

CALCULATION METHOD BASED ON DTG CURVE FOR EVALUATION OF ACTIVATION ENERGY

J. GYÖRE and M. ECET

Ministry of the Interior, Budapest, Hungary

Authors have pointed out three calculation methods based on the weight loss rate of the sample to discuss and to compare them by means of describing kinetically the thermal decomposition of malonic acid. Values of E_A calculated by different methods are well comparable. The method based on the calibrated DTG curve measured by the Derivatograph leads to reliable results and it seems to be convenient for the calculation of E_A of transformations involving weight changes.

Methods of thermal analysis have developed rapidly during the last two decades and have found widespread practical application. Thermoanalytical methods are nowadays important tools in research and routine analysis [1].

It is also a well-known fact that, parallel with the development of thermoanalytical methods, calculation methods have been prepared which are convenient for the determination of kinetic parameters.

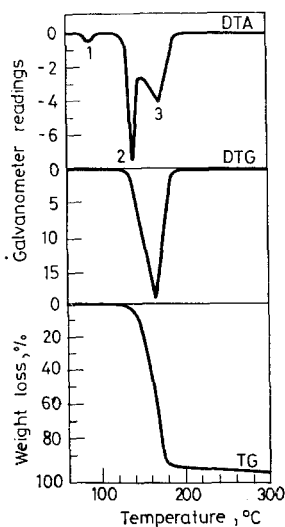


Fig. 1. Thermal decomposition of malonic acid

The kinetic calculation methods based on thermoanalytical measurements can be divided into three main groups:

1. Methods based on thermogravimetric (TG) curves.
2. Methods based on differential thermoanalytical (DTA) curves.
3. Methods based on the modifications of thermoanalytical curves due to different heating rates.

The literature also mentions combinations of the fundamental methods.

Numerous attempts have been made to prepare calculation methods based on the rate of weight loss of a sample, that is to say the derivative function of the TG curve.

There are several possibilities for the preparation of the weight loss curve. We have pointed out three methods to discuss them in detail and to compare them on the example of the kinetics of the thermal decomposition of malonic acid.

We should like to show that the DTG curve obtained with the Derivatograph is suitable for the calculation of kinetic parameters.

Production of the rate function by the construction method of Wiedemann et al. [2]

Wiedemann et al. start from the Arrhenius equation:

$$k = Z \cdot \exp \frac{E_A}{RT}$$

where k is the rate constant.

They state that the relationship is also true in the form:

$$k = f(\alpha) \frac{d\alpha}{dt}$$

For a decomposition reaction of the n th order, $f(\alpha)$ is equal to $(1-\alpha)^n$. The reaction factor is proportional to the weight loss of the sample, α being unity in the case of complete decomposition. The term $\frac{d\alpha}{dt}$ represents the rate of decom-

position of the sample; its value is determined by the slope of the TG curve at individual α values. If α is inserted as a parameter (e.g. $\alpha = 0.5$), then from the relationship for k we obtain that the logarithm of $\frac{d\alpha}{dt}$ is a linear function of the reciprocal of the absolute temperature; thus if $\log \frac{d\alpha}{dt}$, obtained from the TG curve recorded at different heating rates, is plotted as a function of the reciprocal of the corresponding absolute temperature, a straight line is obtained of slope $\text{tg } \beta$.

The activation energy can be calculated from $E_A = 2.3 R \cdot \text{tg } \beta$.

Production of the rate function by the calculation method of Tang [3]

To obtain the rate function by calculation, the data in the TG curve were analysed by the differential method of Tang.

The rate of weight loss and reaction rate constant k at various temperatures are calculated from the relations

$$\frac{dw}{dt} = \frac{dw}{d\tau} \cdot \frac{d\tau}{dt}$$

$$\frac{dw}{dt} = k w_r,$$

where $\frac{dw}{dt}$ = weight loss per minute,

$\frac{dw}{d\tau}$ = weight loss per °C, and

$\frac{d\tau}{dt}$ = heating rate

The residual weight of sample, w_r , at temperature τ is obtained from the relation

$$w_r = w_d - \bar{w}$$

where \bar{w} is the weight loss at temperature τ .

The value E_A may be calculated from the slope of the plot of $\log k$ versus reciprocal absolute temperature by means of the equation

$$E_A = 2.3 R \operatorname{tg} \alpha.$$

Production of the rate function instrumentally and its use for preparation of kinetic equations [4]

It is well-known that the Derivatograph produces the rate of weight loss curve instrumentally, but its graphical construction is also possible. In the latter case slopes of the tangents at individual points of the TG curve are plotted. The instrumentally obtained values may be used instead of data prepared in different ways.

It can be seen that in the Wiedemann method the step involving the calculation of the slope at point $\alpha = 0.5$ on the TG curve corresponds to the reading on the DTG curve at the same value, and thus at this point

$$\frac{d\alpha}{dt} = \frac{dm}{dt}.$$

Thus the term $\frac{d\alpha}{dt}$, the determination of which is rather difficult and inaccurate, may be substituted by the term $\frac{dm}{dt}$ and the equation becomes $k = f(\alpha) \frac{dm}{dt}$.

The numerical value of $\frac{dm}{dt}$ can be obtained precisely by a simple reading from the calibrated DTG curve. For the calculation of the activation energy, $\log \frac{dm}{dt}$ values for identical points on the DTG curves at different heating rates are plotted against the reciprocals of the corresponding absolute temperatures. In this way a straight line is obtained of slope $\text{tg } \beta$. The activation energy may be calculated from $E_A = 2.3 R \text{ tg } \beta$.

Employment of the calculation methods in practice

The calculation methods presented above were employed on the thermal decomposition curves of malonic acid measured under different experimental conditions. Measurements were made with a MOM Paulik–Paulik–Erdey Derivatograph. The DTA and the DTG galvanometers of the instrument were calibrated [1] permitting the determination of temperature differences between the sample and the inert material, as well as the numerical values of $\frac{dm}{dt}$ which represents the rate of decomposition. The experimental conditions are listed in Table 1.

Table 1
Experimental conditions

No.	Weight of sample (mg)	Atmosphere	Sample holder	Heating rate °C min ⁻¹
1	48.0	Ar	crucible	0.8
2	48.5	Ar	poly-plate holder	1.0
3	99.0	Ar	poly-plate holder	2.9
4	465.0	Ar	poly-plate holder	3.0
5	195.0	Ar	poly-plate holder	3.3
6	94.0	air	crucible	4.0
7	191.0	air	poly-plate holder	6.1
8	450.0	Ar	poly-plate holder	7.0
9	453.0	Ar	poly-plate holder	7.3
10	94.6	Ar	poly-plate holder	7.6
11	183.0	Ar	crucible	8.0
12	192.0	air	crucible	7.9
13	188.0	air	crucible	8.4

The thermal decomposition curves of malonic acid recorded under different experimental conditions are very similar, and for this reason only curve number 3 is presented in Fig. 1.

The curves show the known decomposition of malonic acid. According to the DTA curve step one is a crystal modification, peak two indicates the melting of the malonic acid, and peak three marks the decomposition of the sample.

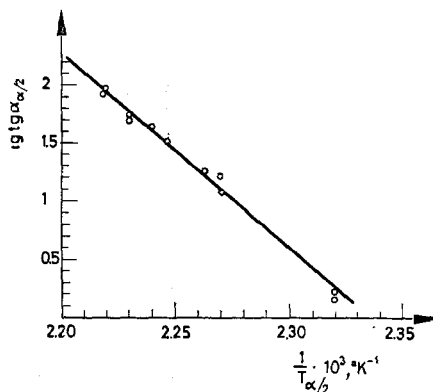


Fig. 2. Estimation of the activation energy by the Wiedemann method

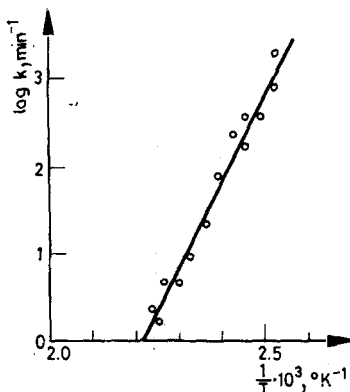


Fig. 3. Estimation of the activation energy by the Tang method

In calculating the activation energy (E_A) by the Wiedemann method we started from the curves recorded at different heating rates. After numerical calculation the logarithmic values of the slope relating to $\alpha = 0.5$ were plotted versus the values of the reciprocal absolute temperature; a straight line was obtained of slope 8.7 (Fig. 2).

In calculating the activation energy by the Tang method we started from only one measurement of the TG curve. After numerical calculation and plotting of the

logarithmic values of the rate constant k versus the values of the reciprocal absolute temperature, a straight line was obtained of slope 8.9 (Fig. 3).

In the calculation of the activation energy by means of the rate of weight loss obtained instrumentally, the starting point was again the curves recorded at different heating rates. After numerical calculation and plotting of the logarithms of the calibrated DTG values given by the Derivatograph versus the values of the reciprocal absolute temperature of the DTG peak, a straight line was obtained of slope 8.6 (Fig. 4). Values of the activation energy of the thermal decomposition of malonic acid calculated by the different methods are around 40 kcal/mole.

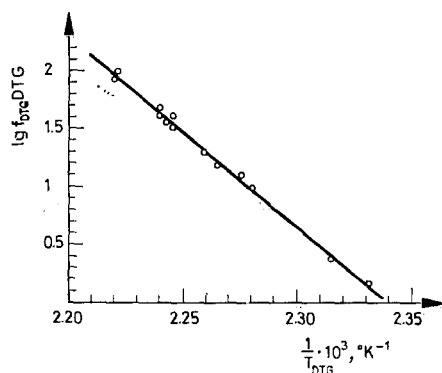


Fig. 4. Estimation of the activation energy by the method based on the calibrated DTG curve

On the basis of this investigation the methods employed could be compared. It was concluded that the thermal decomposition curves of malonic acid obtained by the Derivatograph were suitable for kinetic calculations. Values of E_A calculated by different methods are well comparable. This statement is unambiguous because the basis of all the methods is the Arrhenius equation.

The method of Wiedemann, which permits the calculation of the activation energy, requires more measurements but less numerical calculation.

Application of the method of Tang needs only one measurement, but many numerical calculations.

The method based on the calibrated DTG curve measured by the Derivatograph leads to reliable results. It needs more measurements, but less and very simple numerical calculation. The DTG curve eliminates the difficult and uncertain construction of rates of weight loss, and reduces numerical calculation. The method seems to be convenient for the calculation of the activation energies of transformations involving weight changes.

The accuracy of data is strongly influenced by temperature readings in all the cases presented. They have the advantage that the reaction mechanism need not be known.

References

1. G. LIPTAY (ed.), Atlas of Thermoanalytical Curves, Vol. 1, Heyden and Son Ltd., London, Akadémiai Kiadó, Budapest, 1971.
2. H. G. WIEDEMANN, A. V. TETS and H. P. VAUGHAN, Proceedings of the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, February 21, 1966.
3. W. K. TANG, U. S. Forest Serv. Res. Pap., FPL 71 (1967).
4. J. GYÖRE and M. ECET, J. Thermal Anal., 2 (1970) 397.

RÉSUMÉ — On étudie trois méthodes de calcul reposant sur la vitesse de la perte de poids d'un échantillon dans le but de les discuter et de les comparer à l'aide de la description cinétique de la décomposition thermique. Les valeurs de E_A calculées par ces différentes méthodes sont effectivement comparables. La méthode qui utilise la courbe TGD calibrée enregistrée sur un "Derivatograph" conduit à des résultats plausibles et semble convenir au calcul des valeurs de E_A pour les transformations s'effectuant avec un changement de poids.

ZUSAMMENFASSUNG — Es werden drei auf die Geschwindigkeit des Gewichtsverlustes der Probe basierenden Rechnungsmethoden zwecks Diskussion und Vergleich mit Hilfe der kinetischen Behandlung der thermischen Zersetzung der Malonsäure besprochen. Die mit verschiedenen Methoden gerechneten E_A Werte sind gut vergleichbar. Die auf der mit dem Derivatographen gemessenen kalibrierten DTG Kurve beruhende Methode führt zu verlässlichen Resultaten und scheint zur Errechnung der E_A Werte von mit Gewichtsveränderung einhergehenden Umwandlungen geeignet zu sein.

Резюме — Дано обсуждение и сравнение трех методов расчета, основанного на скорости потери веса образца для кинетического описания термораспада малиновой кислоты. Величины E_A , рассчитанные различными методами, хорошо сравнимы между собой. Метод, основанный на калиброванной кривой ДТГ, измеренной на дериватографе, приводит к надежным результатам и представляется подходящим для расчета величин E_A превращений, сопровождающихся изменением веса.