

KINETIC ANALYSIS OF THERMOGRAVIMETRIC DATA, VI
SOME PROBLEMS OF DERIVING KINETIC PARAMETERS FROM TG CURVES

J. ZSAKÓ

Faculty of Chemistry, Babeş-Bolyai University, Cluj, Rumania

The basic hypotheses of methods used for deriving kinetic parameters from TG data are discussed. The erroneous character of the methods which use more than a single TG curve is shown by comparing the shapes of ideal and real TG curves. The correctness of three integral methods is tested on ideal TG curves. The physical significance of the kinetic parameters and their correlation are discussed.

Thermal decompositions of solids are very complicated processes, involving the decomposition of one chemical compound and the formation of others, the destruction of the initial crystal lattice, the formation of crystallization centres and their growth, the adsorption and desorption of gaseous products, the diffusion of the gases, heat transfer, and many other elementary processes. The overall process is influenced by many procedural variables, such as the heating rate, the heat conductivities of the furnace atmosphere, the sample and the sampler holder, the static or dynamic character of the atmosphere, the physical state of the sample, particle size, compactness, sample weight, etc.

Such a complicated kinetic process cannot be described of course by means of a general equation. This is why in the theoretical treatment of thermal decomposition two main lines have been chosen. The first, used especially for deriving kinetic equations for isothermal conditions, starts from a theoretical model of the process, while the second uses the formal kinetics of homogeneous reactions. In deriving kinetic parameters from TG curves recorded under dynamic temperature conditions, all the methods are based upon relations taken from the formal kinetics of homogeneous reactions.

Basic hypotheses of the kinetic methods

Reaction rate is generally defined as the derivative of conversion. In TG measurements conversion means the ratio of actual weight loss to total weight loss corresponding to a given stage of the reaction:

$$\alpha = \frac{W_0 - W}{W_0 - W_\infty} \quad (1)$$

where W , W_0 and W_∞ are the actual, initial and final weights of the sample, respectively.

In order to obtain the kinetic equation of the thermal decomposition, several more or less justified hypotheses are made.

1. Reaction rate is assumed to be a unique function of conversion and temperature. Formally this is equivalent to

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \cdot \Phi(\alpha, T), \quad (2)$$

2. Function $\Phi(\alpha, T)$ is assumed to be equal to unity, i.e.

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha). \quad (3)$$

These first two hypotheses considerably reduce the general character of kinetic equations, since under isothermal conditions empirical equations of the following form are often found:

$$\frac{d\alpha}{dt} = k \cdot t^m \cdot f(\alpha) \quad (4)$$

where the exponent m may be a function of α . This shows the rate of reaction to be a complicated function of at least conversion, temperature and time.

3. The conversion function $f(\alpha)$ is assumed to be of the form

$$f(\alpha) = \alpha^a (1 - \alpha)^b. \quad (5)$$

Relations of this type have been derived for isothermal conditions from both theoretical models and experimental data [1]. The exponents a and b are frequently called homogeneity factors.

4. The homogeneity factor a is assumed to be zero. In this assumption we have a formal analogy with homogeneous reactions. The homogeneity factor b can formally be called reaction order, and the function $k(T)$ can formally be considered to be the rate constant.

5. The temperature-dependence of the formal rate constant is assumed to obey an Arrhenius-type law:

$$k = Z \cdot T^m \cdot e^{-E/RT} \quad (6)$$

where Z is called the frequency factor, and E the activation energy.

6. The exponent m in Eq. (6) is assumed to be zero.

On the basis of the above 6 hypotheses one obtains the following basic relation

$$\frac{d\alpha}{dt} = Z \cdot e^{-E/RT} \cdot (1 - \alpha)^b \quad (7)$$

which is frequently written without mentioning its formal, hypothetical character.

7. Under dynamic temperature conditions a suitable temperature program is used, i.e. the temperature becomes a unique function of time, expressed by

$$T = \phi(t) \text{ or } t = \Psi(T). \quad (8)$$

In fact only the furnace temperature obeys this program function, but in working out calculation techniques, the sample temperature is generally assumed to be equal to the furnace temperature. Thus, the differential of time may be expressed as

$$dt = \Psi'(T) dT \quad (9)$$

and Eq. (7) takes the form

$$\frac{d\alpha}{(1-\alpha)^b} = \Psi'(T) \cdot Z \cdot e^{-E/RT} dT. \quad (10)$$

This relation is frequently written in a more general form:

$$\frac{d\alpha}{f(\alpha)} = \Psi'(T) \cdot Z e^{-E/RT} dT \quad (11)$$

which formally does not need hypotheses 3 and 4, but almost always in practice only Eq. (10) is used.

By integrating Eq. (10) or (11) one obtains the equation of the TG curve. The integration possibilities depend upon the form of the program function $\Psi(T)$. Eq. (10) can easily be integrated if a hyperbolic temperature program is used, i.e. if the reciprocal absolute temperature is varied linearly [2-4]. However, a linear temperature program is generally used, i.e. a constant heating rate q is used. In this case Eq. (10) becomes:

$$\frac{d\alpha}{(1-\alpha)^b} = \frac{Z}{q} \cdot e^{-E/RT} dT \quad (12)$$

and the right side of it cannot be integrated in finite form.

On the basis of Eq. (12) a large number of calculation techniques have been proposed, and many papers have dealt with their classification too [5-7]. We consider that there are two basic types among these methods, which we shall call one-curve and many-curve methods. The first are based only upon the above 7 hypotheses and aim to derive kinetic parameters from a single TG curve. The latter derive these parameters from several TG curves, recorded under different conditions.

8. The many-curve methods are implicitly based on the following hypothesis: Kinetic parameters b , Z and E characterize a given reaction or substance, irrespective of procedural details, and not only the given TG curve recorded under the given conditions.

The shapes of ideal and real TG curves

If the substitution $x = E/RT$ is performed in Eq. (12) one obtains

$$\frac{d\alpha}{(1-\alpha)^b} = \frac{ZE}{Rq} \frac{e^{-x}}{x^2} dx. \quad (13)$$

The formal integration of this equation gives

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^b} = \frac{ZE}{Rq} \int_{\infty}^x \frac{e^{-x}}{x^2} dx = \frac{ZE}{Rq} p(x) \quad (14)$$

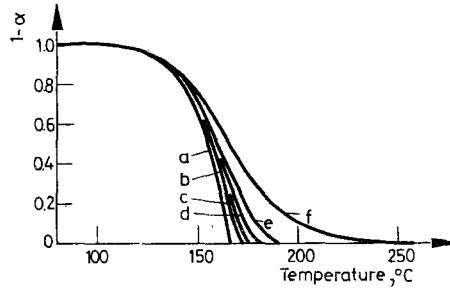


Fig. 1. Influence of the formal reaction order b upon the shapes of TG curves. $E = 24$ kcal/mole; $Z = 10^{10} \text{ s}^{-1}$; $q = 10^\circ/\text{min}$. Reaction order: a) 0; b) 1/3; c) 1/2; d) 2/3; e) 1; f) 2

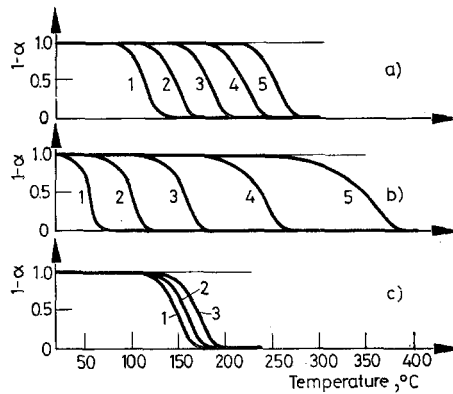


Fig. 2. Influence of E , Z and q upon the shapes of TG curves. a) $Z = 10^{10} \text{ s}^{-1}$, $q = 10^\circ/\text{min}$, $b = 2/3$. E : 1. 20; 2. 22; 3. 24; 4. 26; 5. 28 kcal/mole; b) $E = 24$ kcal/mole, $q = 10^\circ/\text{min}$, $b = 2/3$. Z : 1. 10^{13} ; 2. 10^{12} ; 3. 10^{10} ; 4. 10^8 ; 5. 10^6 s^{-1} ; c) $E = 24$ kcal/mole, $Z = 10^{10} \text{ s}^{-1}$, $b = 2/3$. q : 1. $5^\circ/\text{min}$; 2. $10^\circ/\text{min}$; 3. $20^\circ/\text{min}$

Numerical values of the exponential integral $p(x)$ are given in appropriate tables, and this enables us to construct "ideal" TG curves in order to study influence of kinetic parameters upon the shapes of TG curves [8]. As seen from Fig. 1, the first sections of the TG curves are practically uninfluenced by apparent reaction order, whereas the later sections are very sensitive to this parameter. Increase of the activation energy leads to an almost parallel shift of the TG curves towards higher temperatures, whereas increasing frequency factor Z shifts the curves towards lower temperatures and also increases their slopes (Fig. 2). Increasing heating rate shifts the curves towards higher temperatures, without changing their shapes.

In many-curve methods curves obtained at different heating rates are frequently compared, by assuming their parallel shift with increasing heating rate. In fact the influence of the heating rate is different. As seen from (Fig. 3), the shift is not parallel and with increasing heating rate the slope of the curve decreases [9]. This

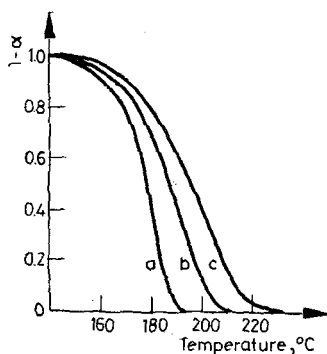


Fig. 3. Conversion-temperature curves of $[\text{Co}(\text{DH})_2(\text{p-toluidine})_2]$ NCS calculated for the release of a p-toluidine molecule. q : a) $5^\circ/\text{min}$; b) $10^\circ/\text{min}$; c) $15^\circ/\text{min}$

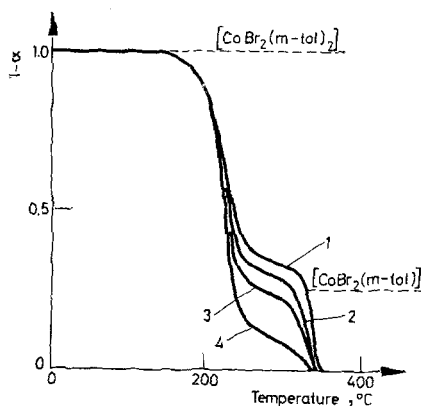


Fig. 4. Influence of sample weight upon the conversion-temperature curve calculated for $[\text{CoBr}_2(\text{m-toluidine})_{2/3}]$ as intermediate; $q = 10^\circ/\text{min}$. Sample weight: 1. 100 mg; 2. 75 mg; 3. 50 mg; 4. 25 mg

means the decrease of the frequency factor Z . According to literature data [e.g. 10–13] and our own observations [9, 14], this decrease of Z is associated with a decrease of the apparent activation energy. It may be concluded that all the many-curve methods based upon the use of TG curves recorded with different heating rates are illusory and worthless. This is true also in the case of Doyle's method [15] based upon the comparison of TG curves recorded under isothermal conditions and under dynamic temperature conditions [16] as well as for its improved form, proposed by ourselves [17].

A similar method proposed by Chatterjee [18] recommends the derivation of kinetic parameters from TG curves recorded with the same heating rate, but by using different sample weights. The value of this method becomes apparent if Fig. 4 is considered. It can be seen that the real shape of conversion–temperature curves depends sensibly on the sample weight [19].

It is obvious that hypothesis 8 is not true and all many-curve methods are erroneous. The kinetic parameters b , Z and E do not characterize a given chemical reaction or a given substance, but a particular overall process. Their numerical value depends on procedural variables such as heating rate, sample weight, particle size, compactness, material and geometry of the sample holder, nature and static or dynamic character of the atmosphere, etc.

As regards the physical meaning of these kinetic parameters, it must never be forgotten that the “general” equation (12) has been obtained on the basis of 7 unjustified hypotheses. Thus, they cannot have the same significance as in homogeneous kinetics. By means of the various calculation techniques we try to describe the TG curve with the help of an equation of type (14), i.e. from a given family of curves we choose a single one, which best fits the experimental curve. We may consider b , Z and E to be variational parameters, and on the basis of only the TG measurements we can tell nothing about their physical content.

Nevertheless, individual TG curves can frequently be characterized very well by means of kinetic parameters b , Z and E . Values of the kinetic parameters can be derived with the help of different differential, integral, differential-difference or special methods [5], if for this purpose only a single TG curve is used and the calculation techniques used are correct.

Comparison of several integral methods

Differential methods are often preferred, especially if DTG curves are recorded automatically. If we have only TG curves, or other conversion–temperature curves, it is recommendable to use integral methods, since the graphical determination of derivatives may introduce considerable errors.

The integral methods are of two main types. Exact methods are based upon the numerical values of the exponential integrals $p(x)$, such as Doyle’s curve fitting method [20], or our statistical method [21], which can easily be applied if a computer is available. The other type uses approximate expressions for $p(x)$, which makes possible the linearization of the TG curves and dispenses with the tiresome calculations characteristic of the “exact” methods.

The correctness of different approaches can easily be tested on “ideal” TG curves. These can be constructed by using numerical values of the exponential integral $p(x)$ and the equation

$$\log g(\alpha) = \log \frac{ZE}{Rq} + \log p(x) \quad (15)$$

obtained from (14) by taking logarithms. In Fig. 5 are given two ideal TG curves. Curve *a* corresponds to “extreme” conditions, when $\log p(x)$ has small absolute values in the temperature interval of the thermal decomposition and the approximation methods generally do not work. Curve *b* represents the “normal” conditions, most frequently met in TG practice.

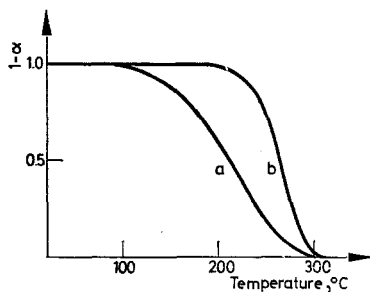


Fig. 5. Ideal TG curves. Reaction order 1. $q = 10^\circ/\text{min}$. a) $E = 10$ kcal/mole, $Z = 10^2 \text{ s}^{-1}$; b) $E = 30$ kcal/mole, $Z = 10^{10} \text{ s}^{-1}$

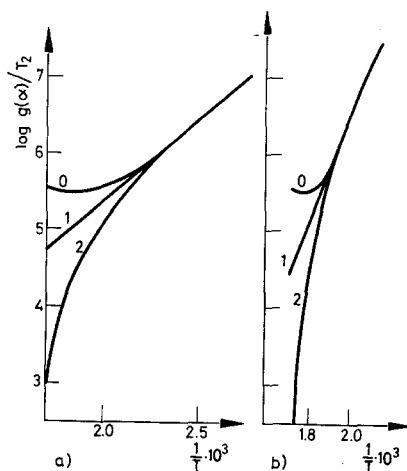


Fig. 6. Coats-Redfern's linearization of the ideal TG curves

As examples we took 3 approximation methods. Coats and Redfern's method is based on the quickly convergent asymptotic expansion of $p(x)$ which gives the relation [22]:

$$\log \frac{g(\alpha)}{T^2} = \log \frac{ZR}{qE} \left(1 - \frac{2RT}{E} \right) - \frac{E}{2.3RT}. \quad (16)$$

Since the first term of the right side of Eq. (16) is practically constant, the graphical plot of $\log [g(\alpha)/T^2]$ vs. $1/T$ must give a straight line if the correct b value is used for the calculation of $g(\alpha)$.

The second method, proposed by van Krevelen et al. [23] uses the asymptotic expansion of $e^{-E/RT}$ in the vicinity of the maximum rate temperature T_m , i.e. the

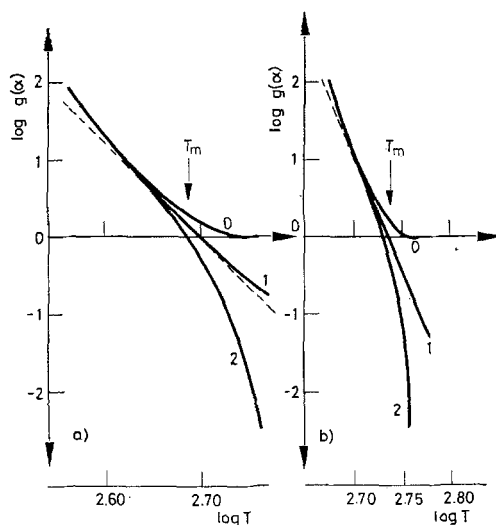


Fig. 7. van Krevelen's linearization of the ideal TG curves

inflection point of the TG curve. On the basis of the equation

$$\log g(\alpha) = \log B + \left(\frac{E}{RT_m} + 1 \right) \log T \quad (17)$$

where

$$B = \frac{Z}{q} \left(\frac{E}{RT_m} + 1 \right)^{-1} \left(\frac{0.368}{T_m} \right)^{E/RT_m}$$

the graphical plot of $\log g(\alpha)$ vs. $\log T$ should also give a straight line with the correct b value.

The third method, given by Horowitz and Metzger [24], is based on the asymptotic expansion of $1/T$ in the vicinity of the same T_m . The basic relation

$$\log g(\alpha) = \frac{E}{2.3 RT_m^2} \vartheta \quad (18)$$

where

$$\vartheta = T - T_m$$

claims $\log g(\alpha)$ to be a linear function of ϑ , i.e. of T .

It is apparent that the last two methods are contradictory, since $\log g(\alpha)$ cannot be simultaneously a linear function of $\log T$ and of T .

In Figs 6, 7 and 8 are presented the linearizations of the ideal TG curves given in Fig. 5, by using the above approximation methods and by presuming the formal reaction orders 0, 1 and 2, respectively. Coats and Redfern's method gives excellent straight lines even under extreme conditions if the correct b value is assumed. In contrast, the other two methods, especially that of Horowitz and Metzger,

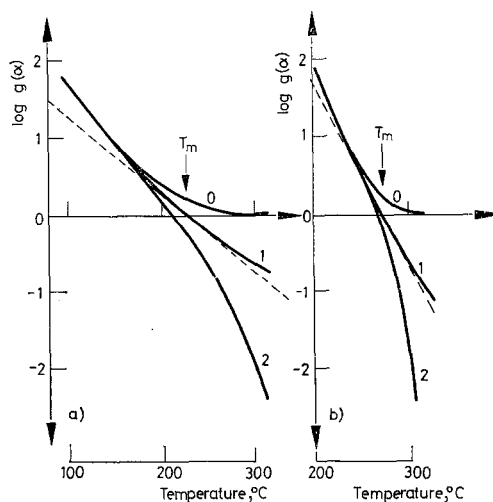


Fig. 8. Horowitz-Metzger's linearization of the ideal TG curves

do not give straight lines but curves with linear portions in the vicinity of T_m . Thus, in the determination of the apparent reaction order the criterion of the best linearity cannot be applied. Even activation energy values calculated from the slope of the linear portion of the curve obtained with the correct b value do not give the exact value. On the other hand, Coats and Redfern's method allows a good linearization and gives correct E values even under extreme conditions; this can be seen from Table 1. It is simpler than the other two methods, since the determination of T_m , which is a source of considerable errors in the other two methods, is not needed.

Table 1

Activation energy values derived from the ideal TG curves given in Fig. 5

Method	10 kcal/mole	30 kcal/mole
Coats-Redfern	9.87 (1.3%)	30.00 (0.0%)
van Krevelen	11.13 (11.3%)	31.02 (3.4%)
Horowitz-Metzger	11.92 (19.2%)	32.46 (8.2%)

The main conclusion of these tests is the clear superiority of Coats and Redfern's method. If this method gives a straight line for a given b value, the TG curve can be taken to obey Eq. (12) and the kinetic parameter values obtained by means of this method can be trusted.

The kinetic compensation effect

All changes in experimental conditions modify the kinetic parameter values. If a larger heating rate is used, the decomposition rate $d\alpha/dt$ increases. Under such conditions the role of diffusion becomes more important, especially in the last stage of the process. This is why the slope of the conversion-temperature curve decreases with increasing heating rate. In terms of kinetic parameters this means the increase of apparent reaction order b , and decrease of the frequency factor Z .

It is very interesting, that there are always parallel variations of Z and E . If Z diminishes, then E also diminishes. The former shifts the TG curve towards higher temperatures, the latter towards lower ones. Thus, we have two effects which act in opposite directions and partially compensate each other. This kinetic compensation effect can frequently be expressed by a linear relationship [25], viz.:

$$\log Z = mE + n . \quad (19)$$

This correlation between Z and E can be observed not only if the same reaction occurs under different conditions. The compensation law (19) has also been observed to operate in the case of the thermal decompositions of compounds of similar structures. Thus, a relation of this type has been found [26] in the case of the first stage (release of an amine molecule) of the thermal decompositions of a large number of $[\text{Co}(\text{DH})_2\text{Am}_2]\text{X}$ type complexes, where DH_2 is an α -dione-dioxime, Am an aromatic amine and X is Cl, Br, I or SCN.

Importance of deriving kinetic parameters

Although nothing can be said on the basis of TG data about the physical meanings of the kinetic parameters b , E and Z , we consider the derivation of these parameters from TG curves very important. They are empirical parameters characterizing the experimental TG curves. Owing to the complexity of thermal decomposition reactions, there is no chance of describing the whole process theoretically at once. This is why successive approaches are needed. Application of the formal kinetics of homogeneous reactions may be considered as a first, rough approach, which enables us to obtain quantitative characteristics of TG curves, though their significance is rather obscure.

This first approach must obviously be followed by a second one. The first steps have already been made in this direction by using for the conversion function the more general form [27]:

$$\frac{d\alpha}{dt} = k\alpha^m(1-\alpha)^n [-\ln(1-\alpha)]^p \quad (20)$$

which is suitable for describing a larger variety of TG curves than Eq. (12) and also seems to be more justified by theoretical model considerations. The corresponding $\log g(\alpha)$ values for eight functions of type (20) have been tabulated by Šatava and Škvara [28]. These authors have suggested a curve-fitting method to derive the kinetic parameters a , b , p , Z and E . By using the tabulated $\log g(\alpha)$ values, the most suitable of these eight kinetic equations can be chosen by other integral methods too, e.g. by means of our statistical method [21] or by using Coats and Redfern's method.

Their physical meanings would not become clearer by taking a larger number of kinetic parameters of course. In order to elucidate these physical meanings and to obtain information on the mechanisms of these complicated heterogeneous processes, we consider the following two tasks the most important:

1. a systematic study of the influence of procedural variables upon the kinetic parameters;
2. combination of TG, DTG and DTA measurements with other physico-chemical investigations such as X-ray analysis, mass-spectrometry, microscopic observations, electric conductivity measurements, etc.

Conclusions

1. All procedures for deriving kinetic parameters from TG data under dynamic temperature conditions are based upon a series of hypotheses which are theoretically not justified.
2. Nevertheless, many TG curves can be well characterized by means of kinetic parameters b , Z and E .
3. In order to derive kinetic parameters, only a single TG curve must be used, since all many-curve methods are erroneous.
4. If different calculation techniques are used, it is very important to test their mathematical correctness.
5. From the integral approximation methods, Coats and Redfern's method can be recommended, since it is simple and gives reliable results.
6. The kinetic parameters derived from TG curves must be considered as variational parameters, and it may not be assumed that they have the same physical meanings as in homogeneous kinetics. Their physical significance cannot be found of the basis of TG data only.
7. In the interpretation of kinetic parameters the kinetic compensation effect must always be taken in account.
8. Kinetic analysis of TG data on the basis of Eq. (11) must be considered as a first approach in the description of the kinetics of heterogeneous reactions under dynamic temperature conditions.

9. A better approach is possible if the number of formal, empirical kinetic parameters is increased.

10. In order to elucidate the physical significance of the empirical kinetic parameters, a systematic study of the influence of procedural variables and the combination of TG, DTG and DTA methods with other physico-chemical investigations is needed.

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RÉSUMÉ — On discute les hypothèses de base des méthodes utilisées pour déduire les paramètres cinétiques des données TG. Le caractère erroné des méthodes utilisant plus d'une courbe TG est mis en évidence en comparant les formes idéales et réelles des courbes TG. Le degré d'exactitude de 3 méthodes intégrales est examiné sur des courbes TG idéales. On discute la signification physique des paramètres cinétiques et leur corrélation.

ZUSAMMENFASSUNG — Die Grundhypothesen der zur Ableitung kinetischer Parameter aus TG-Daten verwendeten Methoden werden erörtert. Der fehlerhafte Charakter der Methoden, welche mehr als eine einzige TG-Kurve verwenden, wird durch den Vergleich der Formen idealer und realer TG-Kurven veranschaulicht. Die Richtigkeit dreier Integralmethoden wird an idealen TG-Kurven geprüft. Die physikalische Bedeutung kinetischer Parameter und ihre Korrelation werden erläutert.

Резюме — Обсуждены основные гипотезы методов, применяемых для выведения кинетических параметров из данных ТГ. Ошибочный характер методов, использующих более чем одну простую кривую ТГ, показан сравнением вида идеальных и реальных кривых ТГ. Проверена надежность 3-х интегральных методов на идеальных кривых. В статье обсуждены физический смысл кинетических параметров и их соотношение.