Journal of Thermal Analysis, Vol. 34 (1988) 909–916

THERMOGRAVIMETRY. FAST METHODS FOR EVALUATION OF KINETIC PARAMETERS

I. Agherghinei

"P. PONI" INSTITUTE OF MACROMOLECULAR CHEMISTRY,
6600 JASSY, ROMANIA

(Received March 9, 1987; in revised form March 23, 1988)

The paper discusses three fast methods for determination of the reaction order, as follows: the single-point method proposed by Kissinger, Horowitz and Metzger, an original two-point method, and the three-point method suggested by a Gorbachev's paper. These methods cannot elucidate the reaction mechanism, but they can help in the rapid derivation of the apparent kinetic parameters n and E.

The fast methods allow the evaluation of kinetic parameters via a small number of calculations if a certain kinetic mechanism is assumed. Due to the fact that these methods process only a small number of experimental data, they do not permit identification of the kinetic mechanism, or of modifications which could appear during the reaction. However, analysis of the experimental data with several of these methods shows whether the phenomenon involved is simple or complex, which can be assessed from the agreement of the results.

The paper presents the following three fast methods of kinetic parameter evaluation: the single-point method of Kissinger [1], Horowitz and Metzger [2], the original two-point method proposed by the present author, and the three-point method suggested by a Gorbachev's paper [3]. The theoretical considerations mainly refer to the kinetic n^{th}-order model, but they could be extended to other kinetic mechanism.

Theoretical

The theoretical study starts from the following well-known differential equation:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = Z \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{1}$$

where the notations are the usual ones.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Under non-isothermal conditions, at a constant heating rate $\beta = \frac{dT}{dt}$, integration of Eq. (1) gives:

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ZE}{\beta R} p(x) \tag{2}$$

where $x = E/RT$ and $p(x) = \int_x^\infty \frac{e^{-u}}{u^2} \mathrm{d}u$.

a) Single-point method

If we take $R_x = (1-\alpha)_{\max}$, the condition $\frac{d^2\alpha}{dt^2} = 0$ leads to

$$\frac{ZE}{\beta R} = \frac{x^2 e^x}{n}(1-\alpha)^{1-n}$$

Substituting this expression into Eq. (2) gives

$$\begin{aligned} n \neq 1: &\quad R_x^{n-1} = 1 + \frac{1-n}{n} p(x)\, x^2 e^x \\ n = 1: &\quad -\ln R_x = p(x)\, x^2 e^x \end{aligned} \tag{3}$$

When $x \to \infty$, we obtain $R_\infty = n^{\frac{1}{1-n}}$, because

$$\lim_{x \to \infty} p(x)\, x^2 e^x = 1$$

Relationships (3) allow tabulation of the values of function R_x against x and n (Table 1). In our calculations we have used the fourth-degree rational approximation for $p(x)$ [4].

The data in Table 1 show that the ratio R_x/R_∞ varies slowly with the reaction order, if x is not too small. Thus, when $x = 30$, the mean value of the ratio R_{30}/R_∞ is 1.062. Accordingly, we can write:

$$R_{30} = 1.062\, n^{\frac{1}{1-n}}$$

This relationship was proposed by Gyulai and Greenhow [5]. A more general relationship was given by Gorbachev [6]. In Eq. (3), Gorbachev substituted the following approximation of the temperature integral:

$$p(x) \approx \frac{e^{-x}}{x(x+2)}$$

Table 1 The values of $(1-\alpha)_{\max}$ for various orders and x's.

x n	10	20	30	40	50	∞
0.1	0.092	0.085	0.082	0.081	0.080	0.077
0.2	0.158	0.146	0.142	0.140	0.139	0.134
0.3	0.211	0.196	0.191	0.188	0.186	0.179
0.4	0.256	0.238	0.231	0.228	0.226	0.217
0.5	0.294	0.273	0.266	0.262	0.260	0.250
0.6	0.328	0.305	0.297	0.292	0.290	0.279
0.7	0.357	0.333	0.324	0.319	0.316	0.305
0.8	0.384	0.358	0.348	0.343	0.340	0.328
0.9	0.408	0.381	0.371	0.365	0.362	0.349
1.0	0.430	0.402	0.391	0.385	0.382	0.368
1.1	0.450	0.420	0.410	0.404	0.400	0.386
1.2	0.469	0.438	0.427	0.421	0.417	0.402
1.3	0.486	0.455	0.443	0.437	0.433	0.417
1.4	0.502	0.470	0.458	0.451	0.448	0.431
1.5	0.517	0.484	0.472	0.465	0.461	0.444
1.6	0.531	0.498	0.485	0.478	0.474	0.457
1.7	0.544	0.510	0.497	0.490	0.486	0.469
1.8	0.556	0.522	0.509	0.502	0.498	0.480
1.9	0.567	0.533	0.520	0.513	0.509	0.490
2.0	0.578	0.544	0.530	0.523	0.519	0.500
2.5	0.625	0.589	0.575	0.568	0.563	0.543
3.0	0.661	0.626	0.611	0.604	0.599	0.577

and obtained

$$n \neq 1: \qquad R_x = \left(1 + \frac{1-n}{n}\frac{x}{x+2}\right)^{\frac{1}{n-1}}$$

$$n = 1: \qquad -\ln R_x = \frac{x}{x+2}$$

Since R_x depends on both n and x (or E), determination of the latter is possible only by means of an iterative procedure. Thus, considering that the value of R_x, determined from the TG curve, corresponds to $x=30$ (a good hypothesis for polymers), by means of Table 1 we can obtain the first approximation of n.

The value obtained allows evaluation of the activation energy using the relationship [7]

$$E = \frac{nRT^2_{\max}}{(1-\alpha)_{\max}}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\max} \tag{4}$$

We can now evaluate a better approximative value of x. The calculation process is repeated until the values of the kinetic parameters for both n and E are not modified by a new iteration.

If we have several values evaluated from the TG curve, the simplest differential method for determining E is an Arrhenius plot of the logarithm of the n^{th}-order rate constant against the reciprocal of absolute temperature:

$$\ln\left[\frac{\frac{d\alpha}{dt}}{(1-\alpha)^n}\right] = \ln Z - \frac{E}{RT}$$

This value of E is fairly precise, even if first approximation of n is not exact. The value of x is the calculated, and with this value it is possible to establish the precise value of n by means of Table 1.

b) Two-point method

The method discussed here is based on our following empirical approximation:

$$p(x) \approx 0.721\, x^{-1.924}\, e^{-x} \tag{5}$$

The relative error of approximation (5) is smaller than 2% in the interval $10 \leqslant x \leqslant 65$, and below 1% for the interval $12 \leqslant x \leqslant 50$. For $x=5$, the relative error is around 10%. The proposed approximation has a practical use, because x lies in the above interval in most situations.

Substituting Eq. (5) into Eq. (2) gives

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = 0.721\frac{Z}{\beta}\left(\frac{R}{E}\right)^{0.924} T^{1.924}\, e^{-\frac{E}{RT}} \tag{6}$$

If we multiply both sides of Eq. (6) by $(1-\alpha)^n$, the following relationship is obtained:

$$\frac{(1-\alpha)^n-(1-\alpha)}{1-n} = 0.721\,\beta^{-1}\left(\frac{R}{E}\right)^{0.924}\frac{d\alpha}{dt}\,T^{1.924} \tag{7}$$

Hence, for two certain conversions, α_1 and α_2, we can write:

$$\frac{(1-\alpha_1)^n-(1-\alpha_1)}{(1-\alpha_2)^n-(1-\alpha_2)} = \frac{\left(\frac{d\alpha}{dt}\right)_1}{\left(\frac{d\alpha}{dt}\right)_2}\left(\frac{T_1}{T_2}\right)^{1.924} \tag{8}$$

In succession, taking $\alpha_1 = 0.25$ and $\alpha_2 = 0.75$, relationship (8) can be written as follows:

$$\frac{0.75^n-0.75}{0.25^n-0.25} = \frac{\left(\frac{d\alpha}{dt}\right)_1}{\left(\frac{d\alpha}{dt}\right)_2}\left(\frac{T_1}{T_2}\right)^{1.924} \tag{9}$$

Let us designate

$$B(n) = \frac{0.75^n-0.75}{0.25^n-0.25} \tag{10}$$

The values of function $B(n)$ as a function of n are listed in Table 2.

The procedure is as follows: we evaluate $(d\alpha/dt)_1$ and T_1 corresponding to $\alpha_1 = 0.25$ (25%), and $(d\alpha/dt)_2$ and T_2 for $\alpha_2 = 0.75$ (75%). With these values, we calculate the right-hand side of Eq. (9). The value obtained is $B(n)$. From Table 2, we determine the values corresponding to n, with eventually a linear interpolation.

The method described above will be exemplified on a mechanism of Kolmogorov, Erofeev, Kazeev, Avrami and Mampel (abbreviated KEKAM) type [3].

Table 2 Values of function $B(n)$ as against values of n

n	$B(n)$	n	$B(n)$
0.0	0.333	1.8	0.920
0.1	0.357	1.9	0.960
0.2	0.382	2.0	1.000
0.3	0.408	2.1	1.040
0.4	0.436	2.2	1.081
0.5	0.464	2.3	1.121
0.6	0.494	2.4	1.161
0.7	0.524	2.5	1.202
0.8	0.556	2.6	1.242
0.9	0.589	2.7	1.282
1.0	0.623	2.8	1.322
1.1	0.657	2.9	1.361
1.2	0.693	3.0	1.400
1.3	0.729	3.1	1.439
1.4	0.766	3.2	1.477
1.5	0.804	3.3	1.515
1.6	0.842	3.4	1.552
1.7	0.881	3.5	1.588

In this case:

$$\frac{d\alpha}{dt} = Z\exp\left(-\frac{E}{RT}\right)(1-\alpha)[-\ln(1-\alpha)]^{1-\frac{1}{m}} \tag{11}$$

At a constant heating rate, integration of Eq. (11) gives

$$m[-\ln 1-\alpha)]^{\frac{1}{m}} = \frac{ZE}{R}p(x)$$

As shown before, we have

$$B = \frac{(1-\alpha_1)\ln(1-\alpha_1)}{(1-\alpha_2)\ln(1-\alpha_2)} = \frac{\left(\frac{d\alpha}{dt}\right)_1}{\left(\frac{d\alpha}{dt}\right)_2}\left(\frac{T_1}{T_2}\right)^{1.924} \tag{12}$$

Relationship (12) shows that B does not depend on the parameter m in Eq. (11). This means that B indicates only the validity of kinetics of KEKAM type.

When $\alpha_1 = 0.25$ and $\alpha_2 = 0.75$, we have

$$B = \frac{0.75\ln 0.75}{0.25\ln 0.25} = 0.623 \tag{13}$$

It is observed that this value of B is identical with that obtained for reaction order $n=1$:

$$\lim_{n\to 1}\frac{0.75^n-0.75}{0.25^n-0.25} = \frac{0.75\ln 0.75}{0.25\ln 0.25} = 0.623$$

The conclusion is that the B value of 0.623 can be assigned either to the n^{th}-order model ($n=1$) or to a model of KEKAM type, indifferently of the pair of values for α_1 and α_2.

c) Three-point method

This method is suggested by a Gorbachev's paper [3]. We consider two arbitrary "points" in the TG curve: α_1, T_1, $(d\alpha/dt)_1$ and α_2, T_2, $(d\alpha/dt)_2$. The harmonic mean of T_1 and T_2 is given by

$$T_{\text{harm}} = \frac{2T_1T_2}{T_1+T_2}$$

In the thermal curve, the values α_{harm} and $(d\alpha/dt)_{\text{harm}}$ correspond to the T_{harm} value.

From Eq. (1), we can write

$$\frac{\left(\frac{d\alpha}{dt}\right)^2_{\text{harm}}}{\left(\frac{d\alpha}{dt}\right)_1\left(\frac{d\alpha}{dt}\right)_2} = \left[\frac{(1-\alpha_{\text{harm}})^2}{(1-\alpha_1)(1-\alpha_2)}\right]^n \tag{14}$$

Gorbachev applied this method for the model of KEKAM type, imposing that one of the two temperatures (T_1 or T_2) is $T_{\max}$ (temperature corresponding to the maximum rate), but this fact is not essential in the demonstration of relation (14).

Equation (14) is an exponential one, which allows evaluation of n. Finally, to diminish the effect of experimental error up to the n value, it is necessary to choose temperatures T_1 and T_2 so that the ratio $(1-\alpha_{\text{harm}})^2/[(1-\alpha_1)(1-\alpha_2)]$ be as different as possible from 1.

Conclusions

Three fast methods for determination of the reaction order n have been discussed. The proposed two-point method has been applied to the model of KEKAM type. For all these models, indifferently of the m values from Eq. (11), we found the same value for B, namely 0.623. This value is identical with the value corresponding to a reaction order of 1.

This fact shows that the fast methods cannot elucidate the mechanism, but they can help in the rapid derivation of apparent kinetic parameters n and E.

References

1 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.

2 H. H. Horowitz and G. Metzger, Anal. Chem., 35 (1963) 1464.

3 V. M. Gorbachev, J. Thermal Anal., 13 (1978) 509.

4 G. I. Senum and R. T. Yang, J. Thermal Anal., 11 (1977) 445.

5 G. Gyulai and E. J. Greenhow, Thermochim. Acta, 6 (1973) 254.

6 V. M. Gorbachev, J. Thermal Anal., 27 (1983) 151.

7 J. H. Flynn and L. A. Wall, J. Res. Nat. Bur. Standards, 70 A (1966) 487.

Zusammenfassung — Es wurden drei Methoden zur Schnellbestimmung von Reaktionsordnungen ausgewertet: eine Einpunktmethode von Kissinger, Horowitz und Metzger, eine Zweipunktmethode und eine Dreipunktmethode nach einer Anregung von Gorbachev. Mittels dieser Methoden kann man zwar nicht den Reaktionsmechanismus bestimmen, wohl aber eine schnelle Bestimmung der kinetischen Scheinparameter n und E durchführen.

Резюме — Обсуждены три быстрых метода определения порядка реакции: метод единственной точки, предложенный Киссинджером, Горовиц и Метцегером, исходный метод двух точек и метод трех точек, предложенный Горбачевым. Все эти методы не могут объяснить механизм реакции, но могут помочь быстро вывести кажущиеся кинетические параметры n и E.