

USEFULNESS OF KINETIC PARAMETERS IN INVESTIGATIONS OF THERMAL DECOMPOSITIONS OF SOLIDS

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The theoretical curves in the coordinates α vs. time for isothermal, and α vs. temperature for non-isothermal experiments are calculated as functions of three kinetic parameters: activation energy E , pre-exponential factor A and the $g(\alpha)$ function describing the mechanism of thermal decomposition of solids. The results show that conclusions not taking into consideration all three parameters can lead to information of little value concerning the mechanism of the decomposition and kinetic calculations. A correlation between non-isothermal and isothermal experiments, important for determination of the thermal stabilities of the compounds, is impossible without a knowledge of the $g(\alpha)$ function.

Independently of the unsolved question of whether kinetic parameters have any real physical meaning, their usefulness only for the description of the kinetics of thermal decomposition of solids is still unclear. The value of the activation energy E is often regarded as a magnitude allowing conclusions to be drawn concerning the temperature-dependence of the rate of the reaction or the amount of energy required to break the bonds in the crystal structure of the decomposing solid. Further, one can find a number of papers concerning the relation between thermal stability (mainly determined as the temperature of the beginning of decomposition) and E . The aim of this paper is to present calculations which confirm the obvious (but rarely taken into consideration) fact that the activation energy itself is not a parameter describing the decomposition process.

It is well known that the relation between the progress of the reaction and time t (in isothermal experiments) or temperature T (in non isothermal runs) is described by three kinetic parameters: A (pre-exponential factor), E (activation energy) and $f(\alpha)$ (or $g(\alpha)$ in integral form), a function the form of which depends on the mechanism of the decomposition (for non-isothermal experiments there is a fourth parameter, the heating rate ϕ). It is generally assumed that increasing the activation energy shifts the beginning of the decomposition into a higher temperature range. This popular opinion causes the situation that in many publications (on the basis of the values of E) conclusions concerning the mechanism of the decomposition are drawn. The above-mentioned relationship: E vs. temperature of the beginning of the

decomposition is shown in Fig. 1, where for three constant parameters ($\phi = 10 \text{ deg min}^{-1}$, $A = 1 \cdot 10^9 \text{ min}^{-1}$, and $g(\alpha) = 1 - (1 - \alpha)^{1/3}$) curves in the coordinates α vs. T are presented. Looking at such a relationship, it is easy to conclude, for example, that bonds in a compound having an E value of $18 \text{ kcal} \cdot \text{mol}^{-1}$ are weaker than in one having an E value of $23 \text{ kcal} \cdot \text{mol}^{-1}$, because the temperature of the beginning of the decomposition is about 100 deg lower in the first case than in the second. This conclusion seems easy, but it is meaningless unless the two other kinetic parameters are identical for both of the above compounds, but this case is really unreliable. Let us take into consideration the second kinetic parameter A . Figure 2 presents the relationships α vs. T for the case when $g(\alpha)$ and the activation energy are constant ($g(\alpha) = 1 - (1 - \alpha)^{1/3}$, $E = 20 \text{ kcal} \cdot \text{mol}^{-1}$) for different A values.

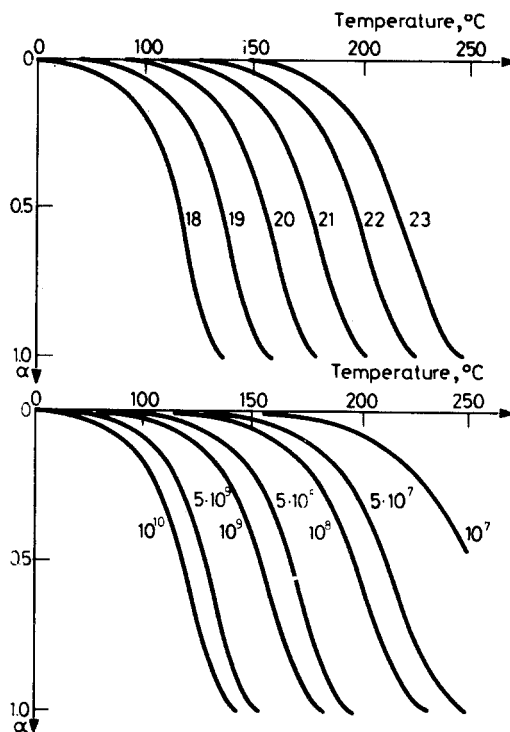


Fig. 1 The progress of the decomposition as a function of temperature and the value of E (in $\text{kcal} \cdot \text{mol}^{-1}$), A in min^{-1} .

$$A = 1 \cdot 10^9, g(\alpha) = 1 - (1 - \alpha)^{1/3}, E = 18 - 23 \text{ kcal} \cdot \text{mol}^{-1}, \phi = 10 \text{ deg} \cdot \text{min}^{-1}$$

Fig. 2 The progress of the decomposition as a function of temperature and the value of the pre-exponential factor A (in min^{-1}).

$$E = 20 \text{ kcal} \cdot \text{mol}^{-1}, g(\alpha) = 1 - (1 - \alpha)^{1/3}, A = 1 \cdot 10^7 - 1 \cdot 10^{10}, \phi = 10 \text{ deg} \cdot \text{min}^{-1}$$

It is evident that a difference of one order of magnitude, for instance $1 \cdot 10^8$ and $1 \cdot 10^9$, very often neglected in discussions, shifts these thermoanalytical curves distinctly. When determining the values of E and A from experimental results, and later using them in kinetic calculations, one must remember that such a problem belongs to the class of ill-posed mathematical problems, having no unique solution. Experimental data can be described by different sets of A and E , which, calculated on the basis of different mathematical approximations, characterize the mathematical method used rather than the reaction itself [1].

The relationship between E and $\ln A$ known in the literature as the "compensation effect" is one of the most controversial problems in the field of the thermal decomposition of solids. Considering the reliability of the compensation effect, it is necessary to bear in mind that this relationship can have a physical meaning only when, under different experimental conditions, the mechanism of the decomposition is constant, but this is not always true. Change of the atmosphere during CaCO_3 decomposition alters the mechanism of the reaction; under different experimental conditions, different form of the $g(\alpha)$ function best describe the process [2]. This leads to the "false compensation effect" described by Agrawal [3], considering kinetic results on CaCO_3 decomposition published by Zsakó [4].

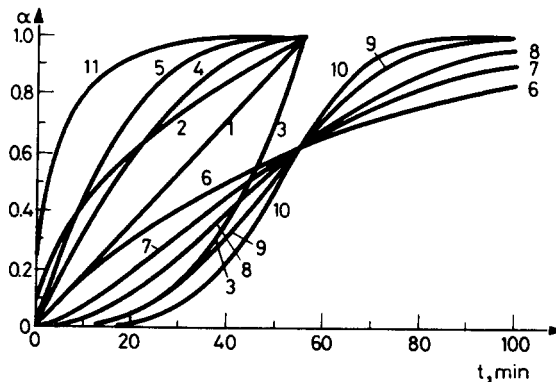


Fig. 3 Theoretical isothermal relationship α - time for the particular $g(\alpha)$ functions. $E = 20$ kcal mol^{-1} , $A = 1 \cdot 10^7$ min^{-1} , $T = 100$ $^{\circ}\text{C}$.

$g(\alpha)$	
1. α	6. $-\ln(1-\alpha)$
2. α^2	7. $[-\ln(1-\alpha)]^{2/3}$
3. $\alpha^{1/3}$	8. $[-\ln(1-\alpha)]^{1/2}$
4. $1-(1-\alpha)^{1/2}$	9. $[-\ln(1-\alpha)]^{1/3}$
5. $1-(1-\alpha)^{1/3}$	10. $[-\ln(1-\alpha)]^{1/4}$
	11. $[1-(1-\alpha)^{1/3}]^2$

Using only the two kinetic parameters, A and E , and not introducing the third one the $g(\alpha)$ function into our considerations, one cannot make any useful and reliable conclusions about the kinetics of the thermal decomposition. These remarks are explained by the curves shown in Figs 3 and 4. A change in the form of the $g(\alpha)$ function can very distinctly change the course of thermoanalytical curves. In Fig. 3, the theoretical isothermal relationships α vs. time are given for the case, when A and E are constant. From these plots it is evident that, without a knowledge of the $g(\alpha)$ form, one can say nothing about "thermal stability" or the range of the decomposition temperatures, even if the compounds under consideration have identical kinetic parameters A and E .

The same situations for non-isothermal conditions is shown in Fig. 4, where for three different equations (describing a reaction controlled by the rate of diffusion, nucleation, and shift of the reactant – product boundary) the curves in the coordinates α vs. T are presented. There are evident differences between the temperatures of the beginning and the end of the decomposition, despite A and E being identical. These curves, considered without a knowledge of the $g(\alpha)$ function, can lead to unreliable conclusions.

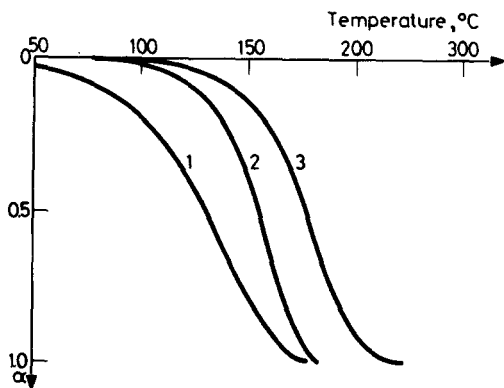


Fig. 4 The relationship $\alpha - T$ as a function of the $g(\alpha)$ form for non-isothermal conditions (heating rate 10 K min^{-1}), E and A are const.

$$E = 20 \text{ kcal} \cdot \text{mol}^{-1}, A = 1 \cdot 10^9 \text{ min}^{-1}, \phi = 10 \text{ deg} \cdot \text{min}^{-1}$$

$$1. [-(1-\alpha)^{1/3}]^2$$

$$2. -\ln(1-\alpha)$$

$$3. 1-(1-\alpha)^{1/2}$$

The application of all three kinetic parameters is very important for correlating isothermal and rising temperature experiments. Two different compounds having the same activation energy, or even more also having identical

temperatures of the beginning of the decomposition in non-isothermal experiments, can show very different α vs. time relationships in isothermal runs, depending on the form of the $g(\alpha)$ function. Using the method of calculation described in detail in [5], the author calculated the course of the theoretical TA curves as functions of E , A and $g(\alpha)$ for dynamic and isothermal experiments (of course, the heating rate or the temperature of decomposition was taken into consideration in both cases, respectively). The results of these calculations will be published later [6]; in this paper, only the most characteristic curves are shown.

If the beginning of the decomposition for compounds having the same reaction mechanism takes place at the same temperature under non-isothermal conditions, then during an isothermal run the progress of the reaction, after an arbitrary chosen period of time, is inversely proportional to the activation energy. This is shown in Fig. 5, where isothermal curves are presented for the case when, under non-isothermal conditions (heating rate 10 deg min^{-1}), the beginning of decomposition ($\alpha = 0.01$) is at a temperature of 130° in each case. The "thermal stability" determined from non-isothermal experiments is always the same (130°), but in isothermal runs the progress of decomposition is greater (after a constant time) when the E value is smaller.

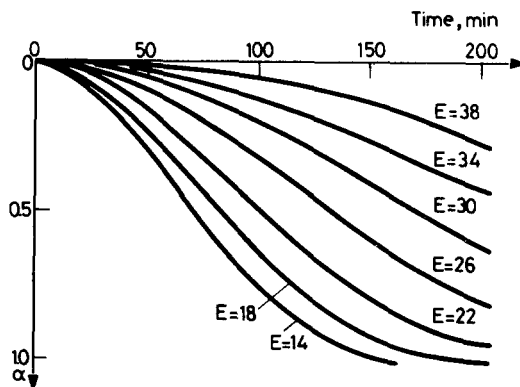


Fig. 5 Isothermal relationship α - time as a function of E value. Temperature of the beginning of the decomposition ($\alpha = 0.01$) was for all curves the same -130°C at $0 = 10 \text{ deg min}^{-1}$.

$$g(\alpha) = [-\ln(1-\alpha)]^{1/2}, T = 100^\circ\text{C},$$

Also for the case when E is constant, but a different $g(\alpha)$ function describes the mechanism, a comparison of the results from non-isothermal runs can give dubious conclusions. In Fig. 6 are presented curves for the case

when E and the "thermal stability" are identical (for each curve $\alpha = 0.01$ at 100° and the heating rate is 10 deg min^{-1}), but of course the curves differ in shape for other $g(\alpha)$ equations. Under isothermal conditions (Fig. 7) these curves show significant differences in the loss of weight after, say, 50 minutes of decomposition at 100° . The situation becomes even more

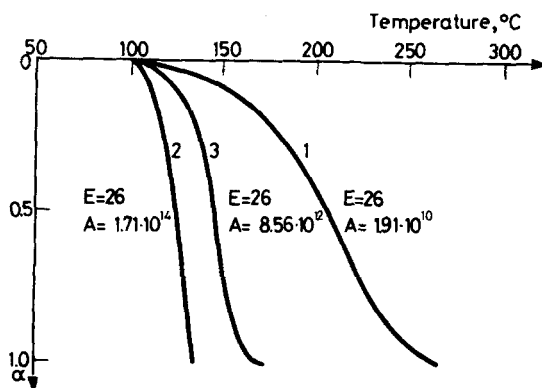


Fig. 6 The relationship $\alpha - T$ for non-isothermal conditions (heating rate 10 deg min^{-1}) for the case when E (26 kcal mol^{-1}) and "thermal stability" ($\alpha = 0.01$ at 100°C) are constant.

1. $[1 - (1 - \alpha)^{1/3}]^2$
2. $[-\ln(1 - \alpha)]^{1/2}$
3. $1 - (1 - \alpha)^{1/2}$

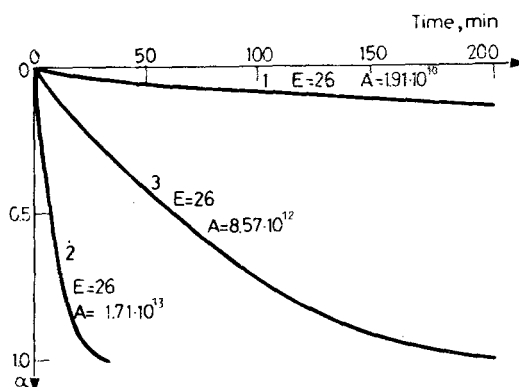


Fig. 7 Isothermal relationship $\alpha - \text{time}$ for the curves presented on Fig. 6

1. $[1 - (1 - \alpha)^{1/3}]^2$
 2. $[-\ln(1 - \alpha)]^{1/2}$
 3. $1 - (1 - \alpha)^{1/2}$
- $T = 100^\circ \text{C}$

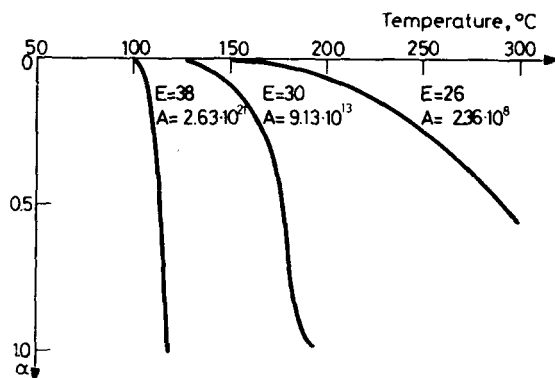


Fig. 8 Relationship $\alpha - T$ for non-isothermal conditions ($\phi = 10 \text{ deg min}^{-1}$). The values of kinetic parameters are marked on the curves.

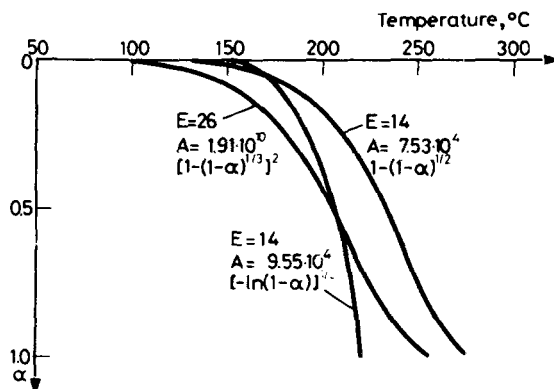


Fig. 9 Relationship $\alpha - T$ for non-isothermal conditions. The values of the kinetic parameters are marked on the curves.

complicated when all three parameters are considered simultaneously. In this case, in contradiction with the often-cited opinion, one can meet curves having higher E values, but showing the beginning of decomposition at lower temperatures. From Fig. 8, where three curves with all kinetic parameters different are presented, it is evident that a compound having an activation energy $E = 38 \text{ kcal mol}^{-1}$ (and $A = 2.63 \cdot 10^{21} \text{ min}^{-1}$ and $g(\alpha) = (-\ln(1-\alpha))^{1/2}$) can decompose at a heating rate of 10 deg min^{-1} 50 deg lower than one having an activation energy $E = 26 \text{ cal mol}^{-1}$ ($A = 2.36 \cdot 10^8$, Jander equation). The difference of these sequences of "thermal stability" determined in isothermal and non-isothermal experiments is shown by the results presented in Figs 9 and 10. After 150 minutes of isothermal decom-

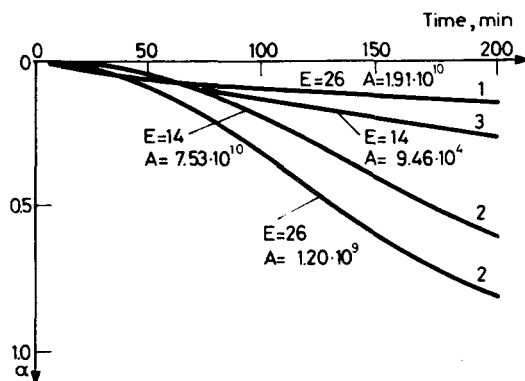


Fig. 10 Isothermal relationship α - time for the curves presented on Fig. 9

1. $[1-(1-\alpha)^{1/3}]^2$
 2. $[-\ln(1-\alpha)]^{1/2}$
 3. $1-(1-\alpha)^{1/2}$
- $T = 100^\circ\text{C}$

position, the most stable (the lowest weight loss) is the compound ($E = 26 \text{ kcal mol}^{-1}$, $A = 1.91 \cdot 10^{10} \text{ min}^{-1}$, Jander equation) for which the decomposition in a dynamic run (10 deg min^{-1}) starts at the lowest temperature ($\alpha = 0.01$ at 100°).

Conclusions

Kinetic parameters are useful in investigations of the progress of the thermal decompositions of solids, or of the correlation between isothermal and rising temperature experiments, only when all three parameters A , E and $g(\alpha)$ are considered. Conclusions concerning the mechanism of the decomposition that are drawn on the basis of a comparison of the activation energies only, are of little value, because they can give reliable information only when, for two or more compounds under investigation, the other two kinetic parameters are identical, which is unrealistic. Also, without a knowledge of the $g(\alpha)$ function, conclusions concerning the thermal stability, determined in non-isothermal runs, are not fully useful. Depending on the values of all three parameters, the thermal stability determined from dynamic experiments can be quite different from that under isothermal conditions.

References

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Zusammenfassung – Theoretische Umsatzkurven α gegen t für isotherme bzw. α gegen Temperatur für nichtisotherme Versuchsführung wurden berechnet in Abhängigkeit von den drei kinetischen Parametern Aktivierungsenergie E , Präexponentialfaktor A und der $g(\alpha)$ -Funktion, die den Mechanismus der Zersetzung von Festkörpern beschreibt. Die Ergebnisse zeigen, dass Schlussfolgerungen, die nicht alle drei Parameter berücksichtigen, zu Ergebnissen von geringer Aussagekraft bezüglich des Zersetzungsmechanismus und der kinetischen Interpretation führen. Eine Korrelation nicht-isothermer und isothermer Experimente, die für die Bestimmung der thermischen Stabilität der Verbindungen wichtig ist, ist ohne Kenntnis der Funktion $g(\alpha)$ unmöglich.

РЕЗЮМЕ — Теоретические кривые α -время для изотермических исследований и α -температура для неізотермических исследований были вычислены как функции трех кинетических параметров: энергии активации E , предэкспоненциального фактора и функции $g(\alpha)$, описывающей механизм термического разложения твердых тел. Результаты показали, что без учета этих трех параметров, получаемая информация о механизме разложения является малоценной, также как и проведенные кинетические вычисления. Важная при определении термоустойчивости соединений корреляция между неізотермическими и изотермическими исследованиями, вообще является невозможной без знания функции $g(\alpha)$.