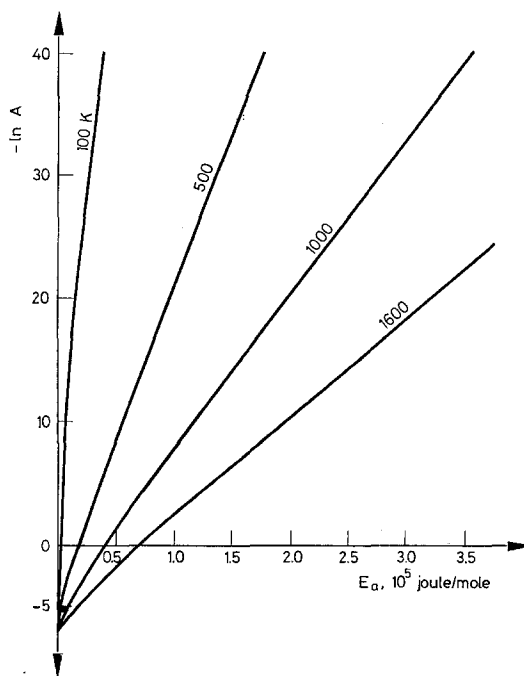


Fig. 1. $-\ln A$ vs. E_a plots at various temperatures

Some significant points of Eq. 6 are that it is independent of the pre-exponential factor Z and the programmed-heating rate r ; it depends only on the activation energy E_a . Figure 2 is a plot of $\ln \frac{A}{A_s}$ vs. E_a with 500 K as a reference temperature.

The use of the semi-logarithmic scale on the ordinate again is for convenience. All calculations in Eqs 4 through 6 were incorporated into a FORTRAN program that was processed on a timesharing terminal of a Honeywell Computer Network System.

Applying Eq. 6, the term A/A_s at a specific temperature can be calculated from the measured quantities as indicated in Eq. 4; the value of E_a then can be derived

from a plot similar to Fig. 2. When E_a is known, A can be readily obtained on Fig. 1. When both A and Q are known, Z can be computed using Eq. 3.

It is important to note that the derivation of Eq. 6 introduces an additional root to the $\ln \frac{A}{A_s}$ vs. E_a plots as reflected on the curves in Fig. 2. This results from the nature of the exponential function in Eq. 5. If only one point on the

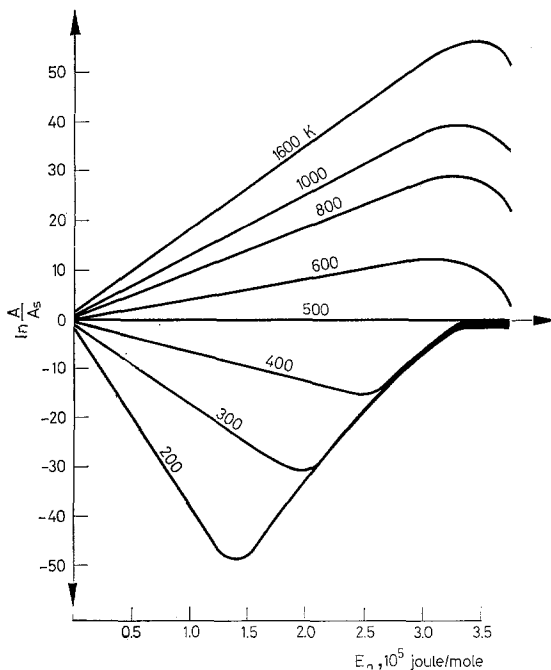


Fig. 2. $\ln \frac{A}{A_s}$ vs. E_a plots at various temperatures

TG curve is used in the calculations, the two solutions of E_a would be confusing. After checking several points, it should be clear that one of the two E_a values is physically implausible. The logical solution is the lower value.

Applications

The integral technique that we have discussed was employed to interpret the thermal decomposition kinetic data of Teflon PTFE in vacuum [4]. The same data were used previously in the differential technique [6]. In the present calculation, two reference temperatures corresponding to approximately 40 and 20 percent reaction were chosen. The data for the computations were obtained from

a smooth curve traced through the original data points. These data and the results of the calculations are summarized in Table 1. There is an excellent agreement between the kinetic parameters derived from the two reference temperatures. However, the precision of the pre-exponential factor Z appears to be poor in each individual standard temperature chosen. It is understandable that a small deviation in the measured activation energy can introduce high deviations in the

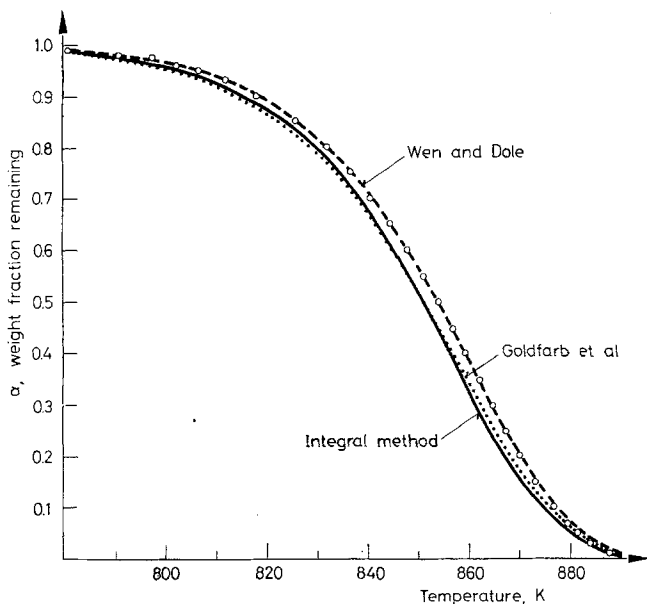


Fig. 3. TG curves of the thermal decomposition reaction of Teflon PTFE in vacuum obtained by various computational methods, as tested by Goldfarb *et al.*; heating rate = 5.66 K/min. O, original data points

Z values as indicated in the data given in Table 1. The values of both E_a and Z appear to pass through a minimum near the reference temperature. This may very well be a consequence of the computational method used. Because of the complex nature of Eq. 6, we do not have a convincing explanation of this phenomenon.

The average value of the results in Table 1 is summarized in Table 2 together with those obtained by different data analysis techniques for comparison. The consistency of the TG curves as calculated from the parameters given in Table 2 is displayed in Fig. 3. The agreements of E_a values among the three computational techniques are excellent. Although the deviations of the Z values of each separate calculation are high, the average Z value is consistent with that obtained by the differential technique. In fact, the differential technique employed a linear regression method that calculates only an average value of the same set of data [8].

Table 1
 Thermal decomposition kinetics of Teflon PTFE in vacuum by Goldfarb, *et al.* [4] as measured using thermogravimetric analysis at 5.66 K/min. Results calculated by the integral method of this work

T K	α	$Q = -\ln z$	Referenced at 850 K				Referenced at 830 K			
			$\ln \frac{Q}{Q_s}$	E_a 10 ³ joule/mole	$-\ln A$	Z 10 ¹⁵ /sec	$\ln \frac{Q}{Q_s}$	E_a 10 ³ joule/mole	$-\ln A$	Z 10 ¹⁵ /sec
790	.983	.0171	-3.4926	3.12	44.70	41.8	-2.4577	3.21	43.98	20.3
795	.977	.0233	-3.1832	3.14	44.68	55.1	-2.1484	3.21	43.61	19.1
800	.968	.0325	-2.8504	3.08	43.56	25.4	-1.8156	3.20	43.25	18.6
805	.956	.0450	-2.5250	3.08	42.78	16.1	-1.4901	3.19	42.74	15.5
810	.941	.0608	-2.2241	3.05	42.38	14.6	-1.1892	3.19	42.45	15.6
815	.918	.0856	-1.8820	2.99	40.96	5.0	-0.8471	3.04	41.20	6.3
820	.889	.1177	-1.5635	2.90	39.54	1.6	-0.5287	2.90	39.86	2.3
825	.857	.1543	-1.2928	2.88	39.00	1.3	-0.2579	2.96	39.98	3.4
830	.819	.1997	-1.0349	2.88	38.76	1.3	0.0			
835	.770	.2613	-0.7660	2.91	38.97	2.1	0.2688	2.96	39.45	3.3
840	.713	.3383	-0.5078	2.85	37.76	0.8	0.5271	2.94	39.04	2.9
845	.643	.4416	-0.2413	2.85	37.73	1.0	0.7936	2.94	38.75	2.8
850	.570	.5621	0.0				1.0349	2.91	38.30	2.3
855	.486	.7215	0.2497	2.89	37.60	1.4	1.2845	2.91	38.04	2.3
860	.395	.9289	0.4991	2.92	37.82	2.3	1.5372	2.93	37.93	2.6
865	.299	1.2073	0.7645	2.99	38.53	6.2	1.7993	2.93	37.70	2.7
870	.202	1.5995	1.0458	3.08	39.61	24.0	2.0806	2.98	37.83	4.1
875	.124	2.0875	1.3120	3.10	39.57	30.1	2.3469	3.01	37.78	5.0
880	.065	2.7646	1.5930	3.03	38.40	12.4	2.6278	3.05	37.82	6.9
		Average		2.98	40.08	11.3		3.03	39.98	7.6
		Deviation		0.10	2.45			0.12	2.29	

Table 2
Kinetic parameters of the data in
Table 1 as calculated by various methods

Reference	E_a 10 ⁵ joule/mole	Z 10 ¹³ /sec
This work	3.01 ± 0.26	9.45
Wen and Dole [6]	3.01 ± 0.06	9.20
Goldfarb <i>et al.</i> [4]	2.90	117.0

It must be noted that Goldfarb *et al.* calculated the pre-exponential factor using the Friedman method [9], which involves several TG curves at different heating rates for determining the kinetic parameters at a specific percent of reaction. The Z value they obtained varies from 10¹³ to 10¹⁸/sec. The result presented in Table 2 is the average of the values as derived from 10 to 80 percent weight loss [4].

Conclusions

Similar to the differential technique, the integral technique is an explicit method for solving an implicit equation like Eq. 3. This technique is unique in the respect that only one single temperature-programmed TG curve is needed in the data reduction. Even though the calculational processes are tedious, the computer programming methods help to relieve most of the burden and allow efficient uses of the complex data processing technique.

The integral technique presented in this work was attempted primarily for TG kinetics of a first-order decomposition reaction, although very few simple first-order reactions in the solid state have been unequivocally identified. Nevertheless, it is readily applicable to other simple order reactions of temperature-programmed experiments as long as their reaction orders are known and the percent of reaction can be monitored as a function of time. Figure 1 is applicable to all first-order reactions, while Fig. 2 can be used for a first-order reaction only when the temperature of 500 K is well within the temperature range of the measurements. It is clear that plots similar to Figs 1 and 2 can be constructed with a different reaction order for a specific problem.

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Nomenclature

- A Eq. 5, K
 A_s A value at reference temperature S K
 E_a Activation energy of a first-order decomposition reaction, KJ/mole
 Q Eq. 4, dimensionless
 Q_s Q value at reference temperature S K

R	Gas constant, 8.318 joule/mole/K
T	Temperature, K
T_1	Lower limit of the integration of Eq. 5, K
T_2	Upper limit of the integration of Eq. 5, K
V	Instantaneous reaction rate, percent reaction per sec
Z	Pre-exponential factor of a first-order reaction, sec^{-1}
f	A function of α and n
k_n	Specific rate constant of reaction order n , sec^{-1}
k_1	First-order specific rate, sec^{-1}
n	Order of reaction, dimensionless
r	Programmed-heating rate, K/sec
t	Laboratory time, sec
α	Percent of material remaining at time t

References

1. L. REICH and S. S. STIVALA, *Elements of Polymer Degradation*, McGraw-Hill Co., New York, 1971.
2. C. B. MURPHY, *Anal. Chem.*, 36 (1964) 347R, *ibid.*, 38 (1966) 443R, *ibid.*, 40 (1968) 380R, *ibid.*, 44 (1972) 513R.
3. C. H. FLYNN and L. A. WALL, *J. Res. Nat. Bur. Std.*, A7 (1960) 487.
4. I. J. GOLDFARB, R. MCGUEHAN and A. C. MEEKS, *Kinetic Analysis of Thermogravimetry; Part II. Programmed Temperature*, Technical Report, AFML-LR-68-181, Part II, Air Force Material Laboratory, Wright-Patterson Air Force Base, Ohio, September 1968.
5. V. SATAVA and F. SKVORA, *J. Am. Ceram. Soc.*, 52 (1969) 591.
6. W. Y. WEN and M. DOLE, *Computer in Chemistry and Instrumentation Series*, Vol. VI, J. S. Mattson, H. B. Mack, Jr., and H. C. MacDonald, Jr., Editors (in press).
7. R. W. FARMER, Technical Report AFML-TR-65-246, Air Force Systems Command, Wright Patterson Air Force Base, Ohio, January 1955.
8. W. Y. WEN, *Intern. J. Chem. Kinet.*, 5 (1973) 621.
9. H. L. FRIEDMAN, *J. Polymer Sci.*, 6c (1965) 183.

RÉSUMÉ — Mise au point d'une technique générale d'intégration pour l'analyse des phénomènes de cinétique du 1^{er} ordre par thermogravimétrie en température programmée. La méthode a été appliquée avec de bons résultats au calcul des paramètres cinétiques de la réaction de décomposition thermique du polytétrafluoroéthylène.

ZUSAMMENFASSUNG — Es wurde eine allgemeine Integraltechnik zur Analyse der Kinetik erster Ordnung bei temperaturprogrammierter Thermogravimetrie entwickelt. Diese Methode wurde zur Berechnung der kinetischen Parameter der thermischen Zersetzungsreaktion von Poly(tetrafluoräthylen) mit Erfolg eingesetzt.

Резюме — Разработана общая интегральная техника для анализа кинетики первого порядка температурно-программируемой термогравиметрии. Метод был успешно применен для вычисления кинетических параметров реакции термического разложения политетрафторэтилена.