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# THERMOGRAVIMETRY. GENERALIZATION OF REICH'S METHOD

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A new method is proposed for the determination of kinetic parameters, where Reich's method is a special case. This method involves a knowledge of the values of the weight loss, the temperature, the rate of weight loss and the derivative of the rate of weight loss, corresponding to a certain point in the TG curve. The findings are in good agreement with those of Reich's method.

Reich's method [1] belongs to the group of differential methods. The advantages and disadvantages of these types of methods have been discussed previously [2].

Roughly speaking, Reich's method involves the measurement of the $w$, $\mathrm{d}w/\mathrm{d}t$, $T$ and $\mathrm{d}T/\mathrm{d}t$ values corresponding to the inflexion point in the integral curve TG.

This method becomes difficult, or impossible, in certain circumstances. Such cases are as follows:

1. Due to the imperfect evolution of gases from a sample, the DTG curve shows a "strong oscillation" in the maximum region, which often makes difficult the measurement of the four values.
2. The DTG peak is very flattened. As a result, the identification of the inflexion point is difficult.
3. The values corresponding to the inflexion point can be strongly affected when a second process overlaps, and therefore the obtained values of the kinetic parameters will be inaccurate.
4. For the peaks corresponding to processes with changing mechanisms, the four values relating to the inflexion point will not be able to characterize the entire process, but only a certain point of it. Incomplete information is obtained, the rest of the region remaining "unexplored".

This paper deals with a generalization of Reich's method, which allows elimination of the above disadvantages.

Let us take into consideration the kinetic equation:

$$-\frac{\mathrm{d}w}{\mathrm{d}t} = Ze^{-\frac{E}{RT}}w^{n} \tag{1}$$

the notations being the usually ones. By differentation of Eq. (1) we obtain:

$$\frac{\mathrm{d}^2w}{\mathrm{d}t^2} = \frac{E}{RT^2}\frac{\mathrm{d}T}{\mathrm{d}t}\frac{\mathrm{d}w}{\mathrm{d}t} + \frac{n}{w}\left(\frac{\mathrm{d}w}{\mathrm{d}t}\right)^2 \tag{2}$$

The above relation can be written as follows:

$$n = \frac{A}{R}E + B \tag{3}$$

where:

$$A = -\frac{w\dfrac{\mathrm{d}T}{\mathrm{d}t}}{\dfrac{\mathrm{d}w}{\mathrm{d}t}T^2}\,;\; B = \frac{w}{\left(\dfrac{\mathrm{d}w}{\mathrm{d}t}\right)^2}\,\frac{\mathrm{d}^2w}{\mathrm{d}t^2}\,.$$

For a certain point $w_j$, the quantities $A$ and $B$ have particular values $A_j$ and $B_j$, so we can write:

$$n = \frac{A_j}{R}E + B_j \tag{4}$$

It may be noted that $A_j$ is always positive $\left(\text{presuming that } \frac{\mathrm{d}T}{\mathrm{d}t} > 0\right)$ while $B_j$ is negative, if $w_j$ is above the inflexion point, and $B_j$ is positive when $w_j$ is below this point.

If logarithms of Eq. (1) are taken, then with consideration of relation (4) we may write:

$$\ln\left(-\frac{\mathrm{d}w}{\mathrm{d}t}\right) - B_j \ln w = \ln Z + \frac{E}{R}\left(A_j \ln w - \frac{1}{T}\right) \tag{5}$$

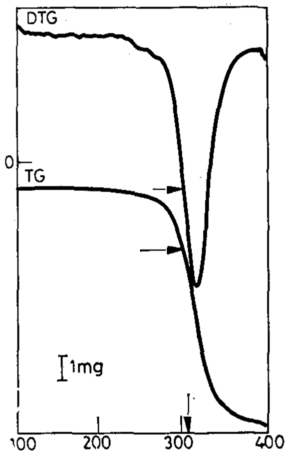

Fig. 1. Thermoanalytical curves of a mixture of poly(acrylonitrile) + poly(vinyl acetate)

In this case the plot $\ln\left(-\dfrac{dw}{dt}\right) - B_j \ln w$ as a function of $A_j \ln w - \dfrac{1}{T}$ should give a straight line whose slope is $E/R$. The magnitude of the reaction order, $n$, can be obtained from Eq. (4).

Thus, as one may expect, relation (5) reduces to the expression obtained by Reich (1), if $w_j$ is the inflexion point, because here $B_j = 0$.

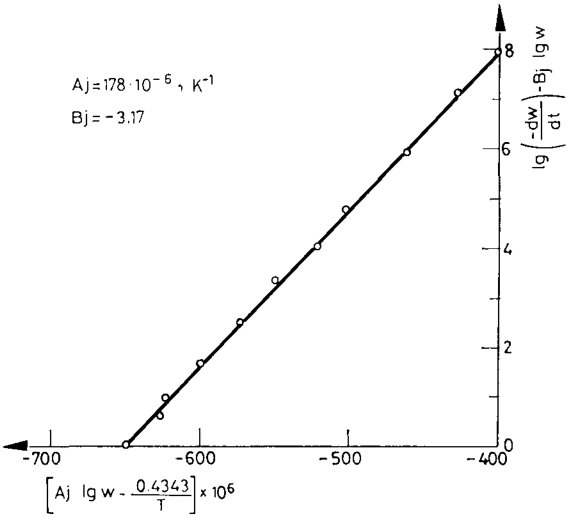

Fig. 2. $\left[\log\left(-\dfrac{dw}{dt}\right) - B_j \log w\right]$ *versus* $\left[A_j \log w - \dfrac{0.4343}{T}\right]$

It is necessary to mention that, although accurate measurement of the second derivative is difficult in the case of the apparatus which gives the DTG curve, this measurement is frequently facilitated, at least for certain regions of the process.

In order to illustrate the method proposed, we have investigated the curves shown in Fig. 1. The arrows in Fig. 1 point to $\left(\dfrac{dw}{dt}\right)_j$ and $T_j$ according to the chosen $w_j$ point, whose second derivative was measured.

The kinetic parameters $n$ and $E$ were determined by both Reich's method and the generalization of this method (Eq. 5).

Figure 2 shows solely the plot corresponding to Eq. (5).

The values obtained were as follows:

$$n = 1.7;\ E = 55 \text{ kcal/mole}$$

$$n = 1.7;\ E = 54 \text{ kcal/mole}$$

by the Reich and the generalization method, respectively. These findings are in very good agreement.

We should mention that relation (2) has been used in the past by several authors [3, 4], but in a different way.

## References

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